Research Journal of Environmental and Earth Sciences 3(1): 56-60, 2011
ISSN: 2041-0492

Received: October 05, 2010 Accepted: October 27, 2010 Published: January 05, 2011

Accumulation Profile of Heavy Metals in Fish Samples from Nsawam, Along the Densu River, Ghana

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Abstract: The present study was carried out to investigate the accumulation profile of heavy metals in five fish species namely; *Heterotis niloticus*, *Channa obscura*, *Hepsetus odoe*, *Tilapia zilli* and *Clarias gariepinus*. Concentrations of Fe, Mn, Cu, Zn, Ca, Cd, and Pb were measured in all the samples analysed. Ni, Co and Cr however, recorded 80, 60 and 20% incidence respectively in the fish samples. The highest mean concentration, 110.56±0.86 mg/kg was recorded for Cu in *Hepsetus odoe*. Ni, Co, and Cr measured relatively lower concentrations from as low as <0.01 mg/kg, <0.005 mg/kg and <0.001 mg/kg respectively been their respective detection limits. The least detectable concentration, 0.08±0.01 mg/kg was measured for Pb in *Clarias gariepinus*. Most of the heavy metals were within the recommended maximum guidelines. The concentration of Cu measured in all the samples however, exceeded the FAO maximum limit of 30 mg/kg. Similarly, the concentration of Mn measured in all the fish samples exceeded the WHO limit of 0.5 mg/L in drinking water. All the concentrations measured for Pb, were below the FAO limit of 0.5 mg/kg except 0.94±0.30 mg/kg, measured in *Hepsetus odoe* which exceeded the limit. The mean of the total concentration of each metal in all the samples indicate that the concentrations of the heavy metals in the samples are generally well below and or within the respective recommended guidelines. Thus fish species from the Densu river, harvested at Nsawam are safe for human consumption.

Key words: Concentration, detectable, guideline, incidence, maximum limit, species

INTRODUCTION

Heavy metals are trace metals that are at least five times denser than water. As a result, they are stable, thus cannot be metabolized by the body and are therefore bio-accumulative. Most heavy metals have no beneficial functions to the body and can be highly toxic. If they enter into the body through inhalation, ingestion and skin absorption they accumulate in the body tissue faster than the body's detoxification pathways can dispose of them (Ekpo *et al.*, 2008). High concentration exposure is not necessary to produce a state of toxicity in the body tissue and, overtime, can reach toxic concentration levels (Prusty, 1994, Khalid *et al.*, 1978). During the past several decades, the increasing usage of heavy metals in industry has led to serious environmental pollution through effluents and emanations (Sericano *et al.*, 1995).

Heavy metals were of particular concern due to their toxicity and ability to be bioaccumulated in aquatic ecosystems (Miller *et al.*, 2002), as well as persistence in the natural environment. Pb, Ba, Cd, Hg, Cr^{4+}, and As are classified as toxic heavy metals and maximum residual levels have been prescribed for humans (FAO, 1983; EC, 2001; FDA, 2001). Essential metals such as Cu, Na, K, Ca, Mn, Se, Fe, Cr^{3+} and Zn, have normal physiological regulatory functions (Hogstrand and Haux, 2001), but may also bioaccumulate and reach toxic levels (Rietzler *et al.*, 2001). Heavy metals pollution in aquatic environment has become a serious problem (Tarrio *et al.*, 1991) and also an important factor in the decline of water, sediments and fish quality.

Fish is often at the top of the aquatic food chain and may concentrate large amount of these metals from the surrounding waters. Most heavy metals find their way into water bodies via, chemical weathering of rocks and soil, agricultural runoffs, industrial waste discharge, mining, batteries, lead based paint and gasoline and improper domestic waste discharge into water ways. Nsawam is a major fishing community along the Densu river in Ghana. The Densu river lies between latitudes 5º30′N to 6º20′ N and longitudes 0º10′W to 0º35′ W and covers an area of about 2488.41 km^2 with an average length of 225.6 km (Kusimi, 2008). Most dwellers in Nsawam depend on the consumption of fish from the Densu basin for their protein requirement. Agricultural runoffs, discharge from mechanical shops, direct disposal of domestic waste find

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their way into the course of the Densu river, particularly at Nsawam and its immediate environs upstream.

