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Research paper

2 **Seasonal variation in heavy metal content of sole, *Solea solea* and croaker,**
 3 ***Pseudotolithus typus* from Lagos and Delta states, Nigeria**

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12 Abstract

13 Fish is a major food product of the Nigerian coastal zone. This study investigated the levels
 14 of lead (Pb), cadmium (Cd), Copper (Cu), Chromium (Cr) and Zinc (Zn) in two economically
 15 important fish species, Sole, *Solea solea* and Croaker, *Pseudotolithus typus* from Makoko and
 16 Koko in Lagos and Delta states respectively. Heavy metal content was determined by air-
 17 acetylene flame Atomic Absorption Spectrophotometer after wet digestion of dried and
 18 milled samples with 1:1 HNO₃: H₂O₂. Metal contents (µg/g, dry weight) for sole in Lagos
 19 and Delta states during the wet season (April – October) were: Pb (0.330 and 0.149), Cd
 20 (0.097 and 0.063), Cu (0.869 and 0.434), Cr (1.184 and 0.826), Zn (7.612 and 7.890); for
 21 croaker: Pb (0.163 and 0.045), Cd (0.115 and 0.029), Cu (0.990 and 0.694), Cr (1.008 and
 22 1.038) and Zn (6.756 and 6.168). For the dry season (November – March) metal contents
 23 obtained were: Pb (0.534 and 0.527), Cd (0.373 and 0.410), Cu (0.437 and 0.556), Cr (0.834
 24 and 0.983), Zn (6.764 and 9.343) for sole; and Pb (0.210 and 0.213), Cd (0.264 and 0.307),
 25 Cu (0.442 and 0.483), Cr (0.577 and 0.597) and Zn (4.783 and 5.924) for croaker. Significant
 26 ($P < 0.05$) variations were observed in metal content between sole and croaker and also
 27 between dry and wet seasons. Generally, metal concentrations were higher in sole than
 28 croaker; and Cadmium content was significantly ($p < 0.05$) higher in fish samples during wet
 29 season, while Chromium and Copper were significantly ($p < 0.05$) higher during the dry
 30 season. Cd and Cr levels in the test species were found to exceed recommended international
 31 tolerable levels. A programme of continuous monitoring and control of the physical and
 32 chemical characteristics of components and food products of Nigeria's coastal zone is
 33 recommended as a management tool for this important ecological zone.

34 **Keywords:** Heavy metal, *Solea solea*, *Pseudotolithus typus*, Lagos, Delta, dry season, wet
 35 season, variation

36 Introduction

37 Sole, *Solea solea* and Croaker, *Pseudotolithus typus* are among the most commonly available
 38 and economically important fish species in Nigeria's maritime states; and contribute
 39 significantly to animal protein intake of the urban population in these states. Lagos and Delta
 40 states are important coastal states with a blossoming shipping and freighting industry
 41 especially in Lagos state, which doubles as the industrial and commercial centre of Nigeria
 42 with the highest number of industries and arguably the largest human population within a
 43 state in the country. As the commercial and industrial nerve centre of Nigeria with an
 44 estimated population of over 9 million people (National Population Commission, NPC,

2006), environmental concerns are normally focused on Lagos State. Over 60% of Nigeria's industries are cited in the state, each discharging its characteristic range of effluents, often containing heavy metals into the terrestrial and aquatic ecosystems within the state. Water pollutants originate from point and non point sources. Point sources are distinct and confined, and include accidental spills from industrial sites that empty into streams or rivers. On the contrary, non-point sources, such as run-off, are diffuse and intermittent; and are largely influenced by factors such as land use, climate, hydrology, topography, native vegetation and geology. Common urban non point sources of pollution include urban run-off from streets or fields which characteristically contain a variety of pollutants from heavy metals to chemicals and sediments. Rural sources of non point pollutants are generally associated with agriculture, mining or forestry. Non point sources are usually difficult to monitor and control (Botkin and Keller, 1998). The hazard presented by a particular water pollutant depends on several factors including the concentration or toxicity of the pollutant in the environment, and the degree of exposure to people or other organisms (Pye and Patrick, 1982).

