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Environmental risk assessments of uses cyanide in gold extraction on water quality parameters and its effect on rhodanese activities in selected organs of *coptodon zillii* in igun reservoir, Southwestern, Nigeria

Abstract

This study was conducted to investigate the effect of cyanide on the pattern of rhodanese activity distribution in selected organs of *Coptodon zillii* and water quality of Igun reservoir. Fish and water samples were collected monthly for period of a year to cover both seasons. The physical parameters such as air and water temperature, conductivity, TDS, pH, depth, and transparency were determined. Air temperature and water temperature were determined *in situ* with a mercury-in-glass thermometer, pH and TDS were determined by calibrated pH meter (PCE-PHD Version 1.1 Model Q656697). Selected organs such as gill, fillet, and liver were used for rhodanese activity analysis while physico-chemical parameters were analyzed based on APHA (2012) standard methods. The pH concentration recorded in this study ranged from 7.1 - 8.1 with a mean of 7.48 ± 0.47 while highest pH mean concentration was observed in dry season (7.61 ± 0.5) compared with the rainy season (7.36 ± 0.24). The mean cyanide concentration was high during the rainy season (0.09 ± 0.03 mg/L) compared with dry season (0.07 ± 0.04 mg/L). The results of rhodanese activity recorded in the gills, fillet, and liver of *Coptodon zillii* (3.66 ± 3.19 RU/mg, 3.73 ± 2.58 RU/mg, and 3.73 ± 2.68 RU/mg) respectively. Water temperature, pH, and depth showed a positive correlation with rhodanese activity in the gills while a negative correlation was observed between water temperature and rhodanese in the fillet and liver of *Coptodon zilllii.* Based on the cyanide concentration recorded in this study shown that Igun reservoir is polluted which can be can harmful to humans and other organisms could due to archaic gold mining method using by local miner around the reservoir. *Coptodon zillii* inhabiting the reservoir showed a high concentration of rhodanese in the different tissues that could serve as the detoxifying mechanism. However, further biochemical analysis of others fish tissue should be examined to determine the effects of mining pollutants on aquatic biota.

Keywords: cyanide, rhodanese, reservoir, physico-chemical parameters, fish

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Abbreviations: APHA, American Public Health Association; BOD_5, Biochemical Oxygen Demand (Over 5 days period); CN, Cyanide; COD, Chemical Oxygen Demand; DO, Dissolved oxygen; E, East of Greenwich Meridian; EC, Electrical Conductivity; EC, Enzyme Commission; *et al.*, *et alli* (and others); Etc, *et cetera* (and the rest, and all others); Fig., Figure(s); kg, Kilogram; L (l), litre; (m), Metre; Max, maximum value; meqL^{-1}, millequivalent per litre; mg, Millgram; min, Minimum value; mL, millilitre; mm, Millimetre; N, North of the Equator; OM, Organic Matter; OC, Organic Carbon; P, Probability level; pH, Potential Hydrogen (Negative logarithm of H^+ in moldm^{-3} in a solution); r, Correlation coefficient; rpm, Revolution Per Minute; RU, Rhodanese Unit; S, Siemens; S.D, Standard deviation; TDS, Total Dissolved solids; TH, Total hardness; TOC, Total Organic Carbon; UNEP, United Nations Environmental Programme; WHO, World Health Organization of the United Nations

Background

In Nigeria, the rate of industrialization has accelerated rapidly, resulting in the introduction of several dangerous compounds into the environment, particularly aquatic environment, which has increased the amount of pollutants discharge into waterbodies.[1,2] The production of iron and steel, metal electroplating, the extraction of gold and silver from ores, petroleum refineries, and the production of synthetic fibers, plastics, fertilizers, and pesticides are just a few of the industrial operations that use cyanide on a global scale.[1] The largest anthropogenic sources of cyanide or/ major pollution events that can quickly release substantial amounts of cyanide compounds into the natural aquatic environment are thought to be the production of cassava, the processing of metals, and mining operations. Highly toxic sodium cyanide (NaCN) is used as the lixiviant by the international mining community to extract gold and other precious metals through milling of high-grade ores and heap leaching of low-grade ores.[2] Gold mining is often associated with positive economic benefits (job creation) and also increased standard of living.[3] However, mining activities may also have negative impacts on the environment due to exploration or/ mining process, inappropriate and wasteful working practices, and use of chemicals like mercury and cyanide in mining activities has been responsible for different types of adverse effects on the physical environment such as ecological disturbance, biodiversity loss, pollution of air, land, soil, water as well as the flora and fauna, landscape degradation and radiation hazards to man.[4] The potential adverse impacts of mining have also been asserted to include displacement of local people from ancestral lands, marginalization, and oppression of people belonging to lower economic classes.[5]

Cyanide is one of the few poisons chemicals that it antidotes exist if inhaled or injected by any organisms which can cause a dramatic and severe poisoning that can quickly result in death. It produces histotoxic (intracellular) hypoxic poisoning by the binding of the cyanide ion to the ferric (Fe^{3+}) iron of mitochondrial cytochrome oxidase. Histotoxic hypoxia is toxic to aerobic organisms because it impairs oxygen transfer in mitochondria, effectively suffocating the organism despite the presence of oxygen in the external environment and the preservation of a "functional" respiratory system. Due to its low boiling point, hydrogen cyanide will rapidly evaporate from the solution at temperatures above 25°C if it does not mix with metal ions that are already present in the water.[6] Greater surface water mixing, higher temperatures, and lower pH all increase the rate of volatilization.[7] However, it is to be expected that the rate of hydrogen cyanide volatilization will be greater in more energetic aquatic environments such as rapidly flowing rivers and larger water bodies during stormy weather. Compared to hydrogen cyanide, which, depending on temperature, has a half-life of a few hours to a few days, the free cyanide ion remains longer in water with a half-life of 15 days.[8] Due to its mode of toxicity, a highly destructive, homicidal, and chemical agent that affects fish can alter enzyme activity, cause behavioral changes, and cause tissue damage at low concentrations, but at higher concentrations in the waterbody, it can kill both its target and non-target organisms in the aquatic environment. Cyanide detoxifying mechanisms allow organisms to tolerate cyanide-polluted environments. Rhodanese is a ubiquitous enzyme that is found in all living things, from bacteria to people, and it is one of the enzymatic pathways.[9] Hence, the major pathway for cyanide metabolism is the conversion of cyanide (CN^-) to thiocyanate (SCN^-), in the presence of a sulphur donor by the enzyme rhodanese (thiosulfate cyanide sulfur transferase; EC 2.8.1.1).[10] Thiocyanate is the primary detoxification metabolite accounting for up to 80 percent of cyanide removal. Rhodanese (thiosulphate: cyanide sulfurtransferase; EC 2.8.1.1).

