CHORS Center for Hydro-Optics & Remote Sensing
San Diego State University 6505 Alvarado Road, Suite 206 San Diego, CA 92120-5005 619/594-2272 or 594-2230

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Nonlinear Relationships Between Particulate Absorption and Chlorophyll: Detritus or Pigment Packaging?

Joan S. Cleveland
Assistant Research Professor
Center for Hydro-Optics and Remote Sensing
San Diego State University
6506 Alvarado Rd. Suite 206
San Diego, CA 92120-5005

(619) 594-2400

Office of Naval Research

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SUMMARY

Relationships for predicting phytoplanktonic absorption at 676 and 436 nm from chlorophyll *a* concentration have been developed for distinct geographic regions defined by latitude. The forms of the predictive equations are controlled by underlying biological mechanisms and lend insight into these mechanisms. Development of these region-specific models allows prediction of phytoplanktonic absorption from more easily measured parameters such as chlorophyll *a* concentration or *in situ* fluorescence and increases accuracy in modelling optical properties or primary production rate using specific absorption coefficients. Temperate and tropical regions exhibited nearly identical relationships at low chlorophyll so these regions were combined and treated as one. Subpolar waters displayed a distinct pattern and were defined as a separate region. Linear relationships between phytoplanktonic absorption and chlorophyll *a* concentration in the subpolar region indicated that influences of pigment packaging on phytoplankton specific absorption coefficients were relatively constant and uncoupled from water column chlorophyll *a* concentration. Nonlinear relationships between phytoplanktonic absorption and chlorophyll *a* concentration for the combined temperate/tropical region suggested that pigment packaging effects were important and variable. The steepness of the relationship at low chlorophyll supported the concept of low pigment packaging effects (thus high absorption per chlorophyll *a*) in oligotrophic, low chlorophyll *a* waters.

Absorption by detritus at 436 nm ranged from 25 to 90% of the total particulate absorption. Differences in coefficients of predictive quadratic equations between particulate and phytoplanktonic absorption indicated that detritus made only a small contribution to the observed nonlinearity. The proportion of absorption by detritus did not exhibit any strong patterns as a function of chlorophyll *a* concentration, arguing against the previously proposed explanation that increases in absorption by detritus as environments become more oligotrophic cause the observed nonlinearity between absorption and chlorophyll *a* concentration.

ACCOMPLISHMENTS

Publications Supported by this Grant:

Cleveland, J.S. and M.J. Perry 1993. A model for partitioning particulate absorption into phytoplanktonic and detrital components. Deep-Sea Research. In Press.

Cleveland, J.S. and A.D. Weidemann 1993. Quantifying absorption by aquatic particles: A multiple scattering correction for glass fiber filters. Limnology and Oceanography. In Press.

Cleveland, J.S. Regional models of phytoplankton absorption from chlorophyll *a* concentration: Influences of pigment packaging and detritus. In Preparation.

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Other Accomplishments:

Chair of Hydrologic Optics session at ASLO 1992 Aquatic Sciences Meeting.

Co-chair of SPIE Ocean Optics XI conference, July 1991.

INTRODUCTION

Recent development of methods for identifying the separate phytoplanktonic and non-phytoplanktonic components of particulate absorption allows examination of the source of nonlinearity in relationships between particulate absorption and chlorophyll *a* concentration. For solutions, absorption increases linearly as a function of concentration. However, previous observations show that absorption or attenuation by oceanic particles increases nonlinearly with chlorophyll *a* concentration, even at the red peak where chlorophyll *a* is the primary absorber (*e.g.*, Smith and Baker 1978; Morel 1988; Gordon 1989). These previous analyses have examined total particulate absorption, without separating the portion of absorption due to phytoplankton from that due to detrital or other non-phytoplanktonic particles. The nonlinearity has been ascribed to an increasing proportion of absorption by detrital particles with respect to chlorophyll-containing particles as the concentration of chlorophyll *a* in the water column decreases, *i.e.*, as waters become more oligotrophic. The observed nonlinearity could also result from an increase in specific absorption coefficients, resulting from a decrease in pigment packaging effects, as waters become more oligotrophic. "Pigment packaging" refers to the consequences of enclosing pigments in cells, where pigment molecules alter the light incident on adjacent molecules. The overall absorption efficiency of pigments in cells decreases compared to the absorption potential for the same molecules in solution (see Morel and Bricaud 1981 for a complete explanation). Decreases in the influence of pigment packaging result from decreases in pigment per cell volume, which can occur either as cell sizes decrease or as internal pigment concentrations decrease for cells of a constant size. Smaller cells tend to occur in low nutrient, oligotrophic environments while low internal pigment concentrations result from photoadaptation to high light. Yentsch and Phinney (1989) suggested that the observed nonlinearity results from the presence of small cells with high specific absorption coefficients in waters of low chlorophyll *a* concentration. This assumes that the concentration of chlorophyll *a* in the water column indicates the trophic status of the environment and that oligotrophic waters always have small cells.

Either scenario, variations in the contribution by detritus or variations in pigment packaging, could cause the observed nonlinearity in relationships between particulate absorption and chlorophyll *a* in the ocean. These alternative hypotheses can be evaluated now that a technique is available for separating detrital from phytoplanktonic absorption. Once the detrital contribution is removed, an algorithm estimating phytoplanktonic absorption as a function of chlorophyll *a* concentration can be developed and used as a subunit in optical models requiring an estimate of absorption (*e.g.*, Stavn and Weidemann, 1989) or bio-optical models of primary production that require an estimate of the chlorophyll *a*-specific absorption coefficient (*e.g.*, Marra *et al.*, 1992). Nonlinearity between absorption and chlorophyll concentration is equivalent to variability in specific absorption coefficients (absorption normalized to chlorophyll *a* concentration). This variability must be considered when modelling optical properties or photosynthesis.

The specific goals of this project were to 1) determine whether the observed nonlinearity between particulate absorption and chlorophyll *a* concentration is due to an increase in the proportion of detrital absorption or a decrease in pigment packaging effects

(or both) as water column concentrations of chlorophyll *a* decrease, 2) produce a predictive model of phytoplanktonic absorption from chlorophyll *a* concentration, whether a single relationship or a family of relationships suitable to diverse oceanic regions, and 3) determine whether the proportional detrital contribution to absorption does indeed increase as chlorophyll *a* concentration decreases. In order to do this, particulate absorption spectra and concentrations of chlorophyll *a* and pheopigments were obtained for samples collected in a variety of oceanic regions. The partitioning model of Cleveland and Perry (1993) was used to estimate the phytoplanktonic component of particulate absorption. Relationships between both total particulate absorption and phytoplanktonic absorption were statistically analyzed as a function of the concentration of either chlorophyll *a* plus pheopimgent or chlorophyll *a*, respectively. Analyses to date have focused on 676 and 436 nm, the red and blue absorption peaks for chlorophyll *a in vivo*. The lack of significant detrital absorption at 676 nm allows more direct examination of pigment packaging effects and less reliance on the results of the partitioning model, while significant absorption by both pigments and detritus at 436 nm allows examination of the changing roles of these particle types.

