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RESEARCH ARTICLE

Seasonal variation of heavy metals (Cd, Pb and Hg) in sediments and in mullet, *Mugil cephalus* (Mugilidae), from the Ghar El Melh Lagoon (Tunisia)

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Abstract

1 - This study investigates the toxic contaminants cadmium (Cd), lead (Pb) and mercury (Hg) in surface sediments and in the fish species *Mugil cephalus* of the lagoon of Ghar El Melh (GEM), Tunisia.

2 - Sampling was conducted seasonally during 2003 and 2004. The results of this study indicated that levels of Cd and Pb varied in sediment from 0.4 to 0.9µgg^{-1}dw and 25 to 70µgg^{-1}dw, respectively. Mercury concentrations in sediment were generally below 1µgg^{-1}dw. The highest level was observed in the north-east of lagoon. In fish muscle, concentrations of Cd, Pb and Hg varied between 0.013 to 0.025µgg^{-1}dw, 0.048 to 0.422µgg^{-1}dw and 0.222 to 0.409µgg^{-1}dw, respectively.

3 - Results of heavy metal analyses in sediment and fish indicated that there were relatively metal contamination problems in GEM lagoon near the harbour due to the anthropogenic activities, notably from the Medjerda River and wastewater from the coastal towns around the lagoon.

Keywords: trace metals, sediments, pollution, lagoon, mullet, Tunisia.

Introduction

Lagoons in northern Tunisia represent a major resource for people and aquatic organisms. One of the most important coastal lagoons is Ghar El Melh (GEM), north of Tunis (37°10 and 10°09). This lagoon has provided a variety of important services for human communities since Roman/Phoenician times. Currently about 10000 people reside within its immediate catchments and much of this area is strongly agricultural. The construction of a new harbour in 1980 on the coast adjacent to the lagoon has made the area an ideal location for the development of fishing and commercial cultivation of marine organisms. The site also has intrinsic value for biodiversity (Hamouda, 1996; Ayache et al, 2006). However, GEM suffers from water contamination problems associated with human activities. Industry, agriculture and population changes have all impacted the lagoon, especially excess nutrients from effluent (Romdhane, 1984, Azzaoui, 1993).

In addition to harboring fishing boats, the lagoon is also a food resource (especially for fish and mollusks) for the region. It is also used for recreational fishing. Previous studies have investigated the ecology of the lagoon (Mahmoudi et al, 2000), water quality (Romdhane, 1985) and contamination by organic compounds (personal communication, 1999). GEM receives land drainage which is diminished since the Medjerda River was diverted away from the lagoon. It is predominantly marine in nature and the main basin is about 1.5m deep. Water circulation system in the lagoon is influenced by the action of winds with main direction North-East. The optimum values of water salinity and temperature were 28-40psu and 15-31°C, respectively.

In recent years, considerable community concern has been expressed about possible metal contamination of the lagoon by groundwater inflow from terrestrial sites industry drainage water from the south slopes of the Eddmina and Jbal Ennadhour mountains and from discharge of urban waste water into the lagoon.

This work was part of the "MELMARINA" project and aims to help understanding of environmental change impacts on coastal lagoons in North Africa, and this study was carried out in order to investigate seasonal bioaccumulation patterns of selected metals in sediments and in fish collected from the GEM lagoon.

Materials and Methods

Nine sediment sampling sites were selected on the basis of possible contamination (Fig. 1). Surface sediment samples were collected during two periods: winter 2003 and summer 2004.

