GESDAV

Journal of Environmental and Occupational Science

available at www.scopemed.org

Original Research

Distribution of mercury in water, sediment and fish from the Volta lake and its major tributaries.

Edward Ebow Kwaansa-Ansah[1], Anthony Apeke Adimado[1], James Hawkins Ephraim[2]

[1]Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana.
[2]Catholic University College, Fiapre, Sunyani, Ghana.

Received: March 22, 2012

Accepted: May 06, 2012

Published: May 10, 2012

DOI : 10.5455/jeos.20120506035722

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

Key words: total mercury, methylmercury, fish, sediment, water.

Abstract
Concentrations of total mercury and methyl mercury were determined in fish and sediment from the waters of the Volta Lake and its main tributaries to understand their distribution in the ecosystem. Total mercury concentrations in fish ranged from 2.11to 355.16 (mean: 75.64) ng/g wet wt. Methyl mercury concentration ranged from 1.77 to 319.48 (mean: 68.44) ng/g wet wt and accounted for, on the average 90% of the total mercury in the muscles of the fish. Methyl mercury concentrations in fish were directly proportional to total mercury concentrations with average correlation coefficient of r = 0.98. The relationship of total mercury and methyl mercury concentrations in fish to those of sediments from corresponding locations was fish-species dependent. Concentrations of total mercury in sediment ranged from 0.96 to 700.25 ng/g dry wt. which is lower than the IAEA threshold of 810ng/g. Water samples from the main tributaries of the Volta and the Volta Lake showed total mercury concentrations of 0.0027 to 0.0862 ng/L and methylmercury concentrations of 0.0004 to 0.0259 ng/L. The methylmercury concentrations accounted for 13.2 to 35.0% of total mercury in the water samples. The results of this study indicate that mean total mercury and methylmercury concentrations in fish increase with increase in trophic level of fish. All the fish samples obtained from the Volta and its major tributaries had mercury concentrations below the WHO/FAO recommended limit of 500 ng/g wet weight. The low levels of mercury in the fish analyzed in this study suggest a comparatively clean aquatic environment which has not yet been impacted by mercury contamination.

INTRODUCTION

Mercury is one of the most toxic elements impacting on human and ecosystem health and therefore is one of the most studied environmental pollutants [1]. Humans and wildlife throughout the world are exposed to mercury, often at levels that raise concern for health and environmental effects [2,3]. Although its potential for toxicity in highly contaminated areas is well documented, research has shown that mercury can be a threat to the health of people and wildlife in many environments that are not obviously polluted [4]. Mercury travels easily through different environmental media, in a variety of chemical forms including its volatile form over long distances leading to global pollution. The risk is determined by the likelihood of exposure, the form of mercury present and the geochemical and ecological factors that influence how mercury moves and changes form in the environment. Mercury cycling in aquatic environments is very complex. The ultimate source of mercury to most aquatic ecosystems is deposition from the atmosphere, primarily associated with rainfall. Once in the aquatic environment, mercury enters a complex cycle in which the various forms can be converted from one form to other with the formation of methylmercury being the most important. The Primary sink for mercury in the aquatic ecosystem is bottom sediments where the inorganic form undergoes methylation to the organic form which can enter the food chain or can be released back to the atmosphere by volatilization. The

biogeochemical factors in sediments greatly influence the transformation of inorganic mercury to methylmercury (MeHg) that, in turn, determines its potential for bioaccumulation and biomagnification in food webs [5]. Although most mercury in the environment is inorganic, some is converted to the highly toxic methyl mercury (MeHg), which bioaccumulates in fish. Fish are an important dietary source in many developed and developing nations. In some communities, fish, shellfish, birds, and marine mammals constitute critical components of the diet or local economies. Fish form an important component of the diet of most Ghanaians, providing up to about 90% of animal protein [6]. MeHg concentrations in fish are commonly high enough to represent a risk to the health of the fish-eating communities [2]. Mercury is potentially accumulated in organisms and sediments, and subsequently transferred to man through the food chain [7]. Although extensive researches have been carried out in many countries to evaluate the presence and distribution of mercury in the aquatic system including fish [8,9], information on mercury contamination of fish and sediments in freshwaters of Ghana remains lacking. Studies carried out in Ghana on mercury contamination have been focused on the Gulf of Guinea and artisanal gold mining areas [10-18]. This research is aimed at assessing the extent of distribution of mercury in the Volta Lake, the largest man-made lake in the world. The Volta is an international river draining five West African countries (Mali, Togo, Burkina Faso, Cote d'Ivoire and Ghana) with a total length of about 1,200 km and a drainage area of about 400,000 km2 with 60% lying in Ghana. Aside the marine (80%), the main source of fish for the general population is the Volta (19%). Volta and its tributaries after the construction of the Akosombo dam which is located downstream of the Volta river has enhanced the accumulation of pollutants in the lake. Potential health risk to humans may arise through the consumption of mercury contaminated fish.