The profile of heavy metals in fish species harvested from Nsawam need to be investigated due to the possible bio-concentration in fishes and consequent bio-accumulation in human beings who occupy the top level on the food chain. This work therefore seeks to take stock of the accumulation profile of heavy metals (iron, manganese, copper, zinc, nickel, calcium, cadmium, lead, cobalt and chromium) in five fish species collected at Nsawam along the Densu river using Atomic Absorption Spectrophotometer, in order to evaluate their hazard level in relation to the maximum residual limit for human consumption.

MATERIALS AND METHODS

This work was carried out at the Chemistry Department of National Nuclear Research Institute, Ghana Atomic Energy Commission from April 2009 to December 2009.

Sample collection: Fresh fish samples were collected directly from the fishermen at their landing site in Nsawam. Different species were placed in different polyethylene bags and were packed on ice in a thermo insulator box and transported to the laboratory. The samples were washed with deionised water and labeled as described in Table 1. The samples were then stored in the freezer prior to preparation.

Reagents: All reagents used were of analytical grade. Hydrogen peroxide (MERCK, Germany) and Nitric acid (Sigma-Aldrich, Germany) were used for digestion. Working standards of iron, manganese, copper, zinc, nickel, calcium, cadmium, lead, cobalt and chromium (Spectrascan, Teknolab AB, Sweden) were prepared by diluting concentrated stock solutions of 1000 mg/L in de-ionised water.

Sample preparation: The tissue portion of five fish samples for each species were homogenized and lyophilized for 72 h (CHRiST LMC-1, Germany) to form a composite sample. The dried samples were ground into powder using mortar and pestle. 0.5 g of dried sample were weighed into Teflon beakers and 6 ml HNO_3 and 1 mL H_2O_2 added. The Teflon beakers were placed in the bomb and closed tightly. The bomb was placed at the center of a microwave oven (ETHOS 900 Microwave, Millestone) and digested for 26 min at full power. The completely digested samples were allowed to cool to room temperature and the volume made up to 20 mL.

Table 1: Identification of fish samples

Sample code	Species scientific name	No. of samples collected
HNF	*Heterotis niloticus*	5
COF	*Channa obscura*	5
HOF	*Hepsetus odoe*	5
TZF	*Tilapia zilli*	5
CGF	*Clarias gariepinus*	5

Table 2: Working conditions for the analysis of trace elements by atomic absorption spectrophotometer

Metals	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Gas	Support
Fe	372.0	0.1	5	Acetylene	Air
Mn	403.1	0.1	5	Acetylene	Air
Cu	327.4	0.1	4	Acetylene	Air
Zn	213.9	0.1	5	Acetylene	Air
Ni	341.5	0.1	4	Acetylene	Air
Ca	422.7	0.1	10	Acetylene	Nitrous oxide/air
Cd	326.1	0.1	4	Acetylene	Air
Pb	405.8	0.1	5	Acetylene	Air
Co	345.4	0.1	7	Acetylene	Air
Cr	425.4	0.1	7	Acetylene	Air

Sample analysis: The digested samples were analyzed in triplicate, using an atomic absorption spectrophotometer (VARIAN AA240 FS). The blanks and calibration standard solutions were also analysed in a similar manner as the samples. The heavy metals were analysed in the fish samples per standard conditions as presented in Table 2. Quantifications were achieved using calibration curves.

RESULTS AND DISCUSSION

The mean concentration of heavy metals in the fish samples are presented in Table 3. The mean concentrations of the total individual metal load in all the fish samples are also presented in Table 4. The heavy metals Fe, Mn, Cu, Zn, Ca, Cd, and Pb all recorded a 100% incidence in fish samples. Cr, Ni, and Co however, recorded 80, 60 and 20% incidence, respectively in the fish samples.

The concentration of Fe ranged between 5.96±0.16 to 10.8±0.43 mg/kg. The highest concentration, 10.8±0.43 mg/kg was recorded in CGF (*Clarias gariepinus*) with the lowest, 5.96±0.16 mg/kg been recorded in TZF (*Tilapia zilli*). Fe is an essential element in human diet. It forms part of haemoglobin, which allows oxygen to be carried from the lungs to the tissues. Severe Fe deficiency causes anaemia in humans.

