

# Assessment of Effluents from Associated Match Industries with Emphasis on Bioaccumulation of Heavy Metals in Crab

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*Received February 15, 2010; revised March 15, 2010; accepted March 30, 2010*

## Abstract

Heavy metals disposed through anthropogenic activities find their way into aquatic environment through factory effluents. These heavy metals resuspend back into the water column along with the sediments and are known to affect aquatic bioresources. Effluent water samples and crabs were collected along top camp stream to evaluate heavy metal concentrations and were assessed to determine the uptake of heavy metals in crabs. Results show fluctuation in acidity/alkalinity of water samples. BOD, COD, DO, conductivity and organic phosphorous were below permissible limit, and metal concentrations (As, Cu, Cr and Zn) in water samples do not constitute a risk factor for human health. However, concentrations of Copper (Cu), Iron (Fe), Arsenate (As) and Manganese (Mn) in crabs were significantly higher than the level found in the effluent water. Heavy metal poisoning has been identified among people that depend on crabs for their protein. Such effects are viewed by international health organization as attenuation of human health. The toxic elements (As, Cu, Fe and Mn) in the effluent and dissolved solid concentrations including potassium and calcium carbonate may be reduced through resource recovery.

**Keywords:** Heavy Metals, Aquatic Environment, Anthropogenic Activity, Aquatic Bioresource

## 1. Introduction

Effluent discharges from industries constitute a serious environmental threat to water quality and aquatic resources; including biodiversity. Likewise, contaminations of soil by the release of heavy metals as a result of industrial and anthropogenic activities are threat to human health and ecosystem [1,2]. Heavy metals are stable and recalcitrant contaminants of aquatic environments. Some metals ions are required for metabolic activity while, many inadvertently may have concentrations that lie in the narrow range between their essentiality and toxicity. Additionally, others may exhibit extreme toxicity even at low levels under certain conditions [3,4]. As distinct from organic substances, they migrate and accumulate in different components of natural ecosystems (water, soil, bottom deposits and aquatic animals). Most heavy metals are supposed to accumulate in aquatic animals and pass their toxic effects onto the upper links of the trophic chain, including human beings [5]. Conse-

quently, regular monitoring of sensitive aquatic environments is quite necessary.

The study of organisms as pollutant monitors has several advantages over the chemical analysis of abiotic compartments. Chemical, toxicological and ecological approaches have been employed extensively in assessing impacts of heavy metal pollution in aquatic environments. Many such studies have concentrated on birds [6], Fish [5,7] in mussels [8] in other invertebrates [9] and vegetation [10].

The tendency of heavy metals to accumulate in aquatic organisms is of scientific interest not only in heavy metal chemistry but also in environmental studies. In particular, the bioavailability of tissue metal levels in crab; an important staple part of food delicacies in some localities, is an indicator of environmental pollution. Ultimately, the contents and properties of effluents could be responsible for possible environmental impact on different matrices (water column, sediment and biota), and possibly contribute to the characteristics of the receiving water.

The aim of this study was to contribute to environ-

mental effect assessment of effluent discharged by Associated Match industry located in Southwest, Nigeria. In particular we report preliminary results regarding heavy metal concentrations in crab, as a bioindicator of heavy metal biomagnifications.

## 2. Materials and Methods

The study area was along the Eleyele industrial layout of Ibadan, North-West Local Government, Oyo State. (Figure 1). The city lies between latitudes 07°22'30" N and 07°25'50" and longitude 003°2'00" E to 003°55'50" E, at an altitude approximately 1500m above sea level. The climate of the area is influenced by Tropical Maritime (mT) and Tropical Continental (cT) air masses. The mean annual rainfall is 1413 mm, while the mean annual temperature ranges from 22.5°C to 31.4°C. The soil in the area support tropical rainforest vegetation while Kaolinite is the main clay mineral present [11-13]. The area is located in the lowland rainforest vegetation zone of Nigeria [14]. It is a major industrial section and various untreated or minimally treated wastes are discharged into the stream.

It encompasses the stretch between ten sampling sta-

tions. Four of these sampling stations were established along the effluent stream (P5<sub>0</sub>, P5<sub>1</sub>, PS<sub>2</sub> and P5<sub>3</sub>) from the industry. One station was at the confluence of the effluent stream, and adjacent natural stream (Topcamp stream, C<sub>1</sub>), three stations were along the TopCamp stream (BC<sub>0</sub>, BC<sub>1</sub> and BC<sub>2</sub>) before the confluence C<sub>1</sub>, and the other two stations after the confluence (AC<sub>1</sub> and AC<sub>2</sub>). A portable Global Position System (GPS) set was used to locate the grid coordinates of sampling stations.

