

# Lambert-Beer law in ocean waters: optical properties of water and of dissolved/suspended material, optical energy budgets

Robert H. Stavn

The role of the Lambert-Beer law in ocean optics is critically examined. The Lambert-Beer law and the three-parameter model of the submarine light field are used to construct an optical energy budget for any hydrosol. It is further applied to the analytical exponential decay coefficient of the light field and used to estimate the optical properties and effects of the dissolved/suspended component in upper ocean layers. The concepts of the empirical exponential decay coefficient (diffuse attenuation coefficient) of the light field and a constant exponential decay coefficient for molecular water are analyzed quantitatively. A constant exponential decay coefficient for water is rejected. The analytical exponential decay coefficient is used to analyze optical gradients in ocean waters.

## I. Introduction

The deep clear ocean waters cover 60% of the earth's surface and are a dominant factor in the energy storage and exchange at the earth's surface. In the clear open ocean the fate of the visible portion of the radiant flux at the air-water interface (about one-half of the total radiant flux) is profoundly influenced by the optical properties of molecular water as opposed to turbid hydrosol systems where the optical properties of suspended or dissolved matter are generally of greater importance. Molecular water is also important in continental slope waters in the longer wavelength region ( $520\text{ nm}^+$ ) of the visible spectrum.<sup>1</sup>

The optical properties of the ocean vary over space and time; this paper proposes an optical energy budget for analyzing the effect of the variation in these optical properties on the energy budget of the upper and near-surface ocean layers. The near-surface region is most important for heat storage and exchange with the atmosphere, and there is growing interest in the effect of optical properties of the ocean on this process.<sup>2,3</sup> The optical energy budget proposed here is derived from

the Lambert-Beer law<sup>4</sup> and the three-parameter model of the submarine light field.<sup>5-7</sup> This budget is applicable to all natural hydrosols; but we confine our attention to the open ocean waters, the optical properties of water and dissolved/suspended material, and the effects of optical gradients on the energy budget. The key factor in constructing an optical energy budget is the ability to extract a true Lambert-Beer absorption coefficient from a diffuse light field as is done routinely with the three-parameter model. Knowing the total absorption coefficient at any point, we can linearly partition it into components due to water and dissolved/suspended matter (material both in solution and suspension). The Lambert-Beer law allows the determination of the absorption coefficient of suspended matter by difference with the total absorption coefficient and the absorption coefficients of material in true solution, mostly the products of the decomposition of organic matter.

It is common in optical oceanography to construct optical energy budgets and estimate the concentration of dissolved/suspended material by calculating empirical optical coefficients from partial measurements of the submarine light field. The usual measurement is the downwelling irradiance  $E_d$ , and the empirical exponential decay coefficient (diffuse attenuation coefficient)  $K_d$  is calculated from it. The  $K_d$  coefficient is then partitioned linearly like a true Lambert-Beer coefficient with the downwelling irradiance assumed to be an adequate measure of the submarine light field. The assumption that the  $K_d$  coefficient has a Lambert-Beer quality to it has been criticized by Morel and Bricaud<sup>8</sup> who assert that this assumption is wrongly

When this work was done the author was with Naval Ocean Research & Development Activity, National Space Technology Laboratories, Mississippi 39529-5004; he has now returned to University of North Carolina, Biology Department, Greensboro, North Carolina 27412.

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invoked and is only an approximation. The rationale for this assumption dates back at least to Riley<sup>9</sup> and probably earlier. A further assumption is that of a constant optical coefficient  $K_w$ , an exponential decay coefficient for molecular water. Heretofore these assumptions have not been analyzed or tested. The three-parameter model provides the basis for quantitatively estimating the consequences of assuming a Lambert-Beer quality to  $K_d$  and a constant  $K_w$  in addition to providing the basis for a universal optical energy budget.

## II. Theory

We shall first construct an optical energy budget employing the three-parameter model<sup>7</sup> and the linear partitioning of true Lambert-Beer absorption coefficients. Then we shall analyze the routine assumptions about the downwelling irradiance and its empirical exponential decay coefficient.

The three-parameter model of the submarine light field is a mathematical reduction of the actual light field to easily measured irradiances, which makes it mathematically equivalent to the actual light field. It allows the simplest valid adaptation of the Lambert-Beer law to a diffused 3-D light field and the derivation of a radiative transfer equation for the light field with an analytical, not an empirical, exponential decay coefficient. This coefficient is the ratio of the Lambert-Beer absorption coefficient and an expression for the mean path of penetration of the submarine light field. All measurements and parameters discussed in this paper are assumed a function of wavelength. The model consists of the downwelling vector irradiance  $E_z$ , scalar irradiance  $E_0$ , and the average cosine  $\bar{\mu}$ . The downwelling vector irradiance is the difference between the downwelling irradiance  $E_d$  and the upwelling irradiance  $E_u$  which yields the net radiant flux per unit area penetrating the hydrosol. The scalar irradiance is the total radiant flux at a point measured by a spherical collecting surface. The average cosine is the average of the cosine for the zenith angle of each radiance vector of the submarine light field, weighted by the magnitude of the radiance vector. The average cosine is also the reciprocal of the mean path of penetration of the submarine light field through the marine hydrosol.<sup>10</sup> The components of the model are related as follows:  $E_z/E_0 = \bar{\mu}$ .

