Original Research Article

Effect of Climate Change through Temperature increase on Heavy Metals Concentrations in Water and Sediment of Ekpan Creek, Delta State, Nigeria

ABSTRACT

Climate change affect the physiochemical characteristics of water bodies directly through temperature increase with resultant effect in reducing heavy metals concentrations in surface water temporarily, and indirectly changing the physical and chemical processes related to temperature in the water columns. This scenario concomitantly increase the rate of biochemical processes with a significant decrease in oxygen concentration, as well as the composition and distribution of metals in water and sediment. The concentrations of heavy metals in water and sediment of Ekpan Creek was investigated from December 2009 to May 2010 at monthly interval. Five sampling stations was designated along the water stretch for water and sediment collection. The Varian Techron Spectr AA – 10 Atomic Absorption Spectrometer (S/N.902 1318) with a printer attached was used for the determination of phosphate, sulphate, nitrate, copper, iron, chromium, manganese, lead, zinc and cadmium.

At the stations, air temperature ranged from 27.9^{0}C to 33.4^{0}C, water temperature from 28^{0}C to 34^{0}C; TDS, 463 to 503mg/L; DO, 4.12 to 7.44 mg/L; hardness, 85.47 to 125 mg/L; phosphate, in water (0.03 to 0.18 mg/L) sediment, 17.85 to 2484 mg/L); nitrate in water 0.02 to 0.04 mg/L, sediment 1.47 to 9.51 mg/L; sulphate in water 19.26 to 50.66 mg/L, sediment 1.47 to 9.51 mg/L; iron in water 0.65 to 0.43 mg/L, sediment 380.37 to 239.17 mg/L; zinc in water 0.32 to 0.13 mg/L, sediment 8.11 to 3.14 mg/L; copper in water 0.0038 to 0.0014 mg/L, sediment 1.33 to 0.05 mg/L; lead in water 0.0042 to 0.001 mg/L; sediment 0.16 to 0.02 mg/L; cadmium in water 0.028 to 0.001 mg/L, 0.504 to 0.019 mg/L; chromium in water 0.0038 to 0.0012 mg/L, sediment 0.801 to 0.001 mg/L; manganese 2.44 to 0.86 mg/L. The present study recommend enforcement of strict regulation of anthropogenic input of these metals to the river and more in-depth study of the impacts of climate change on metals concentrations in aquatic systems.

Keywords: *(*Heavy metals, bioavailability, climate change, temperature, Ekpan Creek, WRPC, Chevron)

1. INTRODUCTION

The impact of climate change on heavy metals concentrations have been qualitatively discussed for different marine ecosystems [1,2]. Climate change have been observed to affect directly the physico-chemical characteristics of water through temperature increase, and indirectly on the physical and chemical processes related to temperature in the water column. The effect of this relationship have been reported to increase the rate of biochemical processes by decreasing oxygen concentrations, change water stratification patterns (the building up of layers in water column) and metals concentrations in aquatic systems.

There is a strong link between the impact of climate change through temperature increase on metal concentrations, turbidity, salinity, dissolved oxygen, biochemical oxygen demand and pH of water bodies, however their knowledge is still very limited with few scientific documentation. A general increase in metal uptake have been observed with increasing temperature in investigated biota, and consequent decrease in dissolved oxygen concentrations and verse versa by Fritioff et al. [3] and Verweij et al. [4]; a natural phenomenon also observed to increase biochemical oxygen demand in surface water causing anoxia.

The most discussed drivers of climate change are the anthropogenic increases in temperature and carbon dioxide, in line with the present study will contribute to the paucity in climate change information by examining other temperature relationships capable of impacting on heavy metal and nutrient concentrations, thus water quality. Increase in surface water temperature for instance, have been noted to alter the physiochemical characteristics of water bodies, with positive effect in reducing heavy metals concentrations in surface water [3], however will significantly increase their concentrations in the bottom sediment, and have been reported in the study area by Oluowo and Isibor [5].

Till date, there are gaps in knowledge in determining climate change scenarios in aquatic ecosystems [4]. The paucity in information of the influence of changing climates on water quality, thus aquatic systems will pose serious challenges to policy makers in the future, to effectively manage aquatic pollution and in assessing their qualities [4,6]. Nevertheless, few studies have outstandingly contributed to this knowledge gap, especially in temperate regions.

The growing concern of anthropogenic climate change causing global warming; a phenomenon associated with atmospheric temperature rise from normal is heightened by human activities such as burning of fossil fuels, deforestation, bad agricultural practices, as well as developmental activities known to elevate the concentrations of greenhouse gases (CO_2, CH_4 and N_2O) in the atmosphere [7]. The impacts of these activities end up in water bodies with negative consequences.

The bioavailability of these gases, thus their concentrations in the atmosphere have been reported to increase air temperature with corresponding increase in water temperature [8]. Shallow water bodies, for instance are more sensitive to temperature increase, which have been observed with lakes in the Netherlands [4]. The usefulness of temperature in assessing the impacts of changing climate in coastal environment is increasingly documented with increase in phytoplankton and other aquatic plant population.

Few empirical studies has documented higher metal bio-accumulation by aquatic plants with increasing temperature, and noteworthy to the present study are the work of [9,10,11,12] report of higher metal bio-accumulation in grown terrestrial plants with increasing temperature. They concluded that, there was a general increase in metal uptake by aquatic plants with increase in temperature.

The usefulness of submerged plants, such as *Eichhornia crasspies* and other floating plants in reducing heavy metal concentrations in water was attributed to their ability to take up substances from surface water and bio-accumulating them in their roots [13,14,15,16,17]; a useful knowledge in the future in ecosystem monitoring. Although, other physiochemical characteristics such as pH, redox potential surrounding metals concentrations and salinity have been widely reported to influence the processes of metal uptake by aquatic plants, however temperature influence them all.

It was also very striking to note that seasonal variation in surface water temperature known to influence metal solubility in water was reported not to have any direct effect in metal solubility [18], as often asserted. The impact of climate change is gradually contradicting previously known monitoring indicators of water bodies, coupled with the complexity in assessing freshwater ecosystems. This is partly due to their slow responses and variability under changing climate; a useful insight in the present study to narrow the knowledge gap on the occurrences and fate of heavy metals in aquatic systems due to climate change.

