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Heavy Metals in Marine Sediments of Gulf of Izmir

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***Abstract*—**In this study, sediment samples were collected from four sampling sites located on the shores of the Gulf of İzmir. In the samples, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn concentrations were determined using inductively coupled, plasma-optical emission spectrometry (ICP-OES). The average heavy metal concentrations were: Cd < LOD (limit of detection); Co 14.145 ± 0.13 µg g^{-1}; Cr 112.868 ± 0.89 µg g^{-1}; Cu 34.045 ± 0.53 µg g^{-1}; Mn 481.43 ± 7.65 µg g^{-1}; Ni 76.538 ± 3.81 µg g^{-1}; Pb 11.059 ± 0.53 µg g^{-1} and Zn 140.133 ± 1.37 µg g^{-1}, respectively. The results were compared with the average abundances of these elements in the Earth's crust. The measured heavy metal concentrations can serve as reference values for further studies carried out on the shores of the Aegean Sea.

***Keywords*—**Heavy metal, Aegean Sea, ICP-OES, sediment.

I. Introduction

VARIOUS human activities, including fishery, agriculture, marine transport (port operations) and industrial activities are carried out in the Gulf of Izmir [1]. As a result of insufficient environmental risk management, chemicals released into the environment by human activities and natural processes enter into the sea environment and can break into particles [2], [3]. The main anthropogenic pollution sources in sea environments are physical and chemical abrasion of parent rocks, waste water discharge, atmospheric deposition, industrial wastes and heavy metals [2]-[4]. Heavy metals are a worldwide problem for ecosystems and human health due to their displacement, settling on the ground in solid form, persistency and biogeochemical cycle [5], [6]. Anthropogenic sources of terrestrial origin carry significant amounts of metals to the seas through water, waves and winds, and these metals bond to marine sediments in various ways: ion exchange, adsorption, precipitation and forming complexes [5]-[7]. Sediments are highly sensitive indicators of natural and anthropogenic pollution variables, and they are also tremendously comprehensive information pools on particulate matters [8], [9]. The properties of sediments vary depending on biological, physical, and chemical conditions, but these are usually measurable variations. Therefore, analyzing marine sediments is highly useful for obtaining information on the anthropogenic impacts on sea environments. High levels of population density and industrial activity directly contribute to the pollution of ecosystems. To investigate the pollution in the study area, heavy metal concentrations of cadmium (Cd), cobalt (Co), chrome (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) were investigated in the sediments collected from the selected locations in the Gulf of İzmir.

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II. Study Area

The samples investigated within the scope of this study were collected from four different sampling locations in the Gulf of Izmir (Fig. 1). The Gulf of İzmir is located at the west of Turkey in the Aegean Sea (38° 41' to 38° 21' N, 26° 30' to 27° 08' E), and it is a natural gulf roughly forming an "L" shape [10]. The total surface area of the gulf is 500 km^2, its water capacity is 11.5 billion m^3 and its total length is 64 km [8]. The gulf is divided into three different regions based on the physical properties of the water bodies: the Inner Region, the Middle Region and the Outer Region [8]-[10]. Water depth in the Outer Gulf is approximately 70 m, and the depth decreases to 15 m towards the Inner Gulf [11]. The Inner Gulf is a center for intense industrial and commercial activities (especially iron, pulp and paper factories, toxic paints, chlorine-alkali facilities, cement plants, wood processing and bottling plants and intense harbor activities) [1]-[12]. The main pollutant factors in the gulf are streams of varying capacities, and over one hundred canals flow into the gulf.

