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Assessment of ocean acidification in a selected tropical coastal lagoon in Mauritius

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Article Information	Abstract: This assessment of ocean acidification at Flic-en-Flac (FF), located in the west of
Received 12 May 2022,	Mauritius, is a first-time study conducted from 2017 to 2021. The variations of pH and
Revised 17 June 2022,	total alkalinity (A_T) were monitored. Over the course of this study, temperature varied from 23 °C to 31 °C, whereas salinity was constant at 35 ‰. The summer season lasted from
Accepted 21 June 2022.	October to March and the winter season from April to September. The lowest mean pH
Published online	value, (7.94 ± 0.02) , was noted in April 2019 winter month whereas the highest mean pH
30 June 2022	value (8.17 ± 0.03) was noted in October 2017 summer month. The overall mean pH values
	(8.06 ± 0.06) were slightly higher in all summer periods compared to winter ones $(8.01 \pm$
	0.07). However, it was observed that the mean pH values in summer 2018 (7.97 \pm 0.03),
	were lower than in 2017 (8.06 \pm 0.06) and 2019 (8.03 \pm 0.05) due to a tropical storm. The
	mean AT for the three sampling periods was (2404.1 \pm 174.8) μ molkg ⁻¹ , in line with the
	global mean of $(2300 \pm 200) \mu\text{molkg}^{-1}$. The mean alkalinity varied from (2094.8 ± 68.0)
	μ mol/kg (September 2019) and the highest mean A _T of (2880.0 ± 14.1) μ mol/kg
	(November 2018). In most cases, results following the t-test show that they were significant
	when the pH values of summer and winter were compared. However, all the t-test results
	were not significant with regards to alkalinity.

Keywords: Ocean acidification, Mauritius, pH, Total Alkalinity, t-tests.

Introduction

Intergovernmental Panel on Climate Change (IPCC) has recently published the latest level of carbon dioxide (CO₂) to be 410 ppm, compared to 280 ppm in the preindustrial times (Masson-Delmotte et al., 2021). The burning of fossil fuels has largely contributed to this large increase in anthropogenic carbon dioxide in the atmosphere. It is a well-known fact that carbon dioxide causes global warming. However, the other environmental concern related to the high levels of CO2 is the lowering of the pH of the ocean; a phenomenon known as ocean acidification (OA). The buffering capacity of the ocean has always maintained the pH of the ocean at about 8.1 (Kapsenberg & Cyronak, 2019; Kleypas, 2019). However, nowadays, with such a high level of carbon dioxide, the ocean's buffering capacity is undermined, leading to a lowering in its pH. In fact, it has been reported that the oceanic pH has already decreased by 0.1 units (Koch, et al., 2013) and is expected to decrease by 0.7 units more under the current trend (Findlay & Turley, 2021). The net effect of this oceanic absorption is an increase in H⁺, HCO₃⁻ and H_2CO_3 and a decrease in CO_3^{2-} and the overall pH (Byrne, 2014).

The Republic of Mauritius constitutes a huge Exclusive Economic Zone (EEZ) of 2 million km² (Ramessur, 2002). Consequently, blue economy has become a major pillar of economy for the island where the sea food hub has been established in the region. A number of adverse effects of OA have been noted. Species with calcium carbonate skeletons, known as calcifying organisms are particularly susceptible to ocean acidification (Baag & Mandal, 2022; Kapsenberg & Cyronak, 2019). As pH decreases, carbonate ion availability also decreases and this results to reduced rate of calcification, leading to the dissolution of shells of aquatic species and reefs. Moreover, an increased level of dissolved carbon dioxide can affect the ability of primary producers to photosynthesize (Gao et al., 2019). A drop in pH can also influence acid-base regulation together with a variety of other physiological processes in aquatic organisms. It is therefore imperative to address and minimise the adverse effects of OA, as indicated by SDG 14 - Life Below Water (UN General Assembly, 2015) and to formulate solutions and policies in the region (Ramessur et al., 2022). Hence, the monitoring of OA at Flic-en-Flac (FF) public beach, one of the popular destinations to tourists and the local population, has been undertaken over the past five years, 2017 to 2021.

