

IMPACT OF ELEME PETROCHEMICALS COMPANY (INDORAMA) ON THE LEVELS OF SOME HEAVY METALS IN PENAUS MONODON (SHRIMP) FROM ELEME CREEKS, RIVERS STATE, NIGERIA

Nwineewii, Jack Dumka¹, Nna, Prince Joe²

Department of Chemistry, Ignatius Ajuru University of Education,
Rumuolumeni, Port Harcourt, NIGERIA.

ABSTRACT

The Eleme petrochemicals company is an olefin based multi- petrochemicals complex with liquid natural gas as its main feedstock, designed to produce a range of intermediate feed-stocks for various downstream process units. With the numerous wastes generated during the production processes, it is hoped that the metals contents of the rich creeks may have been affected which of course will reflect in the shrimp being the indicator species. Therefore, this study was carried out to verify the concentrations of the metals in the creeks (Using Shrimp) with particular reference to the impact of the petrochemicals company. Shrimp samples were collected from ten locations in the creeks after which they were dried, ground, digested and analysed for heavy metals using atomic absorption spectrophotometer model 200A. The mean and standard deviation in mg/kg of the various metal analyzed were as follows: Cd (0.0107±0.006), Cr (7.825±2.313), Pb (0.066±0.022), Fe (233.8±61.98), Zn (18.89±3.094), Ni (8.42±1.681), Mn (57.91±9.187), Cu (7.104±1.491). From the results, it was observed that the concentrations of the metals were high compared with the Eleme Petrochemicals Company EIA (1992) and the maximum permissible limits recommended by the World Health Organization except that of Cd. At the moment, the consumption of shrimp and other Biota from the creeks should be stopped forthwith and it is necessary that the Eleme petrochemicals company treat its waste water properly before discharge while the federal ministry of environment should undertake periodic audit of the company's generated waste.

Keywords: Petrochemicals, Waste, Heavy metal, Environment, Creeks, Shrimp, Audit, Downstream etc.

INTRODUCTION

Various concentrations of heavy metals in aquatic system from varying sources have been reported. In a study carried out by Ibok et al (1989) on heavy metals in fishes from some streams in Ikot Ekpene area of Nigeria, zinc and lead levels in Qua Iboe River were noted to be high. The authors attributed the high metal levels to both domestic sewage and drainage from automobile workshops as well as effluents from Sunshine Batteries Industry. Furthermore, the authors attributed the relatively high levels of chromium, cobalt and lead to their presence in run-off waters, which may contain among other materials, paint waste containing pigments from spraying workshop or renovated buildings. Metals such as cadmium, barium, lead, copper, vanadium, iron and mercury are commonly found in wastes generated from production operations in the petroleum industry (DPR, 1991). In a study carried out by Nwineewii and Edem (2014) on the determination and toxicological effects of some heavy metals in surface water from the Niger Delta, Nigeria it was discovered that the concentrations of the metals were as follows Cd(0.0033mg/l), Cr(0.172mg/l), Pb(0.057mg/l), Fe(0.403mg/l), Zn(0.218mg/l) and Ni(0.865mg/l). The authors attributed the low concentrations of metals recorded in their work to the fact that companies operating within the area may be treating their waste before discharged and that water being a poor accumulator of metals.

Iron and manganese (Mn) are found at relatively high concentrations in freshwater ecosystems and in many respects can be viewed as 'master metals' owing to their ability to influence the cycles of other biologically important elements through both microbial mediated and abiotic reaction (Giblin, 2009). Iron is found at higher concentrations than Mn in most aquatic ecosystems but chemically, Fe and Mn exhibit similar behaviour in natural ecosystem (Giblin, 2009).

