Marine Science Center-University of Basrah

Mesopotamian Journal of Marine Sciences
Print ISSN: 2073-6428
E- ISSN: 2708-6097
www.mjms.uobasrah.edu.iq/index.php/mms

Evaluation of levels of some heavy metals in marine environment, southern Iraq

iD **Salah M. Saleh**[1*], iD **Zuhair A. Abdulnabi**[2], iD **Alaa A. Mizhir**[1], iD **Abbas A. Hantoush**[2], iD **Wesal F. Hassan**[1] and iD **Dhafar Dh. Al-Khion**[2]

1-College of Marine Science, 2-Marine Science Center, University of Basrah, Basrah-Iraq

Corresponding Author *:e-mail:* salah.saleh@uobasrah.edu.iq

Article info.
- ✓ *Received:17 November 2021*
- ✓ *Accepted: 30December 2021*
- ✓ *Published:31 December2021*

Key Words:
Basrah governorate
Heavy metals
Iraq
Marine water

Abstract - Some toxic and essential heavy metals have been evaluated at five stations of the marine water region of Basrah governorate, southern Iraq. Eight of different elements (Pb, Zn, Ni, Mn, Fe, Cu, Cr and Cd) were measured at five stations from various regions these elements were collected by using water sampler at depth 20-25 cm in low tide at summer season in 2016. They have been analyzed using flame-atomic absorption spectrophotometer. The results of all measurements of heavy metals indicated the dominance zinc more than the other elements at St. 1 and St. 4 ranged from 0.144 to 0.193 mg/l, respectively. St. 2 and St. 5 exhibited the dominance of lead in the range between 0.164 and 0.253 mg/l, respectively. While, St. 3 showed the highest concentration of nickel compared with the other elements (0.190 mg/l). Standard deviation was calculated for all elements measured and were in the ranged or(0.008-0.049).

تقييم مستويات بعض العناصر الثقيلة في البيئة البحرية - جنوب العراق

صلاح مهدي صالح[1] وزهير علي عبد النبي[2] وعلاء عادل مزهر[1] وعباس عادل حنتوش[2]
ووصال فخري حسن[1] وظفار ظاهر الخيون[2]

1 - كلية علوم البحار، 2 - مركز علوم البحار، جامعة البصرة، البصرة-العراق

المستخلص- قيست مستويات ثمان من العناصر الثقيلة ذات الخصائص الضرورية والسامة في خمس محطات في المياه البحرية العراقية وهي (الرصاص والزنك والنيكل والمنغنيز والحديد والنحاس والكروم والكادميوم) والتي جمعت من المياه السطحية وبعمق 20 -25 سم باستخدام جهاز جمع عينات المياه في حالة الجزر في فصل الصيف من عام 2016 . حللت جميع العناصر باستخدام جهاز الأمتصاص الذري اللهبي. وقد أظهرت النتائج زيادة في تركيز عنصر الزنك في محطتي St.1 و St.4 عند مقارنته مع مستويات العناصر الأخرى حيث بلغا 0.144 و 0.193 ملغم/لتر على التوالي. كما سجل عنصر الرصاص ارتفاعاً عن بقية العناصر في محطتي St.2 و St.5 حيث بلغا 0.164 و 0.253 ملغم/لتر على التوالي. بينما أظهرت محطة St.3 تركيز أعلى للنيكل عند مقارنته مع تراكيز العناصر الأخرى إذ بلغ 0.190 ملغم/لتر. حسب الأنحراف المعياري لجميع العناصر حيث أظهر بمدى (0.049-0.008).

الكلمات المفتاحية:

Introduction

Although, the heavy metals existed in the earth crust with different ratios, they can occur in biological system as necessary metals such as Fe, Se, Zn, Mn, …. etc. with allowable limits for each organism which need them, accordingly increasing or decreasing of these elements cause lots of diseases for humans, they can damage and alter the function of organs such as the brain, kidney, lungs, liver, and blood (Skinner and Jahren, 2007; Montevecchi, 2018; Karcioglu and Arslan, 2019).

