Evaluation of Iraqi Coasts Contamination Using Littoral and Marine Bivalve Shell

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ABSTRACT
The geochemical analysis of sediments and both *Crassostrea cucullata and Chione californensis* shells and hydrochemical analyses of water are carried out to study the environmental contamination in the Iraqi coasts - north Arabian Gulf. Samples of sediments, shells and water are collected during low tide period from March to August 2011, from seven different stations (Fadakia, Rass Al Bishah, Khor Abdullah, Khor Shytianah , Hacham Island , Khor Al Zubair and Shatt Al-Basra).
The sediments textural analyses revealed that Fadakia, Rass Al Bishah, Khor Al Zubair and Shatt Al-Basra are classified as silty clay sediments while the sediments Khor Abdullah, Khor Shytianah and Hacham Island are classified as sandy silty clay sediments.

The hydrochemical analysis reflect three zones of water salinity, Fadakia and Shatt Al-Basrah of Brackish water with TDS range (15148-18130ppm), Rass Al Bishah of Saline water with TDS range (34123-36521ppm), and the other marine coastal sites of saline water with TDS range (39215-45220ppm).

X-ray diffractometry of shells of *Chione californensis* reveals that they have two layers, an inner layer constitutes of aragonite and outer layer constitutes of calcite, while the shells of *Crassostrea cucullata* have only calcite layer. The geochemical analyses of shells revealed positive correlation between water salinity and chemical constituents. Exception is found for SiO_2, Al_2O_3, and P_2O_5 which have negative correlation with water salinity.

The chemical constituents of SiO_2%, Al_2O_3%, MgO %, Fe_2O_3 %, Co, Zn, Cr, and Pb in the *Chione californensis* shells show direct relation with the calcite whereas CaO %, P_2O_5 %, Na_2O %, K_2O %, Ba, Sr, Rb, and Sr/Ca ratio show direct relation with the aragonite.

The geochemical analysis and differences in the proportion of the calcium carbonate polymorphs within the Iraqi coastal line may reflect the range of influence of pollution effluent from the port of Um Qaser near Hacham Island. Also, It is good to use the mineralogical evidence of *Crassostrea cucullata* and *Chione californensis* shells with their living aqueous habitat to build an aqueous environment pollution models in the Iraqi Coasts.

Key words: Contamination; Littoral and Marine bivalves' shells; chemical constituents; Iraqi coasts.

INTRODUCTION

Marine pollution is a global environmental problem. Human activities in the coastal area and marine water contribute to the discharge of various kinds of pollutants such as major and minor components (CaO %, MgO %, SiO_2 %, Al_2O_3 %, K_2O %, Na_2O %, Fe_2O_3 %, LOI %, Sr/Ca , Mg/Ca)) and Sr, Zn, Cu, Ba, Co, Cr, Pb, Ni, Rb, heavy metals into the marine ecosystems (Censi *et al.*, 2006, Al-Jaberi, 2013). The main reason for the metal contamination is considered as persistent and due to their toxic properties, could create several problems for different kinds of marine ecosystems and could be accumulating in marine organisms (Boening, 1999). Monitoring of chemical components and heavy metals in marine environment as especially coastal zone is very important to assess the contamination in the marine environment (Babukutty and Chacko, 1995, Cravo, et al, 2004). Traditional monitoring of heavy metals in the aquatic environment involves determining and comparing the metal in water, sediment and biota (Al-Dabbas, et al, 1984, Nicholson and Lam, 2005). As a result, biomonitoring process has been widely used to monitoring metals in the last years (Zorita et al., 2006; Hamed and Emara, 2006).

The use of bivalves shells as indicator to the pollution was because they are ubiquitous bivalve organisms found in continental, estuarine, marine and hyper saline waters (Hubbard, et al, 1981, Darvish,2007) .Shells precipitated under differing environmental conditions tends to reflect that deference in the chemistry of shells (Szefer , et al, 2002, Liu and Kueh ,2005). Many of pervious study used these shells as indicator to the pollution in the coastal areas for these shells are very sensitive to pollutant and bivalves are considered as good biomonitor agents for pollutant and heavy metal monitoring in aquatic ecosystems , (Vlahogianni et al., 2007; Maanan, 2008, Aguilar et al ,2012, Berges-Tiznado et al ,2013). Bivalves are believed to incorporate trace elements into their shells in proportion to the concentration of those elements in water (Censi *et al.*, 2006).This incorporation is also influenced by other circumstances, including water temperature and salinity (Al-Dabbas *et al*., 1983 and 1984) .The incorporation of trace elements into marine bivalves could be used to monitor temporal changes in aspects of the marine environment, including the elemental composition of the water (Boening, 1999).

The molluscs bivalves *Crassostrea cucullata* and *Chione californensis* are chosen in this study due to their

high distribution in all the Iraqi shore lines as well as their ability to survive in the intertidal zone, where they are subjected to frequent periods of salinity and temperature changes, as well as their tolerance and adaptability have made them the preferred organisms for monitoring contaminants, and constitute reliable indicators of the quality of given ecosystems (Al-Dabbas, et al, 1983, Al-Jaberi, 2013).

Iraqi Coasts of the Arabian Gulf, Khor Zubair, Shatt Al-Arab and Shatt Al-Basra are developing areas (Fig.1). Water discharge by boats and ships, marine transportation and ballast water discharges are main sources of pollutants in this area. While, wastewater, industrial and agricultural discharges and dredging are another sources of pollutant in this coastal area. These activities along the Iraqi coasts have caused this area to be exposed to different kinds of pollutants especially heavy metals. Although bivalves specially *Crassostrea cucullata* and *Chione californensis* are widely distributed in this area, but there is a lack of information related to heavy metal content of them.

The aim of this research is to study the variation in the chemical and physical characteristics of mollusc's shells which are useful tool for monitoring contamination in the Iraqi aquatic brackish and marine environments within the Iraqi coasts.

