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Full Length Research Paper

Investigation of heavy metals contamination of edible marine seafood

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Levels of trace metals (Co, Cu, Fe, Mn and Zn) were determined in some marine species (*Tilapia zilli, Callinectes sapidus and Littorina litorea*) collected during different seasons from Ondo coastal region, Nigeria. Both species-dependent variability, residency of the organism and temporal variations were pronounced. A general trend in concentration with the following in decreasing order occurred: Fe > Cu >>> Mn > Co > Zn. An overall elevated concentration of these metals was observed during the wet season particularly in crab and periwinkle when low pH and salinity pervaded in the aqueous medium. The highest bioconcentration factor (BCF in brackets) for Mn (0.21) and Zn (2.33) were observed within crab while those of Co (0.98), Cu (2.19) and Fe (9.95) were observed within periwinkles. Significant correlations ($P < 0.05$) were recorded between tissue concentrations and size/length of biota. A continuous monitoring program is recommended to establish the studied organisms as bioindicators and to identify future changes to conserve the 'health' of this fragile ecosystem.

Key words: Bioindicator, heavy metals, pollution, toxicity, water.

INTRODUCTION

Metals including heavy metals are all naturally occurring elements and are usually present to some extent in all environments. These metals in the form of inorganic compounds from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose a serious threat because of their toxicity, long time persistence, bioaccumulation, and biomagnification in the food chain (Papagiannis et al., 2004; Martı´nez-Lo´ pez, 2005). Many of the metals (Co, Cu, Mn, Fe and Zn) are essential trace elements for aquatic organisms and are involved in biochemical processes such as enzyme activation (Leland and Kuwabara, 1985). Above certain levels, however, these elements can have toxic effects. Other metals (e.g. Cd, Pb and Hg) have no known biological functions and consequently detrimental to essential life processes (Thomas and Williams, 2004). Although, the actual physiological consequences to humans vary from one metal to another.

The aquatic environment/ecosystem and their inhabitants are exposed and sensitive to effects of environmental pollution from heavy metal contamination. Aquatic animals accumulate large quantities of these xenobiotics, and the accumulation depends upon the intake and elimination from their body (Karadede et al., 2004). Among different aquatic organisms; oysters, periwinkles, crab and mussels, accumulate large quantities of heavy metals due to their habitat and feeding nature.

There is a growing need to understand the transfer of contaminants such as heavy metals through the food web. Analyzing pollutants in living organisms is more attractive and promising than analyzing pollutants of the abiotic environment, as living organisms provide precise information about the bioavailability of pollutants and the magnification and bio-transference of pollutants (Phillips, 1977). This may assist in predicting pollutants transfer exposure and its possible health consequences to humans. In addition, such information is crucial in making accurate risk assessment for seafood safety purposes. Several aquatic organisms have the ability to bio-accumulate heavy metals to a very toxic level. The impacts of these metals have not only limited the productivity and reproduction capabilities of these organisms, but ulti-

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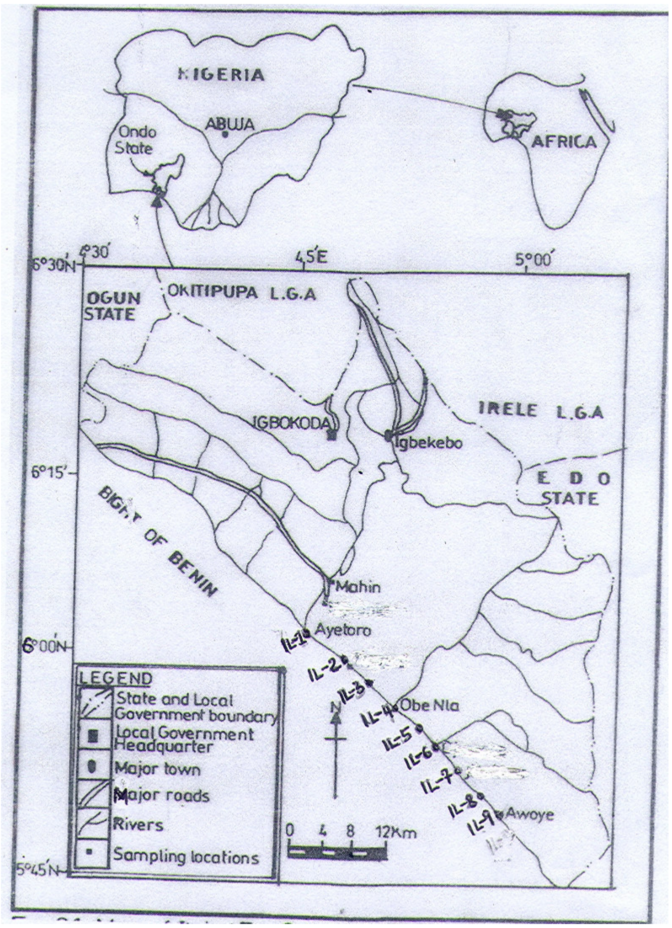

Figure 1. Map of the sampling locations (Inserted is the area map of Nigeria and Africa showing the geographical locations).

mately affect human population due to the food chain relaonship. Although, bioaccumulation in marine invertebrates may be affected by several factors such as environmental condition, age, size, feeding rate and nature of organisms involved (Phillip, 1990). In gasropods, such as dog whelk *Nucella lapillus*, size has been demonstrated as important independent variable influencing levels of metals (Leung et al., 2005). In a similar study, Boyden (1974) in his work on periwinkle *Littorina litorea* (as µg g^{-1} dry soft body weight) showed that concentrations of Fe, Mn, Pb, and Zn decrease with increasing soft body weight while heavy metals contents in individual periwinkles (µg $individual^{-1}$) always increase significantly with size. More recent studies have also demonstrated inverse relationship between weight of soft tissues and some metals such as Cd, Cu and Zn. Others studies have related metal concentration in periwinkles to the shell length (Marigomez et al., 1990; Cain and Luoma, 1986).

