Scientific Research Publishing

Open Journal of Marine Science, 2026, 16(3), 141-162
https://www.scirp.org/journal/ojms
ISSN Online: 2161-7392
ISSN Print: 2161-7384

Variability of Carbon Chemistry at the Marine Protected Area of Savaia Village, Upolu Island, Samoa

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How to cite this paper: Amosa, P., Leauga, A., Vaurasi, V., Latu, F., Leasi, T., Aloi Gray, S., Leung Wai, J. and Taise Uili, A. (2026) Variability of Carbon Chemistry at the Marine Protected Area of Savaia Village, Upolu Island, Samoa. *Open Journal of Marine Science*, **16**, 141-162.
https://doi.org/10.4236/ojms.2026.163009

Received: May 5, 2026
Accepted: July 27, 2026
Published: July 30, 2026

Abstract

The Pacific Small Island Developing States (Pacific SIDS) are at the forefront of climate change impacts, yet these effects remain understudied and therefore poorly understood. Ocean acidification (OA) research in Samoa is in its infancy, with a new OA project established to monitor seawater carbon chemistry in coastal ecosystems. The study measured seawater carbon chemistry—including pH, dissolved carbon dioxide and total alkalinity—within the marine protected area (MPA) of Savaia, Lefaga, on Upolu Island, Samoa. Sampling was conducted over twelve months at four locations within the MPA (Site 1, Site 2, Site 3, Site 4), focusing on spatio-temporal variability in pH, temperature and total alkalinity. Measurements were obtained using water samples and an iSAMI pH sensor. The mean pH recorded was 8.06 ± 0.07, while the mean total alkalinity was 1955.1 ± 25 μmol·kg^{-1}, which is lower than the typical value of 2305 μmol·kg^{-1} observed in tropical environments. This decline in total alkalinity and the corresponding low pH could be a potential source of acidification to downstream coastal ecosystems with potential implications for coral reefs, biodiversity and fishery livelihoods.

Keywords

Ocean Acidification, Total Alkalinity, pH, Samoa, Dissolved Carbon Dioxide

1. Introduction

Samoa (Western) comprises two large volcanic islands—Upolu and Savaii—and several smaller islands with a total land area of approximately 2830 km^2 [1]. The

Samoa Islands are situated in the southwest Pacific and lie between latitudes 13 and 15 south of the equator and longitudes 168 and 173 west [1]. Like other Pacific islands, Samoa exhibits significant geological, biological, cultural and social diversity [2]. The warm tropical ocean of the Samoa archipelago supports a rich diversity of marine habitats, including coral reefs, mangroves and coastal wetlands [3]-[4]. Upolu has well-developed coral reefs encircling the islands [5] [6]. These reefs are a significant natural resource, which not only provides the foundation for important inshore fishery but also plays an integral role in the social and cultural values of the Samoan people [7]-[11]. A few studies have shown that Upolu reefs have degraded due to increasing anthropogenic pressures and climate change [12] [13]. As a result of climate change, reefs of Upolu have been subjected to potential repeated severe disturbances of coral bleaching [13]. However it is not clear to what extent the impacts of a range of climate stressors including increased carbon dioxide levels in the atmosphere will have on Samoa's reef ecosystems.

As atmospheric carbon dioxide (CO_2 atm) levels increase, the partial pressure of CO_2 (pCO_2) in seawater increases. By way of chemical reactions, CO_2 combines with water to form carbonic acid (H_2CO_3), which undergoes a series of acid/base dissociation reactions [14]:

$$CO_2\,(aq) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + \ HCO_3^- \ \leftrightarrow 2H^+ + \ CO_3^{2-} \tag{1}$$

Dissolved inorganic carbon concentration ([DIC]; $\mu mol \cdot kg^{-1}$) is:

$$[DIC] = [CO_2\,(aq) + [H_2CO_3] + [\,HCO_3^-\,] + [\,CO_3^{2-}\,]. \tag{2}$$

Anthropogenic CO_2 uptake increases surface [DIC] and lowers pH.

This rise in pCO_2 poses a major threat to Samoa's coastal and ocean ecosystems. One of the primary consequences of elevated pCO_2 is ocean acidification (OA)—a process that lowers seawater pH due to increased CO_2 atm absorption (Equation (1)). Changes to the carbonate chemistry of seawater will lead to changes in pH and the concentration of different carbonate species such as dissolved carbon dioxide (CO_2), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) [15]. These chemical shifts (Equation (2)) will cause dramatic declines in the saturation state of aragonite and calcite negatively impacting calcifying organisms [2] [16] [17]. Such impacts may include the dissolution of and difficulty in forming carbonate structures [18]-[22]. Coral reefs are negatively impacted by OA due to CO_2 dissolution in the ocean if CO_2 atm levels continue to rise [23] [24]. This prevents a buildup of calcium carbonate ($CaCO_3$), which corals draw from seawater to build their skeleton [25]-[27]. The extent of changing ocean chemistry and impacts on the dissolution of biogenic $CaCO_3$ minerals requires investigations which require the use of specific experimental tools [28]. Non-calcareous macroalga are also impacted by increased pCO_2 and reduced pH; however they are suggested to either not respond to, or be positively impacted by, elevated pCO_2 under OA [29]-[31]. This variability in their responses is due to the differences in dissolved inorganic mechanisms that these organisms possess [31].

Past and recent works related to carbon chemistry assessment of ocean in Sa-

moa is limited to a single study, which focused on developing an automated pH-stat method for the measurement of dissolution rates of calcium carbonate in seawater [28]. A most recent research effort to monitor ocean pH in Samoa by Samoa's Meteorology Division under the Ministry of Natural Resources and Environment, led to the deployment of a buoy in Vaiusu Bay [32]. Despite the project being at its infancy stage, this effort is a positive step forward for ocean acidification monitoring in Samoa. A technical report [2] on the Pacific Islands OA vulnerability assessment projected that by 2050, only about 15% of coral reefs around the world will be in areas where aragonite levels are 'adequate' for sustainable coral growth. The Pacific Island region is expected to experience similar changes, leading to modified reef habitats and subsequent declines in fisheries productivity of some target species (e.g. reef fish and sea cucumbers) and enhanced impacts on calcareous aquaculture commodities (e.g. pearl oysters and marine ornamentals) [2].

While some studies have directly examined the impact of ocean acidification on marine organisms in the Pacific [33]-[35], few have addressed ecosystem-level effects. Most research has primarily focused on the responses of individual species such as the green macroalgae *Caulerpa* spp. [31] and coralline algae [36] rather than evaluating more complex, community-level responses [37]. However, efforts to try to emulate the diversity of such ecosystems are a real challenge due to the complexity in the nature and variability of the natural conditions that exist in those ecosystems. Measurements on Samoan corals showed increased dissolution with increased acidity and decreasing aragonite saturation states [28]. In Samoa, there seems to be no evidential information about ocean acidification and seawater carbon chemistry data or impacts on important ecosystems. In fact, Samoa's State of the Environment (SOE) Report 2023 [38] described the status of coral reefs and other marine habitats based on coverage, diversity and richness without mention of any impacts of seawater carbon chemistry.

