

Physico-Chemical and Heavy Metal Profiles of Marine, Borehole and Sea Water

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Abstract

The extent of water pollution on some rivers and lagoons within Badagry and its environs in Lagos State Nigeria has been critically analyzed with respect to the physico-chemical properties of the surface and underground waters and the results show that total dissolved solids for sea water ranged from 4523-4408 ppm, lagoon water 622-1471 ppm and borehole water 250-61 ppm. Total suspended solid for sea water ranged from 422-231 ppm, lagoon water 129-133 ppm and borehole water 41-146 ppm. Salinity values for sea water ranged from 0.3-0.3 ppm, lagoon 0.5-0.3 ppm and borehole water 0.1-0.3 ppm. Methyl orange alkalinity for sea water ranged from 3.5-3.0 ppm, lagoon water 1.1-1.0 ppm and borehole water 0.5-0.8 ppm. Phenolphthalein alkalinity for sea water ranged from 0.4-0.2 ppm, lagoon water 0.2-0.3 ppm and borehole water 0.1-0.2 ppm. Specific gravity for sea water ranged from 16.371-16.407 ppm, lagoon water 15.878-15.673 ppm and borehole water 15.554-15.839 ppm. Heavy metals such as Ca^{2+} for sea water ranged from 436-427, lagoon water 497-488 and borehole water 345-336. Mg^{2+} for sea water ranged from 128-136, lagoon water 133-189 and borehole water 112-116. Fe^{2+} for sea water ranged from 2.546-2.512, lagoon water 2,786-2.869 and borehole water 1.465-1.354. Cu^{2+} for sea water ranged from 2.84-2.62, lagoon water 3.86-3.86 and borehole water 0.84-0.93. Mn^{2+} for sea water ranged from 0.756-0.726, lagoon water 1.026-1.022 and borehole water 0.450-0.470. Cr^{2+} for sea water ranged from 1.07-1.248, lagoon water 1.897-1.957 and borehole water 0.026-0.028. Bio-chemical analysis such as temperature for sea water ranged from 27.5-28.5 °C, lagoon water 29.8-28.7 °C and borehole water 27.6-27.8 °C. pH for sea water ranged from 6.8-6.8, lagoon water 6.9-7.0 and borehole 7.3-7.2. BOD and COD in sea water ranged from 754-766; 1876-1833 mg/l respectively, lagoon water 978-986; 1943-1982 mg/l respectively whereas the dissolved oxygen for borehole water ranged from 5.54-5.66 mg/l

Key Words : Marine, sea water, heavy metals, Badagry and borehole.

Water pollution and its impacts on the environment have been of serious concern for environmental and industrial experts in the present world. However, to mitigate water pollution and improve the water quality, advanced waste water treatment technologies need to be evoked. These technologies can be accomplished by removing the physical, chemical and biological materials that constitute contaminants from waste water and producing an environmentally safe treated effluent and a solid waste, (Bradley *et al*, 2014; Mancy, 1971). When untreated waste water enters into the surface and ground water resources, serious

environmental and human health risk are the obvious result, (Tchobanoglous *et al*, 1991). In order to minimize the potential risks from untreated waste water entering freshwater resources, industrial waste water plants go through a water quality assessment by monitoring some parameters. Water quality professionals assess water quality by measuring the concentrations of these parameters and comparing with their known standards (Mancy, 1971; Moret *al*, 2006). Biochemical oxygen demand, chemical oxygen demand, taste, odor, color, chlorine demand, hardness, alkalinity and biodegradability tests are

some of the unique analytical parameters of the water pollution (Mancy, 1971; Henze *et al.*, 2002).

