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## Loads of trace metals in Biota, Sediment and Water of Southern Ijaw Creeks of Bayelsa State, Nigeria

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### Abstract

The concentrations of four trace metals Fe, Mn, Pb, and Cd were determined in water snail (*Ancylus fluviatilis*), sediments and water of five creeks in Bayelsa state. Two categories of the aquatic organisms (*Ancylus fluviatilis*) were collected from the creeks. The samples were analyzed for the metals with Atomic Absorption Spectrophotometer model 206 A. The results revealed that in category A, the levels of the metals occurred in the following range in mg/kg Fe (101.69 – 135.4), Mn (30 – 47.73), Cd (0.001 – 0.005) and Pb (4.05 – 8.06). In category B Fe (105.34 – 173.06), Mn (18.11 – 39.12), Cd (<0.001 – 0.006), Pb (0.75 – 4.08). In sediment, the following were obtained; Fe (82.53 – 735.5), Mn (11.06 – 36.1), Cd (0.001 – 0.005) and Pb (2.72 – 7.24). In water, the results were Fe (120.11 – 163.12) mg/l, Mn (7.06 – 38.05) mg/l, Cd (<0.001 – 0.002)mg/l and Pb (0.32 – 0.56)mg/l. The results revealed that the concentrations of the metals obtained in the three samples were within the WHO and USEFA permissible limit in seafood: There was no significant difference at  $p < 0.05$  in the mean concentrations of the metals in the three samples except for Pb in the two categories of (*Ancylus fluviatilis*). However, significant differences occurred between the mean concentrations of trace metals in the aquatic organism, sediment and water samples

**Keywords:** Trace metals, sediments, water snail, anthropogenic, creeks

### Introduction

Since the discovery of crude oil in commercial quantities at Oloibiri in 1956, the area has been constantly polluted with crude oil, petroleum products and effluents from industries. The entire Niger Delta Area, South-South Nigeria is faced with this problem and had caused the degradation of both terrestrial and aquatic phase of the environment. The aquatic system is mostly affected as most of the organisms have been extinct from their natural environment as a result of exploration and exploitation of crude oil. Other human activities also pollute the environment with various toxicants such as heavy metals, plant nutrients and polycyclic aromatic hydrocarbons (PAHs). Heavy metals is among the pollutants that is persistent in the environment as they bioaccumulate in many matrixes until their effect is noticed (Fuge and James, 1973, Bryan 1976, Javed and Munir, 2014) [5, 4, 6].

In the aquatic system, water is the first compartment where any pollutant gets in contacts before being partitioned to aquatic organisms and sediment. Sediments are the most sensitive components of the aquatic system and act as reservoir of the pollutants which take part in maintaining the trophic status for any water reservoir (Alexander and Young 1976 [1], Chakravarty and Patgiri, 2009) [3]. Javed and Munir, (2014) [6] reported that sediment can both act as source and sink for nutrients and heavy metals depending on the physicochemical condition such as temperature, salinity, pH and dissolved oxygen (DO). Aquatic organisms such as cockle, periwinkle, oyster, crab, water snail are non-seasonal benthos are filter feeders. They feed on phytoplankton and zooplankton and in the process they bioaccumulate toxicants, (Mason, 1991, Armstrong *et al.*, 1996) [12, 2].

In the Niger Delta area, aquatic organisms are part of the source of food. These organisms are found in both brackish and fresh water systems. Due to the activities of industries located in the area, the aquatic system of the area is polluted with various pollutants. Of these aquatic organisms, water snail (*Ancylus fluviatilis*) is found in fresh water which exhibit natural variability in physical and chemical properties due to local differences in geology and climate. They are therefore more susceptible to anthropogenic influence than the marine environment (Rainbow and Dallinger, 1993) [15].

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In the Niger Delta, seafood form part of the stable food that is consumed almost on daily bases. It is for this reason that this study was carried out to ascertain the levels of trace metals in water snail (*Ancylus fluviatilis*) in some creeks of Bayelsa state.

