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On the pH and Acid Neutralizing Capacity Profile of Manila Bay Coastal Water Samples in Manila, Philippines

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ABSTRACT

For any body of water, its pH and acid neutralizing capacity (ANC) are two important determinants of its overall condition. The ANC has to be high enough to maintain the pH at an optimal level in order to resist acidification and thereby sustain marine life. An assessment of the pH and ANC of Manila Bay coastal waters along Manila and Pasay, Philippines, was done using 16 collected coastal water samples from four different and equally divided geographic sectors along Roxas Boulevard. The pH of the samples was measured using a pH meter while the ANCs were determined via potentiometric titration against sulfuric acid (H_2SO_4). Results showed that the mean pH of the Manila Bay water samples of 7.84 ± 0.34 was significantly lower compared to the 8.57 mean pH of Laguna de Bay ($p < 0.05$), while the mean ANC of 112.60 ± 16.53 mg $CaCO_3$/L of the Manila Bay water samples does not significantly differ when compared to the 116 mg $CaCO_3$/L mean ANC of all bodies of seawater ($p > 0.05$). Further, both the mean pH and ANC values significantly differ among the four different sectors ($p < 0.05$), and a moderate indirect correlation was identified between pH and ANC of the water samples. More importantly, the coastal waters of Manila Bay have enough buffering components to resist acidification. However, a more holistic study is suggested to accurately assess its capability to indeed sustain marine life.

Keywords: pH, acid neutralizing capacity, Manila Bay, Philippines

INTRODUCTION

Manila Bay is a semi-enclosed estuary facing the South China Sea with major fisheries, shellfisheries, and aquaculture found within this body of water (Global Environment Facility, 2004). It also functions as a port to many ships and has been thriving as a center of economic activity. However, along its coast, many manufacturing industries, such as pharmaceutical, textile, and petrochemical industries, dispose of their waste into the bay. The bay is also the point where many of the domestic sewages of the city converge. Due to the poverty conditions of many of the citizens of the city, many do not have appropriate measures for sewage disposal and end up throwing harmful waste into passageways leading to the bay (Global Environment Facility, 2004).

One important factor that influences water chemistry, specifically pH and buffer capacity, is pollution. Water pollution occurs when there is unwanted dispersion or accumulation of toxic substances in bodies of water. The sources of water pollution can be classified into two: point sources, where discharges can be traced to a specific location, and nonpoint sources, which are diffuse. Globally, nonpoint source pollution from human activities is the leading cause of water pollution (Ashraf et al., 2010).

One of the major abiotic factors in a marine ecosystem is the pH of the water. Although marine life can adjust to wide ranges of pH, water pH levels of 5.0 and lower or 9.0 and higher are lethal to many organisms present in the ocean (Cleveland, 2000). Bodies of saltwater are naturally able to prevent a degree of change on their pH levels through a process called “buffering.” Many weak conjugate acid-base pairs present in saltwater act as buffers, with one of the most common examples being the carbonic acid-bicarbonate pair. However, industrial pollution as well as the aforementioned waste sources may change the concentrations of these buffers present in the water; thus, reducing the capability of the water to buffer against the addition of an acid. The risk of acid rain and other chemical wastes may soon easily increase the acidity of the body of water, which can threaten the sustainability of marine life in the bay.

While pure water has a pH of 7.00, natural unpolluted rainwater actually is acidic in nature, having a pH of 5.60. This acidity is caused by the presence of carbon dioxide (CO_2), nitric oxide (NO), and sulfur dioxide (SO_2) in the lowest layer of the atmosphere, the troposphere. In an unpolluted environment, CO_2 comprises 355 parts per million (ppm), NO comprises 0.01 ppm, and SO_2 comprises 0-0.01 ppm of the air, with SO_2 contributing least in the acidity of rainwater (Casiday & Frey, 1998). Specifically, the presence of SO_2 comes from gases naturally released by volcanoes into the atmosphere. However, with the introduction of fossil fuel combustion and other non-natural sources, the presence of SO_2 is increased to at most 200 times (2.0 ppm). Because of this, at present, most of about 75% of the acidification of rainwater is associated with the presence of sulfuric acid (H_2SO_4), and directly along with it, the presence and quantity of SO_2 and O_2 in the atmosphere. Being a strong acid, H_2SO_4 readily dissociates in water, giving H^+ and HSO_4^- ions. The HSO_4^- ion further dissociates, giving H^+ and SO_4^{2-} ions. Therefore, the presence of H_2SO_4 in the atmosphere drastically increases the amount of H^+ ions present in rainwater, effecting a parallel decrease in the pH of rainwater (Casiday & Frey, 1998).