Excessive levels of some of these parameters often serve as an early warning of problems arising from pollution. Some of these parameters are COD and BOD which indicate the amount of organic pollution and water degradation. There are two major sources of water pollution which include the 'point' sources and 'diffused' sources. Point sources are those sources which can be identified at a single location are known as point sources. Minimization of pollution caused by point sources in all domestic sewage, industrial effluents, cattle field and livestock waste-water etc. can be effected if the wastes are centrally collected, treated up to requisite tolerable level and possibly recycled to serve different useful purposes. Diffused Source however are sources whose location cannot be easily identified are called diffused sources. The water pollution caused by diffused sources like agriculture can be controlled by changing the cropping patterns, tillage particles and advanced farm management practices which do not contaminate the water bodies. Pollution of river bodies has become a major and global problem that is becoming critical in developing nations of the world because of inadequacy or non-existence of surface water quality protection measures and sanitation.

Lagoons, rivers, and streams are sinks for wastes. The discharges of domestic and industrial waste as well as oil spills pose threats to the dilution abilities of the oceans, lagoons, and rivers in major cities (World Bank 1995; UNESCO 2006; Krantz *et al.*, 2007). Heavily polluted water may travel long distances in days before a significant degree of purification is achieved since the natural purification of polluted waters in itself is never fast (Chapman, 1992; Henry *et al.*, 2005; Garg, 2006). This in effect makes pollution of river bodies a global issue that has no respect for national or international boundaries. The

protection of the aquatic life of any potential receiving water body therefore calls for an effective determination of its capacity to assimilate wastes. Hence, constant assessments of the hydraulic and water quality conditions of receiving water bodies are very critical to effective planning and management. The dissolved oxygen (DO) and the biochemical oxygen demand (BOD) are two useful parameters in tracing pollution profile and natural purification of rivers upon which engineering calculations of permissible pollution loads are based (Fair *et al.*, 1971; Garg, 2006). The BOD defines in a comprehensive manner the degradable load added to the receiving water body or remaining in it. It is both time and place specific. BOD therefore measures the oxygen absorbing capacity of an effluent. The DO defines the capacity of the body of water to assimilate the imposed load by itself or with the help of re-aeration through oxygen absorbed mainly from the atmosphere and also through photosynthesis. The amount of dissolved oxygen that can be held by the water depends mainly on the water temperature (Garg, 2006; Agunwamba *et al.*, 2006). The determination of dissolved oxygen concentration relative to its saturation value and the rate of oxygen utilization measured as its BOD become a good measure for identifying the pollution status of a water body. The progressive utilization of oxygen in water bodies has been widely studied over the years and has been used as a measure of the amount of decomposable or organic matter contained in it at a given time. Determination of the self-purification capacity of water bodies has been the subject of researches by scientists around the world (Villeneuve *et al.*, 1998; Rounds, 2001; Radwan *et al.*, 2003; Agunwamba *et al.*, 2006; Alamet *al.*, 2007).

A rapid development in science and technology and a vast usage of industrial processes are generating and releasing more and more

pollutants into the environment. The analysis of chemical pollutants in water therefore has become a serious concern to the professional world and to the authorities in charge of water quality (Chen et al, 2014; World Health Organization, 1993). Water quality depends on these parameters and their characterization tests (Henze, 2002). Acidity of water is determined when reacts with a strong base to a designated pH. Acidity is a measure of an aggregate property of water, and which can be interpreted in terms of specific substances only when the chemical composition of the sample is known (American Public Health Association, 1995; Henze, 2002).

Acidity is classified by the pH value of a titration end point. Acidity caused by mineral acids contains a pH below 4.5 (Cheremisnoff et al, 2015). Industrial waste waters containing high mineral acidity must be neutralized before they are subjected to biological treatment or direct discharge to water sources. A standard method for the examination of water and waste water recommends titration with sodium hydroxide to an end point pH of 3.7 to determine mineral acidity (American Journal of Public Health, 1915). Alkalinity of water indicates the presence of bicarbonate, carbonate, and hydroxide ions. In waste water treatment, alkalinity is a quality parameter to determine the amenability of waste to the treatment process (Henze, 2002). Waste water becomes alkaline when receiving alkalinity from the water supply, ground water, domestic use (detergents and soap-based products) and acid rain (American Public Health Association, 1995). Alkalinity is significant in the treatment processes for water and waste water. Alkalinity is expressed as phenolphthalein alkalinity or total alkalinity (American Journal of Public Health, 1915). Both types can be determined by titration with a standard sulfuric acid solution to an end point pH, evidenced by the color change of a standard indicator solution. The pH also can be determined

