ORIGINAL RESEARCH ARTICLE

Assessment of water and sediment around a lead-acid battery plant dumpsites in South-Western Nigeria

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Abstract

In a quick assessment carried out around dumpsites of a battery manufacturing plant, heavy metals content of sediment, surface water and ground water samples from seven ponds, three streams and a well were assessed using Atomic Absorption Spectrophotometer (AAS). Some physicochemical parameters of the samples were also investigated. Metal concentration in pond and stream sediment samples ranged from 25.71-75,843 µg/gPb, 0.74-4.13 µg/gCd, 32.35-385.31 µg/gCu, 3.17-28.5 µg/gNi, 558.25-908.42 µg/gFe and 10.01-53.59 µg/gZn and these metal concentrations exceeded allowable guidelines for sediment by USEPA. For water samples in general, concentration of metals ranged as Pb(0.001-5.69 mg/L), Cd(0.0006-0.0699 mg/L), Cu(0.001-0.09 mg/L), Ni(0.001-0.38 mg/L), Fe(0.0399-17.099 mg/L) and Zn(0.001-0.14891 mg/L). Physicochemical parameters in water were pH (4.54-7.59), Temperature (25-28 ^{O}C), DO (2.49-6.45 mg/L), TS (296-35,100 mg/L), TSS (2.0-281 mg/L), TDS (290-34,800 mg/L), Cl^- (12.2-52.5 mg/L), NO_3^- (3.2-800 mg/L), PO_4^{3-} (0.14-1.58 mg/L) and SO_4^{2-} (76.0-5,300 mg/L). Results obtained for TSS, TDS, NO_3^-, SO_4^{2-}, Pb, Cd and Fe in water, especially in ponds at Ile-Igbon and Ni in Aweere Stream, exceeded limits set by standard organisations as well as results from similar work.

Chemical: Environmental. Keywords: battery plant dumpsite, heavy metal, sediment

1. Introduction

Indiscriminate dumping of wastes is still an issue in developing nations of the world. Notable among these wastes of diverse origin and nature are those from battery production and usage. Rechargeable batteries are sources of power generation in automobiles and industries and contain metals of environmental concern including lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), manganese (Mn), nickel (Ni), zinc (Zn), palladium (Pd), titanium (Ti), silver (Ag) and lithium (Li) (Biney et al., 2007; Krouse et al., 2009). Heavy metals comprise a group of pollutants that could be anthropogenically introduced into the environment through industrial activities, agricultural run-offs and leaching from solid waste dumps (Biney et al., 2007; Kaushik et al., 2008). They are grouped into one category of 53 elements with density greater than 5.0 g/cm^3 (Gohre and Paszkowski, 2006). Their presence in the environment is of global concern because they are persistent, bioaccumulating and pose health and environmental risks.

Pollutants from waste dumps often end up in rivers and ponds. The removal of heavy metals from water and their accumulation in sediments are controlled by sedimentary processes (Zhang and Shan, 2008). Sediments play a major role in the cycling of heavy metals because they are trace elements traps and can act as sink, reflecting the nature of the overlying waters as at the time of deposition (Bai et al., 2011; Weber et al., 2013). A build-up of metals in sediments has significant environmental implications for the river water quality and the local communities (Demirak et al., 2006). Wastes containing heavy metals pose serious deleterious and health effects when inappropriately disposed. Exposure to some heavy metals, especially Pb, has caused decrease in intelligence quotient in children (Diaz-Barriga et al., 1997), biochemical interference with heme biosynthesis in adults (Goyer and Clarkson, 2001), alteration of physiological processes in plants (Shanker, et al., 2005) and bioaccumulation in some animals (Hsu et al., 2006). This study was therefore predicated on the presence of battery slag dumps around these villages where the residents utilized available water from well and ponds domestically, for irrigation and watering livestock, making contact with such ponds. It aimed at evaluating heavy metal contents of sediments and waters in some ponds, streams and the well around these sites as well as the physicochemical characteristics of the waters and the sediments.

