



Research article

Evaluation of the physicochemical parameters on the water quality of the major rivers of Zamboanga del Norte, Philippines

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Abstract: The province of Zamboanga del Norte is endowed with ample water resources which are the primary sources of domestic water for the people in the area. Nevertheless, these water resources face several man-made and industrial activities that generate unwanted pollution. In this study, the physicochemical characteristics of the major rivers of Zamboanga del Norte, Philippines were investigated to know the present condition and assess the overall water quality. The physicochemical parameters that were investigated includes pH, temperature, nitrate-nitrogen (NO₃-N), total suspended solids (TSS), total phosphates (PO₄²⁻) and total mercury (Hg). The results of the water analyses revealed that the pH, temperature, nitrate as NO₃-N and the total Hg were within the acceptable range prescribed by Department of Environment and Natural Resources (DENR) and World Health Organization (WHO). However, there was a significant increase of the total suspended solids (TSS) concentrations of 138±58.9, 142.3±36.6 and 243±9.5 mg/L, respectively from downstream, midstream and upstream of Sindangan river. The total suspended solids (TSS) concentrations exceeded the permissible limit of 25–65 mg/L recommended by Department of Environment and Natural Resources (DENR). Furthermore, the data showed that all values of the total phosphates for all the river systems exceeded the prescribed limit. Thus, to maintain the water quality of these rivers, proper monitoring and government intervention are very much required.

Keywords: Physicochemical parameters; river water; water quality; Dapitan River; Dipolog River; Dicyo River; Sindangan River; Patawag River

1. Introduction

The lives on Earth depend primarily on water. Humans and other living organisms do not exist without this God-given resource. Water quality is very important for these living organisms to survive. The Philippines in general, and Zamboanga del Norte in particular, rely mainly from streams and rivers as the primary sources of domestic water. Water quality control of the surface water from the river systems is a crucial task not only for the local government authorities involved in formulating policies and regulations but also for the obedient constituents as well. The degraded state of the water resources in the Philippines arises from the absence of an effective system to stop the uncontrolled dumping of untreated sewage, garbage and industrial effluents into water bodies [1]. Thus, proper management and sustainable planning is very much needed [2] to sustain life.

Water pollution affects not only the quality of water but also human health [3]. Contaminants from residential and commercial establishments, industrial and agricultural activities along the rivers can affect the water quality and consequently cause health problems [4,5]. Domestic household wastes, small-scale mining chemicals, oil and grease used in quarrying activities, water run-offs, plastic materials, face masks, face shields, personal care products, debris from construction activities and fertilizers are the main sources of contaminants of these rivers. Additionally, liquid wastes from residences, fishponds and agricultural lands are also spilled into the river systems. Campiseño and Laranjo [6] posited that around 10% of homes have neither toilet facilities nor sewage treatment and some have concentrations of septic tanks or cesspools that leak large amounts of wastes into the shallow waters of Liboran and Dapitan Rivers.

On the other hand, chemicals and heavy metals found in pesticide runoffs and industrial effluents which are drained into the river systems can damage health. Toxic wastes can kill or contaminate marine life while people who eat seafood from polluted areas or who swim in contaminated water become vulnerable to gastric and other infections. Heavy metals are coming from natural sources or anthropogenic in nature [7,8]. Regardless where these metals come from, they still pose health problems to humans and aquatic organisms [7]. Heavy metals tend to accumulate in human organs and nervous system and interfere with their normal functions [4]. Pleto and coworkers [1] asserted that accumulation of heavy metals in fish can also pose health problems through increased blood lead levels of the consumers. Another water quality indicator is the coliform bacteria [9]. Fecal coliforms are commonly used as indicator of sanitary quality that helps to assess possible presence of fecal and pathogenic organisms and thereby ultimately evaluating the quality of the environment [10]. The higher the level of indicator bacteria, the higher the level of fecal contamination and the greater will be the risks of water borne diseases [11].

In the future, managing water quality becomes more complex due to new chemicals that are introduced every year which in turn makes it difficult for the authorities to make decisions as to how many water quality parameters should be measured regularly [12]. In the meantime, scientific laboratory procedures with high-tech instruments are made to assess the water contaminants and maintain high quality standard of potable water. These standard procedures which are followed worldwide include the analysis of different parameters such as pH, turbidity, conductivity, total suspended solids (TSS), total dissolved solids (TDS), total organic carbon (TOC) and heavy metals.

These parameters can affect the drinking water quality if their values are in higher concentrations than the safe limits set by the World Health Organization (WHO) and other regulatory bodies [4, 13].

In the Philippines, The Philippine Clean Water Act of 2004 (RA 9275) was enacted to protect Philippine water bodies from pollution from land-based sources. This act provides for a comprehensive water quality management and for other purposes and preserve it for future generations. In this regard, the Department of Environment and Natural Resources (DENR) was leading the implementation of the law and standard limits for certain physicochemical parameters were determined based on their importance in sustaining aquatic life in the river system [14].

However, despite the present law, man-made activities, industries, commercial establishments, agricultural activities, construction activities, quarries, etc. still dump unnecessary wastes into the water bodies that results to pollution. Thus, the useful indicators to monitor the water quality of the river water were analyzed.

