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Full Length Research Paper

Illegal Dumpsites and it Impact on Groundwater and Fish Resources (*Clarias gariepinus* and *Oreochromis niloticus*)

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The study evaluated the impact of the dumpsite leachate on groundwater at varying horizontal distances from the dumpsite and its biochemical toxicity in two tropical fishes, *Clarias gariepinus and Oreochromis niloticus*. Heavy metal concentration and physiochemical analysis of the leachate inferred that the dumpsite is at the anaerobic acid phase with its impact on groundwater distance depended. Level of heavy metals such as Cd in well 1- 3 (0.004 – 0.009mg/L) and Zn in well 2 (4.10 mg/L) exceeded the World Health Organization (WHO) permissible level. Computed 96-hour lethal concentration data showed that leachate was 1.26 times more toxic to *O. niloticus* (11.69 % v/v) than *C. gariepinus* (14.37 % v/v). In chronic exposure, fishes were exposed to sub-lethal concentrations of the respective 96 hr. LC_{50} data of the test animals for 30 days, and a control group. In the exposed animals, the activities of the enzyme Superoxide dismutase and catalase was significantly inhibited in *C. gariepinus* when compared to the control group. In *O. niloticus*, the enzyme activities of catalase, lipid peroxidation and glutathione S-transferase in the exposed fishes were significantly inhibited when compared to the control group. However, the SOD activity in *O. niloticus* was significantly inducted when compared with control.

Keywords: Dumpsite; Leachate; groundwater; *Clarias gariepinus*; *Oreochromis niloticus*; anti-oxidant.

INTRODUCTION

In the past several decades, the discourse on proper waste management has been on the front burner due to the exponential growth of the global population. The world's population is estimated to be 7.6 billion, growing at an average rate of 1.17 percent per year, yielding approximately 83 million people annually (United Nations, Department of Economic and Social Affairs, Population Division, (2017). In 2012, annual waste generated globally was approximately 1.3 billion tonnes, amounting to a footprint of 1.2 kilograms per person in a day. Municipal waste generation is expected to rise to 2.2 billion tonnes by 2025 due to large quantities of wastes produced throughout the life cycle of consumer products which involves phases from research, production, transportation, distribution, use, and disposal ("Solid Waste Management", 2018).

Like other developing economies, Nigeria is facing a waste management crisis due to the dearth of infrastructures and weak environmental laws to cater for the 25 million tonnes of municipal solid waste generated annually (Beatrice and Jussi, 2013). One of the cities greatly impacted is Lagos state, an economic hub of the nation with an estimated population of 21,000,000, with a daily urban waste generation amounting to 10,000 tonnes (Bakare, 2018). The inefficiency of the authorities to cope with the upsurge in volume of generated municipal solid waste (MSW) resulted to a void in the collection, transportation, recovery, recycling and disposal of solid waste in the state (Adebola, 2006). This void was partially filled by both the formal and informal private sector involved in the house-to-house waste collection and transportation, and the scavengers involved in the on-site waste recovery for recycling benefits (Adebola, 2006). As a result, this has led to the proliferation of unauthorized dumpsites across the

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metropolis to counter the emerging threat of waste accumulation.

Dumpsites by virtue of its heterogeneous composition are capable of generating leachate with potentially significant chemical constituents and pathogenic organisms, with the capacity to negatively impacting groundwater, soil, air and public health qualities. These constituents include regulated hazardous priority pollutants such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, xenobiotic organic compounds (XOCs) and other persistent organic pollutants (POPs) (Ikem *et al.,* 2002; Osibanjo, 2003; Anetor *et al.,* 2008). Despite the deleterious effects of dumpsites, they have historically remained the most utilized and cheapest method of deposing municipal solid waste (MSW) with the widest range of capabilities (Weiss, 1974; El-fadel *et al.,* 1995).

Formation of dumpsite leachate is a complex blend of physical, chemical and biological processes and the waste age which has a profound effect on dumpsites that generate leachate. Discharge of leachate often leads to severe environmental issues such as, through run off resulting to pollution of surface water and ground water resources, through percolation through the subsoil. Historically, since most dumpsites lack engineered liners and leachate collection and treatment systems, the threat of ground water pollution is probably the most severe environmental challenge (Christenen, and Kjeldsen, 1995). These pollutants besides being persistent and bioaccumulative can be ecotoxic, mutagenic, teratogenic, carcinogenic, reactive, corrosive, flammable and generally hazardous to the overall health of the ecosystem (Slacka *et al.,* 2005; Christensen *et al.,* 2001). Examples of such include XOCs and heavy metals. Compounds designated as XOCs are mainly associated with conventional hazardous and industrial wastes; however, they are also present in large quantity in the household or municipal solid wastes (Slack *et al.,* 2007). In addition, household cleaning agents, human and veterinary medicines, paint, garden chemicals, waste electrical and electronic equipment, motor vehicle components and batteries are all potential sources of XOCs (Slack *et al.,* 2005, 2007; Bakare *et al.,* 2013).

