The diurnal variation of the carbonate system – a study of the diurnal $p$CO$_2$ variation and its controlling mechanism in Xiamen Bay

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Abstract
The ocean plays a significant role in the global carbon cycle and its importance as a carbon reservoir is not yet resolved. The ocean zone, highly affected by both land, near shore surface seawater and open ocean, presents a short-term variability in parameters of the carbonate system. The aim of this project was to study the diurnal variation of $pCO_2$ (partial pressure of carbon dioxide) in Xiamen Bay and the cause of this pattern, i.e., which controlling mechanism was responsible for the diurnal variation. Possible controlling mechanisms considered, altering the carbonate system and in turn the $pCO_2$, were temperature variations, biological activities, air-sea gas exchange and physical mixing.

A distinct diurnal variation of $pCO_2$ was observed during the 30-hour study period. The change in $pCO_2$ turned out to be mainly controlled by the tidal difference. The air-sea flux of CO$_2$ and the temperature variation had, according to this study, not a significant effect on the diurnal variation of $pCO_2$ in Xiamen Bay. Biological activities were observed to have a small effect on the $pCO_2$ variation. The conclusion was based on the strong observed relationship between $pCO_2$ and the tidal difference along with the linear relationship between TA and salinity and DIC and salinity. Those trends together with absence of clear correlations between other factors of the carbonate system made the conclusion apparent.

Key words: carbonate system, $pCO_2$, Xiamen Bay, diurnal, tidal difference, controlling mechanism, coastal zone, neap tide, spring tide, physical mixing
Introduction and background

To which extent and to which variability the ocean serves as a carbon reservoir is a global hot spot and an area highly debated. The coastal zone, affected by both land and open ocean, is of very dynamic structure and its feature can rapidly be modified with changing circumstances on a short time-scale. As most studies so far have focused on seasonal variations of the carbonate system in the ocean the call for studies on a more frequent level such as diurnal is getting stronger. It is well known that diurnal variations cause changes in the parameters of the carbonate system (Yates et al., 2007).

The coastal zone, including near-shore banks, lagoons, estuaries and bays, represents approximately 7% of the total ocean area. It is an environment easily affected by human activities causing perturbations in the biogeochemical cycle of carbon. Coastal ocean has due to remineralisation of terrestrial organic material concentrated in a small volume of water a high rate of biological productivity as compared to open ocean (Yates et al., 2007). Moreover, application of nutrients from land activities is common (May et al., 1999). Additionally, the coastal areas have often got a high input of dissolved inorganic carbon from groundwater flow, surface runoff and rivers which also contribute to the change in the biogeochemical cycle of carbon. A question not yet resolved is the magnitude of the coastal ocean’s contribution to the global carbon budget (Yates et al., 2007).

This study has focused on how the \( p\text{CO}_2 \) in the surface seawater in Xiamen Bay changes at a diurnal scale and the cause of this pattern. In other words, which controlling mechanism is responsible for the diurnal \( p\text{CO}_2 \) change? Biological activities, e.g., photosynthesis and respiration, thermodynamic processes such as temperature differences and physical processes, for example tidal differences, are all factors altering measurable parameters of the carbonate system;
pH, total alkalinity (TA), dissolved inorganic carbon (DIC) and partial pressure of carbon dioxide ($pCO_2$). The correlations between these parameters are used for getting a better understanding of the controlling mechanisms of the carbonate system at a particular study site (Yates et al., 2007). In this study dissolved oxygen (DO) was also measured which is a parameter generally not included in the parameters of the carbonate system.

- The carbonate system

The carbonate system in the ocean plays a fundamental role in the global carbon cycle. The partial pressure of carbon dioxide, $pCO_2$, depends on, as mentioned, numerous factors.

