

Temporal Distribution of Seawater pH and Alkalinity Across Five Sites on the North Coast of Upolu, Samoa

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Abstract The ocean plays a crucial role in regulating Earth's climate by absorbing approximately 30% of the carbon dioxide (CO₂) emitted into the atmosphere. This process results in the production of carbonic acid, contributing to the acidification of the ocean and a decrease in seawater pH, which is referred to as ocean acidification. Human activities and natural sources primarily cause this acidification process, and it poses a significant threat to marine ecosystems. One of the key impacts of ocean acidification is the depletion of carbonate ions, which are essential for forming skeletons and shells in many marine organisms, including corals. There is a lack of detailed information regarding the fluctuation of seawater carbonate chemistry in Pacific island coastal regions like Samoa. To bridge this gap in knowledge, a study was conducted to examine the temporal variability of seawater carbonate chemistry at five locations along the North coast of Upolu Island. The mean pH was measured spectrophotometrically using the m-Cresol purple buffer. The total alkalinity (A_T) was measured through titration of seawater with standardized 0.101970 mol/kg HCl. The measured values from the spectrophotometer at three wavelengths: a non-absorbing wavelength (730 nm for m-Cresol purple) and at the wavelengths corresponding to the absorption maxima of the base (I²⁻) and acid (HI⁻) forms of the dye respectively (578 and 434 nm) and the EMF values from the seawater titration were used to calculate the actual pH and A_T. The results showed that these values varied across 5 sites. The overall distribution of mean pH across 5 sites fell below the mean average pH of 8.1 for open ocean water ranging from 7.944 ± 0.090 to 8.087 ± 0.069, while the mean seawater A_T values fell within the normal A_T range of (2100-2500 μmol kg⁻¹). Thus, the variability of these seawater parameters over the study area has indicated healthy coastal waters.

Keywords: Ocean Acidification, SDG14, Total Alkalinity, climate change, seawater CO₂, ocean monitoring, marine ecosystem

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1. Introduction

Climate change is one of the most pressing issues of our time, with far-reaching impacts on ecosystems, economies, and societies worldwide. It refers to long-term alterations in temperature and typical weather patterns in a place. These changes are primarily driven by human activities that release greenhouse gases, such as carbon dioxide (CO₂), into the atmosphere. These gases trap heat, leading to global warming and a range of impacts on ecosystems, weather patterns, sea levels, and human societies. It poses significant threats to livelihoods, biodiversity, and the physical environment.

The ocean, covering over three-quarters of the Earth's surface, plays a crucial role in the planet's ecosystem. It holds about 96.5 percent of all the planet's water and absorbs more than 90 percent of the excess heat in the climate system [1]. Approximately 90% of the planet's biomass lives in the ocean, highlighting its significance as

a vital life-supporting system for our planet. Over time, since the dawn of the Industrial Revolution, the ocean has absorbed roughly 30% of all annual anthropogenic CO₂ emissions [2] showing its ability to moderate climate change impacts on a temporal scale. With ongoing CO₂ emissions, the average ocean pH has decreased from 8.2 to 8.1, exhibiting seasonal and spatial variations of about 0.1 pH units [3]. Projections suggest that the pH could decline by approximately 0.3 to 0.4 units by the end of the 21st century, equivalent to a 100 to 150% increase in acidity if CO₂ emissions remain uncontrolled. Ocean acidification, known as the decrease in ocean pH, poses a global issue, altering ocean carbonate chemistry and leading to adverse effects on marine and environmental resources, particularly for calcifying species. The elevated CO₂ levels linked to the decrease in seawater pH can be particularly challenging not only for calcifying organisms but also for marine species with high metabolisms, such as squid and fish, as the altered seawater pH affects the pH balance in fish blood [4]. An additional critical challenge

confronting the oceanographic community is the inconsistency in measurements of seawater CO₂ system parameters, which arise due to the changing ocean chemistry associated with increasing CO₂ levels. [5]. The characterization of the carbon dioxide system in seawater involves key parameters such as pH, total alkalinity (A_T), dissolved inorganic carbon (DIC), and partial pressure of carbon dioxide (pCO₂). It is noteworthy that these properties can be fully determined by measuring only two of the four parameters (AT, DIC, pH, and pCO₂) [6,7].

