

A Survey on the Accumulation of Trace Metals in Local Fishermen Hair from the Northern Persian Gulf

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Abstract

The concentrations of trace metals in hair of fishermen from the Persian Gulf region were assessed to detect the relationships between element levels in hair and potential factors influencing these relationships. The hair of 19 fishermen were sampled from six stations in the Persian Gulf (*Abadan, Deylam, Bushehr-Nirogah, Dayyer, Lengeh and Bandar Abbas in Khuzestan, Bushehr and Hormozgan provinces*) and analyzed by Inductively Coupled Plasma Mass Spectrometry inductively (ICP-MS) and Cold Vapor Atomic Absorption Spectrometer to detect the trace metals and mercury levels, respectively.

In this study we did not find significant correlation between fish diet and hair element levels, except for mercury ($r=0.74$, $P=0.01$). Our results demonstrated that the average concentrations of Cr, As and V in different stations were almost comparable, while the accumulation of Cu, Zn, Pb and Co in hair samples from Lengeh were much higher than those of other regions. Statistical analysis demonstrated that a positively strong significant correlation ($p<0.05$) existed between V, Cr, Co, Cu and Zn concentrations in the human hair, which might have been originated from similar sources. The accumulation levels of Cd, Cu and Cr in our results were much lower than the corresponding accepted levels. The hair samples contained arsenic in high concentrations, as against arsenic level in normal healthy hair. Ninety percent of detected Pb levels were below $110 \mu\text{g g}^{-1}$ as dangerous level. Among the detected elements in hair, Pb, Ni and As could be used as marker of environmental exposure.

Keywords: *Trace metals, Methylmercury, Fishermen hair, ICP MS, Persian Gulf*

1. Introduction

People are exposed to toxic metals in the environment via food, air, water, and soil, which can produce health risks (Nowak and Chmielnicka, 2000; Passos et al., 2003). Recent researches have indicated that there is a direct relationship between the hair metal contents and environmental exposure

such as vehicular emission and occupational exposure (Vishwanathan et al., 2002). Among the trace metals, there are some elements (As, Ni, Tl, Hg, Cd, Pb and Sb), which are toxic even at quite low concentrations, whereas others (Ca, Co, Cr, Cu, Mn, Mo and Zn) are biologically essential and natural constituents of the aquatic ecosystems and only become toxic at very high concentrations.

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Scalp hair is a metabolic end product that incorporates metals into its structure during the growth process (Ashraf et al., 1994). Trace metal analysis on hair samples have been used to assess human exposure to toxicants, as early as 1931. In recent decades, human hair analysis has attracted attention of more scientists as one of the best methods (Bass et al., 2001), which provides a superior insight into average environmental metals exposure in time-scales ranging from weeks to years.

In comparing blood and urine, which tend to show current or recent body status, analyzing hair samples represents a longer time frame (with an average of 1 cm growth rate per month), potentially years with several advantages namely: (i) easily collected, simple storage and transport; (ii) a high stability; (iii) presence of higher concentrations allowing more sensitive and more accurate results and (iv) cheap analysis (Bass et al., 2001; Pereira et al., 2004).

The main objectives of the present study are investigating the heavy metal levels in human scalp hair from the northern parts of the Persian Gulf and assessing the relationships between element levels in hair and potential factors influencing these relationships. In this study, it is the first time that trace metals as well as methyl mercury in the hair of fishermen and in the muscle of consumed fishes throughout the northern areas of the Persian Gulf are analyzed.

2. Materials and Methods

The Persian Gulf as a shallow sea with an average depth of 30 m, is located in the south and southeast of Iran. The population of the Northern coastal areas in the Persian Gulf is known to consume substantial amounts of fish, and hence fishermen are a good target group to study the relationship between heavy metals accumulation in the body and seafood ingestion. In this investigation, scalp hairs of 19

randomly selected fishermen were collected at six stations in the Iranian coasts of the Persian Gulf, at least three participants in each station. Sampling was performed in January 2004. Figure 1 shows the sampling locations: 1) Abadan, 2) Bandar Deylam, 3) Bushehr-Nirogah, 4) Bandar Dayyer, 5) Bandar Lengeh and 6) Bandar Abbas. The selected sampling sites represent the most important harbors and industrial and agricultural regions in the Khuzestan, Bushehr and Hormozgan provinces. In order to assess the relationship between metals accumulation in hair and consumed fishes, 141 specimens of five fish species were collected from the same stations and analyzed for selected metals. The details are described in Agah et al., (2008).

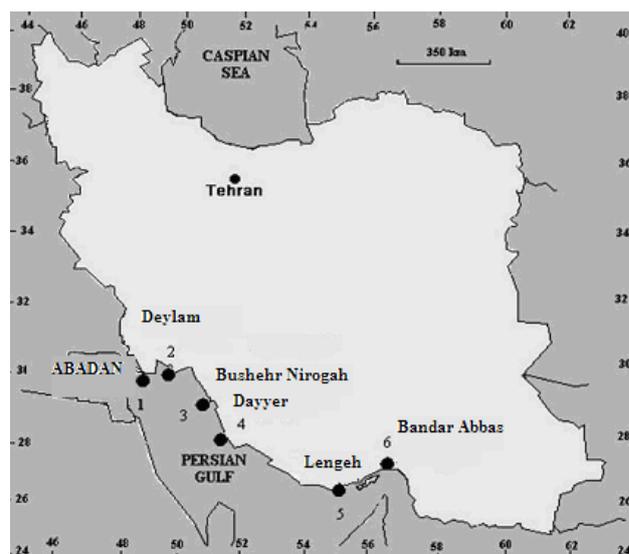


Fig. 1: Study area

In order to eliminate all external elements contamination, hair samples (about 0.5 to 1 gr) were cut by stainless steel scissor as close to the scalp as possible from nape of the neck with less contamination than for example front face hair (Steen, 1991). In this investigation, none of the participants used chemical products on his hair (McDowell et al., 2004). The hair samples were stored in plastic bags with identification tags and shipped to the laboratory for further treatment and analysis. In the laboratory, the hair strands were cut