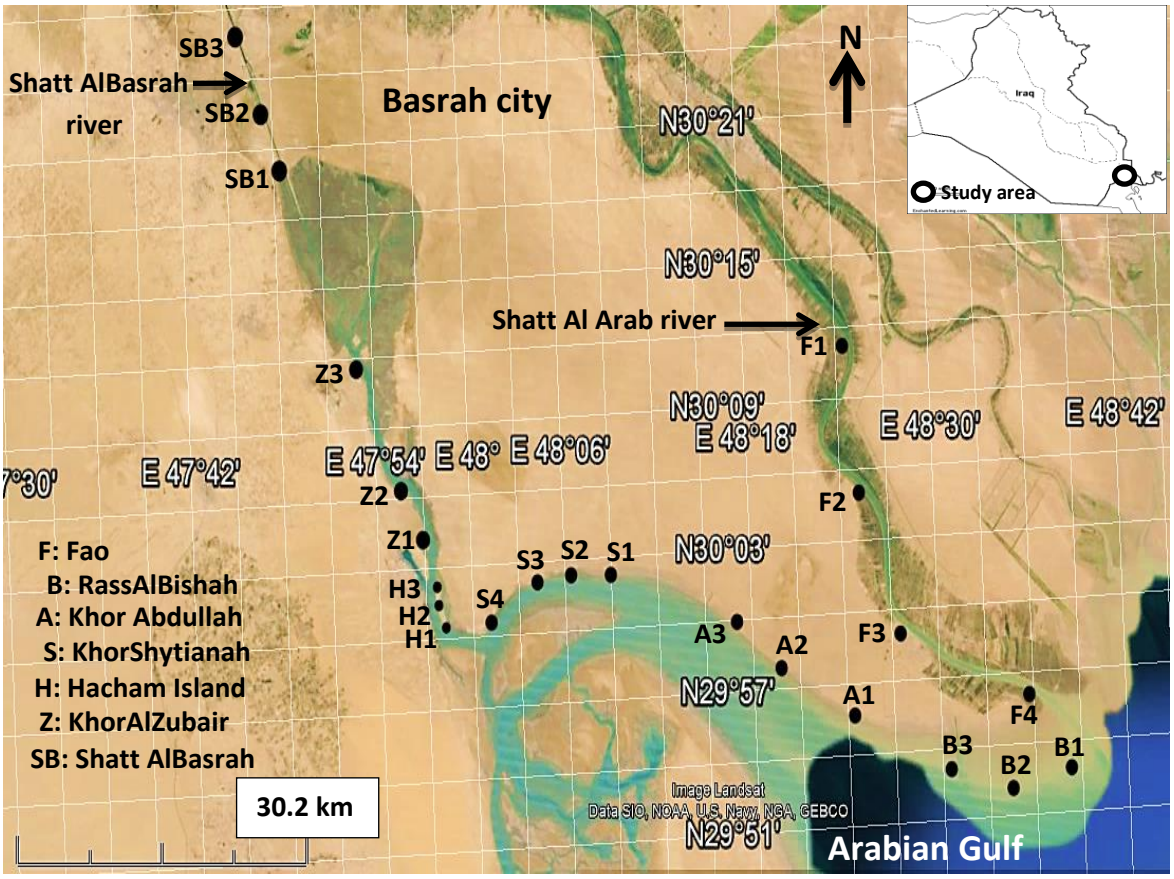

Figure 1- Map of the study area showing location of sampling sites.

MATERIALS AND METHODS

Seven different stations of different aquatic environments were chosen to study the geochemistry of *Crassostrea cucullata* and *Chione californensis* shells along Iraqi coasts and shorelines from Fadakia (at Shatt Al-Arab river at the east of the study area) to Shatt Al-Basra (at the Main Drain Channel at the northwest of the study area) (Fig.1). Samples of shell and water were taken during low tide period from March to August 2011.Four replicates of water and shells samples were collected from each site.

A-Hydrochemical study was done to determine the physical and chemical parameters of the studied sites of Iraqi aquatic environments. Physical parameters include hydrogen number (pH), total dissolve solid (TDS) and electrical conductivity (EC). Chemical parameters include the major cations (K^{+}, Na^{+}, Ca^{+2}, and Mg^{+2}) and anions (Cl^{-}, SO_4^{-2}, HCO_3^{-}, and CO_3^{-2}) (Table 1).

B- Thirty of littoral bivalve *Crassostra cucullata* shells of the same size (3.7 to 6.8 cm) were collected from Fadakia, Rass Al Bishah, Khor Abdullah, Khor shytianah , Hacham Island , Khor Al Zubair and Shatt Al-Basra sampling stations (Fig. 2). As well as thirty of marine bivalve *Chione californensis* shells of the same size (4 to 7 cm) are collected from Khor Abdullah, Khor Shytianah and Hacham Island only due to their absence in other sampling stations.

Crassostrea cucullata is a littoral bivalve shell found in brackish-marine environments (Wang and Guo, 2008) (Fig. 2). *Crassostrea cucullata* is classified using Ahmed, 1975 classifications, as Phylum: Mollusca , -Class: Bivalvia, Subclass: Pteriomorphia, Order: Ostreina Family: Ostreidae , Genus: *Crassostrea cucullata* . Calcite is a main mineral in the *Crassostra cucullata* shell that recognized by X-ray diffraction (CuKq) analysis and SEM-EDAX (Al-Jaberi, 2013).

Chione californensis is a marine bivalve shell found in marine environments only. It is classified using Wang and Guo (2008) classifications, as Phylum: Mollusca, Class: Bivalvia, Subclass: Heterodonta, Order: Ostreina Superfamily: Veneracea, Family: Veneridae, Subfamily: Chioninae, and Genus: *Chione californensis*. Two layers, the inner aragonite layer (nacreous layer) and outer calcite layer (prismatic layer) are recognized by X-ray diffraction (CuKq) analysis and SEM, the percentages of these layers are different from genus to other of *Chione californensis* (Al-Jaberi, 2013). The inner aragonite layer was separated from calcite layer for nine *Chione californiensis* specimens by using an Electric Hand Vibrating Hobby tool since it is the only known method for separation (even that this method may contaminate the samples in the same degree). The purity of aragonite was tested by X-ray diffraction method and about 95% purity is found to have been attained . The crystals of calcite and aragonite was recognized by SEM microscope.

Shell sample was placed in an acid-washed polyethylene bag to analysis. Then they were powdered using glass mortar and were stored in polyethylene pillboxes until digestion (Al-Jaberi, 2013). All of debris's were removed from each sample in laboratory. After washing shells with double distilled water, the scanning electron microscope-EDAX, X-Ray diffraction, and ICP analysis were all employed in this work.

