

# Bioaccumulation of Heavy Metals in the Volta Clam, *Galatea Paradoxa* (Born, 1778) in Relation to Their Geoaccumulation in Benthic Sediments of the Volta Estuary, Ghana

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**Abstract** Heavy metal accumulation in aquatic ecosystems is a common phenomenon among bivalve filter feeders. This study was carried out over an 18-month period at Ada and Aveglo in Ghana, where intense clam fishing represents a major livelihood. The study sought to investigate the concentrations of some heavy metals, zinc, manganese, iron and mercury, in whole soft tissues of three different size classes of the Volta estuary clam, *Galatea paradoxa*, in relation to geoaccumulation of the metals in benthic sediments. The study also sought to examine whether the levels of the metals in clam tissues were within acceptable limits for human consumption. Clam sizes were categorised as small (25–40 mm) medium (41–55 mm) and large (above 55 mm) based on shell lengths and predominant sizes captured in the Volta estuary. Mercury levels in clams and sediments were determined using a Mercury Analyser while Zn, Mn and Fe were determined using an Atomic Absorption Spectrophotometer. Heavy metal concentrations in clams were within permissible limits with reference to WHO safety standards. There were no significant spatial differences ( $p > 0.05$ ) in the concentrations of Mn, Zn, Fe and Hg in clams at Ada and Aveglo. No relationship was observed between heavy metal concentrations in clams and geo-sediments indicating that metal accumulation in clams may not be directly or solely derived from sediments but from other sources such as dissolved metals in the water and seston. Highly significant differences ( $p < 0.0001$ ) were observed between the clam size-classes and sediment samples for iron. Total mercury concentrations

showed highly significant variations ( $p < 0.0001$ ) between all the clam size-classes and the sediment samples.

**Keywords** *Galatea paradoxa* · Clams · Volta estuary · Heavy metals · Sediments · Geoaccumulation

## Introduction

Heavy metal pollution of aquatic environments has become a global issue in both the developing and developed world. Some chemical pollutants, particularly heavy metals, continue to be released to surface waters from industrial and municipal sources resulting in their accumulation in sediments (Mackeviciene et al. 2002). Benthic sediments of aquatic ecosystems are important sinks for heavy metals and a habitat for benthic organisms (Spencer and MacLeod 2002). Exposure of sediment-dwelling organisms to metals may occur via uptake of interstitial waters, ingestion of sediment particles and via the food chain. The occurrence of elevated concentrations of trace metals in sediments found at the bottom of the water column can be a good indicator of man-induced pollution rather than natural enrichment of the sediment by geological weathering (Chang et al. 1998). Sediments are the major repository for heavy metals, in some cases holding over 99% of the total amount of metal present in the system (Chang et al. 1998). Concentrations of bioavailable heavy metal contaminants are needed to evaluate food chain transfer and the potential toxicity of sediment contaminants.

The Volta estuary clam, *Galatea paradoxa* (Born, 1778) is a bivalve filter-feeder, which frequently accumulates high metal concentrations without metabolising the metals appreciably (Gunther et al. 1999; Nasci et al. 1999; Olivier et al. 2002). *Galatea paradoxa* provides a time-integrated

