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Research Article

Physico-chemical variables, heavy metals and macro-invertebrates distribution along a pharmaceutical wastewater impacted stream in minna, Niger state, Nigeria

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This study investigated the effect of Pharmaceutical effluent on the physico-chemical parameters, heavy Metals and macro-invertebrates distribution along a pharmaceutical wastewater impacted stream in Minna. All parameters were determined using Standard method. Collection of sample was done in 4 sites of the Stream in Maitumbi, Minna. The method of APHA, (Abboud, 2014) was employed for the physico-chemical parameters with the use of Multi-parameter meter (H19813) Grochek and Dissolved Oxygen Analyzer model Model JPB-607. The heavy metal determination was carryout using the procedure of (Kruis, 2005; APHA, 2014) and Atomic Absorption Spectrophotometer (AAS) model MY15110001. High performance Liquid Chromatography (HPLC) was used for determination of anti-bionics in the effluent from the four samples sites. Macro-invertebrates samples were collected and analyzed using the procedures of APHA, (2014). Statistical analysis of data was done at 5% level of signiicance (P< 0.05). Results showed that pH (7.6 ± .28-8.94 ± .61), Electrical Conductivity (463.6 ± 115.59-1710.6 ± 682.32 µs/cm), Temperature (26.4 ± .55 -33.46 ± 1.26°c), TDS (223.4 ± 55) (1433 ± 170.79 mg/l). Dissolved Oxygen.(3.44 ± .534.64 ± .14 mg/l), Alkalinity (118 ± 19.54-1238 ± 95.7 mg/l), Calcium (28.592 ± 5.76- 44.66 ± 7.22 mg/l), carbon dioxide (6.084 ± 1.1819.35 ± 4.56 mg/l) Total Hardness (71.4 ± 6.5-153 ± 29.35) was within the acceptable limits set by Nigeria industrial Standard (NIS) and (WHO). Majority of other variables tested have values that are beyond the standard values of WHO, FEPA and USEPA with Conductivity and TDS having outrageous results. Similarly, the results of heavy metals analysis showed Lead to be absent in the effluents, but, indicates that Cadmium (0.00 ± 00-0.35 ± .31 mg/l), Copper (0.25 ± 0.12-29 ± 0.49 mg/l), Manganese (0.14 ± 0.05-25 ± 60 mg/l) was detected at levels above the acceptable limit set by national and international Standard organizations. The results of Macro-invertebrates shows a total of 148 macro-invertebrate taxa, representing 3 orders in 6 families recorded during the 6-month study. Of the major fauna groups, diptera contributed the highest percentage 70.95% of individual abundance which was significantly diferent (P<0.05) among stations. Pollution tolerant (Chironomus) species at sites were better represented at station 2, 3and 4. The results of anti-biotic analyzed are; Ciprofloxacin (concentration 0.049 µ/cm, 0.099 µ/cm, 0.203 µ/cm) and 0.188 µ/cm (Control); Amoxicillin (0.571 µ/cm; 0.3 µ/cm; 0.076 µ/cm; and 0.045 µ/cm (Control) Ampicillin (0.296 µ/cm,0.12 µ/cm,0.597 µ/cm and 0.296 µ/cm(Control); Metronidazole (0.249 µ/cm, 0.125 µ/cm,0.063 µ/cm and 0.011 µ/cm(Control); Tetracycline (0.104 µ/cm, 0.099 µ/cm, 0.048 µ/cm, and 0.023 µ/cm (Control). They are at concentrations more than or equal to detection limits of selected methods. The presence of the drug signifies possible seepage of pharmaceutical effluents into groundwater. The presence of some Dipteran Species associated with low dissolved oxygen levels in the impacted site bears credence to the fact that the chemical components of the waste water were lethal to some aquatic forms. This calls for an abrupt use of modern treatments plants to reduce the level of toxicity that may results from discharge of the effluents which find their way into the water bodies around and pose threat to man and animals that depends on such water for survival. The use of bio-indicator organisms for restoration and remediation programme is highly recommended.

Key words: Physico-chemical variables, heavy metals, macro-invertebrates, pharmaceutical waste-water, impacted stream

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INTRODUCTION

Pharmaceutical effluents are industrial waste generated from pharmaceutical industries from their production processes. The increase in pharmaceutical waste which most time contain substantial amount of heavy metals in Nigeria industrial growth is identified as a major tool for economic development (Adeyeye, 2002). The production of useful consumer product such as drugs is the indicator of this growth. Most of pharmaceutical effluents are known to contain varying concentration of inorganic compounds and total solids including heavy metals and other toxic organic chemicals and phenolic compounds discharged from pharmaceutical industries that are known to affect the surface and ground waters (Anetor, et al., 2000). Due to carcinogenic and mutagenic properties of heavy metal, much attention has been paid to them since they are directly exposed to aquatic organism and human being (Momodu and Anyakora 2010). Heavy metals are not biodegradable so they accumulate in organs in the body and over time begin to fester, leading to various symptoms of diseases. According to Fatoki and Mathaba, (2001), Heavy metals distribution in the sea water and sediment samples were found in high concentrations when compared to regulatory standard. They tend to bio-accumulate and are stored faster than excreted (lentech, 2006) Industrial exposure accounts for a common route of ingestion content in children and adult (Okten, et al., 2007)

However, the use of water polluted from pharmaceutical waste, textile, shoes, cosmetics, plastics, and other household and industrial consumable has its negative consequence on the soil and plants through alteration of the physico-chemical properties of the receiving water body. The aquatic organisms are killed by toxic chemicals with the resultant disruption of the aquatic food chain. The decomposition of the organic materials by micro- organism in the aquatic ecosystem leads to the depletion of the level of dissolved oxygen, which in turn inhibits the growth or course the death of aquatic organisms (Omuegbu, 2008). Soil is a vital component of the aquatic ecosystem that also serves as the major reservoir of contaminants because it possesses the ability to bind various chemicals. Scientist has identified heavy metals as common soil pollutants, although at low concentration some are essential for normal healthy growth and reproduction of plants, animals and human. When ingested into the acidic medium of the stomach, they are converted and combined with the body's bio-molecles such as protein and enzymes to form strong stable chemical bonds. Heavy metals, their deficiency in plant and animals can lead to diseases, however, some, have no known essential function even at very low concentration.