Ndiokwere (1983b) using neutron activation analysis determined the elemental concentrations of As, Au and Hg in fresh tissues of fresh water fish species from the River Niger and Delta areas of Nigeria. Their concentrations of 0.04-0.87µg/g were within the reported range. Concentrations of heavy metals (Cd, Cr, Cu, Pb and Zn) were measured in water, bottom sediments and tissues (muscle and gills) of *Leuciscus cephalus* from the Dipsiz stream in the Yatagan basin (Southwestern Turkey), the site of a thermal power plant. The results obtained showed that the concentrations of Cd, Pb, Zn and Cr in the gills were higher than those in the muscle; however, Cu levels were higher in muscle than that in gills (Ahmet *et al.*, 2006).

One of the most striking investigations in the marine environment is that by Miller *et al.*(1972) who detected mercury in museum specimens of tuna and swordfish species (at concentrations of less than 0.5ppm), and freshly caught fish. In the muscle tissue of black marine (*Makaira indica*) from apparently unpolluted waters of Northeast Australia, Mackey *et al.*(1975) found very high mean levels of mercury and selenium (7.3 and 2.2ppm respectively) (wet weight). Such concentrations were above those permissible for human consumption. Similar, concentrations were also observed in the algae. Michaele *etal* (2006) carried out a study to monitor some heavy metals (Cu, Zn, Cd, Pb) in fish species, plants and benthic macro invertebrates from Danube Delta Biosphere Reserve (Romania). The researchers discovered that the fish organs - in particular the muscles – had very high concentrations of the metals. Fish are very sensitive to cadmium and lead poisoning, but certain species, for example roach, perch and gibel carp in aquatic ecosystem from Danube Delta were found with high concentrations of cadmium and lead. Their concentrations in aquatic plants were higher especially in *Ceratophyllum demersum* for Cd (1.89 mg/kg wet weight) and Pb (23.2 mg/kg wet weight)(Michaele *et al.*,2006).

Study Location

The Eleme creek is 10km North East of Port Harcourt, the capital of Rivers State in the Niger Delta. Port Harcourt is the main industrial city of the Niger Delta region of Nigeria and is 40km South-West of one of the largest commercial town, Aba in 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, Aletto 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 (see Fig.1). Apart from the Petrochemicals Company, other activities take place within the vicinity of the creek. These include dredging, fishing, farming, cow roasting and housing estate.

For purposes of this work, the creek was divided into ten locations with their coordinates using GPS (M 76 GARMIN) as shown in Table 1. The locations were location 1 (Agbonchia 1), location 2 (Agbonchia2), location 3 (petrochemicals), location 4 (Dredging), location5 (slaughter), location 6 (Railway), location 7 (NNPC QTRS), location 8 (Abam), location 9 (Ogan), location 10 (Okrika River).

Sampling Procedure

The sampling locations were chosen on the basis of their accessibility and representation of the environment and the entire aquatic area. Sampling, being an essential part of any analysis, involves collection of a representative portion of the materials being investigated. According to Udosen (1991), the choice of good sampling technique is a prerequisite for accurate data collection. Sampling of biota (shrimp) was carried out monthly for a period of eight months for the determination of the levels of heavy metals (Cr, Cu, Cd, Ni, Zn, Fe, Mn, Pb).

