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REVIEW

A Review of Heavy Metals in Water, Sediment and Living Organisms in the Black Sea

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Abstract

Black Sea waters remain heavily impacted by a number of pollutants originating from different sources such as 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. In this review, heavy metal pollution in water column and sediment, with regard to aquatic organisms living in the Black Sea has been evaluated.

Keywords: heavy metal pollution, heavy metal accumulation, Black Sea ecosystem.

Karadeniz'de Su, Sediment ve Canlı Organizmalardaki Ağır Metal Düzeyleri

Özet

Karadeniz, farklı kaynaklardan gelen, doğrudan ve dolaylı deşarj edilen kirleticiler tarafından oldukca fazla etkilenmektedir. Çok sayıda ülkenin sanayi ve evsel nitelikli atıksuların boşaltılması sonucu Karadeniz’de ekotoksikolojik etkiler oluşmaktaktadır. Ağır metaller, toksik maddeler olup besin zincirinde artan konsantrasyonda birikmektedir. Bu derlemede, Karadeniz’de su kolonunda, sedimentte ve canlı organizmalarda ağır metal düzeyleri incelenmiştir.

Anahtar Kelimeler: Ağır metal kirliliği, ağır metal birikimi, Karadeniz ekosistemi.

Introduction

The pollution of the marine ecosystem by heavy metals is a world-wide 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. Because of settlements, the coastal industries appear to discharge wastes directly into the sea with little or no treatment. The countries of the Black Sea basin do their efforts to protect the nature of the sea. They formulated international rules for the cleaning of water areas from oil and waste and scientifically justified regulations of fishery.

Toxicokinetics of heavy metals in the marine environment has been a major concern since they constitute a potential risk to a number of flora and fauna species, including humans, through food chains. Furthermore, there is increasing evidence that presence of heavy metals is linked to the exacerbation of some microbial diseases in aquatic organisms. At sufficiently high concentrations, heavy metals appear to be toxic to the organism and so it is important to know by how much their concentration may be increased above the normal range in the environment before the effects on marine organisms.

Heavy metals are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to human. They include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them show significant affinity to sulfur and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Cadmium, copper, lead and mercury ions bind to the cell membranes hindering transport processes through the cell wall. Some of the metalloids, elements on the borderline between metals and nonmetals are significant water pollutants (Manahan, 1999).

This manuscript reviews available studies on the heavy metal pollution of the Black Sea. The review summarizes the heavy metal levels in water, sediment and organisms in the Black Sea.

Pollutants in the Black Sea Environment

The Black Sea is a semi-enclosed sea and, located between 40º27'N-46º32'N latitude and 27º27'E- 41º42'E longitude. The Black Sea, together with Azov Sea covers an area of 462,000 km^2, its dimension from east to west is 1150 km and from north to south is 610 km (Grasshoff, 1975). In the main basin of the Black Sea, the depth of water approaches to 2,200 m. The Black Sea is surrounded by six countries and communicates with the Mediterranean Sea to the south and the Azov Sea to the north (Topping and Mee, 1998).

The Black Sea receives considerable quantities of freshwater each year from a number of rivers. Since the sea receives more freshwater than it looses by evaporation, the salinity of the waters is quite low (Topping and Mee, 1998). Because of water budget surplus, there is a surface outflow from the Black Sea to the Aegean Sea of 650 km^3/year of water (Oğuz *et al*., 1995).

However, the Black Sea suffers from serious environmental problems. The shallow, mixed surface waters of the sea receive river discharges which are heavily loaded with nutrients containing nitrogen and phosphorus and contaminated with industrial and mining wastes. In addition, coastal industries appear to discharge wastes directly into the sea with little or no treatment. Thus the water quality of the life-supporting surface layer has seriously deteriorated (Fabry *et al*., 1993).