Heavy metals stressed water; load sourced from weathered soil/rocks Industrial emissions (Oluwatusin, et al., 2016). This may exert unsustainable demand on freshwater by aquatic micro flora/micro fauna and humans who depend on such water and may be exposed to contamination of heavy metals (Ncube, et al., 2017) and other contaminants and their deleterious consequences. Although heavy metals do not remain in water for long period of time, the major concern is if the level of heavy metals in water exceeds healthy guidelines concentration criteria. The protection of water and aquatic ecosystem from adverse effects of pollutants such as heavy metals is central to environmental risk management (Bere and Tundisi, 2011). Understanding the source and impact relationship at the effects of heavy metals in water bodies and biological species is important for effective aquatic ecosystem. This is because trace amount of such metal can accumulate in the food chain, eventually causing disease (Wogun and Okaka, 2011).

Heavy metals exists as natural constituents of the earth crust and are persistent environmental contaminants, because they cannot be degraded or destroyed, while these elements occur naturally, they are often bounded in inert compounds. However, their concentrations have increased several-fold as a result of anthropogenic activities. Human exposure to harmful heavy metals can occur in many ways ranging from the consumption of contaminated food, exposure to air-borne particles, contact or consumption of contaminated water and accumulate over a period of time. High concentration of lead, arsenic and other heavy metal can affect the nervous system and kidney and may cause reproductive disorders, skin lesions, endocrinal damage and vascular diseases.

The increased demand of pharmaceutical products has generated a large number of its manufacturing limits all over the globe and hence, there is increased in pharmaceutical wastewater; most of the drugs are manufactured by the chemical synthesis route, which involves a series of complex chemical reaction which release pharmaceutical wastewater. It is evaluated that about half of the globe wastewater is generated from pharmaceutical industries discharge from the waste plants outlets without it further required processed, which contain different type of chemical ingredient in form of inorganic and organic constituents, spent solvents, catalyst, total solid including heavy metals (Ramola and singh, 2013). Heavy metals are potential ingredients having toxic characteristic to affect the soil surfaces and ground water which have advert effects on the human health and living biota's (Okten, et al., 2007).

In Nigeria, main contribution to the surface and ground water pollution are the by-product of various industries such as fertilizer, pesticides, cement, petrochemical, energy and power, leather sugar processing construction, food processing, mining and others. As industrialization increase in Niger state due to stable power supply, environmental pollution becomes more alarming. This research is therefore aim at investigating the physico-chemical parameters, heavy metals and macro-invertebrates distribution along a pharmaceutical wastewater impacted stream in Minna, Niger state. Nigeria. The result of the research may form basis for intervention by encouraging the pharmaceutical companies to effectively treat their effluent before being discharged in to the environment.

MATERIALS AND METHODS

Study area description

The pharmaceutical industry is located in Maitumbi along Gwada road, Bosso local government area of Niger state and is geographical located between latitude 6.56'6.94"N and longitude 9.33'6.89" E at an altitude of about 299 m. It covers an estimated of the area of 74,244 sq m. the climate of the area is characterized by two distinct season i.e. wet season between April to November with a mean annual rainfall of, 179 mm and the highest mean monthly rainfall is between August and

September. The dry season is between November to march with two hottest Months of February and March. The mean annual temperature and relate humidity of the area is 33.2°C and 61% respectively. The study area was specifically chosen to assess possible impact of wastewater generated from the pharmaceutical industry. The study area covers four samples sites.

The Description of Sites shown in Table 1.

Sample collection

Remote Sensing/Geographical Information System (GIS) Laboratory, Geography Department is shown in Figure 1.

Water sampling

Wastewater sample was collected from each study site on the same day between (8-10 am) monthly. The sample was collected in prewashed polyethene bottles labels according to sampled sites A, B, C and D Each bottle was filled to the brim to exclude air that could oxidize the dissolved organics in the sample. The samples were kept in an ice box and transported to the Laboratory and stored in refrigerator at 4ºC prior to analysis. Physico-chemical water parameters, which include electrical conductivity (µs/cm), pH, Total Dissolved Solids (TDS mg/L), were determine using Multi-parameter meter model Hanna (H19813) Grochek, While Dissolved Oxygen (DO/BOD in mg/l), was measured using a DO Analyzer Model JPB-607 Potable. Temperature (Water/air) was determined using Mercury-in-glass thermometer, Total Hardness, Sodium, Nitrate (No3,), Phosphate (Po4), and Alkalinity was analyze according to APHA, 2014. Description of Sites is shown in Table 1.

