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Distribution and potential risks of heavy metals in fish, water and sediment

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ABSTRACT

Heavy metal pollution in aquatic ecosystem impacts negatively on the organisms that depend on the water. Concentrations of some heavy metals in water, fish and sediment samples from Lake Bosomtwi in Ghana were determined to assess the extent of pollution in the lake. Concentrations of Fe, Zn, Cu, Mn and Ni in the lake were within the permissible levels recommended by World Health Organization. However, Cd and Pb exhibited higher concentrations possibly due to pollution events. The accumulation pattern in the study is in the order of Ni>Fe>Cu>Mn>Pb>Zn>Cd. Concentration of heavy metals in tilapia samples were all below the WHO guidelines. The sediment samples registered pollution load index of 3.317 indicating the sediment was polluted. Bioaccumulation in fish relative to the water was less than unity for all the metals except Mn. With respect to the sediments, bio-concentration factor for Cu was the highest (2.40) followed by Mn (1.72). All other metals recorded values < 1 indicating the fish species have not accumulated significantly from the environment. Except for Pb that registered a target hazard quotient of 1.030, all other metals had quotients well below 1. Consumption of tilapia from the lake can therefore be said to constitute no health risks so far as the heavy metals investigated are concerned. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Heavy metals; Sediment; Bioaccumulation; Target hazard quotient.

INTRODUCTION

Heavy metals are very important in ecotoxicologybecause of theirhigh toxicities (even at lower concentrations<1 mg/L), high enrichment (accumulation capacities), and slow removal rates^[1]. Most heavy metals are released into aquatic systems as a result of anthropogenic (industrial and domestic) activities^[2], atmospheric deposition^[3],

geochemical structure, mining activities and erosion[4].

In the aquatic ecosystem, the water bed sediments serve as sinks for contaminants from diverse sources and provide valuable information on the pollution situation of the water body. Sediments of aquatic environment play vital roles in the uptake of heavy metals^[5] and can also be a potential source of metal pollution by releasing adsorbed metals during

re-suspension episodes^[6]. The sediments reflect the geochemical composition of the bedrock as well as human activities in the surrounding areas. Levels of contaminants in the water, sediments and organisms reveal the extent of contamination in an aquatic ecosystem^[7].

Accumulation of heavy metals in water, organisms and bed sediments can result in ecological changes which may pose risks to human health^[8]. Concentration of a pollutant inside an organism is a good indicator of the pollutant's bioavailability^[9]. Fish and other aquatic life forms are constantly exposed to pollutants released into water bodies. Fish species occupying the top half of the aquatic food chain may bio-concentrate large amounts of contaminants (including heavy metals) from the water bodies and have thereforebeen found to be a good bioindicator of heavy metal contamination in aquatic systems^[10]. In this the work, we used the concentration of heavy metals(Cd, Cu, Fe, Mn, Ni, Pb and Zn) accumulated in the muscles of tilapia (Tilapia busumana) to assess the level of heavy metal pollution in the lake. The possibility of health risks to humans through consumption of tilapia from the lake was modeled using estimated dietary intake and target hazard quotient.

Monitoring the contamination of heavy metal in water systems by the use of fish tissues helps to assess the quality of aquatic ecosystems^[11,12]. Information on the level of contaminants in the lake will help in assessing the health risks that the consumption of fish and water from the lake may pose to human health. It will also inform policy on the proper management of the lake and others water resources nearby.

MATERIALS AND METHODS

Study site

Lake Bosomtwi is the largest natural lake in West Africa. The lake is located in the west central part (06° 32' N and 01° 25' W) of Ghana's Ashanti Region, 35 km south-east of Kumasi – Ghana's second largest city. The lake is one of the six major meteoric lakes in the world and has recently been the focus of international paleoclimate research^[13,14]. It

has a rim diameter of 10.5 km with four streams flowing into it; but the lake lacks an outlet^[15]. It is also the youngest and best-preserved medium-sized impact structure on Earth^[16,17]. The lake serves as a recreational spot and tilapia in the lake is an essential part of human diet in the region. The inhabitants around the lake are predominately vegetable crops farmers who use the lake's water for domestic activities including cooking. In spite of the high dependence of the tilapia fish in the lake as a source of protein, there is little information available on the levels of heavy metals in the lake. This is the first time the biota, sediment and water samples are being determined simultaneously to find out extent of metal contamination in the lake.

