# An Assessment of Environmental Pollution by Some Trace Metals in the Northern Part of Shatt Al-Arab Sediments, Southern Iraq

Faiq A. Al-Manssory

Mohammed A. Abdul Kareem

Department of Marine Geology Marine Science Center Basrah University Department of Soil and Water Sciences College of Agriculture Basrah University

Mohammed M. Yassen

Department of Soil and Water Sciences College of Agriculture Basrah University

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# ABSTRACT

The concentration of five trace metals Cd, Cu, Ni, Pb and Zn wrer determined in the surface sediments of five stations along 17 km of northern part of Shatt Al-Arab River during 1997-1998.

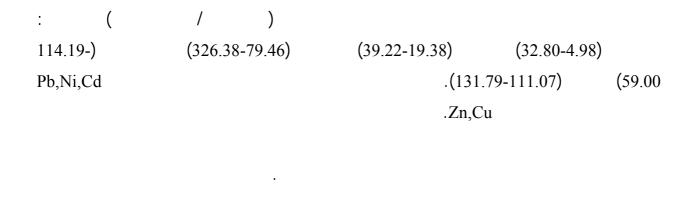
The range of exchangeable trace metals concentrations ( $\mu gg^{-1}$  d.w.) were as following: Cd (4.98-32.80), Cu (19.38-39.22), Ni (79.46-326.38), Pb (59.00-114.19) and Zn (111.07-131.79). Accordingly, the study area environment is heavily polluted by Cd, Ni and Pb, and moderately by Cu and Zn. The northern part of the study area seems to be a source point for pollution by Cd indicating an industrial pullution at the area. While the pollution by Ni reflecting a clear image of hydrocarbon substance contamination, however, the pollution sources of Pb are Basrah port, Ashar channel and Al-Naser oil jetties in Abu Al-Khassib town because these stations have received a sewage effluent indicating anthropogenic pollution for the river ecosystem. The eastern part of Khorah station was found polluted by Cu whereas Dockyard and Ashar channels were polluted by Zn metal.

On the temporal basis, the study area reflects a climbing rate of pollution, especially after the aggression on Iraq.

(Zn,Pb, Ni, Cu, Cd)

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#### **INTRODUCTION**

Trace metal pollution can affect many areas of the world in the developed and developing countries. Pollution of fluvial and coastal marine environments by these metals is being major of concern since may lead to deterioration of natural habits or also cause a serious public health hazard (Anderlini et al., 1986). Trace components in the environment are continuously redistributed in hydrological, hydrochemical as well as biological cycles and pathways (Ledin et al., 1989). The distribution and concentration levels of trace metals have, however, changed drastically during the last decades due to human activities.

Analysis of sediments being a useful method of study environment pollution of trace metals and has been used in numerous investigation in fluvial or marine environments (Johansson, 1989). Only absorbed metals on the sediments and associated with carbonate and organic material are of interest to pollution studies (Anderlini et al., 1982).

There are many studies focusing on this topic at Satt Al-Arab Estuary and the coastal and near by marine environment. Al-Hashimi and Salman (1985) established background levels of the trace metals in the sediments of Shatt Al-Arab Estuary and the NW coast of the Arabian Gulf. Abaychi and Dou Abul (1986) studied the geochemical fractionation of Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the surfacial sediment from the same area and Khor Al-Zubair. Al-Mussawy and Salman (1989) investigated Co, Cu, Fe, Mn, Ni, V and Zn in the surfacial marine sediment of Khor A-Zubair.

There are many studies on these metals in the fluvial and lacustrain environments. Saleh (1982) gave a high record of Cd, Ni, Pb and the moderate one of Cu and Zn at Azair and Qurna. Abaychi and Dou Abul (1985) study Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the northern part of Shatt Al-Arab River. From other view point, Abaychi and Mustafa (1988) uses the Asiatic clam as a bio-indicator of trace metal pollution in Shatt

Al-Arab River. They gave a highest record of Cd and Cu of exchangaeble particulate metals form and moderate value of Zn near Basrah City. There are no such investigations on the lacustrain environment except the study of Al-Dabbas and Hassan (1992). While Mustafa and Al-Saad (1995) concluded that aquatic vascular plants are useful indicator organisms for pollution monitoring studies at this environment.

