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# **Heavy Metal Profiles of Sediment, Macrophytes and Water Quality Parameters of the Stream in Adekunle Ajasin University Fish Farm, Akungba- Akoko.**

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# *A b s t r a c t*

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*Both natural and human activities contribute to the bioaccumulation and transfer of heavy metals, along the food chains resulting in significant environmental and health implications. The worldwide issue of heavy metals contamination in plants and water requires attention, as elevated levels of heavy metals can be extremely harmful to both plant and animal life. In this study, the physico-chemical parameters and heavy metals of water, sediments, and macrophytes from the stream flowing through Adekunle Ajasin University, Akungba-Akoko (AAUA) fish farm were analyzed. The water's physico-chemical parameters were within permissible limits, except for a few parameters such as total dissolved solids, temperature, and electrical conductivity values that were lower than the WHO recommended values. Heavy metals analyses revealed that Zn, Cu, Cr, Ni, Co, and Fe were within the permissible limits, while Mn and Pb exceeded the limits in the water samples. Sediments and macrophytes samples showed that the following Cd, Cr, Cu, Pb, and Fe were above the World Health Organization's (WHO) permissible limits. Conclusively, the water in the stream flowing through AAUA fish farms and Akungba community is suitable for fish culture. However, considering the higher values of sediment and macrophytes beyond permissible limits, it is crucial to broaden the approach beyond continuous monitoring of heavy metal levels through standard assessment studies. The findings presented by this study highlight the need for increased education and awareness regarding the effects of unwholesome anthropogenic activities along the stream.*

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## **INTRODUCTION**

In recent years, the concentrations of heavy metals in aquatic water bodies are reaching unprecedented levels, resulting in worldwide deterioration of water qualities in various water bodies. This is caused by various antropogenic and industrial activities such as: domestic waste, urban sewage and storm water runoff, ex cetera (Zhixiu *et al,* 2014). The pollution of the aquatic environment caused by heavy metals is a growing problem globally and has reached an alarming rate (Bashir *et al*, 2020).

According to Ngumbu (2014), heavy metals are metallic chemical elements that have a high density and can be toxic or poisonous even at low concentrations. Examples of heavy metals include mercury, cadmium, arsenic, chromium, thallium, and lead. Although some heavy metals like copper, iron, zinc, manganese, and selenium are necessary for maintaining human body metabolism as trace elements, their excessive concentrations can cause poisoning (Lenntech, 2014). Heavy metal pollution is of primary concerns, especially in aquatic systems, where their levels have gradually increased due to anthropogenic sources (Oluyemi and Olabanji, 2011).

## Unlike

most organic pollutants, heavy metals exhibit persistence in the environment and are not easily eliminated through biodegradation or chemical means (Briffa *et al*, 2020).

Fish become enriched with accumulated substances and eventually, it's consumed by humans who inevitably suffer from the effects of an enrichment process that takes place at different trophic levels (Zhuang *et al*., 2018). Within aquatic ecosystems, there is an ongoing process of deposition whereby heavy metals permeate waters and subsequently accumulate within various organisms inhabiting them (Mitra, *et al*, 2022). Through the process of bioaccumulation via the food chain, these substances can become potentially toxic to humans as the accumulation can reach significantly high levels, resulting in lethal effects such as renal failure, autism in children, premature births and heart failures (Briffa *et al*, 2020).

Sediments typically represent the ultimate impact of both natural and anthropogenic components of the environment. Sediment quality can serve as an effective indicator of water pollution, as it tends to accumulate heavy metals and other organic pollutants (Samir and Ibrahim, 2008). To measure the concentrations of heavy metals in aquatic ecosystems, scientists typically analyze their levels in water, sediments, and macrophytes present in the aquatic environment. Moreover, sediment significantly contributes to the remobilization of contaminants in aquatic systems.

Plants absorb heavy metals from the soil, and these metals predominantly accumulate in their roots. Some portions of these metals are then transported to other parts of the plant. Aquatic plants are often employed in water quality studies to monitor heavy metals and other pollutants present in water and submerged soil. Because of their selective absorption of certain ions and their sedentary nature, such plants are well-suited as biological monitors (Sawidis *et al*., 1995). Therefore, this study aims to evaluate the concentration levels of heavy metals in the water, sediment, and macrophytes found in the stream that serves as a source of water for fish culture at AAUA farm.