DOI: https://doi.org/10.58629/ mjms.v36i2.250

Anglers' lead weights and hunters' lead shot are both important causes of pollution. Lead poisoning has been blamed for the deaths of swans, marine waterfowl, and seabirds in estuaries and inshore environments, where it lead concentrations are high. This high rate of mortality has stimulated public interest, culminating in the gradual replacement of lead with benign alternatives (although too slowly). Environmental lead levels can be determined via blood and enzyme tests.

Recently, heavy metals and with the development of industry have become critical problems facing aquatic environment because these elements are regarded toxic at low concentration, their ability to insert into the food chain by accumulating in the aquatic organisms such as plant, fish, … etc, and their persistence because they have slow rates of removal (Abdulnabi, 2016).

There are two major sources of heavy metals in the aquatic environment of southern Iraq, natural and anthropogenic (Abdulnabi *et al.*, 2019; Alhello *et al.*, 2020). Natural sources can attribute to natural processes such as fly ash, degradation of biota in water after death, corrosion of the earth crust by weathering, volcanoes, floods and forests fire.

Besides there are many human activities can provide the environment with trace elements such as agriculture activities, for example irrigation and fertilization, petroleum activities by exporting and importing or refinement of oil, mining, discharging the industrial wastes of without treatment and domestic effluents as well as marine navigation activities all these processes represent anthropogenic sources (Hassan *et al.*, 2008 and 2021; Al-Imarah *et al.*, 2015; Al-Khuzie *et al.*, 2021).

In addition, the sediments at the bottom of the water body can play a major role by their ability to accumulate the elements and different types of pollutants, so they can be a source of these elements specially when physicochemical factors changed which help in the release of these elements to the overlying water column (Hassan *et al.*, 2008). Factors like temperature, velocity of water, pH, Eh ionic strength, fine sediment particles, increases the release of heavy metals to the water environment particularly when the surface of sediment is filled with heavy metals and the concentration of them less in the overlying water column (Davis *et al.*, 1991; Karbassi *et al.*, 2005; Al-Atbee, 2018; Hassan, 2018). The aim of this present study is focused on the estimation of some heavy metals in an important regional water of Iraq which considered as marine navigation road (trading and export oil) between Iraq and Iran, and between Iraq and Kuwait. Besides this area is very important fishing ground.

The study stations are located in an important area of Iraqi Marine region. Increasing marine navigation with increases trading processes that including different materials especially production of oil industry. Oil spill is one problem that uncounted this area. Moreover, this region also well known as an increasing ground of fishing operations. These stations were distributed as follows: St. 1 is located close to the estuary of Shatt Al-Arab and the others St. 2-St. 5 are distributed with increasing depth in Khor Abdullah towards Al-Kuwait (Fig. 1).

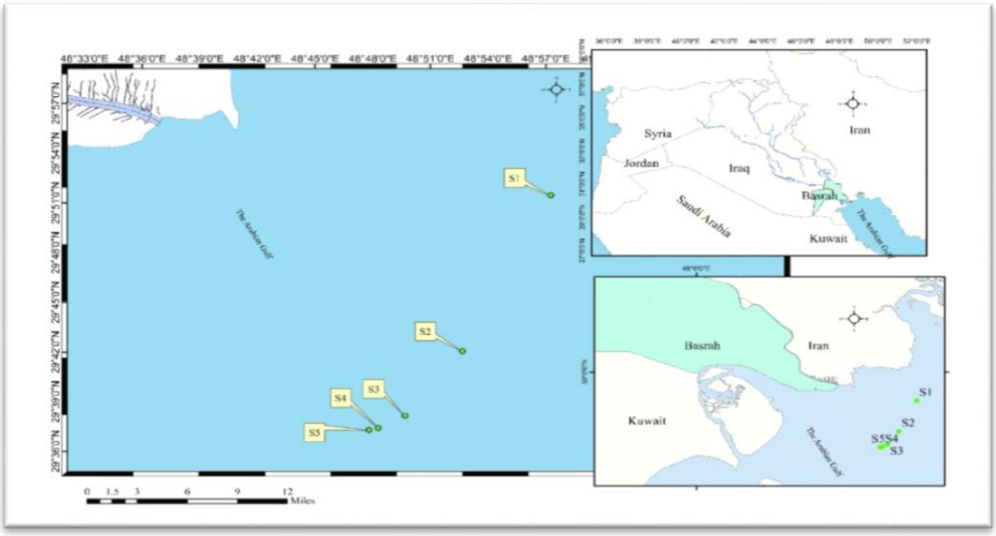

Figure1. Location of sampling stations at the south of Iraq.

