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Impact of Fertilizers on Surface Water Quality in UTHM

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Abstract: Widespread application and excessive usage of fertilizers in agricultural sectors have highly impacted the surface water quality and further deteriorate the nearby waterbody. The objectives of the research are to identify the composition of fertilizers used in the fertilizing activities in G3 lake, UTHM, and to identify the impacts of fertilizers on surface water quality in terms of pH, COD, and AN. Two methods that were used to obtain results which are in-situ measurements and laboratory measurements regarding the APHA standard. The in-situ measurement using DO meter and depth sounder while laboratory measurement using IC, AAS, DR6000, and pH meter. The water samples were taken from the lake using the composite grab sample method which the water samples were stored in HDPE bottles after three days of fertilizing activities. The G3 lake's pH value dropped while the concentration of COD and AN increased due to the acidity of the fertilizers and the composition of fertilizers being dissolved after rainfall events. All of the water depth at all selected points is 0.8 ft or 0.24m were measured using the depth sounder. Dissolved oxygen concentration is between 6.64 mg/l to 6.82 mg/l which all of the three points are categorized as Class II. The pH value resulted classified as neutral water, ranging in between 7.12 and 7.21, thus categorized as Class I. The low temperature during the sampling period favours a more concentration of nitrate, especially in the rainy season. However, there was no presence of phosphate anion within all of the water samples due to phosphatic (P) fixation or retention. In conclusion, deterioration of water quality in G3 lake is not only caused by the fertilizing activities but also by various other aspects. However, sampling procedure can be carried out weekly for three weeks in order to observe more on water quality degradation by the fertilizing activities

Keywords: Surface Water Quality, Fertilizers, Ph, COD And AN

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1. Introduction

Nowadays, the application of fertilizers in the agricultural sector highly impacted the surface water quality of lakes and interrupts the natural aquatic ecosystem. Monitoring the surface water quality is crucial due to its great socio-economic significance [1]. Lakes are most likely to accumulate the contaminants due to their water retention time and cannot self-purify. The lake's water quality can be easily compromised either by natural occurrences such as rainy events or soil erosion and anthropogenic sources [2]. An uncontrolled usage during the fertilizing activities could be a major source of pollutants and could lead to depletion of dissolved oxygen over time [3]. Fertilizers application has spiked causing high demand for chemical fertilizers [4]. Surface water in the UTHM ecosystem is dominated by a tremendous number of the floating-leaf plant which is *Nymphaea* spp. An unpleasant view of water lily packed together competing for the living area which to some extent blocks the water flow of the water body which could cause flooding in UTHM area. The dissolved fertilizers enhance the growth of water lily at the same time blocking the sunlight penetration toward the submerged plant [5].

The purpose of this study is to identify the composition of fertilizers used in the fertilizing activities in UTHM and to identify impacts of fertilizers on surface water quality in terms of pH, COD, and AN. Specific. There are several physical and chemical parameters were observed which are pH value, temperature, water depth, dissolved oxygen, nitrate, nitrite, phosphorus, potassium, sulphur, ammoniacal nitrogen (AN), and chemical oxygen demand (COD). A DO 450 meter and depth sounder instrument was used as an in-situ measurement apparatus. The water sample obtained from the lake was bottled up within a 250ml HDPE bottle each before being brought to the laboratories for testing purposes during the rainy season. There are several laboratory experiments such as determination of anions using ion chromatography (IC) with chemical suppression of eluent conductivity, determination of potassium concentration using atomic absorption spectroscopy (AAS), determination of pH value using ASTM D1293, determination of chemical oxygen demand using Method 8000, and determination of ammoniacal nitrogen ($\text{NH}_3\text{-N}$) using Method 8038. All of the laboratory experiments were conducted according to the American Public Health Association (APHA) standard.

