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Metals (Hg, Pb, Cu, and Zn) Bioaccumulation in Sediment, Fish, and Human Scalp Hair: A Case Study from the City of Mersin Along the Southern Coast of Turkey

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Abstract This study investigates mercury, lead, copper, and zinc concentrations in six most frequently consumed fish species (120 samples), sediments (20 samples) taken from Karaduvar Fishing Area where fish species live, and Mersin Port as a contrary region, and human scalp hair for people regularly consuming these fish species (50 samples) and non-fish-eaters (15 samples) in Mersin, Turkey. On taking living environment into account, the fish groups include pelagic species of *Liza saliens, Liza aurata*, and demersal species of *Merluccius merluccius*, *Mullus barbatus*, *Upeneus moluccensis*, and *Solea solea*. Total Hg (THg) was found to accumulate in muscle tissues at the lowest concentration (0.01 μg/g) in *L. saliens* and at the highest (2.66 μg/g) in *S. solea*. Pb was only detected at high concentrations of 1.86 μg/g in *M. barbatus* and of 2.16 μg/g in *M. merluccius*. Cu and Zn concentrations were below the detection limit within all fish species. In the sediment samples, Pb and Cu concentrations were persistently below their effect range–median (ERM) value, whereas this limiting value only maintained for 15% of THg concentrations. On the other hand, the effect range–low (ERL) of sediment exceeded at Pb in 15% of samples and Cu in 25% of samples. Zn remained below the detection limit for sediment samples. The metal concentrations at scalp hairs of regular consumers of these fish groups and non-fish eaters vary from the range 0.40–3.28 to 0.14–1.02 μg/g for THg, 11.16–107.84 to 8.00–22.38 μg/g for Pb, and 151.67–645.35 to 144.92–343.50 μg/g for Zn. An important finding of the present study is the significant adverse impact of sedimentary heavy metal bioaccumulation to human through the consumption of demersal fishes in the city of Mersin along the southern coast of Turkey.

Keywords Fish · Sediment · Human scalp hair · Metals · Bioaccumulation · Mediterranean Sea · Turkey

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Introduction

Anthropogenic metal pollution of aquatic environments is a critical research issue. Significant advances have been made over the last decade in detecting metal pollution sources, locating metal sinks, and deciphering chronologies of pollution inputs. In addition, significant strides have been made in assessing biotoxicity of a variety of organic and inorganic compounds concentrated in the environment as a result of human activities. Among the heavy metals, mercury, cadmium, and lead are extremely toxic to human. Determination of their toxicity is therefore of fundamental importance for human health. Fish, extensively used in marine pollution monitoring programs, are important in human diet, and therefore, have been subjected to numerous studies [1–12]. Complementary studies have been carried out on metal levels at sediment and human scalp hair (hereafter referred to as HSH) in critically polluted coastal regions throughout the world [13–20] and Turkey [21–24].

The metals Hg and Pb are generally regarded as the most critical pollution indicators, while Cu and Zn are among the essential metals for proper functioning of biological systems. Hg is accumulated more effectively both at aquatic systems and human through its efficient biomagnification in the food chain as documented in microorganisms, fish, crustaceans, and human [25–29]. Another aspect of Hg is its accumulative character in hair than in other biological materials (hair contains 300 times more Hg than blood) [30]. Pb has been used successfully to document population exposure to toxicity by measuring its concentrations on HSH [31, 32]. Pb concentration in hair of healthy persons may be two to five times higher than that in bone, ten to 50 times higher than that of blood and 100–500 times higher than that in urine [33, 34]. Hair can accumulate not only toxic metals but also essential metals such as Zn and Cu and can be taken into consideration when evaluating environmental pollution [35].

Hair offers a good way of discerning long-term variations in trace element concentration by providing a better assessment of normal trace element concentrations. According to the Environmental Protection Agency (EPA), human hair is one of the most important biological materials for worldwide environmental monitoring and the International Atomic Energy Agency uses hair to monitor global trends of element levels [36]. Hair as a biological tissue is unique in respect that it serves as an accumulator for trace elements, and in addition, it is formed in relatively short period of time and remains isolated from the metabolic events in the human body and its metal content can reflect the body status for a long period [34, 37, 38]. Once mercury has been accumulated into the hair, its concentration does not change significantly, whereas mercury contents in blood and urine can only reflect very recent exposures [39]. Because of the simplicity of sampling, storing, and handling, human hair is an attractive biological material for determining the body's trace element status either for nutritional, toxicological, or clinical diagnostic purposes [40, 41]. The advantages of analysis of hair over blood and urine samples for the determination of metals are as follows: (1) the concentrations of most trace elements are higher in hair than in other human materials; (2) specimens can be collected more quickly and easily than specimens of blood, urine, or any other tissue and also special storage conditions are not needed; (3) unlike blood, hair is an inert and chemically homogeneous sample; and (4) serum and urine concentrations provide an acute index in a relatively short period, while the concentrations in hair provide a retrospective index of trace element supplies [42].

