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Ocean Acidification and Carbonate System Geochemistry in the Arabian Gulf

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ABSTRACT

Alkalinity (Alk) and (Dissolved Inorganic Carbon) DIC were measured on high resolution seawater samples, collected on November 2018 and May 2019 at seven stations in the Exclusive Economic Zone (EEZ) of Qatar. Calculated surface P_{CO2} averaged 472 µatm in 2018 and 447 µatm in 2019.

Thus: the Arabian Gulf is degassing CO_2 at present and will not take up atmospheric CO_2 until 2042. Ocean acidification is not yet an issue in the EEZ of Qatar.

The elevated P_{CO2} values are due to $CaCO_3$ formation. Normalized NAlk and NDIC were calculated to remove the impact of increasing salinity. NAlk and NDIC decrease corresponding to a $CaCO_3$/OrgC removal ratio of 2/1. We calculated the nitrate corrected and salinity normalized tracer, Alk*. Values of Alk* were negative, and the change in Alk* relative to Hormuz (DAlk*) indicated that there has been an average decrease of Alk* of -130 mmol kg^{-1}. This decrease is due to $CaCO_3$ formation but previous studies found no evidence for coccolithophorids. One obvious possibility is that Alk removal is due to $CaCO_3$ formation in coral reefs. However, recent study of the composition of particulate matter found that the average particulate Ca concentration was 3.6%, and was easily acid soluble (Yigiterhan et al, 2018). These results suggest that a significant amount of particulate $CaCO_3$ is present in the water column. One hypothesis is that the particulate Ca comes from carbonate rich atmospheric dust. Using Al as a tracer for dust and the average Ca/Al ratio in Qatari dust can only explain about 3% of the particulate Ca. An alternative hypothesis is that particulate $CaCO_3$ may form in the water column due to abiological $CaCO_3$ formation, as proposed recently for the Red Sea (Wurgaft et al., 2016). Precipitation of $CaCO_3$ may be induced by the large inputs of nucleation sites in the form of atmospheric dust.