From ancient times, the Pacific Ocean has not only shaped the cultural and historical identity of island communities but also bestowed upon them significant socio-economic benefits. Coral reefs, for instance, serve as both recreational and tourism attractions, while also providing resources for sustaining stable livelihoods and enhancing the economy. These aspects are integral to the way of life in the Pacific. [8]. The increased ocean temperature, leading to marine heatwaves and coral bleaching [9], along with ocean acidification [10] has resulted in substantial loss of marine resources and coral reefs in Pacific communities. The ongoing phenomenon of global warming, coupled with the increasingly acknowledged effects of atmospheric carbon dioxide on ocean acidification, is expected to have significantly detrimental long-term impacts on reefs [11]. Additionally, coral reefs' importance extends to aquaculture, including pearl oysters and marine ornamentals, and potentially shrimps, as well as their role in coastal protection [12]. Since the beginning of the industrial era, the pH of the tropical Pacific Ocean has decreased by 0.06 units [13], impacting food security and livelihood opportunities for Pacific Island communities. The acidity of the marine environment, intensified by ocean acidification, poses a severe threat to coral reefs, which are habitats for numerous marine species crucial for fish resources in Pacific countries. The economy, largely reliant on fishing and agriculture, is also vulnerable to cyclones and disease [14,15].

Coral reefs fringe the Samoan archipelago, serving as natural barriers to protect coastlines and marine species from the effects of climate change, ocean acidification, and increasing local pressures. [16]. Hence, the reliance of Samoan communities on these ecosystems and the ocean for essential ecosystem services and resources is substantial [17]. Samoa stands out among volcanic islands for its high vulnerability to natural and anthropogenic changes, especially the effects of warming temperatures, ocean acidification, and sea-level rise due to climate change. Despite the majority of international researchers conducting ocean acidification (OA) research in their waters [18,19]. Current knowledge is insufficient to quantify the impact of OA on the marine environment and fish resources. This gap is particularly pronounced in most Pacific countries, where such research has not been extensively carried out. In Samoa, there is a notable absence of information and research on ocean acidification, with no studies conducted along the North coast of Upolu. This study aimed to fill this gap by contributing to the literature and providing baseline seawater chemistry data on Samoa's coastal waters. It conducted a preliminary investigation on the temporal variability of seawater chemistry along the North coast of Upolu. The primary objective was to examine the

seawater chemistry, focusing on measuring seawater pH and alkalinity (A_T) at selected sites across 3 months. The findings are expected to enhance understanding of the status of ocean acidification in Samoa including the temporal trends, which are important for monitoring changes in acidity levels over time. Understanding these trends can help researchers and policymakers develop strategies to mitigate the effects of ocean acidification and protect marine ecosystems. The primary research study is structured into two phases; focusing on spatial and temporal aspects of pH and alkalinity with this article only touching upon temporal variability.

2. Methods

In this study, a quantitative approach was used to collect data through experimental research, focusing on the temporal variability of the seawater carbonate system. The sampling and preservation of samples before analysis followed the Guide to Best Practices for ocean CO₂ measurements [20].

The study aimed to fully describe the seawater carbonate system of the open ocean and nearshore waters by measuring two of its major parameters, along with temperature and salinity [6] Measurements focused on seawater alkalinity and pH, with pH measured using a UV-Vis Spectrophotometer and A_T measured through the open cell potentiometric titration method.

2.1. Study Sites

Five sites along the North coast of Upolu island were selected for this study: Vaiusu, Mulinu'u, Palolo Deep Marine Reserve, Moata'a, and Fagali'i (Figure. 1). These areas were chosen due to their importance in providing ocean services or marine products that are potentially vulnerable to the effects of ocean acidification. Local communities rely on these sites for food, tourism, and income-generating resources. The study covered a period of six months to observe temporal trends in seawater chemistry at these sites.

2.2. Sample Collection and Preservation

Over a six-month period from March to August 2021, samples were collected monthly to study temporal trends in seawater chemistry. Seawater samples were collected using 250 mL and 1000 mL borosilicate glass bottles with polypropylene screw caps. To ensure sample integrity, the bottles were autoclaved at 130°C to destroy any biological wastes or bacterial contaminants. Each bottle was filled with seawater, leaving approximately 3 mL of headspace to prevent breakage due to compression under pressure.