Marine sediment can provide a record for depositional history of metals into the environment. Feltz [43] summarized the significance and use of bed sediments as follows: (1) as an historical water quality integrator, (2) as a reconnaissance tool, (3) in planning analytical schedules, (4) in conducting short-lived studies, (5) for deriving short- and long-term trends,

and (6) for identification of problem areas. Sediments are not only a sink for trace metals, but also a source of resuspended metals, which may be chemically remobilized and enter the water column and food chain [44, 45]. Because of its much longer lifetime in sediment, Hg is considered to be the major tracer of heavy metal pollution in aquatic environments.

The Mediterranean basin has frequently been studied in great deal over the past 20 years because of the anomalous natural presence of mercury. Marine animals of this basin have higher mercury body burdens than the same (or similar) species in the Atlantic and other Oceans. Due to higher mercury levels in many Mediterranean seafood species, the risk for humans living and consuming large amounts of local seafood is therefore higher than in other parts of the world [46]. Mersin, with its long continental coastline along the northeastern end of the Mediterranean Sea, a great variety of marine resources and active shipping, trading, and industry, is prone to heavy metal pollution and its impact on local community. The present study is devoted to exploring the level of human induced pollution in the city of Mersin by monitoring the levels of THg, Pb, Cu, and Zn at fish (two pelagic and four demersal species), sediment from Karaduvar Fishing Area (hereinafter referred to as KFA) and Mersin Port (MP), as well as HSH samples taken from people regularly consuming the fish species and non-fish eaters. More specifically, the aim is to monitor and quantify heavy metal concentrations in the muscle tissue of edible fish species (grey mullet, red mullet, hake, and sole), sediment samples from KFA known as a major fish supplier, and HSH samples from Mersin region of Turkey.

Materials and Methods

Sample Collection

Samples comprised of sediment, fish, and HSH were collected from Mersin along the southern coast of Turkey (Fig. 1) between February and November in 1996. Sampling of heavy metals was avoided in water column because of measuring difficulties.

Fish and sediment samples were taken at KFA (36°48'23.16" N, 34°41'40.64" E). The complementary sediment samples were collected from the heavily polluted MP (36°47'53.35" N, 34°38'11.31" E) for comparison aims (Fig. 1). On taking living environment into account, the fish samples represent pelagic and demersal groups. The pelagic samples include grey mullet [*Liza aurata* (ns, 15) and *Liza saliens* (ns, 15)]. The demersal samples are red mullet [*Upeneus moluccensis* (ns, 15) and *Mullus barbatus* (ns, 15)], hake [*Merluccius merluccius* (ns, 30)], and sole [*Solea solea* (ns, 30)]. These fish species are among the most consumed, commercially valuable and available almost throughout the year. However, the demersal ones have been studied as monitoring species in the Bay of Izmir, Turkey [8].

Fish samples were purchased from the local fish market in the same day of capture and brought to the laboratory on ice as quickly as possible. After having determined their length, weight, sex, and age, the samples were stored in deep freezer (−22°C) until the dissection for their muscle tissues. Fish species were classified according to Whitehead et al. [47]. The properties (length, weight, age, and habitat) of each fish sample are documented in Table 1.

Sediment samples were collected from different depths at each site. A portion of the top 2 cm of sediment was removed using a plastic spoon and placed into pre-cleaned Ziploc plastic bags for trace metals analysis. Sediment samples were frozen at −20°C within an hour of collection.