### Materials and Methods

Description of the study area: Korokorosei River is located in Southern Ijaw local government area of Bayelsa State on longitude 5°30 'O' E and 6° 22'30' E and latitude 4° 19'30'N and 5° 1'30'N South-South Nigeria. Korokorosei River is among the river that forms the delta plane and the river is a freshwater like Orashi, Sombrior, Sagbama and Yenegoa Rivers. These rivers flows north-south of Niger Delta into the Atlantic Ocean. The inhabitants of the area are mainly fishermen and peasant farmers, and the area is contaminated with toxicants from both natural and anthropogenic processes such as transportation in both waterway and land.

### Sample Collection

Composite samples of water, sediment and water snail (*Ancylus fluviatilis*) were collected from five sites namely; 1 (Amassoma), 2 (Ayama), 3 (Azama), 4 (Azuzuma) and 5 (Korokorosei) within three months interval for the period of one year. Two sets of similar sizes of water snails of size range 0 – 3cm, and 0 – 5cm each consisting of twenty organisms were collected. The organisms were hand picked and placed in different baskets labeled according to the sites. The sediment samples were collected with Erkman grab sampler at about 5.0cm depth and were wrapped in aluminum foil. On the other hand, the water samples were collected by dipping plastic containers that were previously washed with de-ionised water at few centimeters below the surface film of the water. Thereafter, few drops of 5M HNO<sub>3</sub> were added to the water samples to prevent chemisorption of the metal ions and were preserved in a refrigerator till the next day.

### Sample preparation and treatment

**Water snail:** Samples of the two categories of the water snail of the size range 0 – 3.0cm and 0 – 5.0cm were cracked with a stainless hard object. The entire flesh parts were taken and was separated with hand into muscles and non-edible parts. The muscles were placed on a petrish dish and oven dried at 105°C to ensure that the water content was driven off.

### Sediment

The sediment samples were air dried and then oven dried at 105°C until a constant weight was obtained.

### Water sample

About 100ml of the water sample of each site was concentrated by heating the acidified water in a 250ml volumetric flask placed in a water bath until the volume was reduced to about 25ml.

### Sample treatment and analysis

The dried samples of sediments and water snail (*Ancylus fluviatilis*) were homogenized with moltar and pestle. Thereafter, 5.0g of each sample were weight and transferred into different conical flasks and digested with a mixture of

5:15 and 15. 1:3, and heated in a water bath at 60°C for about 3hours. On the hand, the water snail samples were digested with 10ml aqua regia HNO<sub>3</sub>: HCl in 1:3.

The digest was allowed to cool to room temperature and 20ml of saturated boric acid solution was added, this was to destroy excess HF by complexation to avoid attack on glass ware, the content of each flask was then filtered with Whatman No. 1 filter paper into 25ml volumetric flasks. Each solution was made up to volume with de-ionized water, the prepared solutions were analysed for iron, manganese, lead and cadmium with Atomic Absorption Spectrophotometer model 206 A.

### Results and Discussion

The concentrations of the trace metal in different compartments of the study area are presented in Table 1 to 3. The results showed that there was variation in the concentrations of trace metals in the different matrixes, while figures 1 to 6 represents the concentrations of trace metals with sites.

**Table 1:** The mean concentration of heavy metals in water snail (*Ancylus fluviatilis*) in mg/kg Category A size range (0 – 3cm)

Site	Heavy metal			
S/N	Fe	Mn	Cd	Pb
1.	101.69 ± 62.01	30.72 ± 2.0	0.005 ± 0.000	6.64 ± 3.21
2.	189.40 ± 32.41	39.86 ± 21.06	0.001 ± 0.000	8.06 ± 2.11
3.	114.34 ± 5.21	47.73 ± 6.33	0.012 ± 0.001	5.05 ± 0.11
4.	135.4 ± 21.11	39.43 ± 11.23	0.008 ± 0.001	6.38 ± 1.22
5.	123.24 ± 17.24	37.02 ± 5.21	0.003 ± 0.000	4.05 ± 1.13

**Table1.1:** Category B size range (0 - 5cm)

Site	Heavy metal			
S/N	Fe	Mn	Cd	Pb
1.	121.09 ± 11.34	28.77 ± 3.05	0.001 ± 0.00	0.75 ± 0.10
2.	163.42 ± 1744	18.11 ± 3.62	0.002 ± 0.00	3.05 ± 1.02
3.	105.34 ± 21.02	32.07 ± 3.01	<0.001 ± 0.00	4.08 ± 0.11
4.	127.05 ± 18.12	39.12 ± 7.22	0.032 ± 0.01	4.05 ± 21
5.	113.06 ± 19.02	31.54 ± 0.94	0.006 ± 0.001	3.75 ± 0.22

