

## COMMENT

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### Absorbance, absorption coefficient, and apparent quantum yield: A comment on common ambiguity in the use of these optical concepts

**Abstract**—Several important optical terms, such as “absorbance” and “absorption coefficient,” are frequently used ambiguously in the current peer-reviewed literature. Because these terms are important when deriving other quantities, such as the apparent quantum yield of photoproduction, ambiguity in the application of these concepts leads to results that are difficult or impossible to interpret correctly. Such ambiguity also hinders comparison of results between studies and ultimately harms proper parameterization of numerical models of oceanic processes, as well as the refinement of remote sensing algorithms. We review these concepts and the implications of such ambiguities. A few simple recommendations that follow conventions developed by optical oceanographers are provided to authors dealing with these concepts. In particular, the symbol  $a$  is recommended for the absorption coefficient (in Napierian form,  $\text{m}^{-1}$ ), which is also preferred over absorbance (dimensionless) when data are presented; the symbol  $A$  is not recommended for absorbance;  $A$  should be used with caution because, although it has been used widely for absorbance in photochemistry and photobiology, it has also been used for absorbance in physics and optical oceanography; the term “absorptivity” is not recommended because of conflicting definitions in the current literature; the pathlength should always be given whenever absorbance data are presented; and normalization of photoproduction rates to absorbance or absorption coefficient should be performed only on optically thin samples, unless the inner filter effects are accounted for and corrected.

#### Absorbance and absorption coefficient

Absorbance (a dimensionless term symbolized as  $D$  or OD by optical oceanographers and as  $A$  by photochemists), absorption coefficient (dimensionless), and absorption coefficient ( $a$ ,  $\text{m}^{-1}$ ) are all measures of the ability of a medium (e.g., a water sample) to absorb light (photons). The definition of these terms can be found in many optical oceanography textbooks (e.g., see p. 14, 15, 49–50 in Kirk 1994; p. 62, 63 in Mobley 1994) or chemistry textbooks (Calvert and Pitts 1966; Balzani and Carassiti 1970; Skoog and West 1971). In this text, we follow the conventions used in optical oceanography (i.e.,  $a$  for absorption coefficient and  $D$  for absorbance). Neglecting scattering,  $D$  is defined as  $\log_{10}$  of the ratio of the collimated incident radiant power ( $P_i$ ) to the transmitted radiant power ( $P_t$ ) through a medium of finite optical pathlength ( $L$ ):  $D \equiv \log_{10}(P_i/P_t)$ . (In practice, to measure the absorbance of dissolved matter in a water sample with a spectrophotometer, a blank [i.e., distilled or MilliQ water] is used as reference and  $P_i$  does not need to be measured because  $D = D_{\text{ws}} - D_{\text{bk}} = \log_{10}[P_i/P_t^{\text{ws}}] - \log_{10}[P_i/P_t^{\text{bk}}]$

$P_t^{\text{bk}}] = \log_{10}[P_t^{\text{bk}}/P_t^{\text{ws}}]$ , where ws means water sample and bk means blank.) Absorbance is defined as the ratio of power loss to the incident power: Absorbance  $\equiv (P_i - P_t)/P_i$ ;  $a$  is defined as the absorbed portion per unit pathlength when the medium is infinitesimally thin (i.e., optical pathlength  $\Delta L \rightarrow 0$ ):  $a$  ( $\text{m}^{-1}$ )  $\equiv (1 - P_t/P_i)/\Delta L$ . More rigorous definitions can be found in the textbooks when scattering is considered. Note that all the parameters but  $\Delta L$  are spectral (dependent on wavelength). By definition, using the Beer–Lambert law, it is easy to derive that  $a = (D \times \ln 10)/L$ , where  $L$  (m) is the optical pathlength of a homogeneous medium for a collimated light beam.  $D$  is proportional to  $L$ , whereas  $a$  is an inherent optical property (IOP) that does not depend on pathlength or illumination condition.

The nomenclature used above (especially the term “absorption coefficient” and the symbol  $a$ ) follows the recommendations of a series of textbooks and reports for optical oceanography, among which are Jerlov (1968, 1976), Preisendorfer (1976), Morel and Smith (1982), UNESCO (1985, Report 45), Kirk (1994), Mobley (1994), and Thomas and Starnes (1999). In the photochemistry literature, the term “absorption coefficient” sometimes takes a decadic form (i.e., absorbance normalized to pathlength:  $\alpha$  [ $\text{m}^{-1}$ ]  $\equiv D/L$ ). In contrast,  $a$  is referred to as the Napierian absorption coefficient ( $a \equiv \alpha \times \ln 10$ ). In the glossary of terms recommended for photochemistry by the International Union of Applied Chemistry (Braslavsky et al. 1996 and references therein), these two symbols ( $a$  and  $\alpha$ ) are reversed.

