



Heavy Metals Pollution on the Environment: A Case Study of Seafood and Humans

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Abstract: Heavy metals pollution on the environment (seafood and humans) is a global problem. The concentrations of copper, cadmium and chromium in prawns, periwinkle and croaker fish from Aba area of Abia State were determined using Atomic Absorption Spectrophotometric (AAS) techniques. The values of copper in periwinkle, prawns and croaker fish were 19.22 ± 8.36 mg/kg, 2.78 ± 3.34 mg/kg and 0.6 ± 0.07 mg/kg respectively whereas the World Health Organization (WHO) limit is 0.5 mg/kg for copper in sea food and all samples examined had results which exceeded the WHO acceptable limits in seafood. Cadmium levels was high in croaker fish (1.10 ± 0.47) mg/kg compared to the WHO limit of 0.5–1.0 mg/kg of cadmium in food and the concentration of cadmium in prawns (0.74 ± 0.5) mg/kg and periwinkle (0.34 ± 0.28) mg/kg were within the WHO acceptable limit of cadmium. The values of chromium levels in periwinkle, prawns and croaker fish were 5.42 ± 3.79 mg/kg, 26.16 ± 2.85 mg/kg and 9.28 ± 8.4 mg/kg respectively and these samples exceeded the WHO acceptable limits of 2.0 mg/kg set for chromium in seafood. The results obtained from this study show that periwinkle and prawns bioaccumulated cadmium.

Keywords: Heavy Metals, Pollution, Environment, Seafood, Humans, Bioaccumulated, Prawns, Periwinkle, Croaker Fish

1. Introduction

Environment is the combination of all things and factors external to the individual or population of organism in question [1]. A pollutant found in the environment damage the natural ecosystem and mans resources [2, 3]. Although many compounds have been shown to exact toxic effects, there was some evidence that heavy metals may be harmful to health at levels recorded in the environment. They are conservative pollutants in that they are not permanent conditions the aquatic environment. They accumulate in organism and some may be seen in food chains. Thus heavy metals continue to enter marine invertebrates against an apparent concentration gradient, contributing to high accumulated body concentration.

1.1. Marine Pollution

The Environmental Protection Agency (EPA) defines pollution as the presence of a substance in the environment that because of its chemical composition or quantity prevents

undesirable environment and health effects. Marine pollution is defined as the introduction by man, directly or indirectly of substances or energy into marine environment which results in harmful effect on organism, hazards to human health, hindrance to marine activities including fishing [4]. In the world today, especially in most African countries, there has been remarkable population growth in activities and a higher exploitation in cultivable land. Transformation have brought about a huge increase in the quantity of discharge and a wide diversification in the types of pollutants that reach the river waters and have undesirable effects on fish and on the potential for fishery exploitation, FAO (1994). There are four basic classes of substance that pollute the marine environment and are heavy metals, domestic and industrial waste, chlorinated hydrocarbon materials and radionuclide.

1.2. Heavy Metals

Heavy metal refers to any chemical elements that has a relatively high density of more of about 5g/cm^3 and is toxic at a lower concentration (Lenntech, 1998). Heavy metals are

perhaps the most common of all the metabolic poisons. These include common elements as Lead (Pb), Mercury (Hg) as well as the uncommon ones such as Cadmium (Cd), Chromium (Cr) and thallium (Tl). Heavy metals are dangerous because they bioaccumulate. They are about sixty (60) naturally occurring heavy metals [5]. Examples include Lead, Arsenic, Vanadium, Thallium, Chromium, Mercury and Cadmium. These metals have no known essential biochemical and physiological functions and are called non-essential biochemical elements [6]. Some heavy metals are trace elements examples are Copper, Cobalt, Iron, Molybdenum, Selenium, and Zinc are essential to maintain the metabolism of the human body. However, at higher concentration, they can lead to poisoning or metabolic anomalies. Heavy metal poisoning could result from drinking contaminated water, intake through the food chain [7-9].