**Table 2:** The mean concentration of heavy metals in sediment in mg/kg

Site	Heavy metal			
S/N	Fe	Mn	Cd	Pb
1.	110.02 ± 73.11	36.1 ± 0.7	0.005 ± 0.00	7.24 ± 3.21
2.	135.2 ± 25.01	34.03 ± 6.2	0.001 ± 0.00	4.02 ± 0.24
3.	735.5 ± 35.24	30.11 ± 3.82	0.001 ± 0.00	3.92 ± 1.04
4.	825.3 ± 41.03	21.27 ± 0.83	0.003 ± 0.000	3.11 ± 0.56
5.	134.2 ± 8.92	11.02 ± 0.45	0.005 ± 0.001	2.72 ± 0.22

**Table 3:** The mean concentrations of heavy metals in water of Korokorosei River in mg/kg

Site	Heavy metal			
S/N	Fe	Mn	Cd	Pb
1.	112.05 ± 92.03	27.09 ± 20.22	0.001 ± 0.00	0.56 ± 0.11
2.	163.12 ± 12.5	14.35 ± 3.74	0.020 ± 0.001	0.622 ± 0.21
3.	145.08 ± 45.26	38.05 ± 3.24	0.002 ± 0.01	0.41 ± 0.314
4.	120.71 ± 6.74	37.05 ± 5.66	<0.001 ± 0.00	0.32 ± 0.27
5.	130.11 ± 43.05	7.06 ± 2.76	0.002 ± 0.001	0.53 ± 0.11

**Table 4:** Paired Samples test

	Paired differences					T	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error mean	95% Confidence interval of the Difference				
				Lower	Upper			
Pair Fe for category A	6.822000	16.378163	7.324537	-13.5142	27.158175	.931	4	.404
1 Fe for category B								
Pair Mn for category A	-9.030000	9.280660	4.150437	-2.493461	20.553461	2.176	4	.095
2 Mn for category B Pair								
Cd for category A	-							
3 Cd for category B	-002600	013126	.005870	-.018898	.013698	-.443	4	.681
Pair Pb for category A	-							
4 Pb for category B	2.900000	2.459776	1.100045	-.154216	5.954214	2.636	4	.058

**Table 5:** One way analysis of variance of heavy metals (ANOVA)

	Sum of Squares	Df	Mean square	F	Sig
Fe Between Groups	215956.6	2	107978.318	2.474	.126
Within Groups	523837.1	12	43653.090		
Total	739793.7	14			
Mn Between Groups	601.071	2	300.535	2.705	.107
Within Groups	1333.228	12	111.102		
Total	1934.299	14			
Cd Between Groups	.000	2	.000	.357	.707
Within Groups	.000	12	.000		
Total	.000	14			
Pb Between Groups	79.884	2	39.942	21.507	.000
Within Groups	22.286	12	1.857		
Total	102.170	14			

**Table 6:** International guidelines for permissible limit of trace metal in food

Element	Usepa	Nafadc	Who
Cd	0.005	0.07	0.005
Cr	0.1	0.05	1.0
Cu	1.0	0.1	0.1
Mn	0.05	0.05	NA
Ni	0.1	0.01	0.001
Hg	0.02	0.01	0.3
Fe	0.3	1.6	6.0
As	6.0	NA	1
Pb	NA	NA	NA
Cu	NA	NA	NA

NA = not available.

