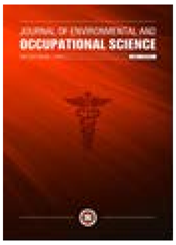
GESDAV

Journal of Environmental and Occupational Science

available at www.scopemed.org



Original Research

Evaluation of mercury and selenium concentrations in the edible tissue of freshwater fish from the Volta Lake in Ghana.

Edward Ebow Kwaansa-Ansah[1], Noah K Asare-Donkor[1], Anthony A Adimado[1], Dong-ha Nam[2]

[1]*Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana.*
[2]*Department of Environmental Health Science, School of Public Health, University of Michigan, Ann Arbor, MI, USA*

Received: August 21, 2013

Accepted: October 10, 2013

Published: October 12, 2013

DOI : 10.5455/jeos.20131010062805

Corresponding Author:
Edward Ebow Kwaansa-Ansah,
Kwame Nkrumah University of Science and Technology, Kumasi, Ghana
eekwaansaansah@yahoo.com

Key words: Total mercury, methylmercury, total selenium, fish species, mercury–selenium relationship.

Abstract

Background: The study of mercury (Hg) and selenium (Se) bioaccumulation in fish is of great importance in order to evaluate the extent of mercury and selenium contamination in the aquatic environment and their possible health risk for humans, considering their antagonistic interactions.

Methods: Total selenium, total mercury, and methyl mercury were determined in one hundred and ninety-nine (199) fish samples belonging to twenty-six (26) different species at various trophic levels in the Volta Lake in Ghana. Total mercury and methyl mercury were determined with a Direct Mercury Analyzer and Selenium with ICP-MS. The concentrations of total mercury, methyl mercury, and total selenium in fish were related to the preferred prey and their bioavailability in the freshwater environment.

Results: There was an increase in concentration of total mercury, methyl mercury and total selenium at successive higher trophic levels of the food chain suggesting that they all biomagnified throughout the food chain. There were statistically significant correlations ($p<0.005$) between total mercury, methyl mercury and total selenium concentrations for all the fish species studied. The molar ratios of total selenium to total mercury and total selenium to methyl mercury in all the fish studied regardless of their positions in the trophic levels were found to be approximately equal to one suggesting protective effects of selenium on methyl mercury toxicity.

Conclusion: This confirms the antagonistic effect of selenium on methyl mercury in fish tissue from the Volta Lake. None of the fish had selenium concentrations above the limit of 3000 ng/g (w/w) considered damaging for fish and other aquatic organisms. Again, none of the fish had methyl mercury and total mercury concentrations exceeding the WHO/FAO guideline values of 300 ng/g and 500 ng/g above which potential health effect could occur.

© 2013 GESDAV

INTRODUCTION

Mercury (Hg) and selenium (Se) are known to be environmental pollutants, although selenium has also been shown to be an essential element in human and animal nutrition. Selenium (Se) is essential to human health and it is a constituent of selenoproteins, which are important antioxidant enzymes and catalyst for the production of active thyroid hormone [1]. Studies have found that Se and certain selenoproteins are well maintained despite prolonged Se deficiency, suggesting the important role of Se in the human body [2, 3]. Methylmercury (MeHg) is a persistent, bioaccumu-lative, and highly toxic form of mercury (Hg) that biomagnifies through aquatic food chains. A major source of MeHg in aquatic systems is the methylation of inorganic Hg by sulfate-reducing bacteria [4]. A major route of exposure to MeHg in humans is the consumption of fish that contain significant amounts of MeHg [5]. One of the factors known to potentially influence fish Hg concentration is the relative trophic level [6]. Experimental studies have suggested that Se may decrease MeHg toxicity under certain exposure conditions [7]. The formation of HgSe likely reduces the amount of Hg available for methylation, leading to less methylmercury (MeHg) accumulation in aquatic food chains. The first report on the protective effects of selenite against mercury toxicity was in 1967 [8]. Since then, numerous studies have shown that selenium supplementation counteracts the negative impacts of exposure to mercury, particularly in regard to neurotoxicity, fetotoxicity, and developmental toxicity with the ability of selenium compounds to decrease the toxic action of mercury being established in all investigated species of mammals, birds and fish [7].

Many studies on the antagonistic effects of selenium (Se) against mercury (Hg) toxicity have been documented [9, 10, and 11]. From experimental studies, MeHg toxicity may occur when the molar ratio of Se: Hg is less than one [12, 13, 14]. There are an increasing number of field studies which assess potential toxicity and bioaccumulation of Hg from aquatic biota using the Se: Hg molar ratio approach [13, 15]. Although we have extensive knowledge on toxic and protective effects of Se in mammals [16, 17], there is very little information on the protective role of Se in fish species. The exact mechanisms of interaction between Hg and Se in fish are not yet fully understood but, data obtained from fish studies indicate that Se, like Hg in aquatic organisms, is mostly found in concentrations that increase proportionally with the trophic species level [18]. However, the relationship between these two elements in fresh-water fish in Africa is currently limited. The Volta Lake in Ghana, one of the world's man-made oligotrophic lakes has three major tributaries which takes their sources from regions where there are some artisanal gold mining activities where mercury is widely used. By measuring Hg and Se concentrations in different fish species with different feeding modes thriving in the same water body such as the Volta Lake in Ghana, a clear understanding of bioaccumulation and biomagnification of mercury in the aquatic food chain could be obtained and compared with that from different aquatic ecosystems to ascertain the extent of mercury and selenium contamination.