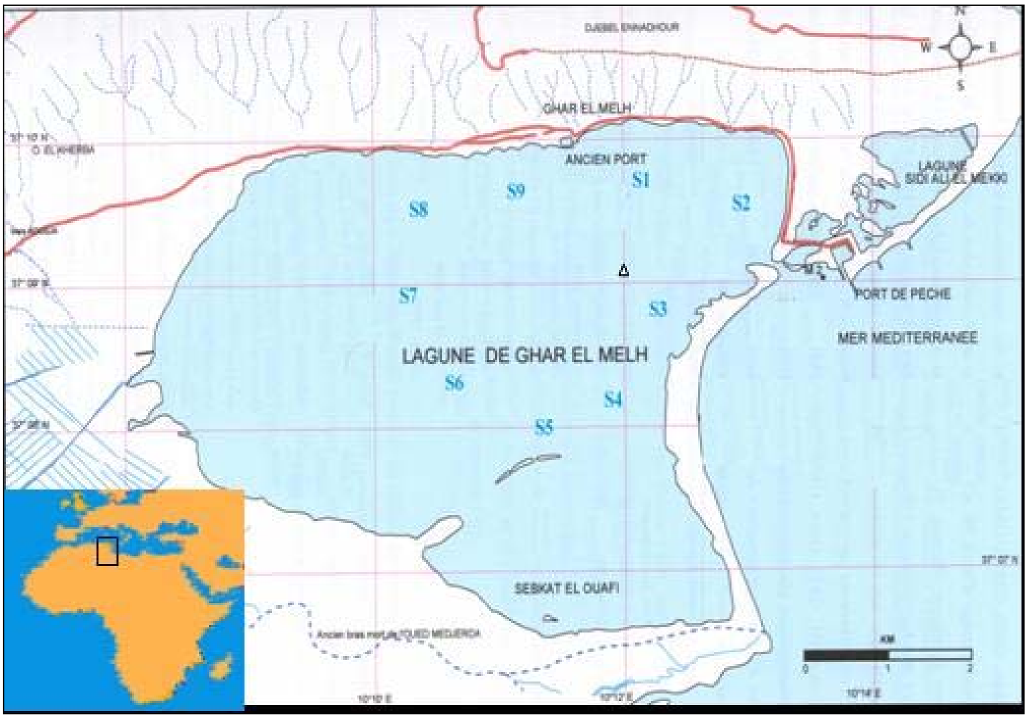

Figure 1. Location of sampling sites for sediments (S), fish (Δ) in Ghar El Melh lagoon.

Sediment sampling was conducted using an Ekman grab. After removing plants and other macro-remains, sediment from the surface (~5cm) was conserved in acid washed plastic bottles. After freeze drying, sediment samples were sieved on a 63µm clean plastic sieve. They were than transferred to individual clean plastic bottles. Approximately 300mg of dried sediment samples were weighed for digestion. Samples were digested in acid-cleaned Teflon microwave vessels with 5ml of ultrapure nitric acid and 2ml ultrapure hydrofluoric acid. A Millestone (ETHOS TCH) system was used and samples were digested for 30min at 200°C. After allowing at least 2h for cooling, the vessels were opened and 0.8g boric acid was added to dissolve the fluoride precipitates (Loring and Rantala, 1992).

Cadmium and lead were analysed by Atomic Absorption Spectrometry (Varian 220Z) and mercury was analysed using Cold Vapour (CV-AAS) following $SnCl_2$ reduction on a Varian

Spectra (AA-10) with a flow injection vapour generator (VGA-77).

Fish samples (*Mugil cephalus*) were collected by trawler net on a seasonal basis from the east coast of lagoon (Fig. 1). The samples were inspected visually (so not to confuse *M. cephalus* with other species), sized and then measured (length). Each individual species was dissected and mass of brain, muscle and liver were placed separately in pre-weighed acid cleaned flasks.

Fish samples were freeze-dried and then ground on agate mortar to obtain affine homogeneous powder. Residual water content was determined by oven drying (105°C for 24h). Fish tissues were digested by microwave using nitric acid (UNEP/IAEA/FAO, 1984) and analyzed using either an atomic absorption spectrophotometer (Varian 220Z) for cadmium (Cd), lead (Pb) or cold vapour AAS (CV-AAS) for mercury (Hg), using $SnCl_2$ reduction on a Varian SpectrA-A10 with a flow injection vapour generator (VGA-77).

Together with a certified reference materiel (sediment IAEA 405, Nist-2976 Mussel tissue and CRM-IAEA-407) obtained from the International Atomic Energy Agency, blanks sample consisting in Milli-Q water were analyzed following the same protocol used for tissue and sediment samples. In order to prevent contamination during preparation and treatment, all sampling materials used were washed in 10% nitric acid, rinsed with double-distilled water and rinsed with Milli-Q water.