Buffers are solutions that resist changes in the pH of a system whenever a strong acid or a base is added, consist of a weak conjugate acid-base pair that is in an ionic equilibrium, and are usually produced by mixing a weak acid or a weak base with its salt (Brown et al., 2015). The buffer capacity of a body of water is measured most commonly in milligrams of calcium carbonate ($CaCO_3$) per liter of seawater. The buffer capacity, specifically the acid neutralizing capacity (ANC), is a significant factor in the maintenance of marine life due to the fact that marine life cannot thrive in an environment with significantly fluctuating pH values. For protection of aquatic life, the ANC should be at least 20 mg $CaCO_3$/L (Laguna Lake Development Authority, 2012). The buffer capacity of seawater has a carbonate ANC of 116.8 mg $CaCO_3$/L (van den Berg & Rogers, 1986). It is observed, however, that the mean ANC value for seawater across all bodies of water is 116 mg $CaCO_3$/L (US Environmental Protection Agency, 2006). Below this quantity, seawater is still capable of neutralizing acid without causing a significant change in the pH. Once the ANC of the seawater has been exceeded, it is noted that marine organisms try to adjust and change their physiological status in order to minimize the sudden change in the conditions of their surroundings - in this case, pH. This is known as "phenotypic plasticity," and it functions to maintain the body processes that sustain homeostasis within the body. However, two main issues arise if the external stress becomes too much for the plasticity: (1) the organism may expire, or (2) the organism may undergo an adaptational change that will be very difficult to reverse (Goobold & Calosi, 2013).

With the unavailability of information regarding the pH and ANC profile of Manila Bay, this study was designed to evaluate these parameters using pH meter and potentiometric titration with sulfuric acid, respectively. In particular, this study compared the mean pH of seawater samples from Manila Bay and Laguna de Bay, compared the mean ANC of seawater samples from Manila Bay and across all bodies of water known to be 116 mg $CaCO_3$/L, compared the mean pH and ANC levels across four geographic sectors of Manila Bay, and determined a possible correlation between pH and ANC levels.

Due to the unavailability of accessible information regarding pH and ANC levels of Manila Bay and other bodies of water for Philippine water samples, comparison and evaluation of the method cannot be carried out. Moreover, an assessment of whether there was a change in the pH and ANC levels over the years similarly cannot be implemented. Likewise, no inference can be made on the causes or possible sources of variations in the measured pH and ANC levels of the water samples. Analysis of the chemical and microbiological composition and identification of other abiotic factors and conditions of the bay were not included in the scope of the study.

MATERIALS AND METHODS

Sampling Design and Sample Size

The probability is small that any body of still water (lake, reservoir, pond, lock, storage pool) is relatively homogeneous with regard to any water-quality characteristic (Wilde, 2006). As such, a single sampling point will not suffice in representing the properties of the water or the distribution of its biological community. Hence, an appropriate sample size was calculated using the means and standard deviations of the pH of the samples from monitoring stations of Laguna de Bay in 2009 and 2012 (Laguna Lake Development Authority, 2012). At 5% level of significance, 80% power, and 5% margin of error, a desired sample size of 16 was obtained.

In this study, the design employed was stratified random sampling with equal allocations for the two outcome measures, namely, pH and ANC levels of the water samples. The geographic stratification of Manila Bay into four sectors and the locations of sampling points employed in this study are shown in Figure 1. Thus, four samples in each of the four sectors were obtained.

Figure 1. Map of Manila Bay divided into four sectors and the locations of sampling points. Image taken from http://maps.google.com/

MATERIALS AND EQUIPMENT

For the potentiometric titration, reagents, glassware, and various other pieces of equipment were used. Specifically, three 250-mL beakers, two glass funnels, and two 10-mL and two 100-mL graduated cylinders were used for the preparation of the titrant and pH measurement of the water samples. Sixteen 250-mL Erlenmeyer flasks were used as the vessel for the analyte, and a pipettor calibrated to thousandths of a milliliter was used for the titrant. Wash bottles were also used during the titration process to rinse the pH meter probe (Orion Model 250A).