into approximately 2-3 mm pieces with stainless steel scissor. Then, they were cleaned according to the IAEA (1997) cleaning procedure (Bass et al., 2001). Samples were washed 5 times with diluted laboratory detergent (Extran), (1:200 v/v) with deionized Milli-Q water, rinsed three times with Milli-Q water, and at the end rinsed with acetone (Analytical grade, Merck).

A washing cycle included 20 minutes immersion in each of the solutions while a mechanical shaker was mixing them intensively, and then, a 2 minutes centrifugation. Finally, the hair samples were dried in an oven at $60 \pm 5^\circ\text{C}$ overnight (Pereira et al., 2004). The pre-washed hair samples were stored in clean plastic bags.

All participating fishermen were asked to fill in a questionnaire providing information regarding their age, career as a fisherman, habitation area, health status (diseases and in particular information about cancer background in their family, number of amalgam filled teeth), source of drinking water and their diet (number of fish meals per week, preferred fish species, vegetable and fruit consumption) to detect potential factors influencing element levels in the human hair.

2.1. Analytical Procedure

All Teflon and glasswares used for extraction and analyses were cleaned thoroughly with laboratory detergent (Extran 2%), soaked overnight in 5% nitric acid solution and finally rinsed with deionized (Milli-Q) water. All reagents were of analytical grade.

To mineralize the hair samples, acid digestion was performed in a closed microwave oven. Aliquots (about 0.15 g) of dry hair samples were accurately weighted into 50 ml digestion vessels, followed by acid digestion using 6 ml HNO_3 (65%, Merck, Suprapur) and 1 ml H_2O_2 (30% Merck, Suprapur) (Muhaya et al., 1998). Trace metals (Co, Ni, Cu, Zn,

As, Cd, Pb, Cr, V) analysis were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a VG-Elemental model PQ2 instrument (Thermo-Finnigan) (Nguyen et al., 2005). Mercury was analyzed using Cold Vapor Atomic Absorption spectrometer (CVAAS, Hg Analyzer II, Thermo Separation Products) (Leermakers, 2003).

Methylmercury was analyzed by aqueous phase ethylation, headspace gas chromatography separation (Perkin Elmer HS 40) of the ethylated compounds, pyrolytic decomposition and atomic fluorescence detection (Tekran 2500) (Leermakers et al., 2003). All pretreatments and analysis were performed in the laboratory of Vrij University of Brussels.

In each sample batch, procedural blanks and Reference Materials were included. The precision and accuracy of the applied analytical method was estimated on Certified Reference Materials (CRMs), IAEA 086 (Mercury and trace metals in human hair-*Monaco*), **Dorm2** (mercury and trace metals in dog fish muscle) and **Tort2** (mercury and trace metals in *Lobster Hepatopancreas*) provided by the National Research Council of Canada. As there are a limited number of CRMs available for elements in hair, forcibly for some elements we used reference materials of other tissues. The results of the certified reference materials showed good agreement with certified values in respect to almost all the elements (Tables 1 and 2) and methylmercury.

The results of zinc and copper (157-177 and 17-19 $\mu\text{g. g}^{-1}$, respectively) analysis in IAEA 086 reference material were in a good agreement with the certified values (159-174 and 16.6-18.5 $\mu\text{g. g}^{-1}$, respectively).

The limits of detection (ng. g^{-1}) were set as three times the standard deviation on the procedural blanks and for methylmercury (MMHg) were set as three times the baseline signal resulting in values of 0.004 ng. g^{-1} . Detection limit of the elements were: As:0.09; Cd:0.14; Cr:4.14; Co:0.14; Cu:3.2; Pb:1.6; Ni:1.04; THg:12; V:0.09; Zn:16 $\mu\text{g. g}^{-1}$.

Table 1: Total mercury concentration in $\mu\text{g. g}^{-1}$

RM	Hg			MMHg		
	Certified value	Our results	Recovery	Certified value	Our results	Recovery
TORT-2	0.27±0.06	0.297±0.005	110±2 (n=6)	0.152±0.013	0.151±0.011	99±7 (n=12)
DOLT-3	3.37±0.14	3.38±0.07	100±2 (n=6)	-	-	-
DORM-2	4.64±0.26	4.39±0.10	95±2 (n=20)	4.470±0.320	4.468±0.023	100±5 (n=7)
IAEA 407	0.216-0.228	0.224±0.002	102±1 (n=4)	0.200±0.021	0.203±0.012	102±6 (n=3)
IAEA 086	0.534-0.612	0.554-0.612	102±4 (n=5)	0.236-0.279	0.238-0.272	96±5 (n=5)

