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Original Research

Determination of Pollution and Heavy Metal Fractions in Golden Horn Sediment Sludge (Istanbul, Turkey)

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Abstract

In our study we studied pollution and heavy metal fractions in the Golden Horn (Istanbul, Turkey). This area has been exposed to domestic and industrial pollution for many years. Concentrations of Zn, Cr, Cu, Pb, Cd, and Ni heavy metals were determined in the study that was conducted to monitor the current state of pollution and changing conditions in the polluted estuary. Mean heavy metal concentrations were found as: Zn 70-260, Cr 26-110, Cu 70-135, Pb 8-50, Cd 0.1-2, and Ni 10-38 mg/kg. Results of the analysis showed that metal concentrations were usually low, indicating that the sediment was not too polluted in the present case. The range of ratios, different fractions of metal concentrations, and total metal concentrations in the samples were critical for potential toxicity and mobility of metals. Results of the analysis showed that heavy metal fractions in the sediment were usually found in residual forms. The values obtained in the study were also compared with the literature. It was found that surface sediments in the Golden Horn were less polluted than other areas. Establishment of sewer collectors and wastewater treatment plants has improved the heavy metal levels in the sediment.

Keywords: heavy metals, wastewater, estuaries, pollution, metal fractions

Introduction

The Golden Horn (Halic in Turkish) is a 7.5 km long marine extension into the land in Istanbul at the entrance to the Marmara Sea. Urban and industrial wastes have been discharged to the Golden Horn for many years. The area is also filled with materials transported by Alibeykoy and Kagithane streams. There were several factories, slaughterhouses, shipyards, and wholesale vegetable and fruit markets in the vicinity of the Golden Horn, and there have been no treatment facilities for many years, while all the facilities discharge their waste into the Golden Horn. As the business opportunities increased in the district, urban sprawl around the Golden Horn increased as well. The diligent work conducted in recent years has partially limited the above-mentioned pollution.

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Pollution sources in the Golden Horn include not only domestic and industrial wastewater but also solid wastes, garbage, and the dreg material transported by Alibeykoy and Kagithane streams, erosion, ballast water drained from ships, and polluted sediment sludge. Emissions along roads also promote an increase in the concentration of pollutants [1]. Approximately 50,000 m^3 of water and 59,000 m^3 of sediment are transferred to the Golden Horn from Alibeykoy and Kagithane stream basins, which have a drainage area of 380 km^2. In the Golden Horn, where the sedimentation is about 3.5 cm/year, inorganic matter, nutrients, heavy metals, and hydrocarbons have accumulated in the benthic sediment [2-3].

Because the municipalities had inadequate solid waste collection facilities in the early 1980s, several organizations around the Golden Horn removed their trash by directly disposing of it into the water. Due to erosion, sediments and residues accumulated in the Golden Horn caused an annual depth reduction of 6-10 cm and filled the Golden Horn basin bed, in addition to being a source of pollutants. Furthermore, the waste that has been thrown into the sea at ship dismantling facilities and the water leakages from garbage disposal sites have also been transferred to the Golden Horn and increased pollution [4].

Although dissolved heavy metals are not present in sediments, they could return to the water column from the sediment via physical and biological processes. The accumulation of pollutants in sediments negatively affects the natural life and organisms in the environment and causes environmental problems. Sediment analysis is quite important in understanding the distribution and transfer of toxic substances. Most common heavy metals that could be conducted in sediment analysis are Zn, Cr, Cu, Pb, Cd, Fe, and Ni [5].

The main objective of the present study was to determine the current pollution level in the Golden Horn, which was exposed to domestic and industrial pollution for several years, and to determine how the current ecological structure of the area, which was attempted to be cleaned at large cost, was affected by the treatment activities.