For example, heavy metals concentrations in interstitial water of sediment decreases with decreasing temperature, because more metals are bounded to sediment colloid at high temperature [19]. This

shortcoming in knowledge was also reported on metal speciation, bioavailability and toxicity [20]; its usefulness have been suggested in understanding the geochemical occurrences of heavy metals in sediments. Especially as sediment has remained an undisputed repository sink for aquatic pollution, by receiving most concentrations released into it.

Ekpan River is one sensitive water stretch in the oil rich Niger Delta believe to receive untreated waste materials from Chevron, Warri Refinery and Petrochemical Company (WRPC) and other human activities capable of compromising the quality of the water over the years. However, available studies have documented heavy metals concentrations within regulatory limits, except iron, zinc and lead as well as significant increase in aquatic plant population [5, 21, 22], substantial increase in heavy metals concentrations and increase in surface water temperature in the present study.

The abundance and increase in aquatic plant (*Eichhornia crassipes*) in the study area, may have been aggravated by climate change through temperature increase. Secondly, these aquatic plants are suspected to have continuously bio-accumulated some of these metals from surface water into their shoot, thus reducing their concentrations. Other temperature-dependent interplay factors, such as flow velocity and natural dilution in the water may have helped to attenuate their concentration and have been reported [5].

The growing misinterpretation of some these relationships could be detrimental to scientific reporting in the future, if not properly understood. The aim of the present study is to examine some of the impact of climate change through temperature increase on the physiochemical characteristic of the study area, their influences on heavy metals concentrations in surface water and sediment. The results will be compared with available studies in the creek to steer up new scientific curiosity in bio-monitoring aquatic ecosystems in the face of climate change.

MATERIAL AND METHODS

Study Area

Ekpan Creek, Effurun, Delta State (fig. 1) is one of the wetlands areas in the oil rich Niger Delta region of Nigeria, located within 5^0 3'5.11"N 5^0 40'44.11"E, altitude 13.5 – 17.5m. The river is about 12km long and

one of the major sinusoidal rivers which in conjunction form an astonishing tributary streams and creeks that drains the wetlands of the western Niger Delta. The river flows westerly into the creek at NNPC jetty and empties into Warri River at Bennet Island [5, 22].

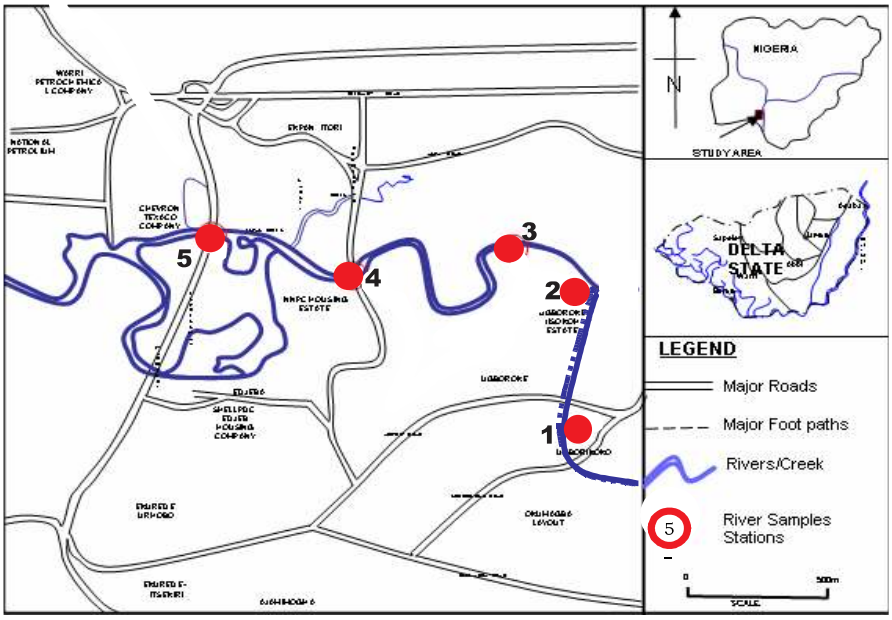


Figure 1: Map of Warri showing sampled points [5].

Notable activities capable of impacting the river were oil exploration activities from Chevron Nigeria Limited and petrochemical refining from the Warri Refinery and Petrochemical Company, a subsidiary of Nigerian National Petroleum Corporation (NNPC), Delta Development Property Agency (DDPA) estate occupants waste dumping directly into the water. Others are logging, laundry, washing, bathing, swimming and agricultural farms.

The study area is known with high relative humidity (80-92%), annual average rainfall above 2800 mm and two distinct seasons (wet and dry) and temperature range between 27^0C to 29^0C.

2.2 Sampling Locations

Five sampling stations were carefully identified for the purpose of the study in proximity to anthropogenic activities and for their proximity to structures with potential impacts on the river from December 2009 to May 2010, to cover wet and dry seasons sampling.

Station I was established downstream of the study area at Olare layout with water depth of 2.47 ± 0.50 m, flow velocity of 1.02 ± 0.30 m/s . Station II was located at the DDPA estate, Station III was the Ekpan new

Layout with water depth (3.56 ± 5.65 m) and flow rate (1.48 ± 0.07 m/s) faster than that of Station II. Station IV was located directly under the Ekpan Bridge, near the NNPC housing complex with water depth (5.12 ± 7.71 m) and flow rate (1.48 ± 0.12 m/s). While Station V was located less than 5km away from Chevron-Texaco Company bridge site; the water depth was 6.38 ± 8.44m, it flows very fast with water velocity of about 1.50 ± 0.18 m/s. A detailing of the study area and sampled stations have been provided by Oluowo and Isibor [5] and Oluowo and Olomukoro [23].

2.3 Temperature Measurement

Temperature readings were collected in-situ using mercury in glass centigrade thermometer. The water was collected in plastic containers, pre-washed and rinsed with distilled water. The thermometer was held in the water for 2 - 4 minutes, while readings were taken with the thermometer still inside the water.

