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Assessment of elemental contaminants in water and selected seafoods from river Benue, Nigeria

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ABSTRACT

Water, soil sediment and seafood [crab (*Sudananautes africanus africanus*), lobster (*Palaemon paucidens*), African catfish (*Clarias gariepinus*) and African catfish (*Synodontis schall*)] samples collected from River Benue (Nigeria) were analysed for sodium (Na), potassium (K), copper (Cu), magnesium (Mg), iron (Fe), calcium (Ca), zinc (Zn), lead (Pb), cadmium (Cd), arsenic (As), selenium (Se), chromium (Cr) and phosphorus (P) using standard analytical techniques. Ca had the highest concentration in both water and sediment followed by Mg while the lowest concentrated metal was Pb. Cd was not at the detectable range in both of the samples. When compared the levels of metals in the water and sediment samples, the highest variability was found in Pb (74.55%) and the least was in Fe (0.89%). The lowest concentration was As in all the seafood samples while the highest was Ca ranging between 134.77 – 333.70μgml^{-1}. Pb and Cd were not at detectable range for all the seafood samples. Cu showed the lowest biocentration while Ca was at the highest side of bioconcentration. All values of the bioconcentration factors showed little or no biological magnification of these trace metal concentrations in the bodies of the sea animals. No manifestation of toxic or pollutant effect has been shown and therefore no possibility of deleterious effect was recorded.

Keywords: Water, sediment, seafoods, River Benue, Pollution.

INTRODUCTION

In Nigeria, the growing rate of industrialization is generally leading to contamination and deterioration of the environment. Thus industrialization and heavy metal pollution are positively correlated[1-5]. The concentration of various elements in the air, water and land may be increased beyond their natural levels due to agricultural, domestic and industrial effluents. When the substances in the effluent discharges in the environment are in very minute amounts in low concentrations, are not toxic to plants and animals and have short residence time in the environment, they are described as “contaminants”[6-7]. In water, insoluble heavy metals may be bound to small slit particles. Metals and other fluvial contaminants, in suspension or solution, do not simply flow downstream, they are complexed with other compounds, settled to the bottom, and ingested by plants and animals, or adsorbed to sediments[8]. Consequently, aquatic organisms may acquire heavy metal burden directly from the river via gills or food chain mechanism[9-11].

Previous work[12-15] revealed high concentrations of heavy metals such as cadmium, lead, iron, copper, nickel, zinc, manganese, magnesium, arsenic and cobalt in some rivers within the proximity of some industrial cities in Nigeria. The discharge of industrial wastes containing toxic heavy metals into water bodies may affect fish and other aquatic organisms, which may endanger public health through consumption of contaminated sea foods and irrigated food crops[16-18]. Heavy metals are commonly found in natural waters. Though some are essential to living organisms yet they may become highly toxic when present in high concentrations[19-20]. Aquatic animals bioaccumulate trace metals in considerable amounts[21-22].

Sea foods serve as excellent food choice for people of all ages. They vary in shape, size, colour, sin, bone and taste[23]. Foods derived on the aquatic environment fall broadly into two major categories, fish and shell fish. Nutritionally, the two groups are not significantly different. There are two groups of shell fish of importance in human food, the mollusca and the anthropoda, while the mollusca consists of bivalves with a 2-piece shells, the anthropoda which are of high relevance to human nutrition comprise of lobster, prawn, shrimps, crayfish and crabs[24]. Biological magnification could lead to toxic levels of minerals in fish, even when the exposure is low. The proven toxicity of high concentrations of heavy metals in water to fishery and wild life[25] poses the problem of an ultimate disequilibrium in the natural ecological balance. Apart from the destabilizing the ecosystem, the accumulation of these toxic metals in the aquatic food organisms is a potent threat to public health. Evidence of potential and observed human hazard due to environmentally acquired heavy metals and their ecological impact have been extensively studied and documented[26-29].

River Benue is a tributary of river Niger, the largest in West Africa[30-31]. The river has the richest source of animal protein by the presence of different kinds of seafoods. Above all it provides the irrigation for both subsistence and commercial agriculture to may communities on its flow. A number of studies have been reported on the geochemistry, pollution assessment and chemical properties of River Benue[30-32] but there is paucity of information on the elemental pollution of the water and seafoods from the lower reaches of River Benue where agricultural activities are highly concentrated.

Therefore, in realization of both the domestic and commercial advantages derived from this great river, this work aims at investigating the pollution level with special interest on the presence of heavy metals and their bioaccumulation in selected seafood; crab (*Sudamanautes africanus africanus*), lobster (*Palaemon paucidens*), African catfish (*Clarias gariepinus*) and African catfish (*Synodontis schall*) being the most popular in the diet of the teeming population along the banks of River Benue.