The common occurrence and hazardous nature of heavy metals in dumpsites are of particular interest in the study. Common heavy metals found in leachates are lead (Pb), Cadmium (Cd), Copper (Cu), Nickel (Ni), Chromium (Cr), Arsenic (Ar), Manganese (Mn), Zinc (Zn) and Mercury (Hg) (Reinhart, 1993). These elements are capable of forming metal colloids or complexes, specifically with organic materials. Consequently, they may amplify the environmental problem if the leachate migrates into surface water or groundwater (Gupta, 2009). Thus, in the last decades, authorities and dumpsite operators have frequently prescribed monitoring of heavy metals in dumpsite as a routine operation (Kjeldsen *et al.,* 2002).

The potential implications of solid waste leachates on the ecosystem has triggered a number of researches on toxicity of leachates on bacteria (Day *et al.,* 1993; Pivato and Gaspari, 2005; Koshy *et al.,* 2007); microalgae (Cheung *et al*., 1993, Bernard *et al*., 1996); plants (Klauck *et al.,* 2013; Cureton *et al.,* 1991; McMurphy *et al*., 1996; Bakare and Wale-Adeyemo, 2004); mussels (Vasiliki and Stefanos, 2012); crustaceans (Bloor *et al.,* 2005; Olivero-Verbel *et al.,* 2008); Daphnia (Wik and Dave,2006); fishes (Adeola *et al.,* 2012; Olujimi *et al.,* 2016; Emenike *et al.,* 2012; Juliardi and Wiyanti, 2018; Oshode *et al.,* 2008; Wong, 1989, Ernst *et al.,* 1994; Bernard *et al*., 1996); amphibians (Adeola *et al.,* 2011) mice (Bakare *et al.,* 2003a; Sang and Li, 2005); rats (Alimba *et al.,* 2006) and human cells (Amahdar *et al.,* 2009;Bakare *et al.,* 2007). Amidst these, there is a need to investigate the ecotoxicological implication of leachates on highly sensitive species like the *Oreochromis Niloticus*.

In Nigeria, fish is considered as one of the commonest sources of proteins, hence is relevant to the success of aquaculture (Hart, 1996). They are considered as suitable bio-indicator species, occupying an important role in the monitoring of water pollution because it responds with great sensitivity to the changes in the aquatic environment (Adeolu *et al.,* 2009). Fresh water species such as *Clarias gariepinus* (benthic) and *Oreochromis niloticus* (pelargic) with diverse spatial niche are systematically deployed as biological models for assessing the presence of pollutants in waters bodies (UNEP/RAMOGE, 1999). Exposure of these species to toxicants through direct contact with contaminated water could result in observable structural and/or functional changes. These alterations are measurable endpoints, generally referred to as stress biomarkers or indices and their investigation is systematically used both in laboratory and field studies (Dailianis, 2011; Moore *et al.,* 2004).

The aim of this study was to investigate the impact of leachates on groundwater resources at varying horizontal distances from the dumpsites and to evaluate its toxic endpoints, such as mortality, as well as its ability to induce biochemical alterations in the organism with aid of oxidative stress indices test, such as lipid peroxidation products and the production of free radicals (in terms of malondialdehyde and superoxide anion contents respectively). Characterization of the response of stress indices in target tissues, such as liver gland of fish, could serve as a veritable tool for assessing the potentially harmful impact of leachate into the aquatic environment as well as its ability to induce cellular alterations in fresh water organisms before observable phenotypic disturbance such as disease and mortality occur.

MATERIALS AND METHODS

The Study Areas

The Iwaya Dumpsite located at Ajoke street is one of the illegal dumpsites in Lagos state Government covering an approximately 183m expanse of land (map,google.com.ng imagery, 2018). This landfill is not equipped with a leachate collection and treatment system; thus, leachate produced is freely discharged into the surrounding aquatic and terrestrial environmental media. The area is largely dominated by fishermen with a population strength of roughly 80,000 inhabitants. It lies between longitude 6°30'7.29"N and latitude 3°23'41.03"E. Figure 1 and plate 1.

Leachate collection and handling

Samples of the leachate discharge from the dumpsite during the raining season in May were analyzed along with samples ground waters at varying horizontal distances (0, 45, 100, 300, 500 and 750 meters) Away from the Dumpsite. Leachate samples were taken from different points and from various vertical column depth to ensure leachate characteristics at different stages of decomposition were collected to form a composite of 20 liters. Samples were immediately transported to the laboratory, filtered and stored in a refrigerator at 4^0C in 2 L plastic bottles to arrest further bio-decomposition of the leachate prior to the commencement of physicochemical analysis and toxicity testing within 3 hr. This was considered as the stock solution and designated as the Iwaya Makoko raw leachate (IMRL).

Leachate Analysis

The physical and chemical parameters of the leachate were analysed in accordance with standard methods as prescribed by USEPA (1996). Standard physical and chemical parameters, including; total suspended solid (TSS), total dissolved solid (TDS), pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved oxygen (DO), oil and grease and conductivity were determined. The concentrations of six heavy metals viz. iron (Fe), lead (Pb), cadmium (Cd), manganese (Mn), zinc (Zn) and chromium (Cr) were estimated in the leachate sample using atomic absorption spectrophotometer (Buck AAS model, United Kingdom).