Although optical oceanographers have progressively adopted the recommendations of the International Association for the Physical Sciences of the Ocean (IAPSO) Working Group on Symbols, Units, and Nomenclature (UNESCO 1985 and references therein), in photochemistry and photobiology, such uniformity is not yet the norm. Instead, these optical terms are used differently among researchers. Clearly this creates some difficulty in exchanging information or comparing results between studies. Other terms, such as absorptivity, molar absorptivity, molar extinction coefficient, and molar absorbancy index, are associated with various symbols and meanings in photochemistry (see p. 21 in Calvert and Pitts 1966; Balzani and Carassiti 1970; Wong 1989; Braslavsky et al. 1996; Miller 1998; Zepp et al. 1998). However, readers should generally feel comfortable with unorthodox uses of nomenclature because it is valid to the extent that the terms are defined and used consistently within any given article. Unfortunately, this is not always the case, and it is important that readers, particularly students of aquatic optics and photochemistry, be aware of such incon-

sistencies and be able to identify them when they are encountered in studying the literature.

In the current literature, “absorbance” frequently has ambiguous meanings, and it has been presented in units of  $m^{-1}$  or  $cm^{-1}$  when it should be unitless (e.g., Zepp and Schlotzhauer 1981; Cooper et al. 1988; Farmer et al. 1993; Moore et al. 1993; Valentine and Zepp 1993; Morris et al. 1995; Wetzel et al. 1995; Scully et al. 1996; Obernosterer and Herndl 2000; Bertilsson and Tranvik 2000).

Absorbance certainly can be defined in other than recommended ways for both optical oceanography and photochemistry (e.g., Kirk 1994; Mobley 1994; Braslavsky et al. 1996 and references therein). Clearly, this practice is not recommended. However, when alternative definitions are used, application of the concept should be self-consistent within a given article. For example, Zepp and Schlotzhauer (1981, p. 481) stated that “ $A_\lambda = \text{absorbance in meters}^{-1}$ ” in definitions of terms for their eq. 2:  $k_h = 2.303A_\lambda/(C_0L)$ , where  $L$  is the pathlength. The inclusion of “meters $^{-1}$ ” was an oversight, which makes it hard to understand the computed values of  $k_h$ . Similarly, Cooper et al. (1988) defined  $\phi$  as inversely proportional to  $(1 - 10^{-\text{Abs}})$ . Abs here should be dimensionless, but they presented their spectral “absorbance” data in units of  $cm^{-1}$  (see table III in Cooper et al. 1988), a possible oversight similar to that in Zepp and Schlotzhauer (1981). Note that  $(1 - 10^{-\text{Abs}})$  is meaningless if Abs has units. A comparable oversight was found in Valentine and Zepp (1993, p. 410). They stated that the samples were diluted so that “the absorbance at 350 nm was less than 0.05  $cm^{-1}$ .”

Moore et al. (1993) and Farmer et al. (1993) stated that their absorbance data were converted to  $m^{-1}$ , but they did not mention how. Does “ $m^{-1}$ ” mean that a 1-m pathlength was used (in this case the converted data are actually the decadic absorption coefficients  $\alpha$ ), or does it represent  $a$ ? Similarly, Obernosterer and Herndl (2000) stated that “absorbance” was measured using a 5-cm quartz cuvette, but presented their data with units of  $m^{-1}$  without explaining why these units were used. It is therefore difficult to judge whether the data are  $D$ ,  $\alpha$ ,  $a$ , or something else.

Wetzel et al. (1995, fig. 2) presented data labeled as “Absorbance (OD).” Because the pathlength was not given, however, such absolute values of absorbance are meaningless except when providing relative comparisons among samples. Morris et al. (1995) stated that  $a = \ln(10^A)$  for a 1-m path. The relationship was correctly stated, but in their fig. 3, data with units of  $m^{-1}$  were presented as “absorbance” and the slope was reported to have units of  $m^{-1} nm^{-1}$  instead of  $nm^{-1}$ . It is therefore unclear whether these results represent  $D$ ,  $a$ , or  $\alpha$ . Unfortunately, none of the three meanings would allow a reader to reproduce their curves (see curves a–c of fig. 3 in Morris et al. 1995) in a manner consistent with the data provided in their table 1.