MATERIAL AND METHODS

Sample collection

Water sample was collected and preserved using Laxen and Harrison method[33]. The sediment was collected by diver at point where the water sample was taken, stored in a polythene bag which have been washed and leached accordingly. Fish samples of two different species namely: African catfish (*Clarias gariepinus*), African catfish (*Synodontis schall*) and lobster (*Palaemon paucidens*) were purchased from fishermen at the river site. The scales were removed, carefully washed and stored at 4^{o}C prior to analysis. Sample of the common West African fresh water crab (*Sudananautes africanus africanus*) was collected from the banks of the river, washed and stored at 4^{o}C. These banks were located at Wadata in Markudi, Benue State, Nigeria. All samples were collected at 6.00 hours Green-Wich Mean Time (GMT) or 7.00 local time while temperature of the water was 27.5^{o}C at the time of collection.

Sample treatment

Five (5) grammes of sieved, air dried soil sample was digested with nitric acid (15ml), perchloric acid (2ml) and hydrofluoric acid (15ml), and placed on a hot plate for 3hours[34]. On cooling, the digest was filtered into 100ml volumetric flask and made up to mark with distilled and deionized water. 5ml of HCl was added to 250ml of water samples and evaporated to 25ml. The concentrate was transferred to a 50ml flask and dilute to the mark with distilled water[35]. The defrozen seafoods were rinsed with deionized water and dried at 105^{o}C until constant weight and blended. 2g of the blended fish part was weighed and digested by following the method described by Ibok *et al*[17]. All chemicals used were of analytical (Analar) grade.

Mineral analysis

Copper (Cu), magnesium (Mg), iron (Fe), calcium (Ca), zinc (Zn), lead (Pb), cadmium (Cd), Arsenic (As), selenium (Se) and chromium (Cr) were determined in all the samples using a Perkin Elmer model 306 Atomic Absorption spectrophotometer. Sodium and potassium were determined using a flame photometer (Jenway, photometer). The instrument settings and operational conditions were done in accordance with the manufacturer's specifications. Phosphorus was determined colorimetrically using Spectronic 20 (Gallenkamp, UK) as described by pearson[36].

Statistical analysis

The results obtained were subjected to statistical evaluation. Parameters evaluated were grand mean, standard deviation and coefficient of variation. All determinations were in duplicate.

RESULTS AND DISCUSSION

Table 1 shows the mean concentrations and the standard deviations of the metals in both the water and the soil sediment. The water temperature was 27.5°C while pH was 6.75±0.02 on average. Cadmium was not detected in both samples. Among those metals detected, calcium had the highest concentration in both water (38.54μgml^{-1}) and sediment (67.40μgml^{-1}) followed by magnesium in water (30.60μgml^{-1}) and sediment (28.27μgml^{-1}) while the least concentrated metal was lead in water (0.04μgml^{-1}) and sediment (0.01μgml^{-1}). However, the values of Ca and Mg (in water) in the present study fall within the World Health Organisation (WHO) recommended range[37]. Magnesium is the second element contributing to both carbonate and non-carbonate hardness in water usually at a concentration much lower than that of the calcium components. Excessive concentrations of Ca and Mg are undesirable in domestic water because of problem of scale formation[38]. Sodium and potassium are the 6th and 7th most abundant elements in the earth's crusts[39]. The solubility of most of the salts of Group I elements in water decreases on descending the group[39]. The results in Table 1 show that the concentration of sodium is higher than potassium both in the water and the soil sediment. The concentrations of Cu, Pb, As, Se, Cr and P were low (< 1.0μgml^{-1}) in both samples. Iron content (in water) in the present study (12.15μgml^{-1}) is higher than the WHO recommended value (0.3μgml^{-1})[37]. Depending on the degree of iron content in water, brown stains on laundry and plumbing fixtures and accumulation of large deposits in the distribution systems are always noticed. These are not only unacceptable to the consumers but give rise to iron-dependent bacteria which in turn can cause further deterioration in the quality of water by the production of slimes or objectionable colour. Unfortunately from this sampling location conducted, the presence of high concentrations of iron will stain laundry and plumbing fixtures and promote bacteria

Table 1: Mean metal concentrations in water and soil sediment (μgml^{-1})

Mineral	Water	Sediment	Grand mean	SD	CV%
Na	8.56±0.10	6.33±0.04	7.45	1.58	21.17
K	4.56±0.00	3.77±0.10	4.17	0.56	13.41
Cu	0.95±0.05	0.52±0.20	0.74	0.30	41.1
Mg	30.60±0.20	28.27±0.03	29.44	1.65	5.60
Fe	12.15±0.04	12.31±0.10	12.23	0.11	0.89
Ca	38.54±0.01	67.40±0.20	52.97	20.41	38.53
Zn	23.38±0.50	21.89±0.04	22.64	1.05	4.65
Pb	0.04±0.03	0.01±0.01	0.03	0.02	74.55
Cd	ND	ND	na	na	na
As	0.11±0.10	0.17±0.00	0.14	0.04	25.75
Se	0.31±0.75	0.28±0.30	0.30	0.02	73.55
Cr	0.68±0.01	0.86±0.20	0.77	0.13	16.53
P	0.68±0.02	0.49±0.10	0.59	0.13	22.8

Mean value ± standard deviation; SD standard deviation; CV% coefficient of variation percent; ND not detectable; na not available.

growth. Thus results obtained may be due to run offs and geological formations of the sample location.

