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TPH And Heavy Metal Analysis Of Petroleum Hydrocarbon Soot Within Aluu Farmed And Feral Aquatic Environment

[1*]Ike-Obasi, J. C., [2]Ezejiofor, T.I.N., [2]Osujgwe., D. I. A & [3]Mgbemena, I. C.

[1]Africa Regional Aquaculture Centre Aluu/Nigerian Institute for Oceanography and Marine Research Lagos, Nigeria
[2&3]Federal University of Technology, Owerri, Imo State, Nigeria
***Corresponding author email: judithikeobasi@gmail.com**

ABSTRACT
The presence of TPH and heavy metals (Copper, Nickel, Lead, Barium, Zinc, Mercury, Cobalt, Chromium, Arsenic, and Cadmium) in aquatic ecosystems remains an issue of public health concern especially in most developing countries like Nigeria. At low concentrations above threshold limit, they are poisonous and can lead to toxicity in humans. The present study was undertaken to evaluate levels of petroleum hydrocarbon soot and heavy metals in Farmed and Feral Nile Tilapia (*Oreochromis niloticus*) from Aluu with Mbaise as control site. Soot samples were collected monthly from the locations for six consecutive months between May and October, 2022 and analyzed. At each sampling month, soot samples were randomly collected monthly per site. The homogenized samples were acid digested and analyzed for selected heavy metals (Pb, Cr, Cu. Ni, Ba, Zn, Co, As, Cd and Hg) using MPAES (Micro Plasma Atomic Emission Spectrophotometer) and compared with WHO permissible limits. Results revealed varying concentrations of heavy metals across the feral and farmed soot samples. Copper concentrations were slightly higher in feral soot (1.728) compared to farmed soot (1.719), while nickel showed negligible differences (2.536 for feral, 2.537 for farmed). Lead concentrations remained consistent (0.45) in both feral and farmed samples. Barium concentrations were markedly higher in feral soot (2.39) compared to farmed (0.4), while cobalt displayed a similar trend with feral soot at 0.3 and farmed soot at 0.029. Chromium concentrations were nearly identical (1.129 for feral, 1.128 for farmed), and arsenic concentrations were below detection limits for both groups. Cadmium concentrations showed minimal differences (0.025 for feral, 0.024 for farmed), whereas zinc concentrations were significantly elevated in feral soot (2.057) compared to farmed soot (0.057). Mercury levels were slightly higher in feral soot (9.9) than farmed soot (9.742). Regarding TPH concentrations, both feral and farmed samples displayed comparable levels across the months. In May, TPH concentrations were 34.8488 for farmed and 34.895 for feral. June showed higher TPH concentrations, with 56.467 for farmed and 57.156 for feral. July had lower concentrations (12.6753 for farmed, 12.676 for feral), while September indicated elevated levels (100.37 for farmed, 100.57 for feral). October and November exhibited consistent TPH concentrations: 100.14 for farmed, 100.7 for feral in October, and 100.74 for farmed, 100.11 for feral in November. Based on this, we recommended that governmental and environment preservation enthusiast to enhanced Monitoring and Regulation of farms and feral aquatic environment as well as engage in public awareness.
Keywords: Aquatic environment, total petroleum hydrocarbons, heavy metals

INTRODUCTION

Rivers State is an oil producing state and for more than 5 years now have been battling with petroleum hydrocarbon soot pollution (Onwuka, 2015; Idemudia, 2019; Pérouse de Montclos, 2022). Soot is an environmental hazard. Its size is two small (2.5U) that it enables it to penetrate anywhere (Sheibani-Tezerji *et al.,* 2018; Daranas *et al.,* 2018). The effects of petroleum hydrocarbon soot pollution within our aquatic environment cannot be under estimated (Daranas *et al*., 2018). According to Kuppusamy *et al.* (2020, P. 4), the term total petroleum hydrocarbons (TPH) is used to describe a group of chemical compounds emanate from crude oil – which are divided into groups called petroleum hydrocarbon fractions. TPH is a mixture of chemicals, this majorly from hydrogen and carbon otherwise called hydrocarbon. This group normally act alike in the presence of soil, water etc (Oparaji *et al*., 2017).