The aim of this study is to determine the change in pH and the alkalinity of seawater at the chosen site over a five-year period, from 2017 to 2021. This study will be very helpful to evaluate the downtrend of these parameters in the long run and from there to conclude the extent of damage that ocean acidification can bring to aquatic species in the Mauritian waters. The objectives are to:

- Determine pH of seawater sample using UV-spectrophotometric method.
- Determining the total alkalinity (AT) of the collected seawater samples using the potentiometric open cell titrator.

• To carry out statistical analysis using the pH and alkalinity data over the summer and winter seasons.

Materials and methods

Study area

Flic-en-Flac public beach (Fig. 1) is found along the west coast of Mauritius (-20.27, 57.37). It is highly visited by the tourists and the local population because of its turquoise waters and coral reefs.

The sandy beach at FF extends over about 5 km. The waters are calm and shallow due to the presence of coral reefs at a distance of about 150 m from the shoreline.



Fig. 1: Flic-en-Flac location on the map of Mauritius

Sampling

Sampling was carried out every two weeks from September 2017 to October 2021 at around 10 am near Anelia Resort & Spa, Flic en Flac. Seawater samples were collected in duplicate in 250 ml borosilicate bottles, followed by the addition of 200 μ L of a mercury (II) chloride (HgCl₂) saturated solution.

Physico-chemical parameters

Temperature and salinity of seawater were measured using a Fluke Calibration 1523 Thermometer with accuracy ± 0.3 °C and an ATO Brix Refractometer with accuracy $\pm 0.1\%$, respectively.

Determination of pH

pH was determined by a spectrophotometric method (Clayton & Byrne, 1993; Liu *et al.*, 2011). Absorbances of each resultant seawater sample, following the addition of purified meta cresol purple dye, were measured at 434 and 578 nm, using a Biochrom Libra S22 UV-Vis spectrophotometer. pH correction following the dye addition to the seawater samples was achieved according to DeGrandpre *et al.* (2014).

Total alkalinity (A_T) determination

An open cell titration was used to determine the total alkalinity of seawater, following the standard operation procedure 3b (Dickson, 1981) and the titrant was 0.1 M HCl in 0.6 M NaCl. A Metrohm pH electrode was used

to monitor the change in EMF. The Gran titration was used to determine the end point.

Quality control

Certified reference materials (CRMs) were obtained from the Scripps Institute of Oceanography, University of California San Diego. Tris buffers and CO₂ in seawater reference materials were required to verify the accuracy and precision of pH and AT measurements, respectively.

Statistical analysis

Normality was tested using the Shapiro-Wilk normality test in R project for statistical computing (Shapiro & Wilk, 1965). To compare the seasonal variation in the data collected over the period of study, unpaired twotailed T-tests were carried out. Since the samples have unequal sizes and unequal variances, the Welch's variant of the T-test was performed with a null hypothesis that the two-population means are equal. All statistical tests were performed at a significance level of 5%.

Results and Discussion

Physico-chemical variations

Within the time frame 2017 to 2021, sampling was carried out over three periods of time; 20-week sampling from 28/09/17 (week 1) to 11/12/19 (week

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20), denoted as sampling period 1; 8-week sampling from 29/10/20 (week 1) to 22/02/21 (week 8), denoted as sampling period 2 and finally 5-week sampling from 01/07/21 (week 1) to 23/09/21 (week 5), denoted as sampling period 3. The summer season is considered to be from October to March and the winter season is considered to be from April to September. The temperature varied between 23 °C and 31 °C while the salinity was constant at 35 ppt throughout the period of study. Figure 2 below shows the variation in the daily mean pH values for the three sampling periods, as follows:

The lowest mean pH value, (7.94 ± 0.02) , was noted in week 15 of April 2019 winter month whereas the

highest mean pH value, (8.17 ± 0.03) , was noted in week 4 of October 2017 summer month and both these pH values are noted in sampling period 1. The highest pH value can be explained by the fact that it was in summer where the water is warmer, and less CO₂ resides in it. The minimum pH value, on the other hand, is due to the fact that it was in winter where the water is colder and hence more CO₂ is present. From week 12 to 16, the values of the mean pH were the lowest since during that period of time, the island was visited by a tropical storm namely Bouchra (9th November 2018 – 17th November 2018), associated heavy rains being slightly acidic, prior to sampling and also, we were heading towards the winter season.