Scully et al. (1996, eqs. 5, 6), defined total absorbed photons at wavelength  $\lambda$  as  $\lambda I_0 \times \lambda(1 - 10^{-\text{Abs}})$ , where  $\lambda I_0$  is the photon flux ( $\mu\text{mol cm}^{-2} \text{s}^{-1}$ ) and  $\lambda(1 - 10^{-\text{Abs}})$  is the fraction of light absorbed. There are two issues here: (1)  $\lambda I_0 \times \lambda(1 - 10^{-\text{Abs}})$  should be divided by the pathlength ( $L$ ) or multiplied by  $S/V$  ( $S$  is the exposed surface area and  $V$  is the cell volume) to obtain units ( $\mu\text{mol cm}^{-3} \text{s}^{-1}$ ) consistent

with the numerator,  $d[\text{H}_2\text{O}_2]/dt$  ( $\text{nM h}^{-1}$ ); (2) as with the work discussed previously, the statement “Abs = absorbance  $cm^{-1}$ ” causes similar concern. Omission of the  $1/L$  term and the use of  $cm^{-1}$  units make it unclear how the quantum yield data were derived. In this situation, the results would be valid only if  $L$  was 1 cm or if the sample was optically thin (see below) so that  $(1 - 10^{-\text{Abs (whole cell)}})/L \cong (1 - 10^{-\text{Abs (1-cm)}})$ . However, neither appears to have been the case in their study.

Similar ambiguities were further introduced in Bertilsson and Tranvik (2000) when they cited Scully et al. (1996). Abs in their eq. 3 was explained as being absorbance with units of  $cm^{-1}$  on the right-hand side but was dimensionless on the left-hand side. Note that Abs in  $10^{-\text{Abs} \cdot L}$  actually means absorbance per centimeter or the decadic absorption coefficient  $\alpha$ , not  $a$ . Hence, it is unclear what the Abs values listed in their tables 1 and 2 really mean.

Another term frequently used by photochemists is “absorptivity.” The term in Braslavsky et al. (1996) is defined as the ratio of *absorptance* (not absorbance!) to optical pathlength, which is different from the meaning found in other articles where “absorptivity” is the decadic absorption coefficient  $\alpha$  normalized to the concentration of the chromophore (e.g., see p. 21 in Calvert and Pitts 1966; Balzani and Carassiti 1970; Zepp 1982; Zepp et al. 1998). This term, as well as other “absorptivity” terms (such as molar absorptivity), is not recommended or should be avoided as suggested by Braslavsky et al. (1996). Absorptivity, like the other optical terms discussed above, although not recommended, can certainly be used if a clear definition is provided and its use is consistent with the definition. Unfortunately, some inconsistencies also can be found in how the term has been used. For example, in Miller (1998), absorptivity is used to describe both  $a$  and  $\alpha$ , making the meaning of the data in the figure unclear.

The ambiguous meanings of absorbance and absorption coefficient, such as those in the examples above, will continue to create confusion. The problem is compounded when people use these or related quantities in deriving other properties such as quantum yields.

### Apparent quantum yield and the inner filter effect

The apparent quantum yield of photoproduction ( $\phi$ ) is a measure of how many molecules of a certain substance (for example  $\text{H}_2\text{O}_2$ , dissolved inorganic carbon (DIC), CO, minerals, etc.) can be produced per photon absorbed by, for example, colored dissolved organic matter (CDOM). It is usually expressed as  $\phi = \text{photoproduction (mol)}/Q_a$  (mol), where  $Q_a$  is the number of photons (mol) absorbed by, as in the above example, CDOM (see Zepp 1982; Miller 1998 and references therein).

The equations and concepts associated with  $\phi$  have been published for decades (e.g., Parker and Barnes 1957; Balzani and Carassiti 1970; Zepp and Cline 1977; Zepp 1978, 1982; Wong 1989). The concepts of inner filter, self shading, or light screening for optically thick solutions have also been discussed (Morowitz 1950; Skoog and West 1971). However, we found that the rules established in these pioneer studies

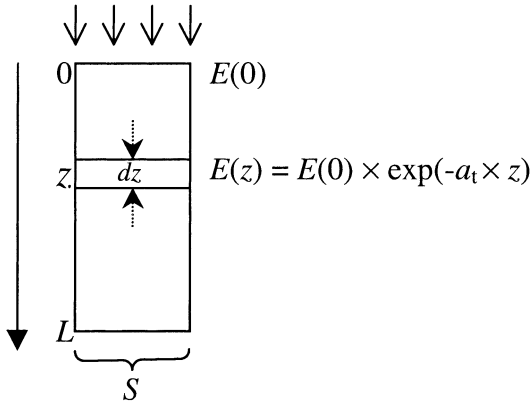


Fig. 1. Schematic of photoproduction measurement cell.  $L$  is the pathlength.

are not always followed in the current literature. Furthermore, the problem is compounded with the ambiguous use of the optical terms discussed previously. For clarification, we review these concepts briefly. We also assess the consequences of ignoring what is called “inner filter effects.”