The construction of an optical energy budget starts with Gershun's equation<sup>11,12</sup>:

$$\frac{dE_z}{dz} = -aE_0, \quad (1)$$

where  $z$  is the geometrical depth in meters and  $a$  is the Lambert-Beer absorption coefficient. Substituting the three-parameter model for  $E_z$  yields a general radiative transfer equation,<sup>5</sup> while substituting the model for  $E_0$  yields an energy budget equation, which requires net radiant flux terms

$$\frac{dE_z}{dz} = -\frac{a}{\bar{\mu}} E_z. \quad (2)$$

This substitution also gives us the analytical exponential decay coefficient ( $a/\bar{\mu}$ ) for the general radiative transfer equation; this coefficient is used for the analysis of the optical properties of the open ocean and their relationship to the optical energy budget. From the Lambert-Beer law it follows that the absorption coefficient can be partitioned linearly into  $n$  components which may be in solution or suspension and that separately absorb light energy:

$$a = a(1) + a(2) + \dots + a(n),$$

and substituting into Eq. (2),

$$\frac{dE_z}{dz} = -\frac{[a(1) + a(2) + \dots + a(n)]}{\bar{\mu}} E_z. \quad (3)$$

The derivative with depth of the energy absorbed from the multicomponent system due to component 1 is then

$$\frac{dE_z^1}{dz} = -\frac{a(1)}{\bar{\mu}} E_z. \quad (4)$$

The differential fraction of the total energy absorbed attributable to component 1 is

$$\frac{dE_z^1/dz}{dE_z/dz} = \frac{-[a(1)/\bar{\mu}]E_z}{-a/\bar{\mu}E_z} = \frac{a(1)}{a}, \quad (5)$$

and the differential of the energy absorbed by component 1 is

$$dE_z^1 = [a(1)/a] dE_z.$$

To obtain the energy absorbed by component 1 in the interval  $\Delta z = z_2 - z_1$  we integrate between  $z_1$  and  $z_2$ , where  $a$  is constant or nearly so in the interval

$$\int_{z_1}^{z_2} dE_z^1 = [a(1)/a] \int_{z_1}^{z_2} dE_z = [a(1)/a] [E_z(z_1) - E_z(z_2)]. \quad (6)$$

This equation is general and valid for all natural hydrosols.

So far we have investigated the Lambert-Beer absorption coefficient  $a$ , the analytical exponential decay coefficient of the submarine light field ( $a/\bar{\mu}$ ), and the general energy budget equation. Consider now the empirical optical coefficients used in optical oceanography and the attempts to approximate these analytical relationships with them. Initially, it is assumed that the downwelling irradiance  $E_d$  is a valid approximation of the net radiant flux penetrating the hydrosol. An empirical exponential decay coefficient is then determined:

$$\frac{dE_d}{E_d dz} = -K_d. \quad (7)$$

The  $K_d$  coefficient is also called the diffuse attenuation coefficient. We see that the function of  $K_d$  is similar to that of  $a/\bar{\mu}$  in Eq. (2), but it is empirical and cannot be analyzed further into fundamental optical parameters from the information that is used to define it. The empirical  $K_d$  coefficient is useful for interpolating  $E_d$  values within a depth interval. However, it is assumed that the  $K_d$  coefficient can be partitioned linearly in the way that the analytical coefficient  $a/\bar{\mu}$  was parti-

tioned in Eq. (3) based on the Lambert-Beer law. The linear partitioning often takes the form

$$K_d = K_w + K_c, \quad (8)$$

where  $K_w$  is an exponential decay coefficient for water and  $K_c$  is an exponential decay coefficient for dissolved/suspended matter in hydrosol.<sup>9</sup> From now on an optical coefficient for water is given a  $w$  subscript, and an optical coefficient for dissolved/suspended matter is given a  $c$  subscript. Furthermore, it has been assumed that  $K_w$  is constant, which preserves a formal similarity to the Lambert-Beer law, where  $a_w$  is the known constant absorption coefficient for molecular water. On the assumption that the  $K_d$  coefficient can be treated like a true Lambert-Beer coefficient,  $K_d$  can be substituted for  $a$  and  $K_w$  can be substituted for  $a(1)$  in Eq. (6), while  $E_d$  can be substituted for  $E_z$  to yield for the interval  $\Delta z$

$$\text{energy abs.} \approx (K_w/K_d)[E_d(z_1) - E_d(z_2)], \quad (9)$$

an approximation for the energy absorbed by water in a multicomponent system. The approximation of the energy absorbed by dissolved/suspended material is obtained by substituting  $K_c$  for  $a(1)$ . Equation (9) is a variant of a form proposed by Tyler<sup>13</sup> with superficial similarity to Eq. (6). Sometimes the energy absorbed per unit volume is estimated with Eq. (1), and the fact that it is a differential equation is ignored. However, the relationship is a derivative, does not refer to an actual volume, and must be integrated over a unit depth to estimate energy absorbed per unit volume. One need only consider what happens to Eq. (1) when the absorption coefficient is  $>1$  and the law of conservation of energy appears to be violated.

To assess quantitatively the consequences of the assumptions of Eq. (8) an analytical expression for  $K_d$  expressed in fundamental optical terms is required. An exact expression can be derived from Schellenberger,<sup>14</sup> which is

$$K_d = (a/\bar{\mu})(1 - R) + RK_w, \quad (10)$$

where  $R$  is the irradiance ratio  $E_u/E_d$  and  $K_u$  is the empirical exponential decay coefficient for the upwelling irradiance  $E_u$ . It must be emphasized that more information about the light field is required than the simple downwelling irradiance to perform the analysis of Eq. (10). The ratio  $R$  varies from  $\sim 1$  to 7% in clear ocean waters,<sup>15</sup>  $K_u$  is the same order of magnitude as  $K_d$ , and thus  $K_d \approx (a/\bar{\mu})$ . In other words we can approximate  $K_d$  with the analytical exponential decay coefficient of the three-parameter model. This approximation of Eq. (10) has been tested with the model of Plass *et al.*<sup>16</sup>; the usual deviation of  $K_d$  from  $a/\bar{\mu}$  is in the range of 0.5%, and the maximum deviation for the optical properties modeled for clear ocean water is 1.8%. This approximation of Eq. (10) also allows us to approximate  $K_w$ . The  $K_w$  coefficient has been defined as constant, and the absorption coefficient for water is a known constant. Therefore, a constant mean cosine is associated with the  $K_w$  coefficient, which we can call