2. Materials and Methods

2.1 Site Description

A total of three dumpsites, each one located at Olodo, Olukunle and Ile-Igbon villages in Oyo state, South-western Nigeria, were investigated. Figure 1 shows the sampling areas at Olodo, Olukunle and Ile-Igbon. These were typical villages characterized by little or no industrial activity. The houses were few, much of the land was used for agriculture and streams were the major source of water supply. Olufa Farm in Olodo village haboured abandoned poultry sheds, a well and an artificial pond greater than 400 m^2 all surrounded by farmlands. The pond served as fishpond before the abandonment and was less than 70 m from the waste piles and their floodplains.

Pond sediment samples (PS1 and PS2) as well as pond water samples (PW1 and PW2) obtained from Olufa Farm were respectively the first two sets of sediment and water samples. PS1 and PW1 were sampled from a point in the pond close to the poultry farm (Figure 1), PS2 and PW2 were collected from the point of discharge to Eegun Stream and water sample (GW) was sampled from the well. Sediment and water samples SS3 and EW respectively were sampled from Eegun Stream which flowed alongside the pond. The point of collection of SS3 and EW from Eegun Stream was upstream to the point of discharge of water from the artificial pond into the stream. Sediment sample (SS4) and water sample (AW) were sampled from Aweere Stream at Olukunle village. The last site was Ile-Igbon village where sediment samples (PS5, PS6, PS7, PS8 and PS9) and water samples (P1, P2, P3 and P4) were collected from some natural ponds within 12.2 m to one another and on a wide area of land with three heaps of the battery and slag waste as well as a big flood-plain. Sediment sample (SS10) and water sample (AS) were sampled from Ajele Stream, also at Ile-Igbon village.

2.2 Sample Collection and Preservation

Three grab samples of sediment were collected from the bottom of each pond using stainless hand trowel, composited and stored in clean separate polythene bags. Grab sampling was also used for water samples using a clean glass bottle. A rope was attached to the bottle only in the case of the well. Water samples for Dissolved Oxygen (DO) determination were taken in a 287 mL brown Winkler bottle and 1.0 mL each of manganous sulphate and alkaline iodide-azide were added to fix the DO. The samples were kept in coolers filled with ice.

