Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2020-207-RC1, 2020

Biogeosciences
Discussions

Interactive comment on "Reproducible determination of dissolved organic matter photosensitivity" *by* Alec W. Armstrong et al.

Patrick Neale (Referee)

nealep@si.edu

Received and published: 30 July 2020

General Comments

Measurements of spectral fluoresence have become a standard part of any study of the dynamics and distribution of dissolved organic matter in both freshwater and marine environments. Methods for deriving standardized metrics from fluorescence data are well established, and most studies of DOM dynamics acquire detailed sets of excitation-emission matrices and analyze them using parallel factor analysis (PARAFAC). In the present contribution, Armstrong, et al., argue that the kinetics of fluorescence photosensitivity are also useful properties to characterize DOM, in particular, the magnitude and rate constants of biexponential kinetics. However, several important considerations

need to be observed if these photosensitivity metrics are to be compared across studies. These are shown in the context of a specialized continuous loop exposure/assay system that the authors have devised, but several are applicable to any photosensitivity study. One is the use of a reference material, SRNOM, to both test the derivation of PARAFAC components and standardize the kinetics for a given exposure set up. Another informative test is the reproducibility of the results in repeated runs including those by different observers, which helps to establish the uncertainty in the estimated kinetic parameters.

I quite agree with these recommendations which are straightforward to implement. For others, it is not clear that they will always contribute to reproducible, or more importantly, interpretable, results. One is the preparation of solid phase extracts of DOM vs using fresh filtrates for the measurements. While extracts are inherently more stable than raw filtrates, the authors demonstrate differences in the photosensitivity kinetics of extracts vs the original filtrates, the reasons for which are not well understood. The authors advise preparing extracts in some situations but not others, this leaves open the question of comparability. The authors also advise using a standard optical density in the sample, yet also show there is a concentration dependence to the kinetics, even for an optically thin exposure conditions. Again, a decision will have to made of whats more important, knowing how the DOM behaves at its natural concentration or being able to compare it to other sources.

The authors also advocate expressing kinetic results as a function of cumulative photon exposure as opposed to time, this will adjust for differences in exposure regime between different studies. In principle, this is a good idea. Any photosensitivity study should include a detailed documentation of the optical setup and exposure measurements such that the results can be expressed either as a function of time or cumulative exposure. Studies do range in how thoroughly exposure conditions are documented. For these kinetic studies, exposure has been measured with a nitrite actinometer. Actinometry is very useful to quantitate the effects within a specific optical set up and is

used effectively by the authors to monitor exposure between experiments, including those with variable working volume. However, the nitrite actinometer only measures quantum fluxes between 330 and 380 nm. For incident solar UV, this is only about 60 per cent of the spectrum (by quanta). For comparison across all photosensitivity studies, I would suggest a more general exposure metric, e.g. total UV radiation. Given the broadband 330-380 nm quantum flux, total UV can be estimated with reference to the manufacturer's stated spectral distribution. But lamp and component aging can change that (even adjusting for constant power), so the best approach is to measure the spectrum in conjunction with actinometry (admittedly, neither of these are trivial to perform).

In the end, investigators will need more information to decide whether the additional insight gained from defining photosensitivity kinetics will be worth the efforts needed to perform all these standardization steps. This report documents experimental tests that show what are sources of variability in the procedure but does not show what new understanding is actually being gained from the results (vs what can already be gained from other optical/chemical measurements typically made on DOM). As far as reproducibility, there is only one instance of repeat determination on a "real world" sample, the small wetland. Further repeat determinations are needed to demonstrate the general reproducibility of the approach. Also, some modification of how the photosensitive fractions are estimated may be needed if the results are to be used in a comparative context (see specific comments below). Despite that this is still a work in progress, it is quite appropriate to have the authors' study and recommendations in a Biogeosciences discussion article. Comments by a wide range of readers should help refine the ideas proposed and ultimately advance the field.

Specific comments:

Line 140 "Solar exposure" – This was not solar exposure, but a laboratory set up. Better (?) "Total sample exposure"

Figure 7 and Table 1 – The captions for these describe kL and kSL with units of mol photons m^{-2}. Those are the units of P, the units of k should be the inverse, m^2 [mol photons]$^{-1}$.

Figure 7 and Table 1 apparently show the same data – and both state the statistics of the comparison. Questionable whether both are necessary. Figure 7 caption, however, says see Fig. 5 for data. It appears that Fig. 6 has the data.

Line 350-360 – Factors affecting storage of filtered water. Previous text only mentioned preparation of filtrates using 0.7 μM glass fiber filters, which allows passage of a substantial bacterial fraction. However, subsequent guidelines caution against used stored material even filtered to 0.2 μM (some bacteria can even get through those). Please clarify what filtration method was used for the stored sample, but in any case (slow) microbial degradation may be another factor resulting in changes in stored material.

Figure 10 – Caption says see Figure 6 for data, data appears to be in Fig. 9. This correction also applies to the caption for Figure A1. Figure 10 could be misleading to the reader, as a quick inspection may suggest that the spread of the multiple points for a particular sample source (and standard deviation in the table) are indications of reproducibility. Actually, only the SRNOM and three of the small wetland points are repeat determinations on the same sample. Separating the points for different sample dates would avoid this confusion, especially given that later on (section 3.3.2) the authors attribute some of the difference in the wetland results with time to possible differences in sample composition and/or previous solar exposure.

Line 456ff, section 3.3.1 Here the relative abundances of kinetic components are considered as metrics of DOM composition or other influences on photosensitivity. A problem with the comparative use of fL and fSL is that the two parameters are not independent. Assuming a good fit to the actual time course the two fractions will always sum to approximately 1, which means that any variation in one fraction will be reflected in a complementary variation in the other. Thus, changes in, e.g. fL, with sample date or

location (as later discussed in 3.3.2) could be caused by change in the concentration of labile or semi-labile fraction, or both. If the focus is on the rate parameters, this is not so important, but if the magnitudes of the fractions are to be comparative metrics, the need to be independent of each other. For example, ft could be the actual component score, score normalized to t0 total fluorescence, or score normalized to DOC.

The authors offer the interpretation that the fractions correspond to “pools” of more or less reactive DOM. However, Murphy et al. (2018) interpret biexponential kinetics as possibly reflecting multiple photoreaction pathways, a fast one involving ROS and slower one related to direct photochemistry. How do the authors reconcile these differing interpretations?

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