Table 2: Metals concentrations in $\mu\text{g. g}^{-1}$

Elements	Dorm 2 (Mussels) n=8			Tort 2 (liver), n=5		
	Certified values	Measured values	Recovery	Certified values	Measured values	Recovery
As	18.0±1.1	17.99±0.45	100±3	21.6±1.8	21.69±1.03	100±5
Cd	0.043±0.008	0.041±0.003	96±8	26.7±0.6	26.4±0.7	99±3
Cr	34.7±5.5	33.67±0.95	107±3	0.77±0.15	0.74±0.075	103±2
Co	0.182±0.031	0.186±0.009	102±5	0.51±0.09	0.52±0.026	103±5
Cu	2.34±0.16	2.31±0.09	94±4	106±10	108.3±3.1	102±3
Pb	0.065±0.007	0.061±0.008	94±13	0.35±0.13	0.34±0.018	98±5
Ni	19.4±3.1	18.77±0.86	97±4	2.5±0.19	2.65±0.21	106±8
V	-	-	-	1.64±0.19	1.76±0.08	107±5
Zn	25.6±2.3	25.25±0.78	99±3	180±6	186.6±4.2	104±2

2.2. Statistical analysis

All statistical analyses of the data including correlation and regression calculations were carried out using SPSS V13. Spearman correlations were calculated between element concentrations. In order to classify and reduce the variables and to detect the relationships between them with greater certainty, Principal Component Analysis (PCA) was performed. Prior to PCA, a Kolmogorov-Smirnov test was performed to analyze normality of data distribution. In addition, one way ANOVA and factor analyses were used to assess significant differences between the mean element levels in different sampling stations. A P-value equal or lower than 5 % indicated that significant relationship between the corresponding variables existed.

3. Results and Discussion

Exposure related factors included in the questionnaires, average concentrations of trace metals in hair of the participants and methylmercury values are summarized in Tables 3 and 4.

In our study, the detected concentrations of the metals and methyl mercury (triplicate measurements)

were higher than the corresponding detection limits. The age of the studied fishermen ranged from 19 to 78 years. Based on a statistical outlier test performed in SPSS 13, participant 11 in Bandar Dayyer exhibited an unusual mercury level in his hair ($39.5\pm 0.5 \mu\text{g g}^{-1}$).

This value was statistically an outlier and not used in subsequent mercury calculations. The total mercury level in the hair of this participant was ten times higher than that for the other participants in the same region and six times higher than the second highest hair level. Fish was the only protein source for this participant. The mean total mercury level in the hair of the fishermen (excluding participant 11) was $2.9\pm 2.2 \mu\text{g g}^{-1}$ with a median of $1.98 \mu\text{g g}^{-1}$.

The relative distribution of the total Hg levels in the hair of the fishermen was as follows: 10 % of the results were lower than $1 \mu\text{g g}^{-1}$, 53 % were between 1 and $3 \mu\text{g g}^{-1}$ (slightly over half were found to have mercury levels above the US EPA advisory level of $1.0 \mu\text{g g}^{-1}$) and 37 % were between 3 and $7 \mu\text{g g}^{-1}$. Methylmercury accounted for 50 to 85 % of the total mercury amount (one exception at 40%) with an average of 68 % (Table 3).

In the present study, the mercury level in the fishermen hair (n=19) was lower than $10 \mu\text{g g}^{-1}$, (the WHO warning limit), except for one participant.

Table 3: Exposure related factors included in the questionnaires, THg and MMHg in the hairs of the participants.

Stations	P*	Age	Career**	Fish meals/week	Amalgam filled tooth	Disease-Cancer background	Consumed fishes	Fruit & vegetables
Abadan	1	42	25	7	0	None-None	To-Ti- G♣	Once per week♣ ▼
	2	22	9	4	0	None-None	Hi-Wh ♣	Once per 10 days ♣ ▼
	3	34	8	3	2	None-None	Ti-To-Hi ♣	Once per week♣ ▼
Deylam	4	27	12	6	0	Head ache-4 persons	Ti-Gr- Na -Ye-Fl ♣	Twice per week ♣ ▼
	5	31	15	3	0	None- 1person	Ti-Gr-Fl-Fo ♣	3-4 times per week ♣ ▼
	6	28	17	6	0	Dizziness-None	Ti-Hi-Fl-Na ♣	Every day ▼
Bushehr	7	36	5	3	3	None-None	G-Fl ♣	4-5 times per week ♣ ▼
Nirogah	8	30	5	2	4	None-None	Na ♣	3-4 times per week ♣ ▼
	9	30	25	9	0	None-None	G-Na- Ti-Ki- Si ♣	Every day ♣ ▼
Dayyer	10	30	6	3	4	Muscle pain-None	G-Ki- Pi-Sk ♣	1-2 times per week ♣
	outlier	11	29	6	11	0	None-None	Gr-Ki-Ti-Wh-In ♣
Lengeh	12	21	8	7	0	Dizziness-None	G-Fo-Ye ♣	Every day ♣ ▼
	13	18	5	6	0	None-None	Sk- Na-Si ♣	3-4 times per week ♣ ▼
	14	33	12	8	0	None-None	Si-Wh-Ki-Ti ♣	4-5 times per week ♣
	15	36	5	4	0	None-None	Sk-Ki-Si ♣	Every day ♣ ▼
	16	19	8	6	0	None-None	Si-Na-Sk ♣	Every day ♣ ▼
Babdar Abbas	17	40	10	5	0	None-None	G-Sk-Ma- Bu-Ka- Pi-♣	3-4 times per week ♣
	18	54	25	4	7	Muscle pain-None	G-Sk-Ti-♣	Every day ♣ ▼
	19	34	12	7	1	Dizziness- None	Sk-G-Pi-Ma ♣	Every day ♣ ▼

*-P: Participants, **-Career as a fisherman,♣ -Orange or apple ▼ -Vegetables ♣ -K: Kawakawa, To: Tonguefish; Ti: Tiger-Tooth; Na: Narrow barred spanish marckerel (Scombridae); Gr: Greasy Grouper; G: Grunt, F: Flathead; Fo:Fourfinger Threadfin; Mu: mullet; Si: Silver Pomfret; Pi: Pinjalo snapper; Sk:Skipjack tuna; Ye: Yellowfin sea bream (Porgies); Ki: King mackerel; Bu: Bull shark (Requin shark); Wh: Whitening Wof-herring; In: Indian Spiny turbot; Ma: Indian Mackerel., Hi: Hisa Shad.