The solubility of a gas in a liquid, in this case CO$_2$ in seawater, is proportional to the partial pressure of the gas above the liquid following Henry’s law. The solubility of a gas decreases with increasing temperature. This is explained by molecules moving more freely between liquid and gas phase with an increased temperature making the probability to find them in gas phase higher. The partial pressure of the gas in the liquid must, with an increase in temperature, also increase. In theory, the correct term to use is fugacity rather than partial pressure, but as the difference in practice is only 1% the term partial pressure is easier related to reality and more understandable (Watson et al., 2003). The carbon dioxide flux between atmosphere and ocean can be described as:

$$F_{\text{air-sea}} = KpCO_{2\text{air}}, \quad F_{\text{sea-air}} = KpCO_{2\text{sea}}$$

where $K$ is the constant of proportionality, i.e., the CO$_2$ gas exchange coefficient independent on CO$_2$ concentrations. The net flux between atmosphere and ocean is described as:

$$F_{\text{net}} = F_{\text{air-sea}} - F_{\text{sea-air}} = K\Delta pCO_2$$

The above relationship shows that the CO$_2$ flux across the air-sea interface, as for other gases, is driven by the difference in $pCO_2$ in the ocean and in the atmosphere (Wates et al., 2003).

In aqueous systems dissolved atmospheric carbon dioxide, CO$_2$(aq), forms carbonic acid, H$_2$CO$_3$ which dissociates into bicarbonate, HCO$_3^-$ and carbonate CO$_3^{2-}$ according to the following system (Follows et al., 2006):

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$
$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$$
$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$$

Carbon is unequally distributed among dissolved and particulate constituents and is generally divided into; dissolved inorganic carbon, DIC = \([\text{H}_2\text{CO}_3] + [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]\) dissolved organic carbon, DOC, and particulate organic carbon, POC. POC is both living organisms and non-living particulate organic detritus. Finally, there is PIC, particulate inorganic carbon, mostly CaCO$_3$ (Watson et al., 2003).
- **Controlling mechanisms**

There are four considered possible controlling mechanisms of the variation of $pCO_2$ in Xiamen Bay; air-sea gas exchange, biological control, temperature control and $pCO_2$ being controlled by physical mixing. Biological activities performed by phytoplankton and benthic communities are influencing the $pCO_2$ in the way that photosynthesis reduces $pCO_2$. The respiration consumes oxygen and makes the $pCO_2$ increase. The influence of tidal difference can be traced by measuring the salinity since the factor is an identifier of different water masses. The salinity in a coastal area is usually lower than in the open ocean due to fresh water runoff and waste water runoff. At spring tide open ocean water is mixed with the seawater in the coastal zone suggesting higher salinity in the coastal area. Besides, the coastal zone has generally got higher $pCO_2$ than the open ocean due to decomposition of waste material from land releasing $CO_2$. At spring tide the above explanation suggests that the $pCO_2$ in the coastal zone decreases, the salinity increases and the opposite effect should be observed at neap tide if the main controlling mechanism is tidal difference.

- **Method**

- **Study site**

Data were collected from an anchored boat during a cruise lasting for 30 hours from July 26th to July 27th in the region of hundred meters from the coastline in Xiamen Bay. The study site is situated at the lower reach of the Jiulong River estuary on the west side of the Taiwan strait. Xiamen Bay, with an average temperature of 21°C, receives domestic seawage and freshwater from Jiulong River. A regular semi-diurnal tide is at a large scale influencing the conditions of the study site.

- **Data recording and sampling**

During the cruise surface seawater was pumped from a depth of approximately 1.5 meters. In situ parameters such as water temperature, salinity and the value of dissolved oxygen, DO, were measured continuously every 10 seconds with an YSI multiparameter sonde. $pCO_2$ was measured by leading the seawater through a so-called shower-head water-air equilibrator, precision: ±0.5matm and accuracy: ±2matm, where the water was mixed with air. The equilibrated air was in turn pumped through a water trap followed by a drier pipe of Mg(ClO$_4$)$_2$ in order to eliminate the water vapour. An air pump was then used enabling the equilibrated air enter a Non-Dispersive Infra-red detector (NDIR) also called Li-cor. The Li-cor measured the $pCO_2$ in the equilibrated air every 15 seconds and was calibrated four times during the data recording using three different $CO_2$ standards; 199 µatm, 415.5 µatm...
μatm and 792 μatm. No correction of temperature difference between in situ pCO₂ and the water in the equilibrator was made because of the short distance from the seawater to the equilibrator. All probe data were directly recorded on a laptop. The whole system, including both the water and the gas line, was checked every 30 minutes.

Additionally, discrete samples were taken every three hours via a side vent of the pumping system. The discrete samples were after the cruise used for measurements of DIC, TA, DO and pH in the laboratory. All sampling bottles were carefully washed three times with seawater, cautiously sealed without air bubbles and taken in duplicates. The samples were poisoned with 50 μl of HgCl₂ in order to prevent biological alteration. 0.05 ml of R1 and R2 were immediately added in the DO samples.

