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Full Length Research Article

DISTRIBUTION OF HEAVY METAL AND PHYTOPLANKTON IN CALABAR RIVER PORT TERMINALS, CALABAR, CROSS RIVER STATE, NIGERIA

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ABSTRACT
An aquatic ecological evaluation of Calabar River Port terminals was carried out from February 2020 to January, 2021 with the aim of assessing seasonal variation of heavy metals and the distribution of phytoplankton. Atomic absorption spectroscopy (AAS) was employed to analyze heavy metal concentration and standard procedure was use in the identification of phytoplankton from three sampling stations namely Eco marine terminal, INTELS terminal and Shoreline terminals in Calabar River port. Results showed elevated levels of lead, Chromium (0.28 ± 0.04), Nickel (0.67 ± 0.03), Lead (0.02 ± 0.02), cupper (0.03 ± 0.01) and Cadmium (0.31 ± 0.09) in all the stations beyond the NESREA recommended limits. The study also showed significant negative relationship between plankton and heavy metals. It recommends a yearly monitoring by regulatory agencies to ensure that shipping activities do not interfere with water quality at the terminals.

Keywords: Water Quality, Heavy Metal, Phytoplankton, Pollution, Port Terminals.

INTRODUCTION
Environmental pollution due to heavy metals is increasingly becoming a problem and has become of great concern due to the adverse effects it has on aquatic ecosystem. Due to the astounding increase of the use of heavy metals, it has resulted in an imminent surge of metallic substances in both the terrestrial and the aquatic environment (Gautam *et al*, 2016). Heavy metal being non bio-degradable, can persist in the environment and become concentrated up in the food chain. (Eja *et al*., 2003)
Phytoplankton is of great importance in bio-monitoring of pollution (Davies *et al.,* 2009). The distribution, abundance, species diversity, species composition of the phytoplankton are used to assess the biological integrity of the water body (Townsend *et al*., 2000). Phytoplankton are good indicators of environmental change due to their quick response to changes in environmental pressures such as nutrient availability (Water report) The biomass of phytoplankton affects the light climate for benthic macrophytes (Sand-Jensen and Borum 1991) as well as the nutrient availability (Sand-Jensen and Borum 1991) and oxygen conditions for benthic macrophytes through their sedimentation (Holmer and Bondgaard, 2001).
Ityavyar and Tyav (2004) defined Environmental pollution as an undesirable change in the environment through harmful substances; waste materials and resources, caused by man's activity or natural disaster which also results to the degradation of the environment with its attendant consequences on biodiversity
According to Elliot (2016), sources of pollution in inland and coastal waters of Nigeria include agro-chemicals (herbicides, pesticides etc.); industrial effluents, domestic sewage and refuse; crude oil spillage and toxic petrochemical by-products. Other sources of harmful chemicals include 'poisonous' plants and plant secondary metabolites which are often used in fishing. These secondary metabolites subsequently, contributes to water pollution with a lot of negative effects on some important aquatic fauna and flora (Omoregie, *et al*., 2015) Results of several studies (Uttah *et al.,* 2008**;** Ibrahim and Abdullahi, 2008; Woke *et al*., 2013; Arazu and Ogbeibu, 2017; Kwen *et al*., 2019; Asiegbu *et. al*., 2019**)** have shown that physical and chemical conditions of aquatic ecosystems determine the occurrence, diversity and density of both flora and fauna in any given habitat, which may change with season of the year (Okogwu and Ugwumba, 2006).
Human activities which include spills from discharging of cargo from vessels, cleaning of oil tanks painting at berth within Calabar River Port Terminals, Calabar, Nigeria may introduce heavy metals and petrochemical effluents that contain hydrocarbons and other toxic organic compounds which are consumed by bacteria and lower the amount of dissolved oxygen in aquatic environments (Fleeger *et al.* 2003).
River ports are extremely complex systems with a wide range of environmental factors such garbage production, noise, dredging, and discharges into the water, air, and soil are just a few (Darbrato *et al*., 2005).

