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HEAVY METAL POLLUTANTS IN WARRI RIVER, NIGERIA

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ABSTRACT: Warri river, a major river in the Delta region of Nigeria, was sampled at three selected industrial locations and the samples analyzed for some heavy metals by Flame atomic absorption spectrophotometry. The total levels of Fe, Cu, Ba, Pb, Cd, Cr, Ni.and Co in ppm were determined specifically at upstream, effluent zone, and downstream of the river in each industrial location. Fe, Cu and Pb were found to be the most abundant metals in the river. The metal distribution pattern of the river clearly indicates the source of pollution to be land-based and implicates the industries in the adjacent area as the most likely source. Correlation analysis of elemental concentrations suggest that some of them are strongly associated, indicating a common source or chemical similarity for the coupled elements. The values of temp (24.00-27.30^{0}c), $_P$H (7.56-7.98), chloride (21.30-159.80mg/l), alkalinity (40.26-97.60mg/l) and suspended solids (0.0008-0.0414mg/l) are also reported.

1. INTRODUCTION

The daily accumulation of heavy metals in our environment (particularly coastal waters) has intensified in recent years with population growth, industrialization and new technological developments. This phenomenon is of great concern because heavy metals constitute considerable hazards to human health due to their toxicity, accumulative tendencies and persistence in the environment with possibilities for environmental transformation into more toxic compounds.

Public awareness on the dangers associated with heavy metals has been partly responsible for alerting governments on the need to protect the health of the communities by keeping constant watch on levels of toxic pollutants, taking steps to reduce them to acceptable levels and ensuring control of emission of pollutants into the environment by legislation. However, these objectives are not being actively pursued in many developing nations.

Water, a prime need for human survival and industrial development is being affected by various activities of man which alters its composition physically, chemically or biologically. Pollution of coastal waters by heavy metals has been widely reported (1). Sources of pollution by trace metals include atmospheric release from fossil fuels burning,

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domestic sewage discharge, land run-off and release from industrial operations such as mining, canning and electroplating (2, 3). With increased diversification in industrialization and particularly with the extensive utilization of crude oil in Nigeria, especially in the Niger-Delta region, the concentration of metal pollutants in the ecosystem has risen (4). Warri River, a major river in Niger-Delta area of Nigeria supports major commercial activities such as shipping of crude oil, fishery and recreational fishing and prawing. The river has been implicated of contamination by heavy metals in the past (4, 5). However, no attempt was made in any of the previous works to establish specifically the sources and distributions of these pollutants in the river. Therefore, this paper attempts to report whether pollution is occurring in the river and if so, to identify the source(s) of the pollution, and the extent of damage to the coastal system.

2. MATERIAL AND METHODS

Samples of water from the river were taken at three selected industrial locations. Location 1 is a refinery, location 2 a steel company, and location 3 an oil drilling company. Samplings were made in October, 1997 at upstream, effluent (discharge) and downstream zones of the river at a distance of 2.5 km either way from the effluent zone.

Water samples were collected just below the water surface using acid-leached polythene bottles. The samples were preserved with Conc. HNO_3 and refrigerated to 4^0C pending analysis. Some water parameters like pH, chloride, temperature, alkalinity, suspended solid, total dissolved solid were performed immediately before preservation.

For assessment of contamination, the method of Arnold (6) was used in which heavy metals extracted by molar nitric acid is assumed to represent the amount that has been acquired through contamination. In this method, 5 mL Conc. HNO_3 was added to 100 mL of well-mixed water sample in 125mL conical flask. The solution was evaporated to about 20ml on hot plate. Another 5mL Conc. HNO_3 was added and the mixture heated until digestion was completed. Additional 10mL Conc. HNO_3 was added and the content filtered and made up to 100 mL with distilled water. Iron, Copper, Barium, Lead, Cadmium, Chromium, Nickel and Cobalt were determined in water samples and blanks with a Computerized Buck Scientific Model 200a/ 210 Flame atomic absorption spectrophotometer (7). The instrument working conditions and parameters for the determinations are shown in Table 1. Standard solutions of the respective metals were used for calibrations. All chemicals were analytical reagents grade obtained from British Drug Houses. The blank was taken on the reagents through the complete procedure except the sample which was omitted (8). Triplicate determinations were made on the samples.