Reagents and equipment

Freshly prepared doubly distilled water was used throughout. All solutions were prepared from analytical grade reagents or were used as received. Standard solutions of Fe, Pb, Zn, Cd, Cu, Ni, and Mn were prepared by appropriate dilution of stock solutions (Merck, Germany). All glassware were thoroughly washed with detergent, soaked in 10% HNO₃ solution overnight and finally rinsed with distilled water and dried at 105 °C in an oven (Gallenkamp, UK) before use. Dissolved oxygen was measured using dissolved oxygen meter [model: HI9142]. Hanna portable conductivity meter [Model: HI 8733] and a microprocessor pH meter equipped with glass electrode were employed for conductivity and pH measurements.

Sampling

Two batches each of water, sediment and fish samples were collected from 4different stations around thelake. A total of 180 samples, consisting of 60 samples each of water, fish and sediments were analysed for 7 heavy metals. At the sampling sites, sample bottles were rinsed three times with stream water before filling. Water samplerwas used to collect surface water from the depth of about 0.3 m into 1Lpre-cleaned plastic bottles and was immediately acidified with 5 mL of 0.5% concentratedHNO₃ to control biological activities. Sediment samples were collected from the bottom layers of the lake into clean polyethylene bags using Peterson sample grabber

(WHL 15). The samples were kept in ice boxes and transported to the laboratory where they were stored in the refrigerator at about 4 °C prior to analysis. Temperature, pH and conductivity of the water samples were measured on-site. Total dissolved solids, and suspended solids were measured gravimetrically after drying in an oven at 105 °C to a constant weight^[18].

Sample preparation

In the laboratory, sediments were spread on plastic trays in fumehood and allowed to dry at room temperature. After air drying for 3 days, the samples were ground in a mortar to homogenize and representative samples taken after sieving through 2 mm mesh^[19]. Fish samples were thoroughly washed in distilled water to remove debris. The non-edible parts such as scales, gut contents and the bones were removed before a representative portion of the edible muscle,reflecting the portion consumed by humans, was taken for analysis.

Digestion procedures

An open-beaker digestion procedure was employed^[20,21]. A 5 mLaliquot of concentrated HNO₃ was added to 50 mL of water sample in a 100 mL beaker. This was heated gently on a hotplateuntil the volume got to about 20 mL. Another 5 mLportion of concentrated HNO₃ was added and the beaker covered with a watch glass and the heating continued for 10 more minutes. The solution was poured into a 50 mL volumetric flask and topped up with distilled water to the mark.

Fish samples(0.5 g of crushed muscle tissue) were weighed into 100 mL glass beaker. A 5 mLaliquot of concentratedHNO₃was added and the mixture heated gently on a hotplate for 30 min. A 3

mL portion of distilled water + 10 mL HNO₃ was added to the beaker and heated gently. The solution was then filtered into a 50 mL volumetric flask and made to the volume using de-ionized water^[22,23].

For sediment samples, 5 g of the sieved sample was placed in 250 mL glass beakerand 3 mL of 30% $\rm H_2O_2$ added. This was left to stand for about 60 min until the vigorous reaction ceased. 75 mL of 0.5 M HCl solution was added and the content gently heated on a hotplate for 2 h. The digest was allowed to cool to room temperature, filtered through a whatman 42 filter paper and finally brought to 100 mLwith HCl^[24].

Metal analysis

Perkin Elmer (5100) atomic absorption spectrophotometer equipped with a deuterium background corrector was used. Determinations of heavy metals were carried out in air/acetylene flame using hollow cathode lamps of each metal as the radiation sources. Prior to analysis, the instrument was calibrated according to the manufacturer's manual. Calibration curves were constructed using internal and external standards. Limits of detection of the analysed metals were determined as thrice the standard deviation of the lowest detectable concentrations from the mean of three replicate analyses. Procedural blanks and triplicates were run alongside as part of the quality assurance scheme.

RESULTS AND DISCUSSION

Physical characteristics of the lake

The physical parameters of the lake during the sampling period are recorded in TABLE 1. The average temperature of the surface water samples ranged from 23.6 to 28.3°C, typical of tropical wa-

