**MARINA MESOPOTAMICA 22 (1): 81 92 2007 *ENVIRONMENTAL ASSESSMENT OF TRACE METALS POLLUTION IN SEDIMENT OF KHOR AL-ZUBAIR, IRAQ H. T. Al-Saad\*, I. A. Abd\*\* M. A. Al-Hello\* and M. K. Zuhkair\*\*\**** \*Marine Science centre-University of Basra, Iraq\*\*Ministry of Environment- Basrah, Iraq\*\*\*Dep. of Biology, col. of science, Basrah University Abstract The purpose of this study was to determined and assess the concentrations of some trace metals in surface sediment from different locations of Khor Al-Zubair sediment during 2006. Samples of sediment were collected from seven stations, treated and analyzed for Cobalt, manganese, Nickel, Iron, Copper and Zinc by Atomic Absorption Spectrometric analysis. The Range and average concentrations measured in ug/g were 21.98-43.97 (30.14) for Co, 353.77-570.60 (507.01) for Mn, 34.56-69.13 (44.98) for Ni, 6676.023-7398.385 (7147.05) for Fe, 7.565-27.739 (14.04) for Cu and 27.41-58.48 (43.04)for Zn. Grain size analyses with total organic carbon have been also determined in those sediment. It is noted that the contamination factors in the investigated sediment were 1.69-3.38 for Co, 0.62-0.70 for Mn, 0.90-1.81 for Ni, 0.142-0.157 for Fe, 0.37-1.38 for Cu and less than one in Zn. In general, the contamination factors of trace metals in the present study could be arranged as following Co>Ni>Mn>Cu>Zn>Fe. Results were also compared with earlier studies carried out on trace metals content of fresh and coastal water in the region including the study area. Diversified natural and anthropogenic inputs may have provided the sources of this pollution. Further studies are needed to characterize the source, fate, biogeochemical processes and impacts of these trace metals on coastal habitats and marine life of the region.

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82 Al-Saad,H. T. et al. ----------------------------------------------------------------------------------- Introduction Heavy metals are widely spread in the aquatic environment, some trace metals are dissolved in water, absorbed by phytoplankton and particles suspended matter by some organism (e.g filter feeding). All of these steps can enter into the food chain, later find in the tissues of living organisms, after the death of these organism the heavy metals may deposit to bottom sediment (Al-Saad et al., 1997). Marine sediments can be sensitive indicators for monitoring contamination in aquatic environments (Heba et al., 2004). The bottom sediments serve as a reservoir for heavy metals and therefore deserve special consideration in the planning and design of aquatic pollution research studies. If a sufficiently large and stable sediment sink can be located and studies, it will allow the investigators to evaluate the geochemical change over time and possibly to established baseline levels against which current conditions can be compared and contrasted (Naser et al., 2006). Heavy metals regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Pekey et al., 2004). Khor AL-Zubair, due to its strategic position in southern Iraq ,link with the North-West Arabian Gulf from the south, and with Shatt Al-Basrah from north, the seawaters from the Arabian Gulf effects on the composition of the water of the Khor (Hussain and Ahmed,1999), the heavy metals entering the Khor are transported by prevailing currents. The main source of pollution in this area are power station, sewage effluent, industrial facilities, port facilities, agricultural activities, coastal construction and oil transportation activities (Al-Saadon, 2002). The aim of the present study is to investigate the distribution of heavy metals(Co, Ni, Mn, ,Fe , Cu and Zn) and to evaluate their levels in the Khor Al-Zubair sediment. Study area Khor Al-Zubair is an extension of the Gulf waters in the lower reaches of Mesopotamia Fig (1). It has an approximate length of 42 km, a wide of 1 km at low tide, and an average depth of 10-20 m, During 1983 this water body was connected to an oligohaline marsh (Hor Al-Hammar,), changing the environment of the Khor from a hypersaline lagoon to an estuary one (Hussain and Ahmed, 1999).The topography of Khor Al-Zubair look like a spindle with tapering ends, at the northern and southern ends. The northern end receives fresh water influx of average 700 m3/sec throughout the tidal cycle. The current in the Khor is characterized by one direction through out the tidal cycle towards the southern end (Arabian Gulf), with velocity

