

[Research]

## The contamination status of trace metals in Sinop coast of the Black Sea, Turkey

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### ABSTRACT

The concentration of some heavy metals in sediment from the Sinop coasts of the Black Sea were measured to monitor metal pollution in 2013. The distribution of the heavy metals in sediments of the Black Sea shows a variable pattern. The objectives of the present study were to elucidate the distribution of heavy metals such as Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Hg and Co in sediment from Sinop coast of the Black Sea. In order to determine. The quality of sediment in the Black Sea, pollution levels of the metals were evaluated using the enrichment factor technique (EF). The lowest EF values were between 0-5 in Cu, Fe, Zn, Ni, Cd, Pb, Mn and Co. These values did not have statistically significant differences. As, Cr and Hg concentrations were estimated relatively higher enrichment values than other the metals. The results indicated that contamination of surface sediments in Sinop Coast is dominated by As (10.2-7.4 mg.kg<sup>-1</sup>), Cr (67-374 mg.kg<sup>-1</sup>) and Hg (0.07-0.03 mg.kg<sup>-1</sup>) and to a lesser extent Cu (7.24-5.09 mg.kg<sup>-1</sup>), Fe (1.76-1.12%), Zn (19.3-13.8 mg.kg<sup>-1</sup>), Ni (16.2-12.5 mg.kg<sup>-1</sup>), Cd (0.06-0.04 mg.kg<sup>-1</sup>), Pb (7.12-6.32 mg.kg<sup>-1</sup>), Mn (470-227 mg.kg<sup>-1</sup>), Co (9.5-5.9 mg.kg<sup>-1</sup>). Also, the requirement of age determination is of great importance to assess the extent of the anthropogenic contribution in pollution.

**Keywords:** Black Sea, Enrichment factor, Heavy metal, Sediment, Sinop coast, Turkey

### INTRODUCTION

Heavy metals are among the most serious environmental pollutants. Their occurrence in water and sediment may become of high ecological significance in the presence of natural or anthropogenic sources. Many metals are essential to organisms but at high concentrations appear to be toxic. Heavy metals found in seawater are continuously released into the marine environment by both natural and artificial processes (Bryan 1976a, b; Rainbow 1993). The natural sources of metals in marine environment are reviewed by Turekian (1971) and categorized by Bryan (1976b) as follows: (a) coastal supply, which includes input from rivers and from erosion due to wave action and glaciers; (b) deep sea supply, which includes metals released from particles or sediments by chemical processes; (c) supply

which by-passes the near-shore environment and includes metals transported in the atmosphere as dust particles or as aerosols; and (d) also material which is produced by glacial erosion in polar regions and is transported by floating ice. In the last few decades, many coastal systems have been increasingly impacted by heavy metals released from anthropogenic activities. To identify pollution problems, the anthropogenic contributions should be distinguished from the natural sources. Anthropogenic sources of metals include: (a) atmospheric input from the burning of fossil fuels, the smelting and refining of metals, the use of leaded petrol in motor vehicles, fly ash from power stations and the use of seawater discharges cooling from operations at power stations. Inputs of some metals to the atmosphere as a result of human

activities are greater than natural inputs and the sea acts as a sink for atmospheric contamination (Clark, 1986); (b) mining activities, such as tailings; (c) industrial processing of ores and the use of metal components, such as electroplating, pigments, electrical wiring, batteries, galvanizing, fertilizers; (d) the release of sewage (Depledge et al. 1994), which was dumped at sea in considerable quantities of high organic content with heavy metals (Clark, 1986); (e) contamination due to ships in docks and harbors from the use of metals such as copper, tin and mercury in antifouling points and other metals such as lead, chromium and zinc in preservative paints (Bellinger & Benham, 1978; Young et al., 1979); (f) dredging spoil, particularly from industrialized estuaries may contain heavy metals and other contaminants which are then transferred to the dumping grounds (Clark, 1986). Sediment plays an important role in the assessment of metal contamination in natural waters and sediments (Wardas *et al.*, 1996). The accumulation of metals in sediment is largely controlled by biogeochemical processes. They accumulate in sediments via waste materials which include organic and inorganic chemicals, terrestrial runoff, disposal of liquid effluents and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities. When heavy metals settle on the sea floor, they finally become part of the sedimentary record (Palanques *et al.*, 1995). When introduced into the sea, organic and inorganic contaminants, particularly heavy metals, eventually accumulate in sediment (Luoma, 1983) which becomes repositories or sinks (Phillips, 1995). Sediments can be sensitive indicators in aquatic environments and may play an important role in mediating the exchange of contaminants between particulate, dissolved and biological phases. Sediments are the major compartment in the coastal environment for heavy metals and other toxic materials by virtue of their small particle size (Davies-Colley *et al.*, 1984) and contain variable concentrations of both essential and non-essential metals (Luoma &

Bryan, 1978). Because of increasing industrial and recreational demands on coastal areas, especially estuarine environments, these systems have come under ever-increasing force which result in habitat deterioration and pollution leading to deleterious effects on benthic and pelagic communities, fisheries and eventually to human health through direct contact of organisms with the sediment or by re-suspension of contaminated particles into the overlying water. Several studies have demonstrated that heavy metal pollution especially in marine environment increased over the last few decades at global scale, therefore, the evaluation of metal distribution in marine sediments is useful to assess the pollution status in marine coasts. Bat and Öztürk (1997) and Bat et al. (2009) point out the local Black Sea environment especially Sinop coasts is not facing a heavy metal pollution problem. The objectives of the present study were to elucidate the distribution heavy metals such as Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Hg and Co in sediment from Sinop coast of the Black Sea. In order to realize the goals of this study, corer sediment samples were collected and analyzed.

