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Assessment of some toxic elements levels in Iraqi marine water

Z.A. Abdulnabi
Marine Science Center, University of Basrah, Basrah, Iraq
e-mail: zuhir38@yahoo.com

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Abstract - Two methods were used for the determination of four toxic elements (mercury, arsenic, cadmium and lead) in the Iraqi marine waters. Water samples were collected from eight stations along the Iraqi marine waters. Three stations were selected from nearby zone of the Fao city in southern of Iraq towards Khor Abdullah, these regions were considered as an important navigation line on one hand between Iraq and Iran and on the other hand between Iraq and Kuwait. The other five stations were extended between Umm Qasr port towards Khor Al-Zubair port while the last station was selected from the nearby zone for confluence zone between Khor Al-Zubair port and Shatt Al-Basra canal. All the samples were collected during low tide at depth of 10 cm from surface water. Mercury and arsenic were analyzed by ICP instrument while lead and cadmium were determined through using Atomic absorption spectroscopy (AAS). The recorded data of the total concentration for all the elements have shown the average of concentration as follows: 0.0060 mg/l, 0.0765 mg/l, 0.0518 mg/l and 0.9229 mg/l for metals mercury, arsenic, cadmium and lead respectively. Moreover, some physico-chemical properties of water were recorded in these stations.

Keywords: ICP analyses, AAS analyses, physico-chemical properties, toxic elements and marine waters.

Introduction

Heavy metals exist naturally in water through two phases dissolved and particulate. They are considered as the constant and stable pollutants in the environment and causes a lot of healthy risk for many organisms in the ecosystem because they have toxic properties with higher concentrations then the allowed limits and their ability on the accumulation (Mwashote, 2003; Salman *et al.*, 2015). Heavy metals are entered into aquatic system *via* several activities which was divided into natural and anthropogenic such as forest fires, volcanoes, erosion of rock, mining, combustion of fossil fuel, domestic effluents, untreated industrial effluents, movement of wind, rain water, waste incineration and agricultural activities (Al-Imarah *et al.*, 2015; Mahdi, 2015; Sylaios *et al.*, 2012; Kokali *et al.*, 2015).

Additionally, the concentration of heavy metals in water was affected by many conditions such as pH, conductance, redox-oxidation potential and mutual interaction between sediment with water because it was represented as an important reservoir for many heavy metals through accumulation operations in various conditions (Balasim, 2013; Al-Khuzaie, 2015).

Arsenic in sea water exist through the four species (arsenate (As^{5+}), arsenite (As^{3+}), monomethylarsinate and dimethylarsinate) these species represent the total concentration for arsenic in sea waters while mercury exist in the waters in different dissolved forms, the most inorganic and organic mercury compounds appear to be associated with particles, colloids and high-molecular organic matter through the coordination with sulphur ligands (UNEP, 1988). Cadmium exist almost as chloride species ($[CdCl]^+$, $CdCl_2$, $[CdCl_5]^{3-}$) and also their ability for complexes formation with chloride ion was increased through increasing of salinity and especially in sea water, while the lead species in water are different between fresh water and sea water, these species depend on pH value for water which in acidic waters the lead was existed as the divalent cation (Pb^{2+}) and forms $PbCO_3$ and $Pb(OH)_2$ under alkaline conditions. Moreover, the lead species in seawater can be described as a function for chloride concentration in water and can exist as follows $[PbCl_5]^{3-} > PbCO_3 > PbCl_2 > [PbCl]^+ >$ and $Pb(OH)^+$(UNEP, 2010a; UNEP, 2010).

Experimental Part

Description of Study Area

Eight stations were chosen extending along the Iraqi marine waters from various regions in southern of Basra governorate and distributed as follows three stations (W_1-W_3) were chosen from nearby zone of the Fao city towards Khor Abdullah, this areas are considered as an important navigation road between Iraq and Iran on one hand and between the Iraq and Kuwait on the other hand and five sites (W_4-W_7) were collected from different regions beginnings from nearby zone of the Umm Qasr port towards Khor Al-Zubair port. This area is important in marine navigation for large number and different loads of oil and commercial ships where they pass through it to the Arabian gulf (Abdulnabi, 2015).

