

Interactive comment on “Diagnosing CO₂ fluxes in the upwelling system off the Oregon coast” by Cao et al.

mdai@xmu.edu.cn

Response to the comments from Dr. Rik Wanninkhof

Cao and co-authors use a conceptual model to estimate CO₂ dynamics/fluxes in upwelling systems. The model is referred to as OceMar (Ocean dominated Margin) and is derived from the work by Dai et al. (2013) in the Caribbean region. In short, it is based on the idea that the carbon to nutrient ratio in upwelling water determines the surface water CO₂ levels. Biological consumption determined from decreasing nutrients concentrations will decrease the *p*CO₂. The final *p*CO₂ value when nutrients are drawn down to zero can either be greater (CO₂ source the atmosphere) or less than atmospheric (CO₂ sink) depending on the C:N ratio of the source water. The concept is elegant and simple, and “works” in some environments and less so in others. For the Pacific upwelling system the authors essentially show that it does not work very well. As described in the paper for the method to work, the system has to fulfill the following:

1. It should be in steady state
 2. Alkalinity needs to be modeled as a function of salinity
 3. Biological uptake needs to follow Redfield stoichiometry, in particular the C:N ratio is assumed to be 6.6:1
 4. Endmembers need to be well described.
 5. The residence time of the water needs to be on the same order as biological response
- The authors use two case studies in the USA West Coast upwelling system, one off the coast of Newport OR, and one at the Oregon-California border. The method “works” at the former and fails at the latter which is attributed to non-steady state conditions. The fundamental issue is that it is difficult to independently determine if the criteria for successful application will be met. Thus, if the calculated *p*CO₂ values end up being reasonable compared to observation it can be assumed that they are, or that compensating errors yield a reasonable value. When the values do not meet expectation it can be assumed that some of the criteria are violated. We know that upwelling systems are highly dynamic; that Alkalinity to salinity ratios are regionally constant for surface waters but not for subsurface (or many upwelling systems); that Redfield stoichiometry is an average that often does not hold in surface water analyses; and that endmembers are difficult to determine. Therefore the applicability and use of the approach seems limited.

[Response]: We appreciate that Dr. Wanninkhof is generally positive with the conceptual model of OceMar and our diagnosis approach which involves essentially two couplings: 1) physics-biogeochemistry; 2) carbon and nutrients. Dr. Wanninkhof well laid out a suite of criteria in the diagnosis approach, which we would further clarify as follows:

- 1) Steady state associated with the water transport (i.e., water input equals water output) in a given system is often assumed in any modeling studies, which is also the basis of our OceMar model. Decomposition of the biological component in a coupled physical-biogeochemical system assumes similar time scales between water mass mixing and biological reactions, and requires conservative tracers to address water mass mixing processes. TALK is often used for the latter purpose because it is relatively widely available

and in most cases is conservative in the upper waters. Such decomposition shall also need to resolve the end-members of the mixing scheme.

- 2) When water mass mixing is decoupled from biogeochemical reactions, the diagnosis approach should be simplified by taking off the biological reaction, which is exactly the case of the nearshore area off the Oregon-California coast shown in the paper.
- 3) Our approach also assumes Redfield ratio in coupling carbon-nutrients as most of the numerical modeling scheme adopts. This is an important assumption that poses challenge to the community. While increasing cases and datasets have inferred non-Redfield C/N uptake ratios, defined departure from the Redfield ratio is very hard to be determined. We are further elaborating this issue below in addressing specific criteria.

The motivation of the exercise of this study is to further test the applicability of the OcéMar model and the diagnosis approach to a well-known upwelling system exerting strong CO₂ sink except (and also known) at the nearshore with intensified upwelling. Specifically, we elucidate as follows the critical issues raised by Dr. Wanninkhof on the conservativity of TAlk, Redfield ratio and end-member determination.