Laboratory Bioassays

Experimental fish and chemical

7 weeks old post juveniles of the *C. gariepinus* of mixed sexes with mean snout to tail length of 22.50cm±0.3, averaging 105g-125g in weight and 12 weeks old post juveniles of *Oreochromis niloticus* of mixed sexes with mean snout to tail length of 15cm±0.5, averaging 55g-65g in weight were purchased from a commercial fish farm located at Agege local government area, Lagos state. The fishes were transferred to the Laboratory where they were stabilized and acclimatized for 7 days in a plastic tank (36 x 30 x 48.5cm). The water used for stocking the organisms in the laboratory was adequately dechlorinated by aerating tap water in a plastic container with an aerator (Cosmo Aquarium, air pump 11,000) for 30 hr. This was done to rapidly vaporize chlorine gas in the water. The test organisms were fed with Coppens fish feed throughout their acclimatization and were fed twice daily at 12 hr. intervals (morning and evening). The holding water was changed once every two days to avoid the accumulation of food residue and waste metabolite. Feeding was terminated 24 hr. before the experiment as recommended by Reish and Oshida (1987).

Measurement of Physico-Chemical Characteristics of Test Media

Physico-chemical parameters were measured at the inception of the experiment and at the end (that is, before the change of test media). The parameters recorded are dissolved oxygen, pH, total dissolved solids, conductivity and salinity using appropriate digital instruments (Jenway).

Acute toxicity testing

Acute bioassay (96 hr. LC_{50}) were conducted in 5 L glass tanks (36.5 x 25 x 28 cm) in a static system with the test medium kept constant throughout the study duration. A set of 10 fish per three replicates was randomly exposed to IMRL at v/v concentration of:
(a) 10, 15, 20, 25% and control without leachate for *C. gariepinus*
(b) 10, 11, 12, 13, 14% and control without leachate for *O. niloticus.*

The quantal response (mortality) was evaluated every 24 hr. over a period of 96 hr. Mortalities were recorded when they showed no response to mechanical stimulation when prodded with a glass rod. Dead specimens were removed to avoid pollution of the water during the experiment.

Sublethal effects of IMRL on *C. gariepinus and O. niloticus*

In the course of the experimental procedure, test organisms were exposed to sublethal concentrations

Figure 1. Map showing the sampling points around the Iwaya Makoko Dumpsite

KEYS: A = Dumpsite (6°30'7.29"N,3°23'41.03"E)
B = Sample Well 1 (6°30'8.79"N,3°23'38.04"E)
C = Sample Well 2 (6°29'58.42"N,3°23'39.03"E)
D = Sample Well 3 (6°30'9.69"N,3°23'31.15"E)
E = Sample Well 4 (6°30'22.73"N,3°23'33.49"E)
F = Sample Well 5 (6°30'28.19"N,3°23'23.83"E)

Plate 1a. Showing the expanse of the Iwaya – Makoko dump site

Plate 1b. Showing Scavengers and Cart pushers at the iwaya – Makoko dump sites with already sorted out plastic containers (indicated by a white arrow)

(1/10th and 1/100th of 96 hr. LC_{50}) of the IMRL extrapolated from the acute toxicity bioassay. A semi-static bioassay test protocol was adopted in which the test media was refreshed once every 24 hr. with the same concentration and untreated control. At the end of the experiment- period on day 30, test organisms were retrieved, Fish specimens were anesthetized with tricaine methane sulfonate (MS-222) to minimize stress and to enable dissection to obtain liver organs required for biochemical assays respectively.

Enzymes Activity Assays

The Reduced Glutathione (GSH): The concentration of reduced glutathione (GSH) was determined according to the method of Beutler *et al.,* (1963), by the reaction of glutathione with the color reagent 5,5-dithiobis- 2-nitrobenzoic acid (DTNB), forming a thiolate anion (TNB), which was measured at 412 nm. The GSH concentration was expressed in µg GSH.mg protein-1.

Superoxide Dismutase (SOD): SOD enzyme activity was analyzed using the method adopted by Sun and Zigman (1978). The SOD enzyme assay measured the difference between superoxide anion disintegration and synthesis i.e, its ability to repress the autoxidation of epinephrine. Enzyme action was observed at absorbance level of 450nm. Concentrations are presented as U/mg or SOD-Unit/mg protein, where one unit is expressed as the level of enzyme required to inhibit 50% epinephrine reduction per minute and per milligram of protein at 25 ^{0}C and pH 7.8.

Catalase (CAT): Catalase activity was analyzed following the protocol adopted by Cohen *et al*. (1970). The protocol focuses on measuring the rate of H_2O_2 disintegration at absorbance levels of 240nm. The results were presented as U/mg or CAT-units/mg protein, where one unit is the level of enzyme that hydrolyzes 1 µmol of H_2O_2 per minute and per milligram of protein at 30 ^{0}C and pH 8.0.

Glutathione-S-Transferase (GST): The level of GST activity was analyzed according to the protocol adopted by Habig and Jakoby (1981). The measurement of GST activity was carried out by monitoring at absorbance level of 340nm, the induction of a conjugate between 1mM GSH and 1mM 1-chloro-2, 4-dinitrobenzene (CDBN). The results were presented as U/mg or GST unit/mg protein, where one unit is expressed as the amount of enzyme that conjugates 1 µmol of CDBN per minute and per milligram of proteins at 25^{0}C and pH 7.4.