The geochemistry of *Crassostrea cucullata and Chione californensis*'s shells were done for the following constituents CaO %, MgO %, SiO_2

%, Al_2O_3 %, K_2O %, Na_2O %, Fe_2O_3 %, P_2O_5 %, as well as Co, Ni, Rb, Sr, Zn, Cu, Ba, Cr, Pb, elements in ppm, LOI %, Sr/Ca , Mg/Ca(Table 2).

These analyses were executed in both calcite and aragonite layers of *Chione californensis* shells. Shells samples from a non-polluted site were collected and analyzed in this study for comparison purposes.

RESULTS AND DISCUSSION:

A-Hydrochemical Analysis:

(1)-Physical parameters

The hydrochemical analysis reflect three zones of water salinity according to Lewis, 1982 and Hem, 1985,.Fadakia and Shatt Al Basrah of Brackish water with TDS range (15148-18130ppm), Rass Al Bishah (south most part of Shatt Al-Arab River) of Saline water with TDS range (34123-36521ppm), and the other marine coastal sites (Khor Al Zubair , Hacham Island , Khor Shytianah , Khor Abdullah) of Saline water with TDS range (39215-45220ppm) (Table 1).

Moreover, due to the positive relationship between electrical conductivity and TDS, the same is true for the EC values. Consequently, three zones had been indicated according to the EC. Fadakia and Shatt Al Basrah with EC range (23-29 mmohs/Cm), Rass Al Bishah with EC range (53-57 mmohs/Cm), and the other marine coastal sites with Ec range (64-71mmohs/Cm). While, the pH values for Fadakia and Shatt Al Basrah with range (7.5-7.9), Rass Al Bishah with range (7.7-8), and the other marine coastal with pH range (7.8-8.2).

(2)-Chemical parameters

The Calcium ion concentration (ppm) for Fadakia and Shatt Al Basrah are ranging from 285 ppm to 412 ppm, Rass Al Bishah with range (465-509ppm), and the other marine coastal with range (513-610 ppm) (Table 1).

The Magnesium concentration (ppm) for Fadakia and Shatt Al Basrah with range (1043- 1208ppm), Rass Al Bishah with range (1441-1478 ppm), and the other marine coastal with range (1482-2040ppm).

The Sodium concentration (ppm) for Fadakia and Shatt Al Basrah with range (4413-4654 ppm), Rass Al Bishah with range (10675-12944 ppm), and the other marine coastal with range (13028-15100 ppm).

The Potassium concentration (ppm) for Fadakia and Shatt Al Basrah with range (78-106 ppm), Rass Al Bishah with range (295-349 ppm), and the other marine coastal with range (311-358 ppm).

The Chloride concentration (ppm) for Fadakia and Shatt Al Basrah with range (8768-9066ppm), Rass Al Bishah with range (20561-21420 ppm), and the other marine coastal with range (22846-26800ppm).

The Sulfate concentration (ppm) for Fadakia and Shatt Al Basrah with range (1089-1990ppm), Rass Al Bishah with range (2026-2577 ppm), and the other marine coastal with range (3082-3700ppm).

The Bicarbonate (HCO_3^-) concentration (ppm) for Fadakia and Shatt Al Basrah with range (41-75ppm), Rass Al Bishah with range (147- 151 ppm), and the other marine coastal with range (150-201ppm).

The Carbonate ($CO3^{-2}$) concentration (ppm) for Fadakia and Shatt Al Basrah with range (6- 22ppm), Rass Al Bishah with range (9-11 ppm), and the other marine coastal with range (13-21ppm).

Table 1: physical and chemical parameters of the studied sites of Iraqi aquatic environments.

Sampling site	pH	EC mmohs/Cm	Na^+ ppm	K^+ ppm	Ca^{+2} ppm	Mg^{+2} ppm	Cl^- ppm	SO_4^{-2} ppm	HCO_3^{-2} ppm	CO_3^{-2} ppm	T.D.S ppm	Water Classi (Lewis, 1982).
KhorAlZubair ,Hacham Island , KhorShytianah , Khor Abdullah	7.8-8.2	64-71	13028-15100	311-358	513-610	1482-2040	22846-26800	3082-3700	150-201	13-21	39215-45220	Saline water
Rass AlBishah	7.7-8	53-57	10675-12944	295-349	465-509	1441-1478	20561-21420	2026-2577	147-151	9-11	34123-36521	Saline water
Fadakia&Shatt AlBasrah	7.5-7.9	23-29	4413-4654	78-106	285-412	1043-1208	8768-9066	1089-1990	41-75	6-22	15148-18130	Brackish water

B- Geochemical Analysis of *Crassostrea cucullata* Shell

The shells of *Crassostrea cucullata* in the studied areas along Iraqi coastal line, show mean contents of 100 % calcite. The range of the measured chemical constituents and heavy metals concentrations (CaO %, MgO %, SiO_2 %, Al_2O_3 %, K_2O %, Na_2O %, Fe_2O_3 %, P_2O_5 %, as well as Co, Ni, Rb, Sr, Zn, Cu, Ba, Cr, Pb, elements in ppm, LOI %, Sr/Ca , Mg/Ca) in the *Crassostrea cucullata*

shells at the studied areas shown in (Table 2).

The results of the geochemical analysis show that positive correlation were found between water salinity of the sampling sites and the chemical constituents in the calcite shell of *Crassostrea cucullata* , as a result to higher content of these ions in the surrounding sea water compared with the Shatt Al Arab river in Fadakia area and Shatt Basra river as continuation of the Main Drain, (Tables 1 and 2) .

Obviously, the results reflect that the relatively higher values of most of the studied chemical constituents and heavy metals (CaO , LOI , MgO , Na_2O , Sr , K_2O , Cu , Zn , Pb ,Cr , Ba ,Rb ,Ni ,Co) lies within the Iraq marine coastlines (Khor Shytianah (S) , Khor Abdullah(A) Rass Al Bishah (B), Hacham Island(H) , and Khor Al Zubair(Z)) . The maximum values of these chemical constituents are indicated in Khor Shytianah site (S), except for SiO_2, Al_2O_3, P_2O_5 and Fe_2O_3 percentages that they had their lower values, while, the minimum values of these chemical constituents are indicated generally in brackish water sites Fadakia (F) at Shatt Al-Arab river and Shatt Al-Basra (SB) site at the Main Drain Channel, (where the water salinity range 15148-18130 ppm ,that classified as brackish water according to Lewis, 1982), except for SiO_2, Al_2O_3, P_2O_5 and Fe percentages that they had their higher values , (Tables 1 and 2) .

