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Heavy metals in water and tilapia fish from Athi-Galana-Sabaki tributaries, Kenya

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Abstract

The well known long term toxic effects of heavy metals lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn), cadmium (Cd) and chromium (Cr) to man are of both scientific and environmental concerns. The presence of these heavy metals in water create a societal health risk in rivers that are otherwise useful for drinking water and fisheries as is of the case of Athi-Galana-Sabaki river in Kenya. Fish play an important role in human nutrition and therefore need to be carefully and routinely screened to ensure that there are no high levels of heavy metals being transferred to man through their consumption. We report levels of Pb, Ni, Mn, Zn, Cd and Cr in tilapia gills and water from tributaries of Athi River measured by Atomic Absorption spectroscopy. The concentration (mg/kg DW) found in the tilapia fish gills ranged; Pb (1.42-4.48), Ni (0.12-1.75), Mn (81.50-158.92), Zn (28.00-76.33), Cd (0.71-1.77) and Cr (ND-0.2). In water, the ranges (mg/l) were; Pb (0.004-0.047), Ni (0.007-0.062), Mn (0.187-1.048), Zn (0.002-0.695), Cd (ND- 0.01) and Cr (ND-0.068). Seasonal variation showed that Zn was significantly high during wet season in fish and water ($p<0.0001$). There was no general trend in levels of heavy metals in water, but in fish gills the elements decreased in the order Mn>Zn>Pb>Cd>Ni>Cr. Results evidence bioaccumulation of heavy metals in the fish and also alarming levels that are higher than the WHO limits, therefore posing potential risk for inhabitants that depend on the river. While the findings are geared towards providing baseline data on the current pollution status of this river, constant monitoring of the levels of contamination to assess the impact of the heavy metals is deemed necessary.

Introduction

The indestructible nature and long term toxic effects of heavy metals including lead (Pb), nickel (Ni), manganese (Mn), zinc (Zn), cadmium (Cd) and chromium (Cr) to man as a result of consumption of organisms obtained from polluted rivers has raised scientific and environmental concerns (Kar *et al*., 2008; Alaa and Werner, 2010; Oronsaye *et al*., 2010 ; Javed and U*smani, 2011; Abdel-Baki et al., 2011; Ekeanyanwu et al*., 2011; Olowoyo *et al*., 2012; Kumar *et al*., 2012). Weathering of soils and rocks and a variety of anthropogenic activities are two independent factors that result into the presence of heavy metals in water hence creating a societal health risk in rivers that are otherwise useful for domestic purposes as is of the case of Athi-Galana-Sabaki River in Kenya. The river has a basin area of 70,000km^2, rises at 1º42'S as Athi River and enters the Indian Ocean as Galana River. It is the second longest river in Kenya and the waters are useful for irrigation, drinking and fisheries. The river and its tributaries flow through major towns, national parks, industrial, agricultural and residential areas.

In aquatic environment, larger animals such as fish have been exposed to heavy metals as a direct consequence of biomagnifications (Ekwanyanwu *et al*., 2011; Javed and Usmani, 2011). The danger is that heavy metals even at low concentrations in fish and water have a particular significance in ecotoxicology and their toxic effects have been widely published for a number of water bodies (Obasohan, 2008; Kar *et al*., 2008; Agatha, 2010; Oronsaye *et al*., 2010; Abdel-Baki *et al*., 2011; Javed and Usmani, 2011; Ekwanyanwu *et al*., 2011). Recently, Ekwanyanwu et al., 2011 reported a concentration of 0.13 mg/l Mn and 0.62 mg/Kg Cd in fish. FAO/WHO has however set recommended limits of individual elements in water and fish (WHO, 1989).

