

Seasonal Variations in Physicochemical and Nutrient Water Quality of River Tano in Ghana

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Abstract: Increasing anthropogenic activities within the catchment of River Tano continues to threaten the river water quality but data is limited. Seasonal variations in some physicochemical and nutrients water quality parameters of River Tano were studied between November, 2016 and October, 2017 using electrometric and standard methods. The objective was to assess changes in physicochemical parameters and nutrient concentrations with the season and to generate useful information for water quality managers and policy makers to ameliorate the problem. The results showed significantly higher rainy season values for all the nutrients and the physicochemical parameters studied. The source of River Tano recorded pH levels lower than WHO minimum permissible level for both seasons but got corrected after 7.2 km from the source. The river was also challenged in terms of colour (61.0 ± 4.6 NTU), total phosphorus content (0.376 ± 0.3 mg/L), total suspended solids (69.7 ± 24 mg/L), turbidity (96.2 ± 21 mg/L) and electrical conductivity ($252\pm33 \mu$ S/cm) since the levels of these parameters exceeded the permissible levels for WHO. Some physicochemical parameters and nutrients correlated strongly to indicate a possible common source to the water body. Cluster analysis extracted two clusters of the seasonal sampling sites for physicochemical parameters and three clusters for nutrients also confirming their respective possible common sources to the river. It is recommended that the buffer zone policy must be enforced to avert further deterioration of the river water quality. Industries must be compelled to treat their effluent before discharging into water bodies

Keywords: Freshwater, Physicochemical, Nutrient, Seasonal Variations, River Tano

1. Introduction

Freshwater bodies serve as conduits for water, nutrients, sediment and biota from the continents to the sea [1]. Its availability is essential for life support on earth [2]. They are known to support numerous ecological services therefore changes in aquatic conservational factors such as pH, redox potential, nutrient loads and temperature may have serious negative effects on the ecosystem functions [3, 4]. Generally, anthroponic activities such as land use changes, discharge of untreated industrial effluent, agricultural and municipal run offs tend to compromise the physical and nutrient river water qualities [5, 6].

River Tano is one of the major rivers in Ghana with

much socioeconomic importance [7]. The water in the river has been dammed at three separate locations along the course of the river by the Ghana Water Company Limited (GWCL) for treatment and distribution to over 1,276,444 people in some communities within the Ahafo, Bono and Bono East Regions [8]. Report received from the Sunyani Regional Office of GWCL showed that the company incurs higher cost of treatment in the rainy season [9]. This might be attributed to increasing anthropogenic activities such as farming, lumbering and urbanization within the catchment [10-13]. Domestic and commercial wastes generated by communities in the basin are channelled into the river untreated [14]. Again, runoffs from farming activities along river banks continue to load nutrients and other organic debris into the river. These

activities pose serious threats to surface water quality and the ecosystem services of the river [14]. Nutrients such as nitrogenous compounds emanating from fertilizer applications, municipal and agricultural runoffs can cause eutrophication [15-18]. Drinking water sources containing high levels of nitrate and nitrite nitrogen may cause health problems like methenoglobinemia commonly called "blue baby" to infants [19]. Phosphorus in water is known to stimulate microbial growth [20]. The question being asked is: how do the concentrations of the pollutants in River Tano change with the seasons and does that inform decision?

In order to ameliorate the seasonal increased treatment cost encountered by the Ghana Water Company Limited and the water quality threats to the Tano basin, there is a need to formulate a policy to guide land use along the banks of the river. Such policies and informed decision making require data on the seasonal variations in physicochemical and nutrient concentrations in the river but such data for the Tano basin is limited. Water quality management involves understanding of data trends and seasonal variations in the physicochemical water quality parameters. Such information is useful to water quality managers and those involved in environmental risk assessment [21, 22]. This study sought to assess the seasonal variations in physicochemical and nutrient water quality parameters of the Tano River.