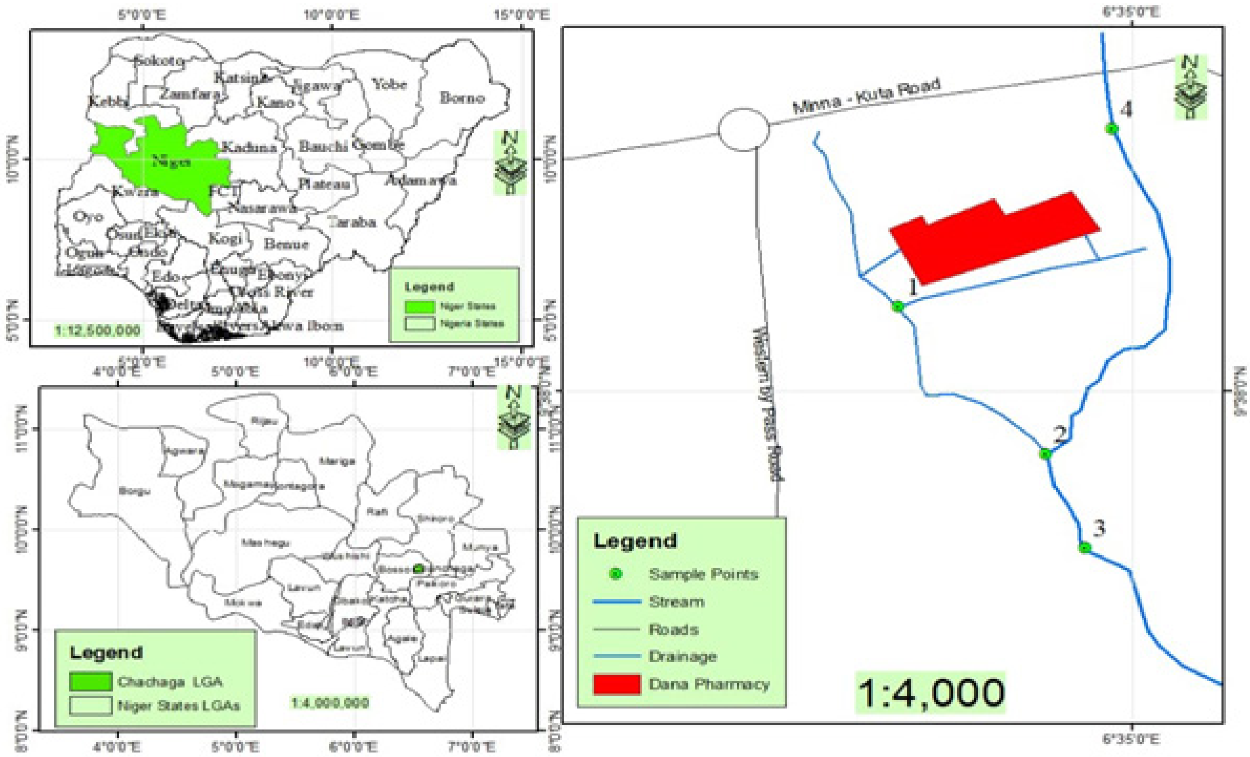

Figure 1. Source: Remote sensing/Geographical Information System (GIS) laboratory, geography department, FUT-MINNA, (2017)
Key:
A- Map of nigeria showing niger state.
B- Map of niger state showing bosso L.G.
C- Map of bosso showing sampling sites

Table 1. Description of sites

Sites	G.P.S Location	Description
Site 1	Latitude 9° 33’3.67″N Longitude 6° 34’59.89″E	This is the main point of industry discharges, connected to the drainage channel, which cut across the settlement surrounding the company. This site has continues flow of the effluent throughout the year.
Site 2	Latitude 9° 33’6.78″N Longitude 6° 34'59.89″E	Sources were the effluent meet the nearby stream that run through the area before the industry which is 500 meters away from site one.
Site 3	Latitude 9° 37'51.66″N Longitude 6° 34'50.26″E	This station is one kilometer away downstream from site two Surrounded by small subsistence farms and shrubs.
Site 4	Latitude 9° 37’45.25″N Longitude 6° 34'59.85″E	The site is upstream of the industrial company. The station is characterize with riparian vegetation and 1 kilometers from station three.

Sample preparation and the determination of physic-chemical variables

Water samples were processed according to the method prescribed by the American Public Health Association (APHA, 2014).

Determination of other parameters

Collected and preserved water sample was used to test the hardness, alkalinity, Co_2, Calcium using the methods of the WHO, (2014)

Determination of antibiotics

High Performance Liquid Chromatography (HPLC) method: Wastewater (effluent) from the company was collected from the four sites sampled into pre-washed and dry sampling bottles and labeled accordingly. The sample was transported in cold condition to the National Agency for Food, Drugs Administration and Control (NAFDAC) Laboratory in Kaduna for High performance liquid Chromatography (HPLC) analysis to quantify the different Antibiotic in the effluent.

Determination of selected antibiotics

In separate vials, four antibiotics were weighed (14 mg). They were then dissolved in methanol in 10 ml volumetric flasks. With ciprofloxacin, a solution of methanol: acetic acid 1:9 (v/v) was used. A mixture of the stock solution was made from these six individual antibiotic solutions by transferring 1.78 mL into a 100 mL volumetric flask and topping up to the mark with methanol.

Macro-invertebrate

Macro-invertebrate samples were collected according to APHA (2013) from four sample Sites of the study area using a hand-held-net, For each sampling Site, the kick sampling technique was used. It involves kicking the water at the sampling Site to stir the macro invertebrates at the bottom to the surface and the net was drag across the water to collect the macro invertebrates at each Site. All collected samples were fixed in 4% formaldehyde and kept in 70% alcohol before transportation to laboratory for sorting and identification.

Heavy metals determination

Heavy metals analyzed include, zinc, Iron, lead, Arsenic, copper, chromium, and cadmium. Analyses for heavy metals were conducted according to standard procedures by KRUIS, (2005); WHO, (2014).

Data analysis

The purpose of this section is to present the different statistical analyses that were used to explore water quality variables, prior to analysing the data in the different statistics software employed in this study; the raw data was entered into Excel. The mean and Standard error of Mean of the physicochemical parameters was determine using Statistical Package for Social Sciences (SPSS), Version:23 and one-way analysis of variance (ANOVA). Duncan multiple test was used to test the level of signiicance ($P<0.05$) among the Stations and Months.