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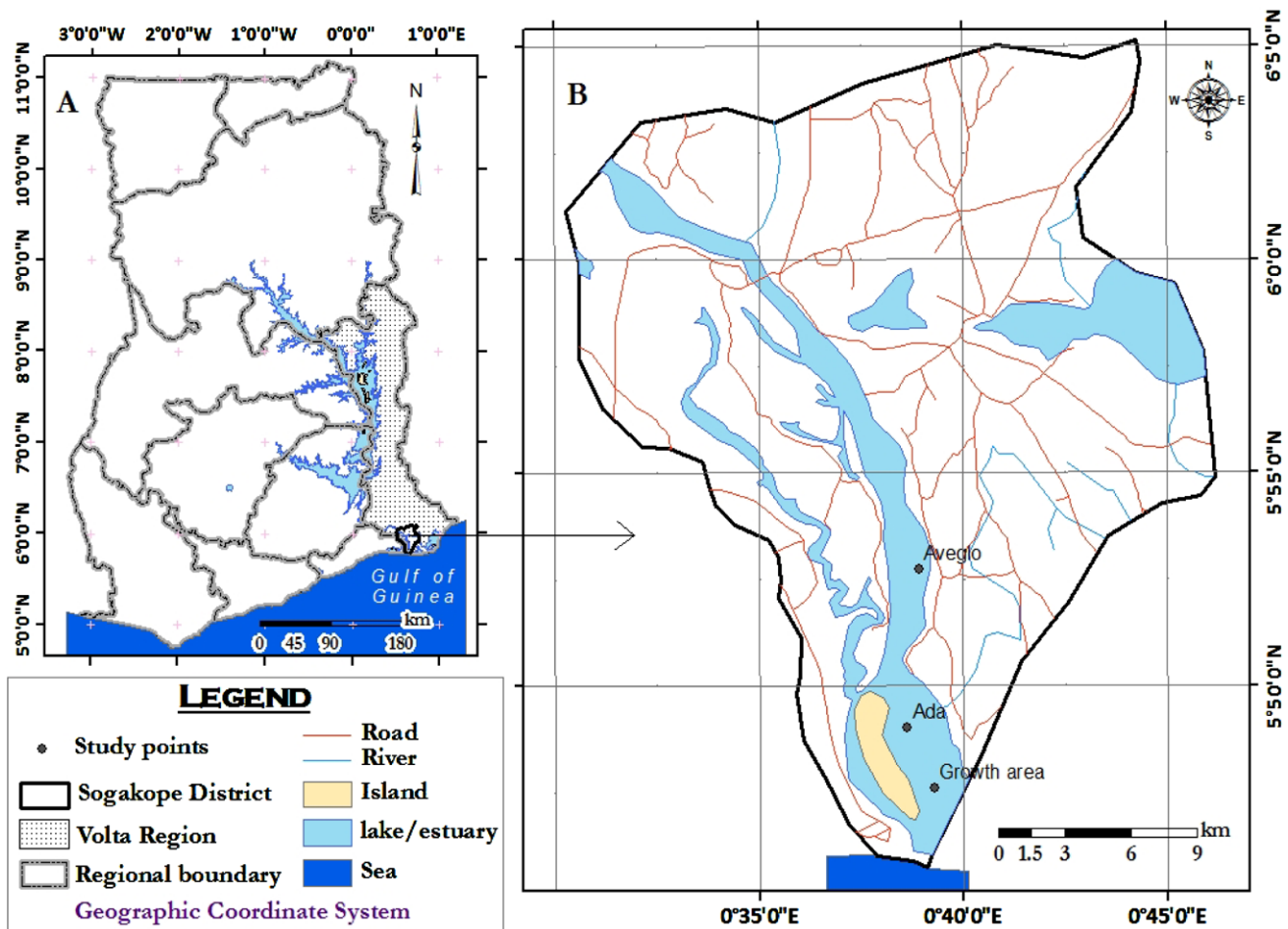
indication of environmental contamination (Regoli 1998; Amisah et al. 2009) and can concentrate pollutants in their tissues at concentrations greater than the ambient water (El-Shenawy 2002). The Volta clam is restricted to a narrow stretch of the south Volta estuary and is not found in any other water body in Ghana (Attipoe and Amoah 1989). Throughout its geographical distribution *Galatea paradoxa* supports a thriving artisanal clam fishery that provides a livelihood to the riparian communities. Increasing population pressure and urban development have led to a proliferation of several rural and metal fabrication industries along the Volta catchment and these have been implicated as potential sources of metal pollution to the estuary (Amisah et al. 2009).

Heavy metal concentrations in clams were determined to assess whether their levels were within permissible limits for human consumption and whether the observed concentrations had any relationship with their geo-concentration in bottom sediments. The metals examined were restricted to mercury (Hg), manganese (Mn), zinc (Zn), iron (Fe) because reconnaissance analysis on seven selected heavy met-

als including the above-mentioned ones and copper (Cu), cadmium (Cd) and lead (Pb) indicated that the last three elements were below detectable limits using an Atomic Absorption Spectrophotometer (AAS). Ada and Aveglo, located in the Volta estuary, were selected for the study because they represent the most active clam fishing sites in Ghana and provide an important livelihood for the communities.

## Materials and Methods

The study was carried out at two most active clam fishing sites, Ada and Aveglo, both in the Volta estuary and over an 18-month period from March 2008 to August 2009. Ada (latitude 05 49' 18.6 N and 00038.46 1E'') and Aveglo (05 53 28.2' N and 00038 24.7E'') represent the southern and northern limits of the most active clam fishing grounds at the Volta estuary (Fig. 1).



**Fig. 1** Map showing clam sampling locations at Ada and Aveglo in the Volta estuary in Ghana

## Collection and Processing of Benthic Sediments

Sediment samples from Ada and Aveglo in the Volta estuary were collected at monthly intervals (over an 18-month period from March 2008 to August 2009) using an Eckman grab. The samples were collected according to standard procedures described in USEPA's sediment sampling guide (USEPA 1994). Samples were kept in LDPE bottles pre-washed with 10% HCl and stored in insulated iced chests for analysis in the laboratory. In the laboratory, sediment subsamples of 500 g from each sampling site were oven-dried to a constant weight (Phillips and Yim 1981). Dried samples were subjected to heavy metal and granulometric analyses (USEPA 1994).

## Heavy Metal Analyses in Whole Soft Tissue of *Galatea Paradoxa*

Clam samples were obtained from the two sampling locations at monthly intervals from fishermen's catch for 18 months from March 2008 to August 2009 and transported to the laboratory, in submerged river water in insulated chests within 12 hours. In the laboratory, clam samples were cleaned with distilled water to remove debris and categorised into three groups, each with 10 individuals for each sampling station based on shell length as follows: small (25–40 mm), medium (41–55 mm), and large (above 55 mm). The groupings were done based on the three dominant size groups in the natural populations to give a broad and fair representative range of metal concentrations in the clams. The various clam size-classes were subjected to a 24-hour depuration. A sterile, stainless steel knife was then used to dislodge and remove the soft tissue of each clam from the shell. Soft tissues of each subsample were oven-dried to a constant weight and ground into fine powder for heavy metal analyses.