Furthermore, the study included on-deck incubation. Four samples were taken every three hours with start at 9.00 am from the same side vent of the pumping system as other samples. Four samples; two for light incubation and two for dark incubation were lowered to approximately the same depth as the water pump, i.e., 1.5 meters. The light incubation samples were kept under water for six hours whereas the samples for dark incubation stayed there for twelve hours. The dark incubation samples were shaded with foil. After the incubation the samples were mixed with 0.05 ml of R1 (MnCl₂) and R2 (NaI, NaOH). The aim of the incubation was to measure the rate of the photosynthesis and respiration by measuring the difference in DO between the samples of initial DO and the incubation samples. If possible, the incubation should also be used for calculating the influence of benthic communities as compared to the phytoplankton in the water column. Data of the total DO from both benthic communities and phytoplankton were collected from the YSI probe. The incubation should reveal the contribution of the phytoplankton as the samples were taken in the water column. The influence of benthic communities should, if the sampling and the incubation were made correctly, be calculated using this relationship:

\[
DO_{TOTAL} = DO_{PHYTO} + DO_{BENTHIC}
\]
- Measurement of sample parameters
In the laboratory measurements of DIC, TA, DO and pH were made. The DIC samples were analysed by a Li-7000 total inorganic carbon analyzer (Apollo Scitech) with a precision of ± 1 mmol/kg and an accuracy of ± 2 mmol/kg of DIC. The principle of the DIC measurement was based on the fact that DIC exists in the form of $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and aqueous $\text{CO}_2$ that absorb certain infrared light. By non-scattering infrared spectroscopy it is possible to measure the absorbance of $\text{CO}_2$. According to the area of the absorbance of $\text{CO}_2$ infrared light the amount of total inorganic carbon can be calculated.

TA was analysed by Gran titration using an automated Gran titration analyzer. For measurements of pH a combined electrode of model WTW SenTix 41 was used. The measuring range for the electrode was between pH -2.00 and +19.99, the accuracy between pH : ±0.01.

The DO measurements were made using Winkler titration. When R1 and R2 are mixed with the seawater samples a white precipitate from which in turn is oxidized by the dissolved oxygen in the water and turns brown. The solution is then acidified with a strong acid making the iodide, (I$^-$), form iodine, (I$_2$). The amount of dissolved oxygen, DO, is proportional to the titration of iodine with thiosulfate, Na$_2$S$_2$O$_3$.

The pH and DO values were measured from the samples as well as measured continuously with the YSI multiparameter sonde. Which one of the two data sets that was the most accurate was investigated by using a computer program named CO2sys (Pelletier, Lewis and Wallace, 1998).

**Results**

Please note that all figures in this part of the report cover a time-scale between approximately 12.00 am July 26$^{th}$ and 15.00 pm July 27$^{th}$. All parameters measured had a diurnal variation during the studied period. Figure 5 shows the change in $p\text{CO}_2$. $p\text{CO}_2$ was observed to have a variation cycle of nearly 12 hours where the $p\text{CO}_2$ varied between approximately 600-1000 uatm. The TA and DIC had similar trends, as can be seen in Figure 6. They increased until approximately 15.00 pm and continued by decreasing until midnight the 26$^{th}$. The following day more or less the same trend was upheld.
The value of the pH change varied in the range of 7.7 and 7.9, according to Figure 6. The change in DO based on measurements from the YSI sonde, presented an inversed correlation with pCO2, Figure 7. Figure 7 also points out that DO, as well as pCO2, has a cycle of nearly 12 hours, i.e., the time of a peak and a minimum value is approximately 12 hours.

Figure 6. The diurnal change of pH and, to the right, DIC and TA variation.

Figure 7. Calibrated in situ pCO2 and DO (YSI).