Table I. Optical Water Types and Sampling Stations

Station	Position	Optical water type
J2	N 38° 20', E 09° 31'	IA
J1A	N 39° 17', E 09° 42'	IB
A	N 36° 00', W 04° 30'	II

$\bar{\mu}_w$ . We determine this coefficient by  $\bar{\mu}_w = a_w/K_w$ . However, the theoretical results of Plass *et al.*<sup>16</sup> and all observations to date indicate that the average cosine of the submarine light field is not constant but decreases in general with depth due to multiple scattering. Layers of dissolved/suspended material if they are highly absorbing can reverse this trend temporarily, but it is still true as a trend over the entire water column. Thus we see that there is a systematic error built into the concept of a constant  $K_w$ ; and it is important to determine how it affects our estimates and calculations. We can analyze the systematic errors incorporated into the assumptions about  $K_d$  and  $K_w$  by substituting  $(a/\bar{\mu})$  for  $K_d$  and  $(a_w/\bar{\mu}_w)$  for  $K_w$  in Eq. (8):

$$K_c = (a/\bar{\mu}) - (a_w/\bar{\mu}_w)$$

or

$$K_c = \frac{[a - (\bar{\mu}/\bar{\mu}_w)a_w]}{\bar{\mu}}, \quad (11)$$

and, therefore, we require measurements of the three-parameter model for the analysis. In essence,  $K_c$  is supposed to be an approximation to  $a_c (= a - a_w)$ ; but it is apparent that  $K_c$  is a function of  $a_c$  and the average cosine of the light field, i.e., the radiance distribution.

### III. Results

Data from Høgerslev<sup>17</sup> represent a complete set of measurements of downwelling, upwelling, and the scalar irradiances for several wavelengths from sampling stations established in the Mediterranean (Table I). Error estimates were given by Høgerslev. These were applied, where appropriate, to various optical coefficients by linear error analysis.<sup>18</sup> The most complete data sets for all the stations sampled were for the wavelengths of 427 and 532 nm. These wavelengths were chosen for further analysis. Høgerslev identified the water masses sampled as the optical water types IA, IB, and II after Jerlov's classification.<sup>19</sup> The progression represented by this series is from most transparent (IA) deep ocean water to least transparent (II) deep ocean water. The irradiance information from these measurements allows the evaluation of Eqs. (6) and (11) so that we can construct optical energy budgets for each water type and also test the assumptions about the empirical coefficient  $K_d$  and the supposed constant  $K_w$ . For this analysis the optical constant  $a_w$  and  $K_w$  values for water were taken from the tables of Smith and Baker.<sup>20</sup>

Consider first the nature of the exponential decay coefficients. The tabled optical constants for water were chosen as close as possible to Høgerslev's reported

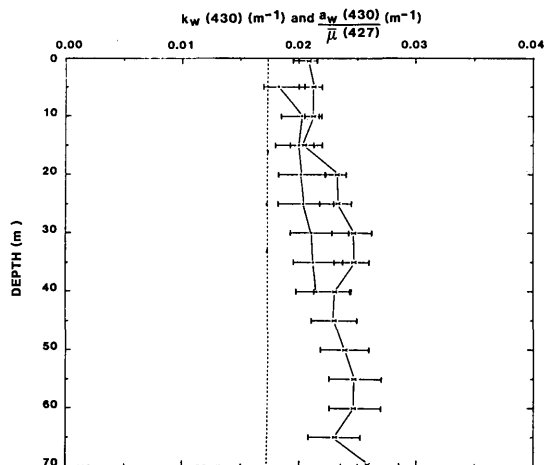


Fig. 1. Comparison of exponential decay coefficient for water types IA,  $a_w(430)/\bar{\mu}(427)$  (×), and II,  $a_w(430)/\bar{\mu}(427)$  (●), with supposed constant exponential decay coefficient for water,  $K_w(430)$  (---). Horizontal lines represent error limits.

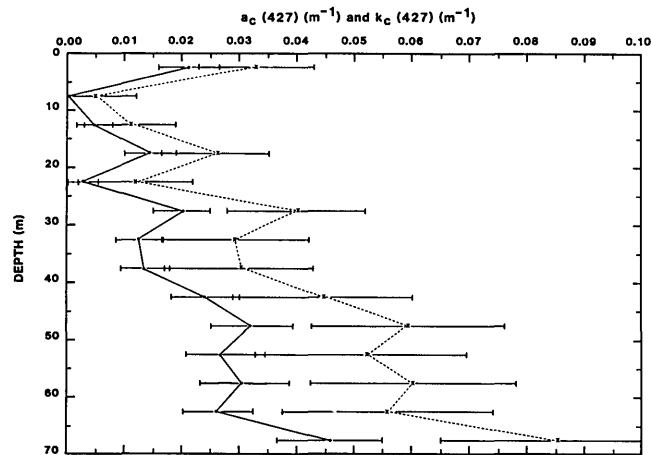


Fig. 3. Concentration of dissolved/suspended material with depth inferred from absorption coefficients  $a_c$  (●) and empirical exponential decay coefficients  $K_c$  (×) for water type IA, 427 nm. Horizontal lines represent error limits.

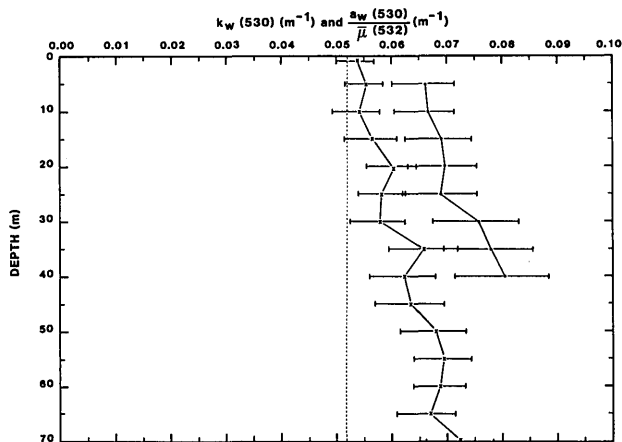


Fig. 2. Comparison of exponential decay coefficient for water types IA,  $a_w(530)/\bar{\mu}(532)$  (×), and II,  $a_w(530)/\bar{\mu}(532)$  (●) with supposed constant exponential decay coefficient for water,  $K_w(530)$  (---). Horizontal lines represent error limits.