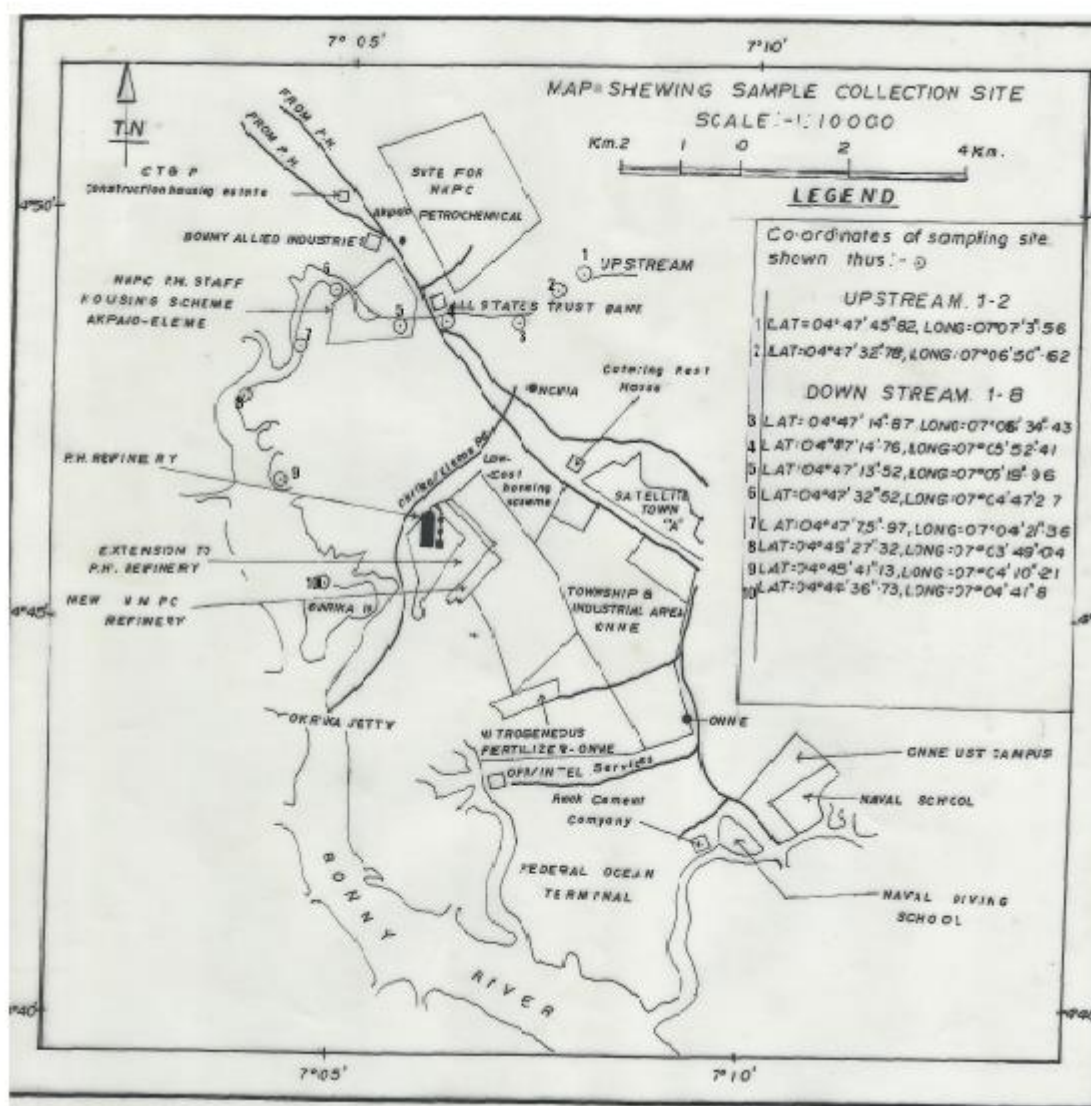


Figure 1: Map of the creek showing sample collection sites

Biota (shrimp) collection

The biota (shrimp) was caught using stake net and in some cases the cast net was used. This was achieved through the help of a field assistant. The shrimps were put in plastic containers and transferred into cool boxes and stored in the refrigerator until ready for analysis.

Determination of the concentrations of heavy metals in biota (shrimp)

The biota (shrimps) samples collected from the creek were heated to a constant weight using an oven (Tecnocalor) at 50°C and individual whole shrimp homogenized. Two grams (2g) of ground body weight were weighed using a high precision microscale, transferred into a

digestion flask and digested with a mixture of 10ml of conc nitric acid and 2ml of 100% perchloric acid. The contents of the flask were digested gently and slowly, by heating in a water bath until near dryness. It was then allowed to cool. The digest was filtered into a 50ml volumetric flask, and made up to the mark with distilled water. The concentrations of heavy metals in biota were determined using the Atomic Absorption Spectrophotometer, Model 200A.

