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HEAVY METALS AND TOTAL HYDROCARBONS IN SURFACE WATER OF ESSENE CREEK, IKOT ABASI, AKWA IBOM STATE, SOUTHERN NIGERIA

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ABSTRACT

Essene Creek is a tributary of the Imo River in Ikot Abasi. However, unlike other major Creeks in the region there is no scientific study or report exclusively on this water body. Thus, the present study was to determine the heavy metal and total hydrocarbon contents in its surface water. It was conducted for 18 months from March 2021 to August 2022. Five stations were stratified based on activities along the Creek. Surface water samples were obtained monthly at intervals of thirty days using one-litre plastic bottles. Standard Atomic Absorption Spectrophotometry (AAS) as prescribed by American Public Health Association (APHA) was employed in determining the concentration of each heavy metal per location, while total hydrocarbon was analyzed in the laboratory using ASTM D 3921 standard procedure. Mean values obtained were iron (1.68 ± 0.11mg/l), zinc (4.57 ± 0.14 mg/l), lead (0.65 ± 0.06 mg/l), cadmium (0.69 ± 0.04 mg/l), chromium (0.52 ± 0.04 mg/l), mercury (0.00 mg/l), nickel (0.42 ± 0.05 mg/l) and total hydrocarbon (0.65 ± 0.06 mg/l). The results show that generally heavy metals have already exceeded their safe limits in the Creek and this should be a cause for concern for stakeholders. It is recommended that a complete hydrobiological survey of the Creek be carried out as soon as possible, especially to establish a benchmark and also ascertain the total health status of the Creek.
Keywords: Heavy metals, total hydrocarbons, surface water, Essene Creek

INTRODUCTION

Rivers have always been very useful to man in various ways, for example it serves to provide water for domestic use, irrigation and even industrial purposes. The quality of water is thus an important component of the natural environment. Water bodies such as creeks and rivers are subject to environmental and human influences. Its variation especially at the surface is a combination of both anthropogenic and natural factors. Liang *et al.* (2018) state that anthropogenic factors constitute a constant source of pollution. Surface run-off is a seasonal phenomenon affected by climate within the catchment or the watershed. Maintaining a good water quality remains a challenge for our environment. (Kusari, 2018).

Heavy metals have been used to refer to any metallic chemical element with relatively high density and is toxic at certain levels. Some heavy metals are either essential nutrients e.g. zinc, iron and cobalt, while others are almost harmless e.g. silver and indium (Balali-Mood *et al.*, 2021). However, other heavy metals, such as lead, mercury, arsenic and cadmium are highly poisonous and may lead to severe complications e.g. bloody diarrhea, abdominal colic pain and kidney failure (Tsai *et al.*, 2021; Bernhoft, 2012). Potential sources of heavy metals in water bodies include agricultural runoff, mining, industrial waste, smelting etc. Organisms require trace metals such as cobalt, iron, magnesium, manganese, zinc, copper, for their normal physiological functioning. However, non-essential trace metals are sometimes present in the food chain and may become toxic at higher concentrations. The environmental risks of trace metals have been, and will continue to be an important issue of great concern and significance (Vincent-Akpu and Offiong, 2015).

Essene creek is not very popular in the scientific community compared to other creeks close to it such as Jaja Creek, Uta Ewa, Stubbs and Douglas creeks, where numerous environmental studies have been exclusively conducted. As a tributary of the Imo River, it meanders through several villages and communities serving as a reliable source of water for the communities. It also serves to provide fish resources and other economic fortunes to the indigenes. For example, both mechanical and non-mechanical sand dredging is ongoing at different locations. It prides itself as a shortest means of transportation between communities that are separated by its waters.

Description of the Study Area

Essene Creek is located in Akwa Ibom State between latitude $4^{o}\ 35^{I}$ N and $4^{\circ}\ 50^{I}$ N and between longitude $7^{o}\ 30^{I}$ E and $7^{o}\ 44^{I}$ E (Figure 1). It traverses about three Local Government Areas in Akwa ibom State viz.: Oruk Anam, Mkpat Enin and Ikot Abasi in the State and empties into the Imo River Estuary at Ikot Abasi LGA. The climate of the area is that of humid tropic. Temperatures are moderate, typically lying between 26ºC and 28ºC. Rainfall is heavy and the mean annual rainfall lies between 2,000-4,000 mm. The wind is generally cold throughout the day, but gets much colder as evening sets in. Usually, the rainy season sets in between March and April and lasts till August or September, while the dry season takes the remainder of the year.

The Creek is dominated by Nipa palm (*Nypa fruticans*) in the areas adjourning its mouth though there are a few remaining mangrove species identified in the area, especially the red mangrove (*Rhizophora racemosa*). Moving upstream, the presence of N. fruticans is reduced and gradually disappears, giving room to a variety of trees and shrubs such as *Elaeis genuineensis*, *Cocos nucifera* and *Avicennia* on both banks of the creek. The creek serves as a fishing ground for artisanal fishers who largely fish along its banks.