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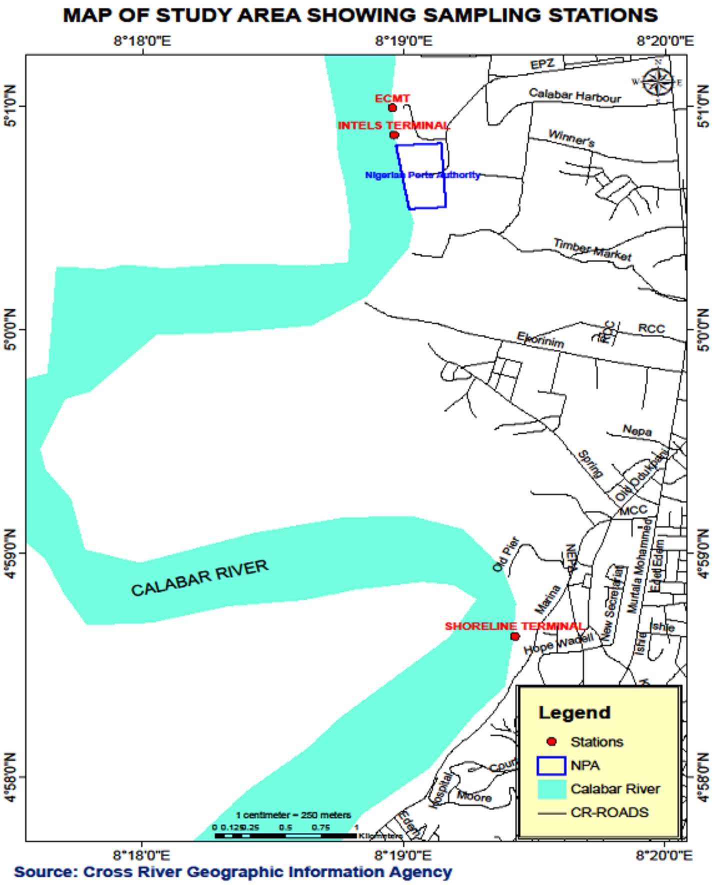

Source: Cross River Geographic Information system (2021)

METHODOLOGY

Plankton identification

Water samples were collected from the three terminals in the Calabar Port—the Eco Marine Terminal (ECMT), the INTELS terminal, and the Shoreline Jetty on a monthly basis for a period of twelve months (February,, 2020 – January, 2021) using the random sampling technique.

Also Sampling for phytoplankton was done monthly for the period of 12 months at the identified sampling stations. Planktons were obtained from 100 liters of water fetched with a plastic bucket and filtered through a 55µm mesh standard plankton net as described by Eni and Andem, (2012**)**. Phytoplanktons were preserved in 4% buffered formalin solution and stored in 500ml plastic sample bottles. The sample was then transported to the Central Analytical Laboratory, Institute of Oceanography, University of Calabar for identification.

For laboratory examination, a total of 144 samples—each representing the water quality and plankton—were taken. At each terminal, two (2) samples were taken each month for water quality analysis and two (2) samples for plankton analysis. Each month, the value for that terminal was determined using the average value for each of the terminals for each parameter.

In the laboratory, samples from the three stations were concentrated to 10ml, 1ml from each sample was taken and all individual taxa present were counted under a microscope. Specimens were sorted, counted using Zeiss binocular microscope at different magnifications (60 x, 100 x and 400 x) Lugol's iodine solution was used to stain the samples in order to improve the ability to distinguish between different species of phytoplankton and to identify them based on their morphological characteristics. (Akpan,1994). Planktons were estimated using Sedgwick-Rafter counting chamber as described by Ovie *et al.* (2015). Phytoplanktons were identified using method of Alfred. *et al.* (1973).