A 2 M H_2SO_4 and distilled water were used in the preparation of the 0.2 M H_2SO_4. The sulfuric acid with 98% purity was procured from RCI Labscan. Deionized water and the buffer solutions of pH 4.0, 7.0, and 10.0 were used in the calibration of the pH meter.

All glassware were washed with liquid detergent, rinsed three to five times with distilled water, and dried before use. Measurements of pH were taken through the use of an electrode pH meter.

Sample Collection and Handling

The protocol for water collection and handling was derived from the surface water sampling methods of Laguna Lake Development Authority, 2012. All samples were collected from the neritic-epipelagic zone, 0.5 to 2.0 m deep from the coastal region, in the four identified geographic sectors along Roxas Boulevard as shown in Figure 1. The samples were collected around 6:00-10:00 in the morning of July 13, 2015. Samples retrieved were tested within 24–48 hr; hence, these samples may only be representative of the date of collection. It is also important to note that there was heavy rainfall approximately three days before the gathering of the samples.

Sixteen 500-mL plastic water bottles (high-density polyethylene bottles recycled from similar bottled distilled water products) were procured, cleaned with liquid detergent, rinsed with distilled water, air dried, and labelled 1-16. The sampling equipment consisted of a polyethylene plastic dipper attached and fastened to a 2.5-m-long metal rod secured with electrical tape. Nitrile gloves were used in order to facilitate better handling of the samples. Using the sampling equipment, water was scooped from the shoreline of the bay at a depth of around 0.5 m. A "control wash" was employed by prerinsing the collection bottle three times with 20 mL of the sample water prior to final collection. Using a funnel, the water collected was transferred to the bottles filled completely to the brim and were capped tightly to avoid inclusion of air. After every batch of samples collected, the filled bottles were placed inside a container with ice that kept them as close as possible to the ideal temperature of 4°C (Canadian Council of Ministers of the Environment, 2011).

Samples were stored in the refrigerator, not cooler than 4°C, and were tested within 24–48 hr. No additional filtration or purification techniques were employed prior to pH and ANC level measurements.

Measurements and Calculations

The protocol for the determination of the pH and measurement of the ANC levels of the water samples was derived from the United States Environmental Protection Agency (2006).

Determination of the pH of the Samples

The measurement associated with the degree of acidity within a system is the pH, measured as the negative logarithmic value of the general activity of hydrogen ions [H^+]. The pH of the water samples was determined using a calibrated pH meter. The calibration of the pH meter was done by dipping the meter first into a buffer solution of pH 4.0; then, it was dipped into a buffer solution of pH 7.0 and, lastly, into a buffer solution of pH 10.0. The pH meter automatically recognizes the buffer set and adjusts its calibration accordingly.

For the pH measurement, 100 mL of each sample was taken and placed in 250-mL beakers. The pH probe was carefully dipped into the beaker, with the bulb fully submerged and not in contact with the glassware. The pH value was noted once the meter has reached a stable reading. Every time a reading was taken, the probe of the pH meter was rinsed with deionized water and dabbed clean using a facial tissue (Purdue University, n.d.).

Titration of the Samples

The acid used in the experiment was H_2SO_4 (River Watch Network, 1992), a strong acid and a major component of acid rain (at 0.1 to 2.0 ppm) (Casiday & Frey, 1998).

For this experiment, the outcomes focused on the ANC of the water samples. Based from the National Field Manual of Collecting Water-Quality Data (Rounds, 2012), the ANC or alkalinity of a sample can be computed as follows:

$$
\begin{aligned}
&\text{Alkalinity}\left(\frac{\text{meq}}{\text{L}}\right)\\
&= \frac{\text{B(mL) x } \text{C}_\text{a}\left(\frac{\text{meq}}{\text{mL}}\right) \text{ x CF}}{\text{V}_\text{s}\text{(mL) x }\left(\frac{1\text{ L}}{1000\text{ mL}}\right)}\\
&= \frac{1000(\text{B})(\text{C}_\text{a})(\text{CF})}{\text{V}_\text{s}}
\end{aligned}
$$

$$
\begin{aligned}
&\text{Alkalinity}(\text{mg CaCO}_3/\text{L})\\
&= \text{Alkalinity}\left(\frac{\text{meq}}{\text{L}}\right) \text{ x } \frac{1\text{ mmol CaCO}_3}{2\text{ meq}} \text{ x } \frac{100.087\text{ mg CaCO}_3}{1\text{ mmol CaCO}_3}\\
&= \frac{50044(\text{B})(\text{C}_\text{a})(\text{CF})}{\text{V}_\text{s}}
\end{aligned}
$$

