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Activation analysis of some elemental concentrations in Sediment and clam (Galatea Paradoxa) from the lower Volta basin in Ghana

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ABSTRACT

This study was carried out to assess the elemental content in the clam (Galatea Paradoxa) and sediment from the lower volta basin in relation to pollution. The concentrations of eighteen elements (Al, As, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Sc, V and Zn) were determined in sediment and whole body tissues of the clam, Galatea paradoxa, by instrumental neutron activation analysis (INAA) without any chemical treatment. From the relatively high levels of metals in the sedimentary habitat of *Galatea pardoxa*, the detrital sediment was likely to be the main source of analyzed elements to the clams, either directly, or indirectly following desorption. The elements in the detrital sediments of the river had average concentrations (in µg/g unless otherwise stated), in decreasing order of 2.25±0.21 %(Fe), 1.67±0.04 %(Mn), 0.84±0.29 %(Ca), 0.44±0.07 %(Na), 0.30±0.03 %(K), 0.24±0.04 %(Mg), 0.18±0.01 %(Al), 37.19±5.58(Cr), 36.51±6.22(V), 29.82±4.48(Ni), 12.67±1.35(Cu), 12.27±1.84(Zn), 10.25±2.22(Co), 2.48±0.16(Sc) and 1.16±0.27(As) while Cd and Hg were below detection limit. Enrichment factor (EF) values indicated moderate enrichment for As, Co and Cr. Apart from As, Co and Cr all the other elements were not enriched in the sediment. Based on geoaccumulation index values, the sediment was considered moderately to strongly contaminated with K but moderately contaminated with Mg. The pollution load index value (0.09) indicated that the sediment was generally not contaminated. In the clams, with the exception of Cd, Hg and Ni which were below detection limits, the levels of elements analyzed in decreasing order were; Fe(0.94±0.26 %) > Ca(0.44±0.04 %) > $K(0.27\pm0.04 \ \%) > Mg(0.16\pm0.03 \ \%) > Cl(0.13\pm0.02 \ \%) > Na(0.12\pm0.001 \$ $Mn(491.18\pm7.53 \ \mu g/g) > Zn(92.29\pm13.84 \ \mu g/g) > Cu(56.42\pm11.20 \ \mu g/g) > Al(54.93\pm2.69)$ $\mu g/g) > As(3.67\pm0.54 \ \mu g/g) > V(2.87\pm0.52 \ \mu g/g) > Cr(1.62\pm0.25 \ \mu g/g) > Sc(0.72\pm0.16)$ μ g/g. Biosediment accumulation factors (BSAF) show that As, Cu and Zn were bioaccumulated and biomagnified (BSAF > 1.00) in the clams.

Introduction

In recent years, much attention has been paid to the chemical composition of aquatic organisms and the associated sediments as a result of environmental pollution. Among environmental pollutants, metals are of particular concern, due to their persistent nature, potential toxic effects and ability to bioaccumulate in aquatic ecosystems (Fernandes et al, 2008). Heavy metals, for instance, has become a worldwide problem because of their indestructible nature (Shyamalendu et al, 2001). A number of infaunal bivalves have been shown to integrate contaminant levels over time and are useful tools for monitoring the state of the sedimentary environment (Langston & Burt, 1991). The Blue mussel, Mytillus edulis, and the Manila clam, Ruditapes philippinarum, for instance, have been utilized for heavy metal pollution monitoring in various countries (Burger & Gochfeld, 2006). The sessile nature, mode of feeding, ability to accumulate contaminants from the environment and availability for human consumption were reported as the criteria for these bivalves to act as indicators for heavy metal pollution (Devagi et al, 2008; Qunfang et al, 2008).

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Some trace metals (such as Fe, Cu, Zn, Co, Mn, Mo, Ca and Sn) are essential for life. Cadmium, V, Ni, Ba and Sr are considered possible essential elements but are useful only within limits which may vary from one organism to the other (Underwood, 1971; Schroeder & Kroll, 1966). Aluminium is toxic to the central nervous system and plays a role in dialysis encelophathy and dialysis oesteodystrophy (Savory & Will, 1991).

