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DETERMINATION OF MERCURY CONCENTRATION IN BANDAR IMAM MARINE SEDIMENTS (PERSIAN GULF)

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The effect of mercury from chloroalkaline unit of Bandar Imam, Iran petrochemical complex (BIPC) has been investigated. 15 stations were chosen in distinct and regular intervals. The samples were taken on depth of 0—10, 10—20 and 20—35 cm in industrial wastewater discharge point to the Persian Gulf. They were transferred to the laboratory and autoclaved at 60-70°C for 48 hours. After drying the samples were mixed and analyzed by using mercury analyzer 254 AMA (Leco). Experiments showed that the concentration of mercury in different samples was high (29-10031 ppb) in comparison with its concentration in Asalloyeh Blank region (12-22 ppb). It was resulted that the concentration of mercury in sediments of Bandar Imam was higher than in standard and blank region because of petrochemical activities and chloride spilling. As the horizontal and vertical distances from the wastewater discharge point were being increased, mercury concentration reduced gradually.

Marine sediments - Persian Gulf - Asalloyeh - Bandar Imam - Mercury

Ուսումնասիրվել է Բանդար Իմամ, Իրան նավթաքիմիական համալիրի քլորալկալիական բլոկից շրջակա միջավայր թափվող սնդիկի ազդեցությունը։ Ընտրվել են միմյանցից կանոնավոր հեռավորությունների վրա գտնվող15 կայաններ։ Նմուշները վերցվել են 0-10, 10-20 և 20-35 սմ խորության վրա՝ Պարսից ծոց արտադրական հոսքաջրերի թափման վայրում։ Նմուշները տեղափոխվել են յաբորատորիա և մշակվել ավտոկյավում 60-70°C պայմաններում 48 ժամվա ընթացքում։ Չորացնելուց հետո նմուշները խառնվել, այնուհետև վերլուծման են ենթարկվել սնդիկի 254 AMA (Leco) վերլուծիչի օգնությամբ։ Ուսումնասիրությունները ցույց են տվել, որ սնդիկի խտությունը տարբեր նմուշներում բարձր է և գտնվում է 29-10031 ppb սահմաններում՝ ի տարբերություն Ասալոյե չաղտոտված վայրի, որտեղ այն կազմում է 12-22 ppb. Արվել է եզրակացություն, որ նավթաքիմիական աշխատանքների և քլորիդների թափման պատձառով սնդիկի խտությունը Բանդար Իմամի նստվածքներում ավելի բարձր է, քան չաղտոտված ստուգիչ տարածքում։ Արտադրական հոսքաջրերի թափման վայրից հորիզոնական և ուղղահայաց հեռացման ժամանակ արձանագրվել է սնդիկի խտության աստիձանական նվազեցում։

Ծովային նստվածքներ - Պարսից ծոց - Ասալոյե - Բանդար Իմամ - սնդիկ

Изучено влияние ртути, поступающей в среду с хлор-щелочного блока нефтехимического комплекса Бандар Имам, Иран. Было выбрано 15 станций в регулярных интервалах. Образцы брались на глубине 0-10, 10-20 и 20-35 см в месте слива в Персидский залив промышленных сточных вод. Образцы переносились в лабораторию и обрабатывались в автоклаве при 60-70°C в течение 48 ч. После высушивания образцы перемешивали и анализировали с использованием ртутного анализатора 254 AMA (Leco). Исследования показали, что концентрация ртути в различных образцах высокая и находится в пределах 29-10031 ppb в отличие от незагрязненного региона Асалойе, где она составляет 12-22 ppb. Было сделано заключение, что концентрация ртути в седиментах Бандар Имама из-за нефтехимических работ и сброса хлоридов была значительно выше, чем в контрольном незагрязненном регионе. При горизонтальном и вертикальном удалении от точки слива промышленных сточных вод было зарегистрировано постепенное уменьшение концентрации ртути.

Морские седименты - Персидский залив – Асалойе - Бандар Имам - ртуть

Hg is amongst the poisonous and heavy metals that pollute water resources and sediments when used in several industries, for example, as an electrode in electrolytic decomposition of the salt (NaCl) to produce chlorine. Hg compounds decompose rarely and accumulate in some organisms such as fish and shrimp. Intoxication due to eating fishes contaminated with Hg has been observed in several parts of the word, including Minamata (Japan) that has attracted the researchers' attention to the detrimental effects of using contaminated sea organisms (fishes). This research was conducted to study the effects of hazardous wastage of the chloroalkaline unit of petrochemical zone of Bandar Imam. In this location where the wastage pours into the sea the sediments were analyzed [1, 2, 3, 7]. In order to measure Hg concentration in the sediments a field inspection of the mentioned area was done, stations were chosen and specified samplings were drawn (0-35 cm).