The results showed the order of chemical constituents and heavy metals accumulation in the shell of oyster in descending order are CaO > LOI > SiO_2 > MgO > Al_2O_3 > Na_2O > Fe_2O_3 % > Sr > K_2O > P_2O_5 > Cu > Zn > Pb > Cr > Ba > Rb > Ni > Co and Mg/Ca > Sr/Ca.
Variation in Mg/Ca and Sr/Ca ratios in the mulluscs shells employed as invironmrntal indicator (Al-Dabbas,1984). Mg/Ca and Sr/Ca values in the coastal line *C. cucullata* shells are higher than in the Fadakia and Shatt Al Basra areas that may be due to increment of salinity in the coastal line compared with Fadakia and Shatt AlBasrah areas. Such finding is in agreement with Al-Dabbas,1984 result.

The average concentration of Magnesium as major ion and Strontium as trace ion of sea water in the *C. cucullata* shells in the coastal line(Khor Shytianah (S) , Khor Abdullah(A) Rass Al Bishah (B), Hacham Island(H) , and Khor Al Zubair(Z)) are higher than Mg and Sr content in the shells of Fadakia(F) and Shatt AlBasrah(SB) , that may be attributed to the higher Mg and Sr content in the sea water .

The bulk of the *Crassostrea cucullata* shell mineral is calcium carbonate

(calcite), accordingly, CaO % and LOI % are the highest percentages of all the analyzed chemical constituents and they have positive correlation between each other and with water salinity,(Tables 1 and 2).

Calcium (CaO%) ,Magnesium (MgO%) ,Sodium (Na_2O%) and Potassium (K_2O) in the *Crassostrea cucullata* shells are relatively higher in the marine coastal sites (Rass Al Bishah ,Khor Al Zubair , Hacham Island , Khor Shytianah , and Khor Abdullah) that may be probably due to increase of these ions in the sea water of these sites compared with the Shatt Al Arab river in Fadakia area and Shatt AlBasrah river.

Dodd (1965) mentioned that the Mg content of the outer calcite layer increase with increase environment temperature, but no so regular as Sr concentration. Mg , Si, Al ,Pb and Zn which have large ionic radii and present in higher concentration in the calcite

SiO_2 %, Al_2O_3 %, P_2O_5 % and Fe_2O_3 % in the Fadakia *C. cucullata* shells were higher than the other sampling sites *C. cucullata* shells (Table 2).

SiO_2 % and Al_2O_3 % are usually residual component in soil. most Si and Al are related to surfcial contamination, related to interstitial grains of amorphous silica or clays.

Si, Al, P and Fe ions may be related to the abundance of the fine fraction clay minerals in the suspended sediment load of Shatt Al-Arab River areas and the Phosphorus-rich fertilizers and organic matter that transported from agricultural land near Fadakia area.

Clay minerals are playing an important role in the environmental cycling of the studied chemical constituents and heavy metals and Clay minerals considered as sink for trace elements (Pendias and Pendias, 2001). The factors controlling trace elements concentration in clay are mainly influenced by: the source of clay minerals, pH – Eh, drainage, climate, time, clay fraction content and organic matter content, pollution, among other factors.

Cobalt (Co): Cobalt is an important and essential element for living organisms (plant and animal nutrition) even though it is present at lower trace level (Hem, 1985). The Co seems to be associated with clay minerals and organic matter. The roles of clays are of significance because of their great sorption capacity and their relatively easy release of Co (Pendias and Pendias, 2001). The cobalt ions in sea water were determined to be about 0.03 ppm, while, it was found in this study that the minimum Co concentration was 0.48 ppm in Shatt Al-Basrah site *Crassostrea cucullata* shells and the

maximum was 2.33 ppm in Khor Shaitana site that may be due to high range of contamination of sea water by this metal.

Nickel (Ni): Nickel can enter to the structure system of clay minerals. The similar ionic radius between Ni^{2+}=0.69A˚ Co^{2+}=0.72A˚ and Fe^{2+}=0.74A˚ Mg^{2+}=0.66A˚ caused to replacement of magnesium and iron by nickel and cobalt in the structure system to the clay mineral .The Ni higher mobility in ionic form increases its toxicity effects compared with Cr and Pb (Pendias and Pendias, 2001). Nickel correlates positively with Al, Cu, Pb, and Fe and to a lesser extent with Cr., suggesting its presence in clay minerals as well as with Fe – oxides. Nickel content in the sea water is about 0.007 ppm, while, it was found in this study that the minimum Ni concentration was 4.5 ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 8.9 ppm in Khor Shaitanah site that may be due to high range of contamination of sea water by this metal. Increase of these elements in the sea water may be attributed to the oil spill from the tanker oil ships that passing in the north and Northwest of Arabian gulf.

Zinc (Zn): The most dangerous elements in scale and size of release are Pb and Zn among the elements of the first class of danger and Ni, Co and Cu are among the second class. Currently, 70 to 95% of all heavy metals are transferred to soil from anthropogenic sources; the rest are from natural source .The anthropogenic sources of Zn are related, first of all, to the nonferric metal industry and then to agricultural practice. Zinc is positively correlated with K, Al, Fe and P demonstrating its association with clay minerals as one host.

It is noted in low amount in the soils, water streams, lakes, oceans and in every living organism (Pendias and Pendias, 2001). While, it was found in this study that the minimum Zn concentration was 213ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 240 ppm in Khor Shaitanah site that may be due to high range of contamination of sea water by this metal.

Copper (Cu): Copper (Cu) forms several minerals of which the common primary minerals are simple and complex sulfides. These minerals are quite easily soluble in weathering processes and release Cu ions, especially in acid environments (Pendias and Pendias, 2001).

The Cu concentration in surface soils reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element, the relative enrichment in copper content that could be due to environmental contamination, (Pendias and Pendias,

2001). Contamination of soil by Cu compounds results from utilization of Cu-containing material such as fertilizers, sprays, and agricultural or municipal wastes as well as from industrial emissions. Some local or incidental Cu input to soils may arise from corrosion of Cu alloy construction materials (e.g., electric wires, pipes). Copper is positively correlated with P, Fe, Al and Ni suggesting clay minerals as host. It was found in this study that the minimum Cu concentration was 451ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 498 ppm in Khor Shaitanah site that may be due to high range of contamination of sea water by this metal.