## Digestion of Clams, Sediment Samples and Heavy Metal Determinations

Digestion of samples was undertaken following the procedures described in Sastre et al. (2002) and Otchere (2003). Zinc, iron and manganese concentrations were determined using a Buck Scientific Model VGP Flame Atomic Absorption Spectrophotometer (AAS) and expressed as total concentrations ( $\mu\text{g/g}$  dry weight (dw)). An Automatic Mercury Analyser (Model HG 6000) with a mercury lamp (wavelength 253.7 nm) was used for the determination of total mercury in clam soft tissues and sediment subsamples and expressed in microgram per gram dry weight ( $\mu\text{g/g}$  dw). Heavy metal contents of sediment samples from the two sampling stations were compared to Unpolluted Sediment Standard (GESAMP 1982) to ascertain the level of pollution (Table 2).

**Table 1** Description of sediment quality: Igeo classification (Müller 1979)

Geoaccumulation index ( $I_{\text{geo}}$ )	Class	Pollution intensity
<0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly to extremely strongly polluted
>5	6	Extremely contaminated

## Determination of Index of Geoaccumulation

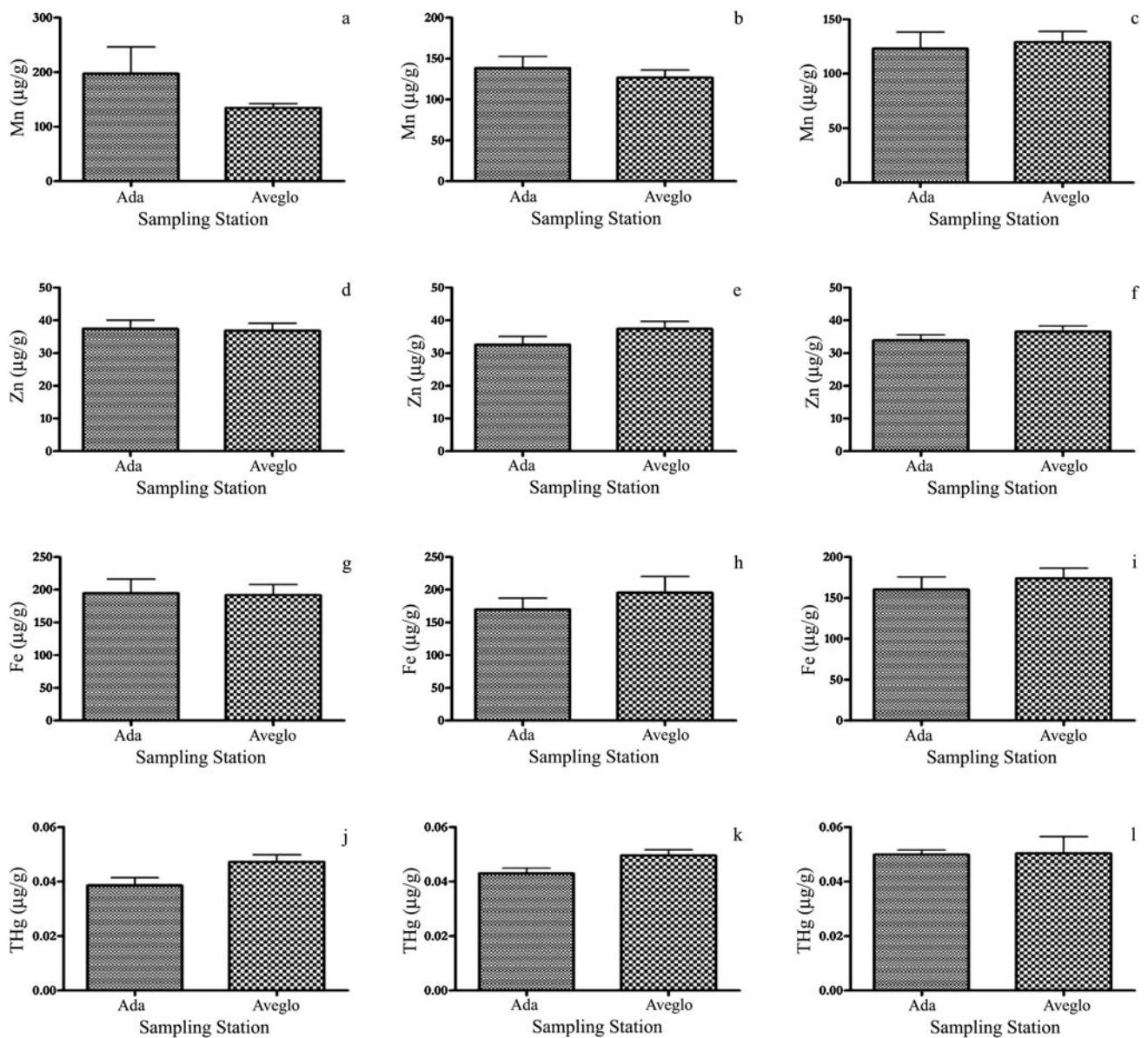
Results of the heavy metal concentrations in the sediments were compared to sediment standards set by GESAMP (1982) to ascertain the extent of heavy metal pollution in the sediments at the two sampling stations. Müller's geochemical index ( $I_{\text{geo}}$ ) was further used to measure the pollution intensities in the study areas (Müller 1979). The  $I_{\text{geo}}$  is associated with a qualitative scale of pollution intensity and samples were classified as unpolluted ( $<0$ ), unpolluted to moderately polluted ( $0 \leq I_{\text{geo}} \leq 1$ ), moderately polluted ( $1 \leq I_{\text{geo}} \leq 2$ ), moderately to strongly polluted ( $2 \leq I_{\text{geo}} \leq 3$ ), strongly polluted ( $3 \leq I_{\text{geo}} \leq 4$ ), strongly to extremely polluted ( $4 \leq I_{\text{geo}} \leq 5$ ) and extremely polluted ( $I_{\text{geo}} \geq 5$ ).