MATERIALS AND METHODS

Sample collection

Sediment and fish samples were collected between June 2009 and January 2010. Sediment samples were collected from a speed boat with an Ekman grab according to the standard procedure described by the USEPA (1994) for sediment sampling. A clean plastic scoop was used to collect the top few centimeters of the bed sediments. Generally, samples were taken from multiple points (four) at each site, which were then pooled, homogenized and then subsampled. The samples were placed in clean dark-polyethylene bags, labeled and stored on ice in an ice container. The samples were transported to the laboratory at Kwame Nkrumah University of Science and Technology, Kumasi and frozen at -20°C within 24 h of collection. Portion of the Sediment samples were air dried, sieved through 2 mm mesh and homogenized by grinding using mortar and pestle and analyzed for their total mercury contents. The fish species were collected from random commercial catches in villages/towns along the Volta Lake and its major tributaries (Black Volta, White Volta, and Oti rivers) depending on the availability of the species for sale. Fish were collected at most locations where sediments had been taken. Samples obtained were therefore reflective of species meant for consumption. A total of 366 fish samples covering fifty-two (52) different species were obtained. The samples were sorted by species, placed in clean plastic bags and stored on ice in ice chest. They were then transported to the laboratory at KNUST, identified and the total length and total weight of each fish taken. In the laboratory, whole fish were dissected, the skin removed, and equal amounts of muscle fillets of several individuals of the same species from each location were pooled, homogenized, and portion analyzed for total mercury content. The remaining portions of sediment and fish samples were stored on dry-ice at a temperature of -20ºC in sterilized polypropylene containers and transported to the Environmental Health Sciences laboratory of the University of Michigan Ann Arbor, USA for chemical analysis. Fish species analyzed included the following: *Auchenoglanis occidentalis, Auchenoglanis biscutatus, Barbus atakorensis, Bagrus docmac, Barbus Guilda, Barbus leonensis, Chelaethiops bibie, Chrysichthys auratus, Citharinops distichodoides,Ctenopoma kingsleyae, Ctenopoma petherici, Chiloglanis voltae, Clarias anguillaris, Chiloglaris occidentalis, Chrysichthys nigrodigitatus, Distchodus rostratus, Distichodus brevipinnis, Gnathonemus senegalensis, Gobiodes sagitta, Gymnarchus niloticus, Hydrocynus forskalii, Hyperopisus bebe, Hemichromis fasciatus, Labeo coubie ,Labeo parvus, Labeo senegalensis, Mormyrops anguilloides Mormyrops breviceps, Mormyrus rume rume, Nannocharax ansorgii, Nannocharax fasciatus, Nannocharax occidentalis, Neolebias unifasciatus, Oreochromis niloticus, Sarotherodon galilaeus, Sarotherodon melanotheron, Sarotherodon obesus, Schilbe Intermedius, Schilbe mystus, Sierrathrissa leonensis, Synodontis batensoda, Synodontis, Synodontis eupterus, Synodontis filamentosus, Synodontis gambiensis, Synodontis membranaceus, Synodontis nigrita, Synodontis ocellifer, Tilapia dageti, Tilapia guineensis, Tilapia Lineatus, Tilapia zilli,*

Water samples were collected with clean polypropylene bottles from the major tributaries (black volta, white volta and oti rivers) as part of the study to determine mercury concentrations in water flowing through the Volta basin before emerging into the lake as well as the

lake waters from all the sites where sediments were taken. Temperature, pH, and dissolved oxygen were measured on site and adequate precautions were exercised to avoid contamination of the water samples during sampling, transport, and handling. Portion of the water samples were analyzed for their physico-chemical parameters and total mercury concentrations at the laboratory in the Department of Chemistry, KNUST and the remaining portion kept in the freezer at -20ºC till it was transported to the USA for methylmercury determination.

Chemical analysis

Fish and sediments samples were digested for total mercury determination by an open flask procedure developed at the National Institute for Minamata Disease (NIMD) in Japan by Akagi and Nishimura [19] and reported earlier [20]. Total mercury concentrations were determined in all the digests by cold vapour atomic absorption spectrophotometry using an automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd., Japan) developed at NIMD. The reducing reagent used in the mercury analysis was 0.5 ml of 10% (w/v) $SnCl_2.2H_2O$ in 1 M HCl. Extraction and digestion of the water samples for total mercury was based on the procedure developed by Akagi and Nishimura.

In the procedure, 1L of water sample was put into a separatory funnel, 10ml of 20N H_2SO_4 and 5ml of 0.5 % $KMnO_4$ were added. The mixture was shaken thoroughly and allowed to stand for 5 minutes. The solution was neutralized with 20 ml 10 N NaOH, and 5 ml of 10% $NH_2OH.HCl$ was added and the mixture shaken. The mixture was allowed to stand for 30 minutes and 5 ml of 10% EDTA were added and the mixture shaken. 10 ml of purified 0.01% dithizone-toluene was added and the mixture shaken for five minutes. The mixture was allowed to stand for 1 hour avoiding direct sunlight. The organic phase was centrifuged at 1200 rpm for 5 minutes and dried with 0.5g Na_2SO_4. Exactly 10ml of the solution was taken in a 50ml digestion flask and evaporated to dryness on a water bath at 60oC with a rotary evaporator. The residue was then subjected to wet digestion with 1ml H_2O, 2ml HNO_3-$HClO_4$ (in the ratio of 1:1) and 5ml H_2SO_4 and heated at 200ºC for 30minutes. The solution was allowed to cooled and made up to 50ml mark and its total mercury content determined by cold vapour atomic absorption spectrometry using an automatic mercury analyzer.

Methyl mercury in sediment and fish tissue was analyzed following the method described by Basu *et al.* [21]. In the procedure, sub-samples were dried (at 60°C) and ground to a powder using a glass Teflon homogenizer. Exactly 40 mg of dried sample was homogenized in 360 µl of 50 mM Tris-HCl buffer (pH 8.5) containing protease (100 µg), and incubated at 50 °C for 1 hour vortexing at every 10 minutes. Following this digestion, 125ul of NaOH (40%), 50µl of cysteine (1%), 50µl of $CuSO_4$ (0.5M) and 50µl of acidic NaBr were sequentially added to the digest and vortexed for 30 seconds.250µl of toluene was added and vortexed for 1minute. 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 the aqueous phase. The aqueous layer (100µl) was collected into another test tube for organic Hg analysis. Water samples (400 µl) were subjected to same treatment for methylmercury analysis. All samples were analyzed by a Direct Mercury Analyzer (DMA-80 Milestone, Inc., Shelton, Connecticut, USA) for their methyl mercury contents.

Quality Assurance

Quality assurance samples analyzed included procedural blanks, replicate samples and post-digestion spikes. The validity of the methodology developed by Akagi and Nishimura and the determination of its accuracy and precision were done by analysis of certified reference material (Dogfish muscle, DORM-2) from the National Research Council (NCR) in Canada and Fish Homogenate Certified Reference Material IAEA-407 from International Atomic Energy Agency, Vienna. Recovery studies were performed by adding increasing amounts of mercuric chloride standard solution to samples of four different fish species and two sediment samples, which were taken through the digestion procedure. The resulting solutions were analyzed for mercury concentration.

For the procedure developed by Basu et al, the validity of the methodology and the determination of its accuracy and precision were obtained from quintuplet analysis of 10mg 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 (equal to 5%). Average recovery rates of DOLT-3, DORM-2 and TORT-2 for total mercury were 98.1 ± 3.5%, 97.6 ± 4.2 and 98.3 ± 4.9%, respectively. Average recovery rates of DOLT-2and TORT-2 for methyl mercury were 97.2 ± 4.5%, 98.4 ± 3.7% and 97.9 ± 5.1% respectively.