A wide range of human activities contribute to the heavy metals pollution in the aquatic environment. The major activities include industrial processing, mining and ore processing, coal and fuel combustion, agricultural and domestic effluents and nuclear activities also, heavy metals input can be from atmospheric fallout leaching or dump from the lithosphere or directly into the aquatic system including rivers, lakes and oceans [8]. The impact of water pollution depends on the magnitude of heavy metals input, duration of input, physical and chemical form and associated chemicals. These factors will determine the elemental concentrations in the water system and their relative availability, transport and toxicity. The most important factor is the chemical form in which the element exists in solution. This depends on the pH, solubility, temperature, the nature of other chemical species and factors of solution chemistry [8, 9].

1.2.1. Heavy Metals Pollution

Many heavy metals contaminant entering the aquatic environment can have strong effects on the bioavailability and toxicity of biological processes. Heavy metals produce their toxicity by forming complexes with organic compound. These modified biological molecules lose their ability to function properly and results in malfunction or death of the affected cells. For example; Mercury, Arsenic, Lead undergoes biomethylation in the water sediment interface, resulting in the productions of more toxic species which are concentrated in shellfish or finfish [8]. Heavy metals are easily absorbed by aquatic life forms and accumulation may be occurring in higher concentration than in the parent water bodies [10]. The accumulation and biomagnifications depends on the available heavy metal concentration in both water and sediments [11]. A number of sea foods such as fish, Periwinkle, Crab, and Crayfish have been used as biological indicators to monitor long term influences within an aquatic ecosystem. This method is dependent on the ability of these organisms to concentrate a metal and to reflect proportionally with the levels of metal in the environment [12-14].

In the other organism, the toxic effects caused by excess concentration of these metals include competition for sites with essential metabolites replacement of vital ions damage

to cell membranes and reactions with the phosphate groups of ADP and ATP. These organisms have homeostatic mechanisms which enable them to tolerate small fluctuation in the supply of most elements but prolonged excesses, eventually to cope and toxicity occurs which if severe can cause the death of organism [6]. Despite these effects, heavy metals are used in electronic, machines, artifacts, domestic utensils, and water system as well as high tech applications. Consequently heavy metals tend to reach the environment from a vast array of anthropogenic sources as well as natural geochemical processes [8, 10, 12].

1.2.2. Arsenic

Arsenic is a metalloid with an atomic number 33 and atomic weight 74.91. It is a group VA element in the periodic table with oxidation state of +3, +5 and -3. In water, arsenic is usually found in the form of arsenate or arsenite, methylated arsenic compounds occur naturally in the environment as a biological activity. Arsenic are use to make insecticides, weed killers, fungicides and are used to preserve wood. Arsenic is the 33rd element with 74.91 molecular mass. Carbon-arsenic bonds are quite stable under a variety of environmental conditions of pH and oxidation potential. Lead arsenate, copper arsenate are only slightly soluble in soluble in water. Arsenic burns at 400°C sesquioxide and it reacts deadly with chlorine, sulphur and most to form arsenide.

1.3. Sources of Environmental Pollution

The burning of coal and smelting of metals are major sources of arsenic in the air. In the surrounding areas of smelters, levels of arsenic in air exceeding $1\mu\text{g}/\text{m}^3$ have been recorded. Al-Bader [13] reported air borne arsenic concentrations in a polluted region of the German Democratic Republic ranging from 0.9- $\mu\text{g}/\text{m}^3$. The arsenic contents of surface waters in unpolluted areas vary but typical values seem to be a few micrograms per litre. When arsenic enters the environment, it does not evaporate. Most arsenic compound can dissolve in water. It gets into air to the ground. Fish and shellfish build up organic arsenic in their tissues.

Arsenic Levels in Food

Marine fish on the average contain arsenic level below 5mg As/kg wet weight [14]. Arsenic levels in food are below 1mg/kg wet weight [15]. Certain bottom feeding fish, crustacean and shell fish may contain arsenic. The use of some organic compound as feed additives for d poultry and swine may lead to accumulation of arsenic in some organs [16].

Effects of Arsenic

Arsenic is a deadly poison and prolonged low dose exposure to arsenic causes cancer in human beings. Breathing a high level of arsenic can give sore throat and irritated lungs and increases the risk of lung cancer. Arsenic damages many tissue including nerves, axonal degeneration. Many rat poisons, insecticide and weed killers contain arsenic. If there is a prolong contact with skin, malignant skin tumors can develop [17].