METHODS

Water samples were collected in a number of different oceans regions (Table 1). Data from below the 1% light level were excluded.

Table 1: Cruises, areas, and dates from which data were obtained.

Project name	Location	Ship	Date	Region	n
Biowatt 1	Sargasso Sea	Knorr	Apr 1985	Temperat	31
Biowatt 1	Sargasso Sea	Knorr	Apr 1985	Sub/trop	12
Biowatt 2 OC1	Sargasso Sea	Oceanus	Mar 1987	Temperat	8
Biowatt 2 OC2	Sargasso Sea	Oceanus	May 1987	Temperat	5
Biowatt 2 OC3	Sargasso Sea	Oceanus	Aug1987	Temperat	7
Biowatt 3 OC4	Sargasso Sea	Oceanus	Nov 1987	Temperat	7
1308-90	NAtl Transect ~60N	Bartlett	July 1990	Subpolar	13
Northern Lights 2	Vestfjord, Norway	Bartlett	Sept 1990	Subpolar	103
1304-91	Sargasso Sea & Canary Basin	Bartlett	Mar 1991	Temperat	23
1306-91	Mediterranean Sea	Bartlett	Apr 1991	Temperat	77
JGOFS Spring Surv	Equatorial Pacific	Thompson	Feb/Mr 1992	Sub/trop	102

On all cruises, water samples for particulate absorption spectra were obtained from Niskin or Go-Flo bottles mounted in a rosette with a CTD. Between 1/2 and 2 liters of water were filtered through a Whatman GF/F (effective pore size 0.7 μm) glass fiber filter at low pressure. Optical density spectra were measured in a dual beam spectrophotometer (Lambda 3B for Biowatt 1 and 2; Kontron Uvikon 860 for all others) using a wet GF/F filter as a blank. During the JGOFS Equatorial Pacific cruise, filters were immediately frozen in liquid nitrogen, returned to CHORS, and spectra were measured in the

laboratory within 3 months. For all other cruises, samples were measured immediately following filtration. Optical density spectra were converted to absorption coefficient spectra [$a_{part}(\lambda)$] by subtracting the optical density at 750 nm from all other wavelengths, dividing by the geometrical pathlength (volume filtered divided by clearance area of the filter), and adjusting for the pathlength amplification factor. The pathlength amplification factor described by Mitchell and Kiefer (1988) was used for data from both Biowatt cruises (data courtesy of D.A. Kiefer and W.S. Chamberlain). The pathlength amplification factor described by Cleveland and Weidemann (1993) was used for all other data.

Water samples for measurement of chlorophyll *a* and pheopigments were filtered through Whatman GF/F filters and pigments were extracted in 90% acetone. Concentrations of chlorophyll *a* and pheopigments were measured fluorometrically for all cruises (Smith *et al.*, 1981). The presence of chlorophyll *b* causes an overestimation of pheopigments in the fluorometric method. When chlorophyll *b* concentrations were available (Biowatt 1; Biowatt 2; JGOFS EqPac), concentrations of pheopigments were corrected using the equation presented by Vernet and Lorenzen (1987). Otherwise, pheopigment concentrations were decreased by 30%, as also suggested by Vernet and Lorenzen (1987).

Particulate absorption spectra [$a_{part}(\lambda)$] were mathematically partitioned into phytoplanktonic [$a_{phyt}(\lambda)$] and detrital [$a_{det}(\lambda)$] components using the approach presented by Cleveland and Perry (1993). The model utilizes measured particulate absorption at the red peak, chlorophyll *a* and pheopigment concentrations, and mean ratios of $a(\lambda)$:$a(676)$ for laboratory-grown phytoplankton cultures. Use of this model relies on the assumption that the spectral shapes, not magnitudes, of absorption by chromophytes (chlorophyll *c*-containing species) and chlorophytes (chlorophyll *b*-containing species) measured in the laboratory are conservative and represent absorption by these groups in the field. The model functions in two stages for two types of phytoplankton assemblages. The first stage, applied to all samples, is based on mean $a(\lambda)$:$a(676)$ spectra for chromophytes and chlorophytes, and constitutes the full model for ocean waters dominated by eukaryotic phytoplankton of these two pigment groups. Phytoplankton of other pigment groups are accounted for in the second stage of the model, which adds the use of the detrital spectral shape to the results of the first stage of the model. The model is described in detail in Cleveland and Perry (1993).

Statistical relationships were analyzed using SYSTAT (Wilkinson, 1989). Particulate absorption was analyzed as a function of the concentration of chlorophyll a plus pheopigments (chl *a* + pheo) while phytoplanktonic absorption was analyzed as a function of the concentration of chlorophyll *a* (chl *a*). Absorption by pheopigments is included in total particulate absorption but not in the phytoplanktonic component.

RESULTS

Intial examination of a scatter plot showing total particulate absorption at the red peak (676 nm) as a function of chl *a* + pheo concentration for the entire data set showed high variability. Both linear and nonlinear fits to the data had poor predictive capability.

Visual inspection suggested a geographic grouping of the data. Data were grouped by latitudinal region, according to *a priori* expectations that specific absorption coefficients should differ for samples from subtropical/tropical (30°N to 30°S), temperate (30°N to 60°N), and subpolar regions (60°N to 70°N) for biological reasons. The subtropical/tropical data set included some values from the southern hemisphere, but all data available for the temperate and subpolar regions were from the northern hemisphere.