The seawater bottles were stored in a cool container and delivered immediately to the laboratory at the National University of Samoa Marine and Environment Research Centre (MERC). Within 6 hours of collection, the samples were poisoned with 0.3 µL mercuric chloride solution to inhibit microbial activity and preserve their composition during long-term storage. [21]. This process involved adding 1 µL of mercuric chloride solution for every kg of artificial seawater. [22,23,24]. After poisoning, each bottle was inverted to ensure thorough mixing, sealed with parafilm, and stored in a cool container for subsequent analysis. [25].

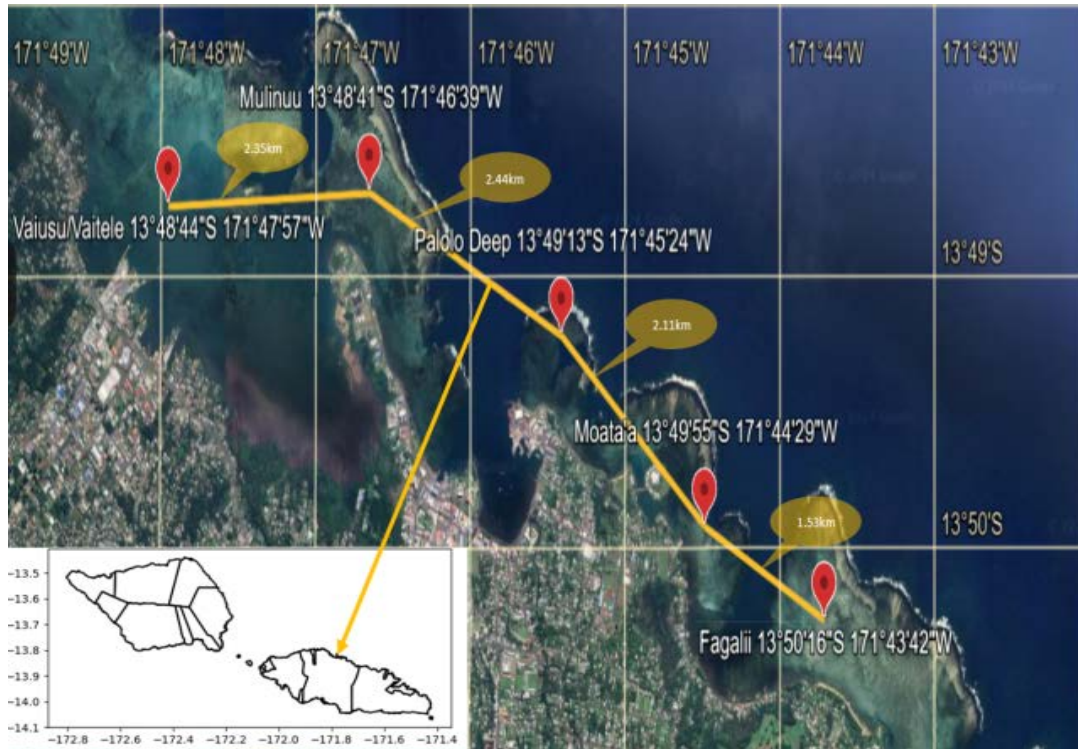


Figure 1. Seawater sampling study sites locations along the North coast of Upolu

2.3. Measurement of Seawater pH

The laboratory pH measurements were conducted following the Standard Operating Procedures proposed by [26] to ensure consistency in analyzing temporal trends in seawater chemistry. Before analyzing seawater samples, the spectrophotometer (Orion™ AquaMate Vis) was operated with the multiwavelength function and cuvettes were placed in a thermostat compartment for a few hours to warm up the sample cells to 25.0°C ($\pm 0.1^\circ\text{C}$). Since pH is sensitive to gas exchange, it is better to work fast once the sample is opened. To minimize errors, the cuvette was rinsed three times with the sample before running the actual test, using a plastic pipette to add a small amount of seawater up to the shoulder of the cuvette while avoiding introducing bubbles. The cuvette was placed in the thermostat sample compartment to ensure alignment of the optical surface of the cell with the light path. Absorbances were recorded for the cell with seawater at three wavelengths: a non-absorbing wavelength (730 nm for m-cresol purple) and at the wavelengths corresponding to the absorption maxima of the base (I^{2-}) and acid (HI^-) forms of the dye respectively (578 and 434 nm). Next, 40 μL of the 2 mmol dm^{-3} m-Cresol purple dye solution was added into the cell using a micropipette, ensuring thorough mixing. The amount of dye added was adjusted to produce absorbance values between 0.4 and 1.0 at each of the two absorbance peaks. The cuvette was returned to the spectrophotometer, and absorbances of the cell with seawater and dye at three wavelengths were measured again. Cells were positioned to maintain consistent alignment between baseline absorbance (seawater sample only) and absorbance of the sample with dye at 730nm, ensuring that the difference was within ± 0.001 to ± 0.003 . Temperature was recorded using the Fluke 51 II handheld digital probe thermometer, and absorbance values were entered into an

excel spreadsheet to calculate the actual and mean pH for each analyzed sample, providing a comprehensive view of temporal variations in seawater pH.