with a pH meter. Phenolphthalein alkalinity is determined by titration to a pH of 8.3 (the phenolphthalein end point) (American Journal of Public Health, 1915). Conductivity is a measure of how substances like oil, alcohol, and sugar present in water conduct impose conductivity on it, (Murdoch *et al*, 1996).

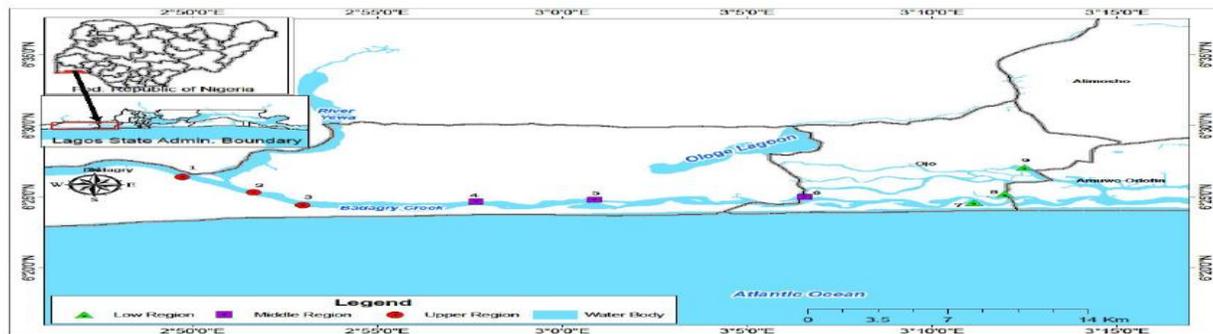
The measurement of conductivity is generally expressed in S/cm (or m S/cm). The scale for conductivity starts at 0.05 μ S/cm (at 25 C) for ultra-pure water (Cable, 2005). The suspended solids are equal to the weight difference between the dissolved solids and the total solids (Murdoch et al., 1996). Components of the total solid load from the treatment plants include phosphorus, nitrogen, and organic matter. The amount of solids in waste water is frequently used to describe the strength of the waste. Gravimetric analysis is the approved procedure for determining total solids, total dissolved solids and total suspended solids, fixed and volatile solids while volumetric analysis is the method for measuring settle-able solids (American Journal of Public Health, 1915). COD is the amount of dissolved oxygen to oxidize and stabilize a sample when organic or inorganic matter of sample solution is responsive by a strong chemical oxidant. The COD value indicates the mass of oxygen consumed per liter of solution and expressed in milligrams per liter (mg/L). The higher the chemical oxygen demand, the higher the amount of pollution in the water sample. However, COD is considered one of the important quality control parameter of an effluent in waste water treatment facility (Wu et al, 2011). The complete oxidation of organic compounds under such strong oxidizing conditions produces carbon dioxide (CO₂) and water (H₂O). The COD for any organic compound can be theoretically calculated from writing a balanced equation (Boyles, 1997). Theoretically infinite time is required for complete biological oxidation of organic matter of domestic sewage.