The activity of an enzyme in a given tissue or organ indicates that tissue or organ's capacity to detoxify cyanide, and rhodanese is more active in tissues that receive greater blood supply and are therefore more exposed to cyanide. Rhodanese is found in the cytosol, mitochondrion, and nucleus, according to research done by Ali et al.[11] on the substance's intracellular distribution. Due to its ability to transform cyanide at a measurable rate and prospective suitability for cleaning up polluted settings, the enzyme rhodanese has a great deal of potential to effectively transform and detoxify cyanide compounds.[12] Okonji et al.[13] reported that rhodanese is a key enzyme involved in the detoxification of cyanide in fish and he also reported reported rhodanese distribution in different tissues of *Clarias gariepinus* and *Heterotis niloticus* in the Osinmo reservoir. Enzymatic parameters are significant in detecting the functional condition of fish exposed to contaminants reported by Aladesanmi et al.,.[14] Because they react to changes in the aquatic environment with great sensitivity, fish are an essential bio-indicator of the environment and play an increasingly important role in the monitoring of water pollution.[15] Fish cannot escape the negative impacts of these contaminants, in contrast to other aquatic animal species, because their habitat is so close to them, according to Dickma and Leung.[16] According to Balali-mood et al.[17] assessing the biochemical and morphological changes in various organs, particularly the liver of the fish, can be used to study the acute, chronic, and long-term effects of chemical substances on biological systems. The red belly tilapia (*Coptodon zillii*) natural habitats are seasonal floodplain streams, lakes, and ponds with marginal vegetation but it has been imported outside of its original area and is widely distributed in Africa and the Middle East.[18] Fish population, distribution, and productivity are greatly influenced by the interaction of the physical and chemical qualities of water. This interaction also sheds light on how aquatic creatures interact with their surroundings.[19]

The hydro-metallurgical method based on the cyanidation process has been reported for the extraction of gold from the Igun gold ore deposit in Atakumosa West Local Government Area of Osun State. Recently, pollution of environment has increasingly gained a global interest especially, contamination of aquatic environment in gold mining communities is a serious environmental problem facing developing countries like Nigeria. The current study is to ascertain the impact of cyanide on water quality and it effect on distribution of rhodanese in the organs of *Coptodon zillii* in Igun reservoir, Southwest of Nigeria. The findings of this investigation will be examined the relationship between the potential function of rhodanese in *Coptodon zillii* organs and water quality.

Methods

Study area

Igun Reservoir five is an abandon gold mining reservoir which was located within Igun-Ijesha gold city in Atakumosa West Local Government Area of Osun State. It Lies on the Latitude 07°35' N to 07°38' N and Longitude 004°30' E to 004° 45' E, fell within a thick equatorial rainforest zone, containing tall trees with dense canopies and thick under growth that covers the rugged hilly terrain (Figure 1). It lies in the steep hills, prevalent narrow valleys and at the intersection of roads from Ile-Ife and Akure.[20] Rivers and Streams like Oika, Eleripon, and Osun rivers were impounded to form reservoirs in order to meet the mining needs of this community. The temperature of the area during the season ranged between 22 °C to 32 °C. Igun village is characterized by two seasons, which are the rainy and dry seasons, with the dry season extending from November to March while April to October marks the rainy season.[20] It has annual rainfall of 1200-1500 mm, which promotes dense vegetation.[21] The Igun village is a rural community of about 3000 populace that are farmers, hunters and other artisanal work are their major occupation. The mining industry has picked up in this area since Federal Government has declared Economic diversification Agenda from Oil and Gas to Agriculture, mining etc. in 1991. There is high increase of migrant miner (both foreign and local miners) into this area due to quality and purity of gold mine in Igun village. Recently, farming, hunting and other agricultural activities as been disrupted due to the archaic method of gold exploration used by the local miner resulted to degradation of environment in this community.

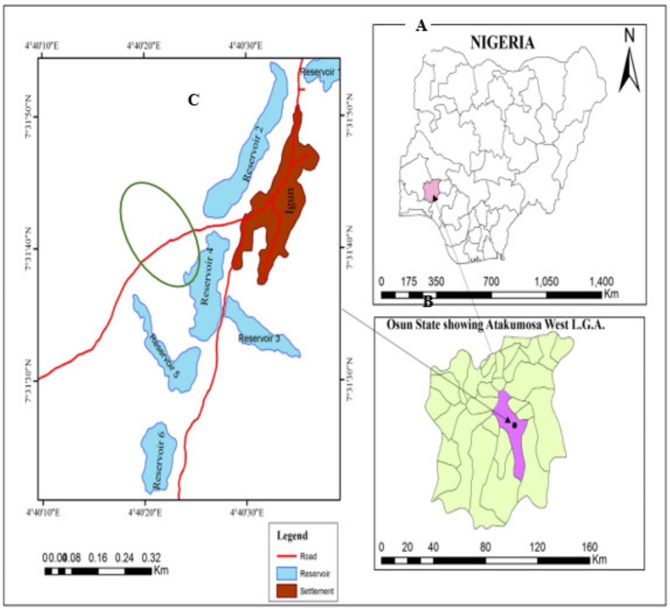

Figure 1 The map showing sampling station of Igun Reservoir 5 in Atakumosa West Local Government, Osun state, Nigeria.