Materials and Methods

Five liters of water were collected from five stations at the Iraqi marine region by using water sampler each of the at a depth (20-25) cm from water surface at low tide. All samples were gathered in polyethylene containers. These samples were directly acidified with nitric acid (65%, supplied from J.T. Baker) to regulate the pH<2 for minimizing precipitation and adsorption of metals on container walls, afterward the samples were transferred into laboratory and preserved at 4^0C in fridge to avoid reducing in volume by evaporation (APHA, 1999).

The laboratory, digestion has been done by taking 100 ml of the marine water sample in a beaker and added to it 5 ml of concentrated nitric acid and a glass watch was used as a cover to the beaker. The solution in the beaker was heated by a hot plate to near drying, then added 5 ml from same acid to insure the of digestion the completion by heating it again to near drying, after that the volume was completed to 50 ml by deionized water and kept in polyethylene bottle (APHA, 1999 and Al-Shmery, 2013). Finally the analyses was conducted by atomic absorption instrument type AA7000, Shimadzu, Japan.

Results and Discussion

The results of lead concentrations shown in Table (1) and Figure (2). The lowest value of lead was recorded at St. 4 and St. 1, while the highest value was recorded at St. 5. The results also showed a significant differences of Pb concentrations between stations. These may due to increase of marine navigation in this area which represents on important navigation path between Iraq and Kuwait (Abdulnabi, 2016; Abdulnabi *et al.*, 2019). Also higher levels at sea surface reflect the effect of increased lead emissions, as this region is characterized by high petroleum extraction activities.

According to Tagliabue (2018) most countries have phased out leaded gasoline, lead now has a unique look, defined by an average water maximum driven by high amounts of lead in the atmosphere when this mass of water was at the surface. pH levels and dissolved salt contents had effect on the solubility of lead in the surface water, when the pH>5.4 with the presence some ions such as SO_4^{-2} , CO_3^{-2} , OH^{-1} and Cl^{-1} the solubility of lead become limited because some species of lead are formed, like $PbSO_4$, $PbCO_3$, $Pb(OH)_2$ and $Pb(Cl)_2$.

Table 1. The concentrations of heavy metals (mg/l) at the Arabian Gulf study during Summer in 2016.

Station	Pb	Zn	Ni	Mn	Fe	Cu	Cr	Cd
$S_{t\,1}$	0.1391	0.1443	0.1333	0.0209	0.0784	0.0112	0.0423	0.0041
St_2	0.1639	0.0694	0.1105	0.1502	0.066	0.0112	0.0423	0.0038
St_3	0.1739	0.1604	0.1903	0.0772	0.1215	0.0306	0.1759	0.0087
St_4	0.1341	0.1927	0.1345	0.0743	0.0858	0.0097	0.069	0.0035
St_5	0.2533	0.0931	0.1812	0.0731	0.1171	0.0097	0.0913	0.033
Mean	0.1728	0.1319	0.1499	0.0791	0.0937	0.0144	0.0841	0.0106
S.D	0.0428	0.0448	0.0305	0.0412	0.0218	0.008	0.0493	0.0113
S.E.	0.0214	0.0224	0.0153	0.0206	0.0109	0.004	0.0247	0.0057
$t_{\text{at } p \leq 0.05}$	8.062	5.881	9.806	3.838	8.587	3.581	3.407	1.871
Sig. (2-tailed)	0.001	0.004	0.001	0.018	0.001	0.023	0.027	0.135
[1]WHO 2011	4	0.01	0.07	0.1	0.3	2	0.05	0.003
[2]CGL 2014	≤5	0.01	-	≤0.05	≤0.3	≤1	0.05	0.005
[3]IQS 2001	3	0.01	0.02	0.1	0.3	1	0.05	0.003

[1]WHO: World Health organization.
[2]CGL: Canadian guidelines.
[3]IQS: Iraqi Standard limits.