2.4 Samples Collection and Analysis

2.4.1 Water and Sediment samples

Water and sediment were collected from five sampling stations from December 2009 to May 2010 at time between 7.00 am and 9:30 am for six (6) months. This sampling time was chosen because human activities in the river were still very low and appropriate to determine the physiochemical conditions of perturbed fresh water bodies. Sampling containers were thoroughly washed with water, soaked in diluted nitric acid for four hours, thereafter rinsed with distilled water. Care was taken to avoid contamination of samples during collection.

Water samples were collected in appropriately labeled bottles as described by Oluowo and Isibor [5]. Those for chemical analysis were collected into 1L polythene bottles without acid, BOD in colored bottles monthly, just below the water surface using direct sampling method describe by APHA, 1989 and modified by USEPA [25]. While sediment, using a 6-inch Ekman grab into appropriately labeled black polythene bags for the same study period. Water samples were pretreated and digested using the wet oxidation method [26] and widely in use. The Varian Techron Spectr AA – 10 Atomic Absorption Spectrometer (S/N.902 1318) with a printer attached was used for the quantitative determination of all heavy metals. The water samples already fixed in nitric acid [27] and filtered through Whatman filtered paper no 1 and aspirated directly into the AAS for metal such as Cd, Cu, Pb, Mn, Ni and Zn. The blanks were prepared accordingly. For quality assurance purposes AAS was calibrated for each metal by

dissolving 1 gram analar grade metal salt in 1 litre of distilled water. Standard and corresponding blanks were run with each set of experimental digest. The detection limits of zinc (0.5 mg/L), manganese (0.5 Mg/L), copper (0.05 Mg/L), nickel (0.02 Mg/L), lead (0.03 mg/L), and cadmium (0.01 mg/L) were carefully observed. To ascertain quality control results of analysis were cross checked using standard reference materials for water and sediment; provided by FEPA [28].

Total organic matter content estimation was conducted using the percentage loss on Ignition (LOI) procedure recommended by Allen 1989 and described by Oluowo and Isibor [5]. The Inductively Coupled Plasma-Mass Spectrometer (ICP) was used to ascertain the presence of possible heavy metals in few samples of water and sediment as suggested by Dojlido and Best [29] and used extensively [5,30 31,32]. The ICP procedure describes a technique for simultaneous or sequential multielement determination of metals and trace elements in solution based on the measurement of atomic emission by an optical spectrometric technique.

2.5 Statistical Analysis

Analysis of variance (ANOVA), regression, and correlation coefficients were carried out on data to show significant differences in the monthly metal concentrations in the water and sediment using the 2007 Excel and SPSS version 19 tool packages. Duncan Multiple Range test (DMR) was employed to ascertain the actual locations of the significant differences which occurred in the ANOVA.

Distribution coefficient (Kd) was used to determine the sorption capacity of the parameters into the sediment. Values less than 6 mg/L were considered insignificant.

$$\text{Distribution coefficient (Kd)} = \frac{M_{ads}}{M_{sol}}$$ [33].

Where M_{ads} = metals adsorbed into the soil and M_{sol} = metal concentration in water.

3.0 RESULTS

3.1 PHYSICAL AND CHEMICAL CHARACTERISTICS

The summary of some of the physical and chemical parameters, heavy metal analysis for water and sediment are presented in Tables 1, 2 and 3.

Table.1: Summary of Physio-Chemical characteristics of Ekpan Creek for sampled stations from December 2009 to May 2010.

PARAMETERS	STATION 1			STATION 2			STATION 3			STATION 4			STATION 5				
	x̄ ± SD	MIN	MAX	x̄ ± SD	MIN	MAX	x̄ ± SD	MIN	MAX	x̄ ± SD	MIN	MAX	x̄ ± SD	MIN	MAX	FEPA 1991	NIS 2007
BOD (mg/L)	2.39 ± 0.919	1.7	4.1	2.50 ± 0.738	2.1	4	2.633 ± 0.65	2.1	3.9	2.41 ± 0.809	1.6	3.9	2.318 ± 0.772	1.5	3.8	30	
COND (µs/cm)	**989.7 ± 32.08***	**966**	**1031**	**893.7 ± 23.91***	**872**	**924**	**843.2 ± 63.39***	**798**	**426**	**1056.7 ±128.06***	**925**	**1210**	**1106.2 ± 177.85***	**891**	**1289**	1000	-
DO (mg/L)	5.177 ± 1.279*	4.2	7.6	4.665 ± 1.298	3.89	7.2	4.652 ± 1.552	3.8	7.8	4.8217 ± 1.22	4	7.2	4.9283 ± 1.232	4.2	7.4	4 - 6	
HCO_3^- (mg/L)	36. ± 9.209	24	50	35.67 ± 6.089	30	44	331.7 ± 7.283	24	42	43.182 ± 17.14	21.09	60	52.677 ± 19.186	28	70	-	-
O & G (mg/L)	0.003 ± 0.002	0.001	0.007	0.004 ± 0.007	0.001	0.018	0.003 ± 0.004	0.001	0.013	0.0035 ± 0.004	0.001	0.011	0.0012 ± 0.0004	0.001	0.002	20	-
pH	6.723 ± 0.065	6.64	6.8	6.743 ± 0.113	6.6	6.9	0.0695 ± 0.117	6.6	6.87	6.783 ± 0.137	6.5	6.9	6.7367 ± 0.095	6.6	6.85	6-9	6.5-8.5
TDS (mg/L)	**476. ± 17.36***	**454**	**492**	**439 ± 26.35***	**406**	**464**	**416.2 ± 37.44***	**380**	**463**	**526.27 ± 60.945***	**460**	**597**	**570.83 ± 102.53***	**449**	**678**	2000	500
TOTAL ALKALINITY (mg/L)	28.77 ± 7.763	19.67	40.96	28.89 ± 4.796	24.59	36.06	27.999 ± 6.4999	19.67	35.79	331.12 ± 11.54	19.67	49.18	35.737 ± 15.282	20.97	57.37	100	
TOTAL HARDNESS(mg/L)	**105.1 ± 14.72***	**88.64**	**125.8**	**93.4 ± 13.58***	**79.45**	**106.8**	**91.48 ± 14.29***	**78.2**	**216.6**	**110.34 ± 26.591***	**75.65**	**188.45**	**124.61 ± 26.015***	**90.25**	**146.39**	100	150

Note: FEPA connote Federal Environmental Protection Agency (Nigeria), NIS means Nigeria Industrial Standard, Bolded and asterisks (*) are values above one of the regulatory limits.