Petroleum hydrocarbon soot, often produced from the incomplete combustion of fossil fuels, poses a significant environmental concern due to its potential adverse impacts on both terrestrial and aquatic ecosystems (Ruiz-Morales, 2022). The discharge of petroleum hydrocarbon soot into the environment can result from various anthropogenic activities such as industrial processes, vehicular emissions, and oil spills (Nazhipkyzy *et al,* 2022). Once released, these contaminants can accumulate in sediments, affecting the health of aquatic organisms and potentially entering the food chain (Gai *et al*., 2017; Azimi *et al*., 2018; Likhanov et al., 2020; Nazhipkyzy *et al,* 2022; Ruiz-Morales, 2022).

TPH is a broad classification of organic compounds derived from crude oil and other petroleum products. They can vary in composition and toxicity, ranging from volatile compounds to more complex, persistent ones (Nazhipkyzy *et al,* 2022; Ruiz-Morales, 2022). TPH contamination is a concern because it can lead to harmful effects on aquatic life, including reduced oxygen levels, smothering of benthic organisms, and alterations in the physical and chemical properties of sediments.

Heavy metals, which include elements like lead, mercury, cadmium, and chromium, are naturally occurring elements that can become pollutants when released into the environment in excessive amounts (Alloway, 2013). Anthropogenic sources such as industrial activities (Li *et al*., 2019), agriculture (Shan et al., 2013, and mining (Rafique *et al*., 2022) can significantly increase heavy metal concentrations in aquatic ecosystems. These metals are persistent, and their accumulation in sediments can impact aquatic organisms, causing toxicity (Jaiswal et al., 2018), reproductive impairments (Zaynab *et al*., 2022), and bio-magnification (Kahlon *et al*., 2018) through the food chain.

Numerous studies have addressed the impacts of petroleum hydrocarbon contamination and heavy metal pollution on aquatic ecosystems. For instance: A study by Wang et al. (2018) conducted in a similar environment demonstrated that petroleum hydrocarbon contamination in sediments can result in altered microbial communities and ecological imbalances. The work of Smith et al. (2019) emphasized the long-term persistence of heavy metals in sediments and their potential to adversely affect aquatic organisms' health and diversity. In a study by Gupta et al. (2020), the authors highlighted the importance of assessing the combined effects of TPH and heavy metals on aquatic biota, as their co-occurrence can amplify toxic effects. A review by Chen et al. (2021) discussed the challenges in remediating petroleum hydrocarbon-contaminated sediments and the role of microbial degradation in reducing TPH concentrations.

The contamination of aquatic environments with petroleum hydrocarbon soot and heavy metals is a concerning issue with potential ecological and human health implications (Idemudia, 2019; Pérouse de Montclos, 2022). The present study seeks to contribute valuable insights into the extent of TPH and heavy metal contamination within the Aluu farmed and feral aquatic environments in Rivers State and Imo State. By integrating literature findings with local data, this study aims to enhance our understanding of the environmental risks posed by these contaminants and inform potential mitigation strategies.

The presence of petroleum hydrocarbon soot and heavy metals in aquatic environments within Aluu, Rivers State, poses a significant environmental and human health concern. Anthropogenic activities, including industrial processes, vehicular emissions, and oil spills, contribute to the release of these contaminants into the environment (Gennadiev *et al*., 2015; Maduka, O., & Ephraim-Emmanuel, 2019). This contamination can lead to detrimental effects on aquatic ecosystems, including altered microbial communities, reduced biodiversity, and potential bioaccumulation through the food chain (Chen *et al*., 2021). Despite the potential risks associated with petroleum hydrocarbon soot and heavy metal contamination, there is a lack of comprehensive research that addresses the specific levels, distribution, and potential impacts of these contaminants in the mentioned regions.