Water samples were drawn from each of these locations mentioned above 20 m apart except C<sub>1</sub> (Topcamp stream) because of its topography beneath rock and the surrounding wetland. The samples were analyzed for pH, electrical conductivity, turbidity, total acidity and alkalinity, oxygen demand (BOD and COD) including major ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>). Water samples were filtered through a 0.45mm whatman no 1 filter paper. Water samples (100ml) were acidized to a final concentration of 2% with nitric acid. Two samples were divided into two and portion of each half was spiked with known concentrations (0, 2.5, 5.0 and 10.0 ppm) of the six analytes in order to determine percent recovery. Unspiked samples, blanks and spiked samples were analyzed by Alpha 4 atomic absorption spectrophotometer (AAS).

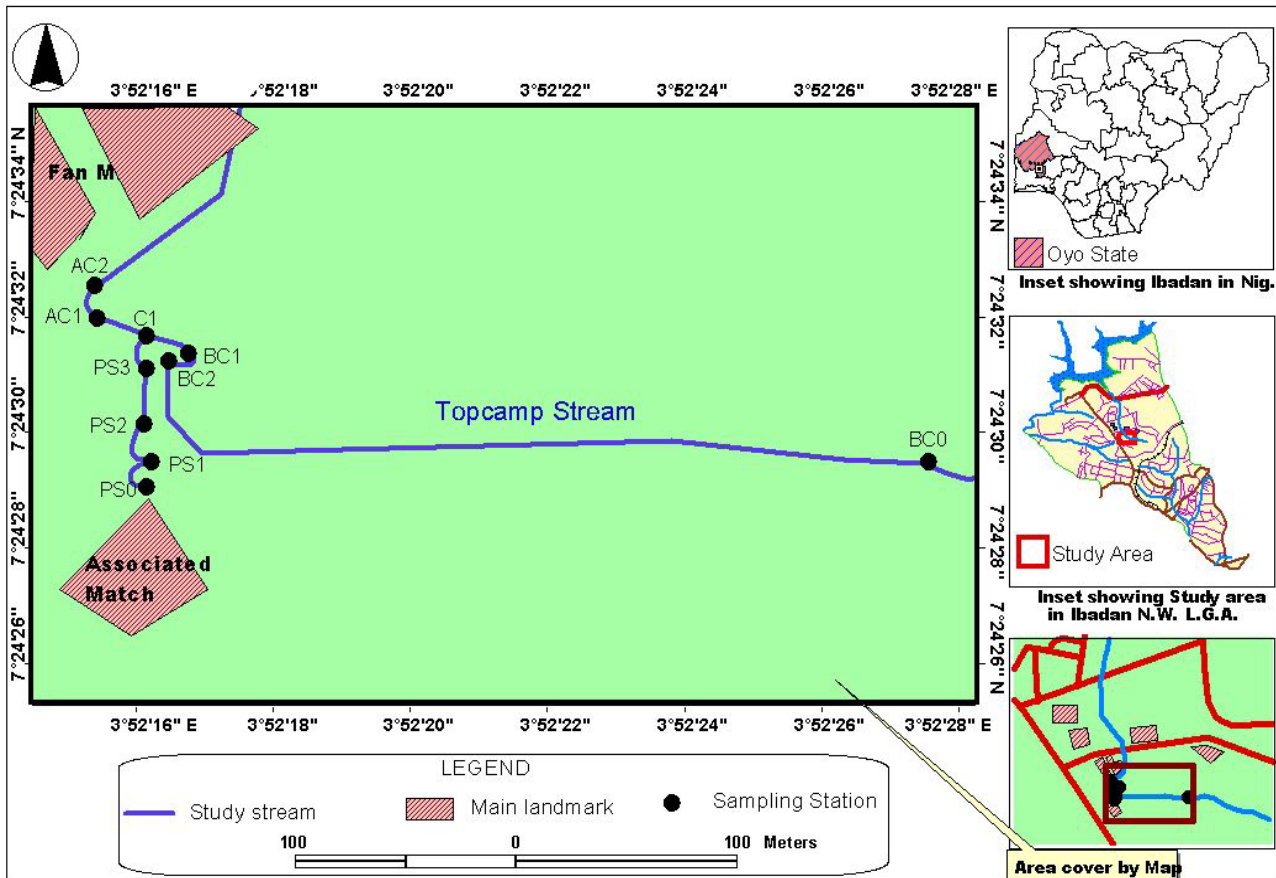


Figure 1. Detailed map of study area showing sampling stations.

The AAS was standardized regularly once after analyzing three samples with matrix-matched standards (Inorganic Ventures, Lakewood, NJ). Standardization was verified with appropriate external standards (Spex Industries Inc., Edison, NJ). Analyte recovery in spiked samples ranged from 92-100%.