Concentrations of pollutants measured in rivers and domestic and industrial discharges provided useful information on the sources that have the potential to create local pollution problems along the Black Sea coast (Tuncer *et al*., 1998). The shallow, biologically productive layer of the Black Sea thus receives water from a waste drainage basin of 17 countries (Bakan and Büyükgüngör, 2000). Pollutants transported by the river constitute the main source of pollution in the Black Sea. According to the estimation of land based sources made by Zaitsev (1992), the Black Sea receives 575,000 tons of mineral nitrogen, 55,000 tons of mineral phosphorus, 30,000 tons of organic phosphorus, 90,000 tons of iron, 206,000 tons of oil and oil products, 48,000 tons of detergents, 12,000 tons of zinc, 45,000 tons of lead, 80 ton of mercury, 2,800 tons of copper, 1,700 tons of arsenic, 1,500 tons of chromium and 2,200 tons of phenol (Polikarpov *et al*., 1994). The annual inputs of Biological Oxygen Demand, total suspended solids, total nitrogen and total phosphorus were high and amounted 1,140,757, 56,603,706, 640,244 and 47,110 tons, respectively (Topping *et al*., 1998).

Heavy Metal Levels in the Black Sea Water Column

Heavy metal pollution in the marine environment is determined by measuring its concentration in water, sediment and living organisms. There is no evidence of significant heavy metal pollution in the Black Sea and further studies are still required (Tuncer *et al*., 1998). Tankere *et al*. (2001) determined the trace metal levels in shelf waters of the northwestern Black Sea. They found out that in the oxic layer of deep station, the suspended particulate fractions of Mn and Fe were a major part of the total metal mass. Dissolved and total particulate concentrations were found 0.038–0.527 µg/L and 0.066–1.593 µg/L for Mn, 0.044–0.184 µg/L and 0.128–0.413 µg/L for Fe, 0.064–0.508 µg/L for dissolved Cu and 0.470–0.704 µg/L for dissolved Ni. Their concentrations did not show any depletion in surface oxic waters, possibly as a result of strong organic complexity. Dissolved Pb concentrations (0.021–0.042 µg/L) were higher than those generally found in the shelf waters. Yemencioglu *et al*. (2006) measured dissolved forms of the redox-sensitive elements manganese and iron (Fe^{+2} and Fe^{+3}) in the oxic/anoxic transition zone, or suboxic zone, of the Black Sea. The maximum dissolved iron (Fe^{+2}) concentrations (16,754 µg/L) were found typically in an order of magnitude smaller than those of dissolved manganese (439,504 µg/L). Lewis and Landing (1992) reported similar values of 11,169–16,754 µg/L for dissolved iron and 439,504–494,442 µg/L for dissolved manganese. In a study related to distribution of mercury compounds in the western Black Sea, total Hg ranged from 0.321×10^{-3} to 2.086×10^{-3} µg/L at the coastal site and from 0.461×10^{-3} to 2.367×10^{-3} µg/L at the gyre site (Lamborg *et al*., 2007).

Altaş and Büyügüngör (2006) investigated the impact of marine activities on heavy metal pollution. Shore and offshore samples of various stations through the Sinop, Samsun and Ordu cities located in the middle Black Sea region between May 2000 and October 2001 were taken. They found that Cd^{+2} and Cu^{+2} levels, generally, and Pb^{+2} and Zn^{+2} levels sometimes, exceeded the levels of Marine General Quality Criteria given in Turkish Water Pollution Control Regulation (2004). In this study it was carried out that heavy metal levels at most sampling points generally fitted the quality criteria. However, determined heavy metal concentration over the criterion especially at some offshore stations shows that the Black Sea is polluted from marine activities.

