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" TOTAL MERCURY LEVELS IN THE COASTAL ENVIRONMENT OF QATAR (ARABIAN GULF)"

By

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ABSTRACT :

The levels of total Mercury (t-Hg) were determined in various segments of the marine environment of Qatar. Several coastal stations, both on the East as well as the West coast of Qatar were worked for t-Hg in seawater, sediments and biological matrices. Nearly 20 stations were worked within the EEZ of Qatar, on the east coast, wherein seawater samples were collected at different depths for t-Hg along with surface sediments and resident biota. Seawater samples were not filtered and results given are for total dissolved Hg. Sediment samples were analyzed for leachable as well as t-Hg contents.

A wide range of 22-198 ng/L values were obtained for the seawater samples, 0.098-317 ug/g dry wt. in sediments and 0.008-0.093 ug/g dry wt. in biota were measured. The leachable fractions amounted to a range of 3-18% of the t-Hg in sediments. The results do not indicate any elevated levels but are discussed in the light of the geographical distribution of stations and sampling sites with respect to their location and possible input sources.

INTRODUCTION :

The Coastal environment of Qatar, a Peninsular projection on the Eastern Arabian Gulf, is subjected to a wide variety of inputs both from domestic as well as industrial sources. Oil and Gas combined with petro-chemical based industries are the mainstay of the economy and are expanding. As part of the ongoing program on investigating the marine environment around Qatar, various segments were analyzed for total Hg concentrations. Information on the levels of Hg around Qatar, as indeed, in the Arabian Gulf are very few and patchy. Al Midfa et al 1994 analyzed Hg species in seawater and sediments around Doha, including the Doha harbour. Fowler 1985, touched upon Hg concentrations in the A. Gulf briefly while Kureishy and Ahmed, 1994 analyzed surface sediments from the whole Gulf for total Hg. Kureishy et al 1995, reported Hg levels in some macroalgal species from the Abu Ali area on the Saudi coast. Findings of ROPME project on Hg is contained in a report (1988). No information is, however, available on Hg concentrations around Qatar. Hence it was thought to investigate the levels of Hg in various segments of the marine environment of Qatar so as to generate information on one of the most toxic trace element and its baseline levels. Hg is the most environmentally significant and potentially hazardous element found in varying quantities in the coastal environment. It is a non-essential heavy metal with no recorded biological function. It is also known that Hg undergoes transformation to more toxic organic (Methyl Hg) forms in organisms.

Materials and Methods

Sampling station positions are given in Fig 1. Briefly, shore samples at 10 different locales were collected. Seawater samples were drawn into precleaned amber-colour glass bottles (2.5L) and acidified to a pH below 2 by adding 9N H_2SO_4. Sediment samples and biota were collected and deep frozen immediately until analysis. Offshore sampling was done on board R.V. Mukhtabar Al-Bahar. The seawater samples were collected by precleaned Niskin Samplers and transferred to 2.5 L amber colour glass bottles and preserved for analysis as before, A Grab (Van Vein) was used to collect surface sediments. Biological specimens were collected by using a dredge and organisms were divided into groups.

On reaching the shore laboratory the samples were analyzed using the following methods :

Briefly sediments were fractionated into two fractions, larger than 2mm and less than 2mm. The < 2mm fractions were used for analysis after eliminating the shell fragments. The sediment samples were leached with 0.5 M suprapure HCl for leachable fraction while for total Hg they were digested with aqua-regia, MOOPAM 1989. Biological specimens were pooled into groups and soft parts dissected for wet digestion using ultrapure acids, and cold vapour techniques. Preconcentration of total Hg in seawater was achieved by complexing it with dithizone at low pH. The complex was extracted in carbon tertrachloride and back extracted in 5 M HCl. The acid extract was shaken with sodium nitrite to

decompose the dithizone and revert Hg to aqueous phase. Excess of nitrite was reduced with hydroxylamine hydrochloride. Inorganic mercury compounds were finally reduced to elemental Hg with a reducing agent ($Sncl_2$) and measured by Cold vapour techniques, Gradner and Riley (1973). Before acidification, the samples were neither filtered nor centrifuged. Therefore, the concentrations reported include the acid leachable mercury associated with particulate material also. Blanks and standard seawater samples were prepared by stripping the seawater by dithizone and spiked with known amount of Hg as Mercury chloride and extracted A. co-efficient of variation of ± 5% was obtained using replicate samples and standards.

Reference materials used for sediment and biological matrices showed > 95% recovery for Hg in all samples with a co-efficient of variation of ± 7%.