# **MATERIALS AND METHODS**

# **Sample Collection:**

The different samples were collected from the AAUA fish farm in Akungba-Akoko, Ondo State at three (3) different depths: below the water surface, mid-water column, and the bottom of the water body. Surface water samples were collected in labeled sterile containers and immediately transported to the laboratory for analysis. Bottom sediment samples were collected in sterile polythene bags, kept in a chilled icebox, and transported to the laboratory for heavy metal determination. All plants were hand-cropped, carefully rinsed to eliminate adhering soil and mud,

and to discard decayed and dead plants. The plant samples were stored in sterile polythene bags and transported to the laboratory for analysis.

# **Physicochemical analysis of the Samples**

The water quality parameters were analyzed on each depth location in-situ using the Hydro lab water quality meter, specifically the Electronic Probe Type Hanna H198106 model. These measurements were performed in triplicates on each sampling site by lowering the Hanna probe vertically into the water bodies. The parameters that were measured include temperature (°C), pH, conductivity (m $\Omega$ /cm), dissolved oxygen (ppm), salinity  $(\%)$ , and total dissolved solids (ppm). Insitu colorimetric test kit methods (Pond Lab 200) were utilized to determine values for total water hardness (ppm), alkalinity (ppm), ammonia (ppm), and nitrate concentrations (ppm) respectively.

Water samples were also collected in transparent, well-labeled bottles and transported in ice-chest containers to the laboratory for chemical analysis. A titrimetric method was used to analyze for sulfates (ppm), carbonates (ppm), and phosphates (ppm). Other ionic constituents of the river systems, such as Na+, K+, and Ca+, were determined using a flame photometric method, specifically the PG Flame Photometer equipment with Model number FP902. The presence of chloride ions (CI-) was determined using the Argentometric method, and heavy metals, such as magnesium, iron, cobalt, manganese, copper, cadmium, nickel, zinc, and lead, were determined using a metal detector Atomic Absorption Spectrophotometer, specifically the Bulk Scientific AAS with Model Number 210 VGP, analytical procedures (AOAC, 2010).

# **Analysis of heavy metals in samples**

**Digestion of Water Samples:** 4 mL of concentrated HCl (10 M) was added to 250 mL of each water sample placed in a 600 mL beaker, and evaporated to 25 mL. The concentrate was then transferred to a 50 mL volumetric flask and diluted to the mark with deionized water. Prior to this process and further analysis, the solutions were filtered through Whatman number 42 filter paper in accordance with Olowu *et al*. (2010). At each step of the digestion process of the samples, acid blanks (laboratory blanks) were performed using an identical procedure to ensure that the samples and chemicals used were not contaminated. They all contained the same digestion reagents as the real samples with the same acid ratios. After digestion, acid blanks were treated as samples and diluted with the same factor. They were analyzed by atomic absorption spectrophotometry before the real samples, and their values were subtracted to

ensure that the equipment read only the exact values of heavy metals in real samples. Each set of digested samples had its own acid blank and was corrected using its blank sample. **Digestion of sediments sample:** 2.0 g of the sediment sample were weighed and poured into a beaker. 5 mL of hydrogen trioxonitrate (V) acid (HNO<sub>3</sub>) were added, together with 2 mL of perchloric acid (HClO<sub>4</sub>) and 5 mL of hydrogen fluoride (HF). The mixture was then heated for 1 hour on a heater at 160°C. After proper digestion, the sample was allowed to cool down and filtered. The filtrate was then transferred into a 100 mL volumetric flask and made up to the mark with distilled water. The prepared sample solution was later transferred into pre-cleaned labeled sample bottles in readiness for Atomic Absorption Spectrophotometer (AAS) analysis.