$Q_a$  needs to be estimated in order to derive  $\phi$ . It is important to note that, rigorously,  $Q_a$  is not proportional to either  $D$  or  $a$  in any experimental setting, although in some cases this may be approximately true. Similarly, photoproduction is not simply proportional to either  $D$  or  $a$  even if  $\phi$  is a constant. This is because any experimental device has a finite pathlength, whereas  $a$ , by definition, is a quantity established using an infinitesimally small pathlength.

Figure 1 illustrates this concept. A collimated beam of spectral irradiance  $E(0)$  ( $\text{mol photons m}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$ ) is projected onto a photoreaction cell. Ignoring scattering and bottom reflection, the total number of photons absorbed by CDOM per unit time at depth  $z$  by an infinitesimally thin layer,  $dz$ , is

$$\begin{aligned} dQ_a \text{ (mol photons s}^{-1} \text{ nm}^{-1}) &= E(z) \times a_{\text{CDOM}} \times S \times dz \\ &= E(0) \times \exp(-a_t \times z) \times a_{\text{CDOM}} \times S \times dz \end{aligned}$$

where  $S$  ( $\text{m}^2$ ) is the cross section of the illuminated area,  $E(z)$  is the irradiance at depth  $z$  (m), and  $a_t$  ( $\text{m}^{-1}$ ) is the total absorption coefficient of the sample. Also,  $a_t = a_{\text{CDOM}} + a_w$ , where  $a_{\text{CDOM}}$  and  $a_w$  are the absorption coefficients of CDOM and water molecules, respectively. Therefore, for the whole cell, we have

$$\begin{aligned} Q_a \text{ (mol photons s}^{-1} \text{ nm}^{-1}) &= \int E(0) \times \exp(-a_t \times z) \times a_{\text{CDOM}} \times S \times dz \\ &= E(0) \times (a_{\text{CDOM}}/a_t) \times S \times [1 - \exp(-a_t \times L)] \quad (1) \end{aligned}$$

where the integration is across the optical pathlength,  $L$ , starting at  $z = 0$ .

The above equation implies that  $Q_a$  is not a linear function of either  $a_{\text{CDOM}}$  or  $L$  because of the exponential term. Because a layer at  $z \neq 0$  receives different illumination than at  $z =$

0, it is referred to as inner filter effects or self-shading. The inner filter effects are negligible when  $a_t \times L \ll 1$ , so that  $E(z) \approx E(0)$  and  $Q_a \approx E(0) \times a_{\text{CDOM}} \times S \times L$ .

The equation used in Cooper et al. (1988) and Moore et al. (1993),  $\phi = [d(\text{H}_2\text{O}_2)/dt]/[I_0(1 - 10^{-\text{Abs}})/L]$ , is a simplification of Eq. 1 because  $a_w$  is not considered ( $\text{Abs} = a_{\text{CDOM}} \times L/\ln 10$ ). It is a valid approximation, of course, because at short wavelengths,  $a_{\text{CDOM}} \approx a_t$  (Quickenden and Irvin 1980; Smith and Baker 1981; Pope and Fry 1997) and at longer wavelengths,  $a_t \times L \ll 1$ .

Using a Taylor expansion (Skoog and West 1971), we have

$$\begin{aligned} Q_a &= E(0) \times a_{\text{CDOM}} \times S \\ &\times \{L - 1/a_t \times [1/2 \times (a_t \times L)^2 - 1/6 \\ &\times (a_t \times L)^3 + \dots]\} \end{aligned}$$

If  $Q_a^0 = E(0) \times a_{\text{CDOM}} \times S \times L$  is assumed to be the first-order approximation to  $Q_a$ , the error term will be  $\sim -1/2 Q_a^0 \times (a_t \times L)$ . Thus, depending on  $L$  and  $a_{\text{CDOM}}$  of the sample, the relative error in the first-order approximation,  $Q_a^0$ , can be very large. For example, if a 10-cm cell is used (Kieber et al. 1990) for estuarine water samples where  $a_{\text{CDOM}}$  (330 nm)  $\approx 5 \text{ m}^{-1}$ , the relative error in  $Q_a^0$  is  $>20\%$ . Normalization of photoproduction rate to absorption coefficient or absorbance (e.g., Kieber et al. 1990; Valentine and Zepp 1993; Miller and Zepp 1995) implies that  $Q_a^0$  is used, which is valid only when  $a_t \times L \ll 1$  (i.e., when the sample is optically thin).

Although the experimental procedure to obtain  $\phi$  is described in many studies (e.g., Valentine and Zepp 1993; Miller and Zepp 1995; Weiss et al. 1995; Gao and Zepp 1998; Andrews et al. 2000), the equation used to determine  $Q_a$  (and therefore  $\phi$ ) is often unclear, which makes it difficult to understand the magnitude of the error and to derive error estimates. Even with a 1-cm pathlength (which is not specified in the publication), some samples in Miller and Zepp (1995) are still not optically thin (specifically, see their SRW1 and SRW1 diluted). Therefore, normalization of their rates to  $a_{\text{CDOM}}$  (350 nm) created uncertainties in the relative response among samples. A similar situation was also found in Kieber et al. (1990), where samples were not diluted sufficiently (or not diluted at all) so that some samples showed absorbance (300 nm, 10-cm pathlength)  $>0.5$  (see fig. 5 in Kieber et al. 1990).