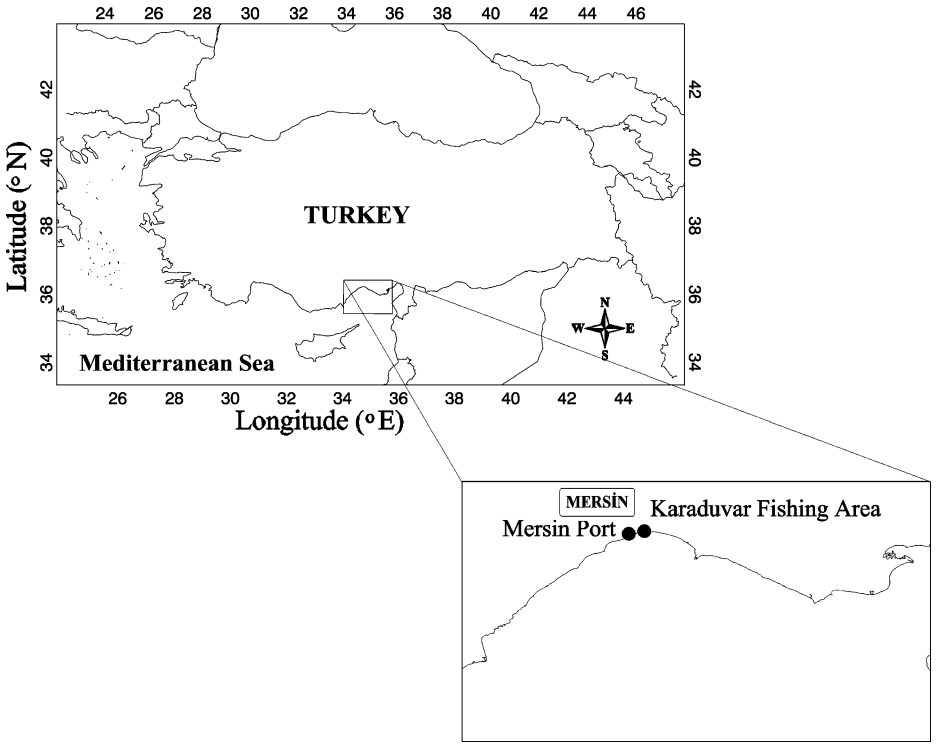

Fig. 1 Map of the study area. Location sites for sediment, fish and HSH samples. Sediment samples were collected from Karaduvar Fishing Area (KFA) and Mersin Port (MP). Fish samples were taken at KFA. HSH samples were taken from the inhabitants of the city of Mersin

HSH samples were collected from a total of 65 subjects (53 male and 12 female) aged from 10 to 73 years in Mersin region in Turkey: 50 samples taken from the people eating regularly the fish species used in this study and 15 samples represent the control group never using fish in their diet. Mersin city has approximately one million inhabitants, thus constituting a subpopulation representing approximately 1.5% of the total Turkish population.

The HSH samples have been chosen from those which have never been dyed or bleached. They were snipped with clean stainless steel scissors from the nape of the neck, and the proximal 0.5 cm of them was collected. The samples were procured by normal cutting and collected with care to avoid any external contamination and sealed immediately in clean and numbered polyethylene bags after collection and transported to laboratory for further analysis. A questionnaire was given to each sampler for describing name, sex, age, domicile, general health, occupation, and living habits (vegetarian/non-vegetarian, smoker/non-smoker, and alcoholic/non-alcoholic).

Sample Analysis

Deionized water was used for preparation of all solutions. All chemicals and standard solutions used in the study were of analytical grade (E. Merck, Darmstadt, Germany). All glasswares were soaked overnight in 10% (*v*/*v*) nitric acid. Glasswares, for the analyses of Pb, Cu, and Zn were rinsed thoroughly with deionized distilled water and dried before use

Table 1 The Age, Habitat, Weight, Length, THg, and Pb Concentrations (μg/g ww) for the Fish (Grey Mullet, Hake, Red Mullet, and Common Sole) from KFA

Sample	Age (year)	Weight (g)	Length (cm)	Habitat	THg (μg/g) $X \pm SD$	n^a	Pb (μg/g) X ± SD	n^b
Grey mullet								
L. aurata	0–6	62.0–274.2	16.4–26.2	Usually inshore, entering lagoons and estuaries	0.13±0.06	0	ND	–
L. saliens	0–7	40.5–445.7	13.8–32.9	Usually inshore, entering lagoons and estuaries	0.12±0.09	0	ND	–
Hake								
M. merluccius	1–5	30.2–208.5	14.2–27.5	Mid water or at bottom, chiefly at 100–300 m.	0.33±0.16	5	1.08±0.49	8
Red mullet								
M. barbatus	1–3	22.5–52.1	10.3–14.1	Muddy bottom of the continental shelf (100–300 m)	0.17±0.16	1	1.46±0.20	8
U. moluccensis	1–2	12.0–38.5	7.4–11.8	Coastal tropical inshore waters at depths of 10–80 m	0.57±0.54	7	1.26±0.31	5
Common sole								
S. solea	0–3+	40.0–118.2	14.4–22.7	Sandy, muddy bottoms, from the shore down to 200 m	0.62±0.50	9	ND	–

Except age groups results are presented in the form of means and their standard deviations

[a] Sample number above the international human consumption advisory limit of 0.5 μg/g ww for THg [58]

[b] Sample number above the accepted limits (1.5 μg/g ww Pb) for human consumption [3]

ND: not detected

and that for Hg analyses was rinsed with distilled water. This was to control the possible Hg contamination of water from the resins used in deionizers.

Fish were sliced for muscle samples using different polyethylene knives for each sample. Edible muscle tissues of 0.85 g of the fish samples were weighed [48]. Thawed sediment samples were weighed in amounts 50–100 g and dried. Then, they were prepared for the experiment and weighed 0.15 g [49]. The HSH samples were washed with a non-ionic detergent and dried. They were weighed 0.10 g [50].