The present study aims to assess the physicochemical attributes of the five (5) major rivers of the province of Zamboanga del Norte, Philippines namely: Dapitan River, Dipolog River, Dicayo River, Sindangan River and Patawag River. The study seeks to investigate the nitrate-nitrogen, temperature, total phosphates, total suspended solids, total mercury and pH at three selected stations (downstream, midstream and upstream) along the rivers over 8 months using standard methods. The researchers hoped that the findings of the study could provide baseline information on the current status of the five major rivers of Zamboanga del Norte, Philippines.

2. Materials and methods

2.1. Study area

Five river systems of Zamboanga del Norte namely: Dapitan River, Dipolog River, Dicayo River, Sindangan River and Patawag River are the study areas of this investigation. The five (5) river systems and the selected stations (downstream, midstream and upstream) are shown in Figure 1. The origin of Dapitan river is Mt. Malindang. It is situated at $8^{\circ} 17' 21.26''$ to $8^{\circ} 39' 3.1''$ north latitudes and $123^{\circ} 23' 42''$ to $123^{\circ} 37' 51.6''$ east latitudes. The sampling sites for the downstream part of Dapitan river comprise the five barangays of Ba-ao, Opao, Ilaya, Sulangon and Polo in the city of Dapitan. The sampling sites for the midstream portion is located at El Paraiso in the municipality of La Libertad and the sampling sites for the upstream part is located at Bergado in the municipality of Mutia.

Dipolog river is situated at $8^{\circ} 17' 10.72''$ to $8^{\circ} 36' 54.22''$ north latitudes and $123^{\circ} 19' 55.2''$ to $123^{\circ} 36' 3.6''$ east latitudes. The sampling sites of the upstream section of Dipolog river comprise of 5 barangays namely: Sinai from the municipality of Sergio Osmeña, Diolen and Pasorio from the municipality of Mutia; and Singaran from the municipality of La Libertad. The midstream section of the river encompasses 3 sampling sites namely: Dionum and Desin from the municipality of Mutia and San Pedro from the municipality of Polanco; and the downstream section covers 5 barangays for the sampling sites namely: Dap-dap and Poblacion North from the municipality of Polanco, Gulayon, Barra and Turno from the city of Dipolog.

On the other hand, Datu Tangkilan was the sampling site for the downstream portion of Sindangan river. Sto. Nino and Baloc were the sampling areas for the midstream part and Nato was the sampling site for the upstream part of Sindangan river (Latitude: $8^{\circ} 13' 5.88''$; Longitude: $122^{\circ} 59' 44.87''$). Dicayo river originates from Mt. Malindang and traverses through Sergio Osmeña, Zamboanga del Norte and passes through the highland barangays of Katipunan, Zamboanga del Norte and flows

towards the Sulu Sea (Latitude: 8° 31' 03" N; Longitude: 123° 17' 30" E). The sampling sites for the downstream portion of Dicayo river consist of Daanglungsod, Barangay Dos and San Antonio. The sampling areas for the midstream part are composed of Sitog and Miatan. Barangay Dabiak is the only sampling site for the upstream portion of the river.

According to history, the name of the Patawag river came from the Cebuano word “Tawag” which means “to call”. When the bridge wasn’t built yet, the people from either side of the river used to call for a boat for them to be able to cross, as they would not dare cross on their own as it was known that the river was infested with crocodiles. Thus, both sides of the river were called “Patawag”. To lessen the confusion, the localities have labeled Patawag-Labason for the Labason-side of the river and Patawag-Liloy on the other side [15]. The sampling stations for Patawag river start from Barangay Patawag in the municipality of Labason for the downstream portion. Barangay San Jose in the municipality of Kalawit for the midstream station and Barangay Molos in the municipality of Tampilisan for the upstream part. River water samples were collected from these locations following the standard methods used in the study.

