Effect of pH, Sulphate Concentration and Total Organic Carbon on Mercury Accumulation in Sediments in the Volta Lake at Yeji, Ghana

E. E. Kwaansa-Ansah · R. B. Voegborlo ·
A. A. Adimado · J. H. Ephraim · J. O. Nriagu

Abstract In this study, pH, total organic carbon, sulphate concentration and mercury concentrations of sediment samples from the Volta Lake at Yeji in the northern part of Ghana were determined. The results indicate that pH ranged from 6.32 to 8.21, total organic carbon ranged from 0.17 to 3.02 g/kg and sulphate concentration from 10.00 to 57.51 mg/kg. Total mercury concentrations ranged from 32.61 to 700 ng/g which is below the International Atomic Energy Agency recommended value of 810 ng/g. Humic substance-bound mercury ranged from 81.15 to 481.31 mg/kg in sediments and its two fractions existed as humic acid-bound mercury > fulvic acid-bound mercury with the ratio of humic substance-bound mercury to fulvic acid-bound mercury as 1.62 on the average. Humic substance-bound mercury and the two fractions fulvic acid-bound mercury and humic substance-bound mercury in sediments were favorably determined and found to correlate significantly positive with total organic carbon (r = 0.538) and total mercury (r = 0.574). However, there were poor correlations between SO_4^{2-} concentrations and humic substance-bound mercury (r = −0.391) as well as the two fractions; fulvic acid (r = −0.406) and humic acid (r = −0.381). By assuming that methyl mercury is mostly formed in sediments, these significant relations suggest that the efficiency of mercury being methylated from a given inorganic form depends on the amount, and most likely biochemical composition of total organic carbon in the lake sediment but not the SO_4^{2-} concentration.

Keywords Total mercury · Sediments · Total organic carbon · pH · Sulphur concentration · Humic substances

Mercury is one of the most serious and scientifically challenging contaminant threats to the world's aquatic resources. Scientific interest in mercury in aquatic ecosystems has been motivated largely by the health risks of consuming fish containing methylmercury, the primary source of mercury in the human diet. Methylmercury (MeHg) is the most stable of the organo-mercury compounds and, hence, is the primary concern regarding human exposure to this type of mercury (European Commission 2006). Due to concerns regarding its bioaccumulation in aquatic food chains, much attention has been focused on factors controlling Methylmercury production under various environmental conditions (Benoit et al. 2001). For most ecosystems, atmospheric deposition is the primary source of mercury, although there are numerous instances of geologic and anthropogenic point source contamination problems. Since the industrial revolution, anthropogenic mercury emission have increased atmospheric levels about threefold to fivefold (Fitzgerald and Watras 1989), and caused corresponding increases in mercury levels in terrestrial and aquatic ecosystems. It is reported that, mercury emission from soils is considered to be the major contributor of global atmospheric mercury inventory (Ericksen et al. 2006). Once discharged into the ecosystem, mercury may undergo a series of transformations to methylmercury which is highly soluble in lipids,

E. E. Kwaansa-Ansah (✉) · R. B. Voegborlo · A. A. Adimado
Department of Chemistry, Kwame Nkrumah University
of Science and Technology, Kumasi, Ghana
e-mail: eekwaansaansah@yahoo.com

J. H. Ephraim
Catholic University College, Fiapre, Sunyani, Ghana

J. O. Nriagu
Department of Environmental Health Science, School of Public Health, University of Michigan, Ann Arbor, MI, USA

with the potential to be incorporated by the aquatic biota, accumulating in food chain, and consequently causing irreversible damage to the central nervous system of man (Grieb et al. 1999). SRB typically live in the upper 5 cm of sediment at the oxic-anoxic interface and mineralize organic matter using sulphate as an electro accepter. Gilmour and Henry (1991) reported that 0.3 mM sulphate ion concentration is optimum for SRB to produce MeHg and at 5 mM sulphate ion concentration MeHg production stops. Organic matter is one of the most important soil components controlling Hg adsorption, mainly in acidic soils (Yin et al. 1996). Organic matter plays a key role in the mobility of Hg in the environment, especially in the catchment areas. Due to specific coordination chemistry, mercury has high affinity for humic substances including fulvic acid (FA) and humic acid (HA). The binding between mercury and humic substances is so strong that the speciation and contents of mercury are largely dominated by humic complexes (Hintelmann et al. 1997). Mercury has been suggested to bind humic substances exclusively via sulphur-containing ligands through inner as well as outer-sphere complexation (Wallschlager et al. 1998).