where B is the volume of titrant (in milliliters) added from the initial pH to the second equivalence point (pH ≈ 4.0), C_a is the concentration of acid titrant in milliequivalents per milliliter or normality (N), V_s is the volume of the sample (in milliliters), and CF is the correction factor. The correction factor is equal to 1.0 for nondigital titration methods. The ANCs of the samples were computed from the volume of acid needed to reach the equivalence point and were recorded in milligrams of $CaCO_3$ per liter (River Watch Network, 1992). Prior to analysis, the glassware and the probe of pH meter were rinsed with distilled water. Instead of a buret, a pipettor was used to ensure greater accuracy in drawing and dispensing the necessary amount of titrant. Twenty-five milliliters of each sample was measured and placed in a 250-mL Erlenmeyer flask. Using a pipettor, the titrant was first dispensed in increments of 0.050 mL. After every titrant addition, the flasks were swirled to dissolve the titrant, and the pH of the samples was taken. When the pH reading was below 6.00, the titrant was dispensed in smaller increments of 0.025 mL, as drastic changes in pH are expected near the equivalence point (which is expected to be around pH 4.00-5.00). Titration was stopped once the pH was below 4.00 and at least eight readings have been recorded per sample.

Calculating the Acid Neutralizing Capacity

In this study, ANC is defined as the ability of the water samples from Manila Bay to resist changes in its pH against H_2SO_4. It is expressed in milligrams of $CaCO_3$ per liter of seawater. The calculation for ANC was done using the Web-based Alkalinity Calculator Version 2.22 of the US Geological Survey (2013) with values recorded in milligrams of $CaCO_3$ per liter.

Statistical Analysis

In order to compare the mean pH of seawater samples from Manila Bay and Laguna de Bay and to compare the mean ANC of the seawater samples obtained from Manila Bay and the mean ANC of seawater across all bodies of water, *t*-test was used. One-way analysis of variance was employed to determine significant differences in the mean pH and ANC levels of seawater samples from the four geographic sectors of Manila Bay. Post hoc multiple comparison tests were further generated via Tukey's honestly significant difference (HSD) test to determine which pairs of sectors were statistically different. Simple linear regression analysis was employed to determine the functional relationship between pH and ANC levels of the water samples. All statistical analyses were carried out at 5% level of significance using Bill Miller's OpenStat software with values reported as means with their respective standard deviations.

Disposal of Materials

The leftover water samples were disposed of inside an inorganic waste bin, and the plastic bottles were properly segregated into the nonbiodegradable waste bin.

RESULTS AND DISCUSSION

pH of the Samples

The pH measurements of the sixteen seawater samples from Manila Bay are presented in Table 1. The samples have a mean pH measurement of 7.84 with a standard deviation of 0.34, and when compared to the 8.57 mean pH of Laguna de Bay, the coastal water samples of Manila Bay are found to be relatively more acidic ($p < 0.05$). Across the four identified geographic sectors in the shoreline of Manila Bay, the highest mean pH of 8.21 was identified at Sector IV with the lowest pH of 7.37 found at Sector II. The average pH and variability values across the four sectors are summarized in Table 1. Further, when the mean pH measurements among the four geographic sectors of Manila Bay were compared, it was found that these sectors significantly differ from each other ($p < 0.05$) suggesting heterogeneity within the water itself, which may be harmful for some marine organisms, such as the milkfish, that are sensitive to changes in the pH. Milkfish or *bangus*, a common fish harvested in the bay, requires an ideal pH from 6.8 to 8.7 (Bureau of Agricultural Research, 2012). When Tukey's HSD test was employed to compare and identify which pairs of sectors significantly differ in the mean pH measurements, only Sectors I and III do not significantly differ ($p > 0.05$) as shown in Table 1.

Table 1. Mean, variability, and post hoc comparisons of the pH and ANC levels in the four geographic sectors of Manila Bay.