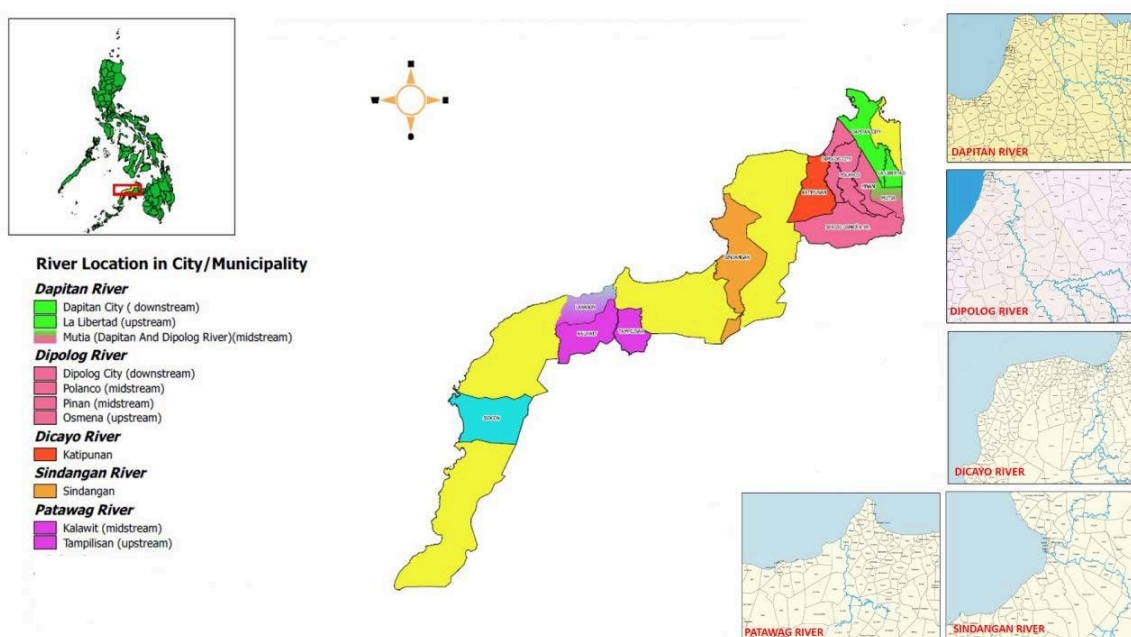


Figure 1. Map of the study area.

2.2. Sample collection

To avoid contamination, all glassware, high-density polyethylene (HDPE) storage bottles for reagent solutions and plastic items were washed first with soap and rinsed with tap water and then acid cleaned following a standard procedure [16]. All items for collecting and storing samples and reagents were washed with distilled water, soaked in a 10% HCl solution for at least 24 h [17] and rinsed three times with distilled water. The washed items were dried and stored in zip locked polyethylene bags.

2.3. Physicochemical measurements

Water samples were obtained from the sampling sites (upstream, midstream and downstream) and portions of the five river systems were used for two replicates for pH, temperature, nitrates (NO₃-N),

total phosphates, total suspended solids (TSS) and total mercury. The previously cleaned polyethylene bottles were washed thrice with river water before filling with water samples. The river water samples were taken at a depth of not more than one meter (1 m). The exact locations of the sampling sites were randomly selected and recorded using the Global Positioning System (GPS).

Water sampling and tide level notations were done in the morning. Water samples were collected from the study area for a period of eight months (January to August 2021) to determine the seasonal fluctuation of these parameters. A liter of water sample was obtained from every station in two replicates for the physical and chemical parameters mentioned. The containers were completely filled with water then capped and properly labeled to prevent from spillage and displacement, respectively. The tests on each sample were done upon return to the laboratory, within one hour of collection. However, the pH and temperature tests were carried out in-situ at the sampling sites using a pH tester from Hanna Instruments model HI98108 pHep+.

The total phosphate concentrations were analyzed using Stannous Chloride Method. The total phosphate can be expressed by [18]

$$mg\ P/L = \frac{mg\ P\ (in\ approximately\ 104.5mL\ final\ volume) \times 1000}{mL\ sample} \quad (1)$$

The nitrates were analyzed as NO₃-N using the Nitrogen, Nitrate (Colorimetric, Brucine) Method [19]. This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H₂SO₄ solution at a temperature of 100 °C and the color of the resulting complex is measured at 410 nm. The total phosphate and NO₃-N concentrations were measured by a UV-Vis Spectrophotometer distributed by SKZ Industrial Co., Limited of Shandong, China. The total suspended solids were measured by filtering the well-mixed water sample through a pre-weighed standard glass-fiber filter. Then the filter and the residue retained on it were dried to a constant weight in a 103–105 °C oven. The increase in filter weight represents the TSS. The TSS concentration can be calculated by the following equation [20,21]:

$$Total\ Suspended\ Solids(mg/L) = \frac{(A - B) \times 1000}{Sample\ Volume(mL)} \quad (2)$$

where *A* represents the final weight of filter + dried residue in *mg* ; and *B* represents the weight of filter in *mg*.

The total mercury of the river water samples was determined using Cold-Vapor Atomic Absorption Spectrometric Method [21]. The analysis was carried out using Shimadzu Atomic Absorption Spectrophotometer model AA-7000.

2.4. Statistical analysis

SPSS 26 was used for the statistical analyses of the study. One-way ANOVA was performed to compare the five (5) river systems.

3. Results

3.1. Physicochemical analysis

The climate of the Philippines can be divided into two major seasons: 1) rainy season and 2) dry season. The rainy season starts from the month of June and ends in November. The dry season, however, starts from December to the month of May. Hence, our sampling period was between these periods from the month of January and ends in August for a span of 8 months. Four months under the dry season (January, February, March and April) and four months under the rainy season (May, June, July and August). Moreover, typhoons have a great influence on the climate and weather conditions of the Philippines that is why the remaining four months (September, October, November and December) were not included because these are considered typhoon - months where heavy rains are experienced in the country.

The summary of the physicochemical analyses of the five rivers are presented in Table 1. These values were compared to the World Health Organization (WHO) [13] and the Department of Environment and Natural Resources (DENR) [22,23] water quality standards. Tables 2, 3 and 4 present the upstream, midstream and downstream, respectively of the one-way ANOVA results of the five rivers of the study. Figure 2 shows the comparison of the different physicochemical parameters of the sampling sites of the five rivers of the study.

Table 1. Physicochemical analyses of the major rivers in this study.