At Shatt Al-Arab River and its estuary, Al-Khafaji et al. (1997) studied concentration of Cd, Cu, Ni, Pb and Zn at two stations in Shatt Al-Arab Estuary in dissolved and particulate phases. Al-Imarah and Al-Khafaji (1998) try to investigate the effect of industrial effluent upon Shatt Al-Arab River water and sediment at three stations in sahatt Al-Arab River.

Al-Hejuje (1999) determines Co, Ni, Mn and Fe in Ashar and Al-Khandk (Dockyard) channels considered (at this time) as a sewage canals influx their polluted materials to the river body. Meanwhile, at the same period of this work 1997-1998 (Al-Imarah, 2001) determine the concentration levels of Cd, Cr, Ni, Pb and Zn of dissolved and particulate phases of Shatt Al-Arab River water.

The aims of this study are to evaluate the possible source of pollution at the study area, and the possible effect of deposition of these metals to the river eosystem.

#### Study area:

Shatt Al-Arab River is formed by the influence of Tigris and Euphrates Rivers at Qurna City about 90 Km northern of Basrah City. It drains into Arabian Gulf with total length of about 195 Km (Fig.1). The sources of sediment in the northern part of the river are from many origins with different proportion (Albadran and Al-Manssory, 1999).

The water of the river considers as an important resource for rural, urban and industrial activities. It is also being as a main waterway between the human residence at both sides. Shatt Al-Arab River water is liable to small oil spills of varying magnitudes, the major source for the input of petroleum substances are Maftiah oil-terminal and Abu-Flous (Al-Naser) oil jetties. Another important source of pollution for the river ecosystem is sewage discharge by tidal channel across Basrah City that connected with the river.

#### MATERIALS AND METHODS

### Field works:

Sampling work was achieved at three sites (east, west and mid-channel) of five stations along 17 Km of the northern segment of Shatt Al-Arab River (Fig.1). These stations were chosen to take surfacial sediment sample to reflect urban and rural activities. Surface sediments were taken by stainless steel Van Veen grab sampler, and only the top few centimeters in the middle of the sample were taken by means of plastic scope. Sampling was carried out during July-August 1997 and January-February 1998.

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Fig.1: Map of Shatt Al-Arab River and position of the samples stations.

### Laboratory methods:

Sediments samples were prepared for metal analysis by leaching air dried samples, with 50% HNO<sub>3</sub> for two hours at 90-95 °C. After leaching, the samples were centrifuged for 20 min., rinsed with de-ionized water and supernatant decanted into 25 ml volumetric flasks. This step was repeated twice, and the samples were stored in capped p;astic bottles for later analysis by PYE Unicam flame atomic absorption spectrophotometer (AAS) type Sp9 (Anderlini et al., 1982), in soil and water department laboratories. A subsample was taken to determine grain size distribution according to Folk (1974). Mean grain-size in phi units (MZ $\phi$ ) of the samples was calculated according to Folk and Ward (1957).

Aliquot of samples were taken to determine calcium carbonate percentage (CaCO<sub>3</sub>%) by adding 1N HCl acid and back titration with 1N NaOH using phenoliphthaline indicator (Jackson, 1958). Total organic carbon percentage (TOC%) was determined following the procedure proposed by Welkly and Black, which mentioned at Pabe et al. (1982). All samples were ruined by two replicates.

