ISSN 1110-0354
*Bull. Nat. Inst. Of Oceanogr. & Fish., A.R.E. 1998. Vol. (24): 403 - 416*

# *TRACE METALS IN WATERS, SEDIMENTS AND FISHES FROM NORTH WEST ARABIAN GULF*

By

**FARIS, J. M.*; Al-IMARAH; BASIM Y.D. AL-KAFAJI AND A.R.M. MOHAMED**

* *Marine Science Center, University of Basrah.*

**Key Words: Trace Metals, Marine Chemistry, Arabian Gulf.**

## *ABSTRACT*

*The concentration and distribution of trace metals in dissolved and particulate phases of water, exchangeable and residual fractions of sediments and different organs of fishes from NW Arabian Gulf were investigated monthly during the period Oct. 94 to Sep. 95. Seasonal variation were observed in the mean concentrations of the studied metals in both phases of water with less account in both fractions of the sediments. Lead recorded clear level in particulate phase of water due to heavy traffic densities and industrial activities, while Cd and Pb were observed in high percent among the metals in the exchangeable fraction of the sediments indicating their anthropogenic sources. The concentration of trace metals in different fish species are different from one species to an other, and the organs of same species. Different accumulation of trace metals were also observed depending on the nature and the function of the tissue and ability of fish on regulating the level of the metals in their bodies during the uptake and elimination processes. For bottom feeder fishes it is found that gill accumulates Mn, liver accumulates Cu and Fe, Kidney accumulates Cd and Cr while gonad accumulates Zn with less accumulation in muscles specially Cd, Cr and Pb, and the levels of some metals are increased with age of the fish. Concentration of trace metals reported in different fishes from NW Arabian Gulf were lower than those reported in the world and within the acceptable world wide range.*

## *INTRODUCTION*

There are numerous types of pollutants found in the aquatic environment such as organic materials, major and trace metals which contribute to both natural and anthropogenic sources. Natural sources include storm dust-fall, erosion or crustal weathering and dead and decomposition of the biota in water, whereas the anthropogenic sources include sewage, industrial, agricultural and automobile waste as - well as shipwrecks and dumping of war materials (Lleyd, 1992; FAO, 1994; Al-Saad, 1995).

As a result of direct discharges of wastes containing trace metals to the environment, their levels increased in water column, while sediments act as archive for many pollutants (Forstner and Wittman, 1979).

As a part of the aquatic environment, fish can accumulate trace metals and act as indicators of pollution (Mersch *et al*, 1993). In the North West Arabian Gulf few studies were done on trace metals accumulation by different organs of fish species (Al-Kafaji, 1996).

This study aimed to determine monthly variations and distribution of trace metals in water, sediments and organs of two commercial fish species ***Liza subviridus*** (Valencilles, 1836) and Nematalosa nasus (Bioch, 1795) from Shatt Al-Arab estuary, North West Arabian Gulf.

## *MATERIALS AND METHODS*

Shatt Al-Arab estuary was selected study area because it represents a fishing ground. Two stations were chosen for sampling (Fig. 1) which performed monthly for the period Oct. 1994-Sep. 1995. Water samples (20 I) were collected in polyethylene bottles by using water sampler held just below water surface. Samples were section filtered immediately by 0.45 um Millipore membrane fitters. Materials passing are dissolved while those retained are particulate. For trace metals determination by atomic absorption spectrophotometry, the procedures adopted followed Riley and Tayler (1968) and Sturgeon ***et al.***, (1982) for dissolved and particulate phases of water respectively.