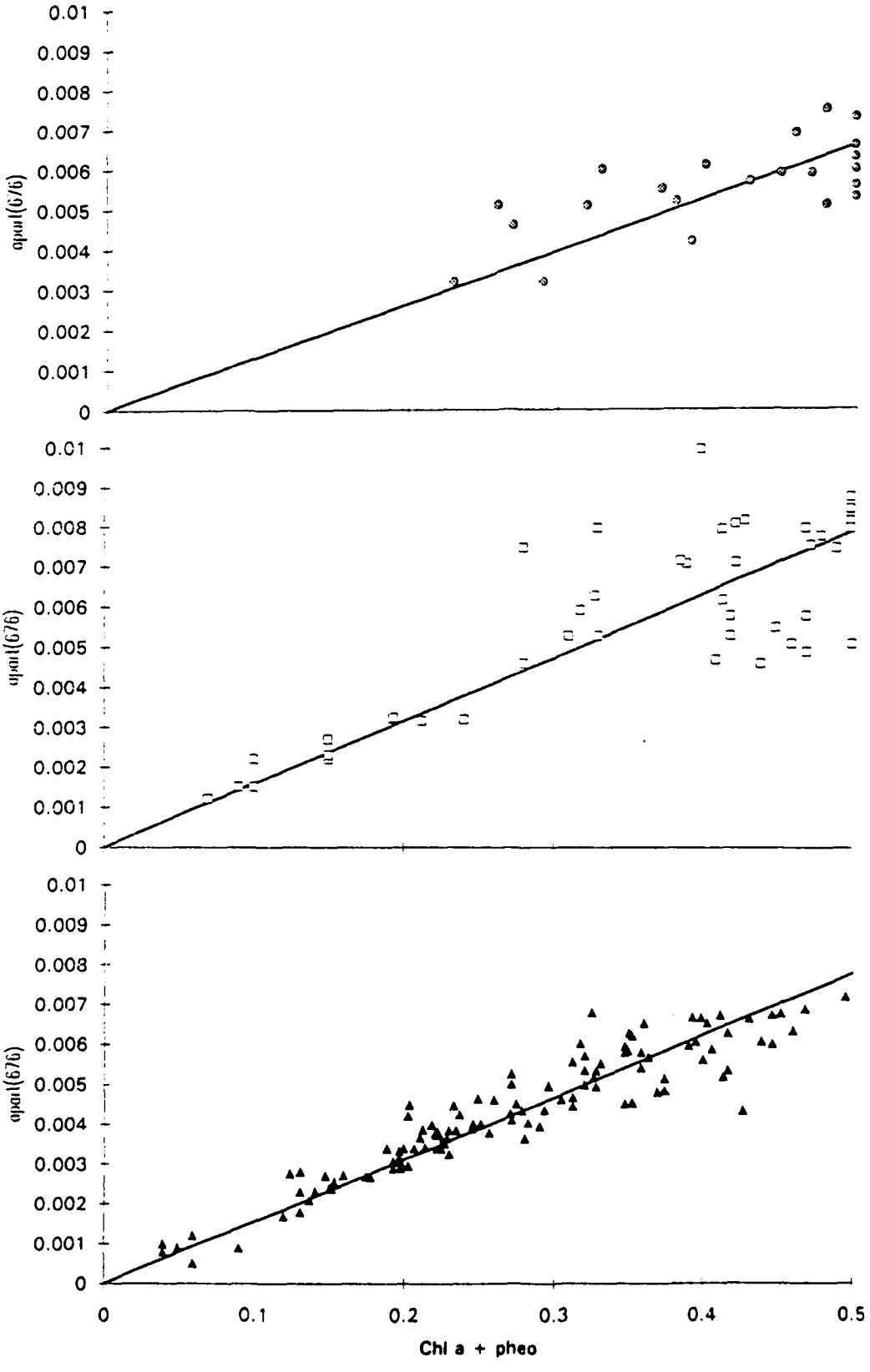
The range of chl *a* + pheo in these three latitudinal regions differed, with maximum values of 5.5 (mg chl *a* + pheo) m^{-3} in the temperate region; 4.0 (mg chl *a* + pheo) m^{-3} in the subpolar region; and 0.5 (mg chl *a* + pheo) m^{-3} in the subtropical/tropical region. These maximum concentrations reflect environmental limits to phytoplankton biomass. Differing data ranges can influence the overall slope or curvature of a nonlinear relationship. To avoid artifacts caused by these varied ranges while attempting to validate or disprove this subjective grouping, data for all three latitudinal regions were restricted to chl *a* + pheo values less than 0.5 (mg chl *a* + pheo) m^{-3}. Within this restricted range, all three regions displayed linear relationships between $a_{part}(676)$ and chl *a* + pheo (Figure 1). Slopes for the subtropical/tropical and temperate regions were not significantly different from each other, while the slope for the subpolar region was significantly different from the other two (Table 2). The similarity between subtropical/tropical and temperate regions suggested that the subtropical/tropical data represented the low chl *a* + pheo portion of a relationship describing subtropical/tropical and temperate data as a single group. Data from these two regions was combined, and the region named temperate/tropical. Particulate absorption for the subpolar region displayed a pattern distinct from this combined temperate/tropical data. A χ^2 test comparing the linear slopes of $a_{part}(676)$ as a function of chl *a* + pheo rejected the null hypothesis that the slope for the subpolar data was identical to that for the temperate/tropical data ($p < 0.05$).

Table 2: Comparison of slopes, correlation coefficients (r^2), and 95% confidence intervals for linear regressions of $a_{part}(676)$ on (chl a + pheo) for the three latitudinal regions. Data were restricted to chl a + pheo less than 0.5 mg m^{-3}.

Region	n	Slope	r^2	lower 95% CI	upper 95% CI
subpolar	24	0.0132	0.97	0.0123	0.0141
temperate	43	0.0158	0.95	0.0147	0.0169
sub/tropical	114	0.0155	0.98	0.0151	0.0159

The restricted data sets were used only for evaluation of the regional separation of data. Remaining analyses were performed using the entire available range of chl *a* + pheo or chl *a*. Second-order quadratic equations ($y = c_1 x + c_2 x^2$) were fit to absorption as a function of pigment concentration. This form was chosen because i) it adequately describes the observed behavior, steep at low chl *a* + pheo and gradually becoming less steep as chl *a* + pheo increases, ii) the derivative of a quadratic, as chl *a* + pheo goes to zero, equals the first-order coefficient (c_1) which represents the maximum specific absorption coefficient for the data being described, iii) as packaging effects become

Figure 1: Data and linear fits to $a_{part}(676)$ as a function of chl a + pheo concentration for the a) subpolar region, b) temperate region, and c) subtropical/tropical region. Data were restricted to chl a + pheo less than 0.5 mg m^{-3}.



important, the second term (c_2) represents the decrease in specific absorption from the maximum described by c_1, and iv) c_2 will be small or zero for relationships that are actually linear, allowing all data to be described with the same general form. No intercepts were used in the models because absorption by components other than chlorophyll *a* and pheopigments is low at 676 nm and particulate absorption at the red peak should be close to zero when chl *a* + pheo equals zero.

