

*Note to the editor and authors: As part of an introductory course to the Master programme Earth & Environment at Wageningen University, students get the assignment to review a scientific paper. Since several years, students have been reviewing papers that are in open online discussion for Copernicus Journals, and the top students in the class have been asked to submit their reports to the discussion in order to help the review process. While these reports are written in the form of official (invited) reviews, they were not requested for by the editor, and we leave it up to the editor and authors to use these reports to their advantage. We hope that these reports will positively contribute to the scientific discussion and to the quality of papers published. This report/review was supervised by Prof. Wouter Peters.*

**Review on “The Oceanic cycle of carbon monoxide and its emissions to the atmosphere” by Conte *et al.***

### **Summary and Scope**

Carbon monoxide (CO) is important in the atmospheric chemistry, because it affects the lifetime of greenhouse gasses, it is a sink for hydroxyl radicals and it affects the ozone chemistry. The ocean is one of the sources of CO. Although it is a minor source, it can be important far away from anthropogenic sources. However, the oceanic CO source is still poorly estimated, mainly because the main driver, biological activity, has a large spatial and temporal variability. This paper aims to overcome this lack of knowledge by using a biochemical model called PISCES (Pelagic Interaction Scheme for Carbon and Ecosystem studies) to assess the CO dynamics at the global scale. It explicitly looks at the interaction between the ocean and the atmosphere. Therefore, they added an extra module to represent the CO sources and sinks. They compared the model output to a gathered dataset of *in situ* CO measurements of the last 50 years. This is the first time a compilation was made of various *in situ* CO measurements. The combination of using a new modified model and this gathered data set, to better estimate the global oceanic CO source, makes this research in particular novel. Moreover, the paper also included the direct production of CO by phytoplankton in their research, which is recently reported as a CO source and only measured once by Gros *et al.* in 2009. Therefore, this paper makes use of new knowledge in their research field.

The paper is well written and a clear structure of the different parts of the research is given. The thorough introduction nicely introduces the topic and describes why it is particularly relevant, which gives the impression that the authors know where they are talking about. In addition, the authors are well aware of the limitations of the used model, which they nicely point out in their conclusion.

The methodology is explained well and is similar to the methods used in other studies in this research field. Stubbins *et al.* (2006), for instance, also multiplied the apparent quantum yield with the moles of photons absorbed (solar irradiance) to calculate the CO photoproduction term. A bit broader spectrum was used though: 280-800 nm. Whereas this paper uses mainly earlier found empirical relationships, Stubbins *et al.* (2006) measured it mainly themselves. They also compared those to

empirical relations, similar to the ones used in the review paper. Hence, although there are some differences in the way data was gathered, the approach to calculate photoproduction is similar.

In general, the paper nicely builds on former research and covers different domains of the earth system with a main focus on the atmosphere, ocean and biology. Therefore, it nicely fits the scope of the journal. For instance, atmospheric models can use the new data of oceanic CO emissions to investigate the oxidizing capacity of the atmosphere in remote oceans. This will replace the outdated model estimation of the global oceanic CO emissions by Erickson (1989), who used a simple empirical relationship between solar radiation and the CO concentration. However, there are a couple of things which need to be improved before the paper can be accepted.

### **Major arguments**

Although the overall methodology is clear to me, there is one main point I would like to be discussed more thoroughly. In the section “Spectral solar irradiance” (p. 4), they use attenuation coefficients from earlier conducted research, to determine the penetration depth of irradiance. The data was not available for all wavelengths in the range used in this paper. Therefore, the authors applied linear interpolation to the remaining wavelengths to retrieve the coefficients. However, I wonder whether they really vary linearly. If not, this may chance the outcome of formula 3 in line 17 of the “Spectral solar irradiance” section (p. 4), which, in turn, affects the outcome of formula 10 in line 17 of the “Photoproduction” section (p. 5). Hence, this could give rise to significant errors in the CO photoproduction term. This will directly affect the values given for photoproduction term in figures 3-5 (p. 28-29). Because the photoproduction term is one of the main sources of CO, a different value of the photoproduction term also chances the CO concentration. Therefore, figure 6 and 7 (p. 30-31), which show the modeled CO concentration, are indirectly affected too.

To make the choice of linear interpolation more straightforward, a figure should be made as figure 1 and 2, showing three coefficients as a function of wavelength (p. 28). In this graph the (linear) trendline with formula and the  $R^2$  should be shown to see how strong the (linear) relationship is of the different coefficients with wavelength. This can be put in the “Spectral solar irradiance section” (p. 4). Furthermore, I would like to see at least a short discussion on the effect of linear interpolation on the CO photoproduction term, preferably under the section “3.3.1. CO photoproduction” (p. 13).

