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Impact of cement effluent on water quality of rivers: A case study of Onyi river at Obajana, Nigeria

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Abstract: Physico-chemical characterisation of industrial effluent is of importance in view of its inherent toxic substances. Effluent from cement plant located in Nigeria was characterised and its impact on the receiving Onyi River was investigated in this study. Effluent, water samples from upstream, discharge point along the river course and downstream location were collected monthly. The river was monitored up to about 1 km downstream from the discharge point for a period of twelve months. The impact of the effluent on the water quality downstream was shown by reduced dissolved oxygen. With respect to upstream, the levels of pH, nitrate, phosphate, total solid, total suspended solids, total dissolved solids, turbidity and biological oxygen demand at downstream were much high, arising from the influx of cement effluent. The cement effluent significantly contributed to the levels of Zn (0.045 ± 0.003 mg/L) and Pb (0.016 ± 0.001 mg/L) downstream such that they exceeded the criteria set by USEPA and WHO respectively. Using Prati method of classification of surface water quality, the Onyi River fell in the class of slightly polluted water. Weight arithmetic water quality index of 85.2 and metal pollution index of 3.46 corroborated the classification. Hence, adequate treatment of downstream water prior to its use for beneficial purposes is required.

Subjects: Environment & Agriculture; Earth Sciences; Environmental Studies & Management

Keywords: cement effluent; Onyi River water contamination; metal pollution; water quality indexes

1. Introduction

Rivers are the major source of surface water for drinking, domestic, irrigation and industrial purposes which are of tremendous benefits to humans. Monitoring of water quality of rivers regularly is quite necessary for the assessment of water quality for beneficial purposes. One of the several approaches that can be used to assess the water quality status of rivers is to adopt water quality index (WQI) method (Goher, Hassan, Abdel-Moniem, Fahmy, & El-sayed, 2014). WQI is a mathematical

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PUBLIC INTEREST STATEMENT

Waste water from industries contaminates rivers if discharged without adequate treatment. Consequently, upon this, most notable rivers in the world whose water resources are to be of benefit to human have been impaired. This study, therefore, focused on the assessment of the degree of contamination of Onyi River in Obajana with waste water from cement production plant. Upon the receipt of such water, the quality of the river was found unfit for beneficial purpose.

expression utilised to transform large number of water quality data into a single number, which denotes the water characteristic (Sutadian, Muttill, Yilmaz, & Perera, 2017). The WQI was first developed in United State by incorporating few commonly used water quality variables, which include dissolved oxygen (DO), pH, conductance, alkalinity and chloride. Since then, several authors have formulated different methods to calculate water quality indices (WQIs). Such WQIs include US national sanitation foundation WQI (Brown, McClelland, Deiniger, & O'Connor, 1972), Canadian council of ministers of the environment WQI (Khan, Paterson, & Khan, 2003) and Oregon WQI (Kannel, Lee, Lee, Kanel, & Khan, 2007). Upon the application of WQI, the quality of rivers can be categorised as excellent, good, medium, bad and very bad based on the WQI results (Chaturvedi & Bassin, 2010). To obtain data for WQIs, large number of samples are required in water quality measurement with long periods of continuous measurement. This requirement set a limitation to the use of these traditional WQIs. Three-dimensional (3D) fluorescence spectrum index method for river water has been developed to circumvent the difficulties in achieving substantial water-quality data for the use of traditional WQIs. The 3D fluorescence spectrum index has been applied to estimate surface water quality of the Ebinur lake watershed in China (Wang et al., 2017).

The availability of fresh surface water for these purposes is becoming hampered nowadays in the world partly due to municipal and industrial pollution. The vulnerability of rivers to especially industrial pollution is unprecedentedly high because of its unhindered accessibility for disposal of wastes. Pollution from industries constitutes a considerable part of total pollution in the world (Bai, Zhang, Sun, Wang, & Zhu, 2006; Pandey et al., 2005). With the development of industries across the world, rivers have become dumping reservoirs for solid wastes and effluents from industries. A navigable Shitalakkhya River in Bangladesh frequently receives waste from textile and dyeing industries located at Narayangany industrial zone. The waste was known to contain untreated dye with heavy metals (Islam, Sarkar, Rahman, & Ahmed, 2015). The major agro-industrial effluents of sugarcane and starch industries were discharged to the River Nile around Cairo city. Their disposal increased the microbial load of the River (Ali, Sabae, Fayez, Monib, & Hegazi, 2011; El-Sayed & Salem, 2015). The industrial effluent disposal into rivers which resulted to pollution was evident for Lake Calumet in Chicago (Roadcap, Kelly, & Bethke, 2005) and Gorka lake in Poland (Czop, Motyka, Sracek, & Szuwarzyński, 2011). Cement kiln dust was generated as by product from a cement plant in India (Kunal, Rajor, & Siddique, 2016). Like all over the world, Obajana community in Nigeria is encountering tremendous challenge of getting fresh water from the Onyi River. The river plays an important role in the supply of fresh water for bathing, household work and irrigation for Obajana community whose population is about 3,500 (Adejoh, 2016). The river is vulnerable to industrial pollution from a cement plant located in the community. Industrial effluent from the plant essentially contains stream of wastewater, solids and gaseous waste. The plant, however, claimed to have effluent treatment plant whose efficiency is uncertain.

The estimated amount of cement produced globally was 3.6 billion tonnes in which the proportion for Africa was 4.7% (Imbabi, Carrigan, & McKenna, 2012). production of cement in the world is increasing constantly and Nigeria is not exempted. Nigeria, being a developing country is experiencing a high demand for infrastructure and housing which places high demand for cement production (Makinde, 2014; Nyaruai, Kinyua, & Gathu, 2016). The cement production sector in Nigeria is playing a vital role in the Nigeria economic development due to its wide spectrum of usage. The by-products in form of effluent and gaseous waste from the cement plant are also increasing as production is stepped up. The dumping station of the effluent from the cement plant at Obajana is Onyi River. Using the Onyi riverwater for bathing and domestic purposes, the Obajana residents and people who are living at farther distance downstream are prone to skin irritation and cholera.