RESULTS

Mean and Standard Error of Mean Values of Physico-Chemical Parameters of Minna Pharmaceutical Effluent

The table below shows the mean and Standard error of mean of the physico-chemical variables of pharmaceutical effluent of Minna. pH, Electrical Conductivity (EC), Carbon Dioxide (CO_2), Temperature (T), Total Dissolved Solute (TDS), Total Alkaline (TA) Total Hardness (TH) Calcium (CA) and Dissolve Oxygen (DO). pH show the degree of hydrogen ion concentration in the effluent which shows no significant diference ($P>0.05$) from the month of March to August with a mean value of 8.7 ± 52 to 8.94 ± 61.

Electrical Conductivity (EC) shows no significant difference ($P>0.05$) from the months of March to August, with mean valves of 1218.2 ± 550.7, 1695.8 ± 806, 1710.6 ± 682.32, 463.6 ± 115.59, 475.4 ± 108.24 and 477.4 ± 103.92 respectively, which show high mean value in dry season (March to May) and reduces in the wet season (June, July and August).

Carbon Dioxide (CO_2) show no significant difference between the months March, April and August, with mean values of 11.7 ± 4.3, 12.85, ± .30 and 11.33 ± 2.1 respectively, no significant difference between the months of June and July, with mean values of 6.064 ± 1.18 and 7.378 ± 1.78. A significant difference in the month of May (19.35 ± 2.1) indicate the end of dry season and beginning of wet season.

Temperature shows no significant difference between the months of March to June, with Mean values varying for a 26.4 ± 57 to 27.16 ± 27 and no significance difference in the months of July and August with mean values of 32.082 ± 1.3 and 33. 46 ± 1.26 it's an indication of mid-wet season. Total Dissolve Solute (TDS) Shows signiicance diference ($P<0.05$) between month of March, May, June, and July with a mean values of 223. 2 ± 57.5, 1433 ± 170.7, 1105.8 ± 18.77 and 960.2 ± 33.5, respectively and no signiicant diference ($P>0.05$) between March, July and April with mean value of 1022. ± 39.60 to 1106.8 ± 28.98 respectively. Total alkalinity: The result show no signiicant diference ($P>0.05$) between March, July and August, with values of 123.0 ± 95.7, 124.41 ± 23.75 and 133 ± 27.15. No significant difference between. April, May and June was observed with mean values of 242.8 ± 49.7, 222.6 ± 36.60 and 116 ± 19.54 respectively. Total Hardness show no significant difference from the months of April to August, with mean values of 134 ± 28.99, 124 ± 22.5, 100 ± 26.14, 71.4 ± 6.58 and 75.2 ± 8.7 respectively while the month, of March has a mean value of 153 ± 29.35.

Calcium (Ca) shows no significant difference throughout the months with mean values from 37.7 ± 9.75 to 31.016 ± 4.68. Dissolved Oxygen (D.O) shows no significant difference between the months of April and June, with mean valves of 3.9 ± and 4.116 ± 13 respectively. There was significant difference ($P<0.05$) between months of March, May, July and August with mean values of 3.44 ± 53, 4.46 ± 12.38 ± 07 and 4.54 ± 14.

Mean and Standard Error of Mean Values of Physico-Chemical Variables are shown in Table 2.

Table 2. Mean and standard error of mean values of physico-chemical variables of minna pharmaceutical effluent between March-August, 2019

	pH	E. Cond	$C0_2$	Tempt	TDS	TA	TH	CA	DO
March	8.7±.52^{a}	1218.2± 550.7^{a}	11.7±4.3^{ab}	26.4±.55^{a}	223.2± 57.5^{bc}	1238± 95.7a	153± 29.35^{b}	37.7± 9.75^{a}	3.44± 53^{a}
April	7.6±.28^{a}	1695.8± 806.98^{a}	12.85±.30^{ab}	26.86±.50^{a}	1106.8± 28.99^{ab}	242.8± 49.79^{ab}	134.6± 28.99^{a}	44.66 ± 7.22^{a}	3.9±.15^{abc}
May	8.17±.52^{a}	1710.6± 682.32^{a}	19.35±4.56^{b}	27.84±.63^{a}	1433± 170.79^{c}	222.6± 36.60^{ab}	124.6± 22.55^{a}	43.84± 7.35^{a}	4.46±.12^{bc}
June	8.38 ±.67^{a}	463.6 ± 115.59^{a}	6.084±1.18^{a}	27.16±.27^{a}	1185.8± 18.77^{abc}	118± 19.54^{ab}	100± 26.14^{a}	28.75± 6.18^{a}	4.116±.13^{abc}
July	8.86±.58^{a}	475.4 ± 108.24^{a}	7.378±1.78^{a}	32.082±1.3^{b}	960.2± 33.51^{a}	124.4± 23.75^{a}	71.4± 6.58^{a}	28.592± 5.76^{a}	3.84±.07^{ab}
Aug	8.94±.61^{a}	477.4± 103.92^{a}	11.33±2.1^{ab}	33.46±1.26^{b}	1022± 39.60^{ab}	133± 27.15^{a}	75.2± 8.76^{a}	31.016± 4.68^{a}	4.64±.14^{c}

Superscript with the same letters across the column are not significant (p>0.05)
Note: a- Acceptable limits
b- Values beyond the standard values of WHO
ab, bc, abc - outrageous results depending on significance

Concentration of antibiotics in minna pharmaceutical effluent

The table below, show different antibiotics in the Sample stations 1 to 4. Ciprofloxacin in of 0.049(µg/L), 0.099(µg/L), 0.203(µg/L) and 0.188(µg/L) respectively. Amoxicillin with 0.57 µg/L in Station 01, and 0.3 µg/L in Station, 2, 0.08 in Station 3 and the least of 0.045 µg/L in station (4), while Metrondanezole decreases from station (1), with 0.249(µg/L), 0.125(µg/L), 0.063(µg/L) and 0.011(µg/L) respectively in all the Station. Tetracycline capsule had the highest concentration in station with 0.104 µg/L, the concentration decrease from the point of discharge and had the least concentration in station 4 (0.023 µg/L). Concentration of Antibiotics in Minna Pharmaceutical Effluent between March-August, 2019 is shown in Table 3.

