Seasonal Investigations into the Level of Toxic Elements in Marine Organisms (Fish and Mollusk) along the Coast of Ghana Using Neutron Activation Analysis

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Abstract: Seasonal investigation was conducted into the occurrence and extent of potentially toxic heavy metals along the coast of Ghana using marine organisms as bioindicators of pollution. The marine organisms sampled were analysed using Instrumental Neutron Activation Analysis coupled with conventional counting system. All the four samples (Dentex macrophthalmus, Sardinella maderensis, Engraulis encrasicolus and Cymbium cymbium) recorded detectable levels of potentially toxic elements which fluctuates between <0.07mg/kg Cd and 699 mg/kg Al. Cymbium cymbium recorded the highest level of (As, Co, Cu, Zn) whiles Engraulis encrasicolus accumulated appreciable amount of V. Al was the most abundant of all the elements. The coast of Ghana was found to be mildly polluted with respect to the elements Al, As, Cd, Co, Cu, Cr, Ni, Hg, V and Zn.

Key words: Ghana, INAA, marine organisms, toxic elements, pollution

INTRODUCTION

The shores of Ghana have for a long period of time been free from reports of serious environmental problems. Despite this, there were a few occasions when dumping of toxic wastes were suspected. Coastal areas have always attracted man and his industries because of the advantages and the ease with which a diverse collection of natural resources can be obtained, the opportunities for waste disposal and recreation and the growing use of the sea lanes for the exchange of commodities. Like most coastal states, the coastal zones, of Ghana, especially Accra, Tema and Takoradi have been the major areas for industrial development. In Ghana, about 90% of the industries and mining activities are concentrated in the southern sector (Serfor-Armah et al., 2001). This trend has led to the continuous migration of prospective workers from inland rural areas to the coastal industrial centres. In these coastal centres of high population densities, discharges into the environment are to a large extent untreated and unregulated, thus increasing the risk of localized pollution and modification of the coastal environment.

The main producers of industrial effluents include the textile, food and petroleum refining industries. Mineral exploitation also contributes to the pollution load. On the whole, industrial development in Ghana is on a relatively low scale and discharges from industry have generally created little impact except in the coastal and other industrial centres. Observations have shown that on the contrary, more materials in the form of municipal sewage are discharge into the marine environment as a result of human and not industrial activities (Middlebrooks et al., 1981). There are not many large city sewage treatment plants or properly planned urban sewage systems. Thus waste waters are mainly discharged untreated into lagoons, estuaries and the immediate inshore areas.

A wide range of toxic elements from these major types of pollutants are expected to be present along the coast of Ghana. Plant materials along the coast of Ghana accumulate these toxic elements and pass it on to the fishes that feed on them and then to human beings through a food chain. Moreover, the study of bio-accumulation of these elements by fishes which are consumed directly by human beings is of interest because some of them are directly or indirectly toxic to marine organisms and ultimately to human life (Quagraine et al., 1996). Hence, the importance in the monitoring of the level of pollution of the Ghanaian coastal waters.

Fish are the major part of the human diet and it is not surprising that numerous studies have been carried out on metal accumulation in different fish species (Zare and
Fig. 1: Map of Ghana showing the sampling sites (all found at the southern part of the country) along the coast

Ebadi, 2005). Fish also have been popular targets of heavy metal monitoring programs in marine environments because sampling, sample preparation and chemical analysis are usually simpler, more rapid and less expensive than alternative choices such as water and sediments (Rayment et al., 2000). Heavy metals may enter fishes and shell fishes by several ways. Small amounts are absorbed by these organisms directly from the water through their gills and other tissues. However most of the pollutants found in aquatic organisms are through the food chain. Phytoplankton, bacteria, fungi and other small organisms absorb these materials from the surrounding water. These are then eaten by larger organisms, and eventually man. Some of these heavy metals exhibit toxicity at low levels in the sea water.

The aim of this study was to determine the concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Ni, V and Zn in flesh of the marine organisms along the coast of Ghana.