The assessments of effluent quality from the plant and of water quality of the Onyi River are very much necessary for safe and sound health of the community and river system. The assessment becomes an important tool to understand the effluent impact of the Onyi River. The classification of water quality of the river equally becomes possible with the assessment. Therefore, the objectives of this study were to investigate the quality of effluent from a cement plant, its impact on the Onyi

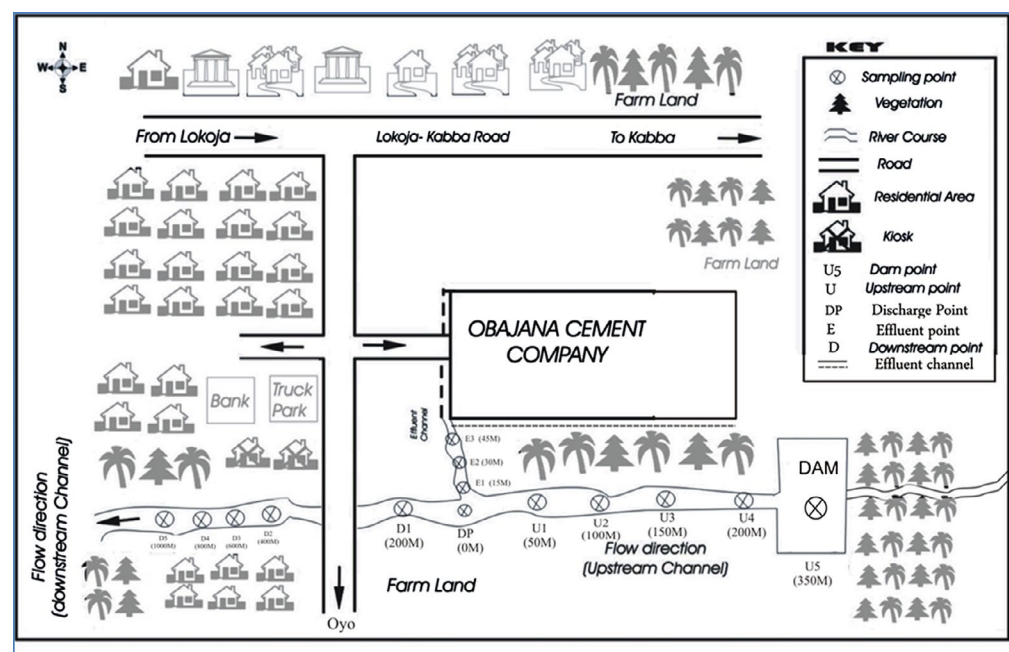
River and to assess the water quality of the river for beneficial purpose. The impact was ascertained by comparison of the effluent quality with the national regulatory standard, National Environment Standards and Regulations Enforcement Agency (2011), for effluent discharges into surface water meant for beneficial purposes such as irrigation, fisheries and swimming and recreation. The consideration of the downstream surface water as fit for drinking and domestic purposes was done by comparison of the water quality with the WHO standard for drinking water. Water-quality indices were also employed to classify the river based on the level of contamination from the effluent discharges. The information about the monitoring of quality of Onyi River in scope and duration is scarce in this regard. Hence, this attempt of frequent monthly monitoring of Onyi River was of environmental essential and could be useful for relevant evaluation of the cement industry. The monitoring covered both wet and dry seasons to study seasonal variations in the water characteristics of the river.

2. Description of study area and sampling design

Obajana Cement plant is the largest cement factory in West Africa and is located in Obajana community on latitude 7.916°N and longitude 6.433°E of Kogi state, The plant is about 60 m away to the Onyi River which frequently receives discharges of effluent directly from the plant. Selected portion of the river with sampling points along the river is shown in Figure 1. Some vegetation grows around the company and the banks of the river. The riverbank is characterised with steep-sided valley. The Fulani settlements are remotely located in the community and access is only via footpaths. The Fulani are nomadic by nature and can settle where there is favourable condition even for their cattle. Occupations of the people in this community include cattle rearing, farming, hunting and petty trading. The crops grown in this area include rice, sweet potatoes, maize, millets, sugarcane, cassava and cowpea.

A portion of the Onyi River under investigation was divided into four zones taking reference from the point of discharge of effluent into the river. These zones are the (1) Dam (2) upstream (3) discharge point at which industrial discharge entered the water course and (4) downstream. All the sampling points along the watercourse before the discharge point were referred to as upstream and it serves as the control points, while all those sampling points after the discharge point were referred to as downstream. The sampling points are designated as follows:

Figure 1. Selected area of Onyi River at Obajana showing sampling points.



- (1) The dam and upstream sampling points were designated as U1–U5 with distances ranging from 50 to 200 m to the discharge point,
- (2) The discharge point at junction where the effluent discharging channel intersected the river and was designated as JP.
- (3) The effluent collection points along the effluent discharging channel and were designated as E1–E3,
- (4) The downstream point as D1–D5 with distances ranging from 200 to 1,000 m away from the discharge point,
- (5) One sampling point was located at the Dam location. This was designated as U5 (350 m).

3. Sampling and chemical analysis of samples

Effluents and water samples of 2.5 L each were collected using grab sampling technique at the designated sampling point monthly for a year. They were kept at 4°C in ice chests and transported to the laboratory. In the laboratory, analyses were carried out immediately. A total of 36 effluent samples and 132 water samples were collected into polyethylene containers soaked in 2 M HNO₃, washed and rinsed with distilled water prior to sampling. All analyses were carried out using standard procedures of the American Public Health Association, American Water Works Association & Water Environmental Federation (1998). The physicochemical qualities of the samples were determined. The pH of samples was determined by electrometric method using a pH meter (HANNA, model HI 96107). Total alkalinity, total hardness, calcium and magnesium were determined by titrimetry. Gravimetry method was used for total solid (TS), total suspended solids (TSS) and total dissolved solids (TDS). Turbidity was determined by turbidimetry method. This method is based on the comparison of the intensity of UV/Visible light scattered by the sample solution with that of 400 FTU. The absorbance values of the solutions were determined using NICOLET Evolution 300 UV/Visible spectrophotometer. Sulphate, nitrate and phosphate were determined by colorimetry. Colorimetric determination of sulphate was performed with barium chloride solution as reagent. Colorimetric phenoldisulphonic acid method was used for nitrate while molybdenum blue method was employed for phosphate. In each of these methods, the absorbance values of the colour solutions were measured with spectrophotometer.

