ISSN:2148-9173 IJEGEO Vol: 4(2) May 2017

International Journal of Environment and Geoinformatics (IJEGEO) is an international, multidisciplinary, peer reviewed, open access journal.

Heavy Metal Levels in Commercial Fishes Caught in the southern Black Sea coast

Levent Bat, Elif Arıcı, Murat Sezgin, Fatih Şahin

IJEGEO International Journal of Environment and Geoinformatics 4(2): 94-102 (2017)

Heavy Metal Levels in Commercial Fishes Caught in the southern Black Sea coast

Levent Bat*[,1], Elif Arıcı[1], Murat Sezgin[1], Fatih Şahin[1]

[1] Address: Sinop University Fisheries Faculty Department of Hydrobiology TR57000 Sinop, Turkey

Corresponding author*
Tel : +90368 2876254
E-mail :leventbat@gmail.com

Received 20 Jan 2017
Accepted 11 March 2017

Abstract

The purpose of the current study is to evaluate the levels of seven heavy metals (arsenic, copper, zinc, mercury, lead, cadmium and iron) and metal (aluminium,) in the edible tissues of *Scophthalmus maximus, Spicara maena, Chelidonichthys lucerna, Alosa fallax* and *Scorpaena porcus* caught in Sinop coasts of the Black Sea. The samples were obtained during the fishing season in 2013 directly from the Turkish fishing vessels. Hg, Cd and Pb were not detected in the edible part of all fish samples. The metal levels in edible tissues did not exceed the standard guideline values. Estimated hazard index (HI) suggest that these metals in the edible tissues of the fish were not toxic for consumers, where the HIs of all the considered metals were below the value of 1.

Keywords: Black Sea, heavy metals, estimated daily intake (EDI), hazard quotient (HQ), hazard index (HI)

Introduction

The concentrations of heavy metal contaminations are an important factor because of its hazards effects on marine coastal ecosystem. These heavy metals are tolerable at even low levels and above certain concentration they become toxic for marine species especially fish. The major risk to consumer is especially non-essential metals such as mercury, arsenic, cadmium and lead. Heavy metal contamination of marine coastal ecosystem is associated with a wide range of sources like dumping of industrial and domestic waste, untreated sewage, spills of toxic chemicals, agricultural chemicals and others, which can impact the health of marine life. It should not be forgotten that fish are natural water inhabitants and cannot escape the harmful effects of heavy metals. Fish are exposed to heavy metals in polluted and contaminated waters. Heavy metals from the human activities and sources are continually released into aquatic ecosystems. They are serious health risks due to of their toxicity, long persistence, bioaccumulation and bio-magnifications in the food chain.

In the Black Sea much is known about the problems caused by the heavy metals in coastal area and their effect on fishing resources, ecosystems and human health. It receives a diversity of toxic compounds from industrial, domestic, agricultural, mining, livestock and other sources through direct dumping from rivers and runoff, posing risks to those people whom base their diet on resources coming from the Black Sea. The Black Sea ecosystem has been seriously damaged as a result of pollution (Algan, et al., 1999 and 2000; Polikarpov et al., 2004; Yüce and Gazioğlu, 2006). Bat (2014) indicated that heavy metal pollution the Black Sea ecosystems are growing at a danger level and have become an important problem.

Fisheries became such a vital part of the commerce of coastal towns in Turkey that their importance in conducive useful nutrition for people, supplying raw material for the industrial sector, composing the employment possibilities and high potential for export (OECD, 2014). Some economic fishes have been significantly declined due to overfishing, industrialisation and urbanisation which have caused fisheries the most favoured species to decrease in the Black Sea coast of Turkey (Kideys, 1994; Bat *et al*., 2007; Güven et al., 2010). Therefore, fish have been found to be good bio-indicators of heavy metal contamination in marine ecosystems (Bat, 2014). Muscle tissue of fish is the most frequently used for analysis because of the main edible part of the fish.

Sinop is considered as the mid-point of the Black Sea in Turkey and is located on Boztepe peninsula which is the most extended point of Turkish Black Sea coastline towards north. The fact that three sides of the peninsula are surrounded by sea has made fisheries a significant means of income. Fishery has an important place in the economy of Sinop.