This study was conducted in collaboration with The Ocean Foundation (TOF) to establish baseline data on the carbon chemistry of seawater in Samoa. This research is vital to support the Government of Samoa's effort in achieving the United Nations (UN) 14th Sustainable Development Goal (SDG) target 14.3, which is to help minimize and address the impacts of OA, including through enhanced scientific cooperation at all levels. This study has intrinsic links to the Pathway for the Development of Samoa 2022-2026 [39], which stipulates stronger environmental surveillance will help maintain cleaner land, water, air and oceans.

The aim of this study was to investigate the variability of carbon chemistry at the Marine Protected Area (MPA) of Savaia village in Lefaga. The study's goals were threefold: i) to characterize the chemistry of seawater, ii) to measure the monthly variability of seawater carbon chemistry, and iii) to compare seasonal variations in seawater chemistry at the Savaia Marine Protected Area (MPA). To achieve these goals, we measured the pH, total alkalinity and temperature of seawater monthly from February 2019 to February 2020. The concentrations of DIC and pCO_2 in

seawater were calculated based on these measurements.

This study provides insights into carbon chemistry variability in Samoa's coastal ecosystems. In addition, this project presents a great opportunity for collaboration between NUS and the local village community to promote publicity outreach programs, environmental awareness, and stewardship of coastal and ocean resources.

2. Materials and Methods

2.1. Study Sites

The Savaia coastal marine protected area (MPA) is located in Lefaga Bay in the south coast of Upolu (**Figure 1**). It is characterized by a fringing reef, often split by freshwater discharge from streamflow, and supported by a low-lying coastal plain [40]. Savaia was selected for our study based on its present coral reef coverage, existing data related to coral and fishery resources, history of successful projects, and community management principles for safeguarding project equipment. Lefaga reefs comprise of 0.1% living coral, which is comparatively lower than other reefs considered to be doing well including Palolo Deep (0.48%), Amaile (0.23%) and Aga (0.3%) [40]. A most recent survey reported Lefaga coral cover decreased from 30% in 1996 to 1% - 5% in 2016 [13]. Savaia is located in an ecotourism area, which is important for subsistence economy in the respective community [40] while at the same time, presenting concerns for reef damage from tourism activities.

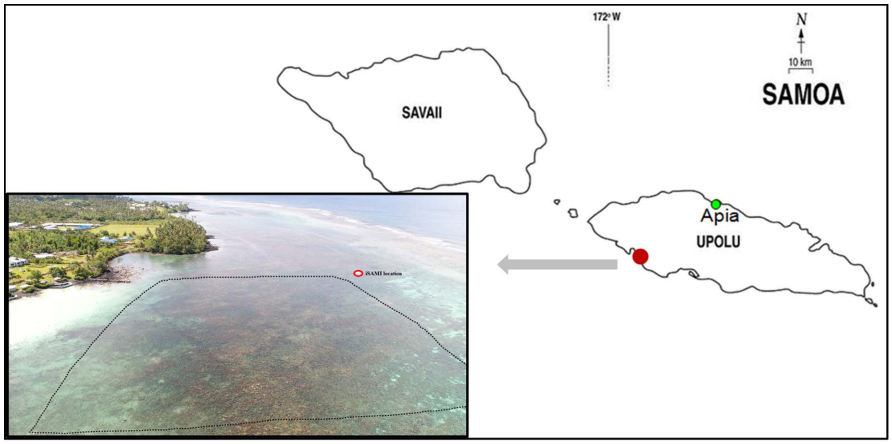


Figure 1. Map of Samoa showing the location of Lefaga District and the location of collection sites (red dot) in Savaia. (image source: NUS drone).

As noted previously, the goal of this study was to characterize the variability in carbon chemistry along the Savaia MPA using surface water quality measurements to identify potential trends and processes affecting pH. Four sites (Site1, Site 2, Site 3, Site 4) (**Figure 2**) have been defined as spatial zones corresponding to distances in km along the coastline and surface water longitudinal gradient of the Savaia MPA (**Table 1**).

Table 1. Description of sampling sites defined as spatial zones corresponding to distances in km along the coastline and surface water longitudinal gradient of the Savaia MPA.

Site	Description	GPS Coordinates
1	iSAMI & CTD site	13˚57′22.8″S 171˚57′40.9″W
2	MPA (furthest from shore)	13˚57′18.0″S 171˚57′44.5″W
3	MPA (middle of reserve)	13˚57′18.1″S 171˚57′41.0″W
4	MPA (closest to shore)	13˚57′18.0″S 171˚57′38.5″W

2.2. Sample Collection

Seawater samples collection followed the method described by Dickson *et al*. (2007) [41]. Bottle samples were collected at four designated sites (Site 1 - Site 4) within the subtidal zone of Savaia Marine Protected Area (MPA), each corresponding to specific distances (**Figure 2**, **Table 1**) along the fringing reef and coastal gradient. Sampling points were located just inside the MPA boundary, with additional comparative samples taken adjacent to the iSAMI deployment point situated outside the boundary. All bottle samples were collected at a consistent depth of approximately 1 m below the surface to minimize variability due to stratification. Seawater was collected in borosilicate glass bottles (or the Niskin bottle) underwater immediately after opening the bottles. This approach was necessary to minimize the exchange of CO_2 with the air space in the collection bottle which affects all carbon parameters except total alkalinity (A_T). Total alkalinity (A_T) is the measure of the capacity of seawater to neutralize acids, measured by titration and expressed in $\mu mol \cdot kg^{-1}$. The samples were immediately transferred into an ice cooler for transport from the collection site to the marine lab at the National University of Samoa ocean campus in Mulinuu. The time to travel from the collection site to the marine lab was 45 minutes. Upon arrival to the lab, the samples were stored in a cool, dark, location (preferably refrigerated but not frozen) until use. For quality assurance, some duplicate sampling was carried out, both from the same sampling bottle (or Niskin bottle) and, if possible, from two

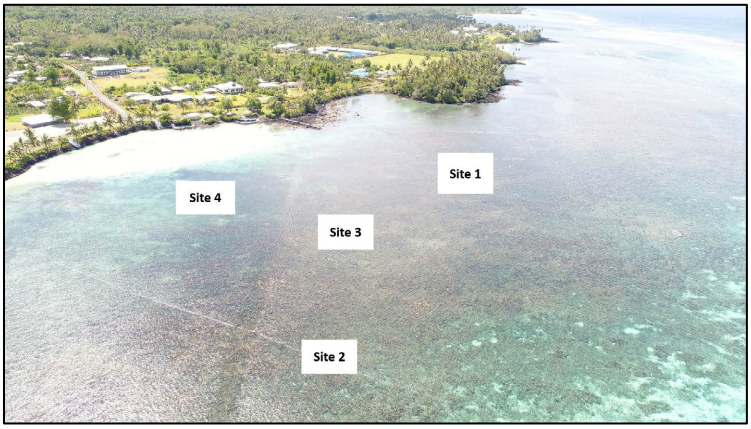


Figure 2. Marine protected area (MPA) and the estimated location of the iSAMI and sampling sites (not to scale).

sampling containers tripped together at the same depth, to assess the quality of the sampling procedures. Samples collected for A_T and pH analysis in the lab were preserved with a mercuric chloride solution [41] to stop biological activity from altering the carbon distributions in the sample container before analysis. Monthly sampling was conducted between February 2019 and February 2020, with the exception of July 2019 due to equipment malfunction. To reduce tidal and diurnal variability, collections were made at approximately whenever possible. Duplicate samples were taken at selected sites to evaluate consistency, and extreme pH values were cross-checked against duplicates before inclusion in the dataset.