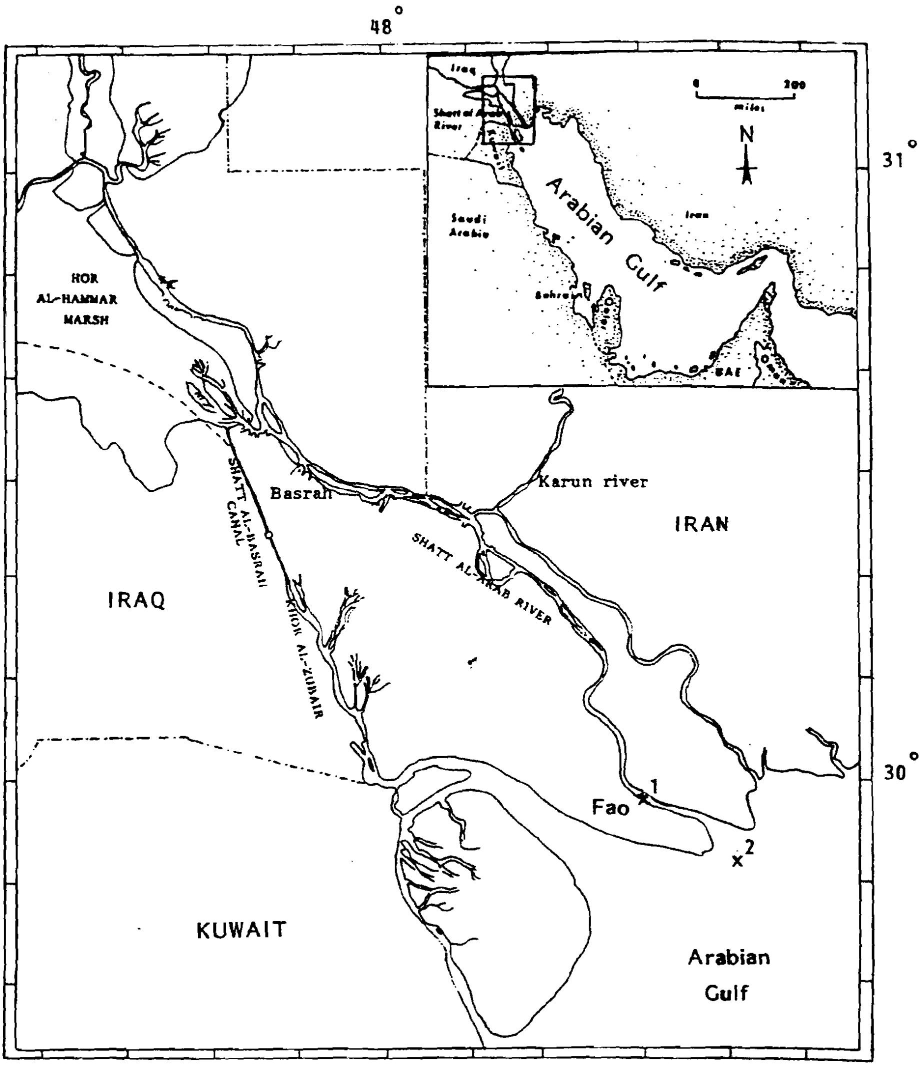


Fig. 1. Map of Shutt Al-Arab estuary and NW Arabian Gulf showing the sampling stations.

Sediments were collected by means of van Veen grab sampler from which subsamples were placed in plastic containers and frozen upon reaching the laboratory. Frozen sediments were dried by Freezer-drier then grinding and sieving. Trace metals analysis was performed on the <63 um fraction of the sediments in which exchangeable trace metals were extracted according to Chester and Voutsinou (1981) while the residual fractions were extracted according to Sturgeon ***et al.***, (1982) procedures.

The total organic contents of the sediments were determined according to El- Wakeel and Riley (1957) by using exothermic heating and oxidation of 1 g grind dry sample with chromic acid.

Two species of commercial fishes ***L. subviridus*** and ***N. nasus*** were collected during sampling by using gill nets 25 x 25 mm mesh. Captures fishes then placed in plastic bags and frozen until reaching to the laboratory. In the lab fishes were thawed, rinsed with deionized water and each species were divided into two length groups. For age determination 5–6 scales were removed from each fish and tested by using projection apparatus model DL5–2.

The abdominal cavity was then opened and the organs gill, liver, gut, gonad and kidney were separated, whereas edible muscle was taken from the left posterior side of each fish. Tissues then freeze dried for 12 h, grind and sieved by 0.5 mm mesh nylon sieve. Tissues were digested by acid mixture following the procedure of ROPME (1982).

Trace metals were determined by Pye Unicum SP-9 atomic absorption spectrophotometer. Acids used were ultrapure and water was deionized.

## *RESULTS*

Mean values for monthly measured salinity, suspended particulate matter and total organic carbon (TOC) for studied stations are listed in Table I. Average value of salinity was greater in station 2 than station 1 while the reverse is true for TOC %.

Sediments consist mostly of silt clay fractions in which annual percentages analyzed were 14.77 and 10.9 for sand 36.31 and 40.1 for silt and 48.92 and 49.0 for clay at stations 1 and 2 respectively.