RESULTS

Table 1. Concentration of Total and Methyl Mercury in sediments collected from the Volta Lake, and its major tributaries.

Location	Sample Size (n)	Total Mercury (ng/g)	Methyl Mercury (ng/g)	r
Akosombo	10	14.64 (11.32 - 19.14)	4.27 (2.16 - 6.73)	0.96
Bui-Pe	10	82.93 (4.51 - 249.00)	33.71 (1.27 - 95.29)	0.98
Kete-Krachie	10	27.96 (9.74 - 56.04)	9.80 (3.15 - 18.91)	0.93
Kpando	10	14.75 (15.85 - 22.02)	5.11 (2.42 - 8.51)	0.73
Saboba	10	5.24 (0.97 - 12.17)	1.56 (0.052 - 3.17)	0.97
Ya-pei	10	30.91 (19.32 - 58.53)	11.70 (7.05 - 22.73)	0.31
Yeji	10	340.61 (32.61 - 700.25)	139.41 (29.72 - 218.94)	0.86

Values in parentheses indicate the range of concentrations.
r is the Correlation coefficient for methyl mercury and total mercury.

DISCUSSION

Mercury in Sediments

Concentrations in sediments ranged from 4.50 to 700.25 ng/g (mean: 74.64 ng/g dry wt) for total mercury and from, 1.27 to 218.94 ng/g (mean: 29.45 ng/g dry wt) for methyl mercury (Table 1). Sediments collected from the Black Volta at Bui-pe and the lake at Yeji had the highest total and methyl mercury concentrations. The large variation of mercury concentrations determined in this survey reflects the wide diversity of sediment characteristics and pollution intensity. Even within a given geographic area, total and methyl mercury concentrations were highly variable. For example, total and methyl mercury concentrations in sediments from Saboba (n = 10) ranged from 0.97 to 12.17 ng/g (dry wt) and from, 0.052 to 3.17 ng/g (dry wt), respectively.

Sediments collected within a 10-m area showed as much variability as samples collected throughout the Volta basin. When our results were compared with levels reported for elsewhere, differences were observed. The levels obtained for sediment from the Brazilian Madeira river (30.0 - 350 ng/g; mean = 130.0) and from Brazilian Tapajos river (170.0 - 430.0 ng/g; mean = 290) were similar to the values reported in this study. However, far higher values were reported for sediments from Philippines Mindanao island (920.0 - 66470.0; mean = 21030).

In a survey of the available African literature Nriagu [22] suggested a baseline value for Hg in sediments as 40 ng Hg/g, and found that the concentration in aquatic African sediments ranged from 50 to 2,200 ng Hg/g. The recently deposited sediments in Itome Bay, Tanzania (0 to 10 cm, ~15 years) had an average concentration of 220 ng Hg/g, above the baseline value, but near the lower end of the range found by Nriagu. Total mercury was positively correlated with methyl mercury concentrations in sediments throughout our study area which is contrary to that of previous studies [23,24]. The percentage of methyl mercury in total mercury concentrations in sediments varied between, 29.2 to 40.9% (mean: 35.4%) which is similar to that reported by Kannan et al [8]. Total mercury was positively correlated ($r = 0.65$; $p < 0.05$) with percent methyl mercury (Figure 1c). In contrast, the ratio of methyl mercury to total mercury increased with its concentration in sediments. Organic carbon (OC) and microbial activity in sediments play an important role in the bioavailability and methylation of inorganic mercury [25]. The mercury concentrations in sediments were compared with the corresponding organic carbon content (Figure 1b, 1e and 1f). Both total mercury and methylmercury were significantly correlated with organic carbon. The correlation coefficients obtained were as follows: total mercury vs. OC = 0.92; methyl mercury vs. OC = 0.93. Percent methyl mercury was positively but poorly correlated with organic carbon with r value of 0.45. The proportion of methyl mercury in total mercury increased with increasing organic carbon content which is the opposite of what was observed by Kannan *et al.* [8] However, OC was poorly correlated with percent methylmercury of the sediments but the inverse of what Kannan *et al.* reported.

Table 2. Concentration of Total and Methyl Mercury in fish collected from the Volta Lake, Black Volta, White Volta and River Oti.

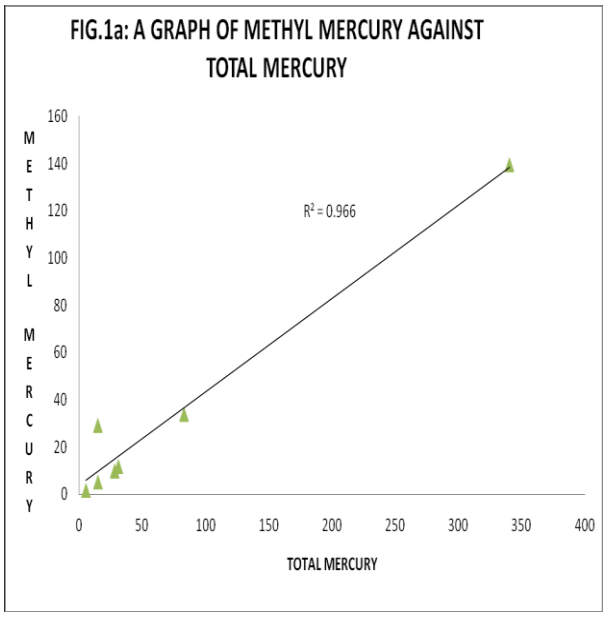
Fish species	Sample size (n)	Total Mercury (ng/g)	Methyl Mercury (ng/g)	Ratio of Me-Hg to T-Hg
Auchenoglanis biscutatus	5	76.78 (68.61 - 110.45)	70.98 (90.04 - 92.99)	0.91
Auchenoglanis occidentalis	6	77.77 (53.81 - 110.45)	70.33 (48.42 - 100.46)	0.90
Bagrus docmac	6	53.94 (49.27 - 57.21)	49.35 (46.36 - 53.20)	0.92
Barbus atakorensis	9	67.03 (40.80 - 90.29)	60.92 (36.92 - 79.72)	0.91
Barbus Guilda	6	24.52 (13.11 - 38.64)	21.88 (11.40 - 33.79)	0.89
Barbus leonensis	6	28.16 (19.38 - 31.49)	23.37 (16.31 - 26.14)	0.83
Chelaethiops bibie	8	25.69 (10.48 - 61.90)	23.30 (9.44 - 56.92)	0.90
Chiloglanis voltae	7	168.5 (80.36 - 305.46)	153.52 (73.93 - 312.77)	0.91
Chiloglaris occidentalis	9	164.42 (80.36 - 305.46)	147.98 (73.16 - 306.14)	0.91
Chrysichthys auratus	12	66.07 (15.27 - 141.46)	60.44 (14.35 - 130.10)	0.92
Chrysichthys nigrodigitatus	16	27.95 (14.42 - 61.27)	25.15 (12.89 - 55.17)	0.90
Citharinops distichodoides	5	32.53 (22.58 - 38.74)	26.33 (18.79 - 33.12)	0.81
Clarias anguillaris	5	237.77 (94.15 - 355.16)	214.86 (87.40 - 319.48)	0.91
Ctenopoma kingsleyae	5	70.62 (45.67 - 91.06)	64.27 (42.41 - 83.72)	0.91
Ctenopoma petherici	7	65.71 (42.76 - 86.58)	56.49 (36.27 - 74.36)	0.86
Distchodus rostratus	6	29.77 (28.75 - 38.46)	27.23 (18.71 - 34.65)	0.92
Distichodus brevipinnis	7	20.7 (16.39 - 25.83)	18.44 (14.76 - 23.02)	0.89
Gnathonemus senegalensis	5	15.52 (4.90 - 22.73)	14.08 (4.30 - 20.66)	0.90
Gobiodes sagitta	4	10.44 (8.36 - 14.29)	9.34 (7.02 - 12.68)	0.89
Gymnarchus niloticus	4	19.21 (12.33 - 24.18)	16.96 (10.82 - 21.02)	0.88
Hemichromis fasciatus	7	24.82 (7.85 - 40.76)	22.47 (7.42 - 35.41)	0.91
Hydrocynus forskalii	3	194.15 (165.24 - 256.17)	176.92 (148.69 - 234.24)	0.91
Hyperopisus bebe	5	28.53 (23.86 - 31.32)	25.87 (21.95 - 28.50)	0.91
Labeo coubie	6	12.18 (4.23 - 24.51)	11.00 (4.23 - 24.51)	0.91
Labeo parvus	4	13.54 (11.00 - 15.75)	12.46 (10.12 - 14.49)	0.92
Labeo senegalensis	9	3.86 (2.11 - 6.43)	3.41 (1.77 - 5.76)	0.88
Mormyrops anguilloides	6	253.98 (199.53 - 309.61)	227.54 (177.14 - 281.19)	0.89
Mormyrops breviceps	7	253.73 (198.53 - 309.61)	229.25 (178.65 - 268.46)	0.90
Mormyrus rume rume	5	49.56 (46.56 - 52.69)	44.76 (43.11 - 46.86)	0.90
Nannocharax ansorgii	10	89.23 (54.23 - 116.40)	79.82 (49.68 - 104.42)	0.90
Nannocharax fasciatus	9	76.47 (51.82 - 107.38)	63.51 (42.78 - 90.22)	0.83
Nannocharax occidentalis	7	84.83 (48.37 - 109.56)	74.65 (41.61 - 96.43)	0.88
Neolebias unifasciatus	5	43.77 (31.29 - 54.18)	38.09 (27.31 - 47.68)	0.87
Oreochromis niloticus	8	54.82 (40.38 - 85.14)	49.98 (38.36 - 77.48)	0.91
Sarotherodon galilaeus	11	30.06 (25.35 - 43.18)	27.57 (22.94 - 40.16)	0.92
Sarotherodon melanotheron	9	43.15 (3.26 - 74.60)	38.59 (2.80 - 70.14)	0.89
Sarotherodon obesus	8	51.36 (39.17 - 88.54)	43.69 (32.86 - 74.98)	0.85
Schilbe Intermedius	5	69.51 (44.17 - 85.88)	62.74 (40.20 - 77.31)	0.90
Schilbe mystus	5	123.94 (100.22 - 158.38)	113.30 (92.16 - 144.14)	0.91
Sierrathrissa leonensis	8	87.23 (51.23 - 116.40)	79.36 (48.14 - 102.76)	0.91
Synodontis batensoda	6	155.4 (131.99 -166.05)	141.54 (120.02 - 152.72)	0.91
Synodontis clarias	6	26.33 (18.32 - 45.14)	23.66 (16.12 - 41.13)	0.90
Synodontis eupterus	8	17.58 (7.67 - 41.97)	15.94 (7.18 - 38.19)	0.91
Synodontis filamentosus	7	14.02 (8.43 - 21.51)	12.64 (7.84 - 19.89)	0.90
Synodontis gambiensis	6	43.56 (31.25 - 70.75)	39.45 (8.80 - 65.95)	0.90
Synodontis membranaceus	8	43.67 (4.81 - 76.14)	39.44 (3.88 - 75.65)	0.90
Synodontis nigrita	11	17.52 (4.08 - 38.52)	15.70 (3.63 - 35.48)	0.89
Synodontis ocellifer	10	100.52 (90.56 - 112.35)	91.25 (82.24 - 104.53)	0.91
Tilapia dageti	7	171.26 (72.20 -309.24)	154.73 (64.98 - 281.19)	0.90
Tilapia guineensis	7	20.05 (11.65 - 28.86)	18.12 (10.67 - 25.63)	0.90
Tilapia Lineatus	5	196.67 (72.20 - 309.24)	178.87 (66.43 - 289.28)	0.91
Tilapia zilli	10	57.74 (51.88 - 71.49)	51.60 (43.14 - 66.50)	0.89