Lipid Peroxidation (LPO) Assay: The levels of homogenized tissue malondialdehyde (MDA), as an index of lipid peroxidation were analyzed by thiobarbituric acid reaction (TBARS Assay). Using the protocol adopted by Yagi (1998). In this method, malondialdehyde is evaluated spectrophotometrically at absorbance levels of 535nm to assay for the amount of lipid peroxidation in a sample.

Statistical Analysis

Acute toxicity data involving quantal response (mortality) were analyzed using the probit analysis after Finney (1971). The enzyme activity and lipid peroxidation assessment data were subjected to a one way analysis of variance (ANOVA) using SPSS 20 statistical package to compare means and to determine the significant differences at a 5% probability level.

RESULTS

Physico-chemical Characterization of Leachate Samples Collected From Iwaya-Makoko Dumpsite

The summary of the physicochemical characterization of the IMRL is presented in Table 1. The pH value of the leachate was found to be 4.79 indicating an acidified medium impacted heavily by heavy metals. The concentration of zinc (Zn), iron (Fe), copper (Cu), manganese (Mn) and Lead (Pb) with the exception of nickel (Ni) were all above the permissible limit of the Nigerian Standard for Drinking Water Quality (NSDWQ), World Health Organization (WHO), United State Environmental Protection Agency (USEPA). Mercury (Hg) was below detectable levels. Zn had the highest concentration of 25.48mg/L, followed by Fe with a concentration of 15.63mg/L. Cu, Mn, Pb and Cd had a concentration 2.11, 1.04, 0.22 and 0.09mg/L respectively. Nickel (Ni) had the lowest concentration of 0.01mg/L. The level of Total suspended solid (TSS: 47 mg/L), Total dissolved solid (TDS:1325 mg/L) and oil and grease (0.64 mg/L) were all above the permissible limit of the NSDWQ. The level of dissolved oxygen (DO) of the leachate was low with a value of 2.60mg/L against the minimum stipulated standard of 6 by the NSDWQ. The concentration of the chemical oxygen demand (COD) and the biological oxygen demand (BOD) were 85.mg/L and 30mg/L respectively, which were all above the permissible limit of the NSDWQ.

Physicochemical Characterization of the Groundwater Samples Collected at Different Distance (0, 45, 100, 300, 500 and 750) away from the Dumpsite

Table 2 shows the physicochemical parameters of the groundwater samples collected at various distance (0, 45, 100, 300, 500 and 750) away from the dumpsite. Groundwater samples were mildly acidic with a mean pH value of 6.38 ranging between 5.85 – 6.74. The concentrations of the total dissolved solids (TDS) (30.00mg/L - 117.30 mg/L) and the chemical oxygen demand (COD) (2.00mg/L – 7.00mg/L) in groundwater samples were within WHO (2011), NSDWQ, and USEPA

Table 1. Physico-chemical characterization of the leachate sample

s/no	Parameter	Level Detected (mg/L)	NSDWQ	WHO	USEPA
1	TSS	47.00	0.25	-	-
2	TDS	1325.00	500	-	500
3	D.O	2.60	Minimum 6.0		-
4	BOD	30.00	3	-	-
5	COD	85.00	30	-	-
6	Oil and grease	0.64	0.01	-	-
7	Cadmium (Cd)	0.09	0.003	0.003	0.005
8	Copper (Cu)	2.11	1	2	1
9	Iron (Fe)	15.63	0.3	-	0.3
10	Mercury (Hg)	ND	0.001	0.006	0.002
11	Manganese (Mn)	1.04	0.2	-	0.05
12	Nickel (Ni)	0.01	0.02	0.07	-
13	Lead (Pb)	0.22	0.01	0.01	0.00 X 10∞
14	Zinc	25.48	3	-	5
15	pH	6.12	6.5 – 8.5	6.5 – 8.5	6.5 – 8.5

NSDWQ – Nigerian Standard for Drinking Water Quality WHO – World Health Organization. USEPA – United State Environmental Protection Agency

permissible level. Levels of BOD in sample location 1 and 4 exceeded the NSDWQ permissible level. The DO level in all the sampled wells exceeded the NSDWQ permissible limits. In all sampled wells, the WHO (2011) and NSDWQ permissible limits of metals such as Cu (1 mg/L), Fe (0.3 mg/L), Mn (0.2 mg/L), Ni (0.02 mg/L), Pb (0.01 mg/L) was not exceeded. The level of Cd (Well 1-3) and Zn (well 2) respectively exceeded the WHO and NSDWQ permissible level of 0.003mg/L and 3 mg/L. However, they were all below the permissible limit of USEPA (2018). With each distance further away from the dumpsite, there was a corresponding 100-fold decrease in all the parameters accessed. Aside Zn in sample well 2, the concentrations of other heavy metals in other sampled wells were negligible (Table 2).

Physico-chemical Characterisation of the Test Media during the Bioassays

The observed physico-chemical parameters of the test media for both test animals are presented in Table 3. The results revealed that the dissolved oxygen level ranged from 5.3mg/L (after each change to a clean media) to 3.3mg/L (after 2 days of exposure). The values of the pH and salinity of the test ranged from 6.59 – 6.99 and 0.3 % – 1.6% respectively. The conductivity and total dissolved solids in the test media increased from 127.87.00µS/m – 822.87µS/m and 65.46ppm-410.16ppm respectively over the period of observation.