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Sample collection and analysis

Fish sampling

Life adult specimens of *Coptodon zillii* was collected from Igun reservoir in Osun State on monthly basis for a year to cover both seasons (November 2016 to October 2017). The fish specimens were collected using cast nets and traps from the reservoir and transported to the laboratory where they were identified using standard identification keys prepared by Paugy et al.[22]

Enzyme isolation and homogenization

The fish specimens were silt open while organs such as gills, liver, and fillet were immediately dissected out and kept in a specimen bottle, and stored in the deep freezer at 4 ˚C until required. For the determinations, the organs were thawed and minced into smaller pieces using porcelain mortar and pestle. The samples homogenate of each fish organ was prepared by homogenizing the 5 g of each fish organ in 15 ml of 0.1 M phosphate buffer pH 6.5. The homogenate samples were filtered through a double layer of cheesecloth, centrifuged at 4000 rpm for 30 minutes using Micro field Centrifuge Model 800D and the supernatants were used as the source of enzyme.

Rhodanese assay

Rhodanese activity was measured according to the method of Agboola and Okonji[23] on the principles of the colorimetric determination of thiocyanate formation. The reaction mixture consisted of 0.5 ml of 50 mM Borate buffer (pH 9.4), 0.2 ml of 250 mM KCN, 0.2 ml of 250 mM $Na_2S_2O_3$, and 0.1 ml of each fish gills, fillet, and liver homogenate in a separate test tube in a total of volume of 1.0 ml. The mixture in each test tube was incubated for 1 minute at room 37 ºC and the reaction was stopped by adding 0.5 ml of 15% formaldehyde, followed by the addition of 1.5 ml of Sorbo reagent. The absorbance was read at a wavelength of 460 nm using Gulfex SM 23A spectrophotometer. One Rhodanese Unit (RU) was defined as the amount of the enzyme that would convert one micro-mole (1 µmol) of cyanide to thiocyanide in one minute at 37 ºC.

Water sampling

The water samples were collected in sterilized 2 litre capacity plastic bottles. Then at the point of collection, the bottles were rinsed thrice with reservoir water, thereafter 2 litres of water samples were taken. The physical parameters such as air and water temperature, conductivity, TDS, pH, depth, and transparency were determined *in situ*. Air temperature and water temperature were determined by a mercury-in-glass thermometer, pH and TDS were determined by calibrated pH meter (PCE-PHD Version 1.1 Model Q656697), and depth was determined by dipping the Secchi disc with a calibrated rope into the reservoir until it reaches the bottom, the calibrated rope was measured with a meter rule. Transparency was also determined by dipping the Secchi disc into the water body and the reading was taken at the point aphotic and photic zones and the average was taking. Nitrate, phosphate, and sulphate were determined using the colorimetric method in accordance with the standard methods of APHA (2017). Total alkalinity was determined by acid-base titration, dissolved oxygen was analyzed in the laboratory using Winkler's titration method. BOD_5 samples were kept in a dark cupboard to prevent photosynthesis to take place and on the fifth day, sample were fixed with Winkler's reagents and analyzed using the same dissolved oxygen procedure and standard (APHA, 2012). Calcium and magnesium were determined by the complexometric titration method. Organic carbon and organic matter were determined by the wet oxidation digestion method.

Cyanide determination in water

The level of cyanide in water was determined by distillation and titration. The water sample was poured into a round bottom flask of a distillation unit and a conical flask containing 50 ml of 1% alcoholic NaOH solution was placed at the collecting end of the distillation unit while the mixture in the flask was being heated. The distillate was collected into an alkaline medium unit, and 200 ml was obtained. The distillate was then titrated against 0.02 M $AgNO_3$ using 1 ml of freshly prepared 0.5% dithizone as an indicator. The endpoint indicated colour change from yellow to purple (Haque and Bradbury, 2002). (1 ml of 0.02 N $AgNO_3$= 1.08 mg HCN).

Statistical analysis

The data were subjected to descriptive statistics and inferential analysis using the SPSS software package (Version 20). Correlation analysis was used to determine the relationship between physico-chemical parameters on rhodanese distribution in the selected organs of the *Coptodon zillii* and Principal component analysis was used to show the interrelationship between the seasonal physicochemical parameters and rhodanese in fish organs.

Results

Air temperature value ranged observed during the sampling period fell between 22.00 - 32.00 ºC with an overall mean of 27.25 ± 4.57ºC, while the highest mean value of air temperature (28.9 ± 2.56 ºC) was recorded in the dry season compared to the rainy season with the mean value of 25.9 ± 3.33 ºC (Table 1). The water temperature value during the period of study ranged from 23 - 30 ºC (27.04 ± 3.11 ºC), while the highest water temperature was recorded during the dry season (28.9 ± 0.74 ºC) than in the rainy season (25.7 ± 1.89 ºC) and there is a significant difference ($p < 0.05$) in water temperature values between the seasons. The depth value recorded during the period of sampling ranged from 1.16 - 4.39 m (2.61 ± 1.37 m). Seasonally, the highest mean depth was recorded during the rainy season (2.93 ± 1.43 m) compared with the dry season (2.26 ± 0.30 m). The transparency value recorded during the period of study ranged from 0.38 - 9.10 m with a mean of 2.92 ± 4.14 m, while high transparency value was observed during the dry season (2.73 ± 3.57 m) than in the rainy season (0.96±0.39 m). The pH concentration recorded in this study ranged from 7.1 - 8.1 with a mean of 7.48 ± 0.47 and highest pH mean concentration was observed in dry season (7.61 ± 0.5) compared with the rainy season (7.36 ± 0.24). Conductivity value observed during the sampling period ranged from 84.1 - 160.5 µS/cm with a mean of 128.60 ± 34.94 µS/cm while lowest value was recorded in the dry season (124.02 ± 27.89 µS/cm) compared with the dry season (130.2 ± 14.34 µS/cm). The total dissolved solids concentration observed during the period of study varied from 72.5 - 117 mg/L (95.31 ± 22.89 mg/L) while highest value was observed in the dry season (93.02 ± 16.62 mg/L) than rainy season (87.19 ± 13.39 mg/L) as presented in Table 1.