Lead (Pb): The accumulation of Pb in the aqueous environments is exposed to various pollution sources and it is of great ecological significance because this metal is known to greatly affect the biological activity in aqueous environments, (Pendias and Pendias, 2001).

Lead is present in Pb^{+2} ions are more spread in the water environment. Lead (as Pb^{2+}) forms carbonates, incorporated in clay minerals, in Fe – Mn oxides and in organic matter, its concentration in the sea water is about 0.0003 ppm , (Pendias and Pendias, 2001). Lead is positively correlated with Fe, Al, P, Cr, Zn, Ni, and K probably suggesting some association with the fertilizers, clay and heavy minerals. It was found in this study that the minimum Pb concentration was 451ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 498 ppm in Khor Shaitanah site that may be due to high range of contamination of sea water by this metal. These concentrations may be due to the gasoline spill in the sea water as a result of activity of ships in these areas caused to contamination by lead ions, especially the sea water in these areas consider as important commercial line to the world ships.

Chromium (Cr): The Cr higher concentration is mainly due to the transportation of suspended sediments as detrital chromite grains by the Shatt Al-Arab River and precipitated in the Iraqi shore lines, and due to pollution from various sources, of which the main ones are several industrial wastes (e.g., electroplating sludge, Cr pigment and tannery wastes, leather manufacturing wastes) and municipal sewage sludge. Chromium main correlation is with Fe, Pb, Ni and Al. It was found in this study that the minimum Cr concentration was 4.4 ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 41 ppm in Khor Shaitanah site that may be due to high range of contamination of sea water by this metal. The high

concentration of Pb in the shell of oyster may be due to replace of Pb ions in the calcareous structure of the shell.

Strontium (Sr) with highly mobility in aqueous environment, by the weathering the minerals of Celestine $SrSO_4$ and Strontianite $SrCO_3$ .It was found in this study that the minimum Sr concentration was 996ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 2015 ppm in Khor Shaitanah site

Rubidium (Rb) has the same chemical characteristics of Potassium (K) and found in Clay minerals as weathered product of the Feldspar minerals and Mica.

It was found in this study that the minimum Rb concentration was 0.85ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 12.23 ppm in Khor Shaitanah site

Barium (Ba) has the same chemical characteristics of Potassium (K) with highly mobility in aqueous environment, by the weathering the minerals of Barite $BaSO_4$ and Witherite $BaCO_3$ It was found in this study that the minimum Ba concentration was 4.3 ppm in Fadakia site *Crassostrea cucullata* shells and the maximum was 27.2 ppm in Khor Shaitanah site

The high concentration of Sr,Rb and Ba may be due to high range of contamination of sea water by these metals.

Afaj and Al-Dabbas, 1998, had studied the C. *cucullata* shells in the Khor Al Zubair coastal area and found that the Iron was (0.0162 %), Zinc was (20 ppm) , and copper (20 ppm) ,while the results of this research indicate that Iron was (0.217%), Zinc was (224 ppm) , and copper (451 ppm) in the *Crassostrea cucullata* shells in Khor Zubair area which may reflect that these trace elements increased more than 10 time within more than decade that might be due to increase contamination with high environmental changes of Khor Al Zubair coastal area. Hence, the studied chemical constituents and heavy metals in the *Crassostrea cucullata* shells are dynamic with the changing in aqueous environment with pollution and evolving with time.

Table 2: The analyzed geochemical constituents of *Crassostrea cucullata* shells for the studied seven sites.

Elements	Shatt Basra (SB)	Khor Zubair (Z)	Hacham Island (H)	Khor Shytianah (S)	Khor Abdullah (A)	Rass Bisha (B)	Fadakia (F)	Constituents Range
CaO %	53.8	54.7	54.8	54.9	54.5	54.3	53.7	53.7 (F) - 54.9(S)
MgO %	0.56	0.75	0.7	0.78	0.66	0.61	0.53	0.53(F) - 0.78(S)
SiO_2 %	0.695	0.413	0.249	0.21	0.345	0.31	0.852	0.21(S) - 0.852(F)
Al_2O_3 %	0.505	0.0976	0.072	0.065	0.096	0.091	0.514	0.065(S), 0.514(F)
K_2O %	0.08	0.178	0.132	0.188	0.14	0.163	0.021	0.021(F)- 0.188(S)
Na_2O %	0.387	0.417	0.399	0.436	0.391	0.393	0.312	0.312 (F)- 0.436(S)
P_2O_5 %	0.098	0.058	0.030	0.0124	0.033	0.0613	0.13	0.0124(S)- 0.13(F)
Fe_2O_3 %	0.26	0.217	0.28	0.19	0.23	0.25	0.29	0.19 (S)- 0.29 (F)
Co ppm	0.48	0.922	1.05	2.33	0.88	0.722	0.52	0.48(SB) - 2.33(S)
Rb ppm	1.3	15.3	11.1	12.23	11.0	11.5	0.85	0.85(F) - 12.23(S)
Sr ppm	1001	1164	1184	2015	1133	1122	996	996(F)- 2015(S)
Zn ppm	214	224	235	240	232	220	213	213(F)- 240(S)
Ba ppm	6.4	10.6	11.9	27.2	14.9	9.4	4.3	4.3 (F)- 27.2 (S)
Pb ppm	32	38	40	43	39	37	31	31(F)- 43(S)
LOI %	41.3	42	42	43.5	43	42	41	41(F) – 43.5(S)
Mg/Ca x 1000	8.8	11.7	10.3	12.0	10.2	9.4	8.3	8.3(F) - 12.0(S)
Sr/Ca x 1000	2.61	3.72	3.73	5.14	3.75	2.93	2.6	2.6(F) – 5.14 (S)

C-Chemical Analysis of Aragonite and Calcite Layers *of Chione californensis* shell:

Concentration of trace elements to specific carbonate shell layers controlled by the relative acceptability of the elements into the lattice and the quantity of foreign elements in the shell reflects the concentration of those elements in the surrounding water (Dodd, 1965; Chow *et al.*, 1976; Phillips, 1977). Infact, filter feeder, such as *Chione californensis*, are particularly valuable in water quality investigation; since shell

variation developing during growth should directly reflect the ambient water condition (temperature, salinity, dissolved and suspended load) (Phillips, 1977). The ranges of the measured chemical constituents (MgO %, SiO_2 %, Al_2O_3 %, K_2O %, Na_2O %, Fe_2O_3 %, and P_2O_5 %, Co, Ni, Rb, Sr, Zn, Cu, Ba, Cr, and Pb, Sr/Ca) of the *Chione californensis* shells at the studied areas in both layers of aragonite and calcite as well as the mean values and standerd diviation of shells samples from a non-polluted site for comparison purposes are shown in the Tables 3.

