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Determining mercury and methylmercury in sediments of the northern parts of the Persian Gulf

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Abstract

In this study. mercury (Hg) and methylmercury (MMHg) concentrations in sediments from the northern parts of the Persian Gulf were assessed. Surface sediments were collected from nine stations in Hormozgan and Bushehr provinces. All analyses were performed on homogenized and lyophilized samples. Total mercury analysis was performed by thermal decomposition, amalgamation, Atomic Absorption Spectrometry (AMA 254) and methylmercury was analyzed by Headspace Gas Chromatography Atomic Fluorescence Spectrometry after aqueous phase ethylation of the extracted samples. Total mercury (THg) in sediments varied from 13 to 40 ng g-1dw and methylmercury accounted for 0.5% to 1.2% of total mercury. The organic carbon (OC) and organic matter (OM) content ranged from 0.5 to 1.4 and from 5 to 11%, respectively.

Keywords: *Mercury, Sediment, Persian Gulf, Headspace AFS, Combustion AAS.*

1. Introduction

Among the toxic metals, mercury (Hg) is probably one of the most hazardous pollutants of aquatic environments (Leermakers et al., 2005) - in both organic and inorganic forms (Stolelli et al., 1998). Mercury occurs naturally as a mineral and is distributed throughout the environment via natural and anthropogenic processes. The major anthropogenic sources are: mining, smelting of sulfide ores, chloride-alkali production facilities, production of cement, coal energy plants medical and municipal waste incinerators and industrial/commercial boilers (Leermakers et al., 2005; US EPA, 2006).

Most of the anthropogenic Hg enters the aquatic system is in inorganic form, which is converted to organic form (MMHg) by aerobic and anaerobic bacterial activity in situ. Sulfur-reducing bacteria are responsible for most of the mercury methylation in the environment (Leermakers et al., 2005; Muhaya et al., 1998; Mason and Lawrence, 1999). The formation of methylmercury increases the number and species of organisms at risk, and makes

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the risk assessment of Hg more difficult. Benthic biota take up mercury accumulaated in sediments and enter it to the food chain (Penedo de Pinho et al., 2002).

The marine environment in the Persian Gulf has been exposed to many natural and anthropogenic polluting episodes. Besides pollution through riverine inputs from adjacent countries (Iran, Iraq, Kuwait, Saudi Arabia, and the United Arab Emirates, Qatar and Oman), the Persian Gulf has been exposed to various additional contaminants as a consequence of marine accidents and wars in recent years. Being located in a major area of petroleum resources, extraction of oil and the passage of oil tankers have an additional disruptive impact on its marine ecosystem.

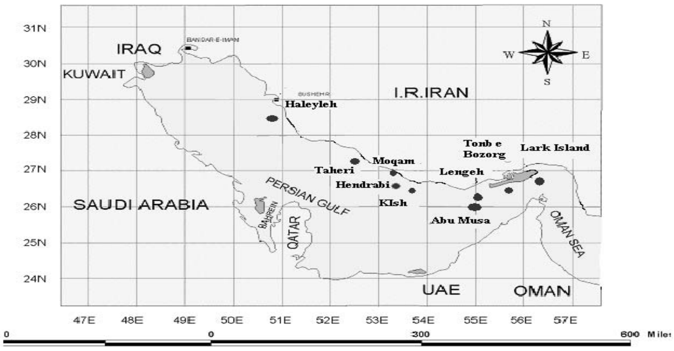
2. Materials and Methods

Sample collection and pretreatment

In order to understand the Hg levels in the northern parts of the Persian Gulf, nine sediment samples belonging to the Hormozgan and Bushehr provinces (Figure 1) were collected using an Ekman Grab (Hydro Bios) and stored frozen in PE bottles. The selected stations, located in industrial as well as rural areas, along ports and harbors in the northern part of the Persian Gulf. Geographical location as well as water depth, water temperature, distance to beach, salinity, PH and water turbidity at each station are summarized (Table 1).