- Total alkalinity-salinity (TAlk-Sal) relationship

The field observed TAlk values were generally well correlated with salinity, telling us that the system was dominated by two end-member mixing schemes in the upper waters off the Oregon-California coast. The non-conservativity, existed though, was not that significant as seen by the deviations of a few data points from each linear regression analysis (Fig. 2 of the original MS). As a matter of fact, Fassbender et al. (2011) have estimated that the contribution of CaCO₃ dissolution to the TAlk addition at Transect 5 was <10 μmol kg⁻¹ (<0.5% of their absolute contents in seawater), close to the analytical precision of TAlk. Such small non-conservative portions would not compromise the application of TAlk as a conservative tracer. On the other hand, the elevated DIC corresponding to the TAlk addition were even smaller (~half of the TAlk deviation), which were <5 μmol kg⁻¹ (Fassbender et al., 2011) and slightly higher than the measurement uncertainties.

In another upwelling system on the northern South China Sea shelf, organic carbon production/remineralization rather than biocalcification/CaCO₃ dissolution exclusively induced the DIC variations during intensified upwelling events nearshore, as supported by the nearly constant salinity normalized values of both TAlk and dissolved Ca²⁺ (Cao et al., 2011).

As the organic carbon metabolism often dominates the biological activities, we contend that TAlk can be well served as a quasiconservative chemical tracer in many coastal upwelling systems, in which the influence of CaCO₃ production/dissolution on TAlk/DIC would be negligible. We have made this point clearer in our revisions.

- Redfield ratio

We agree with Dr. Wanninkhof as well as the other two reviewers that, the real C/N uptake ratio in a given oceanic setting can be different from the Redfield one of ~6.6 (Redfield et al., 1963). However, since the precise estimation of the C/N uptake ratio via e.g. in situ incubation experiments is still problematic, such data are currently scarce over the world's oceans and the empirical stoichiometry is routinely applied into field studies investigating the dynamics and

coupling of carbon and nutrients (e.g., Chen et al., 2008; Fassbender et al., 2011). In the work of Fassbender et al. (2011), another empirical C/N uptake ratio ($\sim 117/16=7.3$; Anderson and Sarmiento, 1994) was applied to the same data set as this study. We thus have done a simple sensitivity analysis using this alternative value of 7.3 (Table R1-1). As $\Delta\text{DIC}-7.3\Delta\text{NO}_3$ were obviously smaller than $\Delta\text{DIC}-6.6\Delta\text{NO}_3$, the new sea-air $\Delta p\text{CO}_2$ were halved. Correspondingly, the newly estimated sea surface $p\text{CO}_2$ were $\sim 35\text{-}45 \mu\text{atm}$ lower than the estimation using the Redfield ratio, which were however consistent with the field measurements. Given that the Redfield ratio also works in our OceMar case studies of the South China Sea and the Caribbean Sea (Dai et al., 2013), we contend that this classic ratio would be preferentially employed if the field observed elemental stoichiometry is not available. Moreover, and as Martz et al. (2014) point out, “treating the Redfield ratios as global or regional constants may be acceptable in the context of interpreting snapshots of the water column captured in shipboard bottle data”.

Table R1-1. Sea-air $\Delta p\text{CO}_2$ and sea surface $p\text{CO}_2$ estimated with different $\Delta\text{DIC}-x\Delta\text{NO}_3$. x denotes the C/N uptake ratio during organic carbon production. T and S represent transect and station(s), respectively.