2. Materials and Method

2.1. Study Area

The Bono East, Bono and Ahafo portions of the Tano basin in Ghana were used in this study. The portion is located within latitudes 7°40'39.04"N-6°57'51.98"N and longitude, 1°52'20.41"W-2°19'37.42"W (Table 1). It begins from the river which is Tuobodom in the Techiman North District of the Bono East Region and runs through the Bono and the Ahafo Regions to the point where it joins the Ashanti Region of Ghana. There are several communities with population of about 1,276,444 people with diverse anthropogenic activities such as agriculture, commercial, wood processing, auto mechanics, food processing and mining within the catchment [23]. In terms of relief and land cover, the area is characterized by both flat and peak surfaces with wet evergreen and moist-semi deciduous ecological zones [8, 24]. The buffer zone of the river bank within the study area has been compromised through human activities leaving few shrubs, tree canopy cover and bare area in some cases [23]. The rainfall pattern is characterized by dry and rainy seasons. The rainy season occurs between April and October, while the dry season occurs between November and March [25]. The average annual rainfall is between 1,140-1,300 mm per annum with temperatures averaging about 25.8°C. The area is warm and moist with relative humidity ranging between 75-85% throughout the year. The annual evapotranspiration is about 1,500 mm with the annual runoffs being about 2,774 million m^3 [8, 26].



Figure 1. Map of Ghana indicating river Tano catchment, sampling sites and land use: Source [23].

2.2. Study Design and Selection of Sampling Site

Periodic sampling of water from nine (9) sampling locations along river Tano course were carried out within the area of study from November, 2016 to October, 2017. The dry season was represented by November, 2016 to March, 2017 whilst April to October, 2017 represented the rainy season. The concentrations of eleven (11) physicochemical parameters namely, temperature, pH, dissolved oxygen (DO), total suspended solids (TSS), total dissolved solids (TDS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), electrical conductivity (EC), turbidity, redox potential and colour as well as five (5) nutrients namely, nitrogen: nitrate (N-NO₃), ammonia (N-NH₃), ammonium (N-NH₄⁺) and nitrite (N-NO₂) as well as total phosphorus (TP) were studied in water samples. The sampling locations starting from the source to downstream were named S₁, S₂, S₃, S₄, S₅, S₆, S₇, S₈ and S₉ [23]. The selected sampling sites were mapped and geo-referenced with the help of a handheld Garmin 62SC Geographical Positioning System (GPS) gadget (Table 1 and Figure 1).

Table 1. GPS Locations of the sampling sites.

Samuling Site	GPS Coordinates		Sites intervals	Sampling sites distance intervals (km)		
Sampring Site	North (°)	West (°)	Sites intervals	Sampling sites distance intervals (kin)		
S ₁ 7.	.67751	-1.87233	S_1	0		
S ₂ 7.	.61532	-1.91023	S_1-S_2	7.283		
S ₃ 7.	.55001	-1.95143	S ₂ -S ₃	7.727		
S ₄ 7.	.45963	-1.94125	S ₃ -S ₄	9.096		
S ₅ 7.	.27958	-2.26844	S ₄ -S ₅	37.35		
S ₆ 7.	.05365	-2.31737	S ₅ -S ₆	23.12		
S ₇ 6	.96822	-2.32827	S ₆ -S ₇	8.612		
S ₈ 6	.80694	-2.42809	S7-S8	18.97		
S ₉ 6	.61289	-2.39906	S ₈ -S ₉	19.62		

Source: [23].

2.3. Sampling and Sample Treatment

Water samples were collected between November, 2016 and October, 2017. Before sampling, sample bottles were treated as previously described by [27]. At the sampling site, the cleaned bottles were again rinsed with the river water for the container to equilibrate with water before sampling [23]. Collection of water samples were done by immersing the sampling bottles to a depth of about 20 cm from the surface of the River with the mouth pointing against direction of flow of the River as previously described by [23]. About 1 L of water was collected in each of the plastic bottles [2]. Collected samples were corked, labelled and kept in an ice chest loaded with ice [23]. This procedure was repeated at all the nine (9) sampling sites. Duplicate samples were taken and preserved.

2.4. On-site Measurements of Some Physical Parameters

All the physical parameters except BOD, COD and colour were measured on-site using their respective meters. All meters were calibrated and rinsed with the water samples before they were used. pH and temperature were measured with a pH meter with a thermometer attached (SmartCHEM model). The electrode of the instrument was dipped into the water samples until the readings were stable and was recorded from the screens. Electrical conductivity (EC), redox potential and Dissolved Oxygen (DO) were also measured (SmartCHEM model). Turbidity (HACH model 2100N meter) and Total Suspended Solids (3150 model TSS meter). Total dissolved solids (TDS: 3150 model meter), colour (HACH 6000 spectrophometer). BOD (Velp Scientific System) and COD (Wagtech Potalab Photometer 7100 model) in mg/L O_2 as previously described by [28-30]were measured in the laboratory.

2.5. Analysis of Nutrients

Analysis of total phosphorus, nitrate, nitrite, ammonium and ammonia were done using APHA 4500, EPA 353.1 with Aquakem 200 discrete analyser methods similar to what was previously described by [31, 32] with some modifications.

2.6. Quality Control (QC) and Quality Assurance (QA)

In order to ensure that the results produced were scientifically acceptable, the normal laboratory regulations and procedures such as proper cleaning of apparatus, calibration of equipment, analyses in duplicates and reagent blanks were strictly observed. For the analysis of nutrients in water samples blanks were included and results were compared to the limit of reporting. Laboratory control samples (LCS) and matrix spike recoveries were measured as percentage of the analyte recovered from the samples compared with the amount of analyte spiked into the sample. Duplicate and matrix spikes relative percentage differences were measured against their original counterpart samples according to the formula:

Laboratory Control Samples =
$$\frac{\text{Absolute difference of the two results}}{\text{Average of the two results}} x 100\%$$
 (1)

The results revealed that Laboratory Control Samples

(LCS) expressed as a percentage ranged between 97–108%.

Nutrient	QC Reference	LCS% Recovery	
NO ₃ -N	LB33707	97	
NH ₃ -N	LB33707	99	
NO ₂ -N	LB33707	104	
NH_4^+-N	LB33707	103	
TP	LB33754	108	

Table 2. Results from the Lab control samples expressed as percentages of quality control and assurance.

TP means total phosphorus.

2.7. Data Analysis

All analytical results were entered in EXCEL Spreadsheet and imported into R software for analysis. The mean and the standard deviation for each of the parameters for each study site as well as for all sampling sites put together were calculated. A t-test was used to compare means of the data for the rainy season and dry the season physicochemical parameters and nutrient concentrations in water samples. The means of the physicochemical parameters and nutrients in water were compared with WHO standards for drinking water. Pearson's product-moment correlations were also used to compare the level of correlation among the physicochemical as well as nutrients in water samples studied. A p-value of less than 0.05 was considered significant. Dendrogram cluster analysis (DCA) was performed using standard method as Squared Euclidean Distances and Centroid linkage [33].

Applied interpolation method based on Inverse Distance Weighted (IDW) and GIS mapping techniques were used to show the spatial distribution of nutrients and physicochemical parameters in water [23, 34]. The interpolation was done by comparing the measured nutrient concentrations and physicochemical parameters at each sampling location with WHO standards. The cell values were calculated for the unmeasured site by averaging the sampled data in the target site using ArcGIS version 10.2.1.

3. Results and Discussion

The results for the physicochemical parameters (temperature, pH, DO, TSS, TDS, BOD, COD, EC, turbidity, redox potential and colour) and nutrients (total phosphorus, ammonia, ammonium, nitrate and nitrite) are shown in Tables 3–8. The results revealed that nitrite (NO₂-N) were not detected in any of the sampling sites for both rainy and dry seasons. This contradicted NO₂-N levels ranging between 0.006 mg/L-0.470 mg/L recorded previously in the study area [27].