Water samples are to be kept at 200°C for proper biodegrading even when it has impact on dissolved oxygen and thus BOD (Pitter et al., 1990). A correlation exists between COD and BOD₅ and BOD₅/COD ratio known as biodegradability index and when domestic waste waters are involved, this value varies from 0.4 to 0.8 (Srinivas, 2008). If BOD₅/COD is ≤ 0.6 then the waste is fairly biodegradable and an effective biological treatment can be possible. If BOD₅/COD ratio is

between 0.3 and 0.6, then seeding is required to treat it biologically. If BOD₅/COD ratio is < 0.3 then the probability of biological treatment is low (Srinivas, 2008). The research aim at determining the physico-chemical and heavy metal profiles of marine, borehole and sea water within Badagry area and to assess to what extent the industries within impact on both the surface and underground waters within the area.

MATERIALS AND METHODS

All samples were collected during the morning hours in Badagry Lagos state Nigeria.



g. 1. Geographical map of Badagry where the samples were collected.

Twelve sampling sites were selected for the sample collection from where water samples were collected. Five samples were collected from the Badagry creek, five samples collected from the

ocean and two borehole samples from residence in Badagry. All samples were collected in a clean transparent plastic container and properly labeled before returning to the laboratory.

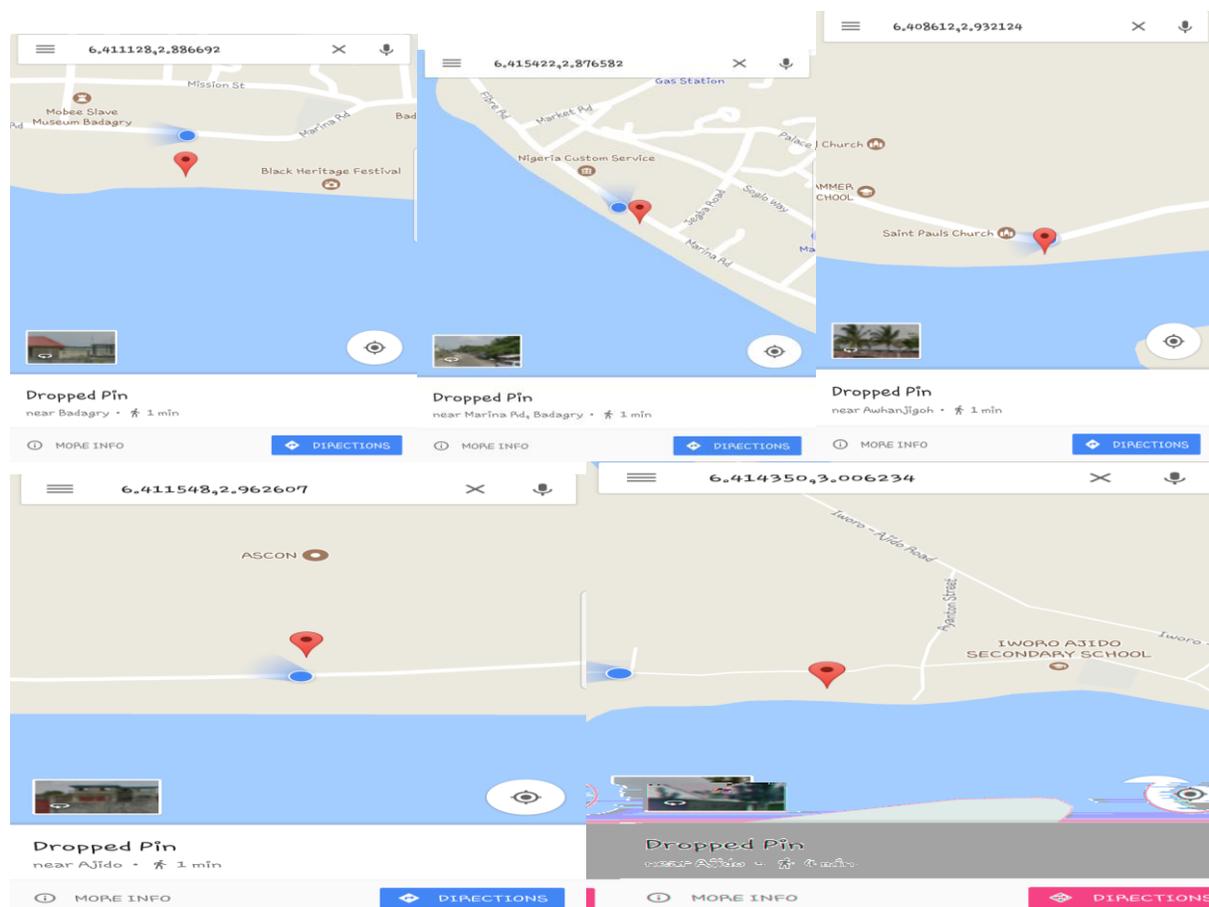


Fig. 2. Locations and GPRS where the samples were collected

The TDS and TSS were determined in the usual manner by filtration, weighing and drying while the salinity was determined by Robert Boyle’s method in which AgCl was precipitated using AgNO₃. The phenolphthalein and methyl orange alkalinities were determined as by titration with HCl using the respective indicators. The pycnometer method was used to determine the specific gravities whereas the TOLEDO’s conductimeter was used to determine the