Coefficients, correlation coefficients, and confidence intervals for the quadratic equations are presented in Table 3 for $a_{part}(676)$ as a function of chl *a* + pheo, $a_{phyt}(676)$ as a function of chl *a*, $a_{part}(436)$ as a function of chl *a* + pheo, and $a_{phyt}(436)$ as a function of chl *a* for the subpolar and temperate/tropical regions. Equations describing phytoplanktonic absorption use chl *a*, rather than chl *a* + pheo, because absorption by pheopigments is not included in the phytoplanktonic component of absorption. Note that these statistical relationships are valid only within the pigment concentration range over which they were developed. Increasing the number of data points at high chl *a* or extending the range to concentrations above 4.0 mg chl *a* m^{-3} may improve the robustness of the relationships and expand the concentration range over which the relationships are valid. For the environments and times sampled here, these data reflect actual chl *a* ranges.

Table 3: Coefficients, 95% confidence intervals, and correlation coefficients (r^2), for quadratic equations [$y = c_1 x + c_2 x^2$] fit to particulate and phytoplanktonic absorption data for temperate/tropical (n=272) and subpolar (n=115) regions. $a_{part}(676)$ and $a_{part}(436)$ were modelled as a function of chl a + pheo while $a_{phyt}(676)$ and $a_{phyt}(436)$ were modelled as a function of chl a.

y	x	Region	c_1	c_2	r^2	95% for c_1	95% for c_2
$a_{part}(676)$	chl+pheo	temp/trop	0.0135	-0.00116	0.96	0.0130 to 0.0140	-0.0013 to -0.0010
$a_{part}(676)$	chl+pheo	subpolar	0.0126	0.00007	0.98	0.0118 to 0.0133	-0.0002 to +0.0003
$a_{phyt}(676)$	chl	temp/trop	0.0166	-0.00184	0.95	0.0159 to 0.0174	-0.0021 to -0.0015
$a_{phyt}(676)$	chl	subpolar	0.0133	0.00123	0.98	0.0124 to 0.0143	0.0007 to 0.0018
$a_{part}(436)$	chl+pheo	temp/trop	0.0369	-0.00434	0.93	0.0352 to 0.0386	-0.0048 to -0.0039
$a_{part}(436)$	chl+pheo	subpolar	0.0388	-0.00260	0.95	0.0357 to 0.0418	-0.0058 to -0.0015
$a_{phyt}(436)$	chl	temp/trop	0.0309	-0.00469	0.91	0.0291 to 0.0326	-0.0054 to -0 0040
$a_{phyt}(436)$	chl	subpolar	0.0297	-0.00114	0.96	0.0274 to 0.0321	-0.0024 to +0.0001

DISCUSSION

Separation of data into distinct latitudinal regions was based on particulate rather than phytoplanktonic absorption so that geographical patterns could be established before the data were mathematically partitioned into phytoplanktonic and detrital components. At the red peak, most of the particulate absorption is caused by chl *a* and pheo, with little absorption by other pigments, detritus, or other types of non-phytoplanktonic particles.

For data restricted to chl *a* + pheo less than 0.5 mg chl *a* m^{-3}, the lack of difference (Figure 1; Table 2) between the temperate and sub/tropical regions indicated that the two data sets represented different portions of a single continuous relationship. The subpolar data set remained distinct, suggesting that different processes control the relationship between absorption and pigments in this region.

As calculated here, $a_{part}(676)$ includes absorption by pheopigments while $a_{phyt}(676)$ does not. Since pheopigments are nonphotosynthetic (except for a small amount in the reaction center of photsystem II), absorption by pheopigments is properly assigned to the detrital component. Discussion of pigment-packaging effects and differences between regions will focus on $a_{phyt}(676)$ rather than $a_{part}(676)$.

SUBPOLAR REGION

Packaging

For $a_{phyt}(676)$ as a function of chl *a* in the subpolar region, c_1 (0.0133) and $a^*_{phyt}(676)$ (0.0145 m^2 (mg chl *a*)$^{-1}$) were consistent with a slight influence by pigment packaging while the linear nature of the relationship (c_2 was positive but close to zero; Figure 2a) implied that this degree of packaging was constant across the observed range of chl *a*. At 676 nm, a reasonable mean value for specific absorption is approximately 0.016 m^2 (mg chl *a*)$^{-1}$, while the maximum value for unpackaged chlorophyll or small cells reaches about 0.025 m^2 (mg chl *a*)$^{-1}$. The value of c_1 was below the expected mean and the maximum, implying a small but definite decrease of specific absorption from the potential unpackaged maximum. This degree of packaging did not vary with water column chl *a*, resulting in a linear relationship and constant specific absorption coefficient across the range of chl *a* represented here. The same was true at the blue peak, with c_1 equal to 0.0297 and c_2 not significantly different than zero (Figure 3a; Table 3).

Pigment packaging in the subpolar region was uncoupled from the water column chl *a* concentration, *i.e.*, the expectation that low chl *a* indicates oligotrophic waters, small cells, and high specific absorption coefficients was invalid for these data. At both 676 and 436 nm, mid-range values of c_1 and $a^*_{phyt}(\lambda)$ indicated that some degree of pigment packaging effects were present but the linear nature of the relationships indicated no change in packaging or pigment per cell volume across the observed range of chl *a*. The variation in chl *a* apparently resulted from a change in cell number not a change in community composition, cell size, or pigment per cell.

These results contrast to those for another polar area. For samples from Antartic waters, the mean $a^*_{part}(435)$, normalized to chl *a* + pheo, was 0.018 m^2 (mg chl *a*)$^{-1}$ (Mitchell and Holm-Hansen, 1991). Photoadaptation to the low irradiance of polar areas, with a subsequent increase in pigment packaging effects and decrease in specific absorption coefficients, was suggested as the cause of relatively low mean specific absorption coefficients in the Antartic. The values of c_1 (0.0297) and mean $a^*_{phyt}(\lambda)$ (0.0296 m^2 (mg chl *a*)$^{-1}$) for the present data, collected in the months of July and Sept. (Table 1), actually suggested the opposite, with relatively small pigment packaging effects. Spectral shapes of absorption suggested increased accessory pigments and low-light photoadaptation for some deep samples in Vestfjord (Cleveland, 1991), but this was not

Figure 2. Data and quadratic fits to $a_{phyt}(676)$ as a function of chl a concentration for the a) subpolar region, and b) combined temperate/tropical region (temperate values as open squares; subtropical/tropical values as solid triangles).