Clearly, if  $\phi$  is to be compared among various samples, photoproduction should be normalized to  $(a_{\text{CDOM}}/a_t) \times (1 - \exp[-a_t \times L])$  and not to  $a_{\text{CDOM}}$ . It should be further normalized to the input irradiance if that is also a variable. Only when  $(a_t \times L) \ll 1$  is normalization to  $a_{\text{CDOM}}$  appropriate, because  $Q_a \approx Q_a^0 = E(0) \times a_{\text{CDOM}} \times S \times L$ . On the other hand, when  $(a_{\text{CDOM}} \times L) \gg 1$ , the incoming photons are absorbed almost entirely by the sample, regardless of the magnitude of  $a_{\text{CDOM}}$ . In such cases, normalization to  $a_{\text{CDOM}}$  is inappropriate.

The consequence is easy to grasp conceptually. If the photoproduction rate is normalized to  $a_{\text{CDOM}}$ , the relative response among samples changes with  $L$  (i.e., the difference among samples depends on the sample volume or at least

the pathlength examined). This makes it difficult to compare results from independent studies because cell size and input irradiance may be different. For example, CO production rate for Suwannee River samples was reported to be 5.1 nmol m L<sup>-1</sup> h<sup>-1</sup> (Miller and Zepp 1995) but was 13 nmol m L<sup>-1</sup> h<sup>-1</sup> in another study (Valentine and Zepp 1993). Without further details revealed for the experimental parameters (the cell size has been published as 25 ml for the former and 10 cm or 13.5 cm × 1.5 cm for the latter, but the actual pathlength was 1 cm for both), it is difficult to know that the difference is due to the difference in the input irradiance (unpubl. data), not to the cell size.

Even in cases when the condition  $a_t \times L \ll 1$  holds, normalization to  $a_{\text{CDOM}}$  at a certain wavelength remains a simplification. Specifically, the reasons are illumination time and wavelength range. Extensive illumination can cause photobleaching (loss of some ability to absorb light, i.e.,  $a_{\text{CDOM}}$  decreases with time). For example,  $a_{\text{CDOM}}$  (300 nm) of an Everglades sample decreased by ~40% after 10 h of illumination (see fig. 7 in Kieber et al. 1990). The measured rate (and therefore  $\phi$  derived from this rate) is an average effect over the illumination period unless the derivative technique of Cooper et al. (1988) is used. If the photobleaching rate is different among samples, normalization to  $a_{\text{CDOM}}$  yields different results for different illumination times. Furthermore, because illumination often covers a wide wavelength range and  $a_{\text{CDOM}}(\lambda)$  and  $\phi(\lambda)$  are both approximately exponential functions of  $\lambda$ , normalization to  $a_{\text{CDOM}}$  at a single wavelength also creates uncertainties in relative response among samples unless the functionality of  $a_{\text{CDOM}}(\lambda)$  and  $\phi(\lambda)$  versus  $\lambda$  is similar among samples.

We can estimate the error encountered due to normalization to  $a_{\text{CDOM}}$  using a simple example that is similar to previous discussions and studies of the inner filter effects (Morowitz 1950; Zepp et al. 1981; Skurlatov et al. 1983). We illustrate the concept from a theoretical point of view, for which no experimental data are needed.

Water samples are frequently put in flasks (volume varies from 250 to 1,000 ml) under solar illumination for incubation (e.g., Cooper et al. 1988; Kieber et al. 1990; Mopper et al. 1991; Moffett and Zafiriou 1993). For simplicity, we consider a single wavelength (e.g., 330 nm) at which the maximum CDOM photolysis rates occur. Assume that solar irradiance ( $E(0)$ , mol photons m<sup>-2</sup> s<sup>-1</sup> nm<sup>-1</sup>) is incident from upper hemisphere directions only and that the effective pathlength is  $L$  (schematic shown in Fig. 1; we use 1, 5, and 10 cm for  $L$  to show the difference). The formula for photoproduction (a rate,  $\eta$  [mol molecules m<sup>-3</sup> s<sup>-1</sup> nm<sup>-1</sup>]) is  $E(0)\phi a_{\text{CDOM}}[1 - \exp(-aL)]/(aL)$ . Normalizing  $\eta$  to  $a_{\text{CDOM}}$  yields  $\eta' = \eta/a_{\text{CDOM}} = E(0)\phi[1 - \exp(-aL)]/(aL)$ . Figure 2 was obtained assuming that  $a_{\text{CDOM}}$  varied between 0.1 m<sup>-1</sup> for clear ocean waters and 100 m<sup>-1</sup> for river waters (e.g., the Suwannee River, Miller and Zepp 1995) and knowing  $a_w$  (330 nm) = 0.0678 m<sup>-1</sup> (Smith and Baker 1981).