RESULTS AND DISCUSSION

As mentioned before Figure-1, illustrates the sampling sites, both coastal and offshore stations. The results are presented in Figures 2 and 3 and tables 1-4 in the text. The results in general show quite low concentrations of t-Hg in various segments, however a few elevated levels are also observed and are discussed below.

The table 1 below gives the dissolved t-Hg in coastal stations analysed at 8 different stations spread across the entire coast of Qatar, including the sensitive sites of Umm-Saeed (C1), Doha (C2), Al-Khor (C3), and Dukhan (C6). As can be seen the highest levels were observed in Umm-Saeed, an industrial area, though no discharges of Hg are known in the area followed by the city of Doha. Al Madfa et al 1994 observed a range of 3.3-30.3 ng/L of t-Hg in Doha waters. Our values are much higher than reported by them.

Table-1

Dissolved t-Hg in Coastal stations (ng/L)

STATION	CONCENTRATION	STATION	CONCENTRATION
C1	128	C5	46
C2	88	C6	68
C3	68	C7	42
C4	42	C8	32

Fig-2 gives the distribution of t-Hg within the EEZ of Qatar with a clear increase around the Island of Halul observed, which may largely be attributed to the discharge of Formation water. Higher values of 198 and 183 were observed at 20 meters around Halul Island. This may now decrease as the discharge of formation water has been largely curtailed due to its reinjection in recent times.

Sediment samples showed varying degree of concentrations. The coastal stations showed a range of 0.132-0.239 µg/g with the station near Umm-Saeed depicting the highest level of 0.239 µg/g suggesting a possible source of Hg from this industrial city as indeed observed in seawater too. This may be due to use of Hg as catalyst in the industrial processes.

Table -2

The concentrations of t-Hg and Leachable Hg in sediment of coastal stations (µg/g dry wt).

STATION No.	LEACHABLE FRACTION	t-Hg	STATION No.	LEACHABLE FRACTION	t-Hg
C1	0.042	0.0239	C5	0.032	0.158
C2	0.038	0.201	C6	0.039	0.162
C3	0.031	0.179	C7	0.039	0.17
C4	0.032	0.172	C8	0.029	0.132

Hg concentrations are lesser at other stations. Al Madfa et al 1994 had reported higher levels of t-Hg in sediments ranging from 0.19-1.75 µg/g in sediments around Doha. They also reported a range of 0.19-2.3 with an average of 0.73 µg/g in 63 µm fraction of sediments with leachable Hg in the range of 0.02-0.42 µg/g As can be seen our values are much lower than those of Al Madfa et al 1994. This may probably be due to the sampling locations. A significant point is the difference in our values of t-Hg (dissolved) being higher than, and sediment values lower than those reported by them.

Fig-3 shows the distribution of t-Hg in surface sediments in the EEZ of Qatar, It is clear again that higher concentrations are observed around Halul Island as well as Umm-Saeed. The overall range of t.Hg in offshore stations ranged from 0.098-0.239 µg/g with two higher values of 0.317 and 0.285 closer to Halul Island. The leachable fractions are given in Table-3-clearly indicating higher values around Halul Islands suggesting anthropogenic inputs of Hg. The rest of the stations show low levels of leachable fractions. Stations closer to Doha and Halul also depict slightly higher values as compared to other stations within the EEZ.

Various authors have reported higher values of t-Hg in sediments from coastal environments and bay e.g Balci and Turgoklu (1993) reported 0.06-0.55 ug/g from Izmir Bay, Turkey; Hitchcock and Thomas (1992) reported 0.005-0.5 µg/g from Cardiff Bay, U.K; Gonzalez and Torres (1990) reported values of 0.48-32 ug/g in sediments around a sewage outfall at Havana, Cuba; while Subramaniam and Mohan Chandran (1990) reported lower values of 0.073-0.163 µg/g in the sediments of Southern east coast of India and Giordano et al (1992) reported an average of 0.23 µg/g along the Italian coast. Kureishy and Ahmad 1994 reported values in sediments of around 0.032-0.27 µg/g from all along the Arabian Gulf. Our values are slightly lower considering the area and the closeness to the shores. The low percentage of leachable fractions 3-18% suggest low enrichment of Hg in sediments, barring a few stations close to a possible source, in the EEZ of Qatar. Higher Calcium Carbonate content of sands around Qatar may also be another reason for lower concentrations observed.