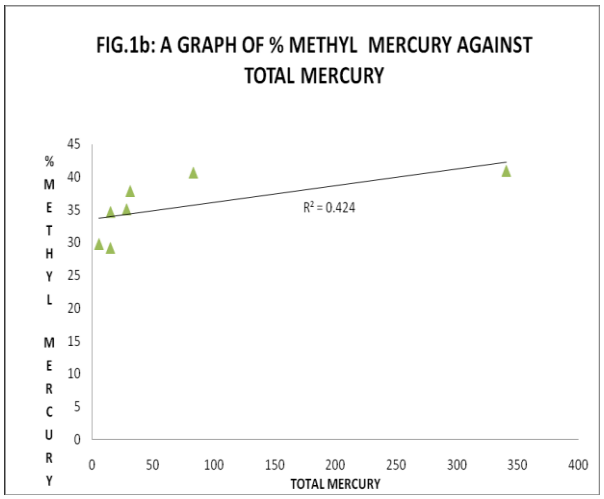
Table 3. Concentrations of total mercury and methyl mercury in water collected from the Black Volta, White Volta, Oti River and the Volta Lake

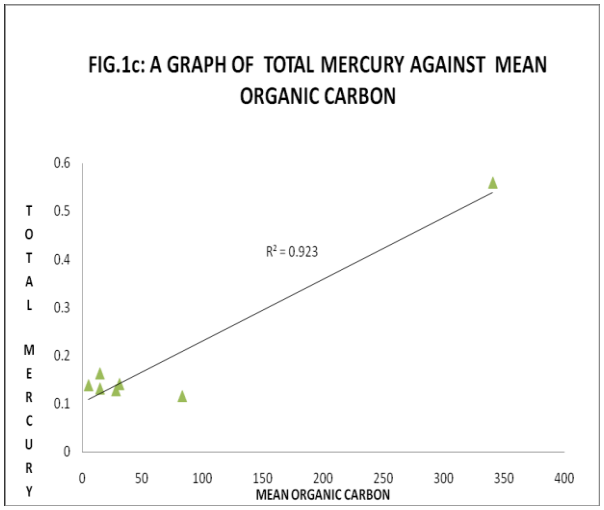
Location	pH	DO (mg/L)	T-Hg (ng/L)	Me-Hg (ng/L)	%Me-Hg to T-Hg
Akosombo	7.5	3.4	0.0462	0.0069	15.1
Bui-Pe	6.8	2.3	0.0304	0.0065	21.3
Kete-Krachie	7.2	2.8	0.0739	0.0259	35.0
Kpando	7.3	2.9	0.0655	0.0184	28.1
Saboba	6.7	1.8	0.0027	0.0004	13.2
Ya-pei	7.3	2.5	0.0463	0.0079	17.0
Yeji	7.4	2.6	0.0862	0.0198	23.0

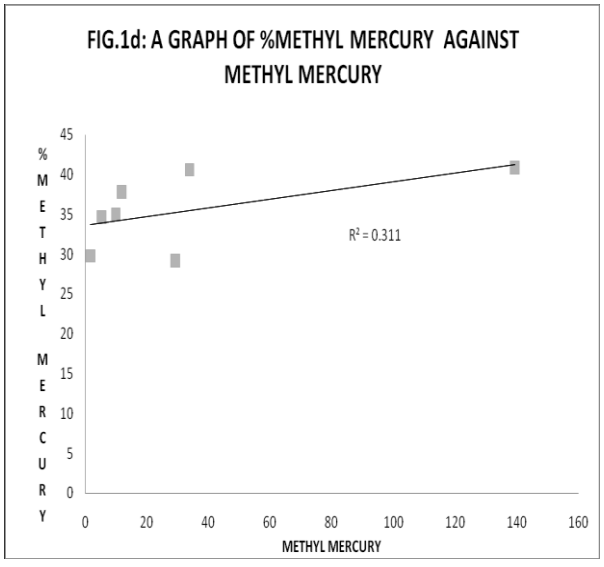
Mercury in Fish

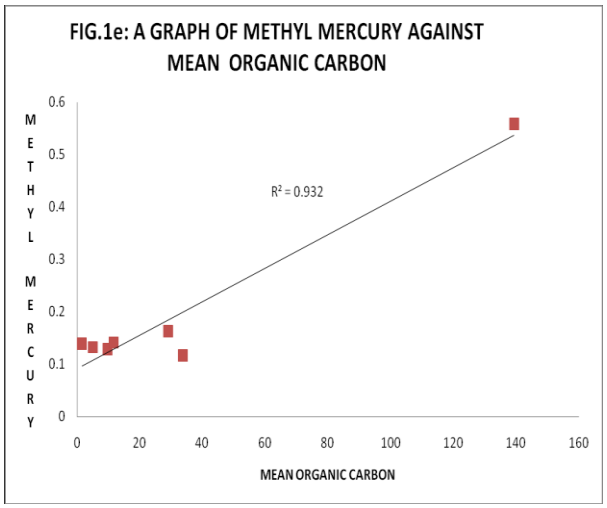
Concentration of total mercury in fish muscle ranged from 2.11 to 355.16(mean: 75.64) ng/g wet wt. and methyl mercury ranged 1.77 to 319.48 (mean: 68.44) ng/g wet wt. (Table 2). Moisture content of fish muscle varied between 39% and 56%. Total mercury concentrations in fish muscle from the Volta were compared to the mean value for freshwater whole fish recorded in other studies. Trasande *et al* [9] reported high levels of mercury (mean 0.87 µg/g) in fish in a subsistence fishing community in Lake Chapala, Mexico.