The distribution and levels of trace metals in water phases and sediment fractions from stations 1 and 2 through the study period are presented in Table II. No doubt trace metals in the particulate phase of water are greater than in the dissolved phase for all trace metals in both station. For sediments trace metals recorded in the residual fraction are higher than in the exchangeable fraction except that for Cd and Pb at both stations during the period of study.

There were considerable differences in the partitioning of trace metals between exchangeable and residual fractions of the sediments. The percentage of exchangeable fractions were: (60,70) Cd, (34,29) CO, (10.7,10.7) Cr, (33,26) Cu, (11.8, 14.9) Fe, (35.6,36.7) Mn, (9.2,6.5)Ni, (70,76) Pb, and (18.6,41.2) Zn for stations 1 and 2 respectively.

The fish specimen were classified into two age groups. The small fish age group $2^{+}$ (160-199 and 140-179 mm) and large fish group$4^{+}$ (200-239 and 180-229 mm) for ***L. subviridus*** and ***N. nasus*** respectively.

Distribution and monthly variations of trace metals in different organs of ***L. subviridus*** and ***N. nasus*** for both age groups are shown in Fig. 2.

For both species it is found that Cd, Cr, and Pb are accumulated in the kidney, Cu in the liver, Mn in the gill and Zn in the gonad, while Co and Fe are accumulated in the gill of ***L. subviridus*** and in the liver of ***N. nasus*** and the reverse is true for Ni.

Maximum values of trace metals were found in the gut of both species as a part of their food chain, while minimum values were recorded in their muscles. The annual mean concentrations of trace metals in the muscles of ***L. subviridus*** for small and large groups were (0.02,0.05) Cd, (0.02,0.1) Co, (0.02, 0.03) Cr, (1.26, 1.88) Cu, (8.41, 8.99) Fe, (1.58,2.0) Mn, (2.06,2.49) Ni, (0.07,0.05) Pb and (8.29,8.87) Zn µg/g dry weight respectively, while for ***N. nasus*** they were (0.01, 0.05) Cd, (0.26, 0.45) Co, (0.25, 0.32) Cr, (2.5, 2.42) Cu, (14.86, 18.9) Fe, (0.88, 1.78) Mn, (1.24, 1.74) Ni, (0.01, 0.05 Pb and (7.76, 6.93) Zn µg/g dry weight respectively.

Table I: Mean values of salinity, suspended particulate matter (SPM) load and total orgenic carbon (TOC%) in Shatt Al-Arab estuary.

| Period | Station 1 | | | Station 2 | | |
|---|---|---|---|---|---|---|
| | Salinity % | SPM, g/l | TOC % | Salinity % | SPM, g/l | TOC % |
| Oct. 94 | 1.26 | 0.134 | 0.94 | 4.42 | 0.163 | 0.53 |
| Nov. | 1.5 | 0.146 | 0.85 | 4.4 | 0.146 | 0.41 |
| Dec. | 1.2 | 0.953 | 0.76 | 4.1 | 0.863 | 0.51 |
| Jan. 95 | 1.2 | 1.275 | 0.84 | 3.2 | 0.965 | 0.65 |
| Feb. | 1.2 | 1.531 | 0.82 | 3.4 | 1.331 | 0.57 |
| Mar. | 1.2 | 0.762 | 0.94 | 2.9 | 0.692 | 0.58 |
| Apr. | 1.1 | 0.680 | 0.82 | 2.5 | 0.673 | 0.68 |
| May | 1.5 | 0.082 | 0.75 | 3.3 | 0.053 | 0.51 |
| Jun | 1.6 | 0.053 | 0.85 | 4.1 | 0.031 | 0.73 |
| Jul. | 1.33 | 0.038 | 1.07 | 5.6 | 0.040 | 0.79 |
| Aug. | 1.7 | 0.020 | 1.09 | 5.4 | 0.042 | 0.62 |
| Sep. | 1.5 | 0.029 | 1.05 | 5.1 | 0.048 | 0.74 |

Table II : Regional mean concentrations of trace metals in water (dissolved , ug / l ; particulate ug / g) and sediments (exchangable and residual, ug/g).

| Metal | Water | | Sediment | |
|---|---|---|---|---|
| | Dissolved | Particulate | Exchangable | Residnal |
| Cd | 0.19 | 24.45 | 0.18 | 0.09 |
| Co | 0.37 | 6.07 | 5.43 | 11.55 |
| Cr | 0.21 | 101.74 | 6.48 | 53.02 |
| Cu | 0.47 | 35.55 | 9.19 | 20.05 |
| Fe | 173.00 | 2454.00 | 686.00 | 4524.5 |
| Mn | 1.52 | 267.05 | 146.05 | 285.00 |
| Ni | 2.85 | 493.65 | 16.15 | 88.05 |
| Pb | 0.23 | 30.99 | 12.92 | 4.82 |
| Zn | 0.82 | 46.23 | 5.81 | 26.18 |

Fig.