Table 4: Concentrations of elements, (mean±sd, µg. g⁻¹), in the hair of fishermen.

stations	V	Cr	Ni	Cu	Zn	Pb	Co	As	Cd	Hg	MMHg %
Abadan	1.3±0.0	1.7±0.1	2.5±0.7	10.1±1.5	217±22	2.3±0.1	0.07±0.00	0.5±0.0	0.11±0.01	6.6±0.4	79
	1.1±0.1	1.5±0.3	1.8±0.0	14.0±2.7	185±24	8.2±0.7	0.07±0.02	0.4±0.1	0.42±0.01	5.5±0.1	75
	1.0±0.0	1.4±0.1	2.3±0.1	11.5±2.3	231±21	2.3±0.1	0.19±0.03	0.4±0.0	0.14±0.00	2.6±0.0	40
Deylam	1.3±0.2	1.9±0.4	3.5±0.2	18.0±0.8	207±4	16.9±0.8	0.12±0.02	0.5±0.1	0.15±0.02	6.1±0.1	79
	1.3±0.1	1.6±0.1	5.1±0.4	11.2±0.1	190±3	5.2±0.2	0.12±0.01	0.4±0.0	0.11±0.01	1.9±0.2	50
	1.2±0.1	1.4±0.0	2.3±0.3	8.0±0.2	172±5	4.2±0.2	0.08±0.00	0.4±0.0	0.13±0.00	6.5±0.5	69
Bushehr Nirogah	1.0±0.0	1.3±0.0	2.1±0.1	8.6±0.3	188±5	1.6±0.03	0.06±0.00	0.4±0.0	0.90±0.02	1.2±0.0	73
	1.1±0.1	1.7±0.1	4.5±0.5	11.6±0.5	168±3	12.9±0.3	0.12±0.0	0.5±0.0	0.19±0.03	0.8±0.1	77
	1.1±0.0	1.4±0.0	4.8±0.2	9.2±0.0	188±1	6.6±0.2	0.19±0.01	0.4±0.0	0.15±0.01	6.0±0.1	68
Dayyer	1.1±0.1	1.4±0.2	2.2±0.2	10.5±0.6	184±2	1.4±0.05	0.06±0.00	0.4±0.1	0.17±0.01	2.1±0.0	74
	1.0±0.0	1.4±0.0	2.5±0.2	9.0±0.2	176±5	1.5±0.1	0.06±0.00	0.4±0.0	0.09±0.00	39.5±0.5	36
	1.0±0.0	1.3±0.1	2.8±0.3	9.6±0.4	242±2	3.7±0.0	0.08±0.01	0.4±0.0	0.19±0.01	2.2±0.0	78
Lengeh	1.0±0.1	1.3±0.1	1.9±0.5	10.6±0.5	201±8	0.6±0.0	0.05±0.00	0.4±0.0	0.06±0.01	3.3±0.1	67
	1.5±0.1	1.9±0.1	2.5±0.3	22.2±0.5	363±2	85.5±1	0.27±0.05	0.4±0.0	0.35±0.02	1.6±0.1	78
	1.3±0.1	1.5±0.0	2.2±0.1	13.0±0.4	268±2	37.1±0.6	0.24±0.01	0.4±0.0	0.20±0.00	1.2±0.0	68
	1.2±0.2	1.5±0.1	4.2±0.1	16.2±8.7	186±2	23.4±0.6	0.25±0.01	0.4±0.0	0.19±0.01	0.8±0.0	65
Bandar Abbas	1.0±0.1	1.4±0.2	2.0±0.2	11.7±1.0	184±15	10.9±0.7	0.05±0.00	0.4±0.0	0.09±0.01	1.0±0.0	62
	1.1±0.1	1.5±0.1	1.9±0.4	12.8±1.3	184±6	1.4±0.1	0.05±0.01	0.4±0.0	0.07±0.01	1.8±0.0	73
	1.1±0.1	1.5±0.1	2.6±0.4	9.9±0.0	182±4	2.0±0.1	0.07±0.00	0.4±0.0	0.08±0.02	1.3±0.0	85

The ranges and median values of the trace metals ($\mu\text{g. g}^{-1}$) were: Zn:162-363 (206); Cu:8-22 (12); Hg:0.8-6.6 (2.9); Pb:0.7-86 (4); Ni:1.8-5.1 (2.8); Cr:1.3-1.9 (1.5); V:1-1.5 (1.2); As: 0.3-0.5 (0.4); Co:0.05-0.3 (0.1) and Cd:0.06-0.9 (0.2). According to the mean metal levels, the metal accumulation levels in the fishermen hairs lead to the following ranking: THg>Zn>Cu>Pb>Ni>Cr>V>As>Co>Cd.