The main aim of this study was to determine the type of association between THg and Se, MeHg and Se in the edible muscle of freshwater fish from the Volta Lake in Ghana.

MATERIALS AND METHODS

Sampling and sample preparation

The fish species were collected from a random commercial catches conducted in villages and towns along the Volta Lake by the local fishermen between April, 2009 and January, 2010. Samples were therefore reflective of species meant for consumption. A total of one hundred and ninety-nine (199) fish covering twenty-six (26) different species of fish were obtained. The samples were sorted by species, placed in clean polyethylene bags and stored on ice in an ice-chest. They were transported to the laboratory at the Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, identified and the length and body weight of each taken. The samples were kept on dry ice and shipped to the laboratory at the Department of Environmental Health Sciences, University of Michigan, Ann Arbor, USA for chemical analysis. At the laboratory, the samples were washed with distilled water, dried on tissue paper and a portion of the edible muscle tissue removed from the dorsal part of each fish and dried in an oven at $60^{o}C$ to constant weight. The dried samples were ground with porcelain mortar and pistol, put into polyethylene bags and labelled for analysis.

Total mercury determination

Total mercury was determined with a Direct Mercury Analyzer (DMA-80 Milestone, Inc., Shelton, Connecticut, USA). In the procedure, known weights (~20 mg) of dried fish tissue were taken in quartz boat sample containers. They were transferred onto the autosampler of the DMA and analyzed for their total mercury contents. Quality assurance samples analyzed included National Research Council of Canada (NRCC) DOLT-3 (dogfish liver), DORM-2 (dogfish muscle), and TORT-2 (lobster hepatopancreas).The results indicated reasonable agreement between the found and claimed values and good coefficient of variation (equal to 5%). Average recovery rates of DOLT-3, DORM-2 and TORT-2 for total mercury were 97.9 ± 3.9%, 97.3 ± 4.1 and 98.1 ± 5.2%, respectively. Detection limit was found to be 0.05 ng THg/sample.

Methylmercury determination

For each fish tissue, methylmercury was extracted using a micro-scale method described by Basu et al (2010). In the procedure, approximately 20 mg of dried sample was homogenized in 50 mM Tris-HCl buffer (pH 8.5) containing protease (100 µg), and incubated at 50 °C for 1 hour. Following this digestion, NaOH (40%), cysteine (1%), $CuSO_4$ (25 μM), acidic NaBr, and toluene were sequentially added to the digest and vortexed. Following centrifugation (13,000 revolutions for 5 min), the top toluene layer was transferred into a test tube and mixed twice with $Na_2S_2O_3$ (5 mM) to permit back-extraction of organic Hg into an aqueous phase. The aqueous layer was placed into another test tube for organic Hg analysis. All samples were directly analyzed by a DMA-80 (DMA-80 Milestone, Inc., Shelton, Connecticut, USA). The validity of the methodology and the determination of its accuracy and precision were obtained from quintuplet analysis of 20mg sample of Standard Reference Materials (SRMs) that were brought into solution following the analytical procedure and analyzed. SRMs included National Research Council of Canada (NRCC) DOLT-3 (dogfish liver), DORM-2 (dogfish muscle), and TORT-2 (lobster hepatopancreas).The results indicate reasonable agreement between the found and claimed values and good coefficient of variation (~ 5%). Average recovery rates of DOLT-3, DORM-2 and TORT-2 for methyl mercury were 97.6 ± 5.3%, 98.4 ± 3.9% and 96.9 ± 4.4% respectively. Detection limit was 0.05 ng MeHg/sample.

Selenium determination

Known weight (10mg) of the samples was open flask digested using Optima Fisher conc. HNO_3 (2.0ml) and H_2O_2 (2.0ml) with stepwise heating from 25^{o}C to 95^{o}C for 2 hours. The solution was cooled to 25^{o}C and diluted to 25ml with milliQ water. An Agilent 7500c Octapole ICP-MS equipped with a dynamic reaction cell and a Cetac ASX-500 auto-sampler was used to measure the concentration of the selenium in the digested samples. For quality assurance, National Research Council of Canada (NRCC) SRM, DORM-2 were brought into solution following the analytical procedure and analyzed using ICP-MS. Average recovery was found to be 96.2 ± 5.7%.

Risk estimates associated with human fish consumption

In this study the risk estimates were based on the WHO/FAO provisional tolerable weekly intake (PTWI) for metals and it is an estimated weekly chemical intake that appears to be without risk if ingested over a period of lifetime. MeHg PTWI of the WHO/FAO has been set at 1.6 µg/kg of body mass to protect vulnerable populations from neurotoxicity. It is established that fish consumption is the major source of human exposure to MeHg. Mean MeHg concentrations therefore were used to determine how much fish can be consumed safely a week.

The amount of Fish A (g) can be computed as follow:

A (g) = W (Kg) x I (µg/Kg body weight) / C (µg/g)

Where W = average body weight (65 or 70 kg for adults woman or man respectively),

I = tolerable weekly intake of fish (µg/kg body weight),

C = metal concentration in fish (µg/g).

From this, the mean number of fish that could be consumed safely a week can be calculated by dividing the amount of Fish "A" (g) by the mean weight (g) of each fish species.

