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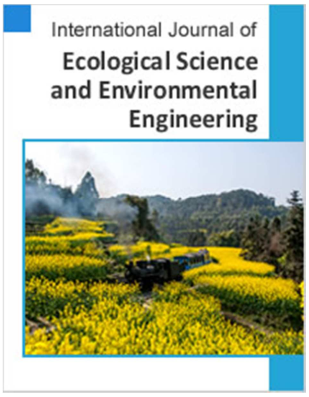

Assessment of the Impact of Pharmaceutical Industry Effluents on Quality of Nearby River

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Abstract

This study is an assessment of the impact of a pharmaceutical industry in Ilorin, Kwara state discharges on the quality of water around the industry. Three locations (point source, upstream and downstream) were chosen spatially along a nearby river course to reflect a consideration of all industrial activities that are capable of changing the quality of river water. Water samples were analysed for its pH, temperature (°C), electrical conductivity (µS/cm), sulphate (SO_4^{2-}), nitrate (NO^{3-}), phosphate (PO_4^{3-}), chloride (Cl^-), total suspended solid (TSS), total dissolved solids (TDS), total solid () (TS), total alkalinity (TA), total hardness (TH) and heavy metals (Zn, Pb, Cd, Mg and Cu) using standard methods. The assessment of the quality of this river water revealed that both upstream and downstream of the rivers were more polluted than the point of effluent discharge. This study also established that the surface water quality of all sampling points of the river was significantly affected by a non-point source of contamination as indicated by the physicochemical parameters monitored. The downstream of the river should be given more attention to as the concentrations of all parameters were higher than other sampling points.

1. Introduction

Water is one of the most indispensable natural resources that constitute about 70% of the body weight of almost all living organisms. It acts as a medium for both chemical and biochemical reactions [1]. Surface water constitutes part of water present as freshwater. Surface water lies not only in its wide spread occurrence and availability but also in its consistent good quality, which makes it an ideal supply for drinking water. However, surface water resources are under serious threat due to growing interest in mechanized agricultural practices, increasing population density and rapid urbanization as well as effluent discharge from industries and healthcare centres. Surface water quality can be affected by varied pollutants ranging from organic and inorganic chemicals and microbes. Water pollution (surface and ground) may be considered as a change in water quality or conditions induced directly or indirectly by man's numerous activities which renders it unsuitable for food, human health, industry, agriculture or leisure pursuit. The menace of water borne diseases and epidemics still threatens the well-being of population, particularly in developing countries. Thus, the quality as well as the quantity of clean water supply is of vital importance for the welfare of mankind [2].

About four to five decades ago, the focus of developed countries was how to prevent industrial and domestic waste from entering the waterways. Treatment plants were employed to improve the quality of water before wastewater was discharged into the lakes and rivers. While industrial waste and domestic waste were being managed, pharmaceutical waste became the emerging contaminant as it was discovered that it was neither completely removed nor degraded in the treatment plants [3]. The studies undertaken in about ten countries, it was detected that more than 80 pharmaceuticals in sewage, ground and surface water to the level of $\mu g/l$ and traces in drinking water [4]. One of the concerns is the possible impact of the accumulation of pharmaceuticals in humans and aquatic animals over a prolonged period as some of them are known to persist in the water environment. Furthermore, pharmaceutical mixtures (ibuprofen, fluoxethin and ciprofloxacin) have been shown to cause mortality of fish in $\mu g/l$ range [5]. The studies reported by [6, 7] buttress the point that pharmaceutical industries, especially in developing countries may be major sources of pharmaceutical waste in the water environment. An indirect effect has also been observed in a study which attributed diclofenac residues to the population decline of vultures in Pakistan [8]. Among the other challenges that face the Nigerian pharmaceutical industry, is the issue of pharmaceutical waste and its impact on the environment and public health. No matter the type/level of production or pharmaceutical business, the pharmaceutical industry generates pharmaceutical waste. While countries such as Italy, United State, United Kingdom, Taiwan and India [9] have been determining and monitoring pharmaceutical waste, there is little indication that Nigeria is monitoring it and there is little or no awareness that pharmaceutical waste is an emerging contaminant with growing concern. Hence, there is need to monitor the impact of pharmaceutical discharge effluents on the nearby river.