The results show positive correlation between the chemical constituents and sea water salinity with relatively higher correlation factor values for most of the studied chemical constituents (MgO, Na_2O, Fe_2O_3, Sr, K_2O, Cu, Zn, Pb, Cr, Ba, Rb, Ni, and Co) of samples collected from Khor Shytianah (S) and Hacham Island (H), as compared with those of Khor Abdullah (A), in both layers of aragonite and calcite, except for SiO_2, Al_2O_3, and P_2O_5 percentages, where higher values were found in Khor Abdullah samples (A) (Tables 1 and 3) .

Some elements are concentrated in the calcite outer layer more than in the aragonite inner layer.
However, the ratio of the elemental distribution in calcite to aragonite layer varies widely from element to other. The studied chemical constituents have different behaviors; they increase within the calcite layer such as MgO, SiO_2, Al_2O_3, Fe_2O_3, Co, Zn and Pb. By contrast others increase within the aragonite layer such as P_2O_5 %, K_2O %, Na_2O %, Ba, Cr, Rb, Sr, and Sr/Ca.

In fact, one major control on trace and minor elements in either calcite or aragonite is crystallochemical. The calcite structure accommodates Ca^{2+} (ionic radius 1.00 Å) as well as minor and trace elements having an ionic radius less than or equal to 1.00 Å. The aragonite structure accommodates Ca^{2+} together with minor and trace elements having radii close or greater that 1.00 Å (Deer *et al.*,1992).

The results reflect that Mg, Si, Al and Zn, which have large ionic radii, are present in higher concentration in the calcite than in aragonite layer, especially Zn element. Pb element, which also has large ionic radus, is present in higher concentration in the calcite layer comprable to the aragonite layer. On other hand, Cr and P elements which have small ionic radii, are present at higher concentrations in aragonite rather than calcite.

Sr/Ca values in the aragonite layer are more than that of the calcite layer.

The surrounding water is the main source for these elements in the structure of *Chione calforniensis*'s shells. Shell composition changes as a result of changing water chemistry (Yatab *et al*., 2000 ;Dalbeck, 2008). Consequently, the aquatic environment had an important role in providing the calcite and aragonite layers by the elements (Tables 1 and 3).

The Sr/Ca ratio can be used for determination of the paleosalinity and paleotemperature of an ancient environment as reported by Chilingar *et al*. (1967); Klein *et al*. (1996) and Thorn *et al*. (1995). The Sr/Ca value is increase with increase of water salinity, so it is higher in the Khor Shytianah and Hacham Island shells in comparison to Khor Abdullah's shells (Table 2).

The Sr and Na were used as indicators to the aragonite layer, while Mg element is indicator to the calcite layer, and these results are clear in the geochemical analysis of the studied shells, which are in accordance with McMillan *et al*.(2005)and Dalbeck (2008). Reeder (1983) showed that Mg^{2+} is able to substitute for Ca^{2+} in hexagonal calcite, but not in orthorhombic aragonite. Therefore, the decrease of calcium element in the calcite layer and increase of the magnesium can be attributed to higher paleotemprature in the Iraqi shorelines.

Generally, most P, Si and Al are related to surfacial contamination and to interstitial grains of amorphous silica or clays.The factors controlling trace elements concentration in clay are influenced by pH – Eh, drainage, climate, time, clay fraction content , organic matter content, pollution and other factors (Caihuan and Wang, 2001). However, it is believed that the clay content is relatively higher in Khor Abdullah, due to the influence of sediment transport loads that are carried annually by Shatt Al-Arab fresh water river to the sea water, consequently, relatively reducing the sea water salinity, as well as the ions concentration. Biomonitors' organisms accumulate the chemical constituents and heavy metals from ambient bioavailable sources of the trace metal over a period (Rainbow, 2006). The *Chione californensis* like other molluscs' is suspension feeder and can uptake the heavy metals from suspended sediment (Caihuan and Wang, 2001). Thus, the shells of *Chione californensis* were found to be useful tool for monitoring contamination (Shulkin *et al*., 2003). The pollution in the Iraqi coasts water may be formed as a result of the oil spill by the oil carrying ships in the navigation channel in the north and northwestern parts of the Arabian Gulf.

Table 3: The geochemical analysis of the Aragonite and Calcite layers for the *Chione californensis* shells of Khor Abdullah (A), Khor Shytianah (S) and Hacham Island (H)

Aragonite						Calcite					
Elements	**A**	**S**	**H**	Mean	S.D.	**Elements**	**A**	**S**	**H**	Mean	S.D.
Al_2O_3 %	0.066	0.04	0.051	0.053	0.013	Al_2O_3 %	0.11	0.09	0.087	0.09	0.012
MgO %	0.047	0.049	0.048	0.0475	0.001	MgO %	0.135	0.142	0.14	0.139	0.003
SiO_2 %	0.075	0.069	0.07	0.071	0.0032	SiO_2 %	0.492	0.473	0.478	0.481	0.009
P_2O_5%	0.069	0.060	0.062	0.063	0.004	P_2O_5 %	0.022	0.013	0.018	0.017	0.004
Na_2O %	0.63	0.67	0.65	0.648	0.021	Na_2O %	0.474	0.562	0.501	0.512	0.04
K_2O %	0.1	0.14	0.12	0.118	0.02	K_2O %	0.07	0.085	0.08	0.078	0.007
Fe_2O_3 %	0.15	0.18	0.16	0.163	0.015	Fe_2O_3 %	0.17	0.20	0.18	0.183	0.015
Ba ppm	13.2	14.1	13.6	13.63	0.45	Ba ppm	10.3	11.5	11.2	11	0.62
Cr ppm	20.1	20.9	20.7	20.56	0.41	Cr ppm	8.7	9.6	9.2	9.16	0.45
Pb ppm	19	24	22	21.6	2.51	Pb ppm	28	32	29	29.6	2.08
Rb ppm	1.18	2.64	1.33	1.71	0.803	Rb ppm	0.53	0.63	0.57	0.57	0.05
Sr ppm	2077	2383	2300	2253	158	Sr ppm	1042	1138	1114	1098	49
Zn ppm	180	211	190	193	15	Zn ppm	218	223	221	220	2.51
Co ppm	0.43	0.95	0.61	0.66	0.26	Co ppm	0.75	1.16	0.89	0.93	0.2
$(Sr/Ca)10^3$	5.32	6.05	5.86	5.74	0.37	$(Sr/Ca)10^3$	2.69	2.92	2.84	2.81	0.11