RESULTS

The mean concentrations of total mercury (THg), methylmercury (MeHg) and total selenium (TSe) in fish from the Volta Lake are presented in Table 1. For easy comparison, the fish species studied were categorized based on their habitat and trophic levels. The various habitats identified were; demersals, benthopelagics and pelagics. The mean concentrations of THg, MeHg and TSe of the fish samples are represented as a bar chart in Fig. 1. The fractions of fish with MeHg concentration likely to cause toxic effects to wildlife and human are presented in table 2. Table 3 presents results of provisional tolerable weekly intake estimates for fish consumptions for men and women. Figure 2 shows graphs for correlations between THg, MeHg and TSe in fish from the study area.

DISCUSSION

The demersal species had average total mercury, methylmercury and total selenium concentrations of 45.79, 41.54 and 44.41ng/g, respectively. Among the demersal species, *auchenoglanis occidentalis* (Claroteidae, invertivore) recorded the highest means for THg, MeHg and TSe. The lowest concentrations were detected in *tilapia dageti* (Cichlidae, detritivores). For the benthopelagic species, the average concentrations for THg, MeHg and TSe were 45.04, 39.79 and 44.39 ng/g, respectively with *clarias anguillaris* (Catfish, Clariidae, omnivore) recording the highest means and *labeo senegalensis* (Cyprinidae, detritivores) recording the least concentrations. The mean concentrations of THg, MeHg and TSe for the demersal and benthopelagic species were found to be similar although they belong to different trophic levels. This could be attributed to the fact that the species are all non-carnivorous and strife for prey in the same aquatic environment.

Table 1. Concentrations of Total-Mercury, Methylmercury and Selenium in fish species from the Volta Lake.

Fish Species	Sample Size (n)	Mean T-Hg (ng/g)	Mean Me-Hg (ng/g)	Mean Se (ng/g)
Auchenoglanis Occidentalis	5	76.78 ± 12.33 (68.61-110.45)	70.98 ± 11.26 (62.43-99.45)	66.89 ± 10.54 (59.42-82.48)
Bagrus Docmac	6	77.77 ± 15.28 (68.61-110.45)	70.33 ± 14.99 (48.20-92.99)	71.16 ± 14.09 (53.47-90.19)
Chrysichthys Auratus	12	66.07 ± 11.38 (53.81-101.45)	60.44 ± 9.81 (50.35-89.10)	65.57 ± 9.11 (51.38-97.92)
Chrysichthys Nigrodigitatus	16	27.95 ± 4.24 (14.42-61.27)	25.15 ± 3.92 (12.89-55.17)	30.44 ± 8.53 (14.36-64.52)
Clarias Anguillanis	5	237.77 ± 26.19 (94.15-355.16)	214.86 ± 24.85 (87.40-319.48)	228.23 ± 23.12 (93.05-322.90)
Dischodus Rostratus	6	29.17 ± 7.14 (24.75-38.46)	27.23 ± 6.82 (18.71-34.65)	28.54 ± 8.78 (24.27-36.85)
Hemichromis elongatus	8	27.96 ± 3.47 (18.56–30.43)	24.85 ± 5.76 (18.24-27.89)	24.89 ± 7.62 (16.84-28.79)
Hydrocynus Forkaii	4	194.15 ± 20.38 (165.24-256.17)	176.92 ± 19.63 (148.69-234.24)	227.86 ± 25.65 (174.69-239.84)
Labeo Coubie	7	13.32 ± 2.55 (9.51-16.02)	11.81 ± 1.43 (8.45-15.08)	13.19 ± 3.28 (9.62-16.23)
Labeo senegalensis	10	3.38 ± 1.42 (0.85-5.26)	3.08 ± 1.06 (0.74-5.09)	3.89 ± 1.29 (1.59-6.06)
Oreochromis niloticus	9	62.33 ± 12.73 (31.86-74.92	54.82 ± 10.56 (28.11-71.69)	65.14 ± 16.78 (39.82-74.13)
Nannocharax Ansorgii	10	89.23 ± 12.47 (54.23-116.40)	79.82 ± 14.53 (49.68-104.42)	87.75 ± 14.92 55.24-119.55)
Schilbe Mystus	5	20.05 ± 4.72 (11.65-28.86)	18.12 ± 3.99 (10.67-25.63)	21.89 ± 3.53 (14.85-28.38)
Schilbe Intermedius	3	166.32 ± 20.24 (158.33-171.56)	147.06 ± 19.55 (142.77-154.43)	156.23 ± 21.45 (146.29-160.91)
Sierrathrissa Leonensis	5	128.52 ± 18.74 (92.19-136.11)	112.64 ± 18.63 (84.73-119.67)	108.52 ± 16.04 (88.24-121.25)
Synodontis batensoda	7	153.47±16.98 (112.39-185.27)	131.98±15.82 (108.27-155.54)	152.62 ± 17.75 (115.68-184.79)
Synodontis black	8	17.56 ± 3.28 (13.92-22.73)	15.98 ± 2.38 (10.64-18.25)	18.94 ± 4.41 (14.68-23.36)
Synodontis clarias	7	29.35 ± 7.85 (17.68-36.44)	25.83 ± 5.64 (17.03-30.16)	28.85 ± 6.78 (16.55-36.14)
Synodontis eupterus	9	19.35 ± 3.96 (14.58-26.35)	17.61 ± 3.13 (13.84-22.08)	18.53 ± 4.95 (14.26-26.94)
Synodontis gambiensis	7	42.82 ± 9.55 (35.14-51.29)	38.11 ± 7.39 (31.55-45.58)	39.84 ± 5.84 (34.11-49.26)
Synodontis membranaceus	10	49.08 ± 7.83 (37.22-60.19)	44.17 ± 6.85 (35.17-51.54)	48.27 ± 6.77 (33.08-57.41)
Synodontis ocellifer	12	24.95 ± 2.79 (16.95-33.53)	21.96 ± 2.55 (15.06-26.72)	26.15 ± 3.95 (16.17-34.18)
Tilapia aurea	9	59.86 ± 4.52 (47.18-73.75)	54.51 ± 4.11 (45.78-63.14)	55.33 ± 4.38 (46.02-74.98)
Tilapia galilaea	8	22.52 ± 3.86 (16.08-27.48)	20.04 ± 3.79 (15.62-26.29)	25.08 ± 4.89 (16.98-29.25)
Tilapia dageti	7	20.05 ± 4.26 (11.65-28.86)	18.12 ± 3.75 (10.67-25.63)	21.32 ± 4.54 (11.86-29.17)
Tilapia zilli	11	66.38 ± 18.77 (50.18-82.92)	57.75 ± 17.46 (41.06-65.98)	65.28 ± 13.58 (47.86-79.02)

