ICP detection of chemical elements in the sediments along Shatt Al Arab Estuary and Khor Abdullah/Southern Iraq

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ICP detection of chemical elements in the sediments along Shatt Al-Arab Estuary and Khor Abdullah/Southern Iraq.

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Abstract

Concentrations of certain chemical elements; Aluminum, Barium, Berylium, Boron, Cadmium, Calcium, Chromium, Cupper, Iron, Magnesium, Manganes, Molybdinum, Nickel, Potassium, Silver, Sodium, Vanadium, and Zinc were detected in sediment samples collected from Ten sites, five each of fresh (Shatt Al-Arab River) and marine (Khor Abdullah) nature within Basrah Governorate, Southern Iraq during 2012.For the detection of the chemical elements Samples were analyzed by using an inductively coupled plasma mass spectrometer (ICP-MS). Concentrations of studied elements in (µg/g) from higher to lower levels were ranged 158926 – 259519 Ca, 13723 – 38140 Fe, 22330 – 39216 Mg, 6687 – 29037 Al, 749 – 28302 Na, 1322 – 6778 K, 392 – 640 Mn, 12.28 – 94.01 Ba, 16.97 – 55.91 Ni, 19.39 – 33.01 V, 9.98 – 29.76 Zn, 5.09 – 26.80 Cu, 0.1 – 9.51 Ag, 5.30 – 8.03 Co, 0.57 – 7.41 B, 0.00 – 0.43 Mo, 0.12 -0.38 Be, 0.20 – 0.38 Cd. Most of these elements are exist in higher levels in stations with compromise salinity between fresh and marine characters, exactly in the Estuary of Shatt Al-Arab, stations 4, 5, 6, and 7.

Key Wards: ICP, Chemical Elements, Sediments, Shatt Al-Arab, Khor Abdullah.

Introduction

In environmental samples, trace elements are normally determined by several techniques. The most widely used ones are flame and graphite furnace atomic absorption spectrometry (Borg, 1987). Water analysis is a typical application of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). ICP-AES is a well established analytical technique with large linear dynamic range, low detection limits, high precision and accuracy, which offers automation, rapid multi-element analysis for the determination of major, minor and trace elements in water samples. Most trace elements in fresh water are present in low concentrations which approach the detection limit of the instrument. It is not good practice to carry out routine analysis close to the detection limit where accurate results are not possible. To avoid this, sample pre-treatment – a ten-fold pre-concentration by evaporation, is applied .

Trace metals enter the aquatic environment of southern Iraq from both natural and anthrapogenic sources (Mustafa, 1985, Abaychi and Al-Saad, 1988, Al-Saad, 1995).

Natural sources include storm dustfall, erosion or crustal weathering and dead and decomposition of the biota in the water, whereas the anthropogenic sources include sewage wastes, industrial effluent, automobile effluent, petroleum and fertilizer industry effluent (FAO,1994). Trace metals are also incorporate through the food chain of fish either from water via gills or from sediments and marine organisms via gut track (Al-Saad *et al*.,1997). Umm-Qaser and Khor Al Zubair area receive trace metals from different sources .

Traditionally, trace elements and heavy metals in soils and sediments are determined with atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometer (ICP-OES) after acid digestion of the samples. With more convenience and multi-element measurement capability, ICP-OES/ICP-MS have become an attractive instrument for simultaneously determining co-contaminants in environmental samples (Han *et al*., 2006)

Inductively coupled plasma mass spectrometry (ICP-MS) have been used for multi elemental determination of V, Mn, Co, Ni, Cu, Zn, Cd and Pb in seawater in which this method involved chelation of the metals onto imino diacetate resins (Veguería et al.2013). Measurements of trace elements in water samples by Inductively Coupled Plasma could be performed after pre concentration and matrix elimination with chitosan-based chelating resin(Kyue-Hyung, 2000).

Trace element contents of crude oil could be determined by ICP-OES by proposing an ultrasound-assisted acid extraction(de Souza, et al., 2006).

In Addition to water sediment samples were also analyzed, and were found higher in magnitude, except for Zinc and Phosphorus, which were relatively lower in comparison with concentrations found in the tissues and shells samples. Comparisons of heavy metals concentrations among the tissue and shell samples showed that the tissue samples contain higher levels of all metals, except for antimony, which was lower. Arsenic concentrations were not detected in all tissue and shell samples. However, Arsenic was found detectable in the sediment samples. Statistical significance ($P < 0.05$) existed between tissue and shell loads for all tested heavy elements. The Bio-Sediment Accumulation Factor (BSAF) for heavy elements in the snail *Bellamyabengalensis* has been estimated in this study. It was observed that Zinc and Phosphorus have high (BSAF) factor in the tissue; and their factors were 12.17, and 8.65 respectively. Other elements were found within normal ranges in load for shell and tissue samples.

Materials and Methods

All chemicals used were analytical grade quality. Ultrapure water was obtained from a Millipore water system (Millipore), ultrapure Nitric acid (HNO_3, Merck) was used to digest the samples. Stock standard solutions of Aluminum, Barium, Berylium, Boron, Cadmium, Calcium, Chromium, Cupper, Iron, Magnesium, Manganes, Molybdinum, Nickel, Potassium, Silver, Sodium, Vanadium, and Zinc were prepared from salts of the studied elements .

Sediment Samples

Sediment samples were collected from mid way of Shatt Al-Arab estuary and Khor Abdullah, Southern Iraq where oil and petroleum products transported as well as presence of sinking vessels since the Iraqi –Iranian war 1980-1988, are the major causes of marine pollution by petroleum hydrocarbons and chemical elements (Al-Saad and Salman, 2012).

The study area is the Estuary of Shatt Al-Arab River which covered the whole of Shatt Al-Arab river from Qurnah (st.1) to Ras Al-Bishah (st.7) and part of Khor Abdullah (Buoys 5, 13 and 29) located in southeastern Iraqi national water ways which lay between 47 ^{o}-49 ^{o} N latitude and 29^{o} -31^{o} E longitude. 10 sites were selected along the study water ways , as shown in Fig.1. Samples of sediment were collected from the bottom surface by means of grab sampler, store in polyethylene containers, and transferred to the lab in cool box which were then stored frozen at -20 ^{o}C until analysis. Samples then were dried in an oven at 50 ^{o}C and homogenized by powdering in an agate mortor.

Standard acid-digestion and analytical detection method were used for determining major and trace elements in the samples. Digestion of sediment samples was proceeded according to Ahmed et al., (2013) in which 0.5 g of each sample is digested in a mixture of acid solutions consist of HNO_3,H_2O_2 and HF.

Samples, standards, and blank solutions were analysed for chemical elements: Aluminum (Al), Barium (Ba), Berylium (Be), Boron (B), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cupper (Cu), Iron (Fe), Magnesium (Mg), Manganes (Mn), Molybdinum (Mo), Nickel (Ni), Potassium (K), Silver (Ag), Sodium (Na), Vanadium (V), and Zinc (Zn) by using ICP-MS instrument.

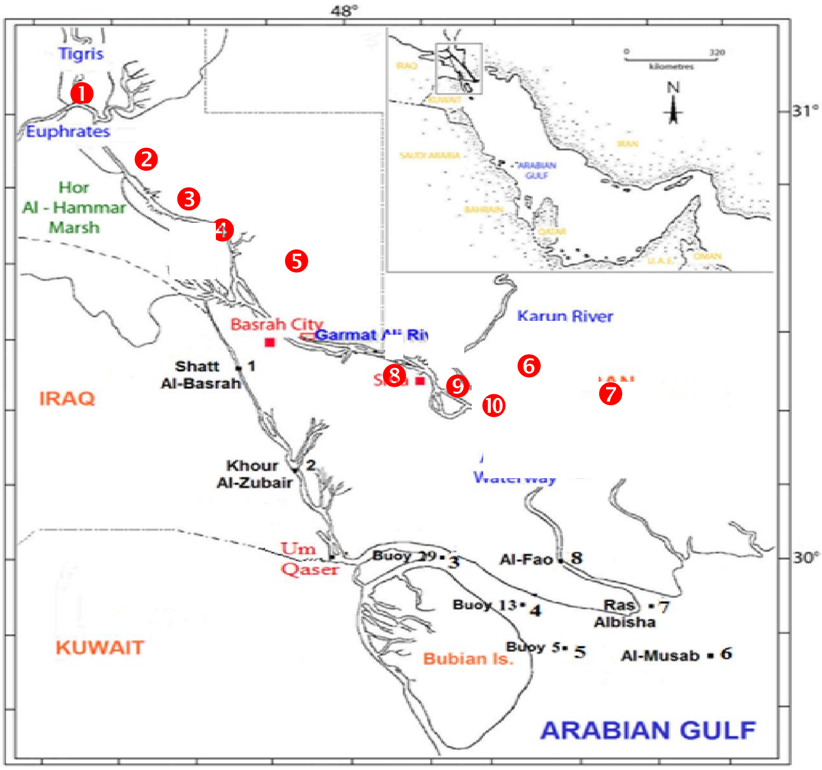

Figure 1. Location map for sampling sites.

Results and Discussion

The levels of concentrations reported for chemical elements in the sediments of Shatt Al-Arab Estuary and Khor Abdullah within the year 2012 are listed in table 1.

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Table 1. Concentrations of chemical elements (µg/g) in sediments from Shatt Al-Arab and Khor Abdullah.

Stations Element	1 Qu rnh	2 De er	3 Sindi bad	4 Asha r	5 Ab oAl k Kaseb	6 Al- Faw	7 Ras El- B Bishah	8 Bo uy 29	9 Bo uy 13	10 Bo uy 5
Aluminum Al	24 511	11 857	2309 1	6687	17 886	290 37	2224 4	22 219	20 773	20 250
Barium Ba	25. 66	18. 98	22.0 9	12.2 8	94. 01	35.2 6	21.67	23. 53	23. 22	24. 68
Berylium Be	0.3 3	0.2 2	0.35	0.12	0.2 8	0.38	0.35	0.3 5	0.3 5	0.3 5
Boron B	4.1 9	3.3 3	5.70	0.57	2.2 5	4.50	6.95	7.4 1	7.2 4	6.7 0
Cadmium Cd	0.3 3	0.2 7	0.35	0.20	0.3 5	0.38	0.37	0.3 5	0.3 2	0.3 5
Calcium Ca	23 3066	21 3715	2184 03	2694 61	25 9519	235 594	1727 90	16 5596	15 9792	15 8926
Cobelt Co	7.1 5	5.3 0	6.98	3.94	6.5 1	7.68	7.80	7.8 1	7.8 6	8.0 3
Cupper Cu	15. 88	9.8 6	16.7 6	5.09	26. 80	17.8 3	16.21	17. 00	17. 48	15. 82
Iron Fe	33 869	18 734	3102 2	1372 3	25 802	381 40	3041 2	29 783	28 338	27 705
Magnesium Mg	35 876	24 157	3389 9	2233 0	22 796	392 16	3443 4	33 144	31 559	31 004
Manganes Mn	64 0	39 2	543	367	71 6	640	514	49 9	47 7	47 1
Molybdinum Mo	0.2 3	0.1 5	0.18	0.05	0.4 3	0.10	0.00	0.2 0	0.0 2	0.0 0
Nickel Ni	45. 16	29. 09	44.7 8	16.9 7	44. 09	50.5 2	55.61	55. 36	55. 43	55. 91
Potassium K	61 97	29 83	6404	1322	35 32	677 8	6281	61 79	56 68	54 91
Silver Ag	8.8 3	0.1 0	8.18	6.81	9.0 2	7.10	9.51	7.0 2	0.2 7	0.0 8
Sodium Na	10 437	60 15	1348 4	749	24 80	905 4	2330 2	27 138	23 869	20 300
Vanadium V	29. 85	22. 68	30.9 0	19.3 9	24. 95	33.0 1	30.83	31. 93	31. 46	31. 76
Zinc Zn	26. 84	17. 25	25.9 7	9.98	42. 33	29.7 6	26.07	26. 82	26. 37	25. 56