2.4. Measurement of Total Alkalinity

Total alkalinity (A_T) was calculated indirectly by measuring first the EMF of seawater using an open-cell potentiometric acid titration system with an 876 Dosimat digital multimeter and a Metrohm Electrode Plus pH electrode developed by the Dickson Lab at Scripps Institution of Oceanography [20,27]. To begin, the multimeter system was connected to the electrode through a current amplifier to allow rapid measurements with the digital multimeter. The stir bar and the vessel were thoroughly rinsed three times with distilled water and completely dried using Kimtech Science Kimwipes before use. The waste sample was disposed into a waste container that contained poisonous mercuric chloride.

For sample preparation, the burette was filled with 0.1N HCl solution and set to the 0 marker of the calibrated burette (0.0 mL). The electrode and burette were attached to the ring stand holder. Using a 50 mL pipette with a bulb (Fisherbrand), 50 mL of seawater was extracted from the sample and poured into the vessel after rinsing the pipette three times. The titration vessel with the stir bar was placed on the stir plate to create a small dip in the middle of the sample. The sleeve part of the probe was submerged in the sample, and the tip of the burette was placed in the sample. Initially, 1.2 mL of acid was added while increasing the speed of the stir bar. The voltage reading should show a negative EMF value before starting the acid addition. Once the reading stabilized, EMF values were recorded.

After degassing the sample, the stir bar speed was reduced, and the acid volume and voltage reading were recorded. Each titration point was recorded with 0.005 mL

increments up to 10 titration points. The measured EMF values were used to calculate alkalinity using a Gran function and a Non-Linear Least Squares (NLSL) method. After daily measurements, the electrode was removed from the ring stand and stored in a KCl storage solution. This method allowed for the analysis of temporal variability in seawater pH and alkalinity trends.

2.5. Data Analysis

The study utilized the SPSS16.0 software from International Business Machines Corporation (Armonk, NY, USA) to conduct statistical and inferential analyses [28] over a span of 3 months at each of the five study sites for the measured pH and A_T . The software generated various tests, including descriptive and frequency tables, to summarize the distribution of means, standard deviation, minimum, and maximum values for all measured and calculated variables at each site over the 3-month analysis period. This approach enabled the examination of temporal variability in pH and A_T across the study sites. [29]

3. Results

3.1. Temporal Variations in pH and A_T

The laboratory pH measurements spanned a total of 6 months of analyses, while the A_T was determined from 3 months of sampling due to a technical malfunction of the multimeter equipment. This temporal variability in data collection duration allows for a comprehensive examination of pH and A_T trends over time at the study sites. Parametric test such as one-way ANOVA analysis was performed to compare means and test for the mean significance difference ($p < 0.050$) between two chemical parameters across the 5 sites over 3 months. The study involved collecting seawater samples from five sites, including a Marine Protected Area (MPA), from July to August. Each site was sampled three times per month, ensuring data reliability and robustness. Over the three-month period, a total of 9 replicate samples were collected per site ($N=9$). This replication accounted for temporal variability, providing a robust dataset for analyzing pH and alkalinity variations in coastal waters.

Temporal variations for pH and A_T recorded below shows distinct differences were observed for the mean pH trend (Figure 2) for July and August and increased across the 5 sites for June. The A_T (Figure 3) increased across 4 sites in June and decreased slightly decrease at the Fagali'i site. For July and August, the mean A_T decreased at Palolo Deep. There were significant differences ($p < 0.005$) for alkalinity across 5 sites in the 3 months; June ($p = 0.000$), July ($p = 0.000$), and August ($p = 0.000$). As for the mean pH distribution, July was the only month with no significant difference ($p = 0.337$) while the months of June ($p = 0.000$) and August ($p = .001$) had significant difference for measured pH.