Heavy metal levels were measured in seawater of the western Black Sea (Zonguldak) shore of Turkey. Maximum concentrations of metals dissolved in seawater were found 1,686 µg/L for Cd, 5,824 µg/L for Cr, 39,281 µg/L for Mn, 7,753 µg/L for Cu, 8,334 µg/L for Ni, 8,081 µg/L for Pb and 54,535 µg/L for Zn. When heavy metal concentrations recorded at Zonguldak are compared with the US EPA limitations, and metal concentrations at the other localities and seawater, the site seems to be more polluted than the other Black Sea shores, but the level of contamination is similar to those found in Rize and Hopa waters. According to recommendations of US EPA under the priority toxic pollutants list, Cd, Cu, Ni, Pb and Zn levels are above the limits in Zonguldak seawater (Coban *et al*., 2009). Balkıs and co-workers (2007a) investigated the effects of the terrestrial inputs originated from natural and industrial sources on the heavy metal distribution along the shore of the Black Sea from Igneada to Hopa. Overall, dissolved and adsorbed suspended trace metal content of the water body was investigated in September 2004 and in April 2005. They found that along the shelf, the amount of dissolved Fe, Mn, Pb, Cd, Hg and Cu and the suspended Fe, Mn, Pb, Cd and Cu matters were above the average values recorded in the shelf waters.

Heavy Metal Levels in Living Organism from the Black Sea

The heavy metal levels in various types of living organism from the Black Sea have been investigated by several researchers (Topçuoğlu *et al*., 2002; Tüzen, 2009; Mendil *et al*., 2010). Some results for heavy metal levels in living organism from the Black Sea investigated by several researchers are summarized in Tables 1 through 6.

According to Turkish Food Codex (2002), the maximum levels of the metals for human consumption may not exceed for As 1 mg/kg fish, for Hg 0.5 and/or 1.0 mg/kg fish, for Zn 50 mg/kg fish, for Cd 0.05 and/or 0.1 mg/kg fish, for Pb 0.2-0.4 mg/kg fish. In the Turkish Food Codex published in 2008, the maximum allowable Pb value was changed to 0.3 mg/kg fish. In the codex, allowable limits for some metals are different in different fish species, i.e., Cd level for *Xiphias gladius* is the 0.3 mg/kg fish while it is 0.1 mg/kg fish *Engraulis* sp.

Measured heavy metal values in some fish species were found to be lower than the maximum permissible levels, but lead level was found to be higher (Nisbet *et al*., 2010). Mendil *et al*. (2010) determined that the lead and cadmium levels were higher than recommended legal limits in Atlantic bonito, red mullet, Atlantic horse mackerel and whiting (Table 2, 3). In the other study, the metal levels in ten different fish species caught from the Black Sea were investigated and it was found out that lead and cadmium levels were higher than the legal limit for human consumption (Tüzen, 2009). Similar results have been found in a study carried out by Uluozlu *et al*. (2007). Tüzen (2003) found that the concentrations of heavy metals in fish samples from the middle Black Sea were below the limits listed in the Public Health Regulation in Turkey (1995). The distribution of some heavy metals in the muscle tissue of *Merlangius merlangus* (whiting), *Mullus barbatus*

Table 1. Mercury levels (µg/g) in living organism from the Black Sea. According to Turkish Food Codex (2008) maximum allowable mercury level in fish meat ranges between 0.5 mg/kg and 1.0 mg/kg

Species	References		
	Nisbet *et al*. (2010)	Tüzen (2009)	Vivien-Harmelin (2009)
Anchovy (*E. encrasicholus*)	ND	0.055	-
Whiting (*M. merlangus*)	ND	0.084	-
Atlantic horse mackerel (*T. trachurus*)	ND	0.078	-
Atlantic bonito (*S. sarda*)	ND	0.025	-
Red mullet (*M. barbatus*)	ND	0.084	0.16*
Flathead mullet (*M. cephalus*)	-	0.070	-
Turbot (*P. maxima*)	ND	0.045	-
Bluefish (*P. saltor*)	ND	0.062	-

Table 2. Lead levels (µg/g) in living organism from the Black Sea. According to Turkish Food Codex (2008) maximum allowable lead level in fish meat is 0.3 mg/kg