Figure 2 shows that for a constant  $\phi$ , normalization to  $a_{\text{CDOM}}$  results in different  $\eta'$  for different  $a_{\text{CDOM}}$ , a consequence of the inner filter effects. Hence,  $\eta'$  does not yield information about  $\phi$  unless  $a_{\text{CDOM}}$  is small. On the other hand, ratios of  $\eta'$  among samples change with sample size if  $a_{\text{CDOM}}$  is large and different among samples. For example,

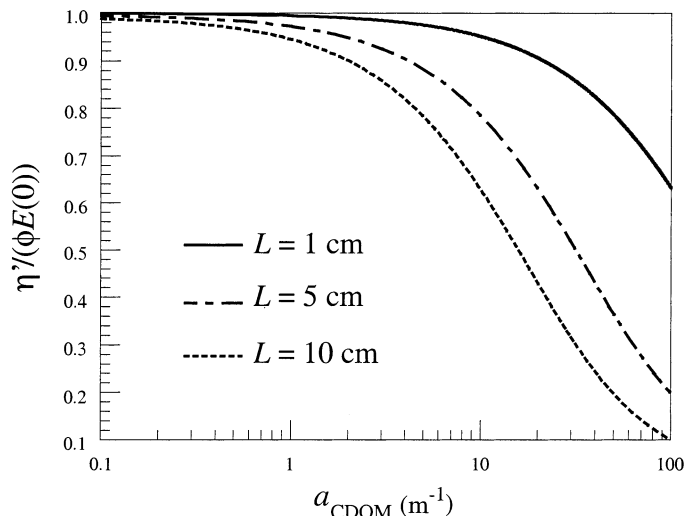


Fig. 2.  $\eta'/(a_{\text{CDOM}}\phi E(0))$  ( $\eta'$  normalized to  $a_{\text{CDOM}}$  and to  $\phi E(0)$ ) as a function of  $a_{\text{CDOM}}$  (m<sup>-1</sup>). The pathlength ( $L$  in Fig. 1) is set to 1, 5, and 10 cm, respectively, to show the difference. The illustration is for a single wavelength at 330 nm. For other UV wavelengths, the results are nearly identical.

if two samples have  $a_{\text{CDOM}}$  of 1 m<sup>-1</sup> and 10 m<sup>-1</sup>, respectively, the ratio of  $\eta'$  is 0.96 for a 1-cm pathlength, 0.81 for a 5-cm pathlength, but 0.66 for a 10-cm pathlength. Thus, even if relative response among samples is to be obtained, a dilution is required to make  $a_{\text{CDOM}}$  small and comparable among samples (Valentine and Zepp 1993). In these cases,  $\eta$ (undiluted) is  $\eta$ (diluted) times the dilution factor. However, this  $\eta$ (undiluted) should only be applied to samples with pathlengths divided by the dilution factor. In a practical example, the corresponding depth of near-surface samples in Valentine and Zepp (1993, table 1) should have been about 20 times smaller for the Suwannee River than for the Intracoastal Waterway because of their different  $a_{\text{CDOM}}$  values and the different dilution factors used.

Another way to correct for the inner filter effects is to use correction curves similar to those in Fig. 2 (i.e., the rates should be normalized to  $a_{\text{CDOM}}[1 - \exp(-aL)]/(aL)$  instead of  $a_{\text{CDOM}}$ . To facilitate comparison between independent studies, it is also a good practice to further normalize the rates to the incident light  $E(0)$  to eliminate differences caused by illumination conditions. For photochemical or photobiological processes in which the action spectra or quantum yield spectra are very similar, such normalization yields data proportional to the apparent quantum yield,  $\phi$ . For optically thick samples, this approach is preferred over the dilution method (Valentine and Zepp 1993) because one must be concerned about the effects of changing photoreactant (e.g., CDOM) concentration on the quantum yield (e.g., Zepp et al. 1981; Skurlatov et al. 1983). However, at least as far as photoproduction of DIC, CO, and photobleaching of CDOM are concerned, the currently available data indicate that dilution effects on apparent quantum yields are not large.

