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Comment

## ***Interactive comment on “Photooxidation of dimethylsulfide (DMS) in the Canadian Arctic” by A. Taalba et al.***

**Anonymous Referee #1**

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### GENERAL COMMENTS

Taalba and coauthors conducted an interesting and extensive study of the factors driving DMS photolysis in the Canadian Arctic, covering the transition from heavily river-influenced shelf areas to the open sea. They measured the spectrally-resolved apparent quantum yield (AQY) of DMS photolysis using appropriate methods, and subsequently used it to calculate water-column integrated photolysis  $k_s$  in the upper mixed layer and to assess the relative impact of DMS photooxidation in these environments. The authors found spatial variability in AQYs related to the variability in known photosensitizers of DMS photolysis: dissolved organic matter of different origin/quality and nitrate.

In my view this is a well-written and well-documented work that makes a relevant addi-

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tion to the field and thus deserves publication in Biogeosciences. However, there are some issues that must be addressed before the paper is published, so I recommend that the paper undergoes a moderate to major revision.

1. (And most relevant): the authors claim that the AQY at 300 or 330 increases exponentially with salinity across different oceanic regimes (Fig. 4), arguing that salinity may be an indicator of CDOM origin (terrestrial vs. marine). However, their calculations do not seem to take into account the variation in AQY due to temperature. The irradiation experiments were conducted at different temperatures in each of the studies, for instance, at 2 – 4 °C in the present study and at 21°C in the Sargasso Sea study done by Toole et al. (2003). That same study showed that a 20°C increase in temperature produced approximately a doubling in AQY. Obviously, this may modify the AQY-salinity correlation encountered, which is one of the core messages of the paper. This issue must be addressed.

2. There is a dearth of information regarding the description of vertical mixing and underwater spectral light attenuation ( $K_d$ ) in the study area. I also have some concerns regarding the measurement of CDOM in highly absorbing and scattering (turbid) waters. These issues deserve a more detailed treatment in the paper. For example:

It should be explained somewhere in “Materials and methods” how the Upper Mixed Layer Depth (UMLD) was calculated. This is relevant for the results of this study, as the authors themselves recognize, because they assumed that the UML was homogeneous in terms of [DMS] and optically-active substances. Using a fine UMLD criterion (e.g.  $< 0.05 \text{ kg m}^{-3}$  density difference) is more likely to render an actively mixing or recently mixed layer. Using a coarser criterion may capture a layer that is not homogeneous in terms of [DMS], because DMS undergoes fast biological/photochemical cycling. The authors calculated DMS photolysis as the water-column integral straight away (Eq. 5 and 6), thus assuming that all the photons capable of promoting DMS photolysis were absorbed in the UMLD. However, they do not state clearly that the photolysis-causing wavelengths were extinguished, e.g., to  $< 1\%$  of subsurface irradi-

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ance within the UML at all stations. There is only a vague sentence in P2101, L14 – 15. Even though spectral  $K_d$ 's in the water column are not reported, they can be approximated from inherent optical properties that do appear in the paper. I used the data in Fig. 3 to make some calculations, which indicate that the authors' assumption was correct (see specific comment on P2101).

In addition, the authors claim that previous studies were wrong in the way they calculated the amount of spectral irradiance absorbed by CDOM (P2108), an affirmation I do not agree with (see detailed argumentation in the specific comments). This should be corrected.

3. Non-technical aspects: I suggest that the authors revise (or reduce) the use of acronyms referred to geographical locations (MRE, MS, CB, SGT-E and SGT-W, etc). The acronyms are not always used in a consistent manner (see specific comments). Replacing some of the acronyms by full words or by more explicit "labels" would help the reader. I also suggest that the authors add a sentence in both the abstract and the summary that conveys the relevance of their findings to the broad audience of Biogeosciences. Although this is speculation, I believe that the methodology used by Taalba et al. to study the relationship between CDOM quality/origin and AQYs might provide results of global significance in the future, and might have implications for the photochemical cycling of compounds other than DMS.

### SPECIFIC COMMENTS

Abstract L5: only in the Arctic? L10 after "salinity,...": in my view, no need to describe the mathematical function. It has no obvious interpretation! Perhaps saying "exponential form" is enough (after checking for temperature effects, general comment 1).

Introduction P2095 L2: "... POTENTIALLY contributing to the formation of cloud..." L2 – 6: A relevant work that might be cited here is "Direct Observations of Atmospheric Aerosol Nucleation, Markku Kulmala et al. Science 339, 943 (2013); DOI: 10.1126/science.1227385. Check out also "Potential for a biogenic influence on cloud microphysics

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over the ocean: a correlation study with satellite-derived data, A. Lana et al., Atmos. Chem. Phys., 12, 7977–7993, 2012”.