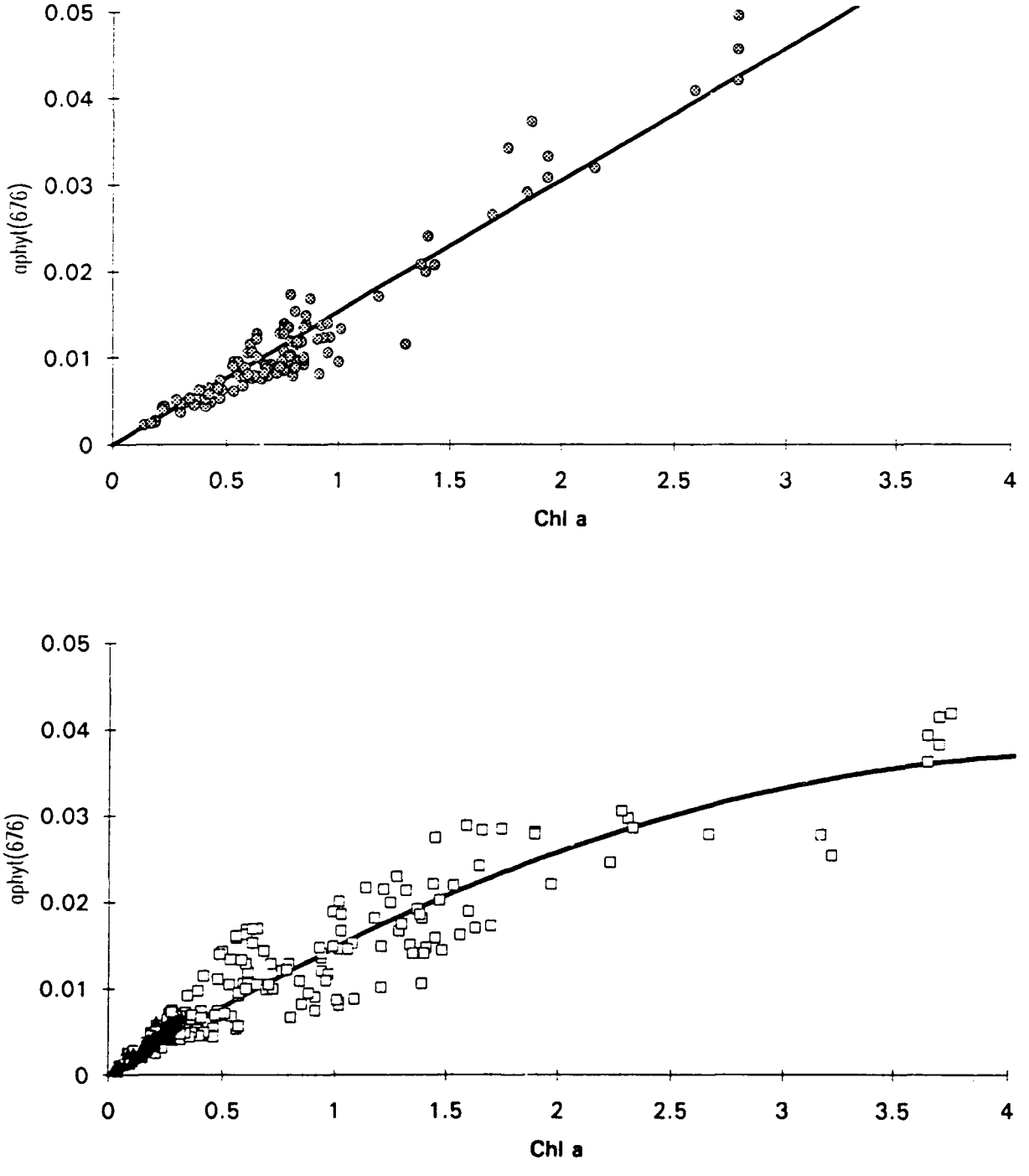
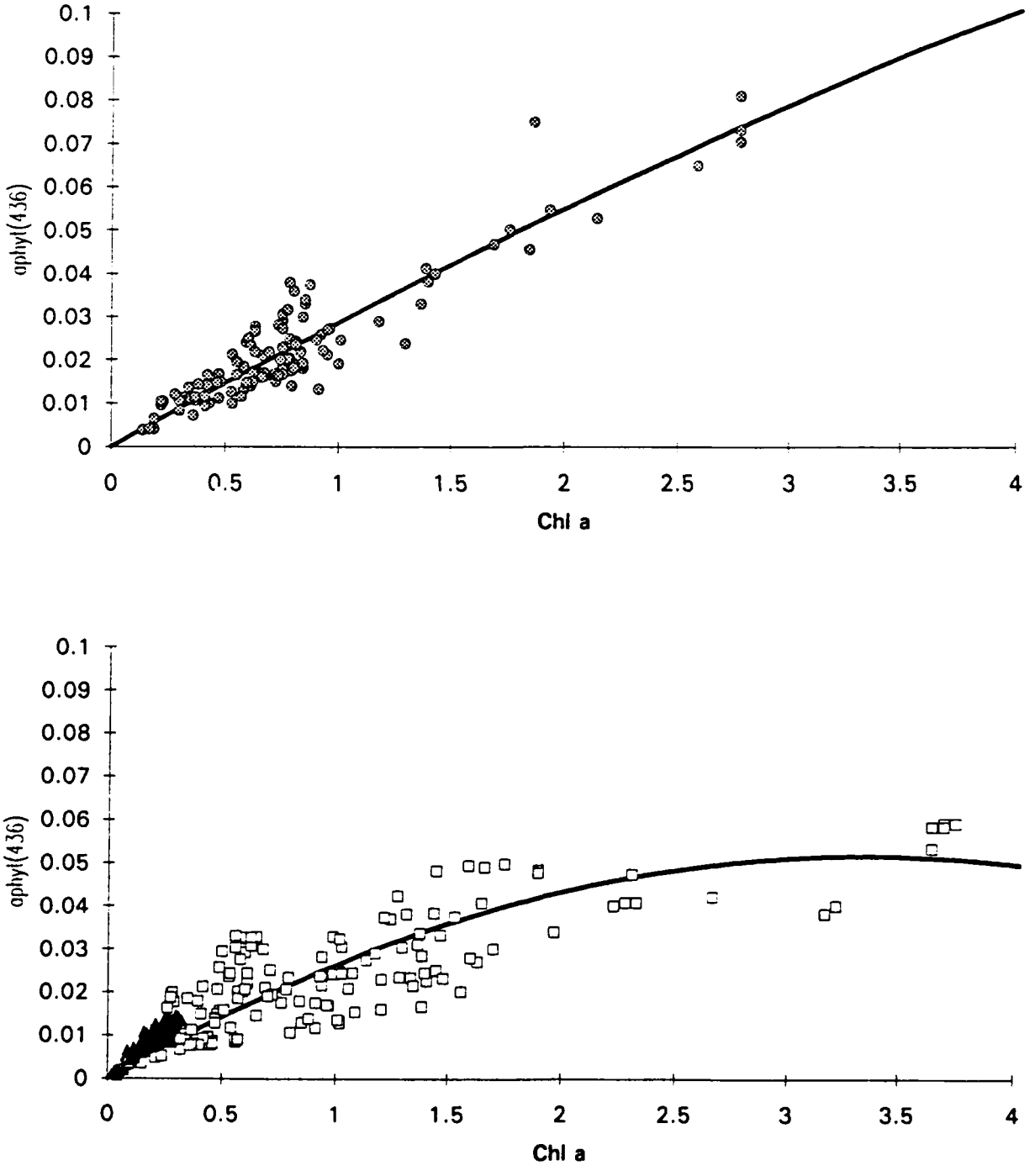