Table 1. Location Name and their Coordinates

<i>Location Number</i>	<i>Location Name</i>	<i>Abbreviations</i>	<i>Coordinates</i>
1	Agbonchia1	AGBA 1	Lat =04°47'45".82, Long 07°07'3".56
2	Agbonchia2	AGBA 2	Lat =04°47'32".78, Long 07° 06'50".62
3	Petrochemicals	PTC	Lat =04°47'14".87, Long 07°06'34".62
4	Dredging	DRG	Lat =04°47'14".76, Long 07°05'52.41
5	Slaughter	SLR	Lat =04°47'13".52, Long 07°05'19".96
6	NNPC Staff Quarters	QTR	Lat =04°47'32".52, Long 07°04'47".27
7	Railway	RLY	Lat =04°47'25".97, Long 07°04'21".36
8	Abam	ABM	Lat =04°46'27".32, Long 07°03'49".04
9	Ogan	OGN	Lat =04°45'41".13, Long 07°04'10".21
10	Okrika	OKR	Lat =04°44'36".73, Long 07°04'41.8

RESULTS AND DISCUSSION

The results of the investigation of the impacts of Eleme Petrochemicals Company on the levels of heavy metals on Biota (Shrimp) are presented in Tables 1 and 2 as shown below. Locations 1 and 2 had no results because the samples were not seen at these locations probably because they were close to the point source where the concentrations of waste generated from the company were high. It was also observed that locations just after the point source (ie location 3) recorded high concentrations of the metals as compared to others. A particular trend was also noticed in the distribution of the metal concentrations; as one move downstream from the point source, the concentrations of metals decreases from one location to another. The concentrations of metals recorded in the dry season were generally high as compared to the wet season (Table 2). The pollutant specific approach is used in the discussion of each of the metals.

Table 2. Mean and standard deviation of heavy metals concentrations in biota (shrimps) from Eleme creeks

<i>Metals</i>	<i>Locations</i>										<i>x ± SD</i>
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>	
Cd	0.011	0.008	NS	NS	0.014	0.011	0.014	0.013	0.007	0.009	0.0107 ± 0.006
Cr	4.125	6.386	NS	NS	9.986	11.624	8.400	6.756	7.542	7.788	7.825 ± 2.313
Pb	0.073	0.045	NS	NS	0.077	0.066	0.068	0.087	0.086	0.034	0.066 ± 0.022
Fe	190.875	148.751	NS	NS	207.477	180.602	249.657	276.302	312.378	304.946	233.8 ± 61.98
Zn	18.355	19.929	NS	NS	21.976	18.216	15.483	21.794	18.973	16.463	18.89 ± 3.094
Mn	53.386	49.091	NS	NS	67.615	55.724	68.641	50.124	59.603	59.116	57.91 ± 9.187
Ni	7.608	6.364	NS	NS	10.906	8.869	9.774	7.908	8.210	7.720	8.42 ± 1.681
Cu	5.545	5.188	NS	NS	7.379	7.776	8.577	8.216	7.290	6.861	7.104 ± 1.491

NS = not seen

Table 3. Seasonal mean and range of heavy metals concentrations (mg/kg) in shrimp from Eleme creeks

<i>Metals</i>	<i>Wet Season</i>		<i>Dry Season</i>	
	<i>Mean</i>	<i>Range</i>	<i>Mean</i>	<i>Range</i>
Cd	0.013	0.0055 - 0.0196	0.009	0.0011 - 0.0192
Cr	7.477	2.8730 - 11.935	8.174	3.4720 - 12.988
Pb	0.059	0.0190 - 0.0970	0.072	0.0180 - 0.0990
Fe	223.320	131.621 - 298.47	244.420	140.84 - 353.786
Zn	17.760	11.4210–58.721	20.037	14.849 - 59.206
Ni	7.697	4.6990 - 11.7230	9.142	6.1670 - 12.071
Mn	55.460	32.608 - 71.3140	60.350	30.499 - 72.140
Cu	6.611	3.8710– 8.7910	7.599	3.9810-9.6080

