Spatial Variability of Alkalinity in the Waters Surrounding the Dangli Island Group of Langkawi, Malaysia

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ABSTRACT

This paper presents a comprehensive assessment of the spatial distribution of alkalinity in the waters surrounding the Dangli Island group of Langkawi during the southwest monsoon. Sampling was conducted at 12 strategically positioned stations around the island, capturing data at three distinct depths—upper, middle, and bottom. The determination of Total Alkalinity (TA) was performed using an Auto-titrator, with synthetic seawater employed as a reference. Alkalinity, indicative of water's capacity to neutralize acids, plays a pivotal role in influencing pH stability. The average alkalinity values for each station revealed notable variations, with Station 11 (ST11) exhibiting the highest (2201.12 µEq/kg) for the surface water, (2260.45 µEq/kg) for the middle water and (2113.7 µEq/kg) for the bottom., while ST5 recorded the lowest among the stations. Analysis of the data indicates a slight elevation in alkalinity levels at the middle (2141.10 µEq/kg) compared to the upper (1982.07 µEq/kg) and bottom depths (2038.50 µEq/kg). Two-way ANOVA results demonstrated a significant difference between sampling stations (p-value = 0.016, p < 0.05), suggesting spatial heterogeneity. Conversely, no significant differences were observed between depth levels (p > 0.05). The study also explores the intricate relationship between salinity and alkalinity, emphasizing the nuanced dynamics of this association in the context of ocean acidification. Notably, a correlation coefficient (r) of -0.06 was obtained, indicating a very weak or negligible inverse relationship between salinity and alkalinity. This observation underscores the complexity of the interplay between these variables, influenced by factors such as biological activity, carbonate system dynamics, and

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human activities. The findings contribute valuable insights into the spatial distribution and factors influencing alkalinity in the marine environment surrounding the Dangli Island group, offering a foundation for future research and environmental management strategies.

INTRODUCTION

Almost 25% of all annual anthropogenic carbon dioxide (CO_2) emissions are absorbed by the ocean [1]. This indicates that absorption of carbon dioxide (CO_2) created by humans is causing a rapid change in the chemistry of the oceans worldwide. This phenomenon, known as ocean acidification (OA), causes adverse effects on many marine species and ecosystem [2]. The origins of ocean acidification are caused by a type of gas known as excess carbon dioxide in the atmosphere that impacts pH and alkalinity. Alkalinity is an important parameter in water chemistry and is closely related to pH. The main contributors to alkalinity in water are bicarbonate ions (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide ions (OH^-). These ions can act as buffers, helping to stabilize and maintain the pH of the water. When acid is added to water, this alkaline substance can neutralize it, preventing a rapid drop in pH. Alkalinity is often expressed in calcium carbonate equivalents ($CaCO_3$) per unit volume of water (milligrams per liter, mg/L) [3,4]. This unit is usually referred to as parts per million (ppm) or milligrams per liter (mg/L).

In natural water systems, alkalinity plays an important role in maintaining ecosystem stability [5]. It can affect nutrient availability, affect mineral solubility, and the overall chemical balance of water. In addition, the health and stability of marine ecosystems depend on the maintenance of seawater alkalinity in the range of 2.2 to 2.5 µEq/L, which is the best value, especially for the support of calcareous species and as a buffer against pH fluctuations [5]. Nowadays, the latest data shows there is a slight decrease in total alkalinity value, which is from 2.1 to 2.4 µEq/L, as shown in Figure 1. Higher alkalinity means that the water body can neutralize acidic pollution from rain or basic inputs from wastewater. A well-buffered lake also means that daily variations in CO_2 concentration only cause minor changes in pH throughout the day. Stable pH values within their optimal range are beneficial to aquatic organisms [6]. Seawater samples change their composition over time as a result of bacterial decay of organic matter, where NH_3 and CO_2 can form within days, and CO_2 exchange with the atmosphere within hours. Microbial activity affects both total alkalinity (A) and total carbonate concentration (C), while CO_2 exchange across the air sample interface only affects concentration [7].

