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RESEARCH ARTICLE

Metal levels in biota from the Southern Black Sea, Turkey

Nuray Balkis[1*], Abdullah Aksu[1], Hakan Hiçsönmez[2]

[1]Department of Chemical Oceanography, Institute of Marine Science and Management, Istanbul University, 34134-00, Vefa Istanbul, TURKEY
[2]Istanbul Province National Education Directorate, TURKEY

***Corresponding author:** nbal@istanbul.edu.tr

Abstract

In this study, toxic metal (Pb, Cd, Hg and As) bioaccumulations in mussel (*Mytilus galloprovincialis*), fish (*Merlangius merlangus euxinus*) and whelk (*Rapana venosa)* were researched along the Southern Black Sea Shelf in 2009. Generally, Pb and Cd contents were higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1 $\mu g\ g^{-1}$ wet wt and 0.1 $\mu g\ g^{-1}$ wet wt, respectively) and European countries (2.0 $\mu g\ g^{-1}$, UNEP, 1985). They showed increases towards the eastern end of the shelf. As concentrations were also observed higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1.0 $\mu g\ g^{-1}$ wet wt) at Terkos, Samsun and Ordu. In contrast, Hg levels were found lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 $\mu g\ g^{-1}$ wet wt) along the shelf.

Keywords: Black Sea, metal, mussel, fish, whelk

Introduction

The Black Sea is an inland marine basin located north of Turkey. Of all the inland seas, such as the Baltic Sea or the Mediterranean, it is the most isolated from the oceans. It is connected to the Mediterrenean via the Istanbul Strait (Bosphorus), the Marmara Sea and the Çanakkale Strait (Dardanelles). The Black Sea, with a surface area of 423,000 km^2, is approximately one-fifth of the surface area of the Mediterranean. It has a total volume of 547,000 km^3 and a maximum depth of around 2200 m.

The Northwestern Shelf (NWS), occupying ~20% of the total area, is the only major shelf region with discharges from three of Europe's largest rivers: the Danube, Dnieper and Dniester (Oğuz *et al.* 2004). The Black Sea has always been a basin with a positive water balance. According to the data presented by

Unluata *et al.* (1989) (see also Ozsoy and Unluata 1997), the sum of fluxes due to precipitation (~300 km^3 yr^{-1}) and runoff (~350 km^3 yr^{-1}) exceeds that of evaporation (~350 km^3 yr^{-1}). The freshwater excess of 300 km^3 yr^{-1} is balanced by the net outflow through the Istanbul Strait, defined as the difference between the transports of its two layers. The Danube River alone brings about 200 km^3 yr^{-1} water discharge, which corresponds to ¾ of the north-western river runoff and 2/3 of the total riverine input (370 km^3 yr^{-1}) into the basin. Turkish rivers (0,275 x 10^3 tons yr^{-1}) account for 1/3 of the Danube (0,913 x 10^3 tons yr^{-1}) and all other rivers on the northern part of the Black Sea (0,977 x 10^3 tons yr^{-1}) (Baştürk *et al.* 1999). Approximately 19 million people live in the coastal zone of the Black Sea. The population is the densest on the Turkish and Ukrainian coasts.

In recent years, aquatic ecosystems have been contaminated by heavy metals; which are of agricultural, industrial, domestic, mining and also natural origins (Ayas and Kolankaya 1996; Han *et al.* 2002). They are potentially toxic to the aquatic environment; if they exceed natural limits, they will be harmful to the aquatic organisms' environments and human health (Förstner and Witmann 1981). Organisms need some metals such as Fe, Cu, Zn, Co, Se, Ni and Mn in certain amounts; however, exceeding these amounts may cause toxic effects for these organisms. Some metals such as Hg, Cr, Pb and Cd are toxic to organisms and marine habitats. These metals are dissolved in sea water or suspended in solid materials and absorbed through the gills or skin of marine organisms; they also accumulate in the bodies of organisms through the food chain (Förstner and Witmann 1981). Mussels, in particular, have been used as biological indicator organisms to monitor marine pollution by toxic heavy metals and potentially toxic chemicals due to their properties of inhabitation (Pempcowiac *et al.* 1999; Hu 2000).

In this study, the metal bioaccumulations in mussel (*Mytilus galloprovincialis*), fish (*Merlangius merlangus euxinus*) and whelk (*Rapana venosa*) have been investigated via one year monitoring program from İğneada to Hopa during 2009. Furthermore, this paper presents the first results of arsenic content in all biaota samples along the Southern Black Sea Shelf. Additionaly, whelks are an important food item in our export. Moreover, Turkey is a member of the "Commission on the Protection of the Black Sea Against Pollution". Thus, these results form a base for future studies.