Table 1: Working conditions of Buck Scientific Spectrometer for the determination of metals

Metal	**Wavelength (nm)**	**Slit width (nm)**	**Lamp current (mA)**	**Characteristic concentration (mg/l)**	**Detection Limit**
Fe	248.3		15	0.06	
Cu	324		4	0.035	
Ba	553.6		11.0	0.008	
Pb	217		5	0.10	
Cd	228		4	0.010	
Cr	357.9		8	0.05	
Ni	232		11	0.059	
Co	240		11	0.048	

3. RESULTS AND DISCUSSION

The values of pH, Temperature, chloride, alkalinity, dissolved solid and suspended solid are presented in Table 1. The temperatures of the waters follow the same pattern with the pH. The values of the temperature are in range of 24.00-27.30^{0}C. Generally, high water temperatures characterize the Nigerian coastal river waters (4, 9). However, these values still fall within the water fishery criteria of 29.9^{0}C (10). The pH values of the water samples are between 7.56 & 7.98 which indicate that the river is slightly mineralized. This shows that there was no industrial pollution from the production of gases such as SO_2 or NO_X which could have been precipitated by rain to make the water of the river acidic. All the pH values obtained favour aquatic life as they fall within the acceptable range of optimum aquatic culture of 6.5-9.0 (10). Warri river is generally alkaline i.e. above 7.0 (4).

Methyl orange alkalinities were recorded for all the water samples. The alkalinity varies from 40.26 HCO_3 mg/l in location 1 upstream to 97.60 HCO_3 mg/l in location 3 effluent point. The values are acceptable for aquatic life as adequate quantities of carbon dioxide will be available to permit plankton production which is the base of the food web as there is close relationship between plankton abundance and aquatic fauna (10).

In terms of chloride content, all the water samples appear to be polluted for marine life. The least value of 21.30mg/l was recorded in location 1 upstream while the sample from location 3 effluent point has the highest value of 159 mg/l. These values exceed the allowable limit for fresh water aquatic culture of 0.002mg/l (10).

The suspended matter of the river, like all Nigerian rivers, was higher in the rainy season than in the dry season. This could be due to the influx of particulate matter into the aquatic systems through run-off in the rainy season. Previous data revealed that the suspended solid range 4-210mg/l was recorded at Udu Bridge, a part of Warri river near the Steel work (4). Surprisingly, low values of 0.0018-0.0414mg/l were obtained in this study. It appears the suspended solid of the river is decreasing. This is expected because of the good drainage system which minimizes the influx of particulate matter into the aquatic systems through run-off in the rainy seasons. These values are allowable as they do not exceed the water quality criteria of 25mg/l for aquatic life (10).

The values of the water parameters obtained varied with different locations. Specifically, highest values of the parameters were observed at the point of effluent discharge while the upstream sections of the river in each industrial location were beyond the range of industrial influence. Therefore, any fluctuations observed in the water at upstream locations may be due to natural phenomenon such as variation in rainfall, salinity, ratio of organic to inorganic materials e.t.c.

Table 2. Water Parameters of Warri River at different locations: (1) Refinery, (2) Steel works, (3) Oil Drilling Station

Location	Zone	Temp (^{o}C)	pH	Chloride (mg/1)	Alkalinity (HCO_3) (mg/1)	Dissolved solid (g/1)	Suspended solid (mg/1)
	Upstream	25.90	7.77	21.30	40.26	0.483	0.002
1	Effluent Point	26.00	7.74	53.30	52.30	0.520	0.003
	Downstream	26.40	7.94	37.30	45.10	0.327	0.006
	Upstream	27.30	7.74	35.50	47.60	0.056	0.004
2	Effluent Point	27.30	7.98	88.80	61.00	0.263	0.007
	Downstream	27.10	7.93	53.30	54.90	0.990	0.008
	Upstream	24.80	7.58	37.30	57.30	0.134	0.044
3	Effluent Point	24.00	7.56	159.80	97.60	0.162	0.006
	Downstream	24.60	7.67	88.80	80.50	0.143	0.015

The dissolved solid obtained in this study was an oily residue. This may indicate contamination by oil possibly from effluent discharge or as a result of natural seepage of crude oil into the river.