Lead levels in majority of samples were below $110 \mu\text{g g}^{-1}$ as dangerous level, and 10 % of samples (in Lengeh) ranged slightly higher than excessive level ($\text{Pb}>30 \mu\text{g g}^{-1}$) (Ajayi et al., 2001). The hair samples contained arsenic in high concentrations, 0.4-0.5 p.p.m, as against 0.08-0.25 p.p.m in normal healthy hair (Health and environment, 2005).

Cadmium levels below 2 p.p.m in hair were considered current normal ranges for body (EBI, 2010). Copper and chromium normal ranges in hair are 11 to 40 and 50 to 100 p.p.m, respectively (ATSDR, 2008). Cadmium, copper and chromium levels in our results were much lower than accepted level.

3.1. Relationship between Trace Metals in Human Hair and in Fish Diet

In order to assess the relationship between element levels in the human hair and fish diet and other exposure factors, 141 fish specimen were sampled at the same hair sampling sites. Details of fish muscle analysis are explained in Agah et al., 2008. The concentration of elements in the fish muscle per species per stations in $\mu\text{g. g}^{-1}$ were: V: 0.003-0.04 Cr: 0.01-0.04, Co: 0.002-0.027, Ni: 0.02-0.08, Cu: 0.1-0.5, Zn: 4-5; As: 0.29-0.9, Cd: 0.002-0.02, Pb: 0.004-0.020 and Hg: 0.01-1.35 (Agah et al., 2008). In this study we did not find any significant correlation between element levels in hair and in the fish diet, except for mercury ($r=0.74$, $P<0.01$). In agreement with the other authors (Pereira et al., 2004; Ashraf et al., 1994), comparing the elements variations in hair and in the consumed fish muscle, demonstrated that the marine food was not the main metal exposure source for the local consumers, except for mercury.

Spearman correlation analysis between element levels in hair and exposure related factors demonstrated that there was a positive correlation between the number of fish meals per week and the MMHg concentrations in hair ($r= 0.43$, $P<0.05$). The Hg concentrations in hair increased from eastern to western sites ($r=0.71$, $P<0.01$). The results of our questionnaire analysis demonstrated that increasing the amount of vegetables and fruit in the daily diet could decrease the mercury accumulation in the human body ($r=-0.41$, $P<0.05$). The details are described in Agah et al., (2011). These results agree with those reported by Carrington and Bolger (2002) and Mahaffey (2000).

3.2. Comparison with literature data

An overview of some of the trace metal concentrations in human hair samples in different societies is shown in Table 5. The elements concentrations in biological samples vary considerably due to geographical differences, nutritional status and environmental factors (Gautam et al., 2004). Also the great variability in the detection of element levels, which usually exists between different laboratories (Seidel et al., 2001; ATSDR, 2003), should be considered in comparing the data with the reference values. Some parameters such as age, sex, dietary habits and environmental status that were sometimes not taken into account in the literature (Nowak and Chmielnicka, 2000), could have very important roles in the elements levels. The metal levels in our study have been compared with other literature data compiled by Iyenger et al., (1978) and Gautam et al., (2004).

Comparing our results for Zn and Ni in hair (206 and $2.8 \mu\text{g. g}^{-1}$, respectively) with other studies and reference value of Zn ($175 \mu\text{g. g}^{-1}$) (Iyenger and Woittiez, 1988) and Ni ($1.25 \pm 0.46 \mu\text{g. g}^{-1}$) (Caroli et al., 1994) demonstrated elevated levels, which indicated an environmental influence on the fishermen. The recommended Zn value in hair is between minimum $115-160 \mu\text{g. g}^{-1}$ to maximum $190-210 \mu\text{g. g}^{-1}$ (Ponzetta et al., 1998).

Table 5: Trace metal levels in the human hair from different societies (mg kg⁻¹).

Reference	Areas	Hg	As	Zn	Pb	Ni	Cd	Cu	Cr	Co
Our study	Persian Gulf/Iran	0.8-6.6(2.9)	0.4	206	12	3	0.2	12	1.5	0.1
ROPME, 1999	Persian Gulf /Kuwait	1.5-5.9	NA	NA	NA	NA	NA	NA	NA	NA
Passos, et al., 2003	Brazilian Amazon	4-20	NA	NA	NA	NA	NA	NA	NA	NA
Feng et al., 1998	Japan	4.6	NA	NA	NA	NA	NA	NA	NA	NA
	Indonesia	3.1								
	China	1.7								
Weihe et al., 2005	North Atlantic, Faroe Island		NA	NA	NA	NA	NA	NA	NA	NA
	-Women consumed whale	3.03								
	-Women without consumed whale	1.88								
Brhun et al., 1997	Chile	0.3-2.5	NA	NA	NA	NA	NA	NA	NA	NA
Shafaei, 2004	Tehran /Iran (Healthy)	0.1-2.4		700-900			0.48-0.85		33-42	NA
Takagi et al., 1986	India	NA	0.6	211	13	0.3	0.3	20	NA	NA
	Japan	NA	0.05	114	4	3	0.3	11	NA	NA
	Canada	NA	0.02	248	5.4	0.3	0.5	9	NA	NA
	USA	NA	0.01	150	2	0.4	0	16	NA	NA
	Poland	NA	0.02	160	2.5	0.5	0.3	9	NA	NA
Gautam , 2004	India Bengal	NA	3.4	152	8	2	0.4	15	NA	NA
Caroli et al., 1992	Italy	NA	0.1	144	8	0.7	0.2	22	NA	NA
Ponzetta et al., 1998	Indonesia	NA	NA	228	16	6	1	29	NA	NA
Oluwole et al., 1994	Nigeria	NA	0.1	129	NA	NA	NA	23	NA	NA
Nowak and Chmielnicka, 2000	Poland	NA	NA	25-276	1-8	2-7	0.3-1	1-13	0.4-3	Nd-1.6
Iyengar et al., 1978	Compiled	NA	0.1-4	99-450	3-70	0.6-6.5	0.2-2.7	11-34	NA	NA
Khalique et al, 2005	Pakistan	NA	NA	170	12	3	1	11	2	1

NA=Not Available; Nd= not detectable

Our results demonstrated that the zinc levels in the hair of 25% of participants were slightly higher than accepted level. Zinc value in the hair of one participant in Bandar Lengeh was much higher than accepted level; however, there is no symptom up to 1000 $\mu\text{g. g}^{-1}$.

