

Dr Jan Kaiser, University of East Anglia, Norwich, United Kingdom

Steinhoff et al. (2012) present a method to calculate net community production (NCP) in upwelling systems using the gases CO₂, O₂ and N₂O. The method consists of mapping of the spatial decrease of the N₂O concentration in the upwelled water mass onto a time axis. The decrease of the N₂O concentration as it is advected westwards is assumed to be entirely due to air-sea exchange. The same time axis is then mapped onto dissolved inorganic carbon (DIC) measurements collocated with the N₂O data. Then, the observed change in DIC as a function of time is compared to the expected change based on CO₂ air-sea exchange and any deviation is attributed to NCP on any given day. The daily NCP estimates are averaged temporally to obtain an NCP value that is taken to represent the upwelling period in the study area.

The mathematical presentation of Steinhoff et al.'s approach appears to be unnecessarily cumbersome. I would like to suggest a more elegant, direct calculation method using the same assumptions made in the paper. This method allows the calculation of NCP directly from the change in dissolved inorganic carbon (DIC) concentration relative to the change in N₂O concentration, at any location.

The temporally averaged flux as calculated by Steinhoff et al. should not be taken to represent a regional average of NCP for the upwelling area. It rather reflects average NCP from a Lagrangian point of view, focussed on the upwelled parcel. To calculate the regional average NCP, the daily NCP estimates would have to be mapped and averaged geographically.

Finally, in addition to the points already made by the other three reviewers, I would also like to comment on the chosen gas exchange parameterisation and the neglect of bubbles in the calculation of the air-sea exchange flux.

Direct calculation method of NCP in an upwelling system

Assuming quasi-Lagrangian transport of upwelled water and neglecting diapycnal mixing and changes in mixed layer-depth the mass balance for N₂O and DIC can be written as follows:

$$z_{\text{mix}} \frac{dc(\text{N}_2\text{O})}{dt} = -k(\text{N}_2\text{O})[c(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})] \quad (1)$$

$$z_{\text{mix}} \frac{dc(\text{DIC})}{dt} = -N - k(\text{CO}_2)K_0(\text{CO}_2)[p(\text{CO}_2) - p_{\text{atm}}(\text{CO}_2)] \quad (2)$$

where z_{mix} is mixed layer-depth, c are mixed-layer concentrations of the corresponding species and N is mixed-layer net community production. The other symbols are the same as in the paper. The symbols "N₂O" and "DIC" used by Steinhoff et al. are not appropriate to represent the concentrations of the corresponding chemical species.

Eqs. (1) and (2) are combined to give

$$N = k(\text{N}_2\text{O})[c(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})] \frac{dc(\text{DIC})}{dc(\text{N}_2\text{O})} - k(\text{CO}_2)K_0(\text{CO}_2)[p(\text{CO}_2) - p_{\text{atm}}(\text{CO}_2)] \quad (3)$$

The gradient $dc(\text{DIC})/dc(\text{N}_2\text{O})$ can be determined from the local slope of a scatter plot of $c(\text{DIC})$ versus $c(\text{N}_2\text{O})$ at any point in time and space. Individual measurements can be grouped where appropriate. It is not necessary to take the route via temporal mappings as chosen by Steinhoff et al. N can then be calculated either by finding the corresponding $c_{\text{equ}}(\text{N}_2\text{O})$ and $p_{\text{atm}}(\text{CO}_2)$ values from the data time series, or by using the regression approach chosen by Steinhoff et al. (cf. their Table 2). I am not sure why "DIC_{equ}" is mentioned in the paper; CO₂ gas exchange needs to be formulated in terms of CO₂ partial pressures (or concentrations), not DIC. In any case, "DIC_{equ}" should be named, more correctly, $c_{\text{equ}}(\text{DIC})$.