Among aquatic species, fishes are the inhabitants that cannot escape from the detrimental effects of heavy metal pollution. This is because of their very

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intimate contact with water that carries the heavy metals in solution or suspension and also fish have to extract oxygen from water by passing water over their gills. The gills particularly are therefore a potential site of absorption of heavy metals and can be considered as one of the most significant indicators in water systems for the estimation of metal pollution level (Rashed, 2001; Ekwanyanwu *et al*., 2011). Infact the transfer factor of heavy metals in fish gills in respect to water has been studied to give information on how these metals are transferred to fish from aquatic ecosystem (Kalfakakour and Akrida-Demertzi, 2000; Abdel-Baki *et al*., 2011). It is worthwhile noting too that other fish organs including the muscles, liver and kidney have also been studied for heavy metal accumulation (Öztürk *et al*., 2009; Begum *et al*., 2009; Edem *et al*., 2009; Ekwanyanwu *et al*., 2011; Javed and Usmani, 2011).

Fish play an important role in human nutrition and therefore need to be carefully and routinely screened to ensure that there are no high levels of heavy metals being transferred to man through consumption. With the assumption that fish and water in Athi River risk exposure of heavy metals and that the inhabitants relying on the river are threatened, we report levels of Pb, Ni, Mn, Zn, Cd and Cr in tilapia gills and water from Ruiru and Mbagathi Rivers which are tributaries of Athi River. The results are geared towards providing baseline data on the current pollution status of this river.

Materials and methods

Sampling sites and sample collection

Tilapia fish and water samples were obtained six times each and at the same sampling time during the wet (April and May 2011) and dry (June and July 2011) seasons and samples homogenized for laboratory analysis. The sampling sites for water (1-10) and tilapia fish (1, 3, 7 and 10) on its tributaries were purposely selected at a distance of 5 Km and based on the surrounding activities as indicated in Table 1.

For water sampling, the procedure described by Öztürk *et al*. (2009) was followed. Polyethylene sampling bottles used were pre-conditioned with 5% HNO_3 and rinsed thoroughly with distilled de-ionized water. At each sampling site, the bottles were rinsed at least three times before sampling. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface. Three 500ml of water were taken at each sampling site, immediately acidified with 10% HNO_3 to a pH of less than 2 and transported to the laboratory in an ice bath. The samples were filtered through a 0.45 μm micropore membrane filter and kept at 4 °C before digestion.

Table 1.Sampling stations and the surrounding activities

Sampling station	Location	Surrounding activities
1	Before town	Fishing point and farming
2	After town	Industrial and residential activities
3	Before Ruiru Coffee plantations	Fishing point and agricultural activities
4	After Ruiru Coffee plantations and also before Ruiru town	Agricultural activities
5	Immediately after Ruiru town	To assess sewage and industrial effluent
6	After Ruiru town	To assess sewage and industrial effluent
7	Downstream of away from pollution points	Fishing point
8	Combined , Mathare, Mbagathi and	Farming,, industries & residential
9	meets	Farming,, industries & residential
10	Downstream of	Fishing point

About 5 Kg of tilapia fish was statistically sampled, the fish was washed to remove loosely held particles before gills being immediately removed at the sampling site using a plastic knife. These were packed in plastic bags for transportation to the laboratory in an iced cooler box for storage at -20 ºC. The fish gills were then dried at 105°C in an oven to obtain a moisture content of less than 10°C. They were ground with a pestle and motor into a fine homogenous powder and stored in well labeled plastic bags before digestion.

Chemicals

All chemicals used were of analytical grade. Concentrated HNO_3, hydrogen peroxide, Pb, Ni, Mn, Zn, Cd and potassium chromate and HCl acid were sourced from Thomas Baker Chemicals Ltd Mumbai India whereas Cr metal was purchased from Fluka Chemicals and GmbH Aldrich Chemical Company, Inc. USA.

Stock and serial standard solutions

Metal salts of annular grade (99.9%) for each metal were first dried at 105 °C, cooled in a desiccator prior to weighing. Stock solutions (1000 mg/ L) of the metal ions were prepared in dilute HNO_3. The working standards of the metal solutions were prepared by appropriate dilutions in distilled water.

Digestion

Water and gill samples were digested in triplicates according to the method described in APHA (2005). Briefly, 10 ml of the filtered water were digested with 5 ml of HNO_3 at 100 ºC with the addition of drops of hydrogen peroxide until there were no brown fumes. The mixture was filtered using Whatman 0.45μm filter paper in a 100 ml volumetric flask and topped with distilled water for aspiration into the atomic absorption spectrophotometer (AAS). For fish, 1g of dried fish gills was accurately weighed and the digestion procedure followed. The transfer factor in fish tissues from water, was calculated according to

Rashed (2001).