For a short pathlength ( $\approx$  centimeters), photoproduction rate is not proportional to  $a_{\text{CDOM}}$  if  $a_{\text{CDOM}}$  is significantly larger than 1 (Fig. 2). Moran and Zepp (1997, p. 1313) normalized previously reported rates to a "DOC concentration

of 83  $\mu\text{M C}$  and absorption coefficients of 5.5  $\text{m}^{-1}$  ( $\text{abs}_{300}$ ) and 2.7  $\text{m}^{-1}$  ( $\text{abs}_{350}$ ).” The Delaware Bay sample of Mopper and Stahovec (1986) had DOC concentrations of 2.4 mg C  $\text{L}^{-1}$ , corresponding to  $\text{abs}_{300} = 13.25 \text{ m}^{-1}$  (1 mol C = 12 g). The size of the flask used to measure production rates was not reported, but even a 3-cm pathlength would make the sample optically thick. The production rate of a sample with  $\text{abs}_{300} = 5.5 \text{ m}^{-1}$  is therefore not a cross product of the sample rate with  $\text{abs}_{300} = 13.25 \text{ m}^{-1} \times 5.5/13.25$ . This is one of the causes of large uncertainties in their normalized data, as addressed in their discussions. Note that this is different from the methodology described in Valentine and Zepp (1993), where the original rate can be a cross product of the measured rate of the diluted sample times the dilution factor because the sample was measured in an optically thin system.

The normalized DIC production rate of Suwannee River water (*see* SRWa in table 2 in Miller and Zepp 1995) was estimated as being 0.36  $\mu\text{M m h}^{-1}$ , where  $a_{\text{CDOM}}$  at 350 nm ( $a_{350}$ ) was 110.2  $\text{m}^{-1}$ . A diluted sample showed 0.63  $\mu\text{M m h}^{-1}$  (SRWh), where  $a_{350} = 34.1 \text{ m}^{-1}$ . This difference can be explained simply by the inner filter effects described above and shown in Fig. 2. For a pathlength of centimeters, Fig. 2 suggests that the normalized rate at  $a_{350} = 34.1 \text{ m}^{-1}$  is more than twice as much as at  $a_{350} = 110.2 \text{ m}^{-1}$  (not shown on the graph, but it is slightly less than that at  $a_{350} = 100 \text{ m}^{-1}$ ).

Figure 2 is based on a single wavelength at 330 nm, but in reality, the full solar spectrum should be used. Assuming  $a_{\text{CDOM}}(\lambda)$  and  $\phi(\lambda)$  decrease exponentially with increasing  $\lambda$ , similar calculations can be performed by integrating  $E(0)\phi a_{\text{CDOM}}[1 - \exp(-aL)]/(aL)$  over the wavelength range. The results are similar to those in Fig. 2 because most of the photoproduction occurs in the UV-B region (Moran and Zepp 1997).

The above analysis shows that if normalization to  $a_{\text{CDOM}}$  is to be performed, three experimental conditions must be satisfied in order to make the results applicable for general studies: (1)  $a_i \times L \ll 1$ ; (2) photobleaching rate among samples is comparable, if significant photobleaching occurs after extensive illumination; and (3) functionality of  $a_{\text{CDOM}}$  and  $\phi$  versus wavelength is comparable among samples when illuminated with a wide spectral range.

In addition, the illumination condition (incident light intensity and the spectral composition) should be considered when comparing results from independent studies.

The key condition is (1) above, which is the concept of an optically thin medium. This is required to minimize the inner filter effects and is critical for accurate estimation of other quantum yield parameters. For example, eq. 3.6 in Blough and Green (1993, p. 35) used an absorbance ratio between the sample and quinine sulfate standard to derive quantum yield. The underlying message is that absorbance of both the sample and the standard must be very small (at least  $<0.1$ ). For example, it may be as low as  $\leq 0.02$  (*see* p. 800 in Calvert and Pitts 1966).

For an optically thick system, the principles to determine  $\phi$  have been described and practiced elsewhere (e.g., Morowitz 1950; Balzani and Carassiti 1970; Skoog and West 1971; Zepp 1978, 1982; Cooper et al. 1988; Moore et al. 1993; Scully et al. 1996; Miller 1998; Zepp et al. 1998),

where formulas similar to Eq. 1 are used. For such systems, a mixing procedure is also required to avoid transport limitations on the kinetics caused by severe inner filter effects.

If uncommon sample cells or cuvettes are used (e.g., spheres), the situation is more complicated than that shown above. In such cases, the approach of Vähätalo et al. (2000) is recommended for error estimates. They mathematically dissected the sample into many thin layers. To determine whether the system is optically thin, however, such rigorous treatment is often not necessary because a rough estimate of the optical pathlength, combined with the absorption coefficient of the sample, can usually yield enough information for such determinations. The conclusion is the same, however: sample response can be normalized to absorption coefficient or absorbance only when the above conditions are met, and particularly only when the data have been properly analyzed as described above to take into account inner filter effects. Otherwise, large uncertainties may be introduced in any attempt to apply the derived relative response among samples for other studies, as has sometimes been the case in the published literature (as shown above).