2.3. Sample Preparation

Preparation for sampling and handling samples was carried out according to the guidelines set out in the Standard Operating Procedures by Dickson *et al*. (2007) [41]. Samples for pH were also analyzed directly from the sample containers. The pH of seawater was measured in the lab by spectrophotometric means. The samples were collected directly into 10 cm path-length optical cells and sealed with polytetrafluoroethylene (Teflon®) caps to ensure that there was no headspace. Samples for DIC and A_T measurements were collected in high-quality borosilicate glass bottles such as Schott Duran (l.c.e. 32×10^{-7} K^{-1}) [41], as they retain sample quality for both temporary and longer-term storage. The bottles were sealed using greased ground glass stoppers held in place with some form of positive closure, or in some alternate gas-tight fashion.

2.4. Sample Analyses

2.4.1. Determination of the pH of Sea Water Using the Indicator Dye m-Cresol Purple

Seawater pH (pH_T, pH measured on the total scale, or hereafter simply pH) is the negative logarithm of hydrogen ion concentration, measured spectrophotometrically and with the iSAMI. A glass Pasteur pipette was used to transfer the sample from the newly opened sample bottle into the spectrophotometric cuvette. This was done carefully and quickly to ensure minimal sample interaction with atmosphere. For work of highest sensitivity and precision, a double-beam spectrophotometer is desirable. However, good results can be obtained with a high-quality single-beam instrument. We used a Thermo Scientific™ Orion™ AquaMate 7000 Vis spectrophotometer provided with the Global Ocean Acidification Observing Network (GOA-ON) Kit for to carry out the pH measurements in this study. The absorbance of the seawater sample was measured and recorded at three wavelengths: 730 nm, 578 nm, and 434 nm. These wavelengths correspond to a non-absorbing wavelength (730 nm) for m-Cresol purple and the absorption maxima of the base (I^{2-}) and acid (HI^{-1}) forms of the m-Cresol dye (respectively 578 and 434 nm).

2.4.2. Determination of the Total Alkalinity of Sea Water

Total alkalinity (A_T) is the measure of the capacity of seawater to neutralize acids,

measured by titration and expressed in μmol·kg^{-1}. A_T of the samples was determined by titration with standardised 0.1N HCl made up in a 0.6M NaCl solution to approximate the ionic strength of the samples being titrated. The results are expressed as micromoles per kilogram (μmol/kg) of sea water. This method is suitable for the lower total alkalinity range with a smaller initial acid addition [41] [42].

2.4.3. *In Situ* pH Measurements by iSAMI Sensor

The iSAMI pH sensor (Sunburst Sensors, Missoula, MT, USA) provided in the GOA-ON Kit is autonomous compared to the spectrophotometry method. It uses a highly accurate colorimetric reagent method and does not suffer from the drift that plagues most electrode-based pH probes. The iSAMI provides valuable in-situ time series data near the surface at depths of up to 3 meters. The iSAMI pH sensor was programmed to take in-situ pH readings every 15 minutes for 3 weeks of each month following the operation manual iSAMI-pH [43], then deployed at about 3m depth in the location 13˚57.366′S and 171˚570744′W. In the fourth week since initial deployment, the instrument was retrieved from the sampling site to extract/download the data onto a laptop, reprogrammed, then deployed again to continue the measurements for the next four weeks. It is noted that the iSAMI experienced technical malfunction after three months (December 2018 and February-March, 2019) and was unavailable for further measurements in the duration of the study. The iSAMI data presented here are the measurements taken from December 2018 and February-March 2019.

2.5. Seawater Temperature and Carbon Chemistry Parameters

The study collected quantitative data on pH, alkalinity, temperature and total dissolved CO_2 in seawater. The other seawater properties such as DIC, pCO_2 were calculated using the CO2SYS spreadsheet [44]. Temperature (˚C) was measured *in situ* at each sampling site. Here, temperature, pH and total alkalinity were measured and used to calculate the remaining carbon parameters. The calculated values include those for partial pressure of CO_2 (pCO_2, μatm) calculated from measured pH and A_T using CO2SYS, total dissolved inorganic carbon (DIC, μmol·kg^{-1}) calculated from pH and A_T, and bicarbonate ion concentration (HCO_3^-, μmol·kg^{-1}) calculated from pH and A_T.

2.6. Data Analysis

The differences in each response variable across sites and months were analysed by using a linear model and One-Way Analysis of Variance (ANOVA). pH, A_T, temperature, pCO_2, DIC, and HCO_3^- were modeled with Site as a fixed factor and Month as a repeated measure. Repeated monthly observations from same sites were handled by a One-Way Repeated Measures ANOVA including Month as a within-subject factor, thereby controlling for temporal autocorrelation. The use of ANOVA and linear models is justified by the balanced sampling design, with repeated monthly measurements across four sites providing sufficient replication

to detect differences in mean values. This approach allows us to test site effects while accounting for temporal variation, ensuring that both spatial and seasonal variability are appropriately represented in the analysis. All the plots and anova tests were created and carried out using R [45].