C/N uptake ratio	$\Delta\text{DIC}-x\Delta\text{NO}_3$ ($\mu\text{mol kg}^{-1}$)			Sea-air $\Delta p\text{CO}_2$ (μatm)			Sea surface $p\text{CO}_2$ (μatm)					
	T4	T5	T6 ^a	T4	T5	T6 ^a	T4	T5	T6 ^a			
	S27-32 ^b	S33 ^c	S35-38 ^c	S45-49 ^c	S27-32 ^b	S33 ^c	S35-38 ^c	S45-49 ^c	S27-32 ^b	S33 ^c	S35-38 ^c	S45-49 ^c
6.6	-23±2	-23±1	-20±3	-23±3	-55±5	-53±3	-48±8	-53±6	335±5	337±3	342±8	337±6
7.3	-42±3	-42±1	-39±3	-42±3	-101±6	-100±3	-92±8	-97±6	289±6	290±3	298±8	293±6

^a T6 represents Transect 6 which is located off the northern California coast (Fig. R1-1). We have added in our revisions the diagnosis of Transect 6 per the suggestion from Referee #1.

^b data for these stations were obtained from waters immediately below the top buoyant layer.

^c data for these stations were obtained from the surface mixed layer.

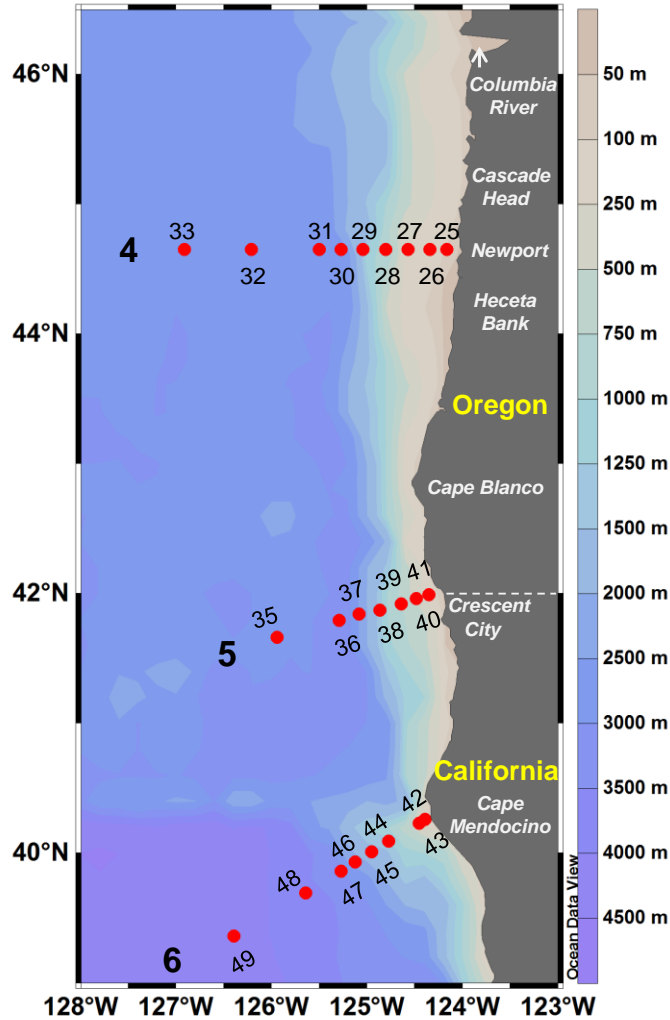


Fig. R1-1. Map of the US west coast off Oregon and northern California showing the topography and the locations of sampling stations along Transects 4, 5 and 6 in spring/early summer 2007.

The above notion was also supported by examining the slope of the linear regression between DIC and NO_3 normalized to a constant salinity, which provides an alternation to the C/N uptake ratio (Sambrotto et al., 1993; Wong et al., 2002; Ianson et al., 2003). Our new analysis with all data from the CO_2 sink zones off the Oregon-California coast revealed a slope of 6.70 ± 0.37 (Fig. R1-2), which is within error comparable to the value of 6.6, suggesting that using the Redfield ratio in our diagnosis approach was in order.