Table 2. Heavy metals and nutrients concentrations in water obtained along the stations from December 2009 to May 2010.

Metals and Nutrients	STATION 1			STATION 2			STATION 3			STATION 4			STATION 5			Regulatory Standards	
	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	FEPA 1991	NIS 2007
Cd (mg/L)	**0.013 ± 0.028***	**0.001**	**0.071**	**0.006 ± 0.011***	**0.001**	**0.028**	**0.003 ± 0.004***	**0.001**	**0.011**	**0.0048 ± 0.007***	**0.007**	**0.021**	**0.003 ± 0.004***	**0.001**	**0.013**	**0.01**	**0.003**
Cr (mg/L)	0.002 ± 0.001	0.001	0.004	0.003 ± 0.004	0.001	0.011	0.002 ± 8E-04 ($8x10^{-4}$)	0.001	0.002	0.0012 ± 0.004	0.001	0.002	0.0017 ± 0.001	0.001	0.003	0.05	0.05
Cu (mg/L)	**0.03± 0.002***	**0.001**	**0.005**	0.001 ± 5E-04 ($5x10^{-4}$)	0.001	0.002	0.003±0.003	0.001	0.008	0.0025 ± 0.003	0.001	0.006	0.0025 ± 0.0014	0.001	0.005	0.05	1
Zn (mg/L)	0.25±0.139	0.117	0.518	0.13±0.088	0.073	0.312	0.2±0.103	0.119	0.398	0.248±0.048	0.201	0.344	0.164±0.121	0.052	0.349	1.5	3
Fe (mg/L)	0.712 ± 0.131	0.492	0.822	0.453 ± 0.011	0.329	0.169	0.631±0.236	0.459	1.032	0.4293 ±0.222	0.18	0.729	0.435 ± 0.15	0.313	0.738	0.3-1.00	0.3
Mn(mg/L)	**0.21 ± 0.027***	**0.008**	**0.076**	0.015 ±0.008	0.007	0.029	0.023± 0.015	0.014	0.043	0.0003 ± 0.01	0.001	0.035	0.0262 ± 0.01	0.013	0.062	N/A	0.20
Pb (Mg/L)	0.01 ± 0.003	0.001	0.007	0.002 ± SE – 4 ($5x10^{-4}$)	0.001	0.002	0.0041 ± 0.003	0.001	0.009	0.0013 ± 0.0008	0.001	0.003	0.0018 ± 0.011	0.001	0.004	0.05	0.01
PO_4^{3-} (mg/L)	0.094 ± 0.08	0.032	0.199	0.077±0.061	0.014	0.152	0.159 ± 0.175	0.039	0.386	0.052±0.040	0.022	0.105	0.0357 ± 0.01	0.017	0.06	-	-
SO_4^{2-} (mg/L)	26.6 ±16.48	14.72	56.86	29.33 ± 12.02	15.14	48.99	27.23 ± 12.17	19.4	51.38	31.7±13.80	18.65	54.82	27.49 ± 9.557	15.73	41.23	-	100
NO_3- (mg/L)	0.034 ± 0.013	0.016	0.047	0.023 ± 0.023	0.001	0.067	0.026 ± 0.015	0.017	0.057	0.0367 ± 0.015	0.014	0.056	0.0375 ± 0.011	0.027	0.051	20	0.2

Note: FEPA connote Federal Environmental Protection Agency (Nigeria), NIS means Nigeria Industrial Standard, Bolded and asterisks (*) are values above one of the regulatory limits.

Table 3. Heavy metals and nutrients concentrations in sediment obtained along the stations from December 2009 to May 2010.

PARAMETER	STATION 1			STATION 2			STATION 3			STATION 4			STATION 5			FEPA 1991	NIS 2007
	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX	ẋ ± SD	MIN	MAX		
Cd (mg/L)	**0.153 ±0.31***	**0.009**	**0.794**	**0.121 ± 0.22***	**0.006**	**0.587**	**0.16 ± 14***	**0.065**	**0.454**	**0.066 ± 0.11***	**0.006**	**0.298**	**0.083 ± 0.15***	**0.011**	**0.39**	0.003	0.003
Cr (mg/L)	0.244 ±0.59	0.001	1.454	0.118 ± 0.28	0.001	0.695	0.055 ± 0.133	0.001	0.328	0.170 ± 0.407	0.001	1.002	0.92 ± 0.21	0.002	0.529	2.000	0.05
Cu (mg/L)	0.471 ± 0.48	0.098	1.265	0.466 ± 0.51	0.0098	1.154	0.725 ± 0.814	0.021	2.074	0.538 ± 0.68	0.021	1.693	0.4215	0.021	1.179	1.000	1.00
Fe (mg/L)	**299.38 ± 52.67***	**210.01**	**374.22**	50625.09 ± 1231.59	283.370	302.023	317.57 ± 92.034	201.216	429.053	313.14 ± 43.14	265.34	385.19	303.07 ± 59.742	220.45	387.23	0.300	0.3
Mn (mg/L)	**1.764 ± 1.23***	**0.108**	**3.397**	**1.567 ± 0.63***	**1.045**	**2.77**	**1.635 ± 0.77***	**1.097**	**3.053**	**1.6 ± 0.51***	**1.032**	**2.22**	**1.489 ± 0.45***	**1.001**	**2.087**	0.050	0.2
Pb (mg/L)	**0.062 ±0.10***	**0.002**	**0.276**	**0.075 ± 0.04***	**0.012**	**0.0123**	**0.041 ± 0.03***	**0.007**	**0.083**	**0.071 ± 0.04***	**0.004**	**0.105**	**0.124 ± 0.26***	**0.003**	**0.655**	0.010	0.01
Zn^{2+} (mg/L)	**6.045 ± 2.56***	**3.453**	**10.876**	**5.566 ± 2.54***	**2.621**	**8.548**	**5.513 ± 1.33***	**3.761**	**7.493**	**5.691 ± 1.89***	**3.005**	**8.939**	**5.501 ± 1.48***	**2.513**	**6.632**	3.000	3.00
$N0_3^-$ (mg/L)	**3.613 ±2.59***	**1.453**	**8.681**	**3.605 ± 419***	**1.005**	**11.47**	**3.649 ±3.38***	**1.202**	**10.41**	**2.852 ± 1.95***	**1.059**	**6.71**	4.241 ± 3.49	1.92	10.31		50
$P0_4^{3-}$ (mg/L)	25.076 ± 11.37	12.982	42.72	30.845 ± 14.26	18.112	56.028	3635.30 ± 5676.06	15.54	12360	24.400 ± 10.62	15.543	44.298	18.569 ± 11.017	10.56	38-058		-
$S0_4^{2-}$ (mg/L)	**2391.7 ± 1938.4***	**2.218**	**4.507**	**2368 ±1902.36***	**1041**	**59.43**	**2780.33 ± 2193.95***	**1003**	**5839**	**1426.98± 1970.76***	**1.054**	**5016**	**946.11 ± 1142.7***	**1.214**	**2673**		100

