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Evaluation of marine pollution by mercury from petrochemical hot spot, west of Libya

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Abstract - Elemental mercury is associated with industrial wastes discharged through the main effluent pipe of the chlorine-Alkali plant at Abo-Kamash area west of Libya. The minimal mercury value of 0.1 ppm dry weight is assumed to be the background level for the uncontaminated sediments in the area. Mercury level ranged from 0.193 to 0.310 ppm in the sediments from the polluted area beyond the plant. The concentration of total mercury in fish muscle ranged from 0.176 and 3.586 µg/g wet wt. The Chlorine-Alkali plant is obviously the major source of mercury pollution.

Keywords: Mercury, Mediterranean Sea, Libya, Chlorine-Alkali plant.

Introduction

Metals, particularly heavy metals such as mercury are toxic to most marine organisms as they are to human being. They can reach them through their food, mainly sea food. It is, therefore, most important to determine such metals in fish, shell fish and other edible marine organisms. Many studies have been done to describe the level of mercury along the northern and eastern coast of the Mediterranean Sea, but a few were carried out along the southern coasts (Joris *et al.*, 1999).

Major sources of contamination are the industrial production of NaOH and plastic, illegal dumping of industrial rubbish, waste incineration and metal smelting (Di-Leonardo *et al.*, 2008).

From 1890 through the mid-20th century, mercury-cell technology was the main commercial process used for the production of chlorine and sodium hydroxide-two of the most commonly used chemicals worldwide.

The process, still used today, involving large quantities of mercury and is a major sources of mercury pollution. Each mercury-cell plant facility may contain hundreds of tons of elemental mercury.

In mercury-contaminated sites, the general improvement of water quality could potentially increase the bioavailability of mercury due to cinnabar or coating contaminated particles which re-suspend lately from the bed sediments providing contaminated particles back to the water column (Gadelha *et al.*, 2010).

Materials and Methods

All environmental samples had been collected on seasonal bases from 1999-2000, fish samples were collected from 3 sites (Fig. 1-a) Sampling gear includes large and small seines, small otter trawls, gill nets and fish traps. Those animals captured in the field were immediately sorted by species and placed in plastic zip lock bags, once labeled the samples were placed into ice chest and stored at -20°C until analysis at the MBRC Laboratories-Libya, were carried out.

Bottom sediments were collected from 7 stations (Fig. 1-c), with one sample from each station, by diving method, and it was impossible to collect samples from the other three stations of the rocky bottom.

Water samples were collected by glass bottles from marine stations distributed around the sea pier (Fig. 1-b). These stations were distributed so that each station was separated from the other by a distance of 0.25 to 2 km.