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Environmental Assessment of trace metals pollution in sediment 83 --------------------------------------------------------------------------- exceeding 2m/sec during ebb tide and 0.66 m/sec in flood tide. At the Southern end, the water discharge reaches 10000 m3/sec with velocity range 0.8-5.78 m/sec. with big tidal range at Umm-Qasar reaching 4.3m. (Al-Badran et al., 1996). Materials and Methods Sediment samples were collected from Khor AL-Zubair area during summer 2006 (Fig.1). Seven stations were selected in this area depending on their special features. Surficial sediment samples were obtained by mean of a Van Veen grab sampler. Trace metals analysis was performed on the <63 um fraction of the sediment which has been separated by sieving after drying and grinding. The determination of trace metals in sediment samples was done according to the following procedure described by Sturgeon et al.,(1982). Concentrated HCl and HNO3 (1:1) were added to each sample and evaporated to near dryness on the hotplate at 80C, then mixture of concentrated HCLO4 and HF (1:1) were added. After heating to near dryness, 20ml of 0.5 HCL were added and cooled for 10 min. The extraction was decanted into 25 ml plastic volumetric flask. This step was repeated twice and all supernatant were combined. Finally samples were stored prior to trace metals analysis using a Pye-Unicam Atomic Figure 1: Sample locations

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84 Al-Saad,H. T. et al. ------------------------------------------------------------------------------------- Absorption type SP9 Pyeunicam. Grain size analysis of the sediment was done according to Folk (1974), the Total Organic Carbon (TOC) of the investigated sediment was determined, using the wet oxidation method as mentioned by El-Wakeel and Riely (1957). Results and Discussion Sea bottom sediment accumulate metals and affect the near-bottom water layer due to resuspension or dissolution processes (Khan et al.,1998). Polluted sediment may act as a secondary pollution source for the aquatic environment. The study of metal concentrations in sediment is also useful for the estimation of polluted trends (Al-Saad, 1995). The concentration of trace metals (Co, Mn, Ni, Fe, Cu, and Zn ) in sediment of Khor Al-Zubair are given in Table (1). The Range and average concentrations measured in ug/g were 21.98-43.97( 30.14) for Co, 353.77-570.60 (507.01) for Mn, 34.56-69.13 (44.98) for Ni, 6676.023-7398.385 (7147.05) for Fe, 7.565-27.739 (14.04) for Cu and 27.41-58.48 (43.04) for Zn. The high values of Mn and Fe were found at station 1, The great amount of Co and Zn were recorded at station 2, while station 4 revealed high concentrations of Ni and Cu. The distribution of the metals in sediment of Khor Al-Zubair were irregular, there concentration were found low to moderate. Copper is an essential elements for all living organism. The irregular fluctuation might be due to regeneration of organic matter with which Cu forms soluble and insoluble metal chelates. The higher concentrations of some of these metals in this environment were due to the contamination of industrial and navigational discharge (Al-Saadon, 2002). The higher concentration might be harmful for the environmental quality as well as for the aquatic and benthic organisms. Zinc play an important role as a micronutrient required for plant growth and its variation in concentration depend on the generic characteristics of the sediment (Khan and Talukder, 1995), and its concentration has been related to the abundance of metal-reactive compound supposedly not significant affected by mans action (Luoma,1990). Mn is one of the more biochemical and active transition metals in aquatic environment, having considerable biological significance. The industrial discharge act as source of Mn. The source of metals in Khor Al-Zubair might be due to the combination of river in input (Shatt Al-Basra), shipping activities, discharge of untreated industrial effluent and domestic waste, city run-off and atmospheric fall-out. The level of contamination expressed by the contamination factor (CF) Pekey et al.,( 2004) and it was calculated as follows:

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86 Al-Saad,H. T. et al. ------------------------------------------------------------------------------------- proper treatment of the waste before discharging into the Khor. (c): The port authority should develop facilities to receive the waste material from ship and oil tanker. Appropriate legislation should be adopted to prevent dumping in the coastal and marine environment and (d): monitoring and evaluation in this area is very important. Table (1): Concentration of trace metals in sediments samples (μg/g) from Khor Al-Zabair Zn CuFeNiMnCoStation No.27.41 7.5657398.38534.56553.4821.981 58.48 12.6097107.11042.24507.8343.972 44.77 17.6527223.62057.60570.6035.173 45.68 27.7397177.01669.13536.3635.174 44.77 15.1307153.71438.40496.4226.385 42.94 7.5657293.52634.56530.6526.386 40.20 10.0876676.02338.40353.7721.987 43.46 14.04 7147.05 44.98 507.01 30.14 Means Table (2): Grain size analysis in sediment samples from Khor Al-Zabair With Total Organic Carbon (TOC%) Stration No. Sand % Silt % Clay % Texture TOC% 1 8 58 34 Silty clay loam 2.56 2 18 62 20 Silty loam 2.45 3 22 58 20 Silty loam 2.00 4 38 34 28 loam 2.60 5 42 24 34 Clay loam 2.62 6 44 32 24 loam 1.80 7 6 54 40 Silty clay 1.98