Figure 3. Data and quadratic fits to $a_{phyt}(436)$ as a function of chl a concentration for the a) subpolar region, and b) combined temperate/tropical region (temperate values as open squares; subtropical/tropical values as solid triangles).



true for all depths or all stations. Photoadaptation was not manifested as low specific absorption coefficients. Perhaps the seasonal cycle resulting in longer days in July and Sept. influenced light availability more than high latitude. It is surprising that the same was not also true for Mitchell and Holm-Hansen's (1991) samples, which were taken during the austral summer when sunlight should have been at an annual maximum.

The hypothesis describing connections between oligotrophic environments, small cells, and high specific absorption coefficients actually applies to a range of water column chl *a* concentrations obtained by sampling a range of environments, rather than a range of chl *a* from within one environment. The data composing this subpolar data set was obtained from only two cruises, one to Vestfjord, Norway (Northern Lights 2; n = 103) and one to a site south of Iceland (1308-90; n = 13). These two sampling sites do not provide much of a gradient in trophic status or chl *a* concentration. More extensive sampling might produce a different pattern. Despite the few samples from south of Iceland compared to Vestfjord, there was close agreement (not shown) between data from the two quite different environments, a coastal fjord and a deep open ocean site. For these two locations, patterns between absorption and chl *a* were the same and linear. The subpolar region remains distinct from the temperate/tropical region, and does not fit in simply as a different chl *a* range or trophic regime.

Detritus

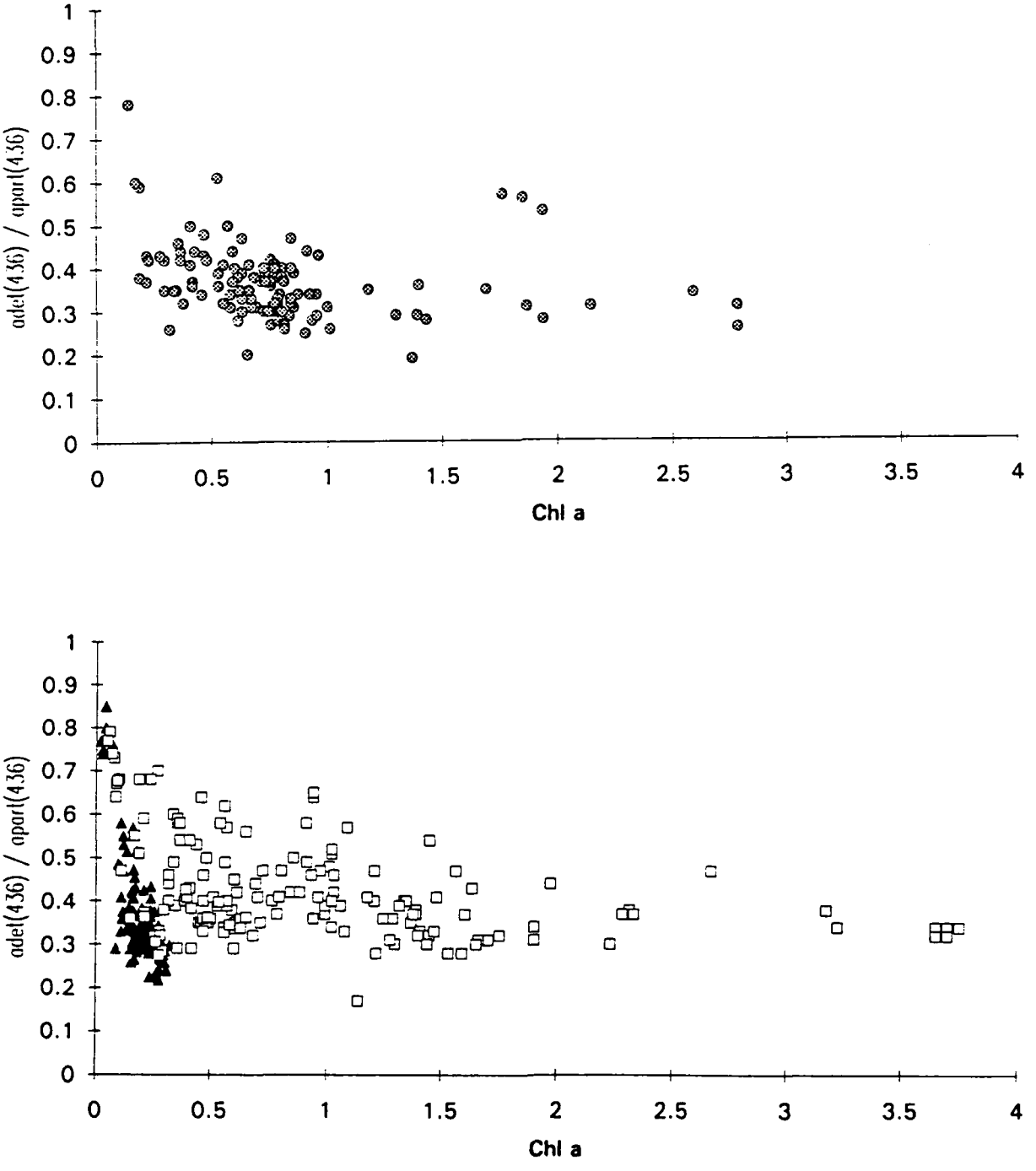
For $a_{part}(436)$ in the subpolar region, c_2 was negative and statistically different from zero, while the confidence interval for c_2 for $a_{phyt}(436)$ included zero, indicating that this relationship was linear (Table 3). The values and change in coefficients implied that the relationship for particulate absorption included a nonlinear contribution by detritus. However, the proportion of particulate absorption due to detritus did not exhibit any trend with chl *a* concentration (Figure 4a). Most of these values were from Vestfjord, a semi-enclosed coastal area, where trophic gradients did not seem to be present. Coastal areas are generally expected to have higher contributions by nonphytoplanktonic particles, either of terrestrial origin or from algal decompostion, but this was not true in this fjord.