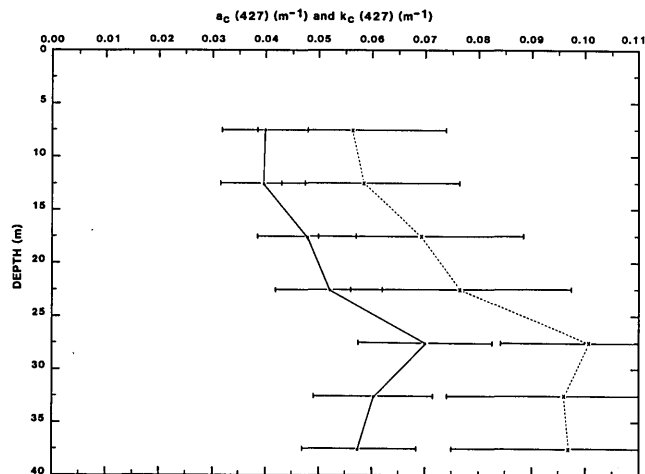


Fig. 4. Concentration of dissolved/suspended material with depth inferred from absorption coefficients  $a_c$  (●), and empirical exponential decay coefficients,  $K_c$  (×), for water type II, 427 nm. Horizontal lines represent error limits.

wavelengths. Interpolation of optical constants from tabled values did not add substantially to the analysis presented here because the tabled values never differed by more than 3 nm from the wavelengths reported by Højerslev. To evaluate how well the  $K_w$  coefficient approximates the actual exponential decay of the light field due to water, we have in Figs. 1 and 2 a comparison of  $K_w$  with the true exponential decay coefficient for water  $a_w/\bar{\mu}$  (types IA and II waters). These two water types represent the extremes of the data. In Fig. 1 all the measured exponential decay coefficients for water type IA were greater than  $K_w(430)$ , while only one coefficient from water type II included  $K_w(430)$  within its range of error. This point was near the surface. All the measured exponential decay coefficients for water type II were greater than  $K_w(530)$  in Fig. 2, while for water type IA only the coefficients of the top 15 m included  $K_w(530)$  within

the range of error. Thus the occasional agreement of  $a_w(530)/\bar{\mu}(532)$  with  $K_w(530)$  was only in the surface layers, and there was no agreement at all below 15 m for any measurement. At the shorter wavelengths (Fig. 1) there is virtually no agreement between  $a_w/\bar{\mu}$  and  $K_w$ , while at the longer wavelengths (Fig. 2) there is poor agreement near the surface for water type IA and no agreement at all for the coefficients of water type II. The source of the systematic error in the use of  $K_w$  as the exponential decay coefficient for water is the variation in  $\bar{\mu}$  between water types and its general decrease with depth for all water types. Thus the systematic error in  $K_w$  causes a greater and greater underestimate of the exponential decay of light due to water as the depth becomes greater and greater. Other systematic errors are due to the individual nature of the average cosine  $\bar{\mu}$  for the different water types. Figures 3 and 4, with data at 427 nm from water types IA and II, illus-

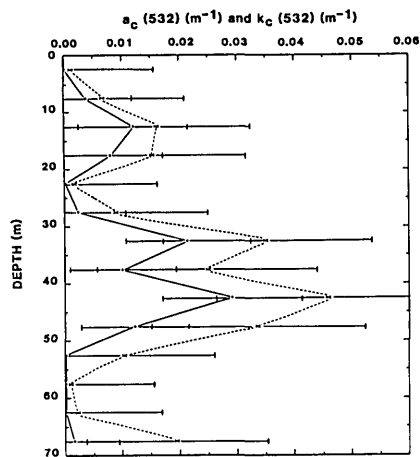


Fig. 5. Concentration of dissolved/suspended material with depth inferred from absorption coefficients  $a_c$  (●) and empirical exponential decay coefficients  $K_c$  (×) for water type IA, 532 nm. Horizontal lines represent error limits.

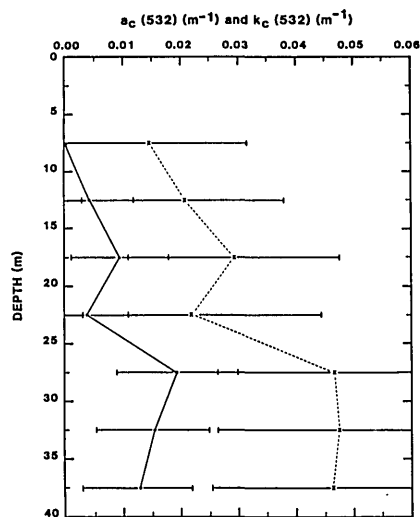


Fig. 6. Concentration of dissolved/suspended material with depth inferred from absorption coefficients  $a_c$  (●) and empirical exponential decay coefficients  $K_c$  (×) for water type II, 532 nm. Horizontal lines represent error limits.

trate two ways to estimate the concentration of dissolved or suspended matter: the differencing of true Lambert-Beer absorption coefficients and the differencing of Eq. (8). The estimates of dissolved/suspended matter for comparable depths are greater in the type II waters than in the type IA waters, which is to be expected for the less transmissive type II water. The estimate of the amount of dissolved/suspended matter from Eq. (8) is always greater than that determined from the true Lambert-Beer absorption coefficients. The measured value of  $K_c$  is predicted by Eq. (11) at each depth from the information on  $a$  and  $\bar{\mu}$  at that depth, and the measured error in  $K_c$  is also predicted by Eq. (11) from the error variation in  $a$  and  $\bar{\mu}$ . Similar results are seen in Figs. 5 and 6 with the observation that the error variance was so high in the type IA

water that the estimates often include zero in the error range and make it difficult to draw reliable conclusions about the vertical variation of dissolved/suspended matter with this particular data set.