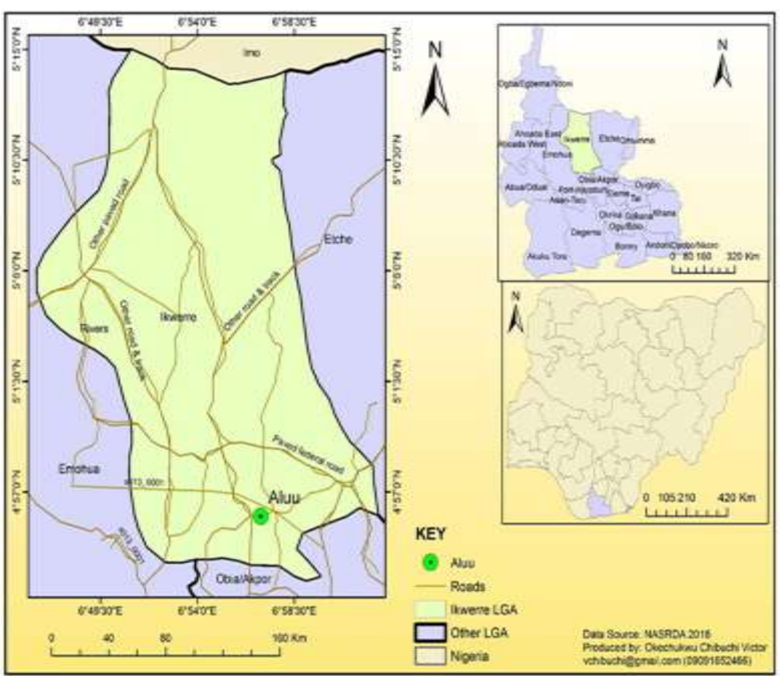
The existing literature on petroleum hydrocarbon and heavy metal contamination in aquatic environments globally lacks a specific focus on the unique context of Aluu, Rivers State. While previous research mainly concentrates on broader pollution concepts like oil spills or industrial discharges (Gupta *et al*., 2020; Chen et al., 2021; Zaynab *et al.*, 2022), there is a distinct absence of studies addressing the characteristics of petroleum hydrocarbon soot, its sources, and its interaction with heavy metals in these Aluu. Moreover, the scarcity of comprehensive assessments comparing contamination levels and impacts between farmed and feral aquatic environments in relation to local factors like land use and anthropogenic activities further underscores the gap. Additionally, current research tends to examine the individual effects of either petroleum hydrocarbon soot or heavy metals (Jaiswal, 2018; Kahlon et al., 20018; Maduka & Ephraim-Emmanuel, 2019; Zaynab et al., 2022), neglecting the combined impacts of these co-occurring contaminants. Thus, there's a pressing need for a region-specific and comprehensive study evaluating contamination levels, sources, interactions, and ecological repercussions of petroleum hydrocarbon soot and heavy metals within both aquatic environments in Aluu, Rivers State, and Imo State. Hence, this research was designed to determine the presence and concentration of some Heavy metals and TPH in the petroleum hydrocarbon soot within ARAC Aluu farmed and feral aquatic environments. With this research, it is quite easy to provide a report that will encourage the government to offer a quick mitigation measures while having in mind the risk associated with the presence of this pollutants. Also, understanding the concentration and distribution of TPH and heavy metals in these environments is crucial for evaluating the potential ecological and human health risks associated with these contaminants. This study is particularly important due to the economic significance of aquatic resources in these states and their contributions to local livelihoods.

MATERIALS AND METHODS

Study Location

This study was conducted in Aluu, Rivers State.