The dissolved oxygen concentration recorded during the study period varied from 5.4 -19.04 mg/L with an overall mean of 10.61 ± 6.21 mg/L, while the lowest dissolved oxygen mean was recorded in in the dry season (7.84 ± 2.36 mg/L) than in the rainy season (10.86 ± 4.13 mg/L). The highest mean concentration of organic matter, total organic carbon, chemical oxygen demands, sulphate, magnesium and hardness (9.19± 4.04 mg/L, 5.33 ± 2.35 mg/L, 14.21 ± 6.26 mg/L, 0.54 ± 0.19 mg/L, 8.35 ± 4.01 mg/L and 34.65 ± 4.35 $CaCO_3$mg/L) were observed during the dry season than in the rainy season (8.59± 4.95 mg/L, 4.99 ± 2.87 mg/L, 13.30 ± 7.65 mg/L, 0.43 ± 0.32 mg/L, 6.38 ± 1.86 mg/L and 34.50 ± 2.62 $CaCO_3$mg/L) while nitrate, phosphate,

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calcium and cyanide concentrations (1.25 ± 0.57 mg/L, 31.33 ± 8.19 mg/L, 28.15 ± 2.13 mg/L and 0.09 ± 0.03 mg/L) were higher in the rainy season (Table 1). A principal component analysis (PCA) was used to find-out the interrelationship between the physico-chemical and rhodanese activities in fish organs among seasons in the reservoir. Four principal components, with eigenvalues >1 (which explained approximately 99.9 % (dry season) and 98.8 % (Rainy season) of the total variance), were obtained (Table 2). The first component for dry season, which accounted for 68.45 % of the total variance, showed strong positive loading (> 0.70) for water temperature, nitrate, TOC, cyanide and rhodanese in gills, fillet and liver, while on the second component account for 31.55 % showed strong correlation between alkalinity and COD. The first component in rainy season accounted for 88.20% showed positive correlation between water temperature, conductivity, DO, BOD, alkalinity, TDS, COD and phosphate while second component contributed to cyanide and rhodanese in fillet elucidating 10.60% of the total variance as shown in Table 2.

The relationship between rhodanese distribution in organs of *C. zillii* and water physico-chemical parameters (Table 2). Water temperature showed a significant positive correlation ($r = 0.835$, $p < 0.05$) with rhodanese distribution in gills and negative relationship with rhodanese in the fillet ($r = -0.674$) and liver ($r = -0.655$) of the *C. zillii*. Air temperature showed a positive relationship with rhodanese distribution in fillet ($r = 0.661$) and liver ($r = 0.731$) at $p < 0.05$. Depth showed a significant positive correlation relationship ($r = 0.855$, $p < 0.05$) with rhodanese specific activity in gills of *Coptodon zillii.* Water pH also had a positive correlation relationship with rhodanese activity in gills ($r = 0.666$) of *Coptodon zillii* presented in Table 3. The mean of rhodanese activity recorded in organs of *Coptodon zillii* such as gills, fillet, and liver are 3.66 ± 3.19 RU/mg, 3.73 ± 2.58 RU/mg, and 3.73 ± 2.68 RU/mg of protein as presented in Figure 2. The lowest mean values of rhodanese-specific activities in organs (gills, fillet, and liver) of *C. zillii* during the dry season were 3.04 ± 2.86, 2.74 ± 2.12, and 2.14 ± 1.04 RU/mg respectively. The rainy season had the highest mean values of rhodanese-specific activities of 4.09 ± 3.55, 4.33 ± 2.8, and 4.86 ± 2.98 RU/mg in the gills, fillet, and liver respectively as presented in Figure 3. There is positive cluster between conductivity, TDS, phosphate, alkalinity, calcium, COD, OM, BOD and water temperature in the rainy season while DO, TOC, nitrate, transparency, air temperature in the dry season and negative correlation between rhodanese in gills, fillet, liver and cyanide in dry season as presented in Figure 4.