LITERATURE REVIEW

Historical data from 1977

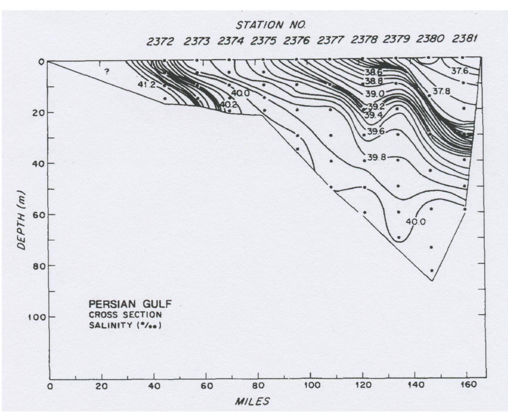


Fig. 2: Surface S in the Gulf

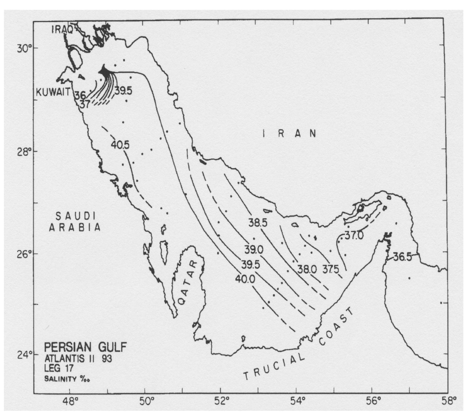


Fig. 3: Salinity (S) - Depth section

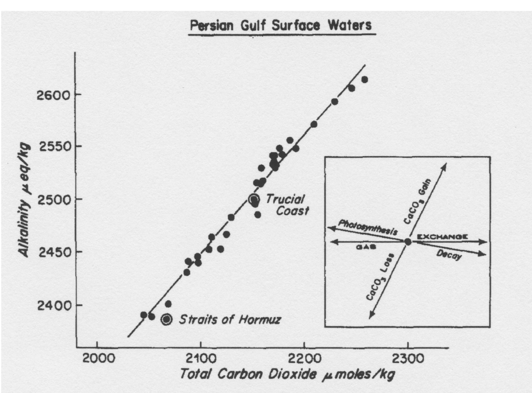


Fig. 4: Alk versus DIC

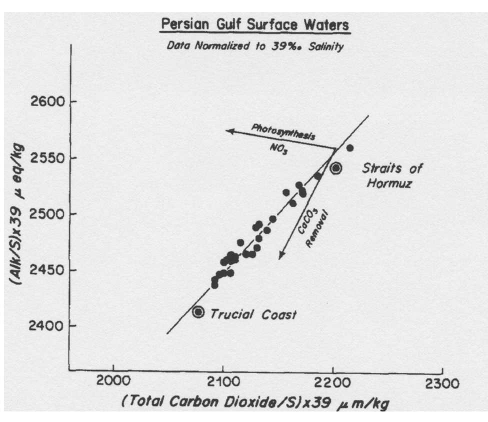


Fig. 5: NAlk versus NDIC

METHODOLOGY

RV *Janan*

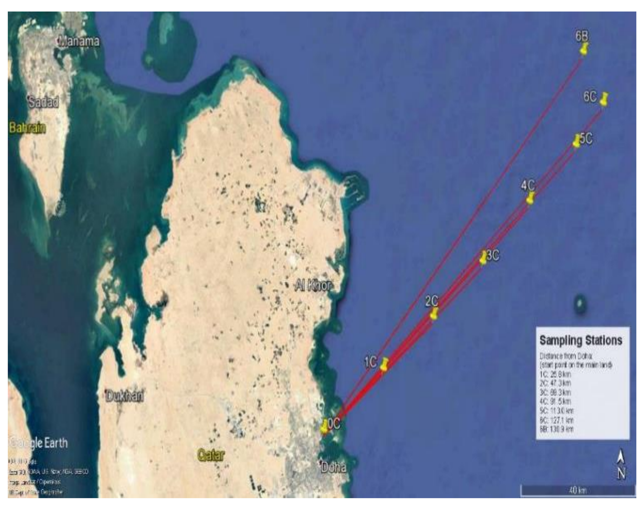
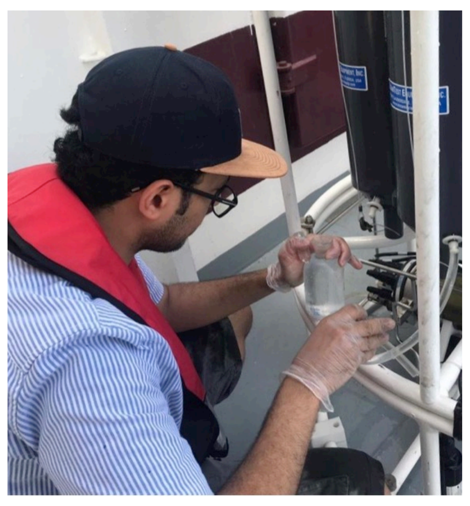


Fig. 1: Station locations in the Qatar Exclusive Economic Zone in the Arabian Gulf sampled on November 2018 and May 2019 by ESC Team, on board R/V Janan.



Sampling Seawater for DIC/Alkalinity

ANALYTICAL METHODS

- DIC was measured by coulometry.
- Alkalinity (Alk) was measured by titration. Dickson standards were used.

REFERENCES

1. Brewer and Dyrssen (1985). Progress in Oceanography 14, pp 41-55.
2. Wanninkhof and McGillis (1999). GRL 26, pp 1889 - 1892
3. Wurgaft, Steiner, Luz and Lazar (2016). Marine Chemistry 186, pp 146-155.
4. Yigiterhan et al (2018). Chemical Geology 476, pp 24-45.