Alkaline-azide modification of Winkler's method was used for dissolved oxygen and biological oxygen demand (BOD). Open reflux method involving the oxidation of organic matter of sample in acidic medium and titration with ferrous ammonium sulphate was used for chemical oxygen demand (COD). Heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) were determined by atomic absorption spectrophotometry using Buck 205 Atomic Spectrophotometer after the digestion of samples with concentrated nitric acid.

All the reagents were of analar grade. Sample blanks were collected for the determinations of anions and metals and appropriate corrections were made. The recovery study of heavy metals in samples was carried out and percentage recoveries of 90.1–110% (Co), 89.4–102% (Cd), 94.3–106% (Cr), 86.7–90.0% (Cu), 90.0–103% (Ni), 98.6–101% (Pb) and 92.5–105% (Zn) were obtained.

4. Application of water quality and pollution indices

The suitability of water from the river downstream was investigated using weighted arithmetic WQI and metal pollution index (PI) as described by Brown et al. (1972) and Caeiro et al. (2005) respectively. The downstream physicochemical parameter values together with WHO standard permissible limits of the parameter were employed to evaluate the mathematical expression for WQI given as follows:

$$WQI = \frac{\sum_{i=1}^n Q_i W_i}{\sum_{i=1}^n W_i}$$

where Q_i is the quality rating scale of each parameter, W is the weight unit of each parameter and n is the number of parameter measured. Q_i was obtained using the following expression:

$$Q_i = 100[(V_i - V_o)/(S_i - V_o)]$$

where V_i is the concentration of each parameter, S_i is the WHO standard permissible value of each parameter and V_o is the ideal value of each parameter in pure water. The V_o values for all parameters are zero except for pH and DO values which are 7.0 and 14.6, respectively (Tripaty & Sahu, 2005). The value of W_i for each water quality parameter is inversely proportional to the WHO recommended standard for the parameter. Therefore, W_i is expressed as follows:

$$W_i = K/S_i$$

The proportionality constant K of the weights for various water quality parameters is given as follows:

$$K = \frac{1}{\sum_{i=1}^n 1/S_i}$$

The metal PI for Onyi River was evaluated using the following expression:

$$PI = \frac{\sqrt{\left(\frac{C_i}{S_i}\right)_{\max}^2 + \left(\frac{C_i}{S_i}\right)_{\min}^2}}{2}$$

where C_i is the concentration of each metal for maximum and minimum values and S_i is the metal level according to WHO water quality criteria.

In view of the utilisation of natural water resources as a source of municipal water supply, a classification was established by Prati, Pavanello, and Pesarin (1971). The classification was based on certain water-quality parameters that are only indicative of most commonly measured parameters. The accepted categories of water quality are excellent, accepted, slightly polluted, polluted and heavily polluted water types. The ranges of concentrations of the parameters for which the classification is based are available in the literature (Prati et al., 1971). The two approaches that seemed to have been used in Prati single index of pollution make the index most preferred for this study. The first approach was based on the characteristics of effluents before their discharge into water bodies. The second approach took into consideration the quality to be maintained in water bodies after dilution of effluents, natural capacity of water bodies for dispersion and self-purification capacity of water bodies. These important considerations were fully considered in the design of this study.

5. Statistical analysis of data

Kruskal-Wallis ANOVA non-parametric ($p = 0.05$) was employed to investigate the difference between the water quality parameters during dry and wet season. This statistical parameter was equally used to determine the difference between water-quality upstream and downstream. Non-parametric test was used because the data were few and were not normally distributed. These statistical analyses were carried out with the aid of OriginPro-8 software package. The results of the analysis were confirmed with Duncan multiple test range.

6. Results and discussions

6.1. Physicochemical characteristics of cement effluent

The production process of cement involves burning of limestone and clay together in a rotary kiln at a temperature of about 1,450°C (Gaharwar, Gaurav, Singh, Singh, & Gariya, 2016). This might be responsible for the observed high average temperature of the effluent. The temperature of the effluent was $28.0 \pm 2.7^\circ\text{C}$ ranging from 24 to 34°C (Table 1). The pH of 9.1 ± 0.9 suggested that the effluent was alkaline in nature. This observation is similar to the report about pH of 8.3 for effluent from cement plant located at Sistan area of Iran (Table 1). Following mixing of calcium carbonate, aluminum silicate, silica oxide and iron oxide as raw materials for cement production in a rotary kiln, water is required in the plant by factory workers for sanitary purpose. This might result in wastewater that is

alkaline. The resulting effluent from the production has potential of imparting high alkalinity to the effluent receiving Onyi River. The total alkalinity of the effluent was 87 ± 33 mg/L with a range of 35–150 mg/L (Table 1). These levels of alkalinity were lower than 625 mg/L observed for cement effluent from Chittak industrial zone of Bangladesh (Table 1).

Most cement plants are well located near a limestone quarry. Quarrying limestone in Obajana community involves drilling and crushing. These operations could be responsible for the TSS of 240 ± 267 mg/L observed for the effluent. In addition, the end product of pyroprocessing at the rotary kiln ranges from dust to lumps of calcium silicate or clinker that can possibly contribute to the TS level of 449 ± 318 mg/L for the effluent. The cement effluent acquires hardness due to dissolved calcium and magnesium salts possibly from the ore. The concentrations of calcium and magnesium in the effluent were in the range of 12.8–58.0 and 5.09–22.8 mg/L, respectively (Table 1). In order to produce cement, limestone as a major raw material undergoes calcination process. The process entails the decomposition of limestone to calcium oxide which reacts with silicate to form cement and carbon(IV) oxide that is given off. In the presence of this gas as a byproduct, a small quantity of limestone (CaCO_3) can readily dissolve in moisture to produce soluble calcium bicarbonate. The soluble calcium of this salt forms about 38% of total hardness of effluent from the Obajana cement plant. The total hardness level of the effluent was 71 ± 32 mg/L ranging from 31 to 153 mg/L. The suspended solids of the effluent ranging from 20 to 1,590 mg/L exceeded NESREA standard limit of 0.75 mg/L for effluent discharge into surface water in Nigeria. This indicates that cement production releases significant amount of solid waste materials not only to the atmosphere, but to surface water as well. The effluent from Sistan cement plant originating principally from cooling operations contained low suspended solids of 5.4 mg/L in comparison to 20–1,590 mg/L observed in this study (Table 1).

The effluent was observed to have turbidity ranging from 7.5 to 804 FTU. Turbid effluent can interfere with Onyi River by reducing sunlight penetration which may affect food supplies and growth of aquatic organism (Mackie & Walsh, 2012). The possibility of microbial pollution in water bodies is often accelerated by high turbid effluent due to high number of foreign microbiota supported by the turbidity (Karikari & Ansa-Asare, 2006).

The chloride (18.0 ± 7.9 mg/L) and sulphate (3.8 ± 1.9 mg/L) contents of the effluent were within the regulatory limits. This suggests that the chloride concentrations of the effluent may not have a discernible impact on the water quality of the river. Nearly all water bodies contain chloride and sulphate, and their levels vary greatly depending on the underlying composition of the river bed. The concern for chloride level, if higher than the background concentration, is that it can corrode metal reinforcement such as bridge that is erected along the water way (Kelly et al., 2007). Sulphate has also been implicated as a corrosive agent in water bodies (Bowell, 2004). The concentrations of chloride and sulphate in cement effluent at Obajana were much less compared with the corresponding concentrations of 3,458 and 2,455 mg/L reported for cement effluent discharged to Surma River in Bangladesh (Table 1).

The phosphate ($29 \pm$ mg/L) and nitrate (141 ± 106 mg/L) levels exceeded the respective NESREA regulatory limits of 3.5 and 40.0 mg/L. Detergents used for washing during sanitation are major sources of phosphate and nitrate in the effluent from cement plant (Lee & Jones, 1986). In spite of water bodies requiring some nutrients such as phosphorus and nitrogen to be healthy, excessive levels of the nutrients can be harmful (George et al., 2010). The eutrophication process on the Onyi River can thus be accelerated with excessive levels of phosphate and nitrate from the effluent.

Biochemical oxygen demand (BOD) and COD are major indicators of the environmental health of effluent receiving water bodies (Patil, Sawant, & Deshmukh, 2012). The level of BOD (5.3 ± 3.7 mg/L) ranging from 3.1 to 12.2 mg/L was below the regulatory limit of 6.0 mg/L, though high level of BOD for effluent was observed for some months (Figure 3). On the other hand, the level of COD (63 ± 43 mg/L) was above 30 mg/L set as standard for effluent discharge into surface water. This is an indication of gross chemical load of the effluent, discharging into the Onyi River. The COD concentration of

Table 1. Physicochemical characteristics of cement effluent discharged to the Onyi river and effluent quality standards

Parameter	Overall average	Range	National Environment Standards and Regulations Enforcement Agency (2011)	World Bank (1995)	Qualities of cements effluents at other locations			
					Bhilai, India ^a	Jamul, India ^a	Sistan, Iran ^b	Chittak, Bangladesh ^c
pH	9.1 ± 0.9	7.5-10.5	6.5-8.5	6-9	6.7	6.9	8.3	6.65
Temperature (°C)	28 ± 2.7	24-34	-	-	-	-	-	29.2
Total alkalinity (mg/L)	87 ± 33	35-150	-	-	-	-	-	625
Total hardness (mg/L)	71 ± 32	34-153	-	-	300	520	-	4,564
Calcium (mg/L)	27 ± 13	12.8-58	180	-	-	-	-	970
Magnesium (mg/L)	10.0 ± 4.6	5.09-22.8	40	-	-	-	-	515
TS (mg/L)	449 ± 318	160-1,840	-	-	-	-	-	34,230
TSS (mg/L)	240 ± 207	20-1,590	0.75	-	-	-	-	1,540
TDS (mg/L)	223 ± 123	40-620	-	-	3,289	3,166	5.4	32,890
Turbidity (FTU)	95 ± 166	7.5-804	-	-	-	-	-	-
Cl ⁻ (mg/L)	18.0 ± 7.9	4.0-37.0	350	-	-	-	-	3,485
SO ₄ ²⁻ (mg/L)	3.8 ± 1.9	1.35-10.1	500	-	-	-	-	2,455
PO ₄ ³⁻ (mg/L)	29 ± 18	10.5-66.6	3.5	-	-	-	-	83
NO ₃ ⁻ (mg/L)	141 ± 106	64-395	40	-	-	-	-	1.45
DO (mg/L)	7.1 ± 1.2	3.9-9.7	4.0	-	6.6	6.5	10.6	1.5
COD (mg/L)	63 ± 43	42-170	30	250	-	-	60	39,060
BOD (mg/L)	5.3 ± 3.7	3.1-12.2	6.0	50	-	-	30.5	-
Co (mg/L)	0.01 ± 0.01	<0.001-0.021	-	-	-	-	-	-
Cd (mg/L)	0.002 ± 0.002	<0.001-0.006	0.01	0.10	-	-	-	-
Cr (mg/L)	0.1 ± 0.1	<0.001-0.431	0.5	0.10	-	-	-	-
Cu (mg/L)	0.01 ± 0.01	<0.001-0.044	0.01	0.50	-	-	-	-
Ni (mg/L)	0.01 ± 0.01	<0.001-0.041	0.1	0.50	-	-	-	-
Pb (mg/L)	0.03 ± 0.03	0.001-0.081	0.1	0.10	-	-	-	-
Zn (mg/L)	0.06 ± 0.03	0.007-0.153	0.2	0.50	-	-	-	-

^aVadav, Rajhans, Ramteke, Sahu, Patel, and Blazhev (2016).