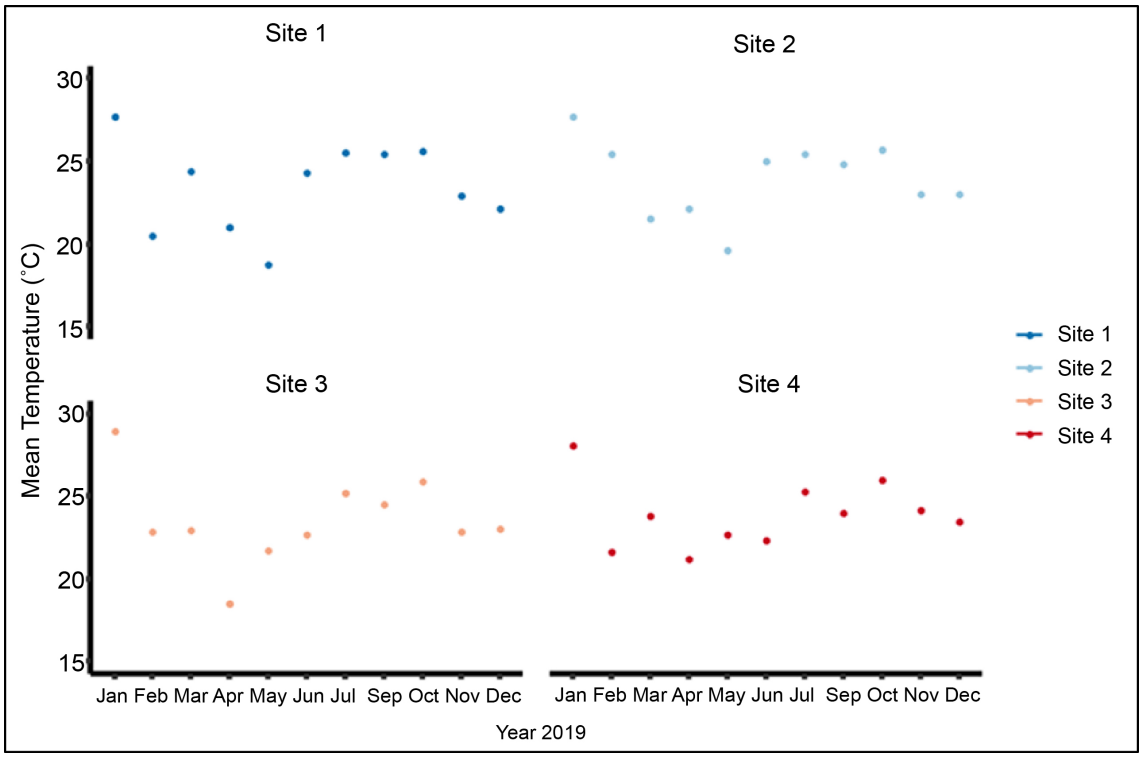
2.7. Quality Control of pH and AT Measurements

All pH and total alkalinity (A_T) samples were subject to quality-control checks prior to analysis. Duplicate samples were collected at selected sites and compared to evaluate consistency in sampling and analytical procedures. Extreme pH values outside the expected seawater range (7.5 - 8.5) were flagged and re-checked against duplicate measurements before inclusion in the dataset. Measurements that did not meet quality-control standards were excluded, resulting in a final dataset of 12 months of observations (February 2019-February 2020, excluding July 2019 due to equipment malfunction).

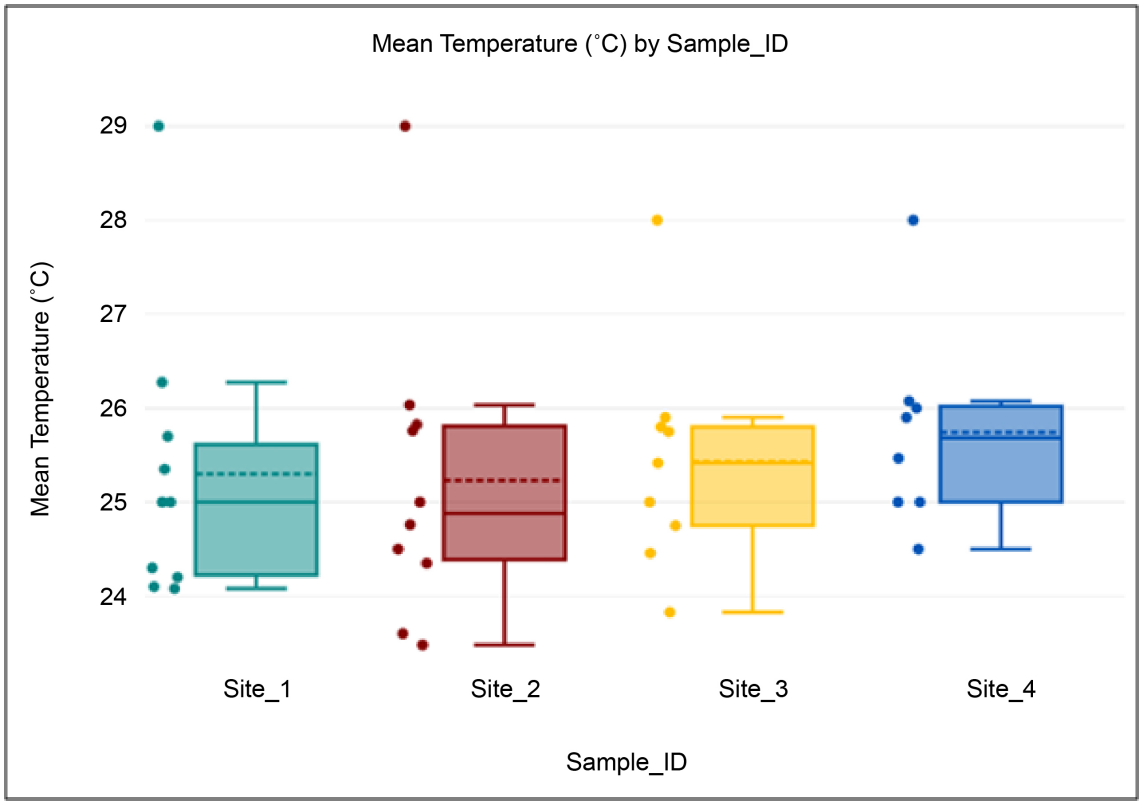
3. Results

3.1. Seawater Temperature

Seawater temperature (˚C) did not show any major differences between each site, showing close synchrony between the values (24˚C - 28˚C) (**Figure 3**). There was an indication of differences in temperature with time (month of year), where the highest mean temperature was in January (28.1˚C ± 0.1˚C) and the lowest mean temperature in April (20.5˚C ± 0.2˚C) across all four sites.



(a) Calculated summary of Mean temperature (˚C) over time (months)



(b) Mean temperature (˚C) showing distribution of data points across the four sites

Figure 3. Mean temperature (˚C) in the four sites with (a) calculated summary of mean temperature (˚C) and (b) mean temperature (˚C) showing distribution of data points across the four sites.

3.2. Total pH

The mean pH (Figure 4), measured on the total scale and denoted pH_T, was not significantly impacted by the site location but rather by the time of year ($p < 0.001$). The differences in means of pH_T for four sites were non-significant ($p = 0.5$, Table 2). However, even though the mean pH_T was not statistically different between the four different sites, there was indication for a consistent pH range of 7.9 - 8.2 across all sites (Figure 4, Figure 5).