Despite many investigations on the subject, suggesting that the organic matter content, sulphate concentration and pH are some of the most important factors which affect Hg behaviors in the soil or sediment, the embedded Hg reaction in soil is still not clear. Furthermore, to the best of our knowledge, no work has been done on the Volta Lake in this respect. The purpose of this study was documenting Hg cycling in this vulnerable ecosystem as important, as both human health and wildlife reproductive potential may be affected by MeHg exposure (Fig. 1).

Materials and Methods

Sediments samples were collected from ten different sites on the Volta Lake at Yeji, one of the major fish landing towns on the Lake in the northern part of Ghana. A clean plastic scoop was used to collect the top few centimeters of the bed sediments. Generally, samples were taken from multiple points (five) at each site, which were then pooled, homogenized and then sub sampled. 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 kept in the freezer at a temperature below 4°C until analysis. All reagents used were of analytical reagent grade (BDH Chemicals Ltd., Poole, England) unless otherwise stated. Double distilled water was used for the preparation of all solutions. Sediment samples were air dried for 7 days until constant weight and sieved with 2 mm mesh. The sediment samples were digested for total mercury

Fig. 1 Map showing the Volta Basin

determination by an open flask procedure developed by Akagi and Nishimura (1991). The accuracy of this method has been verified at NIMD through interlaboratory comparison exercise and by participating in the analyses of Certified Reference Materials (CRM) supplied by the International Atomic Energy Agency (IAEA). In the procedure, about 0.5 g of sample was weighed into 50 mL volumetric digestion flask and a mixture of 1 mL H_2O, 2 mL HNO_3–$HClO_4$ (1:1) and 5 mL H_2SO_4 was added. The mixture was then heated at a temperature of $200 \pm 5°C$ for 30 min. The sample solution was then cooled and diluted to 50 mL with double distilled water. A blank and standard solution digest using 25, 50, and 100 µL of 1 µg/mL standard Hg solution were subjected to the same treatment. The concentrations of the standard solution digest obtained were 25, 50 and 100 ng/L. 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 for the analysis was 0.5 mL of 10% (w/v) $SnCl_2 \cdot 2H_2O$ in 1 M HCl. Quality assurance samples analyzed included procedural blanks, replicate samples and post-digestion spikes. The accuracy of the procedure was determined by analysis of standard reference material (San Joaquin soil, NIST 2709). Recovery studies were performed by adding increasing amounts of mercury chloride standard solution to samples of two different sediment samples, which were

taken through the digestion procedure. The resulting solutions were analyzed for mercury concentration. Statistical analysis of data was carried out using SPSS package program and one-way analysis of variance (ANOVA). Differences in mean values were accepted as being statistically significant if $p < 0.05$ and $p < 0.01$.

In the determination of sulphate concentration, known weight (10.0 g) of the sediment sample was place in a 100 mL beaker, 30.0 mL of 10.0 mM $CaCl_2 \cdot 2H_2O$ added and the mixture shaken for 30 min on an electronic shaker and then filtered. To 5 mL of the filtrate was added 5 mL of 1 M HCl, 10 mL of distilled water and 10 mL of 25% $BaCl_2$ solution. The mixture was place on a vortex mixture for 10 s and allowed to stand for 30 min. The absorbance of the resulting solution was determined with a 21D UV–visible spectrophotometer at a wavelength of 480 nm. The concentration of the sulphate was read from a standard sulphate curve.

For determination of Total Organic Carbon (TOC), 1.00 g of air-dry sediment was weighed into a 500 mL beaker. 10.0 mL of 2.0 M/dm^{-3} $K_2Cr_2O_7$, 20.0 mL conc. H_2SO_4 were added swirled well to mix and allow standing for 30 min to cool. 100.0 mL distilled water, 1.0 mL diphenylamine in sulphuric acid and 10.0 mL orthophosphoric acid were then added. The mixture was swirled well and titrated against 1.0 M/dm^{-3} $FeSO_4$ to a green end point. In determining the pH, 10 g of the soil sample was weighed into a beaker, 30 mL of deionized water added and the mixture stirred continuously for 1 min. The mixture was then allowed to stand for about 10 min. The pH was then measured with a pH 209 pH meter (Romania Instruments). Humic Substance and the two fractions FA and HA were analyzed by the classical fractionation procedure for humic substance including extraction, acidification, separation and purification (Stevenson 1994). HS-Hg was determined by extraction of humic substance followed by determination of Hg. FA-Hg and HA-Hg were separated for FA and HA using the method of Stevenson (1994), followed by determination of Hg. A 50.0 g of the sediment sample was weighed into a beaker, 50 mL: deionized water added and its pH adjusted with 0.1 M HCl to a pH between 1 and 2. The mixture was made up to 80 mL with 0.1 M HCl and allowed to stand for 1 h. The supernatant was separated from the residue and then 0.1 M NaOH added till the pH reached 7. The residue was separated from the supernatant and the residue dried for the determination of mercury.