RESULTS

Research Data from 2018 and 2019 Cruises

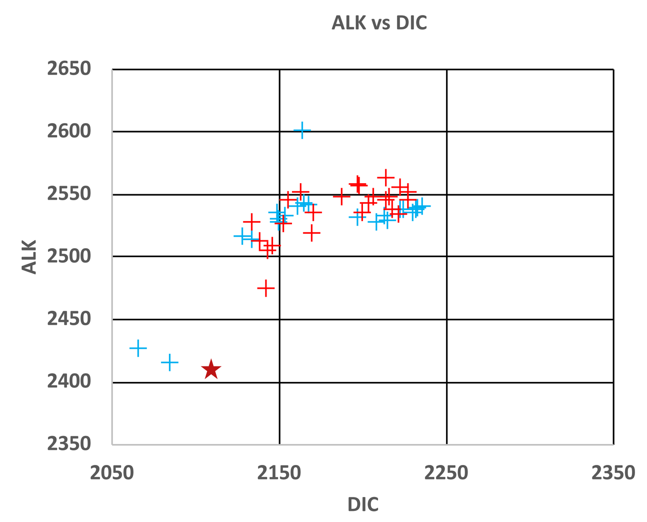


Fig. 6: DIC versus Alkalinity

The red star is the value for inflow through the Strait of Hormuz from Brewer & Dyrssen (1985). DIC and Alkalinity increase from Hormuz to Qatar EEZ due to salinity increase.

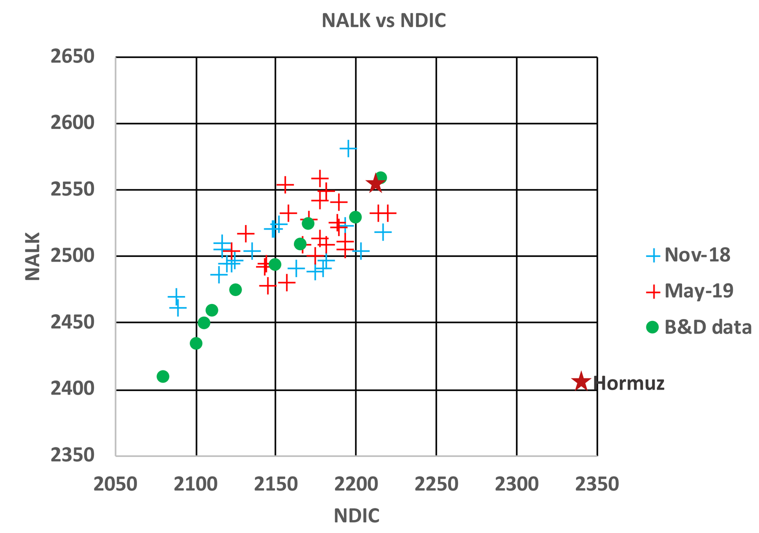


Fig. 7: NALK versus NDIC *(normalized to S = 40)*

When the impact of salinity is removed, NDIC and NAlk decrease from Hormuz to Qatar EEZ. The slope is due to $\Delta CaCO_3$ / $\Delta OrgC$ = 2. The data from Brewer and Dyrssen (1985) show that there has been no change since 1977.