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Environmental Assessment of trace metals pollution in sediment 87 --------------------------------------------------------------------------------- Table (3): Concentration factors (CF) of the sediments of Khor Al-Zabair Zn CuFeNiMnCoStation No.0.39 0.370.1570.900.701.691 0.83 0.630.1511.110.643.382 0.63 0.880.1531.510.722.703 0.65 1.380.1521.810.672.704 0.63 0.750.1521.010.622.025 0.61 0.370.1550.900.672.026 0.57 0.500.1421.010.671.697 Table (4): Correlation coffection between different metals in Khor Al-Zubair Mn NiFeCuZn ----0.346Cu----0.238Fe--0.0380.9440.294Ni-0.3230.9370.2500.028Mn0.3660.5360.1060.4930.844Co

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Table (5): Comparison of trace metal concentrations (μg/g) in sediment of various estuaries, seas and oceans Location Cu Zn Ni Mn Fe References Mrghna estuary 0.595-20.695 0.215-4.258 2.578-25.515 5.877-25.005 369.28-991.75 Khan et al., 1998 NE Bay of Bengal Bengladesh coast 28.92 9.56 49.11 60.10 3499.40 Khan and Talukder, 1995 Ganges estuary, India 26 71 32 553 31036 Subramanian et al., 1988 Veller River estuary, India 9 104 - 619 - Mohanachandran, 1986 Cochin estuary, India 4.81 17.77 - - - Nair et al., 1991 Estuarine, Jave Sea 6-54 33.122 - ND - Everaarts, 1989 Gulf of Thailand 2.6-12.1 15.38 - - - Polprasert et al., 1979 Singapore estuary 10-80 100-500 - - - Sin et al., 1991 North Sea 25-240 400-4000 - ND - Everaarts and Fischer, 1992 River Tees, UK 10-1100 40-2900 - 160-1800 - Davies et al., 1991 Port Said, Egypt 14 50 - - - Saad et al., 1981 Kuwait 20.7 44.6 96.9 409.9 1.5\*105 Samhan et al., 1979 North-West Arabian Gulf 2.59 13.74 10.07 51.54 2400 Al-Hashimi and Salman, 1985 North-West Arabian Gulf 17.3-37.1 27-43 386-637 915-1643 4450-9371 Abaychi and Douabul, 1986 North-West Arabian Gulf 24.2 25.2 39.9 751 5869 Abaychi and Al-Saad, 1988 North-West Arabian Gulf 16 60 94 389 31762 Al-Mussawy and Salman, 1989 Khor Al-Zubair 28 72 90 541 9640 Al-Edanee et al., 1991 Khor Al-Zubair 7.565-27.739 27.41-58.48 34.56-69.13 353.77-570.60 6676.023-7398.385 Present Study 88 Al-Saad,H. T. et al. --------------------------------------------------------------------------------------------

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Environmental Assessment of trace metals pollution in sediment 89 ------------------------------------------------------------------------------- References Abaychi, J.K. and Al-Saad, H.T. 1988. Trace element in fish from the Arabian Gulf and the Shatt Al-Arab River, Iraq. Bull. Envirn. Contam. Toxicol., 40:226-232. Abaychi, J.K. and Douabul, A.A.Z. 1986. Trace element geochemical associations in the Arabian Gulf. Mar. Pollut. Bull., 7: 353-356. Al-Badran,B.,Al-Sadoon,B., and Jassim, T. 1996. Flow characteristic measurement of Shatt Al-Basrah canal, south of Iraq. Mar. meso. 11(2); 299-310. Al-Edanee, T.E.; Al-Kareem, A.A. and Kadum, Sh.A. 1991. An assessment of trace metals pollution in the Khor Al- Zubair environment, Iraq. Mar. Meso. 6:143-154. Al-Hashimi, A.H. and Salman, H.H. 1985. Trace metals in the sediments of the North-Western Coastal of the Arabian Gulf. Mar. Poll. Bull., 16:118-120. Al-Mussawy, S.N. and Salman, H.H. 1989. Heavy metals distribution in Khor Al-Zubair sediments NW Arabian Gulf. Mar. Meso 4: 309-318. Al-Saad, H.T. 1995. Distribution and sources of hydrocarbons in Shatt Al-Arab Estuary and North-West Arabian Gulf. Ph.D. thesis, Basra Univ., 186p. Al-Saad, H.T.; Al-Khafaaji, B.Y. and Sultan, A.A. 1996. Distribution of trace metals in water, sediments and biota samples from Shatt Al-Arab estuary. Iraq. Mar. Meso., 11:63-77. Al-Saad, H.T.; Mustafa, Y.Z. and Al-Imarah, F.J. 1997. Distribution of trace metals in tissues of fish from Shatt Al-Arab estuary. Iraq. Mar. Meso., 11:15-25. Al-Saadon,W.J.F.2002. Determination and distribution of total petroleum hydrocarbons and trace metals in water and sediment from Shatt Al-Basrah and Khor Al-Zubair, southern Iraq. Ph.D. thesis, College of Education, basrah Univ. 151p. Davies, C.A.; Tomlinson, K. and Stephenson, T. 1991. Heavy metals in River Tees estuary sediments. Environ.Technol., 12:961-972. Everaarts, J.M. 1989. Heavy metals (Cu,Zn,Cd,Pb) in sediment of the Java Sea, estuarine and coastal areas of east Java and some deep-sea areas. Neth. J. Sea Res., 23:404-413. Everaarts, J.M. and Fischer, C.V. 1992. The distribution of heavy metals (Cu, Zn, Cd, Pb) in the fine fraction of surface sediments of the North Sea. Neth. J. Sea Res., 29: 323-331. El-Wakeel, S.K. and Riley, J.P. 1957. The determination of organic carbon in marine mud. J. Cons. Int. Explor. Mer., 12:180-183.