Table 1- The geographical locations of the sampling station

Provinces	stations	Location				Sea condition			
		Latitude	Longitude	Depth (m)	Distance to beach (m)	Temperature (°C)	Salinity	PH	Turbidity
Hormozgah	Lark Island	26° 44′ 40 ″	56° 10′ 55″	58	6	28	37.9	8.1	4.6
	Tonb-e Bozorg	26° 10′ 28″	55° 41′ 00’’	94	27.0	28	38.2	8.4	4.9
	Lengeh	26 °27′ 10″	55° 02′00″	14	9.25	25	39.3	8.3	4.6
	Abu Musa	26° 06′ 18″	55° 09′40″	77	37.28	27	38.4	8.5	3.7
	Kish Island	26° 22′ 38″	53° 42′32″	98	19.25	25	37.8	8.6	3.9
	Hendrabi	26° 36′ 00″	53° 24′00″	88	-	25	38.4	8.5	4.1
	Moqam	26° 57′ 10″	53° 27′14″	18	1.24	25	39.2	8.2	4.3
Boshehr	Taheri	27° 06′80″	52° 34′80″	24	-	22	38.6	8.2	4.2
	Haleyleh	28° 34′ 40″	50° 47′10″	39	15.22	26	38.5	8.3	3.5



Sampling stations of the survey area in the Iranian waters of the Persian Gulf

Fig 1. Sampling locations

Prior to analysis, sediment samples were lyophilized (Leybold Heraus Lyophilizer) and passed through a 1mm PE sieve to remove large particles before being grounded in a mechanical mortar

(Fritsch Pulverisette).

3. Analytical procedures:

3.1 Total mercury

THg in sediments was determined by direct combustion atomic absorption spectrometry using the Advanced Mercury Analyzer (AMA 254, Altec, Chech Republic). The details of the analysis are described in Agah et al., (2007).

3.2 Methyl mercury

In order to extract methyl mercury from sediments, approximately 0.5 to 1 g lyophilized and homogenized sample was digested in HNO_3 (4M) in open vessel microwave oven digester (Prolabo A300, France) equipped with Teflon (PTFE) vessels and reflux condenser. Extraction was followed with dichloromethane (CH_2Cl_2) and back-extraction in water, while purging with N_2 in water bath. The digestion and extraction procedures of methylmercury from sediments are based on the work of Bloom et al., (1997) and Tseng et al., (1997). Sodium tetra ethyl borate (0.2% NaBEt4 in 2% KOH) was used for ethylation. The back extracted samples were ethylated during process of separating derivatives (using sodium tetra ethyl borate) and were subsequently transferred to Head space (Perkin Elmer HS40 XL) sampler coupled to a Gas Chromatography (HP 5890) Atomic Fluorescence Spectrometer (Tekran 2500). Signal processes were performed using a Shimadzu A6 integrator. The details of the extractions procedure and analyzing condition are described in Agah et al., (2008) and Leermakers et al., (2003).

3.3 Organic carbon analysis

About 10 mg to 15 mg fine powder sediment (lyophilized and homogenized) was weighed in a silver cup, followed by an addition of HC1 5% (Merck, pro analysis) until all inorganic carbonates were removed and heated at 80°C in a conventional oven overnight. Then the silver cups were folded with tweezers. The organic carbon in sediments was detected by a Carbo Erba NA1500 elemental analyzer (Hellings, 2000).

3.4 Total Organic Matter (TOM)

Total organic matter was determined by loss on ignition (Tung and Tanner, 2003) at 450°C for 8 hours.

3.5 Detection limits and quality control

The detection limits based on three times the standard deviation (3s.d.) of the procedural blanks resulting in values of 0.28 and 4 ng g^{-1} d.w for total and methylmercury, respectively.

Quality control included the use of blanks and certified reference materials (IAEA 356, trace elements and methyl mercury in estuary sediment) in each digestion batch as well as triplicate analysis. The results of certified reference material showed good agreement with certified mercury and methyl mercury values (Table 2).

Table 2- THg and MMHg concentrations in the certified eference material IAEA 356.

	Certified value ($\mu g.g^{-1}$dw)	Experimental (n=6, $\mu g.g^{-1}$dw)
Total mercury	7.34±0.905	6.141±0.69
Methylmercury	5.46±0.39	5.85±0.62

4. Statistical method

Statistical analysis of the data was carried out using SPSS V13. The mercury levels in different transects were compared by Spearman correlation. A Kolmogorov-Smirnov test was performed to analyze the normality of the data distribution. The relationships between total mercury, methylmercury and organic carbon were investigated using regression analysis. In order to assess significant differences between Hg levels at different sampling stations and organic carbon, data were analyzed by one way ANOVA. A p-value of 0.05 or less indicates that a significant relationship between the variables.