It is estimated that over 80% of coastal pollution originates from land-based sources, including industrial, agricultural, oil and gas production and marine oil transportation activities (Ducrotroy, 1966). Recent works suggest that toxic materials threaten the ocean bottom as well as the entire marine ecosystem. The base of the marine food chain consists of planktonic life which occupies the upper 3mm of the ocean water. The young of most fin and shell fishes also reside in the upper few millimeters of the ocean; and tend to concentrate pollutants such as toxic chemicals and heavy metals. It is reported that concentrations of zinc, lead, and copper in the upper 3mm (or micro layer) is from 10 to 1000 times higher than in the deepest waters due to a process referred to as surface film enrichment (Millero, 1996). There is fear that disproportionate pollution of the micro layer will have serious effects on marine organisms (Greig *et. al.*, 1977; Leussen, 1989), resulting in major impacts on people and

70 society as contaminated marine organisms transmit toxic elements or diseases to their
71 consumers (Greig *et. al.*, 1977).

72 Heavy metal contamination of the aquatic environment has become a worldwide challenge,
73 mainly because heavy metals are indestructible; and most of them have toxic effects on
74 organisms (MacFarlane and Burchett, 2000). Among environmental pollutants, metals are of
75 particular concern, due to their potential toxic effects and ability to bio-accumulate in aquatic
76 ecosystems (Censi *et. al.*, 2006). Heavy metal concentrations in aquatic ecosystems are
77 usually monitored by measuring their concentrations in water, sediments and biota (Camusso
78 *et. al.*, 1995; Adegbola *et. al.* 2012). Generally metal concentrations are low in water and
79 attain considerably higher concentration in sediments and biota (Namminga and Wilhm,
80 1976). Heavy metals, including both essential and non-essential elements generally have high
81 significance in eco-toxicology because they are highly persistent and also have the potential
82 to be toxic to living organisms (Storelli *et al.*, 2005). Concerns over heavy metal pollution of
83 the marine environment have been rising due to the human activities that contribute
84 significantly to the release of these metals into the environment. Skejelkvale *et. al.* (2001)
85 reported that heavy metals in the environment are brought about primarily by anthropogenic
86 sources. Though heavy metals are a part of the natural environment and provide numerous
87 benefits to society, those that get deposited in most water bodies result from coal and oil
88 combustion, internal combustion engines, local point sources, and direct deposition from air
89 pollution, bedrock geology and soils (Skejelkvale *et. al.*, 2001).

90 The concern posed by heavy metals in the environment creates an immense threat to the
91 existence of organisms thriving in the area and the ecological integrity of the habitat,
92 particularly as heavy metals may enter the food chains, persist in the environment, bio-
93 accumulate and bio-magnify, then increase exposure of consumers of aquatic products to
94 serious health risks.

95 **Materials and methods**

96 Two fish species, *Pseudotolithus spp* (croaker) and *Solea solea* (sole) which are lenthic and
 97 benthic fishes respectively were used for the study. Sampling was done six times in May,
 98 July, September (Wet season) and November, January, and March (Dry season) at Makoko,
 99 Lagos State and Koko, Delta State, Nigeria. Fish samples were bought fresh from fishermen
 100 at landing sites in the study locations; and preserved by cooling in ice buckets till they were
 101 transferred into deep freezers in the laboratory and kept frozen at -20 °C until analysis.

102 Prior to analysis frozen fish samples were allowed to defrost at room temperatures for about
 103 two hours. The thawed fish samples were oven dried at 105°C for about 12hours until a
 104 constant weight was obtained. Thereafter dried fish samples were homogenized using a
 105 ceramic mortar and pestle. Samples were prepared with utmost care to avoid contamination.
 106 Hand-gloves were worn throughout the analytical procedures, and precautions were taken to
 107 carry out all preparations under strict sanitary laboratory conditions. Where drying was not
 108 completed in one day, samples were kept in desiccators and oven-drying was continued the
 109 following day.