2. Literature Review

Water quality is a term that describes a suitable measure that can indicate the purpose of water usage which varied such as a source of freshwater, plant cultivation, factories, recreational and natural habitat for aquatic life. This required an overall assessment of the physical, chemical, and biological characteristics. The quality of surface water is dependent on the location, time, weather, and presence of either point source or non-point sources pollution [6]. The quality of water is generally controlled by several key factors such as climatic variability, hydrological, biogeochemical, and anthropogenic such as fertilizing activities [7]. There are various sources of freshwater which include rivers, lakes, groundwater, and wetland. These sources of water are used for various purposes such as urban agricultural, and industrial activities while ignoring its original function that supports the natural ecosystem. Aquatic ecosystems are the ones being altered severely or even destroyed from time to time at a pace that the ecosystem cannot restore itself [8].

A lake is commonly a source of freshwater which lack any direct contact with the nearby ocean which consist of physical, chemical, and biological characteristic in the water body. There are four different zones that provide different species their habitat for plants and animals. This zonation includes the littoral zone, limnetic zone, profundal zone, and benthic zone [9]. Lake is considered as an enclosed water body relatively big in size which most of its surroundings are land area except the drains and streams that channel its water to the lakes which can be an important source of freshwater supply, recreational area, and other suitable purposes [10]. Water quality can be very crucial in determining the state of the water which can be classified under the category of clean, slightly polluted, or polluted [11]. Based on the National Water Quality Standards (NWQS) and the Interim National Water Quality Standard (INWQS), Table 1 and 2 shows the categorized class and class definition respectively.

Table 1: National Water Quality Standards (NWQS) for Malaysia [12]

Parameter	Unit	Class					
		I	IIA	IIB	III	IV	V
pH	-	6.5-8.5	6-9	6-9	5-9	5-9	-
DO	mg/L	7	5-7	5-7	3-5	<3	<1
BOD	mg/L	1	3	3	6	12	>12
COD	mg/L	10	25	25	50	100	>100
SS	mg/L	25	50	50	150	300	300
AN	mg/L	0.1	0.3	0.3	0.9	2.7	>2.7

Table 2: Interim National Water Quality Standard (INWQS) Class by Definition [13]

Class	Definition
I	<ul style="list-style-type: none"> • Conservation of natural environment. • Water supply I - Practically no treatment necessary (except by disinfection or boiling only). • Fishery I - Very sensitive aquatic species.
IIA	<ul style="list-style-type: none"> • Water supply II - Conventional treatment required. • Fishery II - Sensitive aquatic species.
IIB	<ul style="list-style-type: none"> • Recreational use with body contact.
III	<ul style="list-style-type: none"> • Water supply III - Extensive treatment required. • Fishery III - Common of economic value, and tolerant species; livestock drinking.
IV	<ul style="list-style-type: none"> • Irrigation.
V	<ul style="list-style-type: none"> • None of the above.

3. Methodology

3.1 Sample of water and data collection

Generally, the study area was carried out at G3 lake, UTHM where the location of water samples was taken. The water sampling process is known as a procedure in selecting a portion of material which sufficient enough in volume to be transported safely and easy to be handled in the laboratory workspace using HDPE bottles. The specific locations were spotted using GPS Coordinate application to get a specific place for next reference which were 1°51'35.14" N 103°05'08.26" E, 1°51'37.35"N 103°05'10.28"E and 1°51'40.50"N 103°05'11.91"E for point A, B, and C respectively. This step was crucial since the error caused by the instrument is lower in comparison with the error caused by the sampling and sample preparation which are significantly high [14]. About 3 liters of water sample were taken which 4 bottles of 250 ml for each point and stored at temporary refrigerator at MPRC laboratory.



Figure 1: The sampling of water using HDPE bottles

For the in-situ measurements, all instruments were rinsed using distilled water after three days of the application of fertilizer within the lake's surrounding area. The measurement of pH and temperature were measured using a pH meter while the measurements for dissolved oxygen used a DO 450 meter. Also, the water depth of the points was measured using a depth sounder. The in-situ measurements were carried out immediately after the sample was taken.