Ranges of concentrations of studied elements (µg/g) in the bottom sediments of the selected sampling stations along the Shatt Al-Arab estuary ranked from higher to lower levels were 158926 – 259519 Ca, 13723 – 38140 Fe, 22330 – 39216 Mg, 6687 – 29037 Al, 749 – 28302 Na, 1322 – 6778 K, 392 – 640 Mn, 12.28 – 94.01 Ba, 16.97 – 55.91 Ni, 19.39 – 33.01 V, 9.98 – 29.76 Zn, 5.09 – 26.80 Cu, 0.1 – 9.51 Ag, 5.30 – 8.03 Co, 0.57 – 7.41 B, 0.00 – 0.43 Mo, 0.12 -0.38 Be, 0.20 – 0.38 Cd. Most of these elements could be arises through certain factors for pollution of Shatt Al-Arab estuary by chemical elements which are incorporated in planktons, as it is maintained by recent study of Ajel et al., (2014) in which they reported concentrations (in µg/g) for major and minor chemical elements in zooplanktons collected from Shatt Al-Arab estuary in the range of (26580-135403 Ca), (791.62-16085.06 P), (4108.15- 12463.09 Mg), (1462.64-11749.05 Al), (406.15-6028.21 Na), (11.66-7086.87 Ba), (110.52-3597.44 Si), (43.38-1849.68 K), (53.55-554.83 Mn), , (81.81-1568.27 Br), (12.59-337.37 Cr), (1.88-29.74 B), (0.42-17.71 Li), (0.04-2.53 Ag), (0.31-1.07 Th), (0.08-1.07 Be), (0.01-1.07 Bi), and (ND-0.07 Ti).

Concentration levels of studied chemical elements showed that the highest values were recorded for Ca, Fe, Mg, Al and Na at all station. This may be attributed to the fact that, these elements are the most abundant elements in earth crust, as concentration ranges (in µg/g) of some of these elements which were reported in bottom sediments of Ismailia Canal, Egypt varied between 14002-22865 Fe; 19125-38025 Al; 288-687 Mn; 40.3-99.5 Zn; 17.2-68.5 Cu and 8.2-28.3 Pb with an average values of 47200, 80000, 850, 95, 45, and 20µg/g respectively (El-Bady, 2015).

High concentrations of Na in Khor Abdullah due to the effect of saline water of the Arabian Gulf, while those for Ni and V could be arises from crude oil pollution in the area. The presence of trace elements Zn, Cu, Co, B, Mo, Be, and Cd in low concentrations could be arises due to pollution from sinking vessels in Shatt Al-Arab estuary since the first Gulf war (Iraqi-Iranian war 1980 -1988).

Levels of chemical elements reported in this study are comparable to those values reported else where by adopting the technique of atomic absorption spectrophotometry, for example in the sediments of Euphrates river within the western district of Iraq, Salah et al.,(2015) reported values for chemical elements in µg/g as follows:Cd 1.87, Co 28.16, Cr 54.4, Cu 18.91, Fe 2249.47, Mn 228.18, Ni 67.08, Pb 22.56, Zn 48.00, and in the sediments of west district of Ghana, levels of heavy metals recorded by means of Atomic Absorption Spectroscopy were range as follows; (0.35 – 0.76) Cd, (6.1 – 10.6) Pb, 2065-3124) Fe, (13.8 – 27.9) Zn, (2.93 – 3.2) Mn, (40.12 – 101.15) Cu, and (49.68 – 128.6) As, all in unit of µg/g (Agyanko,2015). They were found to be polluted to different degrees with those metals compared to WHO(2013).

Though some metals like Fe, Cu and Zn are essential micronutrients, they can be detrimental to man and other living organisms at higher concentrations (Nair et al., 2010).

The uptake of trace metals in fish occurs through food ingestion. Contamination of food with trace elements within the water column which reflects upon contamination of sediments (Jarapala, et al., 2014).

Trace elements can be transferred from sediments to benthic organisms and then become a potential risk to human consumers through the food chain (Soto-Jiménez et al., 2011).

The contamination of sediment, by heavy metals is one of the major concern especially in many industrialized countries because of their toxicity persistence and bioaccumulation (Iken et al., 2003).The present study was, therefore, carried out to examine the distribution of some minor and trace elements in the bottom sediments of Ismailia Canal, along its entire course from Cairo to Ismailia.