Apparenty the tidal height, as mentioned, had a semi-diurnal change according to Figure 8. The data on the tidal height was obtained from a model where the tidal height had been calculated every hour. The average value of the tidal difference in Xiamen Bay is 396 cm (Dai et al., 2005). Lastly, data recording of PAR, the active radiation or light intensity was collected (Dr Kao’s lab, 2009). Naturally the PAR increased during the day and went down to a value of zero during the night in the absence of sunlight. In Figure 9 the variation is plotted in detail.
-Air-sea flux
The average atmospheric pCO$_2$ is known to be 400 uatm. The pCO$_2$ data from Xiamen Bay showed that the seawater pCO$_2$ always was higher than the atmospheric, i.e., did not decline under 400 uatm during the studied period. The air-sea flux depends on the wind speed. A higher wind speed makes the air-sea flux stronger (Warfvinge, 2008). During the studied period the wind speed was approximated to an average of 8 m/s.

The pCO$_2$ flux is driven by the difference in concentration of pCO$_2$ between the atmosphere and the sea water, in this case, the sea water is an atmospheric CO$_2$ source since the difference in pCO$_2$ concentration cause the CO$_2$ to move from the seawater to the atmosphere. The pCO$_2$-flux varied similarly to the pCO$_2$. This means that if, for instance, the pCO$_2$ increase due to respiration the pCO$_2$-flux corresponds by increasing as well. The relationship between the pCO$_2$-flux and pCO$_2$ is showed in Figure 10. The pCO$_2$ also affects the DIC concentration. With uptake or release of DIC the pCO$_2$ should change proportionally. The correlation between pCO$_2$ and DIC can be explained by the homogenous buffer factor, also called Revelle factor (Sundquist and Plummer 1981; Frankgnoule 1994).

\[ \beta = \frac{\Delta pCO_2}{pCO_2} / \frac{\Delta DIC}{DIC} \]

With this expression it is possible to examine what change in pCO$_2$ a change in DIC would cause. The calculations made in this study predict that the change in pCO$_2$ from air-sea exchange was less than 1.28 uatm which is regarded as neglectable according to the diurnal change in pCO$_2$ varying in the range of 400 uatm.
-Temperature variation

The $pCO_2$ should, as described earlier, increase linearly with higher sea surface temperature. In theory the variation of $pCO_2$, if temperature controlled, represent a line with a positive slope. As Figure 11 shows there is a relationship with the $pCO_2$ and the temperature, though the graph does not indicate a clear temperature control of the $pCO_2$ variation. Besides, if temperature controlled, the $pCO_2$ should represent a straight line in relation to time if the temperature variation was eliminated. In Figure 12 the so-called normalized $pCO_2$ is plotted with time when the temperature effect has been deleted according to the following formula (Takahashi, Sutherland et al. 2002):

$$pCO_2_N = pCO_2_T * \exp(0.0423^*(T_{\text{mean}} - T_{\text{obs}}))$$

As can be observed, the difference between the $pCO_2$ curve with temperature effect included, $pCO_2_N$, and the curve without temperature effect, $pCO_2$, are very similar. This is the evidence that the temperature variation does not have a significant controlling effect on the diurnal variation of the $pCO_2$. In Figure 12 the difference of $pCO_2$ with and without temperature effect is plotted as $pCO_2_T$. Undoubtedly, the value of $pCO_2_T$ is very small and therefore to be ignored which is reasonable according to the above motivation.

![Figure 11. The correlation between $pCO_2$ and temperature in this study.](image1)

![Figure 12. $pCO_2$, $pCO_2_N$ and $pCO_2_T$ variation](image2)
Biological effect and influence of physical mixing

Biological activities should in this study site have a 24-hour variation due to change of light intensity during day and night. The PAR data in Figure 9 proves that the light intensity is zero during night time. Consequently the biological activities have a general 24-hour cycle. If the biological activities were the main controlling factor both \( pCO_2 \) and DO should also have a 24-hour trend. As can be observed in Figure 7 both \( pCO_2 \) and DO present a cycle of nearly 12 hours. Evidently, the \( pCO_2 \) variation should not mainly be controlled by biological activities. However, \( pCO_2 \) has a clear correlation with salinity which is an indicator of physical mixing, Figure 13. \( pCO_2 \) is low during high salinity, high salinity indicates spring tide. Apparently, \( pCO_2 \) is largely influenced by tidal difference. Consequently, the opposite trend is observed when the salinity is low, i.e., neap tide occurs. The value of \( pCO_2 \) is at that time relatively high due to absence of mixing with open ocean or near shore surface seawater.

