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Assessment at mid-Black Sea coast of Turkey for recovery valuable heavy metals from sediments

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Abstract: Rapid industrialization and urbanization has led to the contamination of sediments with heavy metals and organic contaminants and created a pervasive problem worldwide. Major sources of contamination include agricultural and urban lands, industrial activities, spills, and accidents. Arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) are often found in sediments and other areas affected by anthropogenic activities. Sediments containing these contaminants act as secondary sources of contamination, posing significant direct and indirect environmental risks through bioaccumulation in aquatic organisms and incorporation into aquatic food webs that may lead to human exposure. Heavy metal accumulation, bioavailability, and toxicity to sediment-dwelling organisms are largely influenced by the physicochemical conditions and geochemical properties of sediments. Ongoing assessment at mid-Black Sea coast of sediment samples was digested using the 1 ml $HClO_4$ % 65, 6 ml HNO_3 % 65, 1 ml H_2O_2 % 30 for metal analysis. Digested samples were analyzed at Perkin Elmer Optima 4300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Samples were taken from the four stations; S1, S2, S3, S4. The results show us that all metals have the highest value in the sample number S4. These values found for Cr 7.65 mg/l, Cu 3.05 mg/l , Zn 6.40 mg/l, Cd 11 mg/l ,Pb 1.32 mg/l and Al 2120 mg/l . According to these results, valuable heavy metals may also be treated and extracted from for recovery.

Key words: Black Sea, Heavy metals, Recovery, Sediments, SEF

1. INTRODUCTION

The pollution of the marine ecosystem by heavy metals is a worldwide problem. The ecosystem of the Black Sea has been damaged as a result of chemical pollution. Much of the pollutants come from major rivers and from smaller sources in all Black Sea coastal countries. Additionally, the Black Sea coastal waters are heavily impacted by sewage, a situation exacerbated by the weak economies of coastal states. Black Sea waters remain heavily impacted by a number of pollutants originating from different sources such as the direct and indirect discharge of land-based pollutants, sewage etc. The Black Sea environment is highly contaminated in many urban and industrialized areas of the many countries, resulting in severe ecotoxicological impacts. Heavy metals are toxic substances that accumulate in food chains with the increasing concentrations.

The Black Sea, a semi-enclosed sea, is situated between 40°55' to 46°32' N and 27°27' to 41°32' E. The Black Sea is surrounded by six countries located in Europe and Asia: Bulgaria, Georgia, and Romania; Russia, Turkey, and Ukraine. In fact, the Black Sea is influenced by seventeen countries, thirteen capital cities and some 160 million people (Bakan and Büyükgüngör, 2000).

Sediments have proved to be excellent indicators of environmental pollution, as they accumulate pollutants to the levels that can be measured reliably by a variety of analytical techniques (Ariman and Bakan, 2008). This phenomenon makes sediment as an effective sink for most heavy metals from both crustal and anthropogenic sources. The Black Sea environment has suffered a catastrophic degradation from the waterborne waste from 17 countries. The objectives of this study were determined concentrations of six heavy metals (Cu, Pb, Cd, Al, Cr, Zn,) in sediments of the mid-Black Sea coast of Turkey. The effects of the accumulation of heavy metals in sediments of the mid-Black Sea coast of Turkey were examined in this study.

2. MATERIALS AND METHODS

2.1 Collection of sediment samples

Marine offshore water samples were collected from 4 stations at 3 miles and 20 miles distance from the coast during the spring season at 2014. The area is bound by the latitude 40° 59' 30 N and 42°22' 12 N and longitude 35°11' 23 E and 37°54' 15 E. The coordinates of the samples collected at four points shown in Table 1.

Table 1. The coordinates of the sediment samples taken from the Mid-Black Sea coast of Turkey

Sampling Points	Station	Coordinates (N-E)
Terme	S1	41.13.397 37.07.776
Fenerköy	S2	41.23.768 36.48.130
Canik	S3	41.23.104 36.17.294
Dereköy	S4	41.34.467 36.12.547

Wet sediments were dried at 103 ºC. After drying to below 63 μm remaining marine sediment samples were digested by adding 1 ml $HClO_4$ % 65, 6 ml HNO_3 % 65, 1 ml H_2O_2 % 30 at the Milestone Start D Digestion System.

