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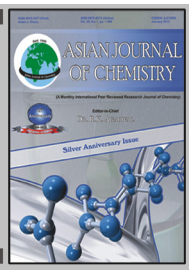

Pollution Monitoring Using *Mytilus galloprovincialis* and Fishes: A Case Study on the Southern Black Sea Shelf

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In this study, the heavy metal bioaccumulations in mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) have been studied along the Southern Black Sea Shelf. Generally, Pb and Cd contents were higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1 μg g^{-1} wet wt. and 0.1 μg g^{-1} wet wt., respectively) and European countries (2.0 μg g^{-1}, UNEP, 1985). They showed increases towards the eastern end of the shelf. As contents were observed 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 in 2009. In contrast, Hg levels were also higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 μg g^{-1} wet wt.) in 2005 and the highest Hg concentrations were found in the west and middle of the shelf.

Key Words: Black sea, Metal, Pollution, *Mytilus galloprovincialis*, Fish.

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 Bosphorus, the Marmara sea and the 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, occupying *ca.* 20 % of the total area, is the only major shelf region with discharges from three of Europe's largest rivers *i.e.*, Danube, Dnieper and Dniester[1]. Black Sea has always been a basin with a positive water balance. According to the data presented by Unluata[2] as well as by Ozsoy and Unluata[3], the sum of fluxes due to precipitation (*ca.* 300 km^3 per year) and runoff (*ca.* 350 km^3 per year) exceeds that of evapouration (*ca.* 350 km^3 per year). The freshwater excess of 300 km^3 per year is balanced by the net outflow through the bosphorus, defined as the difference between the transports of its two layers. Danube river alone brings about 200 km^3/year water discharge, which corresponds to ¾ of the north-western river runoff and 2/3 of the total riverine input (370 km^3/year) into the basin. Turkish rivers (0.275×10^3 tons/year) account for 1/3 of the Danube (0.913×10^3 tons/year) and all other rivers on the northern part of the Black Sea (0.977×10^3 tons/year)[4]. 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[5,6]. 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[7]. 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 habitat. 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[7]. 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[8,9].

In this study, the metal bioaccumulations in mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) have been investigated *via* a four-year monitoring program (2005-2009) from Igneada to Hopa. Furthermore, this paper presents the first results of arsenic content in all biaota samples along the Southern Black Sea shelf. Turkey is

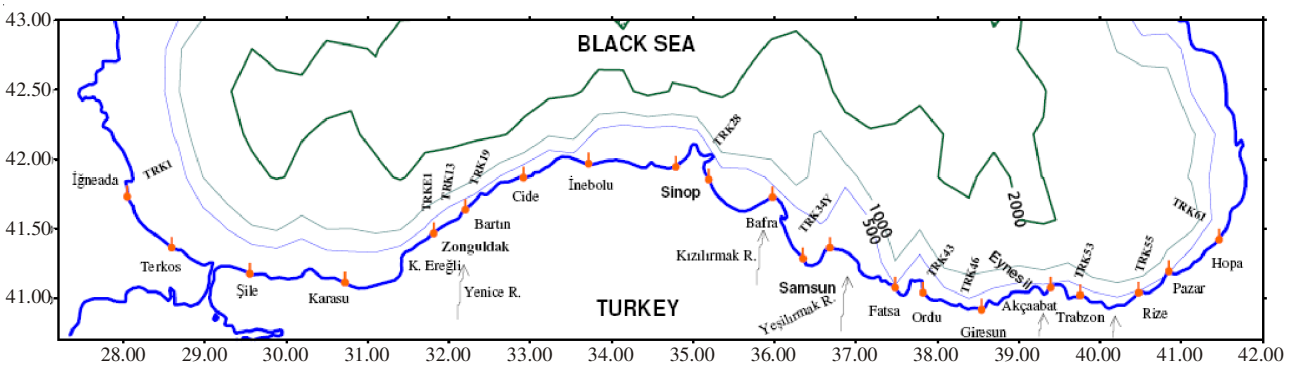

Fig. 1. Location of sampling station along the Southern Black Sea Shelf

a member of the commission on the protection of the Black Sea against pollution. Thus, these results form a base for future studies.