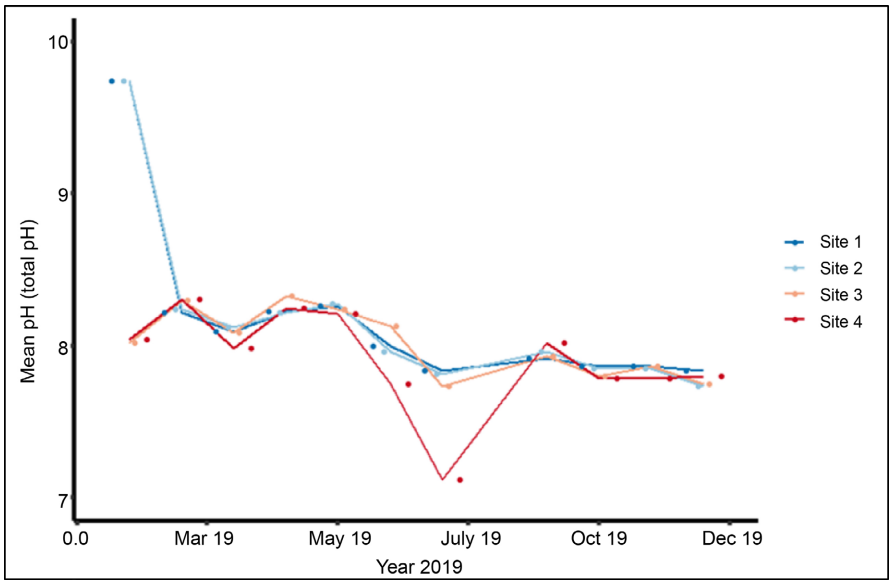
Table 2. Mean pH_T measured in the four sampling sites. Values are Means (±SE).

Mean pH_T		
Site	**pH_T**	**Model stats (Site*pH_T)**
1	8.2 ± 0.2 (n = 11)	p = 0.5 F = 0.9 df = 3
2	8.2 ± 0.2 (n = 11)	
3	8.0 ± 0.1 (n = 11)	
4	7.9 ± 0.1 (n = 11)	

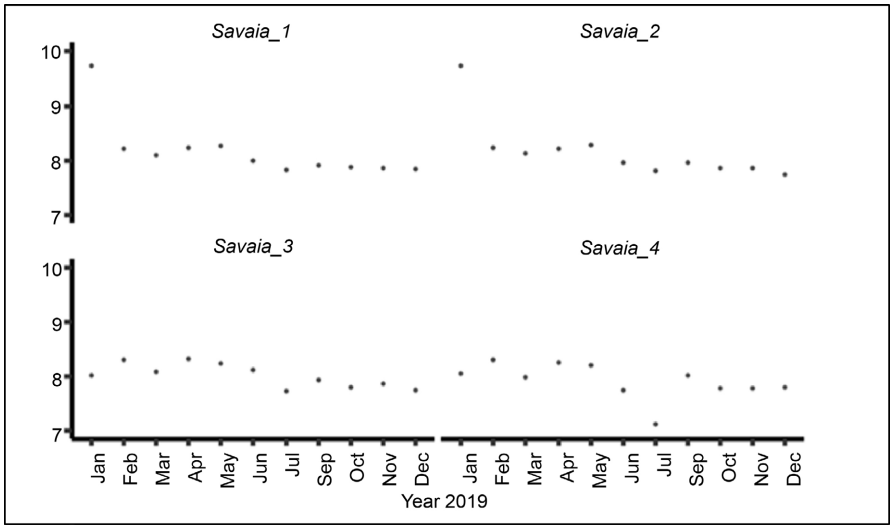
3.3. *In Situ* pH Measurements by iSAMI Sensor

The iSAMI sensor successfully recorded continuous *in situ* pH measurements in

December 2018, February and March 2019. However, despite multiple attempts to reprogram and deploy the sensor, it failed to yield *in situ* pH data for the remaining duration of the study. There was no statistical test done for iSAMI measurements due to negligible sample sizes that lack the power to detect true differences. Running a test would yield a high rate of false negatives.



(a) Calculated summary of Mean pH over time (months) per site



(b) Mean pH of seawater showing distribution of data points across the four sites

Figure 4. Mean pH (total pH or pH_T) for the four sites in Savaia showing (a) calculated mean pH over time across the four sites, and (b) mean pH trends by site.

Based on the parametric data collected by iSAMI, mean pH was 7.9 ± 0.01 and pH range between 7.6 and 8.4 (**Figure 6**). Temperature tended to increase from 17 February until 24 February, with a mean temperature 30.5˚C ± 0.5˚C, after which it decreased to a mean 29˚C ± 0.04˚C.

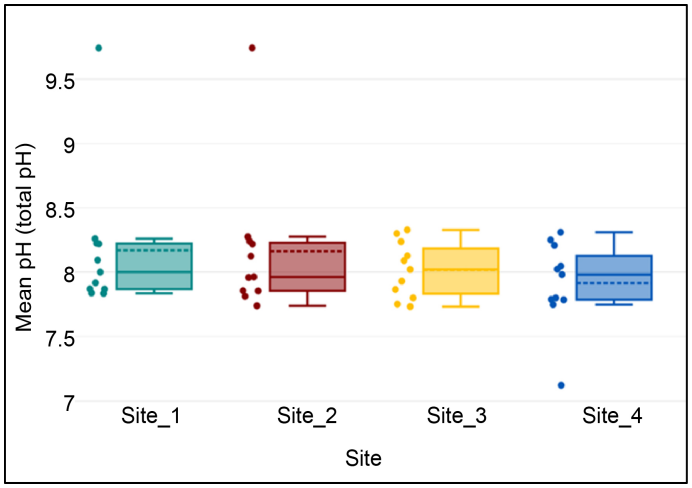


Figure 5. Distribution of measured pH values ranging between 7.1 and 9.7 in the four sites.

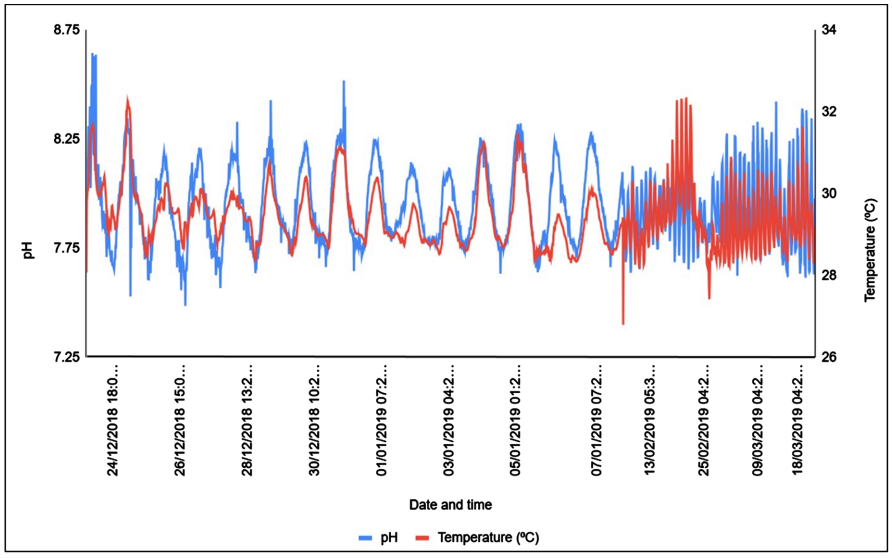


Figure 6. Real-time pH measurements by iSAMI for December 2018, and February-March 2019.