Optical energy budgets calculated by Eqs. (6) and (9) in Table III allow comparison of trends in the energy budgets attributable to the systematic errors inherent in Eq. (9) and comparison of the optical energy budgets with the optical gradient in Table II. The two equations were evaluated over 5-m depth increments, and the results for the increments were summed over the top 40 m to be able to compare all stations. The deviation of the estimated budget [Eq. (9)] from the true budget [Eq. (6)] is defined as  $\Delta\% = 100 [(\text{estim.} - \text{true})/\text{true}]$ . In the 427-nm wavelength region we see that Eq. (9) consistently underestimates the contribution of water to the energy budget by 12–18%. At low concentration of dissolved/suspended matter (water type IA, Table II), the contribution of this material to the energy budget is overestimated by ~51%, and this overestimate decreases as the concentration of dissolved/suspended matter increases (Table II), reaching 7% for water type II. In the wavelength region of 532 nm we can only make reliable calculations for water type II due to the low concentrations and high error variance in the estimates of optical coefficients for dissolved/suspended matter in water types IA and IB. In this longer wavelength region the underestimate of the contribution of water to the energy budget is similar in magnitude (23%) to the underestimates at 427 nm from Eq. (9), but the overestimate of the contribution of dissolved/suspended matter to the energy budget is now 227%. The deviations of estimated energy absorption [Eq. (9)] from true energy absorption [Eq. (6)] for the two wavelengths reflect the optical differences for those wavelengths. The molecular water is the major component of the absorption coefficient and dominates the optical energy budget at 532 nm, accounting for 90% of the absorbed energy for water type II. At 427 nm molecular water dominates only for water type IA, accounting for over 63% of the energy absorbed, then decreases in importance for the other two water types to reach 24% of the budget for type II waters. Another notable trend in Table III is the consistent overestimate of the total energy budget from the use of Eq. (9). Variations in energy absorbed due to layering of dissolved/suspended material are investigated in Table IV. This vertical profile had the next to lowest deviation between Eqs. (6) and (9) for energy absorbed by dissolved/suspended material for the entire water column. However, in individual layers the deviation from the true value with Eq. (9) can still be as high as 200% as is indicated for the 5–10-m interval. It must be emphasized here that we are seeing trends due to systematic error regardless of the variability of individual estimates due to experimental error.

#### IV. Discussion

The results demonstrate the use of an optical energy budget of general validity and applicability when ade-

Table II. Optical Properties of Water and Water Types at Specified Wavelengths

Optical water type	Absorption coefficient: water	Mean absorption coefficient: dissolved/suspended (Surface, 40 m)	Range of average cosines: (surface, 40 m)	Average cosine from $K_w$	Absorption coefficient: water	Mean absorption coefficient: dissolved/suspended (surface, 40 m)	Range of average cosines: (surface, 40 m)	Average cosine from $K_w$	Range of average cosines: (surface, 40 m)
IA	$a_w(430)$ 0.0144	$[a(427)-a_w(430)]$ 0.0111	$\bar{\mu}(427)$ 0.713-0.629 <sup>b</sup>	$\bar{\mu}_w(430)$ 0.837	$a_w(530)$ 0.0507	$[a(532)-a_w(530)]$ 0.0036 <sup>a</sup>	$\bar{\mu}(532)$ 0.948-0.771 <sup>c</sup>	$\bar{\mu}_w(530)$ 0.977	$\bar{\mu}(532)$ 0.948-0.771 <sup>c</sup>
IB	0.0144	0.0163	0.764-0.662	0.837	0.0507	0.0035 <sup>a</sup>	0.836-0.746	0.977	0.836-0.746
II	0.0144	0.0554	0.763-0.650	0.837	0.0507	0.0091	0.769-0.633	0.977	0.769-0.633

<sup>a</sup> May not differ significantly from 0.<sup>b</sup> Continues to decrease to 0.556 at 70 m.<sup>c</sup> Continues to decrease to 0.700 at 70 m.Table III. Optical Energy Budgets<sup>a</sup> at Specified Wavelengths

Optical water type		Energy absorbed: water (427 nm)	Energy absorbed: dissolved/suspended (427 nm)	Total energy absorbed (427 nm)
IA	True	26.0	15.0	41.0
	estim.	21.3	22.7	44.0
	$\Delta\%$	-18	+51	+7
IB	True	30.0	33.9	63.8
	estim.	25.5	41.5	67.0
	$\Delta\%$	-15	+22	+5
II	True	17.7	56.0	73.7
	estim.	15.5	59.9	75.4
	$\Delta\%$	-12	+7	+2

Optical water type		Energy absorbed: water (532 nm)	Energy absorbed: dissolved/suspended (532 nm)	Total energy absorbed (532 nm)
II	True	65.8	7.1	72.9
	estim.	50.7	23.2	73.9
	$\Delta\%$	-23	+227	+1

<sup>a</sup> Normalized to scalar irradiance of 100 at surface.

Table IV. Energy Absorption by Dissolved/Suspended Matter (427 nm) in Vertical Profile: Water Type IB

Depth (m)	Energy absorbed <sup>a</sup>	Estimated energy absorption <sup>a</sup>	$\Delta\%$
0.5	12.5	13.5	8.0
5.0	0.7	2.1	200.0
10.0	6.8	7.9	16.1
15.0	2.6	3.7	42.3
20.0	4.4	5.4	22.7
25.0	2.0	2.9	45.0
30.0	2.7	3.3	22.2
35.0	2.2	2.7	22.7
40.0	2.2	2.7	22.7
Total	33.9	41.5	22.0

<sup>a</sup> Normalized to scalar irradiance of 100 at 0.5 m.

quate measurements of the submarine light field are available. With the Højerslev data set and theoretical limits proposed by Plass *et al.*,<sup>16</sup> we have been able to confirm that the optical properties of water are of great importance in the open ocean; therefore, we must have adequate measurements of the submarine light field and a clear idea of the optical properties of water before we can attempt an optical analysis of deep clear ocean waters.