Materials and Methods

The samples of mussel (*Mytilus galloprovincialis*), fish (*Merlangius merlangus euxinus*) and whelk (*Rapana venosa*) were collected from hot points (harbours and river mouths) in 2009 (Figure 1, Table 1).

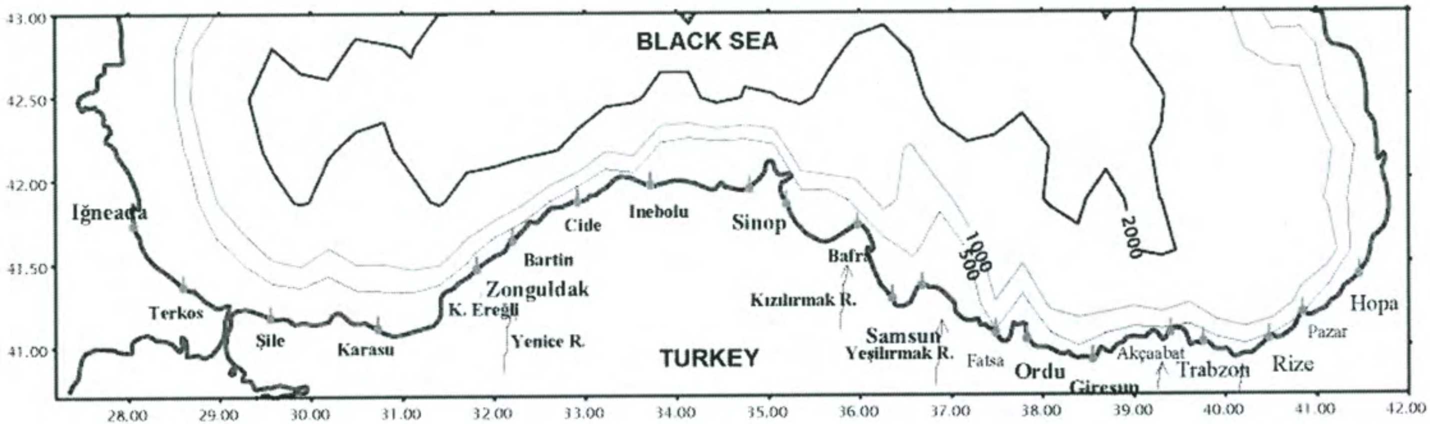

Figure 1. The location of sampling stations along the Southern Black Sea Shelf.

After collection, the samples were placed in polyethylene bags and stored below -20 °C pending analysis (UNEP 1991). For total metal analysis, approximately 10-12 specimens of mussels (the length vary between 10 and 15 cm), fish and whelk taken from each station were dissected according to UNEP (1984). The fillets were homogenized in a blender and approximately 5-7 g of homogenate biota samples were digested with 5:3 HNO_3:H_2SO_4 in microwave digestion system and then diluted to the desired volume with 1 N HNO_3 (UNEP 1984; 1982; 1985). All analyses were performed using an atomic absorption spectrophotometer (SHIMADZU 6701). The total mercury concentration was measured using a cold vapor technique and hydride generator unit (HVG-1 hydride vapor generator). As concentrations were measured using a flame-hydride generator unit (HVG-1 hydride vapor generator). Cd and Pb levels were also determined with a flame furnace; background corrections were used as required. The detection limits for trace metals were Hg: 0.05 and As: 1.0 µg l^{-1}, Cd:0.10 and Pb: 0.10 mg l^{-1}. The accuracy and precision of the analyses was checked by analyzing IAEA-MEL Reference Material IAEA436 and IAEA433 (Table 2). The analytical precision of the analysis was better than 10% at 95% significance level from five replicates.

Table 1. The GPS data of sampling locations in this study.

Station	Longitude	Latutide
Terkos	419.697.679.352	284.268.425.765
Sakarya	412.143.048.056	307.215.560.785
Zonguldak	415.183.334.583	317.997.952.693
Bafra	424.764.806.899	353.201.978.403
Samsun	413.248.601.112	364.076.530.392
Ordu	410.668.977.315	379.005.988.417
Rize	410.761.109.861	404.349.210.528

Table 2. Precision of the analysis from five replicate samples, and certified and measured contents of reference materials in this study.

Reference Material	Element	Precision (%)
IAEA436	Pb	2
IAEA436	Hg	2
IAEA436	Cd	2
IAEA433	As	2

Result and Discussion

Total metal (Pb, Cd, Hg and As) concentrations in mussel, fish and whelk from the Southern Black Sea Shelf were measured during 2009 and listed in Tables 3-5.