3.1. Seasonal Variations of Physicochemical Water Quality Parameters

The results for the seasonal variations in physicochemical water quality of River Tano are shown in Tables 3 and 4. The results revealed that the rainy season physical parameters were generally higher than the dry season. This may be due to influx of eroded materials due to high run offs experienced in the rainy season [35]. The highest temperature was

recorded at S_3 (29.8±1°C) in the dry season while the lowest was recorded at S_7 (25.0±0.3°C) in the dry season. High surface water temperatures are generally associated with discharge of hot effluent into the river or absence of trees to provide shade [36]. Therefore the recorded temperature at sampling site S_3 may be due to absence of trees to provide shade as well as hot effluent discharged from the Techiman main market. Low pH values: 5.34 ± 0.1 for rainy season and 5.42 ± 0.3 for dry season were recorded at sampling site S_1 which is the source of the river. The recorded low pH values at the source were consistent with [7] baseline studies for the Tano basin and were attributed to geological factors. This was corroborated by studies conducted by [27] in some groundwater sources in the study area.

The highest DO was recorded in the dry season at sampling site S_7 (7.3±0.2 mg/L) whereas sampling site S_3 recorded the lowest DO value (4.6±1.2 mg/L). The lowest DO at S₃ may be due to high organic matter in the effluent discharged into the river from the Techiman main market and from the abattoir located around the market. This observation was corroborated by the high BOD (78±9 mg/L), TSS (150 \pm 1 mg/L) and colour (92 \pm 3 Pt. Co unit) recorded at S₃. The measured COD values were relatively higher in the rainy season than the dry season for all sampling sites. Introduction of non-biodegradable materials into the river bodies generally result in high COD [18, 35]). Higher rainy season COD values measured may be attributed to influx of nonbiodegradable materials into the river through runoffs and effluent discharges. High BOD and COD may reduce the oxygen content of the water bodies which may affect aquatic life [2, 37]. Turbidity values recorded were generally higher in the rainy season than the dry season values. The highest was recorded at S_2 in the rainy season (215±3 mg/L) while the least was recorded at sampling site S_7 (10±9 mg/L) in the dry season. Higher turbidity values in rainy season may be due to influx of colloidal particles such as clay, silt, fine organic in the rainy season into the river [38].

Electrical conductivity (EC) is a measure of mobile ions and salts in water bodies [39]. Higher EC and TDS values are generally recorded in the dry season than the rainy season because of high evaporation in dry season and dilution effect experienced in the rainy season [2]. This assertion was corroborated in this study where the highest EC was recorded in the dry season at sampling site S₃ (802±9.0 μ S/cm) and the lowest at sampling site S₁ (21±4.0 μ S/cm) in the rainy season. However, the lowest TDS recorded at sampling site S₁ (10.5±2 mg/L) in the dry season and the highest at sampling site S₈ (152±40 mg/L) in the rainy season contradicts the assertion. High TDS at study site S₈ in the rainy season may be due to the enhanced solubility of salts in the rainy season.

The mean rainy season value for redox potential is significantly higher than the dry season values. This suggests that more oxidation-reduction reactions take place in the dry season than the rainy season probably due to dilution effect during the rainy season [40].

Table 3. Site by site mean rainy and dry seasons physicochemical water quality parameters.