3.4. Total Alkalinity

The mean total alkalinity (A_T μmol·kg^{-1}) between the four sites (**Figure 7**, **Figure 8**) was 1955.1 μmol·kg^{-1} ± 25 and was not significantly different ($p = 0.9$, **Table 3**). However, there was a significant impact of time of year, where there was a significant decrease (red lines on **Figure 8**) in A_T of seawater between the months of April and September ($p < 0.001$).

3.5. Calculated Values of pCO_2

The values for pCO_2 (μatm) (**Table 4**) were variable (150 - 550 μatm) between the four sites (**Figure 9**). There was no significant difference between the means of pCO_2.

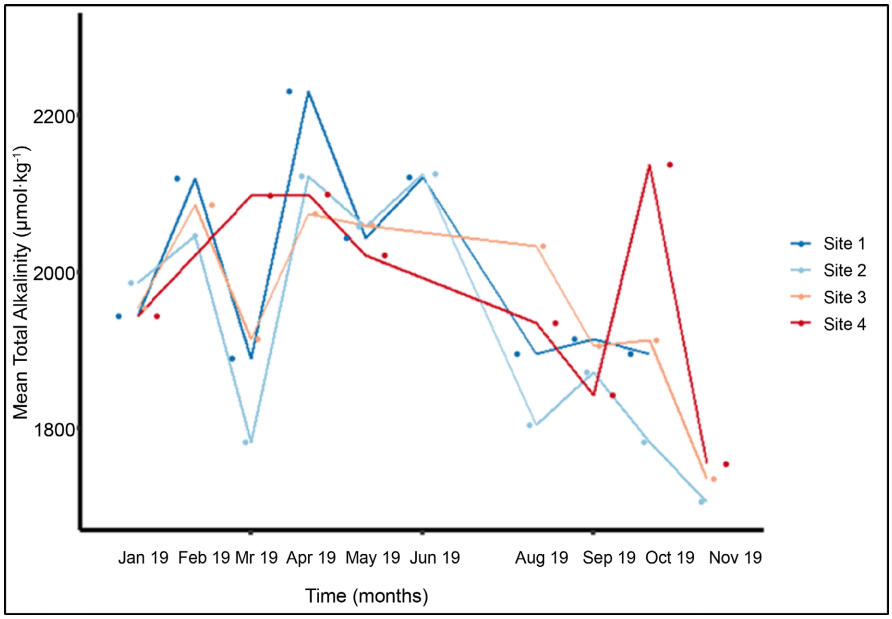


Figure 7. Mean of total alkalinity (A_T) (µmol·kg^{-1}) across the four sites in Savaia.

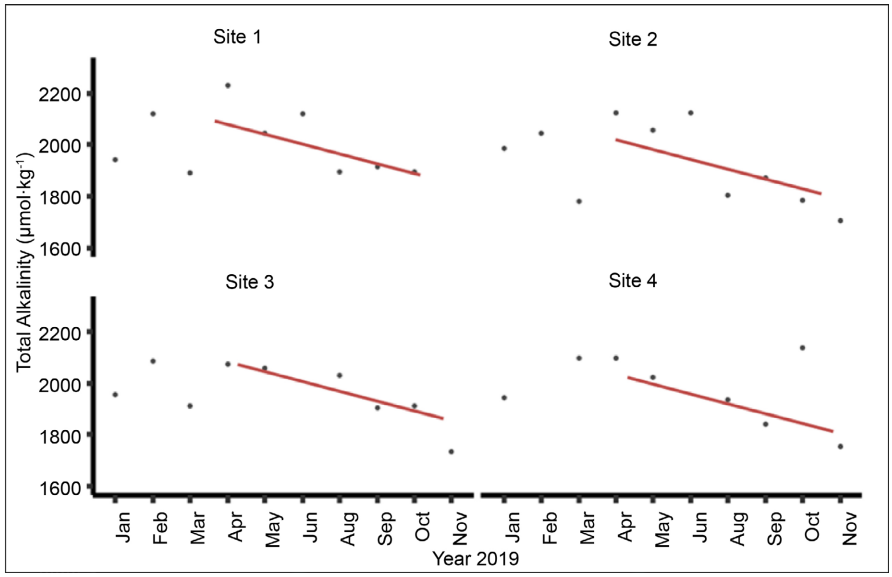


Figure 8. Mean Total alkalinity (A_T) (µmol·kg^{-1}) by site.

Table 3. Total alkalinity (A_T) (µmol·kg^{-1}) measured in the four sampling sites. Values are Means (±SE).

Mean A_T		
Site	**A_T**	**Model stats (Site*A_T)**
1	1954.7 ± 63.5 (n = 10)	
2	1928.8 ± 49.5 (n = 10)	p = 0.9
3	1963.8 ± 37.5 (n = 9)	F = 0.2
4	1978.8 ± 47.5 (n = 8)	df = 3

Table 4. Dissolved carbon dioxide (pCO_2) (µatm) measurements in the four sampling sites. Using the measured values of pH_T and A_T, pCO_2 was calculated using the calculator CO2SYS [44] and applying the constants K1, K2 from Mehrbach *et al.* (1973) [46]. Values are Means (±SE).

Mean pCO_2		
Site	**pCO_2**	**Model stats (Site*pCO_2)**
1	345.0 ± 45 (n = 8)	
2	341.4 ± 50.2 (n = 8)	p = 0.8 F = 0.3 df = 3
3	345.6 ± 61 (n = 8)	
4	410.6 ± 76.4 (n = 7)	

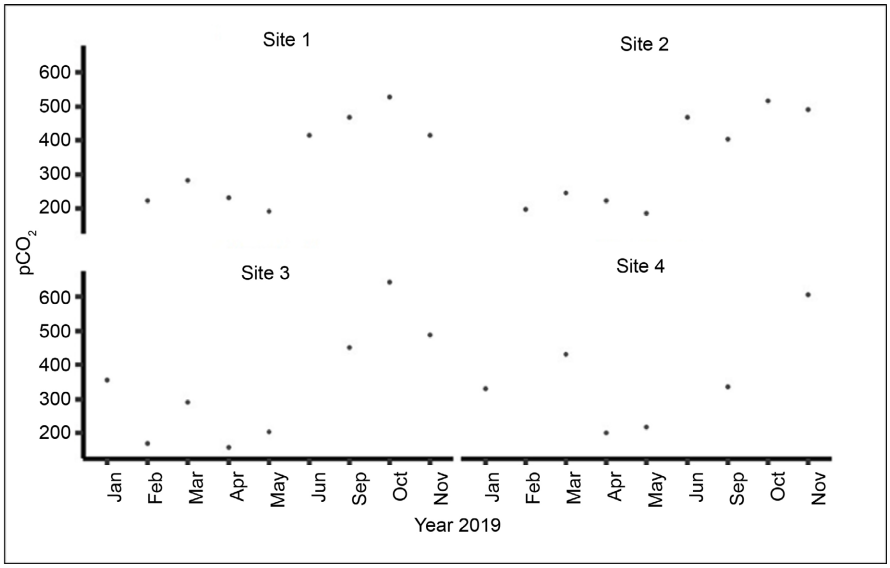


Figure 9. pCO_2 (µatm) measurements across the four sites.

