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Analysis of total hydrocarbon and heavy metal accumulation in sediment, water and associated organisms of Mangrove ecosystem in the Niger Delta

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Abstract

Background /Objectives: This study's objectives are (1) to determine the total hydrocarbon (THC) and heavy metals in sediment and water samples collected from mangrove forest at different locations; (2) to compare the THC and heavy metals across different mangrove associated species; (3) to compare the relationship between THC and heavy metals in different organisms across different locations and (4) to determine the THC and heavy metal concentration between vertebrates and invertebrate organisms in mangrove forest. Methods/Statistical analysis: It is hypothesized that chemical contamination will bioaccumulate across multiple mangrove associated organisms. Physicochemical analysis for Cadmium (Cd), Zinc (Zn), Lead (Pb), Iron (Fe) and total hydrocarbon (THC), was carried out on sediment, water, crabs, fish, insect, anadara and bird droppings, and was measured by spectrophotometric method using HACH DR 890 colorimeter and microwave accelerated reaction system (MARS Xpress, North Carolina). Findings: There was a significant difference in chemical composition between mangrove associated species ($F_{4, 145}$ = 2.83, P=0.03). Anadara has the highest THC (36.44±9/4mg/kg) and Iron (6.97±1.32mg/kg) concentrations while bird droppings had the highest Lead concentration $(10.83\pm1.27$ mg/kg). Fish had the highest Cadmium $(4.20\pm1.01$ mg/kg) and Zinc (15.88±5.53mg/kg) concentrations. The order of organisms contamination is anadara>fish>bird droppings>crab>insect. The order of metal concentration is THC>Zn>Pb>Fe>Cd. In contrast, there was no significant difference between vertebrate and invertebrate organisms ($F_{1, 148} = 0.08$, P=0.78). Vertebrates have higher chemical composition (Cd, Pb and Zn) as compared to invertebrates (Fe and THC). Application/Improvement: Concentration of THC and heavy metals in most mangroves species were above the FAO/WHO standards. This implies that there is a horizontal THC and heavy metal contamination across trophic levels, which is detrimental to public health.

Keywords: Bioaccumulation; heavy metals; invertebrates; Niger delta; pollution; vertebrates

1 Introduction

The Niger Delta region is found in the southern part of Nigeria and covers 20, 000 km² within 70, 000 km² of wetlands ⁽¹⁾. It borders the Atlantic Ocean and has one of the largest mangrove system in Africa, which is estimated to cover 5, 000 km² to 8, 500 km² (²⁾. Apart from the rich mangrove vegetation, it is also rich in crude oil ⁽³⁾, which has made it the host to numerous oil and gas industries such as the Port Harcourt Refinery Company and the Liquified Natural Gas Company. Oil activities in this region have made it one of the most polluted mangrove forests in the world ⁽⁴⁾. Constant offshore and onshore crude oil spillages had contaminated the mangrove environment resulting in increased bioaccumulation of hydrocarbons and heavy metals within the food chain ^(5,6). The study is significant because the major occupation of the people who live in the surrounding coastal towns of the Niger Delta is fishing. They catch the fishes and consume or sell them to other consumers.