Effect of Mercury

Mercury is a silvery white metal and the only metal that is liquid at ordinary temperature. Mercury has an atomic number of 80, molecular weight of 200.59 and found in a group IIB of the periodic table. Mercury melts at -38. Is at 356.6°C at 20°C, its vapour pressure is approximately 200 times the recommended maximum atmospheric concentration. The major uses of mercury are in the electrical industry, production of chlorine, agriculture and paints. Mercury is a global pollutant with complex and unusual chemical and physical properties; the major natural source of mercury is the degassing of the earth's crust, emission from volcanoes and evaporation from natural bodies of water [7]. It also occurs in the earth's crust as sulphide [18]. Worldwide mining of the metal leads to indirect discharges into the environment. Natural biological processes can cause methylated forms of mercury to form which bioaccumulate over a million fold and concentrate in living organisms, especially fish. These forms of mercury: monomethylmercury and dimethylmercury are highly toxic, causing neurotoxicological disorders. The main pathway for mercury to humans is through the food chain and not by inhalation. Methylmercury is more readily taken up by tissues with 95% absorbed by the gut and most of it is retained in the body, less than 1% being excreted.

Mercury acts as a cumulative poison that the body has difficulty eliminating. Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in the living system. There are two types of mercury poisoning, acute and chronic. Acute mercury poisoning results from the ingestion of soluble mercury salts, which violently corrode skin and mucous membranes. Chronic mercury poisoning occurs through regular absorption of small amounts of mercury. This is often a disease of workers in mercury mines, laboratories and industries that use mercury [19]. Mercury is toxic to fish and accumulates to significant concentrations in wild populations.

However, vertebrates feeding on fish from contaminated areas may be at risk. Methylmercury accumulates in the liver, kidneys and brain although, it is slowly excreted, some irreversible damage to the nervous system usually occurs. Symptoms of methylmercury poisoning may not be seen for months; usually subtle neurological changes such as disturbances in coordination, balance and sensory perception, loss of vision along with slurring of speech and memory loss. Mercury also breaks down barriers in the capillaries. This results in edema throughout the body.

Effects of Chromium

Chromium is a hard blue-gray element with atomic number 24 and relative atomic mass of 51.996. It is insoluble in water and occurs in each of the oxidation states from - to +6. Chromium can exist in different forms. Trivalent (chromite) and hexavalent (chromate) are the most important forms. Divalent chromium is unstable in most compounds as it is easily oxidized to the trivalent form by air. The color of chromium metal is steel gray and has a melting point of 187°C and boiling point of 2672°C. Merian [20] compiled the

global sources of chromium in the environment. Total input (100%) consists of input by volcanic emission (less than 1%) biological cycle (30%) including extraction from soil by plants (15%) and weathering of rocks and soils (15%), and man-made emission (70%) including those from general ore and metal products (3%), from metal use (60%) and from coal during and other processes (7%).

Eisler [21] and Abou-Arab [22], in their various studies, indicated a range of 5–250 mg/kg of chromium concentrations in different foodstuffs. Highly refined foods, such as sugar, flour of low extraction, contain the lowest levels <20 µg/kg. Very high concentrations have been reported in pepper [21]. Fresh fish contain <10 µg/kg, meat contains between 10–60 µg/kg. Chromium effects are carcinogenic, causing cancer of the respiratory organs especially in chromate workers chronically exposed to chromium-containing dust [23]. Long-term exposure can cause kidney and liver damage and damage to circulatory and nerve tissue. Low-level exposure can cause irritation to the skin and can also cause ulceration.

Chromium often accumulates in aquatic life; chromium can be less toxic for fish in warm water and decreases in toxicity with increasing pH or water hardness. Chromium can make fish more susceptible to infection; high concentrations can damage various fish tissues and invertebrates such as snails and worms. Chromium (hexavalent) is accumulated by aquatic species through passive diffusion. Ecological factors in the biotic and abiotic environment are involved in the process, which varies according to the sensitivity of different species. The physiological state and activity of the fish also affect accumulation [24]. Trivalent chromium appears to be more toxic than hexavalent chromium, but toxic concentrations for several species of fish range from 0.2–5 µg/mL [23]. Chromium also affects the metabolism of carbohydrates and the concentration of chlorophyll of leaves decreases with increasing hexavalent chromium concentrations (0.01–1 mg/L).