^bKhammar and Darvishi (2016).

^cAlam et al. (2007).

63 ± 43 mg/L observed in this study compared well with COD of 60 mg/L reported by Alam et al. (2007). The average levels of heavy metals in the effluent as shown in Table 1 were Co (0.01 ± 0.01 mg/L), Cd (0.002 ± 0.002 mg/L), Cr (0.1 ± 0.1 mg/L), Cu (0.01 ± 0.01 mg/L), Ni (0.01 ± 0.01 mg/L), Pb (0.03 ± 0.03 mg/L) and Zn (0.06 ± 0.03 mg/L). These levels of metals were within the regulatory limits for effluent discharge into surface water.

7. Characteristics of the Onyi River surface water

The status of water quality at the discharge point, upstream and downstream locations of the river are shown in Table 2. The discharge point is a junction along the Onyi River where outflow effluent mixes with river water. The water quality parameters for the upstream were compared with that for the downstream to evaluate the impact of the effluent. It was observed that after the mixing, alkalinity, total hardness, Ca²⁺, Mg²⁺, solids, Cl⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, COD, BOD, Cd and Cr levels were increased significantly (Table 2). This is temporal indicating that effluent discharges from cement plant have impacted negatively the water quality status of the Onyi River. The effluent was alkaline having pH of 8.32–9.05, but its influx into the Onyi River had no significant impact on the water pH. The alkalinity levels at upstream (51.0 ± 1.8; 71.0 ± 4.0 mg/L) and downstream (58.0 ± 2.5; 81.0 ± 8.4 mg/L) were not also significantly different.

8. Temporal and seasonal variations of water quality Onyi River

The water quality of Onyi River varied with the sampling periods (Figures 2 and 3). Effluent from cement plant showed variation in terms of pollution load from wet season to dry season taking cue from the production rate of cement. There seemed to be low production turn out in wet season than in the dry season. A rainfall during placement of concrete work can pose challenges to achieving a quality concrete, thus making cement demand decreases during wet season. This could result in lower cement production during wet season than dry season and consequently reduces the influx of effluent into the Onyi River. The water quality parameters at discharge point between the wet season and dry season were significantly different as shown in Table 2 (*p* < 0.05). The only exception was the TS of the effluent whose contents varied between 496 ± 208 mg/L for wet season and 493 ± 123 mg/L for dry season. The concentrations of heavy metals at discharge point were higher during the dry season in comparison to the wet season (Table 2). This is probably owing to the low flow of water during dry season. In wet season, much dilution of the effluent would have taken place. In like manner, the water quality upstream and downstream varied significantly between the wet season and dry season. The few parameters that were not affected by seasonal changes were

Figure 2. Monthly variations in pH, turbidity, calcium, magnesium and TS levels.

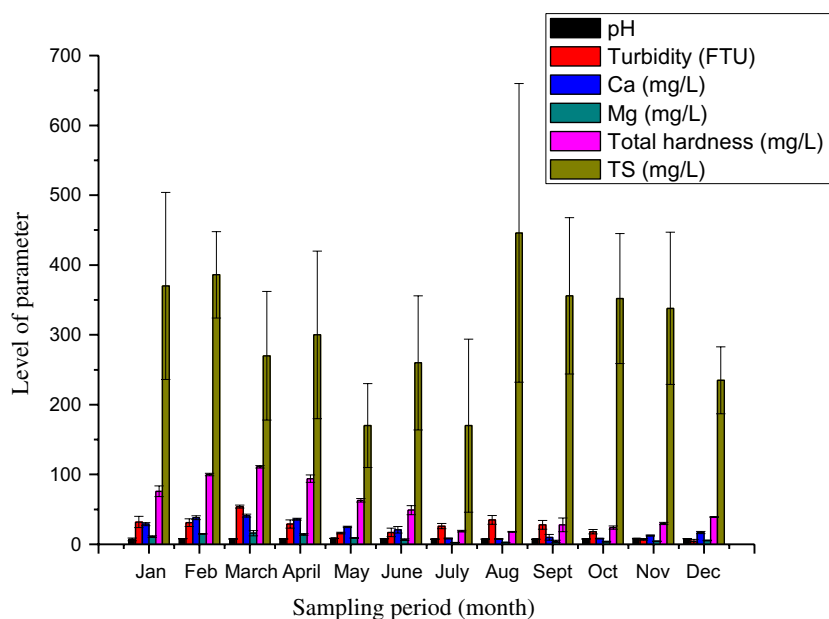


Table 2. Average levels of water quality parameters at discharge point, upstream and downstream of Onyi river during rainy and dry season