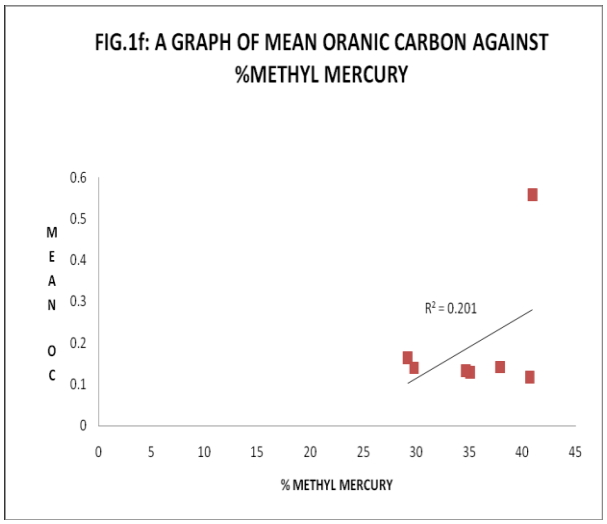












The concentrations recorded in this study were within range of the US national mean concentration for whole fish of 0.26 µg/g wet wt collected in 1990 [26]. Several studies have shown that mercury concentrations in fish generally tend to increase with age, and therefore size, owing to methyl mercury accumulation with increasing exposure time [27]. Fish size is an important factor for methyl mercury concentrations, but the distinct concentrations of mercury observed between sampling locations are probably due to differing amounts of mercury inputs at the various locations of the Lake. This was the general observation among the fish species analyzed from the Volta basin .The following species of fish recorded high total mercury concentrations in the study: chrysichys auratus (a bagride), Chiloglaris occidentalis (a mochokidae), clarias anguillanis (a clariidae), hydrocynus forkalii (an alestiidae), mormyrops anguilloides, mormyrops breviceps, mormyrops rume rume(all mormyridae), schilbe mystus (a schilbeidae), synodontis batensoda, synodontis ocelifer (mochokidae), tilapia dageti, tilapia lineatus (cichlidae) (Table 2). Both total and methyl mercury concentrations were below 0.5 µg/g wet wt in all the fish species collected in this study.

Among the different fishes analyzed, lower concentrations of mercury were encountered in gobiodes sagitta (a gobiidae), labeo coubie, labeo senegalensis (cyprinidae), saratherodon melanotheron (a cichlidae), synodontis filamentous, synodontis membranaceous, synodontis nigrita (all mochokidae) (Table 2). In fish, the percent of methyl mercury to total mercury varied between 81% and 92% (mean: 89%). Factors such as age, sex, habitat and feeding habit of fish may influence such ratios. Total mercury concentration in fish muscle was directly proportional to methyl mercury concentrations for all the species of fish analyzed with correlation coefficients being greater 0.80 which is in agreement with earlier studies [8,28,29]. Total mercury concentrations in fish were positively correlated with the percentage of methyl mercury for all the species of fish studied. The proportion of methyl mercury in total mercury was weakly correlated with methyl mercury concentrations. The concentrations of mercury obtained for fish by Hunter *et al.* [30] are higher than the levels recorded in the fish species under this study even though high levels were obtained for the sediments. Mercury concentrations in bed sediments are not necessarily correlated with concentrations in fish tissues [31]. The results of this study appeared to follow a similar trend as poor correlation was observed between mercury concentration in fish and sediments at all the sampling sites. The relationship between mercury concentrations of fish and sediments vary as a function of factors that affect sediment methylation rates and mercury bioavailability. Although some studies have shown that sediments can be a sink for mercury [32,33], mercury accumulation by fish depends on the combined effect of the abundance of available inorganic mercury in sediments/water column, trophic interaction and the rate at which micro-flora transform mercury into methylmercury in addition to the species- specific accumulation and seasonal variations [27].

In this study, methyl mercury concentrations in individual fish species were not plotted against corresponding sediment concentrations, because the fish were taken from the major landing sites and could not determine actual area where they were harvested. However, Kannan *et al.* [8] reported that the relationship between mercury concentrations of fish and sediments vary as a function of factors that affect sediment methylation rates and mercury bioavailability. A few studies showed that total mercury in sediments from unstratified lakes did not significantly correlate with fish mercury concentrations [33] due to the

variability in methyl mercury production rates in sediments as a result of a variety of factors (such as organic carbon, amount of mercury occurring as sulfides, aerobic or anaerobic conditions, or methylation of mercury in water column).

Burger et al. [34] reported site-specific differences in muscle tissue mercury levels in fish from the Savannah River and found that mercury concentrations generally reflected trophic levels. Fish species at high trophic levels showed higher Hg concentrations whereas those at lower trophic levels recorded low mercury levels. A similar trend was observed in this study as mercury concentrations increased with trophic levels. Fish species have been categorized into numerical trophic values where top predators were assigned a value of 5 and above; between 4.00 and 4.99 fish are classified as high level carnivores; middle level carnivores are assigned 3.00 to 3.99. The omnivores, herbivores or dentritivores are assigned values between 2.00 and 2.99 [35]. All the fish species analyzed can be categorized into the various trophic levels with most of them being natives. Studies have showed that mercury concentration varies with fresh weight of fish and total length. Also, high correlation between mercury concentration and total length and fresh weight of fish are normally observed among carnivorous species whereas poor correlations are observed among herbivorous species [36]. However, this does not hold for some of the species of fish studied (results published elsewhere). All the fish samples from the sampling locations along the Volta Lake recorded mercury concentrations below the World Health Organization's threshold value of 500 ng/g. The results obtained in this study therefore showed that fish from the Volta Lake does not constitute any significant methylmercury exposure to the public through fish consumption from the studied areas. While the levels of mercury of fish in the Volta Lake are currently within the acceptable limits for international markets 500 ng/g in Canada and 1,000 ng/g in the USA) it important to note that for many people living in the lake's region, fish is the major source of animal protein. An individual living close to the lake is likely to consume more fish than is dictated by the World Health Organization (WHO) which suggests limits of consumption for fish containing 500 ng/g mercury.

Mercury in Water

The concentrations of total mercury and methyl mercury in water samples collected from Volta lake and major rivers that flow into the Volta Lake were 0.0027- 0.0862 ng/L (mean: 0.0502 ng/L) and , 0.0004-0.0259 ng/L (mean: 0.0123 ng/L), respectively (Table 3). Concentrations of total mercury in the Black Volta, White Volta, Oti River and the Volta Lake were about 120% lower than that reported from other studies [8,37,38]. While total mercury levels varied little in all the samples of water, methyl mercury levels varied considerably among locations as was reported by Kannan *et al* [8]. Waters from the Black Volta, White Volta and Oti River that flow into the Volta Lake had methyl mercury concentrations far lower than 1 ng/L, accounting for about 21.82% on the average of the total mercury concentrations. The Volta is an oligotrophic lake and the catchments of the rivers that drain into it are intensively cultivated agricultural areas, which may result in the transport of humic substances and methyl mercury from the drainage area.