P2096 L19 – 21: Please consider adding here a reference that documents the freshening trend in the Arctic.

P2097 L3: Please add something like “under shallow stratification conditions” after “summer”. According to Galí et al., bacterial DMS consumption would largely dominate in stations with UMLD > 10 m.

Materials and methods P2099 – 2100 Equations 1, 2 and 3 (and corresponding text): I understand that “I” is the pathlength of the cell used for measuring CDOM absorbance and “L” the pathlength of the irradiation cell. However, I find these symbols a bit confusing at first sight (for instance “L” reminds me of “liter” units). Why not using “r” and “R”?

P2101 L14 – 15: The euphotic layer depth (which I assume is defined as the 1% penetration of PAR) is not really relevant here, given that shortwave UVA accounts for the majority of DMS photolysis. Maybe the authors mean, by saying that, that the surface waters displayed very low transparency to UV and PAR (?); so, despite the very shallow stratification encountered, the UMLD was exposed to a small fraction of subsurface PAR and even a smaller fraction of subsurface UVB and UVA.

If we calculate the total absorption coefficient ( $a_t$ ) from the  $a_{\text{CDOM}}$  (Fig. 3B) and the quotient  $a_{\text{CDOM}}/a_t$  (Fig. 3C), we obtain an  $a_t$  (at 330 nm) of  $\sim 1.5 \text{ m}^{-1}$  at Sta. 640 and 691, and  $\sim 25 \text{ m}^{-1}$  at Sta. 697. If we assimilate  $a_t$  to the  $K_d$  (which is not exact) we obtain a 1% penetration depth for 330 nm radiation of  $\sim 3 \text{ m}$  at Sta. 640-691 and  $\sim 0.2 \text{ m}$  at Sta. 697. This indicates that at these three stations photochemically-active radiation was absorbed at depths shallower than the UMLD. Indeed, the large absorption coefficients of CDOM at 412 nm suggest that a similar situation occurred at most stations.

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In my view, this issue should be explained in more detail (perhaps in the Results section), because the estuarine and shelf waters studied seem to be very different (at least optically) from most open ocean surface waters. I suggest using the concept of “photoactive layer” (sensu Neale et al. 2003, book chapter) rather than “euphotic layer” in this context.

P2102 L8 – 9: “The exponent in Eq. (5) is the photolysis rate constant...” in fact the photolysis  $k$  in Eq. 5 is only the part in parentheses that has (time)<sup>-1</sup> units.

L11 – 14: The authors should be more circumspect about some of these assumptions, which may have an impact on the results. In case the authors measured DMS in vertical profiles, they should mention those profiles in the text to support the ‘homogeneity assumption’. See general comments.

Results and discussion P2102 L17: Naming the stations after the name of the project alone may be confusing for the reader. Please consider using explicit names whenever possible.

P2103 Is there a particular reason to use aCDOM at 412 nm? I would find more useful that the authors reported aCDOM at 330 nm, which is the peak DMS photolysis wavelength (at the water subsurface). Yet, I can assume that there is, roughly, an exponential decrease of aCDOM with increasing wavelength, so that aCDOM 412 is a good predictor of aCDOM 330.

This raises another concern regarding CDOM measurement. On one hand, aCDOM at 412 nm is typically very low in oceanic (“case 1”) waters, so that aCDOM,412 is less sensitive and more error-prone than aCDOM,330 (this may be relevant for Canadian Basin and Baffin Bay stations, Fig. 2). On the other hand, the Lambert-Beer law may not hold when a solution is optically thick (absorbance > 1) and very turbid (which may have happened in samples like Sta. 697). In these cases it may be better to measure aCDOM using 1 cm cuvettes. In fact, the aCDOM,300 at Sta. 697 was  $\sim 20 \text{ m}^{-1}$ . Using Eq. 1 this corresponds to an absorbance of  $\sim 0.87$  in a 0.1 m cuvette. Absorbance was

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likely higher than 1 at wavelengths < 300 nm, which might have affected the calculation of the S275\_295.

Can the authors provide a convincing explanation on these issues?

L1 and 25: It seems there is a typo here (“MatsOUka” instead of “MatsUOka”). The work by “Matsuoka et al.” does not appear in the reference list. Please check through-out.

P2107 L2: Please add “LIKELY” between “anion” and “plays” in that sentence.

P2108 L16 – 20: This sentence seems to imply that previous studies had an important bias: “Note that previous studies often implicitly assumed all underwater light to be absorbed by dissolved chromophores without considering the particulate colored materials, which biased the kdms estimates upward to a certain extent, depending on the fraction of light absorbed by particles”.