3.6. Calculated Values of Total CO_2

Total CO_2 (µmol·kg^{-1}) (**Figure 10**) was not significantly different between the four sites; however, there was a significant difference ($p < 0.001$) in the means between the months of year (**Table 5**).

Table 5. Total carbon dioxide (CO_2) measurements in the four sampling sites. Using the measured values of pH_T and A_T, pCO_2 and CO_2 were calculated using the calculator CO2SYS [44] and applying the constants K1, K2 from Mehrbach *et al.* (1973) [46]. Values are Means (±SE).

Total CO_2			
Site	**CO_2**	**Model stats (Site*CO_2)**	**Model stats (CO_2*Time)**
1	10.2 ± 1.1 (n = 8)		
2	10.0± 1.4 (n = 8)	p = 0.8 F = 0.3 df = 3	$p = 3.9 \times 10^{-8}$ F = 18.7 df = 8
3	10.0 ± 1.6 (n = 8)		
4	11.7 ± 2.1 (n = 7)		

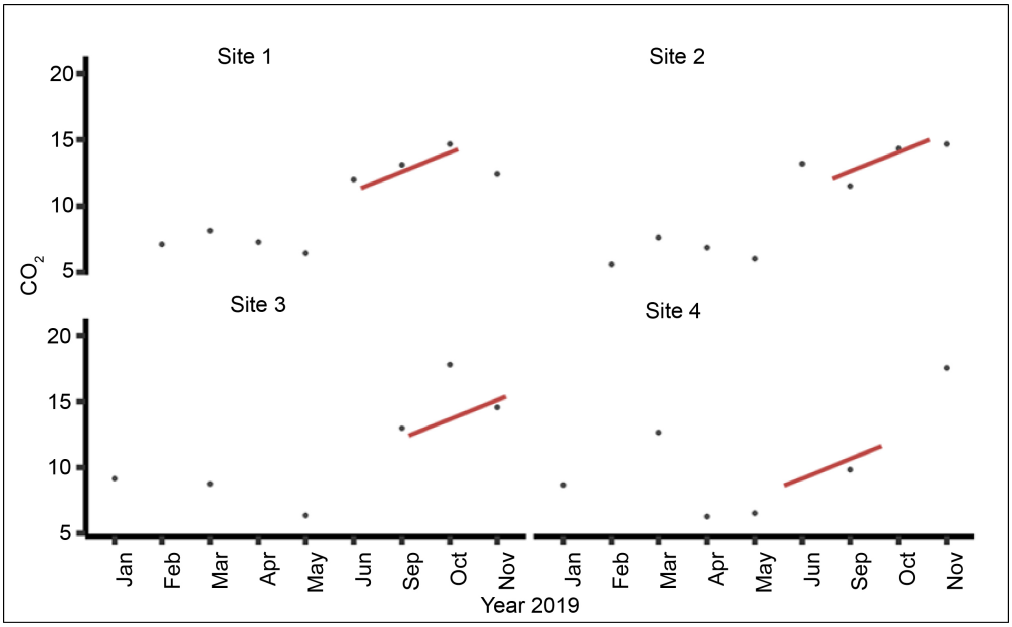


Figure 10. Calculated total CO_2 (μmol·kg^{-1}) values across the four sites.

3.7. Calculated Values of HCO_3^-

The concentration of carbonic acid HCO_3^- (μmol·kg^{-1}) was not significantly different between the four sites; however, there was a significant impact of time of year ($p = 0.04$) (Table 6). The three sites Site 1, Site 2 and Site 3 showed a similar trend of increasing HCO_3^- concentration in the year and declined in November (Figure 11). Site 4 had missing values for February, June and October and may have impacted on the overall trend in the HCO_3^- variability in this location.

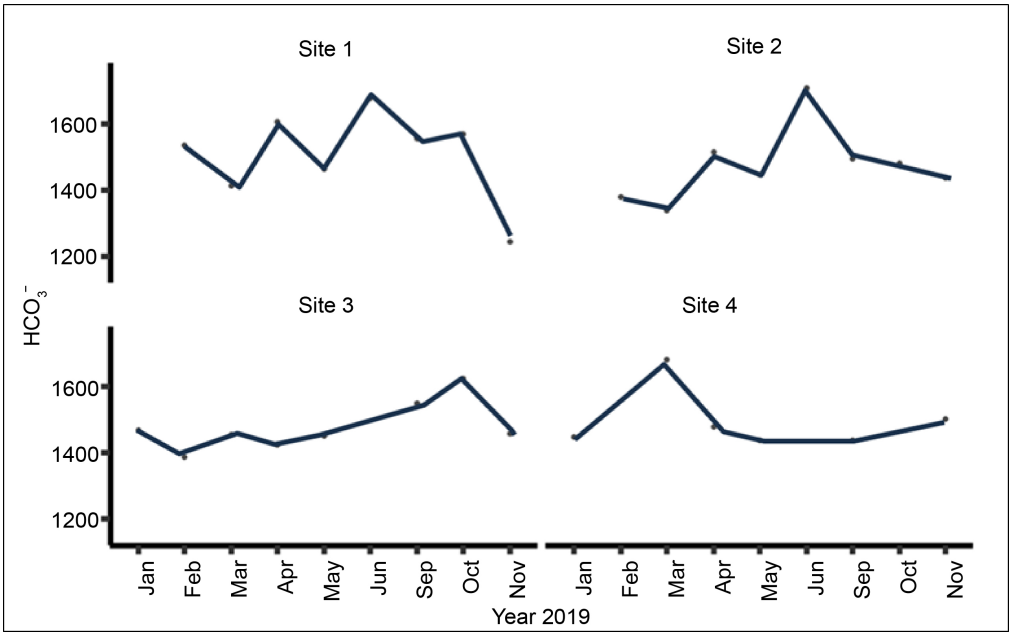


Figure 11. Calculated HCO_3^- (μmol·kg^{-1}) values across the four sites.

Table 6. The concentration of carbonic acid (HCO_3^-) was measured in the four sampling sites. Using the measured values of pH_T and A_T, pCO_2 and CO_2 and HCO_3^- were calculated using the calculator CO2SYS [44] and applying the constants K1, K2 from Mehrbach *et al.* (1973) [46]. Values are Means (±SE).

