# Time series estimation of CO2 exchange during winter and spring at Urayasu in Tokyo Bay

東京湾の浦安における冬から春にかけての CO2 交換の時系列推定

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### 1. Introduction

Coastal blue carbon was defined as vegetated coastal ecosystems, including seagrasses, tidal marshes, and mangroves, due to their high capacity in sequestering carbon dioxide and high controllability by human being [1]. However, in eutrophic bays surrounded by highly urbanized areas, high primary productivity driven by nutrient loading from land effects on the carbon cycle significantly, thus this costal water is thought to have potential in absorbing CO2 [2]. As an important location with potential for CO2 reduction, further understanding of the functions of eutrophicated bays is necessary to arose attention the coastal blue carbon community.

Tokyo Bay is a semi-enclosed bay located in central Japan, surrounded by highly urbanized areas. As one of the most eutrophicated coastal environments, primary production here is reported as one of the highest [3]. Although extensive surveys indicated that the overall bay acts as a strong net sink for atmospheric CO2 [4], the night-time data is completely missing and variation in atmospheric CO2 sequestration in different water environment such as river mouth, ports and harbors still needs to be clarified.

Analytical seawater carbonate system includes

total alkalinity  $(A_T)$ , total dissolved inorganic carbon (DIC), pH and partial pressure of CO2 in seawater (pCO<sub>2sw</sub>). If any two terms are known, the rest two can be calculated. When the ion composition ratio of seawater is constant, the total alkalinity is proportional to the salinity, so that privilege method first estimate  $A_T$  from salinity then use this estimated  $A_T$  along with field measured pH to calculate the rest. Nevertheless, linear salinity -  $A_T$  relation developed in Tokyo Bay [5] was found not robust enough to estimate  $A_T$  at river mouth. Also, the practical approach of using field measured pH as input to CO2SYS [6] leads to underestimation of  $pCO<sub>2sw</sub>$ .

To strengthen the importance of eutrophic coastal water as part of coastal blue carbon, in this study, field survey was conducted to clarify the river water inflow influence and phytoplankton activity influence on seawater carbonate system by time-series sampling. With the collected data, generalized estimation methods for  $A_T$  as well as  $pCO_{2sw}$  are developed as an improvement to privilege methods, which is further applied at Urayasu station to predict the CO2 exchange trend.

#### 2. Materials and Methods

### (1) Outline of survey

Time-series sampling was conducted at the quay of Urayasu City, in the head of the Tokyo Bay as in Figure.1, at Sakai River mouth in December, January, April and June.



# Figure.1 Time-series sampling location (From Google map)

Temperature, salinity, turbidity, chlorophyll-a, and light quantum are measured along vertical direction using a multi-item water quality meter, AAQ-1183 and AAQ-177 (JFE Advantech). DO, pH, electric conductivity, and water level are measured at surface and bottom water by automatic measurement equipment installed on buoy and weight. Water samples were collected from the surface  $(0.5 \text{ m})$  and bottom layers  $(0.5 \text{ m})$ m above bottom) using a water sampler, then transferred into borosilicate glass screw-top Duran bottles with small amount of mercury (II) chloride added to suppress biological activity [7]. Samples were brought back to campus for analysis.

At noon of Jun 2<sup>nd</sup>, an additional survey was further conducted at the upstream and downstream of East water gate of Saki River to gather information about river water quality data.

## (2) Seawater carbonate system

CO2 flux at the sea surface is calculated from the difference of atmospheric pCO2 (pCO<sub>2air</sub>) and  $pCO<sub>2sw</sub>$ . However, this flux is influenced largely by wind that it can hardly reflect the CO2 exchange induced by water environment change. So, in this study only the difference in  $pCO<sub>2air</sub>$ and  $pCO<sub>2sw</sub>$  is compared.  $pCO<sub>2sw</sub>$  larger than  $pCO<sub>2air</sub>$  means releasing CO2 and the vice versa. Unlike  $pCO<sub>2air</sub>$  that is calculated from atmospheric pressure and CO2 concentration in the air, thus with minor variation,  $pCO<sub>2sw</sub>$ varies largely due to water environment condition, so that  $pCO<sub>2sw</sub>$  is regarded as the key parameter in this research.