Even if the above direct calculation method was not used, more of the underlying data should be shown, including scatter plots to show the relationship between different gases. At the moment, the paper only presents $p(\text{CO}_2)$, $c(\text{N}_2\text{O})$ and $c(\text{O}_2)$ data from one transect during cruise P320-1. It is not clear how representative this transect is for the correlation between the three gases and for NCP during that particular season. More data and NCP values derived from these data should be included.

If Steinhoff et al.'s time mapping approach is chosen, the steps described under (A) on p. 4860 can be avoided. Instead, Eq. (1) is integrated to give

$$c(\text{N}_2\text{O}) = [c_0(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})] e^{-k(\text{N}_2\text{O})t/z_{\text{mix}}} + c_{\text{equ}}(\text{N}_2\text{O}) \quad (4)$$

where c_0 is the concentration at the point of upwelling. This can be rearranged to

$$t = -\frac{z_{\text{mix}}}{k(\text{N}_2\text{O})} \ln \frac{c(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})}{c_0(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})} \quad (5)$$

In other words the N_2O concentration can be mapped directly onto a time axis if, as assumed by Steinhoff et al., mixed layer depth and gas exchange coefficient are constant. Furthermore, Steinhoff et al. chose to parameterise $c_{\text{equ}}(\text{N}_2\text{O})$ as a linear function of $c(\text{N}_2\text{O})$, which may be represented by the equation

$$c_{\text{equ}}(\text{N}_2\text{O}) = mc(\text{N}_2\text{O}) + c_{\text{equ},0}(\text{N}_2\text{O}) \quad (6)$$

The N_2O concentration as a function of time is then given by

$$c(\text{N}_2\text{O}) = \left[c_0(\text{N}_2\text{O}) - \frac{c_{\text{equ},0}(\text{N}_2\text{O})}{1-m} \right] e^{-k(\text{N}_2\text{O})(1-m)t/z_{\text{mix}}} + \frac{c_{\text{equ},0}(\text{N}_2\text{O})}{1-m} \quad (7)$$

and the corresponding mapping of the N_2O concentration onto the time axis is

$$t = -\frac{z_{\text{mix}}}{(1-m)k(\text{N}_2\text{O})} \ln \frac{(1-m)c(\text{N}_2\text{O}) - c_{\text{equ},0}(\text{N}_2\text{O})}{(1-m)c_0(\text{N}_2\text{O}) - c_{\text{equ}}(\text{N}_2\text{O})} \quad (8)$$

Temporal versus spatial averaging

Steinhoff et al. average daily NCP estimates (which they designate $\text{DIC}_{\text{bio}}^{\text{tot}}$) over the period from upwelling until when NCP was $<(2 \text{ mmol m}^{-3} \text{ d}^{-1} \times z_{\text{mix}})$, where z_{mix} is mixed layer depth. For example, for $z_{\text{mix}} = 20 \text{ m}$, the last day considered for the average NCP calculation would have $\text{NCP} = 0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$. This approach centres on changes of the DIC inventory in the upwelled water parcel, from a Lagrangian point of view. However, this temporal average does not necessarily represent the spatial average across the upwelling region. Depending on the horizontal velocity of the water parcel, the daily NCP estimates might represent differently sized parts of the study area. To obtain a regionally representative estimate of NCP, individual NCP estimates (obtained with Steinhoff et al.'s approach or using Eq. 3 above) would need to be mapped and averaged geographically. Temporal and regional averages would only match if the velocity of the water parcel were uniform. Whether or not this was the case can be determined from deriving advection rates using Eq. (8) and the corresponding locations of the water samples.