The last station (W_8) was selected from the nearby zone of confluence zone between Khor Al-Zubair port and Shatt Al-Basra canal. All the samples were collected during Winter season, December 2014 by water sampler instrument at depth 10-15 cm from surface water. The physico-chemical parameters of water such as pH, electric conductivity EC, temperature of water and total dissolved solid (TDS), dissolve oxygen (DO), Turbidity and oxidation-reduction potential ORP were measured in the field and the results were compared with some world limits such as World Health Organization (WHO, 2011), European Communities (EC, 1998), Canadian Drink Water Guidelines (CGL, 2014) and Iraqi Standard (IQS, 2001).

All samples were collected in polyethylene containers (Abdulnabi, 2015) and preserved under cooling and then all the samples were transferred immediately to the laboratory for digestion and analyses. The results are shown in Table (1) and the chosen sites in southern of Basra governorate-Iraq as shown in Figure (1).

Materials and Methods

All the samples were collected by water sampler instrument at depth 10-15 cm from surface water and the physico-chemical properties were measured in field by multi meter type, Horiba, model U-5030, then samples were preserved directly through acidifying the samples by using nitric acid (65 %, obtained from Scharlau) in order to adjust of pH solution for the sample at $pH<2$, after that they are transferred immediately to the laboratory and kept in a refrigerator at 4 °C to prevent change in volume due to evaporation (APHA, 1999). All the samples were prepared for digestion and measurement operations through transferred 100 ml from sample to beaker then adding 5 ml of nitric acid to solution and also by using watch glass as cover above it, after that the solution was put on hot plate (almost to dry) and once

Table 1. Physico-chemical properties of selected water samples.

Station	pH	Water Temp. (°C)	Salinity (ppt)	TDS (mg/l)	EC (mS cm^{-1})	EC (mScm^{-1}) at 25 °C	Tur. (NTU)	DO (mg/l)	ORP (mV)
W_1	8.47	19.11	42.5	38000	63.3	71.32	12.1	7.91	163
W_2	8.83	19.5	44.4	39500	65.8	73.52	7.5	8.13	110
W_3	8.38	17.81	41.1	36900	61.6	71.40	159	7.87	176
W_4	8.68	27.33	43	38200	63.6	60.89	142	5.60	78
W_5	8.40	26.90	38.1	34300	57.1	55.10	64.5	6.64	133
W_6	8.24	26.46	35.1	31900	53.1	51.65	40.8	6.60	158
W_7	8.49	26.37	36.8	33200	55.5	54.08	72.7	9.40	143
W_8	8.40	27.23	27.7	26400	43.1	41.33	93.3	6.43	122
WHO 2011	6.5-8.5	-	-	1000	-	-	-	-	-
CGL 2014	6.5-8.5	-	-	500	-	-	1	-	-
EC 1998	6.5-9.5	20	-	1500	2.5	-	1	-	-
IQS 2001	6.5-8.5	-	-	1000	-	-	5	-	-