Sampling Site Location A:



The Aluu people are indigenous to the state of Rivers, more especially the Ikwerre LGA (Figure 3. 1). 40°45′ N, 40°60′ W, 60°40′ E, 70′00′ E are the GPS coordinates for it. The research area is bounded on the northeast by the Ohaji / Egbema LGA and Ndoni LGA, on the southwest by the Emohua, on the south by the Obio/Apkor Local Areas, and on the east by the Etche. The region under study spans a total of 655 km^2, with a population density of $405.2/km^2$, and is home to an estimated 265,400 persons as of the 2006 Nigeria census. The Cretaceous and Tertiary sediments that make up the area were deposited there as a result of gravitational instability and tectonic stress. Mangroves, raffia palms, and a relatively light rainforest thrive there due to the area's favorable drainage (Weli & Ogbonna ,2015; Nwankwoala & Offor, 2018). For both fresh and salt water, it serves as a drain. Agbada, Akata, and Benin coastal formations that date from the ancient to the modern eras of the Niger Delta (Weli & Ogbonna, 2015). Generally speaking, the soils in this region are sandy loams, hummus, alluvium, and the outer belt of saltwater swamps, clay, and muck. Drainage occurs for both fresh and salt water. Between March and October, Port Harcourt receives the most precipitation (Oyegun and Adeyemo, 1999). They experience approximately two meters of rain falls each year on average and the rainy season is at its peak in August, the area where this research work was done has a dry spell termed "August Break." In general, the research region has an average minimum temperature of 22^0C (degrees Celsius) and an average maximum temperature of 32^0C (degrees Celsius)

Sample Collection

Soot samples were collected from sites within Aluu where they are doing artisanal refinery processing. The Mini Vol. Tactical air (TAS) sampler was used to collect the soot samples were collected from three sampling points and then homogenized to form suitable samples, subsequently taken to the laboratory for TPH total petroleum hydrocarbon and heavy metal analyses.

Determination of Total Petroleum Hydrocarbon

This was using the method descript by Nwineewii & Hart, (2019), chromatography principle was use for this extraction which involves separation of mixture through a column having mobile and stationary phase. Here some compounds are retained longer than others.

Principle: Chromatography Principle

This involves the mobile phase and the stationary phase.

$$HETP = A+B/C + (C_{S} + C_{M})\,u$$

HETP =Measure of the resolving power of the column (m)

A=Eddy-diffusion, parameter relating to the channel through,

B =Diffusing coefficient of the eluting particles in the longitudinal direction resulting in dispersion (m^2s^{-1})

C=Resistance to mass transfer coefficient of analyte between mobile and stationary phases interest

C_M = Mass transfer in the mobile phase

C_S = Mass transfer in the stationary phase

U= Representing interest between mobile and stationary phases.

(Wedad *et al*., 2017)

Procedure

Extraction Of Soot Sample.

Extraction of soot samples;

One gram of soot sample was weighed into a 100ml conical flask and 30mls of dichloromethane (extraction solution) was added.

The flask was covered properly and agitated for two minutes.

The extract was allowed to settle for a period of 20 minutes.

Filtration Process

The extract was filtered through a glass wool containing sodium sulphate salt and silica gel.

This will aid total removal of moisture content.

Organomation

The filtrate was transferred into test tubes and placed in an organomation machine for quick evaporation within 30 minutes.

TPH Detection.

The condensed sample was transferred into a vial bottle and inserted into a Gas Chromatography Flame Ionization Detecting machine (GCFID) for TPH detection and recording through a computerized system.

Determination of Method for heavy metal determination of soot.

Determination of heavy metal content of soot was done following the method described by Nwineewii & Hart, (2019).

PRINCIPLE; This was done according to Beer Lambart's law which states that there is a linear relationship between the concentration and absorbance of the solution, this enables the concentration of the solution to be calculated by measuring its absorbance.

A= εbC

A= absorbance

E= molar absorptivity

b =length of light path

c=concentration

Procedure

Digestion of Sample

The soot samples were loaded and digested in an acid mixture, this acid mixture was made up of nitric acid, sulphuric acid and perchloric acid, in a ratio of 2:2:1.

Each filter paper was carefully placed in Teflon tubes and 10 ml of the acid mixture was slowly added to cover the samples.

This was done under a fume cupboard in an ice packed bath.

