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Heavy metal concentrations in sediments from eleme creeks in relation to the eleme (indorama) petrochemicals company, rivers state, Nigeria

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Abstract
The Indorama petrochemical is one of the major companies situated at Eleme suburb, Rivers state, Nigeria. Numerous wastes are generated by this company during it production processes among which are heavy metals. Among the Eleme people, there is this belief that their natural water has been polluted by wastes generated by this company. Hence, this study was undertaken to assess the metal concentrations in the creeks. Sediment samples were collected from ten locations in the creeks during the dry and the wet seasons and subjected to heavy metals analysis using atomic absorption spectrophotometric method. Results of the investigations revealed that the concentrations of heavy metals in the sediments ranged between 0.007 and 67.84mg/kg in the wet season and in the dry season, it ranged between 0.0021 and 71.42mg/kg. However, iron concentrations ranged between 103 and 319.41mg/kg. From the findings, all the eight metals analysed were within the recommended levels set by the national and international community except that of iron that was slightly elevated. Results of the 2-way ANOVA showed that there was significant variation in the concentrations of the metals across locations and the periods of sampling. The Indorama company and other companies located within the vicinity of Eleme need to properly treat their wastes before discharging them to minimize the metal concentrations in the creeks so that the health of the people is not endangered.

Keywords: Petrochemicals, sediments, creeks, company, wet season, dry season, spectrophotometer, anova

Introduction

Pollution with heavy metals in aquatic ecosystems is a worldwide environmental problem that has elicited great concern over the years as a result of the negative effects (Iksander and Keeney, 1974) [7]. Studies carried out by Ramesh *et al.* (2014) revealed that sediments are regarded as ultimate sink and indicator of changes in water column as well as the influence of anthropogenic activities in air and watersheds. Investigation by Vukovic *et al.* (2014) [14] also indicated that heavy metals generated by humans enter into the rivers as inorganic complexes or hydrated ions, which are easily adsorbed into the surface of sediment particles and constitute the labile fraction. Osakwe (2014) [10] showed that environmental and ecosystem variables such as turbulence, water pH, redox potential, seasonal flooding, and storms cause periodic remobilization of contaminated surface and thereby making the bottom sediments a potential source. The levels of Cadmium in sediments obtained by Ekwere *et al.* (1992) [4] from the Bight of Bonny was 0.70mg/kg while in a related study Al-Abdali *et al.* (1996) [1] recorded 1.2-2.0 from the natural background level of unpolluted bottom sediments from the Arabian Gulf. Chronic exposures to cadmium have been noticed to have adverse effects on the reproductive organ, maturation, hatchability and larval development as well as mortality (Svobodova *et al*., 1993; Lloyd, 1992) [13, 8]. Wang *et al.* (2011) [15] conducted some studies on heavy metals in water and the results revealed that 30–98 % of heavy metal concentrations in rivers are transported in sediment-associated forms. EWA (2005) [6] recommended concentrations for some metals in sediments in the city canal of Delft in the Netherlands as follows lead (<530mg/kg), chromium (<380mg/kg), zinc (<380mg/kg), nickel(35mg/kg) and copper (<35mg/kg). Barlas *et al.* (2005) [3] showed that the contamination of aquatic systems by heavy metals, especially in sediments, has become one of the most challenging pollution issues owing to the toxicity, abundance, persistence, and subsequent bio-accumulation of these materials. When discharged into aquatic ecosystems, heavy metals can be absorbed by suspended solids, then strongly accumulated in sediments and bioaccumulated in food

(Yi *et al.*, 2011) [14]. Sediments act as sinks in water column, and may in turn act as sources of heavy metals to the ecosystem (Barles *et al.*, 2005) [3]. Recently, heavy metal pollution in the sediments of aquatic ecosystems has been extensively investigated to effectively manage these ecosystems as to their pollution (Zhang *et al.*, 2013) [18]. Human activities can modify the geochemical cycle of heavy metals resulting in environmental contamination. It is known that heavy metals enter rivers and estuaries from many natural sources, one of the important sources being the municipal sewage. The absence of sewage treatment in Nigeria and of Agricultural runoff is also responsible for the anthropogenic sources of metallic elements in sediments.

Project Location

The Eleme Creek is about 10km North East of Port Harcourt, the capital of Rivers State in the Niger Delta area. Port Harcourt is the main industrial city of the Niger Delta region of Nigeria and lies 40km South-West of one of the largest commercial towns, Aba in neighbouring Abia State. The Port Harcourt Township is located on the South East flank of Niger Delta on the edge of the dry main land which is contiguous with the site of the Petrochemicals Company. The Company occupies about 4, 200 hectares of land in the vicinity of the villages of Akpajo, Aleto and Agbonchia in Eleme, Eleme Local Government area of Rivers State on the Port Harcourt-Bori segment of the East-West road. The Eleme Petrochemicals Company discharges its effluents into the creek which is channeled into the Okrika River which empties finally into the Bonny River.