# **RESULTS AND DISCUSSION**

# **Evaluation of spatial variations:**

Knowledge of the concentrations and distribution of trace metals in sediment can play a key role in detecting sources of pollution in aquatic systems (Forstner and Wittman, 1979). The distribution of Cd, Cu, Ni, Pb and Zn in the study area, (fig.2) shows that the northern part of the study area is a source point of pollution with cadmium (32.80  $\mu$ gg<sup>-1</sup> d.w.) (Table 1). The probable sources of this metal are from petrochemical pigments, fertilizers and petroleum refining (Dean et al., 1972). A further important source is atmospheric emission, which contain cadmiuim from melting scraps (Forstner and Muller, 1973). Basrah port in Maqqal station and Muftiah oil-terminal (formerly petroleum refinery) considered as a possible source for this element to Shatt Al-Arab ecosystem.

	Stations	1	2	3	4	5
Parameters		Maqqal	Silo	Ashar	Khorah	Muhellah
	Cd	32.80	11.25	5.78	6.84	4.98
Trace metal concentrations	Cu	38.44	23.75	39.22	29.81	19.38
$(\mu gg^{-1} d.w.)$	Ni	182.66	326.38	79.46	122.77	256.11
	Pb	79.27	68.89	114.19	59.00	80.98
	Zn	127.18	111.07	131.79	125.28	123.39
	Mz (φ)	8.88	9.74	7.25	9.56	8.73
Sedimentological	Clay %	54.85	62.05	45.56	61.81	56.81
parameters	TOC %	0.88	1.11	1.25	1.03	1.09
	CaCO <sub>3</sub> %	27.28	28.16	24.13	29.97	30.57

Table 1: Average values of exchangeable trace metals (µgg<sup>-1</sup> d.w.) and sedimentological parameters of Shatt Al-Arab River sediment.

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Fig.2: The distribution of exchangeable trace metals ( $\mu gg^{-1} d.w.$ ) in the surface sediment of Shatt al-Arab River. Where the top of each column is East side of the river, while the bottom is the West side.

Contouring pattern of Copper shows a high concentration around the outflow of Salehiah creek at the east side of Shatt Al-Arab River near Khorah station (Fig.1). The highest values were recorded at Ashar station (39.22  $\mu$ gg<sup>-1</sup> d.w.) (Table 1). The possible source of this metal could be from agricultural activities in this area, since fertilizers as one of its sources to the aquatic environment (Dean et al., 1972). Another source may be from corrosion of artillery bombshells and machine gun bullets during the first Gulf war since nearby area being battlefield for many years.

Figure (3) also exhibits Nickel distribution in the surfacial sediment of northern part of Shatt Al-Arab River, which shows the highest concentration among the other studied metals along the study area. The higher average value ( $326.38 \ \mu gg^{-1} d.w.$ ) was recorded at Silo station (Table 1), which is located near Muftiah oil terminal. The abundance of nickel in the river sediment may be related to the petroleum rich substrate (Abaychi and Dou Abal, 1985). Since while field observations show that the water surface of Shatt Al-Arab River seem like a mirror at a day light during summer months, this because of oil spills that coming from Muftiah oil terminal. Another peak of this metal was found at Muhellah station (near Abu Al-Khassib) (Fig.3) which recorded (256.11  $\ \mu gg^{-1}d.w.$ ) (Table 1). This station is located near Al-Naser oil-jetties.

The maximum concentration of lead metal (Pb) was recorded at station 1, 3, and 5 (79.27, 114.19 and 80.98  $\mu$ gg<sup>-1</sup> d.w.) respectively (Table 1). These stations have received a sewage effluent and permit a busy vehicle movement. Since the traffic movement considered as a main source of aquatic environment pollution with lead compounds, this material reaches the environment by air dust or sewage effluent (AbdulRaheem et al., 1987. Ashar station has recorded the highest value of Pb concentration through the study area because of its possess the highest level of TOC% (1.25%) (Table 1).

Zinc concentration is relatively equally also along the study area. Ashar station recorded the highest value (131.79  $\mu$ gg<sup>-1</sup> d.w.) (Table 1) because it possesses the highest level of TOC%, due to relationship between zinc concentration and high levels of detritus (Radwan et al., 1990).