This study highlights the urgency to protect ocean health from extreme changes in alkalinity value. Creating an extensive open-access database will help with long-term tracking and lay the groundwork for upcoming studies and policy development. The analysis will assist in prioritizing research and management efforts by identifying gaps in current knowledge and understanding. The results will help design mitigation strategies for overfishing, which will safeguard coral reef ecosystems and ensure their sustainable use. Moreover, the research endorses worldwide and national endeavours to accomplish Sustainable Development Goal 14, which centers on the preservation and sustainable utilization of oceans, seas, and marine assets.
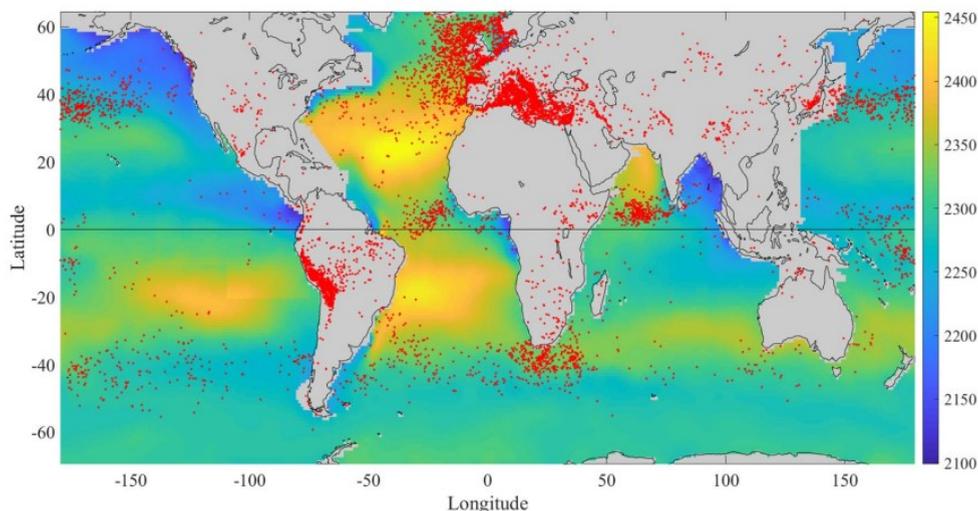
Figure 1. The latest total alkalinity around the world [8]

EXPERIMENTAL

Sample Collection

The sampling point for Dangli Island at Langkawi Kedah is shown as in the Table 1 and Figure 2. The sampling was taken from three different depth (surface, middle and bottom layer) of for each station. A total of 36 seawater samples were collected during the southwest monsoon. A Niskin water sampler was used to collect the seawater sample, which was then preserved by using 100μL of mercury chloride ($HgCl_2$). This is to prevent any biological activity from the organisms found in the water from continuing to affect the rate of the total value of alkalinity and pH of the water. The samples also must be stored in a cold (4°C) and dark place to avoid any other chemical reaction.

Table 1: The latitude and longitude coordinates of Dangli Island, Langkawi.

| Station	Dangli Island	
	Latitude	Longitude
ST1	6.44629444 °	99.76838889 °
ST2	6.44124444 °	99.77355278 °
ST3	6.43628889 °	99.77861944 °
ST4	6.45275000 °	99.77706944 °
ST5	6.44769722 °	99.78226111 °
ST6	6.44266944 °	99.78716667 °
ST7	6.44251667 °	99.78576667 °
ST8	6.45400278 °	99.79099167 °
ST9	6.44911667 °	99.79580278 °
ST10	6.46550278 °	99.79431667 °
ST11	6.46048611 °	99.79932222 °
ST12	6.45561667 °	99.80424722 °
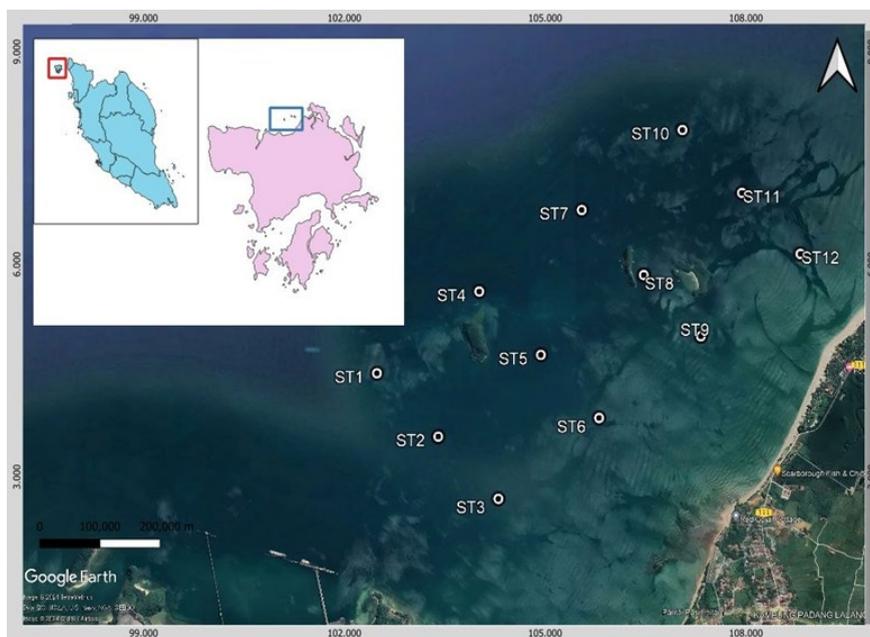
Figure 2: Dangli Coastal Waters.