2. Materials and Methods

2.1. The Study Area

The Pharmaceutical Industry studied is located between latitude 8°28'31.04" N and longitude 4°33'11.20" E in New-Yidi road, Ilorin South local government area, Kwara state, Nigeria. The sampling locations upstream, point of effluents discharge and downstream were recorded using global positioning system (GPS) and Goggle earth (Table 1 and Figure 1). The Pharmaceutical industry supplies drugs across the nation. This river runs a meter behind the industry through a residential area. The effluents from the depot are discharge into the river. This river may constitute a huge health and environmental hazards to humans, aquatic organisms' and other forms of life in New-Yidi road, Ilorin environment, if the river is found contaminated by the effluents from the industry.

Figure 1. *Map showing the sampling points.*

Table 1. *Table showing the sampling points.*

Points	Latitude	Longitude
Upstream	8°28'32.85" N	4°32'46.30" E
Point Source	8°28'33.65" N	4°33'8.16" E
Downstream	8°28'42.06" N	4°33'32.25" E

2.2. Sampling and Preservation

Water samples were collected from the upstream, point source and downstream of the river into 1 L high density polyethylene (HDPE) plastic vials pre-treated with 4 M HNO_3 and properly rinsed with de-ionized water followed by doubly distilled water before use. Samples for metals analysis were collected separately and preserved immediately with 2 ml conc. HNO_3 per 1 L sample. Samples handling and preservation were done in accordance with standard methods [10].

2.3. Water Analysis

The pH, temperature, turbidity and conductivity of the water samples were measured with pH-meter, thermometer, turbidimeter and conductivity meter respectively which were previously calibrated before use. These parameters were determined *in situ* immediately after samples were collected. The total dissolved solid (TDS), Total suspended solid (TSS), total solid (TS), Dissolved oxygen (DO), Biochemical oxygen demand (BOD), Total alkalinity (TA) and Total hardness (TH) were determined using standard methods. Chloride, nitrate, sulphate, phosphate concentrations were determined by Mohr's, sodium salicylate (colorimetric), turbidimetric and ascorbic acid methods respectively [11]. Water samples were digested with aqua regia HCl/HNO_3 (3:1) to release metals in a measurable form by atomic absorption spectrophotometer.

3. Results and Discussion

From Table 2, pH of the water sample for the upstream is 7.3, point of effluents discharge is 7.7 and downstream is 7.1 with a mean value of 7.37±0.306. It was noticed that the pH of the river was within the WHO standard of 6.45 – 8.5, though the pH value at the point of effluent discharge was the highest and this also tells about the influence of the company's effluents on the river body. The company needs to be notified because continuous discharge of these effluents may lead to increase in the pH value of the water. High pH value may turn water into bitter taste [12]. The water temperature is one of the important parameter in river. From Table 2 below, the upstream and point of discharge was $30°C$ while the downstream of the river is $31°C$ with an average value of $30.3±0.577°C$. The temperature difference can be attributed to the time of sampling as the downstream was some distance to the point of discharge. Moreso, Water temperature is largely influenced by incoming solar radiation and the amount shading at the site as well as the ability of light to penetrate the water column [13]. The downstream was less shaded compared to the other sampling sites and this may have resulted to the high temperature value compare to other sampling points. Though, sampling points were within the WHO permissible limits of $25°C$.

Total dissolved solids (TDS) include salt and variety of organic substances, which readily dissolve in water [14]. The value of total dissolved solids at the upstream as 215 mg/l, point of effluents discharge was 205 mg/l while downstream gave 214 mg/l and a mean concentration of 211.33±5.508 (Table 2). The TDS values were below the WHO standard value of 1000 mg/l. As shown in Table 2 below, the TSS of the upstream and point of effluents discharge was 20 mg/l and downstream gave 40 mg/l with an average concentration of 26.67±11.547. The Total Suspended Solid (TSS) were within WHO standard value and the high value of the downstream may be attributed other anthropogenic activities in and around the downstream area. Total Solid (TS) is the summation of the filterable and non-filterable particles found in the river body. Table 2 below revealed that the TS of the upstream was 235 mg/l, point of effluents discharged was 225 mg/l and downstream was 254 mg/l with mean of 238±14.731 mg/l. The water samples were within WHO standard values. The downstream also gave the highest value and this may also be attributed to its exposure to more contaminants as the two other sampling points were within a small forest.