One of the major sources of clams in Ghana is the lower Volta river where majority of clam fishery is conducted by women. Clam fishery is an important poverty alleviation economic activity in the area. This fishing industry is an income generating business in Ghana providing the third most important occupation of the inhabitants. The clams are collected for food and remain an important affordable protein source for the riparian communities in the catchment of the Volta region and across the country. It is also reported to be a delicacy for about 98% of the people along the Volta river (Charkhabi et al, 2008; Olowu et al, 2010). Metals mainly originate from run-off from the surrounding agricultural lands, textile industries and other industrial activities within the study area.

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Since these clams are known to be good bioconcentrators of heavy metals and the fact that sediments acts as repository for metals, it has become important to investigate the concentration levels of these toxic and potentially toxic metals in the detrital sediments and the clams. This work is part of a comprehensive monitoring programme conducted along the Volta basin of Ghana with the aim of assessing the elemental content in the flora, fauna, sediment, water etc in relation to pollution

Objectives

To determine the levels of toxic and potentially toxic elements in sediments and clams *Galatea pardoxa* (= Egeria radiate) in the Lower Volta River using instrumental neutron activation analysis.

To assess the level of pollutants in sediments and the extent to which the sediment quality of the basin has deteriorated.

Materials and methods

Materials and apparatus

Christ freeze-dryer, 5% HNO₃, IAEA Standard reference materials (SRM) - 350,Tuna fish, NIST–SRM 1566b (Oyster tissue), Soldering machine(ERSA MS 6000), cotton wool, Research reactor (GHARR-1), polyethylene vial.

Sample Collection

The Volta Lake is the largest man-made lake in the world taking its source from a low range of hills in Bobo Dioulasso in Burkina Faso. It flows through northwestern Ghana to the east where it enters the sea at Ada passing through several towns, including the sampling village (Alabonu), in the Volta region. The Volta region is between latitude 5°45'N and 8°45'N with the Volta river being defined as the 80 km stretch of river between Kpong and Big Ada (Amisah et al, 2009). Four sampling stations were chosen to represent the portion of the lower Volta river where the research was conducted.

Clams and sediments were sampled from four sampling points from October 2009 to February 2010. The sampling was done at a distance of 150 m apart from one sampling point to the other. Clam samples were collected from the sediment of the river bed by divers while wearing rubber gloves. At each of the four sampling points, 25 clams each were collected at random from five dispersed points (separated by 25m) in the bottom sediment and pooled. A total of 100 pieces of clams were collected. They were washed immediately with some river water to remove mud, algae and organic debrics. The clams were kept in pre-cleaned labeled polyethylene bags and were packaged over ice in a thermo-insulated box (at a temperature of 4°C to help keep them as fresh as possible). All the polyethylene bags used were soaked in 5% HNO₃ for 72 hours.

A total of 28 sediment samples were collected from the four designated sampling points, where the clams were collected, by use of Eckman bottom grab sampler with an attached calibrated cable. At each sampling point, six sediment samples were collected in a similar manner as that of the clam samples. This was done to establish a good correlation between sediment and bivalve heavy metal load. The top 0-2 cm of the sediments, in each case, was sampled. No preservatives were added to the samples. The sediment samples were kept in separately labeled pre-cleaned polyethylene bags and kept over ice in another thermo-insulated box. The samples were then transferred into the laboratory for preparation and analysis.

Sample Preparation for neutron activation anlysis

In the laboratory, the clam samples were washed several times with de-ionised water to remove debris, sediments and other materials adhering to the shells. The size each of the clams

(based on length) was determined by taking the lengths of the shells of the individual clam samples, from the anterior to the posterior end. In order to get a dry weight greater than 0.1 g, clams of similar size (i.e. 8.0 cm to 10.1 cm) were put together. Clam samples within this size range were used in order to minimize the effect of size on the accumulation of metals and other elements by the clams. The shell valves were dislodged and opened aseptically using sterile, stainless, steel knife. The tissues of the clams were then removed and transferred into petri-dishes and kept immediately in a refrigerator for 48 hrs (at a temperature of -6° C). The samples were then removed and freeze-dried using a Christ freeze-dryer for 72 hrs at a temperature of -30°C (corresponding to a vapour pressure of 0.370 mbar). The clam samples were ground and homogenized using a commercial blender with stainless steel blades. About 200 mg each of the pulverized clam samples were weighed, wrapped and heat sealed (using soldering rod) in ultra-clean polyethylene films. Five replicate sub-samples were prepared for each sample. For short lived radioisotopes, the wrapped films were packaged into a 7.0 ml polyethylene vial (i.e. one wrapped film to one polyethylene vial), which were in turn heat-sealed for irradiation. Standard reference materials namely IAEA-SRM 350 (Tuna fish) and NIST-SRM 1566b (Oyster tissue) were prepared and packed similarly as the clam samples. However, for the medium and long lived radioisotopes, the standard reference materials were sandwiched between four wrapped samples and together, packaged into one polyethylene vial for irradiation