Table 1 Seasonal Variation of Physico-chemical parameters from Igun Reservoir

Parameter	Units	Dry Season		Rainy Season		t- test		Overall	
		Min - Max	Mean ± SD	Min - Max	Mean ± SD	t	P	Min - Max	Mean ± SD
Air temperature	°C	25.00 - 32.00	28.90 ± 2.56	22.00 -30.00	25.90 ± 3.33	1.76	0.109	22.00 - 32.00	27.25 ± 4.57
Water temperature	°C	28.00 - 30.00	28.09 ± 0.74	23.00 - 29.00	25.70 ± 1.89	4.05	0.003*	23.00 - 30.00	27.50 ± 3.11
pH		7.10 - 8.10	7.61 ± 0.51	7.12 - 7.60	7.36 ± 0.24	-1.25	0.241	7.10 - 8.10	7.48 ± 0.47
Depth	m	2.07 - 2.80	2.26 ± 0.30	1.16 - 4.39	2.93 ± 1.43	-1.2	0.271	1.16 - 4.39	2.61 ± 1.37
Transparency	m	0.80 - 9.10	2.73 ± 3.57	0.38 - 1.40	0.96 ± 0.39	1.1	0.331	0.38 - 9.10	2.92 ± 4.14
Conductivity	µS/cm	84.10 - 160.50	124.02 ± 27.89	117.8 - 152	130.20 ± 14.34	-0.45	0.667	84.10 - 160.5	128.60 ± 34.94
DO	mg/L	5.40 - 11.60	7.84 ±2.36	6.40 - 19.04	10.86 ± 4.13	-1.61	0.141	5.40 - 19.04	10.61 ± 6.21
BOD	mg/L	2.80 - 9.60	5.60 ± 2.71	2.40 - 15.44	6.32 ± 4.61	-0.34	0.742	2.40 - 15.44	7.56 ± 6.21
Alkalinity	$CaCO_3$mg/L	55.00 - 72.66	62.93 ± 6.39	36.60 - 72.66	58.8 ± 11.68	0.78	0.456	36.60 - 72.66	59.23 ± 17.23
TDS	mg/L	72.50 - 112.90	93.02 ± 16.60	78.80 - 117	87.19 ± 13.39	0.65	0.536	72.50 - 117.00	95.31 ± 22.89
Organic matter	mg/L	3.57 - 13.82	9.19 ± 4.04	2.67 - 15.15	8.59 ± 4.95	0.23	0.825	2.67 - 13.82	8.30 ± 6.00
TOC	mg/L	2.07 - 8.02	5.33 ± 2.35	1.55 - 8.79	4.99 ± 2.87	0.23	0.824	1.55 - 8.79	5.11 ± 3.83
COD	mg/L	5.52 - 21.38	14.21 ± 6.26	4.14 - 23.45	13.30 ± 7.65	0.23	0.827	4.14 - 23.45	13.62 ± 10.20
Sulphate	mg/L	0.32 - 0.79	0.54 ± 0.19	0.02 - 0.81	0.43 ± 0.32	0.71	0.493	0.02 - 0.81	0.49 ± 0.38
Nitrate	mg/L	0.10 - 1.44	0.85 ± 0.52	0.37 - 1.98	1.25 ± 0.57	-1.26	0.293	0.10 - 1.98	0.97 ± 0.89
Phosphate	mg/L	13.75 - 40.79	26.18 ± 10.18	19.16 - 43.49	31.33 ± 8.19	-0.93	0.38	13.75 - 43.49	29.29 ± 15.03
Calcium	mg/L	18.92 - 37.37	26.3 ± 6.78	26.3 - 31.84	28.15 ± 2.13	-0.59	0.584	18.92 - 37.37	28.61 ± 7.88
Magnesium	mg/L	3.38 - 12.94	8.35 ± 4.01	4.34 - 9.11	6.38 ± 1.86	1.02	0.353	3.38 - 12.94	7.44 ± 4.44
Hardness	$CaCO_3$mg/L	30.70 - 40.75	34.65 ± 4.35	31.59 - 39.04	34.50 ± 2.62	0.06	0.958	30.70 - 40.75	35.52 ± 5.11
Cyanide	mg/L	0.04 - 0.10	0.07 ± 0.04	0.06 - 0.13	0.09 ± 0.03	-1.23	0.247	0.04 - 0.13	0.08 ± 0.04

Table 2 Principal component Analysis showing interrelationship between physico-chemical parameters and Rhodanese in the fish organs of Igun reservoir

	Dry season		Rainy season	
	DSPCA 1	DSPCA 2	RSPCA 1	RSPCA 2
Eigenvalue	15.74	7.26	23	4
Total Variance %	68.45	31.55	88.2	10.6
Cumulative variance %	68.45	99.9	88.2	98.8
Air temperature (°C)	0.23	0.17	0.02	0.03
Water temperature (°C)	0.67	0.07	0.85	0.03
pH	0.17	-0.28	0.37	0.19
Depth (m)	0.22	-0.19	0.01	0.06
Transparency (m)	0.23	-0.14	0.01	0.06
Conductivity (µS/cm)	0.22	0.19	0.87	0.13
DO (mg/L)	0.65	0.29	0.55	0.04
BOD (mg/L)	-0.23	0.15	0.52	0.03
Alkalinity (CaCO3mg/L)	0.21	0.81	0.96	0.05
TDS (mg/L)	0.25	0	0.61	0.15
Organic matter (mg/L)	0.25	-0.02	0.74	0.03
TOC (mg/L)	0.74	0.09	0	0.08
COD (mg/L)	0.22	0.77	0.83	0.06

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Table Continued...

	Dry season		Rainy season	
	DSPCA 1	**DSPCA 2**	**RSPCA 1**	**RSPCA 2**
Sulphate (mg/L)	0.14	-0.3	0.01	0.01
Nitrate (mg/L)	0.68	0.07	0.01	0.06
Phosphate (mg/L)	0.13	0.42	0.59	0.04
Calcium (mg/L)	0.19	0.24	-0.15	0.1
Magnesium (mg/L)	0.25	-0.01	0.07	0
Hardness (CaCO3mg/L)	0.08	-0.35	0.05	-0.05
Cyanide (mg/L)	0.56	-0.36	-0.04	0.77
Rhodanese in Gills (RU/mg)	0.87	-0.07	0.82	0.34
Rhodanese in fillet (RU/mg)	0.66	0.29	-0.37	0.87
Rhodanese in Liver (RU/mg)	0.71	-0.07	-0.02	-0.03

Table 3 Correlation matrix showing the relationship between physico-chemical parameters and rhodanese activities in the organs of *Coptodon zillii* in Igun Reservoir