Water turbidity, which reflects transparency, is an important criterion for assessing the quality of water [15]. The turbidity of the river upstream was 55 mg/l, point of effluents discharge 41 mg/l and downstream 36 mg/l with an average of 44±9.849. The turbidity exceed WHO standard value of 5 mg/l. This indicates that the entire river is generally polluted and posing problems to aquatic lives, domestic and irrigation use. This might be due to improper disposal of sewage, surface runoff and wastewater from the Tuyil Pharmaceutical industry activities. Similar higher turbidity values are also recorded by [15]. Table 2 shows upstream of the river had 428 $\mu S/cm$, point of effluents discharge 410 $\mu S/cm$ while downstream 426 $\mu S/cm$ with a mean value of 421.33±9.866 $\mu S/cm$. They were all within the WHO permissible limits of 1500 $\mu S/cm$. There reduction in value at the point of discharge and this may be as result of deionised water been used in the production of drugs.

Dissolved oxygen (DO) is one of the important factors of water quality, which influences the biota present inside the river water [14]. Table 3 shows that the upstream DO was 21.8 mg/l, point of effluents discharge was 14.9 mg/l while downstream gave 17.3 mg/l with a mean concentration of 18±3.503 mg/l. The DO values exceeded the WHO standard values except at the point of discharge which gave approximately the same value as the maximum value of the WHO standard 15 mg/l. High DO are toxic to fish and causes physiological dysfunctions [16]. Biochemical Oxygen Demand (BOD) of the water samples as shown in Table 3, upstream of the river had concentration of 5.9 mg/l, point of effluents discharge gave 8.6 mg/l while the downstream of the river had 6.9 mg/l with a mean concentration of 6.9±1.480 mg/l. All BOD values were within the WHO standard limits.

Hardness is most commonly associated with the ability of water to precipitate soap. As hardness increases, more soap is needed to achieve the same level of cleaning due to the interactions of the hardness ions with the soap [17]. Chemically, hardness is often defined as the sum of polyvalent cation concentrations dissolved in the water [18]. Table 3 shows the upstream had a concentration of 34 mg/l, point effluents discharge 36 mg/l while downstream gave 32 mg/l with a mean of 34±2 mg/l. These concentrations was within the WHO permissible limits of 500 mg/l. Total Alkalinity (TA) of rivers is mainly carbonates and bicarbonates in any the samples which may be resulted due to the weathering of rocks, waste discharge and microbial decomposition of organic matter in the water body [15]. The TA as shown in Table 3 below, upstream of the river had 75 mg/l, point of effluents discharge 80 mg/l while the downstream is 98 mg/l with an average concentration of 84.3±12.097 mg/l. These values were within the WHO maximum contamination limits of 200 mg/l.

The concentration of nitrates is used as indication of level of micronutrients in water bodies and has ability to support plant growth. The upstream of the river had 4.49 mg/l, point of effluents discharge 3.91 mg/l while downstream 8.89 mg/l with a mean concentration of 5.76±2.723 mg/l (Table 3). Nitrate concentration at every sampling points fall within the WHO permissible limits. The mean concentration of phosphate is 1.073±0.452 mg/l. The upstream of the river had 1.25 mg/l, point of effluents discharge gave 0.56 mg/l while the downstream of the river 1.410 mg/l. The concentrations of phosphate for the three sampling points exceeded the WHO standard limits. Discharges of industrial effluents with high phosphate content might be responsible for the high levels observed. It can be noticed that the point of effluent discharge had the least concentration while the downstream of the river had the highest phosphate concentration. This may be attributed to sampling points, because only the downstream of the river is more exposed to pollution while the other sampling points are within a bushy area. Possible sources of phosphate might involve the use of phosphoric acid and phosphate salts as industrial raw materials. In addition, the extensive uses of phosphate based detergents for washing purposes in industries as well as land application of phosphorus-containing fertilisers can be other possible sources [19]. It is one of the major anions in natural waters and is contributed by industrial and household discharges, as contaminant. Sulphate concentration in upstream was 71.13 mg/l, point of effluents discharge 28.05 mg/l while downstream had 63.02 with a mean of all samples 54.07±22.893 mg/l (Table 3). The water samples were within the WHO standard values of 200 mg/l. High chloride content in river waters may indicate pollution by sewage, industrial waste or intrusion of seawater into fresh water bodies. Table 3 reveals that the upstream of the river concentration was 14 mg/l, point of effluents discharge 16 mg/l while downstream gave 13 mg/l with a mean for all samples 14.3±1.528 mg/l. These concentrations are within WHO permissible limits.