Table 2 gives the means and ranges of heavy metal concentrations in the water samples. Nearly all the metals were detected. The concentration ranges were high for most of the metals, thus indicating a lack of uniform distribution in the river. For example, in location 1, Cu ranged from 0.02 to 0.69ppm with the highest values at the effluent points. These higher values at the effluent points as shown in Fig. 2 naturally imply that industrial activities are responsible for elevated levels of metals in Warri river. The mean values of the metals at different zones show Fe to be the most abundant metal in all the three locations followed by Cu, Ba and Pb. The value of Fe is higher at the effluent point of location 2 than other locations, being a major pollutant from iron and steel company (11). The high levels of Ba and Pb in both locations 1 and 3 are due to the composition of Ba in drilling mud and the use of Pb as antiknock in petrol coupled with its high solubility in water bodies (12).

In descending order of predominance, the overall range values of the metals in this study are: Fe (0.11-4.68ppm), Cu (0.02-1.80ppm), Pb (0-1.70ppm), Ba (0-0.67), Cd (0-0.39ppm), Ni (0.03-0.21ppm), Cr (0.07ppm) and Co (0-0.05ppm). The alloying of chromites ore with elements such as iron, nickel and cobalt to form various kinds of chromium metals and ferrochromium compounds by the Steel Company may contribute to their presence in the river. Despite this, low value of chromium was obtained in this study. However, the unexpected low values of some metals in this result may be as a result of physical or chemical phenomenon such as mobility, adsorption or co-precipitation of metals or existence of some respiratory mechanisms by aquatic fauna to eliminate accumulated metal ions in the river. All the metals except barium exceed their allowable limits (10) for aquatic culture. This may explain why there is drastic reduction in marine organisms nowadays than pre-industrial times. This assertion agrees with the study of Tetsola (9) who found low Biomass of fish in Warri river.

Comparing results of this study with previous investigations (13, 14), there is apparently an increase in the periodical accumulation of the metals in the river. This suggests that industrialization must have contributed a fair amount of these metals to the river.

Table 3. Mean total concentrations of heavy metals in Warri River at different locations: (1) Refinery, (2) Steel works, (3) Oil Drilling Station

Location	Zone	Elements (ppm)							
		Fe	Cu	Ba	Pb	Cd	Cr	Ni	Co
	Upstream	3.04	0.02	ND	0.1	0.37	0.06	0.1	0.02
		(0.02)	(0.01)	-	(0.02)	(0.02)	(0.03)	(0.02)	(0.01)
1	Effluent point	3.97	0.69	0.45	0.17	0.39	0.09	0.1	0.05
		(0.02)	(0.02)	(0.04)	(0.02)	(0.02)	(0.02)	(0.03)	(0.02)
	Downstream	3.28	0.43	0.30	0.11	0.07	0.07	0.1	0.02
		(0.02)	(0.03)	(0.02)	(0.06)	(0.01)	(0.01)	(0.01)	(0.01)
	Range	3.04-3.97	0.02-0.69	0-0.30	0.10-0.17	0.07-0.39	0.06-0.09	0.1	0.02-0.05
	Upstream	0.11	0.01	ND	ND	0.05	0.04	0.06	ND
		(0.03)	(0.01)	-	-	(0.03)	(0.01)	(0.01)	-
2	Effluent point	4.68	1.69	ND	0.15	0.02	0.14	0.1	0.01
		(0.04)	(0.02)	-	(0.01)	(0.01)	(0.04)	(0.01)	(0.01)
	Downstream	2.93	1.43	ND	0.1	ND	0.11	0.06	ND
		(0.03)	(0.03)	-	(0.01)	-	(0.01)	(0.02)	-
	Range	0.11-4.68	0.01-1.69	0	0-0.15	0-0.05	0.04-0.14	0.06-0.1	0-0.01
	Upstream	0.65	0.02	ND	ND	0.01	0.01	0.03	0.01
		(0.03)	(0.01)	-	-	(0.01)	(0.01)	(0.01)	(0.01)
3	Effluent point	2.75	1.8	0.67	17	0.33	0.1	0.21	0.03
		(0.03)	(0.02)	(0.02)	(0.02)	(0.02)	(0.02)	(0.03)	(0.01)
	Downstream	1.8	0.27	0.41	0.13	0.17	0.03	0.08	0.02
		(0.02)	(0.02)	(0.05)	(0.02)	(0.02)	(0.01)	(0.03)	(0.01)
	Range	0.65-2.75	0.02-1.8	O-0.67	0-1.70	0.01-0.33	0.01-0.10	0.03-0.21	0.01-0.03
	Overall range	0.11-4.68	0.02-1.80	0-0.67	0-1.70	0-0.39	0.01-0.14	0.03-0.21	0-0.05