A one-way ANOVA test was run to compare different means for measured pH across 5 sites and to identify if there's a significant difference as indicated by the Sig. ($p < .050$) value. The effect size (represented by omega Ω sign) was calculated from 5 values within the ANOVA

table, where ($\Omega^2 = \text{Sum of Squares for between groups} - (\text{df Between groups}) (\text{MS Within groups}) / \text{MS Within groups} + \text{Total Sum of Squares}$) [30].

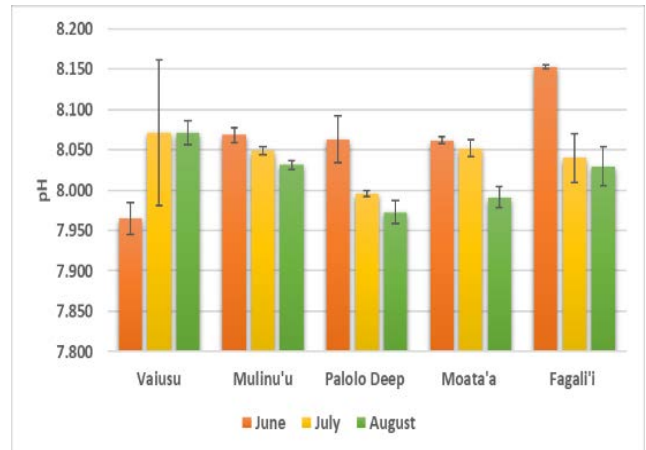


Figure 2. Temporal comparison of mean monthly pH across 5 sites. Error bars indicate standard deviation

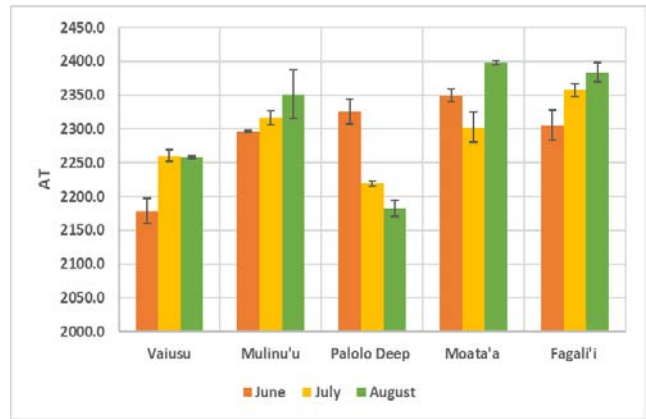


Figure 3. Temporal distribution graph of individual mean AT. Error bars indicate standard deviation across 5 sites

3.1.1. Temporal Variation for pH and A_T

Table 1. A One-way ANOVA analysis for measured pH across 3 months in each site

Month	Sum of Squares (SS)	df	Mean Square (MS)	F	Sig. (p)	
June	Between Groups	.053	4	.013	50.101	.000
	Within Groups	.003	10	.000		
	Total	.056	14			
July	Between Groups	.010	4	.002	1.293	.337
	Within Groups	.018	10	.002		
	Total	.028	14			
August	Between Groups	.011	4	.003	10.664	.001
	Within Groups	.002	10	.000		
	Total	.013	14			

The ANOVA analyses presented in Table 1 indicated significant differences in measured pH levels across the five sites for the months of June ($F(4, 10) = 50.1, p = .000$) and August ($F(4, 10) = 10.7, p = .001$). The effect sizes for these differences were also found to be very meaningful,

with Ω values of 0.946 for June and 0.846 for August. However, no significant difference was found for the month of July ($F(4,10) = 1.3, p = .337$).

Table 2. One-way ANOVA mean comparison for alkalinity across 5 sites

Month		Sum of Squares	df	Mean Square	F	Sig.
June	Between Groups	52502.737	4	13125.684	51.924	.000
	Within Groups	2527.880	10	252.788		
	Total	55030.617	14			
July	Between Groups	33812.513	4	8453.128	53.339	.000
	Within Groups	1584.780	10	158.478		
	Total	35397.293	14			
August	Between Groups	101600.663	4	25400.166	75.777	.000
	Within Groups	3351.967	10	335.197		
	Total	104952.629	14			

The ANOVA in Table 2 indicates a significant difference in alkalinity across sites for all three months:

June ($F(4,10) = 51.9, p = .000$), July ($F(4,10) = 53.3, p = .000$), and August ($F(4,10) = 75.7, p = .000$). As the mean alkalinity differs significantly in all three months according to the ANOVA analysis.