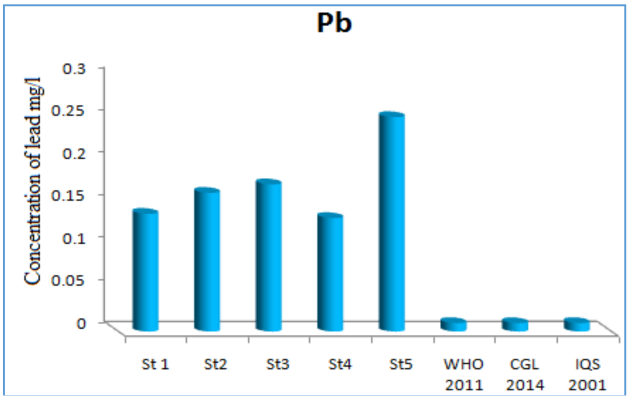

Figure 2. Concentration of Lead in selected sites of the Arabian Gulf during Summer in 2016.

Zinc concentration levels showed the lowest values than the global and local environmental limits at all the selected stations. The results indicated significant differences of Zn concentration between the 5 stations (Table 1 and Fig. 3). Zinc is an important metal because its existence in the biological system of all organisms, many reactions of metalloenzyms used Zn as a catalyst such as Leucine amino peptidase, alcohol dehydrogenises, alkaline phosphates, carbonic anhydrates and superoxide dismutase (ATSDR, 2005).

The main oxidation state of Zacin is (II) which exhibited amphoteric features, where Zn and its compounds dissolved in ds the form hydrate of Zn^{2+} cations, whereas they form zincate anions in strong base which are $[Zn(OH)_3]^-$, $[Zn(OH)_4]^{2-}$ and $[Zn(OH)_4(H_2O)_2]^{-2}$ (EPA, 1979; O’Neil *et al.*, 2001).

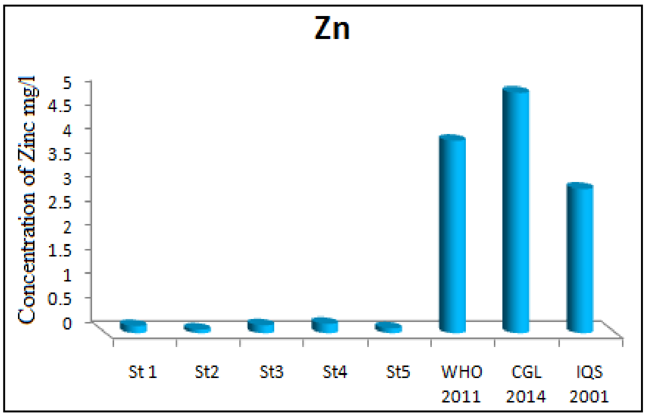

Figure 3. Concentration of Zinc in the selected sites of Arabian Gulf during Summer in 2016.

The concentration of nickel exhibited significant differences between the different stations. The highest concentrations were recorded 0.1903 mg/l and 0.1812 mg/l at St. 3 and St. 5, respectively, while the lowest mean in St. 2 0.1105 mg/l. The high nickel levels may attributed to spills of oil in this region through gathering different ships before loading and unloading in their ports (Abdulnabi, 2016). All stations showed highest levels when compared with global and local limits, the data of nickel levels are shown in Table (1) and Figure (4).

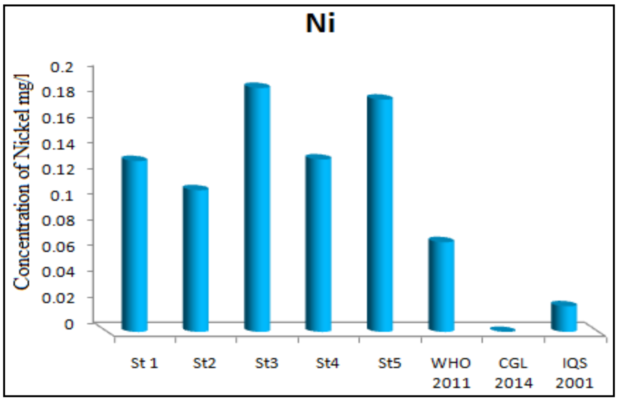

Figure 4. Concentration of Nickel in selected sites of Arabian Gulf during Summer in 2016.