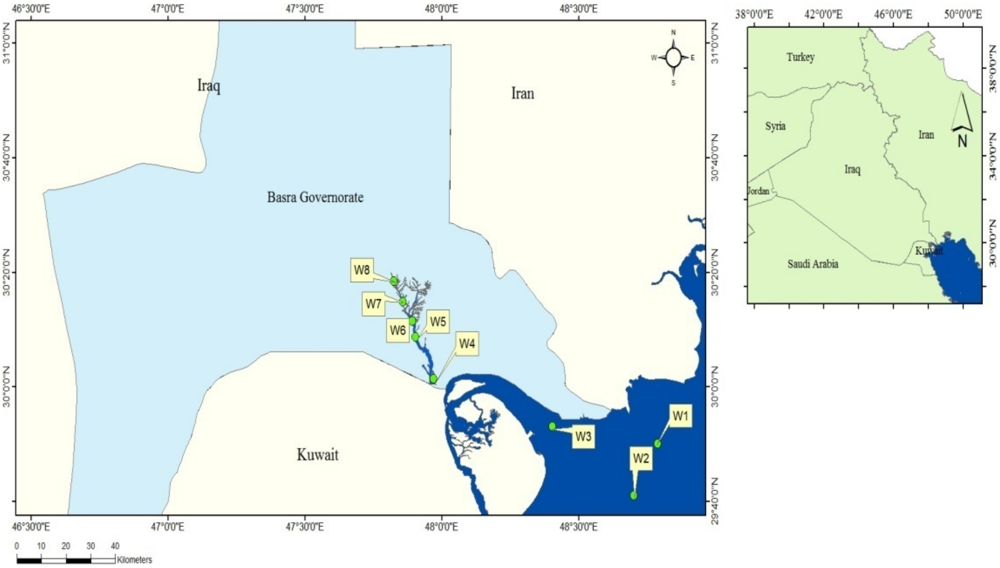


Figure 1. Locations of the samples selected in southern of Iraq.

again 5 ml from nitric acid was added in order toemphasize the completion of digestion operation, then complemented to 50 ml by deionized water and put in polyethylene containers (Alshmery, 2013).

Furthermore, a blank solution was used for all measurements of metals in order to obtain high accuracy of results. Total concentration of mercury and arsenic were measured by using ICP instrument type, ICP-OES HORIBA JY 2000-2, while the atomic absorption spectrometer type, Phoenix-q 86AA was used for measurement of total cadmium and lead. In addition to that, the standard curve method was used for calculated the concentration of metals.

Results and Discussion

Marine samples were selected along marine region of Iraq due to their importance as navigation roads between Iraq and Iran on one hand and between Iraq and Kuwait on the other hand. The physico-chemical properties of waters were measured directly in the field, the results are shown in Table (1). The data recorded for all the stations have shown the pH value at extent (8.24-8.83) and the highest value was recorded in station (W_2) while the lowest value was recorded in station (W_6), generally the marine water tend to behavior alkali, because of the existence of the carbonate system in water such as carbon dioxide, carbonic acid, bicarbonate ions and carbonate ions, this system was responsible for changing the value of pH in water (APHA, 1999).

The pH data was compared with some globally allowed limits for drink water, the results are within the acceptable limits by WHO (2011), (CGL, 2014) and the Iraqi standard (IQS, 2001) except stations (W_2) and (W_4) which were within the acceptable limits of (EC, 1998). Figure (2) shows the location areas of sampling stations. Electric conductivities are an important parameters for selected and knowledge of quality of water and uses, generally the electric conductivity for seawater are recorded the high values compared with freshwater because it consists of high concentration from different salts through several operations especially operations of rocks weathering (Fipps, 1996), conductivity for all samples were measured immediately in field and have recorded various values at range (43.1 mS /cm) in station (W_8) to (65.8 mS /cm) in station (W_2) and also this data was corrected value at 25 °C as shown in Table (1).

Additionally, the measurement of the value of total dissolved solid and salinity have recorded together the highest value in station (W_2) and lowest value in station (W_8) as follows (26.4-39.5 g/l) and (27.7-44.4 ppt) respectively. As well as an important parameters of water quality was turbidity which represents purities of water when in lowest value and also can be considered as an indicator to suspended matter in water (Mahdi, 2015). The turbidity value was recorded for all the stations and showed value at extent (7.5-159 NTU). Dissolve oxygen is one of an important parameters for many organisms in aquatic system, it is impacted through many source as change of temperature and increasing of various pollutants such as chemical and biological, when increasing organic pollutants leads to consumed dissolved oxygen which leads to decrease of its concentration in water therefore it will drive the lives of organisms to risk, furthermore when increasing of dissolved oxygen concentration in water leads to increasing of corrosion operations (WHO, 2011; Gautam, 2011). Dissolved oxygen was measured in the field directly and recorded range between (5.60-9.40 mg/l), this data was consistent with other environmental studies in southern of Iraq (Mahdi, 2015). Further, the oxidation-reduction potential (ORP) was measured, it is one of the important parameters especially in disinfection field for water. The oxidation-reduction potential was used as a measure for consuming dissolved oxygen in water.