Sample Analysis

The overview of this research methodology is focused on the analysis of Total Alkalinity (TA) aspect of ocean acidification that consists of carbonate chemistry and how the way of the water sample that is taken. These data will then be analyzed using other software and also statistical analysis before the results are obtained for further discussion. Numerous studies have been reported on the titration method to measure alkalinity. According to Ahmad [1], titration involves adding exact amounts of reagent to a sample until it reaches a particular pH or endpoint. Standard acids, such as hydrochloric acid (HCl), are frequently used in this procedure as titrants, added until the target pH value is reached. Based on the method described by Dickson [9] and Schulz [10], some adjustments was conducted. The article describes an open-cell, potentiometric titration method for figuring out the total alkalinity of seawater. The findings are presented as moles of seawater per kilogram. The technique works well for measuring total alkalinity in the ocean (2000– 2500 (μEq/kg). Surface polar waters at the coast may have lower readings. To determine the total alkalinity, 25 grams of seawater sample was weighed and placed in a 100 mL beaker. By using a magnetic stir bar in the beaker, it will stir the seawater in the thermostatic bath (Figure 3). Titration of seawater samples with 0.01 M HCl at controlled conditions using temperature (25 °C). The use of HCl 0.01 M, Tris solution and synthetic seawater in the titration is important to calculate the accuracy of the exact results [8]. Finally, the total alkalinity (TA) was calculated using Equation 1.
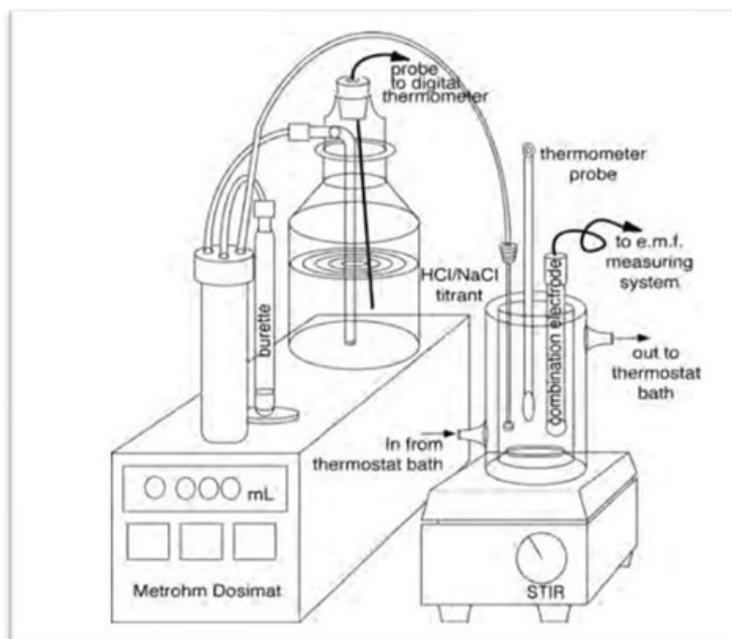
Figure 3. Open-cell alkalinity measurement set-up

$$TA \; (\mu Eq/kg) = [(EP \times C01 \times C02/C00) \times 1{,}000] \times conc. \; of \; HCL \; (used \; for \; titration) \times 1000 \quad (1)$$
$$(change \; from \; g \; to \; kg)$$

Where:

C00 = weight of sample (ml) = 25 g. C01 = actual concentration of HCl (M)
C02 = Correction factor = 100,000 (c=0.01 mol/l of HCl used for titration
EP = end point volume of HCL used for titration
Example: If the endpoint of the titration is 5.60 ml of 0.01 M HCl
TA (μ Eq/kg) = [(5.60 x 0.01 x 100,000/25) x 1,000] x 0.01 = 2,240μEq/kg

RESULTS AND DISCUSSION

The data distribution of various alkalinity values that have been recorded after using the eco-titrator is shown in Table 2 below. Overall, all three sea depths were analysed and showed values of 1900 (μEq/kg) up to 2200 (μEq/kg). The higher the micro equivalent value of an area, the higher the alkalinity value of the sea. The average colour contour of alkalinity for each station by using Surfer Software as shown in the Figure 4.

Table 2: The average and standard deviation data of alkalinity of Dangli group Island, Langkawi.

STATION	SURFACE	MIDDLE	BOTTOM	AVERAGE (µeq/L)
ST1	2077.56	2040.48	2053.51	2057.18 ± 18.81
ST2	2043.47	2130.90	2143.32	2105.90 ± 54.42
ST3	2078.25	2078.57	2131.64	2096.15 ± 30.73
ST4	2085.87	2044.36	2169.70	2099.98 ± 63.85
ST5	1982.07	2141.10	2038.50	2053.89 ± 80.62
ST6	2054.45	2045.89	2066.14	2055.49 ± 10.17
ST7	2026.86	2027.90	2100.60	2051.79 ± 42.28
ST8	2061.56	2035.03	2080.40	2059.00 ± 22.79
ST9	2067.34	2041.87	2054.20	2054.47 ± 12.74
ST10	2056.92	2160.86	2116.67	2111.48 ± 52.16
ST11	2201.12	2260.45	2113.70	2191.76 ± 73.82
ST12	2155.23	2245.39	2188.47	2196.36 ± 45.60
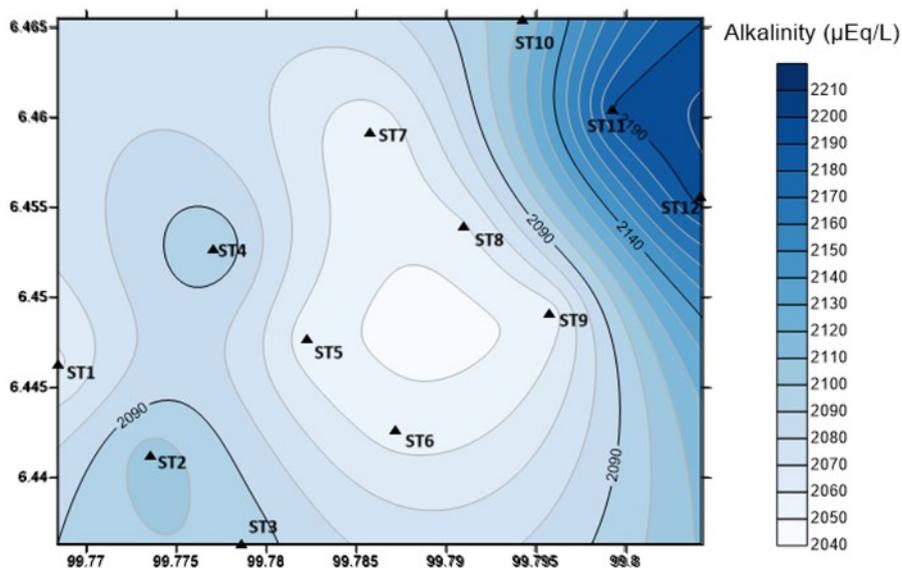
Figure 4: Contour Map of Alkalinity (µEq/L) by using Surfer Software

The distribution of alkalinity value from Dangli Island seawater demonstrates inconsistency data distributed across depths. From the observation, surface alkalinity was generally lower (1982.07–2201.12 µmol/kg), might be influenced by evaporation, freshwater influx, and biological activity. While middle depths exhibit higher alkalinity (2027.9–2260.45 µmol/kg), reflecting reduced surface influences and enhanced mixing with deeper waters. Bottom waters have the most stable and elevated alkalinity (2038.5–2188.47 µmol/kg), attributed to reduced atmospheric interaction and increased mineralization or

carbonate dissolution. According to statistical analysis Two-Way ANOVA, there is no significant difference in the means across different depths with the *p*-value (0.2076) was greater than 0.05. It's may suggest that the measured variable is relatively uniform across depth levels, possibly due to a consistent vertical distribution of influencing factors or the limited depth range. It is shown that the coastal and deep-sea water total alkalinity is strongly influenced by the river flow. In the Black Sea aerobic zone, total alkalinity does not change virtually with depth [11].