The Flame Atomic Absorption Spectrometer (FAAS; Perkin Elmer HGA-600) was employed for the analyses of zinc, iron, manganese, cadmium, chromium, copper, lead, cobalt, and nickel after sample extraction in acid solution (Daniel & Mathew, 2016). The analyses for each metal were done in triplicates.

**Stream Sediment Analysis** The textural and chemical analyses of stream sediments across the sampling locations were conducted by analyzing the bulk density, textural classifications, pH, and organic matter compositions of sediment samples. These samples were collected and analyzed using the methods of Wei *et al* (2019). River sediment samples were collected in triplicate at each of the three (3) sampling locations using a sediment scraper (Hoskin Scientific Equipment, model number: E-411-175- D40). The sediment samples were then poured into well-labeled black polyethylene bags and placed in lidded, dark-colored plastic containers before being transported to the laboratory for subsequent analyses.

**Statistical Analysis:** All data generated were analyzed statistically using one-way ANOVA to obtain the mean and standard deviation. SPSS statistical software (Version 17.0 for Windows; SPSS Inc., Chicago, USA) was used for the analysis. Significant differences were determined at  $(p<0.05)$ .

## **RESULTS**

The concentration of heavy metals in water from the stream at AAUA Fish Farm is presented in Table 1. No regular pattern was observed for the presence of heavy metals across all the sampling points. The concentration of Zinc at all sampling points were well below WHO permissible limits. The highest



**Plate 1: A map of Adekunle Ajasin University showing the sampling site**

concentration of Zinc (0.71mg/l) was recorded midstream with the lowest value of 0.44mg/l recorded downstream. Concentration of Iron at the upstream sampling point was the highest while the lowest was recorded downstream with values of 0.21mg/l and 0.14mg/l respectively. Manganese in the water body exceeded WHO permissible limit at all sampling points. The highest concentration of 0.6mg/l was recorded midstream while the lowest value of 0.33mg/l was recorded upstream. Chromium and lead also exceeded WHO limits across all sampling points. However, Copper, Cadmium, Nickel and cobalt all had values within WHO permissible limit at all sampling points. Interestingly, Cadmium had a negligible value at midstream sampling point, but was not detectable at both upstream and downstream sampling points.

Table 2 shows the concentration of heavy metals in sediments from the stream at AAUA Fish Farm. The amount of heavy metals at all sampling points did not follow the same trend as was found in the water column. With the exception of iron (Fe), the concentration of heavy metals in all the sediments sampled from various points met the standards set by the WHO, (2013). The highest concentration of 238.35mg/kg was recorded upstream, the least value of 180.13mg/kg was recorded midstream.

The concentration of heavy metals in selected plant species at AAUA Fish Farm is presented in Table 3. All three macrophytes had some level of heavy metal presence. Cd and Fe both had concentrations exceeding limits set by the WHO, (2013). Whereas, Zn, Mn, Cu, Ni and Co all had concentrations not exceeding WHO limits. Table 4 shows the Physicochemical parameters of water from the stream in AAUA Fish Farm. All the physico-chemical parameters analyzed were within optimum range for aquaculture except the temperature of the water which was generally low across all sampling points. The highest temperature of  $25.41\textsuperscript{0}\text{C}$  was recorded downstream while the lowest temperature of  $21.12 \text{ °C}$ was recorded upstream.

Metals	Upstream (mg/l)	Midstream (mg/l)	Downstream (mg/l)	Who limits (mg/l)
Zn	$0.50 \pm 0.01^b$	$0.71 \pm 0.00^a$	$0.44 \pm 0.02$ <sup>c</sup>	75
Fe	$0.21 + 0.01^a$	$0.18 \pm 0.23^b$	$0.14 \pm 0.01$ <sup>c</sup>	0.3
Mn	$0.33 + 0.01$ °	$0.61 + 0.00^a$	$0.52+0.01b$	0.1
Cr	$0.17 \pm 0.01^a$	$0.17 \pm 0.02^a$	$0.13 \pm 0.01^b$	0.05
Cu	$0.23 \pm 0.00^b$	$0.26 \pm 0.01^{\text{a}}$	$0.16 \pm 0.01$ <sup>c</sup>	
Pb	$0.09 \pm 0.00^a$	$0.06 \pm 0.01$ <sup>c</sup>	$0.07 \pm 0.00^b$	0.01
C <sub>d</sub>	ND	$0.00+0.00$	ND.	0.003
Ni	$0.01 \pm 0.00^b$	$0.02 \pm 0.00^a$	$0.00 \pm 0.00$ <sup>c</sup>	0.02
Co	$0.01 \pm 0.00^b$	$0.04 \pm 0.00^a$	$0.01 \pm 0.00^b$	0.05

