

Quantitative Comparison of Algorithms for Estimating the Air-sea Exchange of Carbon Dioxide in Malacca Straits

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Abstract

A precise quantification of the sea surface partial pressure of carbon dioxide ($p\text{CO}_{2(\text{water})}$) at the water surface is required in order to define the role of the sea in air-sea exchange of CO_2 . Even though the $p\text{CO}_{2(\text{water})}$ can be measured directly, the semi-empirical model has seen numerous application in determining the $p\text{CO}_{2(\text{water})}$ due to a time-and cost-efficient. This study aims to compare the $p\text{CO}_2$ and FCO_2 (Flux of CO_2) calculated using Zhai and Zhu algorithm with the underway datasets of $p\text{CO}_2$ obtained during the scientific cruise of CISKA-SPICE III in April 2013. The partial pressure of CO_2 ($p\text{CO}_2$) was measured using a high-accuracy electrochemical instrumentation underway HydroC/ CO_2 FT (flow through) with an error $\pm 1 \mu \text{ atm}$. Furthermore, in order to calculate the $p\text{CO}_2$ and the FCO_2 employing widely used algorithms, some data were needed including wind speed, sea surface temperature and chlorophyll-a extracted from MODIS (Moderate Resolution Imaging Spectroradiometer). According to the results obtained, the difference between the $p\text{CO}_2$ and FCO_2 derived from those two algorithms are significant. The underway datasets of $p\text{CO}_2$ are ranging from 409.52-544.01 $\mu \text{ atm}$. Meanwhile, the $p\text{CO}_2$ derived using the Zhai algorithm and Zhu algorithm are between 405.003-422.79 $\mu \text{ atm}$ and 398.94-752.06 $\mu \text{ atm}$ respectively. The FCO_2 are varied between 0.02-0.06 $\text{molC.m}^{-2}.\text{day}^{-1}$ (Zhai algorithm), 0.02-0.57 $\text{molC.m}^{-2}.\text{day}^{-1}$ (Zhu algorithm) dan 0.04-0.23 $\text{molC.m}^{-2}.\text{day}^{-1}$ (the underway datasets). A comparison of the two results reveals that $p\text{CO}_2$ derived using Zhai algorithm is closer with the underway datasets compared with the result of $p\text{CO}_2$ calculated using Zhu algorithm with the MRE (Mean Relative Estimation Error) as large as 19.4% and 39% respectively. Taken together, these results suggest that the Zhai algorithm is more appropriate to determine algorithms for estimating the air-sea exchange of carbon dioxide in the Malacca Straits

Keywords: carbon dioxide, Malacca Straits, $p\text{CO}_2$, FCO_2 , Zhai and Zhu algorithm

Introduction

The rate of CO_2 emission because of anthropogenic mainly originated from land-use change and fossil fuel combustion has increased by around 9.8 $\text{PgC}.\text{year}^{-1}$ since the last a decade (Le Quéré et al., 2015). Indonesia that has a vast area of tropical forest and widely known for its potential CO_2 uptake. However, the role of the forest in absorbing carbon dioxide has decreased due to the conversion of the forest to be a residence area. Indonesia also has a vast area of ocean, which is 3,288,680 km^2 or around 63% of its total area of Indonesia. Ocean has also known having the ability to absorb CO_2 (carbon sink) or to desorb CO_2 (carbon

source). It is fundamental to diagnose the dynamics of the CO_2 transport by an oceanic carbon reservoir in order to make an accurate projection of global warming (Iida et al., 2015).

The Air-sea exchange of carbon dioxide can be examined by calculating the difference between the partial pressure of CO_2 in the atmosphere and the sea ($\Delta p\text{CO}_2$). This $\Delta p\text{CO}_2$ gives a thermodynamic driving force in order to reach equilibrium state of the CO_2 concentration. It can be calculated by using methods such as direct measurement (Yu et al., 2013), the approach of carbonate system (Adi and Rustam, 2010; Wahyono, 2011) and remote sensing data including temperature and chlorophyll-a (Zhai,

2005; Susandi *et al.*, 2006; Ramawijaya *et al.*, 2012).