For quality control samples, results of analytical data for sediment and biota are given in Table 1. The agreement between the measured and certified reference values was, in general, satisfactory.

Statistical analyses of the data were completed using single factor analyses of variance ANOVA to measure significant differences between seasons. Significance was tested at the $P<0.05$ level.

Table 1. Metal concentrations measured in tissue and sediment certified reference materials. All concentrations expressed as $mgKg^{-1}$ on a dry mass basis.

Metal	IAEA 407 Measured	Fish tissue Certified	IAEA 405 Measured	Estuarine sediment
Hg	0.226±0.007	0.222±0.024	0.821±0.022	0.812±0.139
Cd	0.178±0.006	0.189±0.019	0.714±0.008	0.730±0.205
Pb	0.131±0.010	0.12±0.06	74.06±8.44	74.8±9.4

Results

Metals in sediment

All sampled sediment had a predominantly mud-sand composition and after grain-size analysis the mainly part is composed of particles below 63µm.

The metal concentrations in sediments, expressed on a dry weight basis, are presented in Figure 2. The concentrations of Cd and Pb varied from 0.4 to $0.9µgg^{-1}$ and 25 to $65µgg^{-1}$ respectively.

Generally, the higher levels were found in winter, which coincides with high rainfall period and the most intense fishing activities. The elevated elements of terrestrial origin in this period contribute to the highest Pb concentrations, $65µgg^{-1}$ (Fig. 2) (station 9). The levels of Hg varied between 0.3 and $1.4µgg^{-1}$ in winter and summer. Relatively high concentrations of mercury are observed nearby Ghar el Melh town, supporting the hypothesis of a point source of contamination at the site, the effects of which diminish with distance from the source.

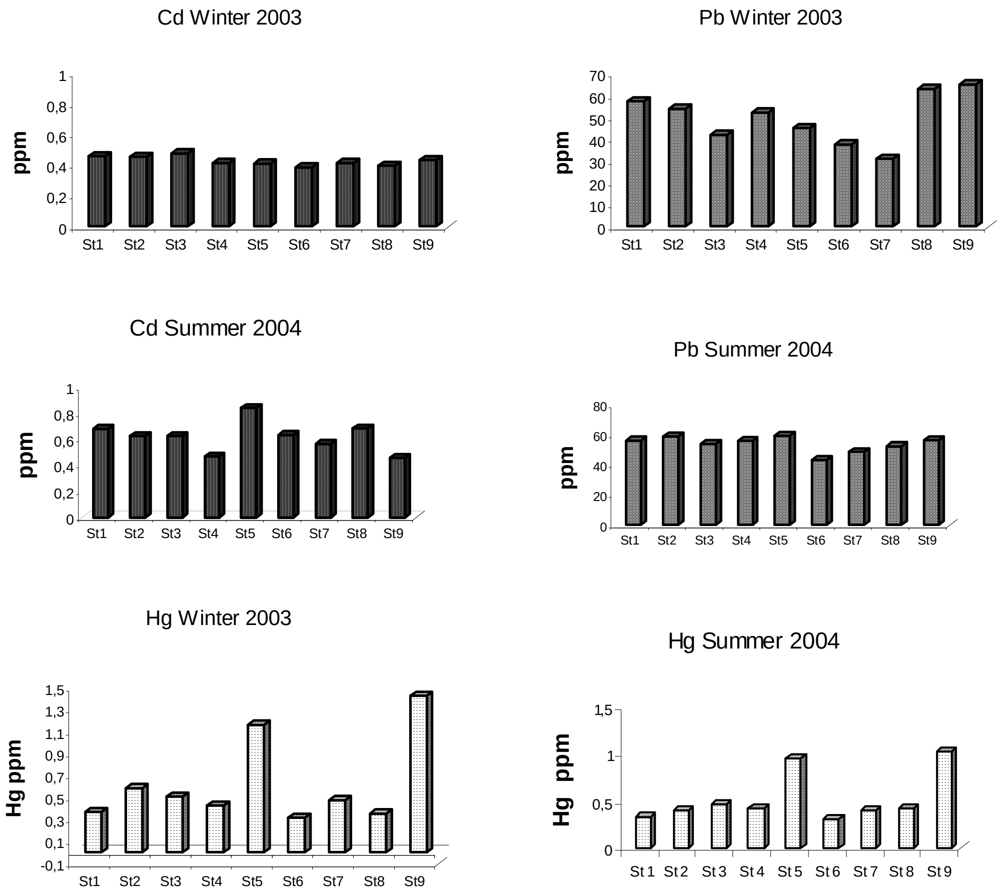

Figure 2. Concentrations of heavy metals (Cd, Pb, Hg) in surface sediments of the GEM lagoon.

Metals in fish

Grey mullet (*Mugil cephalus*) is an important specie in this region. Although, this specie is considered a demersal detritivore, it feeds preferentially on detritus, fish, crustaceans and algae (Farrugio, 1974).

Table 2 summarizes the numbers of fish sampled, length and weight ranges for each period sampled. The seasonal trace metals concentrations in fish muscle, liver and brain are provided in Table 3, in all cases expressed on a dry weight basis.

The highest concentrations of Cd, Pb and Hg were found in liver, while the lowest concentrations were found in muscle (Tab. 3).

No significant seasonal differences ($P<0.05$) were observed for all metals in liver tissue. On the other hand, significant seasonal differences ($P<0.05$) were recorded in Pb and Hg brain concentrations. Seasonally, metals analysis in fish brain samples showed that Cd concentrations were high in spring and autumn; however, those of Pb were high in winter.

Table 2. Number, size and weight of fish sampled in GEM lagoon.

Mugil Cephalus	Number	Length (cm)	Weight (g)
Winter	62	25-30	13.6±2.4
Sprint	70	25-30	15.4±2.3
Summer	55	25-30	14.2±1.9
Autumn	60	25-30	13.8±2.1

Table 3. Heavy metals concentrations in muscle, liver and brain of Mullet (*M. cephalus*) ($\mu g g^{-1}$ dry weight) from GEM lagoon.

Samples	**Cd**	**Pb**	**Hg**
Winter			
Muscle	0.019	0.048	0.391
Liver	0.302	0.927	0.968
Brain	0.027	0.208	0.884
Spring			
Muscle	0.025	0.108	0.335
Liver	0.321	0.620	0.940
Brain	0.017	0.668	0.419
Summer			
Muscle	0.013	0.233	0.222
Liver	0.547	0.633	0.926
Brain	0.002	0.192	0.612
Autumn			
Muscle	0.022	0.422	0.409
Liver	0.678	0.548	0.900
Brain	-	0.796	0.570

Discussion

Despite concerns amongst the local community regarding potential metal contamination of the GEM lagoon, no scientific investigations of the issue have previously been undertaken. Through the collection and analysis of sediment and fish tissue samples this study addressed this significant deficiency.

Metals in sediment

Fine grain particles in sediment usually act as effective collectors and carriers of dissolved metals from the water column to the sediments and thus elevate concentration of heavy metals in sediment. In GEM lagoon, 55 to 65% of the sediment by dry weight was represented by fine particles diameter 40µm or less (SCET, 1999). The abundance of fine particles is assumed to be due to anthropogenic input associated with erosion of upstream agricultural areas and setting out in the lagoon where water currents are generally low.

The levels of Hg, in surface sediments, were generally quite low, ranging from 0.3 to 0.5µgg^{-1}. However, the highest concentration (1.428µgg^{-1}) was recorded in station 9. This station was exceedingly polluted due to human activities within the fishing harbour associated with artesian fishing, such as small boats maintenance and painting. Station 5 also showed high mercury levels which may be explain by the weak currents and sewage discharge. This metal is higher in GEM in winter, probably as a result of run-off from surrounding agricultural land and sewage discharge.