## MATERIALS AND METHODS

### Study Area

The Black Sea which is a large and semi-enclosed sea is located between the latitudes of 40° 55' and 46° 42' with the longitudes of 27° 27' and 41° 42'. It has historically been one of the most biologically and ecologically productive marine ecosystem in the world (Ivanov & Beverton 1985; Mee 1992; Bat et al., 2009). The Black Sea is surrounded by six countries in Europe and Asia: Bulgaria, Georgia, Romania, Russia, Turkey and Ukraine (Altas & Büyükgüngör, 2007). To the South, it is connected to the Mediterranean through the Bosphorus, which is the world's narrowest strait, with an average width of 1.6 km, depth of 36 m and total length of 31 km (Bakan & Büyükgüngör, 2000). To the North, The Black Sea is connected with Sea of Azov through the shallow Kerch Strait, which has a depth of less

than 20 m. Sinop is situated on Boztepe Cape and Peninsula, which is the sharpest point toward the north, on the shore of the Black Sea and extends between latitude of 41°59'40.51"N and longitude of 35°6'47.17"E. The sediment samples were collected four times in July and August of 2013 from İç Liman of Sinop Peninsula at the Black Sea coast of Turkey (Fig. 1). The station was chosen in a way to include

hotspots of pollution around Sinop city such as domestic wastewater discharge points in coastal zone of Sinop (Bat & Gökkurt Baki, 2014).

### Analytical procedure

The core samples obtained was 10 cm in length with a diameter of 4 cm. After the collection of the cores, they were sliced at two

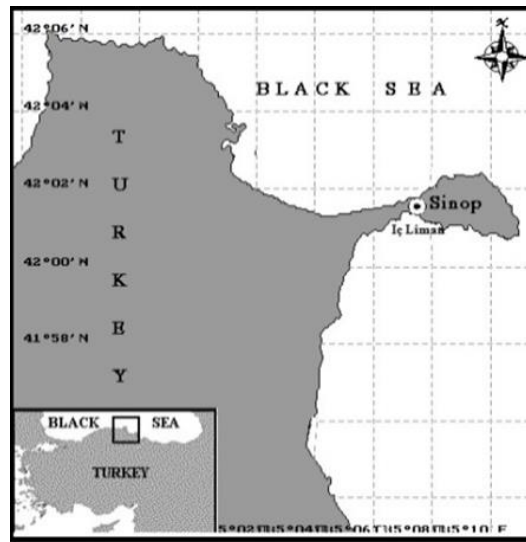


Fig. 1. Map of the study area showing İç Liman station of the Black Sea, Turkey.

cm intervals by using sediment extruding device. The sediment slices were stored in cleaned polyethylene bottles with ice to keep cold and transferred to the laboratory. They were frozen at -21 °C in a deep freezer. Metal analysis (except for Hg) in all subsampling pulverized to 85% passing 200 mesh was performed using 4 acid digestion and ultra-trace ICP-MS method by accredited ACME Analytical Laboratories Ltd. (Vancouver, Canada). Ultra trace Aqua Regia digestion method for Hg analysis was also used by accredited ACME Analytical Laboratories. The average values of duplicates were analyzed for each determination. To better understand the quality of sediment in the Black Sea, pollution levels of metal were evaluated using the enrichment factor technique (EF). EF is a powerful tool used mainly in distinguishing heavy metals coming from anthropogenic and natural sources (Ozkan & Buyukisik, 2012). The

EF represents the heavy metal contamination level in the sediment. In order to identify anomalous metal concentration, geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe and Si were employed. Al was used as reference element to differentiate natural from anthropogenic components, EF was calculated according to the following equation:

$$EF = \frac{(C_x / C_{Al})_{sample}}{(C_x / C_{Al})_{background}}$$

$(C_x / C_{Al})_{sample}$ : is the ratio of metal and Al concentrations of the sample and  $(C_x / C_{Al})_{background}$ : is the ratio of background metal and Al concentrations. Also, the average crust concentrations of elements (Turekian &

Wedepohl, 1961) were taken as background. EF values were interpreted as suggested by Birch (2003) where  $EF < 1$  indicates no enrichment;  $EF < 3$  is minor;  $3 \leq EF \leq 5$  is moderate;  $5 \leq EF \leq 10$  is moderately severe;  $10 \leq EF \leq 25$  is severe;  $25 \leq EF \leq 50$  is very severe and  $EF > 50$  is extremely severe.