### Trace metals in water snail

The concentrations of trace metals Fe, Mn, Cd and Pb in the two categories of water snail (*Ancylus fluviatilis*) are presented in Table 1. The results revealed that iron (Fe) had the highest mean concentrations of all the metals. The levels of iron (Fe) in the two categories of water snail (*Ancylus fluviatilis*) varied from 101.69 to 189.4mg/Kg. In the first category, the highest mean concentration of 189.4mg/kg occurred at station (2) Anyama, while the lowest occurred at station (1) Amassoma. However, in the second category of water snail, iron (Fe) occurred in the range 105.34 to 163.42mg/Kg with the least concentration at station 3 and the highest at station 5, which were Azama and Karokorosei. The concentration of Fe in the two categories of water snail (*Ancylus fluviatilis*) was independent of the stations. In other words, no particular station recorded the lowest or the highest concentration. In a similar study of trace metals in the tissue

of shellfish. (Opune *et al* 2009; Nwabueze *et al* 2001; Kpee and Nwadinigwe 2014) <sup>[14, 10]</sup> obtained similar concentrations of iron in periwinkle and catfish (*Chriysichthys nigrodigitatus*) in the Niger Delta Southern Nigeria. The concentrations of iron in the two categories of water snails (*Ancylus fluviatilis*) were independent of the sample size. The results obtained in this study agreed with the findings of Alexander and Young (1976) <sup>[1]</sup> that reported no influence of size on the metal concentration. Contrary to this, Fuge and James (1973) <sup>[5]</sup> observed a decrease in zinc concentration with increase in size of mussels. Iron is an essential element required by all organisms. In humans, elevated concentrations or chronic exposure of iron compound such as ferrous can cause kidney, liver damage and neurological effect such as convulsion. (Rainbow and Dallinger 1993) <sup>[15]</sup>.

The concentration of Fe in sediments and water followed a similar trend with the concentrations of Fe in water snail (*Ancylus fluviatilis*). In the sediment, the concentration of iron range from 110.03 to 823.3mg/kg while in water, Fe had the range 112.05 to 163.12mg/kg. Water is the first segment of the aquatic medium where any pollutant comes in contact with before being partitioned to other phases. The sediment acts as a trap for the heavy metals, being distributed to the water column, zooplankton and phytoplankton. According to Fuge and James, (1997), Marcus and Jack (2016) <sup>[11]</sup>, sediment accumulates more material than water and biota (aquatic organism) even when the source of pollution has been stopped or controlled. Figure 2 showed the variation of iron with sites, it revealed that station 2 (Ayama) had the highest concentration of iron in the two categories of *Ancylus fluviatilis*

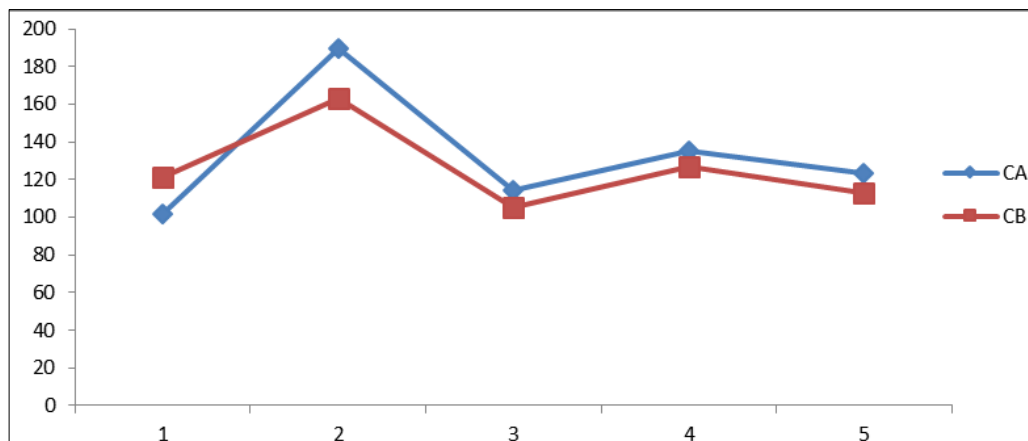


Fig 1: Concentration of iron (Fe) in two categories of water snail

Manganese is an essential metal to human and other organisms as it is required for the metabolism of cells. The concentration of manganese is shown in Table 1 to 3. The mean concentration of manganese in category A of water snail (*Ancylus fluviatilis*) occurred in the range 30.72 to 47.73 mg/Kg and 18.11 to 39.12mg/Kg in category B size range (0 - 5cm). The results revealed that category A had higher mean levels of Mn when compared to category B. The mean levels of Mn in water snail (*Ancylus fluviatilis*) is quite different from that of iron, the larger size (0 - 5cm) had highest concentration of iron than the smaller size (0 - 3cm) Table 1. The mean levels of Mn in water snail agreed with the findings of Fuge and Jame (1973) [5] and Kpee *et al*, (2000) [8] in shellfish Dogwhelk (*Thais haemostoma*). The concentration of Mn in sediment is shown in Table 2. The results revealed that manganese occurred in the range 11.02 to 36.1mg/Kg. The results showed that station (1) Amassoma had the highest