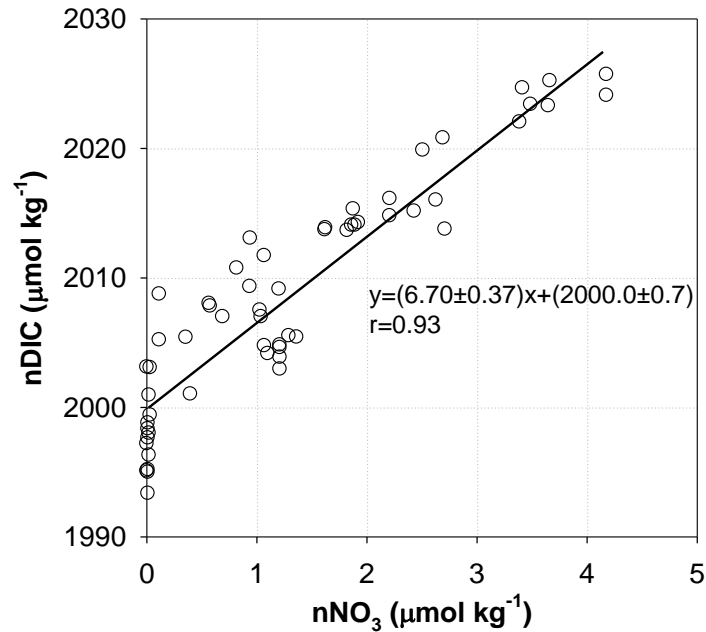


Fig. R1-2. Salinity normalized DIC (nDIC) versus salinity normalized NO₃ (nNO₃) in the CO₂ sink zones off Oregon and northern California in spring/early summer 2007, which included waters immediately below the top buoyant layer at stations 27-32 as well as waters in the surface mixed layer at station 33 on Transect 4, waters in the surface mixed layer at stations 35-38 on Transect 5, and waters in the surface mixed layer at stations 45-49 on Transect 6.

- Identification of end-members

We note that identifications of initial end-members associated with individual water masses are highly complex in any given oceanic regime. To bypass and simplify this issue, the relationship between conservative chemical tracers and salinity was used to reveal the water mass mixing scheme and to identify the end-member values, which might have experienced physical or biological alterations from their original values. Such a method, as one of the core components of the diagnosis approach we are introducing, well worked in two contrasting environments, the coastal upwelling system (this study) and the deep basins of large marginal seas (Dai et al., 2013). Per the suggestion from Dr. Ianson as well, we have performed a sensitivity analysis of end-members including the combined freshwater end-member (Table R1-2) and the deep water end-member (Table R1-3), showing that the influence of variations in either end-member on our diagnosis approach was indeed minor.

Table R1-2. $\Delta\text{DIC}-6.6\Delta\text{NO}_3$, sea-air $\Delta p\text{CO}_2$ and sea surface $p\text{CO}_2$ estimated with different DIC^{eff} , which is the combined freshwater end-member of DIC partly sourced from the Columbia River (CR). The newly diagnosed $\Delta\text{DIC}-6.6\Delta\text{NO}_3$ and sea-air $\Delta p\text{CO}_2$ on Transects 4, 5 and 6 displayed no difference with those with the initial TAlk and DIC of $\sim 1000 \mu\text{mol kg}^{-1}$ in the CR, while all estimated sea surface $p\text{CO}_2$ were within error comparable to the field measurements. Although the TAlk and DIC end-members have large variations of up to $\sim 400 \mu\text{mol kg}^{-1}$ in the main stream of the CR, the corresponding range of DIC^{eff} contributing to waters beyond the CR plume significantly decreases by approximately one order of magnitude, implying minor influence of its variations on our diagnosis of the CO_2 fluxes.