I do not agree with the statement that previous studies assumed that all the photolysis-causing radiation was absorbed by CDOM. Rather, they just assumed that ONLY the radiation absorbed by CDOM was causing DMS photolysis. The confusion here probably stems from the fact that previous studies used a different formulation to calculate photolysis rates in the water column, because they did not assume that all the photons were absorbed within the UML.

See, for instance, Eq. 7 in Toole et al. (2003). There, the amount of photons absorbed at depth  $z$  results from the product of scalar irradiance ( $E_0$ ) and  $a_{CDOM}$ .  $E_0$  at depth  $z$  is calculated from  $E_0$  at the subsurface ( $E_{0-}$ ) and an exponential attenuation factor [ $\exp(-K_d \cdot z)$ ]. If we integrate that equation over a depth interval ( $z_1 - z_2$ ), we get that UML-integrated  $E_0$  and thus photolysis is proportional to  $(1/K_d) \cdot [1 - \exp(-K_d \cdot z_2)]$ .

The case where all photons of a given wavelength are absorbed within the UML is equivalent to setting [ $\exp(-K_d \cdot z_2)$ ] to zero. In this case, photolysis is proportional to  $(1/K_d)$  alone. At this point, it can be noted that both  $K_d$  and  $a_t$  have the same units ( $m^{-1}$ ).

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1), and are closely related variables (although the first is an apparent optical property, deduced from the light field, and the second is an inherent optical property). Now, note that  $a_t$  divides  $a_{CDOM}$  in Eq. 5 and 6, whereas  $K_d$  will divide  $a_{CDOM}$  once Eq. 7 from Toole is integrated with respect to  $z$ . So, the formulation of Toole et al. (2003) and that used in the present study seem to be dimensionally consistent and roughly equivalent when photochemically active photons are completely absorbed within an optically-homogeneous UMLD.

While the formulation used by Taalba and coauthors does not account for scattering (and perhaps does not need so), the formulation of Toole et al accounts for the tridimensional light field (mostly due to scattering) by using scalar irradiance ( $E_0$ ). Furthermore, note that in case 1 waters (oceanic waters where most of the previous studies were one) very little light absorption is expected in the UV and blue light range responsible for DMS photolysis, as shown in Fig. 3C for Sta. 691-640. In particular,  $a_{CDOM}$  will frequently exceed  $a_{particles}$  by around 1 order of magnitude or more.

L25 – 27: In my view this assumption tends to underestimate/overestimate the photolysis rates, not  $k_{DMS}$ . According to Eq. 6,  $k_{DMS}$  is independent of  $[DMS]$  in this approach.

Summary P2110 L9 – 10: Yes, but check the comparison with other studies after accounting for temperature kinetic effects.

References Please check for typos and possible formatting issues. Examples:

P2111 L16: “natural sources” L19: “Global Biogeochem. Cy.,”

P2112 L1: “DelValle” should be “Del Valle”.

Tables and figures Table 1: Why not reporting the approximate depth range sampled? For instance, 0 – 0.5 m. Sampling depth = 0 m does not seem very appropriate.

Table 3: I recommend that, besides the (model-derived) daily quantum irradiance in the 290 – 500 nm band (that causing DMS photolysis), the authors report here the

total shortwave irradiance ('pyranometer irradiance', in  $\text{W m}^{-2}$  units) and even the UVR and PAR irradiance. This will (1) facilitate that expert readers understand the overall irradiance climate at a glimpse, (2) make the information easier to understand by the non-expert audience, and (3) allow the comparison with other studies where only total shortwave irradiance was reported.

Table 4: I suggest changing the column "Layer", which currently adds very little information, and reporting there the UMLD range in each of the studies. This would allow a better understanding of the differences among sites, that is, how much the difference in  $k_{\text{DMS}}$  might have been due to mixing-regulated solar exposure or to differences in quantum yields. Ideally, some information on underwater light attenuation (UV/PAR  $K_d$ ) should be added too, but this information might be hard to find in some studies. In the few studies where a fixed depth horizon of 0 – 20 m was used for computations (Brugger, Hatton and Deal), a note could be added saying that the depth interval did not match the UMLD.

Fig. 1: please add "Beaufort Sea" somewhere in the map or in the caption, because it is mentioned in Fig. 2.

Fig. 2: According to the current nomenclature it seems that the CFL-BS samples (Beaufort Sea) were not located in the Canadian Basin (CB). Is there a reason to give these samples a distinct nomenclature?

Fig. 4: add salinity below the x-axis of the bottom panel. If my concern about the temperature correction was true (see general comments), this figure should be modified. I suggest adding to each panel a twin panel with the temperature-corrected AQYs to see the real variability captured by salinity.

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Interactive comment on Biogeosciences Discuss., 10, 2093, 2013.

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