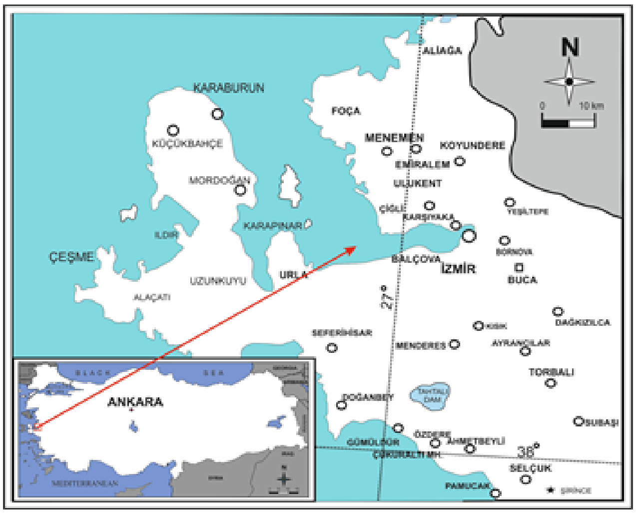

Fig. 1 Location map of the study area: The Gulf of İzmir

III. Materials and Methods

Drilling was carried out in the sediments of the Gulf of Izmir at the locations selected by considering the morphological and topographic properties, waves and flows [13]. Current (young) sediments were collected from four drill zones consisting of Karşıyaka DH-1, Bayraklı DH-5, Inciraltı DH-2 and Çeşmealtı DH-6 (Fig. 2). In these zones, the sea water depth varied between 1 and 13 meters, and the drilling was carried out at depths between 1 and 14 meters (Table I).

The Karşıyaka study area featured a 0.0 to 11.0 m waterbed, and in its blackish-gray, sandy clay parts, towards the lower levels from 12.5 to 13.5 m, it is made up of mud layers containing high amounts of water.

In the Bayraklı location, the waterbed starts at 0.0 to 4.0 m, and in its sandy clay parts towards the lower levels from 6.5 to 7.5 m, it contains blackish-gray mud layers containing high amounts of water. In the Inciraltı region, the waterbed starts at 0.0 to10.0 m, and it is made up of greenish-gray sediments from 10.0 to 12.0 m towards the lower levels with the clay parts containing low levels of sand.

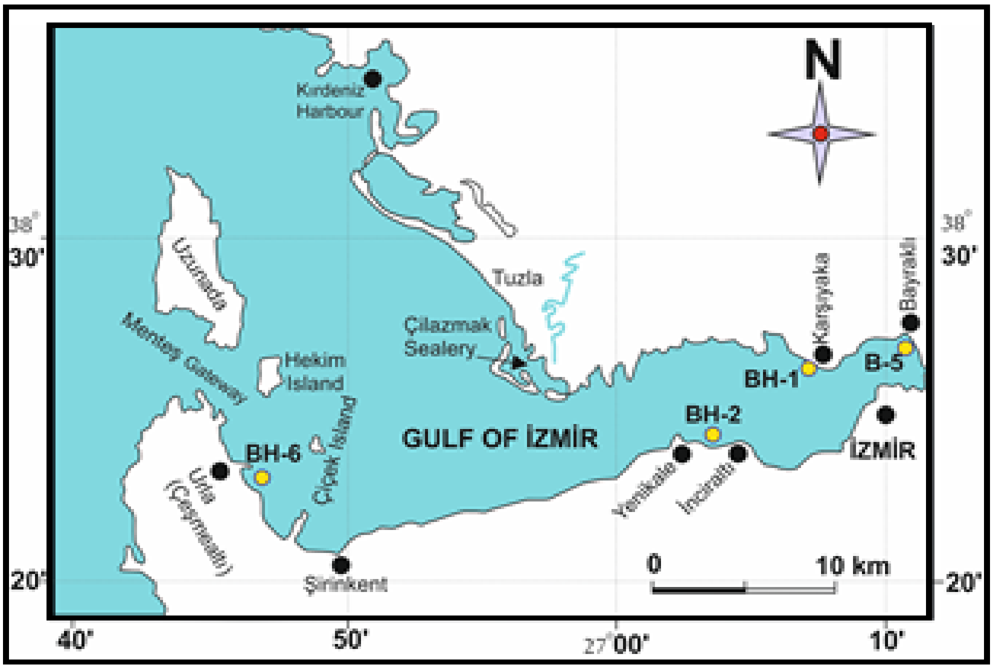

Fig. 2 Location map of the drill hole zones in the Gulf of Izmir (BH-1: Sample location)