WIIO atda	Site by site seasonal mean concentrations ± SD										
who stus.	-	6.5-8.5	-	20	1000	-	-	5-150	5	-	0-15
Parameters	Temp	pН	DO	TSS	TDS	BOD	COD	EC	Turb.	Redox Poten.	Colour
c	26.5±1	5.34±0.1	6.8±0.2	26±7	24±1.1	18±2	26±3	21±4.0	31±16	-1±0.0	20±1
\mathbf{S}_1	25.7±0.4	5.42±0.3	7.0±0.3	18±5	10.5±2	9±4	13±6	23±8.0	18.5±1	-3±0.1	11±1.3
C	26.7±2	7.29±0.5	5.6±0.0	113±2	90.7±9	71±5	96±9	208±5	215±3	-4±1.3	99±10
32	25.7±1	7.10 ± 0.1	4.7±0.1	70±4	56.7±1	31±3	46±8	133±14	66±9	-21±2	51±8
C	27.6±1	7.40±2	5.1±1	150±1	76.0±1	78±9	65±2	402±4	207±11	-7.3±1	92±3
33	29.8±1	7.64±0.1	4.6±1.2	41±3	31.0±1	48±1	57±22	802±9.0	33±25	-23±3	22±3.0
S	27.3±3	7.79±1	6.0±0.5	91 ±4	60±6	51±11	77±20	199±71	108±3	-9±10	65±7
54	23.9±2	6.88±0.6	6.7±1.5	25 ± 3	24±8	45±10	36±16	66±0.4	16±5	-15±9	25±55
S	27.6±1	7.38±5	7.0±0.1	40±10	56±3	31±1	65±1	157±19	48±1	-6.9±5	42±5
35	24.2±0.1	7.15±0.1	7.2±0.4	31±12	32±9	18±13	21±4	81±22	23±11	-0.6±1	24±7
S	27.2±2	7.25±2	7.2±0.0	47±4	76±1	17±3	26±4	285±12	51±10	-2.3±1	33±1
36	24.3±0.4	7.47±0.2	6.9±0.2	34±6	51±10	13±8	16±10	151±18	12±14	-1.1±4	21±4
S	27.0±1	7.44±1	7.27±1	43±1	142±7	32±0.0	49±3	292±14	44±4	-4.9±5	45±3
37	25.0±0.3	7.2±0.01	7.3±0.2	39±4	88±15	16±1.4	19±7	358±11	10±9	-8±2.0	17±2
S.	27.2±6	7.5±4	6.5±8	57±9	152±40	67±0.1	102±40	375±13	59±5	-11±2	60±6
38	27.8±0.2	7.3±0.2	6.6±0.1	47±4	89±11	28±0.2	40±12	278±97	25±10	-16±3	27±8
S.	26.5±3	7.7±1	6.0±3	60±2	130±22	65±2	106±77	326±9	104±8	-2±0.4	92±5
39	25.6±0.1	7.6±0.1	6.5±0.0	60±6	96±14	32±4	47±23	221±8	60±4	-10±1	46±8

Units^b: temperature = °C; DO = mg/L; TSS = mg/L; TDS = mg/L; BOD = mg/L; COD = mg/L; EC = μ S/cm; turbidity = NTU; colour = Pt-Co units; redox potential = mV. Bolded figures represent rainy measurements.

Table 4. Relationship between season and physical water quality parameters.

	Means for all sampling si	tes ± SD	t volue	Davalaa	
Physical water Quality Parameters	Dry Season Rainy Season		t-value	r-value	
Temperature	25.7±1.1	27.1±1.2	-2.52	0.021	
pH	7.03±0.1	7.23±2.0	-0.871	0.390	
DO	6.35±0.7	6.37±1.1	-0.055	0.956	
TSS	38.0±18	69.7±24	-2.82	0.009	
TDS	53.0±9	90.0±11	-2.32	0.027	
BOD	26.7±3.2	47.9±5.4	-3.19	0.003	
COD	32.7±1.2	67.7±2.7	-3.63	0.001	
EC	235±51	252±33	-0.272	0.788	
Turbidity	29.3±15	96.2±21	-3.85	0.001	
Redox potential	-10.8±1.5	-5.27±5.3	-2.37	0.025	
Colour	27.4±0.9	61.0±4.6	-3.90	0.001	