The Shatt Al-Arab estuary has been through substantial environmental stress regarding trace and heavy metals contamination due to the fact that it has been the scene of three wars over the past three decades; most studies have indicated relatively different levels of heavy and trace metale contaminations in a variety of different habitats and organisms of Shatt Al-Arab Estuary (Freije, 2015). It is found that sediments of Shatt Al-Arab estuary are polluted to different degrees with studied chemical elements in this study compared to WHO(2013).

The results obtained by ICP/MS could not be determinrd precislly because during digestion of samples, this technique does not only require the use of strong acids, but also the longer digestion time.

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. Envirn. Contam. Toxicol., 40(2):226-232.

Agyanko,K., Dartey,E., Kuffor, R. A., and Sarkodia, P. A. (2015). Assessment of trace elements levels in sediments and water of some Artisanal and small scale mining localities in Ghana.Current World Environment, 10(1):101-113.

Ahmad, A. Y., Abdullah, M. D. P., Wood, A. Kh., Hamza, A. S. and Othman, M. R. (2013). Determination of some trace elements in marine sediments uasing ICP-MS and XRF: A comparative study. Orie. J. Chem., 29(2):1-9.

Ajeel, Sh. G. Al-Imarah , Faris J. M. and Hameed, M. F. (2014). Distribution of chemical elements in zooplanktons from Southern Iraqi waters. J. Inter. Environm. And Water, 4(2):140-148.

Al-Saad, H.T. (1995). Distribution and sources of hydrocarbons in Shatt Al-Arab estuary and NW of the Arabian Gulf, Ph.D. thesis. University of Basrah. Basrah, Iraq, 186 p.

Al-Saad, H.T., Mustafa, Y.Z. and Al-Imarah, F.J. (1997). Distribution of trace metals in the tissues of fish from Shatt Al_Arab estuary, Iraq. Marina, Mesopotamica, 11: 15-25.

Al-saad, H. T. and Salman, N. A., (2012). Status of oil pollution in the Arabian Gulf and Shatt Al-Arab estuary: A Review. Coastal environment fxus on Assam Regions, pp. 36-46.

Borg, (1987). Trace-metals and water chemistry of forest lakes in Northern Sweden, Water Res. 21:62–72.

De Souza, et al., 2006. Determination of trace elements in crude oil by ICP-OES using ultrasound-assisted acid extraction. J. Anal. At. Spectrom., 21:1345-1349

El-Bady, M. S. M. (2015). Distribution of some minor and trace elements in the bottom sediments of Ismailia Canal, Egypt. Academia,102:20-28 (http://www.academia.edu/8296751).

FAO (1994). Review of pollution in the African aquatic environment. CIFA Technical paper No.25: 118.

Freije, A. M. (2015). Heavy metal, trace element and petroleum hydrocarbon pollution in the Arabian Gulf: Review. J. Asso. of Arab Universities for Basic and Applied Sci. 17:90-100.

Han F.X., Patterson W.D., Xia Y., Sridhar B. B. M., Su. Y.(2006) . Rapid determination of mercury in plant and soil samples using inductively coupled plasma atomic emission spectroscopy, a comparative study.Water, Air and Soil Pollution,170:161–171.

Iken, A., Egiebro, N. O. and Nyavor, K. (2003).Trace elements in water, fish and sediment fromTuskegee Lake, South Eastern, USA. Air, Water and Soil Pollution. 149: 51– 75.

Jarapala, S. R., Kandlakunta, B., and Thingnganing, L. (2014). Evaluation of Trace Metal Content by ICP-MS Using Closed Vessel Microwave Digestion in Fresh Water Fish. J. Environ. and Public Health, 2014:1-8

Kyue-Hyung, L., Mitsuko,O.,Toshio,T., and Shoji, M.(2000). Simultaneous determination of trace elements in river water samples by ICP-MS in combination with a discrete micro sampling technique after enrichment with chitosan – based chelating resin. Analytical Science, 16:731-738.

Mustafa, Y.Z. (1985). Mussel Corbicula fluminca (Muller, 1774) as bio-indicator of heavy metals pollution in Shatt Al-Arab River. M.Sc. thesis, College of Science, University of Basrah.