Correlation of Pharmaceutical Effluent from sites along Zaboyi Stream inMaitumbi between March-August, 2019

The table below correlates the four samples collected and analyzed. From the results, it indicates that site 2 and 1 are positively correlated. Similarly, site 4 and site 3 have a positive correlation. This indicates that these sites accumulate these antibiotics and could affect the biota significantly. Correlation of pharmaceutical effluent from sites along Zaboyi stream in Maitumbi between March-August, 2019 is shown in Table 4.

Table 3. Concentration of antibiotics in minna pharmaceutical effluent between March-August, 2019

Pharmaceutical agent	Therapy group	Analytical methods	Water samples from minna (µg/l)			
		Method	St-1	St-2	St-3	St-4
Ciprofloxacin	Antibiotics	Ciprofloxacin USP.M	0.049	0.099	0.203	0.188
Amoxicillin	Antibiotics	Amoxicillin USP.M2.M	0.571	0.3	0.076	0.0453
Ampicillin	Antibiotics	Ampicillin BP.M	0.296	0.12	0.597	0.296
Metronidazole	Antibiotics	Metronidazole USP.M	0.249	0.125	0.063	0.011
Tetracycline	Antibiotics	Tetracycline USP.M	0.104	0.099	0.048	0.023

Table 4. Correlation of pharmaceutical effluent from sites along zaboyi stream in maitumbi between March-August, 2019
The table below correlates the four samples collected and analysed. From the results, it indicates that site 2 and 1 are positively correlated. Similarly, Site 4 and site 3 have a positive correlation. This indicates that these sites accumulate these antibiotics and could affect the biota significantly.

	St-1	St-2	St-3	St-4
St-1	1			
St-2	0.92*	1		
St-3	0.001	-0.246	1	
St-4	-0.149	-0.289	.942*	1

* Correlation is significant at the 0.05 level (2-tailed).

Average levels of antibiotic concentration in the minna pharmaceutical effluent

The Figure below shows the average antibiotic Concentration from different sample stations of pharmaceutical effluent. The average concentration of the antibiotics analyzed are, Ciprofloxacin Amoxicillin, Ampicillin capsule, metroxinedazole tablet and Tetracycline capsule, with Tetracyline, capsule having the least average concentration of 0.06 µg/L, followed by metroxidazole, tablet, with 0.1 µg/L, ciprofloxacin with 0.15 µg/L, Amoxicillin with 0.25 µg/L and Ampicillin capsule, with the highest average concentration of (0.35 µg/L) which shows that ampicillin capsule is more in the environment comparedto other antibiotic in the efferent collection. Average levels of antibiotic concentration in the minna pharmaceutical effluent between march-august, 2019 are shown in Figure 2.

Composition and distribution of macro-invertebrates in zaboyi stream at maitumbi, minna between March and August, 2019.

The result of macro-invertebrates composition of zaboyi stream maitumbi between March-August, 2021 is shown on the table below. It indicates 3 order, 5 Families and 8 species. The order hemiptera and odanata are pollution non-tolerant species, while the order dipterans is pollution tolerant species with the highest percentage. Pearson correlation co-efficient analysis shows a negatively weak relationship between site 1 and 2(11), while sites 2 and 3 show a positively weak relationship (0.233) and sites 3 and 4 indicate positive relationship of 0.1.

Composition and distribution of macro-invertebrates in zaboyistream at maitumbi, minnabetween march and august, 2019 is shown in Table 5.

Species distribution of macro-invertebrates of zaboiyi stream maitumbi from March-August, 2019

Figure shown the distribution of the various macro-invertebrate species from zaboyi stream in maitumbi, niger State. It shows that the species chironomid transvaalensis has the highest distribution followed by other chironomid larva species indicating high pollution rate in the stream. Species distribution of macro-invertebrates of zaboiyi stream,maitumbi, minna is shown in Figure 3.

Heavy metals concentration in minna pharmaceutical industry

The table 6 below shows results of heavy metals investigated in pharmaceutical industry in Minna from the months of March to August which indicates lead, Cadmium, Copper and Manganese. Lead was not detected throughout the sampling period while Cadmium shows no significant difference throughout the sampling period with mean valves of 0.28 ± 0.02, 0.00 ± 0.02, 0.31 ± 0.27, 0.35 ± 0.31 respectively. Similarly, copper and manganese shows no significant difference with mean values of 0.86 ± 0.39, 0.71 ± 0.49, 0.82 ± 0.43, 0.25 ± 0.12 and 0.29 ± 0.31, 0.45 ± 0.22, 0.75 ± 0.60 and 0.55 ± 26.09 respectively. Heavy metals concentration in minna pharmaceutical industry between March-August, 2019 is shown in Table 6.

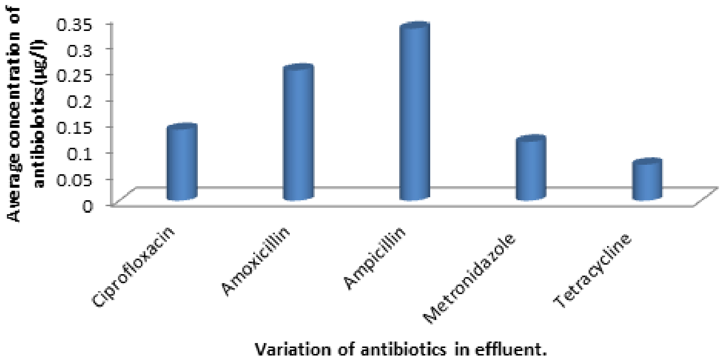

Figure 2. Average levels of antibiotic concentration in the minna pharmaceutical effluent between march-august, 2019

Table 5. Composition and distribution of macro-invertebrates in zaboyistream at maitumbi, minna between March and August, 2019