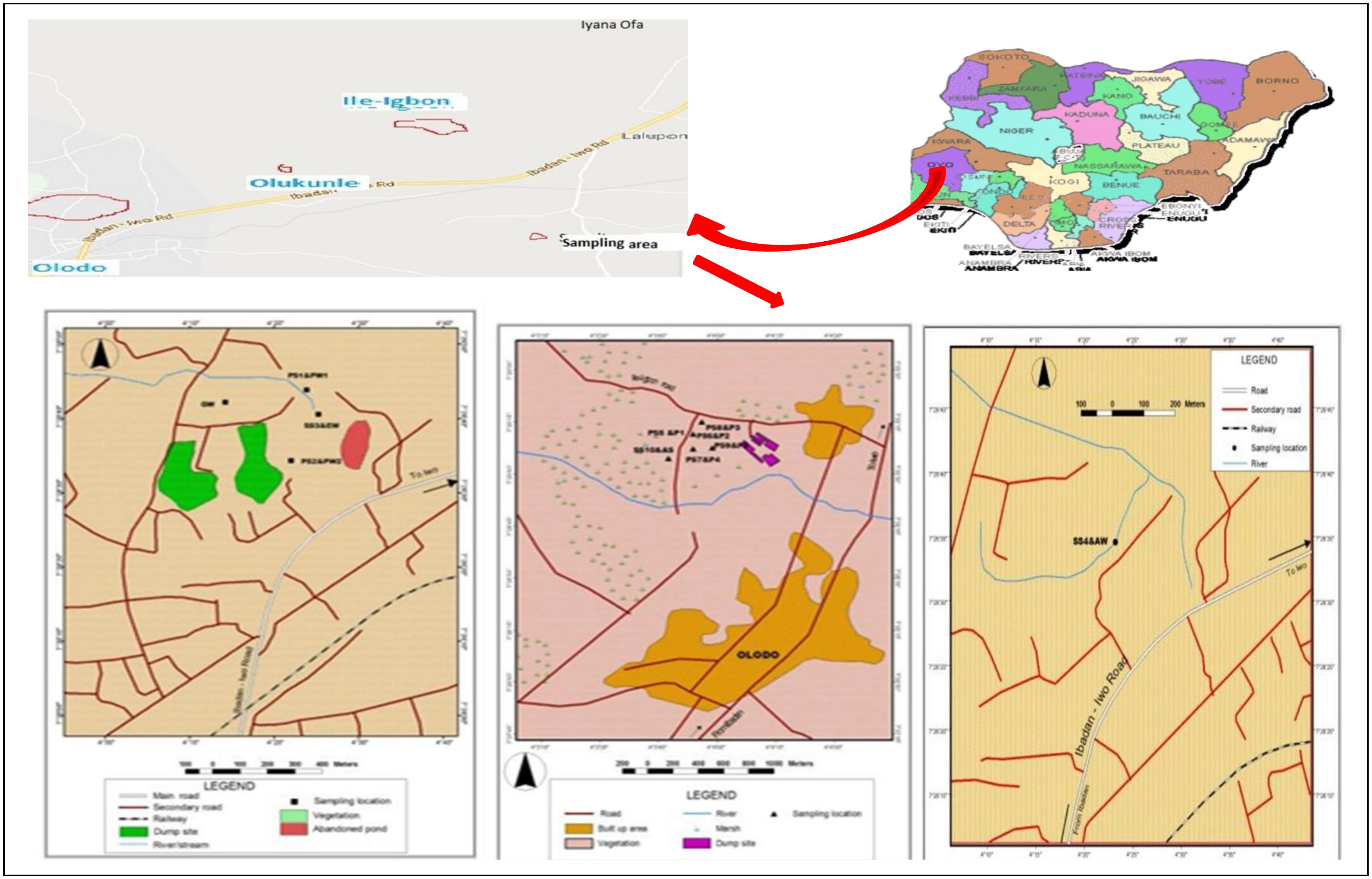

Fig. 1: Map showing sampling areas at Olodo, Olukunle and Ile-Igbon

2.3 Sample Analysis

Fresh moisture content (MC) of sediment was determined by the method of Grinshaw et al. (1989). Clean dishes were oven-dried at 105 ^oC for 2 hours, cooled in a dessicator and then weighed. The process was repeated to a constant weight. Sediment samples, 2 g each, were weighed into different dishes and transferred into the oven. Heating, cooling and weighing were repeated to constant weight. Percentage moisture was calculated from ratio of weight of sediment after and before heating multiplied by 100. Determination of sediment pH was carried out by placing 10 g air-dried sediment samples that had been passed through 2 mm sieve in 20 mL of 0.01 M $CaCl_2$ solution and made to stand for 30 minutes with occasional stirring using a glass rod. The electrode of a pH meter that had been calibrated using buffer solutions of 4 and 7 was gently inserted into each suspension, cleaned with deionized water and wiped with a tissue paper in turn (Grinshaw, et al. 1989). Total Organic Carbon (TOC) and Total Organic Matter (TOM) were determined using Walkey-Black method (1934). Total heavy metals content was extracted from 1 g of air-dried sediment sample in a crucible using 20 mL concentrated HNO_3. This was placed on a water bath and heated for 2 hours to obtain about 5 mL extract. It was then filtered using Whatman (No. 10) filter paper into a 50 mL standard flask and made up to the mark with distilled water. Metals were determined using ALPHA 4 Atomic Absorption Spectrophotometer (AAS) (Chemtech Analytical Model manufactured in Britain) with detection limits, in mg/L, of 0.004 for Pb, 0.002 for Cd, 0.001 for Cu, 0.05 for Ni, 0.003 for Fe and 0.006 for Zn.

The pH and temperature of water samples were determined on the field using a portable pH meter with inbuilt thermometer. Determinations of chloride (Cl^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), DO, Total Solids (TS) and Total Suspended Solids (TSS) were as in Standard Methods for Examination of Water and Wastewater (SMEWW) by American Public Health Association (APHA) (1997) while nitrate (NO_3^-N) was determined according to the method described by Michael (1950). Water sample was digested for heavy metal analysis by adding concentrated nitric acid (2.0 mL) to 50 mL samples. The solution was heated on a water bath for an hour, cooled, filtered into a 50 mL volumetric flask and made up to the mark with distilled water before determination with AAS.