Manganese levels have significant differences between stations. The highest mean was at St. 2 due to their directly effect the Shatt Al-Arab River, on the other hand the lowest concentration was recorded at St. 1 (0.0209 mg/l). All stations showed levels of manganese within the allowable limits excluding the St. 2 (Table 1 and Fig. 5).

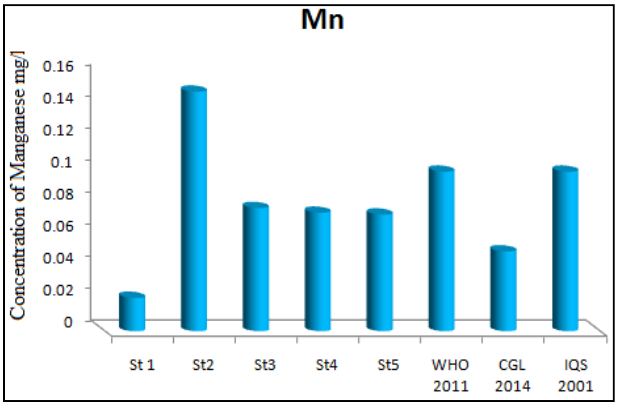

Figure 5. Concentration of Manganese in the selected sites of Arabian Gulf during Summer in 2016.

The results showed significant differences of Fe concentration between stations. The highest concentration of total Iron was at St. 3 (0.1215 mg/l). Whereas, the St. 2 exhibited the lowest mean (0.066 mg/l). The concentration of Iron increased at St. 3 and St. 5 which may be attributed to the presence different immersed iron bodies in this area (Abdulnani *et al.*, 2016). Iron has the fourth domination among the elements. All measurements of Iron at all selected station are within the international regulation limit like IQS (2001), WHO (2011) and CGL (2014) (Table 1 and Fig. 6).

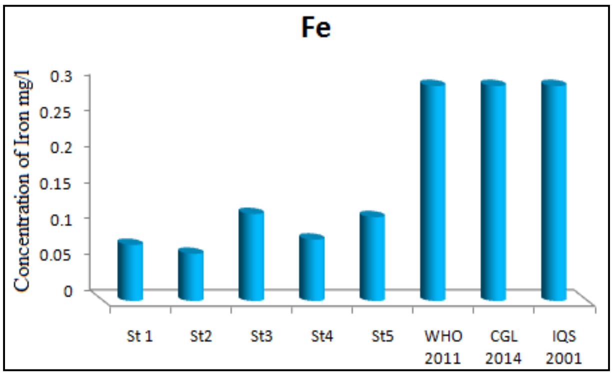

Figure 6. Concentration of Iron in the selected sites of Arabian Gulf during Summer in 2016.

The results of copper concentration showed significant differences between the different stations. The highest mean was recorded at St. 3 and lowest mean at St. 4 and St. 5. Furthermore, all values of copper at all chosen stations are within the allowable limits when compared with global and local limits. The data of copper levels in the marine region of Iraq is given in Table (1) and Figure (7). Copper is one of the elements that had toxic properties in aquatic system when their concentration was above the allowable limits. Moreover, some aquatic organisms had capability of accumulation copper in their body tissue such as fishes which are consumed by human being and causes many risks of health human (Abdulnabi, 2020).

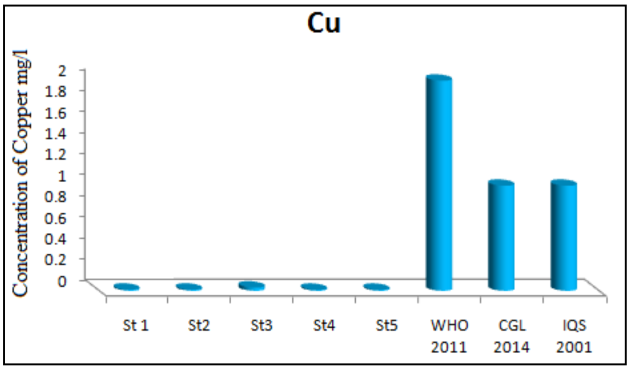

Figure 7. Concentration of Copper at selected sites in Arabian Gulf during Summer in 2016.