Employing the algorithms in which data mainly derived from satellite remote sensing has been widely applied on research related to CO₂ fluxes (Song *et al.*, 2016). The utilization of remote sensing can provide benefits because it produces information of sea surface temperature and chlorophyll-*a*, which cover a vast area and extended periods of time. The cost associated, with the data collection, is also much lower than direct measurement. However, Ramawijaya *et al.* (2012) research at Banten waters shows that the approach for defining the CO₂ flux using Zhu algorithm (Zhu *et al.*, 2009) still contains errors. This Zhu algorithm does not appropriate to be employed in the coastal waters or estuary.

Even though it has advantages of analyzing a large area over time, applying an algorithm for determining the *p*CO₂ can be a challenge due to the complexity as a result of a combination various factors. Thus, finding the most appropriate algorithm to be applied in certain water is crucial (Hernández-Carrasco *et al.*, 2015; Song *et al.*, 2016). Some studies (Wang *et al.*, 2010; Hales *et al.*, 2012; Turi *et al.*, 2014; Hernández-Carrasco *et al.*, 2016; Chen *et al.*, 2016 Song *et al.*, 2016) related to the identification of *p*CO₂ and air-sea CO₂ flux using both algorithms and underway datasets has also been conducted. However, none of them applies this research approach in Malacca strait.

This research aims to compare the *p*CO₂ and FCO₂ (Flux of CO₂) calculated using Zhai and Zhu algorithm, including its comparison to the underway datasets of *p*CO₂ obtained during the scientific cruise of CISKA-SPICE III on April 2013 (Wit *et al.*, 2015). Thus, the most suitable algorithm which has lowest MRE relative to the underway datasets of *p*CO₂ can be used in the future works for examining CO₂ flux in tropical waters mainly in the Malacca strait.

Material and Methods

The materials that are used in this research are aqua-Modis satellite remote sensing, underway datasets of *p*CO₂, and direct measurement of atmospheric *p*CO₂. The Sea Surface Temperature (SST), wind speed and Chlorophyll-*a* are extracted from the satellite imagery using Arc-GIS 10.1. Direct measurement was conducted during the scientific cruise of CISKA-SPICE III Cruise on 02-17 April 2013 (Mayer *et al.*, 2013). CISKA-SPICE III, is a joint research program between Research and Development Center for Marine and Coastal Resources (P3SDLP-Indonesia) and The Leibniz Center for Tropical Marine Ecology (ZMT-Bremen). SPICE (Science for the Protection of Indonesian Coastal Marine Ecosystems), which has a grand topic of “Climate change & the ocean: carbon sequestration in Indonesian Seas & their global significance: generation of scientific Knowledge for formulating strategies for adaptation to climate change” (CISKA). Moreover, the location of sampling station is provided in Figure 1.