**Table1: Concentration of Heavy Metals in Water from the stream at AAUA Fish Farm.**

a, b, c=indicate that means on the same row but with different superscripts are statistically significant (P<0.05) Zn=Zinc, Fe=iron, Mn=manganese, Cr=Chromium, Cu=Copper, Pb=lead, Cd=Cadmium, Ni=Nickel, Co=Cobalt, ND=No Detection





a b, c=indicate that means on the same row but with different superscripts are statistically significant (P<0.05) Zn=Zinc, Fe=iron, Mn=manganese, Cr=Chromium, Cu=Copper, Pb=lead, Cd=Cadmium, Ni=Nickel, Co=Cobalt.





a,b,c=indicate that means on the same row but with different superscripts are statistically significant (P<0.05)

Zn=Zinc, Fe=iron, Mn=manganese, Cr=Chromium, Cu=Copper, Pb=lead, Cd=Cadmium, Ni=Nickel, Co=Cobalt.

		<b>LOCATIONS</b>		
<b>PARAMETERS</b>	<b>UPSTREAM</b>	<b>MIDSTREAM</b>	<b>DOWNSTREAM</b>	<b>WHO Limits</b>
Temperature $(^0C)$	$24.12 \pm 0.00$ <sup>c</sup>	$24.34 \pm 0.01^{\rm b}$	$25.41 \pm 0.00^a$	$28 - 32$ ( <sup>0</sup> C)
pH	$7.32 \pm 0.32^b$	$7.46 + 0.08a$	$7.00+0.00^{\circ}$	$6.5 - 8.5$
Salinity (ppt)	$0.00 \pm 0.00$	$0.00 \pm 0.00$	$0.00 \pm 0.00$	
Conductivity $(mN(M))$	$0.047 + 0.00^a$	$0.040 + 0.03$ <sup>c</sup>	$0.046 \pm 0.00^b$	$1000$ (mN $(M)$ )
Dissolved oxygen (ppm)	$10.87 + 0.22^b$	$10.93 + 0.11^a$	$10.62 + 0.16^c$	5 (Minimum)
Water hardness (ppm)	$71.20 \pm 0.00^{\rm b}$	$71.54 + 0.00^a$	$71.20 + 0.00b$	$0.001$ (ppm)
Alkalinity (ppm)	$89.00 \pm 0.00^a$	$86.01 \pm 0.00^b$	$89.00+0.00^a$	$200$ (ppm)
Total dissolved solid (ppm)	$12.67 \pm 1.53^b$	$13.00 \pm 0.67$ <sup>a</sup>	$11.43 \pm 1.41$ <sup>c</sup>	$500$ (ppm)
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**Table 4: Physico-chemical Parameters of Water from the Stream in AAUA Fish Farm**

a, b, c=indicate that means on the same row but with different superscripts are statistically significant  $(P<0.05)$ Zn=Zinc, Fe=iron, Mn=manganese, Cr=Chromium, Cu=Copper, Pb=lead, Cd=Cadmium, Ni=Nickel, Co=Cobalt.

## **DISCUSSION**

The results of the physico-chemical parameters of the water samples from AAUA Fish Farm are within the permissible limits, except for total hardness and total dissolved solids. The pH values are near the neutral point, which is optimal for fish production and in contrast to what Olagbemide and Owolabi (2019) obtained in water samples from Ureje, Egbe, and Ero dams, all in Ekiti State. The temperature range obtained downstream is within the desirable limits of 24.94°C to 30.68°C for aquaculture, as reported by Phelps and Popma (2000). While the temperature upstream and midstream were below desirable limits. Tropical fishes have been reported to exhibit slower growth rate at temperatures below optimum. The dissolved oxygen (DO) was higher than 5mg/l, which could adversely affect aquatic life if it falls below this concentration (Rao, 2006). Therefore, the result of this work when compared with WHO standards (5mg/l) indicates that the water body contains dissolved oxygen which is at the range ideal for aquaculture. It will not pose a serious threat to the survival of the aquatic biota and may be used for other agricultural and domestic activities (Rao, 2006).