Relative Acute Toxicity of leachate Against *C. gariepinus* and *O. niloticus*

Relative Acute Toxicity of IMRL against C. gariepinus and O. niloticus are presented in figure 2. On the basis of the computed 96 hr. LC_{50} values, Toxicity of the IMRL to *C. gariepinus* (14.37 % v/v) was not significantly (overlap in the 95% C.L of the respective 96 hr LC_{50} values) more toxic than IMRL against juveniles of *O. niloticus* (11.69 % v/v) (Figure 2). Computed toxicity factor shows that IMRL was found to be 1.26 more toxic to *O. niloticus* than *C. gariepinus*.

Enzymatic study

Reduced Glutathione transferase (GSH)

The GSH enzyme activity increased in *C. gariepinus* exposed to the leachate, but the increase was not significant ($P > 0.05$) when compared to control animals (Table 4). The level of GSH activity in *C. gariepinus* was observed to be 0.95µ/mg in control, and 0.75 - 0.83µ/mg in the exposed group (Table 4) The level of GSH activity increased most in exposed *C. gariepinus* to 1/10th (0.14% V/V) LC_{50} sublethal concentration (Table 4).

Measurement of GSH activities in liver of *O. niloticus* exposed to sublethal concentration of the leachate increased ($P > 0.05$) when compared to the control. The

Table 2. Physicochemical Characterization of the Groundwater Samples Collected at Different Distance (0, 45, 103, 312, 530, 742 & 760) m Away from the Dumpsite

Sample location	Distance (m)	TDS (mg/L)	COD (mg/L)	BOD (mg/L)	D.O (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)	pH
Dumpsite (m)	0	1325.00	85.00	30.00	2.60	0.9	2.11	25.48	1.04	0.01	0.22	15.63	4.79
1	45	129.00	7.00	4.00	4.90	0.006	0.017	0.02	0.09	0.002	0.004	0.15	5.90
2	103	117.00	2.00	2.00	5.30	0.009	0.023	0.06	0.014	0.007	0.009	4.10	5.85
3	312	53.00	5.00	3.00	5.00	0.004	0.014	0.04	0.011	0.005	0.007	0.32	6.41
4	530	30.00	3.10	3.30	5.10	0.003	0.012	0.03	0.010	0.004	0.008	0.19	6.74
5	742	54.00	2.00	2.00	5.20	0.002	0.010	0.03	0.008	0.005	0.004	0.37	6.58
NSDWQ		500	30	3	Minimum 6	0.003	1	0.30	0.2	0.02	0.01	3.00	6.5 – 8.5
WHO (2011)		-	-	-	-	0.003	2	-	-		0.01	-	6.5 – 8.5
USEPA (2018)		500	-	-	-	0.005	1	0.30	0.05	0.07	zero	5	6.5 – 8.5

NSDWQ – Nigerian Standard for Drinking Water Quality WHO – World Health Organization. USEPA – United State Environmental Protection Agency

Table 3. Summarized Physico-chemical Characterization of Test Media during the Bioasay

	TDS (ppm)	Temp (0C)	TC (µs/m)	NaCl (%)	pH	D.O
Before Bioassay	65.46	26.10	127.87	0.30	6.99	5.30
After Bioassay	410.16	26.00	822.87	1.60	6.59	3.30

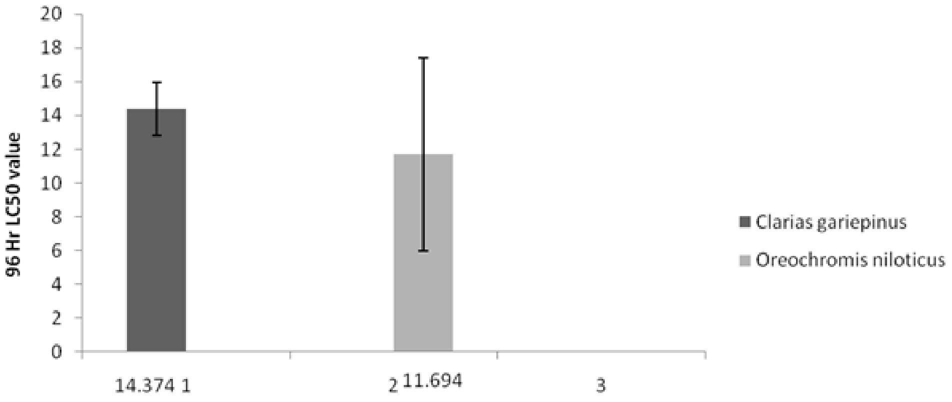

Figure 2. Relative Acute Toxicity of Leachate against *Clarias gariepinus* and *Oreochromis niloticus* based on 96Hr LC_{50} values (V/V)

activity level of GSH was observed to be -0.04µ/mg in the control group, and 0.15 - 0.22µ/mg in the exposed group (Table 4). GSH activity was elevated most in exposed in *O. niloticus* to 1/100th (0.14% V/V) sublethal concentration (Table 4).

