

BIO-MONITORING OF MANGROVE SEDIMENTS AND TISSUES FOR HEAVY METALS ACCUMULATION IN THE MANGROVE FOREST OF CROSS RIVER ESTUARY

ABSTRACT

The need to periodically monitor the mangroves for heavy metals pollution should not be overemphasized given the high premium placed on this ecosystem. The study was aimed at evaluating mangrove sediments and tissues for heavy metals accumulation in the different tidal levels, as an indicator for pollution. Ten random samples of composite surface sediments (0-5cm) were collected from low, mid and high tidal levels using a modified Van Veen (0.1m²) grab sampler. Also samples of senescent leaves, barks and roots of randomly selected ten individual plants of *Nypa fruticans* (low tide), *Rhizophora racemosa* (mid tide) and *Avicennia africana* (high tide) were also collected for heavy metal analyses during the year 2011. Our results showed that there were significant variations ($P < 0.05$) in heavy metals deposition across the tidal levels. In the mangrove sediments, iron (Fe) content (415.8mg/g dry weight) was highest in the high tidal level where *A. africana* was predominantly sampled while *N. fruticans* (low tide) had the lowest deposition of the metal (304.4mg/g dry weight). The accumulation of heavy metals in the mangrove tissues took the general trend of root > bark > leaves, the species notwithstanding. It was also observed that cadmium (Cd) deposition in sediments was comparatively higher than RSV indicating possible cadmium pollution. Generally, accumulation of heavy metals in the mangrove forest of Cross River estuary was within permissible limits. Although the concentrations obtained for the heavy metals studied are generally below documented toxic levels, however, the increasing level of urbanization and industrialization in Calabar municipality and its environs calls for continuous vigilance, surveillance and monitoring of this sensitive and all important ecosystem to protect and ensure that heavy metal pollution is minimal.

Keywords : Cross River, Mangroves, Heavy metals, Pollution

Introduction

Mangroves are halophytic trees that dominate the intertidal zone along coastlines, estuaries and islands in tropical and sub-tropical regions of the world where they exist under conditions of high salinity, extreme tides, strong winds, high temperature with muddy, anaerobic soil (Hogarth, 1999; Middleton & McKee, 2001). They thrive in tropical

41 estuaries, which receive evenly distributed heavy rainfall throughout
42 the year. Mangroves are among the most productive intertidal
43 ecosystems on earth (Wafar *et al.*, 1997; Clough *et al.*, 2000). They serve
44 as nursery and breeding grounds for several commercially important
45 species of marine fauna.

46 However, in spite of their economic and ecological importance,
47 mangrove forests are under threat from over-exploitation, destruction
48 and pollution with heavy metals and petroleum (Rate *et al.*, 2000; Ray
49 *et al.*, 2006; Pekey, 2006 Kairo *et al.*, 2001). According to Mackey and
50 Mackay (1996), mangrove ecosystems serve as sink for the deposition
51 of heavy metals from anthropogenic sources such as domestic,
52 industrial and agricultural discharges. This has led to their use as bio-
53 indicators for pollution monitoring programmes as well as phyto-
54 infiltration and phyto-extraction technology (Wankasi *et al.*, 2006).

55 These pollutants become trapped in mangrove sediments and
56 eventually become partly locked up in detrital particles, making them
57 potentially bio-available to detrital feeders (Chindah *et al.*, 2004; Igwe
58 *et al.*, 2005; Islam *et al.*, 2006). Undoubtedly, they also become
59 accumulated in tissues of these organisms leading to their amplification
60 through bio-accumulation along the food chain. The cycling of heavy
61 metals because of their toxicity, bio-accumulation capacity and
62 persistence, is a serious question recently addressed by many studies
63 on mangrove environments (Mackey & Hodgkinson, 1995; Clark *et al.*,
64 1998). Fillips (2002), Ramasamy and Murugan (2002) observed that

65 heavy metal-mediated pollution affect the development and
66 biochemical activities of soil microorganisms, which might directly
67 or/and indirectly elicit toxic influence on other flora and fauna species
68 in the ecosystem.