Mangrove forests are plant species found in the interface between the land and the sea, and have great affinity for high salinity ⁽⁷⁾. They are mostly found in tropical and subtropical regions of the world because their distributions are influenced by high temperature and precipitation ^(8,9). There are over 73 species and hybrids worldwide ^(10,11), but the most commonly found species are the Rhizophora popularly called the red mangroves ^(12,13). Mangroves are one of the most important economic trees in the world because of the ecosystem services they offer. They purify the air through carbon sequestration (14), and are used to manufacture firewood and charcoal, which are used for cooking ⁽¹⁴⁾. Their leaves have medicinal properties and are used to treat diseases (15,16) in rural and urban areas in the Niger Delta. Furthermore, the mangrove forests are described as the supermarket of the sea (17) because they are made up of a variety of organisms ranging from microbes, invertebrates to vertebrates on both land and sea. The adventitious roots of mangroves serve as a spawning ground for fingerlings of different species of shelled and fin fishes such as tilapia (Sarotherodon melanotheron), sardine (Sardinella maderensis), mullet (Liza falicipinis) and Anadara (Senilia senilis)⁽¹⁸⁾. Two prominent crab species found in the swamps of the Delta are the fiddler crabs (Uca tangeri) and the West African red mangrove crabs (Goniopsis pelii). The G. pelii are good tree climbers that spend most of the day foraging on mangrove trees and feeding on leaves and seeds⁽¹⁹⁾. Their burial of litter materials is to facilitate decomposition, and to reduce the tannin content of the leaves. This is because the tannin, which is an anti-herbivore chemical, makes the litter to be unpalatable for the crabs to consume ⁽²⁰⁾. The insects range from wasps to dragon flies which shuttle between nearby bushes and the mangrove forest in search of food and mates. They also build their nest and lay eggs on the mangrove leaves because they want their young caterpillars, to feed on the leaves (21) to facilitate the process of metamorphosis from young to grown adult. The heron (cattle egrets) also pay visit to the mangrove forest to feed on fingerlings and insects. Furthermore, the mangrove forest serves as the breeding ground for the cattle egret. The biological significance of the relationship between all these species in the complex food web of the mangrove ecosystem⁽²²⁾ is the transmission of harmful chemical via plant-organism and invertebratevertebrate pathways to humans who consume some of these organisms as delicacies, especially the crustaceans and fish ⁽²³⁾. It therefore answers the research question that states that between invertebrate and vertebrate organisms, which one has more chemical concentration? It is thus hypothesized that there will be an accumulation of THC and heavy metals at different trophic levels across the food chains in the mangrove ecosystem. The objectives of the study therefore are; (1) to determine the THC and heavy metals in sediment and water samples collected from mangrove forest; (2) to compare the THC and heavy metals across different mangrove associated species; (3) to compare the relationship between THC and heavy metals in different organisms across different locations and (4) to determine the THC and heavy metal concentrations between vertebrates and invertebrate organisms in mangrove forest.

2 Materials and methods

2.1. Study area and sampling stations

The Niger Delta has tropical climate with rainfall occurring from January to December each year, and has two seasons, the wet and dry seasons ⁽²⁴⁾. The study was conducted in three research sites (Figure 1) namely: Okrika (4°43N and 7°05 E), a host to a major oil refinery with high oiling activities with numerous crude oil pipelines traversing the area; Buguma (4°45N and 6°56 E), a town that has an oil well head with moderate oiling activities and Eagle Island (4°47N and 7°58 E), a community within Port Harcourt, which has little or no oiling activity, but host marine transport activity.

2.2 Description of study species

The dragon flies are of the class insecta, phylum arthropoda and order Odonata. They belong to the suborder anisoptera. Their wings are spread out and the adults are mostly terrestrial while the nymphs are aquatic. They have distinct thorax and the adults are territorial and predatory ⁽²⁵⁾. The wasp belongs to the order hymenoptera, typically known as the "membrane wing". The

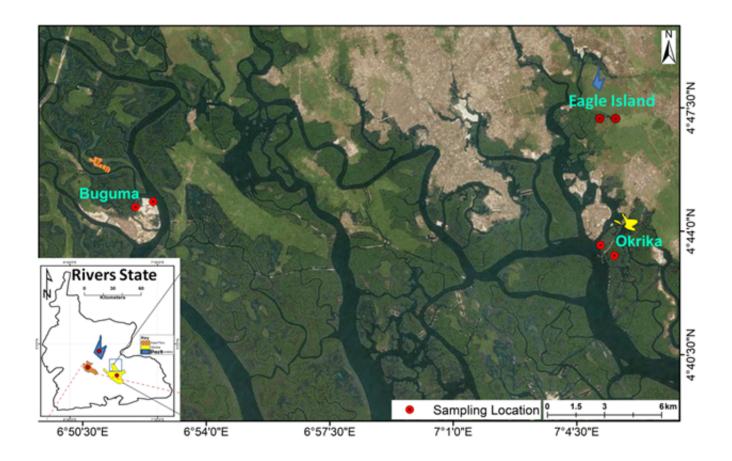


Fig 1. Map of study area showing the sampling points in mangrove forest Niger Delta, Nigeria.

ones captured for this study are grouped in the sub-order Apocrita, this is because their first abdominal segment is fused with the thorax to form mesosoma. They have sucking and chewing mouthparts and are mostly herbivores and parasitic during larval stage ⁽²⁶⁾.

The blue crabs (*Callinectes amnicola*, De Rochebrune, 1883) of the crustacean family are found during ebb tide on the swamp. They have a combination of blue and grey dorsal color while the ventral area is white in color. Their limbs are fragile and partly flattened unlike the land crabs. This crab is consumed in the Niger Delta, but in some other parts of the world like in the Mediterranean they are regarded as an invasive species ⁽²⁷⁾.

