Occurrence of toxic heavy metals (Hg, Pb and Cd) in fish on Ghanaian markets

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\section*{ABSTRACT}
The monitoring of toxic heavy metals in fish is essential for protecting public health against the hazards of metal toxicity. The concentrations of metals (Hg, Pb and Cd), in different fish species were analyzed using Atomic Absorption Spectroscopic (AAS) procedures. The objective of this study was to look at the distribution of heavy metals in different species of fish on Ghanaian markets. Levels of cadmium (Cd) and lead (Pb) were determined by graphite furnace atomic absorption spectrometry (GF-AAS). Mercury (Hg) content was analysed by the cold vapour atomic absorption spectroscopic technique after Hg ions reduction with SnCl\textsubscript{2} (CV-AAS). Amongst the metals analysed, Lead (Pb; 0.1-0.49, average 0.24 mg/kg) showed the highest concentration, followed Mercury (Hg; 0.01-0.37, average 0.073 mg/kg) and Cadmium (Cd; 0.06-0.11, average 0.084 mg/kg). Amongst the species analysed, tuna had high lead concentrations with lobsters having the lowest concentration of lead. With respect to Hg contamination, shark specimen had the highest with cephalopods and octopus having the least Hg concentrations. Levels of cadmium in the examined species averaged from 0.06 mg/kg for octopus to 0.11 mg/kg for tuna. The study revealed that the studied metals concentrations were generally low in species of fish in the two study areas. Although the levels of these heavy metals are not high, a potential danger may emerge in the future depending on pollution sources and frequency of exposure.

\section*{Introduction}
Heavy metals are among the key contaminants of food supply and may be considered the most essential setback to our environment (Zaidi et al., 2005). According to Cui et al. (2005) potentially toxic elements such as cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As) are widely dispersed in the environment naturally by agricultural and industrial utilizations. Once absorbed, heavy metals are known to be persistent in the human body with long excretion half-lives for decades and therefore classified as potentially toxic elements. Fish are often at the top of the aquatic food chain and may concentrate large amounts of heavy metals from the water. In addition, fish are most indicative factors in fresh water systems, for the estimation of trace metal pollution and risk potential of human consumption. Accumulation of metals in different species is a function of their respective membrane permeability and enzyme system, which is highly species specific and because of this fact, different metals accumulate in different orders in different fish samples.

Additionally, the consumption of heavy metal-contaminated food can seriously deplete some essential nutrients in the body causing a decrease in immunological defences, intrauterine growth retardation, impaired psycho-social behaviour, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer. The distribution of metals varies between fish species depending on age, development status and other physiological factors (Kagi and Schaffer, 1998). Accumulation of metals in tissues of fish is dependent upon exposure concentration and duration, as well as other factors such as salinity, temperature, hardness and metabolism of the animals. This study looks at the distribution of heavy metals in different species of fish on Ghanaian markets.

\section*{Materials and Methods}
\textbf{Collection and Preparation of Samples}
Ten specimens each of tuna, octopus, sword fish, cuttle fish, lobster and cephalopod were sampled from markets in the Accra and Tema Metropolitan areas of Ghana. For ten sample obtained from these locations, 100g of each piece were taken and homogenized (10x 100g). Of the 100g homogenized samples, 25 g was taken given a total aggregate sample of 250g. Aggregate samples were divided into three equal parts to form laboratory, trade (defence) and reference samples. Appropriate weight(s) of each species were weighed into vessels of the microwave digester (MA079) with 4ml and 2ml of HNO\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} respectively. The required parameters were entered for the operation of the microwave digester. The digest were transferred into marked or graduated flask and diluted to the 20ml mark with deionized water after rinsing the walls of the vessel into it. Cadmium (Cd) and lead (Pb) were determined by graphite furnace atomic absorption spectrometry (GF-AAS), equipped with a deuterium background corrector. Mercury (Hg) content was analysed the cold vapour atomic absorption technique after Hg ions reduction with SnCl\textsubscript{2} (CV-AAS).

\textbf{Reagents}
All the reagents and chemicals used were of analytical grade Merck (Darmstadt, Germany). Concentrated 65% HNO\textsubscript{3}
and 30% $\text{H}_2\text{O}_2$ were of spectroscopic grades. Standard solutions of heavy metals (1000 mg/l) namely, mercury (Hg), Lead (Pb) and cadmium (Cd), were procured from Aldrich. The standards were prepared from the individual 1000mg/L standards (Merck), in 0.1 N $\text{HNO}_3$. Stock standard solution of chemical modifiers, Mg ($\text{NO}_3$)$_2$ (2.00 gL$^{-1}$), was prepared from Mg ($\text{NO}_3$)$_2$ (Merck) and Pd stock standard solution (3.00 gL$^{-1}$), was prepared from Pd 99.999%.

**Quality Control**

The quantification was performed using a calibration curve of the corresponding standards. Triplicate analyses were performed for each sample. Accuracy was evaluated by certified reference material for trace metals, DORM-2 (Dogfish muscle), was purchased from the National Research Council Canada (Ottawa, Ontario, Canada). The results were found within ± 5% of the certified values.