EXPERIMENTAL

The samples of mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) were collected from hot points (harbours and river mouths) from 2005 to 2009 (Fig. 1, Table-1). After collection, the samples were placed in polyethylene bags and stored below -20 ºC pending analysis[10]. For total metal analysis, approximately 10-12 the ripe mussels (*Mytilus galloprovincialis*) (the length vary between 10 and 15 cm) and fishes (*Merlangius merlangus euxinus*) taken from each station were dissected according to UNEP[11]. The fillets were homogenized in a blender and approximately 5-7 g of homogenate (fish) was 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[11-13]. All the analyses were performed using an atomic absorption spectrophotometer (Shimadzu 6701). The total mercury concentration was measured using a cold vapour technique and hydride generator unit (HVG-1 hydride vapour 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, Cd:0.10 and Pb: 0.10 mg L^{-1}. The accuracy and precision of the analyses was checked by analyzing BCR reference material CRM142 and 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
GPS DATA OF SAMPLING LOCATIONS IN THIS STUDY

Station	Longitude	Latutide
Igneada	417.670.825.834	28.104.292.295
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
13A	418.039.343.519	317.813.632.531
19A	419.421.294.213	329.056.812.341
Sinop	418.960.643.982	352.464.722.761
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
Giresun	409.228.333.333	384.018.333.333
Trabzon	411.129.627.546	393.935.446.441
Rize	410.761.109.861	404.349.210.528
Hopa	41.453.841.926	414.117.866.549

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 (%)	Measured value (this study) (μg g^{-1})	Certified value (μg g^{-1})
CRM142	Fe	8	46000 ± 200	40300 - 41300
CRM142	Cu	8	25 ± 0.9	27.5
CRM142	Zn	4	92 ± 3.0	92.4
IAEA436	Pb	2	0.14 ± 0.01	0.12
IAEA436	Hg	2	4.36 ± 0.05	4.19
IAEA436	Cd	2	0.053 ± 0.02	0.052
IAEA433	As	2	17.2 ± 0.02	18.9
CRM142	Mn	4	523 ± 5.1	569

RESULTS AND DISCUSSION

Total metal (Pb, Cd, Hg, Cu, Zn, Fe and Mn) concentrations in mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) from the Southern Black Sea were investigated from 2005 to 2009. Additionally, as contents were also measured in biota samples along the shelf. The concentrations of these elements are listed in Tables 3-6.

Metals in mussels (*Mytilus galloprovincialis*)

Lead concentrations varied between 4 μg g^{-1} and 25 μg g^{-1} (dry wt.), 3 μg g^{-1} and 10.8 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 1.1 μg g^{-1} (dry wt.) and 11.3 μg g^{-1} and 20.4 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 3a-6a). Lead levels in the Southern Black Sea shelf were found to be 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}, [13]). The highest Pb levels were measured in 2009, whilst the lowest values were measured in 2008.

Cadmium contents varied between 3.0 μg $g^{-1}$and 6.0 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 2.9 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 0.58 μg g^{-1} (dry wt.) and 0.6 μg g^{-1} and 3.5 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 1a-4a). Cadmium levels in the Southern Black Sea shelf were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1 μg g^{-1} wet wt), similar to the previously mentioned Pb levels. While the highest Cd levels were measured in 2005, Cd levels were comparable from 2006 to 2009.

Mercury concentrations varied between 2 μg g^{-1} and 3.6 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 0.24 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 0.02 μg g^{-1} (dry wt) and 0.04 μg g^{-1} and 0.13 μg g^{-1}

(dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 3a-6a). Mercury levels in the Southern Black Sea shelf were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (0.5 μg g^{-1} wet wt.) in 2005. On the other hand, the highest Hg contents were measured in 2005, similar to the Cd findings.

TABLE-3a
METAL CONTENTS OF MUSSELS (*Mytilus galloprovincialis*) IN 2005 (μg g^{-1})

2005	Cu	Zn	Mn	Fe	Cd	Pb	Hg
Terkos	60	208	73	1197	3	7	2
Zonguldak	76	250	52	792	5	13	2.3
Bafra	80	260	86	996	6	4	3.6
Ordu	56	278	26	896	4	25	2.5
Aquatic product directory	**20**	**50**	**-**	**-**	**0.1**	**1.0**	**0.5**

TABLE-3b
METAL CONTENTS OF FISHES (*Merlangius merlangus euxinus*) IN 2005 (μg g^{-1})

2005	Cu	Zn	Mn	Fe	Cd	Pb	Hg
Terkos	11	48	19	609	1	3	<0.01
Zonguldak	10	26	24	92	<0.01	<0.01	<0.01
Bafra	11	22	20	19	3	2	<0.01
Ordu	8	29	17	18	<0.01	<0.01	<0.01
Aquatic product Directory	**20**	**50**	**-**	**-**	**0.1**	**1.0**	**0.5**

TABLE-4a
METAL CONTENTS OF MUSSELS (*Mytilus galloprovincialis*) IN 2006 (μg g^{-1})