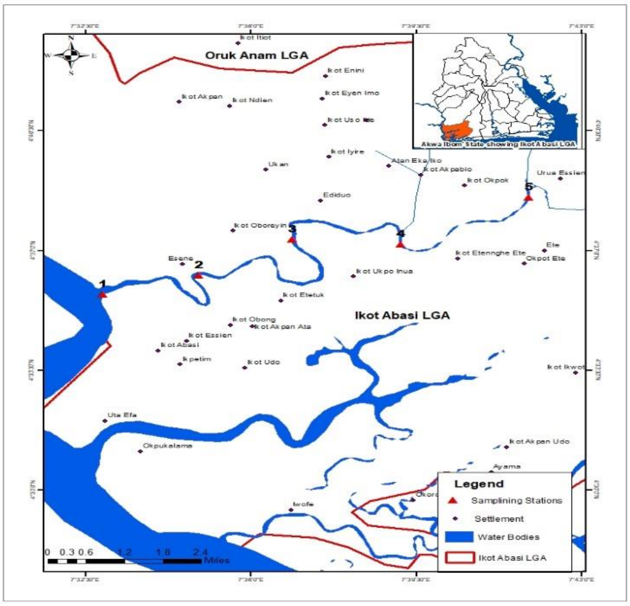

Fig. 1.0: Ikot Abasi LGA showing Essene Creek and Sampling Locations

Data Collection and Water Analysis

Sampling was done between 0800 hrs and 1200 hrs for each sampling day for eighteen months. Surface water samples were collected using 1 litre plastic bottles which had been pre-rinsed with distilled water. The samples were preserved in ice cooled coolers and transported to the laboratory for analysis. All heavy metals (iron, zinc, lead, cadmium, chromium, nickel and mercury) were analyzed in the Akwa Ibom State Ministry of Science and technology laboratory using the standard Atomic Absorption Spectrophotometry (AAS) as set out by APHA (2017). The acidified water sample was filtered using Whatman ashless filter paper and thereafter analyzed with atomic absorption spectrophotometer (Shimadzu AA-6650) using standard method (ASTM D1971/4691) to determine the level of heavy metals. This method of identification employed the use of variable wavelength of light based on the specific metal of interest after standard solutions of each metal has been prepared.

THC was analyzed in the laboratory using ASTM D 3921 standard procedure. ASTM D3921 test method is employed for the determination of oil and grease first. 1000ml of sample was extracted serially thrice, each time with 30ml volume of trichloroethylene (solvent). The extract was diluted to 100ml and a portion was examined by infra-red spectroscopy to measure the amount of oil and grease. For THC, a portion of the oil and grease extract was contacted with de-activated silica gel to remove polar substances thereby providing a solution of total hydrocarbon content. This resulting solution was then examined by infra-red spectroscopy. Calculation of final result was obtained by relating the absorbance of sample to the standard calibration curve plotted.

Statistical Analysis

Various forms of data analyses were performed on the data to extract the relevant outputs. For example, mean, standard error, percentages, minimum and maximum values were extracted using Statistical Package for Social Science (SPSS, version 25) software. All graphical illustrations were done using Microsoft excel 2017. One way Analysis of Variance (ANOVA) at probability level of $p<0.05$ was employed in the estimation of spatial and seasonal variations in heavy metal concentrations. Where applicable, Duncan Multiple Range Tests (DMRT) was used to separate the means. Mean values of heavy metals concentrations were plotted against time of sample collection to give patterns of monthly variation.

RESULTS

Data showing range, mean, standard error of heavy metals and THC concentrations as well as the spatial variations observed along Essene Creek is shown in Tables 1.0 and 2.0. Graphs of mean values of the heavy metal concentration plotted against time of sample collection to give patterns of monthly variations are presented in Figures 2.0 - 7.0.

Table 1.0: Heavy metals and THC measured in Essene Creek from March 2021 to August 2022

Sn	Heavy Metals	Mean	Std. Error	Range	Minimum	Maximum
1	Cadmium	0.69	0.04	1.26	0.07	1.33
2	Chromium	0.52	0.04	1.28	0.01	1.29
3	Iron	1.68	0.11	4.77	0.35	5.12
4	Lead	0.65	0.06	2.11	0.00	2.11
5	Mercury	0.00	0.00	0.00	0.00	0.00
6	Nickel	0.42	0.05	2.1	0.00	2.11
7	Zinc	4.57	0.14	6.41	1.65	8.06
8	THC	0.65	0.06	2.11	0.00	2.11

Table 2.0: Spatial variations in heavy metals and THC in Essene Creek from March 2021 to August 2022