Results and Discussion

The contents of HS-Hg ranged from 81.15 to 498.86 mg/kg with a mean of 274.68 mg/kg (Table 1), accounting for 19.54%–88.1% of sediments total mercury, which is by far

higher than that of free ionic Hg as reported by Wu et al. (2001). Generally, content of humic acid-bound mercury (HA-Hg) in the range of 47.01–310.19 mg/kg was higher than that of fulvic acid-bound mercury (FA-Hg) in the range of 34.25–188.67 mg/kg (Table 1) with the mean ratio of HA-Hg to FA-Hg of 1.62.

HS-Hg is derived from soil organic carbon and Hg in soils. Therefore, soil humic substance and the two fractions, FA and HA, as well as total Hg, serving as material sources were also quantified in this study. The total organic carbon (TOC), pH, sulphate concentration, humic substance bound mercury (HS-Hg) and total mercury (T-Hg) contents were found to be 0.559, 7.59, 24.51, 274.68 and 414.08 mg/kg, respectively on the average (Table 1). HS-Hg was significantly correlated with sediment total carbon, T-Hg, HA-Hg and FA-Hg with the correlation coefficients as 0.538, 0.983, 0.998 and 0.995 respectively (Table 2). In this study, the variation coefficients, calculated by dividing the standard deviation by the mean value of the samples, were comparably high for total carbon (1.56) indicating our samples were diverse in organic matter. However, the variation was not accordingly high for HS-Hg, HA-Hg and FA-Hg, but relatively low, with variation coefficients of 0.56, 0.53 and 0.58. This could be attributable to the narrow range of T-Hg contents of the samples, seen from the lower variation coefficient of 0.48. For natural surroundings with non-point source pollution, mercury in sediments/soils dominantly originates from atmospheric mercury and precipitation of suspended particulate Hg, resulting in the homogeneous dispersion of mercury in air (Yu et al. 2006). Hence, the range of total mercury in sediments was not as wide as that of humic substances. Sediment total mercury was clearly mercury source for forming HS-Hg. Besides, the two fractions of HS-Hg, i.e., FA-Hg and HA-Hg served as mercury source for each other, illustrated by correlation coefficients (Table 2).

Sediments T-Hg, TOC, HS-Hg and HA-Hg were positively correlated with FA-Hg, with correlation coefficient of

Table 1 Summary of mercury levels and sediment properties from the Volta Basin

Measurement	Mean	Standard deviation	Range	Coeff. of variation
pH	7.58	0.53	6.32–8.21	0.0699
SO_4^{2-} (mg/kg)	24.51	14.43	10.00–57.51	0.5887
TOC (g/kg)	0.59	0.87	0.17–3.03	1.4746
T-Hg (mg/kg)	414.09	198.55	110.57–700.25	0.4795
HS-Hg (mg/kg)	274.68	154.23	81.15–481.31	0.5615
FA-Hg (mg/kg)	104.64	55.17	34.15–188.67	0.5272
HA-Hg (mg/kg)	170.02	99.42	47.01–310.19	0.5848

Table 2 Correlation coefficients (R values) of T-Hg and sediment properties (n = 10)

R	pH	TOC	SO_4^{2-}	T-Hg	HS-Hg	FA-Hg	HA-Hg
pH	1.000	0.000	−0.409	0.214	0.251	0.221	0.268
TOC		1.000	−0.173	0.574**	0.538*	0.503*	0.555*
SO_4^{2-}			1.000	−0.272	−0.391	−0.406	−0.381
T-Hg				1.000	0.983*	0.999*	0.981*
HS-Hg					1.000	0.995**	0.998**
FA-Hg						1.000	0.989**
HA-Hg							1.000