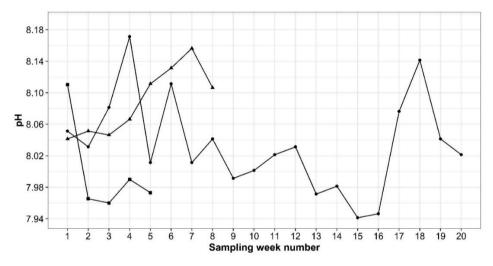


Fig. 2: The variations in the mean pH during the three sampling periods

As for sampling period 2, an upward trend in the mean pH values was noted (October 2020 to February 2021). This is expected since this sampling period occurs well in the summer season and that the temperature kept increasing slightly. On the other hand, there was a downward trend in mean pH during sampling period 3. The reason for this observation is that sampling was carried out well in the winter season and a downward trend is seen and, in this case, temperature was decreasing during the course of study.

Table (1), it is observed that the overall mean pH values (8.06 ± 0.06) were slightly higher in all summer periods than in winter ones (8.01 ± 0.07) and this is in accordance to the fact that more CO₂ is present in the ocean when the temperatures are lower. Similarly, from Table 1, it can be observed that the mean pH values of each summer period is slightly higher those of each winter period.

Interestingly, it was observed that the mean pH values in summer 2018 (7.97 \pm 0.03), were lower than in 2017 (8.06 \pm 0.06) and 2019 (8.03 \pm 0.05) since, as mentioned above, during that period of time, a tropical storm caused a drop in pH.

Table 1: The mean and standard deviation of pH and A_T across the seasons

Season	pН	$A_T (\mu molkg^{-1})$
Summer 2017	8.06 ± 0.06 , n = 16	$2138.9 \pm 55.0, n = 2$
Winter 2018	$8.01 \pm 0.03, n = 8$	$2376.4 \pm 104.2, n=8$
Summer 2018	$7.97 \pm 0.03, n=4$	$2750.0 \pm 127.3, n=4$
Winter 2019	$8.03 \pm 0.11, n=8$	$2358.2 \pm 180.9, n = 8$
Summer 2019	$8.03\pm0.05,$ n =4	2178.1 ± 98.7 , n = 4
Summer 2020	8.09 ± 0.05 , n = 16	2410.6 ± 119.7 , n = 16
Winter 2021	8.00 ± 0.06 , n = 10	$2453.7 \pm 131.5, n = 10$
Summer	8.06 ± 0.06 , n = 40	2406.2 ± 211.7 , n = 26
Winter	8.01 ± 0.07 , n = 26	$2400.5 \pm 142.6, n = 26$

The mean AT for the three sampling periods is (2404.1 \pm 174.8) in line with the global mean of (2300 \pm 200) μ molkg⁻¹ (Williams & Follows, 2011). During sampling period 1 (Fig. 3), mean alkalinity varied from (2094.8 \pm 68.0) μ mol/kg was obtained in week 18 of September 2019 and the highest mean AT of (2880.0 \pm 14.1) μ mol/kg was obtained in week 13 of November 2018. This maximum mean alkalinity value noted is

possibly due to excess nutrient discharge from subsequent runoffs and changes in seawater dilution brought about by the tropical cyclone (Fry *et al.*, 2015). Regarding the other two sampling periods, the mean AT varied from (2238.7 \pm 50.1) µmol/kg to (2550 \pm 70.7) µmol/kg. From Table 1 above, the mean value of the alkalinity for all summer periods was (2407.7 \pm 213.2) μ molkg⁻¹ and (2400.5 ± 134.9) μ molkg⁻¹ for winter, denoting the fact that alkalinity is not affected by air/sea CO₂ exchange and temperature change.

The variations of mean alkalinity for the three sampling periods are shown in Figure 3.

Sampling period • 1 • 2 • 3

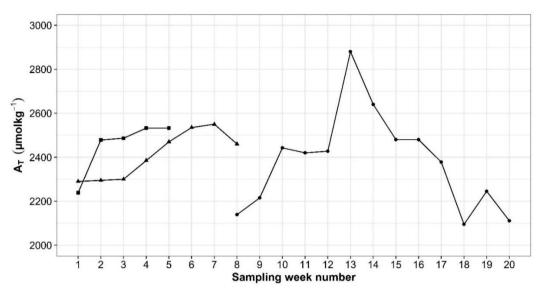


Fig. 3: The variation of AT throughout the years

Quality control

For the pH measurements, quality control experiments using Tris buffers (DelValls and Dickson, 1998) yielded 0.0152 \pm 0.0006, in accordance with Hammer *et al.*, (2014). For A_T, the latter experiments using certified value of the CO₂ in seawater CRM yielded 2.80 \pm 0.87 µmolkg⁻¹.