Order	Family	Species	Common name	Sites					
				1	2	3	4	Total	%
Hemiptera	Nepidae	Ranatra sp.	Water scorpion	0	0	6	0	6	4.05
	Gerridae	Nabonidus Africanus	Water Strider	0	1	8	0	9	6.09
Odonata	Libellulidae	Orthetrum sp.	Dragon flies	0	2	10	0	12	8.1
	Coenagrionidae	Enallagma sp.	Damselflies	0	0	14	2	16	10.81
Diptera	Chironomidae	Transvaalensis	C. Lavae	0	17	11	10	38	25.68
		Tanypus	C.Lavae	0	6	8	9	23	15.54
		Tanytarsus sp.	C.Lavae	0	4	10	11	25	16.9
	Culicidae	Culex Pipiens	Mosquito Larvae	0	0	8	11	19	12.83
								148	100

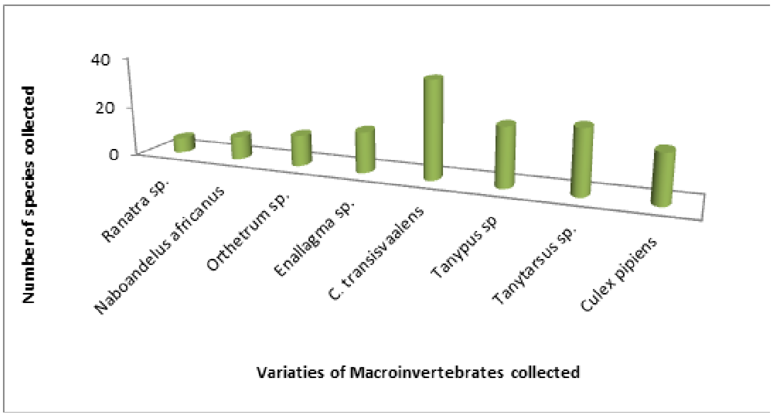

Figure 3. Species distribution of macro-invertebrates of zaboiyi stream,maitumbi, minna.

Table 6. Heavy metals concentration in minna pharmaceutical industry between March-August, 2019

	Pb^+	**Cd^+**	**Cu^+**	**Mn^+**
March	0.00±00[a]	0.28±0.021[a]	0.86±0.39[a]	0.45±0.22[a]
April	0.00±00[a]	.00±002[a]	2.4±0.49[a]	2.5±60[a]
May	0.00±00[a]	.00±00[a]	0.72±48[a]	0.74±0.619[a]
June	0.00±00[a]	0.00±0.00[a]	0.25±0.12[a]	0.14±0.05[a]
July	0.00±00[a]	0.31±.27[a]	0.39±14[a]	0.49±0.27[a]
August	0.00±00[a]	0.35±.31[a]	0.29±.13[a]	0.55±.26[a]
WHO,2015	0.01	0.003	2	0.05
NIS,2015	0.01	0.003	1	0.02