TABLE 1: Some physical parameters of the lake during sampling period

Physical parameter	Mean	Range
Temperature (°C)	24.5	23.6 - 28.3
pH	9.3	8.96 - 9.32
Conductivity (µS/cm)	356.2	310 - 400
Turbidity (NTU)	48	33 - 54
TSS (mg/L)	23.8	16 - 38.5
Dissolved O ₂ (mg/L)	6.4	3.2 -10.4

ters. The average pH of the lake during the sampling period was 9.30. The pH recorded is higher than the natural background value of 7 and the WHO range for drinking and potable water of 6.5 to 8.5^[25]. The high pH of the water body may be due to the lake's carbonaceous bedrock[16] and soaps that are washed into it. Electrical conductivity (EC) reflects the current-carrying capacity of the water body and is a useful indicator of the mineralization in a water sample^[26]. The average value of 356.2 µS/ cmobtained in this study is less than the WHO limit of 700 µS/cm for drinking water^[25]. At high pH, solubility of inorganic substances^[27] is low and may account for the low EC values measured in the water. Total suspended solid level recorded (23.8 mg/L) is slightly higher than the WHO maximum limit (20 mg/L) for drinking water. The high turbidity of the water may be due to run off from the streams that shed into the lake and also fishing and swimming activities that continuously go on in the lake throughout the year. Average amount of dissolved oxygen in the surface waters was 6.4 mg/Lvarying from 3.2 mg/Lto 10.4 mg/L. There was no correlation (p<0.5) between the physical parameters measured.

Quality assurance

Recovery values, based on 1 mg/g spiking levels in fish and sediment samples, were nearly quantitative (>95%) for all the metals. The mean recoveries of the metals ranged from 78.9% for Fe in water to 97.5% for Zn in sediments (TABLE 2).

The high recovery values show that the digestion method used is reproducible. Detection limits ranged from 0.002 mg/g for Cd, Ni, and Cu in water to 0.095 mg/g for Fe in water. This was indicative

that the instrument was sensitive to the analytes. Repeatability studies yielded a relative standard deviation lower than 10% in all cases.

Heavy metals in samples

Concentrations of heavy metals in water, fish and sediment samples from the lake are shown in TABLE 3

Concentrations of the metals at the different sampling point did not show significant differences (p<0.5). Concentration of Fe ranged from 0.085-0.395 mg/L in water samples, 0.013-0.048 mg/g in fish samples and 0.015-0.050 mg/g in sediment samples. The average concentration of Fe in the water samples were very close to the WHO recommended limit of 0.3 mg/L for drinking water^[25]. The concentration of Fe found in the sediments is lower than 54±9 g/kg found in Lake Dianchi in China^[23] and 12587 mg/kg in Lake Ataturk in Turkey[28]. The results on fish (tilapia) was however comparable to that obtained on a couple of fish species sampled from Turkey and Pakistan[29]. Iron helps the body in many important processes. For example, it is an essential part of haemoglobin, the red pigment in our blood that allows it to carry oxygen around the body. Presence of appropriate concentrations of Fe in food items is therefore desirable.

Concentration of Pb ranged from 0.118 - 0.148 mg/L in water, 0.017-0.303 mg/g in fish and 0.50-0.85mg/g in sediment. Concentration of Pb in sediment was higher than that in water and fish hence the sediment could be an influential factor on the level of Pb in the water body. Water samples contained Pb which was slightly higher than $(10 \ \mu\text{g/L})$ safe limit for consumption recommended^[25]. Chronic ex-

TABLE 2: Quality assurance parameters (n=3)

	Water			Fish			Sediment		
	Rec (%)	RSD (%)	LD (mg/g)	Rec (%)	RSD (%)	LD (mg/g)	Rec (%)	RSD (%)	LD (mg/g)
Fe	78.9	0.4	0.095	89.6	2.0	0.097	90.4	1.0	0.012
Pb	87.5	1.0	0.005	96.4	1.6	0.050	93.5	0.2	0.050
Zn	67.8	0.5	0.050	79.8	0.3	0.050	97.5	0.8	0.020
Cd	93.4	0.3	0.002	92.3	5.1	0.003	89.6	5.3	0.040
Ni	96.2	0.2	0.002	94.2	1.2	0.002	97.3	1.2	0.030
Cu	95.0	0.2	0.002	83.9	6.0	0.016	88.6	3.2	0.010
Mn	94.5	1.0	0.040	91.6	0.9	0.006	92.3	0.8	0.020

Mean recovery (%), relative standard deviation (RSD) (%), limits of detection (LD)

TABLE 3: Concentrations heavy metals in water, sediment and fish from Lake Bosomtwi

		Fe	Pb	Zn	Cd	Ni	Cu	Mn
Water (mg/L)	Mean	0.247	0.129	0.081	0.003	0.210	0.194	0.142
	SD	0.135	0.013	0.013	0.001	0.064	0.048	0.061
	Range	0.085-0.395	0.118-0.148	0.061-0.107	0.003-0.004	0.110-0.421	0.126-0.243	0.016-0.216
Fish (mg/g)	Mean	0.02	0.052	0.016	0.001	0.040	0.060	0.210
	SD	0.010	0.018	0.008	0.000	0.016	0.010	0.020
	Range	0.013-0.048	0.017-0.303	0.008-0.038	0.001-0.002	0.008-0.320	0.006-0.045	0.006-0.555
Sediment (mg/g)	Mean	0.032	0.628	0.129	0.025	0.101	0.025	0.254
	SD	0.020	0.320	0.007	0.012	0.048	0.011	0.122
	Range	0.015-0.050	0.500-0.850	0.050-0.250	0.001-0.100	0.025-0.240	0.010-0.200	0.100-0.400

posure to Pb has been linked to growth retardation and infant mortality concentration of Pb greater than 0.1 mg/L is detrimental to foetuses and children^[30].