Analysis of Heavy Metal

Cupper, (Cu), Nickle (Ni), Lead (Pb), Cadmium (Cd), Chromium (Cr) and Mercury (Hg) where analyzed using standard procedure of open digestion set by APHA (2009) for the digestion of water samples. 50 mLwell-mixed, acid preserved sample was measured and transferred into a 42 beaker. 5 mL of concentrated HNO^3 was added to 50 mL of the water sample. The mixture was heated slowly to evaporate to a volume of about 15 – 20 ml on a hot plate. Continues heating and adding of concentrated HNO as necessary was employed until digestion was complete as shown by a light-colored, clear solution. The walls of the beaker were washed down with double distilled water and then filtered with a 0.45 µm pore filter paper. The filtrate was transferred to a 50 ml volumetric flask and topped to the mark. The digested samples were used to measure the individual metal concentrations in the water using an atomic absorption spectrometer (AAS)

RESULT AND DISCUSSION

Table 1: Seasonal variation in the concentration of heavy metals in water in Calabar Port Terminal

Concentration of Heavy Metals	Seasons		p-value	t-test	NESREA standard
	Dry	Wet			
Cupper (Cu)	0.03 ± 0.01	0.03 ± 0.01	0.92	p > 0.05	0.01
Nickel (Ni)	0.67 ± 0.03	0.66 ± 0.03	0.76	p > 0.05	0.01
Lead (Pb)	0.02 ± 0.02	0.02 ± 0.01	0.45	p > 0.05	0.1
Cadmium (Cd)	0.31 ± 0.09	0.31 ± 0.09	0.98	p > 0.05	0.01
Chromium (Cr)	0.28 ± 0.04	0.25 ± 0.05	0.51	p > 0.05	0.5
Mercury (Hg)	0.00 ± 0.00	0.00 ± 0.00	BDL		0.0005

Mean ± S.D values with $p < 0.05$ are significant while $p > 0.05$ are not significant

Where: Cu = Copper; Ni = Nickel; Pb = Lead; Cd = Cadmium; Cr = Chromium; Hg = Mercury. BDL= Below Detection Limit

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Table 2: Seasonal Distribution of Phytoplankton in Calabar River port Terminals during the study Period

Phytoplankton Class	Phytoplankton Species	Dry Season			Wet Seasons			Total	
		ECMT	INTELS	Shorelines	ECMT	INTELS	Shorelines	Dry	Wet
Bacillariophyceae	*Coscinodiscus excentricus*	13	11	7	15	7	13	31	35
	Coscinodiscus radiate	19	12	5	15	26	7	36	48
	Navicula sp.	9	0	0	7	11	0	9	18
	Melosira sp.	0	6	0	0	28	0	6	28
	Melosira granulate	0	0	0	1	0	7	0	7
	Denticum thermalis	2	5	0	6	32	0	7	38
	Diatoma sp.	0	1	0	0	7	0	1	7
	Cyclotella meneghiniana	0	0	0	3	0	0	0	3
Xanthophyceae	*Tribonema minus*	11	0	1	19	3	10	12	32
	Tribonema sp.	0	6	0	0	21	0	6	21
Chlorophyceae	*Spyrogyra sp.*	11	0	1	16	4	0	12	20
	Chlamydomonas sp.	0	0	7	0	0	12	7	12
	Dermatophyton radians	0	0	9	0	0	10	9	19
	Heterothrix ulothricoides	0	0	0	1	0	0	0	1
	Eudorina elegans	0	0	0	5	6	0	0	11
	Closterium gracile	0	0	0	6	8	0	0	14
Euglenodea	*Euglena sp.*	0	0	0	0	0	10	0	10
Cyanophyceae	*Anabaena affinis*	0	0	0	0	9	2	0	11
	Oscillatoria sancta	0	0	0	0	9	16	0	25
	Individuals	**65**	**41**	**30**	**94**	**171**	**87**	**136**	**360**
	Taxa_S	**6**	**6**	**6**	**11**	**13**	**9**		
	Evenness_e^H/S	**0.8797**	**0.8441**	**0.7977**	**0.7556**	**0.7839**	**0.9137**		

Table 3. Correlation coefficient for heavy metals and plankton during the rainy season

	Cu	Ni	Pd	Cd	Cr	Phyto Taxa	Phyto Ind.
Cu	1						
Ni	0.379	1					
Pb	-.828**	-.661**	1				
Cd	.852**	-0.066	-.635**	1			
Cr	.752**	0.0696	-.635**	.806**	1		
Phyto Taxa	0.37504	.742**	-.562**	0.0258	0.083	1	
Phyto Ind.	-0.1286	0.3839	-0.095	-0.327	-0.23	.703**	1