a: Lead is absent in effluents

DISCUSSION

Pharmaceutical compounds are being used for several beneficial purposes in modern society; simultaneously pharmaceutical industries are releasing very toxic contaminants in the environment directly or after chemical modifications (Halling-Sorensen, 2002). Moreover, pharmaceutical compounds may enter the environment through different routes such as discharge, wastewater, and seepage from landfills sites, sewer lines and run-off from animal wastes. (Glass-meyer, et al., 2005). Pharmaceutical industry is a small user of water in terms of quantity, but has a significant impact on water quality draw by the domestic and industrial sectors, return as domestic sewage and industrial effluents which inevitably end up in surface water bodies or in the groundwater, affecting water quality (Mukherjee and Nelliyat, 2006). Many pharmaceutical industries are responsible to generate toxic effluent as a consequence of their operation. The waste water generated from these industries possesses solids, bio-degradable and non-degradable organic compounds. Pharmaceutical effluents offer basic information about the reliability of the aquatic habitat in rivers and streams, into which they are discharged. The physico-chemical analysis of the effluents should indicate that most of these industries obey the standard guidelines of Federal Environmental Protection Agency (FEPA, 2015). An important pollution index of industrial wastewaters is the oxygen content in biological oxygen demand (BOD), where the nutrients status are measured in terms of amount of nitrogen and phosphorus in waste water. Besides this, other significant water quality parameters include pH, temperature and total Dissolved solids. (Ezenobi, 2004). However; pharmaceutical effluents are also categorized by their unusual turbidity, conductivity, TDS and total hardness. Various physical and biological processes occurring in aquatic ecosystem may cause reduction of many pharmaceutical compounds, trace concentrations of human and veterinary pharmaceutical compounds as well as their metabolites have been detected in different water bodies like surface water, groundwater and drinking water sources (Bruce, 2010). Acidic water can also cause problems for human consumption, while slightly acidic water is not dangerous, on its own, it can be quite dangerous when combined with other compounds. Water with a pH that is less than 6.5 can leach metal ions, including Iron, Manganese, Copper, Lead and Zinc from plumbing fixtures and pipes. This, in return, can be quite dangerous. In this research the pH is above 8. On the pH scale, water that has a pH greater than 8.0 can be difficult to disinfect. The World Health Organization (WHO, 2014) recommends that the pH of the water be less than 8.0, because basic water does not allow for effective chlorination. Like TDS, pH is given an aesthetic objective in Canada. The Canadian Guidelines for Drinking Water Quality suggest that the pH of drinking water should be between 7.0 and 10.5. In the United States, pH is, like TDS, a secondary standard; the Secondary Maximum Contaminant Level for pH is between 6.5 and 8.5. According to the EPA, the noticeable effects of a pH that is less than 6.5 include a bitter, metallic taste and corrosion. The noticeable effects of a pH above 8.5 include a slippery feeling, soda-like taste and deposits. The dissolved oxygen value of the effluent recorded (3.44 ± 53 to 4.54 ± 14) is far below W.H.O specification of 7.5 and similar to that obtained by (Idris, et al., 2013). This is an indication of high pollution of the effluent, the value for the groundwater samples were higher than specification. In addition, low DO concentrations mobilize trace Metals. Elevated BOD can be caused due to high levels of organic pollution (caused usually by poorly treated wastewater) and high nitrate levels facilitating high plant growth. Calcium, in the form of the Ca_2 ion, is one of the major inorganic cat ions; it can originate from the dissociation of salts, such as calcium chloride or calcium sulphate, in water. Most calcium in surface water comes from streams flowing over limestone, $CaCO_3$, gypsum, $CaSO_42H_2O$ and other calcium- containing rocks and minerals. Calcium carbonate is relatively insoluble in water, but dissolves more readily in water containing significant levels of dissolved carbon dioxide. The concentration of calcium ions (Ca_2) in the effluent has a mean of (28.75 to 44.66 mg/L) and usually has the highest concentration of any freshwater cat ion (Abboud, 2014). A level of 50 mg/L is recommended as the upper limit for drinking water. High levels are not considered a health concern; however, levels above 50 mg/L can be problematic due to formation of excess calcium carbonate deposits in plumbing or in decreased cleansing action of soaps. If the calcium ion concentration in freshwater drops below 5 mg/L, it can support only sparse plant and animal life, a condition known as oligotrophic. In this research, conductivity shows significant correlation with parameters such as temperature, pH value, alkalinity, total hardness, calcium, total dissolved solids and iron concentration of water. Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Streams that run through areas with granite are composed of more inert materials that do not ionize (dissolve into ionic components) when washed into the water (Gupta, 2010). Ground water inflows can have effects depending on the bedrock they flow through. Discharges to streams can change the conductivity depending on their make-up. A failing sewage system would raise the conductivity because of the presence of Chloride, Phosphate and Nitrate. High conductivity was recorded due to the effluent which has significant effect on the aquatic environment, WHO (2014). Measurement of temperature is an important parameter required to get an idea of self-purification of rivers, reservoirs and control of treatment plant for fish life. In this research, the highest temperature was 33.46ºC. The temperature of surface water is influence by latitude, altitude, season, time of day, air circulation cloud cover, flow and depth of biological process in water bodies (Abboud, 2014). Temperature affects physical, chemical and biological process in water bodies. As water temperature increases the rate of chemical reaction generally increases together with the evaporation and volatilization of substance from the water, (Amoo, 2005). Ground water usually maintains a fairlyconstant temperature, however deep aquifers have higher temperature due to earth's thermal gradient. Factors that may affect temperature are flow rate, industrial discharge sewage outflow. The standard value of alkalinity for river water is 100-200 mg/L for fisheries activities (WHO, 2014). However, the values obtained in the effluent were above the standard range and these makes the effluent unsuitable for aquatic life. However, (Tripathi, et al., 2014) reported that alkalinity show positive correlation with water temperature. Non-steroidal anti-inflammatory drugs (NSAIDs), like Ciprofloxacin, Amoxicillin, Tetracycline and Metronidazole are widely being used and consequently are frequently detected in sewage, surface water and may be found in ground water system. Ibuprofen, indomethacin, diclofenac, acetyl salicylic acid and Tetracycline have been found in surface water system. However, diclofenac, ibuprofen, Metronidazole and Amoxicillin are the most commonly found drugs in the water bodies after clofibric acid. Moreover, Ciprofloxacin has been proven to be highly toxic for vultures and cattle's (Tripathi, et al., 2014). NSAIDs like ibuprofen, naproxen and aspirin are the most commonly used drugs, which are usually found in effective quantities in municipal effluents. (Ashton, et al., 2004). Toxicity due to some pharmaceutical compounds studies on antibiotics have shown that up to 95% of antibiotic compounds can be released unaltered into the sewage system. Moreover, higher concentrations of antibiotics can lead to change in microbial community structure and ultimately affect food chains. In the monitoring study in Four Sites along the stream, out of four pharmaceutical effluent analyzed, some pharmaceuticals like Ciprofloxacin (concentration 0.049 μ/cm, 0.099 μ/cm, 0.203 μ/cm) and 0.188 μ/cm (Control); Amoxicillin (0.571 μ/cm; 0.3 μ/cm; 0.076 μ/cm; and 0.045 μ/cm (Control); Ampicillin (0.296 μ/cm,0.12 μ/cm,0.597 μ/cm and 0.296 μ/cm (Control); Metronidazole Tablet (0.249 μ/cm, 0.125 μ/cm, 0.063 μ/cm and 0.011 μ/cm (Control); Tetracycline (0.104 μ/cm, 0.099 μ/cm, 0.048 μ/cm, and 0.023 μ/cm (Control) have been detected at concentrations more than or equal to detection limits of selected methods. The pharmaceuticals have been identified in water cycle at trace levels by advanced analytical techniques and (HPLC). Several reports have confirmed the presence of pharmaceuticals in effluents of pharmaceutical industries and in municipal wastewaters and these have been recognized as a major source of drugs and pharmaceuticals in drinking water (Pardon, et al., 2019). Most of these research work has been performed on the analysis and detection of pharmaceutical in drinking water samples in developed countries including USA, Japan, the Republic of Korea and some countries in Europe,(WHO 2013). The long term exposure of lower concentration of complex pharmaceutical mixtures on stream biota may result in acute and chronic damages, (Ashton, et al., 2004). Behavioral changes accumulation in tissues (Idris, et al., 2013), reproductive damage and inhibition of cell proliferation, (Abboud, 2014).Several studies have demonstrated that fish exposed to wastewater effluents can exhibit reproductive abnormalities. Moreover, fish exposed to trace levels of birth control pharmaceuticals in the range of concentrations found in the environment show dramatic decreases in reproductive success, suggesting population level impacts are possible, (Babatunde, et al., 2014).The order Hemiptera includes species that are intolerant to various forms of pollution (Sagar, et al., 2012), and in accordance with this, Ranatra sp, and Nabonidus africanus were present at the effluent impacted sites but in very few numbers. Other studies have also reported that the genera tranvaalenssis and Tanypus sp are tolerant to organic pollution (Adamu, et al. 2017). However in this study, these species were somewhat sensitive to pollution as their composition and abundance were significantly reduced at the effluent impact site. The Dipterans were the most ubiquitous group in the present study. They were recorded in all the sampling sites except sites 1 and 2. It has been reported that some aquatic beetles particularly hydrophilids and some dytiscids can renew their oxygen supply directly from the atmosphere, they are probably unaffected by oxygen depletion wastes (Ademola, et al., 2017). The effluent impacted site was dominated by chironomids Particularly C.trivaalensis sp. and certain dipteran species (Chironomus). These species are reportedly more abundant in organic polluted streams and possess the ability to thrive in areas of reduced competition and low concentrations of oxygen (Arimoro, et al., 2007a) Macro-invertebrate community recovered in the downstream sites, at this site, the odonatan, were recorded, possible due to the dilution effects from tributaries and self-purification processes at this part of the stream. Other occurrences at this sampling point were C. Tanytarsus sp, Aedes, (Diptera). Most of these taxa feed on fine particles carried by the water, including algae (Adamu, et al., 2017) and their increase may be related to an increase in the periphyton and phytoplankton, favored by the high nitrogen concentrations from the discharge site. The obvious qualitative changes of macro-invertebrates in this study probably were in response of a combination of natural and anthropogenic influences, including seasonal rainfall patterns. Perhaps the heavy down pour must have altered the substrate stability and the dilution effect must have enhanced the presence of certain tolerant group in the effluent impact site. The concentrations of some heavy metals in the effluents of the pharmaceutical company in Minna were determined. The heavy metals analyzed in this study included Cadmium, Lead, Copper and Manganese. Most of the samples were found to contain the metals in varying concentrations. The highest concentration of heavy metal detected was Copper in the month of April (79 ± 0.49a mg/L) and Manganese also in the month of April with mean concentration of (75 ± 60a mg/L). Mostly, the concentrations were above the WHO, (2014) recommended maximum contaminant concentration level. Lead was not detected throughout the research, However, Cadmium concentration was 0.35 ± .31 mg/L and Manganese was 75 ± 60 mg/L. Chimezie, et al. (2011) had similar results in their findings in Lagos pharmaceutical companies. There are currently no Nigeria industrial Standard (NIS) regulations limiting the levels of pharmaceuticals in wastewater or drinking water, However, the United States Environmental Protection Agency has added four pharmaceutical compounds, which extensively used by human, to the most recent Contaminant Candidate List (CCL) including three birth control substances and one antibiotic. Several reports have confirmed the presence of pharmaceuticals in effluents of pharmaceutical industries and in municipal wastewaters and these have been recognized as a major source of drugs and pharmaceuticals in drinking water. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