The use of downwelling irradiance alone and its empirical exponential decay coefficient  $K_d$  will be demonstrated as inadequate for both a qualitative and quantitative optical analysis of clear ocean waters. All empirical K coefficients have similar limitations; they are composites of both inherent optical properties (independent of the radiance distribution) and apparent optical properties (functions of the radiance distribution).<sup>12,14</sup> The  $K_d$  coefficient is, therefore, not a single or unique optical parameter [Eq. (10)], and serious problems are encountered when attempting to treat it as one that can be partitioned linearly like the Lam-

Table V. Comparison of Exponential Decay Coefficients with Absorption Coefficients for Dissolved/Suspended Matter

Water type	$K_c(427)$	$a_c(427)$	$\bar{\mu}(427)$	$\bar{\mu}_w(430)$	Depth interval $\Delta z$ (m)
IA	$0.056 \pm 0.018$	$0.026 \pm 0.006$	$0.60 \pm 0.06$	0.837	60–65
II	$0.056 \pm 0.018$	$0.040 \pm 0.006$	$0.74 \pm 0.07$	0.837	5–10

Water type	$K_c(532)$	$a_c(532)$	$\bar{\mu}(532)$	$\bar{\mu}_w(530)$	Depth interval $\Delta z$ (m)
IA	$0.046 \pm 0.020$	$0.029 \pm 0.012$	$0.81 \pm 0.06$	0.977	40–45
II	$0.046 \pm 0.021$	$0.013 \pm 0.010$	$0.64 \pm 0.07$	0.977	35–40

bert-Beer absorption coefficient [Eqs. (3) and (8)]. These difficulties become compounded when the exponential decay of the light field due to water is assumed to be caused by a constant  $K_w$ . Furthermore, the  $K_c$  coefficient then determined from Eq. (8) is divided by the concentration of dissolved/suspended matter to obtain a specific diffuse attenuation coefficient. This coefficient is used to convert measured  $K_c$  values to the concentration of dissolved/suspended matter at any region of the open ocean and the clearest coastal waters. It is apparent that treating this  $K_c$  coefficient as both a unique optical parameter and a unique indication of the concentration of dissolved/suspended matter is a dubious proposition.

The question of the uniqueness of  $K_c$  is easily examined from the data in Table V illustrated in Figs. 3–6. The  $K_c$  coefficients were determined for a 5-m increment at each of two different stations in the Mediterranean<sup>17</sup> for 427 and 532 nm, and the coefficients for the two different comparisons are apparently identical with equal error variances in each case. This implies the same concentration of dissolved/suspended matter in the two different layers at the different stations. However, the Lambert-Beer absorption coefficients  $a_c(427)$  determined for the two depth increments of the water types IA and II differ significantly. Moreover the average cosines also differ significantly. The  $a_c(532)$  coefficients for the two depth increments do overlap, but the range of the overlap is only 15% of the total range of experimental error represented by the two coefficients. The two  $K_c(532)$  coefficients are identical, and their error variances cover essentially the identical range, which is definitely not the case for the  $a_c(532)$  coefficients. The average cosine values differ significantly. Thus  $K_c$  is not a unique indicator of the concentration of dissolved/suspended matter, and we shall see presently that there is no firm theoretical basis for ascribing differences in  $K_c$  solely to differences in concentration of dissolved/suspended matter.

We can now assess the systematic errors inherent in the assumptions about  $K_c$ ,  $K_d$ , and  $K_w$  with Eq. (11) derived from the three-parameter model. Consider first the attempt to analyze for concentration of dis-

solved/suspended matter by simple differencing of  $K_d$  and  $K_w$ . In general, the data of Højerslev and the model of Plass *et al.* show that  $\bar{\mu}$  in the open ocean is less than the constant  $\bar{\mu}_w$  associated with  $K_w$  (Table II). This causes the  $\bar{\mu}/\bar{\mu}_w$  ratio in Eq. (11) to become a fraction, and it minimizes the effect of the absorption coefficient for water in the differencing for the  $K_c$  determination. The result is an overestimate of the concentration of dissolved/suspended matter. We may call this systematic error the water error. The grossest overestimates occur when  $a_w \geq a_c$ . The greater the absorption coefficient of dissolved/suspended matter the less the absorption coefficient of water affects the estimate. We still see a considerable overestimate of dissolved/suspended matter concentration up to  $a_c$  at 5 times the magnitude of  $a_w$ , however (Fig. 4, Table II). The range encountered here for the open ocean was of  $a_c$  between 5 times and  $1/6$  the magnitude of  $a_w$  (Table II). Contributing further to the overestimate is the average cosine in the denominator of Eq. (11), which is always  $<1$  and causes the systematic overestimation of dissolved/suspended matter even when the concentration is high. We may call this systemic error the radiance distribution error. An analysis of the data of Table V with Eq. (11) reveals that these two errors are definitely occurring in the optical determinations for clear ocean water. When considering the  $K_c(427)$  value of 0.056 for water types IA and II from Table V, we see that the water error appears from the reduction of  $a_w$  in the type IA layer to 72% of its actual value by the average cosine fraction, while in the type II layer  $a_w$  is reduced to 88% of its actual value. The radiance distribution error enhances the water error when the average cosine increases the estimated dissolved/suspended matter concentration by a factor of 1.7 for the type IA layer and 1.4 for the type II layer. The fact that the concentration of dissolved/suspended matter is greater in the layer of type II water than in the type IA layer causes the two systematic errors to overestimate in a complementary fashion. The result of the complementary overestimates is the spurious equality of dissolved/suspended matter concentration estimated from the