conductivity. The BOD and COD were determined using the manometric method using the HACH manometer. The dissolved metals were measured using the Absorption Spectrophotometer make; THERMOSCIENTIFIC iCE TM 3000 SERIES with dedicated flame and furnace, BUSCH and LOMD colorimeter was used to determine the anions of sulphate, nitrate and chloride, while the HANNA turbidimeter was used to determine the turbidity of the water sample.

RESULTS

The extent of water pollution on some rivers and lagoons within Badagry and its environs in Lagos

State Nigeria has been successfully investigated and results obtained are as shown:

Water sample	TDS (ppm)	TSS (ppm)	Specific Gravity	Deviation (ppm)	TDS	Deviation TSS(ppm)	Deviation SG (ppm)
A1	4523	422	1.637	4023		387	13.871
B1	4384	380	1.636	3884		345	13.866
C1	4439	164	1.618	3939		129	13.689
D1	4446	378	1.621	3946		343	13.710
E1	4408	231	1.640	3908		196	13.907
A2	662	129	1.587	162		94	13.378
B2	944	125	1.573	444		90	13.232
C2	1065	105	1.580	565		70	13.370
D2	1339	96	1.567	839		61	13.179
E2	1471	133	1.567	971		98	13.173
Borehole 1	7.652	1.084	1.554	250		6	13.054
Borehole 2	8.346	1.426	1.583	439		111	13.339

Table 1. TDS, TSS and specific gravity values for water sample Action limits; TDS (ppm) = 500, SG (ppm) = 2.5

Water sample	Methyl orange MOA (mL)	Phenolphthalein PA (mL)	Salinity (mL)	Deviation MO (ppm) from Action Limit	Deviation PA (ppm) from Action Limit	Deviation SA (ppm) from Action Limit
A1	3.5	0.4	0.3	0.2	7.9	34.7
B1	2.9	0.3	0.5	0.8	8.0	34.5
C1	3.0	0.2	0.6	0.7	8.1	34.4
D1	3.3	0.3	0.4	0.4	8.0	34.6
E1	3.0	0.2	0.3	0.7	8.1	34.7
A2	1.1	0.2	0.5	2.6	8.1	0
B2	0.8	0.1	0.3	2.9	8.2	0.2
C2	1.0	0.2	0.2	2.7	8.1	0.3
D2	0.8	0.1	0.4	2.9	8.2	0.1
E2	1.0	0.3	0.3	2.7	8.0	0.2
Borehole 1	0.5	0.1	0.2	3.2	8.2	0.3
Borehole 2	0.8	0.2	0.1	2.9	8.1	0.4
NaCl	0.8	0.1	0.3	2.9	8.2	0.2