The following objectives were in mind while choosing the stations:

- determination of the relationship between Hg concentrations of the sediments and increasing of horizontal distance from the exit,
- determination of the relationship between Hg concentration and increasing of sediment depth,
- determination of the effect of dominant North-west (Nw) winds and ebb and flow on the distribution of Hg contamination in the sediments,
- determination of the relationship between Hg concentration and increasing of water depth.

Materials and Methods. The site is located in the northern part of the Persian Gulf (Bandar Imam) (Fig. 1 and 2).



Fig. 1. Map of the studied area



Fig. 2. Map showing the sampling location area

The geological history of the site reveals that about 500 million years ago in Precambrian period, the solid crust of the earth was united i.e. the continents were connected to each other because of the movement and water penetration into the hole due to the volcanic activities. Some continents and oceans were developed and in the midst of the third era the Persian Gulf was appeared and it was attributed to the extension of Oman Sea into a syncline whose axe is along Zagros, with a little deviation to the west.

Persian Gulf in the south coast is low and sandy. Its floor is muddy and contains some sandy hills and coral reefs which are amongst the most impotent areas of fishing and pearling.

The climate is dry and subtropical. The weather is hot during 7-8 months in a year and the temperature reaches to 50°C, being temperate from November to February.

The bed of the site (Bandar Imam) is composed of clay. Because of the low depth of Persian Gulf, high temperatures and winds the surface evaporation is relatively high. The amount of evaporated water is more than the entering water. Ebb and flow differ in various parts.

Sedimentation occurs because of the wind, ebb and flow and sea streams. The stream wave's speed reaches 11 km/day in a counterclockwise direction. These streams become weak at the end of Persian Gulf (Fig. 2) and don't transfer the sediments.

During the investigation appropriate methods were used [5, 6, 8].

In order to determine Hg concentration in the sediments of Bandar Imam, a field inspection from Khowre-musa, between N= $26^{\circ}-30'$ and E= $7^{\circ}-49'$ in the north of Persian Gulf was conducted, then by sampling instruments and a motorboat the sampling was carried out at the depths from 0.5 to 4.5 m on specified distances (every 200 meters). The direction as in the Fig. 2 was from the fishery propagation center in Mahshahre on Sarbandar road to the point that is located in 18 km from Bandar Imam petrochemical wastage exit. The sampling was done in spring during ebb and flow. At first 15 stations determination was conducted in specified distances with a Garmin model GPS. The sampling was done every 50 meters on the radius of area with 5 samples. Fig. 2 shows the path and position of the station in Bandar Imam.

In order to analyze Hg in the sediments, the samples were taken to the laboratory and placed into autoclave at 60-70°C for 48-hours and often drying, were put in crucible and passed through $N_{\rm P}100$ mesh. Equal amounts of each sample from each known depth were mixed to obtain a homogenous sample. To measure the concentration of Hg in the sediments of the stations, specified amount of each sample was carried to the environmental laboratory of the School of Natural Resources and Sea Sciences of Tarbiat Modarres University for analysis with Leco AMA 254 mercury analyzer. This experiment was replicated three times in each station and the mean of these replications has been reported. The above mentioned instrument before the samples analysis was calibrated with the BCR, NIST standard D67.



Fig. 3. Map showing the sampling stations

Results and Discussion. Results of Hg concentration analysis in different stations of Bandar Imam based on the depth with at least 3 replications and Hg concentration analysis in control station are shown in Tables 1 and 2, respectively. In order to present Hg concentration on different depths more precisely, the histogram chart of Hg mean concentrations in different stations is shown on Fig. 4.

Table 1. Hg concentration analysis (ppb) in different stations of Bandar Imam on the depth
$(Mean \pm SD, 3 replications)$

№ of the station	Depth		
	0-10 cm	10-20 cm	20-35 cm
1	10031	6306	543
2	7593	1931	215
3	7375	7609	2112
4	5703	6933	105
5	4302	3302	2221
6	2769	2820	2405
7	2985	2625	188
8	2917	715	705
9	1969	2225	355
10	1145	801	730
11	643	471	344
12	417	355	145
13	347	176	29
14	146	6015	209
15	101000	26055	247504
Standard of deviation	25366.97	6559.331	247.504

Results of Hg concentration analysis in the sediments of Bandar Imam (Tab. 1) indicate:

- measurement of Hg concentration in the sediments of Bandar Imam (Khowremusa), at the sewage exit of Bandar Imam petrochemical chloroalkaline unit shows that the highest concentration of Hg is in the station 1 that is located in 200 m from the sewage exit point. In most of the stations the highest concentration of Hg is on the depth 0-10 cm,
- by increasing of sediments' depth Hg concentration decreases gradually, so that it becomes near zero in lower depths,
- the station 12 is the place for releasing fishes and shrimps of the fishery propagation center of Mahshahre and is located in 18 km from the chloroalkaline unit sewage exit source and is regarded as the control station of Bandar Imam. Table 1 shows that in the station 12 the pollution amount is higher than the EPA standard (2-5 ppm),
- the results show that the difference between the northern and southern stations' concentration is not significant. So waves of ebb and flow and dominant winds don't transfer the pollution. The station 15 which is located within the petrochemical site (50 m before entering the sea) has the highest Hg concentration in comparison with other stations,
- sampling in the above mentioned stations and the geological history of the area indicate that the origin of sediments' pollution (Hg) is the petrochemical chloroalkaline unit of Bandar Imam,
- in order to get some confidence on the results and the pollution source the sampling procedure was also done in the special zone of Asalloyeh.

Results showed that Hg concentration in Asalloyeh was lower than standard (around 12-22 ppb). Values were much lower than Hg concentration in Bandar Imam sediments (Table 2).



-0-10 cm

- 10-20 cm 20-35 cm

Table 2. Hg concentration analysis (ppb) in different stations of Asalloyeh (Mean±SD, 3 replications)

Fig. 4. Hg concentration analysis (ppb) in stations 1 to 14 of Bandar Imam on the depth (Mean± SD, 3 replications)

9 10 11 12 13 14

7

6000

4000 2000 0

> 2 3 4 5 6 8

1

It has been also designed to measure the least amount of Hg in sediments and liquids which acts on the basis of pure 99.99 oxygen combustion that contains a combustion catalysts tube and decomposes the sample in oxygen–rich media. In this way the unwanted elements are separated. The instrument is calibrated on the standard wavelength of 253.7 nm and includes a golden trap. This trap adsorbs the collected or released Hg from the sample. This method is faster and more confident than the other methods. The phases of the method are:

- 1- decomposition time: 305 s,
- 2- drying time: 60 s,
- 3- degradation time: 200 s,
- 4- waiting time: 45s.

Hg in the petrochemical zone of Bandar Imam is washed in chloroalkaline industries by cellular method. The area sediments have been polluted because of Hg-containing sewage movement into the Persian Gulf. Moreover because of Hg movement attributed to the areas affected by the imposed war, it has entered the waters. This is especially evident in the statistics of Iran's Hg imports to restore the petrochemical zone of Bandar Imam in 1992 [2]. So as the Tab. 1 and 2 and the Fig. 4 show, Hg mean concentrations in the depth 0-10 cm vary from 146 to 10031 ppb, in the depth 10-20 cm they vary from 176 to 7609 ppb and in the depth 20-35 cm - vary from 29 to 2405 ppb. Therefore, it is necessary to separate this metal from the sewage by different processes. As the main origin of Hg movement into the sediments is due to the sewage of chloroalkaline unit of Bandar Imam petrochemical zone, Hg should be refined and recycled.

Results from different stations indicate that:

- 1. by increasing of the horizontal distance from the sewage exit point of chloroalkaline unit of Bandar Imam petrochemical zone, Hg concentration in the sediments decreases gradually,
- 2. according to the area geology, the bed soil is consisted of clay (with negative ions). As Hg is a positive ion, it forms a stable legend complex with clay and remains on the surface so Hg concentration decreases while increasing the sediments depth,
- 3. results of northern and southern stations show that the dominant wind is north-west and the waves (which are in the same direction with the dominant wind) don't move pollution [4],
- 4. according to the geographical position of the area which is located at the end part of the Persian Gulf, ebb and flow of this area are weak and don't transfer the pollution,
- 5. Hg has a high specific weight so it precipitates immediately after entering the low depth areas. Then Hg concentration decreases while increasing water depth,
- 6. the main polluting factor of the area is the chloroalkaline industry sewage of Bandar Imam.

Suggestions

1. In order to control the movement of Hg in the area the sewage exit of Hg factories must be checked.

2. The cellular petrochemical and chloroalkaline industries should be cancelled. In turn, a membrane system has to be used.

3. The factories' sewage must be refined and checked properly.

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