Lead

Lead (Pb), is a heavy bluish-gray chemical element which comes from the Greek word 'plumbum' and it has an atomic number of 82 and atomic weight of 207.19. Lead also has four (4) naturally occurring isotopes. Lead is a widely distributed metal and is soft with little strength. It has a melting point of 327.5°C and boiling point of 174°C. At 20°C, its density is 11.35 grams per cubic centimeter. The oxidation state of lead in inorganic compounds is +2 and most of the inorganic salts of lead have a poor solubility in water. The physical and chemical properties of lead are applied in the manufacturing industries, construction and chemical industries. It is easily shaped and is malleable and ductile. It is also used in batteries, paints, cable sheaths, solder, ammunition and petrol additives.

1.3.1. Environmental Contamination from Natural Sources and Production of Lead

Lead in the environment arises from both natural and

anthropogenic sources. Elevated levels of lead in water arise principally from industrial discharge, highway runoffs and weathering processes in areas of natural lead mineralization. Mining, smelting and refining as well as the manufacture of lead containing compounds and goods can give rise to lead emission. Smelter of lead ores is well known to create pollution problems in local areas. Their influences on the surrounding air and soil depends to a large extent on the height of the stock, the topography and other local features. The emissions can cover a considerable area and also heavy pollution of water bodies through industrial effluents [25-27].

1.3.2. Lead Toxicity in Humans and Sea Foods

In humans, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Exposure can occur mainly through drinking water, food, air and soil. The permissible limits of lead in food by WHO [26] is 2.0mg/kg. Lead in the air contributes to lead in food through deposition of dust and rain containing the metal, on crops and the soil. Lead is absorbed slowly into the body; its rate of excretion is even slower. With constant exposure, lead accumulates gradually in the body. Lead interferes with the formation of haem and the two (2) enzymes affected are aminolaevulinicdehydratase (ALAD) and ferrochelatase. The inhibition of haem synthesis result in anaemia since synthesis of hemoglobin does not take place. Lead can enter into the bone marrow, liver and kidney which in toxic levels lead to disturbances in kidney and liver function, damage to the central nervous system, reproductive organs gas fro-intestinal tract and joint disturbances. There is no correlation between lead concentration in size and length of fish and there is no biomagnifications along food chains along food chains [27].

1.3.3. Source of Environmental Exposure to Cadmium

Cadmium is a relatively rare element that is not found in the pure state in nature, rather, associated with the sulfide ores of zinc, lead and copper. Cadmium has an atomic number of 48 and belongs to group 11b of the periodic table. Cadmium has relative atomic mass of 112.40, has relatively high vapour pressure. Its vapour is oxidized rapidly in air to produce cadmium oxide. Cadmium is widely distributed in the earth's crust at an average concentration of about 0.1mg/kg. High soil concentrations are more commonly found in areas contain deposits of zinc, lead and copper contamination at the local level. Cadmium is use as stabilizer for PVC, in alloys and electronic compounds.

Cadmium is also use in nickel/cadmium batteries, as researchable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Various human activities result in the release of significant quantities of cadmium into the environment. The relative importance of individual source varies considerably from country to country. The major sources of anthropogenic cadmium release can be divided into 3 categories. The first is made up of those activities involved in the mining production and consumption of cadmium. The second category consists of inadvertent sources where the

metal is a natural constituent of the material being processed or consumed and the third category is associated earlier received cadmium discharges or discarded cadmium products. Cadmium is a normal constituent of most food stuffs [28]. The cadmium content of agricultural crops varies according to species, variety cultivated and season. Meat, fish and fruits generally contain similar cadmium levels between 7 and 50µg/kg. The WHO [26] permissible limit for cadmium in food is 2.0mg/kg. Cadmium derives its toxicological properties from its chemical similarity to zinc, an essential micronutrient for plants, animals and humans. In humans, long term exposure is associated with renal dysfunction.