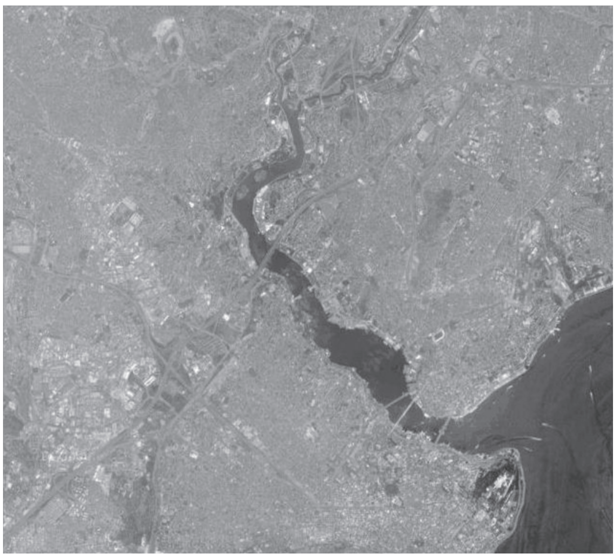

Fig. 1. Satelite view of the Golden Horn.

The present study aimed to analyze various fractions of metals that are significant in sediment pollution. In the analyses, initially the basic parameters such as chemical oxygen demand (COD), total organic carbon (TOC), total solid matter (TSM), total phosphorus (TP), suspended solid material (SSM), total volatile solid matter (TVSM), and total Kjeldahl nitrogen (TKN) were measured, and then the total heavy metal concentrations and concentration values for various fractions were determined.

Material and Methods

Properties of the Golden Horn

Topographic structure of the Golden Horn includes the coastline, hills and ridges, slopes and terraces. On both sides of the Golden Horn there is a flat coastline a few centimeters above sea level and 150 m wide. The most important elements in the Golden Horn region are the hills and extensions, which range between 50 to 130 m and are located on both slopes [4, 6] (Fig. 1).

Experimental Studies

In the study, physical and chemical analyses were conducted on the Golden Horn sediment samples and heavy metal pollution and fractions were determined, and existing pollution and changes were monitored. The sediment samples used in the experiments were obtained from the bottom sludge in the Golden Horn-Sutluce region. Currently, Istanbul Metropolitan Municipality Directorate of Maritime Services is conducting dredging on the estuary sediment sludge to remove erosion and polluting materials in this area. Sludge samples were obtained from this sediment. Received samples were delivered to the laboratory as soon as possible under adequate conditions and kept in the refrigerator at +4°C. COD, TOC, TSM, TP, SSM, TVSM, and TKN analyses were conducted to determine sediment pollution according to Standard Methods [7].

The total heavy metal concentration and the concentrations of various fractions were processed based on the principles depicted in Standard Methods with disintegration techniques and analyzed. The Zn, Cr, Ni, Cu, Fe, and Pb contents in samples obtained from the bottom sludge of the estuary were measured with an atomic absorption spectrometer (AAS) and inductive coupled plasma optical emission spectrometer (ICP-OES) to determine the total heavy metal content and heavy metal fractions. Before chemical analyses, the sludge samples were dried at 103ºC for 24 hours in a Nuve FN 500-type incubator. The analysis method is summarized below.

Table 1. Mean heavy metal concentrations (mg/kg dry weight).

Element	Summer	Winter
Zn	70-200	85-260
Cr	26-90	35-110
Cu	80-135	70-120
Pb	8-50	12-50
Cd	0.1-2	0.2-2
Ni	10-35	12-38

The sediment samples were exposed to the processes of drying, pulverization, sieving, weighing, and disintegration with acid in the laboratory. For metal measurement, 1-2 grams of each homogeneous sample were weighed on a precision scale and placed in beakers. 10 ml 1:1 HNO_3 was added and stirred, then the top was covered with watch glass and heated on a hot plate at 95ºC. After the sample was cooled, 5 ml concentrated HNO_3 was added and the beaker was covered with watch glass and kept for 30 minutes for reflux. After this step was completed, the sample was cooled and 2 ml distilled water and 3 ml 30% H_2O_2 were added. The beaker was covered with watch glass and placed on a hot-plate to initiate the peroxide reaction. After the preliminary treatment, the solutions were filtered through a filter with a pore diameter of 0.45 μm and became ready for analysis.

Although sequential extraction of metals requires more time for analysis, it provides important information on their origin, mode of formation, biochemical and physico-chemical use in the aquatic environment, mobile status or their transmission in the aquatic environment.

In the scope of the study, physicochemical properties and heavy metal content of bottom sludge were determined using the samples obtained from the sediment layer. The obtained results were compared with the range of values used to determine sediment quality in the literature.