The heron birds, also known as cattle egrets (*Bubulcus ibis*, Bonaparte 1855) are of the family Ardeidae, they are under the class aves. They are long-legged freshwater and coastal birds that scavenge for food around the coast and are seen following cattles. Because of massive deforestation in the Niger Delta they are mostly found breeding in pockets of forest situated in urban areas as revealed by the study of ⁽²⁸⁾ in Gujarat.

The shelled organisms used for the study were that of anadara (*Senilia senilis*, Linnaeus, 1758) picked up from the forest floor. They are found in intertidal areas occupied by mangroves ⁽²⁹⁾. The fish species used for this study are the fingerlings of tilapia (*Sarotherodon melanotheron*, Ruppell, 1852) that are found close to the shore in flooded waters. They are dark grey at the dorsal part and light grey at the ventral part, and breed and spawn in mangrove forest ⁽³⁰⁾.

2.3 Sample collection

Water samples were collected with a plastic water sampler from three spots on the river. The water was sealed and sent to the laboratory for further analysis. The soil samples were collected randomly 5 cm below the soil surface with a hand-held soil auger at ten sites in each location. The soils were placed in black polyethylene bags labeled, placed in a cooler at 4° and transported to the laboratory.

The study organisms were picked up or captured within the mangrove forest at three different locations. Several anadara species were picked up from the forest floors, labeled and bagged. The flying insects (i.e. wasps and dragonflies) were captured with a hand-held net, while those walking were hand-picked from their habitat and placed in an insect bottle. The crabs were captured alive or picked up dead on the forest floor when swept ashore during high tide. The droppings of herons were used for this study and were scooped from their breeding ground. The fingerlings of the tilapia were captured live at the edge of the river where they gather in large populations in search of food during high tide.

2.4. Sample preparation and laboratory analysis

2.4.1. Water Samples

Samples from different points and depth were used to produce composite samples for analysis. Thereafter, two hundred and fifty (250) ml of water sample was measured into a separation funnel. The sample container was rinsed with Dichloromethane, thereafter, 25 ml of this substance was added to 250 ml part of the water sample and shaken thoroughly to enable the organic solvent to extract all the available organic materials. The organic extract collected is passed through silica-gel and anhydrous Sodium Sulphate. The collected extract is then injected into a gas chromatograph. The various fractions of the aliphatic compounds are automatically detected by the FID detector. The results are expressed in mg/l.

2.4.2 Sediment sample

The heavy metal analysis of soil was done following the method of $^{(31)}$. Here Five gram (5g) of air-dried, 2mm mesh size sieved soil sample was weighed and transferred into 100 ml glass beaker. A mixture of 2ml of nitric acid, 6ml of hydrochloric acid and about 20 ml of distilled water was added to the soil sample. The mixture was heated and allowed to digest to about 5 ml. digested sample were filtered into 50 ml volumetric flask through filter paper fitted in filter funnels. The atomic absorption spectrophotometer was calibrated using working solutions of 0.5, 1.0, 2.0, 5.0, 10.0 and 100.0 mg/l prepared from 1000 mg/l stock solution for the heavy metals to be analyzed. Sample digests are aspirated into the atomic absorption spectrophotometer immediately after calibration with standard solutions. Concentration values for each metal are expressed in units of mg/kg.

2.4.3 Total hydrocarbon analysis

It involved the use of spectrophotometric method using the HACH DR 890 colorimeter which followed the procedures of ⁽³²⁾. The samples (anadra, fish, crab, insect and bird droppings) were crushed and 2 g of the crushed samples were weighed into a glass beaker and ml of hexane was added, and with the aid of a glass rod, the mixture was homogenized by stirring. Afterwards, the sample was filtered in a glass funnel packed with cotton wool, silica gel and anhydrous sodium sulphate. After this, 10 ml of the filtered organic extract was transferred into a 10 m cuvette and inserted into the colorimeter.

2.4.4 Heavy metal analysis

Aliquots of 0.25 g of air dried samples (shell, fish, crab, insect and bird droppings) were weighed into a Teflon liner of a microwave digestion vessel and 2 mL concentrated (90%) nitric acid (Sigma-Aldrich, Dorset, UK) were added. The metals were extracted using a microwave accelerated reaction system(MARS Xpress, CEM Corporation, Matthews, North Carolina) at 1500 W power (100%), ramped to 175°C in 5.5 min, held for 4.5 min, and allowed to cool down for 1 h. The cool digest solution was filtered through the Whatman 42 filter paper and made up to 100 mL in a volumetric flask by adding de-ionized water. All chemicals and reagents used were of analytical grade and of highest purity possible. Analytical blanks were prepared with each batch of the digestion set and analyzed in the same way as the samples. The sample preparation, analytical validation and quality control followed the procedures of ^(33,34).

2.4.5 Statistical analysis

To determine the significant differences in the concentration of THC and heavy metals in sediment and water, and also in the five mangrove associated species (crab, bird droppings, fish, insect and anadara) analysis of variance (ANOVA) was done. ANOVA was used because there is replication of data, where N>2 $^{(35)}$. The data was first log transformed to ensure that they were

normal and the variances were equal. Bar graphs were then used to illustrate the significance and difference in concentration in vertebrate and invertebrate organisms. All analyses were done in $R^{(36)}$.

3 Results

3.1. THC and heavy metal concentration in water and sediment

Sediment: The result (Table 1) indicates that there is a significant difference among the chemical compositions (i.e. THC and heavy metal concentrations) in sediments ($F_{4, 25} = 6.66$, P< 0.001). But there was no significant difference in THC and heavy metal concentrations in sediment between locations ($F_{2, 27} = 2.55$, P=0.1). Cadmium and Lead concentrations were highest in Buguma while Iron, THC and Zinc were highest in Okrika. The overall order of THC and heavy metal concentration in sediment in the different locations is Fe>THC>Pb>Zn>Cd. Iron has the highest overall concentration in sediment followed by THC and Lead.

Table 1. Levels of total hydrocarbon content (THC) and heavy metals \pm 1 SE in sediments from different locations of the Niger Delta Nigeria

| Location | | | Metals (mg/kg) | | |
|--------------|-------------------|---------------------|------------------|----------------------|--------------------|
| | Cd | Fe | Pb | THC | Zn |
| Okrika | 0.45±0.09 | 1551.05±10.85 | $10.94{\pm}0.85$ | $578.88 {\pm} 28.43$ | $15.46 {\pm} 0.88$ |
| Buguma | $1.85 {\pm} 0.51$ | $908.27{\pm}104.04$ | $20.87{\pm}1.47$ | $145.68{\pm}13.25$ | $8.15 {\pm} 0.27$ |
| Eagle Island | $0.01{\pm}0.01$ | $2.08{\pm}0.16$ | $0.01{\pm}0.01$ | 8.51±0.29 | $2.61 {\pm} 0.41$ |

Water: The result (Table 2) indicates that there is a significant difference among the chemical compositions (i.e. THC and heavy metal concentrations) in water ($F_{4, 25} = 2.81$, P< 0.05). But there was no significant difference in THC and heavy metal concentrations in water between the three locations ($F_{2, 27} = 1.13$, P=0.34). Iron and THC have the highest concentrations in all locations. Iron was highest in Eagle Island (43.06 ± 0.01 mg/l) and THC was highest in Okrika (14.35 ± 0.79 mg/l). Cadmium and Lead have the least concentrations (Table 2). The overall order of THC and heavy metal concentration in water in the different locations is THC>Fe>Pb>Zn>Cd.

Table 2. Levels of total hydrocarbon content (THC) and heavy metals \pm 1 SE in water from different locations of Niger Delta Nigeria

| Location | Metals (mg/l) | | | | | |
|--------------|-----------------|-------------------|-----------------|-----------------|-------------------|--|
| | Cd | Fe | Pb | THC | Zn | |
| Okrika | $0.08{\pm}0.01$ | $1.3 {\pm} 0.04$ | 1.01±0.03 | 14.35±0.79 | $0.05 {\pm} 0.01$ | |
| Buguma | $0.02{\pm}0.01$ | $1.43 {\pm} 0.45$ | $0.47{\pm}0.05$ | $8.56{\pm}1.28$ | $0.15{\pm}0.03$ | |
| Eagle Island | $0.02{\pm}0.01$ | $43.06{\pm}0.01$ | $0.01{\pm}0.01$ | $8.56{\pm}0.16$ | $0.1{\pm}0.01$ | |

3.2 THC and heavy metal concentration in Anadara, crab and insect

Anadara (Senilia senilis): The result (Table 3) indicates that there is a significant difference in THC and heavy metal concentrations in anadara ($F_{2, 57} = 3.60$, P< 0.03). Similarly, there is a significant difference in THC and heavy metal concentrations between locations ($F_{4, 55} = 16.78$, P<0.001). THC concentration in anadara is the highest in all locations followed by Iron and Zinc while Cadmium had the least concentration. The overall order of THC and heavy metal concentration in the different locations is THC>Fe>Zn>Pb>Cd.