CONCLUSIONS

1- The hydrochemical analysis reflect three zones of water salinity, Fadakia and Shatt Al-Basrah of Brackish water with TDS range (15148-18130 ppm), Rass Al Bishah of Saline water with TDS range (34123-36521ppm), and the other marine coastal sites of Saline water with TDS range (39215-45220 ppm).

2- The results show that the TDS in Khor Abdullah, Khor Shytiana and Hacham Island are 39215 – 40100 ppm, 44620 – 45220 ppm, and 41190 – 41220 ppm, respectively. They are, therefore, saline water according to Hem (1985) water classification .Since, there is positive relationship between electrical conductivity (EC) and total dissolved solids (TDS). Three zones have been indicated according to the EC in Khor Abdullah, Khor Shytiana and Hacham Island with EC ranges from 60 – 63mmohs/Cm, 69 – 71mmohs/Cm, and 64 – 65 mmohs/Cm, respectively. The hydrogen number (pH) values for Khor Abdullah ranges from 7.5 to7.9, Khor Shytianah ranges from 7.7 to 8, and

Hacham Island ranges from 7.8 to 8.2.

3- The result of using Schoeller (1972) method to classify the studied water samples, and identifying their water types have clearly indicated that chloride group are the dominant with one major family (Chloride-sodium family) and one water type which is rNa>rMg> rCa: rCl>SO4.

4- This variation can be attributed to the characterization of the marine water or to the spatial variation in controlling factors that are responsible for sedimentation and dissolution of different minerals.

5- The geochemical analysis results show that positive correlation were found between water salinity of the sampling sites and the chemical constituents CaO %, MgO %, K_2O %, Na_2O %, , LOI %, Sr/Ca , Mg/Ca and the trace elements Co, Ni, Rb, Sr, Zn, Cu, Ba, Cr, Pb concentration.

6- Negative correlation were found between water salinity and SiO_2 , Al_2O_3 , P_2O_5 , Fe_2O_3 percentages in the calcite shell of *Crassostrea cucullata*.

7- It is good to use the mineralogical evidence of *Crassostrea cucullata* shells with their living aqueous habitat to build an aqueous environment pollution models and the shell of *Crassostrea cucullata* should be a useful tool for monitoring contamination in the Iraqi aquatic brackish and marine environments.

8- Pollution in the Iraqi coasts water may be formed as a result to the oil spill by the oil bearing ships in the navigation channel in the North and Northwest of Arabian Gulf.

REFERENCES

Afaj, A.H., and Al-Dabbas, M.(1998) Some geochemical aspect of the sediments and mollusk shells from Khor Al-Zubair / south Iraq.The 6th Jordanian geological conference, Vol.6, pp-35-40.

Aguilar , C. A. ; Montalvo , C. ; Rodrı´guez , L. ; Cero´n , J. G. ; Cero´n, R. M. (2012) American oyster (Crassostrea virginica) and sediments as a coastal zone pollution monitor by heavy metals. Int. J. Environ. Sci. Technol. V. 9, pp-579–586.

Ahmed, M.M. (1975) Systematic study on Mollusca from Arabian Gulf and Shatt Al Arab. Center for Arab Gulf studies, Basrah Univ. Iraq, 75 P.

Al-Dabbas, M, F.H. Hubbard and J. McManus (1983) The Proportion of Aragonite in the shells of Mytilus edulis from the Tay Estuary, J.A.W.R.R., vol. 2, No. 2, pp. 73-79.

Al-Dabbas, M., A.M., F.H. Hubbard, and J. McManus (1984) The shell of Mytilus as an Indicator of zonal variations of Water Quality within an Estuary, Estuarine, Coastal and Shelf Science, vol.l8, pp.263-270.

Al-Dabbas, M. A. and Al-Jaberi, M. H. A.(2014)Assessment of heavy metals pollution in the sediments of Iraqi coastlines, IJSR - INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCHVolume : 3 | Issue : 9 | September 2014 • ISSN No 2277 - 8179

Al- Jaberi, Mohanad H. (2013) Study the clastics and shells in the Iraqi shore lines, Unpublished PhD thesis, Baghdad University. 220P.

Babukutty Y and Chacko J (1995) Chemical partitioning and bioavailability of Lead and Nickel in an estuarine system. *Environ Toxic Chem.* 14,427-434.

Bergés-Tiznado,M.E. ;Páez-Osuna, F; Notti,A.; Tegolli, F. (2013) Arsenic and Arsenic Species in Cultured Oyster (Crassostrea gigas and C. corteziensis) from Coastal Lagoons of the SE Gulf of California, Mexico.Biol Trace Elem Res , V.151 ,No.1, pp-43-9.

Boening W (1999) An evaluation of biomonitors of heavy metals pollution in marine waters. *Environ Mon and Assess* 55,459-470.

Caihuan K and Wang W (2001) Bioaccumulation of Cd, Se, and Zn in an estuarine oyster *Crassostrea rivularis* and a coastal oyster *Saccostrea glomerata*. *Aqua Toxic.* 56,33–51.

Censi P, Spoto SE, Saino FM, Sprovieri S, Mazzola A and Nardone G (2006) Heavy metals in coastal water systems: Acase study from the northewestern Gulf of Tailand. *Chem*, 64,1167-1176.

Cravo A, Foster P and Bebianno. MJ (2004) Minor and trace elements in the shell of *Patella aspera*. *Environ Inter.* 28,295-302.

Darvish A (2007) The survey of heavy metals (Cd, Cu, Ni and Hg) in water and soft tissue of *Saccostrea cucullata* in intertidal zone of Hormoz islans, Persian Gulf, M. S. thesis, Environmental Engineering, Azad Univ., of Ahvaz, Iran.