Parameter	Upstream		Discharge point		Downstream		Sig. ($\alpha_{0.05}$) Yes/No?	
	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season		
	Sig. ($\alpha_{0.05}$) Yes/No?		Sig. ($\alpha_{0.05}$) Yes/No?		Sig. ($\alpha_{0.05}$) Yes/No?			
pH	7.69 ± 0.04 ^a	7.70 ± 0.15 ^a	No	8.32 ± 0.71 ^c	9.05 ± 0.62 ^b	7.74 ± 0.01 ^a	7.77 ± 0.23 ^a	No
Temperature (°C)	27.5 ± 0.2 ^a	29.0 ± 0.1 ^b	Yes	26.6 ± 2.3 ^c	28.7 ± 3.0 ^c	26.5 ± 0.3 ^c	27.7 ± 0.2 ^b	Yes
Alkalinity (mg/L)	51 ± 1.8 ^c	71 ± 4.0 ^a	Yes	67 ± 35 ^e	97 ± 4 ^a	58 ± 2.5 ^c	81 ± 8.4 ^a	Yes
Total hardness (mg/L)	37 ± 1.3 ^d	46 ± 2.1 ^b	Yes	57 ± 19 ^c	64 ± 36 ^b	46 ± 2.2 ^b	63 ± 3.7 ^a	Yes
Calcium (mg/L)	14.8 ± 0.3 ^d	17.9 ± 0.7 ^c	Yes	21.9 ± 8.0 ^a	24.8 ± 14.7 ^b	18.2 ± 1.5 ^c	22.2 ± 0.63 ^a	Yes
Magnesium (mg/L)	5.31 ± 0.35 ^d	6.85 ± 0.31 ^b	Yes	8.57 ± 3.0 ^c	9.38 ± 5.17 ^a	6.54 ± 0.22 ^b	9.41 ± 0.77 ^a	Yes
Total solids (mg/L)	196 ± 18 ^a	223 ± 27 ^{ab}	Yes	496 ± 208 ^d	493 ± 123 ^d	284 ± 63 ^c	326 ± 88 ^{bc}	Yes
TSS (mg/L)	112 ± 15 ^{ab}	120 ± 21 ^a	Yes	223 ± 74 ^c	208 ± 41 ^c	123 ± 37 ^a	145 ± 39 ^{ab}	Yes
TDS (mg/L)	84 ± 26 ^a	103 ± 12 ^a	Yes	265 ± 177 ^c	285 ± 124 ^c	161 ± 45 ^b	180 ± 50.4 ^b	Yes
Turbidity (NTU)	25.3 ± 4.1 ^a	16.9 ± 1.7 ^b	Yes	46.3 ± 2.5 ^c	45.2 ± 1.5 ^c	25.4 ± 4.2 ^a	24.4 ± 4.1 ^b	No
Cl ⁻ (mg/L)	7.2 ± 0.7 ^c	12.4 ± 0.8 ^b	Yes	12.6 ± 5.9 ^d	16.1 ± 4.64 ^b	7.8 ± 1.0 ^c	12.5 ± 0.6 ^a	Yes
SO ₄ ²⁻ (mg/L)	0.82 ± 0.04 ^a	0.95 ± 0.10 ^b	Yes	2.98 ± 1.67 ^e	2.79 ± 0.75 ^d	1.59 ± 0.16 ^d	2.05 ± 0.25 ^c	Yes
PO ₄ ³⁻ (mg/L)	22 ± 0.2 ^a	29 ± 1.0 ^{ab}	Yes	28 ± 18 ^d	39 ± 21 ^{bc}	22 ± 2.7 ^c	32 ± 3.3 ^{ab}	Yes
NO ₃ ⁻ (mg/L)	114 ± 46 ^a	140 ± 25 ^{ab}	Yes	155 ± 95 ^c	194 ± 148 ^{bc}	109 ± 18 ^{bc}	156 ± 37 ^a	Yes
DO (mg/L)	8.1 ± 0.5 ^c	9.1 ± 1.5 ^{bc}	No	6.8 ± 0.4 ^{ab}	7.4 ± 1.4 ^a	8.1 ± 0.4 ^{bc}	8.1 ± 1.1 ^{bc}	No
COD (mg/L)	30 ± 3.4 ^{ab}	39 ± 3.2 ^a	No	71 ± 42 ^c	58 ± 16 ^c	43 ± 14 ^{ab}	45 ± 12 ^b	No
BOD (mg/L)	2.9 ± 0.5 ^d	4.4 ± 1.5 ^a	Yes	6.4 ± 5.0 ^c	11 ± 7.5 ^b	4.8 ± 1.4 ^a	7.6 ± 1.9 ^c	Yes
Co (mg/L)	0.0017 ± 0.0002 ^b	0.0028 ± 0.0001 ^a	Yes	0.003 ± 0.001 ^c	0.005 ± 0.004 ^a	0.002 ± 0.001 ^{bc}	0.0031 ± 0.0003 ^a	Yes
Cd (mg/L)	0.01 ± 0.01 ^b	0.0008 ± 0.0003 ^a	Yes	0.002 ± 0.001 ^a	0.004 ± 0.002 ^a	0.003 ± 0.001 ^a	0.0033 ± 0.0002 ⁻	Yes
Cr (mg/L)	0.039 ± 0.002 ^{ab}	0.015 ± 0.002 ^a	Yes	0.02 ± 0.01 ^{ab}	0.08 ± 0.06 ^c	0.06 ± 0.02 ^a	0.012 ± 0.001 ^{bc}	Yes
Cu (mg/L)	<0.0001	0.003 ± 0.001 ^a	Yes	0.0003 ± 0.0008 ^c	0.01 ± 0.01 ^a	0.0001 ± 0.0002 ^c	0.005 ± 0.001 ^a	Yes
Ni (mg/L)	0.0045 ± 0.0003 ^a	0.0067 ± 0.0003 ^{ad}	Yes	0.009 ± 0.004 ^b	0.008 ± 0.003 ^d	0.005 ± 0.001 ^a	0.0082 ± 0.0004 ^c	Yes
Pb (mg/L)	0.008 ± 0.002 ^c	0.03 ± 0.01 ^a	Yes	0.02 ± 0.01 ^d	0.03 ± 0.06 ^a	0.008 ± 0.001 ^b	0.023 ± 0.002 ^a	Yes
Zn (mg/L)	0.06 ± 0.01 ^{ab}	0.034 ± 0.003 ^a	Yes	0.05 ± 0.05 ^b	0.07 ± 0.02 ^a	0.05 ± 0.01 ^a	0.04 ± 0.01 ^{ab}	Yes

Notes: Within a row, mean values with different superscript (a-d) differ significantly.

pH, DO and COD for upstream and downstream. The turbidity level of downstream water was not equally affected by seasonal variation. DO levels at discharge point were lower in comparison with the corresponding levels for either upstream or downstream locations (Table 2). The DO of 6.8 ± 0.4 and 7.4 ± 1.4 mg/L were observed for wet and dry seasons respectively. These were lower than the levels at upstream (8.1 ± 0.5 ; 9.1 ± 1.5 mg/L) and downstream water (8.1 ± 0.4 ; 8.0 ± 1.1 mg/L). The depression in available DO level of the river is an indication of the presence of oxygen demand substances such as suspended materials in cement effluent. When this occurs the DO becomes a limiting factor for aquatic life to survive in Onyi River. However, certain species of fish can resist or tolerate low DO if decline is not abrupt (Vinson & Levesque, 1994).