Note: FEPA connote Federal Environmental Protection Agency (Nigeria), NIS means Nigeria Industrial Standard, Bolded and asterisks (*) are values above one of the regulatory limits.

3.2 Air and Water Temperature

Table 1, fig. 2 presented the temperatures for air and water. The highest monthly air temperature recorded throughout the study period was 33.5°C at station 1 in January 2010. Air temperature values were generally high, compared to previous studies with values in the range of 30ºC and above, except in April and May 2010. The highest water temperature of 34ºC was obtained at station III in December 2009 and was the highest for both air and water in the study. Whereas, the highest air temperature was recorded at station I (33.5°C) in January 2010 followed by February 2010 at station III (33.4°C) and the lowest (27.9°C) at station II in May 2010, water temperature followed a seasonal pattern of being higher in the dry season months (29.5°C to 34°C) than wet (27°C to 30.14°C). December 2009 was the hottest month with very high values of 34°C obtained at station III and 33.2°C at station II, while the lowest of 27ºC was recorded at station I in May 2010.

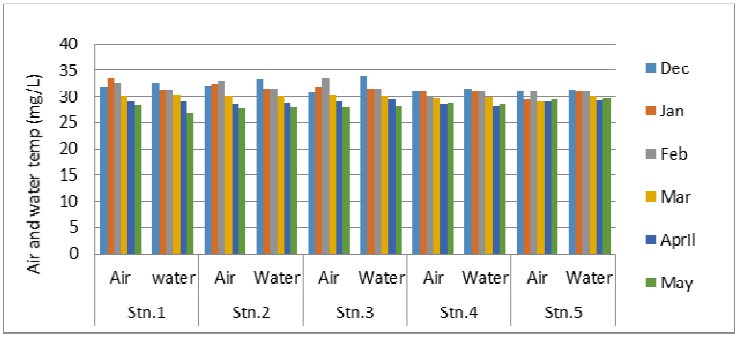


Fig.2: Spatial and monthly variation in air and water temperature.

3.3 Hydrogen ion concentration (pH).

The water was slightly acidic (fig. 3) with pH values ranging between 6.5 and 6.9 mg/L along the sampled stations. The highest pH value of 6.9 mg/L was recorded at stations II and IV in January 2010, while the lowest value of 6.5 at station IV in December 2009. These values were slightly higher than previously reported in the study area, however with observable significant differences ($P < 0.05$) along the stations.

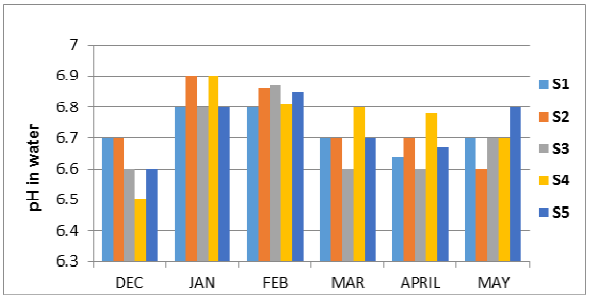


Figure 3: Spatial and monthly variation of pH in water

3.4 Dissolved Oxygen (mg/L)

The monthly concentration of dissolved oxygen as shown in Fig. 4, followed a seasonal prediction of being higher with decreasing water volume (dry season), and reduces as water volumes increases with the rains (wet season). The lowest value of 4.12 mg/L was recorded in May 2010, while the highest value of 7.44 mg/L in December 2008. The values obtained in December 2010 were generally high and above 7.0 mg/L in all the stations. The highest value of 7.8 mg/L was recorded at station III (7.8 mg/L) in December 2009, while the lowest (3.9 mg/L) at station III in March 2010 and station II in April 2010 respectively.

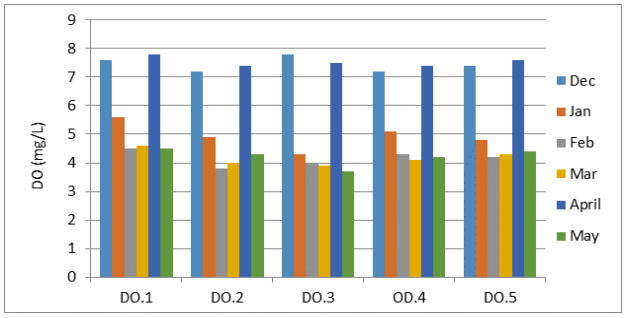


Figure 4: Spatial and monthly variation of dissolved oxygen (DO) in water

3.5 Biochemical Oxygen Demand (BOD)

The values obtained for BOD ranged between 1.5 and 4.1mg/L, with the highest value of 4.1 mg/L recorded in December 2009 at station 1, while the lowest value of 1.5 mg/L was at station V in April 2010 (Table 1, fig 5).

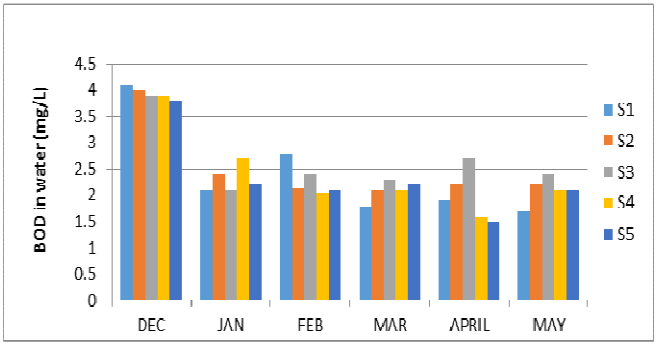


Figure 5: Spatial and monthly variation of biochemical oxygen demand (BOD) in water

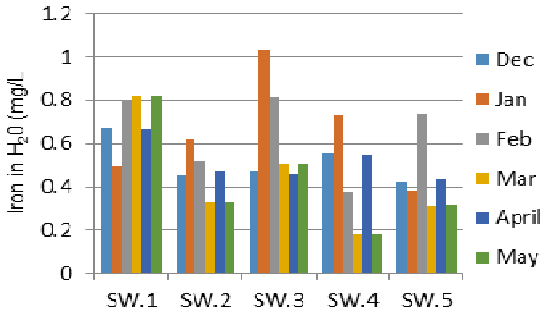
4.1.4 Total Hardness of Water

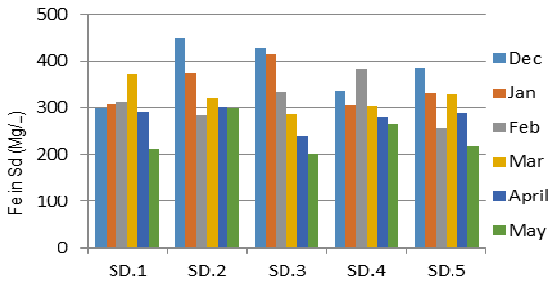
As seen in table 1, water hardness varied largely and did not follow any particular pattern, however was noted to be generally soft. The highest value of 146.39 mg/L was obtained in February, 2010 at station 5, while the lowest of 75.65 mg/L in April 2010 at station 4.

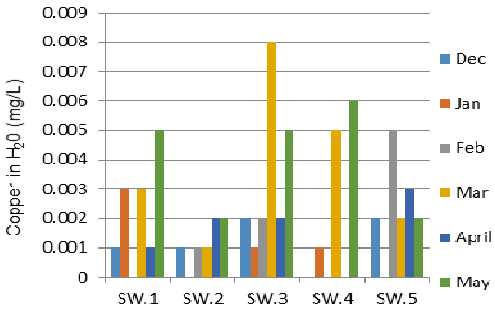
4.1.5 Total Dissolved Solids (mg/L)

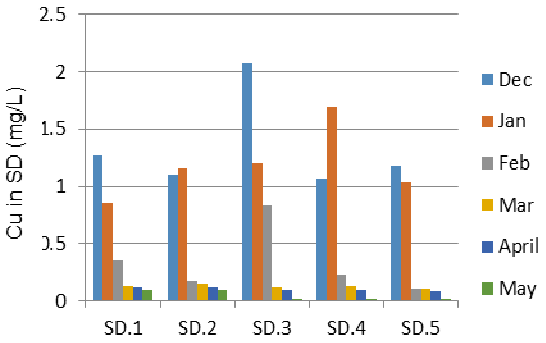
The pattern of distribution of total solids (Table 1); revealed that the highest value of 678 mg/L was obtained at station V in January and February, 2010 respectively. While the lowest value of 380 mg/L at station III in January 2010. The values obtained at station V in all the months were very high and highest through the study period, except in December 2009.

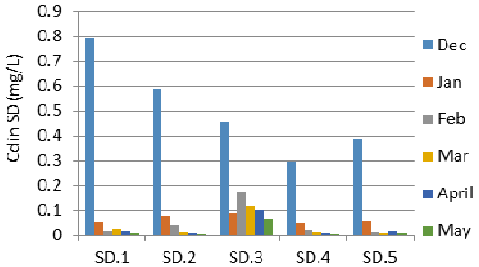
Concentrations of Heavy Metals











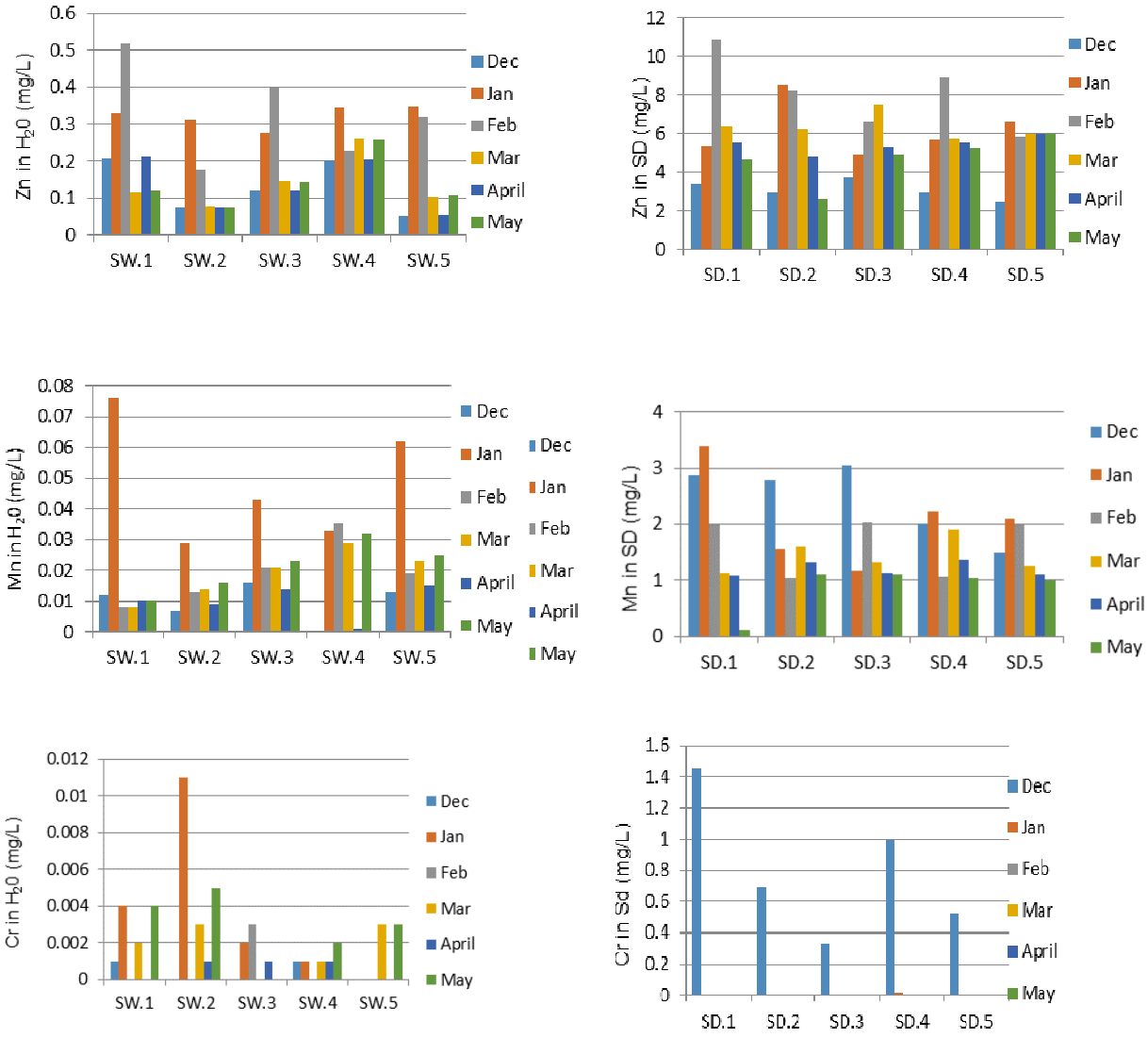


Fig.6: Spatial and monthly variation in heavy metals concentration in water and sediment

DISCUSSION

The concentrations of heavy metals in the surface water throughout the study period were within FEPA safe limits, except for iron in all the stations (Table 2, fig 6), and worrisome levels of zinc recorded at station 1 (0.518 mg/L) and station 3 (0.398 mg/L) in February 2010 (fig. 6), which have been reported previously in the study area by Oluowo and Isibor [5]. Their concentrations however, should not undermine efforts to effectively monitor anthropogenic sources of these metals to the river, especially under climate change scenario, and existing reports of significant increases in heavy metals concentrations found higher than previous studies, their high sorption in bottom sediment [5], as well as increase in aquatic plants population documented by Olomukoro et al. [24]; known to bio-accumulate heavy metals from surface water [4].

Iron has remained the most dominant and consistent metal in the study area, with report of iron and zinc [22], iron and lead [21] and iron and zinc [5] above regulatory limits.

The growing research concern of heavy metals pollution, however with values within recommended limits, except for iron, lead and zinc may have resulted from known oil & gas operations, its allied companies and other human activities that characterized the study area with reports of untreated waste discharge directly into the river has remain a surprise to investigators.

The present study suspect climate change interplay, alongside other physiochemical characteristics of water such as temperature, flow velocity known to increase dilution capacity of water and high sediment sorption capacity reported by Oluowo and Isibor [5], may have influenced the bioavailability of some of these metals and abundance of *Eichhornia crasspies* in the study area.

The concentrations of heavy metals (Table 2) may have been regulated naturally by several physiochemical conditions of water, especially temperature. The air temperature (27.9 to 33.5ºC) and water (27.0 to 34.0°C) recorded (fig. 2) were higher than previously reported in the Creek in almost all the studied stations. Air temperature range between 25°C and 28°C and, water between 22ºC and 25°C was reported by Iloba and Ruejoma [34]. While, [21] reported air temperature range between 19.2 and 32°C, water 25.8 and 30.1°C. This abnormal rise in temperature may have contributed remarkably to the very low concentrations of heavy metals habitually reported. The present study is implicating the population of water hyacinths, the low concentrations of heavy metals to climate change variability. Similar temperature range and above, have been reported elsewhere to support the growth of green algae and other aquatic plants [3,4], are temperature dependent.

The assertion of Verweij et al. [4] that, water temperature increases with increasing air temperature is a growing relationship documented in several studies to increase the population of aquatic plants [35,36,37,38].

Although, temperature in the study followed a seasonal pattern of being higher in the dry season months than wet; a steady increase in values was observed from previously reported, and can be blamed on increasing human activities in the study area and changes in climate. Interestingly, the impact of

temperature is now widely accepted to increase the population and species composition of aquatic plants with the development of new strains. And have been observed in the study area owing to both reports of [21,24] of exponential increase in aquatic plant population.

Increase in metal uptake of Zn, Pb, Ag, Cr and Cd by aquatic plants have been observed with increasing temperature [3,9,10,11,12]. The abundance of these plants in the study area may have played a significant role in attenuating the concentrations of heavy metals in the study area.

Dissolved oxygen (DO), which is one of the most valuable life support requirement in aquaculture for marine lives to perform body metabolic processes as well as in water quality assessment is regulated by temperature. The present study observed a steady decrease in DO concentrations (4.12 to 7.44 mg/L) from previous studies in the Creek. Olomukoro and Osuide [21] reported lower values in the range of 2.3 and 9.6 mg/L than [34] in the range of 1.63 to 3.27 mg/L, as well as BOD concentrations of 0.2 to 8.41 mg/L and 0.57 to 1.5 mg/L respectively in the study area.

Although, BOD and DO concentrations followed a seasonal pattern of being higher in the dry season months than wet, a slight increase was observed in the months of February, March and April 2010. This was expected because biological processes changes rapidly in aquatic systems, with substantial increase in dissolved oxygen concentrations, and consequent increase in biological oxygen demand which will decrease afterwards.

Under climate change conditions, nutrient loads are expected to increase [39]; as such assessing their impacts through eutrophication may not be a straightforward process considering other interplay conditions, for example nutrient availability, light conditions, temperature, residence time and flow conditions [40]. Climate change due to temperature increase have been observed to increase nutrient availability in water, as seen in fig. 7, with very high nutrient concentrations, especially sulphate in water and phosphate in the sediment. Phosphate value ranged between 0.03 and 0.18 mg/L in water and 17.85 and 24.84 mg/L in sediment, nitrate (0.02 and 0.04 in water and 1.47 and 9.51mg/L in sediment), and sulphate (19.26 and 50.66 mg/L in water and 1.47 and 9.51 in sediment). The sequence of nutrient in the water was sulphate > phosphate > nitrate (fig. 7), in line with both reports of Iloba and Ruejoma 2014 and Olomukoro and Osuide 2015) for phosphate and Nitrate (Phosphate > Nitrate). The sequence in the

sediment was Phosphate > Nitrate > Sulphate (Fig. 7). All the physiochemical parameters analyzed in the present study showed significant difference ($P < 0.05$) along the stations.

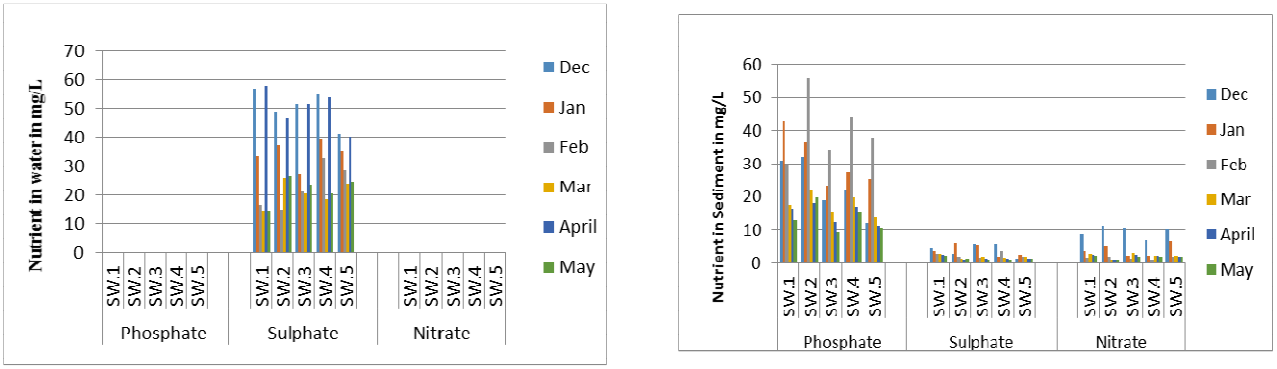


Fig.7. Monthly and spatial nutrient concentrations in water and sediment.

As seen in fig. 7, the bioavailability of nutrients in water and sediment were not in accordance with the anthropogenic source activities of these nutrients in aquatic systems.

High sulphate, according to Whitehead et al. [6] can accelerate corrosion of metals, especially iron. This has implication on the very high concentrations of sulphate recorded and iron consistently reported (fig. 7) in the river above regulatory limits, and may have been exacerbated by increase in temperature from direct effluent release into the river unmonitored. Phosphorus in small quantities is essential for plant growth and metabolic processes of plants and animals; a nutrient in short supply in most fresh waters, even in small amounts result in significant plant growth and alteration of water quality. Phosphate-induced algal blooms may initially increase dissolved oxygen via photosynthesis, which dies afterwards leading to anoxia in most water bodies.

The increase in the population of aquatic plants of the study area, especially *Eichhornia crassipies* reported by Olomukoro and Osuide [21] of 45 taxa group comprising of 4,830 individuals was a significant increase from their earlier study of 1,135 individuals belonging to 19 taxa groups in the bottom sediment [24], could have been exacerbated by climate change, thereby developing exotic and resistant species in the process, in line with [4] assertion of increase in algal community bloom in terms of growth and species composition due to temperature.

The bioavailability of heavy metals in water changes with extreme weather conditions, is a relationship which have been associated with temperature in several studies. The increase in aquatic plants in the

study area may have been responsible for the continuous low levels of metals reported in surface water known to receive untreated waste materials from major oil and gas activities. Fritioff et al. [3] reported increase in metal bioaccumulation of zinc, lead, silver, chromium and cadmium except for iron and zinc in the shoots of aquatic plants with increasing temperature. The low iron concentrations reported in their study was not in conformity with the present study found above [28] recommended limits in all the stations, so also copper in station 3 and 4 during the wet season, however was in line with both reports of [24,41] and [5] in the bottom sediment of the river. Several physiochemical characteristics of the water may have also influenced the abundance of iron in the study area, given that [3] performed their study under controlled experimental conditions.

It is evident in the study that, the very high concentrations of some these metals in the bottom sediment (table 2), and their low concentrations in surface water further implicate climate change through temperature increase, made worse by the constant perturbation of the river from anthropogenic sources, especially as remains a deep sink to heavy metals pollutions in water bodies.

The abnormal increase in temperature may have contributed to their very high concentrations in bottom sediment. This in the future could lead to surface water heavy metal explosion, if not properly regulated. Oluowo and Isibor [5] reported very high concentrations of heavy metals and metal sorption capacity in the bottom sediment, which is believed to have reached its carrying capacity, as well as significant increases in surface water temperature from previous studies in the study area.

Consequentially, every investigated physiochemical characteristics known to signal climate change in surface water and sediment through temperature increase was observed in the present study, and may have helped to influence the bio-concentrations of some of these metals by keeping their concentrations low temporarily.

Conclusion

Notwithstanding, the positive effect of climate change through temperature increase observed to reduce heavy metals concentrations through direct and indirect relationships, can only be temporary. Their long term as well as short term salient impacts cannot be overlooked, especially in assessing changing water quality. Anthropogenic inputs of metals and nutrients to the river should be monitored regularly, especially

anthropogenic sources of untreated effluent and unregulated oil and gas activities to hydrocarbon burning within the study area. The river carrying capacity is suspected to have been reached with worrisome concentrations recorded from previously studies and could be become more devastating in the future.

The present study suggest more in-depth climate change related bio-monitoring studies to investigate heavy metals concentrations in water, sediment, aquatic plants, especially dominant *Eichhornia crassipes* and in edible organism of the study area and Nigeria at large.

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