The purpose of the current study is to evaluate the levels of seven heavy metals arsenic, copper, zinc, mercury, iron, cadmium and lead) and metal (aluminium) in the edible tissues of *Scophthalmus maximus, Spicara maena, Chelidonichthys lucerna, Alosa fallax* and *Scorpaena porcus* caught in Sinop coasts of the Black Sea. It was also attempted to compare the measured values with national and international standards for food and human health.

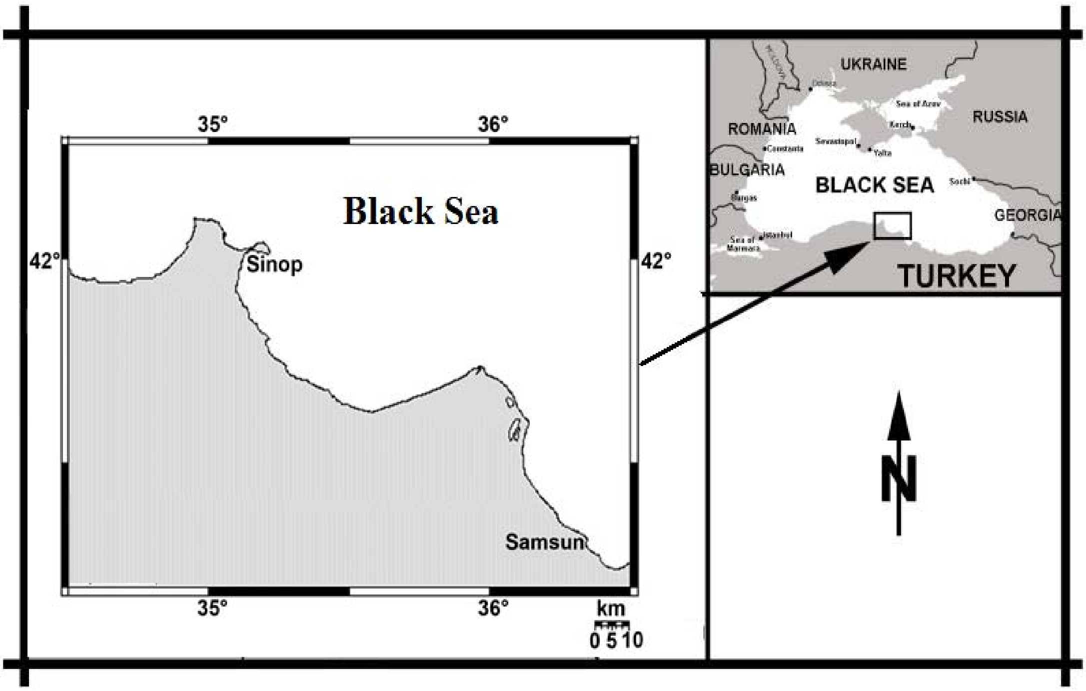

Fig 1. Fish sampling area from Sinop coasts of the Black Sea, Turkey.

Materials and Methods

Study Area

The fish used in the present study were *Scophthalmus maximus, Spicara maena, Chelidonichthys lucerna, Alosa fallax* and *Scorpaena porcus*. Fish were sampled during September 2013 to December 2013 directly from local fishing vessels in Sinop coats of the Black Sea (Figure 1).

Preparation fish samples and determination of heavy metals

The fish samples were taken randomly and only consumable sizes were used. Then fish specimens were measured for total length (TL) by using wooden measuring tray to the nearest 0.1 cm. The mean lengths of *Scophthalmus maximus, Spicara maena, Chelidonichthys lucerna, Alosa fallax* and *Scorpaena porcus* were 47±5, 12±0.6; 28±3; 25±3 and 14±1 cm, respectively.

Fish samples were then labelled, preserved using ice and transported to the main laboratory. All the samples were stored at -21^{0}C prior to pre-treatment and analysis (modified from UNEP 1984).