The concentration of total dissolved solids was found to be highest at the midstream, measuring 13.00 mg/L. It is important to note that this value is significantly lower than the WHO standard range for drinking water, which indicates portability and ranges from 1000 mg/L to 1600 mg/L. However, TDS values in the various sampling points were quite low and "permissible" according to WHO standards (2012), but contrary to the observations of Ladipo *et al*. (2011), who reported values reaching up to 24,896 mg/L. The alkalinity values ranged from 86.01- 89.00 mg/l, which is within the recommended range for drinking water (30 to 400 ppm), but contrary to Boyd's (1982) recommendation for plankton production, which was 20-50 ppm. The observed electrical conductivity values were very low when compared with the findings of Fakayode (2005), who observed high electrical conductivity in Alfaro stream, Ibadan.

## **Zinc**

Zinc plays a vital role in the physiological and metabolic processes of many organisms. The concentration of Zn was highest in the water samples collected midstream  $(0.71\pm0.00$ mg/L) and lowest at downstream  $(0.44\pm0.02 \text{ mg/L})$  which is below the Maximum contaminant level (MCL) of 5 mg/L recommended by USEPA (2009). This level of Zn indicates low anthropogenic activity on the farm. The sediments across all three sampling points had Zn concentrations ranging from  $0.82 \text{ mg/L}$  to  $1.21 \text{ mg/L}$ . The concentration of Zn across the sampling points did not follow the same trend as in the water samples which may be due to differences in the abundance of biota at each sampling point. This is in agreement with the report of Makinde *et al*. (2015) who reported low contamination of Zn in streams and sediments of gold mining areas of southwestern Nigeria. The macrophytes sampled also had similarly low levels of Zn, as with the sediments. This is in contrast to the work of Nirmal *et al*. (2008), who reported the concentration of Zn in selected macrophytes to be half the concentration in sediments.

#### **Iron**

The concentration of iron (Fe) recorded in the water samples ranged from  $0.14 \text{ mg/L}$  to  $0.21 \text{ mg/L}$ , while in the sediments, it ranged from 180.13 mg/kg to 238.35 mg/kg. These values are much lower than those reported by Malami *et al*. (2014) in a study conducted at the Challawa Dam in Kano. The obvious sources of Fe in the water samples may be natural contamination from weathering processes of the soil, leachates from waste dumps, and municipal drain waters flowing into the stream, as suggested by Amoo *et al*. (2004) in their evaluation of heavy metals in fishes, water and sediments of Lake Kainji, Nigeria. However, the Fe contents in all the sediments (183.x50mg/kg – 238.x35mg/kg) are higher than the permissible limit of 131-150 ppm for sediments recommended by the World Health Organization (WHO) in 2013.

#### **Manganese**

Manganese occurs in surface waters that are low in oxygen. Manganese can be released into the atmosphere by both natural and anthropogenic processes, mostly in the form of coarse particles through wind erosion, road dust, agricultural activities, building activities and quarry processes. The Manganese concentrations of water and sediment samples in this study ranged from  $0.33\pm0.01$  mg/L to  $0.61 \pm 0.00$  mg/L and  $0.53$  to  $0.81$  mg/kg. These concentrations are slightly above the recommended MCL for Mn by USEPA (2009) and and below permissible limit of 20 mg/kg set by (WHO,2013) respectively.