TAlk/DIC of CR ($\mu\text{mol kg}^{-1}$)	DIC^{eff} ($\mu\text{mol kg}^{-1}$)	$\Delta\text{DIC}-6.6\Delta\text{NO}_3$ ($\mu\text{mol kg}^{-1}$)		Sea-air $\Delta p\text{CO}_2$ (μatm)		Sea surface $p\text{CO}_2$ (μatm)	
		Transect 4		Transect 4		Transect 4	
		Stations 27-32 ^a	Station 33 ^b	Stations 27-32 ^a	Station 33 ^b	Stations 27-32 ^a	Station 33 ^b
800	435	-24 ± 2	-24 ± 1	-58 ± 5	-55 ± 3	332 ± 5	335 ± 3
1000	450	-23 ± 2	-23 ± 1	-55 ± 5	-53 ± 3	335 ± 5	337 ± 3
1200	460	-22 ± 2	-22 ± 1	-54 ± 5	-53 ± 3	336 ± 5	337 ± 3
		Transect 5 Stations 35-38 ^b		Transect 5 Stations 35-38 ^b		Transect 5 Stations 35-38 ^b	
800	565	-21 ± 3		-51 ± 8		339 ± 8	
1000	585	-20 ± 3		-48 ± 8		342 ± 8	
1200	600	-20 ± 3		-47 ± 8		343 ± 8	
		Transect 6 Stations 45-49 ^b		Transect 6 Stations 45-49 ^b		Transect 6 Stations 45-49 ^b	
800	520	-24 ± 3		-56 ± 6		334 ± 6	
1000	540	-23 ± 3		-53 ± 6		337 ± 6	
1200	550	-23 ± 3		-53 ± 6		337 ± 6	

^a data for these stations were obtained from waters immediately below the top buoyant layer.

^b data for these stations were obtained from the surface mixed layer.

Table R1-3. $\Delta\text{DIC}-6.6\Delta\text{NO}_3$, sea-air $\Delta p\text{CO}_2$ and sea surface $p\text{CO}_2$ estimated with the deep water end-member from different depths. On Transects 4 and 6, the newly estimated $\Delta\text{DIC}-6.6\Delta\text{NO}_3$, sea-air $\Delta p\text{CO}_2$ and sea surface $p\text{CO}_2$ using end-member values at both ~ 150 m and ~ 200 m agreed well with those using end-member values at ~ 175 m, while the three variables were slightly higher using end-member values at ~ 130 m. On Transect 5, the newly estimated $\Delta\text{DIC}-6.6\Delta\text{NO}_3$, sea-air $\Delta p\text{CO}_2$ and sea surface $p\text{CO}_2$ using end-member values at both ~ 130 m and ~ 150 m agreed well with those using end-member values at ~ 175 m, while the three variables were slightly higher using end-member values at ~ 200 m.

Depth of the deep water end-member (m)	$\Delta\text{DIC}-6.6\Delta\text{NO}_3$ ($\mu\text{mol kg}^{-1}$)		Sea-air $\Delta p\text{CO}_2$ (μatm)		Sea surface $p\text{CO}_2$ (μatm)	
	Transect 4		Transect 4		Transect 4	
	Stations 27-32 ^a	Station 33 ^b	Stations 27-32 ^a	Station 33 ^b	Stations 27-32 ^a	Station 33 ^b
~ 130	-23 ± 2	-19 ± 1	-56 ± 5	-45 ± 3	334 ± 5	345 ± 3
~ 150	-23 ± 2	-22 ± 1	-55 ± 5	-52 ± 3	335 ± 5	338 ± 3
~ 175	-23 ± 2	-23 ± 1	-55 ± 5	-53 ± 3	335 ± 5	337 ± 3
~ 200	-23 ± 2	-24 ± 1	-55 ± 5	-56 ± 3	335 ± 5	334 ± 3
	Transect 5		Transect 5		Transect 5	
	Stations 35-38 ^b		Stations 35-38 ^b		Stations 35-38 ^b	
~ 130	-21 ± 3		-51 ± 8		339 ± 8	
~ 150	-20 ± 3		-46 ± 8		344 ± 8	
~ 175	-20 ± 3		-48 ± 8		342 ± 8	
~ 200	-17 ± 3		-40 ± 8		350 ± 8	
	Transect 6		Transect 6		Transect 6	
	Stations 45-49 ^b		Stations 45-49 ^b		Stations 45-49 ^b	
~ 130	-20 ± 3		-46 ± 6		344 ± 6	
~ 150	-22 ± 3		-51 ± 6		339 ± 6	
~ 175	-23 ± 3		-53 ± 6		337 ± 6	
~ 200	-21 ± 3		-50 ± 6		340 ± 6	

^a data for these stations were obtained from waters immediately below the top buoyant layer.