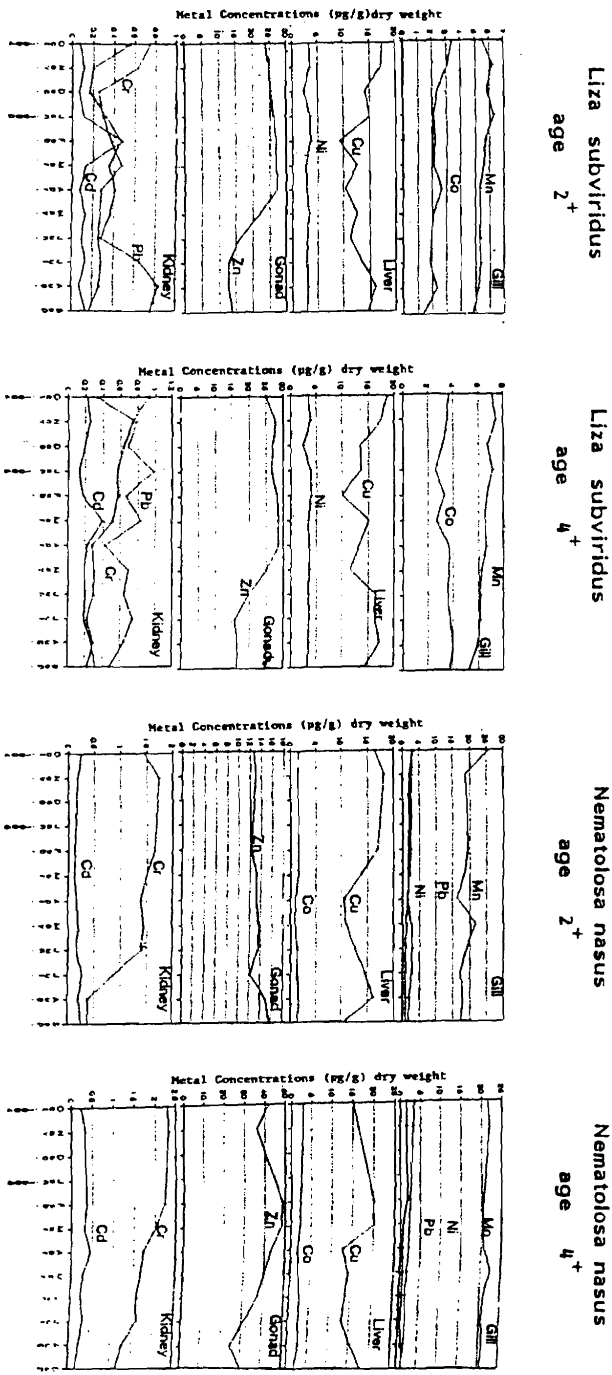


Fig. 2. Monthly variations in metal concentrations (ug/g dry weight) in different tissues of fishes from Shatt Al-Arab estuary during Oct. 1994 to Sep. 1995.

Statistical analysis showed that Cr, Fe and Mn in the dissolved phase of water gave a negative correlation with salinity at both stations, while for Ni and Zn they revealed a significant positive correlation with $P<0.05$ at station 2 only. Regression analysis between trace metals in the dissolved phase of water showed highly significant correlation ($P<0.05$) for Co-Cd, Ni-Zn and Mn-Cd for which $r>0.9$. For sediments a positive with nonsignificant correlation ($P>0.05$) were found for the following pairs: Mn-Fe, Cd-Pb, Fe-Cd, Cu-Mn, Zn-Pb, Ni-Co, Pb-Ni and Cr-Cd, while other pairs showed a negative correlation.