Instrumentation

A computerized Varian Atomic Absorption Spectrometer (model AA-10) was calibrated before sample analysis. The operating parameters were set according to the specification given by the manufacturer. The equation of each generated calibration curve was used in calculating each heavy metal concentrations in the water and fish gills with respect to dilution factors where appropriate.

Data analysis

Data were analyzed with SPSS 17.0 for windows. The mean and standard deviation of means were calculated. The data were analyzed by one-way analysis of variance (ANOVA) and Duncan's multiple range tests was used to separate means ($P < 0.05$).

Results and Discussions

Heavy metals in water from Athi river tributaries

The mean concentration of heavy metals in water is given in Tables 2 and 3 for the wet and dry seasons respectively. There was no pattern observed although Mn was in overall highest in both seasons while Pb or Cr was generally the lowest. For samples found to contain the heavy metals, significant differences were noted between and within elements in various sampling sites ($p<0.05$).

The concentration of Pb in water where detected was found to range from 0.042-0.047 mg/l and 0.032-0.035 mg/l in the wet and dry seasons respectively. Interestingly, while Pb was found to be below the detection limit (BDL) in the wet season at sites 1 (before Athi River town) and 5 (immediately after Ruiru town), during the dry seasons Pb was detected in the waters at these sites. On the other hand water samples from sites 6, 8 and 9 were observed to have Pb only in the wet seasons. This can be attributed to rainfall followed by high river discharge from upstream environment (Khan *et al*., 1998; Kar *et al*., 2008). Of concern however is that all water samples that were detected to have Pb had the levels being higher than 0.01 mg/l, the WHO recommended limit in drinking water thus posing immediate fears of biomagnifications (WHO, 1989).

Except at one site (9) during the dry season, the waters contained Ni ranging from 0.014 to 0.062 mg/l and 0.008 to 0.040 mg/l during the wet and dry season respectively. However, all the water samples found to contain Ni had the concentrations below the drinking water recommended limit of 0.07mg/l Ni (WHO, 1989). These findings are consistent with typical concentrations of Ni reported for unpolluted surface waters although there is caution that continual assessment is highly essential (Salnikow and Denkhaus, 2002; Awofolul *et al*., 2005).

The concentration of Mn ranged from 0.187-0.888 mg/l and 0.533-1.048 mg/l in the wet and dry seasons respectively. In all the sampling sites, Mn was found to be higher than 0.4 mg/l the recommended limit for Mn in drinking water (WHO, 1989). While we describe the waters unfit for human consumption as this would lead to Mn related illnesses, adoption of adequate measures to remove this Mn load are called to avoid further deterioration of the river water quality (Nussey *et al*., 2000; Kar *et al*., 2008; Alaa and Werner, 2010).

Zinc was found to range from 0.046-0.695 mg/l and 0.010-0.055 mg/l and in the wet and dry

Table 2. Concentration of elements in Athi River water during the wet season (mg/l)