Spatial variation in alkalinity values often reflects differences in local environmental factors, which can significantly influence the observed patterns as shown in the Figure 4. Stations like ST11 (2191.76 ± 73.82 µEq/L) and ST12 (2196.36 ± 45.60 µEq/L) show the highest averages due to strong subsurface influences. This happened because the water current was affected by the 2 rivers near the sampling area such as Kilim River and Kubang Badak River. The Kilim and Kubang Badak River in Langkawi has a Ca-HCO3 water type, indicating a high level of surface water-groundwater interaction and limestone dissolution [12]. This high dissolution of limestone significantly impacts the river's water chemistry, contributing to elevated alkalinity levels. When this river water mixes with the seawater near its estuary, it influences the local marine alkalinity, sediment composition, and even the carbonate saturation state. The freshwater from Kubang Badak River and Kilim River might contains bicarbonates and carbonates, coastal areas may also experience high alkalinity. Furthermore, biological processes that affect local alkalinity levels, such as the uptake of carbon dioxide by marine animals, can cause variances in various marine settings [13].

In the other hands, the other stations such as ST5 (2053.89±80.62 µEq/L) has the bright colour of contour map which indicates the area experience the lowest reading of alkalinity. For example, analysis of the data of station 5 indicates a slightly drop in alkalinity levels at surface seawater (1982.07 µEq/L) compared to others station. Processes that dilute seawater and lessen its buffering capability, such as increased freshwater intake from rivers or rainfall, can cause seawater's alkalinity to drop. Alkalinity can also be lowered by biological activity, such as the intake of carbonate ions by marine organisms for the construction of shells and skeletons. Another factor is acidification brought on by too much CO_2 in the atmosphere, which lowers alkalinity by raising the concentration of carbonic acid and consuming carbonate ions [14]. Based on statistical analysis Two-Way ANOVA., indicate that there is a significant difference in the means across different stations, as the $p < 0.05$ (0.0044), leading to the rejection of the null hypothesis. This is because the significant difference in the means across stations could be due to spatial variations in environmental, biological, or physical factors that vary by location, such as differing habitat conditions, resource availability, or pollution levels.

CONCLUSION

For the conclusion, there is proven the different depth will shows no different level of alkalinity in this Dangli Island area, meanwhile spatial distribution has a significant different among the station. Moreover, the alkalinity value was varied due to factors like the type of rocks and minerals in the area, biological activity, climate, and human activities. In regions with more carbonate-rich rocks, will drive alkalinity values higher than other regions. On the other hand, rainfall, runoff, and human impacts like agriculture further affect alkalinity, which is essential for buffering water against changes in pH and maintaining healthy ecosystems. Research on alkalinity and its impact advances the overarching objective of preserving the health of marine ecosystems. It is recommended to increased monitoring and data collection which regularly monitor seawater parameters including pH, alkalinity, temperature, and salinity to provide trend information on ocean acidification. This will provide the important changes in ocean acidification trends. Moreover, the research endorses worldwide and national endeavours to align with

Sustainable Development Goal 14 (SDG14), which focusing on the preservation and sustainable utilization of oceans and marine ecosystem for future generation.

AUTHOR'S CONTRIBUTION

Nurul Hidayah Bt Rosmee carried out the research, wrote and revised the article. Dr Jamil Tajam Mohd Azlan Bin Mohd Ishak, Sabiha Hanim Bt Saleh, Aileen Tan Shau Hwai, Khairul Naim Bin Abd. Aziz and Md Nizam Bin Ismail conceptualised the central research idea and provided the theoretical framework. They also designed the research, supervised research progress, anchored the review, revisions and approved the article submission.

CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare absence of conflicting interests with the funders. The authors declare that there have no personal or financial conflicts of interest that could have influenced the research reported in this paper. All affiliations, funding sources, and other potential conflicts have been fully disclosed and managed in accordance with institutional guidelines to ensure objectivity and transparency in the research process.

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