Figure 2: Reading the pH value and temperature



Figure 3: Reading the dissolved oxygen using DO 450 meter



Figure 4: Reading the water depth using a depth sounder

3.2 Laboratory measurements

The laboratory evaluates the surface water quality parameters such as nitrogen, phosphorus, potassium, sulphur, pH value, chemical oxygen demand (COD), and ammonia nitrogen (AN). First of all, ion chromatography (IC) as shown in Figure 5 was used to determine the anions such as nitrite, nitrate, phosphate, and sulfate. As for the testing procedure, the samples were inserted into the testing vials until filled. Before the analysis was conducted, rinsed the vial with the water sample and deionized water two or three times to remove the dust and other unwanted substances. Later, the samples were inserted into the testing vials until filled. Next, close the vial properly in order with vial cap after being filled with water sample usually up to 2-3 mL of water sample [15]. The outer surface of the vials was cleaned and dried just before inserting it into the machine according to the number that was initially adjusted in the computer. When the vials are already inside the ion chromatography machine, the machine cover was closed. Usually, the test run for each sample takes about 30 minutes, and the result was printed. Finally, the used vials are cleaned by using ultra-purifying water.



Figure 5: Ion chromatography (IC)

The atomic absorption spectroscopy (AAS) as shown in Figure 6 was the most suitable machine in order to determine the single element for heavy metal and has a high detection limit which was potassium. The procedure started by preparing a dilute standard. Next, allowed the gas of oxygen and acetylene from the gas tanks to flow through the pressure-reducing valves. Started the flame using a regular sparkler for determining the potassium [16]. Then, the capillary tube was cleaned using a towel and inserted the capillary tube inside the dilute standard to obtain a “ZERO”. Then, the capillary tube is cleaned again using a towel, this time insert the capillary tube inside the water sample within the polyethylene container. Finally, observed the change of flame colour and the data from the computer for the presence of potassium was recorded [17]



Figure 6: Atomic absorption spectroscopy (AAS)

The apparatus and material that being be used for the determination of pH value include pH meter as shown in Figure 7, beaker, distilled water, water sample kept in high-density polyethylene (HDPE), and stirrer. First of all, the protective cap from the narrow end of the meter was removed and turned on the pH meter. Next, the narrow end of the meter is rinsed using distilled water within a beaker. Then, the electrode was fully submerged into the water sample in the beaker. After that, the electrode was

rinsed using distilled water with a beaker. The button “READ” was pressed and the pH value of the water sample was recorded. Finally, the protective cap was reattached for storage and to switch off the pH meter [17]



Figure 7: pH meter

To determine the chemical oxygen demand (COD). According to the preparation of the sampling procedure, the DRB200 as shown in Figure 8 was turned on and preheated to 150°C. A safety shield was placed in front of the reactor. Next, the COD vials were removed cap carefully at an appropriate range. Then, the COD vials were held at 45 degrees-angle, 2mL of the sample using pipet being transferred into the vials. After that, the exterior of the COD vials was rinsed with deionized water and cleaned with a paper towel. Later, COD vials were inverted several times to mix the content. Finally, place the COD vials in the preheated DRB200 reactor. The same procedure was conducted for the preparation of the blank sample. The COD vials were heated for about two hours and the DRB200 was turned off and let the COD vials cool down for about 20 minutes to 120°C or less. Each of the COD vials was inverted several times while it is warm. The COD vials were placed in vials racks and let to cool at room temperature. The procedure was proceeded by using the Colorimetric determination method to measure the COD.



Figure 8: DRB200

The colorimetric measurement procedure is being carried out as follows. First, the spectrophotometer as shown in Figure 9 was turned on, and set the range programme was either low or high. Next, Icon “STORE” and “PRGM” were pressed and displayed the “mg/L”, COD, and “ZERO” icons. Then, the blank vial’s exterior vials were cleaned with a towel and inserted carefully into the cell until it was solidly inside the adapter. Inserted the COD’s vials into the cell and rotated until it is in place which required a gentle push to fully insert it. After that, the sample is tightly covered with an instrument cap and press “ZERO”. The cursor is moved to the right and the screen displays the result in “mg/L COD”. Finally, the observation result being recorded, the steps are repeated for the other sample vials [18].



Figure 9: DR6000

The presence of ammonia nitrogen according to the procedure, the samples were prepared by a mixing cylinder being filled to the 25-mL line. Next, the blank was prepared by a mixing cylinder to the 25- mL line which fills with deionized water. Three drops of mineral stabilizer were added to each mixing cylinder. Then, put the stopper on the mixing cylinders followed by the mixing cylinders being inverted several times to mix. Three drops of polyvinyl alcohol dispersing agent were added to each mixing cylinder. The stopper was placed on the mixing cylinder later inverted several times to mix.