## RESULTS AND DISCUSSION

Table 1 presents average concentrations of heavy metals in sediments of Sinop coast in the Black Sea. The distribution of heavy metals in sediments shows a variable pattern. The sediment composition and origin depend on the provenance areas, hydrodynamic and lithodynamic activity in the contact zone of the Sea, and on the morphology of the bottom topography. Heavy metal concentrations in surface sediments can provide historical information on heavy metal inputs at that

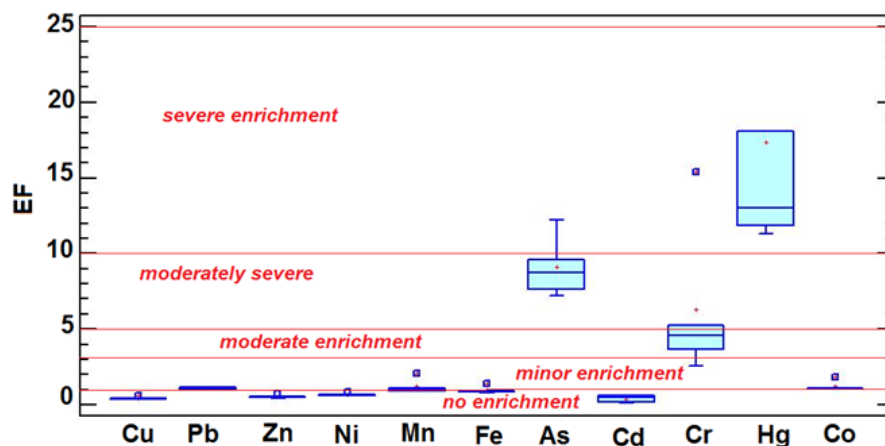
location. Such surface sediment samples are also used as environmental indicators to reflect the current quality of marine systems for many pollutants (Förstner & Solomons, 1980). Nijenhuis *et al.* (1999) reported that the enrichment of trace elements in marine sediments may, in general, originate from the following sources: super and subjacent sediments, through diagenesis: suboxic shelf and slope sediments, hydrothermal input: Aeolian input: fluvial runoff: seawater. The EF value of some metals with respect to the sediment is shown in Table 2. Also, Enrichment factors and classes for core samples were presented in Fig. 2. The results showed that the range of EF values were 0.39- 0.59; 1.00-1.17; 0.42-0.75; 0.62-0.82; 0.92-2.04; 0.79-1.38; 7.2-12.21; 0.1-0.91; 257-15.39; 11.33-32.41 and 1.03-1.85 for Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Hg and Co, respectively.

**Table 1.** Average concentrations of heavy metals in sediments of Sinop coast in the Black Sea (Standard deviation values are given in parentheses).

Depths (cm)	METALS							
	Fe (%)	Ca (%)	Al (%)	Na (%)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppm)
0-2	1.76 (0.33)	3.14 (0.08)	2.17 (0.43)	0.73 (0.23)	7.24 (0.38)	6.32 (0.57)	19.3 (3.89)	252 (19.09)
2-4	1.29 (0.09)	3.03 (0.17)	2.78 (0.08)	1.05 (0.03)	6.70 (0.44)	7.12 (0.31)	13.8 (0.85)	279 (77.78)
4-6	1.42 (0.12)	2.79 (0.01)	2.66 (0.08)	1.01 (0.06)	6.08 (0.35)	6.68 (0.12)	15.0 (0.14)	169 (14.14)
6-8	1.25 (0.09)	2.77 (0.08)	2.54 (0.20)	0.93 (0.11)	5.59 (0.05)	6.51 (0.22)	14.8 (1.99)	189 (35.40)
8-10	1.12 (0.02)	2.63 (0.04)	2.32 (0.05)	0.89 (0.08)	5.09 (0.07)	6.74 (0.30)	15.9 (0.07)	160 (10.61)

Depths (cm)	METALS						
	Ni (ppm)	Co (ppm)	Mn (ppm)	Cd (ppm)	Hg (ppm)	Cr (ppm)	As (ppm)
0-2	15.2 (0.71)	9.5 (1.91)	470 (140.01)	0.05 (0.02)	0.07 (0.01)	374 (183.14)	10.2 (1.98)
2-4	16.2 (1.56)	6.8 (0.21)	272 (20.51)	0.02 (0.01)	0.05 (0.01)	115 (29.70)	7.4 (1.84)
4-6	14.0 (0.35)	6.5 (0.07)	301 (20.51)	0.06 (0.03)	0.03 (0.00)	157 (18.38)	10.0 (0.57)
6-8	13.5 (0.62)	6.4 (1.02)	272 (68.99)	0.02 (0.00)	0.03 (0.01)	131 (92.03)	9.2 (0.78)
8-10	12.5 (0.64)	5.9 (0.28)	227 (17.68)	0.04 (0.01)	0.03 (0.00)	67 (5.66)	7.7 (0.35)