Heavy metals toxicity is frequently the result of long term low level exposure to pollutants common in our environment: air, water, food and numerous consumer products. Given the historical anthropogenic impacts that the Ondo coastal region has been subjected over the past one decade and the few studies that have analyzed sediments and surface water within the ecological area with elevated concentrations of some metals above the interim sediment quality guidelines (ISQG) and WHO guidelines for water [Asaolu, 1998; Canadian Council of Ministers of the Environment (CCME), 1999; WHO, 2002; Ololade et al., 2007a], it becomes inevitable to look into the biota community within the ecological zone. There is consequently the need for the development of monitoring schemes aimed at directly measuring levels of contaminants in various organisms, and biomonitoring schemes that use indicator species to estimate the levels in other parts of the ecosystem. Thus, the aim of the present study is to further complement previous studies on fish, and to investigate for the first time, the natural variation of some metal concentration in certain species of shellfish (crab and periwinkles) at different seasons of the year. The metals determined in the present study (Cu, Mn, Fe, Co and Zn) are generally considered essential micronutrient. Levels of Cd and Pb on the same matrix have been reported (Ololade et al., 2007b).

MATERIALS AND METHODS

Sampling and sample preparation

Samplings were carried out in November 2004 and April 2005. All the locations (IL-1, IL-2, …..IL-9) (Figure 1) which represents different localities is variedly exposed to anthropogenic and/or natural contamination. However, locations such as IL-6, IL-7, IL-8 and IL-9 are exposed to more pollutants due to their proximity to the Atlantic Ocean through which oil spill enters the entire ecosystem. Additionally, economic activities are very high at these locations along with the site IL-1. Water and sediment quality within the area are influenced by sewage, oil spill from Shell and Chevron Companies and run-off from agricultural land (Ololade et al., 2007a). Species targeted for tissue analysis include common non-resident migratory fish species (*Tilapia zilli*) and some resident species with small home ranges (shellfish); periwinkle (*L. litorea*) and crab (*Callinectes sapidus*). The fishes were collected using a single panel gillnets (15 x 2m, 5cm bar mesh) set for approximately 4 h, aided by local fishermen. Basic external appearance survey was conducted on the samples noting any lesions, parasites or to the general indications of health (Albers, 1995). The crabs and periwinkles were picked randomly from their various habitats along the river bank / intertidal zone (sediments). However, crabs and periwinkles were very scarce at some locations. The numbers of samples collected at each location are included in Table 1. Samples were thoroughly washed off any ingested sediment.

Laboratory analysis

The lengths of the fishes and the shell lengths of the periwinkles were individually measured before they are grouped and pooled for metal analysis. The fish were analyzed whole (excluding stomach content) while the soft part of the periwinkles was obtained by cracking the shells. The mean soft body weight for each sample was determined while the water content (% moisture) was obtained after drying at 80°C for 24 h (for fish and periwinkles) and 48 h (for crab) based on literature guidance (Leung and Furness, 1999).

Table 1. Characteristic features of biota

CODE	Sites	Species	No of Samples	MWW*	Mean % Moisture	ML*
IL-1	Ayetoro	C	4	24.3±1.7^{b}	59.8±2.1	—
		F	6	118.4±1.4^{a}	74.8±4.3	8.1±1.7
		P	10	9.5±1.2^{a}	78.1±2.4	2.4±0.9
IL-2	Asumaga	C	4	29.3±2.3^{b}	53.4±2.6	—
		F	5	116.3±2.4^{b}	71.1±4.1	9.2±1.3
		P	10	8.5±1.7^{b}	71.4±2.0	3.1±1.7
IL-3	Ilepete	C	5	43.7±2.4^{a}	59.1±1.4	—
		F	5	126.7±8.9^{a}	76.4±2.8	11.8±1.1
		P	10	8.8±2.1^{a}	69.4±1.6	2.8±1.3
IL-4	Obe Nla	C	4	54.7±0.9^{b}	60.3±2.2	—
		F	6	110.2±8.6^{a}	72.6±3.9	7.0±0.3
		P	10	9.2±3.3^{b}	76.4±2.5	2.8±1.9
IL-5	Ikorigbo	C	5	54.7±10.3^{a}	57.8±2.3	—
		F	6	93.7±10.3^{a}	69.1±3.2	11.9±1.3
		P	10	8.1±3.6^{b}	74.2±3.3	3.2±1.1
IL-6	Ojumole	C	4	54.1±1.9^{b}	58.9±2.2	—
		F	5	120.4±2.4^{b}	76.1±4.3	11.2±1.8
		P	10	10.5±1.5^{a}	78.4±3.1	3.7±1.2
IL-7	Otumara	C	4	52.4±1.4^{a}	61.2±3.2	—
		F	6	128.4±4.7^{c}	80.2±4.3	12.0±2.1
		P	10	10.9±2.2^{b}	78.2±2.9	3.8±1.1
IL-8	Odofado	C	4	50.9±1.9a	59.8±2.4	—
		F	6	122.6±4.8^{b}	76.3±4.7	11.4±1.5
		P	10	10.2±2.4^{b}	79.1±3.3	3.7±0.9
IL-9	Awoye	C	5	52.7±1.6^{b}	60.3±2.6	—
		F	6	125.7±7.4^{b}	78.4±3.9	11.6±1.9
		P	10	9.9±1.8^{b}	79.2±3.2	3.7±1.2

*mean ± standard deviation; C: crab; F: fish and P: periwinkles; ML: mean length.
MWW: mean wet weight.

Chemical analysis

Heavy metal determination in the biota slightly differs based on the type of samples involved. In the present study, the method of Leung and Furness (1999) was employed. The metals were determined with 2.0 g of finely ground tissue samples (for fish and periwinkle) and whole body (for crab) and homogenized with 25ml of de-ionized water after 10mls of concentrated HCl and 2 ml of $HN0_3$ in succession. The mixture was heated and boiled off to near dryness, given a thick yellow liquid. However, for samples of crab, additional 25 ml of 95%, H_20_2 was required for complete digestion. This was probably due to the physiological nature of crab. An analysis for the content of Co, Cu, Fe, Mn and Zn was carried out using atomic absorption spectrophotometer (Alpha 4AAS, Chemical Tech. Analytical Euro). All the metal concentrations were expressed on a dry weight basis. Reagent blanks (distilled water) internal standardization were used to assess any background contamination originnating from sample manipulation and preparation as a control measure. Detection limits in tissues depend on both the detection limit for metals in solution and the amount of tissue used in the analysis. In each case, using same weight of samples, the limits (in µg g^{-1}dw) were; Co (0.005); Cu (0.001); Fe (0.003); Mn (0.001) and Zn (0.006). Data were statistically analyzed by means of ANOVA and Duncan's New Multiple-Range Test. Standard deviation (SD) and Pearson correlation coefficient were calculated. Significance was set at < 0.05.