The results of Cr concentration showed significant differences between stations. St. 3 had the highest concentration of chromium (0.1759 mg/l) than all the other selected stations that may be attributed to spills of oil as region which represent an important navigation canal between Kuwait and Iraq. Moreover, the oil ports are found in this area. The lowest value of chromium concentration was recorded of St. 1
and St. 2 as well as these stations had values the international regulation, while the other stations had values higher than the global and local limits. All the measurements of chromium are listed at Table (1) and Figure (8). Meanwhile chromium is one of the elements that had toxic properties and has three oxidation state Cr^0, Cr^{3+} and Cr^{6+}.
In addition, it is found in the aquatic system by organic and inorganic forms, the well-known of chromium organic compounds have effect less toxic than chromium inorganic compounds, on other hand the oxidation state Cr (IV) has high toxic properties when compared with other oxidation states.

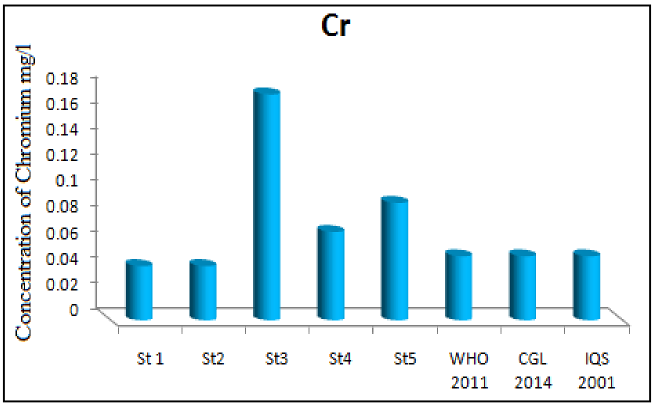

Figure 8. Concentration of Chromium in selected sites Arabian Gulf during Summer in 2016.

There are no significant differences of Cd concentration between the different stations. The data of concentration levels of cadmium in the marine waters of Iraq indicated on elevate on at St. 5 (0.033 mg/l), while there was decreased concentration of cadmium at St. 4 about (0.0035 mg/l). However, the results of cadmium in marine environment of Iraq were compared with those of the international regulation levels and showed that some stations had levels approximately within the allowable limits, while others had high values such as St. 3 and St. 5 (0.0087 and 0.033 mg/l, respectively). The data of cadmium measurements are shown in Table (1) and Figure (9).

Cadmium is unessential elements with toxic effect and some of its compounds have ability to dissolve in water and caused an increase of cadmium in the aquatic system. Besides, it has accumulation properties in the tissue of organisms which then transferred to human though the food chain, hence it caused risk to human health (Abdulnabi *et al.*, 2019).

Cadmium (Cd^{2+}) oxidation state and its complexes such as cadmium hydroxide and cadmium carbonate are predominate in the aquatic system. Virtually, some of cadmium compounds are insoluble in water for example cadmium oxide, cadmium sulfide and cadmium carbonate, but when some conditions are changed like acid, interaction of ligand or oxygen, they changed their state and become soluble (Mc-Comish and Ong, 1988; IARC, 1993). Moreover, the salinity has impact on increasing the cadmium chloride and its species [$CdCl^+$, $CdCl_2$, $CdCl^-{}_3$] especially in sea water. In addition, cadmium may be deposited as cadmium sulfide when the sulfide ion is present (Mc-Comish and Ong, 1988).

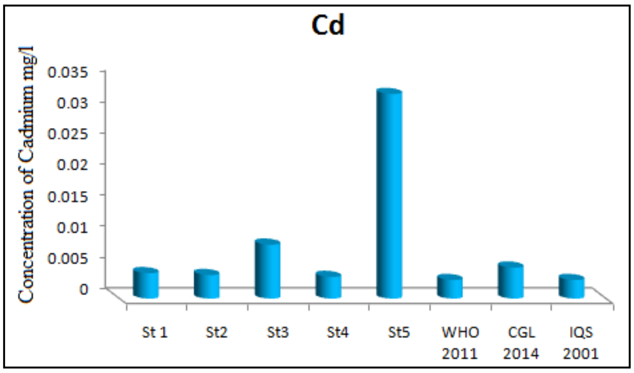

Figure 9. Concentration of Cadmium in selected sites of Arabian Gulf during Summer in 2016.