2.3 Quality Control

Reagent blanks and standards were prepared for both water and sediment analysis. The results of the blanks were subtracted from the sample results. Recovery study was carried out for Zn, Cd and Pb respectively on water samples AS, PW2 and P2 with relatively low, moderately high and relatively very high metal content by spiking the appropriate already analysed samples with standard solutions of the metals. The analysis using AAS was then run again in duplicate and the mean recovery calculated. Besides, precision study was carried out on sample P3 by splitting it into five portions and determining the concentration of Pb in each to get the variance.

3. Results and Discussion

3.1 Sediment physichochemical parameter and metal content

Results of physicochemical parameters and heavy metals concentration of all sediment are shown in Table I while Table II gives the range of metals concentration for this study and the guideline values of metals in sediment by standard organisations. Apart from Fe, metals investigated have been reported as components of lead-acid batteries (Adediran et al., 2010). However, Cu, Cd and Ni, in descending order, were below detection limit in some samples. Where detected, Pb, Cd and Cu occurred at a higher level than the world geochemical background concentration in average shale and world background concnetration. All samples had lower Ni, Fe and Zn than the corresponding average in shale (Table II) and samples were unpolluted by Zn (< 90 mg/kg). Conversely, all samples were polluted at varying degrees by Pb and Cu. Samples within 12.2 m to each other and the slag heap included PS7, in excess of Pb concentration designated as heavily polluted (60 mg/kg), as well as PS8 (52,986 µg/g) and PS9 (75,843 µg/g) with outrageous level. Greipsson et al. (2013) have also observed marked increase in Pb content of surface soil within 3.0 km to a smelter. The pollution was moderate in terms of PS7 (32.7 µg/g) for Cu (25-50 mg/kg) and Pb (40-60 mg/kg) for stream sediments [(25.7 µg/g for SS3 and 51.4 µg/g for SS4)]. All the metals considered were higher in PS2 sampled at the point of discharge of pond to the stream, downstream to SS3, and suggests input from the pond.

Table I: Physicochemical parameters and heavy metal concentration of sediment from Olodo, Olukunle and Ile-Igbon villages

S.C.	pH	MC (%)	TOC (%)	TOM (%)	Pb (µg/g)	Cd (µg/g)	Cu (µg/g)	Ni (µg/g)	Fe (µg/g)	Zn (µg/g)
PS1	5.88	1.57	1.28	2.21	111	1.27	< D.L	9.50	606	15.6
PS2	6.60	1.97	1.60	2.76	68.2	< D.L	< D.L	5.28	710	21.3
SS3	6.09	2.26	0.08	0.14	25.7	< D.L	< D.L	3.17	602	15.0
SS4	6.52	1.76	0.4	0.69	51.4	1.38	< D.L	20.1	908	19.5
PS5	6.35	1.01	0.32	0.55	466	< D.L	< D.L	10.6	618	31.9
PS6	6.53	1.81	0.48	0.83	526	0.74	< D.L	< D.L	558	37.1
PS7	6.26	3.45	2.35	4.07	1,035	0.95	32.4	7.39	681	53.6
PS8	6.49	5.71	2.99	5.18	75,843	4.13	385	28.5	831	12.7
PS9	6.85	4.61	2.15	3.73	52,986	2.86	210	28.5	744	10.0
SS10	4.45	0.56	0.08	0.14	168	< D.L	< D.L	3.17	645	10.6

S.C. = Sample Code; D.L = Detection Limit

Table II: This study and guideline values of heavy metal concentration in sediment

Code	Pb	Cd	Cu	Ni	Fe	Zn
This study (µg/g)	25.7-75,843	0.74-4.13	32.4-385	3.17-28.5	558-908	10.0-37.1
[a]USEPA SQG						
Unpolluted (mg/kg)	< 40	-	< 25	-	-	< 90
Moderate (mg/kg)	40-60	-	25-50	-	-	90-200
Heavily polluted (mg/kg)	> 60	> 6	> 50	-	-	> 200
[b]Average shale (mg/kg)	20.0	0.300	45.0	68.0	46,000	95.0
[c]World average background (µg/g)	14.0	0.38	17.0	-	-	67.0