The formula used for the calculation of  $I_{\text{geo}}$  was:  $I_{\text{geo}} = \text{Log}_2[\frac{C_n}{1.5B_n}]$  (Müller 1979).

$C_n$  is the measured content of element "n", and  $B_n$  is the element's content in "average shale" background concentration. The calculated  $I_{\text{geo}}$  values were compared to description of sediment quality in  $I_{\text{geo}}$  Classification Table (Table 1) (Müller 1979) to determine the pollution intensities of the two sampling sites.

## Granulometric Analysis of Sediments

Granulometric analyses of sediments from the two sampling sites were carried out following the procedures described in Cardoso et al. (2008). Grain size analysis was performed based on a series of sieves of different mesh sizes. Sediments were divided into the following fractions; clay ( $<0.002$  mm), silt (0.002–0.02 mm) and sand (0.02–2 mm). The sand component was further broken down into further fractions: very fine sand (0.02–0.06 mm), fine sand (0.06–0.2 mm), medium sand (0.2–0.6 mm) and coarse sand (0.6–2 mm). Each fraction retained in each sieve was



**Fig. 2** Means  $\pm$  SD of Mn and Zn concentrations in different clam sizes from Ada and Aveglo. (a): Mn small, (b): Mn medium, (c): Mn large, (d): Zn small, (e): Zn medium, (f): Zn large, (g): Fe small, (h): Fe medium, (i): Fe large, (j): THg small, (k): THg medium, (l): THg large

weighed and expressed as a percentage of the total sediment weight.

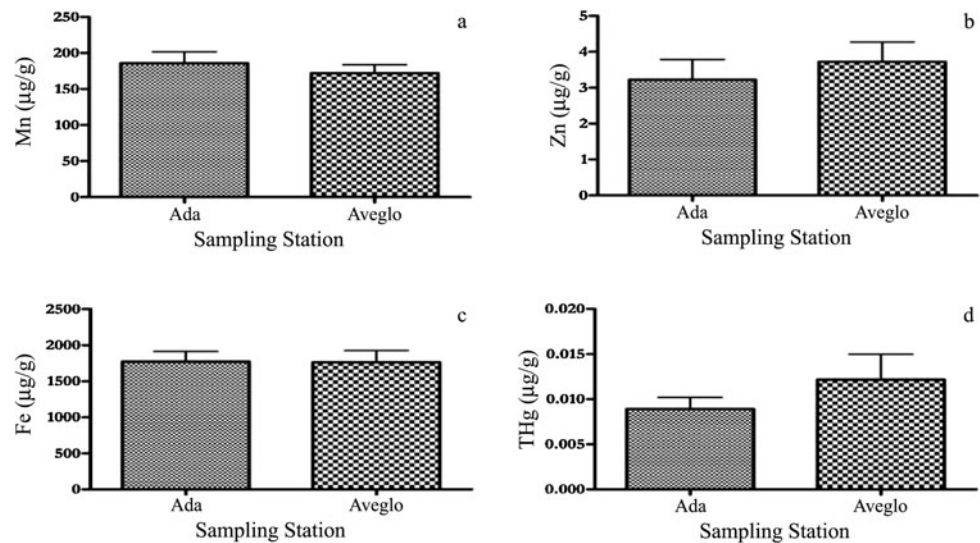
#### Statistical Analysis

Data on the heavy metal analyses were subjected to a one-way analysis of variance (ANOVA) to test for significant differences ( $p < 0.05$ ) in the concentrations of the heavy metals in the tissues of the different class sizes of the clams. Whole tissue concentration for each metal was further subjected to a post-test: the Bonferroni's Multiple Comparison Test to compare all the possible pairs of

columns, i.e. small vs. medium, small vs. large and medium vs. large for significant differences between the compared classes. The Kruskal–Wallis non-parametric test ( $p < 0.05$ ) was used to test for differences in heavy metal concentrations between each clam size group and sediments for the two sites and for spatial variations in metal concentrations in the sediments from the two sampling locations. Column statistics ( $p < 0.05$ ) was used to test for temporal variations in the concentrations of the heavy metals in the clam and sediment samples over the sampling period and graphs were plotted using the GraphPad Prism 5 software.