Results and Discussion

COD was determined by the closed reflux titrimetric method and it was found to average as 2,650 mg/L in the samples analyzed at various periods. SSM and VSSM were determined as 0.26 mg/L and 0.016 mg/L, total solid matter (TSM) was 0.5 g/g, and TVSM was determined as 0.078 g/g, respectively. TP was found as 1,630 mg/kg and finally, TKN was 3.7 mg/g.

In the study, heavy metal concentrations (Zn, Cr, Cu, Pb, Cd, and Ni) that originate from human activity were determined. As shown in Table 1, concentrations were usually low and these values indicated that the sediment was not too polluted presently.

The values determined in the literature that reflect the correlation between water ecosystem quality and the metal concentrations showed that certain descriptions were determined. In these studies, the adequate level

Table 2. Threshold effect concentrations (TEC) values that show sediment quality in clear water ecosystem.

Element (mg/kg dry weight)	Threshold effect concentrations					
	TEL	LEL	MET	ERL	TEL-HA28	TEC
Zn	123	120	150	120	98	121
Cr	37.3	26	55	80	36	43.4
Cu	35.7	16	28	70	28	34.6
Pb	35	31	42	35	37	35.8
Cd	0.6	0.6	0.9	5	0.58	0.99
Ni	18	16	35	30	20	22.7

Table 3. Probable effect concentrations (PEC) values in clear water ecosystem (mg/kg dry weight).

Element (mg/kg dry weight)	Probable effect concentrations					
	PEL	SEL	TET	ERM	PEL-HA28	PEC
Zn	315	820	540	270	540	459
Cr	90	110	100	154	120	111
Cu	197	110	86	390	100	149
Pb	91.3	250	170	110	82	128
Cd	3.53	10	3	9	3.2	4.98
Ni	36	75	61	50	33	48.6

Table 4. Sediment quality threshold values [8].

Element	Sediment quality limit values, Ontario			Temporary criteria for assessment of Lawrence River sediment			Temporary sediment quality evaluation values			Limit values of quality of port sediments		Clean water sediment quality limit values		
	Ineffective	Moderately contaminated	Toxic effect level	Ineffective	Moderately contaminated	Toxic effect level	TEC*	PEC*	Ineffective	Moderately contaminated	Toxic effect level	Ineffective	Moderately contaminated	Toxic effect level
Zn	-	120	820	100	150	540	123.1	314.8	< 90	90-200	> 200	-	-	-
Cr	-	26	110	55	55	100	37.3	90	< 25	25-75	>75	-	-	-
Cu	-	16	110	28	28	86	35.7	196.6	< 25	25-50	>50	< 16	16 -110	> 110
Pb	-	31	250	23	42	170	35	91.3	< 40	40- 60	>60	< 30	30 - 100	> 100
Cd	-	0.6	10	0.2	0.9	3	0.596	3.53	-	-	>6	<0.6	0.6-10	>6
Fe %	-	2	4	-	-	-	-	-	< 1.7	1.7-2.5	> 2.5	-	-	-
Ni	-	16	75	35	35	61	18	35.9	< 20	20-50	>50	-	-	-

Table 5. Sediment quality threshold values (TEC-PEC) (mg/kg, dry weight).

	Range of values for sediment quality		Range of values for clean water sediment quality		TEC and PEC metal concentrations		Sediment quality values			Marine and estuarine sediments, low and medium range regulation values		Average values on Earth	Average sediment value
Elements	TEC	PEC	TEC	PEC	TEC	PEC	LEL	TEL	MET	TEC	PEC	-	-
Zn	124	271	123.1	314.8	121	459	120	123	150	150	410	71	65
Cr	52.3	160	37.3	90	43.4	111	26	37.3	55	81	370	35	74
Cu	18.7	108	35.7	196.6	31.6	149	16	35.7	28	34	270	25	40
Pb	30.2	112	-	-	35.8	128	31	35	42	46.7	218	20	17
Cd	0.676	4.21	0.596	3.53	0.99	4.98	0.6	0.596	0.9	1.2	9.6	0.098	-
Fe %	-	-	-	-	-	-	-	-	-	-	-	35,000	40,000
Ni	15.9	42.8	18	0.359	22.7	48.6	16	18	35	20.9	51.6	20	40

Table 6. Metal concentrations determined in recent studies conducted in certain areas in Marmara region (mg/kg).