Sampling site	Element; Mean±SD (n=3)*						
	Pb	Ni	Mn	Zn	Cd	Cr	p-value
1	BDL	$0.018±0.002^{Aab}$	$0.831±0.010^{Ccd}$	$0.123±0.012^{Ba}$	$0.002±0.000^{Aab}$	BDL	<0.001
2	$0.022±0.005^{Aab}$	$0.014±0.003^{Aab}$	$0.888±0.010^{Cd}$	$0.103±0.011^{Ba}$	$0.004±0.001^{Ac}$	BDL	<0.001
3	BDL	$0.025±0.003^{Ab}$	$0.726±0.009^{Cbcd}$	$0.056±0.006^{Ba}$	BDL	BDL	<0.001
4	BDL	$0.020±0.002^{Aab}$	$0.589±0.090^{Bb}$	$0.047±0.004^{Aa}$	$0.001±0.000^{Aa}$	BDL	<0.001
5	BDL	$0.025±0.004^{Ab}$	$0.187±0.054^{Ba}$	$0.053±0.015^{Aa}$	$0.004±0.002^{Abc}$	BDL	<0.001
6	$0.040±0.004^{Ccd}$	$0.023±0.008^{Bab}$	$0.230±0.008^{Ca}$	$0.046±0.007^{Ca}$	$0.001±0.001^{Aab}$	BDL	<0.001
7	BDL	$0.017±0.003^{Aab}$	$0.560±0.070^{Bb}$	$0.076±0.010^{Aa}$	$0.001±0.001^{Aa}$	BDL	<0.001
8	$0.030±0.007^{Aab}$	$0.062±0.002^{Ac}$	$0.555±0.048^{Cb}$	$0.141±0.003^{Ba}$	$0.001±0.001^{Aab}$	BDL	<0.001
9	$0.047±0.008^{ABd}$	BDL	$0.652±0.041^{Cb}$	$0.095±0.016^{Ba}$	$0.001±0.000^{Aa}$	BDL	<0.001
10	BDL	$0.022±0.006^{Aab}$	$0.681±0.012^{Bbc}$	$0.695±0.288^{Bb}$	BDL	BDL	<0.001
	<0.0001	<0.0001	<0.0001	0.002	0.005		

*Means values followed by the same capital/small letter within the same row/column are not significantly different at 95% confidence level; BDL; below detection limit

Table 3. Concentration of elements in Athi River water during the dry season (mg/l)

Sampling site	Element; Mean±SD (n=3)*						
	Pb	Ni	Mn	Zn	Cd	Cr	p-value
1	0.032 ± 0.002^{Aac}	0.040 ± 0.006^{Aa}	0.928 ± 0.083^{Bbc}	0.016 ± 0.003^{Aab}	0.005 ± 0.001^{Abc}	0.068 ± 0.051^{A}	<0.001
2	0.034 ± 0.003^{Ac}	0.034 ± 0.005^{Aab}	0.773 ± 0.051^{Ba}	0.036 ± 0.001^{Ac}	0.010 ± 0.001^{Ad}	0.035 ± 0.006^{A}	<0.001
3	BDL	0.008 ± 0.002^{Aa}	0.538 ± 0.016^{Ca}	0.035 ± 0.002^{Bc}	0.001 ± 0.000^{Aa}	0.010 ± 0.003^{A}	<0.001
4	BDL	0.032 ± 0.005^{Bab}	0.553 ± 0.014^{Ca}	BDL	0.001 ± 0.000^{Aa}	0.005 ± 0.002^{A}	<0.001
5	0.035 ± 0.002^{Bc}	0.025 ± 0.002^{Babc}	0.702 ± 0.004^{Cab}	BDL	0.008 ± 0.002^{Acd}	0.030 ± 0.004^{B}	<0.001
6	BDL	0.040 ± 0.006^{Ac}	0.772 ± 0.039^{Babc}	0.016 ± 0.003^{Aab}	0.004 ± 0.001^{Aab}	0.015 ± 0.006^{A}	<0.001
7	BDL	0.020 ± 0.007^{Aabc}	0.987 ± 0.036^{Bc}	0.055 ± 0.003^{Ad}	0.002 ± 0.001^{Aab}	BDL	<0.001
8	BDL	0.018 ± 0.005^{Aabc}	1.048 ± 0.088^{Bc}	0.023 ± 0.008^{Ab}	0.003 ± 0.001^{Aab}	BDL	<0.001
9	BDL	0.012 ± 0.007^{Aabc}	0.947 ± 0.024^{Bbc}	BDL	0.001 ± 0.000^{Aa}	BDL	<0.001
10	BDL	0.018 ± 0.003^{Aabc}	0.533 ± 0.099^{Ba}	0.010 ± 0.005^{Aab}	0.001 ± 0.000^{Aa}	0.005 ± 0.002^{A}	<0.001
	<0.001	<0.001	<0.001	<0.001	<0.001	0.385	