Metal analysis in fish was performed using m-AOAC 999.10- ICP/MS (Inductively Coupled Plasma – Mass Spectrometer) method by accredited ÇEVRE Industrial Analysis Laboratory Services Trade Company (TÜRKAK Test TS EN ISO IEC 17025 AB-0364-T). EN 15763 European Standard methods was applied. The limits of detection used for analysis of aluminium (Al), arsenic (As), copper (Cu), zinc (Zn), mercury (Hg), lead (Pb), cadmium (Cd) and iron (Fe) were 0.5, 0.05, 0.5, 0.5, 0.05, 0.05, 0.02 and 0.5, respectively.

Assessments Hazard Quotient (HQ) and Hazard Index (HI) of metals in fish and Intake Levels Calculation

Risk from metals intake through ingestion may be characterized using a Hazard Quotient (HQ) as the ratio of the estimated metal dose (EDI mg/kg of body weight per day) and the reference dose (Rf. D mg/ kg) (Khan *et al*., 2009; Zhuang *et al*., 2013; Ukoha *et al*., 2014; Akoto *et al*., 2014; Ahmed *et al*., 2016). Rf. D values were developed by US EPA and Agency for Toxic Substances and Disease Registry (ATSDR) for consumption as estimates of daily exposures to a contaminant that are probably without a noticeable risk of injurious effects to the general population during a lifespan of exposure (US EPA, 1989, 2002 and 2011a,b; ATSDR, 2005).

If HQ > 1.0, then the EDI of a particular metal exceeds the Rf. D, indicating that there is a potential risk associated with that metal. The estimated daily intake (EDI) depends on both the metal concentration level and the amount of consumption of fish. The average heavy metal daily intake of metals was determined using the following equation.
Metals intake level = average metal content X daily average consumption of fish per person/ body weight.

Total Hazard Index (THI) = Σ HQ = $HQ_{Al} + HQ_{As} + HQ_{Cu} + HQ_{Hg} + HQ_{Fe} + HQ_{Cd} + HQ_{Pb}$ (Ukoha *et al*., 2014).

The annual quantity of fish consumed is 6.3 kg / person in 2013 (TUIK, 2014), which is equivalent to 17.3 g/day for Turkey. The body weight of adult person is 70 kg.

Statistical Analysis

Data were expressed as mean ± standard deviation (SD). Data were analysed by ANOVA at α= 0.05. Comparison of means was performed by Duncan test and difference was considered significant at $p < 0.05$ (Zar, 1984). IBM SPSS Statistics version 21 software is used for statistical analysis.

Results

The analytical data for these metals showed that there was difference in metal content in various fish. In the present study the concentration of metals was in order of Fe > Zn > Cu > Al > As > Pb > Cd > Hg. Figure 2 showed that the concentration levels varied from 0.54 (*S. maximus*) to 1.21 (*A. fallax*) mg/kg wet wt. for Cu; from 2 (C. lucerna) to 8 (*A. fallax*) mg/kg wet wt. for Zn; from 9 (*C. lucerna*) to 19 (*A. fallax*) mg/kg wet wt. for Fe.

The levels of Hg, Pb and Cd in all fish were below the limit of detections (0.05, 0.05 and 0.02 mg/kg, respectively). The As levels in *S. maximus, C. lucerna* and *S. porcus* were below the limit of detection (0.05 mg/kg). However, the highest As (0.29 mg/kg wet wt.) was found in the edible tissues of *S. maena* followed in *A. fallax* (0.25 mg/kg wet wt.). Similarly Al levels in *C. lucerna* and *S. porcus* were below the limit of detection (0.5 mg/kg). However, the highest Al (0.91 mg/kg wet wt.) was found in *A. fallax* followed by S. maena (0.72 mg/kg wet wt.) and *S. maximus* (0.65 mg/kg wet wt.).

In respect to health risk, the tolerable weekly consumes were calculated by means of references for edible tissues of fishes consumed by people. The annual quantity of fish consumed is 6.3 kg/person in 2013 (TUIK, 2014), which is come up to 17.3 g/day for Turkey. The EWI (Estimated Weekly Intake) and EDI (Estimated Daily Intake) worth were given in Table 1. The tolerable weekly intake of heavy metals as PTWI (Provisional Tolerable Weekly Intake), are set by the Food and Agriculture Organization/World Health Organization (FAO/WHO) Joint Expert Committee on Food Additives (JECFA).