Dodd, J.R. (1965) Environmental Control Of Strontium And Magnesium In *Mytilus*: *Geochimica Et Cosmochimica Acta*,V-29, pp-385-398.

Hamed AH and AM Emara (2006) Marine molluscs as biomonitors for heavy metal levels in the Gulf of Suez, Red Sea. *J of Mar Sys.* 60,220–234.

Hem, J. D. (1985)Study and interpretation of the chemical characteristics of natural water (3rd ed.). USGS water- supply papers-2254. 253p.

Hubbard, F., J. McManus and M. AL-Dabbas (1981)Environmental Influences on the shell mineralogy of Mytilus edulis Geo-Marine Letters, vol. L, pp. 267-269.

Lewis, E. L. (1982) The practical salinity scale of 1978 and its antecedents. Marine Geodesy , V- 5 ,No.4,pp-345- 350.

Liu JH and CSW Kueh (2005) Biomonitoring of heavy metals and trace organics using the intertidal mussel *Perna viridis* in hong kong coastal waters. *Mar Pollut Bullet.* 51,857-875.

Maanan M (2008) Heavy metal concentrations in marine mollusks from the Moroccan coastal region. *Environ Pollut* 153,176-183.

Nicholson S and PKS Lam (2005) Pollution monitoring in southeast Asia using biomarkers in the mytilid mussel *Perna viridis* (*Mytilidae*: bivalvia). *Environ Intern.* 31,121-132.

Pendias, K.A. and Pendias, H. (2001) Trace elements in soils and Plants. 3rd edition, CRC Press, Boca Raton, London, New York, Washington, D.C., USA, 388 pp.

Rainbow PS (2006) Biomonitoring of trace metals in estuarine and marine environments. *Aust J of Ecotoxic.* 12:107–122.

Shulkin VM, BJ Presley and VI Kavun (2003) Metal concentrations in mussel *Crenomytilus grayanus* and oyster *Crassostrea gigas* in relation to contamination of ambient sediments. *Environ Intern.* 29,493-502.

Szefer P, K Frelek, K Szefer, CB Lee, BS Kim and J Warzocha (2002) Distribution and relationships of trace metals in soft tissue, byssus and shells of *Mytilus edulis* trossulus from the southern Baltic. *Environ Pollut.* 120,423–444.

Vlahogianni M, M Dassenakis, MJ Scoullos and A Valavanidis (2007) Integrated use of biomarkers (superoxide dismutase, catalase and lipid peroxidation) in mussels *Mytilus galloprovincialis* for assessing heavy metals' pollution in coastal areas from the Saronikos Gulf of Greece, *Mar Pollut Bullet.* 54, no. 9:1361-1371.

Wang, H., and Guo, X. (2008) Identification of Crassostera Ariakensis and related oysters by multiplex species PCR.Journal of shellfish research, V.27, NO.3, pp-481-487.

Zorita I, M Zarragoitia, M Soto and P Gajaraville (2006) Biomarkers in mussels from a copper site gradient (Visnes,Norway) an integrated biochemical, histochemical and histological study. *Aquat Toxic.* 78,109-116.

تقييم تلوث السواحل العراقية باستخدام اصداف الرخويات البحرية والمدية

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المستخلص

تم اجراء التحاليل الجيوكيميائية للرسوبيات واصداف الرخويات كراسوستريا كوكولاتا (بيئة مدية) وكوينو كاليفورنانس (بيئة بحرية) اضافة الى دراسة هيدروكيميائية المياه لغرض تقييم تلوث بيئة السواحل العراقية – شمال الخليج العربي.

جمعت عينات الرسوبيات والاصداف والمياة في فترت المد الواطي (الجزر) للفترة من اذار الى اب 2011 من سبعة محطات هي (الفداغية وراس البيشة ووخور عبد الله وخور شيطانة وجزيرة حجام وخور الزبير وشط البصرة) .

ان تحليل نسيج الرسوبيات للمحطات (الفداغية وراس البيشة ووخور عبد الله وشط البصرة) اظهرت بانها من تصنيف الطين الغريني اما محطات (خور شيطانة وجزيرة حجام وخور الزبير) فاظهرت بانها من تصنيف الطين الغريني الرملي.

بينت الدراسة الهيدروكيميائية بان هناك ثلاثة انطقة لملوحة المياة الاول لمحطات (الفداغية وشط البصرة) حيث كانت الملوحة (15148-18130ppm) والثانية لمحطة راس البيشة حيث كانت الملوحة ,(34123-36521ppm) والثالثة للمحطات (خور عبد الله وخور شيطانة وجزيرة حجام وخور الزبير) حيث كانت الملوحة(39215-45220ppm) .

اظهرت فحوصات الاشعة السينية الحائدة بان صدفة كوينو كاليفورنانس مكونة من طبقتين الداخلية من معدن الاراكونايت والخارجية من معدن الكالسايت اما صدفة كراسوستريا كوكولاتا فكانت من طبقة واحدة من معدن الكالسايت .

وقد بينت التحاليل الجيوكيميائية بوجود علاقة موجبة بين ملوحة المياة ومكونات الاصداف الكيميائية ماعدا المكونات

(SiO_2, Al_2O_3, and P_2O_5) التي اظهرت علاقة سالبة مع ملوحة المياة .

لقد اظهرت المكونات الكيميائية (SiO_2%, Al_2O_3%, MgO %, Fe_2O_3 %, Co, Zn, Cr, Pb) لاصداف كوينو كاليفورنانس علاقة موجبة مع معدن الكالسايت بينما اظهرت المكونات الكيميائية (CaO %, P_2O_5 %, Na_2O %, K_2O %, Ba, Sr, Rb, Sr/Ca) علاقة موجبة مع معدن الاراكونايت.

ان التحاليل الجيوكيميائية و اختلاف نسبة نوعي المعادن الكاربونيتية (اي الكالسايت و الاراكونايت) في السواحل العراقية اظهرت بانها متعرضة الى مدى من التلوث وخاصة قرب ام قصر و جزيرة حجام وان استخدام اصداف الرخويات كراسوستريا كوكولاتا (بيئة مدية) وكوينو كاليفورنانس (بيئة بحرية) كان جيدا في تحديد هذا التلوث بدراسة بيئتها المائية حيث يمكن بناء موديل للتلوث في السواحل العراقية.