Sector	pH		ANC (mg $CaCO_3$/L)	
		Mean (SD)		Mean (SD)
I	7.94		105.10	
	7.78	7.90	105.10	105.10
	7.95	(0.08)^b	105.10	(0.00)^e
	7.93		105.10	
II	7.68		115.10	
	7.35	7.37	145.10	132.60
	7.18	(0.22)^a	145.10	(15.00)^d
	7.25		125.10	
III	7.83		125.10	
	7.89	7.87	125.10	107.60
	7.82	(0.06)^b	95.10	(20.62)^e
	7.94		85.10	
IV	8.37		105.10	
	8.17	8.21	105.10	105.10
	8.20	(0.11)^c	105.10	(0.00)^e
	8.12		105.10	
Total		7.84 (0.34)*		112.60 (16.53)**

^{a,b,c} Mean pH groupings ($p < 0.05$).
^{d,e} Mean ANC groupings ($p < 0.05$).
*Versus 8.57 pH of Laguna de Bay ($p < 0.05$).
**Versus 116 mg $CaCO_3$/L ANC of all bodies of water ($p > 0.05$).

Acid Neutralizing Capacity of the Samples

The values of the ANC levels of the 16 water samples are displayed in Table 1. The mean ANC level was determined to be 112.60 mg $CaCO_3$/L with a standard deviation of 16.53 mg $CaCO_3$/L. The computed 95% confidence interval is 104.50 to 120.70 mg $CaCO_3$/L, which contains the average ANC level across different bodies of water identified to be 116 mg $CaCO_3$/L. As such, there is no enough information to say that there is a significant difference between the ANC of the water samples from Manila Bay and the average ANC level across different bodies of water ($p > 0.05$). Across the four geographic sectors, the highest mean ANC level was found in Sector II while Sectors I and IV have the lowest mean ANC levels. The means and standard deviations of ANC levels among the four sectors are summarized in Table 1. Moreover, the standard deviations of the ANC levels are quite significant to note. The coefficient of variation in Sector III is 19.16%, while that of the total is 14.68%, which is possibly indicative of a need for additional samples involving ANC measurements.

Nonetheless, comparing the possible differences in the mean ANC levels across the four geographic sectors, it was found that the mean ANC levels significantly differ among the four sectors ($p = 0.03$). Using post hoc Tukey's HSD test to further identify which pairs of sectors have significant difference in the ANC levels, results showed that the mean ANC level of Sector II significantly differs from the three other sectors as shown in Table 1.

An attempt to correlate pH and ANC level measurements was considered, using simple linear regression analysis, and the correlation plot is displayed in Figure 2. The correlation coefficient obtained was −0.721, indicating a moderate indirect linear correlation between pH and ANC values. The obtained linear regression model has an intercept of 390.68 and a slope of −35.48, meaning for every unit increase in the pH value, it results to a corresponding 35.48-mg $CaCO_3$/L reduction, on the average, in the ANC level of the water sample. The obtained model is found to be statistically significant ($p < 0.01$). However, the adequacy of this regression model to fully capture the linear relationship between pH and ANC values was only 52.01%, which means that the total variation attributed to the ANC values is further influenced by other factors not identified in this study. Nonetheless, it was found that pH is inversely proportional to the ANC level, which is contrary to the theoretical relationship, where pH is directly proportional to the ANC level (Tölgyessy, 1993). Ideally, the presence of more CO_2 inside the water would lead to an increased concentration of carbonic acid (H_2CO_3) and consequently a decreased concentration of bicarbonate ions (Pytkowicz & Atlas, 1975), which would subsequently both decrease the overall pH and ANC of the water and would eventually result to saltwater acidification.

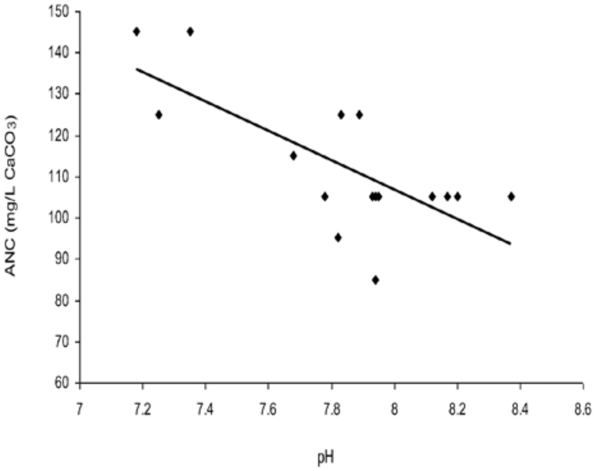

Figure 2. Correlation plot between the pH measurements and the ANC values of the coastal water samples. (ANC = −35.48 (pH) + 390.68; $r = -0.721$; $p < 0.01$).