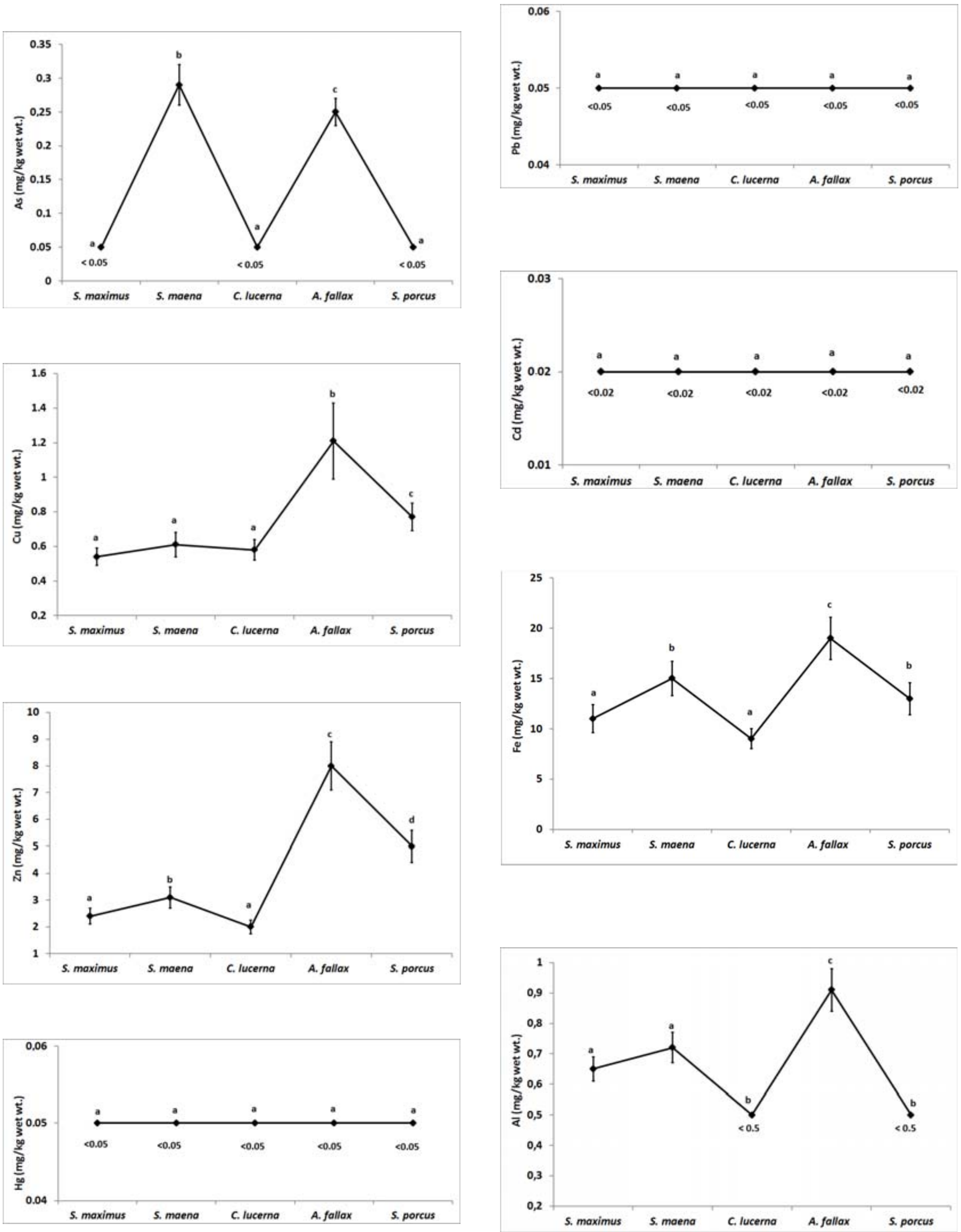

Fig 2. The means with standard deviations (vertical line) of As, Cu, Zn, Hg, Pb, Cd, Fe and Al concentrations (mg/kg wet wt.) in the edible tissues of fish species collected from Sinop coasts of the Black Sea during fishing season in 2013. The same letters beside the vertical bars indicate the values are not significantly different (P>0.05).