For purposes of this work, the creek was divided into ten locations with their coordinates using GPS (M 76 GARMIN). The locations and abbreviations used were: location I(Agbonchia1-ABM 1), location 2(Agbonchia2-AGBA2), location 3(petrochemicals-PTC), location 4(Dredging-DRG), location 5(slaughter-SLT), location 6(Railway-RLY), location 7(NNPC QTRS-NNPC QTRS), location 8(Abam-ABA), location 9(Ogan-OGN), location 10(Okrika River- OKR).

Sediments sample collection

Sediments were collected by the grab method using the Eckman grab sampler at 3 to 4 locations, representing approximately 2-3 cm of surficial bottom sediments, for each sampling site, and wrapped with aluminium foil to avoid contamination. The sediments were taken to the laboratory in cool boxes for the required analyses (APHA, 1998) [2].

Determination of the concentrations of heavy metals in sediments

The sediments collected from each location were thawed and air-dried at ambient temperature and ground to fine particles< 50pm using a shatter-box grinding mill. From each location, 2g of ground sediment samples were weighed with a high precision microscale (Tecnovetro 0), moistened with water and transferred into a 50ml conical flask.Then 10ml of conc nitric acid (assaying 100%) and 2ml of conc perchloric acid (assaying 100%) were added to each sample after which it was heated with a water bath to near dryness. The mild acid treatment was optimal to digest organic matter with associated metals to extract metals linked by adsorption to the sediments. Thereafter, the solution was allowed to cool and filtered into a 50ml volumetric flask. The solution was made up to the mark with distilled water and concentrations of the metals namely Cu, Fe, Pb Cd, Zn, Ni, Mn, and Cr were determined using Atomic Absorption Spectrophotometer Buck Scientific Model 200A spectrophotometer (McConchie *et al.,* 1988) [9].

Results and discussion

The results of the investigation are presented as shown in table 1.

The results indicate that the concentrations of the heavy metals in sediments varied from location to location. It was obvious that the concentrations of metals close to the point source (ie the petrochemicals, location 3) were slightly elevated compared to those far away. It was generally noticed that higher concentrations of metals were obtained in the dry season compared to the wet season. This high level may be attributed to the low volume of water during the dry season which may have led to an increase in the concentration of the metal. The fact that production processes were always on the increase in the company during the dry season bringing about increased output with commensurate waste generation is another plausible contributing factor. The lower levels in the wet season depicted in Table 2 could be due to dilution, continuous water exchange and sedimentation, consequent upon a process where ions bound in previous semi-dry land by decaying macrophytes dissolve as the water level increased with inundation of the fringing swamp and riparian zones (Welcome, 1986) [16].

The discussions are taken under each metal subheading

Table 1: Mean and standard deviation of heavy metal concentrations in sediments from Eleme creeks Locations

Metals	1	2	3	4	5	6	7	8	9	10	x ± SD
Cd	0.002	0.002	0.040	0.038	0.027	0.021	0.018	0.005	0.004	0.003	0.015 ± 0.017
Cr	2.420	2.199	6.013	5.266	5.080	4.869	4.094	3.991	3.473	3.143	4.054 ±1.355
Pb	0.188	0.311	0.591	0.581	0.251	0.299	0.281	0.182	0.184	0.146	0.301 ± 0.277
Fe	124.910	117.443	284.564	262.256	281.510	283.106	276.234	254.464	254.244	204.543	234.3 ± 61.94
Zn	5.137	5.963	7.641	6.854	4.681	4.832	4.181	4.656	4.090	3.122	5.115 ±1.499
Ni	1.780	1.653	3.176	2.374	2.386	2.411	2.052	1.378	1.358	1.138	1.970 ± 0.865
Mn	31.263	43.474	62.672	61.749	57.676	55.707	47.134	35.606	29.535	37.407	46.22 ±12.79
Cu	3.165	3.402	4.267	3.900	3.157	2.180	1.930	2.548	2.129	1.303	2.798 ±1.009

Table 2: Seasonal Mean and range of heavy metal concentrations (mg/kg) in sediments from Eleme creeks Wet Season Dry Season