When compared the levels of metals in the water and sediment samples, the highest variability was found in Pb (74.55%) while Fe was the least varied (0.89%). The order of variation was Pb > Se > Cu > Ca > As > P > Na > Cr > K > Mg > Zn > Fe.

The levels of trace metals determined in the selected seafoods are presented in Table 2. Pb and Cd were not in the dectable range for all the samples. Lead is toxic even at low concentrations and has no known function in biochemical processes[40]. Sources of lead include storage batteries, ammunition and metal type, cable sheaths, solder, pigments and anti-knock compounds in petrol[41]. The onset of lead pollution of surface waters in Nigeria has been reported[42], the major source being the use of leaded gasoline[43]. Lead is known to inhibit active transport mechanisms involving ATP, to depress the activity of the enzyme cholinesterase, to suppress cellular oxidation-reduction reactions and to inhibit protein synthesis[44]. The level of metals in the seafoods is an indication of the level of heavy metals pollution of the water from which they are caught[44]. Since lead was not detected in the seafoods but micro amount was detected in both water and sediment samples, it implies that the results do not explicitly indicate a manifestation of toxic effects. However, the possibility that deleterious effect could manifest a long period of consumption of seafoods caught in this river with trace metals contamination cannot be ruled out.

Table 2: Mean metal concentrations (µgml^{-1}) in the organs of selected seafoods

Mineral	*S. africanus africanus*	*Palaemon paucidens*	*Clarias gariepinus*	*Synodontis schall*
Na	3.44±0.04	5.12±0.60	7.78±0.42	3.68±0.10
K	2.00±0.10	2.10±0.10	1.55±0.10	2.22±0.07
Cu	0.30±0.01	0.29±0.30	0.43±0.01	0.29±0.01
Mg	6.10±0.01	15.29±0.02	0.15±0.02	15.42±0.06
Fe	59.10±0.05	53.27±0.10	62.72±0.10	58.09±0.08
Ca	134.77±0.03	287.09±3.20	271.99±6.50	333.70±0.05
Zn	15.68±0.10	19.81±1.50	15.72±1.00	20.91±0.20
Pb	ND	ND	ND	ND
Cd	ND	ND	ND	ND
As	0.14±0.04	0.25±0.60	0.21±0.10	0.12±0.4
Se	0.36±0.00	0.36±0.50	0.19±0.10	0.25±0.3
Cr	0.27±0.05	0.67±0.40	0.62±0.05	ND
P	22.31±0.10	18.10±1.20	34.20±0.01	27.12±0.10

Mean value ± standard deviation of three determinations; ND Not detectable

Calcium had the highest concentrations ranging between 14.77 – 333.70µgml^{-1}. while the lowest concentration was As ranging from 0.12µgml^{-1} in *Synodontis schall* to 0.25µgml^{-1} in *Palaemon paucidens*. Fe was the second predominant element ranging from 53.27µgml^{-1} in *Palaemon paucidens* to 62.72µgml^{-1} in *Clarias gariepinus*. There is more calcium in the body than any other mineral element, mostly present in teeth and bones. It is also an important constituent of body fluids. It tends to be a kind of coordinator among inorganic elements; if excessive amounts of K, Mg or Na are present in the body; Ca is capable of assuming a corrective role. If the amount of Ca is adequate in the diet, Fe is utilized to better advantage. This an instance of "sparing action"[45]. High values of phosphorus were recorded in all the seafood samples. Good value ratios existed between calcium and phosphorus in the samples (Table 2). Phosphorus is always found in Ca in the body, both contributing to the supportive structures of the body. It is present in cells and in the blood as soluble phosphate ions as well as in lipids, proteins, carbohydrates and energy transfer enzymes[46]. Phosphorus is an essential component in nucleic acids and the nucleoproteins responsible for cell division, reproduction and the transmission of hereditary traits[47].