Statistical tests

The Shapiro-Wilk tests result in p-values of 0.39 for pH and 0.25 for A_T , indicating no significant departure from normality ($\alpha = 0.05$). T-test was then carried out and the results performed on pH data in terms of seasons are summarized in Table 2 below.

pH comparison	t	t(crit)	
Summer 2017 and Winter 2018	2.87	2.08	Significant 0.008945 (p < 0.01)
Winter 2018 and Summer 2018	2.17	2.35	Ns
Summer 2018 and Winter 2019	-1.25	2.29	Ns
Winter 2019 and Summer 2019	-0.12	2.23	Ns
Summer 2020 and Winter 2021	4.01	2.12	Significant 0.0009734 (p < 0.001)
Summer and Winter	2.93	2.01	Significant 0.005192 (p < 0.01)
Summer 2017 and Summer 2018	4.62	2.20	Significant 0.0007304 (p < 0.001)
Summer 2018 and Summer 2019	-2.15	2.62	Ns
Summer 2019 and Summer 2020	-2.17	2.61	Ns
Winter 2018 and Winter 2019	-0.36	2.30	Ns
Winter 2019 and Winter 2021	0.60	2.23	Ns

Table 2: The two-tailed Welch's t-test for pH

In most cases, results following the t-test show that they were significant when the pH values of summer and winter were used due to the fact that in summer the seawater is warmer than in winter. CO_2 sequestration occurs in colder waters (Teng & Zhang, 2018). Consequently, CO_2 molecules have more kinetic energy in summer and are more likely to stay in the air than in water. Hence, in summer, with less CO_2 in the water, the pH is higher whereas lower in winter. These observations are in agreement with the results of Artioli *et al.* (2012) and Chou *et al.* (2011). On the other hand,

t-tests using pH data of the same season on a temporal basis, for example summer 2017 and summer 2018 or winter 2019 and winter 2021, were carried out, the results were mostly not significant. On the whole, a ttest using all of the pH data of summer as opposed to all of winter was conducted; the result was significant, denoting that temperature is an important factor that influences pH of the ocean.

As regards to alkalinity data, t-test was also carried out, as shown in table 3.

A _T comparison	t	t _(crit)	
Summer and Winter (Sampling period 1)	0.30	2.19	Ns
Sampling period 2 (Summer 2020) and Sampling period 3 (Winter 2021)	-0.84	2.10	Ns
Summer and Winter (Whole period)	0.11	2.02	Ns

Table 3: The two-tailed Welch's t-test for alkalinity

We considered two t-test analyses; on a short-term basis using the alkalinity data calculated during the summer and winter periods of sampling period 1 and on a long term basis using all alkalinity data of summer times as opposed to winter times. All the results were not significant and this is attributed to the fact that alkalinity is not affected by air/sea CO_2 exchange and temperature change at that particular location (Yang et al, 2015). Similarly, the results were not significant between sampling period 2 (Summer 2020) and sampling period 3 (Winter 2021).

Conclusion

During 2017-2021, we monitored pH and A_T, chemical parameters closely linked to ocean acidification, at Anelia Resort & Spa, Flic-en-Flac, Mauritius; a pioneering study that has been undertaken. The mean pH values of the different summer periods were slightly above those in the winter ones. However, there was no major variation in the mean alkalinity values regarding the seasons. The Welch's t-test of unequal sample sizes and unequal sample variances was used to test for differences between the summer and winter seasons. The results of this study confirm that there is seasonal variation in the pH between the summer and winter seasons but no variation in the A_T. On the other hand, the t-test results revealed that, when comparing the data sets of the same season but in different years, they were mostly not significant. In view of these findings, we can conclude that the buffer capacity at FF has not really been perturbed. However, it is to be noted that the visit of a cyclone does influence pH and alkalinity of the water in the lagoon.

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All co-authors involved in this paper confirm that we have no relevant financial or non-financial competing interests

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