The discussions and illustrations above are for laboratory experiments only. For in situ experiments in ocean or lake waters, procedures similar to those of Vähätalo et al. (2000) are recommended to estimate the spectral light availability at depth and the spectral quantum yield.

### Concluding remarks

We want to emphasize that the objective of this commentary is to demonstrate the common ambiguity in the use of optical terms in aquatic science experiments. This should alert researchers of possible consequences caused by the ambiguous and inexact use of some basic optical concepts. By no means do these observations diminish the significance of the work of the authors cited.

We find that small errors, such as the use of inappropriate units and inconsistencies in citing references and in the presentation of results, are frequent in the peer-reviewed literature. Many of these errors are obvious and a reader will correctly interpret the results and conclusions if they are careful and erudite. More importantly, many such errors do not affect our understanding of the results. However, inappropriate use of the absorbance and absorption coefficient in calculating other quantities creates difficulty in interpretation of results and can lead to erroneous conclusions, particularly when errors cannot be estimated. Normalization of the production rate to the absorption coefficient is appropriate only when the sample is either optically thin or corrected for the inner filter effects using curves similar to those in Fig. 2. Because of the ambiguity of the absorbance and absorption coefficient terms in several studies, it is difficult to estimate uncertainties in their results. Exposing water samples to solar radiation is a simple, quick, and useful way to estimate photoproduction rates, but caution must be used when interpreting the results.

A question that surfaces in reading these studies is: Will the quantum yields or action spectra derived from different experiments change with the cell pathlength? It is important

to note that absorbance is not the fraction of incident light absorbed, absorption coefficient ( $a$ ,  $m^{-1}$ ) is not the fraction of incident light absorbed per meter although the unit is  $m^{-1}$ , and absorption coefficient is not absorbance normalized to a 1-m pathlength unless the adjective “decadic” is used. However, as discussed above, although not recommended, these optical terms can certainly be defined in other nonstandard ways if they are defined clearly and used consistently in any given article.

Following the uniform use of the nomenclature and symbols among optical oceanographers, we do recommend that the term “absorption coefficient” (symbol  $a$  and in Napierian form,  $m^{-1}$ ) be used to reduce the possible ambiguities. There is no uniform symbol for the term “absorbance.” Kirk (1994) and Mobley (1994) recommended the symbol  $D$ , but even among optical oceanographers its use is rare because the absorption coefficient  $a$ , as an inherent optical property, is always preferred. In the ocean optics protocols recommended for optical oceanographers (Fargion and Muller 2000), absorbance is expressed with the symbol OD, a self-explaining symbol because absorbance is also called optical density. The symbol  $A$  (sometimes Abs) is widely used in the field of photochemistry and photobiology; however, in the physics of radiation, and for over a century,  $A$  has been used for absorptance. Because absorbance depends on pathlength, it is a good practice to use the absorption coefficient rather than absorbance. In the end, no matter what form is used, it is the physical meaning rather than the term or the symbol that explains the results and phenomena.

The production rates derived by exposing bulk samples to solar illuminations (or simulated solar illuminations) are rough and relative estimates because of variation in the absorption coefficient of the samples and also because of the wavelength range and photobleaching effect involved. It is often unclear whether the rates published can be used for other studies or not, mainly because the absorption properties of the samples are unclear (particularly, there is a demonstrable ambiguity between what authors consider absorbance and absorption coefficients in many studies). Alternatively, these properties are simply unknown (e.g., Kieber et al. 1997). This leads to the apparently simple problem of not knowing whether a 250-ml flask will yield the same rate as a 500-ml flask. Furthermore, such results cannot be directly applied to the oceans because the spectral composition of light changes with depth due to the selective attenuation of light by oceanic waters. However, if the spectral quantum yield  $\phi(\lambda)$  is assumed independent of photobleaching and independent of depth (Vähätalo et al. 2000), once the spectral surface irradiance is measured or modeled, oceanic photoproduction per unit area per unit time can be derived easily because UV light (the most productive spectral region, Kieber et al. 1990; Moran and Zepp 1997) is absorbed almost entirely by CDOM. Note that CDOM concentration or the absorption coefficient is not required in this calculation; therefore, the uncertainties associated with CDOM estimates from either field or satellite data (e.g., Hu et al. in press) are eliminated. This is different from carbon fixation by phytoplankton, because the absorption maximum of phytoplankton pigment is  $\sim 440$  nm, and photons at this wavelength are absorbed not only by phytoplankton but also

by CDOM and other detrital particles in marine environments. The photochemical production of DIC provides another, and potentially very large, pathway besides photosynthesis and respiration for carbon cycling in the ocean. Hence, correct use and understanding of the optical terms is necessary to reduce errors in quantifying the processes.

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