Metals	Mean	Range	Mean	Range
Cd	0.011	0.007 - 0.0396	0.021	0.0021 - 0.0626
Cr	3.578	2.0040 - 6.3450	4.532	2.1240 - 6.4600
Pb	0.211	0.0190 - 0.3411	0.392	0.0308 - 1.4730
Fe	225.43	103.67 - 319.41	247.81	119.42 - 298.61
Zn	4.860	2.2490 - 8.4100	5.370	3.2700 - 8.6907
Ni	1.620	0.2110 - 3.8600	2.300	1.0020 - 3.8860
Mn	44.070	24.7640 - 67.842	48.370	30.114 – 71.420
Cu	2.544	0.9290 - 4.5900	3.050	1.1310 - 4.7110

Cadmium

The obtained mean concentration for Cadmium in sediment samples was 0.015mg/kg while the standard deviation was 0.017mg/kg. The lowest concentration of 0.002mg/kg was obtained at locations 1 and 2 ie (AGBA 1) and (AGBA 2) while the highest concentration of 0.04mg/kg was obtained at location 3 (PTC). The mean concentration of cadmium in the wet season was 0.0112mg/kg while 0.0206mg/kg was obtained in the dry season (Table 2). Results of the 2-way ANOVA show that there was significant variation in the concentrations of Cd with locations and the periods of sampling. The levels of Cd in sediments were lower compared to 0.70mg/kg obtained by Ekwere *et al.* (1992) [4] in sediments from the Bight of Bonny and the natural background level of 1.2-2.0mg/kg in unpolluted bottom sediments from the Arabian Gulf (Al-Abdali *et al.*, 1996) [1]. Cadmium is a highly toxic metal. The commonest sources are electroplating, nickel plating, smelting, engraving, batteries, sewage sludge, fertilizer and zinc mine. Chronic exposures have adverse effects on the reproductive organ, maturation, hatchability and larval development as well as mortality (Svobodova *et al.*, 1993; Lloyd, 1992) [13, 8]. Appreciable levels of cadmium in this creek particularly at location5 (NNPC QTRS) may have been as a result of the sewage from this estate believed to be dumped in the creek since it is known that sewage sludge contributes greatly to cadmium levels in aquatic ecosystem.

Chromium

The mean concentration of chromium in sediments from the Eleme creeks with standard deviation was 4.054$\pm$1.355mg/kg. The lowest concentration of 2.199mg/kg was obtained at Location2 (AGBA 2) while the highest concentration of 6.013mg/kg was obtained at location 3 (PTC) (table 1). The mean concentration of Cr of 3.577mg/kg was obtained in the wet season while 4.53mg/kg was obtained in the dry season (Table 2). Results of the 2-way ANOVA showed that there was significant variation in the concentrations of chromium across locations and the sampling periods. EWA (2005) [6] recommended <380mg/kg for class 1 sediments in the city canals of Delft (The Netherlands). The mean level of Cr in sediments obtained in this study is within the internationally approved permissible limits. Chromium is known to have a high corrosive resistance and hardness. It is greatly used for chrome plating. Chromium enters the air, water and soil mostly as chromium (111) and chromium (V1) forms. In air, chromium compounds are present mostly as fine dust particles which eventually settle over land and water. Since Eleme is known to have a lot of industries including those involved in plating, it may have been possible for some particles to have been released into the air which later settled in the creeks.

Lead

The recorded mean concentration for lead in sediments from the Eleme creeks with standard deviation was 0.301 $\pm$ 0.277mg/kg. The lowest concentration of 0.182mg/kg was obtained at location 8 (RLY) while the highest concentration of 0.59mg/kg was obtained at location 3 (PTC). The concentration of Pb in the wet season was 0.2106mg/kg while that in the dry season was 0.3921mg/kg. Results of the 2-way ANOVA showed that there was significant variation in the concentrations of Pb between sampling locations and periods of sampling. EWA (2005) [6] recommended levels of Pb in sediments <530mg/kg. The results obtained from the study for Pb fell within the recommended tolerable levels in sediments. However, it is known that sediments are repository of heavy metals (Ramesh *et al.*; Pepple and Nwineewii, 2008) [11]. Appreciable levels of Pb obtained in this study might well have resulted from accumulation of the metal over a long time. Lead is known to come from building construction, lead-acid batteries, and weights.

Iron

The mean concentration of iron in sediments from the Eleme creeks with standard deviation was 234.3 $\pm$ 61.9mg/kg. The lowest mean concentration of 117.44mg/kg was obtained at location 2 (AGBA 2) while the highest concentration of 284.56mgkg was obtained at location 3 (PTC) as shown in Table 1. The mean concentration of Fe in the wet season was 225.43mg/kg and 247.8mg/kg was obtained during the dry season. Results of 2-way ANOVA show that there was significant variation in the concentrations of iron between the sampling locations and months of sampling. The increase in the concentration of iron may be attributed to construction work and long years of operations within the Petrochemicals Company. This is because iron may have been generated as a result of welding and purification activities that took place within the company plant on a daily basis. There is no doubt that the concentration of iron at location 3 (PTC) was high compared to those at other locations.