Cadmium

The mean concentration of 0.0107mg/kg was obtained for cadmium in shrimp with a standard deviation of 0.006mg/kg. The lowest concentration of 0.008mg/kg was obtained at location 7 (OGN) while the highest concentration of 0.014mg/l was obtained at location 5 (STR) and location 7 (RLY) (see Table 2). The mean concentration obtained in the wet season was 0.0126mg/kg while that in the dry season was 0.0088mg/kg (Table 3). From Table 2, no shrimps were found at location3 (PTC) and location4 (DRG), probably due to high concentrations of pollutants at these locations since they are close to the point source. Results of the two-way ANOVA show that there were significant variation in the mean concentrations of Cd in shrimps with the sampling locations and the sampling periods. Michaele et al (2006) obtained 1.89mg/kg of Cd in fish from Danube delta biosphere reserve, Romania. ANZECC (2000) recommended 0.005mg/kg as the maximum limit for Cd in marine organisms. A Comparison of the result obtained from this work with the ANZECC recommended limit shows that a higher concentration was obtained in this study. These elevated levels may be due to the fact that marine organisms such as shrimps are known to accumulate heavy metals to a very great extent. In fishes, acute toxic exposure to cadmium results in damage of the central nervous system and parenchymatous organs. Chronic exposures have adverse effects on the reproductive organs, motivation, hatchability and larval development as well as mortality (Svobodova *et al.*, 1993; Lloyd, 1992). Cadmium is exceptionally persistent in humans. Low levels of exposure may even result in considerable accumulation especially in kidneys (WHO, 1984). The common pathways of exposure are oyster, clams and some crustaceans.

Chromium

The mean concentration of chromium in shrimp from Eleme creeks with standard deviation was 7.825 ± 2.313 mg/kg. The lowest concentration of 4.125mg/kg was obtained at location 1 (AGA I) while the highest concentration of 11.62mg/kg was obtained at location 5 (SLR). From Table 2, no shrimps were found at locations 3 (PTC) and 4 (DRG). The concentration of Cr obtained during the wet season was 7.447mg/kg while that for the dry season was

8.174mg/kg. The 2-way ANOVA shows that there was a significant variation in the concentration of Cr in shrimps with sampling locations and sampling periods. Opuene (2004) obtained a mean level of 3.26ng/g for *Bagrus bayad* from Taylor creek, Bayelsa State, Nigeria. The levels of chromium obtained from this study were higher. Shrimps are known to accumulate metals up to one hundred times than that of the concentrations in water; therefore this increase in concentration in the shrimps may be as a result of accumulation. The World Bank (1990) has shown that chromium is one of the major effluents generated from Petrochemicals Manufacturing Companies and as such it may also account for some of the chromium in Eleme creeks. Inhalation of high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nose bleeds and ulcers and holes in the nasal septum. Ingestion of large doses of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death.