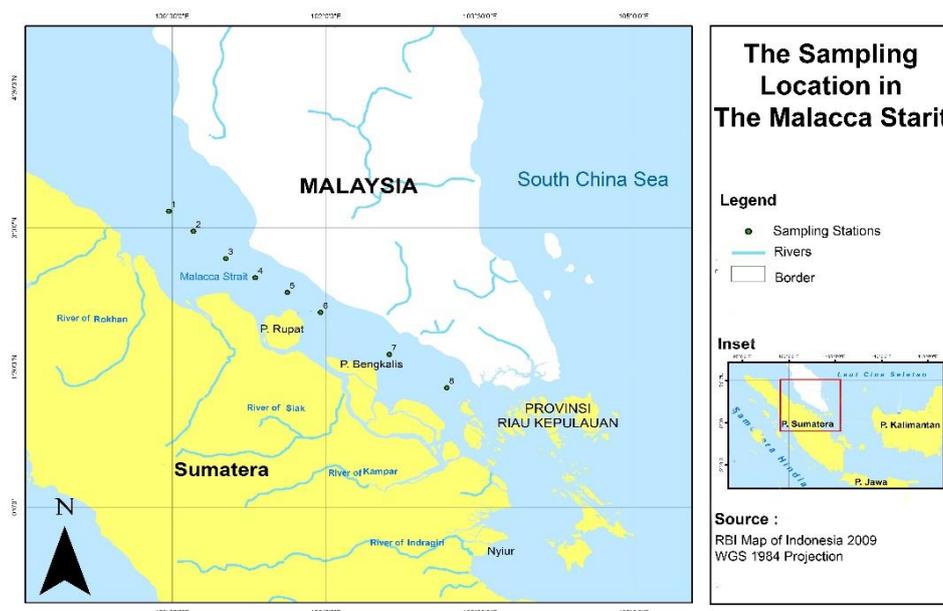


Figure 1. The Location of Sampling Station

Methods for pCO₂ calculation

In addition to the pCO₂ underway datasets, the pCO₂ data was also obtained, pCO₂ is computed using an algorithm that is developed by Zhu et al. (2009), pCO₂ computation using methods that have been employed by Zhai et al. (2005) and the pCO₂ determination through field measurement using HydroC FT flow (±1 µatm).

Carbon dioxide flux calculation

Flux, in here, is known as the transport of CO₂ between the atmosphere and the ocean. It is a function consisting of two variables including the CO₂ concentration gradient between atmosphere and ocean, which is representing of thermodynamic function; and the gas transfer velocity of CO₂ as a function of sea surface hydrodynamics. The equation used is provided as follow.

$$F = K K_0 (pCO_{2(Aq)} - pCO_{2(air)})$$

Where:

- F : Flux of CO₂ (mol.m⁻².d⁻¹)
- k : Velocity of gas transfer (cm.hr⁻¹)
- Ko : Coefficient of CO₂ gas solubility (mol.L⁻¹.y⁻¹)
- pCO₂: Partial pressure of CO₂

CO₂ sink and source

The equation below, was used to define whether a particular seawater acts as sink or source of CO₂.

$$\Delta pCO_{2(Aq)} = \Delta pCO_{2(Aq)} - pCO_{2(air)}$$

In which the pCO_{2atm} measured directly in the Malacca Straits on June 2013 as large as 385 µatm. The ocean will be identified as a source of CO₂ to the atmosphere if the ΔpCO₂ has a positive value. Meanwhile, it is defined as a sink if the ΔpCO₂ has a negative value (Zhai et al., 2005).

Result and Discussion

Partial pressure of CO₂ (pCO₂)

The pCO₂ computation using those three methods shows different results. The pCO₂ values are ranging from 405.003–422.79 µatm (results using the method of Zhai et al. (2005) and around 98.94-752.06 µatm (results using the method of Zhu et al., 2009). Meanwhile, the result of pCO₂ obtained from direct measurement is around 409.52-544.01 µAtm. See Figure 2.

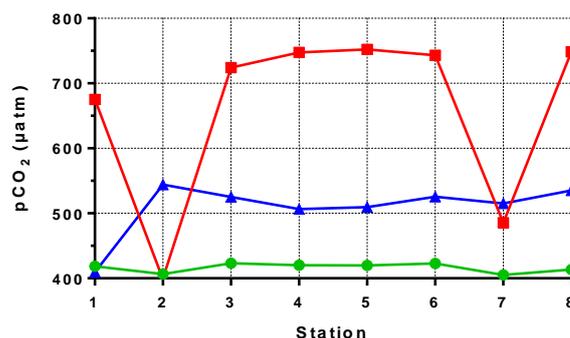


Figure 2. The pCO₂ computation results of All Stations in Malacca Straits using Zhu and Zhai Methods, and its comparison with the field measurement
Note : ● = Zhai; ■ = Zhu; ▲ = Field Measurement

The figure two demonstrates that the pCO₂ computed using the method of Zhu algorithm at station 1, 3, 4, 5, 6, and 8 have the highest pCO₂ compared with another method at the same observation station. Station 2 and 7 computed using the method of Zhu algorithm are identified as the lowest pCO₂ due to the low concentration of chlorophyll-a. In this approach, chlorophyll-a is powered by two which is considerably significant when it comes to the result. The concentration of chlorophyll-a in the station 2 and 7 are extremely low only around 1-2 mg.m⁻³. Unlike Zhu algorithm, the Zhai algorithm relies not only on a single parameter. A parameter of SST and Chl-a is take into account in order to obtain more accurate pCO₂ prediction. According to Zhai et al. (2005), the involvement of diurnal variations of phytoplankton metabolism will affected pCO₂ nonlinearly.