At least 20 crabs *Sudanaea africana africana* samples were collected along the Topcamp stream flow. Each crab was excised. The whole internal organs of the crab were removed by steel pliers and the damp weight was measured. All samples were kept at 85°C for 48h to dry to constant weight. The samples were digested according to the procedure given by US EPA 1996 [15] using concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in beakers placed on a hot plate (1:10). The amount of various essential and non-essential elements like As, Cr, Cu, Fe, Mn and Zn in crab samples was determined by multiplying by the dilution factor given in ppm/g. The detection limits were

as follows: 1 mg/L for Fe; 0.01 mg/L for Cu, As, Cr, Mn and Zn.

Statistical analysis: Data were subjected to Barlett's test for homogeneity, followed by analysis of variance (ANOVA). For post hoc comparison Student Newman Keul's test was employed.

### 3. Results and Discussion

The present study aims in understanding the bioaccumulation patterns and demonstrates the safety of aquatic food as a supplementary source of protein in diet. The results of the physico-chemical characteristics of the discharged effluents in water course, confluence and quality of ensuring water are summarized in **Table 1**. The pH of the effluent water fluctuated between acidic to slightly alkaline. The temperature of the surface water

**Table 1. Physico-chemical characteristics of water quality at various sampling points.**

Parameter	P5 <sub>s</sub>	P5 <sub>1</sub>	P5 <sub>2</sub>	P3 <sub>3</sub>	C <sub>1</sub>	AC <sub>1</sub>	AC <sub>2</sub>	BC <sub>o</sub>	BC <sub>1</sub>	BC <sub>2</sub>
pH	6.49	6.43	6.65	6.47	7.76	8.06	8.01	7.65	8.27	8.09
Temperature Air	30	30	30	29	29	29	29	29	28	30
temp.(°C)	0.4	0.8	0.8	1.6	4.4	4.4	2.3	3.6	2.4	2.0
BOD	5.21	5.07	4.14	5.29	2.37	3.83	2.98	1.47	2.06	2.87
COD	7780	2540	3140	3680	1120	840	780	280	680	480
Total Solid	668	620	180	640	420	160	240	160	140	60
TSS	9.32	3.26	4.35	4.70	1.51	1.13	0.94	0.064	0.65	0.67
Conductivity	298.47	198.48	177.27	153.03	43.95	13.65	16.68	13.65	98.49	1.53
Turbidity	2.6	2.0	2.4	3.2	4.8	4.8	3.8	4.4	5.2	3.2
Dissolved	55.17	17.40	21.39	19.88	07.46	22.86	32.31	3.48	08.45	6.46
Chloride	247.3	205	24.24	43.91	30.51	41.63	27.38	0.24	19.96	33.65
Sulphate	0.418	0.458	0.300	0.305	0.516	0.592	0.658	0.120	0.556	0.760
Inorganic PO <sub>4</sub>	1.150	490	710	675	205	130	125	1.75	95	40
K <sup>+</sup>	34	30	36	40	30	28	24	08	08	1.8
Ca <sup>2+</sup>	41	25	29	28	16	11	17	2.6	8.25	9.6
Na <sup>+</sup>	45.82	51.43	58.03	47.13	48.57	44.77	43.88	1.93	35.90	42.14
Mg <sup>2+</sup>	73.9	69.8	78.35	65.5	53.55	51.09	28.54	24.43	48.73	37.75
NO <sub>3</sub> <sup>-</sup>	720	260	540	540	150	70	60	30	50	40
CaCO <sub>3</sub>										

All the values are in mgL<sup>-1</sup> except pH and Electrical conductivity (µS/cm) and phosphate (µgL<sup>-1</sup>); BOD–Biological Oxygen Demand; COD–Chemical oxygen Demand; TSS–Total suspended solid.

was near constant. However, BOD, COD, conductivity, dissolved oxygen and organic phosphorus were below WHO permissible limit [16]. On the contrary, total solid, turbidity, potassium, nitrate, chloride and calcium levels were markedly high at point source. For example, an electrical conductivity of up to 932  $\mu\text{s}/\text{cm}$  has no effects, but water with a high salinity can be toxic to most plants and may pose salinity hazard [17]. Additionally high sodium levels contribute to salinity problems and interfere with magnesium and calcium availability resulting in sodium hazard.  $\text{CaCO}_3$  representing alkalinity of water is more significant than its pH because it takes into account the principal constituency that influence the water's ability to regulate the pH of the water, thus higher  $\text{CaCO}_3$  results in lower pH and lower  $\text{CaCO}_3$  results in higher pH (Table 1).