Species	References					
	Nisbet *et al*. (2010)	Durali *et al*. (2010)	Tüzen (2009)	Turan *et al*. (2009)	Uluozlu *et al*. (2007)	Tüzen (2003)
Anchovy (*E. encrasicholus*)	0.70*	-	0.30	0.329	0.33	0.39
Whiting (*M. merlangus*)	0.58*	0.46	0.53	0.502	0.93	-
A. horse mackerel (*T. trachurus*)	0.60*	0.64	0.82	-	0.68	0.83
Atlantic bonito (*S. sarda*)	0.90*	0.28	0.61	-	0.76	0.26
Red mullet(*M. barbatus*)	0.92*	0.40	0.36	0.727	0.84	-
Flathead mullet (*M. cephalus*)	-	-	0.68	-	0.61	-
Turbot (*P. maxima*)	0.73*	-	0.28	-	-	-
Bluefish (*P. saltor*)	1.26*	-	0.87	-	0.38	-

*based on dry weight

Table 3. Cadmium levels (µg/g) in living organism from the Black Sea. According to Turkish Food Codex (2008) maximum allowable cadmium level in fish meat ranges between 0.05 mg/kg and 0.10 mg/kg

Species	References					
	Nisbet *et al.* (2010)	Durali *et al.* (2010)	Tüzen (2009)	Turan *et al.* (2009)	Uluozlu *et al.* (2007)	Tüzen (2003)
Anchovy (*E. encrasicholus*)	0.035*	-	0.27	0.124	0.65	0.18
Whiting (*M. merlangus*)	0.002*	0.18	0.21	0.192	0.55	-
A. horse mackerel (*T. trachurus*)	0.012*	0.22	0.32	-	0.50	0.48
Atlantic bonito (*S. sarda*)	0.025*	0.35	0.13	-	0.90	0.10
Red mullet (*M.barbatus*)	0.020*	0.23	0.17	0.208	0.45	-
Flathead mullet (*M. cephalus*)	-	-	0.35	-	0.45	-
Turbot (*P. maxima*)	0.022*	-	0.10	-	-	-
Bluefish (*P. saltor*)	0.025*	-	0.23	-	0.60	-

*based on dry weight

Table 4. Zinc levels (µg/g) in living organism from the Black Sea. According to Turkish Food Codex (2002) maximum allowable zinc level in fish meat is 50 mg/kg

Species	References					
	Nisbet *et al.* (2010)	Durali *et al.* (2010)	Tüzen (2009)	Turan *et al.* (2009)	Uluozlu *et al.* (2007)	Tüzen (2003)
European anchovy (*E. encrasicholus*)	26.25*	-	38.8	25.416	40.2	18.85
Whiting (*M. merlangus*)	31.34*	27.7	65.4	6.029	48.6	
A. horse mackerel (*T. trachurus*)	27.70*	25.7	52.7	-	37.4	11.41
Atlantic bonito (*S. sarda*)	19.55*	21.0	64.9	-	48.7	13.72
Red mullet (*M. barbatus*)	23.71*	17.8	75.5	7.573	106.0	-
Flathead mullet (*M. cephalus*)	-	-	86.2	-	40.2	-
Turbot (*P. maxima*)	24.83*	-	45.2	-	-	-
Bluefish (*P. saltor*)	25.51*	-	93.4	-	35.4	-

*based on dry weight

Table 5. Copper levels (µg/g) in living organism from the Black Sea. According to Turkish Food Codex (2002) maximum allowable copper level in fish meat is 20 mg/kg

Species	References				
	Nisbet *et al.* (2010)	Durali *et al.* (2010)	Tüzen (2009)	Uluozlu *et al.* (2007)	Tüzen (2003)
Anchovy (*E. encrasicholus*)	2.73*	-	1.96	0.95	1.96
Whiting (*M. merlangus*)	3.72*	1.8	1.32	1.25	-
A. horse mackerel (*T. trachurus*)	1.79*	2.4	0.65	0.95	1.55
Atlantic bonito (*S. sarda*)	1.74*	1.9	1.43	0.84	1.29
Red mullet (*M. barbatus*)	3.14*	1.4	0.96	0.98	-
Flathead mullet (*M. cephalus*)	-	-	2.14	1.26	-
Turbot (*P. maxima*)	2.13*	-	0.75	-	
Bluefish (*P. saltor*)	2.86*	-	2.78	1.83	