**Fig. 3** Mean  $\pm$  SD of Mn, Zn, Fe and THg concentrations in the sediment samples from Ada and Aveglo



## Results

### Heavy Metal Concentrations in Clams

All four heavy metals were detected in whole soft tissues for the various clam sizes in the estuary at Ada and Aveglo (Fig. 2(a–l)) comparisons among the different clam size-classes (small vs. small, medium vs. medium and large vs. large) from the two locations using the Kruskal–Wallis non-parametric test ( $p < 0.05$ ) did not show any significant differences ( $p > 0.05$ ) for Mn, Zn, Fe and Hg concentrations in the tissues of the clams (Fig. 2(a–l)). Graphs are presented as means of all monthly concentrations for each metal  $\pm$  SD for the period.

### Granulometric Analysis of the Sediment Samples

Composition analyses of sediments from both sampling stations were predominantly sand (between 98.18 and 99.48%). Silt and clay jointly constituted less than 2% of the sediment. Further analyses of the sand component of the sediment revealed that it was predominantly coarse sand (between 63.36 and 98.71%).

### Heavy Metal Concentrations in Sediment Samples

As in the clams, all four heavy metals were present in the estuary sediments. Result of the Kruskal–Wallis test for independent samples revealed no significant differences ( $p > 0.05$ ) in the concentrations of Mn, Zn, Fe and THg between the two sampling sites (Fig. 3 (a–d)).

### Comparative Analyses of Heavy Metal Concentrations in Clams and Sediments

#### Ada Sampling Station

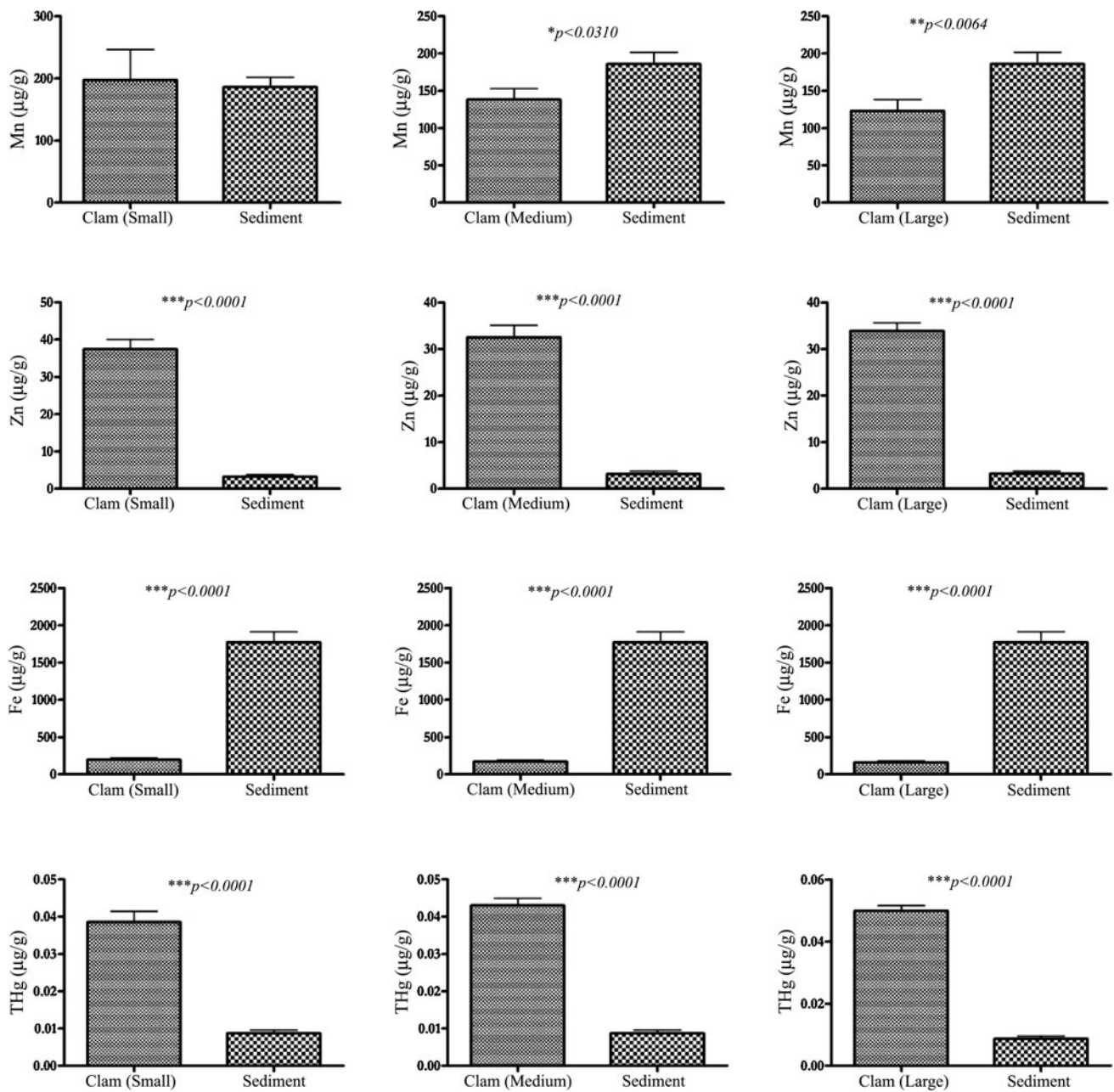
No significant differences ( $p > 0.05$ ) were found in manganese concentrations between the small-sized clams and sediment samples (Fig. 4). Significant variations were, however, observed in the Mn concentrations between the clams and the sediment samples. Zinc concentrations were significantly higher ( $***p < 0.0001$ ) in all the clam sizes compared to sediments. Highly significant differences ( $***p < 0.0001$ ) were observed in all clam size-classes and sediment samples for iron (Fig. 4). Total Hg concentrations also showed highly significant variations ( $***p < 0.0001$ ) between all the clam size-classes and sediments (Fig. 4).