Therefore, the lower values of ORP refer to the existence of contamination in aquatic system while the higher values of the ORP leads to more ability of water to destroy foreign contaminants such as microbes or contaminants that depend on carbon. Also from knowledge of ORP values can identify the reduction operation that occur for various oxidation states and it converted to metal (0) (APHA, 1999). The measurements of all samples were recorded and its showed at range (78-176 mV). This data refer to more contamination in station (W_4) because this region was an important commercial port, due to the many different loading and unloading operations that occur inside the port. Also in this study, the measurement of four toxic elements in marine environment of Iraq such as Mercury, Arsenic, Cadmium and lead was done by using two techniques ICP and AAS.

Mercury is one of the toxic elementthat exist in the environment, it was distributed in the lithosphere, hydrosphere, atmosphere and biosphere by many activities as natural and anthropogenic sources. The toxicity of mercury depends on its chemical state and some forms of mercury are relatively non-toxic and have been entered to contents of some drugs. Methyl mercury is the most toxic form of mercury as well as it has ability for accumulation especially in fish tissues, therefore it has reach to human through eating. Increasing of mercury levels that causes of many diseases as Minamata disease which causes mental disturbance, loss of balance, speech, sight and hearing difficulty in swallowing and degeneration of brain (UNEP, 1988; Morita*et al.*, 1998; Ahmed and Alam, 2003). Mercury in all samples were measured and recorded the highest value in station (W_3) while the lowest value in station (W_5) because the site (W_3) is an important navigation road between Iraq and Kuwait and many of different ships and various loads as oil and commercial ships pass through it. The station (W_4) and (W_7) recorded high value of mercury because these regions are commercial and contain the oil port while station (W_8) recorded the high concentration of mercury about 0.0068 mg/l which might be due to the release of the wastewater and industrial waste into Basra canal which was connected with station (W_8). The results are shown in Table (2) and Figure (2). This data was compared with globally allowed limits and shows that four stations are within the acceptable limits 0.006 mg/l for WHO (2011) while the other stations have recorded the highest value of it. Moreover, the concentration of mercury for all stations are higher than the allowed reported limits of 0.001, 0.001 and 0.002 mg/l by CGL (2014), IQS (2001) and EPA (2009) respectively.

Arsenic is an ubiquitous element that was found in the atmosphere, soils and rocks, natural waters and organisms, arsenic concentration in waters are shows various values from <0.5 to 5000 mg/l and depend on under natural conditions through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through many anthropogenic activities such as combustion of fossil fuels, domestic waste, industrial effluent, mining, farming, pulp and paper production, cement manufacturing, and also used some compounds of arsenic as Insecticides and herbicides (Panagiotaras *et al.*, 2012; Sindhu *et al.*, 2015). However, the presence of Iron oxyhydroxide in water works interaction with organic carbon and leads to release of arsenic to the environment (Panagiotaras *et al.*, 2012).

These activities leads to provide a nurturing environment for increasing concentration of arsenic. Arsenic can form both inorganic and organic compounds. It exists in nature in the oxidation states as arsine (-III), arsenic (0), arsenite (+III) and arsenate (+V). Nevertheless, the valence states of arsine and arsenic occur only rarely in nature also arsenite and arsenate constitute the dominant species in waters (UNEP, 1988; Panagiotaras *et al.*, 2012). Arsenic is one of toxic element and their toxicity depend on chemical form and state of valence moreover it has ability for accumulation in fish tissues and marine algae and thus it causes a lot of risks health for humans and animal that feeds them, arsenic compounds are classified as human carcinogen especially it causes lung cancers in humans and animals exposed by inhalation or via contaminated feeding (UNEP, 1988).