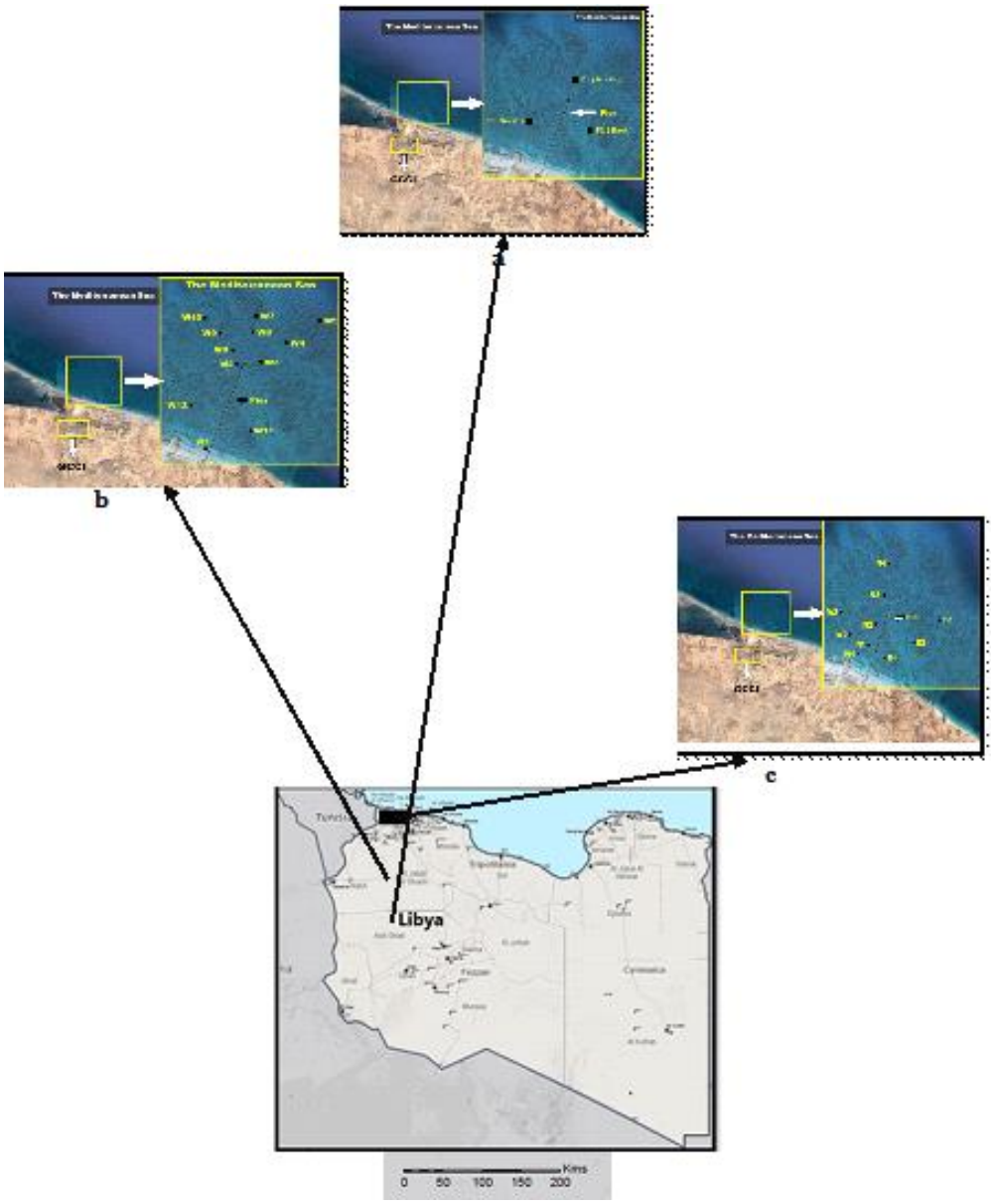

Figure 1. Map of the sampling sites, a-fish, b-water, c-sediments.

Total mercury (T Hg) was determined by atomic absorption spectrophotometer (Mas-50) mercury analyzer Perkin-Elmer after mineralization of samples with sulfuric acid oxidizing the mercury with stannous chloride, the volatile Hg bubbled into closed system of the MAS-50 analyzer (wave length: 253.7) (Hatch and Ott, 1968).

Results & Discussion

Table (1) shows the results of the elemental mercury in seawater samples collected from the study stations at the marine area in front of Abo Kamash industrial complex for the summer and autumn seasons of 1999 and the winter and spring seasons of 2000.

It is apparent that the average concentration of mercury in seawater samples ranged from 0.1 µg/l in the sample collected in the spring and 0.25 µg/l in the samples collected during autumn season, in the samples collected in the summer of 1999, the mercury concentration ranged between 0.1 µg/l and 1.6 µg/l with an average of 1.4 µg/l.

It is a common knowledge that the concentration of mercury in the non-polluted open sea water ranges from a fraction of nanograms to a few nanograms per liter (Bruland, 1983).

Aston and Fouler (1985) pointed out that the open water of the Mediterranean contains a total mercury concentration of 0.5 to 2.5 ng/l.

The concentration of total mercury in water samples collected from the area were 0.1-1.6 µg/l (Table 1).