The mixture was allowed to cool for about 5minutes.

The Teflon tubes were closed and placed in stainless steel bumbs and placed on a hot plate '

The were heated at 150°C for 6 hours.

The digested samples were allowed to cool to room temperature.

Filtration of Samples

The mixture was filtered and transferred into polypropylene graduated tubes.

The Teflon tubes were rinsed three times with distilled water.

Deionized water was added to make it up to 100mls.

The filtrate was transferred into a Poly bottle for heavy metal detection.

Instrumentation

The samples were connected to a Microplasm Atomic Emission Spectrophotometer (MPAES) with the help of an Enablelizer which carried the sample through a plasma touch.

At various wavelengths, the elements were calibrated and identified through computerized system.

Statistical Analysis

All experiments were done in triplicates. Available data were subjected to descriptive test, analysis of variance using Graph Pad Prism Software to determine significant differences. Duncan multiple range test under the probability of 0.05 was used to compare the mean values. The study employed Logistic regression.

RESULTS

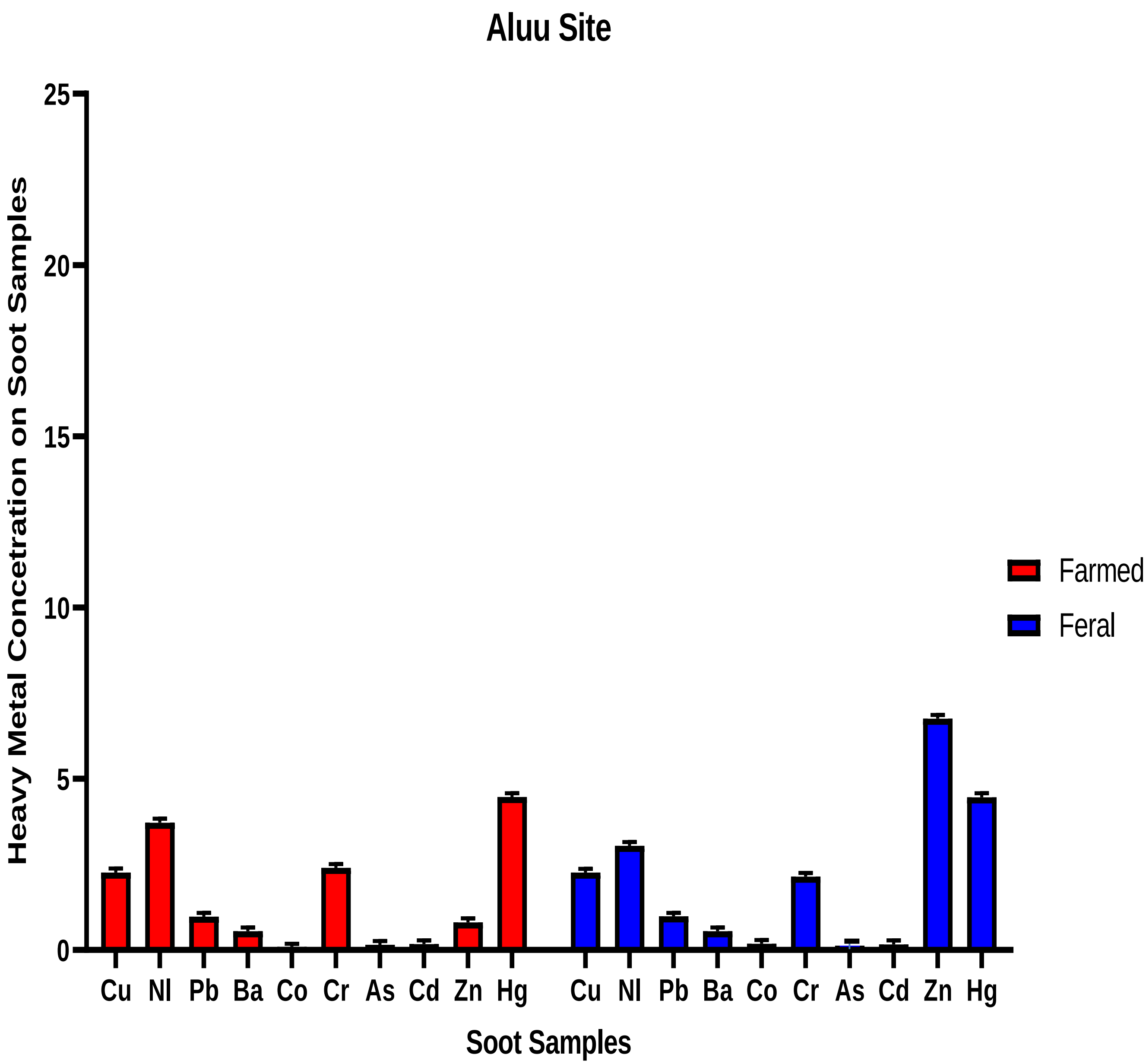


Figure 1: Monthly variation in Heavy metal concentrations in Aluu farmed and feral aquatic environment.

Copper (Cu): Feral soot had a concentration of 1.728, while farmed soot had a concentration of 1.719. Nickel (Nl): Both feral and farmed soot had similar concentrations, with 2.536 and 2.537, respectively. Lead (Pb): Both feral and farmed soot had the same concentration of 0.45. Barium (Ba): Feral soot had a concentration of 2.39, whereas farmed soot had a lower concentration of 0.4. Cobalt (Co): Feral soot had a concentration of 0.3, while farmed soot had a lower concentration of 0.029. Chromium (Cr): Both feral and farmed soot had similar concentrations, with 1.129 and 1.128, respectively. Arsenic (As): The concentrations were below the detection limits for both feral and farmed soot. Cadmium (Cd): Feral soot had a concentration of 0.025, while farmed soot had a slightly lower concentration of 0.024. Zinc (Zn):

Feral soot had a concentration of 2.057, whereas farmed soot had a significantly lower concentration of 0.057. Mercury (Hg): Feral soot had a concentration of 9.9, while farmed soot had a slightly lower concentration of 9.742.