2006	Pb	Cd	Zn	Mn	Fe	Cu	Hg
Ordu	5.3	2.6	156	51	1317	62	<0.01
Rize	10.8	<0.01	63	56	1834	73	0.05
Giresun	3.8	1.5	79	28	924	8.0	0.02
TRK13A	1.7	0.2	118	23	930	12	0.08
Sinop	3.0	0.2	55	12	307	4.0	0.02
Samsun	3.4	1.3	122	12	521	26	0.17
Trabzon	7.1	2.9	31	63	2363	17	0.24
TRK19A	3.6	1.0	51	20	735	6.0	0.02
Igne ada	3.3	0.5	48	10	646	5.2	0.02
Hopa	7.5	1.0	232	17	430	29	0.02
Aquatic product directory	**1.0**	**0.1**	**50**	**-**	**-**	**20**	**0.5**

TABLE-4b
METAL CONTENTS OF FISHES (*Merlangius merlangus euxinus*) IN 2006 (μg g^{-1})

2006	Pb	Cd	Zn	Mn	Fe	Cu	Hg
Ordu	18.0	0.5	85	<0.01	91.2	0.5	0.02
Samsun	9.3	<0.01	21	7.4	216.4	1.0	<0.01
Zonguldak	8.9	<0.01	38	<0.01	87.7	0.8	<0.01
Aquatic product directory	**1.0**	**0.1**	**50**	**-**	**-**	**20**	**0.5**

TABLE-5
METAL CONTENTS OF MUSSELS (*Mytilus galloprovincialis*) AND FISHES (*Merlangius merlangus euxinus*) IN 2008 (μg g^{-1})

2008	Cd	Fe	Mn	Pb	Cu	Hg
Terkos	0.13	394	1.8	1.1	1.7	0.41
Zonguldak	0.58	132	2.6	<0.01	45	0.50
Ordu	<0.01	21	1.1	<0.01	0.8	0.14
Aquatic Product Directory	**0.1**	**-**	**-**	**1.0**	**20**	**0.5**

Copper contents varied between 56 μg g^{-1} and 80 μg g^{-1} (dry wt.), 4.0 μg g^{-1} and 73 μg g^{-1} (dry wt.), 0.8 μg g^{-1} and 45 μg g^{-1} (dry wt.) and 3.4 μg g^{-1} and 10.5 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 3a-6a). Copper levels in the Southern Black Sea shelf were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (20 μg g^{-1} wet wt.) in 2005, similar to the Hg findings. While the highest Cu levels were observed in 2005, the lowest Cu levels were found in 2009.

TABLE-6a
METAL CONTENTS OF MUSSELS (*Mytilus galloprovincialis*) IN 2009 (μg g^{-1})

2009	Cu	Cd	Pb	Fe	Zn	As	Hg
Terkos	7.7	3.5	12	109	450	1.23	0.04
Sakarya	5.2	1.3	17	576	425	0.86	0.07
Zonguldak	7.7	0.6	13	122	108	0.41	0.09
Samsun	3.4	0.9	11	24	43	4.85	0.13
Bafra	4.3	1.4	20	83	146	0.53	0.12
Ordu	6.0	3.0	15	45	801	3.22	0.13
Rize	10.5	2.4	18	132	13	0.19	0.07
Aquatic product directory	**20**	**0.1**	**1.0**	**-**	**50**	**1**	**0.5**

TABLE-6b
METAL CONTENTS OF AND FISHES (*Merlangius merlangus euxinus*) IN 2009 (μg g^{-1})

2009	Cu	Cd	Pb	Fe	Zn	As	Hg
Terkos	2.7	0.35	15	26	12	0.09	0.07
Sakarya	2.1	0.24	12	30	22	0.06	<0.01
Bafra	2.9	0.07	15	29	23	0.10	0.09
Ordu	3.4	0.22	13	106	41	0.03	0.5
Aquatic product directory	**20**	**0.1**	**1.0**		**50**	**1**	**0.5**

Zinc concentrations varied between 208 μg g^{-1} and 278 μg g^{-1} (dry wt.), 31 μg g^{-1} and 232 μg g^{-1} (dry wt.) and 13 μg g^{-1} and 801 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 3a - 6a). Zinc contents in the Southern Black Sea shelf were observed to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (20 μg g^{-1} wet wt.) from 2005 to 2009. The highest Zn levels were found in all sampling periods at the eastern of the shelf.

Iron contents varied between 792 μg g^{-1} and 1197 μg g^{-1} (dry wt.), 307 μg g^{-1} and 1834 μg g^{-1} (dry wt.), 21 μg g^{-1} and 394 μg g^{-1} (dry wt.) and 24 μg g^{-1} and 576 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2009, respectively (Tables 3a-6a). The highest Fe levels were found in 2005 and 2006, whilst the lowest Fe levels were measured in 2008 and 2009 along the shelf.