*Means values followed by the same capital/small letter within the same row/column are not significantly different at 95% confidence level; BDL; below detection limit

Table 4. Concentration of elements in Athi River fish during the wet season (mg/kg)

Sampling site	Element; Mean±SD (n=3)*						p-value
	Pb	Ni	Mn	Zn	Cd	Cr	
1	1.73 ± 0.05^{A}	0.67 ± 0.11^{Aa}	148.71 ± 0.99^{Ca}	48.79 ± 5.28^{Ba}	1.29 ± 0.19^{A}	0.02 ± 0.00^{A}	<0.001
3	2.21 ± 0.10^{A}	1.75 ± 0.62^{Aab}	158.92 ± 1.88^{Cc}	76.33 ± 8.53^{Bc}	1.44 ± 0.12^{A}	0.02 ± 0.01^{A}	<0.001
7	3.31 ± 0.85^{A}	0.29 ± 0.06^{Aa}	149.13 ± 2.26^{Cb}	53.96 ± 3.82^{Bc}	0.96 ± 0.23^{A}	0.02 ± 0.01^{A}	<0.001
10	1.94 ± 0.04^{A}	0.83 ± 0.23^{Aab}	107.96 ± 1.32^{Cb}	69.17 ± 0.20^{Bbc}	1.60 ± 0.12^{A}	0.02 ± 0.00^{A}	<0.001
p-value	0.073	0.039	<0.001	0.005	0.081	0.873	

*Means values followed by the same capital/small letter within the same column/row are not significantly different at 95% confidence level

Table 5. Concentration of elements in Athi River fish during the dry season (mg/kg)

Sampling site	Element; Mean±SD (n=3)*						p-value
	Pb	Ni	Mn	Zn	Cd	Cr	
1	1.71 ± 0.08^{Ab}	0.87 ± 0.15^{Ab}	81.50 ± 17.21^{C}	49.50 ± 0.92^{Bc}	1.52 ± 0.10^{Ac}	0.07 ± 0.06^{A}	<0.0001
3	1.42 ± 0.05^{Aa}	0.54 ± 0.13^{Aab}	132.17 ± 42.29^{B}	35.00 ± 0.12^{Ab}	1.23 ± 0.06^{Ab}	0.05 ± 0.04^{A}	<0.0001
7	4.48 ± 0.05^{Ad}	$0.58\pm0.18A^{ab}$	132.67 ± 44.89^{B}	37.00 ± 1.71^{Ab}	0.71 ± 0.15^{Aa}	0.02 ± 0.01^{A}	<0.0001
10	2.10 ± 0.05^{Bc}	0.12 ± 0.06^{Ba}	124.04 ± 44.06^{C}	28.00 ± 4.17^{Ba}	1.77 ± 0.12^{Bc}	ND	<0.0001
p-value	<0.0001	<0.0001	0.759	<0.0001	<0.0001	0.57	

*Means values followed by the same capital/small letter within the same column/row are not significantly different at 95% confidence level.

seasons respectively. With respect to WHO limits of Zn in drinking water, the waters did not constitute immediate hazard to aquatic fauna and human consumers (WHO, 1989; Oguzie, 2003; Fernandes *et al*., 2007; Agatha, 2010).

Concentration of Cd was found to range from 0.001 to 0.004 mg/l and 0.001 to 0.010 mg/l during the wet and dry seasons respectively. Surprisingly, levels of Cd at site 3 (before Ruiru Coffee plantations) and 10 (downstream of Athi River) were BDL during the wet season while in the dry season Cd was found in waters at these sites. In addition, the levels indicated minimal fears of Cd poisoning during the wet seasons but in the dry season levels higher than the 0.003 mg/l Cd, the recommended limit for drinking water were recorded (WHO, 1989).

Chromium levels were BDL during the wet season. In the dry season, the levels ranged from 0.005 to 0.068 mg/l except at site 1 (before Athi river town) Cr levels lower than 0.05 mg/l, the recommended limit of Cr in drinking water (WHO, 1989). Based on the location of this site however, this would be expected.