A 1 mL of Nessler reagent needs to be added to each mixing cylinder. The stopper is put on the mixing cylinders followed by the mixing cylinders by inverting it several times to mix. Start the instrument times which one minute reaction time starts. A 10mL needs to be poured from the blank cylinder into a sample cell when the timer expires, the blank sample cell is clean using a towel. The blank is inserted into the cell holder. Push the “ZERO” button which the display shows 0.00 g/L NH₃-N. A 10mL from the sample cylinder is poured into a second sample cell. The prepared sample cell is clean by using a towel. Insert the prepared sample into the cell holder. Push the “READ” button later the results show in mg/L NH₃ [19]

4. Result and Discussion

4.1 Data results

Table 3: Sampling data at G3 lake, UTHM

Parameter	Point A	Point B	Point C
Water Depth(m)	0.24	0.24	0.24
pH (in-situ)	6.96	7.19	7.20
Dissolve Oxygen (mg/l)	6.64	6.63	6.82
Temperature (°C)	30.9	29.5	29.3
pH (laboratory)	7.16	7.18	7.30
Chemical Oxygen Demand (mg/l)	26	30	23
Ammoniacal Nitrogen (mg/l)	0.50	0.51	0.57
Nitrate (mg/l)	1.4005	1.3794	1.5898
Nitrite (mg/l)	0.1654	0.1627	0.1650
Orthophosphate (mg/l)	n.a	n.a	n.a
Potassium (mg/l)	4.251	3.810	3.369
Chloride (mg/l)	10.7495	10.9527	12.3718

4.2 The impacts of fertilizers on surface water quality in terms of pH, COD, and AN.

The pH value was obtained from both site measurement and laboratory measurement to measure the overall free hydrogen and hydroxyl ions which to determine the acidity or alkalinity of three sampling points at the water body [20]. From the in-situ measurement, the highest pH value was 7.20 at point C followed by 7.19 and 6.96 at points B and A respectively. Meanwhile, the laboratory measurements show that the highest pH value is 7.30 followed by 7.18 and 7.16 at points B and A. Based on both measurements, the average pH value is 7.12 and 7.21 which ranged between 6.96 to 7.2 and 7.16 to 7.30 for both measurements. The average pH value at the G3 lake bank is pH 8 [21] so the value becomes the baseline reference for the changes of pH value for this study. All of the pH values measured were taken below the baseline value. This is because the fertilizer applied is acidic which reduces the pH value of the waterbody. The least reduction between the baseline value and the measured value is 0.8 and 0.7 for in-situ measurement and laboratory measurement respectively. In the meantime, the most reduction between the baseline value and the measured value is 1.04 and 0.84 for in-situ measurement and laboratory measurement respectively. The range of pH value reduction between the baseline and both measurements is 0.8 to 1.04 and 0.7 to 0.84 respectively. Based on the National Water Quality Standards (NWQS), all of the measured water samples are within the range of 6.5 to 8.5 categorized as Class I (Water supply I and Fishery I). It is concluded that after the fertilizing activities the pH value dropped which altered its surface water quality.