Table 2. Methyl orange, phenolphthalein Alkalinity and salinity values for samples. Action limits; (ppm) = 3.7, salinity (ppm) = 35ppt in ocean water; 0.5 in river water

Sample Metal mg/L	A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	Borehole 1	Borehole 2
Ca ²⁺	436	458	432	448	427	497	489	487	492	488	345	336
Mg ²⁺	128	126	124	132	136	133	186	197	194	189	112	116
Fe ²⁺	2.546	2.463	2.538	2.446	2.512	2.786	2.872	2.886	2.967	2.869	1.465	1.354
Cu ²⁺	2.84	2.65	2.68	2.64	2.62	3.86	3.82	3.88	4.02	3.86	0.84	0.93
Mn ²⁺	0.756	0.687	0.684	0.788	0.726	1.026	1.032	1.019	1.028	1.022	0.450	0.470
Cr ²⁺	1.07	1.289	1.278	1.265	1.248	1.897	1.876	1.846	1.986	1.957	0.026	0.028
Zn ²⁺	0.674	0.764	0.698	0.647	0.687	1.098	1.026	1.058	1.038	1.107	0.010	0.012
As ²⁺	0.075	0.076	0.073	0.078	0.075	0.859	0.896	0.917	0.925	0.946	0.189	0.158
Cd ²⁺	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.001	0.001
Pb ²⁺	0.354	0.356	0.356	0.368	0.363	0.847	0.864	0.978	0.947	0.965	0.007	0.008
Ni ²⁺	2.056	2.106	2.106	2.108	2.027	3.287	3.178	3.178	3.194	3.168	0.01	0.02

Table 3: result of metal analysis. Action limit= Ca²⁺<75; Mg²⁺<30; Fe²⁺=2.0; Cu²⁺=0.5; Mn²⁺=0.2; Cr²⁺=0.05; Zn²⁺=2.0; As²⁺=0.1; Cd²⁺=0.01; Pb²⁺=0.05; Ni²⁺=0.1;

Sample	A1	B1	C1	D1	E1	A2	B2	C2	D2	E2	Borehole1	Borehole 2
Temp. °C	27.5	28.41	27.9	29.6	28.5	29.8	28.9	28.6	28.9	28.7	27.612	27.823
pH	6.82	6.72	6.74	6.82	6.83	6.94	6.93	7.04	7.12	7.04	7.324	7.241
Turbidity	3.53	4.73	3.93	4.64	4.52	6.53	7.24	6.53	8.13	7.52	1.812	1.902
BOD mg/l	754	765	760	756	766	978	967	965	978	986	1.435	1.643
COD mg/l	1876	1786	1854	1836	1833	1992	1943	1922	1937	1982	5.832	7.341
SO ₄ ²⁺ g/l	14.51	14.32	14.23	14.81	14.62	17.91	17.23	17.74	17.42	17.13	5.562	7.681
NO ³⁻ mg/l	4.63	4.73	4.77	4.25	4.21	6.37	6.46	6.28	6.93	6.88	1.065	1.440
Cl g/l	15.66	14.99	15.24	15.83	15.44	18.26	18.66	18.36	18.67	18.55	9.562	10.482

Table 4. Results of Bio-chemical analyses for water samples Action limit = Temp = 40; pH=5-9; Turbidity = 5.0; BOD=40; COD=120; SO₄²⁺=750; NO³⁻=1; Cl=750; DO=0-