Table 4. Correlation coefficient for heavy metals and plankton during the dry season

	Cu	Ni	Pd	Cd	Cr	Phyto Taxa	Phyto Ind.
Cu	1						
Ni	.560*	1					
Pb	-.955**	-.649**	1				
Cd	.846**	0.0514	-.770**	1			
Cr	.803**	0.0424	-.655**	.911**	1		
Phyto Taxa	.574*	.633*	-.721**	0.3456	0.26	1	
Phyto Ind.	-.606*	0.3729	-.732**	.551*	0.39	.678**	1

Seasonal correlation between heavy metal and plankton distribution shows a positive correlation between Cu and phytoplankton distribution in terms of diversity in both season and negative relationship in terms of individual (abundance) in both seasons. The correlation coefficients for phytoplankton was positive for dry and wet season respectively but negatively correlated with individual species in both seasons. This implies that increase in Cu concentration led to increase in phytoplankton diversity during both seasons but negligible decrease in phytoplankton abundance in both season. This agrees with the findings of Rodgers *et al*. (2010) that the 13^{C} assay showed an impact of copper on phytoplankton, through reduction in 13^{C} uptake, suggesting a reduction in photosynthetic activity. It is possible that Cu concentrations toxic to marine phytoplankton are confined to areas impacted by heavy anthropogenic emissions. Sholkovitz *et al*. (2012) showed that significant correlation between Cu concentrations in phytoplankton with various phytoplankton that were abundant at Blanakan Ponds was Nitzschia with correlation coefficient (r) = 0.7518. It showed that the higher Cu concentration in phytoplankton, the higher Nitzschia abundance (Siswantining, 2017).

Nickel showed strong positive correlation with phytoplankton distribution in both seasons. Thus, increase in nickel showed increase in phytoplankton abundance and diversity. Lead showed negative correlation with both diversity and abundance in dry and wet. However, only phyto taxa had strong negative correlation in dry season. The correlation coefficients for phyto taxa were -0.56 and -0.10 for dry and wet season respectively but -0.10 for individual in both seasons affects phytoplankton communities at different levels - abundance, growth strategies, and dominance and succession patterns. However, Guo *et al*., 2022 posits that's That Ni sensitivity of phytoplankton varied between the 11 species tested within the study but was generally rather 435 low. This may be partly due to the use of nitrate as a nitrogen source in his experiments as other studies have revealed higher Ni sensitivities when growth is fuelled by other nitrogen-sources, such as urea. The reduced sensitivity observed in his study may also be due to the use of the high concentration of organic ligand (EDTA) added to our media, which complexed Ni making it less available for biological interactions (Guo *et al*.2022)

Cadmium had negligible correlation with phytoplankton abundance and diversity in both seasons. However, the negligible correlation was positive in dry season taxa S but negative in wet season. The correlation coefficients were 0.03 and 0.33 for diversity and abundance in dry season but -0.33 and -0.31 in wet season. Chromium also had negligible correlation with phytoplankton abundance and diversity in both seasons. Hindarti and Larasati, (2019) reported the increasing heavy metals concentration lead to the decreasing of cell density and intracellular pigment content of Nitzschia sp., thus the lower correlation value during the dry season. However, the negligible correlation was positive in dry season but negative in wet season. The. The negative correlation observed in Cd and Pb corroborate the report of Echeveste *et al*. (2012) that Cd and Pb are lethal to oceanic marine phytoplankton. The positive correlation between Nickel and phytoplankton affirmed the report of Boyce *et al*. (2010) that Nickel act as nutrient that is essential for the growth of cells in water organism. Some phytoplankton utilize heavy metals for their growth, they multiply increase in population when they get Fe, Zn, Cu, Mn etc. Thus, some phytoplankton are considered pollution indicator.

Conclusion

The quality of water influences the abundance, diversity and specie evenness of phytoplankton in water. There was observed an elevated heavy metal concentration in Calabar River port terminals. These varied spatially due to tidal influence and variation in human activities. All Heavy metals in the study showed negative relationship with plankton except nickel which had a strong positive relationship Thus, pollution of water body with heavy metal has significant impact on planktons distribution and consequently on food chain

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