3.2. Geospatial Analysis of Physicochemical Quality Analysis

Geospatial analysis was done for only parameters with WHO standards (pH, colour, TDS, TSS, turbidity, conductivity). The results for the geospatial analysis of the physical water quality (interpolation) are shown in Figure 2. The results showed that the River Tano is challenged in terms of colour, TSS, turbidity and conductivity for both rainy and dry seasons at all sampling points except the source. Both dry and rainy seasons recorded values higher than the WHO standards for drinking water for colour, TSS and turbidity. This means that the high water treatment cost as purported by GWCL will not only happen in the rainy season but in the dry season as well. Turbid and high TSS laden water is unfit for domestic use [2, 18]. It is aesthetically unacceptable and it is the cause of unpleasant taste and odours and choke the gills of

aquatic fish [41]. They may also lead to reduction in light penetration which may affect photosynthetic activities in the river as well as being a conduit for other pollutants such as pathogens, nutrients and heavy metals into the Tano River [42]. Consequently, GWCL may have to use more chemicals for water treatment in order to ensure that all contaminants are removed from the water before consumption.

The pH at the source is also challenged since the measured pH at the source was lower than WHO range of 6.5–8.5. It however, got corrected after the source probably due to the discharge of alkaline effluent into the river [10-11, 14]. This observation is consistent with [7] baseline studies at the Tano basin due to geological factors. The geological make-up of the basin is alternate formations of Birimian, greywacke and granitoids which may account for the low pH at the source as well as the observed TDS [7]. Low pH water tends to corrode metal pipes as well as posing serious health problems to people who may consume the water [40, 43].



Figure 2. Geospatial analysis of physicochemical parameters.

3.3. Seasonal Variations of Nutrients Water Quality Parameters

The results for the seasonal variations in nutrients water quality parameters are shown in Table 5. The results showed that the measured rainy season nitrate concentrations were significantly higher than the dry season concentrations for all sampling sites. The highest nitrate concentration was recorded at sampling site S_4 (11.6±0.4 mg/L) in the rainy season whereas the lowest nitrate concentration was recorded at sampling site S_9 (0.43±0.2 mg/L) in the dry season. The source of nitrates to water bodies may be through the use of

fertilizers and fuels for blasting in mining. During the rainy seasons, farming activities increase with intense use of chemical fertilizers along river banks. Therefore runoffs in compromised buffers along river banks may carry them into water bodies [16]. This was corroborated by studies conducted by [31] at Tejgaon industrial area of Bangladesh and was attributed to high runoffs in the rainy season. Higher nitrate concentrations in surface water may lead to eutrophication. Unlike nitrate that recorded higher concentrations in the rainy season than the dry season, 6 of the sampling sites recorded higher ammonia and ammonium concentrations in the dry season than the rainy season. This may be due to higher decomposition and accelerated oxidation of NH₄⁺ to NH₃ which was aided by high temperatures [44, 45]. Nitrite was not detected in any of the sampling sites. Total phosphorus concentrations were insignificantly higher in the rainy season than the dry season. The highest TP concentration was recorded at sampling site S₄ (0.35±0.4 mg/L) in the rainy season while the lowest was recorded at sampling site S₁ (0.06±0.1mg/L) in the dry season. This may be due to influx of higher runoffs in the rainy season than the dry season.

Table 5. Site by site seasonal nutrient concentrations.