Crab (*Callinectes amnicola*): The result (Table 3) indicates that there is a significant difference in THC and heavy metal concentrations in crab ($F_{4, 25} = 29.16$, P< 0.001). But there was no significant difference in THC and heavy metal concentrations in crab between locations ($F_{2, 27} = 1.03$, P=0.37). Lead concentration was the highest in crab in all locations followed by Cadmium, Iron, THC and Zinc. Therefore, the overall order of THC and heavy metal concentration in crab in the different locations is Pb>Cd>Fe>THC>Zn.

Insect (dragonfly+wasp): The result (Table 3) indicates that there is a significant difference in THC and heavy metal concentrations in insect ($F_{4, 25} = 35.97$, P< 0.001). But there was no significant difference in THC and heavy metal concentrations in insects between locations ($F_{2, 27} = 0.54$, P=0.59). THC concentration was the highest in insects in all locations followed by Zinc, Lead, Iron and Cadmium. Therefore, the overall order of THC and heavy metal concentration in insects in the different locations is THC>Zn>Pb>Fe>Cd.

| Sampling Location | Species | THC and heavy metal concentration (mg/kg) | | | | | |
|----------------------|---------|---|-------------------|-------------------|-------------------|-------------------|--|
| | | Cd | Fe | Pb | THC | Zn | |
| | Anadara | 0.1±0.01 | 11.15±0.38 | 3.97±0.18 | 82.06±1.72 | 5.69±0.12 | |
| Okrika | Crab | $2.98{\pm}0.34$ | $2.85{\pm}0.6$ | $11.23{\pm}1.01$ | $1.42{\pm}0.06$ | $0.02{\pm}0.01$ | |
| | Insect | $2.22{\pm}0.1$ | $1.76 {\pm} 0.22$ | 4.15±0.43 | 14.5±1.85 | 5.78±0.25 | |
| Buguma | Anadara | 0.08±0.03 | 6.51±0.21 | 2.54±0.23 | 22.11±1.2 | 3.26±0.15 | |
| | Crab | $1.72{\pm}0.1$ | $1.19{\pm}0.03$ | $7.21 {\pm} 0.46$ | $0.58{\pm}0.03$ | $0.01{\pm}0.01$ | |
| | Insect | $1.84{\pm}0.2$ | $1.21 {\pm} 0.02$ | 3.61±0.28 | 9.45±0.44 | 4.34±0.23 | |
| Eagle Island | Anadara | $0.02{\pm}0.02$ | 6.84±0.45 | 3.68±0.2 | 16.53±0.73 | 3.19±0.15 | |
| | Crab | $2.95{\pm}0.09$ | $3.29{\pm}0.17$ | $7.65{\pm}0.77$ | $4.03{\pm}0.01$ | 2.1 ± 0.12 | |
| | Insect | $1.4{\pm}0.16$ | $2.84{\pm}0.17$ | $2.85 {\pm} 0.36$ | $8.56 {\pm} 0.13$ | $5.85 {\pm} 0.19$ | |

| Table 3. THC and heavy metal concentration in anadara (S. senilis), crab (C. amnicola) and insect (dragonfly+wasp) collected from |
|---|
| mangrove forest in different locations in the Niger Delta |

3.3 THC and heavy metal concentration in fish and bird droppings

Fish: The result (Table 4) indicates that there is a significant difference in THC and heavy metal concentrations in fish ($F_{4, 25} = 5.74$, P< 0.001). Similarly, there was a significant difference in THC and heavy metal concentrations in fish between locations ($F_{2, 27} = 3.51$, P=0.04). Zinc concentration was the highest in fish in all locations followed by Cadmium, THC, Iron, and Lead. Therefore, the overall order of THC and heavy metal concentration in crab in the different locations is Zn>Cd>THC>Fe>Pb.