The U.S. EPA mercury water quality criterion for protection of freshwater is 12 ng Hg/L [39]. The water quality criterion for mercury proposed for Minnesota's freshwater is 7 ng Hg/L while a value of 2 ng Hg/L has been established for Wisconsin waters [40]. The mercury concentrations found in this study were far below the U.S. EPA tolerance limit, and those established in Minnesota and Wisconsin. Methyl mercury accounted for, 13.2 - 35.0% (mean: 21.8%) of the total mercury in waters from our study area. In freshwater areas [41], the proportion of methyl mercury was variable but generally higher, with an average of 25% and ranged up to 80%. Methyl mercury accounted for 6-13% of the total dissolved mercury in inland surface waters from Sweden [42]. In anoxic lake water, the percentage of methyl mercury was as high as 58% of the total mercury [43]. The wide range of methyl mercury proportions in water depends on several variables such as acidity, dissolved organic carbon, sulfate, and hydrological and geochemical factors [43].

Some of the key characteristics of Reservoirs/Lakes that mitigate against the formation and accumulation of methyl mercury include short hydraulic residence time, low organic content of the sediments, high pH and high dissolved oxygen concentrations. Methylation occurs in low-oxygen environments, and thus water column methylation is unlikely in the Volta Lake from the levels of dissolved oxygen recorded in this study. Sediment methylation is still possible since low oxygen conditions are undoubtedly present in the deeper sediments. There are some characteristics of Volta Lake that suggest it may be susceptible to enhanced methylation and/or accumulation of bioavailable mercury. Methyl mercury is formed in zones where water shifts from oxygenated (or oxic) conditions to deoxygenated (or anoxic) conditions due to physical impediments to the movement of oxygen and\or biological activity. Drawdown has the potential to create transitional oxic/anoxic zones within the reservoir that favor the formation of bioavailable mercury. This may occur in portions of the lake where bottom sediments are often exposed. Methylation in these transitional oxic/anoxic zones can be related to

changes in microbial activity or changing speciation of sulfur, which then stimulates methylation. There are no data to suggest that this is indeed happening in the Volta Lake sediments, but neither are there data to refute it.

CONCLUSION

Total mercury and methyl mercury were found in fish, water and sediment from the Volta Lake and its main tributaries. In general, the concentrations obtained from the study indicate low levels of mercury in the Volta basin as compared to other studies elsewhere. All the fish samples from the Volta Lake and its major tributaries recorded mercury concentrations below the World Health Organization's threshold value of 500 ng/g. The results therefore showed that fish from the Volta Lake and its major tributaries does not constitute any significant methyl mercury exposure to the general public through fish consumption from the studied areas. Concentrations of total mercury in sediment were lower than the IAEA threshold of 810ng/g. The low concentration of mercury in fish, water and sediments in this study suggest that the Volta aquatic environment has not yet been significantly impacted by mercury contamination. . However, the mercury concentrations in fish, water, and sediments should be monitored to ensure the safety of the residents in the Volta Lake region, because these vital resources cannot be replaced if they begin to accumulate unacceptable mercury concentrations.

ACKNOWLEDGMENT

We thank Mr. Munir Abdullah Dawood of Pure and Applied Biology Department, College of Science, Kwame Nkrumah University of Science and Technology for identifying the fish species. We acknowledge the support of the African Study Center, University of Michigan in shipping and carrying out the analysis in the USA. The academic and technical support of Professors Jerome O. Nriagu and Niladri Basu, and Dr Dong-Ha Nam of the Department of Environmental Health Sciences, University of Michigan School of Public Health is acknowledged.

REFERENCES:

1. Leopold K, Foulkes M, Worsfold P. Methods for the determination and speciation of mercury in natural waters - A review. Analytica Chimica Acta 2010; 663:127 - 138.
2. Mergler D, Anderson HA, Hing LMC, Mahaffey K, Murray R, Sakamoto M, Stern A. H. Methylmercury Exposure and Health Effects in Humans: A Worldwide Concern. Ambio. 2007; 36, 3-11.
3. Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW. Effects of Environmental Methylmercury on the Health of Wild Birds, Mammals, and Fish. Ambio. 2007; 36, 12-18.
4. Covelli S, Acquavita A, Piani R, Predonzani S, De Vittor C. Recent contamination of mercury in an estuarine environment (Marano lagoon, Northern Adriatic, Italy). Estuarine, Coastal and Shelf Science. 2009; 82: 273-284.
5. Chen C, Amirbahman A, Fisher N, Harding G, Lamborg C, Nacci D, Taylor D. Methylmercury in Marine Ecosystems: Spatial Patterns and Processes of Production, Bioaccumulation, and Biomagnification. Ecohealth. 2008; 5(4): 399-408.
6. Koranteng KA, Hutchful G, Tetebo AY. Informationon Fisheries in Ghana. Min. of Food and Agriculture. The Directorate of Fisheries. 2004; Pp10.
7. Chen CY, Dionnea M, Mayesb B.M, Ward D.M, Sturupc S, Jacksond BP. Mercury Bioavailability and Bioaccumulation in Estuarine Food Webs in the Gulf of Maine. Environ Sci Technol. 2009; 43(6): 1804-1810.
8. Kannan K, Smith Jr. RG, Lee RF, Windom HL, Heitmuller PT, Macauley JM, Summers JK. Distribution of Total Mercury and Methyl Mercury inWater, Sediment, and Fish from South Florida Estuaries. Arch. Environ. Contam. Toxicol. 1998; 34, 109-118.
9. Trasand L, Cortes JE, Landrigan PJ, Abercrombi MI, Bopp RF, Cifuentes E. Methylmercury exposure in a subsistence fishing community in Lake Chapala, Mexico: an ecological approach. Environmental Health. 2010; 9:1.
10. Adimado AA, Baah DA. Mercury in Human Blood, Urine, Hair, Nail, and Fish from the Ankobra and Tano river basins in south-western Ghana. Bull. Environ. Contam. Toxicol. 2002; 68: 339-346.
11. Golow AA, Adzei EA. Mercury in the surface soil and cassava crop near an alluvial goldmine at Dunkwa-on-Offin, Ghana. Bull. Environ. Contam. Toxicol. 2003; 69: 228-235.
12. Babut M, Sekyi R, Rambaud A. Improving the Environmental Management of small scale gold mining in Ghana: a case study of Dumas. J. Cleaner Prod. 2003; 11: 215-221.
13. Bannerman W, Potin-Gautier M, Amouroux D, Tellier S, Rambaud A, Babut M, Adimado A, Beinhoff C. Mercury and arsenic in the gold mining regions of the Ankobra river basin in Ghana. J. Phys. IV 2003; 107: 107-110.
14. Bonzongo JC, Donkor AK, Nartey VK. Environmental impacts of mercury related to artisanal gold mining in Ghana. J. Phys. IV France. 2003;107: 217-220.
15. Golow AA, Mingle LC. Mercury in river water and sediments in some rivers near Dunkwa-on-Offin, an alluvial goldmine, Ghana. Bull. Environ. Contam. Toxicol. 2002; 70: 379-384.
16. Donkor AK, Bonzongo JC, Nartey VK, Adotey DK. Mercury in different environmental compartments of the Pra river basin, Ghana. Sci. Total Environ. 2006; 368:164 - 176.
17. Voegborlo RB, Adimado AA, Ephraim JH. Mercury Distribution in Different Fish Species Representing