Heavy metals in tilapia fish from Athi river tributaries

The mean levels of Pb, Ni, Mn, Zn, Cd and Cr in the fish gills obtained in the wet and dry seasons at four fishing points (sites 1, 3, 7 and 10) are presented in Tables 4 and 5. Generally, the concentration of heavy metal in the fish gills decreased with an observed trend of Mn>Zn>Pb>Cd>Ni>Cr. There were significant differences between and within elements at the sampling sites ($p<0.05$).

The concentration of Pb in the fish gills was found to range between 1.73-3.31 mg/kg DW and 1.42-4.48 mg/kg dry weight (DW) in the wet and dry seasons respectively. These values were higher than the WHO recommended limit for fish and fish products in both seasons; at sites 3 and 7 during the wet season and at sites 7 and 10 during the dry season. While these levels are attributed to industrial and urban centers that are along the river, they pose threat to human life. The otherwise low levels may as well pose fear of Pb poisoning since low levels of Pb are also known to be toxic (Obasohan and Oronsaye, 2004; Agatha, 2010).

The concentrations off Ni ranged from 0.29-1.75 mg/kg DW and 0.12-0.87 mg/kg DW in the wet and dry seasons respectively. With the exception of sites 10 and 3 in the dry and wet seasons respectively, Ni concentrations were higher than 0.4mg/kg the WHO recommended limit (WHO, 1989). The concentration of manganese was found to range from 81.50-132.67 mg/kg DW and 107.96-158.92 mg/kg DW in the dry and wet seasons respectively. These were higher than 2.50 mg/kg, the WHO recommended limit (WHO, 1989).

Zinc levels ranged between 28.00-49.50 mg/kg DW and 48.79 to 76.33 mg/kg DW in the dry and wet seasons respectively. These values though were below the 75 mg/kg recommended limit for Zn in fish and fish products with an exception of fish obtained from site 3 (before coffee plantations). The concentration of cadmium was found to range from 0.96 to 1.60mg/kg DW and 0.71-1.77 mg/kg DW in the wet and dry seasons respectively. The levels were all below the recommended limit of 2.0mg/kg for fish and fish products. The range of Cr in both wet and dry seasons was lower than the recommended limit of 0.15 mg/kg for Cr in fish and fish products (WHO, 1989). The consumption of fish should be cautious as cumulative effects might constitute health hazards to aquatic life and to man (Oronsaye *et al*., 2010).

The concentrations of heavy metals in the fish gills were always higher than that in water. These findings are consistent with previous studies (Kar *et al*., 2008; Alaa and Werner, 2010; Agatha, 2010; Oronsaye *et al*., 2010; Javed and Usmani, 2011; Abdel-Baki, 2011; Ekwanyanwu *et al*., 2011). We calculated the transfer factor (TF) of all elements in fish from water and this was found to be greater than 1 giving evidence of bioaccumulation of the elements from water (Kalfakakour and Akrida-Demertzi, 2000; Rashed, 2001; Abdel-Baki *et al*., 2011). There were higher concentrations of the elements in fish during the dry season, attributed to the obviously higher water temperatures at these periods. Higher temperatures can result in; higher activity and ventilation rates in fish, tend to lower oxygen affinity of the blood and thus increase the rate of pollutant accumulation, and can lead to higher metabolic rates, which could induce more feeding and in turn result in increased metal concentration, if the metals are taken up via food chain (Obasohan, 2008). However, it is quite evident that there was bioaccumulation of heavy metals in the fish gills and the condition may get worse potentially risking man through consumption of the fish. Therefore, a regular monitoring of heavy metal levels in water and fishes in Athi river is necessary.

Conclusion

The concentration of Pb, Mn, Cd and Cr in water, and Pb, Ni and Mn in fish gills where detected was found to be higher than the WHO recommended limit thus posing immediate fears of biomagnifications to man. We recommend constant monitoring of heavy metals concentration in Athi River since the river serves as a source of drinking water, irrigation and fisheries for the local inhabitants. While these results give precautionary use of the water from Athi river, these will also be a basis to sensitize authorities towards management of discharge into this very important river in order to avoid further deterioration of the river water quality.

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