RECOMMENDATIONS

This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards on the water quality and biota. The side effects on human, aquatic and animal health need to be investigated through thorough safety and toxicological studies. Sincere efforts are required to reduce the problem along with some adequate regulations to control them.

The limitations of time and funding reinforce the need for intelligent approaches and predictive tools to gauge the environmental concentrations and the effects of pharmaceuticals on aquatic organisms. Water quality guidelines enforced in Nigeria needs to include analysis of most commonly used pharmaceutical compounds in drinking water sources. Moreover, the latest remedial measures need to be adopted at large in effluent treatment plants of pharmaceutical industrial units to check long term environmental health hazards.

CONCLUSION

All the antibiotics were below the detection limit in all four wastewater sample points except for ciprofloxacin. The mean concentration of ciprofloxacin in the effluents for the four investigated sites has the highest concentration of 0.208 µg/L. Pharmaceuticals have been detected in wastewater treatment plant effluents and drinking water source. Trace amount of pharmaceuticals in drinking water for longer duration may cause considerable adverse effects to human health and aquatic life, though concentrations of pharmaceuticals detected in drinking water (in micro gram per liter range µg/L) are several orders of lower magnitude than the minimum therapeutic dose, though concentrations of pharmaceuticals detected in drinking water (in micro gram per liter range µg/L) are several orders of lower magnitude than the minimum therapeutic dose. There are currently no Nigeria Industrial Standard (NIS) regulations limiting the levels of pharmaceuticals in wastewater or drinking water. It is not going to be possible to measure, monitor, or conduct robust long-term studies of the effects of all pharmaceuticals, or probably even 10% of them, on aquatic organisms. The occurrence of high concentrations of pharmaceuticals at specific sites and the reports of effects occurring in the low µg/L range of some pharmaceuticals suggest that possible effects as a result of the presence of pharmaceuticals in the environment do occur, notwithstanding their low ranking here. Classifying pharmaceuticals as “not a problem” would be premature; but in comparison with other chemicals and based on the current state of the science, this preliminary risk assessment ranks them as less of a threat. Direct exposure to pharmaceuticals at levels normally found in drinking water (up to 100 µg/L) is generally not considered to pose human health risks, (Johnson, et al. 2008). However, the present study shows that drinking water in areas with high levels of industrial waste may be contaminated to considerably higher levels

Similarly, in this research, the surface water has high levels of Total Dissolved Solids (TDS) and Electrical Conductivity (EC). The BOD of the effluent water showed that the water was contaminated and the use of the water for domestic purposes by the inhabitants could lead to hazardous side effects. The presence of pollution tolerance organisms along the sample stream indicates the impacted nature of the effluent on biota. The highest concentration of heavy metal detected was Copper and Manganese in April. The concentrations of all the heavy metals (except Lead) were above the WHO, (2014) recommended maximum contaminant concentration level.

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