Zinc

The mean concentration of zinc in sediments from Eleme creeks with standard deviation was 5.115 $\pm$ 1.499 mg/kg. The lowest concentration of 3.122mg/kg was obtained at location 10 (OKR) while the highest concentration of 7.41mg/kg was obtained at location 3 (PTC). The mean concentration of zinc obtained in the wet season was 4.86mg/kg while in the dry season the mean concentration obtained was 5.37mg/kg. Results from the 2-way ANOVA showed that there was a significant variation in the mean concentration of zinc across the sampling locations and sampling periods. EWA (2005) [6] recommended zinc concentrations of<380mg/kg for sediments from Delft, Netherlands. Surface runoff arising from battery industry around Eleme and long years of operations of the Petrochemicals Company may have contributed to appreciable levels of zinc in the creeks. Although zinc is an essential requirement for a healthy body, excess zinc can be harmful and may cause zinc toxicity (Formire, 1990).

Nickel

The mean concentration of nickel in sediments from the Eleme creeks with standard deviation was 1.970 $\pm$ 0.865mg/kg. The lowest concentration of 1.138mg/kg was obtained at location 10 (OKR) while the highest concentration of 3.176mg/kg was obtained at location 3 (PTC) as shown in Table 1. The concentration of nickel obtained in the wet season was 1.62mg/kg while the concentration obtained during the dry season was 2.3mg/kg. Results of the 2-way ANOVA show that there was a significant variation in the concentration of nickel from sampling locations and the sampling periods. EWA (2005) [6] recommended Ni concentration of <35mg/kg in sediments. It is known that nickel compounds are used for nickel plating, to colour ceramics, for manufacture of some batteries, and as catalysts to increase the rate of chemical reactions. It is possible that nickel may have been used in one of these processes in the Petrochemicals Company which of course ultimately resulted in the increase in its high concentration in sediments especially at location 3 (PTC) which was the first receiving point of effluents from the Petrochemicals Company.

Manganese

The recorded mean concentration for manganese in sediments was 46.22mg/kg while the standard deviation was 12.79mg/kg. The lowest concentration of 29.53mg/kg was obtained at location 9 (OGN) while the highest concentration of 62.67mg/kg was obtained at location 3 (PTC) as shown in Table 1. The mean concentration of Mn in the wet season was 44.07mg/kg while the mean concentration in the dry season was 48.37mg/kg (Table 2). Results of the 2-way ANOVA show that there was a significant variation in the mean concentration of manganese from one sampling location to another and between the sampling periods. The concentrations of Mn obtained from this study were higher than those obtained during the analyses of Eleme Petrochemicals Company EIA for water. This elevated level might be attributable to the wastes generated from the Petrochemicals Company in the area.

Copper

The mean concentration of copper in sediments was 2.798mg/kg and the standard deviation was 1.009mg/kg. The lowest mean concentration of copper of 1.303mg/kg was obtained at location 10 (OKR) while the highest mean concentration of 4.260mg/kg was obtained at location 3 (PTC) as shown in Table 1. The concentration of Cu in the wet season was 2.5mg/kg while 3.05mg/kg was the concentration obtained in the dry season (Table 2). Results of the 2-way ANOVA showed that there was a significant variation in the concentration of Cu between the sampling locations and sampling periods. EWA (2005) [6] recommended concentration of <35mg/kg for Cu in the sediments in the city canal of Delft in the Netherlands. The levels of Cu in sediments obtained from this study fell within the internationally recommended permissible limit although it is far higher than the levels obtained during the Petrochemicals Company EIA study for water. This increase, no doubt might be attributed to construction and operational activities which were being carried out at the Petrochemicals Company. Pepple and Nwineewii (2008) [11] reported their findings that sediments were repositories for heavy metals. The U.S. Environmental Protection Agency maximum tolerable contaminant level (MCL) for drinking water is 1.3mg/l.

Conclusion

The numerous industries situated at Eleme suburb especially the Eleme (Indorama) petrochemicals has been a teething problem for the inhabitants since they assumed that their creeks had been polluted with heavy metals. The study conducted to assess the metal levels in the creeks revealed that the metal levels were still within the national and international recommended limits and did not pose any treat to those who depended on the creeks for consumable. However, it is our utmost view that companies operating within the vicinity of Eleme treat their generated wastes before discharging them so as to reduce the possibility of contaminating the creeks for the locals.

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