TOC in the sediments showed a positive correlation with Cd, Co, Cr, Fe, Ni, Pb and Zn and significant correlation ($P<0.05$) were observed with the exception of Cd, while Cu showed a negative correlation with TOC at both stations.

Possessive correlation were also observed between concentrations of trace metals in the particulate matter and their concentrations in the gut of studied fish species. Trace metals correlate positively were Cd, Cu, Mn and Pb for ***L. subviridus*** and Cd, Co, Cu, Mn, Ni and Pb for ***N. nasus,*** while Cr, Fe and Zn showed a negative correlation for both groups of studied fish species.

Concentrations of most metals in the gut and their concentrations in the muscles were correlated positively, while levels of Cd and Pb in the livers and gill of ***L. subviridus*** were correlated negatively for both age groups. A negative correlation was observed between Fe and Pb concentration in muscles and their concentrations in the gill, while negative correlation were observed for Co, Cu and Zn concentrations in kidney with their concentrations in the gut.

For ***N. nasus,*** significant correlation ($P<0.05$) was observed between Cu concentration in gill and its concentration in muscle with $r = 0.765$ and 0.608 for small and large fish groups respectively. Good correlation was observed between concentration of Cr in gill and its concentration in the liver with $r= 0.970$ and 0.769 for small and large fish groups respectively and correlate significantly with P values of $<0.05$.

Negative correlation was observed between Zn concentration in the muscle and its concentration in the gonad, and its concentration in the muscle. The results also showed an inverse correlation between Cu, Fe and Zn concentrations in the gonad and their concentrations in the liver.

## *DISCUSSION*

With the exception of Co, Fe and Ni mean concentrations of trace metals in the dissolved phase of water from Shatt Al-Arab estuary were generally lower than the world wide average (Burton, 1976) due to limited population and sources of trace metal pollutants, whereas the relatively high Co and Ni due to petroleum rich substrate of the area (Al-Saadm 1995).

Most of studied metals recorded lower levels during winter and spring months due to dilution by highly discharging of the river during this period (Mohamed ***et al.***, 1995).

There is a tendency for trace metals to be higher in station 2 compared to station 1. This is probably due to the deposition of metals from particulate matter because of mixing processes that happen in estuarine region (Klinkhammer and Bender, 1981).

The negative correlation between salinity and most dissolved trace metals was due to their inverse solubility (Phillips, 1980).

The highly significant correlation between trace metals Cd-Co, Cu-Mn, Fe-Zn and Ni-Zn with $r>0.8$ may be due to the same ratio of existence of these metals in the study area.

Compared to Shatt Al-Arab river, trace metal concentrations as a particulate matter in the water from Shatt Al-Arab estuary were lower (Abaychi and DouAbul, 1985), but for Mn, Ni and Pb they higher (Abaychi and Mustafa, 1988). With the exception of Ni, values reported in this study were less than those reported elsewhere (MAFF, 1993).

Concentrations of trace metals in the particulate matter of the showed high values during spring months that explained on the basis of flood during this period.

Grain size analysis for the sediments revealed their silt clay feature with higher amount at station 2, while sediments at station 1, which is close to the city of Fao, contain higher TOC as well as higher concentrations of trace metals in which statistical analysis showed a significant correlation with $P<0.05$. Trace metal concentrations in the residual fraction were greater than exchangeable fraction with the exception of Cd, and Pb due to their anthropogenic sources.

Trace metals accumulation in the sediment from both stations with elevated values for some metals clearly indicated considerable anthropogenic inputs, mostly industrial waste (Kakulu and Osibango, 1992) which reflects the negative or nonsignificant correlation between different metals.

For both fish species Cd was found to accumulate in the Kidney (Khalaf ***et al.***, 1982) while it is lower in muscle and gonad. The concentration of Cd in the Kidney of small ***L. subviridus*** showed a significant correlation with age ($P<0.05$) in which higher amount of Cd was observed in their food indicating its active feeding in the age, while high correlation was found between Cd in the Kidney of large ***N. nasus*** and age.

Despite age, Co found to be accumulated in gill of ***L. subviridus*** and liver of ***N. nasus.*** It is explain on the basis of high Co concentrations in particulate and sediment and confirmed by its high level at spring and autumn, which may be related to, suspended particulate matter during this period. Negative correlation between Co in gill and liver of ***L. subviridus*** ($r= -0.201$ and $-0.680$ for small and large groups respectively) indicated that this metal accumulates in one of these tissues more than the other, while positive correlation for Co, in gill and liver of ***N. nasus*** ($r= 0.471$ and $0.349$ for small and large groups respectively) indicated that Co accumulates in both tissues in different amounts.