equal  $K_c$  values. The systematic overestimation built into Eq. (8) when  $\bar{\mu}_w > \bar{\mu}$  will also cause an estimate of measurable quantities of dissolved/suspended matter when none is detectable, as can be seen at 532 nm in Fig. 6. The source of this error is found again in the two systematic errors outlined above. For example, in the 10–15-m layer of Fig. 6 where the estimate of dissolved/suspended matter includes 0.0 in the error variance, the fraction  $\bar{\mu}/\bar{\mu}_w = 0.77$  for a significant water error, and  $\bar{\mu}$  for this layer is 0.75, which gives a factor of 1.3 for the radiance distribution error. Both of these errors work together to give a spurious indication of dissolved/suspended matter. The general low concentration of dissolved/suspended matter at 532 nm for the open ocean<sup>1,17,21</sup> implies that a false indication of algae containing fucoxanthin such as diatoms and brown forms may be an additional problem with the general overestimate of pigment concentration when green forms are not present. In Table II the lowest values for  $a_c(427)$  indicate similar problems for green forms in the clearest ocean waters. Moreover Arnott *et al.*<sup>1</sup> indicate a general low level of material absorbing at 532 nm in continental slope water in addition to low levels of material absorbing in the 600-nm<sup>+</sup> region for both clear ocean water and continental slope water. The previous difficulties of estimation are to be expected for inferring the presence and concentration of cyanobacteria, which contain pigments absorbing in the 600-nm<sup>+</sup> region.

Although we have identified and assessed the systematic errors inherent in the use of  $K_c$  as an indicator of the concentration of dissolved/suspended matter, it is possible to consider whether  $K_c$  could be used as an approximation to  $a_c$ . A perusal of Figs. 3, 5, and 6, which have reliable indications of the vertical variation in  $K_c$  and  $a_c$ , shows that the determinations of  $K_c$  and  $a_c$  have overlapping error variances in the upper 25 m or so of the water column and then diverge as we go deeper; Eq. (11) and Table II show us why this is so. The measured values of  $\bar{\mu}$  make their closest approach to  $\bar{\mu}_w$  in the surface layers, and thus the systematic errors delineated by Eq. (11) become smaller. However, the errors are systematic, and the overestimation from the use of  $K_c$  is always occurring. Thus the overlapping of error variances of  $K_c$  and  $a_c$  in the upper layers does not mean that an overestimate is less likely; it means that we have an overestimate that cannot be predicted or controlled without knowledge of  $\bar{\mu}$  for a given water mass. Stated another way,  $K_c$  is a function of  $a_c$ , not an approximation of it.

Considering the importance of molecular water in the optics and radiant energy transfer of clear ocean waters, we must examine carefully the contribution of molecular water to the exponential decay of the submarine light field. The analytical exponential decay coefficient ( $a/\bar{\mu}$ ) from the three-parameter model allows analysis of the contribution of the various components of the hydrosol to the exponential decay of the light field. Spectrophotometry gives us a known constant Lambert-Beer absorption coefficient for water  $a_w$ <sup>20</sup>. From Eqs. (3) and (4) we see that the exponen-

tial decay coefficient of water is  $a_w/\bar{\mu}$ . Thus the exponential decay of the submarine light field due to molecular water is a function of the average cosine  $\bar{\mu}$ , which in turn is a function of the radiance distribution of the light field. The radiance distribution of the submarine light field is affected by many factors, the initial factor being the radiance distribution of the light field external to the marine hydrosol. Gordon *et al.*<sup>22</sup> have demonstrated with their quasi-single-scattering model that the exponential decay of the submarine light field in the surface layers is definitely a function of the incident radiance distribution when considering a level sea surface. These changes in the radiance distribution of the surface layers as a function of the incident radiance distribution will be incorporated in the average cosine  $\bar{\mu}$ . In general, we expect an increase in  $\bar{\mu}$  with a near zenith sun and a decrease in  $\bar{\mu}$  with an overcast sky. This shows up as a decrease in the exponential decay due to molecular water in the surface layers with a zenith sun and an increase in the exponential decay due to water with an overcast sky. However, the nature of the radiance distribution in the surface layers is further altered by the sea state as differing configurations of surface gravity waves alter the radiance distribution by wave focusing, altered surface reflectivities, etc.<sup>23</sup> Then as the light field penetrates to greater depths multiple scattering becomes important and acts to decrease the average cosine as the radiance distribution becomes more diffused.<sup>5,19</sup> Therefore, the exponential decay due to water tends to increase on deeper penetration of the light field. Recent observations<sup>24</sup> document the existence of a deep chlorophyll maximum that may be 150 m deep in the tropical regions and becomes shallower in depth as one moves poleward until it is apparently quite near the surface in arctic seas. Complex interactions of absorption by chlorophyll and scattering by small cellular particles in these layers can further alter the radiance distribution and temporarily reverse the general trend toward the decrease of  $\bar{\mu}$  with depth. The species composition of this layer can vary seasonally as can the number density of particles depending on whether bloom conditions exist within the particle layer. Such alterations contribute to optical heterogeneity of the open ocean and have differing effects on the radiance distribution and the exponential decay due to water. It is possible to consider whether the concept of a constant  $K_w$  can be replaced with a  $K_w$  that is a function of depth. If the deep clear ocean regions were optically homogeneous and never subject to wave action or changing sky conditions such a concept might be workable. However, the results plotted in Figs. 1 and 2 indicate how complex the deep clear ocean regions really are. The exponential decay coefficient for water at 427 nm (Fig. 1) is always larger than  $K_w$  for water type IA, and only one surface point for water type II overlaps with the value for  $K_w$ . The coefficients at 532 nm show no agreement with  $K_w$  for water type II and agreement for only the upper 15 m for water type IA. It is clear that all the factors elucidated above are interacting in complex ways to give the final deter-



mination for the exponential decay coefficient due to water. When we consider further the practice of using a constant  $K_w$  for estimating the concentration of dissolved/suspended matter from  $K_d$  determinations a paradoxical situation develops because of the overestimate of dissolved/suspended matter when the exponential decay coefficient for water is greater than  $K_w$ ; an underestimate would be expected from the uncritical use of Eq. (8).