PTWI is the maximum level of a pollutant to which a person can be exposed per week over a lifetime without an unacceptable risk of health effects (National Academy of Sciences, 1989; WHO, 1996; Council of Europe, 2001; FAO/WHO, 2010; EFSA 2010, 2012a,b).

Estimated hazard quotient (HQ) of Al, As, Cu, Zn, Hg, Pb, Cd and Fe suggest that these metals in the edible tissues of *S. maximus, S. maena, C. lucerna, A. fallax* and *S. porcus* do not pose any apparent threat to people, where the HIs of all the considered metals (Total Hazard Index (THI) = Σ HQ_n = 0.034) were below the value of 1 (Figure 3).

If the total hazard index (THI) is below 1.0, no health risk may occur as a result of ingestion of the fish and the greater the value of THI above 1, the greater is the level of risk associated with the fish consumption. Hence, THI = 0.0 to 1 means no hazard; 1.1 to 10 means moderate hazard while greater than 10 means high hazard or risk (Ukoha *et al*., 2014).

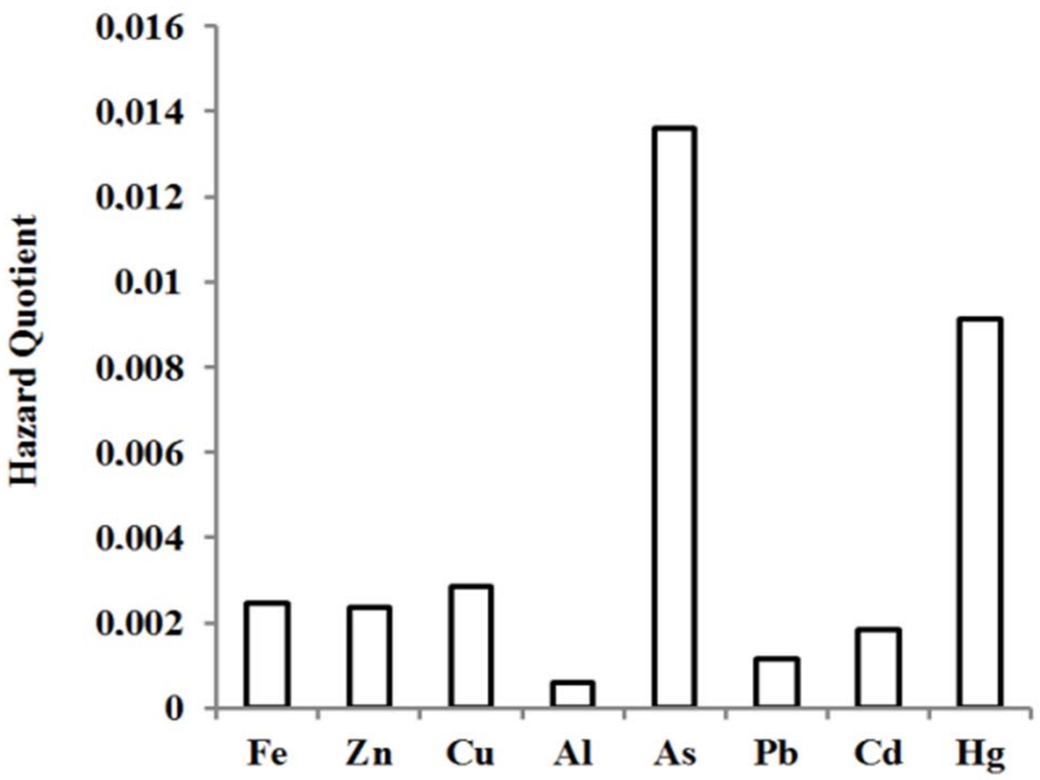

Fig 3. Total hazard quotient of As, Cu, Zn, Hg, Pb, Cd, Fe and Al via consumption of *S. maximus, S. maena, C. lucerna, A. fallax* and *S. porcus.*

Table 1. Estimated Weekly Intakes (EWI) and Estimated Daily Intakes (EDI) of metals in edible tissues of commercial fish from Sinop coastal waters of the Black Sea, Turkey.