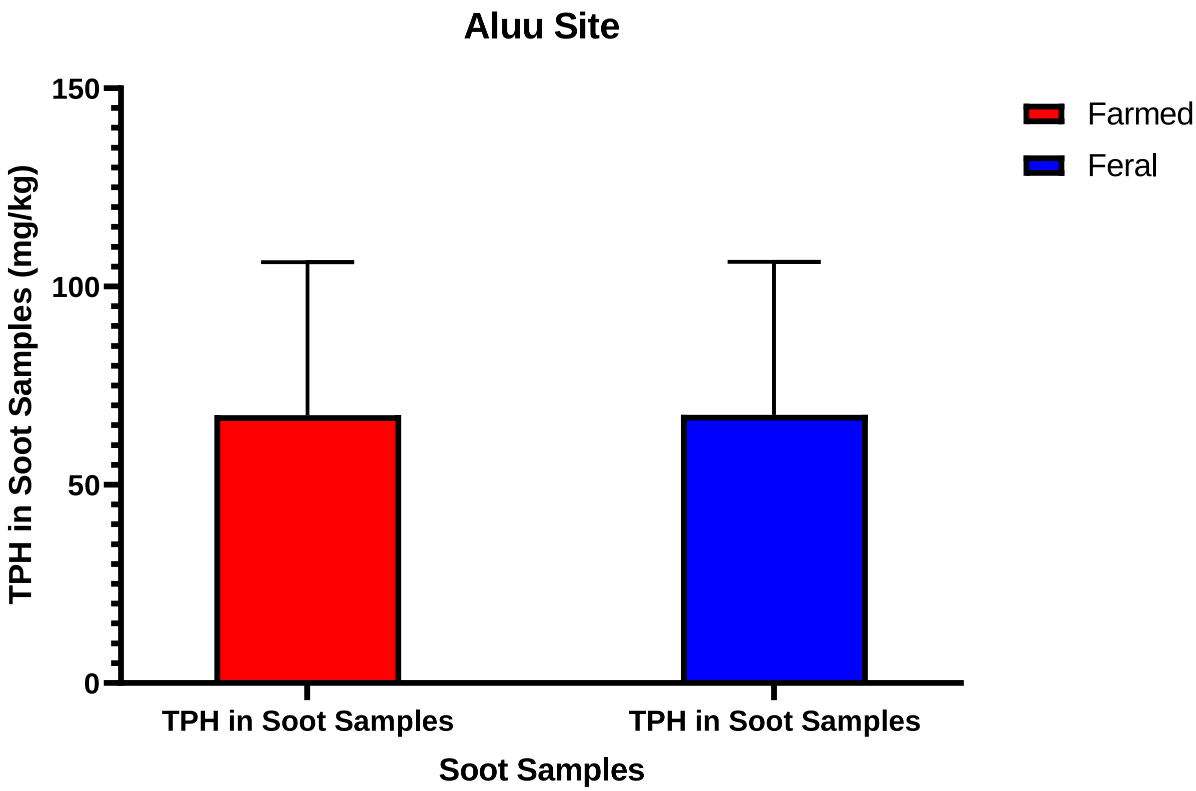


Figure 2: TPH on soot samples from farmed and feral environments (Aluu Site)

The data provided represents the total petroleum hydrocarbon (TPH) concentrations in soot samples collected from the Aluu sites, specifically in the farmed and feral samples. Let's analyze the data for each month (May, June, July, September, October, and November):

May: The TPH concentration in the farmed sample for May is 34.8488 while the TPH concentration in the feral sample for May is 34.895. For June, the TPH concentration in the farmed sample for June is 56.467, while the TPH concentration in the feral sample for June is 57.156. For July, the TPH concentration in the farmed sample for July is 12.6753, while the TPH concentration in the feral sample for July is 12.676. In September, the TPH concentration in the farmed sample for September is 100.37, while the TPH concentration in the feral sample for September is 100.57. For October, the TPH concentration in the farmed sample for October is 100.14, while the TPH concentration in the feral sample for October is 100.7. In November, the TPH concentration in the farmed sample for November is 100.74, while the TPH concentration in the feral sample for November is 100.11.

DISCUSSION OF FINDINGS

The analysis of heavy metal concentrations in feral and farmed soot from Aluu sites shows a consistent pattern, with feral soot exhibiting higher metal concentrations like copper, nickel, barium, cobalt, zinc, and mercury. Lead concentrations remain uniform, while chromium, arsenic, and cadmium concentrations show stability. These variations can be attributed to environmental factors, contamination sources, natural processes, and farming practices. Understanding these variations is crucial for comprehensively deciphering the factors influencing heavy metal dynamics and TPH concentrations in distinct environments.

The results of the present study, which investigated TPH concentrations and heavy metal levels in soot from Aluu aquatic environments, are consistent with and complement findings from previous research studies that have explored similar themes. The study conducted by Onwuka (2015) emphasized the relationship between oil extraction, environmental degradation, and poverty in the Niger Delta region of Nigeria, highlighting the detrimental consequences of petroleum-related activities on the local ecosystem and communities. This aligns with the current study's identification of elevated TPH concentrations, underlining the ongoing issue of hydrocarbon contamination in the region.

Furthermore, the work by Oparaji et al. (2017) assessed polycyclic aliphatic hydrocarbon and TPH levels in aquatic fauna from the Forcados Terminal River in Port Harcourt. While their focus was on aquatic fauna rather than soot, their findings of hydrocarbon contamination in aquatic organisms corroborate the present study's concerns about contamination's potential impact on aquatic life. Similarly, the study by Gennadiev et al. (2015) explored hydrocarbon status in soils and provided insights into the factors influencing soil contamination, which may contribute to TPH levels in sediment samples as observed in the current study.