^b data for these stations were obtained from the surface mixed layer.

Taken together, the OceMar conceptual model is applicable to other marginal systems but the diagnosis will have to be adjusted to individual settings with different water mass dynamics and biological responses.

The paper is nicely written and well-researched. A minor issue is that the Revelle Factor appears to be misinterpreted and incorrectly used by assuming that a fractional change in $p\text{CO}_2$ is the same as the air-water concentration difference (plus that temperature, alkalinity, and salinity do not change).

[Response]: We thank the comment and have made it right in our revisions.

References

- Anderson, L. A., and Sarmiento, J. L.: Redfield ratios of remineralization determined by nutrient data analysis, *Global Biogeochem. Cycles*, 8, 65-80, 1994.
- Cao, Z., Dai, M., Zheng, N., Wang, D., Li, Q., Zhai, W., Meng, F., and Gan, J.: Dynamics of the carbonate system in a large continental shelf system under the influence of both a river plume and coastal upwelling, *J. Geophys. Res.*, 116, G02010, doi:10.1029/2010JG001596, 2011.
- Chen, F., Cai, W.-J., Wang, Y., Rii, Y. M., Bidigare, R. R., and Benitez-Nelson, C. R.: The carbon dioxide system and net community production within a cyclonic eddy in the lee of Hawaii, *Deep-Sea Res. II*, 55, 1412-1425, 2008.
- Dai, M., Cao, Z., Guo, X., Zhai, W., Liu, Z., Yin, Z., Xu, Y., Gan, J., Hu, J., and Du, C.: Why are some marginal seas sources of atmospheric CO₂?, *Geophys. Res. Lett.*, 40, 2154-2158, doi:10.1002/grl.50390, 2013.
- Fassbender, A. J., Sabine, C. L., Feely, R. A., Langdon, C., and Mordy, C. W.: Inorganic carbon dynamics during northern California coastal upwelling, *Cont. Shelf Res.*, 31, 1180-1192, 2011.
- Ianson, D., Allen, S. E., Harris, S. L., Orians, K. J., Varela, D. E., and Wong, C. S.: The inorganic carbon system in the coastal upwelling region west of Vancouver Island, Canada, *Deep-Sea Res. I*, 50, 1023-1042, 2003.
- Martz, T., Send, U., Ohman, M. D., Takeshita, Y., Bresnahan, P., Kim, H.-J., and Nam, S. H.: Dynamic variability of biogeochemical ratios in the Southern California Current System, *Geophys. Res. Lett.*, 41, 2496-2501, doi:10.1002/2014GL059332, 2014.
- Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of seawater, in: *The Sea*, edited by M. N. Hill, Wiley, New York, 26-77, 1963.
- Sambrotto, R. M., Savidge, G., Robinson, C., Boyd, P., Takahashi, T., Karl, D. M., Langdon, C., Chipman, D., Marra, J., and Codispoti, L.: Elevated consumption of carbon relative to nitrogen in the surface ocean, *Nature*, 363, 248-250, 1993.
- Wong, C. S., Waser, N. A. D., Nojiri, Y., Whitney, F. A., Page J. S., and Zeng, J.: Seasonal cycles of nutrients and dissolved inorganic carbon at high and mid latitudes in the North Pacific Ocean during the Skaugran cruises: determination of new production and nutrient uptake ratios, *Deep-Sea Res. II*, 49, 5317-5338, 2002.