#### Aveglo Sampling Site

Differences in Mn concentrations between the clam and sediment samples were significant ( $p < 0.05$ ) for all clam size-classes. Zinc showed highly significant variations ( $p < 0.0001$ ) between all clam size-classes and sediments (Fig. 5). Very significant differences ( $p < 0.001$ ) were found for iron between all clam size-classes and sediments (Fig. 5). Again, highly significant differences ( $p < 0.0001$ ) were observed for THg concentrations in the clam and sediments (Fig. 5).

#### Sediment Geoaccumulation Indices for Ada and Aveglo

Sediments from the two sampling stations are unpolluted (class 0) with the heavy metals: manganese, zinc, iron and mercury (Tables 1 and 2).  $I_{geo}$  values were well below zero for all metals with manganese values ranging between  $-1.69$  and  $-3.64$ .  $I_{geo}$  values for zinc were between  $-4.57$



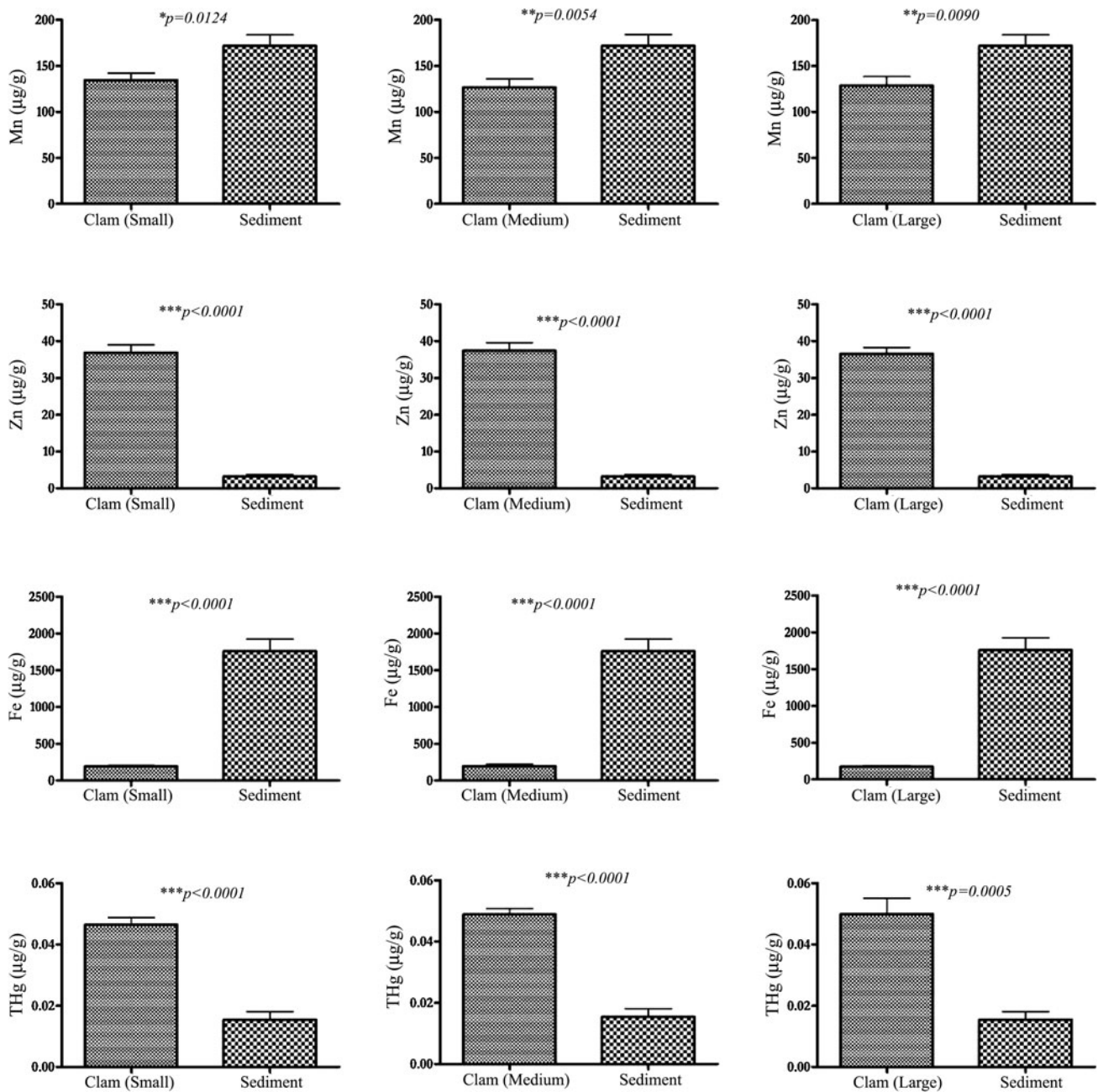
**Fig. 4** Mean  $\pm$  SD of Mn, Zn, Fe and THg concentrations in the clam and sediment samples from Ada