Superoxide dismutase (SOD)

The results showed that the activity of the SOD enzyme was significantly ($P < 0.05$) inhibited in *C. gariepinus* exposed to 1/100th (0.14% V/V) LC_{50} sublethal concentration of the leachate. The level SOD activity significantly decreased from a ranged from 4.48µ/mg in the control group, to 1.98µ/mg in the exposed group (Table 4). The level of SOD activity decreased most in *C. gariepinus* exposed to 1/100th LC_{50} sublethal concentration.

Similar to *C. gariepinus*, SOD enzyme activity in *O. niloticus* was also inhibited in 1/100th (0.14% V/V) LC_{50} sublethal concentration of the leachate (Table 4). However, there was a significantly ($P < 0.05$) induction in SOD activity in *O. niloticus* exposed to 1/10th (1.36% V/V) LC_{50} sublethal concentration when compared to the control group. The level of SOD activity significantly increased from 6.54µ/mg in the control group to 21.51µ/mg in the exposed group (Table 4). The level of SOD activity decreased most in *O. niloticus* exposed to 1/10th LC_{50} sublethal concentration.

Catalase (CAT)

The CAT enzyme activity was significantly ($P < 0.05$) inhibited in *C. gariepinus* exposed to 1/100th (0.14% V/V) LC_{50} sublethal concentration of the leachate when compared with the control. The level of CAT activity significantly reduced from 20.32µ/mg in control, to 7.45µ/mg in the exposed group (Table 4). The level of CAT activity decreased most in *C. gariepinus* exposed to 1/100th LC_{50} sublethal concentration.

Measurement of CAT activities in liver of *O. niloticus* exposed to 1/100th LC_{50} sublethal concentration was significantly inducted ($P < 0.05$) when compared to the control. The level of CAT activity significantly increased from 35.59µ/mg in control to 84.86µ/mg in the exposed group (Table 4). Furthermore, the level of CAT activity decreased most in *O. niloticus* exposed to 1/10th LC_{50} sublethal concentration.

Lipid Peroxidation (LPO) Assay

The results of the lipid peroxidation assay showed that the level of malonaldehyde (MDA) in the liver of *C. gariepinus* exposed to the leachate was induced but the increase was not significant ($P > 0.05$) when compared to control animals. The level of MDA formation was 0.28µ/mg in control, 0.07µ/mg in the exposed groups (Table 4). The level of peroxidation was highest in animals exposed to 1/100th sublethal concentration of leachate (Table 4).

The liver of *O. niloticus* exposed to 1.36% V/V and 0.14 % V/V sublethal concentrations of leachate revealed a significant ($P < 0.05$) decline in LPO when compared to the control animals. The peroxidation level on day 30 was found to be 0.66µ/mg in control group, and 0.17 - 0.18µ/mg in the exposed group (Table 4). The level of peroxidation was lowest in animals exposed to 1/10th (1.36% V/V) sublethal concentration of leachate (Table 4).

Glutathione S - Transferase (GST)

The GST enzyme activity was inhibited in *C. gariepinus* exposed to the leachate, but the decrease was not significant ($P >0.05$) when compared to control animals. The level of GST activity was 13.02µ/mg in control group, and 11.48 - 11.80µ/mg in the exposed group (Table 4). The GST activity decreased most in *C. gariepinus* exposed to 1/100th (0.14% V/V) LC_{50} sublethal concentration.

GST activity in liver of *O. niloticus* exposed to sublethal concentration of the leachate was significantly ($P < 0.05$) inhibited in the exposed groups when compared to the control group. The level of GST activity significantly declined from 12.73µ/mg in control group, to 1.94 - 4.13µ/mg in the exposed group (Table 4). The level of GST activity decreased most in exposed *O. niloticus* to 1/100th LC_{50} sublethal concentration.

DISCUSSION

Leachate composition varies significantly among landfills, depending on waste composition, waste age, climate and hydrogeological conditions, landfilling technology, as well as inherent conditions in the landfill such as moisture, pH, temperature and biochemical activity. (Lema *et al.,* 1988). Generally, landfills are known to undergo at least four phases of decomposition, an initial aerobic phase, an anaerobic acid phase, an initial methanogenic phase and a stable methanogenic phase (Christensen and Kjelson, 1995).

In this study, the results of the physicochemical parameters of the leachate indicate an anaerobic acid phase. This stage is usually characterized with low pH, high concentrations of many compounds, and in particularly high concentrations of easily degradable organic compounds as volatile fatty acids (Kjeldsen *et al.,* 2002). The mildly acidic nature of the groundwater indicates the presence of metals, particularly toxic metals. Metals such as zinc, damaged battery cells (lead, mercury and alkaline) and improperly disposed electronic wastes, cans of aerosol and other

Table 4. Impacts of IWRL on Biochemical Parameters of *C. gariepinus* and *O. niloticus*