In order to obtain statistically more reliable data, the samples contained six replicates, and all the measurements were performed at triplicate samples for THg and other metals. THg represents the sum of methyl Hg, Hg^{2+}, Hg, and other Hg compounds that are measured in an environmental sample, and it is the most commonly measured component because of the high cost of compound-specific Hg analysis. Using different methods, the digestion of THg was performed for fish [48], for sediment [49] and for HSH samples [50]. All six digests were subsequently diluted to the fixed volume (25 mL) with deionized water. Total Hg concentrations were then measured at triplicate ones using hydride generation

atomic absorption spectrometry (HGAAS; UNICAM 939 AA spectrometer equipped with a VP-90 vapor system, UK).

In order to measure Pb, Cu, and Zn concentrations, triplicate 25 mL samples prepared were first adjusted to pH range of 2.2–2.8 and then subjected to ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone (MIBK) extraction according the Standard Methods [51]. The samples were enriched to 5 mL and kept in refrigerator at 4°C for the subsequent Pb, Cu, and Zn analysis using flame atomic absorption spectrometry (Perkin Elmer 3100, Norwalk, CT). MIBK was used as a blank.

The concentrations of heavy metals are expressed as microgram per gram wet weight of muscle tissue of fish samples and microgram per gram dry weight of sediment and HSH samples. The absorption wavelength and detection limits were 253.7 nm and 0.002 ppm for Hg, 283.3 nm and 0.022 ppm for Pb, 324.8 nm and 0.012 ppm for Cu, and 213.9 nm and 0.002 ppm for Zn, respectively.

Statistical Analyses

All statistical calculations were performed with SPSS packet program. Because some of the variables were not normally distributed, the non-parametric *t* test (Mann–Whitney *U*) was applied to identify differentiation of fish species, of regional differences in sediment samples, and of HSH from people consuming the fish and non-fish eaters. Kendall test provided the correlation between toxic metal concentration and the parameters (such as length, weight, age, depth, etc.) of the samples. Possibilities less than 0.05 ($P<0.05$) were considered statistically significant.

Results and Discussion

Fish

The length and weight of the fish samples varied from 14.4 to 22.7 cm and 40.0 to 118.2 g for sole, 7.4 to 14.1 cm and 12.0 to 52.1 g for red mullet, 13.4 to 27.5 cm and 30.2 to 208.5 g for hake, and 13.8 to 32.9 cm and 40.5 to 445.7 g for grey mullet. The ranges of all samples for each species group are listed in Table 1, which further includes the overall mean and standard deviations of the THg and Pb concentrations in the muscle tissues. The highest concentrations of THg (2.66 μg/g) were observed within the demersal fish species *S. solea* living close to the bottom, which were likely to be impacted by nearshore anthropogenic activities (Fig. 2). Soles are known to be a target fish species for bioindicator of marine ecosystem health because of its food uptake from highly polluted sediment [52, 53]. The overall mean THg concentration of the samples is 0.62 μg/g. The second highest overall mean THg concentration of 0.57 μg/g is found for the another demersal red mullet, *U. moluccensis* (Fig. 2). Significant correlations ($P<0.01$) were only observed between THg concentration in *U. moluccensis* muscle and their total length and body weight. Due to high mobility, red mullets, being bottom dwellers to a certain extent, are species that tend to increase contaminants to a higher degree than other species. For this reason, it was recommended as monitoring species in coastal eutrophication programs by FAO/UNEP [54]. Although *M. barbatus* and *U. moluccensis* are both red mullet, these species differ in terms of living regions and feeding behavior. While *M. barbatus* lives over the muddy bottom of the continental shelf (100–300 m), *U. moluccensis* lives in coastal tropical inshore waters at depths of 10–80 m. The results of this study show that THg seems to be