TEMPERATE/TROPICAL REGION

Packaging

Data from the temperate/tropical region were obtained from 8 cruises in diverse locations at varied times of year (Table 1), and compose a more appropriate data set than do the subpolar data for examining the hypothesis that low water column chl *a* indicates the presence of small cells with low pigment packaging effects. Nonlinear relationships for both $a_{phyt}(676)$ and $a_{phyt}(436)$ (Figures 2b and 3b; Table 3) do indeed support this hypothesis. Specific absorption coefficients are high at low chl *a* and decrease as chl *a* concentration in the water column increases. For $a_{phyt}(676)$, c_1 was 0.0166, compared to a general expected mean $a^*_{phyt}(676)$ near 0.016 and maximum of 0.025 m^2 (mg chl *a*)$^{-1}$. Values of $a^*_{phyt}(436)$ measured in the laboratory range from 0.016 to 0.065 (Bricaud *et al.*, 1988), 0.014 to 0.03 (Mitchell and Kiefer, 1988), or 0.02 to 0.05 m^2 (mg chl *a*)$^{-1}$ (Sathyendranath *et al.*, 1987). For the blue peak, c_1 (0.0309) was intermediate among these laboratory values. The quadratic formulation is useful because it allows interpretation of c_1 as the specific absorption coefficient at low chl *a*, which should be the

Figure 4. Proportion of particulate absorption at 436 nm due to detritus as a function of chl a concentration for the a) subpolar region, and b) combined temperate/tropical region (temperate values as open squares; subtropical/tropical values as solid triangles).



maximum for the region being described. In the temperate/tropical waters sampled here, the maximum specific absorption coefficients as represented by c_1 were fairly high for both the red and blue peaks, consistent with the expectation that areas of low chl *a* concentration have small cells with high specific absorption coefficients. Many of the data in the low chl *a* portion of Figure 3b were from the Equatorial Pacific, where cells smaller than 10 μm dominate the phytoplankton community (Chavez 1989).

Yentsch and Phinney (1989) performed a similar analysis for the Gulf of Maine. Mean absorption and mean chl *a* values were calculated for a series of chl *a* ranges, and a power equation was fit to particulate absorption at the red peak. They used particulate absorption because estimates of phytoplanktonic absorption were not available, but most of the particulate absorption at this wavelength is due to phytoplankton. The equation given by Yentsch and Phinney (1989) is in absorbance (log base 10), rather than absorption (log base e) units, and was not corrected for pathlength amplifcation within the glass fiber filters. Laboratory measurements by Yentsch and Phinney (1990) show 2.17 as the mean pathlength amplification factor at 670 nm for their spectrophotometer. Applying this pathlength amplification factor and converting to absorption units produces the curve shown in Figure 5. For direct comparison with the results of Yentsch and Phinney (1989), the present temperate/tropical $a_{part}(676)$ data were also fit with a power equation. These two predictive models are nearly identical, with a maximum difference of 11% (Figure 5). Data used to develop the two models shown in Figure 5 originated in diverse temperate and tropical areas of the world's oceans: the Gulf of Maine (Yentsch and Phinney, 1989), the Sargasso Sea (Biowatt 1 and 2; 1304-91), the Canary Basin (1304-91), the Mediterranean Sea (1306-91), and the Equatorial Pacific (JOGFS EqPac) (Table 1). Inclusion of Yentsch and Phinney's data would probably cause only small changes in the quadratic equation developed here (Table 3). A single quadratic equation for prediction of phytoplanktonic absorption from chl *a* concentration should be suitable throughout temperate and tropical areas of the ocean.

Specific absorption coefficients at 436 nm were plotted on log-log axes for comparison to the model of Carder *et al.* (1991; Figure 6). Carder *et al.* (1991) chose a hyberbolic tangent formulation because it provides asymptopes that can be described by maximum and minimum specific absorption coefficients. Using very few data points and assuming that subtropical waters have higher specific absorption coefficients than temperate waters, Carder *et al.* (1991) presented separate regional relationships describing specific absorption as a function of chl *a* concentration. While values from the present synthesis generally fall near the predictions of Carder's models, the separation into subtropical and temperate regions is not confirmed and measured specific absorption coefficients do not follow the hyperbolic tangent function (Figures 1b, 1c, and 6).

Detritus

The detrital portion of particulate absorption at 436 nm did not follow a simple pattern as chl *a* concentration changed (Figure 4b). At all chl *a* concentrations, there was a minimum detrital contribution of 25%, while the maximum possible contribution increased as chl *a* decreased. Variability at any single chl *a* concentration was high. The

Figure 5. Comparison of power equation fit to $a_{part}(676)$ as a function of chl a + pheo for temperate/tropical data (solid line) with equation from Yentsch and Phinney (1989; dashed line).