With the samples collected from survey,  $A_T$ and DIC were measured by neutralization titration. Sample pH is measured at lab condition as well.  $pCO<sub>2sw</sub>$  was then calculated with CO2SYS [6] developed by CDIAC (Carbon Dioxide Information Analysis Center) using one of the pH and  $A_T$ , pH and DIC, or DIC and  $A_T$ combination, since the final  $pCO<sub>2sw</sub>$  result is consistent.

### 3. Results and Discussion

## (1)  $pCO<sub>2sw</sub>$  in the field

In the river survey at noon of June.2<sup>nd</sup>, the East Watergate is closed, so samples at the surface and bottom in the downstream of East Watergate as well as a sample in the upstream (shallower water) was collected. The river survey result shows that pCO2 of river water at downstream is much higher than  $pCO<sub>2sw</sub>$  at the time-series sampling site, so river water inflow will cause the  $pCO<sub>2sw</sub>$  at the time-series sampling site to be higher.



# Figure.2 River survey results at downstream of East Watergate (12:05)

Time-series  $p_{CO2sw}$  are shown in Figure.3, with shadow area in all figures demonstrating the night-time condition. The survey in December was under complete no-bloom condition, while during the survey in February,  $\frac{2020.12}{\frac{3}{20000} \times 2021.4}$ we captured the beginning of the phytoplankton  $\frac{a}{2}$ bloom, but the biological process influence was too weak to be reflected in the  $p_{CO2sw}$  trend.





observed during nighttime because of higher phytoplankton concentration at the time-series sampling site.

## (2) Improvement in  $pCO<sub>2sw</sub>$  calculation

Privilege method of feeding field pH and estimated  $A_T$  into CO2SYS [6] to calculate  $pCO<sub>2sw</sub>$  was first tested. As plotted in Figure.4, comparing to the accurate  $pCO<sub>2sw</sub>$  calculated using parameters measured in lab condition, the  $pCO<sub>2sw</sub>$  calculated with privilege method caused severe underestimation. And the cause lies in the biasness of field pH value.







Figure.5  $pCO<sub>2sw</sub>$  predicted using trained Gradient Boosting model (Y axis) to accurate  $pCO_{2sw}$  (X axis)

To avoid the underestimation of  $pCO<sub>2sw</sub>$ , datadriven approach is applied. Gradient Boosting model trained using pH, salinity, chl-a, DO and temperature as input reached highest  $R^2$  value of 0.921. Though outliers still exist in the Figure. 5, underestimation has been avoided to large extend.

# (3) Application of the developed  $pCO<sub>2sw</sub>$ estimation model

All the collected data was used to train the model, and prediction was made using data at Urayasu monitoring station from December to June. The prediction result in Figure.6 indicates that With the collected data, a data-driven  $pCO<sub>2sw</sub>$ Urayasu is a source for CO2 especially in December and January when biological influence is weak.



Figure.6 Time-series prediction of  $pCO<sub>2sw</sub>$ 

#### at Urayasu

<sup>2</sup> value Edo River water inflow is considered as the reason for this CO2 releasing result. Though further evidence needs to be collected to prove the reliability.

### 4. Conclusion

 $pCO<sub>2sw</sub>$  fluctuation at river mouth in the head of the Tokyo Bay due to river water inflow and phytoplankton activity was clarified through time-series sampling from December to June.

estimation method was developed, which avoids the underestimation in privilege method.

The developed estimation method is applied for time-series prediction of  $pCO<sub>2sw</sub>$  in Urayasu, and this location is revealed to be a source for CO2.

#### 5.References

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