A wide range of biological matrices, grouped into taxonomical order of broad categories, were analysed and have shown interesting results, (Table-4) Seagrass showed the lowest concentrations in the range of 0.008-0.022 µg/g while seaweeds depicted slightly higher values of t-Hg in the range of 0.026-0.048 µg/g suggesting a possible buildup in higher plants. In the animal category again mixed plankton, though having a large surface area, showed lowest rang of t-Hg of 0.008-0.018 at different stations while Gastropods and Bivalves (mostly clams and oysters) depicted ranges of 0.022-0.062 and 0.038-0.093 µg/g respectively suggesting that dietary habits have a significant role in t-Hg concentrations in tissues of organisms. Time related accumulation of t-Hg is also noticeable in the ranges observed in marine organisms. Kureishy 1993, has earller reported a wide range of t-Hg, 0.002-0.46 µg/g (wet wt) in a variety of marine organisms form Qatari waters. This study had concluded that larger organisms (large carnivores) had higher concentrations of t-Hg which were largely time related as well as depended on the dietary habits. A positive correlation of t-Hg with size in Hamoor (E. tauvina) was also observed in Qatari waters. In all though the levels of t-Hg in marine organisms around Qatar are quite low and do not suggest any significant biomagnification related to anthropogenic inputs. In a related study by ROPME, it was also shown that large carnivorous species of fish was more likely to have higher levels of t-Hg in the Arabian Gulf, In this report the mean t-Hg levels were reported as 0.15 µg/g from this region, though higher values in organisms and sediments were observed around the outfall of a closed chloralkali plant in Kuwait (ROPME 1988).

In conclusion it can be said that the coastal environment of Qatar including its EEZ is relatively «clean» as regards Hg contamination in this area. Area of concern, however, remain such as around

Halul Island and Umm-Saeed where slightly higher levels were observed. Since the formation water discharge is now almost stopped around Halul station regarding Hg, as well as other "oil derived" contaminants, will further improve.

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REFERENCES

1) **Al Madfa, H; Aboul Dahab, Q; and Holail, H. 1994** : Mercury pollution in Doha (Qatar) coastal environment. Environment Toxicology and chemistry, Vol. 13, No. 5, pp 725-735.

2) **Fowler, S. 1985** : Coastal baseline studies of pollutants in Bahrain, United Arab Emirates, Oman. Proceedings, Regional Symposium for the evaluation for Marine monitoring and Research Program, Al Ain, United Arab Emirates, Dec 8-11, pp71-80.

3) **Kureishy, Tariq W., and Ahmad, Mahmoud H. 1994 :** Total mercury distribution in surface sediments from the Arabian Gulf. Qatar University Science Journal, 14 (2) pp 390-394.

4) **ROPME 1988** : Mercury Project : Review of data and recommendations - Annex IX; ROPME/WG-39/2, ROPME, KUWAIT.

5) **Kureishy, Tariq W.; Abdel - Moati, M.A.R; and Muftah, A. R. 1995 :** Marine Algae as bioindicators of pollution levels in the Arabian Gulf. Qatar Univ. Sci. J. 15 (1)pp 215-221.

6) **MOOPAM 1989** : Manual of Oceanographic observations and pollutant analysis methods. Regional Organization for the protection of marine Environment (ROPME), Kuwait 458p.

7) **Gardner D., and Riley, J.P. 1973** : Mercury in the Atlantic around Iceland J. Cons. Int. Explor. Mar, 35 (2); pp 202-204.

8) **Balci A, and Turkogle, M. 1993** : Heavy Metals in sediments from Izmir Bay, Turkey. Mar. Poll. Bull. 26(2) pp 106-107.

9) **Hitchcock, D.R. and Thomas. B.R. 1992 :** Some trace metals in sediments from Cardiff Bay, U.K. Mar. Poll. Bull. 24(9) pp464-466.

10) **Gonzalez H. and Torres, I. 1990** : Heavy metals in sediments around a sewage outfall at Havana, Cuba. Mar. Poll Bull. 21 (5) pp 253-255.

11) **Subramaniam V. and MohanChandran G. 1990:** Heavy metal distribution and enrichment in the sediments of Southern East Coast of India. Mar. Poll. Bull. 21(7)pp 324-330.

12) **Kureishy, Tariq W. 1993** : Concentrations of Heavy metals in marine organisms around Qatar before and after the Gulf War Oil spill. Mar. Poll. Bull. 27 pp 183-186.