Kidney is found to be the major organ for Cr accumulation in both species, which is in a good agreement with the findings, by Phillips and Russo (1978). Negative correlations were found between Cr in kidney and the age of both species.

It is found that Cu is accumulated in the liver of both species due to Cupper retaining in the liver (Latif, 1980) which is appeared with other findings of other workers for different species (Khalaf ***et al.***, 1985).

For all groups and both species, Fe and Mn found to be accumulated in gill (Khalaf ***et al.***, 1985) with the exception of Fe which accumulates in liver of *N.* ***nasus*** (Rehwoldt, 1976). Iron in gill and liver correlates positively for ***L. subviridus*** and negatively for *N.* ***nasus*** for all age groups indicating that accumulation in these tissues is similar for ***L. subviridus*** and different for *N.* ***nasus.***

Tissues of studied fishes for all ages have different pattern for Ni accumulation in which high concentrations were recorded in liver of ***L. subviridus*** and gill of *N.* ***nasus.*** No correlation was observed between lead in kidney of ***L. subviridus*** and gill of *N.* ***nasus.*** No correlations were found for Ni with age for both species, which indicated that Ni accumulation dose not affected by age and probably act under physiological control.

Lead found to be accumulates in the kidney of ***L. subviridus*** and gill of N. nasus for both age groups, and it is increased during summer months in both tissues. No correlation was observed between lead in kidney of ***L. subviridus*** and gill of *N.* ***nasus*** with age of fishes due to homeostatic control of lead in their tissues.

With the exception of gut, high Zn is found in the gonad of both species, which increased during winter and spring due to maintenance the gonad maturation of both species, while it decreases during summer after releasing eggs. No correlation was observed between concentration of Zn in gonad and age for both species which is agreed with the findings of Murphy ***et al.***, (1978).

All studied trace metals reported in a high concentrations in the gut of both species due to natural food for omnivorous fishes. (Al-Hisnawi, 1990; Majeed, 1989). On the other hand, concentrations of trace metals were recorded in the muscles of both species with the elevation of Fe and Zn and very low concentrations of Cd and Pb which indicates that both fishes are actively regulate metals in their muscles. The highly correlation observed between trace metals in the muscles and guts of both species indicate that gut contents of food is the main source of the metals in the muscles.

In conclusion, trace metals reported in this study for ***L. subviridus*** and *N.* ***nasus*** were lower than those reported for ***L. subviridus*** from Arabian Gulf (Abaychi and Al-Saad, 1988), Khor Al-Zubair (El-Edanee ***et al.***, 1991) and

Shatt Al-Arab (Abdullah and Abdul-Hassan, 1993) as well as lower than world wide values (Bryan, 1976). Tissues indicated that they have variable capacities and storage for trace metals, which are related to their biological functions.

## *REFERENCES*

Abaychi, J.K. and Al-Saad, H.T., 1988. Trace elements in fish from the Arabian Gulf and the Shatt Al-Arab river, Iraq. Bull. Environ. Contam. Toxicol., 40: 226-232.

Abaychi, J.K. and DouAbul, A.A.Z., 1985. Trace metals in Shatt Al-Arab river, Iraq. Water Res., 19: 457-462.

Abaychi, J.K. and Mustafa, Y.Z., 1988. The Asiatic clam corbicula flaminea: An indicator of trace metal pollution in the Shatt Al-Arab river, Iraq. Environ. Poll., 54: 109-122.

Abdullah, A.A.M. and Abdul-Hassan, J.K., 1994. Distribution of zinc and cupper in the tissues of some marine fishes around the coast of Fao, South Iraq. J. Basrah Res., *10: 17-23.*

Al-Hisnawi, F.M.J., 1990. Biology of Green Back Gray Mullet, Liza subvidirdus (Valenciennes, 1836) in Khor Al-Zubair, South Iraq. M. Sc. Thesis, University of Basrah.

Al-Khafaji, B.Y.D., 1996. Trace metals in water sediments and fishes from Shatt Al-Arab estuary, NW Arabian Gulf. Ph. D. Thesis, University of Basrah.