*based on dry weight

(red mullet), *Engraulis encrasicholus* (anchovy) from Black Sea and Mediterranean Sea was studied by Turan *et al*. (2009). They suggested that this may reflect a considerable pollution of the Mediterranean and Black Seas. The authors proposed the polluted areas to be taken into consideration in order to protect the biodiversity and human health in this ecosystem.

Topçuoğlu *et al*. (2003a) investigated the metal concentration in macroalgae samples from 1998 to 2000 collected from the Turkish coast of the Black Sea. According to the findings of this study, the heavy metal pollution decreased in Turkish coast of the Black Sea during the years investigated (Table 6). In another study, it was determined that the Turkish Black Sea coast faced heavy metal pollution and the metal concentrations in macroalgae, sea snail and mussel were very high (Topçuoğlu *et al*., 2002). In a study of Romeo *et al*. (2005), accumulated trace metal concentrations have been measured in the mussel collected in the Black Sea. The authors found that Cd, Cu, Zn, Hg, Fe, Mn concentration changed between 0.96-1.74 µg/g, 6.64-8.05 µg/g, 108-190 µg/g, 26-33 ng/g, 95-106 µg/g and 14.5-24.5 µg/g mussel, respectively.

Tüzen *et al*. (2009) measured the trace element concentration in different marine algae (*Antithamnion*

Table 6. Heavy metal levels (µg/g dry wt) in some living organism from the Black Sea

Species	Metals								References
	Cd	Co	Cr	Zn	Mn	Fe	Pb	Cu	
Mussel	<0.02-6.44	<0.05-5.36	<0.06-7.58	78.12-512.5	5.66-22.8	151-598	<0.05-2.60	7.21-11.52	Topçuoğlu *et al.* (2002)
Sea snail (soft part)	2.01-41.13	<0.05-0.7	<0.06-1.45	73.3-255.9	3.90-10.01	87-550	<0.5	36.19-72.20	
**Ulva lactuca* 1998/1999	<0.02/<0.02	<0.05/<0.05	<0.06/<0.06	21.2/9.6	45.1/21.8	778/550	<0.1/<0.1	13.8/3.87	Topçuoğlu *et al.* (2003)
* *Cystoseira barbata* 1998/1999	<0.02/<0.02	<0.05/<0.05	<0.06/<0.06	35.1/13.9	32.1/6.7	427/130	<0.1/<0.1	5.7/2.2	
* *Pterocladiella capillacea* 1998/1999	1.53/1.36	<0.05/<0.05	<0.06/<0.06	119.8/86.2	91.1/52.1	158/288	<0.1/<0.1	10.3/5.3	
***Ulva lactuca* 1998/1999	<0.2/<0.2	<0.05/<0.05	<0.06 <0.06	13.5/394.4	41.1/12.5	902/357	<0.1/<0.1	11.3/7.7	
** *Cystoseira barbata* 1998/1999	<002/<0.02	<0.05/<0.05	<0.06 <0.06	43.9/191.5	27.3-22.7	593/590	<0.1/<0.1	593-590	
***Pterocladiella capillacea* 1999	<0.02	<0.05	<0.06	176.8	10.8	407	<0.1	<0.03	
Cystoseira crinita	0.22-1.87	-	-	-	9-60	510-510	0.4-6.3	0.3-6.0	Strezov and Nonova (2003)
Cystoseira barbata	0.10-1.25	-	-	-	9-54	111-567	0.7-2.4	0.6-9.0	
Mussel	<0.02	-	7.65-11.3	312.2-396.5	46.9-73.05	-	<0.05-108.6	11.75-23.25	Bakan and Böke-Özkoç (2008)
Different marine alga species	0.5-23.6^	1.56-42.6^	0.5-11.6	3.64-64.8	9.98-285	99-3949	1.54-3969^	1.70-17.1	Tüzen *et al.* (2009)