Rivers		Parameters					
		pH	T (°C)	PO ₄ ²⁻ (mg/L)	NO ₃ -N (mg/L)	TSS (mg/L)	Total Hg (µg/L)
Dapitan	DENR	6.5–8.5	26–30	0.025	7	25–65	1–2
	Downstream	7.42±0.56	27.3±0.26	0.28±0.01	0.14±0.03	11±1.87	0.3±0.3
	Midstream	6.89±1.1	29.57±0.64	0.28±0.008	0.02±0.0001	1.9±0.04	0.1±0.006
	Upstream	7.46±0.81	25.97±0.72	0.31±0.03	0.02±0.0003	1.9±0.04	0.1±0.006
Dipolog	DENR	6.5–8.5	26–30	0.025	7	25–65	1–2
	Downstream	7.45±0.3	29.78±1.19	0.28±0.009	0.1±0.05	27.86±5.7	0.4±0.3
	Midstream	7.71±0.55	27.59±0.92	0.34±0.05	0.06±0.01	5.31±2.8	0.3±0.1
	Upstream	7.67±0.36	26.9±1.99	0.33±0.07	0.05±0.03	5.16±6.3	0.4±0.1
Sindangan	DENR	6.5–8.5	26–30	0.025	7	25–65	1–2
	Downstream	7.47±0.12	28.65±0.5	0.29±0.008	0.29±0.04	138±58.9	0.4±0.2
	Midstream	7.26±0.24	29.02±0.36	0.3±0.02	0.42±0.03	142.3±36.6	0.8±0.15
	Upstream	7.27±0.34	29.23±0.21	0.29±0.004	0.39±0.02	243±9.5	0.53±0.15
Dicayo	DENR	6.5–8.5	26–30	0.025	7	25–65	1–2
	Downstream	7.35±0.13	28.07±0.74	0.36±0.11	0.18±0.10	24±9.5	0.1
	Midstream	8.24±0.22	29±0.28	0.29±0.005	0.1±0.08	4.2±1.2	0.1
	Upstream	8.26±0.09	26.5±1.1	0.29±0.004	0.06±0.06	4.0±1	0.1±0.002
Patawag	DENR	6.5–8.5	26–30	0.025	7	25–65	1–2
	Downstream	7.56±0.06	30.8±0.71	0.29±0.01	0.13±0.09	49.7±19.75	0.18±0.21
	Midstream	7.5±0.04	25.95±1.57	0.29±0.008	0.2±0.1	33±15.72	0.2±0.14
	Upstream	7.49±0.05	26.57±0.06	0.29±0.004	0.04±0.03	20±6.56	0.093±0.092

Table 2. One-way ANOVA results for the upstream sites.

River	Upstream											
	pH		Temperature		PO ₄ ²⁻		TSS		NO ₃ -N		Total Hg	
	Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, ST Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level	
Dapitan	7.4647 M	Sig.	25.9667M	Sig.	0.3100 M	Sig	1.9000 M	Sig.	0.0191 M	Sig.	0.00013 M	Sig.
	0.8088 SD	0.057	0.7234 SD	0.139	0.02615 SD	0.718	0.0400 SD	0.000	0.0003 SD	0.000	0.0000058 SD	0.000
Dipolog	7.6686 M		26.9417 M		3268 M		5.1625 M		0.0509 M		0.000417 M	
	0.3609 SD		1.9866 SD		0.0674 SD		6.3388 SD		0.0287 SD		0.000141 SD	
Dicayo	8.2620 M		26.4667 M		0.2920 M		4.0000 M		0.0563 M		0.000097 M	
	0.0890 SD		1.1547 SD		0.0036 SD		1.0000 SD		0.0638 SD		0.0000017 SD	
Sindangan	7.2667 M		29.2333 M		0.2940 M		243.0000 M		0.3867 M		0.000533 M	
	0.3423 SD		0.2082 SD		0.0036 SD		9.5394 SD		0.0208 SD		0.0001528 SD	
Patawag	7.4897 M		26.5667 M		0.2947 M		20.0000 M		0.0433 M		0.000093 M	
	0.0532 SD		0.0577 SD		0.0035 SD		6.5575 SD		0.0289 SD		0.0000923 SD	

Table 3. One-way ANOVA results for the midstream sites.

River	Midstream											
	pH		Temperature		PO ₄ ²⁻		TSS		NO ₃ -N		Total Hg	
	Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, ST Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level	
Dapitan	6.8873 M	Sig.	29.567 M	Sig.	0.2830 M	Sig	1.9233 M	Sig.	0.0197 M	Sig.	0.00013 M	Sig.
	1.1084 SD	0.002	0.6429 SD	0.000	0.0079 SD	0.026	0.0352 SD	0.000	0.00012 SD	0.000	0.000006 SD	0.000
Dipolog	7.7108 M		27.589 M		0.3436 M		5.31444 M		0.05530 M		0.000344 M	
	0.5537 SD		0.9158 SD		0.0541 SD		2.7645 SD		0.01030 SD		0.000142 SD	
Dicayo	8.2410 M		29.000 M		0.2917 M		4.1667 M		0.41500 M		0.000100 M	
	0.2202 SD		0.2757 SD		0.0047 SD		1.1691 SD		0.02811 SD		0.000000 SD	
Sindangan	7.2621 M		29.017 M		0.2997		142.333 M		0.09833 M		0.000800 M	
	0.2369 SD		0.3657 SD		0.0201 SD		36.5987 SD		0.08377 SD		0.000154 SD	
Patawag	7.4985 M		25.950 M		0.29133		33.0000 M		0.20000 M		0.000193 M	
	0.0429 SD		1.566 SD		0.0082 SD		15.7162 SD		0.10000 SD		0.000136 SD	

Table 4. One-way ANOVA results for the downstream sites.