Zinc had concentrations ranging from 15.68µgml^{-1} in *S. africanus africanus* to 20.91µgml^{-1} in *Synodontis schall*. The levels of zinc reported herein is comparable with fish from river in Ikot Ekpene located in Nigeria[17]. It has been reported that zinc contamination affects the hepatic distribution of other trace metals in fish[48]. Zinc, copper and manganese which are essential elements, compete for the same site in animals. This, no doubt, would affect tissue metal concentrations as well as certain physiological processes. The amounts of zinc determined in the seafood samples were very much below the 1000µgml^{-1} set for zinc in seafoods by the Australian National Health and Medical Research Council[49].

The different levels of sodium and potassium observed in the seafood samples caught from the same river (Table 2) may be due to the different physiological activities of the sea animals. Animal tissues, in general, are much less rich in potassium but on the other hand, they usually contain more sodium[50]. This observation is consistent with the report in this work.

Potassium forms loose associations with proteins and is an activator of pyruvate kinase and numerous other enzymes. Over 40 enzymes are known which require a univalent cation for maximum activity; potassium is usually the most effective. Transport ATP-uses from animal sources require sodium as well as potassium ions for maximum activity. Sodium influences osmotic pressure and contributes to normal pH equilibrium[50,51]. All the seafoods under discussion are not good sources of sodium and potassium.

The levels of Cu, As, Se and Cr determined in the seafoods samples were relatively low with As having the lowest concentrations ranging from 0.12µgml^{-1} in *Synodontis schall* to 0.25 µgml^{-1} in *Palaemon paucidens*. The levels of chromium obtained in this study are below the values (2.50 – 9.50µgml^{-1}) reported for fish from three rivers in Ikot-Ekpene area[17]. The chemical toxicity of arsenic compounds has been well studied because of their extensive medicinal use and as garden herbicide in the past[52]. The acute effect of arsenic poisoning by oral intake are intense abdominal pairs, nausea, vomiting, diarrhea resulting from gastro-intestinal tract damage and all terminating in coma and death[53]. In Chile and Taiwan, 0.2µgml^{-1} arsenic in drinking water and taken for a long time has been calculated as the threshold for skin cancer. The usual arsenic level in drinking water is about 0.002µgml^{-1} [(54-55)]. However, it can be reported that the levels of As in the present study have posed threat to human health.

Table 3 shows the bioconcentration factors for the various seafood samples. No biocentration factors were calculated for Pb and Cd in any of the seafood samples because those metals were not at detectable range. Biocentration factor for Cr in *Synodontis schall* was not calculated too because the metal was not detected in the sample. Cu showed the least biocentration while Ca showed the highest bioconcentration followed by Fe in all the seafood samples. The high bioamplification for Ca and Fe in this study, suggests that either the River Benue has high concentration of these metal ions or the sea animals have poor mechanism for the digestion and elimination of these heavy metals. The rate of bioaccumulation of heavy metals in organisms depends on the ability of the organism to digest the metals and strength of such metal in the river per se as well as the levels of the metals in the surrounding soils and the feeding habits of the fish species and sea animals[56-57]. Na, K, Cu, Mg, Zn, Cr and P had bioconcentration factor less than one (<1) while Fe, Ca, As and Se were greater than one (>1). However, the metal concentrations observed here are consistent with the biological magnification hypothesis[58].

Petrides[59] had indicated that fish and meat from wild animals are the chief source of animal protein in the diets of the rural communities especially in the southern part and middle belt of Nigeria. Adeyeye[10] and Osajuyigbe[59] have reported

Table 3: Bio-concentration factors[a] of the various metals in the organs of selected seafoods

Mineral	*S. africanus africanus*	*Palaemon paucidens*	*Clarias gariepinus*	*Synodontis schall*
Na	0.40	0.60	0.44	0.43
K	0.45	0.44	0.34	0.49
Cu	0.32	031	0.45	0.31
Mg	0.20	0.50	0.00	0.50
Fe	4.86	4.38	5.16	4.78
Ca	3.50	7.45	7.06	8.66
Zn	0.67	0.85	0.67	0.89
Pb	na	na	na	na
Cd	na	na	na	na
As	1.27	2.27	1.91	1.09
Se	1.16	1.16	0.61	0.81
Cr	0.40	0.99	0.91	na
P	0.32	0.26	0.50	0.40

na not available
[a]Ratio of concentration in seafoods ($\mu g ml^{-1}$) to concentration in water ($\mu g ml^{-1}$).

that the relatively high consumption of fish has bean attributed to greater availability of this product at relatively cheaper prices. Currently about 45% of animal protein consumed in Nigeria is derived from fish. With this revelation, it is suggested that both the rivers and the seafoods therein should be regularly monitored to avoid the consumption of contaminated sea animals. It is gratifying, however, that the selected seafoods studied in the current report contained reasonable levels of beneficial metals (Na, K Fe, Ca and Zn) and the levels are well below the safety limits.

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