Metals	PTWI[a]	PTDI[b]	EWI[c]		EDI[d]	
			Minimum	Maximum	Minimum	Maximum
Al	70	10	--	0.040	--	0.006
As	*	*	--	0.013	--	0.002
Cu	245	35	0.024	0.053	0.003	0.008
Zn	490	70	0.088	0.353	0.013	0.050
Fe	392	56	0.397	0.838	0.057	0.120
Cd	0.49	0.07	Below Detection Limit			
Pb	1.75	0.25	Below Detection Limit			
Hg	0.28	0.04	Below Detection Limit			

[a]PTWI (Provisional Tolerable Weekly Intake) (mg/week/70 kg body wt.)
[b]PTDI (Permissible Tolerable Daily Intake) (mg/day/70 kg body wt.)
[c]EWI (Estimated Weekly Intake) (mg/week/ kg body wt.)
[d]EDI (Estimated Daily Intake) (mg/day/ kg body wt.)
*There is no PTWI set for As

Discussion and Conclusios

Legal thresholds are not available for essential elements in European Commission Regulation (EC, 2006). There is also no maximum level set for As in foods at EU level. However European Commission Regulation (EC, 2006) indicates that maximum levels of Hg, Pb and Cd are 0.5, 0.30 and 0.05 mg/kg wet wt., respectively. Overall, the findings from the present study revealed that Al, As, Cu, Zn, Hg, Fe, Cd and Pb concentrations in the edible tissues of fish species were lower than the maximum permissible limit as recommended by the Turkish Food Codex (TFC, 2002) and European Commission Regulation (EC, 2006). The concentrations of these metals in muscle tissues of the samples were not risky to human health. These data provide a useful baseline to measure any future changes in local pollution.

In the present study values in edible tissues were lower than those reported by other studies in the Turkish Black Sea coast. Cd, Pb, Cu and Zn concentrations were found to be highest in *Spicara smaris* at Rize and Pazar (Topcuoğlu *et al*., 2003) compared to *S. maena* in this study.

Similarly, Pb and Cd concentrations were found to be highest in *Psetta maxima* at Igneada (Topçuoğlu *et al*., 1990) and very high levels of Fe, Zn, Cu, Pb and Cd in *P. maxima* at Samsun, Sinop, Terme, Fatsa and Ordu (Nisbet *et al*., 2010) when compared to *Scophthalmus maximus* in this study.

Cd, Pb, Cu and Zn levels in *Alosa caspia* from Samsun were also high (Tüzen, 2003), but Fe levels were similar in *A. fallax* from Sinop in this study. Moreover, Nisbet *et al*. (2010) found very high concentrations of Fe, Zn, Cu, Pb and Cd in *Alosa caspia* from Samsun, Sinop, Terme, Fatsa and Ordu when compare to *A. fallax* in this study. Bat *et al.* (2012) have investigated heavy metal levels in *Scorpaena porcus* and *Spicara maena* of the same sampling area and found higher Zn, Cu, Cd and Pb accumulation in fish species. Balkıs *et al.* (2012) also found Cd and Pb levels in Merlangius merlangus euxinus from the southern Black Sea coast were higher than those in the critical levels. These studies indicated that different levels of heavy metals in different fish species could be the result of ecological needs, metabolism and feeding patterns (Yılmaz, 2003), behaviour and body size (Tüzen, 2003).

Estimated hazarded quotients of all the considered metals were below the value of 1, therefore the metals in fish samples do not pose any apparent threat to the population and these fishes are healthy for consumption.

The present study has demonstrated that metal levels in five species of these sea fish caught in Sinop coasts of the Black Sea do not have inordinately high levels in the edible muscle tissue. Whether essential or not heavy metals toxic to man (Al, As, Cu, Zn, Hg, Pb, Cd and Fe) have natural levels in *S. maximus, S. maena, C. lucerna, A. fallax* and *S. porcus* which are well below those likely to cause a problem in public health. Sinop coast is relatively unpolluted and is relatively far from large urban centres along the coastline. Therefore it is concluded that the metal levels may be taken as a convenient base line against which any future pollution trends might be measured.

Acknowledgements

This study was presented as a oral presentation with abstract only in Protection of Natural Resources and Environmental Management: The main Tools for Sustainability. (PRONASEM) 11-13 November 2016, Bucharest, Romania. It was supported by the Department of Hydrobiology of Fisheries Faculty, Sinop University.