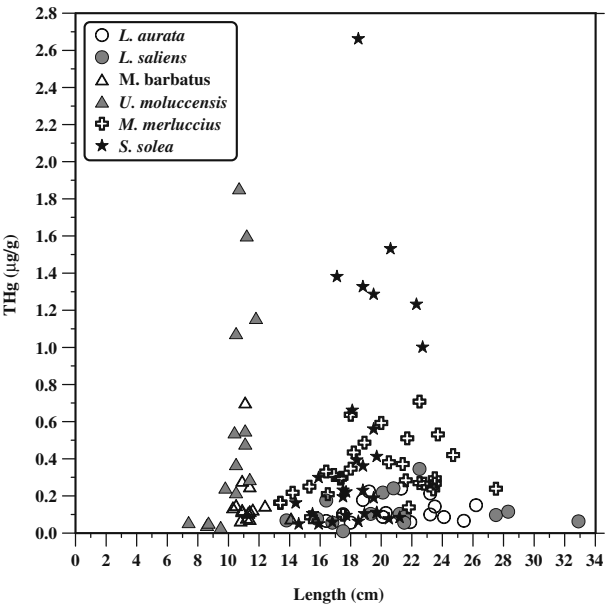

Fig. 2 Variations of THg concentrations with respect to length of fish samples

more concentrated in *U. moluccensis*. On the contrary, grey mullet (*L. aurata* and *L. saliens*) species living preferentially close to the surface and feeding on the bottom, attained relatively less overall mean THg concentrations of 0.13 and 0.12 µg/g, respectively (Table 1, Fig. 2). Considering the fact that international marketing limit for THg concentration in fish muscle tissues set in the European Union, the USA, and Canada (based on WHO guidelines) is 0.5 µg/g ww [55–57], the demersal fish species of *S. solea* and *U. moluccensis* caught in the KFA region in Mersin are considered to be contaminated by fairly high THg, and therefore. are highly harmful for people, especially pregnant women, children under 15 years of age, and frequent fish consumers. The recommended WHO limit for these consumer groups is even lower and set to 0.2 µg/g ww [13, 58]. We recall that the toxicity analysis in our samples was performed in fish muscles because it is the main fish part consumed by humans and implicated in health risk, and therefore, the THg concentrations were found slightly lower than those reported elsewhere in other tissues such as liver, kidneys, gills, and gonads of fish [9, 20, 22, 59]. Fish has been known as a source of nonoccupational mercury exposure to fish-consuming population groups [16]. Therefore, we were interested in the contamination level accumulated at the consumable parts of the fish.

We found that Pb concentration in *U. moluccensis* ($P<0.01$) and *M. merluccius* ($P<0.05$) muscle significantly correlated with both their total length and body weight. The further data suggested a different Pb accumulation in the fish groups (Table 1). Red mullets and hake revealed highest overall mean Pb concentrations greater than 1.0 µg/g, whereas the maximum concentrations exceed 2.0 µg/g (Fig. 3). Pb concentrations in most of the red mullets and hake samples either comparable or greater than the limit of 1.5 µg/g set by the Australian National Health and Medical Research Council [3, 60]. These Pb values are also higher than those found in Mersin and Izmir Bay of Turkey [8, 61]. Interestingly, *S. solea* did not show any significant Pb accumulation contrary to the case of THg. For all *S. solea* samples, Pb concentrations were too low to be measured because they were below the detection limit of the instrument. The lowest concentration of 0.009 µg/g in sole was found

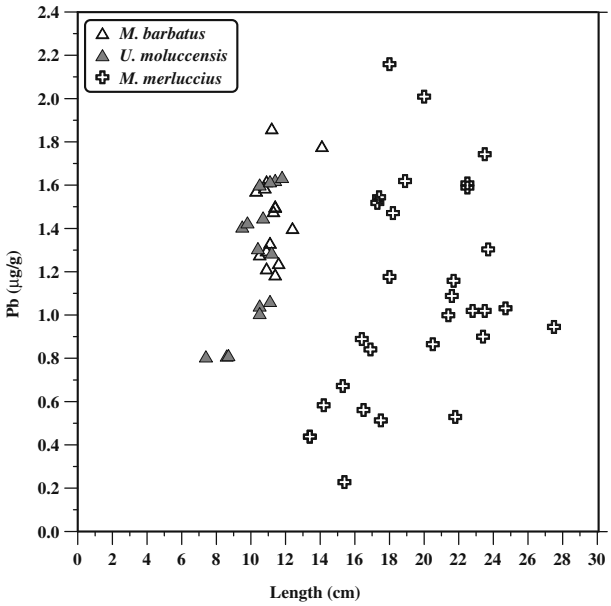

Fig. 3 Variations of Pb concentrations with respect to length of fish samples

as well by Celik et al. [61] in Izmir Outer Bay, Turkey. We observed similar low Pb concentrations at grey mullet species, as also reported by Usero et al. [53].

We determined an increasing tendency in the samples, indicating that THg and Pb concentrations ranged from the pelagic grey mullet (*L. saliens*), to the demersal species hake (*M. merluccius*), red mullet (*U. moluccensis*), and sole (*S. solea*), but Pb concentrations for *S. solea* were low. On the other hand, Cu and Zn concentrations were always below the detection limit of the instrument for all fish species. Thus, our findings are generally consistent with the studies indicating lower concentrations of heavy metals in pelagic fish species as compared to their benthic counterparts [9, 62].

Sediment

The Numerical Sediment Quality Guidelines (SQGs) have been developed using a variety of approaches (Table 2). They have been selected by individual jurisdictions depending on the receptors that are to be considered (e.g., sediment-dwelling organisms, wildlife, or humans), the degree of protection that is to be afforded, the geographic area to which the values are intended to apply (e.g., site-specific, regional, or national), and their intended uses (e.g., screening tools, remediation objectives, identifying toxic and not-toxic samples, and bioaccumulation assessment) [63].