Values in parenthesis represent the range of concentrations

Table 2. Fraction of fish with MeHg concentrations likely to cause toxic effect to wildlife and humans

Potential risk for	MeHg Criteria	Demersals (71)		Benthopelagics (106)		Pelagics (22)		Total (199)	
		n	%	n	%	n	%	n	%
Wildlife	≥ 100 ng/g	0	0	10	9.43	15	68.10	25	12.56
	Se:Hg≤1	5	7.00	0	0	5	22.72	10	5.03
Human	≥300 ng/g	0	0	2	1.98	0	0	2	1.01
	Se:Hg≤1	5	7.04	0	0	5	22.72	10	5.03

*n represents the number of fish in each trophic level above the threshold limits of each risk criterion and "%" represents the percentage of this number to the total number in the group. MeHg criteria are those of USEPA (2001) for wildlife (≤100 ng/g) and humans (≤300 ng/g) protection.

Table 3. Provisional Tolerable Weekly Intake estimates.

Fish Species	Mean Wt. (g)	Mean MeHg (μg/g)	Amount of fish per week (g)	
			Woman	Man
Auchenoglanis Occidental	280	0.071 ± 0.011	1465	1577
Bagrus Docmac	260	0.070 ± 0.015	1486	1600
Chrysichthys Auratus	32	0.060 ± 0.011	1733	1867
Chrysichthys Nigrodigitatus	145	0.025 ± 0.004	4160	4480
Clarias Anguillanis	240	0.215 ± 0.026	484	521
Dischodus Rostratus	65	0.027 ± 0.007	3852	4148
Hemichromis elongatus	20	0.025 ± 0.006	4160	4480
Hydrocynus Forkaii	120	0.177 ± 0.020	588	633
Labeo Coubie	98	0.012 ± 0.001	8667	9333
Labeo senegalensis	38	0.003 ± 0.001	34667	37333
Oreochromis niloticus	186	0.055 ± 0.011	1891	2036
Nannocharax Ansorgii	214	0.080 ± 0.014	1300	1400
Schilbe Mystus	96	0.018 ± 0.004	5778	6222
Schilbe Intermedius	123	0.147 ± 0.019	707	762
Sierrathrissa Leonensis	231	0.113 ± 0.018	920	991
Synodontis batensoda	226	0.132 ± 0.016	788	848
Synodontis black	78	0.016 ± 0.002	6500	7000
Synodontis clarias	67	0.026 ± 0.006	4000	4308
Synodontis eupterus	29	0.018 ± 0.003	5778	6222
Synodontis gambiensis	110	0.038 ± 0.007	2736	3733
Synodontis membranaceus	234	0.044 ± 0.007	2364	2545
Synodontis ocellifer	109	0.022 ± 0.003	4727	5090
Tilapia aurea	102	0.055 ± 0.004	1891	2036
Tilapia galilaea	156	0.020 ± 0.004	5200	5600
Tilapia dageti	120	0.018 ± 0.004	5778	6222
Tilapia zilli	116	0.058 ± 0.017	1793	1931

*Mean MeHg concentration of each fish species were used in calculation. Average body weight of 65 and 70 kg for woman and man respectively was considered.