The mercury level at stations 1 & 2 is higher than in the samples collected 2 Km away from the jet except station 9.

Table 1. Mercury concentration (µg/l) in the sea water from 10 stations around the hot spot location.

Station No.	Range	Average
1	0.1-1.6	0.530
2	0.1-1.5	0.575
3	0.1-1.4	0.481
4	0.1-1.4	0.481
5	0.1-1.4	0.481
6	0.1-1.3	0.451
7	0.1-1.4	0.481
8	0.1-1.2	0.431
9	0.1-1.4	0.568
10	0.1-1.3	0.456

The total mercury was determined in marine fish collected from the sampling area, as shown in Table (2) the levels of mercury were high. The highest concentrations were found in the species of Scorpion fish (3.586 µg/g) and the lowest value was found in *Sarpa salpa* (0.1765 µg/g).

Variations in mercury are related to a number of intrinsic factors (size, age and sex) together with the accumulation mechanisms for mercury in each species.

Table 2. Mercury concentration (µg/g) in fish collected from 3 sites of the sampling area.

Species	No. of Fishes	Sample Average
Sarpa salpa	2	0.1765
Spondyliosoma cantharus	2	0.793
Mullus surmuletus	4	0.9836
Diplodusannularis	4	0.9836
Scorpaena elongate	1	3.586
Pagellus erythrinus	4	0.950
Labrus spp	2	2.343
Lithognathus mormyrus	2	0.802
Dipoldus vulgaris	3	1.471
Sciaena umbra	3	1.202
Euscarus cretensis	1	0.319
Epinephelus costae	1	2.116
Umbrina cirrosa	3	0.844
Trygon pastinaca	1	0.779
Epinephelus guaza	1	2.422
Dentex dentex	1	0.87
Pagrus pagrus	1	1.192

To compare the results obtained from the present study, fish samples were collected from a station located 110 km east of the petrochemical complex, which is considered as a non-polluted area and the results are presented in Table (3).

Samples of the limpet *Patella* were mercury collected and analyzed during 1999 and 2000, representing the summer, autumn, winter and spring seasons. The concentrations of mercury in the tissues of these limpets ranged from 0.213 mg/kg wet weight in winter 2000 and 1.244 mg/kg wet weight in autumn 1999. The general average of these samples was 0.673 mg/kg wet weight. The mussel *Mytilus*, was also used for the presence of mercury.

Table 3. Mercury concentration (µg/g) in fish collected from a reference site (unpolluted).

Species	No. of Fishes	Sample Average
Mullus sp.	2	0.073
Epinephelus guaza	1	0.349
Sciaena umbra	3	0.217
Lithognathus mormyrus	4	0.079
Scorpaena elongate	3	0.133
Trachurus trachurus	3	0.122
Pagellus erythrinus	3	0.199

The concentration of the mercury was between 1-370 µg/g wet weight. The *Octopus* had between 50 to 370 µg/kg (GESAMP, 1986). By comparing the results of the concentration of mercury in the collected *Patella* from the study area with the results obtained above, a significant increase is observed.

The International Council for the Exploration of the Sea carried out studies covering the North Atlantic, the North Sea, the Baltic Sea and the Mediterranean region with a view to tracking the level of mercury pollution in the bottom, the concentration of mercury in this type of limpets in the Mediterranean region ranged between 4-7000 µg/g wet weight UNEP, 1983).

The heavily contaminated biota in the marine environment around GCCI represent a main source for sea food, so it is very important to treat industrial waste waters to avoid risk of human poisoning by mercury (Banana *et al.*, 2016)

Sediments:

Samples Deposits:

Sediment is the main site or location of mercury accumulation in the marine environment. The mercury concentration in the coastal sediments off Abo-Kamash ranged from 0.066 µg/g dry weight at stations N3 and N4 (Spring) to 0.554 µg/g at station E2 (Autumn) (Table 4). However, the concentration of mercury in the sediments was ranging from 0.095 µg/g dry weight at station W2 to 0.428 µg/g dry weight at station E1.