Parameters	**Fish organs**			**Anova**	
	Gills	**Fillet**	**Liver**	**F**	**P**
Air temperature (°C)	0.329	0.661	0.731	189.4	0
Water temperature (°C)	0.835*	-0.674	-0 .655	226.6	0
pH	0.666	0.46	0.378	8.27	0
Depth (m)	0.855*	0.521	0.536	0.53	0.66
Transparency (m)	0.13	0.464	0.385	1.63	0.19
Conductivity (µS/cm)	0.343	-0.136	-0.188	429.4	0
DO (mg/L)	-0.177	-0.049	-0.044	11.06	0
BOD (mg/L)	-0.205	0.085	0.064	1.68	0.19
Alkalinity (CaCO3mg/L)	-0.004	-0.259	-0.228	329.4	0
TDS (mg/L)	-0.136	0.254	0.305	382.8	0
Organic matter (mg/L)	0.317	-0.204	-0.184	7.298	0
TOC (mg/L)	0.317	-0.204	-0.184	2.461	0.08
COD (mg/L)	0.318	-0.203	0.183	16.95	0
Sulphate (mg/L)	-0.022	0.479	0.512	5.187	0.003
Nitrate (mg/L)	0.487	0.282	0.297	3.39	0.03
Phosphate (mg/L)	0.31	0.373	0.444	74.01	0
Calcium (mg/L)	-0.2	-0.365	-0.377	152.5	0
Magnesium (mg/L)	-0.004	0.169	0.262	4.48	0.007
Hardness (CaCO3mg/L)	-0.304	-0 .408	-0.347	330.4	0
Cyanide (mg/L)	0.056	-0 .159	-0.172	6.68	0

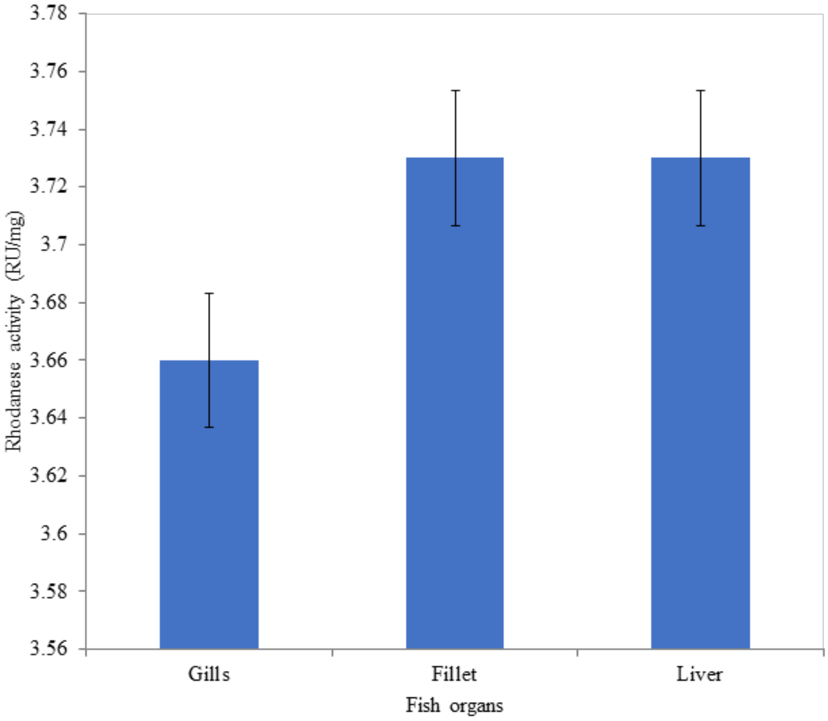

Figure 2 The Mean rhodanese activities in organs of *Coptodon zillii* in Igun reservoir.

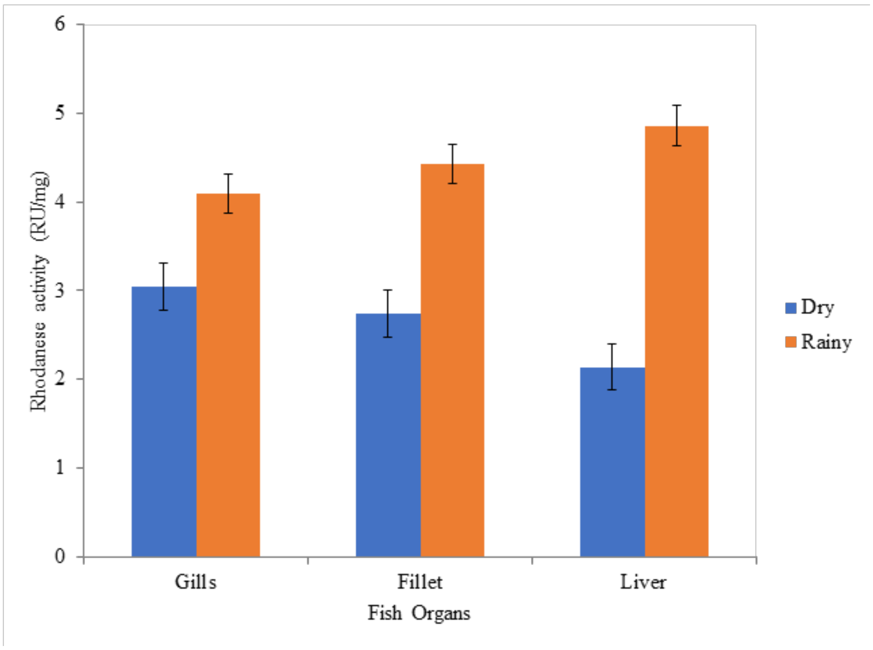

Figure 3 Seasonal variation in rhodanese activity in organs of *Coptodon zillii* in Igun Reservoir.