Arsenic of all samples for all selected stations were measured by using ICP technique, the data are shown in Table (2) and Figure (3) and showed concentration range of (0.057-0.112 mg/l) and the highest value was recorded in station (W_2) because this region undergoes continuous marine navigation as well as it can be described as gathering station for different loads of ships, furthermore the stations (W_1) and (W_4) recorded the high value when compared with all measurements except for station (W_2) because station (W_1) represents the estuary of Shatt Al-Arab and thus it can be loaded by various contaminations while station (W_4) is an important region as commercial port, after that, the concentration is decreased from station (W_4) towards station (W_6) and then also noted the increase of concentration value once again in station (W_7) because this area is an important port as commercial and oil port, also 0.057 mg/l was recorded in station (W_8) because this area is effected by fishing that may include the use of some arsenic compounds, on the other hand through the release of wastewater and industrial waste without treatment into Basrah canal which are connected with station (W_8), moreover arsenic is one of the metals that are considered as rich metals and exist in sewage sludge (Sindhu *et al.*, 2015).

The result of measurements of arsenic was compared with the globally allowed limits and showed the high values when compared with WHO (2011), CGL (2014), IQS (2001) and EPA (2009).

Cadmium and lead were measured in the waters of all stations after the selection, collection and digestion operations through using flame atomic absorption spectroscopy. Cadmium is a non-essential element and exist in environmental and also it was considered a rare element even though it was extensively distributed over the earth's crust (UNEP, 2010a). It has one oxidation state, Cd^{2+}, therefore it is usually found as a mineral combined with other elements such as oxygen, chlorine and sulfur in environment and it tends to complexe formation with chlorine in case of the increasing of salinity and especially it occur at clearly in seawater.

Cadmium is released by various natural and anthropogenic sources to the atmosphere, aquatic environments such as mining, farming, burning coal and household wastes, industrial effluents, erosion of rocks, mineral fertilizers and movement of wind (UNEP, 2010a; IARC, 1993). Cadmium is one of the toxic element that does not break down in the environment, but can change forms. Some cadmium compounds are soluble in water therefore they exist in low concentration in plant, animal, fish and bird and they have an ability of accumulation mainly in the kidneys and liver of vertebrates and in aquatic invertebrates and algae and thus they causes many risks on health of human and mainly affecting on kidneys and the skeleton because they have the ability of accumulation in bone and furthermore they form a carcinogen by inhalation (UNEP, 2010a). Cadmium in all samples were measured and recorded.

The total concentration at range between (0.045-0.066 mg/l), station (W_1) was recorded the highest value when compared with all measurements while the lowest value was recorded in stations (W_3) and (W_4). This may be attributed to carrying out dredge works in this area mainly because they are important regions as marine navigation roads and then because they are far from contamination sources as untreated domestic waste (WHO, 2011), while station (W_1) was affected by various pollutants and that loaded from Shatt Al-Arab. Additionally, station (W_8) also recorded high value when compared with all the measurements of stations except stations (W_1) and (W_6) because these stations are the confluence zone between Shatt

Al-Basrah and Khor Al-Zubair port, Shatt Al-Basrah canal was consider as drainage canal which contain untreated waste water where industrial waste was released directly towards the canal.

The results of cadmium measurements are shown in Table (2) and Figure (4). Also the data of cadmium concentration was compared with various globally allowed limits and showed higher values when compared with WHO (2011), CGL (2014), IQS (2001) and EPA (2009).