**Fig. 2.** Mean, median, 95% confidence levels, minimum, maximum values and outliers of EF for 11 elements in the sediments of Sinop Peninsula

**Table 2.** EF values for sediments.

Depths (cm)	EF (Cu)	EF (Pb)	EF (Zn)	EF(Ni)	EF(Mn)	EF (Fe)	EF (As)	EF(Cd)	EF(Cr)	EF (Hg)	EF (Co)
0-2	0.5961	1.1708	0.7527	0.8282	2.0487	1.3874	7.6160	0.6175	15.3966	32.4194	1.8525
2-4	0.4306	1.0296	0.4201	0.6890	0.9255	0.7938	12.2110	0.1928	3.6954	18.0755	1.0351
4-6	0.4084	1.0095	0.4772	0.6223	1.0703	0.9132	8.7318	0.6045	5.2727	11.3346	1.0340
6-8	0.3932	1.0303	0.4931	0.6284	1.0129	0.8418	7.2100	0.1055	4.6073	11.8701	1.0662
8-10	0.3920	1.1679	0.5800	0.6370	0.9255	0.8258	9.6264	0.4621	2.5799	12.9957	1.0761

The lowest EF values were determined between 0-5 in Cu, Fe, Zn, Ni, Cd, Pb, Mn and Co. These values have not been considered significant. Cr, As and Hg concentrations were estimated relatively higher enrichment values than other metals. It is assumed that the high EF values indicate an anthropogenic source of heavy metals, mainly from activities such as industrialization, urbanization, deposition of industrial wastes. The major industries and their type of waste in Sinop coast of the Black Sea region were food manufacturing such slaughtering, dairy products, canning of fruits/vegetables/fish, grain mill and bakery products, sugar factories, etc. (Bakan & Büyükgüngör, 2000). However, Bat and Gökkurt Baki (2014) showed that the research area of Sinop coasts, affected with intensive land-based pollution and organic matter originating from domestic discharge. These findings are supporting our results. Solid waste storage areas are available in the vicinity of Samsun and Sinop. The batteries contained in solid waste may be cause to increase of mercury. Moreover, mercury enters the atmosphere from thermal plant, from burning, incinerating trash, things like that. Uslu & Gökmeşe (2009) pointed out that Turkey comes second after France as regards to mercury contamination in Europe. In Samsun near Sinop there is thermal plant and Hg may be transported the atmosphere as vapour then near coast environment. In the present study the results indicated that contamination of surface sediments in Sinop coast is dominated As (10.2-7.4 mg. kg<sup>-1</sup>), Cr (67-374 mg.kg<sup>-1</sup>) and Hg (0.07-0.03 mg.kg<sup>-1</sup>) and to a lesser extent Cu (7.24-5.09 mg.kg<sup>-1</sup>), Fe (1.76-1.12%), Zn (19.3-13.8 mg.kg<sup>-1</sup>), Ni (16.2-12.5 mg.kg<sup>-1</sup>), Cd (0.06-0.04 mg.kg<sup>-1</sup>), Pb (7.12-6.32 mg.kg<sup>-1</sup>), Mn (470-227 mg.kg<sup>-1</sup>), Co (9.5-5.9 mg.kg<sup>-1</sup>). In the last two years, the local population in Sinop has been about 35000, increasing to 200000 in

summer. The increased sewage pollution in late spring and summer from the population of Sinop was reflected in changes in the species composition of *Ulva* and in an increase in biomass and production and invertebrates mainly Arthropods and Mollusks (Bat *et al.*, 2001). These changes may effect increase organic pollution. The organic matter loads are usually originating from domestic discharges and the percentage of organic content in the sediment of Iç Liman area was maximum 2.18% (Bat & Gökkurt Baki 2014). It is well known that metals bound to organic matter in sediment (Buchanan 1984, Bryan & Langston 1992). Thus, untreated domestic wastes and human activity along the coastal zone of Sinop increase in July and August and most probably give rise to high metal concentrations (Bat *et al.*, 1999). Since, the bioavailability and toxicity of any trace metals in sediments depend upon the chemical form and concentration of the metals (Kwon *et al.*, 2001), it can be inferred that trace metals in sediments samples with the highest EF values, along with higher labile fractions in sediments are potential sources for mobility and bioavailability in the aquatic ecosystems (Mohiuddin *et al.*, 2010). Heavy metal pollution in sediments of the Black Sea has attracted considerable research attention since the 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 combustion residues and activities (Boran & Altınok, 2010). Heavy metal levels sediment from the Black Sea were investigated by many researchers. (Table 3).