If the above motivation that the tidal difference has a significant effect on \( pCO_2 \) is correct, \( pCO_2 \) should naturally have a clear relationship with the tidal height data. Figure 14 shows that this is the case, the tidal difference does correspond to the variation in \( pCO_2 \). As seen in Figure 14 the \( pCO_2 \) is high during neap tide and low during spring tide. The peak in \( pCO_2 \) does not exactly correspond to the minimum value of the tidal height, but this is regarded as a result of the tidal height data being calculated from a model and not measured.

Furthermore, TA and DIC should increase linearly with salinity if the tidal difference was the main controlling factor. By thinking of two different water masses being mixed in spring tide it can easily be understood that TA and DIC increases with salinity according to discussion above. Figure 15 and Figure 16 strengthen this conclusion.

The relationship between DIC and salinity and TA and salinity should, in more detail, be linear. According to the R2 values the linearity, in Figure 15 and 16, is evident. The small alternations from the straight line are due to other controlling mechanisms. It has already been concluded that temperature
difference had no significant effect on the variation of $pCO_2$. In addition, temperature has no direct effect on DIC (umol/kg), although it does influence the physical properties of the water such as the density and dissolution constants. Moreover, the influence of air-sea gas exchange has also been described as minor and of no important significance. Therefore, these alternations from the straight line indicate the effect of biological activities. If the biological activities had a significant importance the relationship between TA and salinity and DIC and salinity would not present a linear correlation. The small alternations from the straight line do suggest that biological activities have got an effect on the variation of $pCO_2$. Based on the above reasoning the biological activities can, together with the fact that the $pCO_2$ and DO did not have a 24-hour cycle, be excluded from the important controlling mechanisms, but does have a minor effect on the $pCO_2$ variation.

The light and dark incubation made in this project would have made it possible to calculate the rate of photosynthesis and respiration. In the samples the biomass is constant as opposed to the in situ DO measurements from the YSI which is largely influenced by physical mixing. During the dark incubation only respiration occurs due to the absence of light. The DO should decrease during the night and increase during the day when photosynthesis is dominating. By comparing the initial DO values at a certain time with the incubated samples a conclusion of the rate of photosynthesis and respiration could have been drawn. The incubation procedure in this project unfortunately failed due to lack of required sampling experience. The DO data from the incubation was regarded as inaccurate and not possible to use as part of the results. Due to other results excluding the biological activities as the main controlling mechanism of the change of $pCO_2$ the failure of the incubation was not seen as serious.
Conclusions

The controlling mechanisms of the carbonate system are apparently complex in the way that a vast number of parameters affect the outcome. To comprehend which mechanisms that have the most fundamental impact, each specific testing site has to be taken into consideration separately.

This study has showed that all the examined parameters varied at a diurnal scale in Xiamen Bay at the specific studied period. The $pCO_2$ varied between approximately 600-1000 uatm during the experiment. Among four possible controlling mechanisms; air-sea gas exchange, temperature variations, biological activities and physical mixing the variation of $pCO_2$ was, according to observed correlations between parameters measured, caused by physical mixing. The conclusion was based on a number of observed circumstances. Firstly, the tidal difference turned out to have a strong correlation with the $pCO_2$ variation. Secondly, the salinity and $pCO_2$ had inversed correlation indicating the effect of physical mixing. Generally, relationships between salinity, tidal height and $pCO_2$ are strong indicators of a strong influence from tidal differences. Finally, the salinity had a linear relationship with both TA and DIC which, if not controlled by tidal difference, would have been non-linear. The conclusion corresponds with other studies on the diurnal change of $pCO_2$ in Xiamen Bay (Dai et al., 2007). Even though the main controlling mechanism was evidenced to be physical mixing the biological activities had a small effect on the $pCO_2$ variation as opposed to air-sea gas exchange and temperature differences which had a neglectable effect on the $pCO_2$ change.

In this study only a number of possible measurable parameters were examined in order to get greater understanding of the cause of the $pCO_2$ variation. A more detailed study could, for example, include measurements of nutrient levels. It is essential that studies on the carbonate system are accomplished with local data for the region examined. In this case data on the tidal height was fundamental. Another possibility would have been to measure the tidal height as part of the project and avoid using a model. Probably, the results and conclusion had been even clearer.

It is important to point out that this project had a very short study period. To obtain a more reliable result diurnal variation should have been examined during a longer period of time to be able to compare the diurnal cycles and possibly observe a more general diurnal trend.


References

Books:

Articles:


