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Heavy metal accumulation of water, sediment and some organisms in the Marmara Sea (Turkey)

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Increasing human populations and activities depending on the industrial and agricultural improvements cause worldwide disappearance of usable water resources. The harmful effects from polluted waters reach the human body by the food chain. In particular, heavy metals, which are known as some of the most important pollutants to nature, can stay in the ecosystem for a long time, lead to harmful effects in food chain by accumulations, and have direct or indirect toxic effects on aquatic organisms. These metals can be deposited in the body of the organisms which are an important ring in food chain in aquatic environments. In this study, a total of five heavy metals (Cu, Fe, Zn, Cd, and Pb) in water, sediment, some macroinvertebrates and fish at the Sea of Marmara (Turkey), which is a bridge between Black Sea and Aegean Sea, were investigated. For this aim, water, sediment and organism samplings were done in 2009, the date before the planned construction of a channel in the Marmara Sea. Thus, it was aimed to contribute to the researches which have been performed in the Marmara Sea. According to the results, while the levels of Cd and Zn were determined to have high values in the water samples, the obtained concentration levels in sediment and accumulation rates in the organisms were compared in this study.

Keywords: Marmara Sea, heavy metal, accumulation, essential elements

INTRODUCTION

Environmental pollution has negative effects on the living things. Especially the pollution of water resources leads to uncontrolled problems in both aquatic environments and human economy-social life. Among the pollutants, heavy metals stay in the first order depending on their harmful and destroying effects. Although living things need some trace elements like Cu, Zn, Fe for their biological systems, some of them like Cd, Pb, As, and Hg cause very high toxic effects at very low concentrations. Furthermore, a lot of studies reported that these metals accumulate in the bodies of different organisms [1–4].

In recent years, a lot of studies have been performed on the accumulation of heavy metals in aquatic environments. The Marmara Sea is located on north-west of Turkey and it is surrounded by settlements, agricultural and industrial areas. Also, the Marmara Sea, a small inner sea, is a bridge between Black Sea and Aegean Sea *via* Bosphorus Strait and Dardanelles Strait, respectively. Thus, the Marmara Sea separates two important continents, Asia and Europe. Also, the Marmara Sea is an important immigration way between Black Sea and Mediterranean Sea for fish which are fed on benthic invertebrates. Fisheries are very important bazaar for the economy of the local people living around the Marmara Sea. But the Sea is under the influence of anthropogenic effects due to the discharges from settlements, industrial and agricultural activities [5]. There is a project on opening a channel between the Marmara Sea and Black Sea [6]. Therefore, environmental studies on water and sediment quality of the Marmara Sea gain importance day by day. Thus, we can assess environmental effects of the channel on the Sea by the before/after researches.

There are a lot of studies on heavy metal accumulation in the water column or sediment of Marmara Sea [7–28]. Also, some heavy metal accumulations in mollusc species which are a very important group in benthic macroinvertebrates and the other groups, were studied in Marmara Sea [5, 7, 9, 10, 15, 17, 18, 20, 21, 23-25, 28-36]. Physicochemical analyses can inform on the current water quality at a particular time of an aquatic environment. Therefore, to monitor the changes in the chemicals like heavy metals in aquatic environments, samplings made by seasonal intervals at least will be useful. But benthic macroinvertebrates and fish are useful organisms to follow heavy metal pollution in an aquatic ecosystem by the accumulation talents of the heavy metals in their bodies. They can tell us past and present situation of the ecosystem.

In this study, it was intended to contribute to the researches which have been performed in the Marmara Sea. For this aim, the heavy metal concentrations in both water/ sediment and some tissues of different macroinvertebrates (starfish, crab and shrimp) / fish in the Sea of Marmara at the same time samplings were determined.

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Thus, different organism groups in the Sea were evaluated for their roles on heavy metal accumulations in this study.

EXPERIMENTAL

The samplings were made in December 2009 in Marmara Sea between the coordinates 41.01968N - 28.36683E and 40.96936N - 28.51225E. The organisms belonging to invertebrate (starfish *Astropecten* sp., shrimp *Parapenaeus* sp., and crab *Carcinus* sp.) and fish (*Gobius* sp., *Trigla* sp., *Hippocampus* sp., *Spicara* sp.) were sampled by a beam trawl (3 m mouth width, 60 cm length and 3 m bag length, 40 mm pore diameter). The sampling for the organisms was started at the bottom four km from the shore and the beam trawl was used during 15 km (Fig. 1).

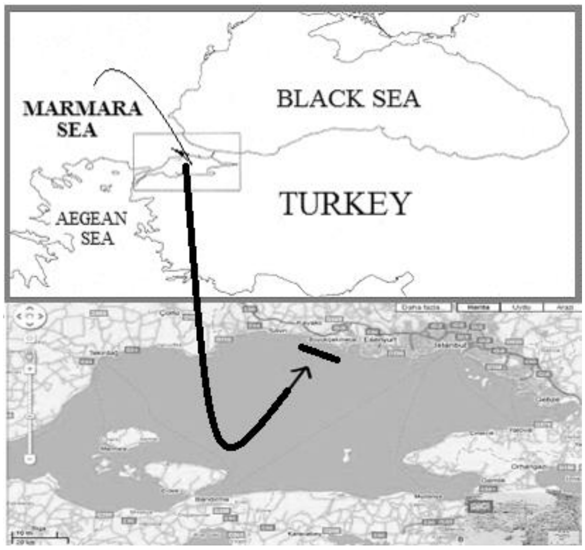

Fig. 1. The location of Marmara Sea and the sampling locality

The obtained materials belonging to the macroinvertebrates and fish were put into sterile plastic bags and transported to the laboratory for their dissection. Also, the water samples were obtained from 40 m depth by a Nansen water sampler (1.5 L) and the sediment materials were taken from 50 m depth by an Ekman grab (15 × 15 cm). The water and sediment samples were put into polypropylene bottles that were cleaned by 1:1 HCl and 1:1 HNO_3, separately and transported to the laboratory to perform the heavy metal analyses.

In the laboratory, a total of 10 mL of water samples was put into a solution of HNO_3/HCl (5:2) with 8 mL of pure water and was filtered before measuring the concentrations of heavy metals. The sediment samples were homogenized and about 1 g of sediment samples was taken and dried in a drying oven at 85°C for 48 h before putting into a solution of HNO_3/HCl (5:2) with 3 mL of pure water and the residue was filtered. The sampled organisms were measured by a calliper and scales. The dissection was made in the laboratory and some tissues of them (muscle tissue, bowel, liver, and gills) were obtained and about 1 g parts of the organs were put into a solution of HNO_3/HCl (5:2) with 3 mL of pure water. All prepared samples were drained by filter paper and were preserved at a temperature of -20°C until measuring the heavy metal contents.

The concentrations of Cu, Fe, Zn, Cd, and Pb were determined on an Analyst 800 Model Perkin Elmer AAS flame atomic absorption spectrometer (FAAS) with deuterium lamp and air acetylene burner. All values were expressed as the mean of three replicate analyses for each sample.

RESULTS AND DISCUSSION

In this study, a total of five heavy metal (Cd, Fe, Zn, Cu, and Pb) contents were determined in water, sediment and some tissues of organisms living in the Sea of Marmara (Table 1).

Table 1. Length and weight sizes of sampled organisms

Material		Length (cm)	Weight (g)
Astropecten sp.	INVERTEBRATES	4.5	13.20
Carcinus sp.		2.0	3.729
Parapenaeus sp.		13.0	12.0
Gobius sp.	FISH	11.5	15.273
Trigla sp.		18.0	59.071
Hippocampus sp.		10.0	4.84
Spicara sp.		12.0	21.0

Water samples

The literature suggests to measure the concentration levels of Cd, Pb and Cu in sea water for determining the pollution level [28]. In this study, the concentrations of Pb and Cu were determined as UAL (under analysable limit) in the water samples (Table 2 and Fig. 2).

But the levels of Cd and Zn were found at high rations in the sea water samples according to the limits in the WPCR of Turkey (Water Pollution Control Regulation) and the limits in the literature [28, 37] (Fig. 2). It is reported that Cd is more likely related to anthropogenic effluents and Zn is widely detected in industrial and mining wastewater [38]. Also, they can enter the sea from the settlements.

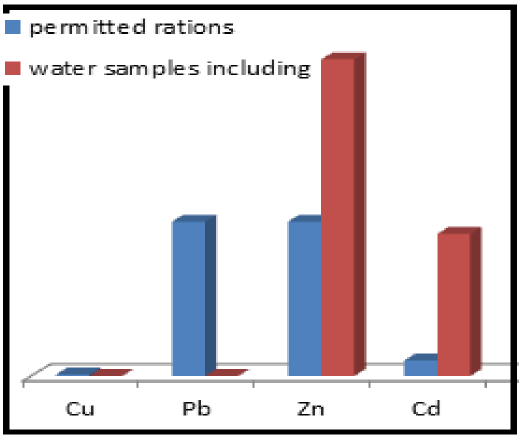

Fig. 2. Comparison of the heavy metal levels in sea water as permitted and measured rations.

Sediment samples

It is reported that many heavy metal concentrations in sediment are higher than the those in the surrounding water [18]. The heavy metals in the sediments of aquatic environments which they tend to transport to the water column are the results of urban discharge and industrial wastes. Therefore, the analysis of heavy metals in the sediment helps in the interpretation of water quality [39]. In the previous study performed by Balkıs *et al.* [18] in the Marmara Sea, it was reported that Cd is rather high in the sediments of Bosphorus and Marmara Sea. Also, Otansev *et al*. [24] reported a widespread heavy metal enrichment in sediments of the Marmara Sea.

Table 2. Measured levels of some heavy metals in water, sediment and some organisms in the Sea of Marmara (ppm)

Sample	Cd	Cu	Zn	Pb	Fe
Water	0.092	UAL	0.205	UAL	3.138
Sediment	0.176	2.043	4.179	2.373	81.770
Astropecten sp. (muscle)	0.227	0.808	0.643	0.170	5.147
Carcinus sp. (muscle)	0.122	1.648	1.092	UAL	3.362
Parapenaeus sp. (gill)	0.134	4.626	1.455	UAL	13.440
Parapenaeus sp. (bowel)	0.126	0.185	2.255	UAL	1.710
Parapenaeus sp. (muscle)	0.128	0.809	1.122	UAL	1.549
Gobius sp. (gill)	0.142	0.294	2.242	UAL	28.830
Trigla sp. (liver)	0.132	UAL	1.350	UAL	11.28
Trigla sp. (gill)	0.141	0.121	1.977	UAL	10.63
Hippocampus sp. (gill)	0.152	UAL	2.782	UAL	5.479
Spicara sp. (gill)	0.145	UAL	1.464	UAL	9.735

UAL: Under Analysable Limit

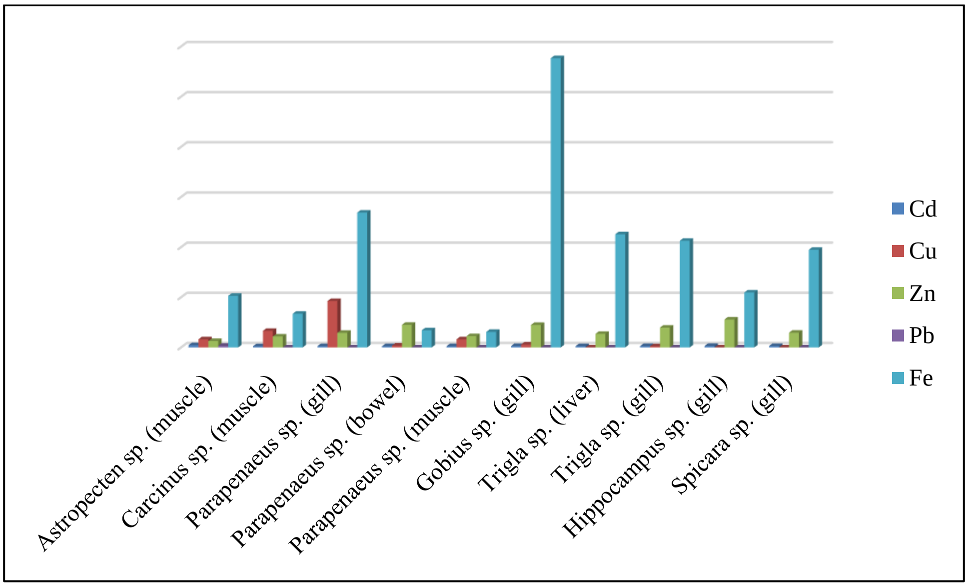

Fig. 3. Comparison of the heavy metal levels in the organisms at measured rations.

Turkish Thrace region has highly intensive agricultural and industrial activities which lead to continuous pollution of water resources. In the previous study carried out by Balkıs and Çağatay [16], the heavy metal distributions and sources were investigated in the sediments of Marmara Sea. The results show that the erosion products by two rivers from the south are the main sources to the relatively high metal concentrations in the studied area [16]. In our study, the concentrations of the heavy metals were found at 0.176 mg/kg for Cd, 2.043 mg/kg for Cu, 4.179 mg/kg for Zn, 2.373 mg/kg for Pb and 81.770 mg/kg for Fe. These rations were found as very low levels compared with the literature [40]. But the measured heavy metal concentrations in the sediment samples were found higher than in the water samples (Table 2).

Organism samples

The heavy metal contents of the tissues in some marine species were also studied in this study. Although, Cd and Zn concentration levels were found similar to those in the tissues of the macroinvertebrate samples, Cu and Fe concentrations in the gills of shrimps (*Parapenaeus* sp.) were found higher than in the muscles and bowels. The Pb concentrations in the macroinvertebrate samples were found at UAL except starfish muscle (Table 2). When the heavy metal findings were evaluated according to their accumulation in the gills of the fish samples, the levels of Cd, Zn, Cu were found at similar rations and the Pb concentrations were found at UAL (Table 2). The concentrations of Fe were found at high levels in demersal goby fish (*Gobius* sp.) (Fig. 3).

In a study performed on heavy metal concentrations in the sea water, sediment and starfish of Marmara Sea, it was reported that industrial activities lead to heavy metal accumulation [32]. In another study performed in shrimps (*Parapenaeus longirostris*) living in the Sea of Marmara, some heavy metal concentrations were reported at high rations [22].

The studies which were performed on heavy metal accumulations in the organisms show that the different accumulation rations can be observed in different tissues depending on the species and age. The gills are an important way to enter the heavy metal inside the organisms. In this study, the concentrations of Cu and Fe in shrimp gills were found higher than in the other tissues. Also, the measured heavy metal concentrations in sediment were found at a higher level than in water samples. It was observed that the concentration of Fe was at a high level in goby fish which is living and feeding depending on sedimental material.

Heavy metals are among the important environmental pollutants and they can enter the aquatic surroundings by different ways. Their accumulations have increased due to the settlements, industrial and agricultural wastes. Although other pollutants can be removed from the natural environments by biological degradation, the heavy metals can accumulate [41]. The studies reported that the toxicity and accumulation of heavy metals in the aquatic environments lead to serious problems for ecosystems. These ecological problems can affect human health directly or indirectly because heavy metals can enter the biological structures by the food chain. It was reported that the heavy metal Cd had led to Itai-itai disaster in Japan by feeding on contaminated rice. This heavy metal affects the kidneys in humans and leads to chronic poisoning. The other heavy metals Pb and Zn can be transmitted by superficial water flood to sea, and they can accumulate in the tissues of aquatic organisms. Although Zn is needed for the physiology of living things, it can cause toxic effects at high concentrations. Pb is toxic for aquatic organisms [28].

As a result, to prevent the accumulation of the heavy metals in human body, their transporting to the aquatic environments must be prevented. Also, it is suggested that similar studies should be repeated periodically in the Marmara Sea before opening a channel between Marmara Sea and Black Sea. Thus, controlled monitoring can be provided for sustainable usage and rational management of the Marmara Sea.

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