Lead exists in the environment naturally through three oxidation states Pb(0), Pb(II) and Pb(IV), the valence state (II) represent the main valence state of lead in water while the fourth oxidation state of lead may exist in water only in extreme conditions outside the environmental such as pH and oxidation-reduction potential, generally the fourth oxidation state for lead compounds as tetraethyl lead, it was extensively used as an antiknock agent in gasoline fuel (Nagbal, 1987; UNEP, 2010). The species of lead in water depend on pH value when being in acidic medium it tends to exist in forms such as Pb(II), $PbSO_4$ and $[PbCl]^+$, whereas in alkaline medium it tends for complexes formation with carbonate ($PbCO_3$), hydroxide $[PbOH]^+$ and organic matter (UNEP, 2010).

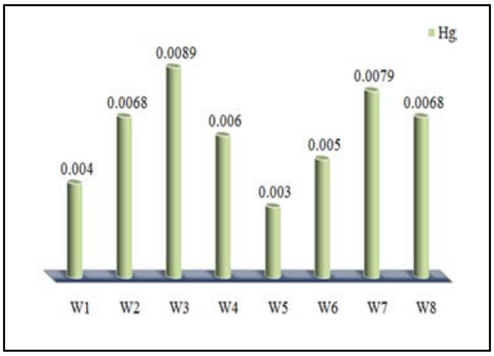
Lead is a non-essential and was considered as a toxic elements at very low exposure levels and it has ability on accumulation in most organisms, therefore the increase of lead concentration in environment leads to many healthy risks for human, plant and animal, lead has the ability of accumulation in bone and thus may causes neurological, cardiovascular, renal, gastrointestinal, hematologic and reproductive effects (Nagbal, 1987; UNEP, 2010). Lead was released into the environment *via* many natural and anthropogenic sources such as combustion of leaded fuel, movement of wind, untreated industrial effluents, automobile effluents, domestic waste, weathering of rocks and mining (UNEP, 2010; Nagbal, 1987; Lovering, 1976).

Lead was measured and recorded for all stations, the total concentrations at extent were (0.8460-1.0769 mg/l). Station (W_4) and (W_6) recorded the highest values when compared with all the stations measurements because station (W_4) was an important commercial port (Umm Qaser), therefore it undergoes several activities as marine navigation and loads and unloads operations that occur inside the port while stations (W_2), (W_3) and (W_5) recorded equal values of total concentrations for lead about 0.846 mg/l. Also stations (W_1), (W_7) and (W_8) recorded the high values because these stations are important areas and affected by several activities as natural and anthropogenic sources, also station (W_1) represents the Shatt Al-Arab estuary therefore was affected by river and marine navigation and the various pollutants loaded from Shatt Al-Arab through tide, whereas station (W_7) is an important region as commercial and oil port and affected by many pollutants and that may be due to the marine navigation and loads and unloads operations for different ships, in addition it recorded the high value at 0.922 mg/l for station (W_8) that may be attributed to being the confluence zone between the Shatt Al-Basrah canal with Khor Al-Zubair as well as the Shatt Al-Basrah canal was drainage canal and industrial waste and wastewater which are released into the canal without treatment.

The data for all the measurements of lead are shown in Table (2) and Figure (5), the data recorded higher values for lead concentration when compared with some globally allowed limits as WHO (2011), CGL (2014), IQS (2001) and EPA (2009) that recorded about 0.01 mg/l.

Table 2. Concentration of total Mercury, Arsenic, Cadmium and Lead of stations selected from surface waters of marine samples.

No. of samples	Conc. of Hg mg/l	Conc. of As mg/l	Conc. of Cd mg/l	Conc. of Pb mg/l
W_1	0.0040	0.0905	0.0660	0.9230
W_2	0.0068	0.1120	0.0480	0.8461
W_3	0.0089	0.0680	0.0450	0.8461
W_4	0.0060	0.0840	0.0450	1.0000
W_5	0.0030	0.0760	0.0480	0.8460
W_6	0.0050	0.0570	0.0630	1.0769
W_7	0.0079	0.0680	0.0480	0.9230
W_8	0.0068	0.0570	0.0510	0.9220
Average	0.0060	0.0765	0.0518	0.9229
WHO 2011	0.0060	0.0100	0.0030	0.0100
CGL 2014	0.0010	0.0100	0.0050	0.0100
EPA 1998	0.0020	0.0100	0.0050	0.01500
IQS 2001	0.0010	0.0100	0.0030	0.0100



Figuer 2. Concentration of total mercury (mg/l) in Iraqi marine water.