Parameters	Station 1 (Mean± S.E) Min-Max	Station 2 (Mean± S.E) Min-Max	Station 3 (Mean± S.E) Min-Max	Station 4 (Mean±S.E) Min-Max	Station 5 (Mean±S.E) Min-Max	Total Mean (Mean±S.E) Min-Max
Iron	1.97 ± 0.32^{a}	1.86 ± 0.18^{a}	1.73 ± 0.22^{a}	1.57 ± 0.28^{a}	1.27 ± 0.14^{a}	1.68±0.11
	(0.60-5.12)	(0.51-3.12)	(0.36-3.09)	(0.56-5.11)	(0.35-2.15)	(0.35-5.12)
Zinc	5.46 ± 0.33^{a}	4.55 ± 0.11^{bc}	3.85 ± 0.37^{cd}	5.31 ± 0.26^{ab}	3.66 ± 0.10^{d}	4.57±0.14
	(2.68-8.06)	(3.76-5.20)	(1.65-6.1)	(4.03-8.06)	(2.57-4.31)	(1.65-8.06)
Lead	0.79 ± 0.17^{a}	0.50 ± 0.10^{b}	0.76 ± 0.15^{a}	0.71 ± 0.13^{a}	0.48 ± 0.11^{b}	0.65±0.06
	(0.05-2.11)	(0.06-1.11)	(0.00-2.03)	(0.00-1.35)	(0.04-1.19)	(0.00-2.11)
Cadmium	0.90 ± 0.08^{a}	0.73 ± 0.06^{b}	0.53 ± 0.09^{c}	0.81 ± 0.08^{b}	0.49 ± 0.05^{c}	0.69±0.04
	(0.35-1.3)	(0.39-1.13)	(0.07-1.16)	(0.32-1.30)	(0.24-0.93)	(0.07-1.33)
Chromium	0.44 ± 0.08^{b}	0.51 ± 0.07^{b}	0.78 ± 0.09^{a}	0.56 ± 0.12^{b}	0.33 ± 0.06^{c}	0.52±0.04
	(0.02-1.03)	(0.04-1.00)	(0.14-1.21)	(0.06-1.29)	(0.01-0.69)	(0.01-1.29)
Nickel	0.73 ± 0.19^{a}	0.37 ± 0.10^{b}	0.43 ± 0.09^{ab}	0.36 ± 0.08^{b}	0.20 ± 0.04^{b}	0.42±0.05
	(0.06-2.11)	(0.03-1.31)	(0.06-1.07)	(0.02-1.11)	(0.00-0.42)	(0.00-2.11)
Mercury	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00±0.00
	(0.00-0.00)	(0.00-0.00)	(0.00-0.00)	(0.00-0.00)	(0.00-0.00)	(0.00-0.00)
THC	1.23 ± 0.19^{a}	0.70 ± 0.13^{b}	0.33 ± 0.07^{b}	0.34 ± 0.10^{b}	0.63 ± 0.10^{b}	0.65±0.06
	(0.00-2.10)	(0.00-2.11)	(0.01-0.93)	(0.00-1.22)	(0.00-1.14)	(0.00-2.11)

Means with different superscripts along the same row are significantly different (Duncan's test) $p<0.05$

The relative concentrations of heavy metals in the study area were observed in the following sequence: Zn>Fe>Cd>Pb>Cr>Ni>Hg. Zinc ranged from 1.65 to 8.06 mg/l with a mean value of 4.57 ± 0.14 mg/l; iron ranged from 0.35 to 5.12 mg/l with a mean of 1.68 ± 0.11 mg/l; cadmium ranged from 007 to 1.33 mg/l with a mean of 0.69 ± 0.04 mg/l; lead had a range of 0 to 2.11 mg/l with a mean value of 0.65 ± 0.06. Chromium ranged from 0.01 to 1.29 mg/l with a mean value of 0.52 ± 004 mg/l, while Nickel ranged from 0 to 2.11 mg/l with a mean of 0.42 ± 0.05 mg/l. Mercury was found below detectable limits throughout the sampling stations. Apart from iron, every other heavy metal found showed significant ($p>0.05$) spatial variations along the Creek, whereas, no significant($p>0.05$) seasonal variation was noticed in all the stations. Iron, zinc and nickel had higher wet season values, while lead, cadmium and chromium had higher dry season values.

Figure 8.0 depicts mean and seasonal variations of THC concentrations in Essene Creek during the study period. The maximum value found was 2.11mg/l, while the mean value was 0.65mg/l. Mean variation in THC concentrations across the five stations were in the order: ST1>ST2>ST5>ST4>ST3. There was no significant ($p>0.05$) difference in THC concentrations between the seasons.