2.2 Determination of sediment enrichment factor (SEF)

Digested samples were analyzed at Perkin Elmer Optima 4300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for concentrations of the metals Cr, Cd, Cu, Al, Zn, and Pb.

The extent of metal contamination compared to the background area was assessed using the enrichment factor, EF (Selvaraj et al., 2004; Woitke et al., 2003).The concentration of each metal measured in the Mid-Black Sea coast sediments is normalized to aluminum data and to the aluminum crystal value. Aluminum, being a conservative element, is generally assumed to have a uniform flux to the sediments over the past century from crustal rock sources. The sediment enrichment factor (SEF) for metal concentration in sediments at all stations were calculated from:

$$SEF = \frac{X/Al\ (\mathrm{sediment})}{X/Al\ (\mathrm{Earth's\ crust})} \tag{1}$$

where X is the metal studied and X/Al is the ratio of the concentration of element X to aluminum. Aluminum was chosen as the element of normalization also because of natural sources (98%)vastly dominates its input (Kamau, 2002).

2.3 Determination of geo-accumulation index

A first quantitative check of metal pollution in aquatic sediments has been proposed by Müller and Suess (1979) in an equation and it is called the "Index of Geoaccumulation", that is, the enrichment on the geological substrate:

$$I_{geo} = \ln (C_n / 1.5 * B_n) \tag{2}$$

where:

Cn: measured concentration,

Bn: geochemical background value

1.5: a factor for lithologic variations of the heavy metals.

The sediment pollution was investigated by following the concentration of 5 studied heavy metals such as Zn, Cr, Pb, Cu, and Cd. The factor 1.5 was introduced to minimize the effect of possible variations in the background values which might be attributed to lithologic variations in the sediments (Al-Haidarey et al., 2010). According to the crustal abundance data of Krauskopf and Bird (1995) the reference samples were Zn:70, Cr:100, Pb:13, Al:81300 Cu:55 and Cd:0.2 mg/kg.

3. RESULTS AND DISCUSSION

This study investigated the effects of heavy metals pollutants in the mid-Black Sea coastline. heavy metal concentrations measured at four different stations are given in Table 2.

Table 2. Heavy metal concentrations in sediments collected from the mid-Black Sea coast of Turkey

Station	Cr(mg/kg)	Cu (mg/kg)	Zn(mg/kg)	Cd(mg/kg)	Pb (mg/kg)	Al(mg/kg)
S1	2.052	0.56	1.148	2.72	0.092	380
S2	1.764	0.648	1.176	2.56	0.1	420
S3	2.292	0.516	1.288	3.28	0.076	372
S4	3.06	1.22	2.56	4.615	0.528	848

The results are given Figure 1, all heavy metal concentrations are high at S4 station.

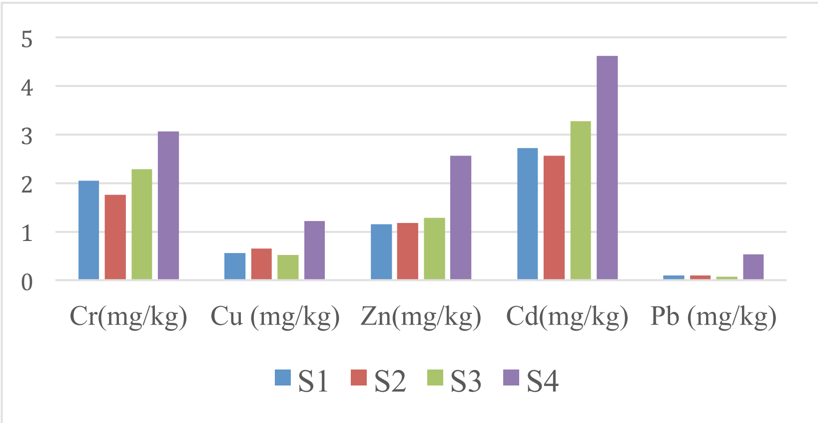

Figure 1. Schematic representation of the heavy metal concentrations in sediments collected from the mid-Black Sea coast of Turkey

3.1 Sediment enrichment factor

The sediment enrichment factor (SEF) is a convenient measure of geochemical trends and is used for making comparisons between areas (Sinex and Helz, 1981). A value of unity denotes neither enrichment nor depletion relative to the Earth's crust.