The average lead value in our study (12 $\mu\text{g. g}^{-1}$) was relatively lower than that in other studies, i.e. Compiled (Iyengar et al., 1978) and Indonesia (Ponzetta et al., 1998), while the concentration of lead in our study was comparable with India (Takagi et al., 1986) and Pakistan (Khalique et al., 2005). Lead concentration in the hair of fishermen in our study was higher than that in the hair of Japanese (Feng et al., 1998), Americans (Takagi et al., 1986) and Poles (Nowak and Chmielnicka, 2000), Italians (Caroli et al., 1992), Indians, Bengals (Gautam et al., 2004) and Canadians (Takagi et al., 1986). It reveals that the concentration of lead in the human hair in our sampling areas is influenced by the environmental

exposure. The concentration of lead in the hair of fishermen in Bandar Lengeh (12 $\mu\text{g. g}^{-1}$) was 4 to 17 times higher than that in the other stations. Hence, considering the industrial outputs in the Bandar Lengeh is recommended. Concentrations of Cu (12 $\mu\text{g. g}^{-1}$) and Cd (0.2 $\mu\text{g. g}^{-1}$) in our research were lower than that in other societies, i.e. Canada (Takagi et al., 1986), Italy (Caroli et al., 1992) and Nigeria (Oluwole et al., 1994).

Although arsenic level in the fishermen hair in our study (0.4 $\mu\text{g. g}^{-1}$) was lower than that in the human hair in India (0.6 $\mu\text{g. g}^{-1}$; Takagi et al., 1986) and arsenic victims in the West Bengal (3.4 $\mu\text{g. g}^{-1}$; Gautam et al., 2004), but it was 10 to 40 times higher than that in the other societies (Table 5). The concentrations of arsenic in all the sampling areas were almost similar and high. In agreement with the high concentration of arsenic in fish muscle in the same sampling areas (Agah et al., 2009), high arsenic concentration in the human hair might have originated from natural sources.

The mean Cr level in our research was almost in the same level reported from the Poland (0.4-2.7 $\mu\text{g. g}^{-1}$; Nowak and Chmielnicka, 2000) and Pakistan (1.9 $\mu\text{g. g}^{-1}$; Khalique et al., 2005). The mean cobalt concentration in our data (0.12 $\mu\text{g. g}^{-1}$) was six times less than Pakistan hair samples (0.7 $\mu\text{g. g}^{-1}$).

The average mercury level observed in the hair of fishermen from the Persian Gulf region was lower than that in human hair from the Amazon regions (Passos, et al., 2003) and Japan (Feng, et al., 1998), but was comparable with the Hg concentrations reported in hair of fish consumers in Indonesia (Feng et al., 1998), in North Atlantic women who used to consume whale meat (Weihe et al., 2005), in Kuwaiti fishermen (ROPME, 1999), and Chilean fish consumers (Brhun, et al., 1997).

4. Conclusion

Our results demonstrated that the concentrations of V, Cr, As and Zn in and between stations were almost comparable, while other elements (Cu, Ni, Cd, Pb and Co) displayed high variation in and between stations with the highest levels at Lengeh. In order to detect the pollution source(s), it is necessary to check the

industrial outputs in Lengeh.

A Spearman correlation matrix (Table 6) between all elements, as well as the fishermen ages, career and fish meals per week was calculated. In addition, a Principle Component Analysis and associated loading plot were performed on all variables.

The regression analysis between the element concentrations and the age of the participants and occupational exposures did not show any significant relationships. Vanadium had significant relationship with other elements except for Zn and Cd.

Three principal components or groups of elements were extracted from the element concentrations in the fishermen hair, explaining 75 % of the total variation. Factor 1 (expressing 41 % of total variance) includes V, Co, Cr, Zn, Pb and Cu, which may reflect a similar behavior originated from common sources. Factor 2 (explaining 21 % of total variance) includes As and Ni with anti correlation with Cd; Factor 3 (explaining 13 % of total variance) includes Hg.

From the Principal Component Analysis, Spearman correlation matrix and the loading plot (Figure 2), it appeared that a positive strong significant correlation ($p < 0.05$) existed between V, Cr, Co, Cu and Zn concentrations in the human hair, which might have originated from similar sources.

Table 6: Spearman Correlation Coefficients between the concentrations of trace metal in the hair samples.