Saltwater acidification is commonly attributed to CO_2 and during increased concentrations; the compound readily bypasses biological membranes towards the blood and other intracellular cavities (Fabry et al., 2008). Organisms may attempt to passively buffer the CO_2 out through natural processes, but there may come a point where the physiological need of the organism matches the status of the surrounding pH. These newly adapted species then thrive and proliferate within the ecosystem, possibly leading to the extinction of another organism. One of the notable spreading-diminishing species pairs is the algae and the calcifers, which require the carbonate ion (CO_3^{2-}) in order to undergo calcification (Connell et al., 2013). The carbonic acid-bicarbonate buffer system within the water generally maintains the need of carbon for both species in their survival. However, due to the increasing CO_2 levels within the water, a substance that the algae can easily tap for carbon fixation, the ecosystem then proceeds in favor of the increasing algae, which then forces the buffer system to shift at the expense of the calcifers (Fabry et al., 2008).

The buffering capacity of a body of water protects it from rapid changes in pH that may be brought about by external factors such as water pollution. However, long-term pollution may eventually consume the buffer capacity of water. Specifically, CO_2 emissions from human activities get absorbed by the ocean, thereby producing substances that lower the pH (Shaw et al., 2013). As these acidic substances accumulate, the buffering components of the water body are gradually consumed until the buffer capacity of the water is exceeded (i.e., the carbonate ions are used up). When this happens, the water becomes highly susceptible to changes in pH. This is detrimental to organisms as extreme acidification makes the water body unfit for marine life (Addy et al., 2004). With lower pH, the availability of plant nutrients such as ammonia, phosphate, and iron may also decrease. In addition to that, slight shifts in the pH can cause significant changes in the solubility of heavy metals (e.g., iron and copper). These, which are found in the sediments of water, are more soluble in water with lower pH levels. Thus, a decrease in pH will cause these potentially toxic metals to be resuspended in the water, where they could be ingested by marine organisms (Shaw et al., 2013).

However, it is important to note that a high buffer capacity is not always indicative of ideal water-body characteristics. For instance, when a toxic substance accumulates in the body of water, it is possible that the organisms most susceptible to it will die, while survivors will use up the toxic substance and decrease its concentration. In this case, diversity is low, but the buffer capacity is maintained (Jorgensen, 1999). As such, in order to get a proper risk assessment of a body of water, a holistic approach is advised - one that includes other abiotic factors such as temperature and the level of eutrophication.

CONCLUSION

A significant difference between the mean pH of the coastal water samples of Manila Bay and Laguna de Bay was identified in this study. There is also a significant difference in the mean pH levels among the geographic sectors of Manila Bay suggesting heterogeneity within the water itself, which may be harmful for some marine organisms. However, based on the obtained results, there is no sufficient evidence to say that the average ANC of the water samples is significantly different from 116 mg $CaCO_3$/L mean ANC of all bodies of seawater. Thus, despite the differences among the mean ANCs of the sectors, it can be said that the coastal waters of Manila Bay, in its entirety, still have enough buffering components to resist acidification and to sustain marine life.

Expert organizations in ecology or marine biology can make use of the baseline information obtained in this study to evaluate which marine organisms found in the bay should be closely monitored, especially in the event of acid rain or other certain conditions that would significantly alter the acidity of the water. The data of the research may also inform the authorities maintaining the bay on its current status and whether or not an action plan, designed to regulate the conditions of its waters, should be implemented. However, to accurately describe the capability of Manila Bay to indeed sustain marine life, a more comprehensive study regarding the chemical and microbiological composition of the water samples is recommended. Other than the pH and ANC levels, the amount of pollution, chemical composition (e.g., amount of dissolved oxygen and chlorine levels), and other essential physicochemical properties of seawater may provide additional information in better assessing the sustainability of marine culture in Manila Bay. Moreover, this study could be used to further encourage the need for a holistic ecological risk assessment of the bay, given that pH levels and buffer capacity, specifically its ANC, are only two of the factors indicating the sustainability of a marine ecosystem. Manila Bay has been a significant Philippine landmark over the years and serves as a large avenue for aquaculture; therefore, it is highly important and just to uphold its capability to maintain life.

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