Recently, two SQGs have been developed independently for marine environment by the National Oceanic and Atmospheric Administration (NOAA) [64] and for Florida [65] The NOAA guidelines provide two values for each chemical, which identify sediment that is rarely (less than effects range low, or ERL) and frequently (greater than ERM) associated with adverse biological effects. Threshold effect level (TEL) and probable effect level (PEL) are counterparts of ERL and ERM, respectively developed specifically for Florida. Low-range values (i.e., ERLs or TELs) were intended as concentrations below which adverse effects upon sediment-dwelling fauna would be expected only infrequently. In contrast, the ERMs and PELs represent chemical concentrations above which adverse effects are likely to occur.

Table 2 Descriptions of the Published Numerical Sediment Quality Guidelines (SQGs) for Marine Environment

Type of SQG	Acronym	Description	Ref
Threshold effect concentration SQGs			
Threshold effect level	TEL	Sediments are considered to be clean to marginally polluted. No effects on the majority of sediment-dwelling organisms are expected below this concentration	[65]
Effect range–low	ERL	Represents the chemical concentration below which adverse effects would be rarely observed	[64]
Probable effect concentration SQGs			
Probable effect level	PEL	Sediments are considered to be heavily polluted. Adverse effects on the majority of sediment-dwelling organisms are expected when this concentration is exceeded	[65]
Effect range–median	ERM	Represents the chemical concentration above which adverse effects would frequently occur	[64]

Evaluations of the reliability and predictive ability of the SQGs indicate that they can be used effectively to assess the quality of soft, aqueous, sedimentary deposits. The SQGs can be used to classify sediment samples for toxicity, to identify contaminants of concern, and to prioritize areas of concern based on the frequency and degree to which guidelines are exceeded [66].

A variety of SQGs can be used to rank and prioritize chemicals in samples. The choice of whether to use the ERL/TEL or ERM/PEL values or others should be predicated upon the probability of toxicity (i.e., level of risk) that is considered tolerable or acceptable (Table 2). If a relatively low level of risk to sediment dwelling organisms is tolerable, ERL/TEL values should be used. However, they should be used with an understanding that concentrations exceeding these values by minor amounts are likely to be associated with relatively low probabilities of toxicity. If a higher level of risk is tolerable, then the ERM/PEL values should be used to identify chemicals of potential concern [66].

The mean of each triplicate THg, Pb, and Cu concentrations at the MP site varied from 0.17 to 5.00 μg/g, from 6.23 to 32.37 μg/g, and from 5.19 to 34.17 μg/g, respectively. The overall means of all measurements are 2.30, 19.02, and 18.23 μg/g, respectively. Considering the fact that the corresponding ERM and PEL value of Hg is 0.7 μg/g, the mercury contamination at the MP site is comparable with the ERM and PEL (Table 3). However, THg concentrations around 1.0–5.0 μg/g were measured at eight locations out of ten (Table 4). The triplicate mean THg concentration of every depth is however an order of magnitude higher than its ERL value of 0.15 μg/g, which indicates the level of contamination tolerated by the majority of benthic organisms. On the other hand, Pb and Cu contaminations were found to be insignificant with the overall mean concentrations in order of magnitude less than their ERM values of 218 and 270 μg/g, respectively. Their maximum concentrations were measured not more than about 30 μg/g. The overall mean concentrations of Pb and Cu are comparable with their corresponding TEL values.

At KFA site, the concentrations were generally higher. The overall mean concentrations of all measurements are 2.65, 45.61 and 44.67 μg/g for THg, Pb, and Cu, respectively (Table 4). This implies twofold increase of the Pb and Cu concentrations with respect to those measured in the MP site. This increase was found to be related to their rather high concentrations (more than 100 μg/g) in some locations of the KFA region. These values are still below the ERM value of 270 μg/g for Cu and 218 μg/g for Pb. On the other hand, the

Table 3 Comparison of Maximum Sedimentary Heavy Metal Concentrations Measured at MP and KFA Regions with the Threshold and Probable Effect Concentration Values Reported at Sediment Quality Guidelines (SQGs)

Element	Type of SQG				Maximum Detection	Location
	Threshold effect concentration SQGs		Probable effect concentration SQGs			
	TEL	ERL	PEL	ERM		
Hg	0.13	0.15	0.70	0.71	5.00	MP
Pb	30.2	46.7	112	218	143.5	KFA
Cu	18.7	34	108	270	143.4	KFA

All values are given as microgram per gram dw

triplicate mean THg concentrations lie within the range of 0.56–4.75 μg/g, and their overall mean exceeds ERM and PEL values of the MP site.