References

Ahmed, Q., Bat, L., Yousuf F, Arıcı E. (2016). Heavy metals in *Acanthopagrus arabicus* Iwatsuki, 2013 from Karachi coasts, Pakistan and potential risk of human health. International Journal of Fisheries and Aquatic Studies, 4(1): 203-208.

Akoto, O., Bismark Eshun, F., Darko, G., Adei, E. (2014). Concentrations and health risk assessments of heavy metals in fish from the Fosu Lagoon. Int. J. Environ. Res., 8(2):403-410.

Algan O, Gazioğlu C, Çağatay N, Yücel ZY, Gönençgil B. (1999). Sediment and water influxes into the Black Sea by Anatolian rivers. Zeitschrift für Geomorphologie 43: 61–79.

Algan O., Gazioğlu C., Yücel Z., Çağatay N., Gönençgil B., (2000). Sediment and Freshwater Discharges of the Anatolian River into the Black Sea, IOC-BSRC Workshop «Black Sea Fluxes», Workshop Report No. 145. Paris: UNESCO, 38–50.

ATSDR. (2005). Public Health Assessment Guidance Manual (Update). U.S. Department of Health and Human Services Public Health Service Agency for Toxic Substances and Disease Registry Atlanta, Georgia, 357p.

Balkıs, N., Aksu, A., Hiçsönmez, H. (2012). Metal levels in biota from the Southern Black Sea, Turkey. Journal of the Black Sea / Mediterranean Environment, 18 (2):134-143.

Bat, L., Şahin, F., Satılmış, H. H., Üstün, F., Özdemir, Z.B., Kıdeyş, A. E., Shulman, G. E. 2007. The changed ecosystem of the Black Sea and its impact on anchovy fisheries. (in Turkish). Journal of FisheriesSciences.com, 1(4):191-227.

Bat, L., Sezgin, M., Üstün, F., Şahin, F. 2012. Heavy metal concentrations in ten species of fishes caught in Sinop coastal waters of the Black Sea, Turkey. Turkish Journal of Fisheries and Aquatic Sciences, 12: 371-376.

Bat L. 2014. Heavy metal pollution in the Black Sea. In: Düzgüneş E, Öztürk B, Zengin M. (Eds.). Turkish Fisheries in the Black Sea. Published by Turkish Marine Research Foundation (TUDAV), Publication number: 40, ISBN: 987-975-8825-32-5 Istanbul, Turkey, 71-107.

Council of Europe. (2001). Council of Europe's policy statements concerning materials and articles intended to come into contact with foodstuffs. Policy Statement concerning materials and alloys. Technical Document. Guidelines on metals and alloys used as food contact materials. (09.03.2001), Strasbourg. 67p.

EFSA Panel on Contaminants in the Food Chain (CONTAM). 2010. Scientific Opinion on Lead in Food. EFSA Journal, 8 (4): 1570.

EFSA (European Food Safety Authority). 2012a. Cadmium dietary exposure in the European population. EFSA Journal, 10 (1), 2551. 37p.

EFSA Panel on Contaminants in the Food Chain (CONTAM). (2012b). Scientific Opinion on the risk for public health related to the presence of mercury and methylmercury in food. EFSA Journal, 10 (12): 2985, 241p.

European Commission Regulation (EC). (2006). Setting maximum levels for certain contaminants in foodstuffs, No 1881.

FAO/WHO. (2010). Summary report of the seventy-third meeting of JECFA, Joint FAO/WHO Expert Committee on Food Additives, Geneva.

Güven, KC., Nesimigil, F., Cumalı, S., Yalçın, A., Gazioğlu, C. and Çoban, M. (2010). Anionic Detergent LAS pollution and Discharged amount from Turkish coasts to the Black Sea during 2004-2007. J. Black Sea/Medi,t. Environ., 16(1):5-24.

Khan, S., Farooq, R., Shahbaz, S., Khan, M.A., Sadique, M. (2009). Health Risk Assessment of Heavy Metals for Population via Consumption of Vegetables. World Appl Sci J., Vol.6 (12):1602-1606.