and  $-7.54$  for the sediments from the two sites for the 18-month period, indicating the sediments were practically very unpolluted as far as zinc was concerned.  $I_{geo}$  index for iron ranged between  $-4.32$  and  $-6.66$  while that of mercury ranged between  $-1.32$  and  $-2.98$  (Table 2), indicating that the sediments were unpolluted by the metals.

## Discussion

Geo-sediment grain size plays an important role in accumulation of heavy metals at the benthos. Increases in

heavy metal concentrations are associated with finer grain sediment sizes and organic matter (GESAMP 1982). At Ada and Aveglo, metal concentrations were low due to the coarse nature of the sediments. Sediments are the major repository of metals, in some cases holding more than 99% of metal present in the aquatic system (Odiete 1999). Fe concentrations in the sediments were relatively high. This can be due to natural processes rather than anthropogenic activities as Fe occurs abundantly in the environment and may come from background levels in the sediments (Din 1992). Agricultural activities around the Volta



**Fig. 5** Mean  $\pm$  SD of Mn, Zn, Fe and THg concentrations in the clam and sediment samples from Aveglo. Significant variations:  $***p < 0.0001$

Estuary are usually limited to small-scale holdings and subsistence agriculture, and poverty often causes the farmers to open more land for cultivation. Manganese and zinc are present in most of the agrochemicals used around the estuary. The use of agrochemicals in the catchment is not widespread, but the major users of these agrochemicals are smallholders who have little or no skills in handling and disposal of the chemicals. The amount of chemicals entering the estuarine environment, although presently insignificant, might have potential adverse environmental effects.

Metal concentrations in the clams were generally low with reference to WHO safety standards and within acceptable safety standards of the organisation (Table 3). This may well suggest that metal levels in the surroundings are low and are not interfering with the normal metabolic processes of *G. paradoxa* (Vazquez et al. 1993). Although variations in the concentrations of the metals were significant, clear-cut trends were not observed. Seasonal variations of the heavy metal levels in *G. paradoxa* were irregular and did not follow any pattern. Most of the metals, however, exhibited peak levels just prior to or during the



**Table 2** Sediment geoaccumulation indices for Mn, Zn, Fe and Hg at Ada and Aveglo

Period	Sampling site	Mn	Zn	Fe	Hg
March 2008	Ada	-2.84	-5.57	-4.68	-2.95
	Aveglo	-2.94	-5.57	-5.51	-1.51
April 2008	Ada	-2.74	-5.57	-5.51	-2.95
	Aveglo	-2.74	-6.16	-5.88	-1.32
May 2008	Ada	-2.64	-5.57	-4.80	-2.95
	Aveglo	-3.64	-6.16	-5.88	-2.60
June 2008	Ada	-2.74	-5.57	-4.80	-2.91
	Aveglo	-3.64	-6.16	-5.97	-1.38
July 2008	Ada	-3.06	-7.16	-5.38	-2.94
	Aveglo	-3.18	-5.57	-5.38	-2.91
Aug. 2008	Ada	-3.06	-5.64	-6.66	-2.10
	Aveglo	-2.12	-4.84	-4.32	-2.58
Sept. 2008	Ada	-2.12	*	-6.16	-3.12
	Aveglo	-2.40	-4.57	-4.44	-2.33
Oct. 2008	Ada	-3.06	-6.16	-6.16	-2.76
	Aveglo	-2.94	-7.16	-5.32	-2.70
Nov. 2008	Ada	-3.47	-7.16	-5.38	-2.98
	Aveglo	-2.74	-7.16	-5.27	-2.76
Dec. 2008	Ada	-2.64	-6.16	-5.01	-2.58
	Aveglo	-2.74	-6.16	-5.97	-2.67
Jan. 2009	Ada	-3.18	-5.64	-5.80	-2.67
	Aveglo	-3.32	-6.16	-5.44	-2.50
Feb. 2009	Ada	-3.47	-6.16	-5.72	-2.85
	Aveglo	-2.64	-5.57	-5.88	-2.63
March 2009	Ada	-1.69	-5.64	-5.11	-2.85
	Aveglo	-3.18	-5.57	-5.51	-2.66
April 2009	Ada	-3.06	-5.64	-5.44	-2.92
	Aveglo	-3.18	-5.57	-5.57	-2.89
May 2009	Ada	-2.64	-6.16	-5.51	-2.75
	Aveglo	-3.32	-4.16	-5.51	-2.85
June 2009	Ada	-2.84	-4.16	-5.44	-2.89
	Aveglo	-3.06	-4.16	-5.38	-2.84
July 2009	Ada	-2.84	-5.57	-5.21	-2.71
	Aveglo	-2.40	-4.34	-4.60	-2.71
Aug. 2009	Ada	-2.84	-4.57	-5.51	-2.75
	Aveglo	-2.74	-4.57	-5.44	-2.66