	HCO_3^-		
Site	**HCO_3^-**	**Model stats (Site* HCO_3^-)**	**Model stats (HCO_3^- *Time)**
1	1508.3 ± 47.2 (n = 8)		
2	1474 ± 39 (n = 8)	p = 0.7 F = 0.6 df = 3	p = 0.04 F = 2.6 df = 8
3	1477 ± 26.2 (n = 8)		
4	1544.3 ± 57 (n = 7)		

4. Discussion

4.1. Overview of pH Profile Sites

The pH environment of the four sites (Site 1, Site 2, Site 3, Site 4) was typical of natural tropical shallow intertidal environments, with a mean pH of 8.06 ± 0.07 displaying regular monthly periodicity [47]-[49]. The monthly variation in pH was low for each site, indicating a potentially less dramatic impact of the combined influence of different factors, including temperature changes, freshwater input and biological activity. Studies have shown that seasonal or monthly variations are generally lower than daily variations in coastal areas. This is because daily pH fluctuations are driven by biological processes like photosynthesis and respiration, which can cause large and rapid changes in pH [50] [51]. Monthly or seasonal variations in pH may be less pronounced because the shorter and more intense fluctuations in pH are averaged out by seasonal changes in other factors, including temperature and biological cycles [51] [52]. In hindsight, daily pH measurements would have been an important analysis by itself in this study because of the large and rapid changes in pH within a 24-hour cycle. We have noted this crucial aspect for future research. Although the occurrence of the lowest mean pH 7.1 (Site 4) and highest pH 9.7 (Site 1) was not statistically significant, the large difference between the lowest and highest pH across the four sites is significant in itself, and could be an indicator of several potential factors. These may include seawater thermal stratification and high phytoplankton biomass [50] [53] in site (Site 1) where the highest pH values occurred (**Figure 4**). Such disparity in pH values is unsurprising in a highly productive coastal zone in summer [54], with a summer pH of similar level [55] and higher elsewhere [56]. In such areas, CO_2 depletion due to net photosynthetic production exceeds its replenishment from atmospheric infiltration, respiration or from other sources [57]. It should be noted however, that sources of CO_2 for example calcification, can cause oversaturation of surface waters, even in the presence of high photosynthetic production such as reported on some coral reefs [58] [59].

The sharp low seawater pH of 7.1 in Site 4 is likely to be due to benthic CO_2 sources such as respiration and calcification combined with its potential separa-

tion from surface waters by minor temperature stratification [60]. The site is part of a community marine reserve with aquaculture activities present such as the giant clam farm, seaweed beds and seagrass meadows here which likely contributed CO_2 via respiration and calcification. Another reason for the very sharp decrease in seawater pH in Site 4 site could be due to a freshwater source from rivers in the vicinity of the coastal area. It is well established that freshwater from rivers has a lower pH of 7 than seawater pH 8 [61] [62] due to low salinity levels [63].

4.2. The Monthly Decrease of Low Total Alkalinity (μmol·kg^{-1}) at the Four Sampling Sites

Total alkalinity (A_T μmol·kg^{-1}) is an important property affecting pH due to its buffering capacity to resist large changes in pH levels in the natural seawater environment [41]. Coastal and estuarine ecosystems such as our sampling sites in Savaia are highly dynamic and therefore can be classified as weakly or strongly buffered depending on whether the A_T was below or above that of ocean water [64].

The spread of low A_T was consistent across the four sampling sites and corresponds with our pH_T values, which demonstrated lower mean pH_T from June to December with decreasing A_T (**Figure 6**, **Figure 7**). This relationship between pH_T and A_T was evident in the trends in the mean values (**Figure 4**, **Figure 5**). The reason for this decreasing pH and A_T is likely due to two reasons: first, the effect of marine biota via the buildup of nutrient and organic matter cause AT to decrease [65] and secondly the variation in sea surface temperature (SST) where higher temperatures (˚C) have been found to lower A_T in some tropical seawater environments [66]. Our data are in agreement with those findings, where in the Savaia sampling sites, all of the four sites demonstrated a high mean temperature 23.7˚C ± 0.4˚C, with the highest temperature of 28.9˚C in Site 3. There is a pattern of consistently higher temperatures in June-October. The other possible reason for lower A_T is potentially low salinity or salinity fluctuations in our sampling sites; however, this was not well documented in our measurements, and we have acknowledged this oversight for consideration in our continued monitoring work.

4.3. Drivers of pH Variability in Coastal Ecosystems

Studies have shown that the high pH variability of coastal ecosystems is primarily driven by inputs from land [67]. These include freshwater inputs from rivers, streams and estuaries, which typically dilute the alkalinity of seawater [68]. This results in reduced buffering, nutrients enhancing productivity and pH, as well as organic matter supporting excess respiration driving acidification [64]. In our study, we overlooked the existence of freshwater sources near the site and we assumed the level of salinity at 35 ppt in our calculated values of carbon parameters. We acknowledge this oversight and have addressed this for improvement in our ongoing seawater monitoring activities. In hindsight, our results have highlighted for the first time, the natural pH variability in Savaia where the geophysical profile

is highly dynamic with potential significant influence of freshwater input. This is important given this site is a popular giant clam sanctuary. Additional factors that can affect pH variability in coastal regions include geochemical changes associated with land use changes, hydrodynamic circulations and coastal water table or aquifer discharges [68]. Our study site at Savaia is located within the village MPA and has integrated ecotourism to promote sustainable development. There have been developments in the area in terms of infrastructure [69] and although the developments may be small-scale, it can have potential impact on the coastal environment and carbonate chemistry of seawater.

5. Conclusions

In summary, the patterns of change in the measured values of pH and total alkalinity, and the calculated values of pCO_2, CO_2 and HCO_3^- in the coastal area of Savaia provided here demonstrate a large variability in pH (7.1 - 9.7) in this area. The results can only be compared to those in literature [50]-[52] due to limited or no published information available for the carbon chemistry profile of coastal areas in Samoa. The mean pH 8.06 ± 0.07 is in accordance with mean pH in tropical seawaters [57] [70] and is expected to decrease in the future due to increased levels of anthropogenic pCO_2 in the atmosphere [71]. The mean A_T values were lower than the values of 2305 μmol·kg^{-1} typically measured for tropical environments [72] [73]. This spread of low A_T and corresponding low pH is likely due to nutrients and organic matter, and freshwater flow from rivers in the vicinity of the coastal areas.

This study used water sampling techniques and analysis methods well accepted and practiced by ocean chemists and our data have shed light on a much-needed understanding of carbon chemistry changes in seawater of the coastal environments of Samoa. The study demonstrated significant temporal (monthly) differences in measured pH and A_T across the four sampling sites. These trends must be understood further within temporal and daily changes in salinity and freshwater input and nutrient loading processes.

The results of this study add to the emerging literature on carbon chemistry variability and water quality sampling in Pacific SIDS. Currently, science-based evidence of changing seawater quality in the coastal and ocean water of Samoa is still relatively limited to null or unpublished literature, baseline environmental assessments and project reports. This study provides baseline information and contributes to Samoa's information resource to assist in future research and monitoring efforts, and to suggest management and protection strategies by the government and local communities.

Acknowledgements

We thank the funding support of both the National University of Samoa's University Research Ethics Committee and The Ocean Foundation. We also thank the technical support of GOA-ON through The Ocean Foundation, which provided

the OA-in-a-box kit, which was instrumental in completing the work.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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