Explanation	Ni	Cu	As	Cd	Pb	Zn
Average range in surface sediment	-	77-149		0.15-0.74	22-76	-
Shale average value	-	50		0	20	-
2001	-	417		67	203	-
2003	-	131		2	81	-
Surface	90	194		6	510	890
Bottom	54	274		1	420	128
Halic sediment	84 - 167	297-3,900		-	124-702	450-8,750
<63µm	-	16-724		-	10.5-260	39-793
>63µm	-	3.5-481		-	3.13-175	10-241
Balat	-	476		-	95	614
Unkapani	-	522		-	152	585
Kabatas	-	68		2	48	147
Tarabya	-	12		2	6	19
R. Kavagi	-	56		1	17	82
Garipce	-	-		-	-	78
R. Feneri	-	-		-	-	120
Poyraz	-	-		-	-	40
Sarköy	54	13		<0.02	23	44
M. Eregli	21	30		<0.02	32	34
Menekse	41	17		1	22	50
Marmara	46	154		-	70	389
Valide Sultan Bridge	74	520		-	168	640
Eyup	54	230		-	63	434
Adalar Sonrasi	49	124		-	47	284

for each metal was indicated. These values are defined by parameters such as threshold effect level, lowest effect level, minimal effect threshold level, low effect range, possible effect level, high effect level, toxic effect threshold, and medium effect range (Tables 2-3).

Tables 4-6 show the metal concentrations and their impact on the ecosystem applied in studies conducted in certain regions [8]. As a result of analysis in certain sample measurements, metal concentrations exceeded toxic effect levels when compared to sediment quality limit values and were above TEC and PEC. In analyzes of sample measurements, the metal concentration represented moderate contamination levels and remained between TEC and PEC.

The heavy metal values determined in previous studies conducted on the Marmara Region are listed in Table 6. As could be observed in these studies, the following ranges were determined as: Zn 10.7-8750 mg/kg, Cr 4.73-485 mg/kg, Cu 3.45-3900 mg/kg, Pb 3.13-702 mg/kg, Cd <0.02-2.04 mg/kg, Fe 5,956-55,100 mg/kg, and Ni 20.53-90 mg/kg. When these values were compared with the results of the present study, it was observed that the heavy metal concentrations determined in this study were generally lower than the other studies in the literature.

Heavy metals that enter the marine environment due to various factors tend to accumulate in fine grain fractions of sediments. Thus, the sediments with a small diameter would result in higher heavy metal concentrations in the structure [9]. When heavy metal concentrations in the sediment samples collected from the Golden Horn-Sutluce region were compared, we observed that the rehabilitation efforts had a positive effect. Other studies conducted in the Marmara region and the Golden Horn also demonstrated that heavy metal concentrations were higher in coastal regions in inner gulfs and inland seas when compared to high seas and middle and outer gulfs.

Table 7. Percentages in different metal fractions (%).

Element	F0	F1	F2	F3	F4
Zn	5-11	7-15	4-13	7-14	2-12
Cr	1-3	6-16	2-15	8-24	3-18
Cu	2-6	6-16	4-12	6-14	2-17
Pb	2-4	7-9	5-11	2-10	2-11
Cd	3-5	5-7	4-8	2-12	3-9
Ni	6-9	5-8	5-12	12-16	3-13

Analysis results demonstrated that metal concentrations exceeded TEC values and/or were between TEC and PEC. Concentrations between TEC and PEC values are also considered to have poor effects in certain cases. Other values were below TEC. Under TEC, it is accepted that adverse effects were observed only rarely. The metal concentrations obtained in the present study were ordered by the heavy metal content in the sediment as follows: Zn> Cu> Cr> Pb> Ni> Cd.

Although the metals may remain fixed in the sediment for a long time, they could be freed by degradation under oxidizing conditions. This situation is explained by the presence of metal fractions. Heavy metals are separated into fractions based on their reaction with soil particles due to environmental conditions. In sequential metal extractions on sediment samples, F0 represents the fraction of water-soluble metals, F1 represents the fraction of exchangeable metals, F2 represents the fraction of carbonate-bound metals, F3 represents the fraction of Fe-Mn oxide-bound metals, F4 represents the fraction of organic matter and sulfide-bound metals, and F5 represents the fraction of metals in the residual section.