Manganese recorded lower concentrations in the fish samples compared to Fe. The lowest concentration of 1.6±0.23 mg/kg was measured in TZF (*Tilapia zilli*) whiles the highest concentration, 2.72±0.13 mg/kg of Mn was measured in COF (*Channa obscura*). It is interesting to note that the least concentrations for both Fe and Mn

Table 3: Mean concentration of heavy metals in fish samples

Sample code	Heavy metal (mg/kg) Fe	Mn	Cu	Zn	Ni	Ca	Cd	Pb	Co	Cr
HNF	6.96±0.12	1.72±0.01	56.04±0.10	18.92±0.15	<0.01	8.21±0.20	0.32±0.01	0.16±0.03	0.24±0.01	0.64±0.12
COF	6.40±0.02	2.72±0.13	74.84±1.02	23.68±0.44	<0.01	30.40±0.40	0.16±0.01	0.48±0.01	<0.005	0.40±0.03
HOF	9.40±0.31	2.52±0.10	110.56±0.86	30.04±0.13	0.84±0.01	45.20±0.72	0.24±0.10	0.94±0.30	<0.005	0.44±0.20
TZF	5.96±0.16	1.60±0.23	91.08±1.04	28.24±0.84	0.24±0.02	36.40±0.51	0.24±0.21	0.34±0.02	<0.005	<0.001
CGF	10.80±0.43	2.16±0.91	45.60±0.74	19.84±0.16	0.20±0.04	24.80±0.76	0.36±0.03	0.08±0.01	<0.005	0.16±0.20

Table 4: A comparison of mean of total metal concentration (mg/kg) with maximum limits

Heavy metal	Mean of total concentration	Maximum limit	Reference
Fe	7.90	-	-
Mn	2.14	0.5	WHO (1985)
Cu	75.62	30	FAO (1983)
Zn	24.14	30	FAO (1983)
Ni	0.43	70-80	USFDA (1993b)
Ca	29.00	-	-
Cd	0.26	0.5	FAO (1983)
Pb	0.40	0.5	FAO (1983)
Co	0.24	-	-
Cr	0.41	12-13	USFDA (1993a)

were measured in TZF (*Tilapia zilli*). The concentrations of Mn in all the fish samples exceeded the WHO (1985) guideline of 0.5 mg/L in drinking water. Thus the mean of the total concentration of Mn in all the fish samples, 2.14 mg/kg (Table 4) also exceed the WHO guideline. Mn is an essential element for both animals and plants. Deficiencies of Mn result in severe skeletal and reproductive abnormalities in mammals. It is widely distributed throughout the body with little variation and does not accumulate with age (Sivapermal *et al.*, 2007).

The concentration of Cu in fish samples were extremely higher compared to the concentration of the other heavy metals that were analysed in the fish samples. The concentrations of Cu in the samples analysed ranged from 45.6±0.74 to 110.56±0.86 mg/kg, with the highest concentration, 110.56±0.86 mg/kg in HOF (*Hepsetus odoe*). However, the lowest concentration of 45.6±0.74 mg/kg measured in CGF (*Clarias gariepinus*) was above the FAO guideline of 30 mg/kg. Thus the concentrations of Cu in the fish samples analysed were all above the FAO recommended guideline (FAO, 1983). Cu is an essential part of several enzymes and it is necessary for the synthesis of haemoglobin. The mean of the total concentration of Cu, 75.62 mg/kg was also above the FAO guideline.

Zn measured the highest concentration, 30.04±0.13 mg/kg in HOF (*Hepsetus odoe*) while the lowest concentration, 18.92±0.15 mg/kg was measured in HNF (*Heterotis niloticus*). The FAO maximum guideline for Zn is 30 mg/kg (FAO, 1983). Thus the concentrations of Zn in the fish samples were within the FAO guideline. The mean of the total concentration of Zn in all the fish samples, 24.14 mg/kg (Table 4) was therefore within the FAO guideline. Zn is an essential trace metal for both animals and humans. A deficiency of zinc is marked by retarded growth, loss of taste and hypogonadism, leading to decreased fertility (Sivapermal *et al.*, 2007). Zn toxicity is rare but, at concentrations in water up to 40 mg/kg, may induce toxicity, characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea (NAS-NRC, 1974).

Ni recorded very low concentrations in the samples relative to the other heavy metals apart from Co which recorded the lowest concentration relatively. The concentrations of Ni in the samples ranged between <0.01 to 0.84±0.01 mg/kg. The highest concentration, 0.84±0.01 mg/kg was measured in HOF (*Hepsetus odoe*) with the lowest detectable concentration, 0.20±0.04 mg/kg measured in CGF (*Clarias gariepinus*). The estimated maximum guideline (USFDA, 1993b) for Ni is 70-80 mg/kg. Thus the concentrations of Ni in all the samples were far below the stipulated limit. The major source of Ni for humans is food and uptake from natural sources, as well as food processing (NAS-NRC, 1975). Increased incidence of cancer of the lung and nasal cavity caused by high intake of Ni has been also been reported in workers in Ni smelters.