The average seasonal concentration of mercury in the sediment samples collected from the study stations was 0.193, 0.310, 0.260, 0.212 ug/g during the summer, autumn, winter and spring seasons, respectively.

Background concentrations of 0.08 µg/g dry weight were recorded for a range of sediments including the Australian coast (0.004 to 0.005 µg/g dry weight), multiple polar coastal areas (0.02 to 0.08 µg/g dry weight), Baffin Bay Greenland kernels (0.5 µg/g dry weight) (GESAMP, 1986).

However, concentrations of 0.05 to 0.1 mg/kg dry weight can be considered as typical background concentrations of mercury in the Mediterranean sediments (UNEP, 1989).

It is apparent that the levels of mercury concentration in the sediment of Abo-Kamash region are very much higher than those recommended for the Mediterranean sediments. Mean while, the concentration of mercury from an area over 10-20 km from the site of the plant, on the Egyptian coast, were well above the levels recorded near Abo Kamash plant, as the concentration of mercury has increased to 1.4 µg/g dry weight.

While the concentration of sediment samples collected from the Italian coast ranged from 0.1 to 1.11 µg/g dry weight. Moreover, in Minamata region the concentration was about 0.10 µg/g dry weight, while in the Gulf of Trieste, Italy it was 40 µg/g dry weight, as this Gulf received waste from the Hg mercury mine area (GESAMP, 1986).

Mercury values from the east section show higher values (0.369 µg/g) than those recorded from the north and west sections with values of 0.182 µg/g and 0.176 µg/g, respectively, and that can be attributed to the typical currents dominated the studied area.

The minimal mercury value of 0.1 ppm dry weight is assumed to be the background level for uncontaminated sediments (El-Sayed *et al.*, 1979).

Table (5) shows the results of sediments and fish recorded in the present study compared with those of Banana *et al.* (2016).

Table 4. Mercury concentration µg/g dry weight in sediment collected from 10 sites.

Stations	Summer	Autumn	Winter	Spring	Average
E1	---	0.485	0.485	0.314	0.428
E2	0.212	0.554	0.304	0.369	0.366
E3	0.236	0.449	0.449	0.450	0.396
N1	0.185	0.291	0.231	0.128	0.208
N2	0.180	0.229	0.376	0.122	0.226
N3	---	0.158	0.158	0.066	0.127
N4	0.099	0250	0.267	0.066	0.170
W1	0.129	0.313	0.121	0.231	0.198
W2	---	0.085	0.085	0.117	0.095
W3	0.311	0.291	0.121	0.228	0.237

Table 5. Total mercury concentration (µg/g) in the sediments and fishes from the same site study.

Sample type	Range	References
Sediment	0.02-0.75	Banana *et al.* (2016)
Sediments	0.095-0.428	Present study
Fishes	0.34-3.13	Banana *et al.* (2016)
Fish	0.319-3.586	Present study

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تقييم التلوث البحري بالزئبق، غرب ليبيا

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المستخلص- يرتبط عنصر الزئبق بالملوثات الصناعية التي يتم تفريغها من خلال الأنبوب الرئيسي لمصنع البتروكيمياويات في منطقة أبو كماش غرب ليبيا. ومن

المفترض أن تكون القيمة الدنيا للزئبق البالغة 0.1 جزء في المليون من الوزن الجاف هي المستوى الأساسي للرواسب غير الملوثة في المنطقة في حين تراوح مستوى الزئبق من 0.193 إلى 0.310 جزء في المليون في الترسبات من المنطقة الملوثة خارج المصنع. بلغ تركيز الزئبق الكلي في عضلات الاسماك ما بين 0.176 و 3.586 ميكروغرام/غرام وزن الرطب. كما أنه من الواضح أن مصنع الكلور القلوي هو المصدر الرئيسي للتلوث بالزئبق.