Lead

The obtained mean concentration for lead in shrimp was 0.301mg/kg and standard deviation was 0.277mg/kg. The lowest concentration of 0.146mg/kg was obtained at location 2 (AGA2) while the highest concentration of 0.591mg/kg was obtained at location 3 (PTC). The mean concentration of Pb obtained in the wet season was 0.659mg/kg while that of the dry season was 0.7234mg/kg. Results from the 2-way ANOVA indicate that there was a significant variation in the mean concentration of Pb in shrimps with sampling points and locations. Michaele et al (2006) obtained a higher level (23.2kg/g) in fish from Danube delta biosphere reserves, Romania. The maximum level recommended for lead in fishes is 0.007mg/kg (ANZECC 2000). The results obtained in this work are high compared to the recommended levels for lead in fishes and aquatic organisms. Shrimps are known to be a bioaccumulator, hence most of the metals found in this organism may have been accumulated over time. Also lead is known to come from exhausts from vehicles in the atmosphere, batteries, and waste from lead ore mines, lead smelters and sewage discharge. The Eleme creeks transverses the east-west road and is also very close to the NNPC quarters where sewages from the estate are believed to be discharged into the creeks. Thus, smokes emitted from cars through the east-west road and the sewage from the NNPC estate are potential routes for generation of lead into the Eleme creeks. The toxic effects of lead on fish increase at lower pH level, low alkalinity and low solubility in hard water. Chronic lead toxicity in fish may lead to nervous damage which can be determined by the blackening of the fins (Dojlido and Best, 1993). Acute toxicity on the other hand may cause gill damage and suffocation (Svobodova *et al.*, 1993). These are consistent with the fact that no shrimps were found at locations 3 and 4 which are close to the source where this metal may have been discharged into the creeks.

Iron

The mean concentration of iron in shrimps from Eleme creeks with standard deviation was 233.8 ± 61.98 mg/kg. The lowest concentration of iron of 148.75mg/kg was obtained at location 1 (AGA I) while the highest concentration of 276.3mg/kg was obtained at location 8 (ABM). The mean concentration of iron in the wet season was 223.32mg/kg and that in the dry season was 244.42mg/kg. Results of the 2-way ANOVA show that there was a significant difference in the mean concentration of iron in shrimps from sampling locations and sampling periods. Eleme petrochemicals Company EIA (1992) gave the concentration of iron in Eleme water of 0.69mg/l. It was found that the concentration of iron in shrimps from the study was very high. Iron has varieties of uses; it is used for welding and purifying ores. It is also used at active site of many important redox reactions. All these processes are used in the industries like the petrochemicals which can lead to generation of iron in the

waste waters. Iron is an essential element forming part of haemoglobin, myoglobin and many enzymes. The element is estimated to be 60-70mg/g in humans. Exposure to excess levels of iron greater than 50-100mg/day can result in pathological deposition of iron in the body tissues, the symptoms of which are fibrosis of the pancreas, diabetes mellitus and liver cirrhosis (Richard, 1996).

Zinc

The recorded mean concentration for zinc in shrimp was 18.89mg/kg while the standard deviation was 3.094mg/kg. The lowest concentration of 15.483mg/kg was obtained at location 7 (RLY) while the highest concentration of 21.97mg/kg was obtained at location 5 (STR). The concentration of zinc obtained in the wet season was 17.76mg/kg while that in the dry season was 20.03mg/kg (Table 3). Results of the 2-way ANOVA show that there was a significant variation in the mean concentrations of zinc with locations and in the periods of sampling. The Eleme Petrochemicals Company EIA (1992) obtained 0.20mg/l as the concentration of zinc in Eleme water. The level of zinc obtained in this study is rather high compared to the EIA result suggesting that construction and operations within the Petrochemicals Company may have contributed to the high levels of zinc in the creeks. Zinc is known to be an essential requirement for a healthy body. However, excess zinc can be harmful due to zinc toxicity (Foremire, 1990).

Manganese

The mean concentration of manganese in shrimp and standard deviation was 59.91 ± 9.18 mg/kg as shown in Table 2. The lowest concentration of 49.09mg/kg was obtained at location 2 (AGA2) while the highest concentration of 68.64mg/kg was obtained at location 7 (RLY). The mean concentration of Mn in the wet season was 55.46mg/kg while 60.35mg/kg was recorded in the dry season. Results of the 2-way ANOVA show that there was a significant variation in the concentration of Mn with locations and sampling points. Opuene (2004) recorded a mean level of 41.25ng/g dry weight in *Bagrus bayad* from Taylor creek, Bayelsa State. The Eleme Petrochemicals Company EIA (1992) obtained 0.01mg/l as the concentration of manganese in water from Eleme. From the level of Mn obtained in this study, it is apparent that there was an increase in the concentration of Mn compared to the EIA data, suggesting that the increase might have been caused by waste generated from the Petrochemicals Company. Manganese compounds are less toxic than those of other widespread metals such as nickel and copper (Hasan, 2008). Exposure to manganese dusts and fumes should not exceed the maximum tolerable limit of 50mg/m³ even for short periods because of its toxicity (MCB, 2008). Manganism has occurred in persons employed in the production or processing of manganese alloys, patients receiving total parenteral nutrition, workers exposed to manganese – containing fungicides such as maneb, and glaciers of drugs such as methcenthinone made with potassium permanganate.