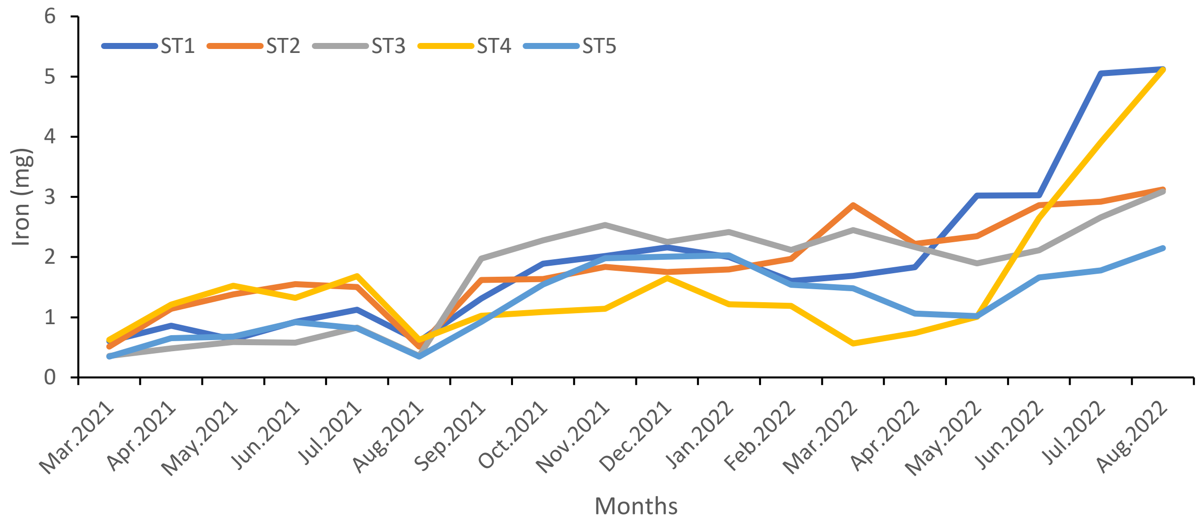

Fig. 2.0: Iron concentration by month in Essene Creek

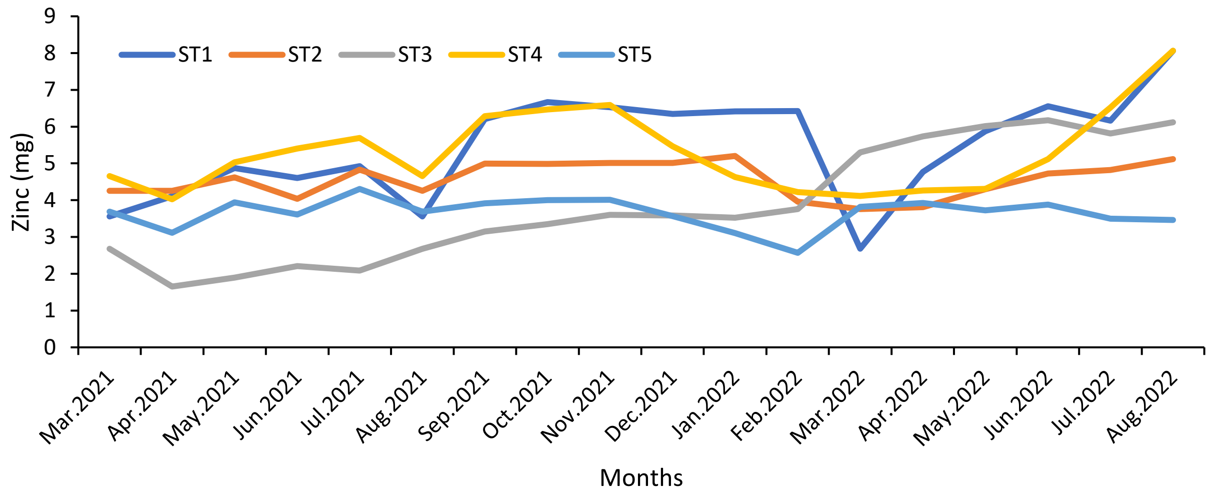

Fig. 3.0: Zinc concentration by month in Essene Creek

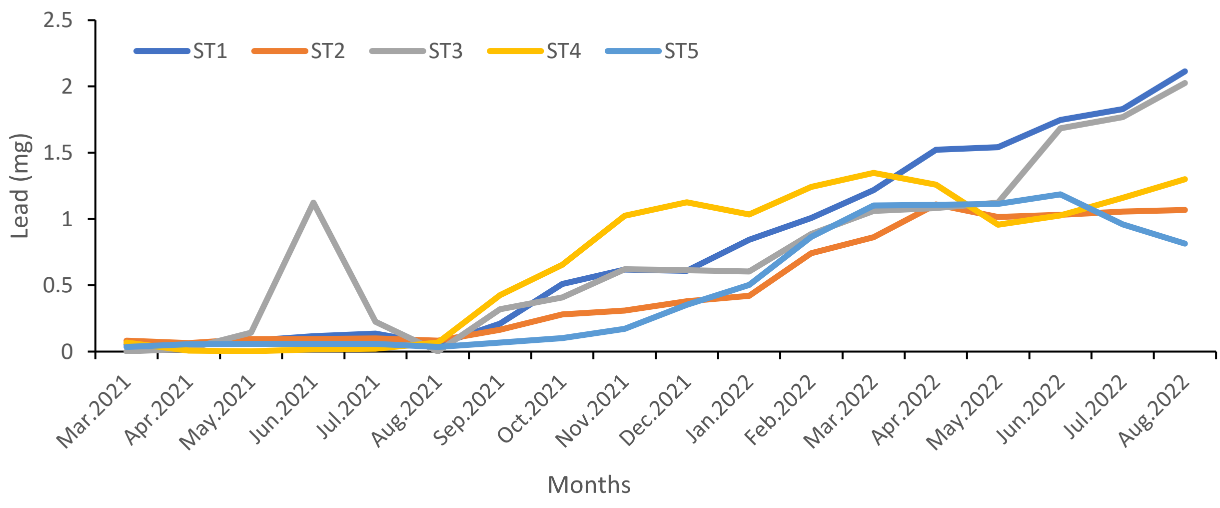

Fig. 4.0: Lead concentration by month in Essene Creek

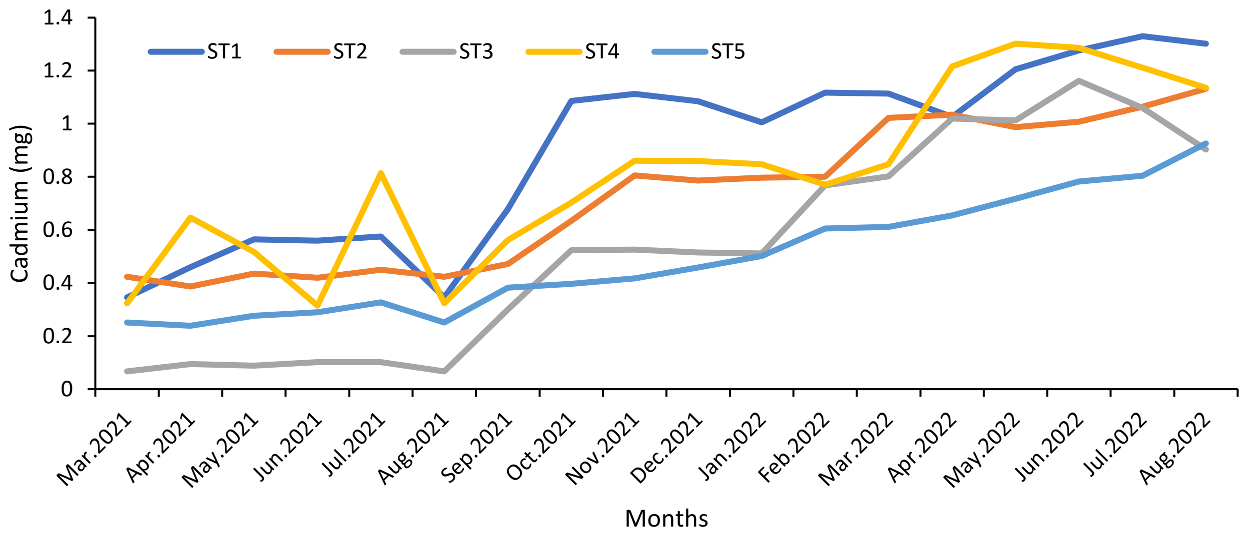

Fig. 5.0: Cadmium concentration by month in Essene Creek

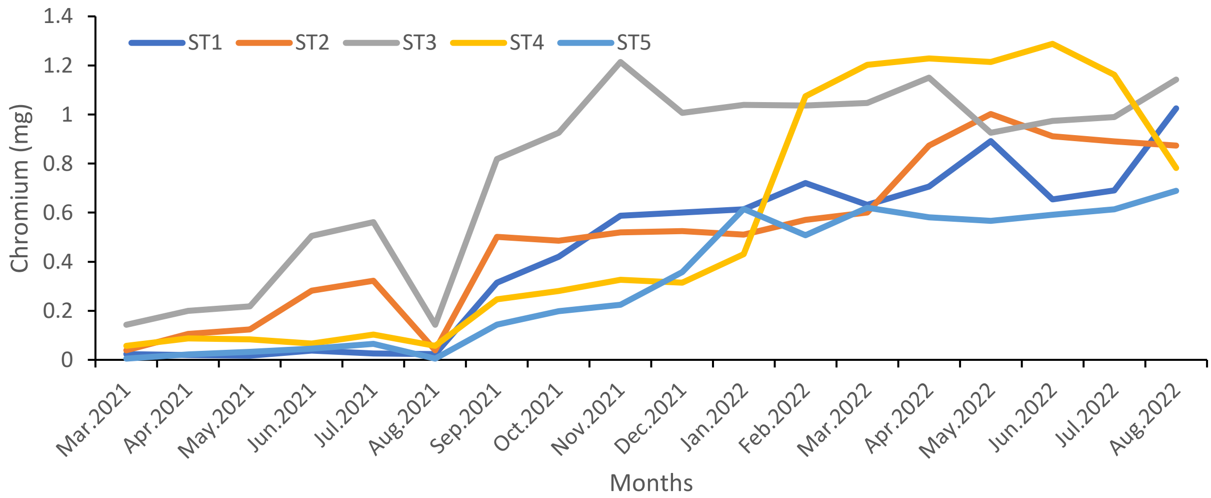

Fig. 6.0: Chromium concentration by month in Essene Creek

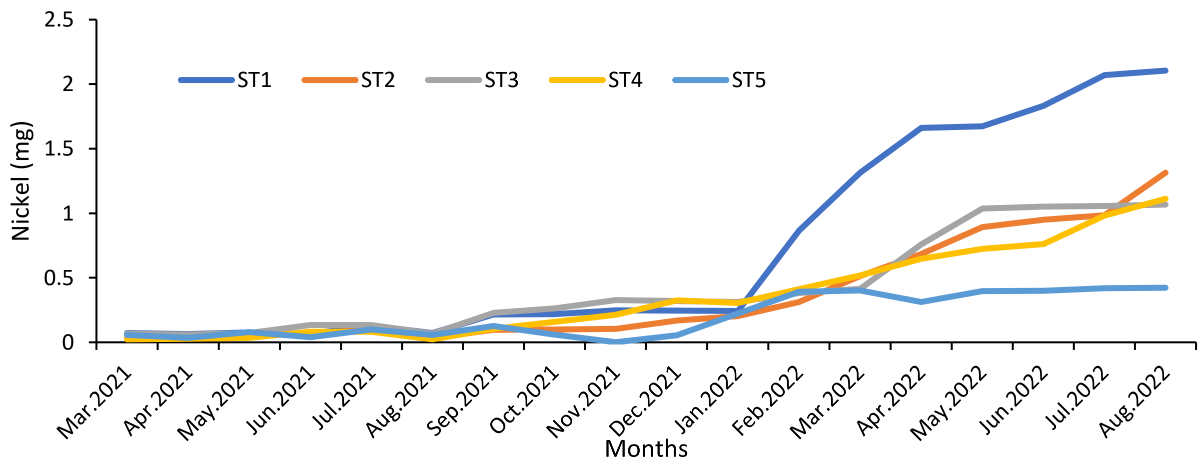