Kideys, A.E. (1994). Recent dramatic changes in the Black Sea ecosystem: The reason for the sharp decline in Turkish anchovy fisheries. J. Mar. Syst., 5: 171-181.

National Academy of Science. (1989). Recommended Dietary Allowances, 10th Edition, National Academy Press, Washington, D.C. 298p.

Nisbet, C., Terzi, G., Pilger, O., Sarac, N. (2010). Determination of heavy metal levels in fish sample collected from the Middle Black Sea. Kafkas Üniv.Veteriner Fak. Dergisi, 16 (1): 119-125.

OECD. (2014). http://www.oecd.org/turkey. Country note on national fisheries management systems, Turkey. (Accessed 6th of March 2014).

Polikarpov, G.G., Egorov, V.N., Gulin, S.B., Mirzoyeva, N.Yu. (2004). Pollution of the Black sea and suggestions on solutions. (In: The Black Sea Foundation for Education Culture and Protection of Nature, Ed. M.S. Çelikkale) Workshop A glance to the Black Sea, 31 October 2003, Istanbul, Turkey, 91-128.

Topçuoğlu, S., Erentürk, N., Saygı, N., Kut, D., Esen, N., Başsarı, A., Seddigh, E. (1990). Trace metal levels of fish from the Marmara and Black Sea. Toxicological and Environmental Chemistry, 29:95–99.

Topçuoğlu, S., Ergül, H.A., Baysal, A., Ölmez, E., Kut, D. (2003). Determination radionuclide and heavy metal concentrations in biota and sediment samples from Pazar and Rize stations in the eastern Black Sea. Fresenius Environmental Bulletin, 12 (7):695-699.

TFC (Turkish Food Codex). (2002). Official Gazette of Republic of Turkey. Notifications about determination of the maximum levels for certain contaminants in foodstuffs of Turkish Food Codex (in Turkish). (Notification No: 2002/63), Issue: 24885.

TUIK, Turkish Fishery Statistics. 2014. Available online: http://www.tuik.gov.tr/

Tüzen, M. (2003). Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chemistry, 80: 119–123.

Ukoha, P.O., Ekere, N.R., Udeogu, U.V., Agbazue, V.E. (2014). Potential health risk assessment of heavy metals [Cd, Cu and Fe] concentrations in some imported frozen fish species consumed in Nigeria. Int. J. Chem. Sci., 12 (2): 366-374.

UNEP (The United Nations Environment Programme). (1984). Determination of Total Cd, Zn, Pb and Cu in Selected Marine Organisms by flameless AAS. Reference Methods for Marine Pollution Studies, 11 Rev 1.

U.S. EPA (Environmental Protection Agency). (2002). A Review of the Reference Dose and Reference Concentration Processes. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC, EPA/630/P-02/002F.

U.S. EPA (Environmental Protection Agency). (2011a). Exposure factors handbook: National Center for Environmental Assessment, Washington, DC; EPA/600/R-09/052F. Available from the National Technical Information

Service, Springfield, VA, and online at http://www.epa.gov/ncea/efh
U.S. EPA (Environmental Protection Agency). (2011b). Highlights of the Exposure Factors Handbook. National Center for Environmental Assessment, Washington, DC; EPA/600/R-10/030. Available from the National Technical Information Service, Springfield, VA and online at http://www.epa.gov/ncea.
WHO. (1996). Trace elements in human nutrition and health. ISBN 92 4 156173 4 (NLM Classification: QU 130), Geneva.
Yilmaz, A.B. (2003). Levels of heavy metals (Fe, Cu, Ni, Cr, Pb and Zn) in tissue of Mugil cephalus and Trachurus mediterraneus from Iskenderun Bay. Turk. Environ. Res., 92, 277–281.
Yüce H. and Gazioğlu C. (2006). "Maritime Security Challenges Ahead in the Black Sea", Journal of Black Sea/Mediterranean Environment, Vol.12 (3): 233-250.
Zar, J.H. (1984). Biostatistical analysis. Second edition. Prentice Hall, Int., New Jersey.
Zhuang, P., Li, Z., McBride, M.B., Zou, B. (2013). Health risk assessment for consumption of fish originating from ponds near Dabaoshan mine, South China. Environ Sci Pollut Res., 20(8):5844-5854.