69 The monitoring of mangrove ecosystems for heavy metal
70 pollution has become imperative given the high premium placed on
71 this economic and ecological important ecosystem. Recently, the
72 upsurge of human activities along the Great Kwa Basin, urbanization
73 and industrialization, uncontrolled and mismanagement of open
74 dumpsters in Cross River State, Nigeria has ignited severe panic for eco-
75 toxicologists, especially as it concerns heavy metal pollution. This paper
76 is aimed at evaluating the extent of pollution using heavy metal bio-
77 indicators on the mangrove sediments and tissues.

78 **Materials and methods**

79 **Sampling site**

80 The study area covered the mangrove forests of the Great Kwa
81 River, East of the Cross River estuary, which flows into the Gulf of
82 Guinea. This area lies within latitudes 04° 45' and 04° 15' North of the
83 Equator and longitudes 008° 15' and 008° 30' East of Greenwich
84 Meridian along the eastern border of the University of Calabar, Nigeria.
85 The research was undertaken 2011 spanning January to December.

86 **Sampling methods**

87 Ten random samples of composite surface sediments (0-5cm)
88 were collected from low, mid and high tidal levels using a modified

89 Van Veen (0.1m²) grab sampler. Samples of senescent leaves, barks
90 and roots of randomly selected ten individual plants of *Nypa fruticans*,
91 *Rhizophora racemosa* and *Avicennia africana* were also collected for
92 heavy metal analyses. It should be clearly noted that in the Great Kwa
93 River estuary, *N. fruticans* is predominantly found in low tidal level while
94 *R. racemosa* and *A. africana* are found in the mid and high tidal levels,
95 respectively.

96 **Sample preparation and heavy metal analysis**

97 The tissue samples were rinsed with de-ionized water, placed in
98 black polyethylene bags, tagged and stored in cool boxes at -4°C to
99 avoid oxidation. Sediments and plant tissue samples were then oven-
100 dried at 80°C to constant weight. The dry samples were ground, and
101 sieved through a 250µm mesh screen. 1g of the each sample was
102 digested in Kjeldahl Digester using a mixture of concentrated HNO₃
103 and HCl. The digested samples were analyzed for heavy metals (Iron
104 (Fe), manganese (Mn), cadmium (Cd), chromium (Cr), copper (Cu),
105 zinc (Zn), nickel (Ni), and lead (Pb) by flame atomic absorption
106 spectrophotometry (FAAS) (Perkin Elmer- Model 3030, Germany).

107 **Statistical analysis**

108 Data collected from the analyses were subjected to analysis of
109 variance (ANOVA) using Predictive Analytics SoftWare (PASW), version
110 18.0 while significant means were separated using Least Significant
111 Difference Test Statistics (LSD). The results were compared with global
112 average shale and fossil rhine (ASV) concentrations of metal (Turekian

113 and Wedepohl, 1961) while concentration factor (CF) was calculated
114 using Alberts *et al.* (1990) method.

115 **Results**

116 **Heavy metal deposition in the mangrove sediments**

117 There were significant differences ($P < 0.05$) in the deposition and
118 accumulation of heavy metals in the mangrove sediments. In the
119 mangrove sediments, iron (Fe) content (415.8mg/g dry weight) was
120 highest in the high tidal level where *A. africana* was predominantly
121 sampled while *N. fruticans* (low tide) had the lowest deposition of the
122 metal (304.4mg/g dry weight). However, there was no significant
123 differences ($P > 0.05$) observed in zinc (Zn), Nickel (Ni) and chromium
124 (Cr) deposit in the mangrove sediments in the low and high tidal levels.
125 For manganese (Mn), there were no significant variations among the
126 tidal levels. The deposition of cadmium was highest in the low tide
127 inhabiting *N. fruticans* while lead (Pb) and copper (Cu) were observed
128 to be high in the sediment of *R. racemosa* (Mid tide) comparing with
129 the sediments in other tidal levels (Figure 1).