Fig. 7.0: Nickel concentration by month in Essene Creek

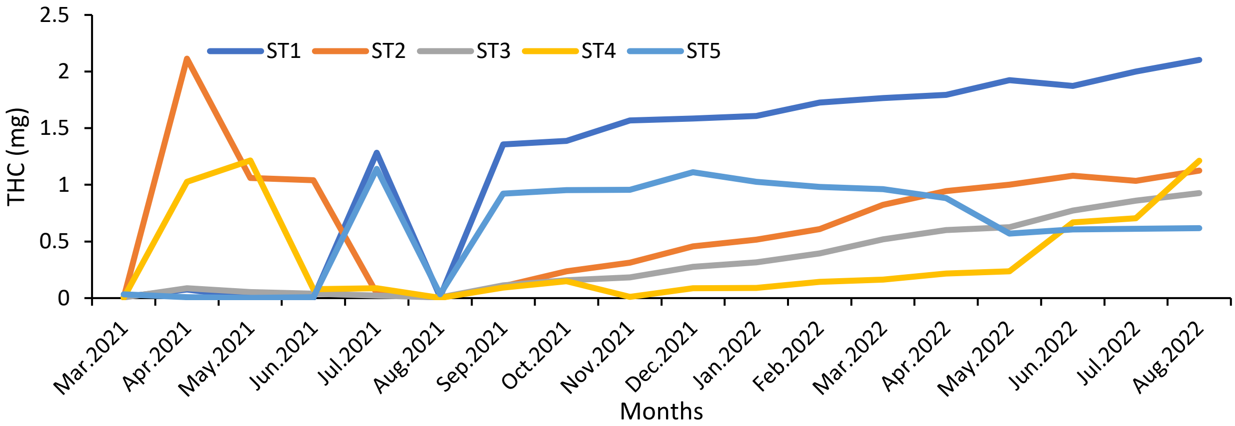

Fig. 8.0: THC concentration by month in Essene Creek

DISCUSSION

The use of heavy metals as indicators of pollution has been widely applied by many scientists, because at higher levels, most heavy metals can be deleterious to both human and aquatic life (Oribhabor and Ogbeibu 2009; Woju and Okaka 2011; Bawa-Allah 2023). The order of abundance of heavy metals from the study is Zn > Fe > Cd > Pb > Cr > Ni > Hg, very similar to the sequence (Zn > Fe > Cu > Pb > Cr > Ni > Mn > Cd) reported by Wangboje and Ekundajo (2013) for River Ikpoba. Station 5 had the least concentrations for all the heavy metals, whereas station 1 had the highest concentrations for all except for Cr. Some of the heavy metals (Fe, Zn and Ni) recorded higher wet season mean values as opposed to Pd, Cr and Cd which had higher dry season values. Both scenarios have been reported by other researchers such as Achi *et al.* (2021) and Iwegbue *et al.* (2023).