	Concentration	GSH (μ/mg)	SOD (μ/mg)	CAT (μ/mg)	MDA (μ/mg)	GST (μ/mg)
C. gariepinus	Control	0.95 ± 0.09^{a}	4.48 ± 0.67^{b}	20.32 ± 2.87^{b}	0.28 ± 0.21^{a}	13.02 ± 1.29^{a}
	1/100th	0.83 ± 0.05^{a}	1.98 ± 0.51^{a}	7.45 ± 1.57^{a}	0.07 ± 0.01^{a}	11.48 ± 0.64^{a}
	1/10th	0.75 ± 0.20^{a}	6.80 ± 1.28^{b}	32.31 ± 5.96^{b}	0.07 ± 0.01^{a}	11.80 ± 2.53^{a}
O. niloticus	Control	-0.04 ± 0.22^{a}	6.54 ± 1.38^{a}	35.59 ± 6.62^{b}	0.66 ± 0.02^{a}	12.73 ± 1.38^{b}
	1/100th	0.22 ± 016^{a}	1.86 ± 0.49^{a}	8.57 ± 2.25^{a}	0.17 ± 0.03^{b}	4.13 ± 1.90^{a}
	1/10th	0.15 ± 0.01^{a}	21.51 ± 6.93^{b}	84.86 ± 29.90^{b}	0.18 ± 0.01^{b}	1.94 ± 0.15^{a}

Values followed by same superscript along the same column are not significantly different from each other

disinfectants deposited in the landfill as waste, after exposure to air and water and may have found their ways to the groundwater through seepage to give the toxic, acidic nature it currently possesses (Akinbile and Yusoff, 2011 Another explanation could be that the acidic nature of Lagos groundwater is characteristic of the coastal groundwater whose pH is primarily controlled by its hydrogeological setting (Longe *et al*., 1987). The pH findings from this study agree with Longe and Balogun (2010) who observed that the Solus landfill located at Igando, Lagos State, Nigeria impacted on adjoining groundwater samples with pH ranging between 5.30 and 7.07. The depleted levels of DO in all the sampled wells are typical of all underground water resources (Minnesota Pollution Control Agency, 2009).

Prohibitory levels of heavy metals such as Cd (Well 1-3) and Zn (well 2) in the groundwater source closest to dumpsite could be as a result of the low pH around the dumpsite area. The pH of the subsurface affects the mobility of the metals by affecting the sorption/desorption of metals, precipitation/dissolution, complex formation and oxidation/reduction reactions that take place in the subsurface (McLean and Bledsoe, 1992). A similar observation was reported by Chirenje (1999), that at pH conditions below 9 the soil cation exchange capacity was reduced and the mobility of Cd and Ni was increased. Furthermore, zinc ligands are known to be soluble in neutral and acidic solutions, hence readily transported in most natural waters (USEPA 1980, 1987). Although Zinc has beneficial use in an organism by enabling the normal functioning of cells by via DNA synthesis and regulation of the immune system is still hazardous when found in high concentration. Soluble chemical species of zinc are the most bioavailable and most toxic (Spear, 1981) having the ability to bioaccumulate in aquatic fauna which eventually biomagnifies along the food chain. The biomagnification potential of zinc could spell harm to people resident at Iwaya/Makoko environs due to their usual dependence fish as their major source protein. Unborn and newborn children are even more susceptible to zinc poisoning due to the possibility that their mothers having absorbed large concentrations may expose the children through blood or milk supply during suckling. This is also coupled with the poorly developed excretory and defense mechanism of infants. In contrast to zinc which is an essential metal, Cadmium (Cd) is one of the most toxic heavy metals (Sanita di and Gabrielli, 1999). The high Cd concentration in underground sources of drinking water causes damage to kidneys. Cadmium (Cd) is one of the most toxic heavy metals in the arable soil for crop growth and yield formation (Sanita di and Gabrielli, 1999).

The toxicity of the leachate was found to be 1.23 more toxic to *O. niloticus* (96LC$_{50}$ of 11.694% (v/v) than to *C. gariepinus* (96LC$_{50}$ of 14.374% (v/v) (Fig: 2). the differential sensitivity of both test organisms to the leachate can be attributed to the unique morphological and physiological differences of both species. These, in turn, influenced their susceptibility to the leachate sample.

Glutathione (GSH) is a sulflrydryl antioxidant and tripeptide which plays a functional role in reactions of oxidation/reduction, amino acid transport and detoxification of many toxic agents. It is the first line of defense against cellular damage mediated by oxidants (Van der Oost *et al.,* 2003). In this study, the apparent decrease in GSH levels in the exposed fishes indicates an oxidizing state of the cell induced by heavy metals present in the IWRL. Glutathione (GSH) is a key component in such metal scavenging due to the high affinity of metals to its thiol (-SH) group. Heavy metals increase GSH oxidation, resulting in depletion of cellular GSH levels (Zhu and Pilon-smits, (1999), this is an adaptive and protective role of biomolecule against oxidative stress. Cytosolic depletion of GSH causes a readjustment of the intracellular redox environment and oxidative signaling (Vivancos *et al*., 2010), this result is in agreement with the findings of Semane *et al.,* (2007). They observed a decrease in GSH content and a more oxidized GSSG/GSH ratio after Cd treatment (1 and 10 μM) in *Arabidopsis.*

The activity of the enzyme Superoxide Dismutase (SOD) was significantly inducted in the liver of *O. niloticus* exposed to IWRL at the end of the 28-day study. This enzyme SOD is known to act as cytoprotection against free radical-induced injury by converting superoxide radicals (O2-) generated in peroxisomes and mitochondria to hydrogen peroxides. The hydrogen peroxide is then eliminated from the system by the Catalase (CAT) enzyme, which transforms it into water and molecular oxygen (O_2). The significant increase of SOD activity observed during the study demonstrates that IWRL induced an adaptive response by scavenging the overproduction of superoxide ions under the oxidative stress. Therefore, an increase in SOD activity indicates that there is O_2-generation and this generation can be expelled. Otherwise, if the overproduction of superoxide anions to an extent exceeds the function of SOD elimination, these anions can inactivate the enzyme (Kaur and Jingal, 2017).