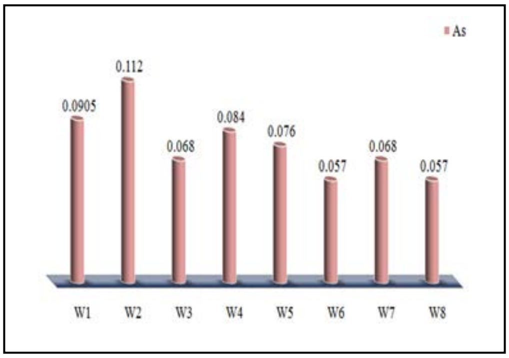


Figure 3. Concentration of total arsenic (mg/l) in Iraqi marine water.

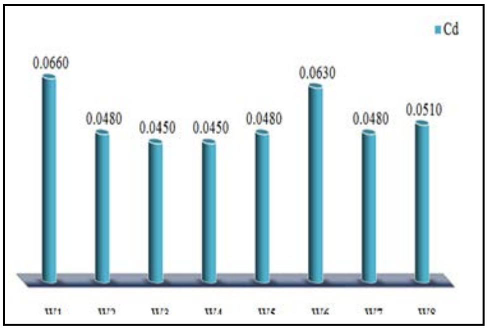


Figure 4. Concentration of total Cadmium (mg/l) in Iraqi marine water.

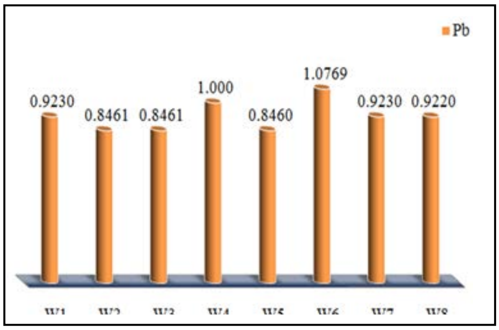


Figure 5. Concentration of total lead (mg/l) in Iraqi marine water.

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تقييم مستويات بعض العناصر السامة في المياه البحرية العراقية

زهير علي عبد النبي
مركز علوم البحار، جامعة البصرة، البصرة - العراق

المستخلص - جمعت النماذج من ثمان محطات على طول المياه الأقليمية العراقية. تم اختيار ثلاث محطات من المناطق القريبة من مدينة الفاو في جنوبي العراق بأتجاه خور عبدالله، إذ تعتبر هذه المنطقة خط ملاحي مهم بين العراق وايران من جهة ومن جهة اخرى بين العراق والكويت. المحطات الخمس الأخرى تكون ممتدة بين ميناء ام قصر بأتجاه ميناء خور الزبير بينما أختيرت المحطة الأخيرة في منطقة الألتقاء بين ميناء خور الزبير وقناة شط البصرة. جميع النماذج جمعت على عمق 10 سم من سطح الماء وبوقت الجزر.إستخدمت طريقتين لتقدير أربع عناصر سامة هي (الزئبق والزرنيخ والكادميوم والرصاص) في المياه البحرية العراقية، فقد إستخدم جهاز ICP لتقدير الزئبق والزرنيخ بينما الرصاص والكادميوم تم تقديرهما بأستخدام مطيافية الأمتصاص الذري. بلغ معدل التركيز الكلي للعناصر الزئبق والزرنيخ والكادميوم والرصاص (0.0060 و 0.0765 و 0.0518 و 0.9229) ملغم/لتر على التوالي، كذلك سجلت بعض الخصائص الكيميائية والفيزيائية للمياه في محطات الدراسة.