Elements	V	Cr	Co	Ni	Cu	Zn	As	Cd	Pb	Age	Career	Fish meal
V	1.00											
Cr	.89**	1.00										
Co	.65**	.54**	1.00									
Ni	.43*	.45*	.62**	1.00								
Cu	.44*	.56**	.31	-.1	1.00							
Zn	.27	.15	.45*	.05	.29	1.00						
As	.79**	.83**	.33	.30	.36	-.03	1.00					
Cd	.24	.10	.51*	.07	.26	.31	-.04	1.00				
Pb	.60**	.58**	.75**	.381	.57**	.28	.43*	.53**	1.00			
age	-.23	-.00	-.67**	-.47*	.03	-.15	-.01	-.32	-.32	1.00		
Career	.34	.37	.11	.23	-.06	.17	.36	-.32	.23	.27	1.00	
Fishmeal	.22	.06	.22	.34	-.30	.25	-.06	-.25	.01	-.18	.37	1.00

** Correlation is significant at the 0.01 level (1-tailed). * Correlation is significant at the 0.05 level (1-tailed).

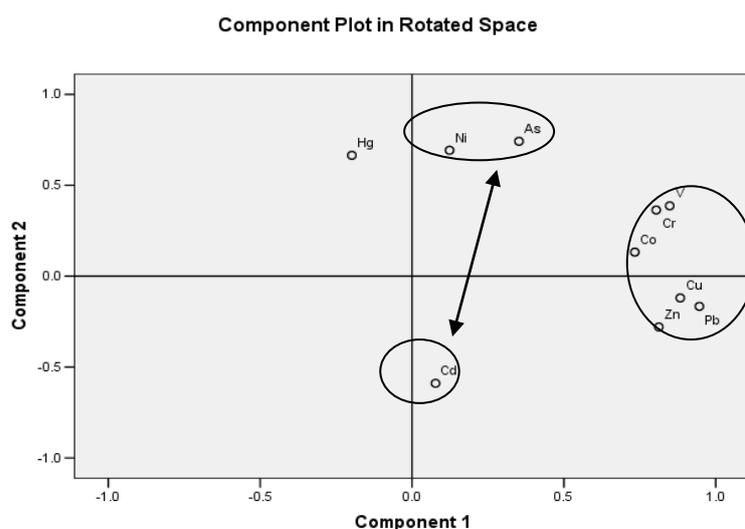


Fig. 2: PCA loading plot of the 10 elements in the fishermen hair.

Among the analyzed elements in the hair samples, lead, nickel and arsenic could be considered as markers of environmental exposure. In order to assess human exposure to toxic elements in the sampling area, it is important to have more comprehensive collection of samples, as well as complete questionnaires through larger classified population.

The questionnaire can provide all the data about occupational exposure, dietary habit and their sources (to be local or exported), especially for the main food sources, cigarette smoking and health background. Contaminated water is one of the main sources for human exposure to toxicants like arsenic (Gautam et al., 2004).

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Abbreviations

As: Arsenic, Cd: Cadmium, Co: Cobalt, Cr: Chromium; Cu: Copper, Hg: Mercury; Ni: Nickel, Pb: Lead, Tl: Thallium; Sb: Antimony; V: Vanadium; Zn: Zinc

References

- Agah H., Leermakers, M., Elskens, M., Fatemi, S. M. R and Baeyens, W., 2008. Accumulation of heavy metals in the muscle and liver of five fish species from the Iranian borders of the Persian Gulf. *The Journal of Environmental Monitoring and Assessment*.157(1-4): 499-514.
- Agah H., Leermakers, M., Gao, Y., Fatemi, S. M. R., Mohseni Katal, M., Baeyens, W and Elskens, M., 2010. Mercury accumulation in fish species from the Persian Gulf and in human hair from fishermen. *Environmental Monitoring and Assessment*. 169(1-4): 203-216.
- Agah, H., S. Hashtroodi, M., Eghtesadi Eraghi, P., Fatemi, S. M. R., Leermakers, M. and Baeyens, W., 2011. Trace metals and major elements in the Persian Gulf sediments. *Journal of the Persian Gulf* 3 (7): 45-57.
- Ajayi, SO., Odukoye, OO. and Onianwa, PC., 2001. Lead content of human scalp and air in Southwestern Nigeria. *Nigeria. Journal of Science*. 35 (2): 183-187.
- Ashraf, W., Jaffar, M. and Mohammad, D., 1994. Age and sex dependence of selected trace metals in scalp hair of urban population of Pakistan. *Science of the Total Environment*. 151(3):227-33.
- ATSDR. Agency for Toxic Substances and Disease Registry. 2003. Hair Analysis Panel Discussion