River	Downstream											
	pH		Temperature		PO ₄ ²⁻		TSS		NO ₃ -N		Total Hg	
	Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level		Mean, Std Dev and Significance Level	
Dapitan	7.3605 M	Sig.	26.6200 M	Sig.	0.2890 M	Sig.	11.000 M	Sig.	0.14200 M	Sig.	0.00029 M	Sig.
	0.52885 SD	0.793	1.2946 SD	0.000	0.00704 SD	0.044	1.8708 SD	0.000	0.032711 SD	0.011	0.000297 SD	0.356
Dipolog	7.4506 M		29.7778 M		0.2850 M		27.857 M		0.10259 M		0.00037 M	
	0.29875 SD		1.1946 SD		0.00896 SD		5.6988 SD		0.049535 SD		0.000263 SD	
Dicayo	7.3513 M		28.0667 M		0.3600 M		24.000 M		0.18000 M		0.00010 M	
	0.13349 SD		0.74207 SD		0.11259 SD		9.5395 SD		0.096436 SD		0.000000 SD	
Sindangan	7.4710 M		28.6500 M		0.2880 M		138.000 M		0.29000 M		0.00037 M	
	0.11926 SD		0.5010 SD		0.00794 SD		58.8982 SD		0.043589 SD		0.000231 SD	
Patawag	7.5573 M		30.800 M		0.28478 M		49.6667 M		0.12667 M		0.00018 M	
	0.06292 SD		0.7127 SD		0.01240 SD		19.7547 SD		0.090970 SD		0.000210 SD	

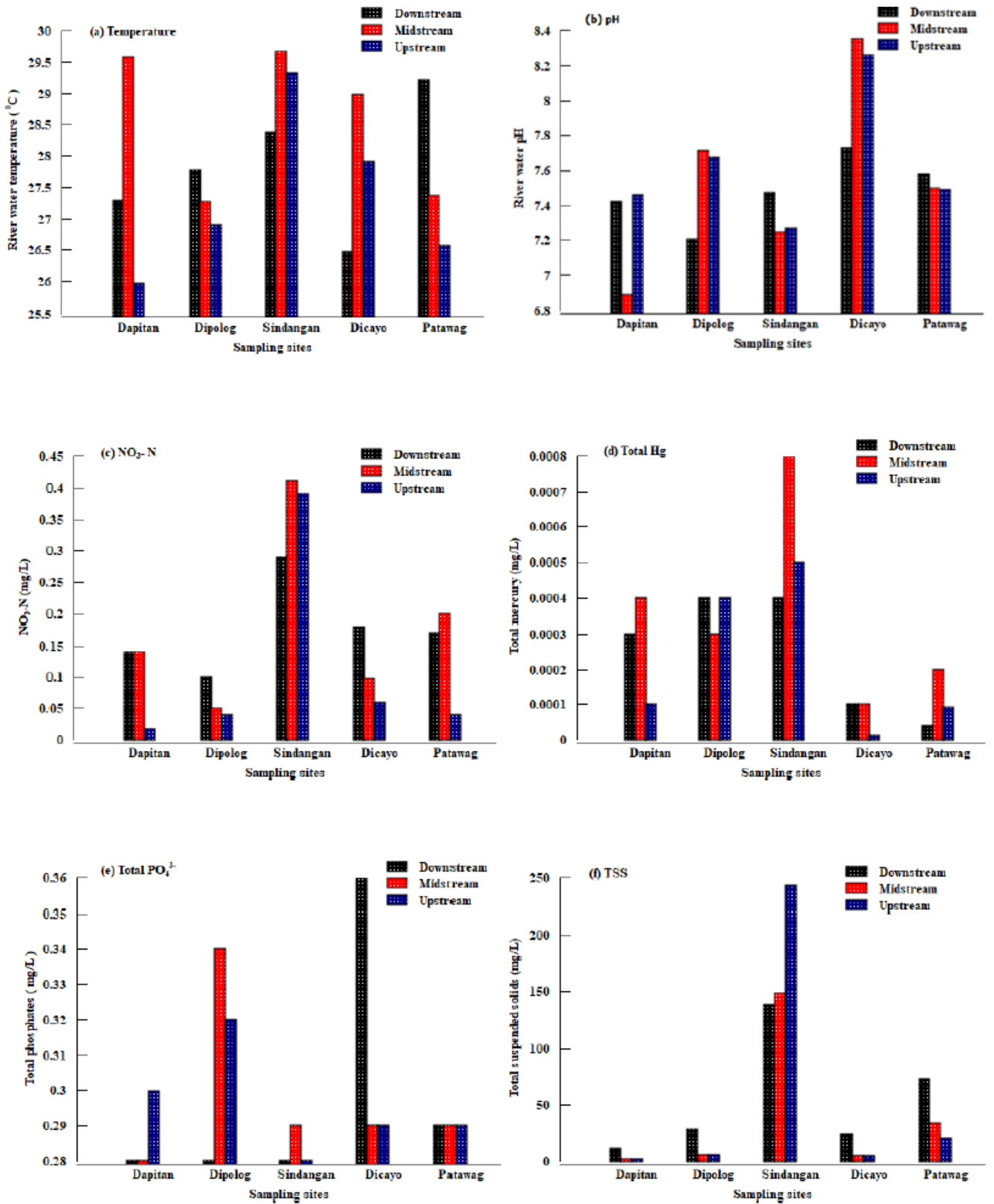


Figure 2. Comparison of the different physicochemical parameters of the sampling sites.