9. Comparison of water quality of Onyi river with some water quality standards

The average levels of water quality parameters for upstream and downstream are shown in Table 3. No significant differences were found between the average values of pH, temperature, DO and zinc for upstream and downstream. Except temperature, DO, cadmium and lead, the levels of water quality parameters for downstream were above the corresponding levels for upstream. This trend has implication on the aquatic system. For instance, the environmental effects of alkaline wastewater on the receiving river can be severe (Roadcap et al., 2005). The impacts include increased water pH, high COD and oxygen depletion in the water, high sulphate loading and increase in metal concentration (Mayer, Younger, & Aumonier, 2008).

In spite of alkaline nature of cement effluent as observed in this study the downstream water pH could only increase by 0.1 units in comparison with the upstream water pH. The water pH for upstream was within the pH range of 6.5–9.0 for drinking water and aquatic life (Table 3). The total hardness level of 54.4 ± 2.4 mg/L for upstream was not above 500 mg/L set as a limit by WHO for drinking water. There is no adverse effect associated yet with water hardness in the WHO guidelines; however undesirable roles of hard water in heart disease and domestic utility have been mentioned by Schroeder (1960). Based on the classification in terms of degree of hardness, the Onyi River water is soft as total hardness level is less than 75 mg/L being mentioned for soft surface water (El-Sayed & Salem, 2015). The low level water hardness could be attributed to cement kiln dust that possibly flowed along with effluent as part of by product from cement plant. This dust is a significant resource material for lime substitute that can be utilised as a chemical addition for stabilising wastewater receiving river. The dust is known to contain high CaO content that can act as a precipitant. TSS as

Figure 3. Monthly variations in alkalinity, TSS, DO, BOD and COD levels.

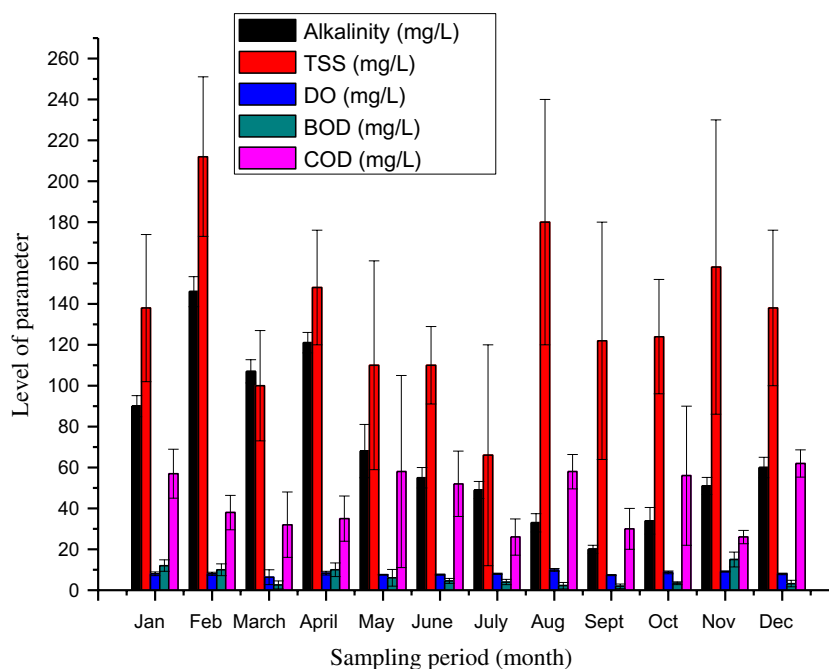


Table 3. Comparison of average water quality of Onyi river with some water quality standards

Parameters	Upstream	Downstream	WHO ^g	USEPA ^h	CQC ⁱ	Surface water quality by Prati et al. (1971)		
						Acceptable	Slightly polluted	Polluted
pH	7.7 ± 0.1	7.8 ± 0.1	6.5-8.0	6.5-8.0	6.5-9.0	6.0-8.4	5.0-9.0	3.9-10.1
Temperature (°C)	28.3 ± 0.1	27.1 ± 0.2	-	-	-	-	-	-
Total alkalinity (mg/L)	61.1 ± 2.5	69.5 ± 3.7	-	-	-	-	-	-
Total hardness (mg/L)	41.6 ± 1.5	54.4 ± 2.4	500	-	-	-	-	-
Calcium (mg/L)	16.3 ± 0.3	20.3 ± 0.8	-	-	-	-	-	-
Magnesium (mg/L)	6.08 ± 0.27	7.97 ± 0.38	-	-	-	-	-	-
Total solids (mg/L)	209 ± 14	305 ± 65	-	-	-	-	-	-
TSS (mg/L)	116 ± 15	134 ± 34	-	-	-	40	100	278
TDS (mg/L)	93.1 ± 6.25	170 ± 36	<600	500	500	-	-	-
Turbidity (FTU)	21.1 ± 1.33	24.9 ± 3.68	5	-	-	-	-	-
Cl ⁻ (mg/L)	9.77 ± 0.23	10.1 ± 0.60	250	250	250	-	-	-
SO ₄ ²⁻ (mg/L)	0.88 ± 0.06	1.82 ± 0.16	500	-	500	-	-	-
PO ₄ ³⁻ (mg/L)	25.5 ± 0.45	27.4 ± 2.41	-	-	-	-	-	-
NO ₃ ⁻ (mg/L)	127 ± 13	132 ± 24	50.0	10.0	-	12	36	108
DO (mg/L)	8.63 ± 0.54	8.10 ± 0.63	-	-	5.5-9.5	75-125	50-150	20-200
COD (mg/L)	34.0 ± 1.4	44 ± 11	-	-	-	20	6.0	12.0
BOD (mg/L)	3.66 ± 0.75	6.20 ± 1.39	-	-	-	3.0	6.0	12.0
Co (mg/L)	0.002 ± 0.001	0.003 ± 0.001	-	-	0.05	-	-	-
Cd (mg/L)	0.004 ± 0.002	0.002 ± 0.001	0.003	0.002	-	-	-	-
Cr (mg/L)	0.027 ± 0.001	0.034 ± 0.011	0.05	0.10	0.05	-	-	-
Cu (mg/L)	0.002 ± 0.001	0.003 ± 0.001	2.0	0.009	0.024	-	-	-
Ni (mg/L)	0.006 ± 0.002	0.007 ± 0.001	0.07	0.05	0.025	-	-	-
Pb (mg/L)	0.018 ± 0.002	0.016 ± 0.001	0.01	0.003	0.017	-	-	-
Zn (mg/L)	0.040 ± 0.004	0.045 ± 0.003	0.01	0.12	0.03	-	-	-