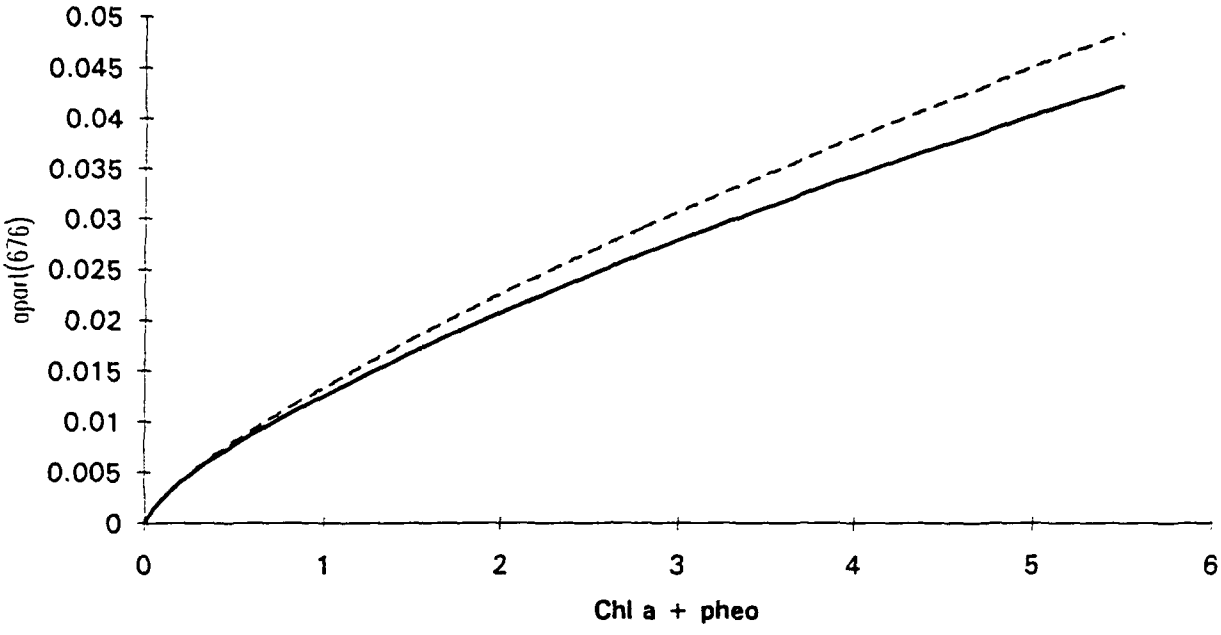
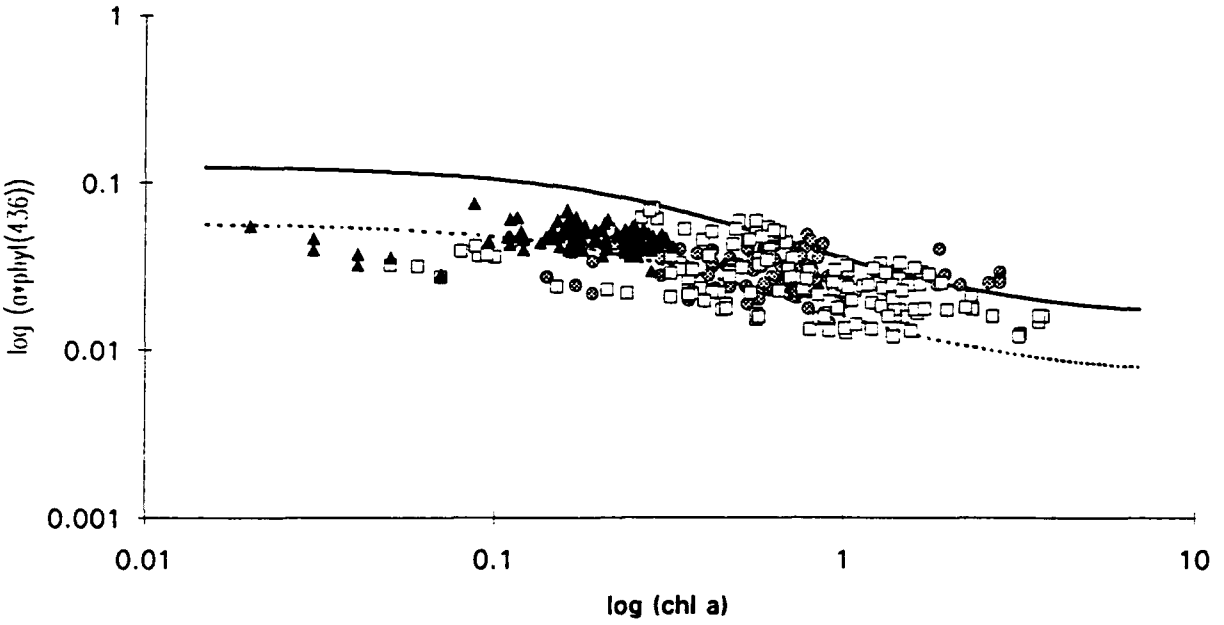


Figure 6. Comparison of measured $a^*_{phyt}(436)$ to the hyperbolic tangent model of Carder et al. (1991). Data are from the polar (grey circles), temperate (open squares), and subtropical/tropical (solid triangles) regions.



previously invoked explanation that the proportion of absorption by detritus increases as water column chl *a* concentration decreases was not supported by these data.

Other Sources of Variability

Even though a quadratic equation fits the data better than a linear equation, differences between measured and predicted values of absorption were high. For example, at 1 mg chl *a* m^{-3}, the lowest measured value of $a^*_{phyt}(676)$ was 0.008 while the highest was 0.021, with the quadratic model predicting 0.0125 m^2 (mg chl *a*)$^{-1}$ (Fig. 2b). This observed range of specific absorption at a single chl *a* concentration is reasonable, being similar to that found in laboratory studies. Figures presented by Sathyendranath *et al.* (1987) show a range of *in vivo* $a^*_{phyt}(676)$ from 0.012 to 0.024 m^2 (mg chl *a*)$^{-1}$ for 7 species grown at three different irradiance levels. At the red peak, chl *a* is the primary absorber thus the variability must be due to variation in pigment packaging effects rather than accessory pigment composition.

The hypothesis linking chl *a* concentration to cell size and specific absorption uses water column chlorophyll *a* to identify the "trophic status" of an environment, *i.e.*, low water column chl *a* means low nutrients and small cells. This hypothesis ignores other potential sources of variation in specific absorption coefficients. Reduction of internal pigment concentrations without a concurrent change in cell size or community composition, as occurs during photoadaptation to high light or sudden nutrient limitation, could also decrease specific absorption coefficients. In an effort to identify the source of the remaining variability in the relationship between $a_{phyt}(676)$ and chl *a*, a stepwise multiple linear regression was applied to data from the temperate/tropical region. Along with chl *a* concentration, percent light depth (optical depth) was selected as a variable at the 1% level of significance, but the improvement in predictive capability was small. Residuals from the multiple regression were greater and the correlation coefficient was lower than those for the quadratic curve, indicating that the nonlinear relationship remained a better description of the data. If appropriate supporting data can be obtained for all cruises, other variables known to influence pigment packaging and specific absorption (optical depth, nutrients or nutricline depth, mixed layer depth) may be included in the multiple regression in the future.

CONCLUSION

Ecological differences between phytoplankton communities in subpolar and temperate/tropical waters underlie the forms of models predicting phytoplanktonic absorption. The quadratic model for temperate/tropical waters has a basis in the expectation of high specific absorption coefficients in waters of low nutrients, low chl *a*, and small cell size. The linear model for subpolar waters means that specific absorption coefficients are constant and pigment packaging effects are uncoupled from variations in water column chl *a* concentration. Some mechanism(s) other than nutrient availability controls cell size and chl *a*. Concentrations of chl *a* do not convey information on cell size, thus the connection between chl *a* and specific absorption is not present. The region-specific models presented here provide estimates of either total particulate absorption or of phytoplanktonic absorption alone which can be used to in models of optical properties or primary production rates in the ocean.

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