4. Discussion

Most of the aquatic habitats require water with a pH between 6.5–8.5. Chemical and biological changes due to some pollutants which occur in the river water can affect the pH level. Moreover, the presence of dissolved gases, salts, bases and acids are the many factors that greatly affect the pH of water [24]. Any change of the pH level, whether below or above the required range, can cause health problems not only to the living organisms of the river but also to human beings that rely on the aquatic products coming from the river. On-site analyses of pH and temperature were carried out at the sampling sites following the standard protocols mentioned in the analytical procedures. Figure 2b shows that the upstream portion of Dicayo river had the highest pH value of 8.26 ± 0.09 and the lowest pH value of 6.89 ± 1.11 was found in the midstream portion of Dapitan river. The plot also shows that Dicayo river registered the highest reading of 7.35 ± 0.13 , 8.24 ± 0.22 and 8.26 ± 0.09 , for the downstream, midstream and upstream sites of the river, respectively. It can be deduced from the results that the water of Dicayo river was slightly basic whereas the midstream portion of Dapitan river was a little bit acidic compared to the other rivers. However, the pH of the streams of Dapitan and Dicayo rivers was observed to be at the acceptable range prescribed by Department of Environment and Natural Resources in the Philippines. On the other hand, the pH values of all the river water samples of Dipolog, Sindangan and Patawag rivers were also found to be within the acceptable range of 6.5–8.5 prescribed by World Health Organization (WHO) and Department of Environment and Natural Resources in the Philippines. Additionally, Gupta et al., [25] observed that the narrow variations of pH could be attributed to low variation in free CO_2 . The absence of industrial activities along the river can also be a factor that may be responsible for non-interference of ionic species with the pH due to fewer concentrations present [26]. The present study confirmed these observations.

Temperature governs the kinds of organisms that can live in rivers and lakes. All aquatic organisms have their preferred temperature range. Warm water holds less dissolved oxygen than cool water and may not contain enough dissolved oxygen for the survival of different species of aquatic life [27]. In addition, the rate of metabolism of aquatic plants and animals is greatly affected by the prevailing water temperature [28]. Increasing number of insoluble pollutants [5], like macro and microplastics, make the water hotter, thereby increasing the water temperature. As depicted in Figure 2a, the highest temperature in the upstream portion was recorded at Sindangan river (29.23 ± 0.21), while the temperature of Dapitan river was colder (25.97 ± 0.72 °C) compared to the other rivers which was found to be below the minimum limit of 26 °C prescribed by WHO and DENR. This could be attributed to the trees present in the surroundings of the upstream area. In the midstream portion, Dapitan river obtained the highest water temperature of 29.57 ± 0.64 °C. This was slightly above the water temperature of Sindanga river (29.02 ± 0.36 °C) and the lowest temperature (25.95 ± 1.57 °C) was observed in Patawag river. It was also observed that the downstream temperature of Patawag river (30.8 ± 0.71 °C) was the highest among the five downstream sites of the river systems and Dapitan river had the lowest downstream temperature of 26.62 ± 1.29 °C. Furthermore, as shown in Table 1, the mean temperatures of the downstream, midstream and upstream portions of Dipolog, Sindangan, Dicayo and Patawag rivers did not vary significantly and were observed to be within the allowable range of 26–30 °C.

Phosphates are introduced into the aquatic environment in the form of phosphorus, which is a vital nutrient required for growth and proper functions of cells and tissues [28] to support aquatic lives. The results for the total phosphate concentrations of the five river systems of the study exceeded the

permissible limit (0.025 mg/L) in the revised guideline set by the Department of Environment and Natural Resources [23]. However, these values are lower than the WHO requirement for drinking water of 0.5 mg/L. It was observed that the sampling sites at the downstream portion of Dicayo river got the highest value of total phosphate concentration of 0.36 ± 0.11 mg/L. Compared to other rivers, it was observed that Dipolog river obtained the highest values at the midstream and upstream portions of 0.34 ± 0.05 mg/L and 0.33 ± 0.07 mg/L, respectively (Figure 2e). This could be attributed to the anthropogenic and farming activities of the inhabitants along the river using chemical fertilizers [29], as well as open dumping of municipal wastes into the river [30]. The presence of high concentrations of total phosphate is due to Zamboanga del Norte is an agricultural province in general and the people living near the vicinity of the rivers being studied are engaging in farming activities in particular. Excess fertilizers from their farmlands that drift into the rivers might be the cause of the higher phosphate concentration.