MATERIALS AND METHODS

Study area: Ghana is situated at 5.5° N of the equator. The study areas are all located at the southern part of the country (Fig. 1). The coastline of Ghana stretches for approximately 550 km. It is generally a low lying area,
not more than 200 m above sea level, and has a narrow coastal shelf extending outward between 20 and 35 km except off Takoradi, where it reaches up to 90 km (Armah and Amlalo, 1998). Generally, the climate of Ghana is tropical. The eastern belt is warm and comparatively dry, while the south-west corner is hot and humid. It becomes progressively drier from south-west to the north-east of Accra. Two-thirds of the coastal zone falls within the dry coastal savanna strip where annual rainfall ranges from 625 mm to 1000mm and average of 900 mm. Peak rainfall is in June and the lowest in January (Akpati, 1990) minimum temperatures occur in June to August and in January to March. The relatively dry coastal climate of the south-east is believed to be caused by the prevailing south-south-westerly winds blowing parallel to the coast, and a cool current of water immediately. Cold nutrient-rich water from the depths of the oceans regularly wells up to the surface. On the Ghanaian coast from July to September, a major upwelling of cool, high salinity south Atlantic central water occurs on the continental shelf. A second minor upwelling takes place in December to January. Studies of beach temperatures have shown that upwelling intensity is greater in the vicinity of Takoradi where temperatures are usually lower than other Ghanaian coastal waters (Armah and Amlalo, 1998). The coastal water is characterized by an eastward flowing current and an upwelling with varying annual intensities. Water masses offshore of the Ghanaian coast consist of five principal layers (Armah and Amlalo, 1998). A tropical surface water (warm and of variable salinity) extends down to a maximum of about 45 m depending on the seasonal position of the thermocline. Below the thermocline occurs the south Atlantic central water (cool and high salinity) down to a depth of about 700m. Also, below this are the three cold layers: the Antarctic deep water (700-1500 m); the north Atlantic deep water (1500-3500 m); and the Antarctic bottom water (3500-3800 m) (Akpati, 1990). The warm Guinea current flows along the coast at the surface in an eastward direction. It is approximately 370 km wide and at its southern edge, encounters the westward flowing south equatorial current with maximum velocity in June to July. Surface water velocities range from 0.5-1.5 m/s. The sub-surface water could have velocities ranging between 0.5-1.0 m/s and 0.05-1.02 m/s near the bottom (Armah and Amlalo, 1998).

Ghana has two seasons, the raining season and dry season. The raining season is between late April to October, and the dry season is between November and late March.

**Sampling:** Four different species of marine organisms (fish and mollusk) were sampled along the coast of six selected communities in Ghana by the research team. The communities are Prampram, Tema, Apam, Elmina, Sekondi, and Axim. At each sampling site, the marine organisms freshly brought to the coast were bought and collected into well labelled polyethylene bags. The samples collected were made up of three fish species: *Dentex macrophthalmus*, *Sardinella maderensis*, and *Engraulis encrasicolus*, and a mollusk specie, *Cymbium cymbium*. The samples were transferred into a thermo-insulated box and kept on ice, sent to the laboratory and stored in the refrigerator. Sample collection was on monthly basis from May 2009 to April 2010.

In this study, the various marine organisms were chosen for the investigations into the levels of toxic elements along some selected coastal towns in Ghana. This is because:

- The organisms are available and abundant throughout the year.
- They are widely consumed by the Ghanaian populace.
- They are easy to sample and identify and also have sufficient tissue for the analysis of the contaminants of interest.

Also the various sampling sites were chosen because they are very active sites when it comes to fishing as well as being the coastlines that always harvest the marine organisms chosen for this study.

**Sample preparation:** At the Laboratory, the research team prepared the samples for analysis through the following steps.

The samples were washed several times with de-ionized water to clean them from sand and other entangled materials. The scales of the fish samples were removed using a stainless steel knife. The shell of the mollusk species were crushed and removed leaving only the tissue. The samples were washed several times again with de-ionized water. The tissue of both the fish and mollusk species were cut into pieces, put in Petri-dishes and then kept in the refrigerator for about 48 hrs. The fish and mollusk samples were then removed and freeze-dried using the freeze-dryer (Christ freezedryer) for 72 h. The individual fish and mollusk species were ground and homogenized using a blender. 200 mg each of the samples was weighed and packaged into an ultra-clean polyethylene foil and wrapped. The foil was heat-sealed and packaged into polyethylene vials and heat-sealed.

**Sample irradiation, counting and analysis:** All prepared samples and standards were irradiated using the Ghana Research Reactor -1 (GHARR-1) facility at the GHARR-1 centre of the National Nuclear Research Institute (NNRI) of the Ghana Atomic Energy Commission (GAEC). The reactor was operated at a half-full power of...
The total concentrations of Al, As, Cd, Co, Cu, Cr, Hg, V, Ni and Zn in four different marine organisms, *Dentex macrophthalmus*, *Sardinella maderensis*, *Engraulis encrasicolus* (fin fishes) and *Cymbium cymbium* (mollusk) collected along the coast of Ghana are presented in Table 3. Almost all the marine organisms collected along the coast of Ghana, contained detectable amounts of many elements (Al, As, Co, Cr, Cu, Hg, Ni, Cd, V, and Zn).

* RESULTS AND DISCUSSION

The total concentrations of Al, As, Cd, Co, Cu, Cr, Hg, V, Ni and Zn in four different marine organisms, *Dentex macrophthalmus*, *Sardinella maderensis*, *Engraulis encrasicolus* (fin fishes) and *Cymbium cymbium* (mollusk) collected along the coast of Ghana are presented in Table 3. Almost all the marine organisms collected along the coast of Ghana, contained detectable amounts of many elements (Al, As, Co, Cr, Cu, Hg, Ni, Cd, V, and Zn).