The two major sources of optical variability, creating horizontal optical gradients in the ocean, that are determinable from the analytical exponential decay coefficient ( $a/\bar{\mu}$ ) are the absorption coefficient  $a$  and average cosine  $\bar{\mu}$ . Optical gradients in the ocean can be defined in terms of changes in transparency or the change in the exponential decay coefficient ( $a/\bar{\mu}$ ) of the light field. The limiting cases for changes in optical transparency, or changes in the optical gradient, would be a gradient in  $a$  with  $\bar{\mu}$  remaining constant or a gradient in  $\bar{\mu}$  with  $a$  remaining constant. It is also possible to have an increasing gradient in  $a$  with a corresponding increase in  $\bar{\mu}$ , which gives a constant exponential decay coefficient ( $a/\bar{\mu}$ ) and thus no change in transparency. The same applies to a decreasing gradient in  $a$  with a corresponding decrease in  $\bar{\mu}$ . Although there would not be a change in transparency there would still be an optical gradient present. And there are many possible combinations of these conditions to affect the horizontal optical gradient. It is of interest to consider the effect that changes in oceanic transparency or optical gradients have on the optical energy budget. At 427 nm the change in transparency (increase in  $a/\bar{\mu}$ ) creating the gradient from water types IA to II is due to the increase in  $a_c$ , while the range of the  $\bar{\mu}$  coefficient remains nearly constant for each water type (Table II). Along this optical gradient the energy budget reflects the relative magnitudes of  $a_w$  and  $a_c$ . That is, less energy is being absorbed by water in the upper 40 m as the concentration of dissolved/suspended matter increases; and the contribution of the two components to the energy budget is proportional to  $a_w/a$  and  $a_c/a$ , respectively [Eq. (6)]. The use of Eq. (9) to estimate the optical energy budget does not reveal this trend as the underestimate of energy absorbed by water is nearly constant with water type, but the overestimate of energy absorbed by dissolved/suspended matter decreases from water type IA to II. The dominance of the energy budget by molecular water in water type IA and the decrease in its percentage of the energy budget along the optical gradient are obscured by Eq. (9) where the estimated budget is apparently dominated by dissolved/suspended matter in water type IA. The optical energy budget for 532 nm indicates an overall dominance of the water contribution to the energy budget because the  $a$  coefficient is dominated by molecular water. The systematic overestimate of energy absorbed by the dissolved/suspended component in all conditions by Eq. (9) gives a systematic underestimate to all quantum efficiency calculations for photosynthesis and fluorescence.

The trends outlined above for the horizontal optical gradient are also true for the vertical optical gradient. The vertical gradient is made much more complex by layering of the dissolved/suspended matter, and the effects on the optical energy budget for the different layers are correspondingly more complex. Layers of dissolved/suspended matter have been identified as areas of enhanced heating rate due to increases in  $a_c$  (Ref. 25) and decreases in  $\bar{\mu}$ .<sup>6,7</sup> Given the known changes in  $\bar{\mu}$  in a layered system, the curve of heating rate with depth for molecular water will not be the smooth exponential curve of the textbooks but will have irregularities due to the irregularities of  $\bar{\mu}$ , and there is at least the potential for water to contribute to layers of enhanced heating rate along with the layers of dissolved/suspended matter.

## V. Summary

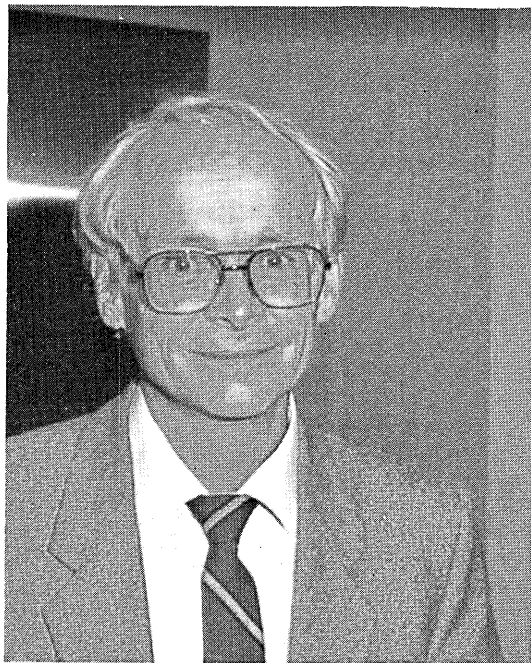
A general equation has been developed for evaluating the optical energy budget of any hydrosol. In addition an equation has been proposed to evaluate quantitatively the systematic errors inherent in assuming a Lambert-Beer quality to the empirical exponential decay coefficient  $K_d$ . Two systematic errors have been identified and assessed. These equations reveal that great care must be taken when optical analyses of clear ocean water are undertaken because the optical properties of water are so important. It has been demonstrated that use of the  $K_d$  coefficient to estimate the concentration of dissolved/suspended material leads to systematic overestimates. This leads further to overestimating the amount of radiant energy absorbed by dissolved/suspended material. It has also been demonstrated that the exponential decay of the penetrating light field due to the action of molecular water is not constant but variable and is a function of the radiance distribution of the submarine light field. The assumption of a constant exponential decay coefficient for molecular water leads to a systematic underestimate of the radiant energy absorbed by water in the visible wavelengths. Two sources of optical variability have been identified to account for gradients of transmissivity in clear ocean waters: the absorption coefficient and the average cosine.

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Lawrence Mertz of Lockheed Research Laboratories, a 1987 AMOSA participant. Photo: F. S. Harris, Jr.