mean concentration of Mn  $36.1 \pm 0.7$ mg/Kg. However, in category A of the water snail (*Ancylus fluviatilis*), a contrary results was obtained where the lowest concentration of Mn  $30.72 \pm 2.0$ mg/Kg was reported at station 1. The levels of Mn in water samples of the stations is shown in Table 3; the mean concentration range from 7.06 to 38.05mg/l with the highest concentration at station (3) Azama and the lowest at station (5) Karokorosei. Manganese is widely distributed in the earth crust mostly in igneous, sedimentary and metamorphic rock. Permissible levels of and manganese in the environment do not pose a threat to man and mammals. However, elevated or chronic exposure can result to psychiatric disorder, including impairment, disorientation and speech disturbances. Manganese is used in many materials that are commonly found in the environment such as, paints, electronic and alloys. This implies that the major source of manganese in the environment is anthropogenic.

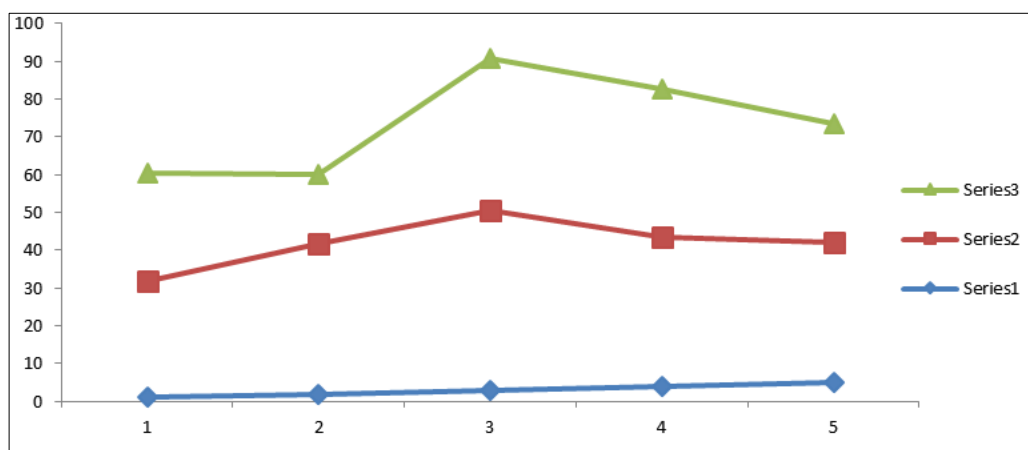


Fig 2: Concentration of manganese in two categories of water snail

The mean concentration of cadmium is shown in Table 1 to 3. The results revealed that low concentration of cadmium (Cd) was reported in the three samples, water snail, sediment and surface water. In the water snail (*Ancylus fluviatilis*); the mean concentration in category A of size range (0 - 3cm) occurred in the range 0.003 to 0.012mg/Kg. Location (3) Azama had the highest concentration whilst location (5) Korokorosei had the lowest, while in the sediment, cadmium had the range 0.001 to 0.095 mg/Kg. On the other hand, the mean concentration of cadmium in water occurred in the range <0.001 (BDL) to 0.002mg/l. Generally, low concentration of cadmium was obtained in all the samples (water snail, sediment and water) investigated in this study.

The low concentrations of cadmium in these samples may be attributed to the fact that, the metal is not found in nature, rather, it is distributed to the environment as a result of anthropogenic activities such mining of ores, manufacturing of household materials, exploration and exploitation of crude oil. The study area is very close to where crude oil was first discovered in Southern Ijaw. However, low concentrations of cadmium in the environment, may be attributed to the fact that, the bunkery activities and other oil companies operating in area have no impacts on the levels of cadmium. A similar results were obtained by several researchers in the area, (Kakulu, 1985 Kpee and Nwadinigwe 2014 [7, 10], and Marcus and Jack 2016) [11].