Note: (-) = not available.

^gWorld Health Organisation (2006).

^hUSEPA (1999).

ⁱCanadian Council of Ministers of the Environment (1999).

Table 4. Classification of surface water using water quality and metal pollution indices

Weight arithmetic water quality index		Metal pollution index	
WQI value	Rating of water quality	PI value	Class
0–25	Excellent	<1	No effect
26–50	Good	1–2	Slightly affected
51–75	Poor	2–3	Moderately affected
76–100	Very poor	3–5	Strongly affected
Above 100	Unsuitable for drinking purpose	>5	Seriously affected

Source: Goher et al. (2014).

low as 134 ± 34 mg/L was observed possibly owing to the presence of CaO, which could have enhanced settling of much of suspended solids from the effluent. The total dissolved solid level of the downstream water was well below the WHO limit of 600 mg/L (Table 3).

10. WQI for classification of Onyi River water quality

There was a need to determine the water quality of Onyi River downstream in view of its utilisation for domestic purpose. On this basis, a single index of pollution established by Prati et al. (1971) for the classification revealed that Onyi river water downstream fell in the class of slightly polluted water (Table 3).

Table 5. Measured quality rating (Q_i), weight unit (W_i) of each parameter and metal index variables

Parameters	S_i	Q_i	W_i	$(C_i/S_i)_{\max}$	$(C_i/S_i)_{\min}$
pH	8	80	0.00026	-	-
Temperature	NA	-	-	-	-
Total alkalinity	NA	-	-	-	-
Total hardness	500	10.98	4.09×10^{-6}	-	-
Calcium	NA	-	-	-	-
Magnesium	NA	-	-	-	-
Total solids	NA	-	-	-	-
TSS	NA	-	-	-	-
TDS	600	28.33	3.41×10^{-6}	-	-
Turbidity	5	498	4.09×10^{-4}	-	-
Cl ⁻	250	4.04	8.19×10^{-6}	-	-
SO ₄ ²⁻	500	0.364	4.09×10^{-6}	-	-
PO ₄ ³⁻	NA	-	-	-	-
NO ₃ ⁻	50	264	4.09×10^{-5}	-	-
DO	5.5	71.43	3.72×10^{-3}	-	-
COD	NA	-	-	-	-
BOD	NA	-	-	-	-
Co	NA	-	-	-	-
Cd	0.003	66.67	0.6821	1	0.33
Cr	0.05	68	0.0409	0.9	0.46
Cu	2	0.15	0.00102	0.002	0.001
Ni	0.07	10	0.02924	0.114	0.086
Pb	0.01	100	0.20464	1.7	1.5
Zn	0.05	90	0.04093	4.8	4.2

Note: NA = Not available (WHO standard is unavailable).

Using WQI and metal PI approaches for classification of water quality (Table 4), Onyi River can be classified on the basis of degree of metal contamination. The values obtained for Q_p , W_i and C/S_i variables are shown in Table 5. The values for the variables were obtainable because of the availability of WHO limits for the selected parameters. The WQI for the Onyi River was 85.2 with respect to drinking and domestic purposes. This indicates that the water quality of the river is very poor for such purposes. The metal PI of 3.46 was obtained showing that the river was strongly contaminated with heavy metal.

11. Proposed potential mitigating actions

Process for the manufacture of cement should include provision not only for ensuring a standard product, but also for avoiding the release of treated effluent into surface water. Nigeria is a temperate region with insufficient natural water resources especially in the dry season. Reuse of adequate treated cement effluent for irrigation is necessary to compensate for the shortage. Much of this practice should be embraced worldwide. Reuse of wastewater is a usual practice in Israel where 65–70% of wastewater of industrial origin is reused in agriculture after biological treatment (Ickson-Tal, Avraham, Sack, & Cikurel, 2003).

The inorganic load of the effluent will be greatly reduced by installing equipment for precipitation. In this case, sodium sulphate can be added to aid precipitation of most metals. It is necessary to increase the number of septic tank systems to sufficiently remove TSS from the effluent by sedimentation, flocculation and skimming. These processes are expected to also reduce organic load.

12. Conclusions

The Onyi river water was vulnerable to pollution by the discharge of cement effluent of inadequate quality. The effluent contained high load of suspended solid and COD substances. The magnitude of nitrate and phosphorus in the effluent were above the allowable limits and may allow for algal growth in the river. With upstream dilution of the effluent the Onyi River water at downstream location is still very poor and remains unfit for drinking and domestic purposes. Hence, the Onyi River water has potential to impact humans' health negatively if ingested. The river was strongly impacted with metal pollution. Intense treatment is therefore required for the effluent prior to discharges and regular monitoring of the Onyi river is equally recommended. More research is still needed particularly to determine the characteristic of sediments and assess the impact of the effluent on the sediments of the Onyi river.

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