S1''4-	Site by site mean seasonal nutrient concentration ± SD (mg/L)							
Sampling site	NO ₃ -N	NH ₃ -N	N-NO ₂	N-NH4 ⁺	ТР			
C1	(2.79±0.6)	(0.07±2.2)	< 0.05	(0.01±0.1)	(0.18±0.1)			
51	0.58±0.1	0.6±0.2	< 0.05	$0.01{\pm}0.01$	0.06±0.1			
S2	(3.79±1.4)	(0.97±1.3)	< 0.05	(0.23±0.4)	(0.55±0.7)			
52	0.75±0.4	0.9±0.1	< 0.05	0.35±0.5	0.27±0.4			
\$2	(9.4±2.0)	(1.64±4.0)	< 0.05	(3.11±1.3)	(1.5±0.7)			
55	5.4±5.0	1.41±0.1	< 0.05	5.95 ± 8.0	0.38±0.5			
S 4	(11.6±0.4)	(0.09±8.0)	< 0.05	(0.06±0.04)	(0.35±0.4)			
54	0.65±0.4	0.39±0.5	< 0.05	0.14±0.1	0.28±0.4			
85	(5.23±0.5)	(0.21±3.8)	< 0.05	(0.08±0.05)	(0.19±0.2)			
55	0.95±0.9	0.53±0.8	< 0.05	0.11±0.4	0.26±0.3			
84	7.79±1.4	0.23±6	< 0.05	(0.14±0.1)	0.06±0.1			
50	0.49±0.4	0.46±0.4	< 0.05	0.86±0.1	0.26±0.3			
\$7	(7.87±1.1)	(0.25±5)	< 0.05	(0.08±0.04)	(0.1±0.02)			
57	0.55±0.4	$0.44{\pm}0.4$	< 0.05	0.86±0.1	0.28±0.4			
00	(6.85±1.5)	(0.04±5)	< 0.05	(0.05±0.04)	(0.20±0.1)			
58	0.65±0.1	0.88±0.2	< 0.05	0.04±0.2)	0.34±0.4			
20	(7.54±0.8)	(0.56±5.3)	< 0.05	(0.03±0.3)	(0.25±0.2)			
59	0.43±0.2	0.55±0.1	< 0.05	0.08±0.1	0.08±0.4			
WHO standards	10	1.5	1-1.5	-	0.07			

TP means total phosphorus: <0.05 means below detection limits: bolded figures in brackets represent rainy season measurements.

Table 6.	Means	ofall	l sampling sites.	
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Nutrionta	Means of all sampling sites ± SD) (mg/L)	4 and be a	p-value	
Nutrients	Dry Season	Rainy Season	t-value		
Nitrate	1.16±0.9	6.97±1.3	-7.17	4.83e-08	
Ammonia	0.674±1.1	0.486±0.2	1.19	0.244	
Ammonium	0.786±0.4	0.418±2.2	0.538	0.596	
Nitrite	< 0.05	< 0.05	N/A	N/A	
Total phosphorus	0.266±1.0	0.376±0.3	-0.805	0.428	

3.4. Geospatial Nutrient Analysis

Geospatial analysis was done for only nutrients with WHO standards. The results are shown in Figure 3. The results showed that the Tano River is challenged in terms of total phosphorus concentration for both seasons since the levels for both seasons exceeded the [46] standards for total phosphorus in drinking water. Generally, phosphorus in water bodies are attributed to agricultural runoffs [20] but higher levels are rarely found in surface water bodies since they are usually taken up by acquatic plants [1]. In this particular study, higher total phosphorus in the Tano River may be attributed to discharge of untreated industrial effluent into the river. Higher levels of phosphorus in water bodies (above WHO standards) may stimulate microbial growth and eutrophication when combined with nitrogenous compounds [15, 16-18]. The study site S_4 recorded levels that exceeded the WHO standards for nitrate and ammonia in the rainy season. This may also be due to agricultural runoff and industrial discharges in the rainy season [17, 31]. Drinking water sources containing high levels of nitrate may cause health problems like methenoglobinemia commonly called "blue baby" to infants [19].



Figure 3. Geospatial analysis of nutrients distribution at the different sampling sites.

3.5. Dendrogram for Physical and Nutrient Water Quality Parameters

The results of the dendrogram for the physical and nutrient water quality parameters are shown in Figures 4 and 5. The horizontal axis of the dendrogram represents the dissimilarities between clusters while the vertical represents the seasonal sampling points. The results showed that two clusters were extracted for physicochemical parameters while three clusters were extracted for nutrient water quality. The clusters may suggest similar pollution sources (point and non-point sources) to the river [33]. The clusters for the physical parameters were: cluster 1: DS₁, RS₁, DS₄, DS₅, DS₂, RS₅, DS₆ and RS₄. Cluster 2: RS₈, RS₉, DS₈, RS₆, RS₇, DS₉, DS₇, RS₂, RS₃ and DS₃ (Figure 4). The clusters for the nutrients were: cluster 1: RS₅, RS₉, RS₈, RS₂, DS₄ and DS₅; cluster 2: DS_1 , DS_2 , DS_6 , DS_7 , DS_8 , DS_9 , DS_9 and RS_7 ; cluster 3: RS₁, RS₄, RS₆ and RS₃ (Figure 5).