The sediment samples were homogenized using a polyethylene spatula and air-dried at 20°C for five days in a clean, dry environment. Organic debris, Shelly fragments and macro-organisms were removed from the sample. The dried samples were then crushed using an agate mortar and pestle. It was then sieved through a 64 μ m-mesh U.S.A standard testing sieve (Fisher Scientific Company, U.S.A). About 100 mg of each sample was weighed into ultra-clean polyethylene films which were wrapped and heat sealed. Five replicate sub-samples were prepared for each sample. Standard reference material, namely NIST-SRM 1646a (estuarine sediments) was prepared and packed in a similar mannar as that of the samples.

For short irradiations, one wrapped film was packaged into one 7.0 ml polyethylene vial (i.e. in a 1:1 ratio) where as for medium and long lived radioisotopes, the reference material was sandwiched between four wrapped samples and, together, packaged into one polyethylene vial for irradiation. All polyethylene films and polyethylene vials used for the irradiation processes were soaked in 5% HNO₃ for 72 hours. This was followed by rinsing (with de-ionized water) and drying in an oven at 15°C. This was done to eliminate possible contamination that might arise from the use of these materials. *Sample Irradiation and counting*

The irradiation and counting of samples have been described previously by Serfor-Armah, 2006. The prepared samples, standards and empty polyethylene vials were all irradiated in the Ghana Research Reactor-1(GHARR-1) facility at the Ghana Atomic Energy Commission, Kwabenya, operating at 15 KW at a thermal neutron flux of $5x10^{11}$ ns⁻¹cm⁻². Samples were transferred into the irradiation sites via pneumatic transfer system at a pressure of 0.6 Mpa. The categorization of irradiation time (ti), decay time (t_d) and counting time (t_c) for short-lived radionuclides with half-life less than few

hours (i.e. ²⁸Al, ⁴⁰Ca, ³⁸Cl, ⁶⁶Cu, ²⁷Mg and ⁵²V) were 2 minutes, 1-10 minutes and 10 minutes respectively. For medium-lived radionuclides with half-life of several hours (⁷⁶As, ¹¹⁵Cd, ⁴²K, ²⁴Na and ⁶⁹Zn), the irradiation time used was 1hour, decay time 24hours and a counting time of 1hour. The long lived radionuclides with half-life in days and years (i.e. ⁶⁰Co, ⁵¹Cr, ²⁰³Hg, ⁵⁹Fe, ⁵⁹Ni, and ⁴⁶Sc) were irradiated for four hours and decayed for two weeks with ten hours counting. In short irradiation, each of the sealed samples in the polyethylene capsules were sent for irradiation one after the other in one of the inner irradiation channels. Table 1 describes the nuclear data for the elements of interest.

Evaluation of peak area of y-spectrum

The counting of the induced radioactivity was performed by a PC- based γ -ray spectrometry. It consists of an n-type high purity Germanium (HPGe) detector (model GR2518) coupled to a computer-based Multichannel Analyzer via electronic modules and a spectroscopy amplifier (model 2020, Canberra Industries Incorporated). The relative efficiency of the detector is 25% with an energy resolution of 1.8 KeV at γ -ray energy of 1332 KeV of ⁶⁰Co.

The γ -ray product radionuclides were qualitatively identified by the energies emitted and the quantitative analysis was done by converting the counts as area under the photo peaks by the comparator method. Through appropriate choice of cooling time, the detector's dead time was controlled to be less than 10 %. Both qualitative and quantitative analyses were done using the γ -ray spectrum analysis software, MAESTRO-32.