High exposure can lead to obstructive lung disease and has been linked to lung cancer. Cadmium concentrations in aquatic and terrestrial biota from uncontaminated localities are low. Phytoplankton in areas of oceanic upwelling contains raised cadmium levels [29], and filter-feeding mollusks can accumulate significant concentrations of cadmium even in coasted localities that are moderately contaminated [30]. Oysters are well known cadmium accumulators, levels of up to 8mg/kg wet weight in New Zealand [31]. Also edible crustaceans such as crab and lobster contain relatively high cadmium [31].

1.3.4. Sources of Copper in the Environment to Copper

Copper is the 29th element found in group 1B of the periodic table. Copper has an atomic mass of 63.546. Copper metal is a chill, lustrous reddish brown metal. The metallic form is very stable to dry air at low temperatures but undergoes a slow reaction in moist air to produce a hydroxyl carbonate or hydroxyl sulfate that forms a greenish-grey amorphous film over the surface which protects the underlying metal from further attack. The metal is sparingly soluble in water, in salt solutions and in mildly acidic solution but can be dissolved in nitric acid and sulphuric acid as well as in basic solution of NH_4OH , NH_4CO_3 , in the presence of oxygen [32]. Copper occurs naturally in many minerals such as chalcocite (Cu_2S), Azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). These minerals are components of rocks and the earth crust. Through weathering of rock, volcanic activity, wind, copper gain its way in free or combined form into the atmosphere, soil and water surfaces. These disturbances affect the average background concentration of copper in the environment. Anthropogenic source of copper include emissions from mines, smelters. Environmental copper can arise from the burning of coal for power generation and other sources include its use as antifouling agent in paints, human sewage sludge and animals manure. Copper is also deliberately released into some water bodies to control the growth of algae [33, 34]. Copper is an essential substance to human life, but high doses can cause anaemia, liver and kidney damage, stomach and intestinal irritation. Copper may also induce allergic responses in sensitive individuals.

Haemodialysis patients and those with chronic liver disease are sensitive to excess copper. Gastrointestinal effects have also resulted from single and repeated ingestion of

drinking water containing high copper concentration and liver failure has been reported following chronic use of copper. In plants, copper is a component of several enzymes involved in carbohydrate, nitrogen and cell wall metabolism. Copper has been shown to exert negative reproductive, biochemical, physiological and behavioural effects on a variety of aquatic organisms. Copper concentration as low as 1–2µg/L have been demonstrated to have adverse effects on aquatic organisms, however, they may be variations due to species sensitivity and bioavailability. A high soil levels copper can be very toxic to plant.

Symptoms of metal toxicity are early leaf fall, stunted growth, poor roof development and small chlorotic leaves. At the cellular level, copper inhibits a large number of enzymes and interferes with several aspects of plant biochemistry. Tolerance to copper has been shown in the environment for aquatic and terrestrial invertebrates, fish, and phytoplankton and land plants using their tolerance mechanism. The aim of this project is to ascertain the degree of pollution through the levels of heavy metals on the environment especially on sea foods and humans.

2. Materials and Methods

2.1. Sample Collection

The seafood samples (dried prawns and periwinkle) were purchased from different sellers in Mdokiline and the fish (croaker fish) were purchased from Cameroun road all Aba area of Abia State. The samples were transferred to the laboratory for analysis. In order to prevent post mortem changes, the samples were stored frozen in a refrigerator till analysis. The samples were washed several times with distilled water and were placed on a foil differently and oven dried at 105°C to constant weight. The samples were later

sliced to pieces with plastic knife into a crucible and weighing balance. The samples were then place into a heated furnace and allow to ash at which the samples were thereafter, removed from the furnace into the desiccators where it was further dried and allowed to cool.