110 All glass wares used were washed and rinsed severally with distilled water; then washed in
 111 10% HCl before use.

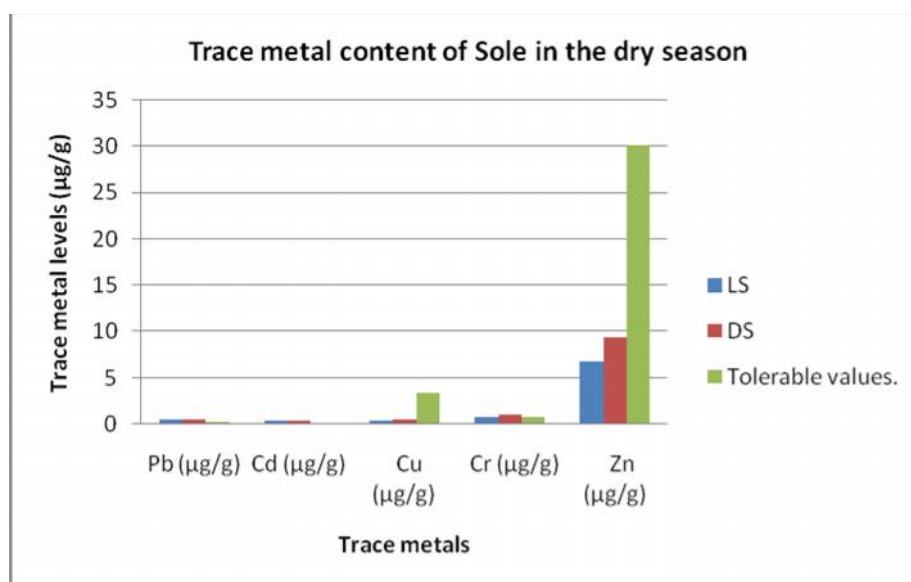
112 Samples were digested according to the wet digestion procedure of Asegbeloyin *et al.* (2010),
 113 by digesting 10.00 g of dried sample in 60 ml of freshly prepared 1:1 HNO₃/ H₂O₂ solution at
 114 160 °C on a hot plate for about one hour until the volume of contents was reduced to about
 115 5.00 ml. Contents were then filtered and the filtrate transferred to a standard flask and made
 116 up to 25.00 ml with distilled de-ionized water. This was stored in plastic bottles and the
 117 concentrations of Pb, Cr, Cu, Cd and Zn were evaluated using air-acetylene flame AAS
 118 (AAnalyst 200, Perkin Elmer).

119 Data obtained were subjected to one-way Analysis of Variance (ANOVA) according to the
 120 procedure of Steel and Torrie (1980). Significantly different means were separated using the
 121 methods of Duncan. The values obtained were presented as Least Significance Differences
 122 (LSD) of means at ($p < 0.05$).

123 Results and discussion

124 Levels of Pb, Cd, Cu, Zn, Cr and As observed in the Sole and Croaker during the dry season
 125 (November – March) at both study locations compared with international tolerable values are
 126 presented in Fig. 1 and Fig. 2; while those for the wet season (April – October) are presented
 127 in Fig. 3 and Fig. 4.

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130 **Figure 1: Trace metal content of sole in dry season (November – March)**

131 **LS (Sole from Lagos state), DS (Sole from Delta state)*

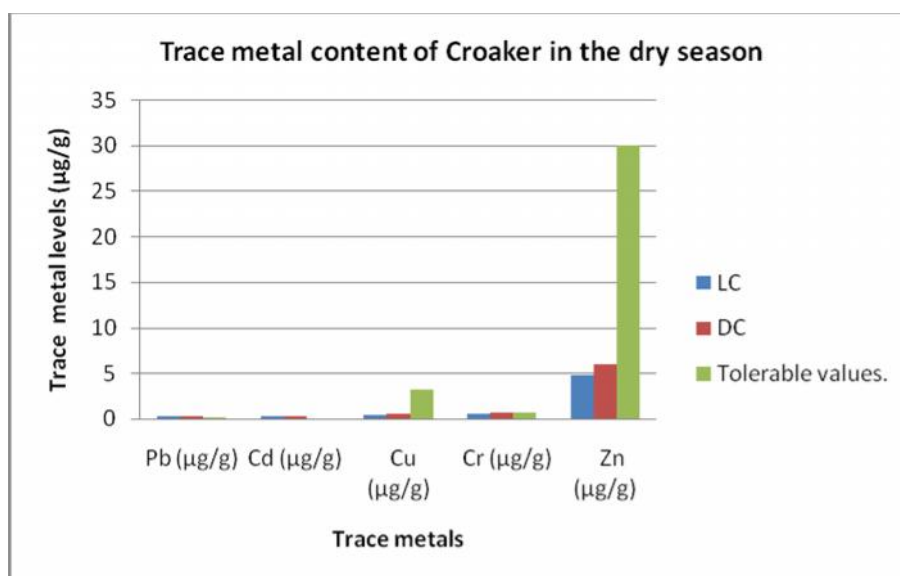


Figure 2: Trace metal content of croaker in the dry season (November – March)

**LC (Croaker from Lagos state), DC (Croaker from Delta state)*

Levels of Pb and Cd in sole during the dry season were similar in both study locations but higher than tolerable values, while Cr levels were higher in Delta than Lagos state. Levels of Cu and Zn in sole were higher in Delta during the dry season, but lower than tolerable values. Similar trends as reported above were observed for all trace metals in Croaker during the dry season. With the exception of Cu and Zn, trace metal content of sole was higher in Lagos than Delta state, with Pb and Cr levels higher than reported tolerable levels during the wet season. Zn and Cu levels of Croaker were higher in Lagos than Delta state, but lower than tolerable values during the wet season.