In order to identify the suitability of the methods relative to the field measurement, a comparison of the Mean Relative Error (MRE), between indirect measurement and the value from direct measurement, is one of the best approaches. The computation results shows that the MRE based on Zhai algorithm is around 19.40%, while based on Zhu algorithm is about 38.96%. Thus, it can be said that the result obtained using the Zhai algorithm is closer to the real data from direct measurement. Even though, the Zhu Algorithm employing more complex equation, involving the derivation of Chl-a and SST rather than a single parameter. It is almost certain that this method only suitable for the pCO₂ estimation in the South China Sea that has been conducted by Zhu et al. (2009). According to their finding, the algorithm produces smaller MRE relative to the field datasets. It is suggested that this algorithm, for Malacca Strait application, should be

further modified in order to obtain a more accurate pCO_2 prediction. The Zhu algorithm can be used to obtain a closer result, with the field underway datasets, by reducing its constant from 5,715.94 to 5,500.

Carbon dioxide flux

CO_2 flux varies from one method to another, and from one station to another. See Figure 3. The computation results using Zhu algorithm shows the value is relatively higher compared with the other methods. The flux is highly positive correlated with the ΔpCO_2 between atmosphere and the ocean. Since the atmospheric pressure of CO_2 is assumed to be remain stable, the pattern of CO_2 fluxes and their MRE are almost similar, with the pCO_2 analysis in Figure 3.

The results of the CO_2 flux (FCO_2) calculation are varied from 0.02–0.06 $mol.m^{-2}.d^{-1}$ (using Zhai algorithm), 0.02-0.57 $mol.m^{-2}.d^{-1}$ (using Zhu algorithm), and 0.04-0.23 $mol.m^{-2}.d^{-1}$ (based on direct measurement). According to Susandi *et al.* (2008), using the method of Zhai *et al.* (2005) in the northern part of Indonesian waters reveals a CO_2 flux as large flux as $2.6 mol m^{-2}.y^{-1}$ ($0.07 mol.m^{-2}.d^{-1}$). There is no FCO_2 prediction that has been computed in the Malacca strait. However, generally speaking, this value is still much lower compared with the value computed in Florida Bay, using a method of CO_2 system approach. It is ranging of $59.9-40.3 mmol m^{-2}.d^{-1}$, with the average of $29.6 mmol m^{-2}.d^{-1}$ (Dufore, 2012). According to Ekayanti and As-syakur (2011), the average of CO_2 flux in Indonesian waters is around $3.8 mol m^{-2}.y^{-1}$. It is completely very lower than in the South China Sea. In the South China Sea, the maximum CO_2 flux is $36.14 (mol m^{-2}.y^{-1})$, with the SST values of $22.51^{\circ}C$ to $29.32^{\circ}C$ (Zhai *et al.*, 2013). Meanwhile, The Zhai *et al.* (2013) explained that the South China Sea acts as a CO_2 source to the atmosphere only during the fall season, which the flux is around $0.4-0.5 mmol.m^{-2}.d^{-1}$.

The Malacca strait has a unique characteristic due to its physical and chemical properties of seawater, which influences by the water supply from some big rivers in Indonesia and Malaysia. The study that was carried out by Wit *et al.* (2015), suggests that CO_2 fluxes from those rivers amount to $66.9 \pm 15.7 TgC$ per year, of which Indonesia and Malaysian rivers releases $53.9 \pm 12.4 TgC$ per year and $6.2 \pm 1.6 TgC$ per year respectively. Furthermore, Wit *et al.* (2015) said that the CO_2 , which is potentially caused by the primary source of DOC near the coast, is transported by the river. The DOC is most likely transported to the Malacca strait and

contributes to the outgassing of CO_2 in the Malacca Strait (Wit *et al.*, 2015).