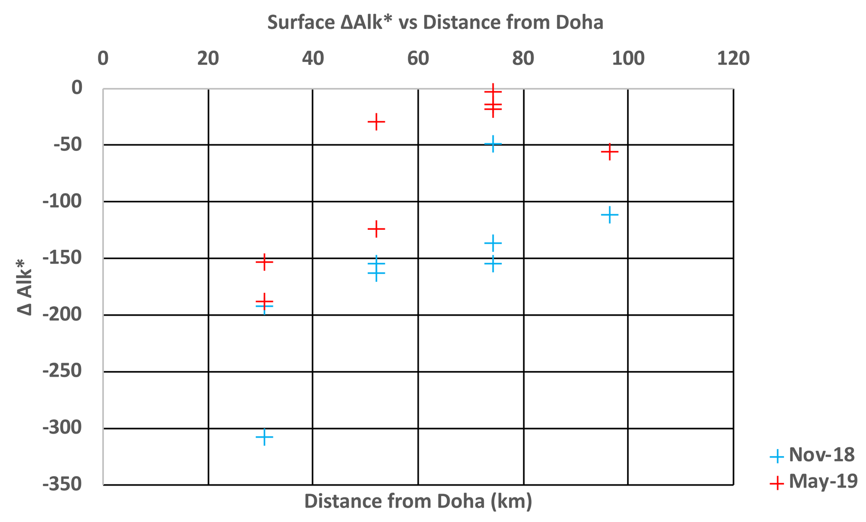


Fig. 8: Calculate Alk*

Plot of ΔAlk* relative to Strait of Hormuz.

1. Calculate Potential Alkalinity:
   $A_P = A_T + 1.26 \times NO_3$
2. Normalize to S = 40
   $A^C_P = S \times A_P / S$
3. Then: $Alk^* = A_P - A^C_P$
   ALK* is negative
   ΔAlk* is negative (relative to Hormuz)

CaCO$_3$ Formation:

Alk versus DIC and NAlk versus NDIC
Data from 1977 by Brewer and Dyrssen (1985)
Insert shows vectors for specific processes
For this data set the decrease in NAlk and NDIC correspond to a $CaCO_3$ removal / Photosynthesis ratio of 2:1

Reverse Estuarine Circulation:

Surface Seawater enters through the Strait of Hormuz and salinity increases to the north because of large net evaporation. The high salinity return flow to the south exits the Strait of Hormuz at depth, by Brewer and Dyrssen (1985).

Calculation of Gas Exchange Flux of CO$_2$:

The gas exchange flux of CO_2 equals the rate of $CaCO_3$ formation. We calculated the flux of CO_2 using the stagnant boundary layer model and piston velocity from Wanninkhof (1999). Assuming an average wind speed of 10 knots, the CO_2 flux equals 6.9 mol C m^{-2} y^{-1}. This is much greater than the rate of net calcification seen for pristine corals.

DISCUSSION

Why does Alk* decrease?

A decrease in Alk* means that $CaCO_3$ is being formed. The concentration of particulate $CaCO_3$ in the water column is high and acid soluble. It can't come from dust. However there is no evidence of $CaCO_3$ forming plankton. Could be growth of coral reefs or abiological formation. But present day corals are not healthy and occupy a small area (0.7% of sea floor).

Is there Ocean Acidification today?

Surface P_{CO2} was calculated from DIC and Alkalinity

2018 Average P_{CO2} = 472 µatm
2019 Average P_{CO2} = 447 µatm

At present rate of increase of atm CO_2, there will be no uptake of atm CO_2 until about 2042!
Ocean Acidification is not occurring in the Arabian Gulf.

Why is P_{CO2} so high?

Due to $CaCO_3$ formation and this reaction:

$CaCO_3 + CO_2 + H_2O =$
$2\,HCO_3^- + Ca^{2+}$

When $CaCO_3$ forms, reaction shifts to left and CO_2 goes up!

CONCLUSION

1. P_{CO2} in the surface water of the Arabian Gulf is higher than atmospheric.

2. Ocean Acidification is not a present issue.

2. The tracer DAlk* is negative suggesting that $CaCO_3$ formation is occurring.

3. P_{CO2} is high because of $CaCO_3$ formation. There is high particulate $CaCO_3$ but there are no $CaCO_3$ forming plankton. It can't come from dust.

4. It could be growth of coral reefs or abiological formation.

5. Coral reefs in the Arabian Gulf are not healthy.

6. The rate of calcification can be calculated from the gas exchange flux of CO_2.

7. Assuming average winds, the gas exchange flux of CO_2 (and rate of formation of $CaCO_3$) equals 6.9 mol C m^{-2} y^{-1}.

8. This is much greater than previously measured net calcification rates of healthy coral reefs in other locations.

9. Abiological $CaCO_3$ formation appears to be a possibility!

ACKNOWLEDGMENT

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