Values in parenthesis are standard deviation of triplicate analysis
ND- Not detected

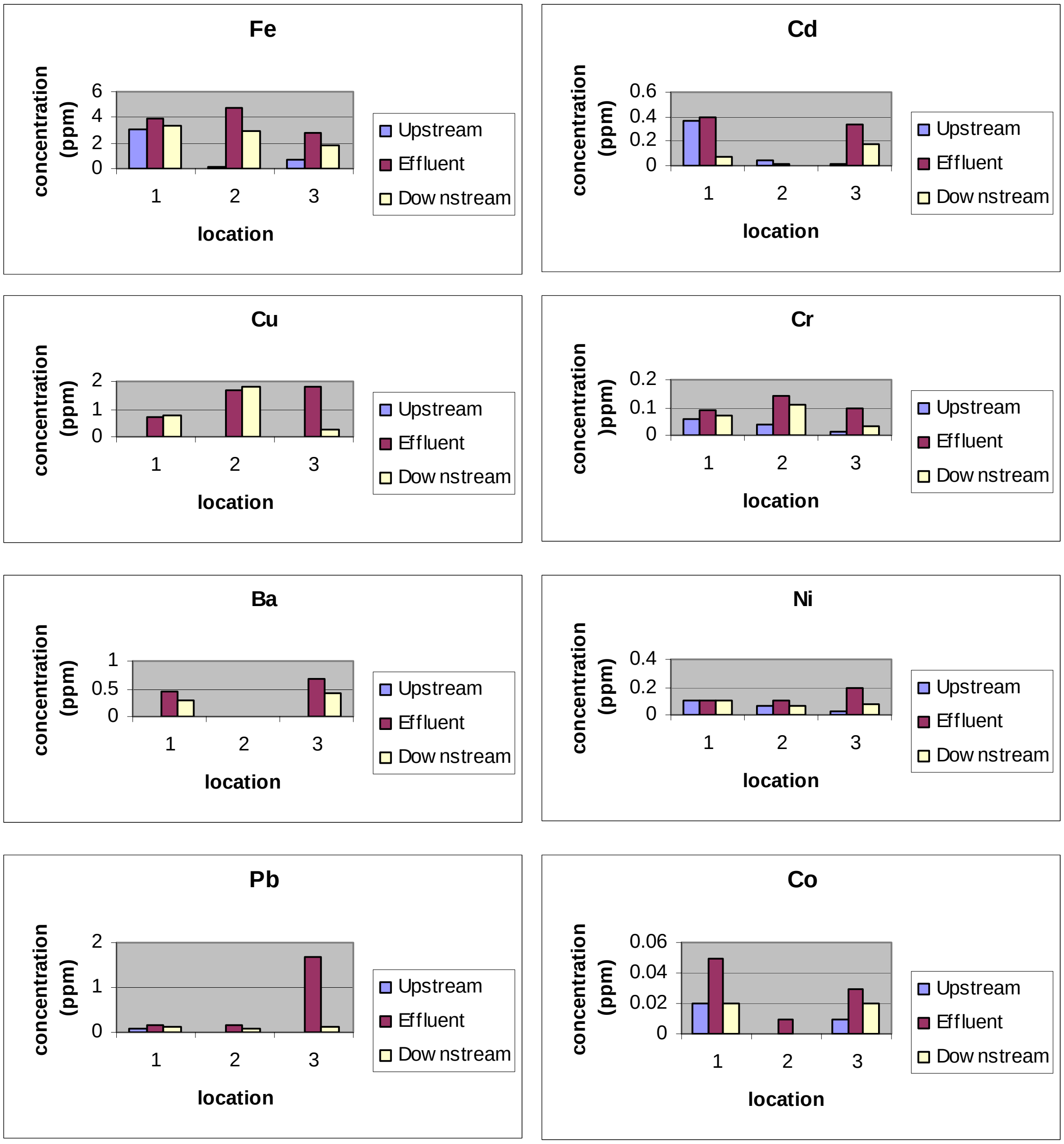

Fig. 1. Chart showing concentrations of metals at different locations: (1) Refinery (2) Steel works (3) Oil Drilling Station.

The correlation matrix with the significant values highlighted is presented in Table 4. The linear regression data was obtained by calculating the Pearson's correlation coefficient, r, with a computer programme PROCC CORR of SAS.

Nearly, all the metal pairs have positive coefficients and to indicate which of these are "significant" in the statistical terms, the critical multiple correlation coefficient, R, was obtained from the table of significant values.

The critical value of R with n=9, $\alpha = 0.05$, is 0.360. By extracting the values $r \geq R$ from Table 4, a reduction of the dimensionality of the data matrix which resulted in exposing the number of significant relationships between the parameters became clear as shown in Table 5.

There is a strong association between the elements coupled. This suggests a common source or chemical similarity for the couples involved (15)

Table4. Pearson's correlation matrix of the analyzed metals

	Fe	Cu	Ba	Pb	Cd	Cr	Ni	Co
Fe	1	0.0608	0.205	0.8723	0.382	0.775	0.435	0.364
Cu		1	0.302	0.626	-0.095	0.81	0.582	0.102
Ba			1	0.635	0.632	0.115	0.711	0.657