RESULTS AND DISCUSSION

Results

Summary statistics of the concentrations of Co, Cu, Fe, Mn and Zn in the species of fish, crab and periwinkles are presented in Table 2. The levels of metal can be seen to follow two patterns with Cu and Fe occurring at much higher concentrations while the remaining metals, Co, Mn and Zn levels across the biota are not particularly high. This indicates that the metals are either not bio-concentrated or generally low in abundance within the area. The metals have been investigated individually and the distributions of each metal at each sampling site during both seasons are presented in Figures 3(A-C). The values represent the mean concentrations measured in the respective composite samples collected from each site in the study area. The data shows seasonal dependent variations in tissue metal concentrations.

Concentrations (in mg kg^{-1} dw) of Cu in fish, crab and periwinkles during the dry season (wet season in bracket) were in the range 101.3 –292.8 (109.2-426.3), 20.1– 44.1

Table 2. Summary statistics of trace metals concentration$^{\#}$ (mg kg^{-1} dw) in fish, crab and periwinkles from Ondo coastal river, Nigeria.

Species	Variables	Cu	Co	Fe	Mn	Zn
Crab	Mean	34.33 (45.57)	0.2 (0.13)	42.01 (53.37)	2.18 (2.71)	0.61 (0..28)
	Minimum	20.1 (19.4)	0.08 (0.03)	23.2 (24.4)	0.71 (1.83)	0.25 (0.14)
	Maximum	44.1 (63.2)	0.27 (0.19)	91.3 (73.9)	2.90 (4.01)	0.98 (0.47)
	S.D	9.14 (13.34)	0.06 (0.05)	21.52 (17.59)	1.29 (0.63)	0.31 (0.11)
	C.V(%)	27 (29)	30 (38)	51 (33)	59 (23)	44 (41)
Fish	Mean	194.45 (271.14)	0.18 (0.11)	204.72 (261.13)	1.05 (1.76)	0.23 (0.16)
	Minimum	101.3 (109.2)	0.03 (0.02)	105.2 (122.5)	0.51 (0.82)	0.07 (0.09)
	Maximum	292.8 (426.3)	0.38 (0.21)	269.4 (419.3)	1.90 (2.93)	0.36 (0.22)
	S.D	65.75 (122.67)	0.16 (0.07)	57.38 (103.88)	0.44 (0.69)	0.09 (0.05)
	C.V(%)	34 (45)	89 (64)	20 (37)	42 (39)	39 (31)
Periwinkles	Mean	310.2 (351.5)	0.33 (0.24)	1315.5 (1052.6)	0.78 (0.99)	0.10 (0.11)
	Maximum	186.2 (209.3)	0.19 (0.12)	243.1 (392.9)	0.53 (0.72)	0.01 (0.01)
	Minimum	467.3 (492.4)	0.46 (0.34)	2210.1 (2411.2)	0.81 (1.48)	0.31 (0.26)
	S.D	88.5 (29.2)	0.1 (0.02)	714.3 (252.4)	0.19 (0.20)	0.10 (0.09)
	C.V(%)	29 (25)	30 (29)	54 (72)	24 (20)	100 (82)

#: Concentrations are mean of triplicate analysis. Values in parenthesis are results of the wet season
S.D: Standard Deviation; C.V: Coefficient of variation;

(19.4–63.2) and 186.2 – 467.3z(209.3–492.9) respecttively. The lowest concentrations were observed in crab while highest concentration was recorded at site IL-5 especially in fish and periwinkles. There was substantial variation between the respective composite samples collected from each sampling sites and amongst the biota.

Cobalt concentrations in fish during the dry season (wet season in bracket) were in the range 0.03 – 0.38 (0.02 – 0.21) mg kg^{-1} dw. For the crab and periwinkles, the range were 0.08 – 0.26 (0.09 – 0.19) mg kg^{-1} and 0.19 – 0.46 (0.12 – 0.34) mg kg^{-1} dw. No discernible pattern was observed across the biota in their Co concentration. All the biota recorded Co concentrations below 0.50 mg kg^{-1} dw.

The levels of Zn in both the dry and wet seasons in fish (in mg kg^{-1}dw) ranged from 0.09 - 0.36. However, higher mean concentration of 0.23 ± 0.09 mg kg^{-1}dw was recorded during the dry season over the 0.16 ± 0.05 mg kg^{-1}dw obtained during the wet season. For crab, the upper limit recorded Zn level of 0.98 mg kg^{-1}dw and 0.47 mg kg^{-1} dw with mean levels of 0.61 ± 0.31 mg kg^{-1}dw and 0.28 ± 0.11 mg kg^{-1}dw in the dry and wet seasons respecttively. In periwinkles, the tissue Zn values ranged from <0.01 in wet season to 0.31 mg kg^{-1}dw during dry season. The mean Zn concentration in periwinkles is 0.10 ± 0.11 and 0.11 ± 0.09 mg kg^{-1}dw for the dry wet season respectively.

Like Cu, the concentrations of Fe were equally high with values < 23, 105 and 243 mg kg^{-1}dw in crab, fish, and periwinkles respectively. The range in mean concentrations (mg kg^{-1}dw) during the dry season (wet season in brackets) were 20.1 – 44.1 (19.4 – 63.2), 101.3 – 292.8(109.2 – 426.3) and 186.2 – 467.3(209.3 – 492.4) for crab, fish and periwinkles respectively. The Cu levels were generally higher during the wet seasons.

Manganese concentrations (in mg kg^{-1}dw) in crab, fish, and periwinkles during the dry season (wet season in brackets) ranged from 0.71 – 2.90 (1.83 – 4.01), 0.51 – 1.90 (0.82 – 2.93) and 0.53 – 1.17 (0.92 – 1.48) respectively. Like some of the metals, the concentrations are generally higher during the wet season.