Lead concentrations in sediments of Tunisian lagoons are generally lower than 30µgg^{-1} (Chouba et al, 2002). The highest concentration of Pb in GEM sediments was 65µgg^{-1}. Thus, it could be attributed to the geological environment surrounding lagoon, fishing activities and sewage discharges.

Cadmium levels in sediments were quite low in summer and winter and don’t exceeded sediment toxicity guidelines value (Long et al, 1995).

This investigation demonstrated that metal levels in sediments in GEM lagoon are higher than those measured in Bizerte lagoon (Mzoughi et al, 2002). The GEM lagoon demonstrates a homogenous distribution pattern for metallic pollution. This pollution could be attributed to the consequence of old communication between this lagoon and Medjerda River as well as to waste discharges.

The present data, when compared with those reported in other studies focuses on different North African lakes, show high metals levels than in Egyptian lakes (Tab. 4). However, metals levels of Cd and Pb in GEM were very low compared to those found in Lagos Lake (Nigeria) (Tab. 4).

Table 4. Comparison of heavy metals concentrations in sediments in different African lake (mean values on µgg^{-1} dry weight).

Regions	Hg	Cd	Pb	References
Lake Muriat (Egypt)	0.07	0.20	7.3	Saad et al, 1985
Lake Manzala (Egypt)	-	0.17	9.6	Saad et al, 1985
Lagos Lake (Niger)	0.10	4.10	178.9	Okoye et al, 1991
GEM Lagoon (Tunisia)	0.41	0.52	50.4	Present work

Metals in Fish

Studies have shown that heavy metals accumulate mainly in metabolic organs such as the liver which stores metals to detoxificate by producing metallothioneins (Kargin and Erdem, 1991; Olsson, 1996). The different concentrations of metals determined in different organs were shown in Table 3. The liver appeared to be the main location of Cd, Pb and Hg accumulation in *M. cephalus*. This could well result from changes in metabolic activities of the fish according to season and spawning period. Same results were found in previous work conducted in other regions (Sultana and

Rao, 1998; Hmzimela et al, 2003; Canli and Atli, 2003).

In the muscle tissue of *M. cephalus* in GEM lagoon, metals concentrations were comparable to levels recorded in muscle tissue of estuarine and marine fish from different areas such as the Gulf of Gabes (Tunisia) and Lake Manzala (Egypt) (Sultana and Rao, 1998; Saad et al, 1985; Hamza-Chaffai et al, 1996; Karadede and Unlü, 2000; Canli and Atli, 2003; Mzimela et al, 2003). All metals concentrations in fish liver reported in the above mentioned studies were higher than those measured in GEM fish.

A seasonally pattern was not observed for the distribution of each metal in the muscle tissue. This could be related to the presence of young individuals (not mature) and the subsequent storage of excess metals not affected by spawning season.

Consequently, it can be concluded that the concentrations of heavy metals in fish tissues from GEM lagoon were lower than levels admitted for food consumption. Although, there were generally no high levels of heavy metals in sediment, except near the village region where a potential danger could occur in the future depending on the management in this region such as the threaten caused by the implantation of the new fishing harbour

Conclusions

This survey permitted to assess the degree of temporal and spatial contamination by trace metals (Cd, Pb, Hg) in the superficial sediments and fish of GEM lagoon. The concentrations of Pb recorded were higher in winter than in summer but inversely those of Cd were high in summer. The north area of the lagoon, near village of Ghar El Melh, is more contaminated by these metals than the southern and western parts of the lagoon.

Mullet accumulates trace metals specifically in liver. The muscle contains the lowest concentration of trace metals compared to that recorded in the brain and the liver. The mullet tissue is not contaminated and it does not show any danger for human consumption.

These data provide insights into the chemical contamination of the lagoon which help to understand its ecosystem functioning and may be useful for its future management.

While measured concentrations are within international limits (ASMO, 1997), there is cause for concern since metal concentrations in the sediment samples were elevated near sources of effluent. Furthermore, grab sampling collects the upper 3-5cm of sediment and higher resolution sampling using only the upper 0.5 or 1cm of most recent sediment could indicate a different pattern of contamination and would meet future investigation.

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