Ca is one of the essential elements in humans. The concentrations of Ca in the samples ranged between 8.21±0.20 to 45.2±0.72 mg/kg. The highest concentration (45.2±0.72 mg/kg) was measured in HOF (*Hepsetus odoe*) while the lowest concentration, 8.21±0.20 mg/kg was measured in HNF(*Heterotis niloticus*). Ca, in combination with phosphorus and other elements, is necessary to give strength to bones and teeth. It is also essential for normal clotting of blood and a vital link in transmission of nerve impulses. Ca is identified as an essential element in enzyme regulation, in the secretion of insulin in adults, and in regulation of muscle function. A decrease in Ca causes osteoporosis, a decrease in the density of the bone, evident in woman after menopause.

The lowest concentration of Cd, 0.16±0.01 mg/kg was measured in COF (*Channa obscura*) while the highest concentration, 0.36±0.03 mg/kg was measured in CGF. Interestingly, the concentration of 0.24 mg/kg was measured for both HOF (*Hepsetus odoe*) and TZF (*Tilapia zilli*). The concentrations of Cd in all the fish samples, however, fell below the FAO guideline (FAO, 1983) of 0.5 mg/kg. The source of Cd in humans is through food consumption. Severe toxic symptoms resulting from Cd ingestion are reported between 10 to

326 mg (Sivapermal *et al*., 2007). Fatal ingestions of Cd, producing shock and acute renal failure, occur from ingestions exceeding 350 mg (NAS-NRC, 1982).

Pb is classified as one of the most toxic heavy metals. The lowest concentration of 0.08±0.01 mg/kg was measured in CGF(*Clarias gariepinus*) while the highest concentration of 0.94±0.30 mg/kg was measured in HOF(*Hepsetus odoe*). The highest concentration, 0.94±0.30 mg/kg measured in HOF (*Hepsetus odoe*) was however, above FAO (1983) guideline of 0.5 mg/kg. The mean of the total concentration of Pb, 0.4 mg/kg (Table 4) in all the samples was however below the estimated FAO limit. Lead causes renal failure and liver damage in humans.

Co recorded the least incidence in all the samples analysed. A concentration of 0.24±0.01 mg/kg was measured in HNF (*Heterotis niloticus*). All the other samples had Co concentrations below 0.005 mg/kg, the detection limit. Co is an essential nutrient for humans, and also forms an integral part of vitamin B_{12} (Sivapermal *et al*., 2007). Co, has also been found to enhance proper thyroid function. Deficiency resulting from Co intake causes anaemia. Excessive intake of Co is however, reported to cause congestive heart failure and polycythemia (Alexander, 1972).

Cr is an essential trace metal and the biologically usable form of Cr plays an essential role in glucose metabolism. The concentrations of Cr in the fish samples were in the range of <0.001 to 0.64±0.12 mg/kg. The lowest detectable concentration, 0.16±0.20 mg/kg was measured in CGF (*Clarias gariepinus*) while the highest concentration, 0.64±0.12 mg/kg was measured in HNF (*Heterotis niloticus*). The maximum guideline, 12-13 mg/kg stipulated by the USFDA (1993a) was however, higher than the concentrations of Cr measured in all the fish samples. Deficiency of Cr results in impaired growth and disturbances in glucose, lipid and protein metabolism (Calabrese *et al*., 1985).

CONCLUSION

The profile of heavy metals in the analysed fish samples indicate the presence of the heavy metals in fishes obtained from the Densu river at Nsawam. The accumulation patterns of heavy metal contaminants in fish depend on uptake and elimination rate. In exception of Mn, Cu and Pb, the concentration of all the heavy metals measured were below the recommended maximum limits. The concentrations of Cu and Mn in all the fish samples were above the respective recommended maximum limits. The concentrations of Pb in HOF (*Hepsetus odoe*) was also above the maximum guideline. The results can be used to evaluate the possible health risk associated with the consumption of the species that were analysed. Regarding the mean concentration of the total heavy metal concentration for each metal, it can be said that the concentrations in the samples are generally well below and or within the recommended maximum limits, hence the samples are safe for human consumption.

ACKNOWLEDGMENT

The authors wish to acknowledge the Chemistry Department of the National Nuclear Research Institute, Ghana Atomic Energy Commission for making available the equipment and materials for the analysis.

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