[a]United States Environmental Protection Agency Sediment Quality Guidelines (Pedersen et al., 1998)

[b]World geochemical background concentration in average shale (Harikumar et al., 2009; Jonathan et al., 2016)

[c]World background concentration (Bervoets and Blust, 2003; Demirak et al., 2006)

SS10, with similarity to SS3, was sampled from a stream and had the lowest MC (0.56%) and TOC (0.08%) as well as concentrations of some metals. This was probably because of its texture, likely more sandy, and acidic nature (pH 4.45) making the metals labile and not bound. Unlike the heavily polluted PS1 and PS2 from Olufa Farm close to the slag pile and its flood plain, SS3 from Eegun Stream was moderately polluted. This was probably because it was upstream to the point of discharge of the pond into it as well as sandy (unpublished data). Nevertheless, some sediment samples were polluted and harmful because in comparison with other heavy metals at low concentration, Pb puts life in marine environment in danger (Sadiq et al., 2003; Bai et al., 2011).

The pH of sediment samples ranged from 4.45 to 6.85, SS10 being the lowest (4.45) and moderately acidic (Table I). Others were less acidic and PS9 was almost neutral. pH governs stability of metals bound to sediment as inorganic compounds such as metal oxides, hydroxides, carbonates and sulfides. Metals are released in the more mobile forms at strongly acidic conditions. As in organic matter, increase in pH induces precipitation of amorphous ferric and manganese oxides which scavenge much of Pb, Zn and Cd from contaminated water (Warren, 1981). TOM of sediment ranged from 0.14 to 5.18%. Due to its strong complexing potential for metallic contaminants, organic matter acts as a major sink for trace metals (Gonzalez et al., 2006; Bai et al., 2011). PS8 with the highest TOM (5.18 %) had highest Pb (75,843 µg/g), Cu (385 µg/g) and Cd (4.31 µg/g) while SS3 and SS10 with the lowest TOM (0.14 %) had lowest Pb (25.7 µg/g) and Fe (602 µg/g). PS5, PS6 and PS7 with relatively high pH and TOC had high Pb and Fe contents. This is also true for Fe in PS2 with pH 6.6 and TOC 2.76 %. Moreover, Cu and Pb concentrations in sediments showed similarity in trends and the highest concentrations of both metals were found in sediments with elevated TOC content. This agrees with the results of Al-Abdali et al. (1996) and suggests derivation from pollutant sources.

Tables III and IV respectively display the results of heavy metals concentration and the physicochemical parameters of water samples from all the sites. Water quality criteria for different parts of the world and range for this study are shown in Table V. Cu and Zn had certain similarities: both were the only metals detected in all samples (Table III), their concentrations were above that for world background average and in all samples, Cu (0.001-0.09 mg/L) and Zn (0.001-0.149 mg/L) respectively occurred below the Nigerian Standard for Drinking Water Quality (1 mg/L) and (3 mg/L) set by Nigerian Industrial Standard (NIS) (Table V). Besides, concentration of Cu in water was also lower than WHO’s limit (2 mg/L) and the water samples were therefore safe for drinking with respect to Cu and Zn. Contrariwise, most of the water samples where Cd, Ni, Pb and Fe were detected, in ascending order, were polluted in comparison with the world average background concentration and the permissible limits by some of FMWR, NIS and WHO, among others (Table V). These include all except PW1 and AW for Pb, EW for Cd, PW1, EW, P2, P3, AS and GW for Ni and only P1 for Fe. P2 from one of the ponds close to the slag pile (within 12.2 m) actually had the highest Pb (5.69 mg/L), Cu (0.09 mg/L) and Fe (17.10 mg/L), suggesting point source polution. Consequently, all these were unfit for drinking. Beyond consumption by man, some of the water samples (PW1, AW, P2 and GW for Cd as well as AW and P4 for Ni) exceeded the water quality criteria for irigational waters by Food and Agriculture Organization (FAO) and Nigeria (0.01 mg/L Cd and 0.2 mg/L Ni) (FAO, 1985; FEPA, 1991) and also 0.01 mg/L Cd for groundwater protection by FEPA (1991) thus, were unsuitable for irrigation and would be deleterious to plants, soil and the food chain.