The concentrations of Cd ranged from 0.003-0.004 mg/L in water, 0.001-0.002 mg/g in fish and 0.001-0.100 mg/g in sediment. The concentration range obtained from water was lower than the tentative South African Target Water Quality Range (TWQR) guideline of 0-0.005mg/L in water for domestic use^[31] and also lower than the 0.005mg/Lfor USA maximum contaminant level^[32]. However, the concentration of Cd in water was considerably higher than the permissible levels recommended for consumption^[25].

A high level of Cd in the lake's waters is of great concern. Cd is extremely toxic. Cd interferes with metabolic processes in plants andbio accumulatesin aquatic organisms and then enters the food chain^[33]. Cd replaces Zn in the arteries causing inflammation and hardening of the arteries. Concentration of Cd in fish was slightly lower than that in water and sediments. Fishfrom the lake had lower amount of Cd than the safe limits proposed by Food and Agriculture Organisation[34]. Levels of Cd obtained in sediment samples were within the TWQR for both domestic and irrigation purposes. A similar level of Cd(0.01-0.260 mg/g) has been reported for sediment samples from Umtata^[20].

Concentration of Zn ranged from 0.061-0.107 mg/L in water, 0.008-0.038 mg/g in fish and 0.050-0.250 mg/g in sediment samples. Concentration of Zn inwater was lower than the US-EPA limits of 5 mg/L and TWQR for domestic use of 3.0 mg/L. Hence the water has no detrimental effects with re-

gards to the concentration of Zn, at the prevailing pH.

Concentration of Ni ranged from 0.110-0.421 mg/L in water, 0.008-0.032mg/gin fish and 0.025-0.240 mg/g in sediment. Since the concentration of Ni determined was lower than the WHO limit of 20 mg/L, the water can be said to be safe for drinking in terms of its Ni concentration. Concentration of Ni determined was higher than 1-6 μ g/L in Lake Diorani, 1-12 μ g/L in Lake Texoma and 500-900 μ g/L in Lake Ataturk^[28]. Fish samples contained the lowest levels of Ni as compared with water and sediments.

Levels of Cu ranged from 0.126 -0.243 mg/L in water, 0.006-0.045 mg/g in fish and 0.100-0.400 mg/g in sediments. South African Guideline for Cu in domestic water supply is 0 to 1.0 mg/L^[31] whilst^[25,34] and US-EPA limits for Cu in water are 2, 10 and 1 mg/L respectively. Concentration of Cu in water of the lake was lower than the set values, hence adverse effects from domestic use of the water are not expected as far as copper is concerned. The mean concentration of Cu in fish was lower compared with water and sediments. The fish samples also had Cu concentrations below permissible values^[25]. The Cu determined in these diment is within the acceptable range of 30 mg/g.

The levels of Mn ranged from 0.016-0.216 mg/Lin water, 0.006-0.555mg/g in fish and 0.100-0.400 mg/g in sediments. Water contained the lowest levels of Mn compared with fish and sediment. The WHO limits for Mn in water is 0.1mg/L^[25]. Since the concentrations of Mn in water sampled from Bosomtwi is below theset value, the water is suitable fordomestic use with respect to Mn.

In the present study, tilapia fish is used as a bioassay organism for sensitivity to trace and toxic elements effects. The order of accumulation in *Tilapia* busuman is Mn>Fe>Cu>Zn>Ni>Pb>Cd. All the heavy metals determined in the tilapia were below the set value recommended by the Food and Agriculture Organisation^[34].

Bio-concentration factor

Bio-concentration factor (BCF) was used to evaluate the extent of metal bio-accumulation^[32] in the fish samples. Bio-concentration factor is the ratio of the concentration of a metal in organism to that in water environment. The BCF of fish relative to the water was less than unity for all the metals except Mn (0.08, 0.40, 0.20, 0.33, 0.19, 0.31 and 1.48 for Fe, Pb, Zn, Cd, Ni, Cu and Mn respectively). With respect to the sediments, BCF for Cu was the highest (2.40) followed by Mn (1.72). All other metals recorded values < 1 indicating the fish species have not accumulated significantly from the environment. It is known that inorganic species such as heavy metals do not bio-concentrate as much as the organic contaminants^[35].