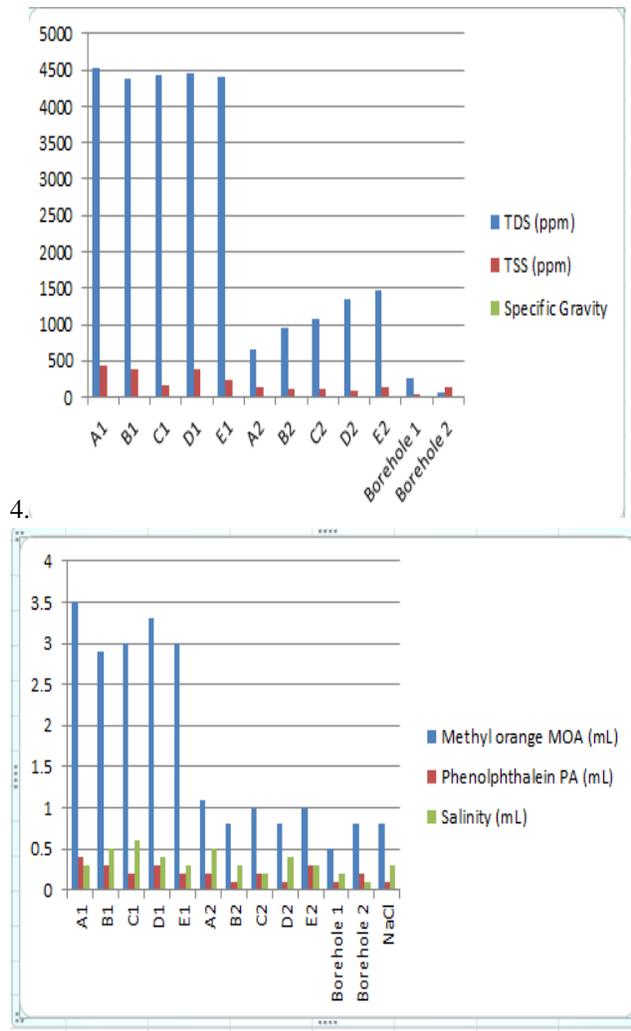


Fig.3: A bar chart showing (a) the TDS, TSS and specific gravity (b) Alkalinity and salinity values for water samples

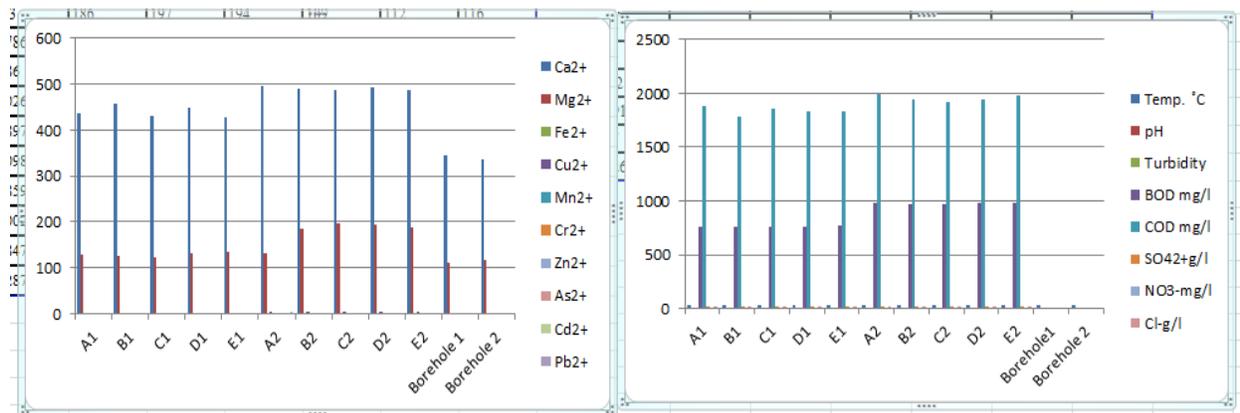


Fig.4: A bar chart showing (a) the concentration of heavy metals and (b) Biochemical properties of water samples