## CONCLUSION

The current lack of comparable data will make it impossible to measure future trends in contamination or to adequately protect ecosystems and public health. In the Black Sea

**Table 3.** Heavy metal levels ( ppm, except for Fe dry wt.) in sediment from Turkish coast of the Black Sea.

Fe (%)	Zn	Ni	Cu	Mn	Pb	Cd	Cr	Co	Hg	References
-	-	-	-	-	3.06-617.8	-	-	-	-	Ünsal 2001
-	-	-	-	-	2.9-42.0	-	-	-	-	Ünsal 2001
-	12-238	-	2-47	-	5-143	1-225 (ppb)	-	-	9-91 (ppb)	Ünsal et al. 1998
-	-	-	0.08-0.42	-	3.06-3.77	-	-	-	0.05-0.40	Ünsal et al. 1995
-	-	-	11.80-356.56	-	6.22-11.32	-	-	-	0.86-4.0	Ünsal et al. 1995
-	-	-	528.12 ± 357.0	-	38.74 ± 39.5	-	-	-	0.29-2.02	Ünsal et al. 1995
1.3-4.3	50-108	38-130	29-68	355-751	14-35	-	32-171	7-37	-	Kıratlı and Ergin 1996
0.2-4.9	24-138	11-202	15-87	112-1064	12-66	-	13-224	< 20	-	Yücesoy and Ergin 1992
1.9-3.9	50-111	34-88	20-47	312-995	19-51	-	51-135	9-19	-	Ergin et al. 2003
2.6-4.9	57-127	2.2-69.1	23-75	354-902	11-30	0.6-0.9	22-122	5.2-17.2	-	Topçuoglu 2000
-	-	-	-	-	-	-	218.1±20.1	-	-	Topçuoglu et al. 1998
-	50.1±0.4	-	15.5±0.5	414.4±0.8	<0.5	<0.02	-	-	-	Topçuoglu et al. 2003
-	484.2±1.1	-	506.5±1.5	647.5±1.9	39.2±4.3	<0.02	-	-	-	Topçuoglu et al. 2003
2.9	119.3 ± 0.7	31.57 ± 0.51	13.57 ± 0.08	519.1 ± 4.5	< 0.05	< 0.02	74.7 ± 1.4	21.45 ± 4.44	-	Topçuoglu et al. 2002
0.5	33.9 ± 0.1	13.55 ± 0.38	4.00 ± 0.02	206.6 ± 1.0	< 0.05	< 0.02	10.8 ± 0.2	< 0.05	-	Topçuoglu et al. 2002
2.7	92.6 ± 0.37	33.50 ± 0.77	27.60 ± 0.24	338.2 ± 0.3	21.4 ± 5.6	0.73 ± 0.08	58.5 ± 0.4	8.28 ± 0.51	-	Topçuoglu et al. 2002
3.5	91.5 ± 0.45	65.20 ± 0.71	37.3 ± 0.14	424.3 ± 1.3	15.1 ± 2.9	0.89 ± 0.11	115.5 ± 0.5	13.40 ± 0.71	-	Topçuoglu et al. 2002
4.4	82.9 ± 0.16	18.50 ± 0.22	69.9 ± 0.20	514.1 ± 1.1	31.1 ± 2.0	0.93 ± 0.04	21.8 ± 0.1	16.8 ± 0.97	-	Topçuoglu et al. 2002
5.4	267.4 ± 0.26	37.26 ± 0.38	95.5 ± 0.19	870.3 ± 3.5	< 0.05	< 0.02	38.88 ± 0.34	36.44 ± 10.5	-	Topçuoglu et al. 2002
-	109.55-261.65	7.9-49.25	32.9-64.85	441.55-668.75	12.13-223.7	<0.02	53.05-99.3	-	-	Bakan & Özkoç 2007
4.7±0.01	325.3	128.1	59.9±1.0	2915±5	<0.01	<0.02	1276.5	63.7±2.3	-	Balkıs et al. 2007
8.5±3.87	119.8	129.9±1	43.7±2.1	864±3	<0.01	<0.02	370.8±1	33.6±1.9	-	Balkıs et al. 2007
4.9±0.01	91.4±0.5	104.6±1	23.0±0.3	989±4	<0.01	<0.02	231.9±1	22.7±1.2	-	Balkıs et al. 2007
7.8±0.03	119.5	120.0±2	27.6±0.7	1206±1	<0.01	<0.02	720.6±1	27.4±1.2	-	Balkıs et al. 2007
6.05± 0.50	182 ± 17	26.53± 0.79	56.86± 0.34	672.8± 3.0	<0.1	<0.02	74.24±7.00	23.90± 1.40	-	Ergül et al. 2008
5.68± 0.50	169 ± 16	23.61± 2.19	52.03± 0.61	651.9± 2.27	<0.1	<0.02	70.02± 7.04	22.60±1.30	-	Ergül et al. 2008
47,200	146	-	66	3140	26	0.38	135	22.8	-	Yığiterhan & Murray 2008
-	56.5-286.3	10.6-29.2	13.68-315.99	-	12.34-83.78	-	-	-	-	Özşeker & Erüz 2011
33800-45900	82.8-183.9	56.9-93.3	39.8-72.46	416-763	20.29-37.76	0.18-0.53	73-117	12.9-21	0.03-0.13	Ozkan & Buyukisik 2012
43800-50100	83.9-124.2	49.5-140.6	57.83-71.83	383-755	18.13-44.33	0.24-0.45	54-147	19.7-28.9	0.04-0.07	Ozkan & Buyukisik 2012
-	-	-	2.87- 407.93	-	2.51-79.78	0.03-1.04	-	-	0.47 - 2.86	Sur et al. 2012

coastal waters the data on heavy metals in sediments are available but variable; it results from studies using methodologies that are not inter-comparable. Independent investigations and available data (Table 3) suggest that this situation is serious and warrants urgent action. Although high trace metal concentrations were found in some regions of the Black Sea coast, Turkey (see Table 3), the level of most often of the trace metals were not extremely enriched in these surface sediments of Sinop coast and did not present a serious threat to the local fauna and flora. It is recommended that further investigations and future monitoring will be useful to assess long term effects of anthropogenic inputs on the Black Sea.