The Cr, Cu, Cd, Ni, Pb, and Zn concentrations in different samples and rate ranges found in different fractions in the total concentrations are presented in Table 7. Chemical fractions distinguish metals of natural origin and/or metals of anthropogenic sources. Metal fractionation possesses a critical significance for potential toxicity and mobility of metals [10]. The sequential extraction technique was introduced for this purpose to provide information on the strength and forms of the metals associated with the sediments [11]. According to the analysis results, it could be clearly observed that the distribution of heavy metal fractions in different areas in the sediment varied significantly due to various factors.

As seen in the analysis results, Cr, Cu, Cd, Ni, Pb, and Zn were mostly found in the residual fractions of the samples, indicating that these metals were bound to mineral mesh in the samples. The highest concentrations after the residual fractions were found in reducible fractions (i.e., metals were bound to Fe and Mn oxides).

The Zn concentrations were predominantly in persistent/bound fractions (mean 50%) and the average Zn concentrations in the exchangeable, reducible fractions were 20% of the total concentration. It was observed that Zn in the sediment found in this study region might be detrimental to biota in the aquatic environment, since it could be re-mobilized when environmental conditions change. The average Zn concentration in oxidizable fractions was about 10% of the mean total concentration.

High amounts of Cr and Cu were found in residual fractions, while large rates (18% Cr and 11% Cu) were found in reducible fractions. Fraction F3 (associated with Fe and Mn oxides) was defined as the reducible fraction, and metals in this fraction could be released if exposed to sediment reduction conditions according to the information available in the literature [12-13]. Fe (II) and Mn (II), Fe (III) and Mn (IV) are oxidized to form oxide or hydroxide precipitates in increasing oxygen concentrations (Eh>100 mV) and neutral pH media. Several metal types can be adsorbed on this type of precipitate.

The non-fixed Cr, Cu, and Zn fractions (F1, F2, F3) were higher than the fixed fractions. Fixed Pb and Ni concentrations were also relatively high. This demonstrated that the natural structure could contribute to certain Pb values in the sediment in the study area. Ni was probably immobilized in aluminosilicate minerals and might be found in biologically negligible amounts [14-15]. Ni and Zn concentrations in highly variable-exchangeable fractions could be easily absorbed and utilized by the organisms.

Only small amounts (<9% of total concentrations) of Cr, Cu, Ni, and Pb were found in the exchangeable fractions in the sediment samples, indicating that these metals would not pose a significant risk to aquatic biota because only small amounts could be reactivated when environmental conditions change [16]. The multitude of exchangeable fractions suggested that anthropogenic activities (mainly due to the discharge of sewer and industrial wastewater into the streams) affected the metal concentrations in the study area [17, 18].

Conclusions

In the analyses, the concentrations of human activity-originated Zn, Cr, Cu, Pb, Cd, and Ni heavy metals were determined from sediment, and mean heavy metal concentrations were found as follows: Zn 70-260, Cr 26-110, Cu 70-135, Pb 8-50, Cd 0.1-2, and Ni 10-38 mg/kg. Concentrations were usually low and indicated that the sediment was not too polluted in the present. When the values obtained in the study were compared with the literature, we could conclude that the bed dredging works in the Golden Horn, the channels established around the estuary to prevent wastewater discharge, building of wastewater treatment plants, and the closure of the existing factories improved the rehabilitation of heavy metal levels in the sediment. However, contaminants that were concentrated in the sediment could persist in the sediment structure in the Golden Horn, even if the pollutant discharge to the water environment is reduced or even prevented.

Since the Golden Horn has been exposed to heavy metal pollution during the past, it would take a long time to clean up the pollution in the sediment and to reduce the heavy metal pollution in the living organisms inhabiting this area, even if all the pollution sources are restricted. To prevent pollution in the Golden Horn, all uncontrolled discharges from land, air and water sources should be identified and prevented. Industrial organizations located around the Golden Horn should be prevented from conducting illegal discharges by regular inspections, and treatment plant effluents complying with the discharge standards should be controlled.

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