The concentration of zinc in the upstream was 0.139 mg/l, point of effluent discharge 0.098 mg/l while the downstream of the river was 0.167 mg/l. Mean and standard deviation of zinc are 0.135±0.035 mg/l. Zinc concentration at both upstream and downstream of the river were above WHO standard while the point of effluents discharge was within the permissible limit. Lead is one of the oldest metals known to man and is discharged in the surface water through paints, solders, pipes, building material, gasoline etc. [20]. Lead is a well-known metal toxicant and it is gradually being phased out of the materials that human beings regularly use. Atmospheric fallout is usually the most important source of lead in the freshwaters [21]. The concentration of lead was below detectable limits in the three sampling points tested. Hence the water is not polluted with lead ion. An exposure to cadmium enhances calcium excretion thus causes skeletal demineralization and probably leading to increases in bone fragility and risk of fractures [22]. Table 3 shows that cadmium concentration in the upstream was 0.440 mg/l, point of effluents discharge 0.290 mg/l while the downstream was below detectable limits. The mean concentration is 0.243±0.22 mg/l and 0.22 mg/l. Cadmium concentrations at both upstream and downstream of the river were far above the maximum permissible limits of WHO. Hence, the river is polluted with cadmium and this should draw the public concern, since they use both points water for rearing fishes. From Table 3, magnesium ranged between 5.1 to 7.2 mg/l a value higher than WHO permissible limit of 0.05 mg/l in drinking water. The maximum value recorded for copper was 0.01 mg/l (Table 3). This value fell below WHO permissible limit of 0.02 mg/l.

Table 2. *Average concentration of physical parameters of water samples with reference to WHO standards.*

Physical Parameters	Upstream	Point source	Downstream	WHO standard	Mean	Standard Deviation
pH	7.3	7.7	7.1	6.5 – 8.5	7.367	0.306
Temp. (°C)	30	30	31	25	30.333	0.577
TDS (mg/L)	215	205	214	1000	211.333	5.508
TSS (mg/L)	20	20	40	80	26.667	11.547
TS (mg/L)	235	225	254	1500	238	14.731
Turbidity (NTU)	55	41	36	5	44	9.849
EC	428	410	426	1500	421.333	9.866

Table 3. *Chemical parameters (mg/l) of water samples with reference to WHO standards.*

Chemical Parameters	Upstream	Point source	Downstream	WHO standard	Mean	Standard Deviation
DO (mg/l)	21.8	14.9	17.3	15	18	3.503
BOD (mg/l)	5.9	8.6	6.2	10	6.9	1.48
TH (mg/l)	34	36	32	500	34	2
TA (mg/l)	75	80	98	200	84.333	12.097
NO_3^{2-} (mg/l)	4.49	3.91	8.89	10	5.763	2.723
PO_4^{3-} (mg/l)	1.25	0.56	1.41	0.5	1.073	0.452
SO_4^{2-} (mg/l)	71.13	28.05	63.02	200	54.067	22.893
Cl (mg/l)	14	16	13	250	14.333	1.528
Zn (mg/l)	0.139	0.098	0.167	0.01 – 0.05	0.135	0.035
Pb (mg/l)	ND	ND	ND	0.01	ND	ND
Cd (mg/l)	0.44	0.29	ND	0.003	0.243	0.224
Mg (mg/l)	7.2	7.2	5.1	0.05	6.5	0.99
Cu (mg/l)	ND	ND	0.01	0.02	0.003	0.005

ND: Not Detected

4. Conclusion

The assessment of the quality of this river water revealed that both upstream and downstream of the rivers were more polluted than the point of effluent discharge. The levels of most parameters monitored were generally lower in the industrial zones of the river while downstream of river is more polluted and this may be attributed to it exposure to contaminant than the upstream and point of effluents discharge into this river. This study also established that the surface water quality of all sampling points of the river was significantly affected by a non-point source of contamination as indicated by the physico-chemical parameters monitored.

Recommendation

More research should be carried out on this river in order to monitor the continuous effects of the effluents on the river. The downstream of the river should be given more attention to as the concentrations of all parameters were higher than other sampling points.

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