clam spawning season. The studies revealed that the clam starts spawning in June (when mean dry tissue weight maximum occurs), and is completed between October and November (when mean dry tissue weight minimum occurs). This observation corroborates earlier studies by Etim et al. (1991). The spawning season coincides with the onset of the second rainy season in Ghana and is completed by the start of the dry season. The pattern of variation of heavy metal accumulation in the clams is, therefore, largely influenced by the reproductive cycle of the organism. Metal

**Table 3** Heavy metal concentrations in whole clam tissues at Ada and Aveglo with reference to WHO safety standards for bivalves

	Mn	Zn	Fe	Hg
Ada sampling site				
Min. conc. ( $\mu\text{g}/\text{dw}$ )	49	13	79	0.028
Max. conc. ( $\mu\text{g}/\text{dw}$ )	867	46	316	0.059
WHO standard (2004)	**	1000	**	0.5
Aveglo sampling site				
Min conc. ( $\mu\text{g}/\text{dw}$ )	49	16	123	0.037
Max conc. ( $\mu\text{g}/\text{dw}$ )	206	49	539	0.074
WHO standard (2004)	**	1000	**	0.5

\*\*No health-based guideline values provided

bioaccumulation in *G. paradoxa* is synergistically influenced by both biotic and abiotic factors (Gold-Bouchot et al. 1995).

Intense clam fishing is carried out at Ada and Aveglo during the onset of rains to the start of the dry season. During this period, heavy metals are introduced into the estuary from fuel leakages, paint coatings of the fishing boats, fumes from outboard motors and motorised air compressors used for clam fishing. The elevated concentrations of heavy metals during the fishing period could also be attributed to surface water run-off into the Volta estuary during periods of rainfall.

Similarities in bioavailability of the metals and homogeneity in ambient and physicochemical conditions (Ferreira et al. 2004) might explain why there were no significant differences ( $p > 0.05$ ) when size classes (small vs. small, medium vs. medium and large vs. large) were compared. Manganese Zn and Fe have been shown to be essential for intracellular regulatory mechanisms in clams (Ferreira et al. 2004). This, possibly, explains the absence of any significant spatial variations in metal concentrations between the two sampling sites. The results possibly suggest that the levels of contamination of these metals do not exceed the clam's capacity of regulation (Wang et al. 2002).

Clams and sediment samples revealed no distinct relationship between heavy metal concentrations in clam tissues and sediments in which they thrive. Correlation analysis of all the clam size-classes and sediments from the two stations were not significant, indicating no distinct trend in metal uptake by the clams. Heavy metal accumulation in clams may, therefore, not be directly or solely derived from sediments but from other sources. Higher concentrations of Zn in clam tissues compared to those found in the sediments suggest a high rate of accumulation by the clams, a physiological mechanism induced by exposure (Cardoso et al. 2008).

Iron concentrations in the sediments from both sites were generally higher. This occurs because Fe is deposited much



more quickly but is strongly bound to the sediments under the estuarine conditions (Huanxin et al. 1999). Iron is, thus, not readily available to the clams. Manganese on the other hand can be said to be released much more easily from sediments than Fe and thus becomes more available to the clams. Mercury is a non-essential trace metal, which is not metabolised in the tissues of the clam and thus accumulates in the clams. Earlier studies by Amisah et al. (2009) and Obirikorang et al. (2009) revealed that peak values for most of the heavy metals occurred just prior to or at the onset of the spawning season. This study did not need to revisit this aspect but it is worthwhile to note this as it relates to timing of clam fishing to avoid heavy metal transfer through the food chain. The release of heavy metals from sediments is controlled by complex dynamics of heavy metals and the physical and chemical conditions of the environment. There was no clearly defined relationship between the heavy metal concentrations in the clam tissues and in the sediments. Other factors of the environment are certainly implicated.

## Conclusions

All the size classes of *Galatea paradoxa* have the capacity to accumulate Mn, Zn, Fe and Hg. Higher concentrations of Zn in clam tissues compared to those found in the sediments suggest a high rate of accumulation by the clams, a physiological mechanism induced by exposure. The clams did not appear to be able to regulate Hg in their tissues because it might not be required for gonadal recrudescence (Amisah et al. 2009). There were, however, no significant spatial variations in the concentrations of heavy metals in the clams. The findings further suggest that the levels of contamination of these metals in the estuary do not exceed the clams' capacity of regulation. Analyses of the clam and sediment samples revealed no distinct relationship between heavy metal levels in clam tissues and sediments in which they are found. This indicates that heavy metal accumulation in clams may not be directly or solely derived from sediments but from other sources such as seston and from dissolved metals in the water.

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