### **Evaluation of temporal variations:**

Values of exchangeable trace metal concentrations of Abaychi and Dou Abal (1985) at the northern part of Shatt Al-Arab River between Qurna and Basrah City, is consider as a background level for this study in order to clarify the temporal variations. Figure (3) summarizes the results of this study and shows clearly that there is a large-scale contamination with all of the studied metals, especially for cadmium and zinc (Table 2).

This study is compared with the former studies at Shatt Al-Arab River, its estuary and the northern part of Arabian Gulf. Only the studies that use Unicam AAS type Sp9 exclusively were put under comparison while the other that didn't use this type of AAS were excluded. The trace metal concentration in the NW Arabian Gulf and Kuwaiti marine environment during mid-eighteen of the 20<sup>th</sup> Century were shown in Table (2). For Shatt Al-Arab Estuary, Al-Khafaji et al. (1997) and Al-Imarah et al. (1998) represent the latest studies upon this topic during the end of nineties of the last century. Second study gave lower values for the studied metals concentration at the same time and space, except of nickel (Table 2). But it still higher the background levels that given by Al-Hashimi and Salman (1985). Faiq A. Al-Manssory et al.

Fig.3: Differences of exchangeable trace metal concentrations ( $\mu gg^{-1}$  d.w.) of Shatt Al-Arab River sediment, plotted over a general background (shaded strips). The vertical lines represent mean standard error of the samples.

Location		Trace metal conc. (µgg <sup>-1</sup> d.w.)					References
		Cd	Cu	Ni	Pb	Zn	References
NW Arabian	Arabian Gulf	0.17	7.00	91.00	5.00	3.40	Abaychi and Dou Abul (1986)
Gulf K	Kuwaiti Marine Env.	1.40	23.00	91.00	27.00	57.00	Anderlini et al. (1986)
Azair-QurnaQurna-BasrahQurna-Abu Al-KhaRiverFao-Ras Al-BishaDeer-HarthaFao-Ras Al-BishaMaqqal-Muhellah	Azair-Qurna	6.00	33.75	284.00	87.50	76.00	Saleh (1982)
	Qurna-Basrah	0.15	11.90	42.00	12.20	6.0	Abaychi and Dou Abul (1985)
	Qurna-Abu Al-Khassib	51.65	216.63	13.60	5.43	108.85	Abaychi and Mustafa (1988)
	Fao-Ras Al-Bisha	0.20	13.85	25.80	17.05	8.00	Al-Khafaji et al. (1997)
	Deer-Hartha	10.40	6.66	42.40	25.17	24.70	Al-Imarah and Al-Khafaji (1998)
	Fao-Ras Al-Bisha	0.18	9.19	16.15	12.92	5.81	Al-Imarah et al. (1998)
	Maqqal-Muhellah	12.26	30.12	189.39	80.47	125.09	Present study

Table 2: Mean concentration of exchangeable trace metal (µgg<sup>-1</sup> d.w.) of the NW Arabian Gulf and Shatt Al-Arab River sediments.

Whereas Abaychi and Mustafa (1988) gave the highest levels of Cd and Cu, even though higher than this study. But it gives a nearby estimation of zinc metal of our study (Table 2), On close sight of Table (2), we could see that the studied trace metals concentration were going to rise in climbing rate especially after the aggression on Iraq. Figure (3) also exhibits a large-scale concentration of Cd, Cu and Pb metals of anthropogenic origin in the northern part of the study area.

### The assessment of environmental ecosystem:

Results show that there is a real difference between the metals under consideration through the study area because of high values of standard deviation and a high coefficient of variation, especially for Cd, Ni and Pb (Table 3).