4. Discussion

Temperature is one parameter that is often used in physical, chemical and biological processes and therefore varies between times and places. Normal ocean surface temperatures in the equatorial Pacific Ocean range from 18 to 30°C [31], therefore the mean seawater temperature for this study in Figure 4 range from 28.1 to 30.4°C. This increase in temperature was caused by the amount of time to transport seawater samples at the laboratory for measurements instead of on-site measurements. This is presented to correlate the findings on the spatial, temporal and seasonal variations of pH and alkalinity across the 5 study sites to these parameters. Therefore the lowest seawater temperature was recorded for Palolo Deep site in August however it was the highest in June. In July, the highest temperature was recorded at Mulinu’u site.

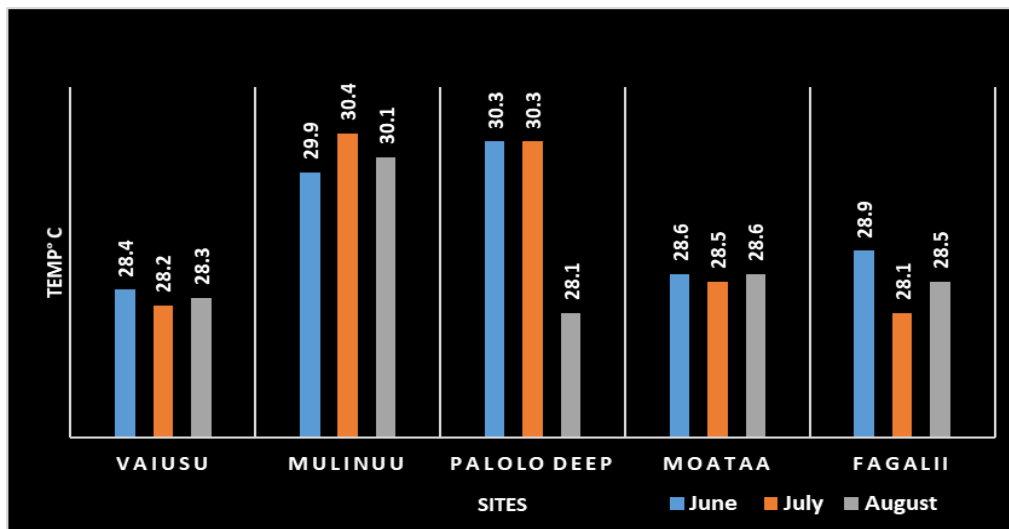


Figure 4. Composition of Mean Temperature recorded across 5 sites over 3 months

4.1. Temporal Variability in Seawater Parameters

When referring to pH and alkalinity in seawater, temporal variability describes how these parameters change over time. pH measures the acidity or basicity of a solution, while alkalinity measures the water's ability to neutralize acids. Both pH and alkalinity in seawater can vary due to natural processes and human activities. Monitoring temporal variability in pH and alkalinity is crucial for understanding the health of marine ecosystems, as changes in these parameters can impact marine life, including corals, shellfish, and other organisms. It can also help assess the effectiveness of conservation and management efforts aimed at protecting marine environments from the impacts of climate change and pollution.

4.1.1. Temporal Variability in pH

The pH of seawater is a critical parameter in oceanography, reflecting the thermodynamic state of the

solution. It is calculated using the equation $pH = -\log [H^+]$ [32]. An ANOVA analysis (Table 1) was conducted to explore the temporal variations in mean pH across five sites—Vaiusu, Mulinu’u, Palolo Deep, Moata’a, and Fagali’i—over the months of June to August. The results indicated significant differences in pH for both June and August, highlighting temporal variability in pH levels during these months ($p < 0.05$).

In June, the mean pH ascended across 5 sites and dropped significantly lower at Vaiusu ($F(4, 10) = 50.1, p = .000$) compared to the other 4 remaining sites. This is due to the highest levels of pCO_2 recorded in Vaiusu over 4 sites. It is well-aligned with the discoveries from a report by Raven et al. [13],- which stated that changes in the chemistry of the oceans are caused by increased concentration of CO_2 in the atmosphere, consequently lowering ocean pH. As atmospheric CO_2 dissolves in seawater, the partial pressure of this gas increases as well in the surface waters, therefore decreasing the concentration of the ocean’s pH [33]. This supports

another similar study on pH data on ocean chemistry at Aloha Ocean Station from the Royal Society report where the lowest pH values correspond to the acidity of the ocean with high carbon dioxide concentration [34]. Most CO₂ studies presented correlations and ecological consequences of lower pH, lower carbonate saturation state and higher CO₂ [21,34]. The temperature for Vaiusu site was the lowest across 4 of the remaining sites with the lowest mean pH as well. This is in contrast to a study where the pH is dependent on temperature in surface seawater and vice versa which was investigated as a function of salinity and composition [35].