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#### REFERENCES

- Altas, L. & Büyükgüngör, H. (2007) Heavy metal pollution in the Black Sea shore and offshore of Turkey. *Environmental Geology*. 52: 469-476.
- Bakan, G. & Büyükgüngör, H. (2000) The Black Sea. *Marine Pollution Bulletin*. 41: 24-43.
- Bakan, G. & Özkoç, H.B. (2007) An ecological risk assessment of the impact of heavy metals in surface sediments on biota from the mid-Black Sea coast of Turkey. *International Journal of Environmental Studies*. 64: 45-57.
- Balkıs, N. Topcuoglu, S. Güven, K. C. Öztürk, B. Topaloglu, B. Kırbasoglu, Ç. & Aksu, A. (2007) Heavy metals in shallow sediments from the Black Sea, Marmara Sea and Aegean Sea regions of Turkey. *Journal of the Black Sea / Mediterranean Environment*. 13: 147-153.
- Bat, L. & Gökkurt Baki, O. (2014) Seasonal variations of sediment and water quality correlated to land-based pollution sources in the middle of the Black Sea coast, Turkey. *International Journal of Marine Science*. 4: 108-118.
- Bat, L. & Öztürk, M. (1997) Heavy metal levels in some organisms from Sinop Peninsula of the Black Sea. *Turkish Journal of Engineering and Environmental Sciences*. 21: 29-33.
- Bat, L. Gökkurt, O. Sezgin, M. Üstün, F. & Sahin, F. (2009) Evaluation of the Black Sea land based sources of pollution the coastal region of Turkey. *The Open Marine Biology Journal*. 3: 112-124.
- Bat, L., Akbulut, M., Sezgin, M. & Çulha, M. (2001) Effects of sewage pollution the structure of the community of *Ulva lactuca*, *Enteromorpha linza* and rocky macrofauna in Dışlıman of Sinop. *Turkish Journal of Biology*. 25: 93-102.
- Bat, L., Gündoğdu, A., Öztürk, M. & Öztürk, M. (1999) Copper, zinc, lead and cadmium concentrations in the Mediterranean mussel *Mytilus galloprovincialis* Lamarck 1819 from Sinop coast of the Black Sea. *Turkish Journal of Zoology*. 23: 321-326.
- Bellinger, E.G. & Benham, B.R. (1978) The levels of metals in dock-yard sediments with particular reference to the contributions from ship-bottom paints. *Environmental Pollution*. 15: 71-81.
- Birch, G. (2003). A scheme for assessing human impacts on coastal aquatic environments using sediments. in: Woodcoffe, C. D., Furness, R. A. (Eds.), Coastal GIS 2003. Wollongong University Papers in Center for Maritime Policy, 14, Australia.
- Boran, M. & Altınok, I. (2010) A review of heavy metals in water, sediment and living organisms in the Black Sea. *Turkish Journal of Fisheries and Aquatic Sciences*. 10: 565-572.
- Bryan, G.W. (1976a) Some aspects of heavy metal tolerance in aquatic organisms. In: A.P.M. Lockwood (Ed.), Effects of Pollutants on Aquatic organisms. Cambridge University Press., pp. 7-34.
- Bryan, G.W. (1976b) Heavy metal contamination in the sea. In: R. Johnston (Ed.), Marine Pollution. London Academic Press. pp. 185-302.
- Bryan, G.W. & Langston, W.J. (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution*. 76: 89-131.
- Buchanan, J.B. (1984) Sediment analysis. In: N.A. Holme and A.D. McIntyre (Eds.), Methods for the Study of Marine Benthos. Blackwell Science Publication, pp. 41-65.