With the support of the classification of Taylor, 1964 (Table 3) the sediment enrichment factor (SEF) values were interpreted (Table 4).

Table 3. The degree of metal pollution based on seven sediment enrichment factor classes (Taylor, 1964).

SEF value	Designation of sediment quality
50	Extremely severe enrichment
25-<50	Very severe enrichment
10-<25	Severe enrichment
5-<10	Moderately severe enrichment
3-<5	Moderate enrichment
1-<3	Minor enrichment
<1	No enrichment

Table 4. The results of enrichment factor of some heavy metals of sediment samples from the mid-Black Sea coast of Turkey.

Station	S1	S2	S3	S4	Sediment quality
Cr	1.756	1.36	2.00	1.17	Minor enrichment
Cu	0.87	0.91	0.82	0.85	No enrichment
Zn	1.40	1.30	1.60	1.40	Minor enrichment
Cd	1164	991	1434	885	Extremely severe enrichment
Pb	0.6	0.59	0.51	1.55	Minor enrichment

The sediment enrichment factor for 5 studied heavy metals for each station was listed in Table 4. According to Taylor (1964) classification, the EF value of some heavy metals as Cr, Cu, Zn, and Pb was < 1 and 1-<3, indicated that there was no enrichment or minor enrichment by these metals in the sediments of the mid-Black Sea coast. But heavy metal Cd is greater than 50, so sediment extremely severe enrichment.

3.2 The geo-accumulation index

The geo-accumulation index (I_{geo}) values were interpreted (Table 5) with support of the classification of Abrahim and Parker (2008). Generally, the I_{geo} consists of 7 grades or classes.

Table 5. The degree of metal pollution in terms of seven enrichment classes (Abrahim and Parker, 2008).

I_{geo}	Value I_{geo}	Class designation of sediment quality
>5	6	Extremely contaminated
4-5	5	Strongly to extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

The I_{geo} classes for 5 studied heavy metals for each station are listed in Table 6. The I_{geo} values revealed that the value of Cr, Cu, Zn and Pb in all stations fell into class 0. But also Cd value is 2 at S1 station and ın all other stations, the value is 3. According to this sediment was moderately to strongly contaminated.

Table 6. The results of geo-accumulation index classes of some heavy metals of the mid-Black Sea coast of Turkey.

Station	S1	S2	S3	S4	Sediment quality
Cr	0	0	0	0	uncontaminated
Cu	0	0	0	0	uncontaminated
Zn	0	0	0	0	uncontaminated
Cd	2	3	3	3	moderately to strongly contaminated
Pb	0	0	0	0	uncontaminated

So, this analysis revealed that the sediments of the mid-Black Sea coast were suffering from slight contamination to moderately to strongly contamination with the studied heavy metals according to I_{geo} values. All station were suffering moderately from Cd metal.

4. CONCLUSIONS

Heavy metal pollution in the Black Sea has attracted considerable research attention since last 20 years. Sources of heavy metals in the Black Sea environment can be mainly attributed to terrestrially derived wastewater discharges, agricultural and industrial run-off, river run-off atmospheric deposition of combustion residues, and shipping activities. It is clear from many studies conducted that the heavy metal pollution should be taken into account in the Black Sea.

Additionally, the sediment enrichment factor and geo-accumulation index results show that Cd metal was created moderate pollution in the mid-Black Sea coast of Turkey. Therefore heavy metal recovery will be provided to using suitable treatment techniques of one of these: the sequential extraction, thermal extraction, bioremediation, chemical oxidation, solidification, vitrification methods.

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