Different Trophic Levels from the Atlantic Coastal Waters of Ghana. J Sci Technol. 2010; vol. 30 No. 1

18. Oppong SOB, Voegborlo RB, Agorku SE, Adimado AA. Total Mercury in Fish, Sediments and Soil from the River Pra Basin, Southwestern Ghana. Bull Environ Contam Toxicol. 2010; 85(3): 324-329
19. Akagi H, Nishimura H. Speciation of mercury in the environment. In: Suzuki T, Imura N, Clarkson TW (eds) Advances in mercury toxicology. Plenum Press, New York, USA. 1991; pp 53-76.
20. Voegborlo RB, Baah DA, Kwaansa-Ansah EE, Adimado AA, Ephraim JH. Mercury concentrations in fish species from the Gulf of Guinea, Ghana. Bull Environ Contam Toxicol. 2004; 73:1057-1064.
21. Basu N, Nam D. Rapid methods to detect organic mercury and total selenium in biological samples. Chem Cent J 5:3.
22. Nriagu JO. Toxic metal pollution in Africa. Sci. Total Environ. 2010; 121; 1-37.
23. Craig PJ, Moreton PA. Total mercury, methyl mercury and sulphide in River Carron sediments. Mar Pollut Bull. 1983; 14:408-411.
24. Kannan K, Falandysz J. Speciation and concentrations of mercury in certain coastal marine sediments.Water Air Soil Pollut. 1998; 103 (1-4): 129-136
25. Andersson I, Parkman H, Jernelov A. The role of sediments as sink or source for environmental contaminants: A case study of mercury and chlorinated organic compounds. Limnologica 1990; 20:347- 359.
26. Bahnick D, Sauer C, Butterworth B, Kuehl DW. A national study of mercury contamination of fish. IV. Analytical methods and results. Chemosphere. 1994; 29:537-546.
27. Jackson TA. Biological and environmental control of mercury accumulation by fish in lakes and reservoirs of northern Manitoba, Canada. Can J Fish Aquat Sci. 1990; 48:2449-2470.
28. Grieb TM, Driscoll CT, Gloss SP, Schofield CL, Bowie GL, Porcella DB. Factors affecting mercury accumulation in fish in the upper Michigan peninsula. Environ Toxicol Chem. 1990; 9:919-930.
29. Kim JP. Methylmercury in rainbow trout (*Oncorhynchus mykiss*) from lakes Okareka, Okaro, Rotomahana, Rotorua and Tarawera, North Island, New Zealand. Sci Total Environ. 1995; 164:209-219.
30. Hunter DB, Leatherland JF, Stokes PM. The effects of polychlorinated biphenyls and methyl mercury, singly adding combination on mink II. Reproduction and kit development. Arch Environ Contam Toxicol. 1987; 16:449-454.
31. Rose R, Hutcheson MS, West CR, Pancorbo O, Hulme K, Cooperman A, DeCesare G, Isaac R, Screpetis A. Fish mercury distribution in Massachusetts, USA lakes. Environ Toxicol Chem. 1999; 18:1370-1379.
32. Rudd JWM, Turner MA. Suppression of mercury and selenium bioaccumulation by suspended and bottom sediments. Can J Fish Aquat Sci. 1983; 40:2218-2227.
33. Sorensen JA, Glass GE, Schmidt KW, Huber JK, Rapp GR Jr. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton and fish of eighty northern Minnesota lakes. Environ Sci Technol. 1990; 24:1716-1727.
34. Burger J, Gaines KF, Boring CS, Stephens WL Jr, Snodgrass J, Gochfeld M. Mercury and selenium in fish from Savannah River: species, trophic levels and differences. Environ Res. 2001; 87:108-118.
35. Froese R, Pauly D. Editors 2009. Fish Base World Wide Web electronic publication www.fishbase.org version (10/2009).
36. Lange TR, Royals HE, Connor LL. Mercury accumulation in largemouth bass (Micropterus salmoides) in a Florida. Lake Fla Game Freshw Fish Comm. 1994; 32:727.
37. Schroeder WH. Developments in the speciation of mercury in natural waters. Trends Anal Chem. 1989; 8:339-345.
38. Stein ED, Cohen Y, Winer AM. Environmental distribution and transformation of mercury compounds. Crit Rev Environ Sci Technol. 1996; 26:1-43.
39. US EPA. Water Quality for Mercury. 440/5-84-026, Office of Water, U. S. Environmental Protection Agency,Washington, DC. 1985.
40. Glass GE, Sorensen JA, Schmidt KW, Rapp GR. New source identification of mercury contamination in the Great Lakes. Environ Sci Technol. 1990; 24:1059-1069.
41. Gill GA, Bruland KW. Mercury speciation in surface freshwater systems in California and other areas. Environ Sci Technol. 1990; 24:1392-1400.
42. Lee YH, Hultberg H. Methyl mercury in some Swedish surface waters. Environ Toxicol Chem. 1990; 9:833-841.
43. Gilmour CC, Henry EA. Mercury methylation in aquatic systems affected by acid deposition. Environ Pollut. 1991; 71:131-169.