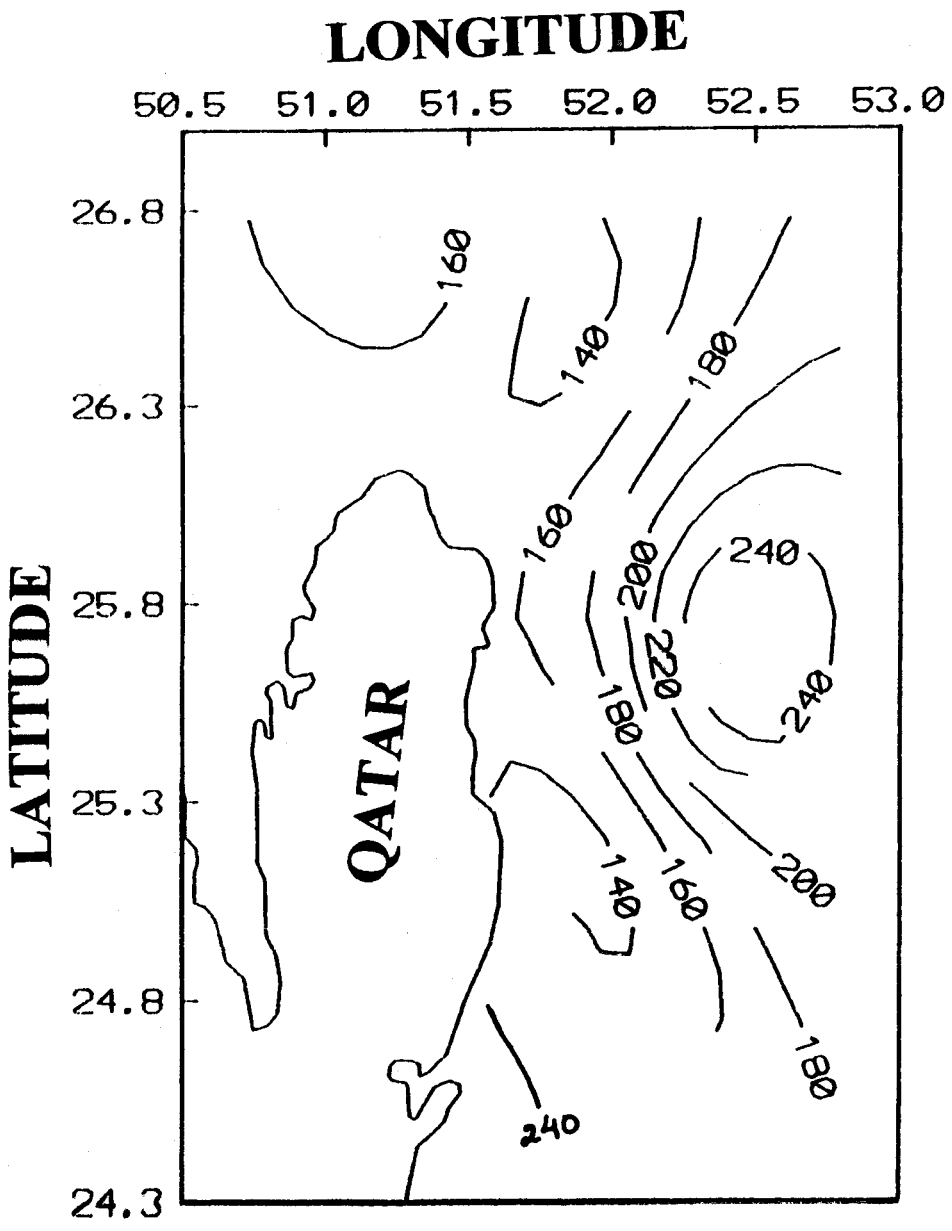

FIG - 1 Hg Concentrations in Sediment x 10^3 ug/g dry wt

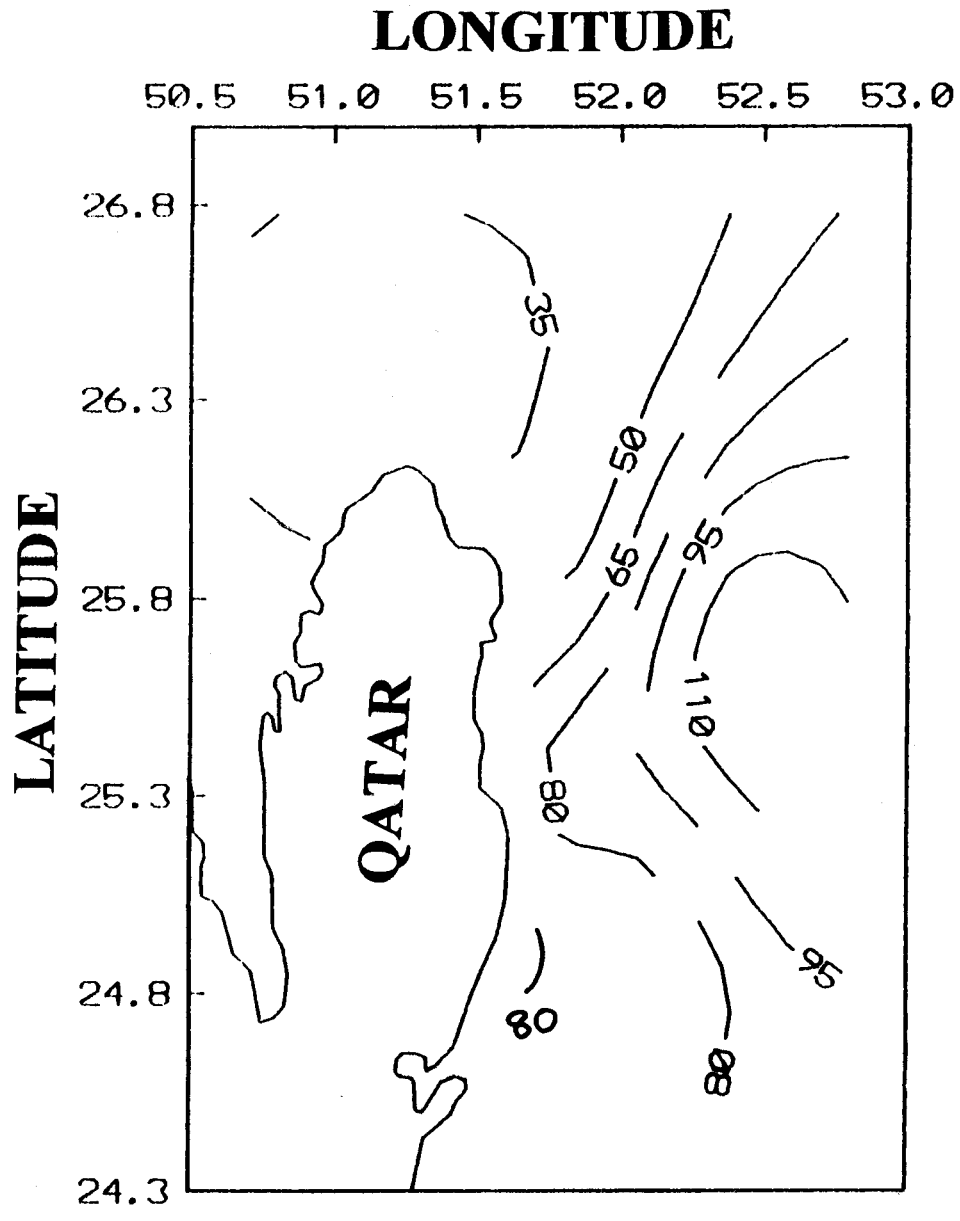

FIG - 2 Hg concentrations in surface sea water ng/L

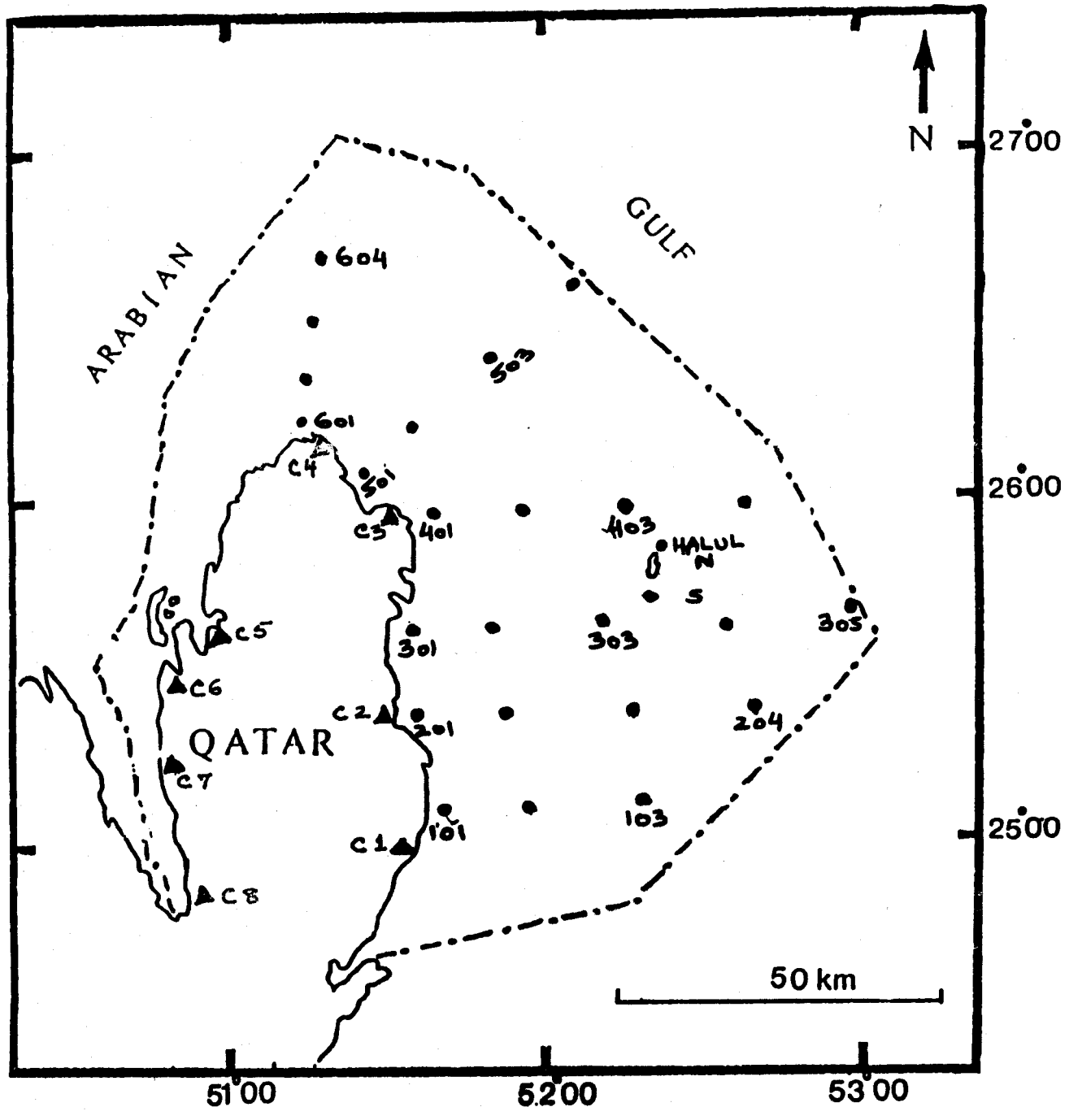

FIG – 3 STATION POSITIONS

▲ **COASTAL STATIONS**

● **OFFSHORE STATIONS**

TABLE-3

Leachable Fractions of Total Hg levels in Surface Sediments

Station No.	Total Hg ug /g
101	0.032
102	0.021
103	0.009
201	0.039
202	0.029
203	0.003
302	0.005
303	0.009