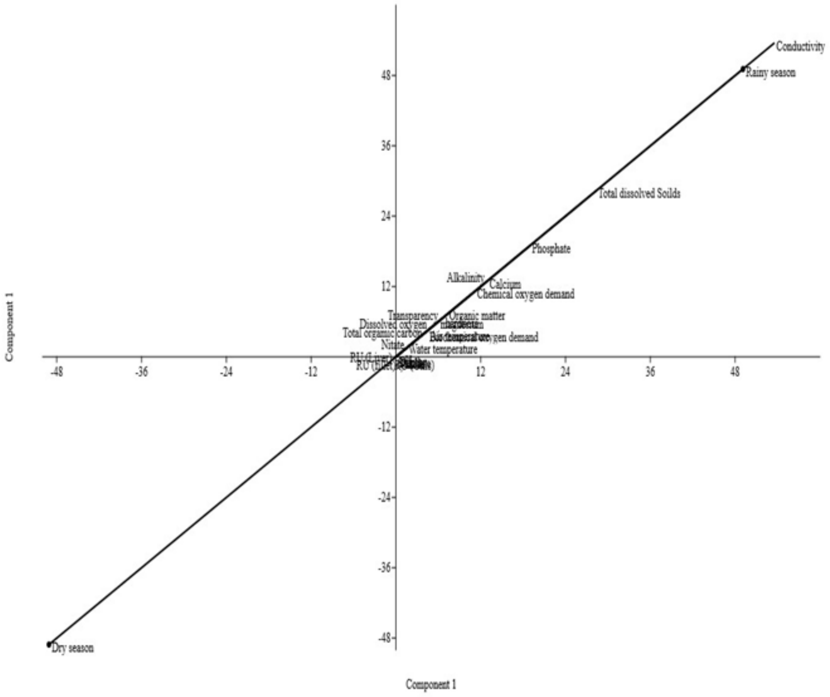

Figure 4 Principal component Analysis (PCA) showing relationship between seasonal variation in physico-chemial and Rhodanese activity in fish organs of Igun reservoir.

Discussion

Air and water temperature values ranged between 22 - 32ºC and 23 - 30ºC respectively for Igun reservoir was similar to the report of Arimiro *et al*., (2007) who recorded a range of 24.4 - 30.4ºC in Orogodo River and align with other temperature range observed in African tropical water bodies (Adagha (2017). The pH values of Igun reservoir ranged from 7.1 - 8.10 was similar to report of Ayoade et al.[24] that recorded pH range of 6.2 - 8.5 in Awba Reservoir. The pH observed in this study was within the range for inland waters (6.5 - 8.5) which make the reservoir water to be alkaline in nature and it adequate for fish production and.[6] The pH range recorded in this reservoir could be described as neutral with slight fluctuation to the alkaline condition due to cooling or the dilution effects of the rains.[25] Water is governed by function of the mineralogical and geochemical characteristics of the rocks underlying of the area which could alter

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the water quality such pH, conductivity etc..[26] The highest reservoir water depth (4.39 m) recorded was probably due to the high rainfall and the high surface water inflow from the upstream surrounding area. The lowest depth recorded during the dry season was probably due to the presence of high evaporation of water from the reservoir Ayoade et al.[24] Water transparency values ranges from 0.38 to 9.1 m was recorded in Igun reservoir fell within oligotrophic class as reported by Wetzel[27] who classified lakes at 0.8 - 7.0 m Secchi disc reading as eutrophic lakes while 5.4 - 28.3 m (oligotrophic lakes) and 1.5 - 8.1 m (mesotrophic lakes) respectively. This result also agreed with previous studies by Onozeyi[28] (River Ogun) and Mustapha, 2009 (Oyun lake) who recorded higher transparency during the dry season. Electrical conductivity values of 84.1 - 160.5 µS/cm were recorded in the Igun Reservoir during the period of study with a mean value of 124.02 ± 27.89 µS/cm in the dry season while a mean value of 130.2 ± 14.34 µS/cm was observed in the rainy season. Ioryue et al.[29] reported that an increase in conductivity values during the dry season might be due to a high rate of evaporation as well as sulphide-bearing rocks, which is facilitated by the past mining effect on the reservoir water while the decrease in conductivity value during the rainy season can be due to dilution by rainwater.[30]

Dissolved oxygen values (5.40 -19.40) recorded in Igun reservoir was similar to the report of Ikenweiwe and Otubusin[31] who recorded 1.75 - 11.20 mg/l in Aiba reservoir. The high concentrations of dissolved oxygen observed in this study might be due to low organic enrichment. The overall BOD_5 mean values of 6.02 ± 3.79 mg/L recorded during the period of study in Igun reservoir suggests that water has less concentration of organic matter and they could support aquatic biota.[32] The alkalinity was higher in the dry season than in the rainy season could be due to low water levels with its high concentration of salts and the lower value in the rainy season could be because of dilution as reported by Teame and Zebib.[33] The high TDS value recorded during the study period might be due to runoff from the mining grounds to the reservoir as well as runoffs from farmlands.[4,30] Nmerukini et al.[34] reported that high total dissolved solids could be due to the release of carbonates, bicarbonates, chlorides, phosphates, nitrates, calcium, magnesium, sodium, potassium, manganese, and organic matter. The high organic matter concentration observed during the period of study was within the range of 2.67 - 15.15 mg/L (8.84 ± 4.40 mg/L). The higher mean value of organic matter during the dry season compared to low value recorded in the rainy season, might be a result of reduction in water level due to evaporation, and the decay of falling leaves into the reservoir. The nitrate concentration range observed during the period of study, fairly exceeded the typical concentration of freshwaters (< 1.0 mg/L), though it was tolerable for fish growth and satisfied surface water quality standards (< 5 mg/L) according to WHO[6] and Amah-jeray et al.[35] Vushe and Herta[36] reported that initial rains flush out deposited nitrates from soil hence, the nitrate value in this study was less compared to WHO[6] recommended guideline value of 50 mg/L.