Al-Saad, H.T., 1995. Distribution and sources of hydrocarbons in Shatt Al-Arab estuary and NW Arabian Gulf. Ph. D. Thesis, University of Basrah.

Bryan, G.W., 1976. Metal concentration in the sea. Mar. Poll. Bull., 7: 353-356.

Burton, J.D., 1976. Basic properties and processes in estuarian chemistry. In: Estuarian Chemistry. Burlon, J.D. and Liss, P.S. (Eds.). Academic Press, London.

Chester, R. and Voutsinou, F.G., 1981. The initial assessment of trace metal pollution in coastal sediments. Mar. Poll. Bull., 12: 84-91.

Edl-Edanee, T.J.Z., Al-Kareem, A.A. and Kadum, S.A., 1991. An assessment of trace metal polltuion in the Khor Al-Zubair environment. Marine Mesopotamica, 6: 143-154.

El-Wakeel, S.K. and Riley, J.P., 1957. The determination of organic carbon in marine mud. J. Cons. Int. Explot. Mer., 12: 180-183.

FAO, 1994. Rivew of pollution in the African aquatic environment. CIFA Technical Paper No. 25.

Forstner, U. and Wittman, G.T.W., 1979. Metal pollution in the aquatic environment. Springer Verlag, New York.

Kakulu, S.E. and Osibanjo, O., 1990. Pollution studies of Nigerian rivers. Trace metals levels of surface water in Niger Delta area. Int. J. Environ. Stud., 30: 309-317.

Khalaf, A.N.; Al-Jaafery, A.R.; Khalid, B.Y.; Elias, S.S. and Ishaq, M.W., 1985. The pattern of accumulation of some heavy metals in Barbus grypus (Heckel) from a polluted river. J. Biol. Sci. Res., 16: 51-75.

Klinkhammer, G.P. and Bender, H.L., 1981. Trace metal distribution in Hudson river estuary. Estuar. Coast. Mar. Sci., 12: 629-643.

Latif, M.A., 1980. Metal content of fish tissues. M. Sc. Thesis, Wales University, UK.

Lioyd, R., 1992. Pollution and fresh water fish. Fishing News Books, Oxford, U.K.

MAFF, 1993. Monitoring of contamination in marine fish and shell fish. Aquatic Environ. Monit. Rep., MAFF, Direct. Fish. Res., Lowestoft, 36: 7-16.

Majeed, S.A., 1989. Biology of Gizzard shad ***Nematolosa nasus*** (Block, 1975) in Khor Al-Zubair, South Iraq. M.Sc. Thesis, University of Basrah.

Mersch, J.; Dubost, N. and Pihan, J., 1993. Comparsion of several inert and biological substart to assess the trace metal concentration in the reservoir of the nuclear power plant in Cattenom France-Ann. Limnol., 29: 325-337.

Mohamed, A.R.M.; Hussain, N.A. and Ali, T.S., 1995. Effects of Shatt Al-Basrah Cannal on the hydrobiology of the NW Arabian Gulf. Marine Mesopotamica, 10: 84-104.

Murphy, B.R.; Atchison, G.J.; Alan, W. and Kolar, D.J., 1978. Cadmium and zinc content of fish from an industrial contaminated lake. J. Fish. Biol., 13: 327-335.

Phillips, D.J.H., 1980. Quantitative aquatic biological indicators. Applied Science Publisher, London.

Phillips, G.R. and Russo, R.C., 1978. Metal bioaccumulation in fishes and aquatic invertebrate. A Literature Review, U.S. EPA. 60013-78.

Rehwoldt, R. Karimian, D. and Altmann, H., 1976. Distribution of selected metals in tissue samples of carp ***Cyprinus carpio***. Bull. Environ. Contam. Toxicol., 15: 374-377.

Riley, J.P. and Taylor, D., 1968. Chelating resins for the concentration of trace elements from sea water and their analytical use in conjuction with atomic absorption spectrophotometry. Anal. Chem. Acta, 40: 479-485.

ROPME, 1982. Manual of oceanographic observation and pollutant analysis methods. ROPME, P.O. Box 26388, 13124 Safat, Kuwait.

Sturgeon, R.E.; Desaulnicrs, J.A.; Berman, S.S. and Russell, D.S., 1982. Determination of trace metals in estuarian sediment by graphite furnace atomic absorption spectrpphotometry. Anal. Chem. Acta, 134: 288-291.