Manganese concentrations varied between 26 μg g^{-1} and 86 μg g^{-1} (dry wt.), 10 μg g^{-1} and 63 μg g^{-1} (dry wt.) and 1.1 μg g^{-1} and 2.6 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* from 2005 to 2008, respectively (Tables 3a-5). The highest Mn levels were found in 2005 and 2006. On the other hand, the lowest Mn values were measured in 2008 along the Southern Black Sea shelf. The highest Mn levels were found in 2005 and 2006 whilst the lowest Mn values were measured in 2008.

Arsenic concentrations ranged from 0.19 μg g^{-1} and 4.85 μg g^{-1} (dry wt.) in *Mytilus galloprovincialis* in 2009 (Table-6a). Contents 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 in Terkos, Samsun and Ordu. The lowest value was measured as 0.19 μg g^{-1} (dry wt.) at Rize station.

Metals in fishes (*Merlangius merlangus euxinus*): Lead concentrations varied between < 0.01 μg g^{-1} and 3 μg g^{-1} (dry wt.), 9 μg g^{-1} and 18 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 1.1 μg g^{-1} (dry wt.) and 11.5 μg g^{-1} and 14.9 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2009, respectively (Tables 3b-6b). Lead levels in the Southern Black Sea shelf were found to be 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},[13]). The highest Pb values were measured in 2006 and 2009, whilst the lowest values were measured in 2005 and 2008.

Cadmium contents varied between < 0.01 μg $g^{-1}$and 3 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 0.5 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 0.58 μg g^{-1} (dry wt.) and 0.07 μg g^{-1} and 0.35 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2009, respectively (Tables 3b-6b). Cadmium levels in the Southern Black Sea shelf were found to be higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (1 μg g^{-1} wet wt), similar to Pb findings. The variation in Cd levels was found to be similar during the 2005-2009 period.

While mercury concentrations were measured at the limit of the method (< 0.01 μg g^{-1} dry wet) in 2005, they varied between < 0.01 μg g^{-1} and 0.02 μg g^{-1} (dry wt.), 0.14 μg g^{-1} and 0.50 μg g^{-1} (dry wt.) and < 0.01 μg g^{-1} and 0.09 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2006 to 2009, respectively (Tables 3b-6b). Mercury contents were measured at their the highest values in 2008 along the shelf and they 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.) at all sampling periods. However, mercury levels in fish from the Southern Black Sea shelf were observed to have higher mercury levels those from the Marmara Sea[14].

Copper contents varied between 8.0 μg g^{-1} and 11 μg g^{-1} (dry wt.), 0.5 μg g^{-1} and 1.0 μg g^{-1} (dry wt.), 0.8 μg g^{-1} and 45 μg g^{-1} (dry wt.) and 2.1 μg g^{-1} and 3.4 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2009, respectively (Tables 3b-4b). Copper levels in the Southern Black Sea shelf were determined to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (20 μg g^{-1} wet wt.) in all the sampling periods, similar to the Hg findings. The highest Cu level found, which was higher than the critical limit, was measured at Zonguldak station in 2008.

Zinc concentrations varied between 22 μg g^{-1} and 48 μg g^{-1} (dry wt.), 21 μg g^{-1} and 85 μg g^{-1} (dry wt.) and 12 μg g^{-1} and 41 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2009, respectively (Tables 3b-6b). Zinc contents in the Southern Black Sea shelf were found to be lower than the critical limits set by the Turkish Ministry of Environment for Aquatic Products (20 μg g^{-1} wet wt.) during 2005-2009 period. The highest Zn level, which was higher than the critical limit, was measured at Ordu station in 2006.

Iron contents varied between 18 μg g^{-1} and 609 μg g^{-1} (dry wt), 88 μg g^{-1} and 216 μg g^{-1} (dry wt.), 21 μg g^{-1} and 394 μg g^{-1} (dry wt.) and 26 μg g^{-1} and 106 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2009, respectively (Tables 3b-6b). The highest Fe values were measured at Terkos, Samsun and Ordu Stations along the shelf.

Manganese concentrations varied between 17 μg g^{-1} and 24 μg g^{-1} (dry wt.), < 0.01 μg g^{-1} and 7.4 μg g^{-1} (dry wt.) and 1.1 μg g^{-1} and 2.6 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from 2005 to 2008, respectively (Tables 3b-5). The highest Mn levels were found in 2005 along the shelf. On the other hand, Mn values were lower than the detection limit of the method used (< 0.01 μg g^{-1}) in 2006.