Since electroplanting works may increase the concentrations of cadmium in nearby sediment by over one hundred times (Warren, 1981), and because of Maqqal station is located relatively close to two major power plants in Basrah City, it recorded the highest average level of contamination with Cd along the study area (32.80  $\mu$ gg<sup>-1</sup> d.w.) representing a hot spot of contamination with this metal for the river ecosystem. Concentration of this metal decreases in a semi-linear pattern throughout the study area but in overall the river environment condition is considered as a heavily polluted with this metal (Table 3). This highly poisonous metal in the environment is considered as an index of industrial pollution (AbdulRaheem et al., 1987).

Table 3: Statistical parameters of exchangeable trace metal concentrations (µgg<sup>-1</sup> d.w.) of Shatt Al-Arab River sediment, and the environmental condition according to U.S. Environmental Protection Agency

	Range			Standard	Mean Standard	Coefficient of	Environm.
Metal	Min.	Max.	Mean ** Deviation		Error (M.S.E)	Variation (C>V%)	Condition
Cadmium (Cd)	0.00 *	81.25	12.26	19.35	±4.33	154	Heavily polluted
Copper (Cu)	0.00	62.38	30.12	14.80	± 3.31	48	Moderately polluted
Nickel (Ni)	0.00	594.53	189.39	176.78	± 39.53	91	Heavily polluted
Lead (Pb)	1.20	126.32	80.47	41.94	$\pm 9.38$	51	Heavily polluted
Zinc (Zn)	72.23	238.98	125.09	37.21	± 8.32	29	Moderately polluted

\* The lower limit is not detected.

\*\* Sample number=40.

In view of the fact that the dominance of nickel metal in the river ecosystem may be related to the petroleum rich substace (Abaychi and Dou Abal, 1985); Silo station which is located nearby a formerly petroleum refinery and recently as an oil-terminal. It has been recorded the highest average concentration (326.38  $\mu$ gg<sup>-1</sup> d.w.). The northern part of Shatt Al-Arab River seem to be heavily polluted by this metal (Table 3) reflecting a clear image of contamination by hydrocarbon substances.

Organic detritus may contain of the order of ten times the concentration of lead in the whole sediment (Warren, 1981). Due to the ecosystem state of the northern part of Shatt Al-Arab River which contain a high percentage og organic detritus (0.88-1.25%) (Table 1); which come from sewage outflow; cause to rising of the level of contamination with trace metal especially with lead. So, the environmental condition of the study area is persumed a heavily polluted by lead according to U.S. Environmental Protection Agency (Table 4). This condition reflects a man-made pollution because of the concentration of lead in sediment is used as an indicator of anthropogenic pollution (AbdulRaheem et al., 1987).

Tabble 4: Criteria used by United States Environmental Protection Agency in defining polluted sediments prior to dredging operations; bulk sediment analysis; ranges in (mg kg<sup>-1</sup> d.w.). After (Anderlini et al., 1982).

Parameters		Non polluted	Moderately polluted	Heavily polluted
Cadmium (Cd)	а	с	с	> 6
Copper (Cu)	а	< 25	25-50	> 50
Nickel (Ni)	а	< 20	20-50	> 50
Lead (Pb)	b	< 40	40-60	> 60
Zinc (Zn)	b	< 90	90-200	> 200

a=These ranges are based on 260 samples from 34 harbors during 1975-1976.

b=These ranges are based on compilation of data from more than 100 different harbors since 1967.

c=Lower limits not established.

# CONCLUSIONS

Shatt Al-Arab River considered as a heavily polluted by Cd, Ni and Pb, while it was moderately polluted by Cu and Zn.

The northern part of the study area seem to be a source point for pollution by Cd, indicating an industrial pollution caused by electroplanting works which located nearby this area.

Nickel concentration of the surfacial sediment records the highest value among the other studied metals along the study area. This was reflecting a clear image of hydrocarbon substance contamination.

There are three peaks of lead concentration through the study area, clearing that there is anthropogenic pollution in the river ecosystem.

There are large scales temporal variations of the studied trace metals, reflecting a climbing rate of river pollution especially after the aggression on Iraq.

Stations with higher level of TOC% have also high level of trace metal concentrations, reflecting a contamination state by sewage effluent.

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