3.6. Correlation Relationships Between the Physicochemical Parameters and Nutrients

The correlation relationships between the physicochemical parameters and that of nutrients are shown in Tables 7 and 8 respectively. The results showed strong positive relationships between temperature and COD, temperature and EC, pH and TDS, pH and BOD, pH and COD, pH and EC, DO and redox potential, TSS and BOD, TSS and COD, TSS and turbidity, TSS and colour, TDS and colour, TDS and COD, BOD and colour, turbidity and colour. The strong correlation relationships may suggest that those physicochemical parameters are from a common source to the River Tano and are likely to be anthropogenic activities such as farming and effluent discharge [23]. The following pairs exhibited strong negative relationships. They were: BOD and DO, COD and DO, DO and colour, DO and redox potential, EC and redox potential.

For the nutrient relationships, a strong positive relationship was observed between total phosphorus and NH_4^+ -N.



Figure 1. Dendrogram of the seasonal sampling sites for physical parameters.



Figure 2. Dendrogram of the seasonal sampling sites for nutrients.

Table 7. Correlation relationships between physical water quality parameters.

	Temp	pН	DO	TSS	TDS	BOD	COD	EC	Turb	Redox P	Colour
Temp	1										
pH	0.267	1									
DO	-0.455	-0.281	1								
TSS	0.356	0.407	-0.605	1							
TDS	0.237	0.545*	0.052	0.287	1						
BOD	0.430	0.491*	-0.615	0.760*	0.451	1					
COD	0.488*	0.527*	-0.461	0.575*	0.609*	0.881*	1				
EC	0.695*	0.565*	-0.493	0.260	0.332	0.432	0.359	1			
Turbidity	0.315	0.296	-0.539	0.932*	0.299	0.794*	0.663*	0.163	1		
Redox P	-0.347	-0.246	0.609*	-0.033	0.055	-0.126	-0.129	-0.498*	0.123	1	
Colour	0.294	0.466	-0.487*	0.833*	0.550*	0.863*	0.851*	0.176	0.913*	0.100	1

TP = total phosphorus; Redox P = redox potential; temp = temperature; * means relationship is significant at $p < 0.05^d$.

Table 8. Correlation relationships among nutrients in water.

	NO ₃ -N	NH ₃ -N	ТР	NH4 ⁺ -N
NO ₃ -N	1			
NH ₃ -N	-0.007	1		
TP	0.302	0.728*	1	
NH4 ⁺ -N	0.183	0.731	0.476*	1

4. Conclusion

The seasonal variations in some physicochemical parameters and nutrients in the River Tano were studied. The results showed significantly higher mean rainy season concentrations for most of the physicochemical parameters studied. The water quality of River Tano is challenged in terms of EC, colour, TSS and turbidity since their measured levels exceeded the respective WHO permissible levels. The pH at the source of the river is below the WHO minimum permissible level for pH (acidic) but gets corrected right after the source due to anthropogenic activities.

For nutrient water quality, River Tano is challenged in terms of total phosphorus (TP) levels and NO_3 -N around the Techiman market. The levels of TP exceeded the WHO standards for drinking water throughout the basin as well as NO_3 -N around the main market.

Cluster analysis for the seasonal sampling points extracted two clusters for the physicochemical parameters and three clusters for nutrient water quality which suggested similar pollution sources. Most of the physicochemical parameters and the nutrients showed significant relationships except for BOD and DO, COD and DO, DO and colour, DO and redox potential, EC and redox potential where the relationships were significantly negative.

It is recommended that the buffer zone policy must be enforced to avert further deterioration of the Tano River quality. The Environmental Protection Agency, Ghana, must compel industries to treat their effluent before discharging into the external environment.

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