2.2. Sample Preparation and Digestion

The Food and Agriculture Organization method which involves the digestion of samples in a beaker on a hot plate was adopted for the breakdown of organic matter [35]. In a tall Pyrex beaker were 3.24g of prawn (A), 4.92g of periwinkle (A), 3.99g of croaker, fish (A) and 5g each of the second and third samples of prawns, periwinkle and croaker fish diluted with distilled water were placed 5ml of 10% conc. HCl acid was then added. The beaker and its content were heated on a hot plate and it contained boiling until the organic matters were broken down for volume reduction. After heating, the beaker was removed from the hot plate and allowed to cool. The contents were then transfer to a 100ml volumetric flask using a filter paper and made up to mark 20ml with distilled water. The diluted samples were transferred into samples bottles and labeled. The total metal concentration of the samples was then determined by Atomic Absorption Spectrophotometer (AAS) bi direct aspiration.

3. Results

The results obtained for the analysis of heavy metals in seafood such as prawns, periwinkle and croaker fish sold in Aba Area in Abia State are as presented in Table 1 while Table 2 show the World Health Organization (WHO) mean concentration of heavy metals limits recommended for seafood quality.

Table 1. Mean concentration of Copper, Cadmium and Chromium in seafood samples.

S/No	Seafood Samples	Cu (mg/kg)	Cd (mg/kg)	Cr (mg/kg)
1	Prawns	2.78± 3.34	0.74 ± 0.56	26.16 ± 2.85
2	Periwinkle	19.22 ± 8.26	0.34 ± 0.28	5.42 ± 3.79
3	Croaker Fish	0.6 ± 0.07	1.10 ± 0.47	9.28±8.41

*Experiments were carried out in triplicate and the mean and standard deviation are presented.

Table 2. The WHO mean concentration of heavy metals in seafood.

	Copper (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)
WHO limits	0.5	0.5- 1.0	2.0

4. Discussion

The average level of cadmium in prawns was (0.74± 0.56) mg/kg and comparing it with the WHO limit which was (0.5-1.0)mg/kg and the European commission [36] maximum limit of cadmium in seafood which is 0.5mg/kg. Prawns fell between the W.H.O maximum limit and was higher than those previously reported by Wegwu et al. [10] in crayfish which was (0.07 ± 0.02) mg/kg. The highest level of cadmium was found in croaker fish which was

(1.10±0.47)mg/kg and comparing it to WHO maximum limit of cadmium in seafood (0.5-1.0)mg/kg. Croaker fish exceeded the maximum limit. The average level of cadmium in periwinkle was (0.34±0.28)mg/kg and it fell between the acceptable limit when compared with the WHO acceptable limit.

In the analysis the copper concentration in prawns was 2.78± 3.34 mg/kg which exceeded the WHO limit of 0.5 mg/kg recommended for copper in seafood [10-15]. Periwinkle (19.22±8.36)mg/kg exceeded the WHO acceptable limit of copper in periwinkle and this is toxic to

the living system when accumulated gradually causing in croaker fish (0.60 ± 0.07)mg/kg fell a little above the FAO/WHO Expert committee (JECFA) limit when compared with it and so it is free from toxicity of copper in the living system of consumers. Prawns (26.16 ± 2.85)mg/kg was greater than WHO acceptable limit of 2.0mg/kg when compared with the WHO limit and it was discovered that chromium competitively interfere with copper metabolism [37]. Periwinkle (5.42 ± 3.79)mg/kg exceeded the WHO acceptable limit of 2.0 mg/kg in food. High concentration of chromium in fishes can damage their tissues [38]. Currently there is no formal recommended dietary allowance for chromium but the U.S Food and Nutrition board derived Adequate intake (A.I) for Chromium for different age groups [39].

5. Conclusion

The results from this study show that periwinkle and prawns bioaccumulated cadmium. Chromium levels were high in the three samples, this shows that periwinkle, prawn and croaker fish were not toxic free from chromium at the time of analysis and also prawns, periwinkle and croaker fish were high in copper concentration. This implies that long term consumption of these sea foods can cause the accumulation of these toxic metals in the body. For future research, the sources of these sea foods should be analyzed to know whether these sources were polluted or unpolluted and a comparative study of the heavy metals in some vital organs like the lungs, liver and the kidney should be analyzed to determine the degree of bioaccumulation in the individual organs.

Conflicting Interests

The authors declare that they have no conflicting interests.

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