*West Black Sea
** East Black Sea
^ µg/kg

cruciatum and *Phyllophora nervosa*) collected from the central and eastern Black Sea. They found that the highest trace element concentration was determined for iron and the lowest for cadmium (Table 6). The authors suggested that the marine algae samples should be analyzed more often in Turkey with respect to toxic elements. Edible marine algae samples could be used as a food supplement to help meet the recommended daily intakes of some mineral and trace elements.

Zinc, copper, cadmium, lead and cobalt concentrations in demersal fishes (*Mullus barbatus*, *Merlangius merlangius euxinus*, *Spicara smaris*, *Raja clavata*), Mediterranean mussel *Mytilus galloprovincialis* and sea snail *Rapana venosa* from the Sinop coasts of the Black Sea have been measured (Turk-Culha *et al*., 2007). Significant differences were found in metal concentrations between the species. Similar significant differences observed with regard to different metals. The concentrations of Pb, Cd and Co were determined under detection limit for the species. The other metal levels in the Mediterranean mussel and the sea snail were significantly higher than those in fishes.

From 1996 to 2002; Fe, Mn, Cu, Pb and Cd distribution in six green macroalgae species from the Bulgarian Black Sea coast were determined by Strezov and Nonova (2005a). Average heavy metal concentrations were for all algae 650 µg/g for Fe, 184 µg /g for Mn, 5.6 µg/g for Cu, 3.3 µg/g for Pb and 1.1 µg/g for Cd. They suggested that heavy metal contents in different species demonstrate various degree of metal accumulation and the obtained higher values in the northern part of the studied zone can be attributed to the discharge influence of the big rivers entering the Black Sea, such as Danube, Dnieper, Dniester, and local pollutant emissions, as well. The data of Strezov and Nonova show also that there is no serious contamination in green macroalgae with heavy and toxic metals along the whole Bulgarian Black Sea coast.

Environmental metal contamination in the Black Sea alga species (green and red) was studied from 1992 to 2003, using radionuclide approach (Strezov and Nonova, 2005b). They found that radionuclide and metal concentrations depend on the macrophyte and all data show the lack of serious pollution along the Bulgarian Black Sea coast.

Heavy Metal Levels in Sediment from the Black Sea

The distribution of the recent bottom sediments in the Black Sea 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. Sediment formation is also influenced by the solid riverine runoff and coastal abrasion, slope-derived supply, and biogenic and chemogenic matter (Ignatov, 2008).

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, 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. Heavy metal levels in sediment from the Black Sea were investigated by many researchers (Ergül *et al*., 2008; Topçuoğlu *et al*., 2002; Topçuoğlu *et al*., 2004). Results of their studies are summarized in Table 7.

Heavy metal levels in sediment were determined for the rivers of Sakarya, Kızılırmak and Yeşilırmak in the Black Sea (Balkıs *et al*., 2007b). The highest amount of Co, Cr, Zn, Fe and Mn were found outside of the Yeşilırmak and Sakarya River mouth. However, lower concentrations of all the metals were observed at the zone outside Kızılırmak. The authors also indicated sources of metal pollution. They were: fertilizer plant and copper smelter located near Yeşilırmak River, iron and steel complex industry and thermal power plant in the eastern coastal site of the Sakarya River.

Ergül *et al*. (2008) demonstrated that heavy metal concentrations in sediment trap samples and resultant vertical fluxes in the eastern Black Sea coastal waters are variable, and are likely to be dependent upon seasonal changes within the water column as well as anthropogenic and geological inputs such as weathering and run-off from land-based sources. Furthermore, metal concentrations in both surface sediments and sinking particles also suggest that heavy metal concentration is generally enhanced in the eastern region along the Black Sea coast of Turkey. Topçuoğlu *et al*. (2002) investigated heavy metal levels in sediment sampled from different location of the Turkish Black Sea coast, and they found that sediments sampled from Rize and from Igneada are more polluted than those near Kilyos, Amasra, Sinop, and Perşembe.