The formation of ²⁸Al arises not only from the ²⁷Al (n, γ) ²⁸Al but also from the ³¹P (n, α) ²⁸Al and ²⁸Si (n, p) ²⁸Al reactions. This creates interferences during the determination of Al. These interferences were evaluated by the method described by Serfor-Armah et al, 2010.

Pollution Assessment

Determination of enrichment factor

In the present study enrichment factor was used to assess the level of contamination and the possible anthropogenic impact in the sediments.

To evaluate the magnitude of contamination in this sediment, the enrichment factors (EF) were computed relative to the abundance of species in source material to that found in the Earth's crust.

Many authors (Baptista Neto *et al.*, 2000; Mucha *et al.*, 2003) have used conservative elements such as Al and Fe to identify and normalize anomalous metal concentration, Aluminium has been used in this study to normalize metal contaminant and differentiate natural from anthropogenic components. According to Ergin *et al.* (1991) the metal enrichment factor (EF) is defined as follows:

$EF = \frac{(X/Al)sediments}{(X/Al)Earth Crust}$

Where EF is the enrichment factor, X is the metal studied and X/Al is the ratio of the concentration of element X to Al. Many authors prefer to express the metal contamination with respect to average shale to quantify the extent and degree of metal pollution (Muller, 1969; Forstner and Muller, 1973). In this study, the background concentrations of Mn, Al, K, V, Na, Mg and Ca were taken from Taylor (1964). According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate the metal is entirely from crustal materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic.

Index of Geoaccumulation (Igeo)

The geoaccumulation index, Igeo, values calculated for different metals as introduced by Muller (1969) is as follows:

Igeo =
$$ln(\frac{c_n}{1.5 \times Bn})$$

Where Cn is the measured concentration of element n in the sediment sample and Bn is the geochemical background for the element n which is taken from the literature (Taylor, 1964). The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations. The seven grades or classes of geo accumulation index proposed by Muller were used in this study.

Pollution Load Index

The extent of pollution by trace metals has been assessed by employing the method based on Pollution Load Index (PLI) developed by Thomilson *et al*, 1980. The relation is shown below

PLI =
$$\sqrt[n]{(product of n number of CF value)}$$

Where CF = contamination factor and n= number of metals PLI provides a simple, comparative means for assessing a site or estuarine quality. A value of zero indicates perfection, a value of one indicates only baseline levels of pollutants present and values above one indicate progressive deterioration of the site (Thomilson et al, 1980).

Results and Discussion

The results for the analysis of standard reference materials, the elemental content of sediments and clams are presented on Tables 2, 3 and 4 respectively.

None of the elements of interest were present in detectable amounts in the empty polyethylene irradiation vials. The number of counts obtained for the irradiated samples were therefore considered to be entirely due to the samples and not from the polyethylene irradiation vials used.

The accuracy of the method was evaluated by repeated analyses of compositionally appropriate certified reference materials; NIST –SRM 1566b (Oyster Tissue), IAEA-SRM 350 (Tuna Fish) and NIST-SRM 1646a (Estuarine Sediments) under the same experimental conditions as the samples. The results of this is shown on table 3. The accuracy of the measurements, in terms of the relative deviation from the IAEA certified values were all within $\pm 4\%$. From this, it was realized that, the agreement between the IAEA certified values and the values obtained in this work was generally good.

Elemental distribution in sediments

From table 4, it can be seen that, the elements in the detrital sediments of the river had average concentrations (in µg/g unless otherwise stated), in decreasing order of 2.25±0.21 %(Fe), 1.67±0.04 %(Mn), 0.84±0.29 %(Ca), 0.44±0.07 %(Na), 0.30±0.03 %(K), 0.24±0.04 %(Mg), 0.18±0.01 %(Al), 37.19±5.58 (Cr), 36.51±6.22 (V), 29.82±4.48 (Ni), 12.67±1.35 (Cu),12.27±1.84 (Zn), 10.25±2.22 (Co), 2.48±0.16 (Sc) and 1.16±0.27(As). Cadmium and Hg were below detection limit. The mean concentrations of the heavy metals As, Cd, Cr, Cu, Hg and Zn in sediment were within the permissible limits of standards as stated in Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG) (Wisconsin Department of Natural Resources, 2003) with Fe and Mn exceeding the CBSQG values as shown on Table 5. All the metals, however, recorded concentrations that were below the threshold effect levels (concentrations below which adverse effects upon sediment dwelling fauna would infrequently be expected). According to Amisah et al, 2010, the concentrations of Mn, Fe, Hg and Zn in sediments of the Volta estuary of Ghana were also within permissible limits with reference to WHO safety standards.