Mussel (Mytilus galloprovincialis)

Lead (Pb) concentrations varied between 11 µg $g^{-1}$and 20 µg g^{-1} (dry wt) (Table 3). Pb levels in the Southern Black Sea Shelf were found to be considerably higher than the critical limits set by the both Turkish Ministry of Environment for Aquatic Products (1 µg g^{-1} wet wt) and European countries (2.0 µg g^{-1}, UNEP 1985). The highest Pb levels were measured at Station Bafra, whilst the lowest values were determined at Station Samsun.

Cadmium (Cd) contents varied between 0.6 µg $g^{-1}$and 3.5 µg g^{-1} (dry wt) (Table 3). Cd levels were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.1 µg g^{-1} wet wt) in all the staions, similar to the previously mentioned Pb levels. While the highest Cd levels were measured at Stations Terkos and Ordu, the lowest Cd contents were observed at Station Zonguldak.

Mercury (Hg) concentrations varied between 0.07 µg $g^{-1}$and 0.13 µg g^{-1} (dry wt) (Table 3). Hg levels were found to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 µg g^{-1} wet wt) along the shelf.

Arsenic (As) contents ranged from 0.19 µg g^{-1} and 4.85 µg g^{-1} (dry wt) (Table 3). As levels were observed to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1.0 µg g^{-1} wet wt) at Stations Terkos, Samsun and Ordu. The lowest As value was measured as 0.19 µg g^{-1} (dry wt) at Station Rize.

Table 3. Metal contents of mussel (*Mytilus galloprovincialis*) in 2009 (µg g^{-1}).

Station	**Cd**	**Pb**	**As**	**Hg**
Terkos	**3.5**	**12**	**1.23**	0.04
Sakarya	**1.3**	**17**	0.86	0.07
Zonguldak	**0.6**	**13**	0.41	0.09
Samsun	**0.9**	**11**	**4.85**	0.13
Bafra	**1.4**	**20**	0.53	0.12
Ordu	**3.0**	**15**	**3.22**	0.13
Rize	2.4	**18**	0.19	0.07
Aquatic Product Directory	**0.1**	**1.0**	**1**	**0.5**

Fish (Merlangius merlangus euxinus)

Lead concentrations varied between 12 µg $g^{-1}$and 15 µg g^{-1} (dry wt) (Table 4). Pb levels in all the staions along the Southern Black Sea Shelf were found to be considerably higher than the critical limits set by the both the Turkish

Ministry of Environment for Aquatic Products (1 μg g^{-1} wet wt) and European countries (2.0 μg g^{-1}, UNEP 1985).

Cadmium contents ranged from 0.07 μg $g^{-1}$and 0.35 μg g^{-1} (dry wt) (Table 4). Cd levels were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.1 μg g^{-1} wet wt) except Station Bafra.

Mercury concentrations varied between <0.01 μg $g^{-1}$and 0.5 μg g^{-1} (dry wt) (Table 4). Hg levels were found to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 μg g^{-1} wet wt) except station Ordu along the shelf.

Arsenic contents ranged from 0.03 μg g^{-1} and 0.1 μg g^{-1} (dry wt) (Table 4). As levels were determined to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1.0 μg g^{-1} wet wt) along the shelf similar to Hg levels.

Table 4. Metal contents of fish (*Merlangius merlangus euxinus*) in 2009 (μg g^{-1}).

Station	Cd	Pb	As	Hg
Terkos	**0.35**	**15**	0.09	0.07
Sakarya	**0.24**	**12**	0.06	<0.01
Bafra	0.07	**15**	0.10	0.09
Ordu	**0.22**	**13**	0.03	**0.5**
Aquatic Product Directory	**0.1**	**1.0**	1	**0.5**

Whelk (Rapana venosa)

In this study, the whelk (*Rapana venosa*) were collected at stations Sakarya and Bafra, whilst they did not found other stations along the Southern Black Sea Shelf.

Lead concentrations varied between 12 μg $g^{-1}$and 32 μg g^{-1} (dry wt) (Table 5). Pb levels were found to be considerably higher than the critical limits set by the both the Turkish Ministry of Environment for Aquatic Products (1 μg g^{-1} wet wt) and European countries (2.0 μg g^{-1},UNEP 1985).

Cadmium contents ranged from 0.6 μg $g^{-1}$and 1.0 μg g^{-1} (dry wt) (Table 5). Cd levels were observed to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.1 μg g^{-1} wet wt) similar to Pb levels.

Mercury concentrations varied between <0.01 μg $g^{-1}$and 0.05 μg g^{-1} (dry wt) (Table 5). Hg levels were determined to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 μg g^{-1} wet wt) along the shelf.