5. Results and Discussion

The results of the THg and MMHg concentrations in sediments companying with organic matter, organic carbon and methylmercury fraction are shown in Table 3.

In our study the detected concentrations of Hg and MMHg were higher than the corresponding detection limits. THg in the sediments varied from 12.8±0.7 ngg^{-1}dw (Abu Musa Island, depth=77 m) to 40.0±1.0 ngg^{-1}dw (Kish Island, depth=98 m) in the Hormozgan province, with median value of 18 ngg^{-1}d.w. Variations in sediment mercury levels were negligible, except in Kish with a relatively higher value than other stations. Concentrations of MMHg in the sediments were relatively low, varied from 0.09 ng.g^{-1} d.w in Lengeh port to 0.21 ng.g^{-1}d.w in Taheri port. The fraction of MMHg ranged from 0.5% at Kish Island to 1.3% at Haleyleh Port. The lowest and the highest OC were detected in sediments of Taheri port (0.50%, Depth of 24 m) and Moqham (1.2%, Depth of 18 m), respectively (Table 3). The results of Hg and MMHg in sediment samples were correlated with each other (Pearson correlation r^2=0.64, p=0.004, except for Halyleh).

Figures 2a and 2b show THg and MMHg levels in the sediments versus the sampling stations. The pattern of MMHg variation in the sediments is comparable with that of THg.

Table 3- THg, MMHg levels, fraction of MMHg (%), organic matter and organic carbons in the Persian Gulf sediments.

Provinces	Stations	Depth (m)	THg ng g^{-1}d.w	RSD %	MMHg ng g^{-1}d.w	MMHg %	OM%	OC%
Hormozgan	Larak Island	58	18.6±0.6	3	0.10	0.5	6	1
	Tonb e Bozorg	94	17.7±0.2	1	0.12	0.7	6	0.6
	Lengeh	14	15.3±0.4	3	0.09	0.6	6	0.7
	Abu Musa	77	12.8±0.7	5	0.12	0.9	5	0.6
	Kish	98	40.0±1.0	4	0.19	0.5	7	0.7
	Hendrabi	88	19.3±0.3	1	0.12	0.6	7	0.7
	Moqham	18	13.1±0.9	6	0.12	0.9	10	1.4
Bushehr	Taheri Port	24	27.4±2.0	7	0.21	0.8	6	0.5
	Haleyleh Port	39	15.2±0.2	1	0.20	1.3	11	0.7

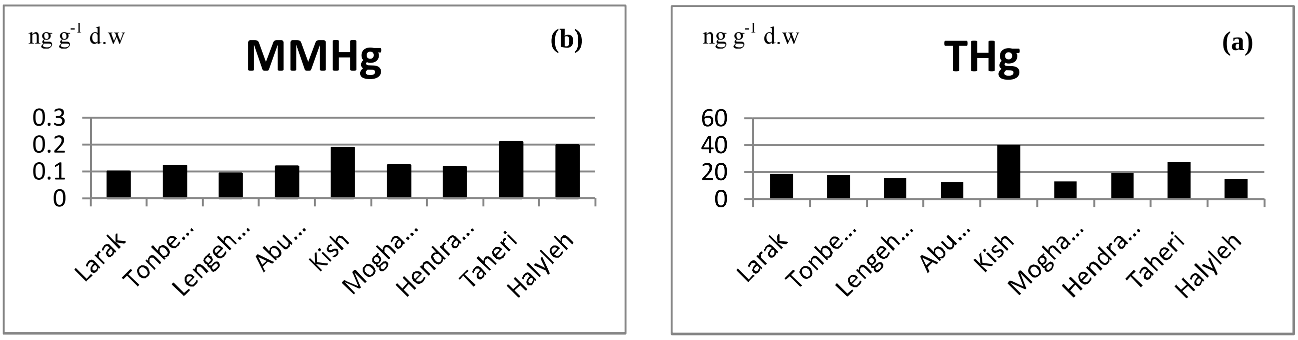


Fig 2. The mean of THg and MMHg levels versus the sampling stations

Organic carbon and organic matter concentrations in the sediments (Except for Halyleh) were significantly correlated (Figure 3, Pearson correlation $r^2=0.68$, $p<0.005$).