Results for enrichment factor values (EF), geoaccumulation index (Igeo) and pollution load index (PLI) are shown on table 5. Enrichment Factor (EF) of the heavy metals in sediment showed that Al (1.00), Ca (0.009), Cu (1.05), Fe (0.02), Mn (0.79), Na (0.006), Ni (0.0003), Sc (0.51), V (1.28) and Zn (0.82) had no enrichment; Co (1.86) and Cr (1.69) had minimal enrichment. The sediment was therefore not contaminated with Co and Cr, since their EF values were less than 2 (Gonzalez et al., 2000), but are more likely to have anthropogenic sources. Arsenic (2.93) had moderate enrichment. According to Gonzalez et al., 2000, EF value higher than 2 is an indication of contaminated sites. Hence with respect to As, the sediment can be said to be contaminated. The concentrations of Na, Mg and Co could be due to erosion and leaching from nearby soil as they are already natural components of the earth crust (Lenntech, 2009; O'brien et al, 1990).

The geoaccumulation indexes (Igeo) of metals and their corresponding contamination intensities have been described by Forstner et al, 1993. Apart from K and Mg all the metals analysed exhibited a zero class, indicating practically unpolluted sediment quality. The sediment was classified to be moderately to strongly polluted (2 < Igeo < 3) with K but moderately polluted (1 < Igeo < 2) with Mg.

From Tomlinson *et al*, 1980, the extent of pollution of the sediment was assessed using the pollution load index (PLI). The PLI value obtained was 0.09. This indicates that the sediment as a whole was unpolluted. The observed high level of metals in the detrital sediments was in agreement with the findings from Davies et al, 2006. According to them, sediments are known to hold more than 90% of the total amount of metals present in an aquatic ecosystem. Suspended sediments and metallic chemical solids usually aggregate to form large denser- than- water particles that settle from the water to the sediments (O'brien, Rianbow & Nugegoda, 1990).

Distribution of elements in clams

The concentration of elements analyzed in the clams in decreasing order were; Fe(0.94±0.26 %) > Ca (0.44±0.04 %) > K (0.27±0.04 %) >Mg (0.16±0.03 %) > Cl (0.13±0.02 %) > Na $(0.12\pm0.001 \text{ \%}) > Mn (491.18\pm7.53 \mu g/g) > Zn (92.29\pm13.84$ $\mu g/g$ > Cu (56.42±11.20 $\mu g/g$) > Al (54.93±2.69 $\mu g/g$) > As $(3.67\pm0.54 \ \mu g/g) > V \ (2.87\pm0.52 \ \mu g/g) > Cr \ (1.62\pm0.25 \ \mu g/g) >$ Sc $(0.72\pm0.16 \,\mu\text{g/g})$. Cadmium, Hg and Ni were below detection limit. Among the eighteen elements studied in the clams, Fe recorded the highest concentration with Sc recording the lowest. According to Etuke et al,2000, the other of tissue elemental concentration in Galatea paradoxa from the Cross River, Nigeria, was Mg>Ca>Fe>Cu>Zn. Aluminium, Cu, Mg, Mn, V, as well as Fe, were observed to have concentrations relatively higher than those of the clams from the Volta estuary studied by Serfor-Armah et al, 2010. On the contrary, Ca, Co, Na and K (in this work) recorded lower concentrations than those from Serfor-Armah et al, 2010.

Manganese, Fe, Ca, Co, Mg, Na, K and V are known to be essential for life. Manganese has no noxious effects. It is a micronutrient for bone formation and aids in enzymatic actions. Manganese is also known to aid in nerve and heartbeat functions (Bakhru, 2002). Iron on the other hand, is essential for red blood cell formation. It is also known to be essential for cognitive development and proper functioning of the immune system. Deficiency of Fe can lead to fatigue, low blood level and low blood pressure (Wardlaw & Smith, 2006). Calcium is a metal that is known to be essential for blood clotting and muscle contraction. It also plays a role in the formation and maintenance of bones (Witney & Rolfes, 2005). Cobalt is an important component of vitamin B12 which participates as a coenzyme in many vital enzymatic reactions (Cheggour et al, 2000). Magnesium is an important electrolyte responsible for proper nerve and muscle function. It also works as co-factor in many metabolic reactions (Yamashitaet al, 2005). However, sodium is required for nerve and muscle functioning whereas potassium aids in the fluid balance and nerve impulse transmission within the cells of bivalves (Witney & Rolfes, 2005).