Fe is one of the most abundant elements on earth and occurs freely in the earth crust. It is an essential component in human systems. However, elevated levels have been reported to cause development of taste, colour and other aesthetic problems (Fatoki *et al.* 2002). Elevated levels of Fe also impair the ability of body to regulate Fe absorption leading to siderosis in liver, pancreas and heart (Achi *et al.* 2021). While WHO sets a guideline value of 0.3mg/l, the present study records an average of 1.68mg/l in the Creek with the highest mean value of 1.97mg/l in station 1. This may be attributed to the contributions of the Imo River which sweeps through this point and could also be a direct result of run-off from the watershed. Several authors have reported high values of Fe including Igbinosa *et al.* (2012), Seiyaboh *et al.* (2017), Anyawu and Nwachukwu (2020) and Iwegbue *et al.* (2023). The generally higher wet season average found in the present study reflects the results of Iwegbue *et al.* (2023). However, low values have been reported by other researchers like Oribhabor and Ogbeibu (2009), who reported an average of 0.7mg/l for Buguma Creek, while Favour and Obi (2014) reported a mean value of 0.4mg/l at a site in New Calabar River.

Zn is one of the heavy metals naturally found in the environment. It is a very useful component of water, but can cause a number of health risks if present in amounts higher than useful (Sankhla *et al.* 2019). According to Edori and Iyama (2020), Zn is useful in the human system because of the different biochemical and metabolic roles it plays in tissues and cell development. The WHO (2011) recommends a safe limit of 3.0mg/l for Zn in drinking water, whereas Standards Organization of Nigeria (SON) (2007) states that 3.0mg/l is fine, above which water is unsuitable for industrial uses. Oyem *et al.* (2015) suggests that above 3.0mg/l, Zn gives water an undesirable taste. The average Zn concentration found in the present study is 4.57mg/l, with significant variations along the length of the Creek. The Eastern Obolo Estuary as reported by Udoh *et al*, (2013) showed high concentration of Zn, above the allowed standards for drinking water, while Obasi and Akudinobi (2020) and Atama *et al.* (2020) reports high Zn values in some communities in Abakaliki and Iva valley in Enugu state respectively. These differ from reports of Iwegbue *et al.* (2023) for Bomadi Creek and Obot and Afia (2023) for Stubbs Creek, where Zn was found in quantities within the permissible range. In the same vein, Uzairu *et al.* (2014), Okereke and Nnoli (2010) and Obaroh *et al.* (2015) all had similarly low values in their study. The high concentrations of Zn found in the present study is likely due to inputs from the immediate environment via drainage or from the corrosion of the galvanized equipment used in some of the stations for mechanical dredging. It could also be due to industrial waste disposal from the defunct ALSCON quarters situated by the river bank or generally because Zn is a major component of roofing sheets which somehow is drained into the water channel.

Pb was averagely detected in levels (0.65mg/l) higher than the benchmark set by WHO (0.01mg/l) during the study. This is not different from what has been reported in water bodies in the region. For example, Oribhabor and Ogbeibu (2009) for Buguma Creek, Igbinosa *et al.* (2012) for Shanomi Creek, Ehiemere *et al.* (2022) and Obot and Afia (2023) for Stubbs Creek. Sources of Pb in rivers have been shown to be burning of leaded fuel, burning of domestic or industrial wastes containing lead components where the water eventually washes into the river as well as corrosion of products of Pb (Adesiyan *et al.* 2018). Pb has been reported to be potentially deleterious to most forms of life (WHO, 2002) and dangerous to humans which can lead to behavioral changes and impaired performance in IQ tests (Isangedighi and David, 2019). This means that the Creek has a potentially high health risk if consumed. Higher dry season values for Pb have been reported by Uzairu *et al.* (2014) and Achi *et al.* (2021) for Challawa River and River Ogbere respectively. This is similar to what was found in this study and is possibly due to the volume of water available in the Creek (Uzairu *et al.* 2014), however, there was no seasonal variation within the sampling stations.

WHO specifies the safe limit for Cd to be 0.003mg/l. This is far below what was detected in the study, where the mean value was 0.69mg/l. By implication, the Creek is polluted as respects Cd. Potential Cd sources to the Creek could include natural erosion of Cd containing rocks, discharge and domestic effluents, industrial activity, atmospheric emission and deposition of organic and fine grain sediments (Zhong *et al.* 2020). Higher Cd levels have been reported in the region by several researchers such as Igbinosa *et al.* (2012), Otene and Alfred-Ockiya, (2019) for Elechi Creek, Tesi *et al.* (2019) for parts of Warri River and Obot and Afia, (2023) for Stubbs Creek. However, Ighariemu *et al.* (2019) reports low Cd concentration Ikoli Creek. Cd can be retained for up to 20-30 years in the kidney (WHO, 1993) and continuous exposure may eventually accumulate to toxic levels which may lead to anaemia, damage of proximal tubules, severe bone pain, and mineral loss in humans (Hodgson and Levi, 2002). In excess doses, it can interfere with calcium regulation in biological systems in man, fish and other aquatic organisms (Yan and Allen, 2021).