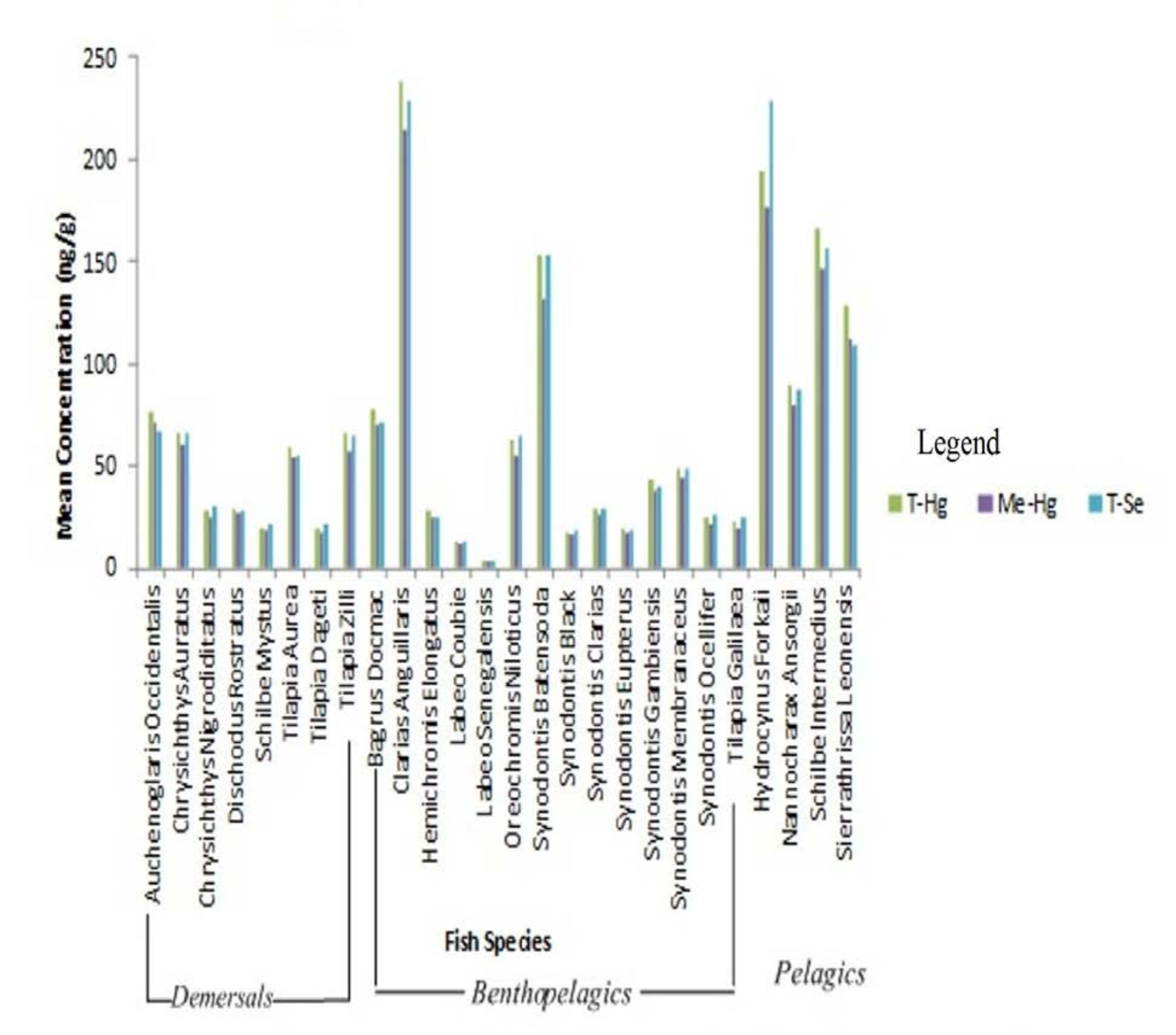


Fig. 1. Concentrations of total mercury (THg), methyl mercury (MeHg) and total selenium in tissues (dry weight) of different fish species from the Volta Lake.

The average THg, MeHg and TSe concentrations for the pelagic species were 144.56, 128.93 and 145.09 ng/g respectively with *hydrocynus forkaii* (Alestidae, piscivore) recording the highest means and *nanncharax ansorgii* (Citharinidae, piscivore) recording the least.

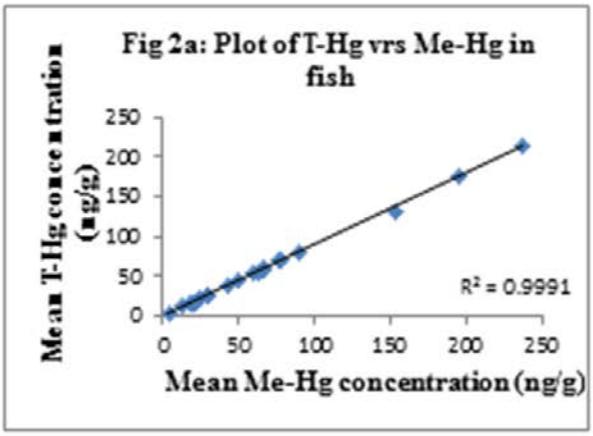
The mercury and selenium concentrations varied depending on the trophic position of the fish species as demonstrated in Fig 1. Hg and Se concentrations in fish tissues were observed to increase from the bottom feeders to the piscivorous species suggesting biomagnification of these elements along the food webs which is in accordance with some studies from the tropical and temperate regions [19, 20]. When the feeding habits for the species were considered, the carnivorous species (pelagics) were observed to accumulate higher levels of THg, MeHg and TSe than the non-carnivorous species (demersals and bethopelagics) which was similar to the results reported by Lima et al [21] from the Para State, Brazil. The carnivorous species were about three (3) times more contaminated than the non-carnivorous species interms of mercury (Fig. 1). This observation was similar to the TSe concentrations recorded by the carnivorous and the non-carnivorous species.

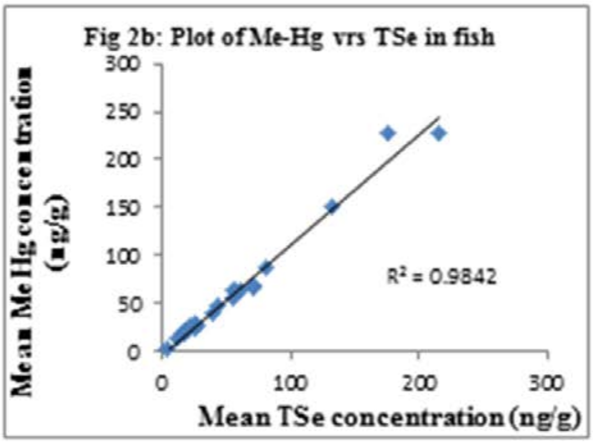
THg levels varied widely among the fish species studied with the highest value of 355.16 ng/g occurring in *clarias auguillaris* (Clariidae, omnivore) and the lowest value of 0.85 ng/g occurring in *labeo senegalensis* (cyprinidae/omnivore). The highest THg was found to be in the order of 417 magnitudes higher than the lowest one. MeHg varied between 0.74 ng/g and 319.48 ng/g with the highest value occurring in *clarias auguillanis* and the lowest in *labeo senegalensis.* This observed trend was similar to that of THg. Ouédraogo et al [18] reported high levels of THg and MeHg in *clarias auguillanis* from lakes in Burkina Faso which is similar to the current results obtained from the Volta lake in Ghana. The highest MeHg was found to be in the order of 432 magnitudes higher than the lowest. All the fish samples from the Volta Lake recorded THg concentrations below the World Health Organization's threshold value of 500 ng/g [22].

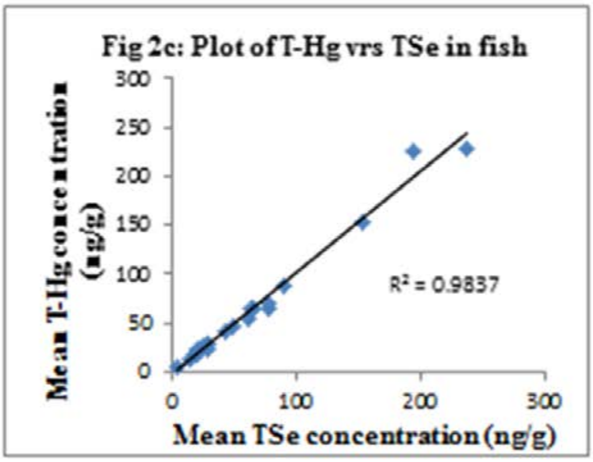
The TSe concentrations in the fish varied in a similar manner as the THg and MeHg levels with the highest value being up to 203 orders of magnitude higher than the lowest. The highest TSe concentration of 322.90 ng/g was detected in *clarias auguillanis* and the lowest value of 1.59 ng/g recorded in *labeo senegalensis.* However, all the fish species studied had TSe concentrations lower than threshold (500 ng/g) established by Watanabe et al. [23]. Although some individual fish recorded high levels of mercury (THg and MeHg), these individuals also presented the highest selenium contents and mean molar ratio obtained between these elements (Fig 1), indicating that both Hg and Se are equivalently present in these fish samples.

There were statistically significant correlations ($p<0.005$) between THg, MeHg and TSe concentrations for all the fish species studied (Fig 2a, 2b, 2c). The mercury and selenium concentrations were significantly correlated with weight for some species of the fish studied (mostly the piscivorous). The correlations between these elements have also been studied in some fish samples from other freshwater and marine waters of the world [18, 24, 25, 26] and similar results were reported. Hagmar et al. [27] reported a significant correlation between fish intake and blood selenium and selenoproteins by some Latvian subjects, indicating that fish had a considerable impact on selenium status of human.

Since all the species investigated lived far from local man-made sources of pollution, their Hg and Se levels may be from natural sources. Differences in THg concentrations and the relative proportion of the MeHg in the tissue of these freshwater fish may be considered to be the consequence of some factors which includes the dietary mercury intake and storage, elimination and detoxication capabilities and capacity of migration. Several papers have reported that the chemical interaction between mercury and selenium is one of the possible mechanisms leading to mercury detoxication [15, 28, and 29]. From the high concentrations of TSe as compared to the MeHg levels, it could be suggested that the interactions between mercury and selenium in the tissue of fresh-water fish from the Volta Lake is one of antagonism rather than synergism. This suggestion is also evident from the significantly positive correlations ($p<0.005$ in all cases) between the concentrations of selenium and mercury in the tissue of the fish studied as demonstrated in fig. 2a, 2b and 2c.







Potential health hazard assessment

The levels of Se found in the fish samples studied could be said not to pose health risk for both humans and wildlife. This conclusion was based on the fact that none of the fish had TSe concentrations above the set limit of 3000 ng/g (w.w) considered to be damaging for fish. The risk assessment was therefore estimated only on the threat posed by MeHg content of the fish (Table 2). Considering the total number of fish samples analyzed (n=199), 12.56% exceeded the wildlife Hg threshold of 100 ng MeHg/g w/w set by the USEPA [30]. Out of this, 15% of the total number of the pelagics, 10% of the benthopelagics and 0% of the demersals had their MeHg contents exceeding the set limit. Only 1.01% of the total number of fish (1.98% of benthopelagics) had MeHg content exceeding 300 ng MeHg/g w.w for human health protection (corresponding to the 500 ng THg/g w.w threshold limit of W.H.O.) set to protect individuals prone to Hg toxicity.

In recent times, it has been proposed that the molar ratio of Se:Hg ≥ 1 is safe for fish health [13]. Taking into consideration the Se-Hg interactions, 10 individual fish samples (corresponding to 5.03% of the total fish samples) had molar ratio of Se:Hg≤ 1 (Table 2). It could therefore be suggested that 5.03% of the total number of fish from the Volta lake in Ghana analyzed could pose health risk when the protective effect of Se on Hg is considered. Although approximately 95% of freshwater fish samples from the Volta Lake analyzed could be said to be safe for human consumption in terms of Hg toxicity, care must be taken since other contaminants that could reduce the concentration of Se may be present in the aquatic system. We therefore agree with Burger et al [31] who suggested that care should be taken before integrating Se:Hg ratios in risk assessments for Hg toxicity due to other factors that could influence it.

Estimation of Provisional Tolerable Weekly Intake of Fish.

Fish dietary intake studies in the Volta River basin particularly Ghana are needed in order to relate the actual fish consumption patterns among populations to potential health effects, since the main source of methylmercury intake by humans is through fish diet. The Provisional Tolerable Weekly Intake (PTWI) estimates are summarized in Table 3. The results show that all the fish species had MeHg concentrations below the WHO/FAO threshold of 0.50 µg/g above which would be deemed hazardous to human health.

However, fish such as *clarias anguillanis* with mean MeHg concentration of 0.215 µg/g should be consumed with care since the levels could bioaccumulate with time. Again, the pelagic, piscivorous species *hydrocynus forkaii, nannocharax ansorgii, schilbe intermedius* and *sierrathrissa leonensis* should also be consumed with moderation since almost all had considerable mean concentrations of MeHg in the ranges of 0.08, 0.113, 0.147 and 0.177 µg/g respectively. The consumption could be limited to at most one fish per week for both men and women to forestall any eventuality in Hg contamination.

CONCLUSION

The study demonstrated that there is a generally low concentration of Se and Hg in fish species from the Volta Lake suggesting that the aquatic environment has not been impacted significantly by the metals. TSe was positively and significantly correlated with both THg and MeHg concentrations in the tissue of the fish species studied. Taking into consideration the Se-Hg interactions and Se:Hg molar ratio as a criterion for fish safety, about 95% of the freshwater fish samples from the Volta Lake could be said to be safe for human consumption in terms of Hg toxicity. The *clarias anguillanis* species and large piscivorous fish such as *hydrocynus forkaii, nannocharax ansorgii, schilbe intermedius* and *sierrathrissa leonensis* were found to accumulate high levels of MeHg therefore their consumption should be regulated and care taken since other contaminants such as arsenic that could reduce the concentration of Se may be present in the aquatic system. However, the low contents of Hg found in this study and the absence of any official reports on mercury poisoning in the inhabitants of Volta Lake region that consume the fish suggest that Se can be acting as a detoxification agent for Hg. A more comprehensive study concerning the interaction of various Hg and Se chemical forms is necessary and Hg toxicity should be determined in general foods of the population in the Volta River basin.

ACKNOWLEDGMENT

The authors wish to thank Mr. D. O. Abdul Rahaman, Department of Fisheries, Yeji and Mr. Munir Abdullah Dawood of Department of Theoritical and Applied Biology, Kwame Nkrumah University of Science and Technology for their assistance in obtaining and identifying the fish species. The immense support of the African Study Center, University of Michigan in shipping and carrying out the analysis in the USA is also acknowledged. Finally, Professors Jerome O. Nriagu and Niladri Basu of the Department of Environmental Health Sciences, School of Public Health, University of Michigan are also acknowledged for their academic and technical support.