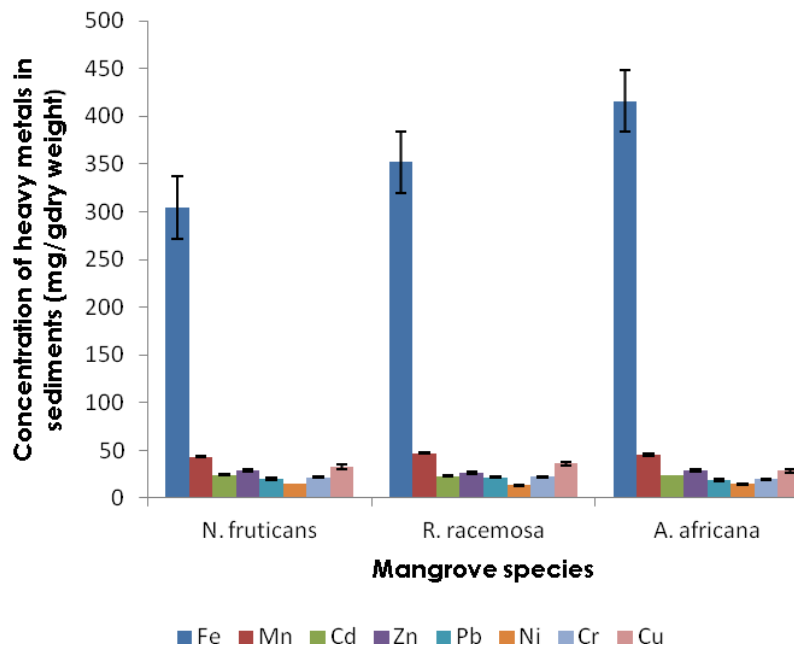
130 **Heavy metal deposition in the mangrove tissues**

131 Heavy metals accumulation in the mangrove tissues varied
132 significantly ($P < 0.05$) across the tidal levels as well as specific to
133 mangrove tissues. Iron (Fe) accumulation was more in the roots of the
134 mangrove, the species notwithstanding but however, was lowest on
135 the bark of *R. racemosa* (mid tide). For manganese, its accumulation in

136 the roots of *A. africana* (high tide) was the same with that of the bark
 137 of *R. racemosa* while its deposition in the leaves of *N. fruticans* was
 138 significantly higher than the leaves of *R. racemosa* and *A. africana*,
 139 respectively. The bark of *A. africana* accumulated more cadmium.
 140 However, other mangrove tissues showed no significant differences,
 141 except the leaves of *N. fruticans* and *R. racemosa* .

142 Accumulation of zinc was high in the bark of *A. africana* when
 143 compared with other tissue parts of the different mangroves. For
 144 copper, its accumulation was highest in the barks of *N. fruticans* and *A.*
 145 *africana*. Although there were instances of deviations, the general
 146 trend in the deposition and accumulation of heavy metals was
 147 sediments>roots>barks> leaves (Table 1). Additionally, the Average
 148 Shale Value (ASV) for the metals was within permissible range except
 149 for cadmium, where ASV was lower than its accumulation in the
 150 sediments and plant tissues. It was also observed that the
 151 concentration factor (CF) for zinc (Zn) was in the three tidal levels
 152 (Figure 2). This was followed by copper and manganese. However, the
 153 concentration of cadmium was very low comparatively.