* Cymbium cymbium recorded the highest levels of As, Co, Cu and Zn in both seasons whilst the highest level of V was recorded in *Engraulis encrasicolus* also in both seasons. Al was found in all the marine organisms at varying concentrations (237-699 mg/kg) during the dry season and 243-687 mg/kg during the wet season. Such...

**Table 3:** Mean values of elemental concentration of seafood species with standard deviations (mg/kg, unless indicated otherwise)  

<table>
<thead>
<tr>
<th>Element</th>
<th>Cymbium cymbium</th>
<th>Dentex macrophthalmus</th>
<th>Sardinella maderensis</th>
<th>Engraulis encrasicolus</th>
<th>Accepted level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>23.7 ± 9.5</td>
<td>55 ± 10</td>
<td>23.7 ± 9.5</td>
<td>55 ± 10</td>
<td>40 ± 5</td>
</tr>
<tr>
<td>As</td>
<td>0.19 ± 0.1</td>
<td>0.31 ± 0.08</td>
<td>0.19 ± 0.1</td>
<td>0.31 ± 0.08</td>
<td>0.15 ± 0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>0.88 ± 0.01</td>
<td>0.85 ± 0.08</td>
<td>0.88 ± 0.01</td>
<td>0.85 ± 0.08</td>
<td>0.80 ± 0.08</td>
</tr>
<tr>
<td>Co</td>
<td>15 ± 1.2</td>
<td>12.12 ± 1.82</td>
<td>15 ± 1.2</td>
<td>12.12 ± 1.82</td>
<td>10 ± 1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>0.99 ± 0.01</td>
<td>0.94 ± 0.01</td>
<td>0.99 ± 0.01</td>
<td>0.94 ± 0.01</td>
<td>0.90 ± 0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.035 ± 0.005</td>
<td>0.041 ± 0.003</td>
<td>0.035 ± 0.005</td>
<td>0.041 ± 0.003</td>
<td>0.04 ± 0.05</td>
</tr>
<tr>
<td>Hg</td>
<td>12 ± 1.2</td>
<td>3.82 ± 0.57</td>
<td>12 ± 1.2</td>
<td>3.82 ± 0.57</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.045 ± 0.007</td>
<td>0.045 ± 0.006</td>
<td>0.045 ± 0.007</td>
<td>0.045 ± 0.006</td>
<td>0.05 ± 0.05</td>
</tr>
<tr>
<td>V</td>
<td>-0.07 ± 0.01</td>
<td>0.19 ± 0.03</td>
<td>-0.07 ± 0.01</td>
<td>0.19 ± 0.03</td>
<td>-0.20 ± 0.05</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.19 ± 0.1</td>
<td>-0.19 ± 0.1</td>
<td>-0.19 ± 0.1</td>
<td>-0.19 ± 0.1</td>
<td>-0.19 ± 0.1</td>
</tr>
</tbody>
</table>

**Table 4:** Pearson’s correlation coefficient matrix of heavy metals in the marine organisms  

<table>
<thead>
<tr>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1</td>
<td>-0.95**</td>
<td>1</td>
<td>-0.90**</td>
<td>1</td>
<td>-0.48</td>
<td>1</td>
<td>-0.59</td>
<td>1</td>
</tr>
<tr>
<td>As</td>
<td></td>
<td>0.182</td>
<td>-0.215</td>
<td>0.539</td>
<td>-0.258</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td>0.93**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.525</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.906</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.317</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.141</td>
<td>1</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**: Correlation is significant at 0.05 level  

**Notes:**  
1. Detection limit; Values in parenthesis are results of the wet season  
2. The levels of toxic or potentially toxic industrial pollutants (Valchos et al., 1998) measured in the studied marine organisms were as follows: As (1.11-37.9 mg/kg), Co (0.032-0.13 mg/kg), Cu (3.82-12.12 mg/kg), V (0.46-0.96 mg/kg) and Zn (20.74-84.19 mg/kg) all in the dry season and As (1.56-34.2 mg/kg), Co (0.034-0.24 mg/kg), Cu (6.63-15.36 mg/kg), V (0.60-0.89 mg/kg) and Zn (24.74-44.16 mg/kg) recorded during the wet season. These values were found to be comparable to that reported in other polluted oceans of the world (Gadde et al., 2007). For example levels of 1.74±0.86 mg/kg As, 0.24±0.05 mg/kg Co, 0.45-8.79 mg/kg Cu, 2.39-38.24 mg/kg Zn, 0.16-0.59 mg/kg Ni. Olodade et al. (2008), determined the levels of the trace metals (Co, Cu, Mn, Fe and Zn) in marine fish (Tilapia zilli) from Nigeria, and reported the following mean concentrations: 194.45 (271.14) mg/kg Cu, 0.18 (0.11) mg/kg Co, 204.72 (261.13) mg/kg Fe, 1.05 (1.76) mg/kg Mn, and 0.23 (0.16) mg/kg Zn. Values in parenthesis are results of the wet season. The presence of the above elements in the study area perhaps could be associated with the heavy industrial and human activities along the southern sector of Ghana’s coastline.  