For samples of sediment where metals were detected, the level in sediment was higher than in water sampled from the same point. This is in line with previous reports by Hambuckers-Berhin et al. (1997) as well as Rozan and Benoit (1999).

Table III: Concentration of Heavy Metals in Water from Olodo, Olukunle and Ile-Igbon villages

Sample Code	Pb (mg/L)	Cd (mg/L)	Cu (mg/L)	Ni (mg/L)	Fe (mg/L)	Zn (mg/L)
PW1	0.001	0.02	0.045	0.002	1.13	0.072
PW2	0.88	< D.L	0.034	< D.L	1.25	0.149
EW	0.28	0.001	0.022	0.001	1.28	0.126
AW	0.001	0.04	0.022	0.38	2.17	0.081
P1	0.62	0.01	0.004	0.08	0.04	0.001
P2	5.69	0.05	0.09	0.001	17.10	0.001
P3	0.83	0.003	0.003	0.013	5.95	0.003
P4	0.37	0.01	0.001	0.021	5.20	0.009
AS	0.17	< D.L	0.001	0.004	< D.L	0.009
GW	< D.L	0.07	0.034	0.004	0.95	0.063

D.L = Detection Limit

Table IV: Physicochemical parameters of water from Olodo, Olukunle and Ile-Igbon villages

Sample Code	pH	Temp °C	DO mg/L	TS mg/L	TSS mg/L	TDS mg/L	Cl^- mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	SO_4^{2-} mg/L
PW1	7.59	27	4.06	482	42.0	440	13.9	6.6	< D.L	230
PW2	7.19	27	2.49	406	22.0	384	14.7	6.6	0.14	310
EW	7.22	27	3.80	450	8.0	442	19.0	8.2	0.26	193
AW	7.38	26	5.65	363	4.0	359	15.9	5.0	0.22	76.0
P1	6.57	28	6.45	482	81.0	401	< D.L	80.0	< D.L	3,740
P3	6.99	29	< D.L	12,700	231	12,500	< D.L	660	0.3	3,740
P4	4.54	29	< D.L	11,000	91.0	10,900	< D.L	160	< D.L	5,300
AS	6.64	25	5.28	296	6.0	290	12.2	5.0	< D.L	115
GW	6.70	28	3.40	320	2.0	318	52.5	3.2	< D.L	103

D.L = Detection Limit

Table V: Water Quality Criteria and range for this study

		Water Quality Criteria					
Parameter	**Range for this study**	**FMWR[a]**	**NIS (Nigeria)[b]**	**WHO[c]**	**GCDWQ (Canada)[d]**	**NPDWR (USA)[d]**	**Background concentration world average[f]**
Pb (mg/L)	0.001-5.69	-	0.01	0.01	0.01	0.015	0.0002
Cd (mg/L)	0.001-0.07	-	0.003	0.003	0.005	0.005	0.00002
Cu (mg/L)	0.001-0.09	-	1.0	2.0	-	1.3	0.001
Ni (mg/L)	0.001-0.38	-	0.02	0.07	-	-	-
Fe (mg/L)	0.04-17.10	-	0.3	-	-	-	-
Zn (mg/L)	0.001-0.149	-	3.0	-	-	-	0.01
pH	4.54-7.59	6.5-8.5	6.5-8.5	-	-	-	-
Temp. (°C)	25-29	<35.0	Ambient	Ambient	-	-	-
DO (mg/L)	2.49-6.45	7.5	-	-	-	-	-
TS (mg/L)	296-12,700	-	-	-	-	-	-
TSS (mg/L)	2-231	-	-	250	-	-	-
TDS (mg/L)	290-12,500	-	500	≤500[e]	-	-	-
Cl^- (mg/L)	12.2-52.5	250	250	≤250[e]	-	-	-
NO_3^- (mg/L)	3.2-660	50	50	≤45[e]	45	10	-
PO_4^{3-} (mg/L)	0.14-0.3	<13.5		≤100[e]	-	-	-
SO_4^{2-} (mg/L)	76-5,300	100	100	≤100[e]	-	-	-

[a]Andong et al. (2019); [b]SON (2007); [c]Ukpong and Peter (2012); [d]SDWF (2017); [e]Awonyemi et al. (2014); [f](Klavins et al. 2000; Demirak et al., 2006)

[a] https://www.researchgate.net/publication/337906407

[b]https://www.unicef.org/nigeria/ng_publications_Nigerian_Standard_for_Drinking_Water_Quality.pdf was obtained online on 16/01/2019.