CAT and SOD enzymes have associated functions. SOD catalyzes the dismutation of the superoxide anion radical to H_2O and H_2O_2, which is detoxified by both CAT and GSH-Px activities. The significant reduction in CAT activity in *O. niloticus* could stem from decreases in reaction rates resulting from the excess production of H_2O_2. This could have been because of the flux of superoxide radicals, which has been shown to inhibit CAT activity (Ahmad *et al*. 2000). Similarly, Jee and Kang (2005) also observed a decrease in catalase activity in the gills, livers, and kidneys of *Paralichthys olivaceus* after phenanthrene exposure. Recently, Tripathi and Singh (2013) observed a decrease in CAT activity in the brains, gills, livers, and skeletal muscles of *Channa punctatus*. The increase or decrease in enzyme activity is related to the intensity of cellular damage. Bagnyukova *et al*. (2005) reported a reduction of CAT activity by a systemic herbicide, 3-amino 1,2,4-triazole in the brain of *Carassius auratus* and the activity of GSHPx increased. The authors suggested that this increase might represent a compensatory response to lowered CAT activity, and these changes could provide compensatory mechanisms for detoxifying H_2O_2 or elevated amounts of hydroperoxides.

Lipid peroxidation in vivo has been identified as one of the basic deteriorative reactions in cellular mechanisms of metals-induced oxidative stress in freshwater fishes. The inhibited activity of hepatic antioxidative enzymes, such as superoxide dismutase and catalase, would result in enhanced levels of lipids peroxidation index (MDA). In the present study, however, the inhibited activity of antioxidant enzymes was not necessarily related to the enhancement of MDA levels. In other words, there was a marked reduction ($P < 0.05$) in the MDA level in *O. niloticus* exposed to IWRL when compared to the control group. The marked reduction in MDA level in *O. niloticus* could be attributed to the increased oxidative stress caused by the induced generation of ROS and depletion of tissue contents coupled with diminution in enzymatic antioxidative defense mechanism (Achudume *et al*., 2009)

GST is a cytosolic or microsomal enzyme that catalyses the conjugation of reduced glutathione (GSH) with oxidative products, such as 4-hydroxyalkenals (membrane peroxides) and/or base propenals, resulting from DNA oxidative degradation (Leaver and George, 1998). Therefore, it also plays an important role in protecting tissues from oxidative stress (Fournier *et al*., 1992; Jifa *et al*., 2006). The enzyme GST has been reported to respond differently to numerous compounds, for example, Paulino *et al.,* (2012) observed an increase in GST activity in gills of the Neotropical fish *Prochilodus lineatus* after sub-chronic exposure to atrazine, an herbicide broadly used to control undesirable organisms in corn crops, while Rendón-von Osten *et al*., (2004), reported a significant inhibition of GST activity in mosquito fish (*Gambusia yucatana*) gills after 24 h exposure to 0.06 mg L-1 of carbofuran.. In this study, the GST activity was significantly inhibited in the liver of *O. niloticus* compared to control. A similar observation of marked GST inhibition was observed in a study Botte *et al*., (2012), they reported that hepatic GST activity decreased after 5 days of exposure to a cocktail of pesticides. Similarly, Cavalheiro de Menezes *et al.,* (2012) reported that of fish fed with a standard diet and exposed to the herbicide quinclorac showed a marked inhibition of GST activity indicating that some conjugation products catalyzed by GST may hinder this process, indicating that oxidative products can in fact reduce the conjugation capabilities.

CONCLUSION

With the passage of time, the world's mega manufacturing and processing plants are gradually expanding to meet global market demands, thus, leading to an inevitable solid waste generation and accumulation. Forecast for the next 2 decades indicates a progressive increase in waste production and, subsequently in leachate infiltration. The discharge of leachate into the ecosystem is one of the major environmental burdens of waste disposal.

In this study, the polluting impact of such discharge on groundwater resources declined away from the polluting source. This infers that the contamination of the groundwater was more dependent on proximity to dump sites. The less dependency has been attributed to the influence of topography and to some extent, the hydrogeology of the area. Furthermore, Presence of Cd and Zn concentration above safety limits of the WHO and NSDWQ is an indication of the toxic potential of the groundwater and therefore poses a grave risk to both biotic and abiotic resources.

The evaluation of stress indices in target tissues of teleosts exposed to leachate reflects a reliable approach for the risk assessment of its potentially harmful impact on aquatic biota, thus providing an accurate picture of the overall health and status of the environment. The present study established the potential of leachate to induce oxidative effects in tissues of *C. gariepinus* and *O. niloticus*, although *O. niloticus* proved to be more sensitive to ROS inducing xenobiotics than *C. gariepinus*. To conclude, SOD, CAT, MDA and GST anti-defense enzymes demonstrated to be reliable biomarkers of effect after exposure to dumpsite leachate, and *O. niloticus* proved to be more sensitive for bio monitoring programs in the aquatic environments.

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