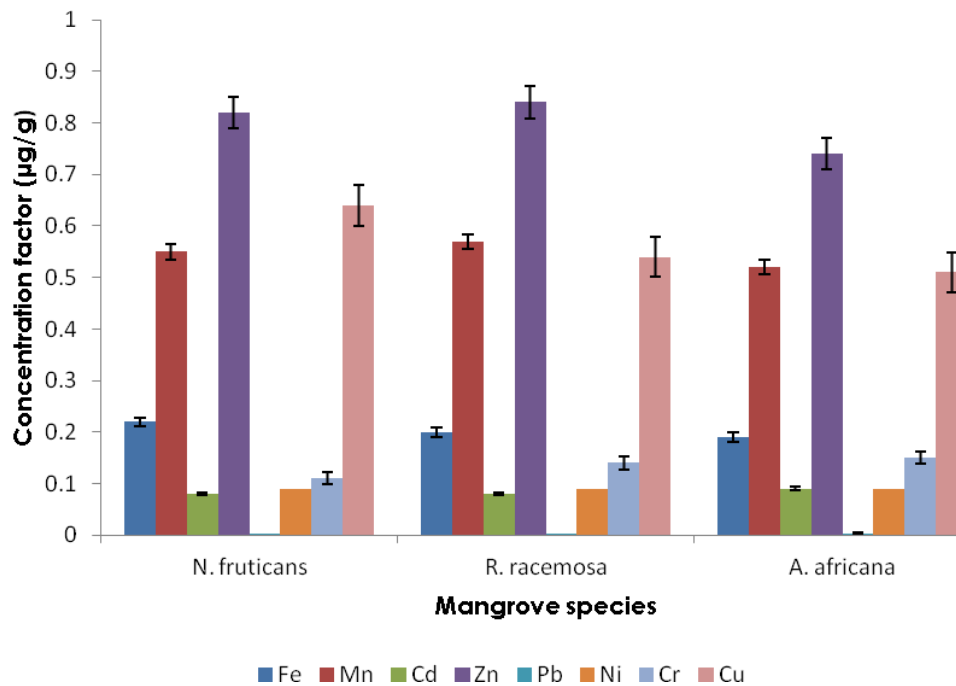
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157 **Figure 1:** Concentration heavy metals in the mangrove sediments.

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162 **Figure 2:** Concentration factor for heavy metals in the mangrove
163 sediment and plant tissues.

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Table 1. Average concentration of heavy metals (mg g⁻¹, dry weight) in plant tissues and sediments of mangrove species in the mangrove forest of Great Kwa River, East of the Cross River estuary, Nigeria

Mangrove species	Samples parts	Heavy metal (mg/g dry weight)							
		Fe	Mn	Cd	Zn	Pb	Ni	Cr	Cu
<i>N. fruticans</i>	Root	81.47c±0.46	24.11b±0.23	1.73b±0.32	28.02d±1.23	0.42b±0.01	1.49b±0.02	5.17c±0.21	15.87b±0.34
	Bark	52.52a±1.21	27.25c±0.37	2.21b±0.32	32.61e±0.46	0.018b±0.48	1.54b±0.37	1.66b±0.03	26.48d±0.25
	Leaves	67.73b±2.02	19.88b±0.43	0.83a±0.01	11.54b±0.05	0.038b±0.001	0.84b±0.01	0.61a±0.01	20.44c±0.78
<i>R. racemosa</i>	Root	88.78c±1.34	24.19b±0.38	1.77b±0.48	25.35c±0.56	0.11b±0.001	1.54b±0.01	6.76d±0.04	15.88b±0.24
	Bark	64.01a±1.23	37.84d±0.76	2.20b±0.02	29.17d±0.34	0.014a±0.0001	1.67b±0.01	1.58b±0.02	21.34c±0.45
	Leaves	64.94b±0.78	19.54a±0.54	1.32a±0.03	11.54a±0.45	0.04b±0.001	0.66a±0.01	0.77b±0.01	21.25c±0.32
<i>A. africana</i>	Root	82.23c±0.32	32.82d±0.76	1.73b±0.85	25.12c±0.53	0.102b±0.001	1.63b±0.14	6.53c±0.05	13.27a±0.11
	Bark	81.20c±0.33	29.52c±0.86	3.04c±0.23	29.55d±0.67	0.014a±0.001	1.56b±0.24	1.91b±0.02	24.33d±0.07
	Leaves	67.68b±0.35	19.67a±0.45	1.59b±0.46	10.81a±0.54	0.038b±0.002	0.70a±0.05	0.69a±0.001	21.85c±0.06
Average value (ASV)	Shale	4700	600	1.31	45	20	68	83	45