REFERENCES

1. Rayman MP. The importance of selenium to human health. Lancet. 2000; 356, 233 – 241.
2. Chen J, Berry MJ. Selenium and selenoproteins in the brainand brain disease. J. Neurochem. 2003; 86, 1-12.
3. Whanger PD. Selenium and the brain: a review. Nutr. Neurosci. 2001; 4 (2): 81 – 97.
4. Regnell O, Hammer T, Helgee A, Troedsson B. Effect of anoxia and sulphide on concentrations of total and methyl mercury in sediment and water in two mercury polluted lakes. Ca . J. Fish Aquat. Sci. 2001; 58, 506 – 517
5. Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW. Effect of environmental methylmercury on the health of wild birds, mammals and fish. Ambio. 2007; 36, 12-18.
6. Weech S, Scheuhammer AM, Elliott J, Cheng K. Mercury in fish from Pinchi lake region, British Columbia, Canada. Envron. Pollut. 2004; 131, 275 – 286.
7. Choi AL, Budtz-Jorgensen E, Jorgensen PJ, Steuerwald U, Debes F, Weihe P, Grandjean P. Selenium as a potential protective factor against mercury developmental neurotoxicity. Environ. Res. 2008; 107, 45 – 52.
8. Parizek J, Ostadalova I. The protective effect of small amounts of selenite in sublimate intoxication. Experimental. 1967; 23 (2): 142 – 143.
9. Yang DY, Chen YW, Gunn JM, Belzile N. Selenium and mercury in organisms: interactions and mechanisms. Environ Res 2008; 16:71–92.
10. Berry MJ, Ralston NVC. Mercury toxicity and the mitigating role of selenium. EcoHealth 2008; 5:456–9
11. Khan MAK, Wang F. Mercury–selenium compounds and their toxicological significance toward a molecular understanding of the mercury–selenium antagonism. Environ Toxicol Chem 2009; 28:1567–77.
12. Ralston NVC, Raymond LJ. Dietary selenium's protective effects against methylmercury toxicity. Toxicology 2010; 278:112–23.
13. Yang DY, Ye X, Chen YW, Belzile N. Inverse relationships between selenium and mercury in tissues of young walleye (Stizosedion vitreum) from Canadian boreal lakes. Sci Total Environ. 2010; 408:1676–83.
14. Peterson SA, Ralston NVC, Peek DV, Spate VL, Morris JS. How might selenium moderate the toxic effects of mercury in stream fish of the western US? Environ Sci Technol 2009; 43:3919–25.
15. Belzile N, Chen Y-W, Gunn JM, Tong J, Alarie Y, Delonchamp T, Lang C-Y. The effect of selenium on mercury assimilation by freshwater organisms. Can J Fish Aquat Sci 2006; 63:1-10.
16. Tran D, Moody AS, Fisher, Foulkes ME, Jha N. “Protective effects of selenium on mercury-induced DNA damage in mussel haemocytes”, Aquat. Toxicol. 2007; 84:11-18
17. Agusa T, Nomura K, Kunito T , Anan Y, Iwata H, Miyazaki N, Tatsukawa R, Tanabe S. Interelment relationships and age-related variation of trace element concentration in liver of striped dolphins (Stenella coeruleoalba) from Japanese coastal waters. Mar. Pollut. Bull. 2008; Vol.57 (6-12): 807 - 815.
18. Ouédraogo O, Amyot M. Mercury, arsenic and selenium concentrations in water and fish from sub-Saharan semi-arid freshwater reservoirs (Burkina Faso) Sci. Total Environ. 2013; 444:243–254.
19. Chen C-Y, Stemberger RS, Klaune F, Blum JD, Pickhardt PC, Folt CL. Accumulation of heavy metals in foodweb components across a gradient of lakes. Limnol Oceanogr 2000; 45:1525–36.
20. Campbell L, Verburg P, Dixon DG, Hecky RE. Mercury biomagnification in the food web of Lake Tanganyika (Tanzania, East Africa). Sci Total Environ 2008; 402:184–91.
21. Lima APS, Sarkis JES, Shihomatsu HM, Muller RC. Mercury and Selenium concentrations in fish samples from Cachoeira do Piria Municipality, Para State, Brazil. Environ. Res. 2005; 97:236 – 244.
22. FAO/WHO. Safety evaluation of certain food additives and contaminants. WHO Food Additives. Geneva: World Health Organization; 2004.
23. Watanabe T, Kiron V, Satoh S. Trace minerals in fish nutrition. Aquaculture 1997; 151, 185–207.
24. Farias LA, Déborah IT, Fávaro, Curcho MRSM, Fonseca BC, Nascimento SM, Kunioshi L, Braga ES. Mercury and Selenium accumulation assessment in fish most consumed by Cubatão community, São Paulo, Brazil. *2009 International Nuclear Atlantic Conference - INAC 2009 Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009 Associação Brasileira de Energia Nuclear – ABEN ISBN:* 978-85-99141-03-8
25. Ikemoto T, Kunito T, Tanaka H, Baba N, Miyazaki N, Tanabe S. “Detoxification mechanism of heavy metals in marine mammals and seabirds: interaction of selenium with mercury, silver, copper, zinc and cadmium in liver”, Arch. Environ. Contam. Toxicol.. 2004; 47: 402-413.
26. Burger J, Gaines KF, Boring CS, Stephens Jr. WL, Snodgrass J, Gochfeld M. Mercury and selenium in fish from the Savannah River: species, trophic level, and locational differences. Environ. Res. Sect. A 2001; 87, 108–118.
27. Hagmar L, Persson-Morchos M, Akesson B, Schutz A. Plasma levels of selenium, selenoprotein P and glutathione peroxidase and their correlations to fish intake and serum levels of thyrotropin and thyroid hormones: a study on Latvian fish consumers. Eur. J. Clin. Nutr. 1998; 52, 796–800.
28. Cuvin-Aralar LAM, Furness RW. Mercury and selenium interaction: A rewiew. Ecotoxicol Environ Saf. 1991; 21, 348 – 364.
29. Gailer J. Arsenic–selenium and mercury–selenium bonds in biology. Coord Chem Rev 2007; 251:234–54.

30. USEPA. Water quality criterion for protection of human health: methylmercury EPA 823/R 01/001. Washington, DC: EPA; 2001.

31. Burger J, Gochfeld M. Selenium and mercury molar ratios in saltwater fish from New Jersey: individual and species variability complicate use in human health fish consumption advisories. Environ Res 2012; 114:12–23.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.