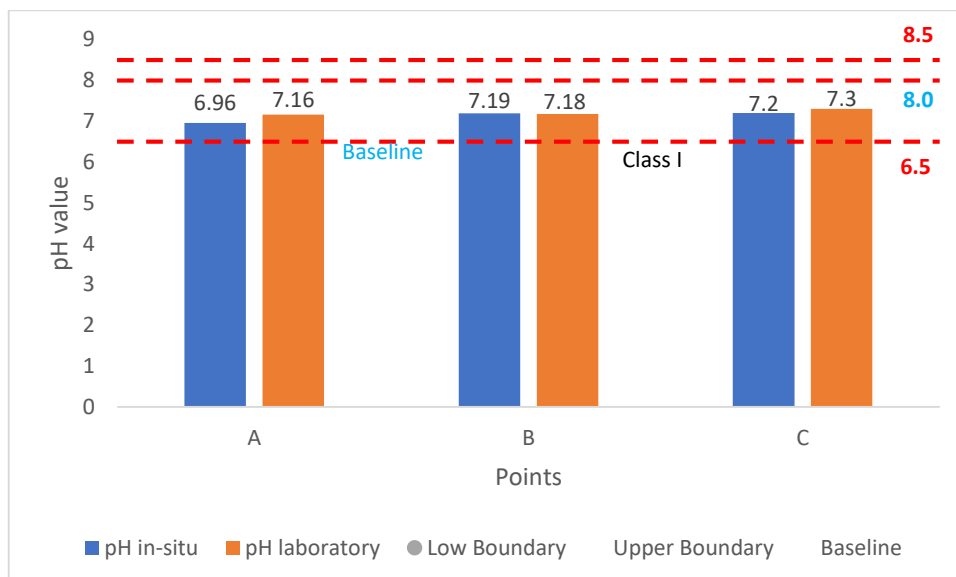


Figure 10: pH value for in-situ and laboratory measurements

Ammoniacal nitrogen (AN) is all kinds of toxic pollutants usually waste products, leachate that is present in the water body [20]. the range of ammoniacal nitrogen (AN) for the sample was between 0.50 to 0.57 with an average of 0.53 mg/l. The highest concentration obtained from the laboratory testing is 0.57 mg/l at point C followed by 0.51 mg/l at point B. The lowest concentration recorded is 0.5mg/l at point A and the baseline was 0.49 mg/l. The average concentration of ammoniacal nitrogen (AN) at G3 lake was 0.49 mg/l [7] so the value becomes the baseline reference for the changes in AN concentration related to fertilizing activities for this study. All of the AN value measured was taken slightly above the baseline value. This is because the fertilizers that were used contain 15% of total nitrogen from its overall composition which later leached to the waterbody after a rainfall event. The least increment of AN concentration is 0.1 mg/l at point A followed by a 0.2 mg/l increase at point B. The highest increment in AN concentration is 0.08 mg/l at point C. Based on the National Water Quality Standards (NWQS), all of the measured water samples are above 0.3 mg/l and below 0.9 mg/l so it's categorized as Class II (Water supply II and Fishery II). It is summarized that after the fertilizing

activities the AN concentration increase slightly which could be more in term of concentration from time to time until the fertilizers fully dissolve to the soils and nearby waterbody usually due to rainfall.