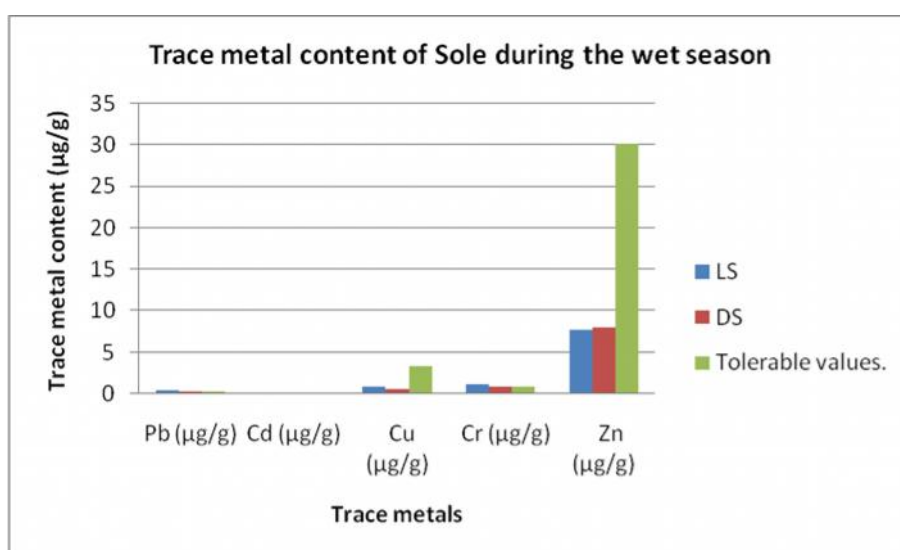
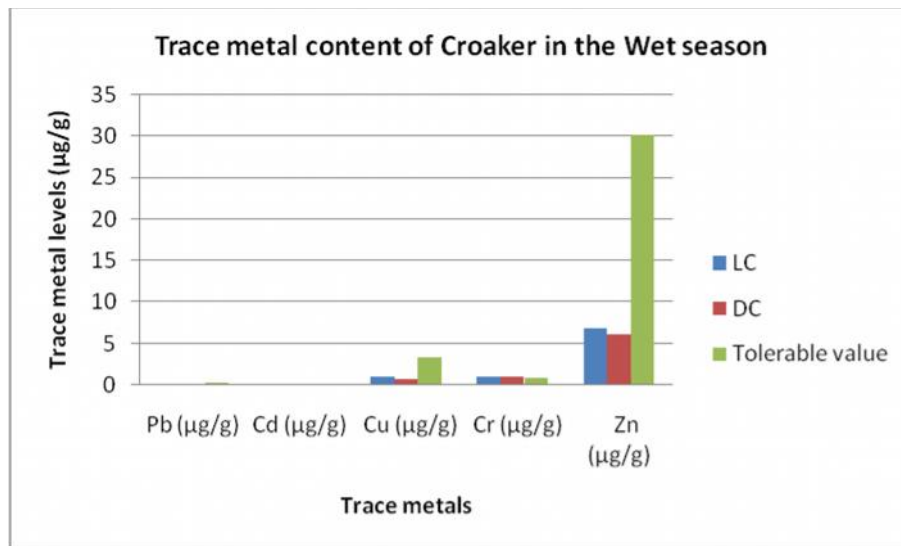


Figure 3: Trace metal content of sole during wet season (April – October)

146 *LS (Sole from Lagos state), DS (Sole from Delta state)

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148

149 **Fig. 4: Trace metal content of Croaker in the wet season (April – October)**

150 *LC (Croaker from Lagos state), DC (Croaker from Delta state)

151 Table 1 describes variation in metal contents between seasons. Generally, significant ($p < 0.5$) variation was observed between seasons in Cd, Cu and Cr levels, with Cu and Cr being
 152 higher during the dry than wet season; and Cd being higher during the wet season. Table 2
 153 describes variation in metal content between experimental fish species. Pb and Zn were
 154 significantly ($p < 0.5$) higher in Sole than in Croaker. As shown in Table 3, observed
 155 differences in metal content in Sole and Croaker between Lagos and Delta states were not
 156 statistically significant.