The heavy metal Cu in appropriate concentrations is essential but above the threshold concentrations could also be toxic. Copper aid hormone synthesis and protein metabolism (Bakhru, 2002). Ironically, excessive amounts of copper can induce chlorosis and Fe deficiency (Sarkany-Kiss, Michaela & Fodor, 1997).

In this study, the concentration of Cu in the clams (56.42 $\mu g/g$) was lower than the WHO limit of 100 $\mu g/g$. This concentration (of Cu in the clams) compared well with that obtained by Bogatov et al, 2009, (i.e. 54µg/g) in freshwater hydrobionts from Russia. Chromium is known to potentiate insulin actions (Cheggour, 2000). However, long term exposure to chromium can cause liver and kidney damage. The concentration of Cr (1.62±0.25 µg/g) was comparatively lower than the WHO limit of 8 µg/g (for Cr). Zinc recorded a concentration of 92.29 ± 13.84 µg/g in the clams which was lower than the WHO limit of 250 μ g/g. Zinc is an essential trace element in our diet and is required for the synthesis of DNA, RNA, and protein and thus for cell division (Prasad, 1983). However, harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting. Taken longer, it can cause anemia and decrease the levels of good cholesterol (ATSDR, 2005). According to Etuke and co workers, the concentration of Zn in Galatea paradoxa (Donacidae) from the Cross River, Nigeria was 5.56% in 2000 (Etuk et al, 2000). This concentration was however greater than the concentration of $92.29\pm13.84 \ \mu g/g$ obtained in this present studies.

But for Cl, all the elements recorded in the sediments were also detected in the clams. Biosediment accumulation factor (BSAF) which is the ratio between the metal concentration in whole tissue of an organism (i.e clams) and that in the sediment was calculated for and is shown on Table 4. Zinc recorded the highest BSAF value of 7.35 with Co recording the least BSAF value of 0.016. The BSAF values for clams in decreasing order follows; were as Zn>Cu>As>K>Mg>Ca>Fe>Sc>Na>V>Cr>Mn,Al>Co. The clam bio-accumulated and biomagnified As, Cu and Zn (with their BSAF>1.00) in their tissues. This indicates that, though Zn, Cu and As were considered minor elements (i.e. concentration from 1-100 μ g/g), they are likely to trigger toxic effects readily than the major elements (elements with concentrations >100 µg/g).

Adjei-Boateng *et al*, 2010, also reported BSAF values of the order Hg>Mn>Fe from the volta clam, *Galatea paradoxa*, from the volta estuary. This indicates that clams from the Volta estuary analysed by Adjei-Boateng accumulated Mn more the Fe whilst the opposite was observed in this current studies.

Conclusions

The analytical data obtained in this work indicates that, the concentrations of Al, Ca, Co, Cr, Fe, Mn, Ni, Sc and V in the sediments were higher than that in the clams. However As, Cl, Cu, Mg, Na, K and Zn had relatively higher concentrations in the clams than in the sediment. The high concentration of Zinc and hence its accumulation in the clam tissues than in the sediment may be as a results of its essential requirements by the clams. Zinc (and metals like Cd) tends to be rather labile in sediments, compared with other metals, hence its lower concentration in the sediment relative to the clams. This pattern has been observed in a number of Moroccan estuaries (Cheggour et al. 2000). The higher levels of Mg. Na and K recorded in the clams could be an indication of their natural capacity to regulate and accommodate elevated concentrations of these metals as well as the bioavailability of these metals to the clams (Devagi et al, 2008). Enrichment factor values show that As were moderately enriched with Co and Cr having minimal enrichment. Apart from K and Mg all the metals analysed exhibited a zero class, with respect to Igeo, indicating practically unpolluted sediment quality. The sediment was classified to be moderately to strongly polluted (2 < Igeo < 3) with K but moderately polluted (1 < Igeo < 2) with Mg. Though some essentialities are associated with these metals, above some concentration levels, they are accompanied with some toxic effects. Hence depuration which is known to reduce the concentration levels of these metals is recommended before consumption. To avoid the associated accumulative effects of consuming unhealthy quantities of heavy metals, the consumption of a diversity of sea and freshwater foods by the large number of people depending on the clam, Galatea paradoxa, is also recommended. Toxicity however is known not to depend entirely on the concentration levels of these elements in sea and freshwater food but also on the chemical forms in which metals exist in an organism. Toxicity studies as well as Speciation studies are therefore recommended for future studies for elements such As, Cr etc.