Cr is a potentially toxic metal occurring in water. Leaching from top soil and rocks are the most significant natural sources, however, industrial activities such as electroplating and leather tanning also injects relatively large amounts into water bodies. It occurs in two oxidation states viz: Cr(III) and Cr(VI) in water, but Cr(VI) causes public health concerns because it is toxic to humans, animals, aquatic flora and fauna (Engwa *et al.* 2018, Tumolo *et al.* 2020). The safe benchmark for Cr is 0.05mg/l, (WHO, 2004) whereas the mean value found in this study is 0.52mg/l with station 3 contributing the most. There was no seasonal variation, but highest values occurred in the dry season. Achi *et al.* (2021) reports similar values and trend for Challewa River, while Obasi and Akudinobi (2020) as well as Ehiereme *et al.* (2022) report much higher values for some communities in Abakaliki and Niger delta region. Thus, Essene Creek is polluted in terms of Cr.

Ni occurs naturally in water, with a concentration of about 0.02mg/l (WHO, 2011). Inputs from anthropogenic activities has been noted by Farhang *et al.* (2004) as a contributor to nickel toxicity to living organisms. Aremu *et al.* (2002) notes that water is a minor contributor to the daily oral intake of Ni, while Cempel and Nikel (2006) agrees with Engwa (2018) that at excess amounts, Ni is carcinogenic. The permissible limit by WHO (2011) is 0.07mg/l, but the mean occurrence as found by the present study is 0.42mg/l, indicating Ni pollution of the study area. There was a significant variation in the mean concentration across the Creek. Aside from station 2, Ni increased toward the mouth of the Creek. Obasi and Akudinobi (2020) reports higher values compared to the present study and what was reported by Achi *et al.* (2021).

Hg is released into the environment through natural phenomena such as volcanoes, degradation of minerals or evaporation from soils and manmade processes. The mining industry, especially artisanal miners, use mercury in the extraction process, leading to the leaching of Hg into the environment (Veiga *et al.*, 2014). However, Hg was not detected at any location during the study period and was thus discarded. It means therefore, that the Creek is free from Hg contamination at the moment

THC is a water pollution indicator widely used in conjunction with heavy metals in determining the pollution status of a water body primarily due to its enhanced bio-accumulative potential (Dumka, 2018). Natural sources of hydrocarbons include petroleum and natural gas deposits as well as the conversion of organic molecules in the environment through chemical or biological processes (Neff *et al*. 2005). It has also been shown that contamination of an aquatic ecosystem by both natural and anthropogenic THC is attributable to industrial and maritime sources (Dumka 2018). Hydrocarbons have a tendency to form a waterproof layer on water which prevents oxygen exchange between the environment and water. This can be fatal to aquatic flora and fauna as well as man (Srivastava *et al.*, 2019). WHO stipulates a maximum limit for THC of 10mg/l, beyond which implies contamination. The mean THC values for this study (0.65mg/l) is far below the stipulated value and indicates that the Creek is not polluted based on this parameter. Dumka (2018) reported an average THC value of 8.08mg/l for Otamiri River, while Asuquo *et al.* (2004) notes that the fishes of Cross River have higher concentrations of THC, indicating that the water contains significant quantities of THC. Inyang *et al.* (2018) noted that the waters of Qua Iboe River at Ibeno were significantly contaminated viz a viz hydrocarbons, similar to what Akpan (2013) reported for the Imo River Estuary, but higher than what Obot and Afia (2023) reported for Stubbs Creek. There was spatial variation between the sampling locations, but no seasonal variation was recorded in the present study. The low values of THC found during the study suggests that the Creek is free from oil and gas and its related activities at the moment.

CONCLUSION

The Essene Creek is an important landmark in the state and source of income for communities where it meanders through. It sure has abundant resources which could be tapped by indigenes and the government at large. The results of this study indicated that iron, zinc, lead, cadmium, chromium and nickel have already exceeded their safe limits and this should be a cause for concern. However, there is a real need to conduct more comprehensive research in the

Creek to validate the baseline data presented via this study. This should include aspects of hydrological survey not covered in this work, for example, sediment analysis and microbenthic survey.

RECOMMENDATIONS

Based on the results of this study, the following recommendations are made:

i. More comprehensive studies be conducted on the Creek to include all aspects of water quality determinants. Micro and macro benthos in the Creek should be studied to also establish a baseline as there is no record of such at the moment.

ii. Federal Ministry of Water Resources (FMWR), The Nigeria Hydrological Services Agency (NIHSA) should lead other stakeholders at increasing the level of awareness in riverine communities especially as to the safe environmental practices which will not unduly stress the water body.

iii. Regular water monitoring should be conducted by FMWR and NISHA, because it usually will give a first-hand indication of environmental pollution.

iv. Strict legislation should not just be in place, but enforcement done on environmental degradation.

v. Operational industries should be forced to conform with existing environmental laws and the polluter pays principle should equally be enforced.

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