A second concern is the conclusion which states: “the model is able to predict most of the ~300 *In situ* data points within a factor 2. However, this means that it is possible that the model can over or underestimates a concentration by 100%! Hence, this is an extremely weak formulation, since this states that the model actually is not performing that well. Before further consideration of this script, I need to see an alternative metric for model performance implemented, which will be used to thoroughly discuss the prediction offsets of the model to the in-situ measurements, especially the large offsets. The RMSE error is a possible alternative metric, which is already calculated in the paper to test different parameterizations (p. 9 in the “2.4 Comparison to in situ” section). It is, however, not used in the main conclusion about the model performance. Besides that, such metric should not only be calculated for the entire sample of *in situ* measurements (285 subsamples), but also calculated for the subdivisions, in other words latitude groups representing different climate zones. This can be put in a new table and the results can subsequently be discussed in section 3.2.1. Surface CO concentrations (p. 11-12). Lines 5 and 15, which state “within a factor of 2”, should then be edited in this section. Also,

figure 6C should then be replaced by a figure showing the offsets of the model simulation from the observed data (residuals).

Finally, the paper shows in figure 6 (p. 28) the locations of the different *in situ* measurements and how well the model predicts the CO concentration of these points for a given latitude. This is definitely an important figure. However, it could certainly be improved, since it contains a lot of information, and is hard to read and interpret. Especially 6B is messy: latitude on the x axis is shown in a different way than in the figure 6A (shows the locations of the *in situ* measurements). Also, shaded areas of mean minimum and maximum CO concentration are shown for latitude and longitude. I would recommend to leave the shaded area of the longitude out, since it does not tell more than the latitude averages and makes it even harder to read. Actually, I do not know what the longitudinal mean stands for in that graph, since for a particular latitude you have only one point for every longitude. Hence, it is the mean minima and maxima of one point. Only if it is of real importance for this research and it can be clearly motivated, it can be kept in.

In addition, the section that describes the figure uses a lot of information, which is hard to obtain from this figure. To make the graph more readable, figure 6A should be split from 6B and 6C and put it in a separate figure. Moreover, the colors and symbols of the different types of *in situ* data need to be adjusted. Now, the *in situ* data are hard to distinguish from each other, especially the ones with a dark color. I would like to see the dots slightly bigger and a clear distinct color set should be chosen.

### **Minor arguments**

Besides these three main concerns, there are some minor issues and typos that have to be revised:

- Minor issue 1: the explanation of the used PISCES model is very short. I like the chosen model, but I wonder why in particular the PISCES model is chosen. Is it because the authors are most familiar with this model or is it because it simulates the phytoplankton concentration best? Secondly, I do not know what the type and resolution (both temporal as spatial) of the in- and output data are. This can be important, since this determines what conclusion can be drawn. Please, provide a longer description of the model including the above-mentioned information in the section 2.1 Oceanic CO model description.
- Minor issue 2: in the section "Efficiency of the excited CDOM to produce CO", the average of two parametrization is used to calculate the apparent quantum yield. Here, a short motivation should be provided.
- Minor issue 3: in section "3.2.1. Spatial patterns of the sources and sinks", it is mentioned that the annual mean of the CO concentration is vertically integrated over a depth of 1000 meters. Please provide a short motivation, why in particular a depth of 1000 meters is chosen.
- Minor issue 4: in the section "Sensitivity of the oceanic CO budget to changes in the photoproduction", the parameterization test is discussed. It is concluded that the Launois et al. showed the best results compared to the standard one of Morel. However, no reason was

given why still the standard parametrization of Morel is used. An argument should be given in this section.

- P. 3, line 5: a comma should be placed after “Hence”
- P. 4, line 11: reference missing of the SMARTs2 model
- P. 12, line 27: “April” should be changed to “August”.
- P. 16, line 33: replace “from” by “to”
- P. 17, line 6: a comma should be placed after “In figure 10” and “is shown” should be placed after “PISCES”
- P. 29, figure 4:  $\text{nmol m}^{-2}\text{yr}^{-1}$  as unit for the graphs of photoproduction, phytoplankton production and bacterial sink, whereas in section “3.1.2. Spatial patterns of the sources and sinks” the unit  $\text{mmol m}^{-2}\text{yr}^{-1}$ . Hence, the units in figure 4 should be changed to  $\text{mmol m}^{-2}\text{yr}^{-1}$
- P.31, figure 7: the x axis values are with and without commas. This should be changed.

#### References:

- Erickson, D. J. (1989). Ocean to atmosphere carbon monoxide flux: Global inventory and climate implications. *Global Biogeochemical Cycles*, 3(4), 305-314.
- Gros, V., Peeken, I., Bluhm, K., Zöllner, E., Sarda-Esteve, R., & Bonsang, B. (2009). Carbon monoxide emissions by phytoplankton: evidence from laboratory experiments. *Environmental chemistry*, 6(5), 369-379.
- Stubbins, A., Uher, G., Law, C. S., Mopper, K., Robinson, C., & Upstill-Goddard, R. C. (2006). Open-ocean carbon monoxide photoproduction. *Deep Sea Research Part II: Topical Studies in Oceanography*, 53(14-16), 1695-1705.