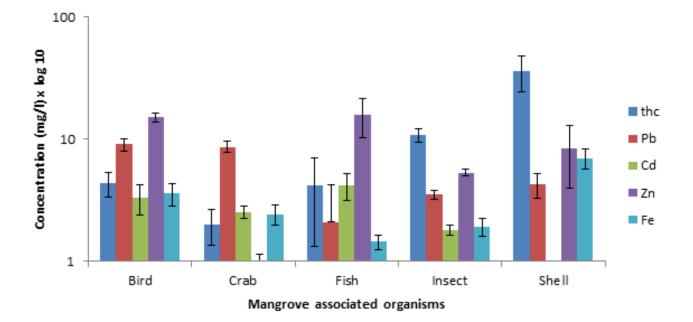
Bird (*B. ibis***) droppings**: The result (Table 4) indicates that there is a significant difference in THC and heavy metal concentrations in bird droppings ($F_{4, 25} = 25.28$, P< 0.001). But there was no significant difference in THC and heavy metal concentrations in bird droppings between locations ($F_{2, 27} = 0.87$, P=0.43). Zinc concentration was the highest in all locations followed by Lead, THC, Cadmium and Iron. Therefore, the overall order of THC and heavy metal concentration in the different locations is Zn>Pb>THC>Cd>Fe.

| | | ulli | erent locations in th | e Niger Della | | | | |
|--------------|---------|-----------------|---|-------------------|------------------|------------------|--|--|
| Sampling | Species | THC and heav | THC and heavy metal concentration (mg/kg) | | | | | |
| Location | | Cd | Fe | Pb | THC | Zn | | |
| Okrika | Fish | 5.88±0.9 | $1.84{\pm}0.28$ | $0.01 {\pm} 0.01$ | $2.46{\pm}0.11$ | 9.79±0.56 | | |
| | Bird | 5.9±0.45 | 4.58±1.04 | $10.42{\pm}2.04$ | 4.23±0.39 | 18.29±1.95 | | |
| Buguma | Fish | 4.31±0.09 | $1.34{\pm}0.11$ | $0.01{\pm}0.01$ | 0.27±0.06 | 10.93±0.15 | | |
| | Bird | 2.35±0.23 | 1.39±0.16 | 9.16±0.18 | 2.99±0.25 | 12.45±0.11 | | |
| Eagle Island | Fish | 0.64±0.03 | $0.81{\pm}0.07$ | 10.2±0.33 | $14.54{\pm}1.08$ | 36.65±1.31 | | |
| | Bird | $1.76{\pm}1.68$ | $4.84{\pm}0.27$ | $7.79{\pm}3.08$ | $5.83{\pm}3.05$ | $14.45{\pm}1.23$ | | |
| | | | | | | | | |

 Table 4. THC and heavy metal concentration in fish (S. melanotheron) and bird (B. ibis) droppings collected from mangrove forest in different locations in the Niger Delta

3.4 Comparison of THC and heavy metal concentration of all mangrove associated organisms

The result (Figure 2) indicate that there is significant difference in THC and heavy metals between mangrove associated organisms ($F_{4, 145} = 2.83$, P=0.03). Anadara has the highest THC concentration (36.44 ± 11.94 mg/kg) followed by insects (10.83 ± 1.27 mg/kg) and bird droppings (4.35 ± 0.95 mg/kg). Bird droppings have the highest Lead concentration (9.12 ± 1.07 mg/kg) followed by crab (8.69 ± 0.88 mg/kg) and shell (4.26 ± 0.97 mg/kg). Fish has the highest Cadmium concentration (4.20 ± 1.01 mg/kg) followed by bird (3.33 ± 0.93 mg/kg) and crab (2.55 ± 0.28 mg/kg). Fish has the highest Zinc concentration (15.88 ± 5.53 mg/kg) followed by bird (15.06 ± 1.24 mg/kg) and shell (8.48 ± 4.50 mg/kg). Anadara has the highest Iron concentration (6.97 ± 1.32 mg/kg) followed by bird (3.60 ± 0.76 mg/kg) and crab (2.44 ± 0.44 mg/kg). The order of organism contamination is anadara>fish>bird droppings>crab>insects. This means anadara has the highest overall chemical



contamination followed by fish and bird droppings.