* $p < 0.05$, ** $p < 0.01$

0.99, 0.51, 0.99 and 0.98, respectively. It suggested that sediments mercury could be bound to FA upon being incorporated with humic substance. FA-Hg was not significantly correlated with sediment pH, for whole sediment samples (Table 2). FA-Hg was not significantly correlated with sulphate content. Basically, in sandy soil with very good permeability, bases tend to leach, which promotes the development of soil acidic circumstance and aerobic conditions. Under this condition, FA-Hg thus appreciably produced and accumulated (Stevenson 1994). In acidic soil with rich organic matter, the more acidic the soil is, the more FA-Hg is. On the other hand, FA-Hg and humic acid appear to counteract each other on neutral sediments. HA-Hg was positively correlated with TOC, T-Hg, HS-Hg and FA-Hg with correlation coefficients of 0.56, 0.99, 0.99 and 0.98, respectively (Table 2) revealing that all types of mercury resources were in favor for the formation of HA-Hg. Again, HA-Hg was found not to significantly correlated with sediment sulphate content. Sediment pH, as the strongest influencing factor for the formation of HA-Hg showed positive but poor significance with correlation coefficient of 0.27. With sediments of low pH the acidity is derived from acidic humic substance and organic matter, thereby promoting the formation of HA-Hg.

T-Hg concentrations are significantly correlated to the TOC concentrations as was previously reported in other studies. Humic substance-bound mercury (HS-Hg) and the two fractions FA-Hg and HA-Hg in sediments were found to correlate significantly with TOC and T-Hg. However, SO_4^{2-} concentrations were found not to correlate significantly with HS-Hg as well as the two fractions. By assuming that MeHg is mostly formed in sediments, the significant relations suggest that the efficiency of inorganic Hg being methylated from a given inorganic Hg depends on the amount, and most likely biochemical composition of TOC in the lake sediment.

References

Akagi H, Nishimura H (1991) Speciation of mercury in the environment. In: Suzuki T, Imura N, Clarkson TW (eds) Advances in mercury toxicology. Plenum Press, USA, pp 53–76

Benoit JM, Gilmour CC, Mason RP (2001) Aspects of bioavailability of mercury for methylation in pure cultures of desulfobulbus propionicus. Appl Environ Microbiol 67(1):51–58

Ericksen JA, Gustin MS, Xin M (2006) Air-soil exchange of mercury from background soils in the United States. Sci Total Environ 366(2/3):81–863

European Commission Directorate General-Environment. (2006) Report on the Mercury Conference: how to reduce supply and demand; 26–27 October. Brussels, Belgium

Fitzgerald WF, Watras CJ (1989) Mercury in surficial water of rural Wisconsin lakes. Sci Total Environ 87/88:223–232

Gilmour CC, Henry E (1991) Mercury methylation in aquatic systems affected by acid deposition. Environ Pollut 71:131–169

Grieb TM, Driscoll CT, Gloss SP, Schofield CL, Browie GL, Porcella DB (1999) Factors affecting mercury accumulation in fish in the upper Michigan peninsula. Environ Toxicol Chem 9:919–408

Hintelmann H, Welbourn PM, Evans RD (1997) Measurement of complexation of methylmercury (II) compounds by freshwater humic substances using equilibrium dialysis. Environ Sci Technol 31:489–495

Stevenson FJ 1994. Humus chemistry, genesis, composition, reactions. 2nd Edn. Wiley, New York

Wallschalager D, Desai MVM, Spengler M (1998) How humic substances dominate mercury geochemistry in contaminated floodplain soils and sediments. J Environ Qual 27(5):1044–1054

Wang DY, He L, Wei SQ (2006) Estimate of mercury emission from different sources to atmosphere in Chongqing, China. Sci Total Environ 366(2/3):722–728

Wu HT, Yu GF, Qing CL (2001) Relationship between soil properties and different fractions of soil Hg. Pedosphere 11(3):257–262

Yin YY, Allen HE, Huang CP (1996) Adsorption of mercury (II) by soil: effect of pH, chloride and organic matter. J Environ Qual 25(4):837–844

Yu G, Wu H, Jiang X, He W, Qing C (2006) Relation between humic substance-bound mercury content and soil properties in subtropical zone. J Environ Sci 18(5):951–957