Pb				1	0.524	0.615	0.663	0.587
Cd					1	0.071	0.58	0.602
Cr						1	0.483	0.089
Ni							1	0.369
Co								1

n=9, α=0.05, if r≥0.360, then value is significant**.**

Table 5**.** Number of significant relationships between parameters obtained by linear regression Analysis, R.

Couples	Significant correlation values
Fe-Cu	0.608
Fe-Pb	0.823
Fe-Cd	0.382
Fe-Cd	0.775
Fe-Ni	0.435
Fe-Co	0.364
Cu-Pb	0.626
Cu-Cr	0.81
Cu-Ni	0.582
Ba-Pb	0.635
Ba-Cd	0.632
Ba-Ni	0.711
Ba-Co	0.657
Pb-Cd	0.524
Pb-Cr	0.615
Pb-Ni	0.663
Pb-Co	0.587
Cd-Ni	0.58
Cd-Co	0.602
Cr-Ni	0.483
Ni-Co	0.369

n=9, α=0.05, if r≥0.360

Conclusively, the variability in the concentrations of the metals obtained in different parts of the river suggests that different industries contribute significantly to the heavy metal load of the river. The highest values of the metals observed at the effluent zone in each industrial location suggest (or confirm) that industrial activities are responsible for heavy metal pollution of Warri River. The result of this study emphasizes the value of constant monitoring of rivers and water bodies receiving effluents in order to forestall cumulative effects of the metals in the river which may lead to sub- lethal consequences in the aquatic fauna and ensuing clinical poisoning to man.

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