Motsara M.R., Roy R.N.(2008), Guide to laboratory establishment for plant nutrient analysis. FAO, Fertilizer and Plant Nutrition, Bulletin 19. Rome .

Nair I.V., Singh K., Arumugam M., Gangadhar K., Clarson D.(2010). Trace metal quality of Meenachil River at Kottayam, Kerala (India) by principal component analysis, World Appl. Sci. J. 9:1100-1107.

Salah,E. A., Zaidan, T. A. and Al-Eawi, A. S., (2015). Identification of sources of heavy metals pollution in Euphrates river sediments (Iraq) using MSA. Inter. J. Env. And water,4(2):50-61.

Soto-Jiménez M. F., Arellano-Fiore C, Rocha-Velarde R, Jara-Marini M. E., Ruelas-Inzunza J,
Páez-Osuna F. (2011). Trophic transfer of lead through a model marine four-level food chain: Tetraselmis suecica, Artemia franciscana, Litopenaeus vannamei, and Haemulon scudderi. Arch. of Env. Cont. and Tox..61(2):280–291.

Veguería, S.F.J., Godoy, J. M., de Campos, R. C., and Gonçalves, R. A., (2013). Trace element determination in seawater by ICP-MS using online, offline and bath procedures of pre concentration and matrix elimination. Micro chemical Journal 106 (2013) 121–128.

World Health Organization (WHO) (2013). Guidelines for Drinking-Water Quality – Second Edition – Volume 2 – Health Criteria and Other Supporting Information. International Programme On Chemical Safety, http//www.who.int/water_sanitation_health/ dwq/2edvol2p1.pdf. (1996). Retrieved in October 2013.

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بلازما الحث المزدوج (ICP) لتقدير العناصر الكيمياوية في رواسب من مصب شط العرب وخور عبدالله / جنوب العراق.

فارس جاسم محمد الامارة وحامد طالب السعد وعبدالزهرة عبدالرسول الحلو ونادية عبدالامير المظفر و صلاح مهدي صالح

قسم الكيمياء وتلوث البيئة البحرية
مركز علوم البحار/جامعة البصرة
البصرة – العراق

الخلاصة

تم تقدير عدد من العناصر الكيمياوية : الالمنيوم والباريوم والبريليوم والبورون والكادميوم والكالسيوم والكروم والنحاس والحديد والمغنيسيوم والمنغنيز والموليبديوم والنيكل والبوتاسيوم والفضة والصوديوم والفناديوم والخارصين في عينات رواسب من عشرة مواقع خمساً منها لمياه نهرية ضمن مصب شط العرب وخمساً لمياه بحرية ضمن خور عبدالله \ محافظة البصرة جنوب العراق خلال عام 2012. قدرت العناصرالكيمياوية باستخدام تقنية بلازما الحث المزدوج والمرتبط بمطياف الكتلة (ICP-MS) . كانت تراكيز العناصر المدروسة بوحدات مايكروغرام \غرام من الاعلى الى الادنى كما يلي: كالسيوم 158926 – 259519, والحديد 13723 – 38140 , والمغنيسيوم 22330 – 39216 , والالمنيوم 6687 – 29037 , والصوديوم 749 – 28302 , و البوتاسيوم 1322 – 6778 , والمنغنيز 392 – 640 , والباريوم 12.28 – 94.01 , و النيكل 16.97 – 55.91, والفناديوم 19.39 – 33.01 , والخارصين 9.98 – 29.76 , والنحاس 5.09 – 26.80 , والفضة 0.1 – 9.51 , والكوبلت 5.30 – 8.03 , والبورون 0.57 – 7.41 , والمولبدينوم 0.00 – 0.43 , والبيريليوم 0.12 – 0.38 , والكادميوم 0.20 – 0.38 . معظم هذه العناصر يتواجد بمستويات عالية في مياه تتميز بملوحة معتدلة بين الصفات العذبة والبحرية وبالتحديد في مصب شط العرب للمحطات 4 و 5 و 6 و 7.

كلمات مفتاحية: بلازما الحث المزدوج, العناصر الكيمياوية, الرواسب, شط العرب, خور عبدالله.