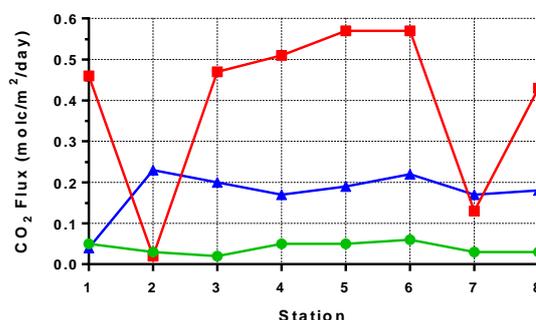


Figure 3. The FCO_2 computation results of All Stations in Malacca Straits using Zhu and Zhai Methods, and its comparison with the field measurement
Note : ● = Zhai; ■ = Zhu; ▲ = Field Measurement

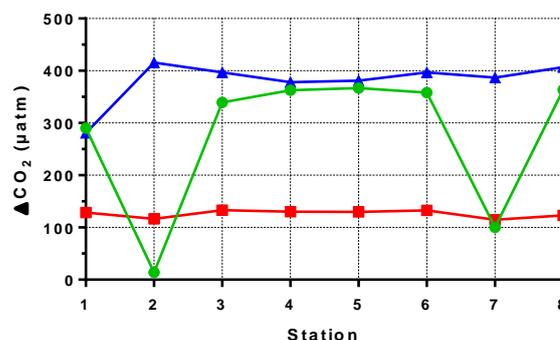


Figure 4. The $(\Delta)pCO_2$ between ocean and atmosphere in all stations of Malacca Straits based on Zhu and Zhai Algorithms, including its filed measurement.
Note : ● = Zhai; ■ = Zhu; ▲ = Field Measurement

In order to identify whether the waters is considered as a source or a sink of CO_2 , can be done by defining the differences between pCO_2 value in the seawaters and pCO_2 value in the atmosphere. The computation result shows that, the seawater acts as a CO_2 sources. The differences of pCO_2 (ΔpCO_2) values can be seen in Figure 4.

Conclusion

The pCO_2 computation results based on Zhai algorithm and Zhu algorithm are ranging from $405.003-422.79 \mu atm$ and $398.94-752.06 \mu atm$ respectively. Meanwhile, the pCO_2 from the field observation is ranging from $409.52-544.01 \mu atm$. It is the evidence that the Malacca Straits act as a CO_2 sources to the atmosphere. The computation result of the partial pressure of CO_2 (pCO_2) in the ocean by

using the Zhai algorithm is closer (MRE ~19.4%), to the $p\text{CO}_2$ value of field measurement, than its computed based on Zhu algorithm (MRE ~39%).