Conclusions

Eight of the heavy metals were found in marine region of Iraq where, the elements were introduced in the marine environment by two ways as natural sources and anthropogenic sources, the results were compared with international guidelines such as IQS (2001), WHO (2011) and CGL (2014) and showed that all the metals were within permissible limits excepted some heavy metals like lead, nickel and chromium. The data of cadmium and lead were approximately consistent with those of Abdulnabi *et al.* (2019) study that obtained at the same region. The metals were ordered according to the increase of their concentrations and showed as follows:

St. 1 showed the highest value of zinc concentration and lowest value of cadmium and they were ordered as Zn>Pb>Ni>Fe>Cr>Mn>Cu>Cd, while at St. 2 they were form of Pb>Mn>Ni>Zn>Fe>Cr>Cu>Cd. The concentration of nickel was high concentration at St. 3 when compared with the other of heavy metals, and was in the order of Ni>Cr>Pb>Zn>Fe>Mn>Cu>Cd. St.4 exhibited approximately order of heavy as that of metals St. 1, Zn>Ni>Pb>Fe>Mn>Cr>Cu>Cd, while the concentration of these elements at St. 5 were Pb>Ni>Fe>Zn>Cr>Mn>Cd>Cu.

Elements like Al, Fe and Cu are classified as hybrid elements which have a vertical profile that is a combination of nutrient-like and scavenged profile. This behavior occurs as a result of horizontal and vertical variation; At the deepest waters, iron nutrient-like activity gives place to loss owing to scavenging, while element like Pb is classified as an Anthropogenic or transitory elements frequently exhibit behavior similar to that of nutrient-like, scavenged, or hybrid elements, but their signature is temporally variable. Although lead has a scavenged profile, emissions from leaded gasoline have increased the upper ocean concentrations. Surprisingly, due to the widespread phase-out of leaded gasoline, lead now has a unique profile, with an intermediate water maximum caused by greater atmospheric lead levels while this water mass was at the surface. Reduced lead emissions have resulted in lower levels at the ocean's surface (Tagliabue, 2018).

References

Abdulnabi, Z.A. 2016. Assessment of some toxic elements levels in Iraqi marine water. Mesopot. J. Mar. Sci., 31(1): 85-94.URL

Abdulnabi, Z.A. 2020. Assessment of free and total cyanide levels in the water environment of Shatt Al-Arab. Indones. J. Chem., 20(4): 880-886.https://doi.org/10.22146/ijc.47369

Abdulnabi, Z.A., Al-Khuzaie, D.K.K., Jarallah, H.M., Hassan, W.F. and Saleh, S.M. 2016. Evaluation of selenium and iron levels in Shatt Al-Arab sediment and the Iraqi Marine environment. Ind. J. Nat. Sci., 6(34): 10475-10482. URL.

Abdulnabi, Z.A., Altememi, M.K., Hassan, W.F., Al-Khuzaie, D.K.K. and Saleh, S.M. 2019. Assessing of Some Toxic Heavy Metals Levels and Using Geo Accumulation Index in Sediment of Shatt Al-Arab and the Iraqi Marine Region. Baghdad Sci. J., 16(2): 323-331.URL

Al-Atbee, R.S.K. 2018. Assessment of some heavy metals and hydrocarbons in water, sediments and dominate aquatic plants at Al-Chibayish marshes. M.Sc. Thesis, University of Basrah, Iraq.URL

Alhello, M.A., Al-Khuzie, D.K., Saleh, S.M., Alhello, A., Al-Saad, H. and Hassan, W.F. 2020. Heavy metals indices in Shatt Al-Arab river, Basrah province, Iraq. I: sediments. Poll. Res., 39: S14-S19.URL

Al-Imarah, F.J.M., Al-Saad, H.T., Al-Hillo, A.A., Al-Mudhafar, N.A. and Saleh, S.M. 2015. ICP detection of chemical elements in the sediments along Shatt Al-Arab estuary and Khor Abdullah/southern Iraq. Int. J. Environ. and Water, 4(4): 11-18.URL