The sources of nitrate contamination of the sampling sites may be derived mainly from excess fertilization, forest denudation and household activities of the inhabitants along the riverbanks. The Nitrate-Nitrogen ($\text{NO}_3\text{-N}$) concentrations of the five river systems are shown in Figure 2c. As evident in the figure, the mean $\text{NO}_3\text{-N}$ concentrations of the sampling sites at the downstream, midstream and upstream of Sindangan river obtained the highest values of 0.29 ± 0.04 , 0.42 ± 0.03 and 0.39 ± 0.02 mg/L, respectively. Bakure and coworkers [31] reported that the mean $\text{NO}_3\text{-N}$ concentration decreased at downstream sites when compared with upstream sites for agricultural streams due to the denitrification process. This is similar to the present study since the primary occupation of the people surrounding Sindangan river is farming. However, the data revealed that Nitrate-Nitrogen concentrations of the river systems were still in the acceptable limit prescribed by Department of Environment and Natural Resources of the Philippines and World Health Organization since all the values of $\text{NO}_3\text{-N}$ observed were below the 7 mg/L recommended for drinking water.

A body of water begins to lose its ability to support a diversity of aquatic life when levels of TSS increase. Photosynthetic activity decreases since less light penetrates the water, so less oxygen is produced causing a drop in dissolved oxygen levels. As shown in Figure 2f, there was a general decrease of the TSS concentrations from the downstream, midstream and upstream portions, respectively, of Dapitan, Dipolog, Dicayo and Patawag rivers. The sweeping increase of TSS in the downstream parts of the said rivers could be due to the anthropogenic activities of the residents along the river since the sampling sites in the downstream portions were within the city. Increased TSS in water by anthropogenic factor could be due to farming, construction of road, quarrying and grubbing which lead to resuspension of particles from sediment back to surface water [28]. Nevertheless, the total suspended solids were well within the standard range of 25–65 mg/L set by DENR. Conversely, in the Sindangan river, there was a significant increase of the TSS concentrations of 138 ± 58.9 , 142.3 ± 36.6 and 243 ± 9.5 mg/L from downstream, midstream and upstream portions, respectively, which were found to be higher than the maximum limit of 65 mg/L. The high concentration of the suspended sediments could be due to the soil runoffs, debris from twigs and insoluble particles. During the time of sampling in the upstream portion of the river, heavy rains were experienced and flooding was observed. This could be the reason why the TSS was a little bit higher in the upstream area. Besides, quarrying activities were also observed in the area during the sampling period.

As, Cd, Cr, Cu, Ni, Hg, Pb and Zn are examples of heavy metals which cause water pollution. Some of these metals (e. g., Cu, Fe, Mn, Ni and Zn) are required as nutrients in trace amount for life

processes in plants and microorganisms but become toxic at higher concentrations [32]. In the present study, only the total mercury (Hg) was analyzed. The data in Figure 2d reveal that the total concentrations of Hg in Sindangan river were the highest at the downstream, midstream and upstream sections, respectively. However, it was found that the total Hg concentrations of Sindangan river were well below the acceptable range. Significantly, it was found that the total mercury of the five major rivers of Zamboanga del Norte in the Philippines were well below the acceptable range of 0.001–0.002 mg/L suggested by DENR and WHO. Though it was less than what is considered a threat to human health, a trace of this heavy metal can gradually become a source of water contamination [33].

In the upstream sites (shown in Table 2), the results of the ANOVA test for $\text{NO}_3\text{-N}$ indicated that the data differed significantly ($F_{4,19}=73.958$, $p < 0.05$). In order to test the individual differences between the sites, post-hoc comparison was performed. The post-hoc analysis using Scheffe disclosed that the mean scores for Dapitan ($M=0.0191$, $SD=0.0003$), Dipolog ($M=0.0509$, $SD=0.0287$), Dicayo ($M=0.0563$, $SD=0.0638$) and Patawag ($M=0.0433$, $SD=0.0289$) statistically vary from that of Sindangan ($M=0.3867$, $SD=0.0208$). The ANOVA results for TSS revealed that a significant difference existed between the overall data ($F_{4,19}=982.617$, $p < 0.05$). The Scheffe post-hoc test confirmed that the significant difference occurred between the mean scores of Dapitan ($M=1.9$, $SD=0.04$), Dipolog ($M=5.1625$, $SD=6.3388$), Dicayo ($M=4.00$, $SD=1.00$) and Patawag ($M=20.000$, $SD=6.5575$) with that of Sindangan ($M=243.000$, $SD=9.5394$), and between the mean scores of Dapitan and Dipolog with that of Patawag. Moreover, the total mercury in the upstream sites differ significantly ($F_{4,19}=11.110 < 0.05$). The differences between groups were determined using Scheffe in the post-hoc analysis. The test indicated that the mean score for Sindangan ($M=0.000533$, $SD=0.0001528$) was significantly different from Dapitan ($M=0.00013$, $SD=0.0000058$), Dicayo ($M=0.000097$, $SD=0.0000017$) and Patawag ($M=0.000093$, $SD=0.0000923$). Similarly, Scheffe test also showed that the mean score of Dipolog ($M=0.000417$, $SD=0.000141$) vary significantly from that of Dapitan, Dicayo and Patawag. Other parameters like pH, temperature and total PO_4^{2-} which were not statistically significant, post-hoc comparison was not performed.