#### **Chromium**

The concentrations of Cr were  $0.13\pm0.01$  mg/L downstream and as high as 0.17±0.01 mg/L upstream at the sampling points. These values were higher than the  $(MCL)$  of  $\overline{0.1}$  mg/L recommended by USEPA (2010) for unpolluted water. This may be due to the discharges of agricultural wastes into the stream, because the source of the water been used in the AAUA Fish Farm is surrounded with farms Fish Farm is surrounded with farms cultivated by the community or as a result of cassava processing and cloth washing effluents as suggested by Ehiemere *et al*. (2022). Chromium concentrations found in the macrophytes ranged from 1.26 mg/kg to 1.47 mg/kg, T these values are lower than the values of 12–13 mg/kg stipulated by USFDA (2017).

## **Copper**

Copper was detected in water from all the sampling points, with the highest concentration of 0.26mg/l found midstream. Although the concentration of copper detected across all sampling points is below the 2mg/l limit set by the USEPA (2010), the presence of copper in the water samples may be attributed to the use of copper-rich attributed to the use of copper-rich herbicides/algaecides, as suggested by Ehiemere *et al*. (2022). Concentrations of copper in both the sampled sediments and macrophytes were below the recommended limits set by WHO (2003).

#### **Lead**

The concentrations of Pb in the water samples were above the recommended MCL for Pb, which was 0.0015 mg/L (USEPA, 2010). A probable source of the high lead concentration could be from used drycell batteries and tires from dump sites, as suggested by Lawson (2011). The sediments also had high lead concentrations ranging from 0.18 mg/L to 0.21 mg/L, which are lower than the values reported by Adekoya *et al*. (2006) in the Ojora River, Lagos State. However, the lead concentrations in the sediments are within the WHO recommended value of 1 ppm. There were non-detectable levels of lead concentrations in the Macrophytes collected from the sampling points.

#### **Cadmium**

Cadmium was not detected or was present in negligible amounts in all water samples collected. However, the sediments had some level of cadmium, ranging from 0.03mg/kg to 0.08mg/kg across all sampling points. The concentration of cadmium detected in all sediments was below the 4.9mg/kg limit recommended by WHO (2003). The limit recommended by Macrophytes sampled had cadmium concentrations ranging from 1.45mg/kg to 1.55mg/kg. Interestingly, the Macrophytes had a higher concentration of cadmium than both the water and the sediments. This may be due to the Macrophytes acting as sinks and accumulating cadmium over time, as suggested by Nirmal *et al*. (2008).

#### **Nickel**

Nickel is considered an essential trace element for human and animal health (Zigham *et al*., 2012). Water samples collected downstream showed negligible amounts of nickel, while concentrations of 0.01mg/L and 0.02mg/L were recorded upstream and downstream, respectively. The maximum permissible limit for nickel in water is 0.2 mg/L, and the concentration of nickel in the water samples collected was below this limit. The observations of this research is in agreement with Ruqia *et al*. (2015) report on the accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water, and plants, as well as the analysis of physicochemical parameters of soil and water.

The sediments had nickel concentrations ranging from 0.12mg/kg to 1.10mg/kg across the sampling points, while nickel concentration in the macrophytes ranged from 0.29mg/kg to 0.34mg/kg. The higher concentration of nickel in the sediments and macrophytes might be due to the fact that heavy metals have a tendency to be absorbed in living tissues or bottom sediments, rather than being carried around in water, as suggested by Alagoa (2019).

#### **Conclusion**

In conclusion, this study demonstrates that the physico-chemical parameters of the water in the stream been used in Adekunle Ajasin University, Akungba - Akoko Fish Farm are favorable for fish production. The majority of the physico-chemical parameters were found to be within the stipulated range for fish production, indicating that the water quality is suitable for fish growth and survival.

Moreover, the results indicate that heavy metal pollution on the farm is not severe. Only three heavy metals: lead, chromium, and manganese, were found to have concentrations above permissible limits. This

suggests that there is a need for regular monitoring of the water quality to prevent any further increase in heavy metal concentrations, which could adversely affect the aquatic ecosystem.

To ensure sustainable fish production, it is recommended that the University farm management implements proper waste management practices to prevent heavy metal contamination of the stream. Additionally, continuous monitoring and periodic assessment of the water quality should be conducted to ensure that the physico-chemical parameters remain within the acceptable range for fish production.

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