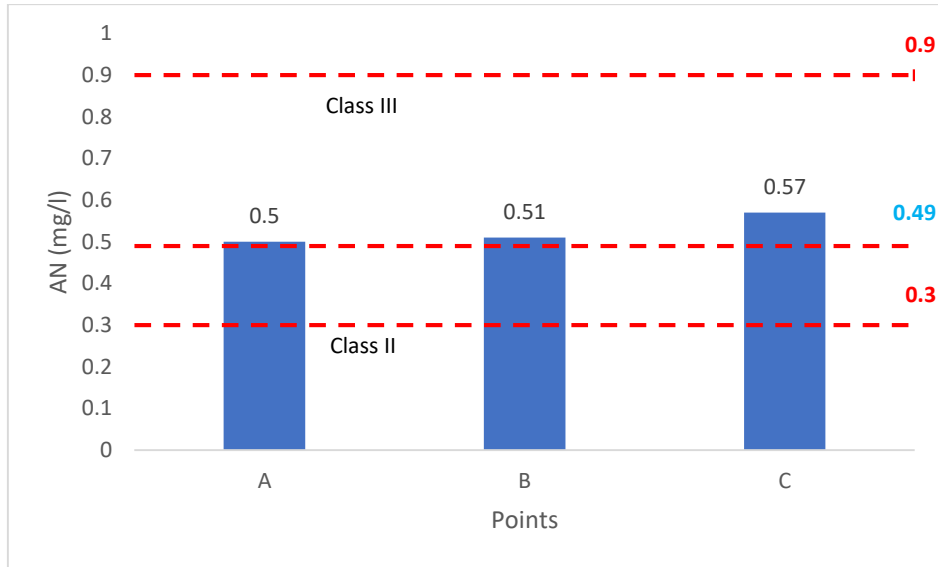


Figure 11: AN (mg/l) vs points

COD is an advantageous measurement for the concentration of organic pollution within the waterbody. Other than fertilizing activities, an increase in the value of COD concentration could be caused by the rise of organic substances and inorganic pollutant that comes from the runoff of the nearby cafeteria food waste and other water waste that is channeled to the lake [22]. The range of chemical oxygen demand (COD) for the samples was from 23 mg/l to 30 mg/l, with a mean of 26.33 mg/l. Point B shows the greatest value of COD which is 30 mg/l followed by point A at 26mg/l. Meanwhile, the COD value obtained from point C is the lowest at 23mg/l. Based on the National Water Quality Standards (NWQS), the COD measured at the samples of points A and B were categorized as Class II (Water supply II and Fishery II) while the COD measured sample at point C was categorized as Class I (Water supply I and Fishery I).

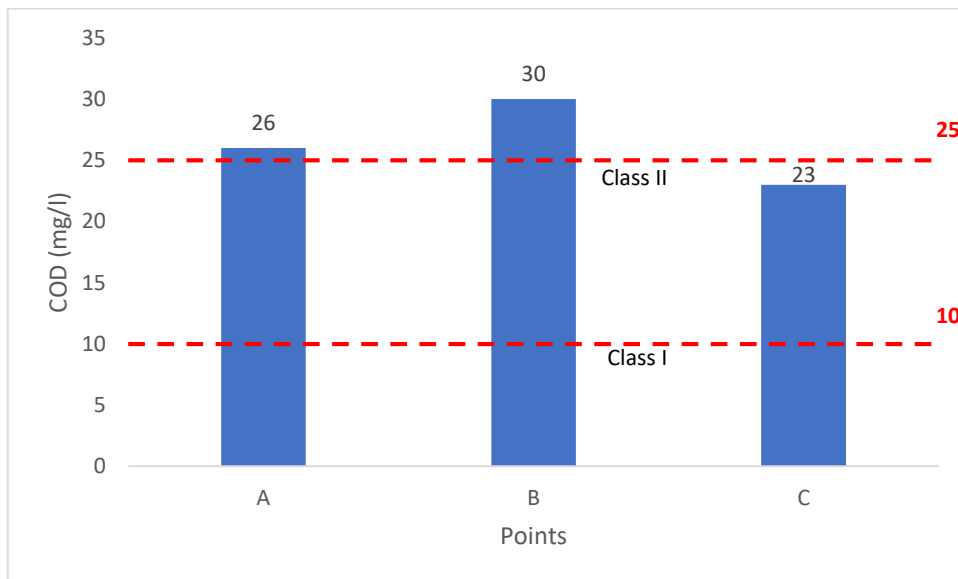


Figure 12: COD (mg/l) vs points

5. Conclusion

The overall pH value within the study area for both in-situ and laboratory measurement can be categorized as Class I and neutral water which dropped from slightly alkaline water due to the soluble acidic composition of the fertilizer. Also, the baseline for the pH value according to the previous study is pH 8, all of the pH values measured were taken below the baseline value. This is because the fertilizer applied is acidic which reduces the pH value of the waterbody. The chemical oxygen demand (COD) concentration of G3 lake ranged between 23 mg/l to 30 mg/l which points A and B categorized as Class II while Class I for point C. Other than the application of fertilizers, a high concentration of COD could be caused by the rising of organic substances and inorganic that come through the nearby runoff nearby cafeteria. Lastly, the ammoniacal nitrogen (AN) concentration at the study area ranged between 0.50 mg/l to 0.57 mg/l which all of the points categorized as Class II. All of the obtained value has slightly more in comparison with the baseline value which was 0.49mg/l. The least increment of AN concentration is 0.1 mg/l at point A followed by a 0.2 mg/l increase at point B. The highest increment in AN concentration is 0.08 mg/l at point C. In a conclusion, deterioration of water quality in G3 lake is not only caused by the fertilizing activities but also by various other aspects such as soil weathering, nearby cafeteria water outflow, and hydrological cycle which related to the lake retention time.

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