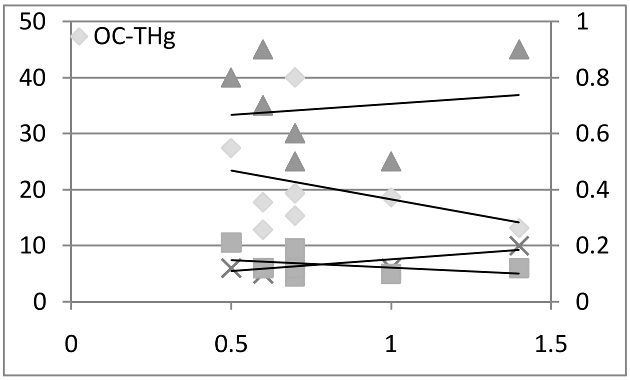


Fig 3. Relationships between OC and THg, MMHg (ng g^{-1} d.w), MMHg (%) and OM (%) levels in the sediments

An overview of Hg concentrations in sediments in different regions of the world is presented in Table 4. The total mercury levels in our study (13-40 ng g^{-1}dw) were relatively higher than that in the sediments of the southern parts (0.6-17 ng g^{-1}dw, ROPME, 1999) of the Persian Gulf, except for that in Kuwait (1.2-39 ng g^{-1}dw, ROPME, 1999) with similar values. Relatively higher mercury levels in the northern parts of the Persian Gulf may be related to hydrological conditions causing finer particles to settle in the deeper waters at the northern parts of the Persian Gulf.

Total mercury levels in the sediment in our study were lower than those found in the North Sea and Scheldt Estuary-Belgium (Baeyens et al., 1998; Leermakers et al., 2001); Lake Balaton-Hangry; (Nguyen et al., 2005); Anadyr Estuary-Russia (Blanco et al., 2000), Nerbi´on-Ibaizabal Estuary-Spain (Landaluze et al., 2004), Husainsagar Lake-India (Prahalad et al., 1988), Western Oregon, Ontario lake_USA (Marvin et al., 2002).

Table 4- Comparing the mercury levels in sediments (ng g^{-1} d.w) in different seas

Location	THg	MMHg	Reference
Persian Gulf ;Iran	13-40 Mean: 20	0.09-0.21	Our study
Persian Gulf, Emirate	0.6-2.2		ROPME, 1999
Saudi Arabia	Max 5.4		
Kuwait	1.2-39.4		
North Sea, Belgium	4–701	0.005–0.45	Leermakers et al., 2001
Scheldt Estuary, Belgium	7–730	0.007–0.47	Leermakers et al., 2001
	800-1400	5–15	Baeyens et al., 1998
Lake Balaton, Hangry	9–160	0.07–0.84	Nguyen et al., 2005
Anadyr Estuary, Russia	80-2100	0.1-0.6	Blanco et al., 2000
Nerbion-Ibaizabal Estuary, Bilbo Basque, Spain	690-5700	8-80	Landaluze et al., 2004
Lake Ontario, US	5-1400		Marvin et, al., 2002
Husainsagar Lake, India	12 400		Prahalad et al., 1988

4. Conclusion

Mercury levels in our study were compared with the Canadian Sediment Quality Guidelines (SQGs), the threshold effect level (TEL[1], 0.17 µg g^{-1}) and probable effect level (PEL[2], 0.486 µg g^{-1}) (US EPA, 2006; MacDonald et al., 2000). Our results were in the range of unpolluted areas regarding Hg<100 ng g^{-1} (IAEA, 1990, ROPME, 1999), and also were 8 to 9 times lower than the threshold effect level.

However mercury concentrations in our study were

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[1] TEL: The level below which adverse biological effects are expected to occur rarely.

[2] PEL: Represents the level above which adverse effects are expected to occur frequently.

lower than other seas, but comprise much higher methylmercury potential (Table 4), except for Lake Balaton.

The THg and MMHg concentrations and the fraction of MMHg were not significantly correlated with TOC contents, which indicate that the concentrations of THg and MMHg in sediments of the sampling areas were not significantly influenced by TOC contents in them.

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