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References

- Adi, N.S. & Rustam, A. 2010. Studi Awal Pengukuran Sistem CO_2 Di Teluk Banten. Prosiding Pertemuan Ilmiah Tahunan VI. Ikatan Sarjana Oseanologi Indonesia. Jakarta.
- Chen, S., Hu, C., Byrne, R.H., Robbins, L.L. & Yang, B. 2016. Remote estimation of surface $p\text{CO}_2$ on the West Florida Shelf. *Continental Shelf Res.* 128:10–25. doi: 10.1016/j.csr.2016.09.004
- Dufore, C.M. 2012. Spatial and Temporal Variations in the Air-Sea Carbon Dioxide Fluxes of Florida Bay. Graduate Theses and Dissertations. University of South Florida. 69p.
- Ekayanti, N.W. & As-Syakur, A.R. 2011. CO_2 Flux in Indonesian Water Determined by Satellite Data. *Int. J. Remote Sensing Earth Sci.* 8:1-12
- Hales, B., Strutton, P.G., Saraceno, M., Letelier, R., Takahashi, T., Feely, R., & Chavez, F. 2012. Satellite-based prediction of $p\text{CO}_2$ in coastal waters of the eastern North Pacific. *Prog. Oceanog.* 103:1–15. doi: 10.1016/j.pocean.2012.03.001
- Hernández-Carrasco, I., Sudre, J., Garçon, V., Yahia, H., Garbe, C., Paulmier, A., Dewitte, B., Illig, S., Dadou, I., González-Dávila, M. & Santana-Casiano, J.M., 2015. Reconstruction of super-resolution ocean $p\text{CO}_2$ and air-sea fluxes of CO_2 from satellite imagery in the southeastern Atlantic. *Biogeosciences*, 12(17): 5229-5245. doi: 10.5194/bg-12-5229-2015
- Iida, Y., Kojima, A., Takatani, Y., Nakano, T., Sugimoto, H., Midorikawa, T. & Ishii, M. 2015. Trends in $p\text{CO}_2$ and sea-air CO_2 flux over the global open oceans for the last two decades. *J. Oceanog.* 71(6):637-661. doi: 10.1007/s10872-015-0306-4
- Le Quéré, C., Moriarty, R., Andrew, R.M., Peters, G.P., Ciais, P., Friedlingstein, P., Jones, S.D., Sitch, S., Tans, P., Arneeth, A. & Boden, T.A. 2015. Global carbon budget 2014. *Earth System Sci. Data*, 7(1):47-85. doi: 10.5194/essd-7-47-2015
- Mayer, B., Samiaji, J. & Elizal, H. 2013. Report of Research Cruise MTK-2013. Indonesia-German Science for the Protection of Indonesian Coastal marine Ecosystems. 12 pp.
- Ramawijaya, M.Y., Awaludin, Pranowo, W.S. & Rosidah. 2012. Pemanfaatan Algoritma Zhu untuk Analisis Karbon Laut di Teluk Banten. *J. Horpodon Borneo.* 5(2):131-136.
- Song, X., Bai, Y., Cai, W.-J., Chen, C.-T., Pan, D., He, X. & Zhu, Q. 2016. Remote Sensing of Sea Surface $p\text{CO}_2$ in the Bering Sea in Summer Based on a Mechanistic Semi-Analytical Algorithm (MeSAA). *Remote Sensing.* 8(7): 558. doi: 10.3390/rs8070558
- Turi, G., Lachkar, Z. & Gruber, N. 2014. Spatio-temporal variability and drivers of $p\text{CO}_2$ and air-sea CO_2 fluxes in the California Current System: an eddy-resolving modeling study. *Biogeosciences*, 11(3):671-690. doi: 10.5194/bg-11-671-2014
- Wahyono, I.B. 2011. Kajian Biogeokimia Perairan Selat Sunda dan Barat Sumatera ditinjau dari Pertukaran Gas Karbondioksida (CO_2) antara laut dan udara. Thesis. FMIPA. Universitas Indonesia (UI). Jakarta.
- Wang, X.J. 2010. Spatial and temporal variations in the sea surface $p\text{CO}_2$ and air-sea CO_2 flux in the equatorial Pacific: model sensitivity to gas exchange and biological formulations. *Biogeosciences Discussions.* 7(3):3879–3910. doi: 10.5194/bgd-7-3879-2010
- Wit, F., Müller, D., Baum, A., Warneke, T., Pranowo, W.S., Müller, M. & Rixen, T. 2015. The impact of disturbed peatlands on river outgassing in

- Southeast Asia. *Nature Communications*, 6:10155. doi: 10.1038/ncomms10155
- Yu, P., Zhang, H., Zheng, M., Pan, J. & Bai, Y. 2013. The partial pressure of carbon dioxide and air-sea fluxes in the Changjiang River Estuary and adjacent Hangzhou Bay. *Acta Oceanologica Sinica*, 32(6):13-17. doi: 10.1007/s13131-013-0320-6
- Zhai, W., Dai, M., Cai, W.J., Wang, Y. & Hong, H. 2005. The partial pressure of carbon dioxide and air-sea fluxes in the northern South China Sea in spring, summer and autumn. *Mar. Chem.* 96(1):87-97. doi: 10.1016/j.marchem.2004.12.002
- Zhai, W.D., Dai, M.H., Chen, B.S., Guo, X.H., Li, Q., Shang, S.L., Zhang, C.Y., Zhai, W.D., Chen, B.S., Cai, W.J. & Cai, W.J. 2013. Seasonal variations of sea-air CO₂ fluxes in the largest tropical marginal sea (South China Sea) based on multiple-year underway measurements. *Biogeosciences*. 10:7775-7791. doi: 10.5194/bg-10-7775-2013
- Zhu, Y., Shang, S., Zhai, W. & Dai, M. 2009. Satellite-derived surface water pCO₂ and air-sea CO₂ fluxes in the northern South China Sea in summer. *Prog. Natural Sci.* 19(6):775-779. doi: 10.1016/j.pnsc.2008.09.004