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DISTRIBUTION AND LEVELS OF TRACE METALS IN THE RED SEA COASTS AND COMPARISON WITH THEIR LEVELS IN THE ARABIAN GULF

H. T. Al-Saad F. J. M. Al-Imarah * M. A. R. Saeed

Dept. chemistry & Marine Pollution, Marine Science Centre, Basrah Univ.– Iraq
**Faculty of Marine Science & Environment, Hodeidah University, Yemen*

Abstract

The marine environment of Seas is suffered from pollution by trace metals as well as petroleum hydrocarbons from different sources. Different studies were conducted to evaluate the levels of trace metals, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in water, sediments, plants, fishes and shrimps from Red Sea and Arabian Gulf coasts. Most of these studies revealed that levels of trace metals were acceptable when compared with world wide standards and comparable to those for unpolluted environments. Higher concentrations of trace metals in the environmental media or biota were observed close to the coastal cities due to anthropogenic activities, while lower values were reported for remote areas. Dissolved trace metals in µ g/l reported were: 0.19,0.04-2.65, 0.02 (Cd), 0.21, 0.024-29.05, ND (Cr), 0.47, 5.32-174, 7.0 (Cu), 173, 3.48- 206.50, 40 (Fe), 1.52, 0.12-8.05, 7.00 (Mn), 2.85, 0.12- 22.43, 1.66 (Ni), 0.23, 0.10-2.85, 3.00 (Pb) and 0.82, 0.0-9.45, 20 (Zn) in coastal waters of Arabian Gulf, Red Sea and World wide. Exceptions were reported for certain studies such as recording of high concentration of mercury in the edible flesh of the fish Hammrah from North West Arabian Gulf waters which explained on the basis of natural sources. Elevated levels of lead from automobile emission were reported in bottom surface sediments nearby Kuwaiti coasts.

Introduction

Heavy metals are elements having atomic weights between 63.546 and 200.590 AMU (Kennish, 1992) and a specific gravity greater than 4.0 g/l(Connell and Miller, 1984).. Living organisms require trace amounts of some heavy metals such as: Co, Cu, Fe, Mn, Mo, V, Sr, and Zn. Excessive levels of some metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to biological water systems are: Cd, Cr, Hg, Pb and As (Kennish, 1992). Heavy metals are usually taken up by both fauna and flora which could be provokes an increase in the concentration of the metal in the organisms by a factor of 1000- 10000 times (Kinne, 1984). If the excretion is slow, it can lead to the bioaccumulation phenomenon.

Within the Egyptian area of Mediterranean Sea, trace metals in certain levels were reported in muscles of fishes *Saurida undosquamis* sampled from Al-Exanddria, Port Said and Gulf of Suez waters (El-Moselhy, 2003). In most Red Sea coasts of Yemen, certain levels of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were reported in surface water and sediments (Al-Shawafi *et al.*, 2005).

Compared with other sites of Red Sea, high levels of trace metals in fauna and sediments from Al-Hodeidah and Al-Salif at the Yemeni coasts of Red Sea were recorded in which shrimp and snails were accumulated higher trace metal concentrations compared with fish species (Hassan and Nadia, 2000).

On the other hand, in the area of Northern Arabian Gulf, trace metals input may derive from a number of anthropogenic and natural sources. Among trace metals, the potentially toxic mercury, cadmium and lead may inter coastal waters by sewage and other waste water effluents, power plant cooling water discharges, auto emission, petroleum and petrochemical industry wastes, storm drain outfalls and solid waste landfills (UNEP, 1980).

In the Northern Arabian Gulf, the concentrations of some heavy metals in surface and core sediments were recorded (Rose and Stoffers,1978), reported data for the concentrations of trace metals in surface sediments and commercial shrimp and fish from various regions of Kuwait (Anderlini *et al.*,1982), while mercury in a certain concentration was reported in shrimp and fish species from Iran (Parvaneh,1977).

Recently, trace metals Cr, Cu, Fe, Mn, Ni, Pb, Zn and V in Sulaibikhat bay of Kuwait Northwest Arabian Gulf, were recoded (Al-Sarawi *et al.*, 2002).

Materials and Methods

Concentrations of trace metals in environmental samples are usually determined by Atomic Absorption Spectrophotometer after a certain analytical processes. Water samples of 5 litters each required for trace metal analysis is filtered in the lab through pre-washed and pre-weighted 0.45 µm Millipore membrane filters. Those who pass through the membrane is known as dissolved phase of water, while material retained as particulate phase of water.

Filtered water samples were run through 50x 2 cm ion exchange column filled with 50 – 100 mesh Chelex-100 resin in a flow rate of 5 ml/min, then column is washed by 200 ml deionized water and the trace metals eluted by 30 ml 2 M nitric acid which was collected in 50 ml plastic beaker. The eluate was evaporated to near dryness, the residue was then dissolved in 1 ml 0.5 N hydrochloric acid and made up to 25 ml with deionized water and stored in 25 ml nalgen screw cap bottles and sealed for trace metals analysis.

For particulate matter, the same procedure used for sediment digestion is adopted.

Bottom surface sediments are collected by Van-veen Grab sampler, put in plastic bags, transfer to the lab and store in deep freezer. Frozen sediments were dried by freeze-drier then grinding for homogenization and sieving through a 63 µm screen. Then less than 1 g from sieved samples were digested with HNO_3 , HF, HCl and $HClO_4$ (Loring and Rantala,1992). Samples then kept in nalgen screw cap bottles and sealed for trace metals analysis.

For collection of fishes, gill nets were used, caught fishes were put in plastic bags and transfer to the lab in ice box. In the lab fishes were cut from abdomen cleaned by rinsing with water, the edible muscle was taken from the left posterior side of each fish. Muscles then freeze dried for 12 hours, grind and sieved by 0.5 mm mesh nylon sieve, then tissues were digested by acid mixture following ROPME (1982).

For the trace metal analysis, flame or flameless atomic absorption spectrophotometer is used, which is fitted with special Hallow Cathode Lamps for each metal.

Results

In waters from Red Sea and Arabian Gulf, Concentrations of trace metals as a total, dissolved or particulate phases were investigated and most of the results are tabulated in table 1. In the sediments, Concentrations of trace metals as a total, exchangeable or particulate matters were investigated and most of the results are tabulated in table 2. In edible muscles of shrimps

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from Red Sea and Arabian Gulf, Concentrations of trace metals as a total were investigated and most of the results are tabulated in table 3. In fishes from Red Sea and Arabian Gulf, Concentrations of trace metals in edible muscles were investigated and most of the results are tabulated in table 4.

Table 1. Concentration mean/range of trace metals in waters dissolved phase (W_d) µg/l and particulate phase (W_p) µg/g from Red Sea and N. W. Arabian Gulf.

Trace metals → Locations ↓	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Port Said W_d	0.15-0.68	-	0.15-2.9	-	-	-	0.38-1.99	0.62-7.62	Abdelmoneim, and Fattouh, A. 1994
W_p	0.00-0.25	-	0.08-0.92	-	-	-	0.1-1.52	1.16-9.92	
Gulf of Suez W_d		-	1.6-9.6	-	-	-	1.0	1.62-29.2	AbdelSalam,1980.
Gulf of Suez W_d	0.14-0.29	-	8.55-10.7	-	-	-	1.79-1.85	9.09-29.5	El-Mosellhy, 1993.
Hodeidah, W_d	0.04-2.65	0.024-29.05	5.32-174	3.48-206.5	0.12-8.0	0.12-22.43	0.10-2.85	0.0-9.45	Heba, *et al.*, 2004
W_p	0.22-101.36	1.60-534.6	2.72-199	6.20-691.77	98.10-6966.6	4.32-158.0	2.64-832.5	1.11-472.6	
Shatt Al-Arab Estuary, W_d									Al-Saad, *et al.*, 1996
W_p	112.3	193.4	63.7	9466.0	35.7	81.5	22.5	10.04	
NW Arabian Gulf W_d	0.19	0.21	0.47	173.0	1.52	2.85	0.23	0.83	Al-Khafaji, 1996.
W_p	46.23	493.65	267.05	2454.0	35.55	101.74	6.07	24.45	
Kuwait Bay W_d	-	1.16	4.23	100.0	2.6	0.8	2.02	36.11	Al-Sarawi *et al.*, 2002
W_p	-	152.3	90.5	28,000	54.8	37.3	70.4	451.4	
World wide rivers, W_d	0.02	-	7.0	40.0	7.0	1.66	3.0	20.0	Burton, 1976

Table 2. Concentration mean / range of trace metals in surface bottom sediments (in µg/g) from Red Sea and North West Arabian Gulf.

Trace metals → Locations ↓	Concentration of trace metals									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Hodeidah, S_e	12.1		38.46	332.5	219.98	196.52	116.40	17.4	19.8	Al-Edrise, 2002.
Hodeidah	0.2-5.80		6.38-38.4	36.7-79.0	99.67-199.76	9.17-24.21	7.10-116.4	4.99-6.26	4.02-18.35	Heba, *et al.*, 2004
Aden Port		23.97	82.19	19.89		335.5	34.54	77.28	128.59	Nasr, et al., 2006
Kuwait	1.50		2.85	20.50	15000.0	4099.0	96.90	22.7	280.0	Samhan, *et al.*, 1986
NW Arabian Gulf S_e	0.03		50.40	24.20	5869.0	751.00	39.80	6.60	25.20	Abaychi,and Al-Saad, 1988
NW Arabian Gulf	1.2-3-9		17-121	8-72	200-2300	25-950	15-193	17-48	12-123	Anderlini, *et al.*,1986.
Saudi Arabia	0.16		56.85	3.68	6296.7	94.63	14.53	3.05	7.72	Fowler,et al.,1993.
Sulaibikhat Bay (Kuwait)			55.6	26.98	24900	187.4	12.95	5.6	73.5	Al-Sarawi *et al.*, 2002
Unpolluted sediments	0.11	-	-	33.0	41.0	770.0	-	19.0	95.00	GESAMP, 1993.

Table 3. Concentration mean/range of trace metals in edible muscles of shrimp (in µg/g) from Red Sea and North West Arabian Gulf.

Trace metals → Locations ↓	Concentration rang of trace metals									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Red Sea	0.6-7.9	0.13-2.5	0.03-17.9	29-171	50-3400	-	-	-	52-118	Heba,et al., 2001
Al-Salife, Yemen	2.4	1.33	1.20	5.93	7.30	-	3.85	1.06	123.86	Hassan & Nadia 2000
Hodeidah	0.2-5.80		6.38-38.4	36.7-79.0	99.67-199.76	9.17-24.21	7.10-116.4	4.99-6.26	4.02-18.35	Heba, *et al.*, 2004
Hodeidah,	12.1		38.46	332.5	219.98	196.52	116.40	17.4	19.8	Al-Edrise, 2002.
Aden Port		23.97	82.19	19.89		335.5	34.54	77.28	128.59	Nasr, *et al.*, 2006
NW Arabian Gulf	0.03		50.40	24.20	5869.0	751.00	39.80	6.60	25.20	Abaychi,& Al-Saad, 1988
Kuwait	0.8	0.1	0.2	14	-	-	0.6	0.7	46	Anderlini, *et al.*,1986.
Shatt Al-Arab Estuary	0.5	-	-	37	52.2	7.9	32.3	5.9	97.5	Al-Imarah, 2001.
Saudi Arabia	0.16		56.85	3.68	6296.7	94.63	14.53	3.05	7.72	Fowler,*et al.*,1993.
Worldwide	1.0	0.2	0.3	70	-	-	1	1	80	Bryan, 1976

Table 4. Concentrations mean/range of trace metals in the edible muscles of fishes from Red Sea and NW Arabian Gulf.

Trace metals → Species/Locations	Concentration rang of trace metals									
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Lethrinus sp., Suez Gulf	0.39-0.51	-	0.34-0.45	0.43-0.45	19.25-20.14	0.23-1.13	-	0.64-1.14	4.31-4.87	Abdelmoneim, & El-Deek, 1992
Acanthopagurus bifaclatus, Red Sea	0.26	-	0.72	0.51	16.39	0.45	-	3.36	4.34	Abdelmonei, *et al.,* 1994.
Marine Fish,Red Sea Coast of Yemen	1.5-2.5	-	0.80-1.30	1.30-2.00	3.20-6.00	0.20-0.60	1.00-2.00	1.00-1.30	8.00-20.0	Heba,*et al.,* 2001
*Scomberomrus commerson,*Al-Hodeidah coast, Yemen	0.39-1.6	-	0.9-1.51	1.3-2.79	3.6-4.76	0.3-0..94	0.9-1.0	1.0-2.6	8.0-39.5	Al-Edrise, 2002.
Liza subviridus, Shatt Al-Arab	0.03		0.02	1.57	8.55	1.79	2.27	0.06	8.58	Al-Khafaji, 1996.
*Epinephelus tauvina,*NW Arabian Gulf	0.2		0.3	1.0	-	-	0.5	2.9	20	Anderlini, *et al.,* 1986.
Kuwait	0.8	0.4	0.6	9	148.0	2.0	0.6	1.4	70	Anderlini *et al.,* 1982
Marine fishes, World wide	0.15-3.0	-	0.2-1.0	4.0-50	400	1.0-60	0.4-25	0.5	6.0-1500	Bowen, 1966
World wide	0.2	0.1	0.5	3.0	50.0	10.0	1.00	3.0	80.0	Bryan, 1976

Table 5. Concentration mean/range of trace metals in aquatic plants from Red Sea and NW Arabian Gulf.

Trace metals → Species/Locations ↓	Concentration rang of trace metals									
	Cd	[illegible]	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Marine plants, Al-Hodeidah coast of Yemen	0.82-1.70	7.25-11.70	6.25-20.20	10.50-46.50	-	-	0.50-13.25	3.60-5.90	3.30-29.70	Heba,*et al.*, 2000
Polygonum spp *Salvinia natans* *Sallinsneria spiralis* Hammar marsh Iraq	5.23 1.42 1.19	- - -	2.11 3.17 3.09	- - -	- - -	- - -	10.53 7.39 2.02	0.09 0.28 0.29	0.11 0.11 0.12	Al-Saad,*et al.*, 1997
Ceratophylum demersum, Shat Al-Hilla River, Iraq	10.29	49.8	8.96	13.92	-	-	153.74	34.90	62.23	Al-Taee, 1999.
Myriophyllum verticillatum, Shatt Al-Hilla River, Iraq	9.73	46.7	2.54	9.06			119.01	45.63	24.83	
Typha domengensis				29.8				20.06	26.3	Aziz, *et al.*, 2006
Phragmites australis Shatt Al-Basrah canal, Iraq				28.2				19.9	24.7	

Discussion

Although trace metals are not considered as global pollutants, but their concentrations can and does affect many coastal areas of the word's oceans, Such pollution is most prevalent in highly industrialized nations with long histories of industrial development and in less developed nations undergoing rapid expansion of industrial facilities. This pollution may lead to deterioration of natural habitats by depleting ecologically sensitive species or to destruction of valuable marine resources by eliminating or tainting commercial species (Anderlini, *et al.*,1986).

The marine environment could be polluted with effluent containing trace metals from both anthropogenic and natural processes, maximum effective inputs are from untreated municipal industrial wastes, agricultural runoff and input from atmosphere (Heba, et al., 2003) with special concern to disposal of automobile and industrial lubricants, spillage from all these factors will lead to a local eutrophication, increased of biological oxygen demand (BOD_5) and algal blooms (Heba, *et al.*, 2001).

The increases of sewage and industrial effluent discharged into the Gulf of Aden have seriously endangered the ecosystem (Heba, *et al.*, 2003).

Studies of trace metals in water, fishes from Suez Gulf (Abdelmoneim, and Fattouh, 1994) showed that the highest accumulated elements were Fe and Zn, while the lowest one was Cd.

The trace metal levels in the dissolved phase of water from Gulf of Suez were nearly fixed for more than decade, as shown in table 1, the same source of trace metal pollution is expected which is the heavy navigation (Ben-Yami, M. 1998). Trace metal concentrations in Gulf of Suez waters were comparable to those for world wide Rivers (Heba and Al-Mudhaffer, 2000). For other parts of Red Sea, the characterizations of sea water plays a great role in determination of trace metal concentrations. The salinity, dissolved oxygen, quantity of Sewage effluent discharges and water mixing currents are different (Heba, *et al.*, 2004).

In the sediments of Red Sea coast of Yemen, Degree of some trace metal pollution showed different levels of pollution in the area depending upon their sources, mainly was natural (MAFF, 1993).

The fate of trace metals in the marine environment is determined by their partitioning between dissolved and particulate phases of water (Castro,

& Huber, 1997). Distribution of heavy metals as particulate matter from sewage effluents are greatly effected by mixing rate with the sea water

The principal source of Pb in the marine environment appears to be the exhaust of vehicles which run with leaded fuels (Heba, *et al.*, 2004). Also, lead reaches the sea by rain and wind blow dust (Williams, *et al.*, 1978).

As a natural sources for trace metals introduction to Northern Arabian Gulf are airborne and waterborne particulates. Dissolved and adsorbed metal pollutants derived from the urban, industrial and agricultural centers of Iraq, Iran and Kuwait may be entering to the Northern Arabian Gulf. The majority of the suspended particulate load of Shatt Al-Arab is expected to be deposited in its estuary before they reach the Gulf in which adsorbed trace metals are released their (Al-Khafaji, 1996;).

Sediments could be used as indicator for trace metal pollution (Little and Smith, 1994; F?rstner and Wittmann,1981). Moreover, the concentrations of trace metals in sediments are 1000 – 100000 times higher than their concentrations in overlying water (Heba, *et al.*, 2000), and their concentrations are effected by a number of factors such as grain size, total organic carbon and carbonate content of the sediments as well as other physical and chemical parameters. The high concentration of trace metals in the sediments of areas close to highly dense cities could be arises from sewage discharge as well as industrial pollution, ship wrecks, oil enrichment and transportation, Moreover, high concentrations of lead (Pb) is found every where which associated with high traffic density of automobile running by leaded gasoline (Al-Khafaji,1996; Riley and Chester, 1981).

Aquatic plants are useful indicator for pollution monitoring studies. Plants have a great capacity to accumulate heavy metals from aquatic environment (Aziz, *et al.*, 2006; MAFF, 1993; Abaychi and Al-Obaidy,1987; Al-Saad, *et al.*,1994). Few studies were conducted for the investigation of trace metals in aquatic plants from Red Sea and Arabian Gulf. In Red Sea, the levels of trace metals in five marine plants; *Sargsum latifolium, Sagasum lacifolium, Padania spp., Taonia dicotoma and Avicina marina* from different areas of Red Sea were studied (Al-Edrise, 2002). The study revealed that different plants accumulate different concentrations of trace metals. For NW Arabian Gulf, trace metal concentrations in three aquatic vescular plants from Shatt Al-Arab River were investigated and found that there are noticeable variations in the mean concentration of some of these trace metals in the studied plants (Abaychi, and Al-Obaidy,1987). The distribution and concentrations of trace metals in aquatic plants from the marshes of Iraq have been studied, it is found that the concentrations of Fe, Mn, Ni, Pb and Zn in the studied aquatic plants

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were lower than the baseline concentrations and those for Cd, Cr and V were relatively higher (Al-Saad, et al., 1994). Phragmites australis and Typha domengesis aquatic plants from Shatt Al-Basrah canal, southern of Hammar marsh in Iraq were found as good bioaccumulators and biomonitors for Cu, Pb and Zn in water of Shatt Al-Basrah canal (Aziz, *et al.*, 2006).

Conclusion

In view of high rate of population growth and Industrial development, which released huge amounts of waste water to the environment, as well as crude oil production and transportation, in addition to heavy navigation of vessels in the seas, as well as erosion and other effects of engineering According to the levels of trace metal concentrations in water, sediments, shrimps, fishes and plants from Red Sea and North West Arabian Gulf and comparison with word wide areas as well as limits of pollution it seams that the studied areas do not consider polluted by trace metals, and if the levels of trace metals were little bit high the pollution is expected in the area which effected by the source of pollution and the effect will be diminished abroad.

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توزيع ومستويات المعادن النزرة في سواحل البحر الاحمر ومقارنتها مع مستوياتها في الخليج العربي

حامد طالب السعد و فارس جاسم محمد الامارة
قسم الكيمياء وتلوث البيئة البحرية، مركز علوم البحار، جامعة البصرة، البصرة – العراق
و
مهيوب سعيد
كلية علوم البحار والبيئة، جامعة الحديدة، الحديدة، اليمن

الخلاصة

تعاني البيئة الساحلية للبحار من تلوث بالمعادن النزرة فضلا" عن التلوث بالهيدروكاربونات النفطية ومن مصادر مختلفة. وقد اجريت دراسات مختلفة لتقيم مستويات المعادن النزرة:الكادميوم والكروم والنحاس والحديد والمنغنيز والنيكل والرصاص والخارصين في مياه ورواسب واسماك وروبيان سواحل البحر الاحمر والخليج العربي. وافرزت معظم هذه الدراسات ان مستويات المعادن النزرة كانت مقبولة عند مقارنتها مع الحدود القياسية العالمية ومقاربة لتلك في البيئات غير الملوثة. ان اعلى التراكيز المسجلة لهذه المعادن في البيئات المختلفة والكائنات الحية وجدت قرب المدن الساحلية بسبب النشاطات الصناعية، بينما كانت اوطأ القيم قرب المناطق النائية والبعيدة عن مصادر التلوث. كان تركيز المعادن النزرة في الجزء الذائب من المياه (بوحدات مايكروغرام/ لتر) بحدود:١٩،٠ و ٠،٠٤ – ٢،٦٥ و ٠،٠٢(كادميوم) و ٠،٢١ و ٠،٠٢٤ – ٢٩،٠٥ و غير محسوس (كروم) و ٠،٤٧ و ٥،٣٢ – ١٧٤ و ٧،٠ (نحاس) و ١٧٣ و ٣،٤٨ – ٢٠٦،٥٠ و ٤٠ (حديد) و ١،٥٢ و ٠،١٢ – ٨،٠٥ و ٧،٠ (منغنيز) و ٢،٨٥ و ٠،١٢ – ٢٢،٤٣ و ١،٦٦ (نيكل) و ٠،٢٣ و ٠،١٠ – ٢،٨٥ و ٣،٠٠ (رصاص) و ٠،٨٢ و ٠،٠ – ٩،٤٥ و ٢٠ (خارصين) في المياه الساحلية للخليج العربي والبحر الاحمر والمياه العالمية على التوالي. وقد سجلت بعض الاختلافات لعدد من الدراسات مثل تسجيل قيم عالية من الزئبق في عظلات سمكة الحمرة من مياه شمال غرب الخليج العربي والذي تم تفسيره اعتمادا" على مصادر طبيعية. وسجلت مستويات غير متوقعة للرصاص في الرواسب القاعية لسواحل الكويت واعزيت الى مصادر الانبعاث من وسائط النقل.