In August, the low amount of rainfall contributed to the decrease in mean pH in Vaiusu compared to Mulinu'u and Fagali'i by 0.1 and 2.6mm. If rainfall was low or decreased, it implies the non-dilution of ocean acidity. Although the temperature was higher at Mulinu'u and Fagali'i sites than Vaiusu, it did not affect the levels of measured pH as it was more statistically significantly lower in Vaiusu than Mulinu'u and Fagali'i and similar to Palolo Deep site. Although the temperature was lowest for Vaiusu site, the mean pH was significantly lower than Mulinu'u and Fagali'i. This is aligned with a past study from Gao et al. [25] where spatial and temporal variations in pH and A_T were analyzed across different stations in Changjiang Estuary, China. The results showed temporal variations in pH versus temperature and no significant correlations were found between pH and temperature for some stations. Therefore, the pH of coastal waters responds to the changes in dissolved carbon dioxide concentrations, alkalinity, hydrogen ion concentrations and, in a lesser way, to temperature. Other contributing factors to lowering pH are excess nutrients along the waterways, organic matter, nitrate and sulfate concentration from fertilizers, wastewater, automobile exhaust, and animal waste [25]. These can be decomposed adding CO₂ to seawater. These factors end up on the coast of Vaiusu site. Since Vaitoloa is a previous landfill, the leachate from this landfill can contaminate groundwater. These leachates will potentially end up in coastal ecosystems resulting in a high pCO₂ and low pH [36]. Similarly, in Western Europe and North America in the late 20th century, nitrate and sulfate concentrations in precipitation over the eastern United States are strongly associated with pH. All in all, the mean pH values for this study are well within a range similar to long-term trends in pH for 4 selected coastal ecosystems; the Chesapeake Bay, Danish Straits, Southern North Sea, and Tampa Bay [25] but differ in findings in another study where an extreme pH such as the 6.2 values recorded in coastal waters following an underwater eruption gave rise to a novel shallow submarine volcano south of the island of El [37]. This low pH is expected as the eruption releases acidic gases such as CO₂, SO₂ and nitrous oxides.

4.1.2. Temporal Variability in A_T

Alkalinity serves as the buffering capacity that neutralizes acid by accepting hydrogen ions (H⁺) during titration with hydrochloric acid to the carbonic acid endpoint [38]. An ANOVA analysis was run to determine monthly significance mean comparison between A_T across 5 sites. Therefore all 3 months were significantly different across 5 sites (p<0.05). An observed temporal trend

illustrated a decline in mean A_T across June. For July and August mean A_T was recorded the lowest for Palolo Deep site.

In June, levels of alkalinity dropped significantly lower in Vaiusu than in the other 4 sites. In July, the mean A_T dropped significantly in Palolo Deep than the other 4 sites as illustrated by Figure 3. This means the ability to neutralize acid (low pH) at Vaiusu and Palolo Deep is low and can be explained by the immediate change in pH. Similar to the finding in August, observed temporal trends illustrated a decline in mean A_T across June and were lower in Palolo Deep. Also, the decline in A_T for Palolo Deep was in equilibrium with the mean levels of pH, whereby a decrease in pH causes alkalinity to decrease as well [39].