- http://www.atsdr.cdc.gov/HAC/hair_analysisy.
- ATSDR, Agency for Toxic Substances and Disease Registry. 2008. Case Studies in Environmental Medicine (CSEM). Chromium Toxicity Course: WB 1466.
<http://www.atsdr.cdc.gov/csem/chromium/docs/chromium.pdf>
- Bass, D., Hickok Darrell, A., Quig, D. and Urek, K., 2001. Trace element analysis in hair: Factors determining accuracy, precision and reliability. *Alternative Medicine Review*. 6(5):472-481.
- Brhun, C.G., Rodriguez, A.A., Barrios, C.A., Jaramillo, V.H., Becerra, J., Gras, N.T., Nunez, E. and Reyes, O.C., 1997. Total mercury and methylmercury levels in scalp hair and blood of pregnant women residents of fishing villages in the eighth region of Chile. *ACS Symposium Series*. 654:151-177.
- Caroli, S., Senofonte, O., Violante, N., Fornarelli, L. and Powar, A., 1992. Assessment of reference values for elements in hair of urban normal subjects. *Microchemical Journal*. 46:174-183.
- Carrington, C. and Bolger, M., 2002. An exposure assessment for methylmercury from seafood from consumers in the United States. *Risk Analysis* 22:701-712.
- EBI. 2010. Environmental bureau of investigation. <http://www.eprf.ca/ebi/contaminants/cadmium.html>
- Feng, Q., Suzuki, Y. and Hisashige, A., 1998. Hair mercury levels of residents in China, Indonesia, and Japan. *Archives of Environmental Health* 53(1):36-43.
- Gautam, S., Sharma, R., Roychowdhury, T. and Chakaborti, D., 2004. Arsenic and other elements in hair, nail and skin-scales of arsenic victims in west Bengal, India. *Science of Total Environment* 326 33-47.
- Health and environment, 2005. Centre for science and environment
http://old.cseindia.org/html/healthnews/jan_feb05/lead_story.htm
- Iyenger, V. and Woittiez, J., 1988. Trace elements in human clinical specimens: Evaluation of literature data to identify reference values. *Clinical Chemistry*, 34: 474-481.
- Iyenger, G. V., Tanner, J.T., Wolf, W. R. and Zeisler, R., 1987. Preparation of a mixed human diet material for the determination of nutrient elements, selected toxic elements and organic nutrients: a preliminary report. *Science Total Environment*. 61: 235-252.
- Khalique, By, A., Shah Munir, H., Jaffar, M. and Shaheen, N. 2005. Status of Selected Trace Metal Distribution in Scalp Hair of Traffic Control Personnel Exposed to Vehicular. IDG Tech panel. http://www.redorbit.com/news/science/281076/status_of_selected_trace_metal_distribution_in_scalp_hair_of/?source=r_science
- Leermakers, M., Nguyen, H.L., Kurunczi, S., Vanneste, B., Galletti, S. and Baeyens, W., 2003. Determination of methylmercury in environmental samples using static headspace gas chromatography and atomic fluorescence detection after aqueous phase ethylation. *Analytical and Bioanalytical Chemistry*. 377: 327-333.
- Mahaffey, K. R., 2000. Recent advances in recognition of low-level methylmercury poisoning. *Current Opinion Neurology*. 13:677-707.
- McDowell, M.A., Dillon, C.F., Osterloh, J., Bolger, P.M., Pellizzari, E., Fernando, R., de Oca, R.M., Schober, S.E., Sinks, T., Jones, Robert, L. and Mahaffey, K.R., 2004. Hair mercury levels in U.S. Children and women of childbearing age: Reference range data from NHANES 1999-2000. *Environmental Health Perspectives*. 112 (11-112(11)):1165-1171.
- Muhaya, B., Leermakers, M. and Baeyens. W., 1998. Influence of sediment preservation on total mercury and methylmercury analysis. *Water, Air Soil pollution*107: 277-288
- Nguyen, H.L., Leermakers, M., Kurunczic, S., Bozod, L. and Baeyens, W., 2005. Mercury distribution and speciation in Lake Balaton, Hungary- *Science of the Total Environment*. 340: 231- 246.
- Nowak, B., and Chmielnicka, J., 2000. Relationship of lead and cadmium to essential elements in hair,

- teeth, and nails of environmentally exposed people. *Journal of Ecotoxicology and Environmental Safety*. 46: 265-274
- Oluwole, AF., Ojom JO., Durosinmi, MA., Asubiojo, OI., Akanle, OA., Spyrou, NM. and Filby, RH., 1994. Elemental composition of head hair and fingernails of some Nigerian subjects. *Biol Trace Element Research*. 43: 452.
- Passos, C.J., Mergler, D., Gaspar, E., Morais, S., Lucotte, M., Larribe, F., Davidson, R. and de Grosbois, S., 2003. Eating tropical fruit reduces mercury exposure from fish consumption in the Brazilian Amazon. *Environmental research*. 93:123-130.
- Pereira, R., Ribeiro, R. and Goncalves, F., 2004. Scalp hair analysis as a tool in assessing human exposure to heavy metals. *Science of the Total Environment*. 327: 81-92.
- Ponzetta, MT., Nardi, S., Calliari, I. and Lucchese, M., 1998. Trace elements in human scalp hair and soil in Irian Jaya. *Biological Trace Element Research* 62: 199 -212.
- ROPME., 1999. Regional report of the state of marine environment (ROPME Sea Area) translated by Fatemi, M.R. Marine Environment Bureau of Iran, p: 167.
- Seidel, S., Kreutzer, R., Smith, D., McNeel, S. and Gilliss, D., 2001. Assessment of commercial laboratories performing hair mineral analysis. *Journal of American Medical Association*. 285(1):67 -72.
- Shafaei, F., 2004. Determination of trace metals in human hair, Chemistry Department, North Tehran Branch, Islamic Azad University, Thesis for Master of Science, 120 P. (in Persian).
- Steen, K., 1991. The molecular and structural biology of hair. *Annals of the New York Academy of Sciences*. Vol.642, N.Y.
- Takagi, Y., Matsuda, S., Imai, S., Ohmori, Y., Masuda, T., Vinson, J.A., Mehra, M.C., Puri, B.K. and Kaniewski, A., 1986. Trace elements in human hair: an international comparison. *Bulltein of Environmental Contamination Toxicology* 36: 793-800.
- Vishwanathan, H., Hema, A. and Deepa E., 2002. Trace metal concentration in scalp hair of occupationally exposed autodivers. *Environmental Monitorig Assessment* 77: 149-54.
- Weihe, P., Grandjean, P. and Jorgensen, P.J. 2005. Application of hair mercury analysis to determine the impact of seafood advisory. *Environmental Research*. 97: 201-208.