The mean concentration of sulphate observed during this study was 0.48 mg/L which was below the WHO[6] guideline limit of 250 mg/L for wastewater. High levels of sulphate can cause a laxative effect in human.[37] The phosphate value during the period of study was high when compared to the WHO (2011) permissible limit of 5 mg/L. The phosphate range recorded might be due to allochthonous substance deposited into the reservoir from surrounding farmlands[19] and detergents used by miners and people of this community in washing of their clothes. In the present study, calcium concentration ranged between 18.92 - 37.37 mg/L, and magnesium values 3.38 - 12.93 mg/L recorded from this study were within the permissible limit recommended by (WHO, 2011). The water hardness also ranged between 30.70 - 40.75 $CaCO_3$mg/L with a mean concentration of 34.57 ± 3.25 $CaCO_3$mg/L recorded in Igun reservoir during the period of study which fell within soft water class. Higher values of water hardness during the dry season might probably be due to low water levels and a high rate of evaporation.

The cyanide concentration range of 0.04 - 0.13 mg/L observed from Igun reservoir with a mean concentration of 0.08 ± 0.03 mg/L was higher than the prescribed limit (0.07 mg/L) of WHO[6] for drinking water. The cyanide value recorded in this study corroborated with the study of Oriyomi et al.[38] who reported that the level of cyanide in Igun reservoir is higher in the rainy season compared to the dry season. The cyanide concentration in the study area was high and might be attributed to local techniques which involved using of chemicals such as cyanide and mercury in gold mining activities in Igun Reservoir. People living in this community are exposed to most hazardous toxic chemicals especially young hardworking youths who were struggling to earn for living with little or no regards for their health safety and degradation of the environment. Based on the report of medical expertise that using of archaic method of gold exploration could lead to serious health issues such as infertility, severe cough, itching and can also damage internal organs like kidneys and livers and pollution of rivers, streams, groundwater as well as the flora and fauna in that environment. The highest rhodanese activities of 3.74 Ru/mg in the organs of *Coptodon zillii* were found in the liver and fillet could the due to the different activity of rhodanese in different fish organs which play primarily physiological role in each fish organ.[39] Rhodanese has been reported to be present in high concentrations in the liver of animals and also reveals the ability of that organ to detoxify cyanide.[11,23]

The result of this study was similar to the report of Suganthi et al.[40] Kaloyianni et al, (2021), Schuijt et al.[41] that toxicological studies revealed the impacts of contaminants on the aquatic ecosystem through the measurement of biochemical parameters in the liver of the fish. The higher activity of rhodanese in the liver of *Coptodon zillii* might be attributed to the role of the liver as the main organ of biotransformation in detoxification processes in general.[42] Aminlari et al.[43] were of the view that the level of rhodanese in different tissues of animals is correlated with the level of exposure to cyanide. The high rhodanese activity observed during the rainy season could be because the enzyme was being induced in the presence of cyanide.[44] This result corroborates with the findings of Okonji et al.[45] who reported high rhodanese activity in *Clarias gariepinus* and *Heterotis niloticus* during the rainy season at Osinmo reservoir. The high level of pollution increases the metabolic activities of the reservoir, hence leading to high air and water temperature that in turn increases the rhodanese activity in the *Coptodon zillii* organs. PCA data exploration analysis revealed the possible contribution of anthropogenic pollutants such as mining activities to high concentration of cyanide in this reservoir and when there is concentration in water during dry season, it affects rhodanese activity in fishes. Akinsiku et al.[46] had earlier reported that a high level of pollution in a water body increases metabolic activities in the water hence resulting in the release of heat, which favors enzyme activity. Shinde et al.[47] reported that positive correlation between rhodanese activity and other environmental variables means that as a one parameter increases the other parameter also increases vice versa while negative correlation means as a parameter increases, the other parameter decreases.

In this study, the air temperature was positively correlated with rhodanese activity in the fillet and liver of *C. zillii*, Water temperature showed a significant positive correlation with the gills of *C. zillii*, pH was positively correlated with rhodanese activities in the gills of *C.*

zillii, and sulphate was positively correlated with rhodanese activity in the liver of *C. zillii*. Hence, the interrelationships among these variables viz physico-chemical parameters and rhodanese activity in *Coptodon zillii* showed the level of dependency on each other which align with report of Aladesanmi et al.[14] The positive significant relationship of rhodanese with water temperature was probably due to an increase in water temperature that resulted in to increase in biochemical activities in the fish organs. Furthermore, the water temperature has direct effects on enzyme activity,[48] as temperature directly affects the metabolic rate in organisms, hence affecting other processes.[49] There was no correlation between cyanide concentration in water and rhodanese activity in the organs of *Coptodon zillii.* This study is in agreement with Okonji et al.[9] who reported that rhodanese though plays a role in cyanide detoxification, but no correlation between cyanide accumulation and rhodanese activity has been observed.[50–56]

Conclusion

Based on these results obtained from this study showed that Igun reservoir is heavily polluted with cyanide which can harmful to humans living in this community and aquatic organisms while *Coptodon zillii* can survival in this environment is due to rhodanese present in the fish that detoxified cyanide. Due to the importance of fish as a cheap source of protein to the populace, regular monitoring of water and fish should be ensured to avail portable water and food safety to humans. However, further biochemical analysis of others fish tissue should be examined to determine the effects of mining pollutants on aquatic biotas.

Declarations

Ethics approval and consent to participate

The experimental procedures conformed with the national and international standards on the use of laboratory animals in accordance with the National Institutes of Health Guide for the Care and Use of Laboratory Animals (NACLAR, 2004).

Consent for publication

Not applicable.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Competing interests

No competing interest exists in the research outcome presented in the article.

Funding

Not applicable.

Authors' contributions

OOK designed, and supervised the study, proofread and approve the manuscript, and REO co-supervised the biochemical aspect of the research. OVK carried out the fieldwork, laboratory analysis, and statistical analysis and wrote the manuscript. OEO, TAA, and STA proofread the manuscript. All authors read and approved the final manuscripts.

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