TABLE I
PROPERTIES OF CORE SEDIMENTS [14]

Sample No	Depth of Sample (m)	Quantity of Sample (gr)	Sample Coordinates (WGS-84, 6^0)	
			X	Y
Karsiyaka DH-1	12,50-13,50	1047	4255697	510456
Bayrakli DH-5	6,50-7,50	1021	4258790	513920
Inciralti DH-2	10,00-12,00	1023,5	4253810	502590
Cesmealti DH-6	4,50-5,00	1035,7	4249770	478170

As in the other regions, towards the lower levels of the Çeşmealtı region, there are sediments with high water content in the blackish-gray, caked, sandy clay parts. Core sediments were collected to a depth of 1.5 meters and aligned in core boxes. At the end of drilling, sediment samples were put in secure plastic bags and immediately sent to the laboratory where they were dried at room temperature and sieved with a polyurethane sieve in preparation for heavy metal analysis in their powder form.

For heavy metal analysis, sediments were firstly dissolved in an acid mixture containing nitric (HNO3), hydrofluoric (HF), perchloric (HClO4) and hydrochloric (HCl) acids and then placed in a microwave digestion system [15]-[17]. The presence of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn heavy metals was determined by using a Perkin Elmer® Optima™ 7000 DV model using a charge-coupled device (CCD) detector. For the investigated heavy metals, data were stored and processed by WinLab32, ICP Version 4.0 software. All data were obtained with axial imaging, a nebulizer and a cyclonic spraying chamber with a 10 second integration time.

Standard calibrated solutions of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were prepared from a stock primer standard solution, and a calibration curve with an 0.999 correlation coefficient was obtained with three study standards over a range of 0.25 $\mu g\,L^{-1}$ to 1.0 $\mu g\,L^{-1}$. In the calibration space, ultrapure water acidified with Suprapur® nitric acid (HNO_3) was used. An empty solution, study standards and samples were kept under acidic conditions at 2.5% (v/v) volume.

IV. RESULTS AND DISCUSSION

The average concentrations of heavy metals detected in the sediment samples from the Gulf of İzmir were, respectively, Cd < LOD; Co 14.145 ± 0.13 $\mu g\,g^{-1}$; Cr 112.8618 ± 0.89 $\mu g\,g^{-1}$; Cu 34.045 ± 0.53 $\mu g\,g^{-1}$; Mn 481.43 ± 7.65 $\mu g\,g^{-1}$; Ni 76.538 ± 3.81 $\mu g\,g^{-1}$; Pb 11.059 ± 0.53 $\mu g\,g^{-1}$ and Zn 140.133 ± 1.37 $\mu g\,g^{-1}$ (Table II).

The Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn heavy metals in µg/g units found in the sampling locations show a tendency to increase and decrease in parallel with each other (Fig. 3). The comparison of the samples to the average abundances of these elements in the Earth's crust [18] revealed that Cd, Mn and Pb values in all sediments were lower than the reference values, except for Çeşmealtı where the Pb value was similar to the reference value. In Inciraltı, Co and Ni levels were high, while Ni and Cu levels were high in Karşıyaka. Çeşmealtı was the only location in which Cr and Zn levels were low. In summary, Cr, Cu, Ni and Zn were high in Karşıyaka; Co, Cr, Ni and Zn were high in Inciraltı; Cu and Zn were high in Bayraklı. In the samples from Çeşmealtı, levels of all elements, except for Pb, were lower than the samples from other locations. This is attributable to heavy metals entering into the water environment, the absorptive capacity and textural composition of sediments, the chemical structure of metals and their ability to accumulate on the seabed by bonding to other compounds [19]. In this study, the Çeşmealtı core sample was collected from a region that was closer to the surface compared to the other locations. Furthermore, Karşıyaka and Inciraltı were determined to be more polluted due to the intense industrial activities in the Inner Gulf [20].