DISCUSSION

Concentration of heavy metals in the soft tissue in relation to body £weight

A comparative examination of the data in Tables 1 and 2 showed that considerable differences occurred in the metal concentration on a weight specific basis (mg kg^{-1}dw) in the soft tissue of fish and periwinkles and whole body of crab from the same locality. Historically, this has been related to varieties in the body weight of individual as reported by other authors (Boyden, 1974). For example, using the dry season results, the metal variation with length and/or mean wet weight of soft tissues of fish, crab and periwinkles is as represented in the correlation graph in Figures 2(A - H). The length of the fish showed no significant correlations with the concentration of all the metals with correlation coefficient, R^2 ranging from R^2 = 0.0099 in Cu to R^2 = 0.4563 in Co. However, significant correlation was observed between concentration of Co and tissue weight of fish (R^2 = 0.9336). In periwinkle, apart from the concentration of Fe (R^2 = 0.7138), no other metals displayed significant correlation between mean wet weight and tissue metal burden and for crab, none of the metals showed any significant correlation in wet weight and tissue metal burden. Thus, the observed higher heavy metal concentration in the large periwinkles (those with higher shell length and consequently, mean wet weight) and crabs (with higher mean wet weight) may be attributed to higher metabolic rate of these organisms. This is agreement with other authors (Platz – Osuma and Fernandez, 1989; Nott and Hagstar, 1989).

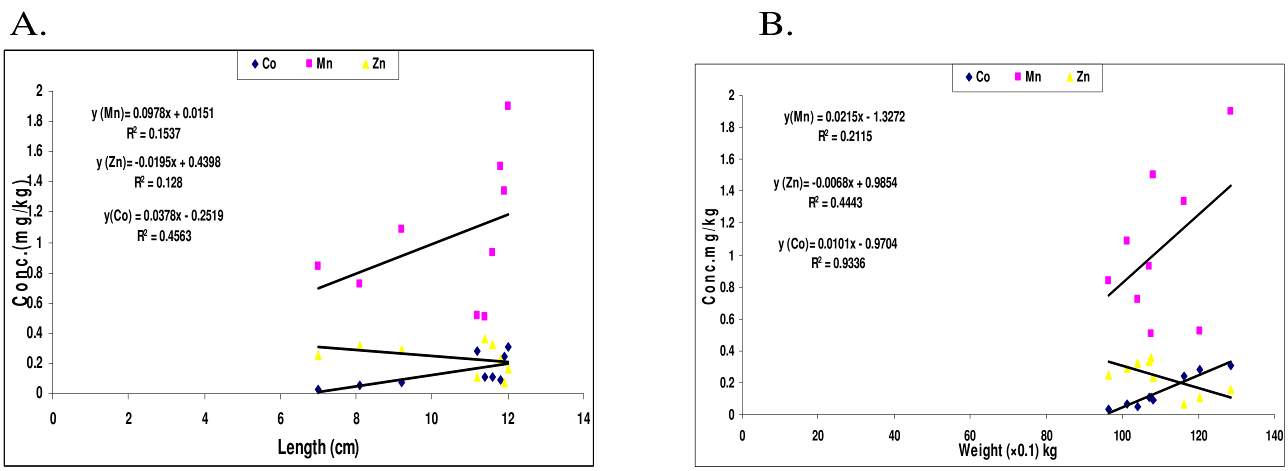

Figure 2. Size relationship for Co, Mn and Zn in Fish, by both length (A) and Size (B) using data from all sites and all seasons (P = 0.05 for both correlation)

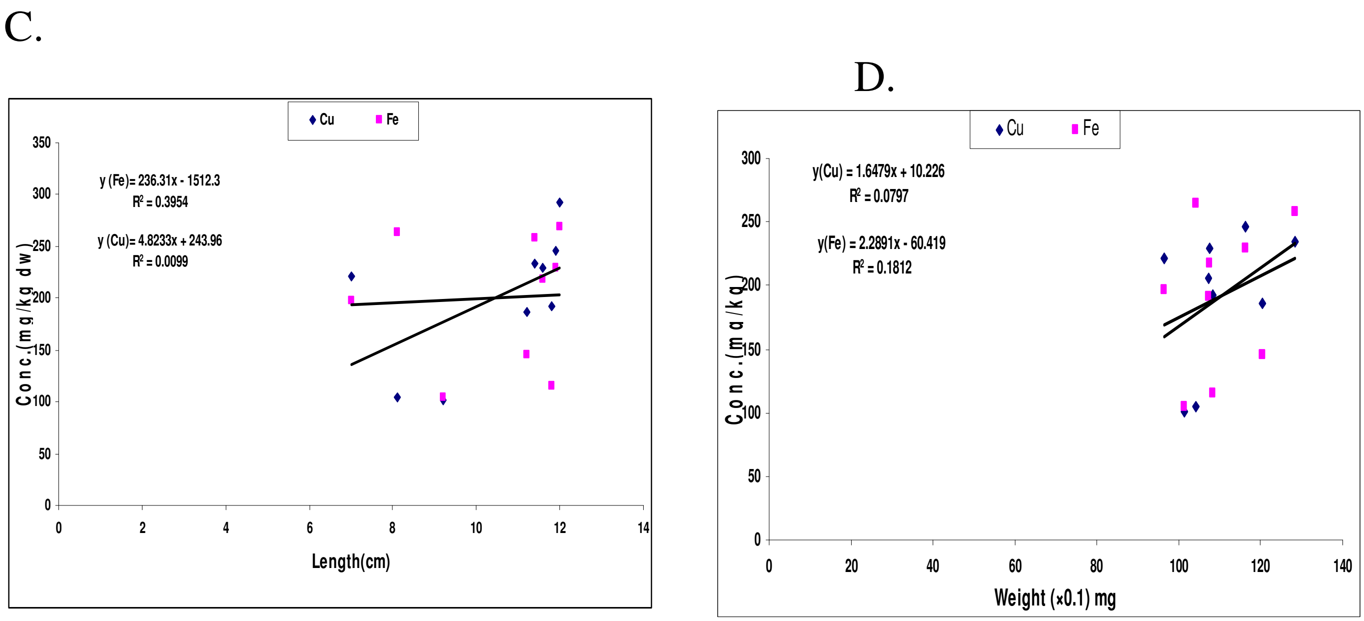

Figure 2. Size relationship for Cu and Fe in Fish, by both length (C) and Size (D) using data from all sites and all seasons (P = 0.05 for both correlation).