Regarding heavy metals, the investigation conducted by Alloway (2013) discussed sources of heavy metals and metalloids in soils, aligning with the discussion of heavy metal variations in the present study. The study by Kahlon et al. (2018) delved into the impact of heavy metals on aquatic biota, paralleling the present study's emphasis on the potential ecological consequences of varying heavy metal concentrations. Additionally, the work by Li et al. (2019) and Shan et al. (2013) examined heavy metal contamination, its sources, and identification using multivariate analysis and GIS, respectively, providing context for the variations in heavy metal levels observed between the farmed and feral samples in the current study.

In comparison to the findings from Ruiz-Morales (2022) and Nazhipkyzy et al. (2022), which focus on characterization and separation of hydrocarbon-related materials, the present study expands on these works by directly assessing TPH concentrations in soot samples from distinct aquatic environments. Moreover, the current study's observations of higher heavy metal concentrations in feral tilapia align with the conclusions of studies such as Azimi et al. (2018), which investigated sources of heavy metals in urban environments, and Likhanov and Rossokhin (2020), which explored the impact of fuel type on soot particles. These connections emphasize the interconnectedness of hydrocarbon contamination and heavy metal exposure in aquatic environments.

The practical implications of these results are significant for both environmental management and human health. The higher heavy metal concentrations in feral aquatic environments suggest potential contamination sources, warranting increased monitoring and mitigation efforts to safeguard aquatic ecosystems. Additionally, the presence of varying TPH concentrations underscores petroleum hydrocarbon pollution, necessitating proactive measures to prevent ecological disruption. Comprehensive understanding of these implications is vital for formulating targeted strategies that address contamination sources, protect ecosystems, and promote safe consumption practices.

CONCLUSION

In conclusion, this study has shed light on the critical issues of Total Petroleum Hydrocarbon (TPH) contamination and heavy metal concentrations in aquatic environments within the Aluu region, specifically in farmed and feral areas. The observed variations in TPH concentrations and heavy metal levels between these environments emphasize the need for a comprehensive understanding of the sources, mechanisms, and potential ecological impacts of these contaminants. The consistent pattern of higher heavy metal concentrations in feral tilapia underscores the significance of pollution sources in aquatic ecosystems. The presence of TPH and heavy metals raises concerns for both environmental health and human well-being. These findings underscore the importance of tailored strategies for pollution management, ecosystem protection, and safe food consumption practices. To ensure sustainable aquatic environments and safeguard public health, collaborative efforts are essential in addressing these challenges through effective regulations, remediation initiatives, and ongoing research.

RECOMMENDATIONS

Based on the findings of the study, two key recommendations are proposed to address the challenges posed by TPH contamination and heavy metal concentrations in the Aluu aquatic environments:

Governmental and environment preservation enthusiast must enhanced Monitoring and Regulation of farmes and feral aquatic environment. It is crucial to establish a comprehensive and continuous monitoring program for TPH contamination and heavy metal levels in both farmed and feral aquatic environments. Regular monitoring will provide real-time data on contamination trends and potential sources, enabling timely intervention and adaptive management strategies. Regulatory authorities should implement and enforce stringent standards for permissible TPH and heavy metal concentrations in aquatic environments, considering both ecological and human health perspectives. These regulations should encompass guidelines for industries, agricultural practices, waste disposal, and other potential pollution sources to prevent further contamination.

Public and environmental health experts in collaboration with government must design and implement a full Public Awareness and Education programme. Raising public awareness about the potential risks associated with TPH contamination and heavy metal exposure is essential. Educational campaigns should target both local communities and industries to emphasize the importance of responsible waste disposal, sustainable farming practices, and the safe handling of chemicals. Additionally, information on the potential health risks associated with consuming fish and other aquatic products with elevated heavy metal concentrations should be disseminated to the public. By fostering understanding and promoting informed decision-making, public awareness efforts can encourage support for pollution reduction initiatives and responsible consumption habits.

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