Palolo deep had the lowest mean pH value across 5 sites in July and August, this is associated with having the lowest mean alkalinity value for these 2 months specifically (Figure 3). This is quite interesting as Palolo Deep is indeed a marine protected area [40] compared to the other 4 sites which are more exposed to physical and chemical contaminations from human activities. However, a different result was observed in a study in subtropical regions, where increasing surface A_T from increasing salinity and temperature related to climate change causes pH to decrease. For example, for seawater with pCO₂ 400 μatm and A_T of 2400 μmol kg⁻¹ at 25°C, an increase in the salinity of 1‰ will decrease the pH by 0.003 and an increase in temperature of 1°C will decrease the pH by 0.001 as estimated using the CO2SYS software (Peterson, 2018). Many human-derived pollution and biological processes around Palolo Deep influence the levels of A_T, which includes damaging the corals through tourist and local snorkeling and swimming activities-, and increasing urban sprawls near the coastline with ship routing. These causes fundamental changes in coastal environments, including land-use changes and increasing environmental pollution often leading to seawater intrusion and contamination. This is evident in accordance with Torres-Martínez et al. [41]. The variability in alkalinity was observed to be mainly controlled by the simple dilution or concentration (SDC) effect of precipitation and evaporation, and the measured concentrations of alkalinity are well aligned with those predicted from salinity and temperature [42], however prior to another study, the removal or addition of CO₂ gas and temperature changes did not affect the levels of alkalinity [43]. Although sea surface temperature does not affect A_T, it can influence the upwelling of cold waters to the surface, according to Fiedler et al. [44] where an oceanographic survey was performed on the eastern tropical Pacific Ocean in August-November 1990 and found a productive, nutrient-rich, moderately high-chlorophyll surface layer in two oceanic upwellings. Coastal upwelling is when winds blow across the ocean surface water both north and south, allowing upwelling of deeper water. Upwelling brings CO₂-rich deep water to the surface. Biological production and upwelling or some combination of both may potentially be responsible for the A_T variability in our precipitation-limited coastal environment [45]. Near the equator, upwelling also increases A_T relative to salinity, particularly in the Pacific. A_T variation due to combined organic production and denitrification on the order of ~15 μmol kg⁻¹ SW, a potentially minor (<1%) contribution to

the observed degree of variability at Stearns Wharf. Yang [46]. Riverine discharges significantly affected the carbonate system, as they are an input of total alkalinity and nutrients [47]. Another similar study on Puget Sound at Fjord Estuary receives waters upwelled along the Pacific Coast that are already burdened with increasing concentrations of anthropogenic CO₂, which will continue to increase over the proceeding decades regardless of possible changes to atmospheric pCO₂ [46].

5. Conclusion

The measured pH and A_T varied temporally depending on the condition of the site. A comparison was made across 5 sites, and Vaiusu site had the lowest mean pH and A_T over June, while Palolo Deep had the lowest mean pH and A_T for July and August. The contributions to a decline in coastal pH and A_T were from anthropogenic emissions (Klinckhamers, 1992) that may have been in operation over centuries to millennia [48]. The effects of these contribution takes hundreds of years for the coastal ocean to recover from. As Palolo Deep is considered a marine protected area, it has the lowest mean pH and A_T value across 5 sites in 2 months which was expected to increase. This is due to anthropogenic and natural hazards such as cyclones damaging the coral reef sites. Since Samoa has two distinct weather regimes, the research question was investigated by collecting seawater samples from 2 months of the wet season and 4 months of the dry season. Mulinu'u was the only significant site from the ANOVA analyses. The pH was below the normal mean pH of 8.1 and the characteristics seemed to be strongly influenced by heavy rainfall season as well as the various anthropogenic sources (Klinckhamers, 1992). Excess nutrients such as phosphorus and sulfur from agriculture and riverine inputs from past years still have an effect on the ocean chemistry as well as the mixing process of freshwater from mangroves and seawater (Iakopo, 2006). High nutrient input increases pH in the developing world whereas excess amount can cause oligotrophication (partial reversal of the eutrophication process) and eutrophication (a gradual increase in the concentration of phosphorus, nitrogen, and other plant nutrients in an aging aquatic ecosystem) which may lead to acidification, adding to the same trend imposed by anthropogenic CO₂ emission [49]. In the future, the dominant driver that needs to be managed is nutrient input [50].

Disclosure Conflict of Interest

Authors Name:

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Conflict of Interest Disclosure Statement

I, Tina Taitaifono Mareko, hereby disclose the following potential conflicts of interest related to my involvement in the research publication titled "Spatial and temporal distribution of seawater pH and alkalinity across

five sites on the North coast of Upolu, Samoa". The authors of this research paper declare that they have no actual or potential conflicts of interest related to this study. I have no personal relationships, interests, affiliations, or business activity with individuals or entities that have a vested interest in the research presented in the Publication.

Financial Disclosure:

This research received no specific grant from any funding agency in the public, commercial, or nonprofit sectors. I also understand that I must promptly reveal any changes in my personal business interests, affiliations, or activities that may give rise to a conflict of interest, by updating my Disclosure Statement.

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