Halul North	0.048
Halul South	0.057
401	0.041
402	0.029
501	0.005
502	0.005
503	0.004
601	0.005
602	0.006
603	0.006

TABLE-4
Total Concentrations in Biota ug/g dry wt.

Groups	Station. No.	Concentrations and ranges.
Seaweeds	Coastal station	0.03-0.048
	101,102,103	0.028-0.034
	201,202,203	0.026-0.029
	302,303	0.031-0.033
	401,402	0.03-0.033
	501,502,503	0.028-0.036
Seagrass	Coastal stations	0.009-0.02
	101,102,103	0.008-0.012
	202	0.013
	303	0.021
	401	0.018
	501	0.022
Mixed Plankton	101,102,103	0.009-0.011
	201,202,203,204	0.011-0.014
	301,302,303,304,305	0.012-0.018
	401,402,403,404	0.012-0.018
	501,502,503,504	0.009-0.014
	601,602,603,604	0.008-0.016
Gastropodes	Coastal stations	0.022-0.032
	101,102	0.03-0.032
	202	0.029
	302,303	0.034-0.036
	402	0.062
	501,502	0.043-0.049
	601,602	0.039-0.042
Bivalves	Coastal stations	0.038-0.065
(mostly oysters&clams)	103	0.058
	201,202	0.062-0.073
	302,303	0.086-0.092
	402	0.093
	502,503	0.082-0.09
	601,602	0.076-0.082