Deionized water was obtained from a Pure Lab Classic machine. All glasswares were soaked in nitric acid solution for 24 hours and rinsed with deionized water before analysis. Analyses were duplicated to ascertain the reproducibility of results.

**Results and Discussion**

<table>
<thead>
<tr>
<th>Species</th>
<th>Cadmium (Cd)</th>
<th>Mercury (Hg)</th>
<th>Lead (Pb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tuna</td>
<td>0.11</td>
<td>0.02</td>
<td>0.49</td>
</tr>
<tr>
<td>Shark</td>
<td>0.1</td>
<td>0.37</td>
<td>0.23</td>
</tr>
<tr>
<td>Octopus</td>
<td>0.06</td>
<td>0.01</td>
<td>0.24</td>
</tr>
<tr>
<td>Sword fish</td>
<td>0.08</td>
<td>0.04</td>
<td>0.25</td>
</tr>
<tr>
<td>Cuttle fish</td>
<td>0.07</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>Lobster</td>
<td>0.09</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Cephalopod</td>
<td>0.08</td>
<td>0.01</td>
<td>0.24</td>
</tr>
</tbody>
</table>

As shown in Fig 1.0, all tested heavy metals were found in the different species of fish at different concentrations depending on the type of fish and the heavy metal itself. Amongst the metals analysed, Lead (Pb; 0.1-0.49, average 0.24 mg/kg) showed the highest concentration, followed by Mercury (Hg; 0.01-0.37, average 0.073mg/kg) and Cadmium (Cd; 0.06-0.11, average 0.084 mg/kg). The analysis of Pb revealed strong differences in species contamination. Amongst the species analysed, tuna had high lead concentrations with lobsters having the lowest concentration. The trend in the level of contamination is largely explained by factors such as season, diet, location and age of the fish. The high levels of Pb contamination in tuna may also be explained by the size of the fish. This finding corroborates with work done by Storelli et al., (2002) who reported that size and mercury levels were highly correlated for blue fin tuna. Accumulation of heavy metals in different species is the function of their respective membrane permeability and enzyme system, which is highly species specific and by virtue of this different heavy metals accumulate in different orders in different fish samples. The extremely high levels of Pb in tuna may indicate that the environment is highly stressed with respect to lead. Lead has the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards (Puel et al., 1987).

The shark specimen showed a high mercury contamination followed by lobsters with cephalopods and octopus having the least Hg concentrations. This suggests a trend in the residues based on sample size. Many studies have also shown that mercury is bioamplified in the food chain with high-trophic-level predatory species, such as sharks, tuna and sword fish having generally high mercury concentrations. Specimen size can therefore be considered as a key parameter which
determines high exposure levels. Hg intakes can therefore be associated with the consumption of larger specimens, whereas the amount of Hg ingested remained within safe levels with the consumption of smaller species of fish. The differences in Hg content may indicate the degree of pollution in sediments and seawater based on geographical location which agrees with work done by (Sadiq, 1992). Mercury enters the coastal waters by sewage and other wastewater effluents, power plant cooling water discharges, vehicle emissions, petroleum and petrochemical industrial wastes, storm drain outfalls and solid waste landfills (Al-Mohanna and Subrahmanyam, 2001). According to the same authors, contaminants cannot be regulated by crustaceans and therefore, bioaccumulation of these elements occurs in specimens edible tissues.

Levels of cadmium in the examined species averaged from 0.06 mg/kg for octopus to 0.11 mg/kg for tuna. Although Cd is a toxic element that would deposit in human body and pose hazard to human health. The concentration in fish samples in the study were far lower than the consumption safety tolerance in fish set by the European Union (E.U). Similar situation was reported by Szefer et al. (2003) from Szczecin Lagoon. Also Turkmen and Ciminli (2007) found Cd levels below 0.001 mg/kg in fish (Clarias gariepinus) from Lake Golbasi. Cadmium is toxic to many organisms since the ion form combines with sulphhydryl (thiol) groups of many enzymes preventing their normal function (Walker et al., 2001).

The variability in heavy metal levels in different species depends on feeding habits, ecological needs, and metabolism (Rom´eo et al, 1999), age, size, and length of the fish and fish habitat (Canli and Furness, 1993).There was no significant difference in contamination levels with respect to sampling sources as shown in figures (2.0,3.0 and 4.0).

Conclusion

This study was carried out to provide information on heavy metal concentrations on seven species of fish in the Accra and Tema Metropolis. The highest metal concentrations were found in the shark species where as the lowest heavy metal concentrations were found in lobster. The study revealed that most of the fish species analyzed accumulated high levels of lead than mercury and cadmium. This study revealed that the heavy metals concentrations were generally low in species of fish in the two study areas and the differences were not significant. Although the levels of these toxic heavy metals were not high, a potential danger may emerge in the future depending on pollution sources and frequency of exposure.

Recommendations

Further studies should be conducted to determine levels of heavy metals in fish based on size, length and habitat as well as studies on rate of metabolism in fish species based on heavy metal residues.

References