Pollution load index (PLI)

Pollution load index, defined as the nth root of the multiplicity of the presumed contaminants, is used to determine the quality of the sediment samples. The PLI tells how polluted the sediment is- an indication of the overall toxicity of the soil^[8]. PLI is computed using the relationship

$$PLI = \sqrt[n]{(p_1 p_2 p_3 \dots p_n)}$$
 (1)

Where p is the ratio between the mean concentrations of each metals determined and their baseline concentrations in the sediment. The baseline concentration was taken as the minimum.

While PLI value of zero is an ideal and represents uncontaminated sediment, a value of one indicates the metals are only present at their background levels and a value greater one shows a progressive level of contamination. The PLI computed for the metals under investigation was 3.317 whichshows that the sediment is somehow contaminated. The value is also higher than 1.85 recorded for Lake Veeranam in India^[8].

Estimated daily intake of metals (EDI)

The daily intake of each of the metals was estimated as

$$EDI = \frac{E_f \times E_d \times F_{ir} \times C_f \times C_m}{W_{ab} \times T_a} \times 10^{-3}$$
 (2)

where E_F is the exposure frequency (365 days/year); E_d is the exposure duration, equivalent to average lifetime (70 years); F_{IR} is the fish ingestion rate (g/person/day), which was considered to be 20 g/person/day^[36]; C_f is the conversion factor (0.208) to convert fresh weight to dry weight considering 79% of moisture content; C_m is the concentration of heavy metal in fish (mg/kg); W_{ab} is the average body weight (average adult body weight was considered to be 60 kg); and T_a is the average exposure time for non-carcinogens (which is equal to $E_F \times E_d$)^[36].

Target hazard quotient (THQ)

The THQ, which is a ratio of the estimated exposure (EDI) to the oral reference dose (R_f D), is used to assess the potential non-carcinogenic risk of the consumers of the perceived contaminated food.

$$THQ = \frac{EDI}{R_r D}$$
 (3)

Where the R_fD for Cu, Zn, Ni, Pb, and Cd are 0.04, 0.3, 0.2, 0.0035 and 0.001 mg/kg/dayrespectively^[37]. Health risk assessment of consumers from the

TABLE 4: Estimated dietary intake, food reference dose and target health quotient of tilapia fish from Lake Bosomtwi

	EDI	$\mathbf{R_{f}D}$	THQ
Fe	0.002		
Pb	0.004	0.004	1.030
Zn	0.001	0.300	0.004
Cd	0.000	0.001	0.069
Ni	0.003	0.200	0.014
Cu	0.004	0.040	0.104

intake of metal-contaminated fish was characterised by using the THQ. THQ <1 means the exposed population is unlikely to experience some non-carcinogenic adverse effects during the life time. Otherwise, THQ> 1 means that there is a chance of non-carcinogenic effects, with an increasing probability as the value increases. Except for Pb that registered a THQ greater 1 (1.030), all other metals had THQ well below 1 (TABLE 4).

Consumption of tilapia from the lake can therefore be said to constitute no health risks so far as the heavy metals investigated are concerned. This is based on the assumption that the individual obtains all their fish supplies from the lake and that food processing (such as cooking) has no effects on the levels of heavy metals present in the fish.

CONCLUSION

Because of the closeness of the lake to a major city, it is possible that anthropogenic activities related to industrialization and urbanization have impacted negatively on the quality of the lake. The concentrations of Fe, Zn, Cu, Mn and Ni in Lake Bosomtwi are within the permissible levels recommended by WHO. However, Cd and Pb exhibited higherconcentrations. The accumulation pattern in the study is in the order of Ni>Fe>Cu>Mn>Pb>Zn>Cd. Possible sources of these heavy metals in water may be attributed toanthropogenic sources. Generally, the concentration of heavy metals in sediments was found to be higher than in water and fish with the exception of Ni and Cu. Sediments play a vital role in the adsorption of heavy metals in aquatic environment. Accumulation pattern insediments in the lake is Pb>Mn>Zn>Ni>Cu>Cd>Fe. With reference to the concentrations of heavy metals obtained in this study, water from the lake is unsuitable for domestic and irrigation purposes. Consumption of tilapia fish from the lake was found to pose no health risks to humans. The data provides an insight into the potential impact of heavy metals in the environment and estimate the contamination levels of fish tissues with regards to metals.

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