In summary, the level of mercury contamination is severe in both sites, whereas the other contaminations stay around their effect range low. Zn concentrations were always below the

Table 4 THg, Pb, and Cu Concentrations (μg/g dw) in the Sediment Samples Measured at Different Depths at the KFA and MP Regions

Sample No	Region	Depth (m)	THg (μg/g) X[a]±SD	Pb (μg/g) X[a]±SD	Cu (μg/g) X[a]±SD
1	KFA	0.15	2.69±0.14	28.92±2.24	12.71±0.15
2	KFA	0.30	1.16±0.39	49.92±3.32	13.44±0.39
3	KFA	0.70	1.25±0.48	9.83±1.89	5.85±0.48
4	KFA	2.50	3.75±0.07	143.5±4.74	57.03±0.07
5	KFA	2.75	2.76±0.31	46.83±0.94	143.4±0.31
6	KFA	3.00	0.56±0.04	16.00±0.24	9.95±0.03
7	KFA	3.50	3.68±0.03	117.1±1.92	141.5±0.03
8	KFA	4.00	3.25±0.07	12.58±0.12	8.80±0.07
9	KFA	4.50	4.75±0.35	17.50±1.42	35.04±1.35
10	KFA	6.00	2.69±0.71	13.89±0.95	18.95±0.70
		Overall mean[b]	2.65±0.26	45.61±1.78	44.67±0.36
11	MP	7.50	2.02±0.23	17.81±0.41	18.80±0.63
12	MP	10.00	0.75±0.06	21.61±0.39	15.33±0.06
13	MP	10.25	3.67±0.45	32.37±0.60	34.17±0.08
14	MP	11.00	3.40±0.70	30.00±0.67	31.67±0.67
15	MP	12.50	0.85±0.29	17.94±1.27	5.39±0.29
16	MP	13.00	2.82±0.89	9.50±0.24	10.94±0.89
17	MP	13.50	3.82±0.04	19.67±1.73	17.54±0.03
18	MP	14.30	0.47±0.06	17.28±1.27	14.38±0.06
19	MP	16.30	5.00±0.43	17.78±2.78	28.88±0.43
20	MP	20.00	0.17±0.07	6.23±0.54	5.19±0.06
		Overall mean[b]	2.30±0.32	19.02±0.99	18.23±0.32

[a] Results are presented in the form of triplicate means and their standard deviations

[b] Overall mean values of ten determinations in every region

detection limit for all the sediment samples. The results we obtained revealed no statistically significant differences in Hg, Pb, and Cu concentrations between two sampling regions (Mann Whitney U, $P<0.05$). The mean mercury concentrations in our sampling sites seem to be half of those measured in the Gulf of Trieste (5.04 μg/g), which is an exceedingly polluted region due to historic cinnabar mining in the catchment [67]. They are however comparable with those in the Yatsushiro Sea off Japan [68]. High mercury levels were reported at a number of sites in Azerbaijan, exceeding the ERL value of 0.15 μg/g. On the other hand, our results agree with the low sediment Pb and Cu concentrations investigated in Caspian Sea. The maximum concentration of 28.6 μg/g was found just south of Baku Bay, but the Pb levels never exceeded the ERL value of 47 μg/g. Although one hot spot of 49.5 μg/g was observed off southern Kazakhstan, Cu concentrations were much lower in the northern Caspian Sea as it was in our MP values. In contrast, the Cu content exceeded the ERL value of 34 μg/g at several locations in Azerbaijan and Iran [69] like our data obtained from KFA.

Human Scalp Hair

Figure 4 illustrate the THg, Pb, and Zn concentrations in HSH samples from fish consumer and non-consumer groups, respectively, for their age groups. Expectedly, the HSH samples reflect a similar trend of contamination detected at fish and sediment. The THg concentrations lie within the mean of triplicate samples 0.143–1.019 μg/g (Fig. 4) with the overall mean value of 0.43 μg/g (Table 5) at samples collected from people who never consumed fish. For the samples collected from people who regularly consume the fish chosen in the study, both the range and mean THg concentration showed considerable differences. The measurements covered a wider range between 0.403 and 3.284 μg/g (Fig. 4) with their overall mean of 1.06 μg/g (Table 5), which is almost twice of the former case.