The common African crab is one of the few species found all year round. Heavy metals absorbed by the crabs have a possibility to get accumulated in different parts of the body and the residual amount can build up to a toxic level as is the case with Cu, Fe, and Mn. The concentration patterns in the water effluent revealed the following order  $\text{Mn} > \text{Fe} > \text{Cu} > \text{Cr} > \text{Zn} > \text{As}$  (Figure 2) whereas the accumulation of heavy metals in crabs followed different sequence of  $\text{Ca} > \text{Fe} > \text{Mn} > \text{Cu} > \text{As} > \text{Cr} > \text{Zn}$  (Figure 3). The order of accumulation in crab is proportional to various metal deposits in the effluent. The concentrations of heavy metals in unimpacted (up-stream) sections of Topcamp are illustrated in Figure 4. The crabs, hepatopancreas showed higher concentration of all metals, especially, calcium this condition might be due to the fact that hepatopancreas plays a prime role in binding the metals and act as primary route of excretion.

The water analysis of heavy metals in the study area was compared to the accumulating pattern in hepatopancreas of indigenous crab, *Sudanaenautes africanus africanus* (Figure 2). Metal concentration of arsenic, chromium, copper and zinc in water samples in this study do not constitute a risk factor for human health and appear to be below the permissible limits set by the UNEP (1993) [18]. However, metal concentration of Cu,

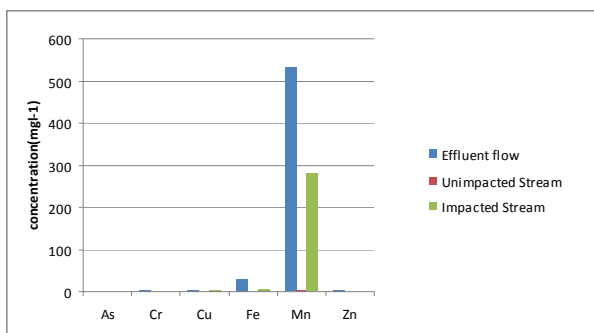


Figure 2. Mean concentration of heavy metal content of water/effluent sample ( $\text{mg l}^{-1}$ ).

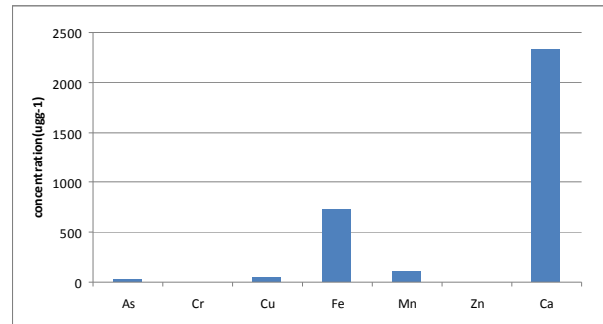


Figure 3. Mean concentration of heavy metals in crab specimen ( $\mu\text{g g}^{-1}$ ) from impacted section of Topcamp Stream.

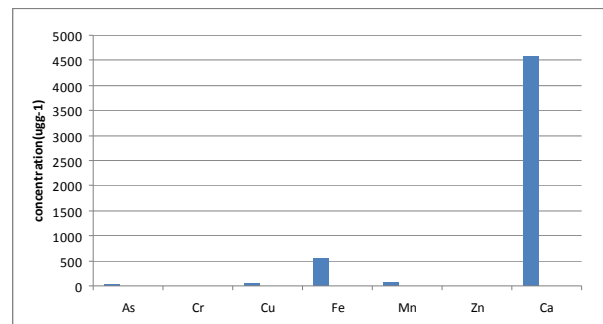


Figure 4. Mean concentration of heavy metals in crab specimens ( $\mu\text{g g}^{-1}$ ) from unimpacted section of Topcamp Stream.

Fe and Mn in crabs is significantly higher than the levels found in the effluent water. Consequently, in terms of ecological, crab is irreplaceable bioindicators of the degree of damage to the water environment. Moreover, it is also important to monitor the contamination of crab with heavy metals, because frequent consumption of the contaminated crab presents a very serious health risk. The results of the present study enabled us to determine the background concentrations of these metals in both water and crab. These data will constitute a reference to future studies on the evolution of contamination in this area. On the other hand, a potential danger may occur in the future depending on the agricultural, recreational activities and effluents from the Associated Match Industries.

The crab, *sudanaenautes africanus africanus* is economically important and forms a large part of aquatic catch in the area of study. However, heavy metal poisoning had been identified among people that depend on crabs for their protein [19]. The effects of heavy metal contamination are viewed as an international problem because of the effects on human health and ecosystem [20,21]. The concentrations of most toxic elements, other than As, Fe, Cu and Mn are not dramatically excessive. These heavy metals, the high dissolved solids concentration, including potassium and calcium carbonate may as well be withheld for corrective treatment before release

into the aquatic environment.

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