Gas exchange parameterisation

The choice of gas exchange parameterisation is critical for the NCP calculation. O_2 is used to constrain the chosen parameterisation, but only in case of one of the three cruises (P320-1), with a stated O_2 measurement accuracy of $3 \mu\text{mol l}^{-1}$. In case of the other two cruises (M68-3, P399-2), the measurement accuracy of $5 \mu\text{mol l}^{-1}$ was cited as too high to be able to calculate O_2 air-sea exchange fluxes. However, even an accuracy of $5 \mu\text{mol l}^{-1}$ would represent less than 10 % of the O_2 concentration gradient across the air-sea interface, based on Fig. 2 and

Fig. 3 in Löscher et al. (2012). It should therefore be possible to calculate NCP for these two cruises, too. In any case, it would be good to see the NCP values based on O₂ for all cruises included in Table 3, including their corresponding uncertainties.

Since surfactant films are likely to break up at higher wind speeds, it is rather perplexing that the authors have chosen a gas exchange parameterisation that is taking surfactant films into account (Tsai and Liu, 2003) for cruises P320-1 and P399-2, which experience significantly higher wind speeds than cruise M68-3, for which the parameterisation of Wanninkhof (1992) was chosen. The stated reason is the lower productivity during M68-3, but it is not known under what conditions the interplay between wind, waves and productivity lead to the establishment of surfactant films. If the same parameterisation was chosen for M68-3 as for the other cruises, the relationship between upwelling index and NCP in Fig. 4B would be significantly different. In any case, the radiocarbon budget-based parameterisation of Wanninkhof (1992) has been updated by Sweeney et al. (2007) and the updated parameterisation should be used instead. Also, it would be good to list the actual equations used because there are several listed in the papers mentioned. For example, Wanninkhof (1992) has equations for short-term and long-term averaged winds as well as equations that include chemical CO₂ enhancement effects. How were the Schmidt numbers calculated and which exponent was used for the Schmidt number and why?

Lastly, the solubility of O₂ is significantly different to that of N₂O and CO₂. Due to bubble injection and bubble exchange, the atmospheric equilibrium concentration of O₂ may not accurately represent the diffusive air-sea exchange flux. Calculations of NCP based on O₂ need to take this into account (Craig and Hayward, 1987; Emerson et al., 2008; Kaiser et al., 2005), but this does not appear to be done in the present paper.

References

Craig, H., and Hayward, T.: Oxygen supersaturation in the ocean: Biological versus physical contributions, *Science*, 235, 199-202, 1987.

Emerson, S., Stump, C., and Nicholson, D.: Net biological oxygen production in the ocean: Remote in situ measurements of O₂ and N₂ in surface waters, *Global Biogeochem. Cycles*, 22, GB3023, doi:10.1029/2007GB003095, 2008.

Kaiser, J., Reuer, M. K., Barnett, B., and Bender, M. L.: Marine productivity estimates from continuous oxygen/argon ratio measurements by shipboard membrane inlet mass spectrometry, *Geophys. Res. Lett.*, 32, L19605, 10.1029/2005GL023459, 2005.

Löscher, C. R., Kock, A., Könneke, M., LaRoche, J., Bange, H. W., and Schmitz, R. A.: Production of oceanic nitrous oxide by ammonia-oxidizing archaea, *Biogeosciences*, 9, 2419-2429, 10.5194/bg-9-2419-2012, 2012.

Steinhoff, T., Bange, H. W., Kock, A., Wallace, D. W. R., and Körtzinger, A.: Biological productivity in the Mauritanian upwelling estimated with a triple gas approach, *Biogeosciences Discuss.*, 9, 4853-4875, 10.5194/bgd-9-4853-2012, 2012.

Sweeney, C., Gloo, E., Jacobson, A. R., Key, R. M., McKinley, G., Sarmiento, J. L., and Wanninkhof, R.: Constraining global air-sea exchange for CO₂ with recent bomb ¹⁴C measurements, *Global Biogeochem. Cycles*, 21, GB2015, 10.1029/2006GB002784, 2007.

Tsai, W.-t., and Liu, K.-L.: An assessment of the effect of sea surface surfactant on global atmosphere-ocean CO₂ flux, *J. Geophys. Res.*, 108, 3127, doi:10.1029/2000JC000740, 2003.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373-7382, 1992.