Nickel

The recorded mean concentration for Ni in shrimp from Eleme creeks was 8.42mg/kg and the standard deviation was 1.68mg/kg as shown in Table 2. The lowest concentration of 6.364mg/kg was obtained at location 2 (AGA) while the highest concentration of 10.90mg/kg was obtained at location 5 (STR). The mean concentration of Ni in the wet season was 7.69mg/kg while that in the dry season was 9.14mg/kg (Table 3). Results of the two-way ANOVA show that there was a significant variation in the mean concentration of Ni with sampling points and periods of sampling. The recommended concentration of nickel in surface water is 0.02mg/l (WHO, 1984, ANZECC, 2000). The levels of Ni in this study were significantly higher than those obtained for Iko River (Benson and Etesin, 2008) and

those reported by Mba (1980) and Egwelle (1992). The highest concentration of Ni obtained at location 5 (STR) close to the Petrochemicals Company suggests that most of the nickel may have come from the petrochemicals Company waste waters, consequent upon catalytic hydrogenation processes that uses Ni or its compounds as catalysts. Nickel is an essential trace element involved in enzyme processes, but the essential nutrient is very low. High doses are toxic. Nickel and many of its compounds are human carcinogens and poison. Ingestion of large doses of nickel compounds (1-3g/kg) has been shown to cause intestinal disorders, convulsion and asphyxia.

Copper

The mean concentration of copper in shrimp from Eleme creeks was 7.10 ± 1.491 mg/kg. The lowest concentration of 5.188mg/kg was obtained at locations 2 (AGA2) while the highest concentration of 8.57mg/kg was obtained at location 7 (RLY). The mean concentration obtained in the wet season was 6.11mg/kg while that in the dry season was 9.142mg/kg (Table 3). Results of the 2-way ANOVA show that there was a significant variation in the concentrations of Cu with sampling locations and sampling periods.

Eleme Petrochemicals Company EIA (1992) obtained 0.1mg/l as the concentration of copper in the water from Eleme. The liquid effluents from Petrochemicals Manufacturing have 0.5mg/l as the maximum level of Cu (World Bank, 1990). These levels are less than those obtained from the study implying that the concentration of copper is high. Copper as known is one of the major wastes generated from the petrochemicals industries during its production processes. Consequently, those locations close to the Petrochemicals Company have high levels of copper. In humans, excessive doses of copper may lead to severe gastro intestinal and mucosal irritation, hepatic and renal damage, irritation of the nervous system, nausea, vomiting, diarrhea and depression. In most cases, narcotic changes in the livers and kidneys may occur (WHO, 1984).

CONCLUSION

The impact of Eleme Petrochemicals Company on the levels of some heavy metals in shrimp was studied. The results of the investigation revealed that the Petrochemicals Company impacted negatively on the aquatic system as shown in the high concentrations of almost all the metals in shrimps. The concentrations of metals recorded in the Biota were more than the national and international recommended limits. This revealed that the company may not have given adequate treatment to its wastes before discharged, and based on the results of the study, it is the opinion of the researchers that consumption of Biota from the creeks should be stop forthwith pending when a proper remediation exercise is carried out. It also necessary that the company should do a proper treatment of its wastes before discharged.

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