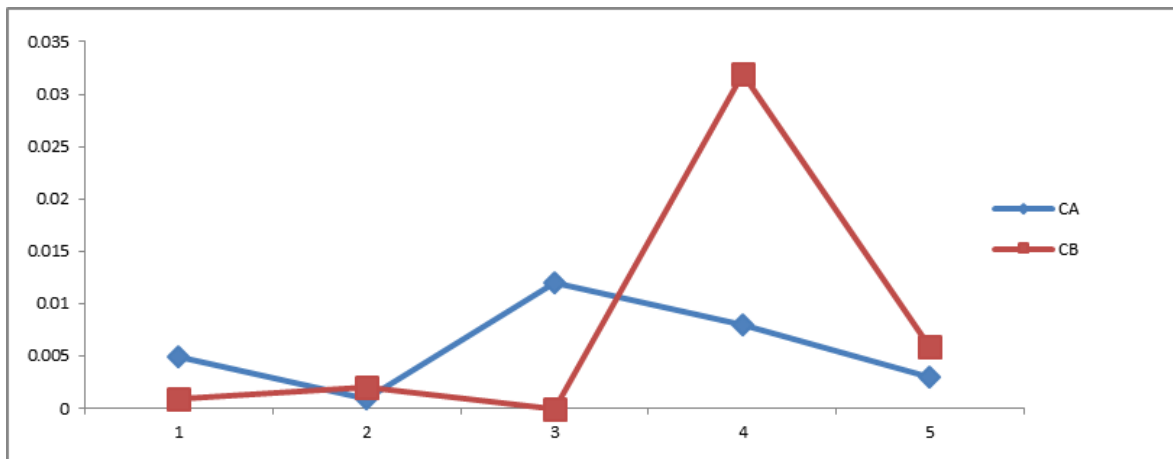


Fig 3: Concentration of cadmium (Cd) in two categories of water snail

The mean concentration of lead (Pb) is shown in Table 1 to 3. The results revealed that Pb occurred in the range 4.05 to 8.06mg/Kg in category A of the size range (0 – 3cm) and in category B (0.-5cm). The concentrations occurred in the range 0.75 to 4.08 mg/Kg. In the sediment, the range was 2.72 to 7.24 mg/Kg while in water the range of 0.3 to 0.62 mg/kg levels of Pb was obtained. The concentration of lead (Pb) in the samples varied with the stations, no particular station had the highest and the lowest concentrations of the metals. Lead is an example of non-essential metal that is not required by any organism. It is mostly distributed to the environment as a result of human activities. Some sources of Pb to environment include transportation; paint, crude oil, alloys and lead based products such accumulated motor batteries. An appreciable concentration of lead was obtained in water snail (Table 1). This result agreed with the finding of Kakulu (1985) [7] who

obtained a maximum lead level of 6.4 mg/Kg in fish of the Niger Delta, a maximum of 3.800 mg/Kg was reported by Kpee *et al* (2009) [9] of Ipo stream while Marcus and Jack, (2016) [11] obtained a maximum concentration of 52.48 mg/Kg in pumpkin (*Telfeiria occidentalis*). Lead is distributed through anthropogenic activities and elevated levels of lead (Pb) in human may cause many disorder and diseases. According to Waldichuk, (1980), food intake by man contribute to about 92% of lead, while drinking water and air contribute 6% and 2% respectively. Lead (Pb) has great affinity for the carboxyl groups of the glutamic and aspartic acids, the sulphur hydryl groups of cystein and phenoxy groups of tyrosive whether present in protein, cell membranes or enzyme system as was reported by Standslead, (1977).