Variability in species bioaccumulation

The results as obtained in the present study show that not all chemical elements and chemical compounds are subject to bioaccumulation and among those that are, the extent of bioaccumulation varies considerably. This implies that inorganic contaminants such as heavy metals entering coastal waters may be concentrated by edible marine organisms to varying degrees from either water, their food or sediments. This is in agreement with other work on pollutant transfer and transport in the sea (Fowler, 1982).

The results in Figures 3(A - F) show that the metals were not evenly distributed across the biota. Copper, Fe, Mn and Zn are essential macronutrients for fish, crab and periwinkles. However, elevated levels as observed with Cu, Fe and to some extent, Mn in the present work may likely show elicit adverse physiological reactions in these faunas and other aquatic lives within the environment and consequently on humans that depend on them as delicacies. This increase in metal content can be informative sublethal response, indicating increased metal availability and potential metal stress. Thus, the ability to regulate the internal metal levels is impaired. This might be sufficient to cause chronic toxicity or mortality during early development. It is therefore not surprising that the

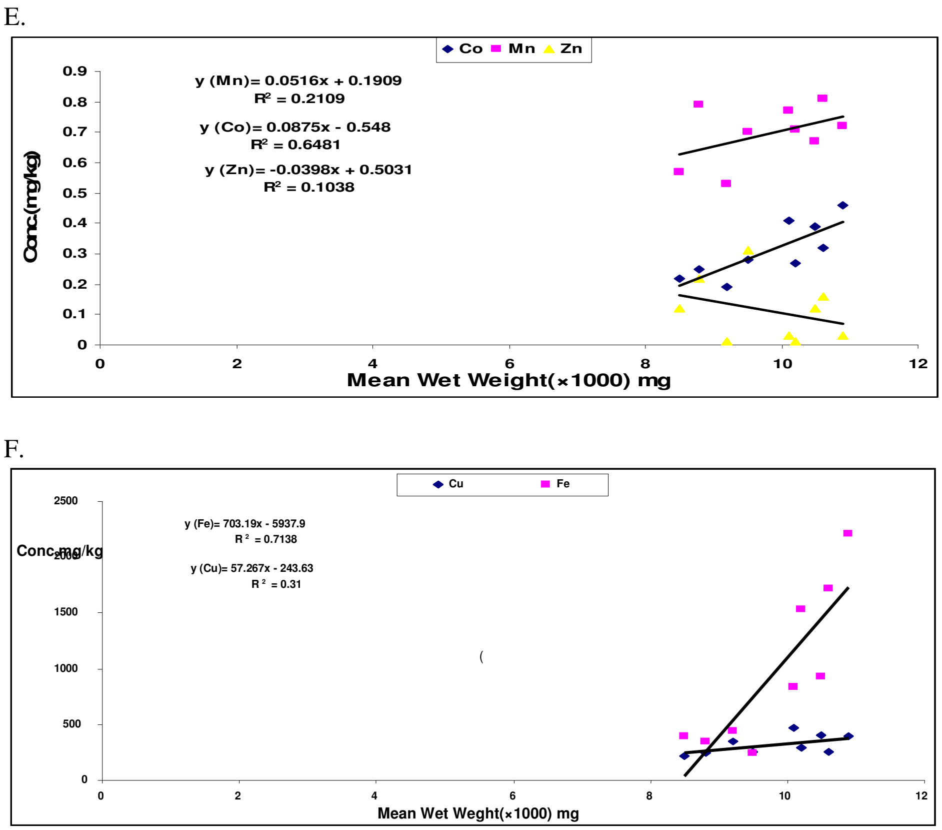

Figure 2. Size relationship for Co, Cu, Fe, Mn and Zn in Periwinkle by Size (E and F) using data from all sites and all seasons (P = 0.05 for both correlation)

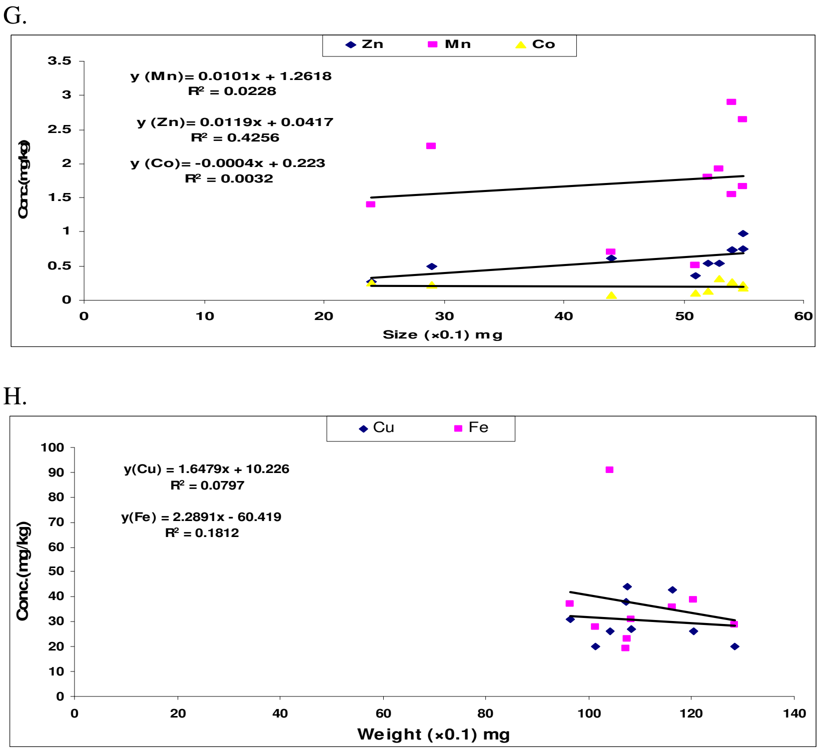

Figure 2. Size relationship for Co, Cu, Fe, Mn and Zn in crab by size (G and H) using data from all sites and all seasons (P = 0.05 for both correlation).