- Clark, R.B. (1986). Marine pollution. Clarendon Press, Oxford.
- Davies-Colley, R.J. Nelson, P.O. & Williamson, K.J. (1984) Copper and cadmium uptake by estuarine sedimentary phases. *Environmental Science & Technology*. 18: 491-499.
- Depledge, M.H. Weeks, J.M. & Bjerregard, P. (1994) Heavy metals. In: P. Calow (Ed.), Handbook of Ecotoxicology. Oxford Blackwell Sci. Publ., London. 2: 79-105.
- Ergin, M. Keskin, Ş. Algan, O. Alpar, B. Ongan, D. Kırıcı, E. Bayhan, E. & Temel, A. (2003) Güneybatı Karadeniz kıta sahanlığının geç Kuvaterner jeolojisi: sedimantolojik, sığ sismik stratigrafik, mineralojik ve jeokimyasal araştırmalar. TÜBİTAK Sonuç Raporu, Ankara, 175 (Ed. Güven, K.C. ve Öztürk, B., 2005. *Deniz Kirliliği, Tüdev Yayınları* No: 21, İstanbul, 512 s.) (in Turkish).
- Ergül, H.A. Topçuoğlu, S. Ölmez, E. & Kırbaçoğlu, Ç. (2008) Heavy metals in sinking particles and bottom sediments from the eastern Turkish coast of the Black Sea. *Estuarine, Coastal and Shelf Science*. 78: 396-402.
- Förstner, U. & Solomons, W. (1980) Trace metal analysis on polluted sediments, I: assessment of sources and intensities. *Environmental Technology Letters*. 1: 494-505.
- Ivanov, L. & Beverton, R.J.H. (1985) The fisheries resources of the Mediterranean. Part Two: Black Sea. *Etud.Rev. CGPM / Stud. Rev. GFCM*.
- Kiratli, N. & Ergin, M. (1996) Partitioning of heavy metals in surface Black Sea sediments. *Applied Geochemistry*. 11: 775-788.
- Kwon Y.T. Lee, C.W. & Ahn, B.Y. (2001) Sedimentation pattern and sediments bioavailability in a wastewater discharging area by sequential metal analysis. *Microchemical Journal*. 68: 135-141.
- Luoma, S.N. (1983) Bioavailability of trace metals to aquatic organisms- A review. *Science of the Total Environment*. 28: 1-22.
- Luoma, S.N. & Bryan, G.W. (1978) Factors controlling the ability of sediment-bound lead to the estuarine bivalve *Scrobicularia plana*. *Journal of the Marine Biological Association of the United Kingdom*. 58: 793-802.
- Mee, L.D. (1992) The Black Sea in Crisis: A Need for Concerted International Action. *Ambio*. 21: 278-286.
- Mouhiddin, K.M. Zakir, H.M. Otomo, K. Sharmin, S. & Shikazono, N. (2010) Geochemical distribution of trace metals pollutants in water and sediments of downstream of an urban river. *International Journal of Environmental Science and Technology*. 7: 17-28.
- Nijenhuis, I.A. Bosch, H.J. Sinninghe Damste, J.S. Burmsack, H.J. & De Lange, G.J. (1999) Organic matter and trace element rich sapropels and blackshales: a geochemical comparison. *Earth and Planetary Science Letters*. 169: 277-290.
- Ozkan, E.Y. & Buyukisik, B. (2012) Geochemical and statistical approach for assessing heavy metal accumulation in the Southern Black Sea sediments. *Ekoloji*. 21: 11-24.
- Özşeker, K. & Erüz, C. (2011) Heavy metal (Ni, Cu, Pb, Zn) distribution in sediments from Trabzon in the Black Sea. *Indian Journal of Geo-Marine Sciences*. 40: 48-54.
- Palanques, A. Diaz, J.I. & Farran, M. (1995) Contamination of heavy metals in the suspended and surface sediment of the Gulf of Cadiz (Spain): the role of sources currents, pathways and sinks. *Oceanologica Acta*. 18: 469-477.
- Phillips, D.J.H. (1995) The chemistries and environmental fates of trace metals and organochlorines in aquatic ecosystems. *Marine Pollution Bulletin*. 31: 193-200.
- Rainbow, P.S. (1993) The significance of trace metal concentrations in marine invertebrates. In: R. Dallinger and P.S. Rainbow (Eds.), *Ecotoxicology of metals in invertebrates*, Lewis Publishers. pp. 3-23.
- Sur, M. Sur, H.İ. Apak, R. & Erçağ, E. (2012) The Pollution Status of Bottom Surface Sediments Along the Turkish Coast of the Black Sea. *Turkish Journal of Fisheries and Aquatic Sciences*. 12: 453-460.
- Topçuoğlu, S. Kırbaçoğlu, Ç. & Güngör, N. (2002) Heavy metals in organisms and sediments from Turkish coast of the Black Sea, 1997-1998. *Environment International*. 27: 521-526.
- Topçuoğlu, S. (2000) Black Sea ecology pollution research in Turkey of the marine environment. *IAEA Bulletin*. 42: 12-14.