Fig 2. Concentration of THC and heavy metals in five mangrove associated organisms in the NigerDelta (i.e.shelled organism is anadara)

3.5 Comparison of Invertebrate and vertebrate mangrove associated organisms

The result (Figure 3) shows that there is no significant difference in THC and heavy metal concentrations between invertebrates and vertebrates ($F_{1, 148} = 0.08$, P = 0.78). But there was a significant difference between the chemical compositions ($F_{4, 145} = 5.19$, P < 0.001). Invertebrates have higher Iron (4.13 ± 0.75) and THC (17.70 ± 5.79) contents than vertebrates while vertebrates have higher Cadmium (3.47 ± 0.66), Lead (6.28 ± 1.43) and Zinc (17.09 ± 2.78) than invertebrates (Figure 3). In all vertebrates have more chemical contaminations than invertebrates.

4 Discussion

Lead concentration for Okrika and Buguma were higher than the international standard ⁽³⁷⁾ about 0.3mg/kg. This shows that during the time of sample collection there was an active oil spillage in the location. This is because the Okrika sampling site is a host to a major refinery, and has numerous crude oil pipelines that convey petrochemical products from the refinery to the wharf for evacuation by oil tankers that transport the products abroad ⁽²⁴⁾. There are thus constant spillages of crude oil into rivers in the Niger Delta as corroborated by ⁽²³⁾. In addition, to accidental spills as a result of faulty pipes, oil spillages do occur because of deliberate sabotage by locals who puncture pipelines to siphon crude oil which they sell to the black market ⁽³⁸⁾.

Moreover, it is not surprising that the highest concentration of iron was recorded at Eagle Island; this is because water contaminated with iron III frequently oozes out from the parent rock underneath to create rusty coloration on the soil surface. In the same vein, higher THC was recorded in Okrika because the area is a host to a refinery and has several pipelines ⁽³⁹⁾. The pipelines of the Port Harcourt Refining Company (PHRC) had recorded thousands of oil spillages over the years, which flow into the adjoining rivers. This leads to contamination and increase in THC as compared to other locations that have limited oiling activities. This study revealed that there is a difference in chemical concentration as one goes from highly to lowly polluted location as a result of reduction in oiling activities (Tables 1 and 2).

S. senilis (anadara) is staple seafood consumed by the local people; therefore, high concentration of THC would be hazardous to the consuming public⁽⁴⁰⁾. Anadara is a benthic organism that is often collected at the bottom of the river during low tide. Bottom dwelling habit predisposes this organism to contamination from settling pollutants from offshore oil spillages. The chemical compositions in the shell reveal the pattern of oiling activities across the three study sites, which grades from less to

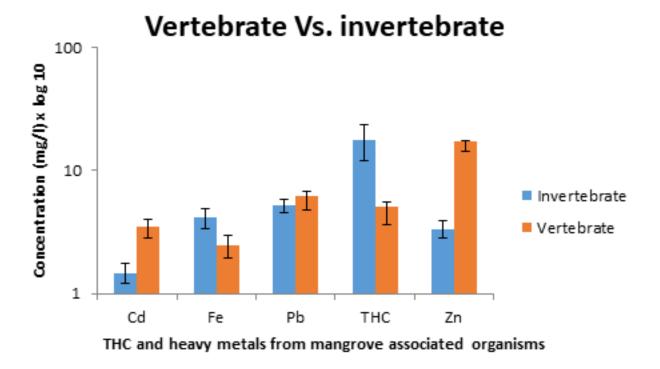


Fig 3. Concentration of THC and heavy metals in vertebrate and invertebrate mangrove associated organisms in the Niger Delta.

high pollution. Previous studies have shown that bivalves can be used to monitor heavy metals as well as detect unfavorable environmental conditions ⁽⁴¹⁾. This result agrees with the findings of ⁽⁴²⁾ on the bioaccumulation of metals in edible bivalves (*Ruditapes decussatus and Paphia undulata*) in Egypt. The value of lead in the Niger Delta (2.54-3.97 mg/kg) is higher than the result obtained in the fishing zone of south India (1.16-2.64 mg/kg) ⁽⁴³⁾. However, the Cadmium range in the Niger Delta (0.02-0.1 mg/kg) is lower than that from India (0.04-5.33 mg/kg). Bivalve especially has high heavy metal concentration because of their filter feeding habit, which makes them to gulp food materials from the bottom of the river.

C. amnicola has high concentration of lead, a poisonous substance, which is harmful to consumers ⁽⁴⁴⁾. This crab species is mainly aquatic and is caught in fishing net along with other fish species in waters of the Niger Delta that are already polluted. High concentration of lead was also reported by ⁽⁴⁵⁾ in a perturbed river in the Niger Delta. The concentration of lead and cadmium were equally above values of ⁽³⁶⁾. But both results were higher than the permissible level for cadmium (2.0 mg/kg) and lead (0.3 mg/kg) ⁽⁴⁵⁾.

Dragon flies and wasp are not typical mangroves insects, but migrate into the mangrove forest from nearby bushes and feed on smaller insects or leaves of mangroves. Feeding on leaves directly expose them to contamination by THC and heavy metals lodged in the mangroves leaves, which had been absorbed via the roots from polluted soils ^(21,46). For instance, aquatic plants such as mangroves have the capability of absorbing copper, zinc and cadmium via their root system from polluted water ⁽⁴⁶⁾. These heavy metals are in turn sucked in by piercing and sucking insects from plant leaves. Dragon flies have mandibulate mouth parts and are predatory because they feed on other smaller insects. Similarly, wasps are predators and herbivores and feed on the juice of prey or leaves. These feeding habits help to transfer pollutants across the food chain to other species. For instance, cattle egrets that feed on these insects get contaminated. The THC and heavy metal concentrations in these insects were higher than the international standards. Although, levels of the studied chemicals have not been found in previous studies, but by the FAO/WHO standard the concentration were high.

High zinc concentration in fish captured at Eagle Island is as a result of high zinc content in the water, which comes from the bedrock of the sea as reported by⁽¹⁹⁾, who revealed high zinc concentration in crab *Uca tangeri* at Eagle Island. This result is in line with the study of⁽¹⁸⁾ who revealed high concentration of lead, cadmium and zinc in tilapia and sardine caught from the Bonny River, Niger Delta. This study further showed that the operations of the Liquefied Natural Gas (LNG) project in Bonny contributed greatly to the high chemical contamination of the river. The chemically contaminated waters are in turn distributed

to other neighboring rivers by tidal currents.

Furthermore, there was high zinc concentration in the droppings of *B. ibis*, which is as a result of high zinc concentration in the study environment ⁽¹⁹⁾. Similarly, high Zinc concentration was also reported in the feathers of song bird (*Parus major*) ⁽⁴⁷⁾. This study further showed that excrement of *P. major* can be used as a biomonitor for lead, cadmium, arsenic and copper. Other studies have also found high concentration of lead and cadmium in feathers of cattle egret (*B. ibis*) in Pakistan. These authors revealed that contamination of cattle egret can lead to contamination of the cattle, which eventually gets to humans who consume the meat. The findings of this study reveal that there is a vertical heavy metal contamination across taxa from lower to higher organisms within the mangrove ecosystem.

Anadara (*S. senilis*) has the highest chemical composition because of their benthic and sedentary lifestyle that predisposes them to high chemical intake in the aquatic environment (Figure 2). They are usually found attached to mangrove tree stem, or floating objects or hard surfaces at the river bottom. Their immobility exposes them to contamination from oil spillage, which increases their absorption of heavy metals. Aquatic organisms are more exposed to pollutants than land organisms such as crabs and flying organisms such as birds and insects. This is because birds and insects take in contaminants via food and drinking water while fish and shelled organisms consume polluted food items and are bathed daily with polluted water.

Vertebrates have more chemical contamination than invertebrates along the food chain because of their higher exposure to polluted environment such as air, water and land whereas invertebrates have limited exposure from food and the environment.

5 Conclusion

Study on multiple species bioaccumulation of chemicals is important to understand the movement of pollutants up the food chain. Vertebrate and invertebrate species are significant components of the mangrove ecosystem; they are thus significant in bioaccumulation of THC and heavy metals. High level of contamination of water, soil and mangrove associated organisms is caused by numerous oil industries located in the region that constantly release crude oil and industrial waste into the aquatic and terrestrial environment. Therefore, based on the fact that a large population of biodiversity do exist in mangrove forest it is necessary to carry out constant monitoring across multiple species to determine the health status of the forest in order to prevent people from inadvertently getting contaminated when they consume seafood. Similarly, the use of terrestrial, aquatic and arboreal organisms together is a new strategy adopted in this study to determine the levels of bio accumulation at different levels of the food chain. It is therefore recommended that waste materials should be recycled rather than being dumped into the rivers. Also oil industries should do constant surveillance check of their pipelines to prevent leakages leading to oil spillages. Lastly, public health officers should do more constant checkups of seafood caught in the Niger Delta Rivers before they are sold in the market to be bought by consumers

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