[d]https://static1.squarespace.com/static/583ca2f2d482e9bbbef7dad9/t/59139087d2b857f06e95c1dd/1494454412093/guidelinesBW-2017.pdf was obtained online on 16/01/2019.

Water samples ranged from 4.54 to 7.59 in pH (Table V). Only P4, leachate from the dump, has pH (4.54) outside the range (6.5-8.5) set by Federal Ministry of Water Resources (FMWR) and Nigerian Industrial Standard (Table IV). It was thus acidic probably due to sulfuric acid from the battery slag dump and supported by the SO_4^{2-} that was the highest (5,300 mg/L). Besides, it had very high TS (11,000 mg/L), TSS (91.0 mg/L), TDS (10,900 mg/L) and NO_3^- (160 mg/L), following P3, from within 12.2 m from P4, with highest TS (12,700 mg/L), TSS (231 mg/L), TDS (12,500 mg/L), NO_3^- (660 mg/L) and PO_4^{3-} (0.3 mg/L). The temperature of water samples ranged from 25^{o}C to 29^{o}C. This was likely due to the variation in time of collection that spanned over many hours: from late morning for PW1, PW2, ES (27^{o}C) and GW (28^{o}C) being groundwater; till late afternoon for AS (25^{o}C), because these were different villages. Besides, AW (26^{o}C) and AS (25^{o}C) were streams with different depth, stream flow and activities while P1 to P4 (28-29^{o}C) were stagnant water bodies with less activities. The level of DO in water is affected by a number of factors including temperature, aquatic life, turbulence and elevation, among others. Some of these probably resulted in PW1, PW2 and EW at 27^{o}C as well as P1 and GW at 28^{o}C to have different values of DO. Moreover, DO and Cl^- were not detected in P3 and P4, the water samples with very high values for majority of the detected physicochemical parameters. Non-detection of DO in P3 and P4 suggested high organic pollution and suggested non-sustainability of life because the quality of water varies directly with the DO content (Prati et al., 1971). Sulphates and nitrates have been used as electrolytes of lead accumulators. Consequently, NO_3^- and SO_4^{2-} were high in P1, P3 and P4 probably because of leaching of these electrolytes from these close waste piles into the pond water. Some of the water samples were non-consumable to man due to their SO_4^{2-}, TDS and NO_3^- levels relative to the criteria by some regulatory bodies. Furthermore, some were improper for watering livestock because of their NO_3^-, SO_4^{2-} and TDS status that exceeded the corresponding 100 mg/L, 1000 mg/L and 3000 mg/L by FEPA (1991).

Finally, the result of recovery study as a mean (n = 2) for Zn in AS was 67.50%, Cd in P2 was 76.70% and Pb in PW2 was 71.17%. Besides, the precision result of Pb in P3 as a mean (n = 5) was 0.83338 mg/L, standard deviation was 0.00358 mg/L and the coefficient of variation was 0.43 %. The method could therefore be said to have high repeatability under the same condition.

4. Conclusion

The physicochemical parameters of surface and ground water as well as sediments from Olodo, Olukunle and Ile-Igbon villages were investigated. The results showed a general pollution of the sediments at the sites and in varying degree especially by Pb. Sediments close to the slag dump showed outrageously high values of Pb while those farther indicated lower level. Some of the water samples showed contamination with respect to sulphates, nitrates and heavy metals. Solids in slag leachates were also very high. With no industrial activity in these villages, these pollutions no doubt, must have come from the point source of the slag and battery waste dumps. The health implication of water pollution and indirectly, sediment pollution, in tropical rivers is very important because the people utilize untreated water for many domestic and farm uses including drinking. It will be a worthwhile venture therefore to clean up the sites in these villages.

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