Arsenic concentrations ranged from 0.03 μg g^{-1} and 0.1 μg g^{-1} (dry wt.) in fishes (*Merlangius merlangus euxinus*) from the Southern Black Sea shelf in 2009 (Table-6b). Levels were found to be much 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. Arsenic levels in fishes are comparable to or slightly higher than those found in the Marmara Sea[14].

Total metal (Cu, Zn, Cd, Pb and Hg) contents of mussels (*Mytilus galloprovincialis*) were found to be much higher than the critical limits set by the Turkish Ministry of Environment for Aquatic Products along the Southern Black Sea shelf in 2005 (Table-3a). However, Cu, Zn Fe, Mn and Hg contents of fishes (*Merlangius merlangus euxinus*) were low, contrary to the high Pb and Cd levels. While Pb, Cd, Cu and Zn contents were determined to be higher than the critical limits of Aquatic Product Directory along the shelf, Hg values were found to be lower (Table-2a) in 2006.

Cadmium and lead contents of fishes (*Merlangius merlangus euxinus*) were found at their highest values at Terkos and Bafra stations in 2005 (Table-3b). Copper, mercury and cadmium contents of fishes were measured at their lowest values, whereas Pb contents were higher than the critical limits of aquatic product directory in 2006 (Table-4b). In 2008, the highest Cd and Cu contents of mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) were found at the Zonguldak station and the highest Pb values were measured at the Terkos station (Table-5). However, the Hg contents of all biota (*Mytilus galloprovincialis* and *Merlangius merlangus euxinus*) samples were lower than the limits of the aquatic product directory along the shelf. In addition, Pb contents were lower than the detection limit (< 0.01 μg/L) of the method used at Zonguldak and Bafra stations. In 2009, Pb and Cd levels were found higher than the critical limits set by the Turkish Ministry of Environment for aquatic products (1.0 μg g^{-1} and 0.1 μg g^{-1} dry wt, respectively) along the shelf. Iron contents were measured at their highest values at all stations, similar to the Pb and Cd levels encountered and zinc level in fishes (*Merlangius merlangus euxinus*) was measured as the highest value at station Ordu in 2006. In addition, the highest metal values, excluding mercury, were found in the eastern part of shelf.

Although Fe and Mn values had been set in the aquatic product directory, it was observed that these metal levels were quite high along the Southern Black Sea shelf during 2005-2009 period (Tables 3-6). It is known that Mn and Fe oxides and hydroxides coming to marine systems *via* rivers adsorb and co-precipitate dissolved metals and affects their enrichment[15,16]. In addition, the high Mn values in the western region can be correlated to inputs from the Binkiliç manganese mining zone[17].

In this monitoring programme (2005-2009), metal contents in mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius*

merlangus euxinus) ranked as follows: Zn > Fe > Pb > Cu > Cd > As > Hg and Fe > Zn > Pb > Cu > Cd > As > Hg, respectively. The highest values were generally found at harbours and river mouths. Several domestic discharge stations are exist at Zonguldak, Samsun, Ordu, Giresun, Trabzon and Rize. Besides, some industrial discharges stations such as iron and steel industry, thermal power plant, copper smelter and fertilizer plant are also exist at Eregli, Zonguldak and Samsun. For this reason, this study results are 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 observed that Cu, Hg and Zn contamination levels in fishes (*Merlangius merlangus euxinus*) from the Southern Black Sea shelf were higher than those of the Marmara sea, contrary to Pb levels encountered, which were much lower. Furthermore, Cd and As levels were comparable to or slightly higher than those from the Marmara Sea[14,18,19] and Eastern Egean Sea[20]. Topçuoglu[21] have also confirmed the heavy metal pollution in mytilus, fishes and surface sediments of the Middle and Eastern Black Sea shelf.

Conclusion

Lead, cadmium, mercury, zinc and arsenic levels of mussels (*Mytilus galloprovincialis*) and lead and cadmium contents of fishes (*Merlangius merlangus euxinus*) from the Southern Black Sea shelf are higher than the critical limits by the Turkish Ministry of Environment for Aquatic Products. On the other hand, the highest metal values are generally found at Harbours Eregli, Zonguldak, Samsun, Trabzon, Giresun, Ordu and Hopa and River mouths Sakarya, Yenice, Kozlu, Filyos, Kizilirmak and Yesilirmak and they show 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 is 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 both mussels (*Mytilus galloprovincialis*) and fishes (*Merlangius merlangus euxinus*) along the Southern Black Sea shelf is rising rapidly and the toxic effects, particularly of Pb, Cd, As and Zn, will pose serious threats for human health.

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