Bulk heavy metal (Fe, Mn, Co, Cr, Ni, Cu, Zn and Pb) distributions and their chemical partitioning together with total organic carbon and carbonate data were studied in 0-2 cm oxic to anoxic surface sediments obtained at 18 stations throughout the Black Sea by Kıratlı and Ergin (1996). High Cr and Ni contents in the sediments are interpreted to reflect, in part, the weathering of basic-ultrabasic rocks on the Turkish mainland. Maximum carbonate-free levels of Mn (4,347 mg/kg), Ni (355 mg/kg) and Co (64 mg/kg) obtained for sediment from the shallow-water station (102 m) probably result from redox cycling at the so-called 'Mn pump zone' where scavenging-precipitation processes of Mn prevail. Chemical partitioning of the heavy metals revealed that Cu, Cr and Fe seem to be significantly bound to the detrital phases whereas carbonate phases tend to hold considerable amounts of Mn and Pb.

In another study carried out by Coban *et al*. (2009), heavy metals in sediment were found at significant levels of 0.47 µg/g for Cd, 67.95 µg/g for Cr, 30.21 µg/g for Cu, 274.4 µg/g for Mn, 37.03 for µg/g Ni, 39.14 µg/g for Pb and 84.6 µg/g for Zn, that were comparable with those found in the estuarine areas of other countries in the region.

Topçuoğlu *et al*. (2003b) determined the radionuclides ^{137}Cs, ^{238}U, ^{232}Th and ^{40}K and Cd, Pb, Cu, Zn and Mn in sediment samples collected from two stations at the eastern Turkish coast of the Black Sea. The result from this study showed that radionuclide concentrations in the sediment fraction were significantly higher because of the influence of the collection sites. At the same time, Pb, Cu, Zn and Mn concentrations in Rize sediment were also higher than in Pazar sediment of similar grain size. In general, the heavy metal concentrations in that study were not higher than those previously observed. However, Pb and Cu levels increased in sediment in the Turkish area of the Black Sea during the years investigated.

In conclusion, heavy metal pollution in the Black Sea has attracted considerable research attention since last 20 years. Sources of heavy metals

Table 7. Heavy metal levels (µg/g dry wt) in surface sediment from the Black Sea

Metals	References				
	Ergül *et al*. (2008)	Balkıs (2007)	Topçuoğlu *et al*. (2004)	Topçuoğlu *et al*. (2002)	Yücesoy and Ergin (1992)
Cd	<0.02	<0.02	<0.02	<0.02-0.93	-
Cu	52.03-56.86	23.0-59.9	47-111	69.9-95.5	15-119
Cr	70.02-74.24	231.9-2496.8	39-245	21.8-38.9	13-238
Co	22.60-23.90	22.7-79.2	22.5-86.2	16.8-36.4	0-22
Ni	23.61-26.53	104.6-128.1	36.5-79.2	18.5-37.3	11-22
Zn	169-182	91.4-456.6	68-148	82.9-267.4	24-141
Fe		4.7-48.1	4.2-29.6	4.4-5.4	0.2-5.3
Mn	651.9-672.8	989-3696	907-2830	314.1-870.3	112-1109
Pb	<0.1	<0.01	<0.1-52.9	<0.05-31.1	12-69
As	12.60-13.10	-	-	-	-

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. During the last 20 years, in some areas of Black Sea, metal concentrations in sea water exceeded the levels of Marine General Quality Criteria given in Turkish Water Pollution Control Regulation. Especially, lead and cadmium levels were found higher in fish species than the legal limit for human consumption. Additionally, high levels of heavy metals have been reported by the authors in algae and sediments from certain regions of the Black Sea, suggesting that heavy metal pollution in the Black Sea is remarkable.

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