Other potentially toxic elements that were measured in the marine organisms with varying low concentrations were: Hg and Cd. Cadmium was below the detection limit during the dry season while a low concentration range of mercury (0.012-0.038 mg/kg) was measured in the samples also during the dry season. Cr was measured in all the marine organisms with Cymbium Cymbium showing the highest content. The highest level of Hg (0.038 mg/kg) was measured in Dentex macrophthalmus and the lowest value (0.12 mg/kg) was found in Engraulis encrasicolus. The following concentrations of Cd (0.23 mg/kg) Cr (0.77 mg/kg) and Hg (0.97 mg/kg) have been reported elsewhere (Gadde et al., 2007). In general, Cd, Hg, Ni, Cr, and Co tend to be the least recorded compared to the other elements.  

The metal concentrations in aquatic systems usually remain either in solution or suspension form and finally settle down to the bottom or are taken up by the organism. The progressive and irreversible accumulation of these metals in various organs of marine species ultimately leads to metal-related diseases because of their toxicity, thereby endangering the aquatic biota and their organisms (Gadde et al., 2007).  

The metal data (Table 4) was examined on the basis of linear correlation between metal pairs in terms of strong positive correlation. Strong positive correlation were observed for As-Co, As-Cr, As-Cu, As-Ni, Co-Cr, Co-Zn, Co-Hg, Co-Ni, Cr-Ni, Cu-Ni, Cu-Zn and Hg-Zn. indicating the existence of a common source/origin of these metals in the marine organisms under investigation.  

The concentrations of the various elements in Cymbium cymbium serve as a baseline data, since it’s not been used in previous studies. However Tay et al. (2008) used various fish species (Cynosoglossus cadenali, Dentex congoensis, Trachinotus Ovatus, Trachurus trachurus, Sardinella eba, Solar crumophthalmus and Panulirus regius) to assess the state and trend of contamination of the coastal waters of Accra and Tema for the elements Fe, Mn, Cu, Zn and Cd, and came out with the following mean concentration values: 11.74 mg/kg Fe, 4.0 mg/kg Mn, 6.19 mg/kg Cu, 11.1 mg/kg Zn, 0.19 mg/kg Cd. Cymbium cymbium accumulated the highest level of the toxic elements (As, Co, Cu, Zn, Cr, Ni), This is because Cymbium cymbium is a bottom feeder and is
generally expected to concentrate more metals than surface feeders like fish. Additionally, the higher concentration of metals in *Cymbium cymbium* over fish was not very surprising because as resident species, the concentrations of contaminants in their tissue are likely to be more representative of the site than some mobile species, such as fish. If analysis for instance indicate that *Cymbium cymbium* is safe to eat, then consumption of other more mobile species should also be safe.

A critical assessment of Table 3 shows a consistent higher concentration of Co, Cd, Zn and Cu in all the marine organisms during the wet season. In general higher concentrations of most of the metals in individual marine organisms were obtained during the wet season across all the biota.

A major upwelling phenomena on local scale during the wet season may have increased the bioavailability of most of the metals (Table 4), whiles one factor that may contribute significantly to seasonal changes in the metal concentration as observed in this work is increased productivity. This has been reported to influence a dramatical rise in the metabolic concentration in seawater, the resultant effect of which is the possibility of organic complexation and subsequent changes in metal bioavailability (Olodade *et al.*, 2008).

**CONCLUSION**

Potentially toxic elements in the chosen marine organisms along the coast of Ghana has been investigated using INAA. Almost all the marine organisms studied contain detectable levels of potentially toxic elements. Al was the most abundant (237-699 mg/kg) of all the elements. *Cymbium cymbium* accumulated the highest level of the toxic elements (As, Co, Cu, Zn) in both seasons, whiles the highest level of V was found in *Engraulis encrasicolus* also in both seasons. The levels recorded were within the permissible acceptable limit with the exception of As and Cr in *Cymbium cymbium* but comparable to studies elsewhere, the presence of these potentially toxic elements in the studied marine organisms in Ghana is of much concern, since they bioaccumulate. Anthropogenic activities were found to have impacted negatively on the coastal waters of Ghana, since they were identified as the main source of the contaminants. Prudent measures should therefore be adopted to mitigate the effect on these waters.

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