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90 Al-Saad,H. T. et al. ------------------------------------------------------------------------------------- Folk, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill Publishing Co., Austin, Texas, USA, 182p. Heba, H.M.A.; Al-Edresi, M.A.M.; Al-Saad, H.T. and Abdelmoneim, M.A. 2004. Background levels of heavy metals in dissolved, particulate phase of water and sediment of Al-Hodeidah Red Sea Coast of Yemen. JKAU: MAR. Sci.,15:53-71. Hussain, N.A. and Ahmed, S.M. 1999. Influenced of hydrographic conditions on the interaction between ichthyoplankton and macrozooplankton at Khor Al-Zubair lagoon, Iraq, Arabian Gulf. Qatar Univ. Sci.J. 18; 247-259. Khan, Y.S.A. and Talukder, A.B.M. 1995. Accumulation of trace elements and organochlorine pesticides from the sediments of the south coast of Bangladesh, Bay of Bengal. M.Sc. Thesis, Institute of Marine Science, University of Chittagong, 82p. Khan, Y.S.A.; Hossain, M.S.; Hossain, S.M.G.A. and Halimuzzaman, A.H.M. 1998. An environmental assessment of trace metals in the Ganges- Brahmaputra- Megahna estuary. J. of Remote Sensing and Environment, 2:103-117. Luoma, S.N. 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Heavy metals in the marine Environments, (Edited by Lurness, R.W. and Rainbow, P.S.), pp. 51-66. CRC Press, Boca Raton, FL. Mahanachandran, G.1986. Heavy metal distribution in deltaic and coastal sediments in between Polar and Cauvery River. M. Phill. Dissertation, Jawaharlal Nehru University, New Delhi, India, 156p. Nair, C.K.; Balchand A.N. and Nambisan, P.N.C. 1991. Heavy metal speciation in sediments of Cochin estuary determined using chemical extraction techniques. Sci. of the Total Environ., 102:113-128. Nasr,S.M.,Okban,M.A. and Kasem,S.M.2006. Environmental assessment of heavy metals pollution in bottom sediments of Aden Port, Yemen. Intern J. of Ocean and Oceangra.1(1):99-109 Pekey, H.; Karakas, D.; Aybert, S.; Tolun, L. and Bakoglu, M. 2004. Ecological risk assessment using trace elements from surface sediments of Izmit Bay (Northeastern Marmara Sea) Turkey. Mar. Pollut Bull, 48: 946-953. Polprasert, C.; Vangvisessomjai, S.; Lohani, B.N.; Muttamara, S.; Arbhabhirama, A.; Traichaiyaporn, S.; Khan, P.A. and Wangsuphachart, S. 1979. Heavy metals, DDT and PCR in the upper Gulf of Thailand. Research Report. Division of Engineering, Asian Institute of Technology, Bangkok, 316p.

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Environmental Assessment of trace metals pollution in sediment 91 --------------------------------------------------------------------------------- Saad, M.A.H.; El-Rayis, O.A. and El-Nady, F.E. 1981. Occurrence of some trace metals in bottom deposits from Abu- Kir Bay. Egypt J. Etud. Pollut. CIESM., 5:555-560. Samhan, O.; Anderlini, V. and Zarba, M. 1979. Preliminary investigation of the trace metal levels in the sediments of Kuwait. K.I.S.R., Ann. Sci. Rep., 93-96. Sin, Y.M.; Wong, M.K.; Chou, L.M. and Normala, A. 1991. A study of heavy metal contents of the Singapore River. Environ. Monit. Assessment, 19: 484-494. Subramanian, V.; Tha, P.K. and JerGrieken, R. 1988. Heavy metals in the Ganges estuary. Mar Pollt.Bull, 19(6): 290-3. Sturgeon, R.E.; Desaulniers, J.A.; Berman, S.S. and Russell, D.S. 1982. Determination of trace metals in estuarine sediments by graphic furnace atomic absorption spectrophotometry. Anal. Chim. Acta, 134: 283-291.

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