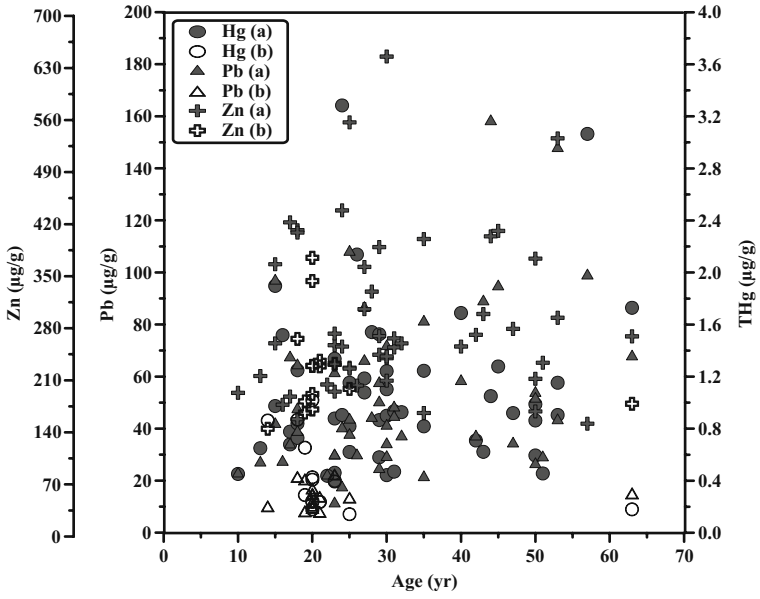

Fig. 4 Variations of THg, Pb, and Zn concentrations in the HSH samples with respect to age groups of people consuming regularly the fish (**a**) and non-fish eaters (**b**)

Table 5 THg, Pb and Cu Concentrations (μg/g dw) in the HSH Samples with Respect to Age Groups

Sample	Age (year)	THg (μg/g) $X \pm SD$	Pb (μg/g) $X \pm SD$	Zn (μg/g) $X \pm SD$
A	10–63	1.06±0.59	52.37±31.16	292±108
B	14–73	0.43±0.29	14.11±4.64	225±64

Except age groups results are presented in the form of means and their standard deviations

A: HSH samples taken from people consuming regularly the fish, *B*: HSH samples taken from non-fish eaters (control group)

Based on studies of the major THg poisoning event in Minamata (Japan), Harada et al. [70] have suggested 50 mg/g in hair as the threshold concentration for the onset of Hg poisoning. Our THg concentrations were below the "Minimata threshold" criterion (Table 5). Even for people regularly consuming fish in Mersin, hair THg concentrations are below the WHO criterion of 2 mg/g [58]. Although our data involve only THg measurements, they are consistent with the previous study in this region, indicating higher concentrations of methyl Hg in HSH samples from fish consumer as compared to non-consumer groups [24]. In other parts of the world, the mean hair THg levels of fish eaters were found markedly higher than the non-fish eaters, e.g., 21.9 μg/g in the Lake Murray area and 0.75 μg/g in the upper-Strickland area of Papua New Guinea, around 4.07 and 0.38 μg/g in Hong Kong [17, 71].

Pb concentration varies between the range of 8.00 and 22.38 μg/g and 11.16–158.04 μg/g in HSH samples collected from people non-consuming and consuming the fish, respectively (Fig. 4). Its overall mean concentration of 14.11 μg/g for the non-fish consumers is three times smaller than that of 52.37 μg/g for the fish consumers (Table 5). However, the means of HSH Pb concentrations obtained in the present study were much higher than the critical value of 20.0 μg/g reported by the German Federal Health Agency [32, 72]. Thus, Pb content in hair samples suggests the exposure of individuals to this element. The differences of THg and Pb concentrations between HSH samples from these two different groups were found to be statistically significant at the level of $P<0.001$ [73, 74].

Zn concentrations exhibited a different character as compared to THg and Pb because it is an essential element abundantly available in human hair. Therefore, their co-occurrence in the scalp hair of individuals should be considered normal, and its limitation leads to alopecia. Therefore, its toxic contamination is not expected to be significant as for the other elements as suggested by the mean Zn concentrations of 292.2 and 224.8 μg/g for the fish consumer and non-fish consumer groups, respectively (Table 5). Their range lies between 144.9 and 645.3 μg/g (Fig. 4). On the other hand, Cu concentrations were always below the detection limit for all the HSH samples.

Conclusions

This study fills a gap on the bioaccumulation of heavy metals in sediment, fish, and HSH along the southern coast of Turkey. Because sediments serve as a repository for a large number of environmental contaminants, it is comprehensible that demersal fish may accumulate more toxic compounds, given their close contact with sediment particles and interstitial water for extended periods of their life cycle. Fish samples for this study involve pelagic and demersal species. In fact, both sediment and demersal samples showed highest THg and Pb levels. Muscle analyses provided a first picture of metal concentration levels in

fish frequently consumed by Mersin inhabitants. KFA is mantled with sediment containing 90% of the samples exceeding their respective ERM concentrations, and based on NOAA data, these sediments may be referred to as toxic. Forty percent of sediment samples for Pb and Cu exceed their respective ERL and TEL, indicating a threshold level. Our findings demonstrate that there are high levels of THg in the sediments of KFA due possibly to heavy industry around the site. The imminent risk of THg contamination through the consumption of fish from this water body could represent a human health risk. Assimilated by humans, the incorporation of mercury into the food chain is in fact a universally recognized potential health hazard. Considering the risk to human health, preventive measures should be taken. In addition, the levels of metals detected in HSH samples are at acceptable levels for human. A potential danger may however occur in the future depending on the agricultural and industrial development in this region.

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