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Table 1: Nuclear data [IAEA-TECDOC-564] for the elements of interest

Element	Isotope (% abund.)	Nuclide	Cross-section(b)	Half-life	γ-ray energy(KeV)
Al	²⁷ Al(100)	²⁸ Al	0.232	2.241min	1779.0
As	⁷⁵ As(100)	⁷⁶ As	43±1	26.3 h	559.1
Br	⁸¹ Br(49.31)	^{82}Br	2.69±0.09	35.3 h	554.3, 776.5
Ca	⁴⁸ Ca(0.187)	⁴⁹ Ca	1.1±0.2	8.72min	3084.4
Cd	¹¹⁴ Cd(28.73)	115Cd	0.300±0.015	53.5 h	336.3, 527.91
Cr	50 Cr(4.35)	⁵¹ Cr	15.9±0.2	27.72 d	320.0
Cu	65Cu(30.9)	⁶⁶ Cu	2.17±0.03	5.09min	1039.2
Cl	³⁷ Cl(24.23)	³⁸ C1	0.428 ± 0.005	37.2min	1642.7
Co	⁵⁹ Co(100)	⁶⁰ Co	17±2	5.272a	1173.5,1332.5
Fe	⁵⁸ Fe(0.28)	⁵⁹ Fe	1.15±0.02	44.5d	192.3, 1099.3
Hg	²⁰² Hg(29.7)	²⁰³ Hg	4.9±0.1	46.6 d	279.2
K	41 K(6.73)	^{42}K	1.46±0.03	12.38h	442.9,1524.7
Mg	²⁶ Mg(11.01)	²⁷ Mg	0.0382±0.001	9.46min	843.8,1014.4
Mn	⁵⁵ Mn(100)	⁵⁶ Mn	13.3±0.2	2.58h	846.8
Na	²³ Na(100)	²⁴ Na	0.530±0.005	14.95h	1368.6,2754.0
Ni	⁵⁸ Ni(68.08)	⁵⁹ Ni	0.113±0.007	70.82 d	810.8
Sc	45 Sc(100)	⁴⁶ Sc	16.9±1	83.8 d	898.3, 1120.5
V	⁵¹ V(99.75)	⁵² V	4.88 ± 0.04	3.743min	1434.1
Zn	⁶⁸ Zn(18.6)	^{69m} Zn	0.072±0.004	13.76 h	438.6

Element	NIST –SRM 1566b (Oyster Tissue)		IAEA-SRM 350 (Tuna Fish)		NIST-SRM 1646a (Estuarine Sediments)	
	This work	Certified value	This work	Certified value	This work	Certified value
A1	193.0±7.0	197.2±6.0			2.336±0.020%	$2.297 \pm 0.018\%$
As	7.48±0.32	7.6±0.65	5.08	5.28	5.99±0.09	6.23 ±0.21
Ca	0.0806±0.002%	0.0838±0.0020%	102	100	0.498±0.071%	0.519 ±0.020%
Cd	2.52±0.1	2.48±0.08	0.019	0.020	0.151±0.005	0.148 ± 0.007
Cl	$0.498 \pm 0.02\%$	0.514±0.010%				
Со	0.359±0.02	0.371±0.009	0.038	0.037	(5.1)*	(5.0)*
Cr			0.63	0.65	42.3 ±3.6	40.9 ± 1.9
Cu	69.5±2.9	71.6±1.6	2.91	2.83	9.89 ±0.40	10.01±0.34
Fe	201±5.0	205±6.8	70.19	72.1	1.952±0.271%	2.008±0.039%
Hg	0.0359±0.002	0.0371±0.0013	4.86	4.68	(0.039)*	(0.040)*
K	0.646±0.005% 0.1101±0.004%	0.652±0.009% 0.1085±0.0023%			0.891±0.023%	$0.864 \pm 0.016\%$
Mg	19.2±0.7 0.3181±0.005%	18.5±0.2 0.3297±0.0053%			0.378±0.01%	$0.388 \pm 0.009\%$
Mn	1.02±0.07	1.04±0.09	0.58	0.60	239.5±3.5	234.5±2.8
Na					0.765±0.029%	0.741±0.017%
Ni	0.600±0.027	0.577±0.023	0.31	0.32	(22.2)*	(23)*
Sc	1416±49	1424±46			(4.8)*	(5)*
V					43.64 ±0.91	44.84 ± 0.76
Zn			16.9	17.4	50.6 ±2.1	48.9 ± 1.6