Arsenic contents ranged from 0.45 μg g^{-1} and 0.62 μg g^{-1} (dry wt) (Table 5). As levels were found to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1.0 μg g^{-1} wet wt) similar to Hg levels.

Table 5. Metal contents of whelks (*Rapana venosa*) in 2009 (μg g^{-1}).

Station	Cd	Pb	As	Hg
Sakarya	**1.0**	**32**	0.62	<0.01
Bafra	**0.6**	**12**	0.45	0.05
Aquatic Product Directory	**0.1**	**1.0**	**1**	**0.5**

In this one year monitoring programme in 2009, metal contents in mussel, fish and whelk ranked as follows: Pb > Cd > As > Hg. The highest values were generally found at harbours and river mouths. Several domestic discharge stations exist at Zonguldak, Samsun, Ordu, Giresun, Trabzon and Rize. Besides, some industrial discharge stations such as iron and steel industry, thermal power plant, copper smelter and fertilizer plant also exist at Ereğli, Zonguldak and Samsun. For this reason, these results showed both the anthropogenic discharges (domestic + industrial) and terrestrial inputs from the mining zone in the rest of the shelf (Turkey mining Map, MTA; the scale of the map is 2,000,000) via rivers.

When our results were compared those of previous studies, it was clearly seen that Pb contamination levels in mussel, fish and whelk from the Southern Black Sea Shelf were higher than those of the Marmara Sea (Aksu *et al.* 2011). Furthermore, Hg, Cd and As levels were comparable to or slightly higher than those from the Marmara Sea (Aksu *et al.* 2011; Kayhan *et al.* 2006; Kayhan *et al.* 2007) and Eastern Aegean Sea (Küçüksezgin *et al.* 2001). Topçuoğlu *et al.* (2002, 2003) and Ergül *et al.* (2008) have also confirmed the heavy metal pollution in mussels, fish and surface sediments of the Middle and Eastern Black Sea Shelf.

Conclusion

Lead, cadmium and arsenic levels of mussel (*Mytilus galloprovincialis*) and lead and cadmium contents of fish (*Merlangius merlangus euxinus*) and whelk (*Rapana venosa*) from the Southern Black Sea Shelf were higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products in 2009. On the other hand, the highest metal values were generally found at Harbours Ereğli, Zonguldak, Samsun, Trabzon, Giresun, Ordu and Hopa and river mouths of the Sakarya, Yenice, Kozlu, Filyos, Kızılırmak and Yeşilırmak. They showed an increase towards the eastern end of the shelf.

The effects of the Danube River can be observed in metal distributions, especially in the Hg levels of the west and middle of the Southern Black Sea Shelf. The effect of deep discharges was seen at hot points Zonguldak, Samsun, Ordu, Giresun, Trabzon and Rize. Additionally, the anticyclone cycles significantly affect the vertical variations throughout the shelf. In this study, the results indicate the implications of the inputs from the mining zone on the rest of the shelf (Turkey mining Map, MTA; as the scale of the map 2.000.000) and the terrestrial anthropogenic (domestic + industrial) inputs via rivers.

In conclusion, consumption of the mussel, fish and whelk along the Southern Black Sea Shelf is rising rapidly, and the toxic effects, particularly of Pb, Cd and As may pose serious threats for human health.

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Güney Karadeniz Şelfi'nde biyotada metal seviyeleri

Özet

Bu çalışmada canlı organizmalarda toksik (Pb, Cd, Hg ve As) elementler analizi ile Güney Karadeniz Şelfi'nin kirlenme yükünün tespiti hedeflenmiştir. Bu amaçla 2009 yılında şelf boyunca sıcak noktalardan (limanlar ve nehir ağızları) ve Trol istasyonlarından midye, mezgit ve deniz salyangozu toplanmıştır. Tüm örneklerde toplam Pb, Cd, Hg ve As içerikleri incelenmiştir. Yapılan analizlerde Pb, Cd ve As içerikleri genel olarak şelf boyunca yüksek bulunmuştur. Ayrıca metal değerleri şelfin doğusuna doğru da artışlar göstermiştir. Sonuçlar şelfin gerisindeki maden yataklarından ve cevherleşme zonlarından yağmur ve nehirlerle olan taşınımları ve karasal kaynaklı antropojenik girdileri (evsel + endüstriyel) göstermektedir (Türkiye Maden Yatakları Haritası, MTA; ölçek: 1/ 2.000.000). Sonuç olarak, midye ve balık örneklerinde Pb ve Cd gibi toksik elementlerin kabul edilen değerlerin üzerinde olması insan sağlığı açısından önemli bir risk unsuru oluşturmaktadır.

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