- Topcuoğlu, S. Ergül, H.A. Baysal, A. Ölmez, E. & Kut, D. (2003) Determination of radionuclide and heavy metal concentrations in biota and sediment samples from Pazar and Rize stations in the Eastern Black Sea. *Fresenius Environmental Bulletin*. 12: 695-699.
- Topcuoğlu, S., Guven, K.C., Okus, E., Esen, N., Gungor, N., Eğilli, E., Kut, D., Doğan, E. & Unlu, S. (1998) Metal contents of algae and Sediments of Turkish coasts in the Black Sea In: The Proceedings of the First International Symposium on Fisheries and Ecology, Trabzon, Turkey, 437-439.
- Turekian, K.K. (1971) Rivers, tributaries, and estuaries. In: D.W. Hood (Ed.), *Impingement of man on the oceans*. Wiley-Interscience, New York. pp. 9-73.
- Turekian, K.K. & Wedepohl, K.H. (1961) Distribution of elements in some major units of the earth's crust. *The Geological Society America*. 72: 175-192.
- Ünsal, M. (2001) Lead pollution and its sources along the Turkish coast of the Black Sea. *Mediterranean Marine Science*. 2: 33-44.
- Ünsal, M. Bekiroğlu, Y. Beşiktepe (Akdoğan), Ş. Kayıkçı, Y. Alemdağ, Y. Aktaş, M. & Yıldırım, C. (1995) Determination of the land-based sources of heavy pollution in the middle and eastern Black Sea Coast. *Tarım ve Köyişleri Bakanlığı Trabzon Su Ürünleri Araştırma Enstitüsü*. Project No: DEBAG-121/G; pp: 59 (in Turkish).
- Ünsal, M. Çağatay, N. Bekiroğlu, Y. Kıratlı, N. Alemdağ, Y. Aktaş, M. & Sarı, E. (1998) Heavy metal pollution in the Black Sea. *Tarım ve Köyişleri Bakanlığı Trabzon Su Ürünleri Araştırma Enstitüsü*. Project No: YDABCAG-456/G-457/G; pp: 51 (in Turkish).
- Uslu, I. & Gökmeşe, F. (2009) Mercury pollution coming from coal-fired power plants. *TÜBAV Biim. Dergisi*. 2: 10-13 (in Turkish).
- Wardas, M. Budek L. & Rybicka E.H. (1996) Variability of heavy metals content in bottom sediments of the Wilga River, a tributary of the Vistula River (Krokaw area, Poland). *Applied Geochemistry*. 11: 197-202.
- Yiğiterhan, O. & Murray, J.W. (2008) Trace metal composition of particulate matter of the Danube River and Turkish rivers draining into the Black Sea. *Marine Chemistry*. 111: 63-76.
- Young, D.R. Alexander, G.V. & McDermott-Ehrlich, D. (1979) Vessel-related contamination of Southern California Harbours by copper and other metals. *Marine Pollution Bulletin*. 10: 50-56.
- Yücesoy, F. & Ergin, M. (1992) Heavy-metal geochemistry of surface sediments the southern Black Sea shelf and upper slope. *Chemical Geology*. 99: 265-287.

## وضعیت آلودگی فلزات کمیاب در ساحل سینوپ دریای سیاه، ترکیه

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### چکیده

غلظت‌های بعضی از فلزات سنگین در رسوب سواحل Sinop دریای سیاه اندازه‌گیری شد تا آلودگی به فلزات در سال ۲۰۱۳ پایش شود. انتشار فلزات سنگین در رسوبات دریای سیاه، الگوی متغیری را نشان می‌دهد. هدف مطالعه حاضر، تعیین انتشار فلزات سنگین چون مس، سرب، روی، نیکل، منگنز، آهن، آرسنیک، کادمیم، کرم، جیوه و کبالت در رسوب سواحل Sinop دریای سیاه بود. کیفیت رسوب در دریای سیاه، سطوح آلودگی فلزات با استفاده از تکنیک فاکتور غنی سازی (EF) مورد ارزیابی قرار گرفت. پایین‌ترین مقادیر EF بین صفر تا ۵ در مس، آهن، روی، نیکل، کادمیم، سرب و کبالت بود. این مقادیر تفاوت معنی‌داری با هم نداشتند. غلظت‌های آرسنیک، کرم و جیوه اندازه‌گیری شده، غنی‌سازی به نسبت بالاتری از فلزات دیگر داشتند. نتایج نشان داد که آلودگی رسوبات سطحی در سواحل Sinop به طور غالب شاخص آرسنیک ( $10/2-7/4 \text{ mg.kg}^{-1}$ )، کرم ( $67-374 \text{ mg.kg}^{-1}$ ) و جیوه ( $0/07-0/03 \text{ mg.kg}^{-1}$ ) و تا حداکثر مس ( $5/09 \text{ mg.kg}^{-1}$ ) آهن ( $7/24$ )، آهن ( $1/76-1/12\%$ )، روی ( $19/3-13/8 \text{ mg.kg}^{-1}$ )، نیکل ( $16/2-12/5 \text{ mg.kg}^{-1}$ )، کادمیم ( $0/06-0/04 \text{ mg.kg}^{-1}$ )، سرب ( $7/12-6/32 \text{ mg.kg}^{-1}$ )، منگنز ( $470-227 \text{ mg.kg}^{-1}$ ) و کبالت ( $9/5-5/9 \text{ mg.kg}^{-1}$ ) هستند. هم چنین، نیاز به تعیین سن اهمیت زیادی در ارزیابی وسعت مشارکت انسانی در ایجاد آلودگی دارد.

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