158 **Table 1: Seasonal variation in metal content of Sole and Croaker**

Season	*Metal contents (µg/g)				
	Pb	Cd	Cu	Cr	Zn
Wet	0.34 ± 0.11	0.34 ± 0.04 ^a	0.48 ± 0.04 ^b	0.73 ± 0.10 ^b	6.70 ± 0.64
Dry	0.17 ± 0.05	0.08 ± 0.02 ^b	0.75 ± 0.12 ^a	1.01 ± 0.09 ^a	7.11 ± 0.30

159 **Columns with similar superscripts are not significantly ($P < 0.05$) different*

160 **Table 2: Variation in metal content between fish species**

Fish Species	*Metal contents ($\mu\text{g/g}$)				
	Pb	Cd	Cu	Cr	Zn
Sole	0.41 ± 0.12^a	0.26 ± 0.06	0.56 ± 0.08	0.95 ± 0.10	7.92 ± 0.51^a
Croaker	0.13 ± 0.04^b	0.19 ± 0.04	0.62 ± 0.10	0.76 ± 0.10	5.83 ± 0.44^b

161

162 **Columns with similar superscripts are not significantly ($P < 0.05$) different*

163

164 **Table 3: Variation in metal content of Sole and Croaker between Lagos and Delta states**

Location (States)	Metal contents ($\mu\text{g/g}$)				
	Pb	Cd	Cu	Cr	Zn
Delta	0.28 ± 0.10	0.23 ± 0.04	0.65 ± 0.11	0.86 ± 0.11	6.38 ± 0.46
Lagos	0.27 ± 0.11	0.23 ± 0.06	0.54 ± 0.05	0.85 ± 0.09	7.37 ± 0.61

165

166 Metal (Pb, Cd, Cu, Cr and Zn) concentrations in the two fish species and sampling locations

167 were compared with international standards. As expected, the metals were more concentrated

168 in sole (a benthic fish) fish than croaker, a pelagic fish; except for Cu where the

169 concentrations in croaker were higher than in sole and Cd where concentrations found in
170 Croaker from Lagos State (LC) was higher than those found in Sole.

171 In general, lead values obtained in this study were similar to those reported in previous
172 studies (Eletta *et al.*, 2002). Lead is known to exert its most significant effects on the nervous
173 system, the hematopoietic system and the kidney. It has effects on the nervous system
174 including motor disturbances.

175 The concentration of Cadmium in all the experimental fish were higher than the EC 2005
176 limit of 0.05µg/g, except in Delta croaker with a concentration of 0.029µg/g. Cadmium
177 concentrations in this study were higher than those reported earlier by Edem *et al.* (2009).
178 Adverse effects of excessive chronic cadmium exposure may include chronic renal failure,
179 kidney stones, liver damage, lung cancer, osteomalacia, possibly hypertension, prostate
180 cancer, and proteinuria. Chronic cadmium exposure has been reported to cause mild anemia,
181 skeletal lesions, Itai-itai disease, anosmia, and yellowing of teeth. Cadmium is a cumulative
182 toxin. Its level in the body increases over time because of its slow elimination. It accumulates
183 chiefly in the liver and kidneys, and also in muscles and bone.

184 Chromium concentrations in this study were found to be lower than levels previously
185 reported Burgera and Gochfeld (2005), but higher than the IAEA standard for chromium
186 (0.730µg/g; IAEA-407, 2003). Reported health effects of chromium toxicity include
187 haemolysis, renal and liver failure, cancer and damage to circulatory and nervous tissues.

188 Mean concentrations of zinc in this study were lower than the reported standard of 3.280ppm
189 (IAEA-407, 2003). Zinc deficiency has been associated with dermatitis, anorexia, growth
190 retardation; poor wound healing, hypogonadism with impaired reproductive capacity.

191 Also, the study showed more heavy metals' pollution in Lagos lagoon fish samples than in
192 Koko lagoon except for Zn, where the concentrations in Delta were more than those of Lagos
193 state. The concentrations of Zinc were much lower than the international tolerable values.

194 **Conclusion**

195 Trace metal contents of the two economically important fish species evaluated varied with
196 season and among species, with the benthic species studied (Sole) having significant higher
197 levels of Pb and Zn than the pelagic species, Croaker. Cu and Cr levels were significantly
198 higher during the dry season; and Cd level in fish species were significantly higher during the
199 wet season. Reported studies on variation in metal content of economically important
200 Nigerian fish species are generally lacking, thus it is important that finding of this research be
201 published to educate consumers on possible health hazards associated with fish consumption.

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