 Table 2: Comparism of elemental concentrations in reference materials analyzed by INAA with certified/recommended values, n = 5

*Non certified/Recommended values

Table 3: Mean value of elemental concentration in Clams, Mussels and Sediment ($\mu g/g dry$

weign	weight, unless indicated otherwise)				
Element	Clams	Sediment	BSAF		
Al	54.93±2.69	1.81±0.01%	0.03		
As	3.67±0.54	1.16±0.27	3.16		
Ca	$0.44 \pm 0.04\%$	$0.84 \pm 0.29\%$	0.52		
Cd	< 0.07	< 0.07	-		
Cl	0.13±0.02%	< 0.001	-		
Co	0.17 ± 0.04	10.25±2.22	0.016		
Cr	1.62 ± 0.25	37.19 ± 5.58	0.04		
Cu	56.42.±11.20	12.67±1.35	4.5		
Fe	0.94±26.03%	2.25±0.21%	0.42		
Hg	< 0.02	< 0.02	-		
K	0.27±0.04%	0.30±0.03	0.89		
Mg	0.16±0.03%	0.24 ± 0.04	0.66		
Mn	491.18.±7.53	$1.67 \pm 0.04\%$	0.03		
Na	$0.12 \pm 0.001\%$	29.82 ± 4.48	0.28		
Ni	< 0.92	$0.44 \pm 0.07\%$	-		
Sc	0.72 ± 0.11	2.48±0.16	0.29		
V	2.87 ± 0.52	36.51±6.22	0.08		
Zn	92 29+13 84	12 56+1 88	7 35		

Biosediment Accumulation Factor (BSAF) = concentration of metal in bivalve/concentration of metal in sediments

Table 4: Concentration of trace metals of sediment samples and the toxicological reference values for sediments (µg/g dry weight, unless indicated otherwise) Enrichment factor and Geoaccumulation

index values.							
Elements	Concentration	Sediment Quality Guidelines values	5 TEL	Enrichment factor	Igeo		
Al	1.81±0.01%		2.55%	1.00	< 0.0		
As	1.16 ± 0.27	9.8	10798	2.93	$<\!\!0.0$		
Ca	$0.84 \pm 0.29\%$			0.009	$<\!\!0.0$		
Cd	< 0.07	0.99	583				
Cl	< 0.001						
Co	10.25 ± 2.22			1.86	$<\!\!0.0$		
Cr	37.19 ± 5.58	43	36286	1.69	$<\!\!0.0$		
Cu	12.67±1.35	32	28012	1.05	$<\!\!0.0$		
Fe	2.25±0.21%	2.0%	18.84%	0.02	$<\!\!0.0$		
Hg	< 0.02	0.18					
K	0.30±0.03			65.27	2.26		
Mg	0.24 ± 0.04			46.84	1.93		
Mn	1.67±0.04%	0.04%	63.00%	0.79	$<\!\!0.0$		
Na	29.82 ± 4.48			0.006	$<\!\!0.0$		
Ni	$0.44 \pm 0.07\%$	0.0023%	1.95%	0.0003	$<\!\!0.0$		
Sc	2.48±0.16			0.51	$<\!\!0.0$		
V	36.51±6.22			1.28	$<\!\!0.0$		
Zn	12.56 ± 1.88	120	98000	0.82	< 0.0		