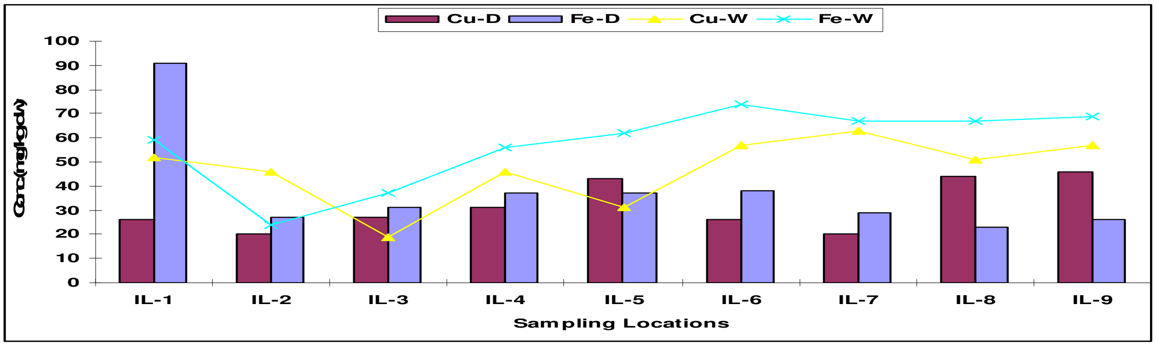

Figure 3A. Seasonal variation of Cu and Fe in crab across sampling locations.

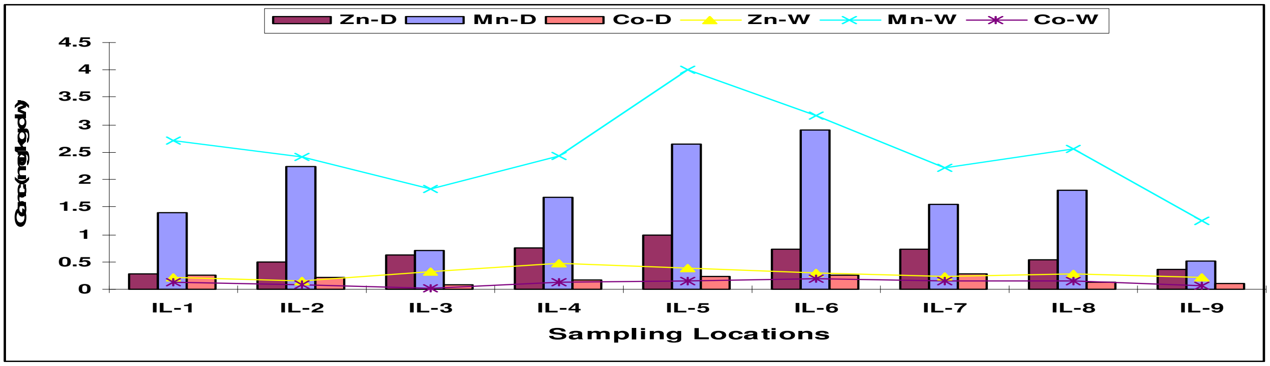

Figure 3B. Seasonal variation of Co, Mn and Zn in crab across sampling locations.

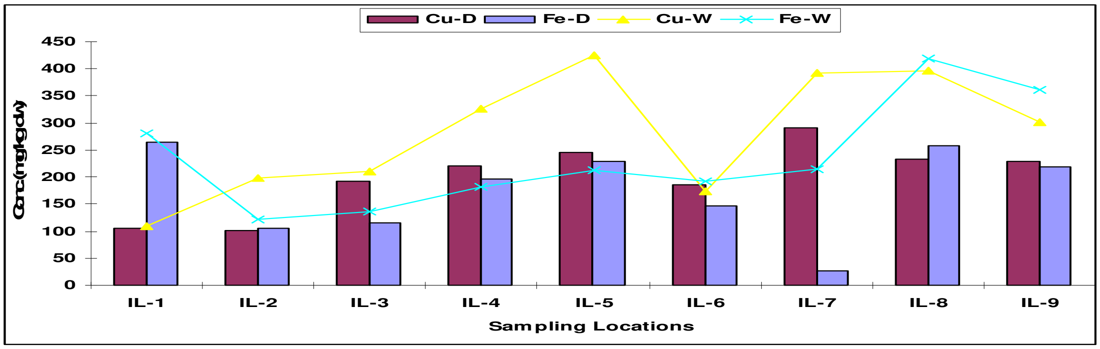

Figure 3C. Seasonal variation of Cu and Fe in fish across sampling locations.

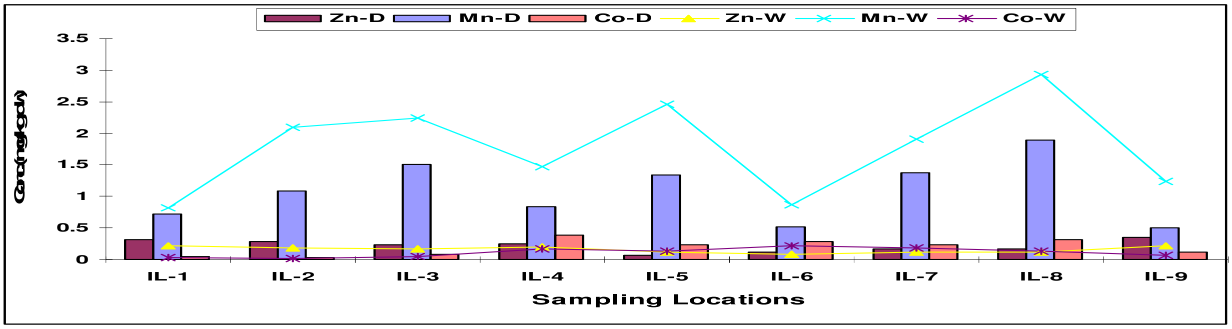

Figure 3D. Seasonal variation of Co, Mn and Zn in fish across sampling locations.

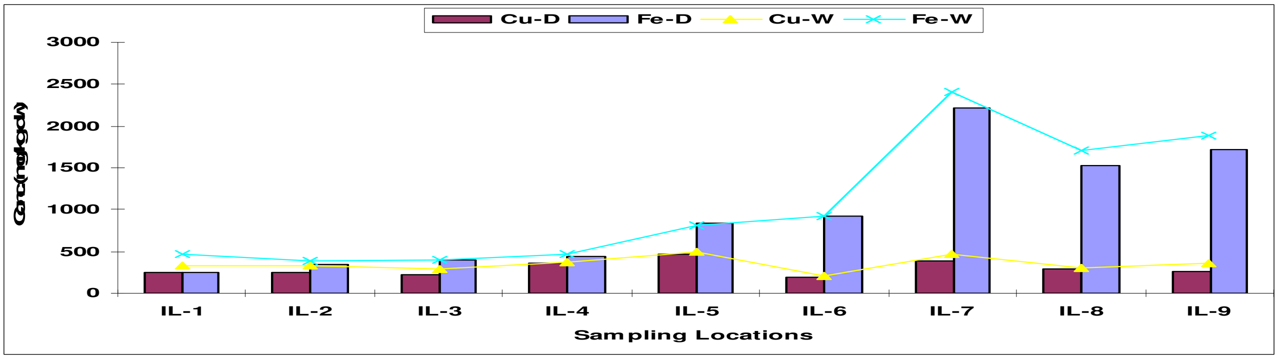

Figure 3E. Seasonal variation of Cu and Fe in periwinkles across sampling locations.