DISCUSSION

This work aims at evaluating the extent to which the nearby industries impact on surface and underground water in Badagry and its environs with respect to adequacy of otherwise of their effluent discharge system. The values obtained for sea water for total dissolved solids were much higher than lagoon water and borehole water. This shows that the samples A1-E1 has high values of combined content of inorganic content that are found in water. The qualitative test results of total dissolved solid in samples A2-E2 and borehole1-borehole2 shows that the water sample there are little inorganic content in them. High levels of TDS are often caused by the presence of potassium, chlorides and sodium. These ions have little or no short term effects, but toxic ions (lead, arsenic, cadmium, nitrate and others) may also be dissolved in water. The TDS for samples A1-E1 showed undesirably high values which could be salty, bitter, or metallic. It could also indicate the presence of toxic metals. These high values of TDS point to hard water, which causes scale build-up in pipes and valves reducing their performance. Total suspended Solids TSS are solids in water that can be trapped by filtration. TSS values for samples A1-E1 show high values as compared to values in sample A2-Borehole2 while samples A1-E1 have more suspended solid than A2-Borehole2. Salinity measures the amount of salts in dissolved water. From the deviations it shows that there is high salinity in samples A1-E1, and little values of salinity in A2-Borehole2. The alkalinity values in samples A1-E1 are relatively low from the deviation showing that it is not suitable for drinking. The positive part of having alkalinity in water keeps it less susceptible to acids. Values in A1-E1 means that the water is packed with minerals and can cause water to become fogged. The specific gravity is a measure of relative density and the values obtained in samples A1-E1

show high specific gravity compared to A2-Borehole2. The values of calcium Ca^{2+} and magnesium ions Mg^{2+} in samples A2-E2 presented high values showing that the water samples contain ions that cause hardness in water. Heavy metals ions generally were higher in samples A2-E2 than samples A1-E1. Borehole1-Borehole2 show little amount of calcium and magnesium. The temperature values were observed to be normal within the ranges 25-30 °C in all water samples. High levels of COD and minimal levels of BOD in all sea and lagoon water samples which mean that the waste water contains highly non-biodegradable wastes.

CONCLUSION

Pollutants entering a river can be washed away to sea, or degraded by microorganisms present in the river. Excess pollution in a river can damage the plant and animal life present in the river by reducing the oxygen content of the water. Point sources of pollution are discharge points where pollutants collected by a network of pipes or channels are released. Diffuse sources, on the other hand, are characterized by multiple discharge points that cannot be located exactly. Point sources can be easily controlled, while diffuse sources pose great difficulty in terms of collection and control. Lakes are much more prone than rivers to pollution as they do not have the flushing effect of rivers. They also do not have the dilution effect of large bodies of water such as the sea. Eutrophication can be a particular problem for lakes. The major sources of water pollution will include discharges from sewage works, often containing industrial wastes, discharges from manufacturing and industrial plants, including mines, discharges from animal rearing, fish farming and agriculture, seepage from domestic and industrial landfill sites and urban surface

water run-off. Different pollutants affect the aquatic environment in different ways. While at low concentrations many pollutants (e.g. organic materials, N and P) may be beneficial, at high levels they can adversely affect the ecology of the system. Excess nitrate can be particularly harmful to babies. Many of the toxic pollutants in effluents are synthetic, and therefore do not easily biodegrade naturally. The effects of physical pollution on the ecology of a river system can be complex, affecting the feeding and breeding habits of the different species. Biological pollutants can spread disease through water, and also disrupt the ecology. The measurement and control of water quality is therefore of crucial importance in the interests of public health and the maintenance of the environment. Having all these in mind, it becomes very pertinent to ensure the quality of water used for drinking cooking, washing, industrial purposes and irrigation. The increased BOD and COD values are higher in lagoon water samples than sea water and borehole water. This is because the accumulations of industrial and vegetal wastes are heavy contaminants of lagoon water. The sea water has more dilution as the water flows past unlike lagoon water that is a receptacle to heavy industrial sewage. The heavy metals are also higher in lagoon in line with expectations. This is so because most industrial effluents are heavily loaded with heavy metals and mostly these come from ineffective sewage disposal system.

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