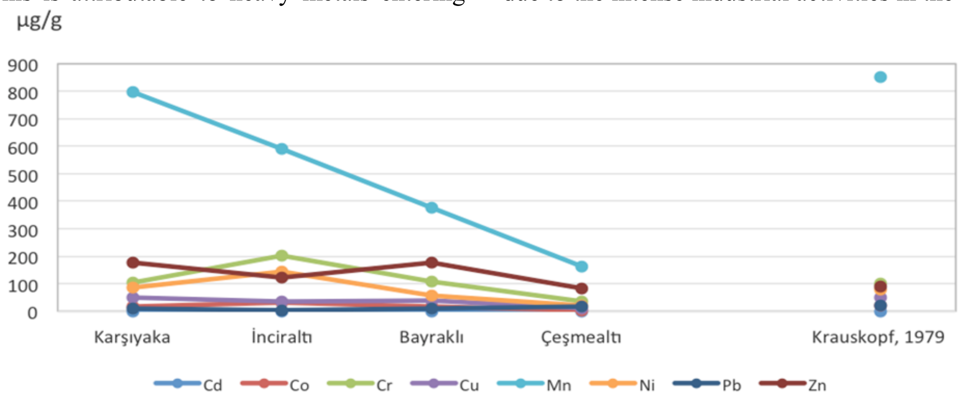

Fig. 3 Distribution of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn heavy metals by investigated regions [18]

TABLE II
ICP-OES ANALYSIS RESULTS OF THE SEDIMENT SAMPLES FROM THE GULF OF İZMIR

Heavy Metals	Wavelength (nm)	Unit	Karsiyaka (DH-1)	Inciralti (DH-2)	Bayrakli (DH-5)	Cesmealti (DH-6)	Limit of Detection (LOD) µg/L	µg/g
Cd	228.802	µg/g	< LOD	< LOD	< LOD	< LOD	0,584	0,096
Co	228.616	µg/g	16,17 ± 0,27	20,62 ± 0,04	16,34 ± 0,18	3,448 ± 0,046	0,808	0,133
Cr	267.716	µg/g	104,9 ± 1,9	203,8 ± 0,8	106,7 ± 0,6	36,07 ± 0,26	1,54	0,254
Cu	327.393	µg/g	51,55 ± 0,75	35,46 ± 0,41	37,65 ± 0,35	11,52 ± 0,60	0,761	0,125
Mn	257.610	µg/g	795,9 ± 19,9	590,0 ± 6,6	376,4 □ 2,9	163,4 ± 1,2	1,23	0,202
Ni	231.604	µg/g	85,78 ± 0,73	143,8 ± 2,1	56,12 □ 0,81	20,45 ± 0,17	2,05	0,339
Pb	220.353	µg/g	10,53 ± 0,44	3,685 ± 0,558	11,30 ± 0,54	18,72 ± 0,57	5,79	0,955
Zn	206.200	µg/g	176,8 ± 1,9	123,2 ± 1,1	177,2 ± 1,3	83,33 ± 1,18	0,66	0,109

V. CONCLUSION

Heavy metal concentrations (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) of the core samples collected from four different locations in the Gulf of İzmir (Karşıyaka, Bayraklı, Inciraltı and Çeşmealtı) were analyzed with ICP-OES. The results showed that pollution gradually decreased from the Inner Gulf to the outer regions and, moreover, there was not significant pollution in Çeşmealtı (Urla). The geochemical structure of sediments can become deformed as a result of natural and anthropogenic factors. However, when seas reach a point where they cannot eliminate the accumulated anthropogenic pollution by their own means, the pollution starts to harm humans and organisms living in the seas. This leads to the emergence of diseases that necessitate long-term treatments. Researching the particles that gradually settle on the seabed through various ways is of great importance in controlling heavy metal pollution.

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