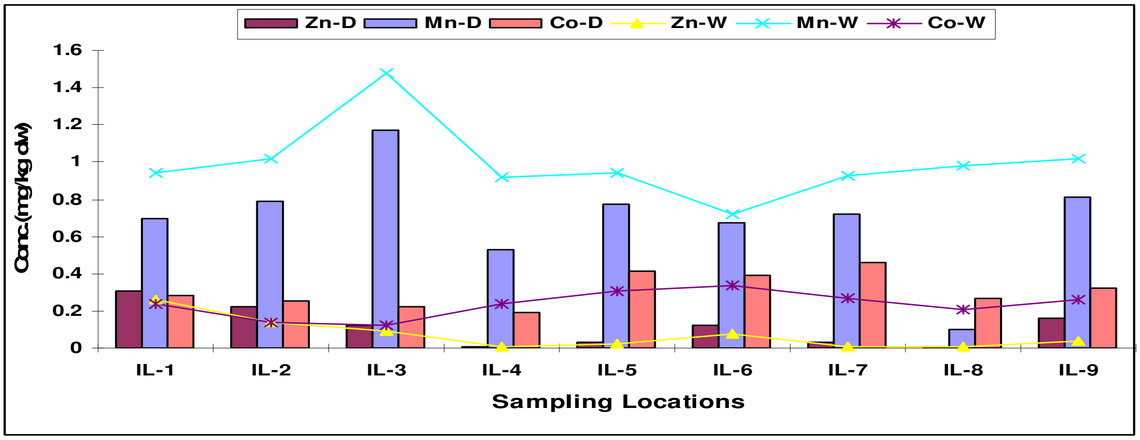

Figure 3F. Seasonal variation of Co, Mn and Zn in periwinkles across sampling locations.

fish populations were observed to be scarce and even of small sizes during sampling. While metal toxicity in fish has been widely observed and investigated in the laboratory settings, it is difficult to asses in field situations. Here, metal induced fish mortality can be greatly underestimated as dead or dying fish may not be readily observed.

Each element had somewhat different distributions from the others. Highest concentrations of most of the metals occur in periwinkles *L. littorea* and blue crab *C. sapidus*. Several factors may be responsible for this variation in metal uptake within the same locality. Thevariation is also indicative of the degree to which particular species pick up particulate matter from the surrounding water and in particular, sediment while feeding. Both crab and periwinkles are bottom feeders and are generally expected to concentrate more metals than surface feeders like fish. Additionally, the higher concentration of metals in periwinkles and crab over fish was not very surprising because as resident species, the concentrations of contaminants in their tissue are likely to be more representtative of the site than some mobile species, such as fish. If analysis for instance indicate that periwinkles are safe to eat, then consumption of other more mobile species should also be safe. Though, previous studies showed that metals such as Zn bioaccumulate poorly in fish (Wilson et al., 1981; Bradley and Morris, 1986), the present study equally revealed that periwinkle *L. littorea* are less sensitive to Zn than fish. Zn is a neurotoxin. By its ability to chelate and deplete the neuronal concentration of glutathione (GSH), it causes neuronal cell death in a dose dependent manner (Chen-Jung and Su-Lan, 2003). All the biota were not polluted with respect to Zn when compared with the WHO standards of 150 mg/g (WHO, 2002).

Periwinkles has shown to be most sensitive to Cu, Co and Fe and least to Mn and Zn while fish tends to be most sensitive indicator for Mn and Zn. This differential preferences for metals also show that no one particularly organism can truly be suitable as indicator for heavy metal monitoring. It may be expected that levels of metals in individual biota should be the same or very close within each locality; other factors such as economic activities, human population, and variation in agricultural activities may be responsible for the variation. No doubt, sex-specific differences in metal concentration have been suggested in crab (Sastre et al., 1999), but unfortunately, gender differences were not examined due to the small size. However, male crabs, which are more resident especially in low salinity area, are expected to have

Table 4. Comparison of present metal status (mg kg-1 dw) in biota with results from other studies.

Country/year	Location	Sample Type	Fe	Cu	Zn	Co	Mn
Present study, Nigeria, 2004/2005	Ondo- State	Fish	105.2 – 419.3	101.3 – 426.3	0.07 – 0.36	0.02 – 0.38	0.51 – 2.93
		Crab	23.2 – 91.3	19.4 – 63.2	0.14 – 0.98	0.03 - 027	0.71 – 4.01
		Periwinkles	243.1 – 2411.2	186.2 – 492.4	0.01 – 0.31	0.12 – 0.46	0.53 – 1.48
Asaolu, Nigeria, 1998	Ondo- State	*Oreochromis niloticus*	13.82-91.78	0.25-4.29	1.53-48.95	1.50-1.55	41.25
		Synodontis spp.	42.61-292.35	0.63-3.13	1.86-57.42	3.80-3.86	30
Okoye, Nigeria, 1989	Lagos- Lagoon	*T. guineaysis*	53.55-131.48	9.37-13.75	17.80-37.02	0.32-0.75	4.65-20.89
		M. cephlus	45.47-145.60	2.63-2.99	9.29-10.62	0.68-1.38	3.52-8.22
Kakulu, Nigeria, 1985	Niger-Delta	Fish	0.49-57.15	nd - 13.43	1.03-17.65	-	0.08-12.77
Talbot, Australia,1983	Albany	Crab	14.8 – 26.6	0.67 – 1.36	32.4 – 48.3	nd	0.54 – 1.01

Table 3. Bioconcentration factor (BCF)# of metals in biota

Species	Season	Cu	Co	Fe	Mn	Zn
Crab	Dry	0.16	0.65	0.37	0.18	2.33
	Wet	0.28	0.42	0.50	0.21	1.68
Fish	Dry	0.93	0.58	1.78	0.09	0.77
	Wet	1.69	0.35	2.47	0.14	1.00
Periwinkle	Dry	1.40	0.98	8.38	0.006	0.04
	Wet	2.19	0.77	9.95	0.078	0.69

#: Values are calculated using the mean concentrations of metals in each season
BCF = Concentration of metals in organism / Concentration in wat

Table 4. ANOVA ($p = 0.05$) for metal concentration.