The ANOVA results (shown in Table 3) suggested that the midstream pH of the five rivers differ significantly ($F_{4,25}=5.565$, $P<0.05$). The Scheffe post-hoc test further revealed that the significant difference lies between the pH of Dapitan ($M=6.8873$, $SD=1.1084$) and Sindangan ($M=7.2621$, $SD=0.2369$) with that of Dicayo ($M=8.2410$, $SD=0.2202$). When the data are analyzed in terms of midstream temperature, the ANOVA results revealed that the data significantly differ ($F_{4,25}=13.880$, $P<0.05$). The subsequent post-hoc comparison indicated that the mean scores for Dapitan ($M=29.567$, $SD=0.6429$), Dipolog ($M=27.589$, $SD=0.9158$), Dicayo ($M=29.000$, $SD=0.2757$) and Sindangan ($M=29.017$, $SD=0.3657$) vary significantly from that of Patawag ($M=25.950$, $SD=1.566$). When analyzed across midstream PO_4^{2-} , the ANOVA test showed that there exists significant difference ($F_{4,22}=52.83$, $P<0.05$) between the data. The following post-hoc comparison revealed further that the mean scores of Dapitan ($M=0.0197333$, $SD=0.00011547$), Dipolog ($M=0.0553000$, $SD=0.01030024$), Sindangan ($M=0.0983333$, $SD=0.08376555$) and Patawag ($M=0.2000000$, $SD=0.10000000$) significantly differ from that of Dicayo ($M=0.4150000$, $SD=0.02810694$), and the mean scores of Dapitan and Dipolog significantly differ from that of Patawag. In terms of midstream TSS, results of the ANOVA test indicated that the data differ significantly ($F_{4,22}=64.987$, $P<0.05$). The post-hoc analysis disclosed that the mean scores for Dapitan ($M=1.9233$, $SD=0.0352$), Dipolog ($M=5.31444$, $SD=2.7645$), Dicayo ($M=4.1667$, $SD=1.1691$) and Patawag ($M=33.0000$, $SD=15.7162$) statistically vary from that of Sindangan ($M=142.333$, $SD=36.5987$). When analyzed

along midstream NO₃-N, ANOVA results suggested that there exists significant difference between the data. The Scheffe test disclosed that the mean scores of Dapitan (M=0.0197, SD=0.00012), Dipolog (M=0.05530, SD=0.01030), Sindangan (M=0.09833, SD=0.08377) and Patawag (M=0.20000, SD=0.1000) differ significantly from that of Dicayo (M=0.41500, SD=0.02811). Similarly, Scheffe test also showed that the mean scores of Dapitan and Dipolog vary significantly from that of Patawag. When the data were analyzed in terms of midstream total Hg, results of ANOVA test indicated that a significant difference exists between the data. The Scheffe post-hoc test showed that the significant difference occurred between the mean scores of Dapitan (M=0.00013, SD=0.000006), Dipolog (M=0.000344, SD=0.000142), Dicayo (M=0.000100, SD=0.000001) and Patawag (M=0.000193, SD=0.000136) with that of Sindangan (M=0.000800, SD=0.000154), and between the mean score of Dipolog and Dicayo.

It can be gleaned from the ANOVA results in Table 4 that there is no significant difference in the downstream pH ($F_{4,37}=0.420$, $P>0.05$) and total Hg ($F_{4,22}=1.158$, $P>0.05$) between the five rivers. However, in terms of downstream temperature ($F_{4,37}=22.374$, $P<0.05$), TSS ($F_{4,22}=18.559$, $P<0.05$), NO₃-N ($F_{4,22}=4.205$, $P<0.05$) and PO₄²⁻ ($F_{4,22}=2.938$, $P<0.05$), results showed that the data significantly differ. The succeeding post-hoc analysis revealed the following statistical differences between individual groups across each parameter. For downstream temperature, the mean scores of Dipolog (M=29.7778, SD=1.1946), Sindangan (M=28.6500, SD=0.5010) and Patawag (M=30.800, SD=0.7127) differ significantly from that of Dapitan (M=26.6200, SD=1.2946). Similarly, the mean scores of Dicayo (M=28.0667, SD=0.74207) and Sindangan also differ significantly from that of Patawag. For TSS, the mean scores of Dapitan (M=11.000, SD=1.8708), Dipolog (M=27.857, SD=5.6988), Dicayo (M=24.000, SD=9.5395) and Patawag (M=49.6667, SD=19.7547) vary significantly from that of Sindangan (M=138.000, SD=58.8982). For NO₃-N, the mean scores of Patawag (M=0.12667, SD=0.090970) and Dipolog (M=0.10259, SD=0.049535) vary significantly from that of Sindangan (M=0.29000, SD=0.12667). While the ANOVA test found significant difference in PO₄²⁻ between the five rivers, the subsequent post-hoc analysis suggested otherwise.

5. Conclusion

The values of the water quality parameters, such as pH, temperature, NO₃-N and total mercury from all water samples collected from the downstream, midstream and upstream sites of the 5 major rivers of the study were found to be within the recommended limits of WHO and DENR. However, in the revised guidelines of DENR for the total phosphates, the data showed that all values of the total phosphates for all the river systems exceeded the prescribed limit. The total suspended solids (TSS) at the downstream, midstream and upstream sites of Sindangan river were higher than the permissible limit recommended by DENR. Agricultural wastes and domestic sewage possibly pollute the 5 major rivers of Zamboanga del Norte, Philippines.

The baseline data from this investigation could be used for further assessments by future researchers. The results could also serve as the basis in formulating government policies regarding the preservation and management of the major rivers of Zamboanga del Norte, Philippines to enhance health and prevent pollution for future generation.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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