Al-Khuzie, D.K.K., Al-Hatem, Z.A., Shabar, H.A., Hassan, W.F. and Abdulnabi, Z.A. 2021. Heavy metal distribution in grain size fraction in surface sediments: pollution assessment of Iraqi Coasts. Eco. Environ. & Cons., 27: S388-S398.URL

Al-Shmery, A.Y.H. 2013. Estimation of some heavy metals in clams, sediments and water from Shatt Al-Arab and treatment rocks porcellanite. M.Sc. Thesis, University of Basrah, Iraq.URL.

APHA, Standard Methods for the examination of water and wastewater 1998. Ed^{20th}, American Public Health Association.URL

ATSDR (Agency for Toxic Substances and Disease Registry) 2005. Toxicological profile for zinc.URL

CGL 2014. Guidelines for Canadian Drinking Water Quality-Summary Table, Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.

Davis, C.A., Tomlinson, K. and Stephenson, T., 1991. Heavy metals in River Tees estuary sediments. Environ. Technol., 12: 961-972.https://doi.org/10.1080/09593339109385095

EPA. (Environmental Protection Agency), 1979. Water-related environmental fate of 129 priority pollutants. Washington, DC: U.S. Environmental Protection Agency, Office of Water Planning and Standards.URL

Hassan, I.F., Al-Khuzaie, D.K.K., Kzaal, R.S., Hassan, W.F. and Abdulnabi, Z.A. 2021. Spatial and temporal distribution of heavy metals in dust fallout in Basra city/Iraq. IOP Conf. Series: Earth and Environmental Science, 779: 1-7.DOI 10.1088/1755-1315/779/1/012070

Hassan, W.F. 2018. Metal contamination in the sediments of tidal flat for Iraq costal. International Journal of Science and Research, 7(3): 120-125.URL

Hassan, W.F., Albadran, B.N. and Faraj, M.A. 2008. The geochemical distribution of trace metals in Shatt Al-Arab river sediments. Marina Mesopotamica, 23(2): 419-436.URL

IARC. 1993. Cadmium and certain cadmium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Beryllium, cadmium, mercury and exposures in the glass manufacturing industry. IARC monographs, Vol. 58. Lyon, France: World Health Organization. International Agency for Research on Cancer, pp: 119-236.URL

IQS (The Iraqi Standards for Drink Water) 2001. Iraqi Legislation. No. 417.

Karbassi, A.R., Nabi-Bidhendi, GH.R. and Bayati, I. 2005. Environment geochemistry of heavy metals a sediment core of Bushehr, Persian Gulf. Iran. J. Environ. Health. Sci. Eng., 2(4): 255-260.URL

Karcioglu, O. and Arslan, B. 2019. Poisoning in the Modern World-New Tricks for an Old Dog? Mechanism and Health Effects of Heavy Metal Toxicity in Humans. 10.5772/intechopen.73906(Chapter 5). doi:10.5772/intechopen.82511

Mc-Comish, M.F. and Ong, J.H. 1988. Cadmium. In: I. Bodek, W.J. Lyman, W.F. Reehl, *et al.*, eds. Environmental inorganic chemistry: Properties, processes, and estimation methods. New York, Pergamon Press, 7.5-1 to 7.5-12.URL

Montevecchi, W.A. 2018. Reference Module in Earth Systems and Environmental Sciences Seabirds as Indicators of Ocean Pollution. doi:10.1016/B978-0-12-409548-9.10821-8

O'Neil, M.J., Smith, A., Heckelman, P.E. 2001. Merck index. 10th ed. Rahway, NJ: Merck & Co., Inc.URL

Skinner, H.C.W. and Jahren A.H. ٢٠٠٧. Biomineralization. pp: 1-69.https://doi.org/10.1016/B0-08-043751-6/08128-7

Tagliabue, A. 2018. Reference Module in Earth Systems and Environmental Sciences Elemental Distribution: Overview. doi:10.1016/B978-0-12-409548-9.10774-2

WHO 2011. Guidelines for Drinking Water quality. 4th ed., Switzerland.URL