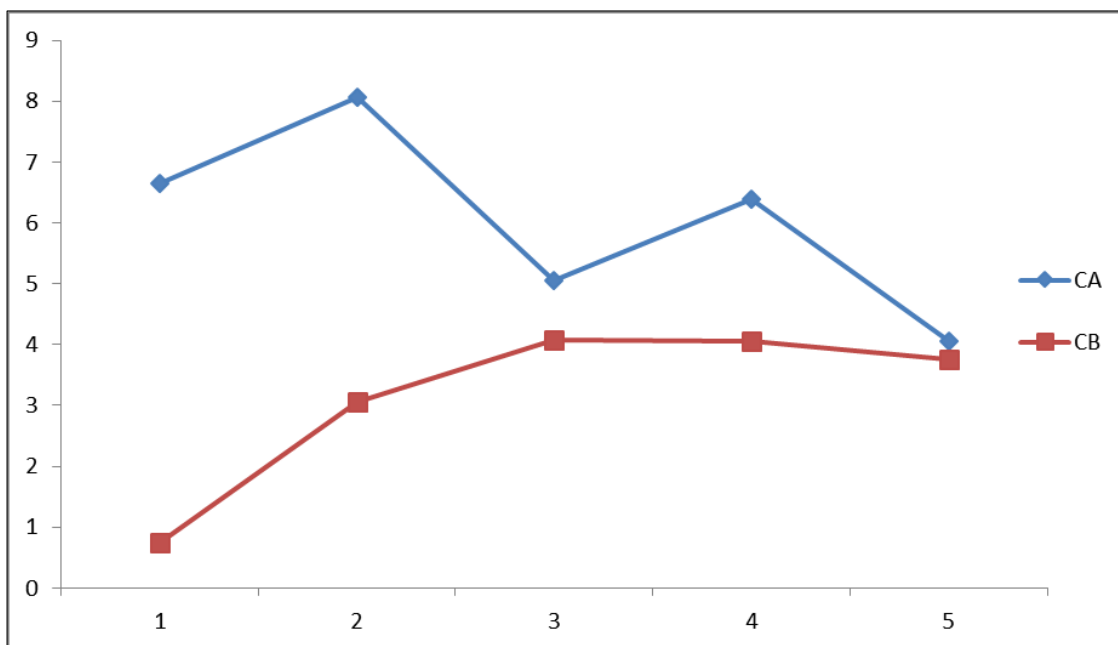


Fig 4: concentration of lead (Pb) in two categories of water snail

The results of students T-test revealed that there was no significant difference in the mean concentrations of (Fe, Mn, Pb and Cd) in the two categories of water snail (*Ancylus fluviatilis*) examined Table 4. However, the results of ANOVA revealed significant difference in the mean levels of lead in the samples. On the other hand, post Hoc Test (PHT) revealed significant difference among water snail, water and

sediment. In category A of the water snail (0 – 3cm), the trace metals occurred in following order Fe > Mn > Pb > Cd. A similar order was reported in category B of the water snail. This trend of the distribution of trace metals in the two categories of the water snail may suggest that the metals might have emanate from the same sources such as waterway transportation, dumping of household waste into the river and

spillage of crude oil from pipeline and vessels that carried crude oil and other petroleum products to and from Brass river terminal. The overall mean concentration of metal in the three sample indicated that the metal occurred as in the following order Fe > Mn > Pd > Cd. The results revealed that, the essential elements Fe and Mn had elevated concentrations when compared to the non-essential metals Pb and Cd. The mean levels of the metals (Fe, Mn, Pb and Cd) obtained in the three samples were within the permissible levels recommended by WHO, NAFDAC and USEPA in food.

### Conclusion

The results of the study revealed that the two categories of the water snail (*Ancylus fluviatilis*) investigated showed that both have the mean concentration of the trace metals in the following decreasing order of magnitude Fe > Mn > Pb > Cd. The students T-test revealed no significant difference in the mean levels of metals in the samples. However, there was significant difference in the mean levels of metals among the samples with respect to Pb at  $p < 0.05$  and the levels of metal in the samples occurred in the order; water snail > sediment > water. The study also revealed that the mean concentrations of metals varied with the stations, where no particular station had the highest or least concentrations of the metals. Rather, the concentration fluctuates from one station to the other. The results revealed that appreciable levels of lead (Pb) were reported in all the samples and this implies that lead (Pb) may have contaminated the environment. The consumer of water snail (*Ancylus fluviatilis*) from the river may suffer of diseases caused by Pb contamination.

Based on the results obtained in this study, the researchers would recommend that

1. More research should be carrying out on the area to examine the concentration of trace metals and other pollutants.
2. The inhabitants of the area should be educated against dumping domestic and waste-water directly into the river.
3. The government should mandate oil companies operating in Bayelsa state to clean up the area.
4. The Federal Ministry of Environment should enact law that will guide the operation of oil companies in the Niger Delta area.

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