169 **Discussion**

170 Industrial wastes laden with toxic metals are of great concern in
 171 the marine ecosystem given that they are not easily degradable,
 172 leading to their persistency in the ecosystem. Worst still is the fact that
 173 these metals accumulate in different trophic levels of food chain.
 174 Pollution monitoring, especially in the mangrove ecosystem is very
 175 strategic. This is premised on the menace orchestrated by this condition
 176 and which has caused government and her agencies globally huge
 177 sums of money. While acting as reservoir for the phyto-filtration and
 178 extraction of metals (Wankasi *et al.*, 2006), mangrove is also used as
 179 bio-indicators for heavy metal pollution.

180 However, their accumulation and subsequent distribution
 181 according to Guo *et al.* (1997), depend on various factors, which
 182 includes redox conditions and organic contents of the sediments in the
 183 ecosystem. These factors as also observed by Mason *et al.* (1994) may
 184 influence the toxicity of metals through processes such as mercury
 185 methylation as well as controlling metals' availability for living
 186 organisms. Quémerais *et al.* (1998), Dong *et al.* (2000) observed that
 187 metals can be absorbed onto the surface of minerals like clay, iron
 188 and/or manganese oxy-hydroxides, thus hindering their availability.

189 Our results showed that there were significant variations in the
 190 depositions and accumulation of these heavy metals in the mangrove
 191 sediments along the tidal levels. Among the heavy metals, iron
 192 deposition was highest in the sediments of *A. africana* in the high tide

193 while cadmium and lead were in highest deposition in the *N. fruticans*
 194 sediment that was sampled in the low tide. However, in the mid tide (*R.*
 195 *racemosa*) sediment, copper was found to be high. The elevated
 196 concentration of iron in the high tidal level might probably be due to
 197 redox conditions in sedimentary columns and the relation of the iron in
 198 the organic fractions as well as in the water soluble and exchangeable
 199 fractions (Sundby *et al.*, 1981; Izquierdo *et al.*, 1997; Akpan *et al.*, 2002).
 200 Undoubtedly, the extent of pollution in the mangrove ecosystem is
 201 proportional to anthropogenic disturbances of the mangrove due to
 202 the rate of urbanization and industrialization in the municipality (Rate *et*
 203 *al.*, 2001; Pekey, 2006; Ray *et al.*, 2006) and adjoining communities
 204 surrounding the mangrove. Such perturbations affect sediment
 205 properties as water currents, tidal flow and the ability of mangrove
 206 trees to capture sediments are altered (Kaly *et al.*, 1997).

207

208 Our current results on the accumulation of these heavy metals in
 209 mangrove tissues revealed that there were significant variations in their
 210 concentrations in the mangrove plants, which indicated that the trend
 211 in the accumulation was roots > barks > leaves, the mangrove
 212 notwithstanding. The significant variation in the accumulation of heavy
 213 metals in the tissues of mangrove plants might be basically due to (a)
 214 the metal need of the specific tissues (b) the amount/quantity of
 215 metals deposition in the sediments of the mangrove and (c) sea water
 216 intrusion during high tide. Expectedly, besides the high deposition of

217 these metals on the mangrove sediments, their accumulation was
 218 more in the roots than other plant tissues. The explanation probably is
 219 that the roots first receive the metals and depending on the need of
 220 the other tissues, roots supply. This alteration occasioned by the
 221 perturbation may as well affect the heavy metals that get deposited in
 222 the sediments of the different tidal levels where the different
 223 mangroves were sampled.

224 According to Alberts *et al.* (1990), metals such as chromium and
 225 lead, have low rates of translocation and as such are much more
 226 concentrated in the roots than in stems or leaves. Apart from copper
 227 whose concentration was higher in the leaves, concentrations of other
 228 metals were least in the leaves. This obviously suggests active
 229 translocation, transport and biomass production processes (Markert,
 230 1993; Phillips, 1995). This also suggests that copper can be sequestered
 231 in the leaves for the remediation of metal ions pollution in the
 232 mangrove forest of Cross River estuary. The concentration factor (CF)
 233 indicated that zinc was high in the soil for the plants to assimilate.
 234 Though this factor increases the risk of the metal entering into food
 235 chain, however, zinc is a micronutrient and its accumulation might not
 236 pose threat to the plant. The implication is that there is the possibility
 237 that a metal can be present in the soil but not available for plant to
 238 absorb or assimilate. This might be the case of other heavy metals with
 239 low CF.

240 The high CF of zinc, copper and manganese in the tissues of the
241 mangrove plants across the tidal levels might suggest active uptake
242 and possible storage of these metals needed for the plant growth and
243 development. Bioavailability of metals and their transfer from soil to
244 plants are affected by physicochemical parameters (Ross, 1994; Tam &
245 Wong, 1996; Izquierdo *et al.*, 1997). Although the concentration of
246 cadmium in the sediments was very high, CF in the mangrove species
247 was low. This may be due to the high concentrations of other metal
248 ions, especially zinc in the soil, which had been reported to inhibit
249 uptake of cadmium (Thornton, 1981). The low CF obtained for nickel
250 and lead may be indications of lack of storage of these metals in plant
251 tissues (Ross, 1994). This might presuppose that there may be cadmium
252 and lead pollution given the high presence of these metals.

253

254 The accumulation and the seeming tolerable and permissible limits of
255 the heavy metals sampled except cadmium notwithstanding, the
256 levels of these metals could obstruct the food chain of aquatic
257 organisms inhabiting the mangrove. This was the positions of Kramer and
258 Chardonens (2001); Zhou *et al.* (2004); Uzair *et al.* (2009).

259 It should be understood that copper and zinc are micronutrients
260 essential for plant growth, thus their concentrations in the leaves and
261 barks may reflect physiological requirements of the mangroves.
262 According to Wankassi *et al.* (2006), the shoot of mangrove trees may
263 act as a good absorber for the remediation of metal ion polluted

264 environments. Going by our result, the possibility of the leaves and
 265 barks of these mangrove species being used as copper sink might not
 266 be in contention. This low bioaccumulation of heavy metals in the
 267 mangrove leaves might indirectly imply also low accumulation of these
 268 metals in the tissue of organisms in the ecosystem. This is premised on
 269 the fact that leaf litter constitutes major components of detrital food
 270 chain. Comparing heavy metals in sediments and plant tissues may be
 271 convenient for assessment of some measure of pollution, the limitations
 272 of this method, notwithstanding (Wang and Fan, 2001).

273 The ability of any plant to accumulate heavy metals in its tissues
 274 is genetically controlled as well as its capacity to withstand heavy
 275 metal pollution. Genetic engineering approach can be used for further
 276 studies to understand and enhance the phyto-remediation properties
 277 of these mangroves (Fulekar *et al.*, 2009). This could be a good source
 278 of alien genes that will be used for plants improvements towards aiding
 279 phyto-remediation process.

280

281 **Conclusion**

282 Although the concentrations obtained for the heavy metals
 283 studied are generally below documented toxic levels, however, the
 284 increasing level of urbanization and industrialization in Calabar
 285 municipality and its environs calls for continuous vigilance, surveillance
 286 and monitoring of this sensitive and all important ecosystem to protect
 287 and ensure that heavy metal pollution is minimal.

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