Metals	Crab	Fish	Periwinkles
Cu	0.048	0.089	0.194
Co	0.023	0.103	**0.048**
Fe	0.011	0.118	0.794
Mn	0.472	**0.017**	**0.020**
Zn	0.002	**0.048**	0.396

Results in bold shows significant mean differences

higher metal concentrations. This is because; female crabs are generally noted for seasonal migratory behaviour especially for reproductive purposes. Thus, exchange of metallic ions into the environment can occur especially when migrated into a clean environment. Therefore, locality with high metal burden in crab may likely be more represented by the male species. This conclusion deserves attention in future studies.

The elevated Cu and Fe concentration appear to be a general incidence which is indicative of overall concentrations in the river. The results indicate that crab and fish from Ondo coastal region of Western Nigeria should be safe for human consumption. The levels of some of the metals, particularly Zn, Mn and Co in fish has serious ecological consequences especially in terms of biomagnifications by larger resident predatory species and the death or adverse effect/impacts that may result as a consequence of ingesting such resident prey.

The results in Table 3 are that of the biological concentration factors (BCFs). It is an estimate of the ratios of the concentrations (mg kg^{-1}) of the given metal in the respective biota to the concentrations (mg L^{-1}) in the ambient water during the respective seasons. Levels of metals in water from the same study area has been reported somewhere (Ololade et al., 2008). The trends in BCF in both seasons were observed to follow similar pattern .The highest BCF (in bracket) for Zn (2.33) and Mn (0.21) were observed within crab and those of Cu (2.19), Co (0.98) and Fe (9.95) were observed within periwinkles. Bioconcentration factors are equally high for Cu in fish. This indicates that crab and periwinkles have a high preferential potential to concentrate those metals in their soft tissues (Eja et al., 2003). It is worthy to note, that, while fish and periwinkles concentrate Cu and Fe in their body efficiently, crab seems to be far less sensitive to bioaccumulate Cu and Fe. Since the BCF values is important when comparing the order of uptake of metals (Canteford et al., 1978), such correlations serve a predictive function in that biouptake may be estimated for other heavy metals.

Seasonal metal variation

Some variations were observed in biota metal concentration between the two seasons. The seasonal dependent variation in tissue concentration of the heavy metals may be associated with several factors such as nature of sediment scavenged, type of food, nature of runoff, and or the water quality (Karbassi et al., 2008; Khadka and Khanal, 2008; Mtethiwa et al., 2008; Nouri et al., 2008). A critical assessment of Figures 3(A - F) shows a consistent higher concentration of Co and Cu in

Table 5. ANOVA (p = 0.05) for metal concentration.

Metals	Crab	Fish	Periwinkles
Cu	**0.048**	0.089	0.194
Co	**0.023**	0.103	**0.048**
Fe	**0.011**	0.118	0.794
Mn	0.472	**0.017**	**0.020**
Zn	**0.002**	**0.048**	0.396

Results in bold shows significant mean differences

all the biota during the dry season. This trend has been reported by other authors from similar studies (Kakulu and Osibanjo, 1986; Biney, 1991; Okoye et al., 1991). The pattern, however, is different with other metals (Fe, Mn and Zn). Higher concentrations of these metals were obtained during the wet season across all the biota. One factor that may contribute significantly to seasonal changes in the metal concentration as observed in this report 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 (Tan and Wong, 1995; Joiris and Azokwu, 1999). Comparatively, the concentrations of Zn, Co and Mn (Table 4) were found within the range obtained by other authors while those of Fe and Cu were far above those reported by similar authors (Talbot, 1983; Kakulu, 1985; Okoye, 1989; Asaolu, 1998).

The least Mn concentration in water at both seasons was 8.2 mg L^{-1} (Ololade et al., 2008), a value considered very high and far above the WHO reference standard of 0.5 mg L^{-1}. With highest concentrations (mg kg^{-1}dw) of 4.01, 2.93 and1.48 in crab, fish and periwinkles at both seasons respectively, it can be said that the biota do not extensively accumulate Mn into their bodies when compared with the concentration in water. While consumption of these biota may not produce any toxicity due to Mn, some neuropsychiatric disorders which may manifests in the form of impulsive and aggressive behaviors may results from the use of the water from the study area (Kosneth, 2001). The analysis of variance (ANOVA) report (Table 5) showed that significant mean differences occurred in all the metals in crab except Mn (p = 0.472). Similarly, significant mean differences were recorded in the concentration of Mn (p = 0.017) and Zn (p = 0.048) in fish and Mo (p = 0.048) and Mn (p = 0.020) in periwinkles.

Conclusion

The safety (health risk) of Ondo coastal river for some species of fish, crab, and periwinkle has been assessed. The wide distribution of these species coupled with their domestic and economic advantages, especially by recreational fishers, is sufficient to make the data particularly relevant. The five investigated metals (Co, Cu, Fe, Mn and Zn) were found to be selectively distributed in different biota. The study also shows that the larger biota represent greater risk due to increased metal burden in their soft tissue through bioaccumulation. Furthermore, the warmer months, when recreational activities like fishing takes place, may present the greater risk for Co and Zn while greater risk for Cu, Fe and Mn are expected during the winter season. Though, there is there are no reported cases of metal toxicity arising from the direct use of the water or fish consumption from the area. The work has provided some data and information that may be useful for such studies and policy formulation. There is the need for regular public health checks on the level of heavy metals among the community that border the study area. It is therefore recommended that more species be sought for proper evaluation. This will demonstrate the extent of the trophic transfer of the metals and organics in the area. Also, that, continued contaminants monitoring of the Ondo Coastal regions are essential if relevant agencies are to ascertain the quality of habitats for resident and migratory wildlife. Consequently, a contaminant monitoring programme should be established not only for trace metals but also for hydrocarbons and organochlorine pesticides.

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