Calcium carbonate measurements in the surface global ocean based on Moderate-Resolution Imaging Spectroradiometer data

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[1] We describe a two-band algorithm for the remote quantification of the ocean's suspended calcium carbonate (also known as particulate inorganic carbon (PIC)), based on normalized water-leaving radiance at 440 and 550 nm. We tested this algorithm using ship-derived and satellite-derived results from a variety of marine environments. From this validation work we calculated the overall accuracy of the satellite-based PIC estimates, assuming different timescales and space scales for binning. After performing the validation work we applied the two-band algorithm to water-leaving radiance data from 2002, sampled by Moderate-Resolution Imaging Spectroradiometer (MODIS)/Terra (a 36-band satellite spectrometer designed to observe land, ocean, and atmosphere), and we derived seasonal, global maps of the standing stock of pelagic PIC as well as particulate organic carbon (POC). These data, along with limited observations on the turnover time of calcium carbonate coccoliths in the euphotic zone, provide some new insights into global rates of pelagic calcite production.

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1. Introduction

1.1. Production and Distribution of Particulate Inorganic Carbon in the Surface Ocean

[2] Particulate inorganic carbon (PIC; or CaCO₃) is found throughout the coastal and open oceans of the world and it represents about 1/4 of all marine sediments [Broecker and Peng, 1982; Seibold and Berger, 1982]. CaCO₃ is produced in shallow waters by either coral reefs or macrophytic algae (e.g., Halimeda), or in the plankton, by coccolithophores, foraminifera, and pteropods [Milliman, 1993]. These plankton eventually fall through the water column, and are deposited in shallow and deep sea sediments. Mineralization of their CaCO₃ shells can involve five allotropic modifications, with calcite and aragonite being the most abundant [Stumm and Morgan, 1981]. Previous calculations of the inventory of total alkalinity and residence times of various water masses have demonstrated that calcification by oceanic and shelf plankton accounts for $\sim 2/3$ of global calcification [Milliman, 1993]. The current global CaCO₃ production rate is thought to be ~ 0.6 Gt C as CaCO₃ yr⁻ with ~ 0.3 Gt C produced in the deep sea [Milliman, 1993]. Two other estimates of global calcification in shelf,

slope and oceanic waters are ~0.9 Gt C yr⁻¹ [Morse and Mackenzie, 1990] and ~1.1 Gt C yr⁻¹ [Wollast, 1994], almost 2 × higher than Milliman [1993]. Wollast [1994] suggested that sediment trap artifacts or overestimates of dissolution were the cause of lower global calcification estimates. Milliman et al. [1999] estimated that pelagic production of calcium carbonate was 0.7 Gt PIC yr⁻¹. This value was closer to the range of deep sea CaCO₃ dissolution estimates (0.7–0.9 Gt PIC yr⁻¹) given by Archer [1997], but still less than the estimated global CaCO₃ rain rate of ~1 Gt PIC yr⁻¹ [Archer and Maier-Reimer, 1994; Archer, 1997]. More recently, Feely et al. [2004] used the seasonal cycle of euphotic zone alkalinity to estimate the range of annual calcite production. Their values varied from 0.8–1.4 Gt PIC yr⁻¹.

1.2. Marine CaCO₃ Cycle: Biogeochemistry Implications

[3] The burning of fossil fuels appears to have major impact on oceanographic, ecological and physiological conditions [Sabine et al., 2004] through effects (sometimes opposing) on temperature, stratification, pH, etc. [Bates et al., 1996; Lavrentyev et al., 2001; Peng et al., 1998; Riebesell et al., 1993, 2000, 2001; Stockwell et al., 2000]. Nonetheless, it is not yet known whether the net effect of

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increased pCO₂ will shift the ratio of export of particulate organic carbon to particulate inorganic carbon. Such a change could then affect the ability of the ocean to act as a CO₂ sink. It is clear that not enough is known about the calcium carbonate standing stock in the sea to allow unambiguous prediction of its response to different forcing.

[4] Anthropogenic CO₂ can be neutralized by reactions with marine calcium carbonate via the dissolution reaction

$$CO_2 + CaCO_3 + H_2O = 2HCO_3^- + Ca^{2+}.$$
 (1)

As the oceans become enriched in fossil fuel-derived CO_2 , the locations and extent of dissolution will increase as a function of changes in the CaCO₃ saturation state. Feely et al. [2004] estimated that the depths of calcite and aragonite saturation have shoaled as much as several hundred meters since the beginning of the industrial revolution, due to the ventilation of anthropogenic CO₂ into the sea. On longer timescales, variations in calcium carbonate cycling have been proposed to account for a significant fraction of the ~80 ppm increase in atmospheric CO₂ from glacial to interglacial times [Archer and Maier-Reimer, 1994; Boyle, 1988; Broecker and Peng, 1989]. Even on thousand year timescales, sedimentary CaCO3 is a major buffer of atmospheric CO2 [Archer et al., 1998; Broecker and Takahashi, 1977; Sundquist, 1993]. Surface production and deep dissolution of CaCO₃, the ocean "carbonate pump," has the effect of raising atmospheric pCO₂ by roughly 25 ppm [Maier-Reimer, 1996; Najjar et al., 1992; Volk and Hoffert, 1985], with local surface ocean impacts as high as 50 ppm in coccolithophore blooms [Holligan et al., 1983; Robertson et al., 1994]. Thus even on short timescales, changes in the carbonate standing stocks could be significant to atmospheric CO₂ budgets.

[5] Knowledge of the global distribution of calcium carbonate may help explain significant anomalies in alkalinity that can be found in the surface ocean, which ultimately result from variability in calcification and dissolution. While calcium carbonate is generally oversaturated in the surface ocean (as much as 5 times), significant negative Ca++ anomalies can be seen in the top 200 m presumably due to net calcification and subsequent sinking of the CaCO₃. In slightly deeper waters (while still above the lysoclines for aragonite and calcite), there are welldocumented positive anomalies in Ca⁺⁺, suggesting net calcite dissolution [Milliman et al., 1999]. Taken together with sediment trap measurements, it appears that at least half of the surface-produced calcium carbonate must dissolve shallower than 1000 m to be consistent with sediment trap fluxes at that depth [Balch et al., 2000; Balch and Kilpatrick, 1996; Feely et al., 2004; Troy et al., 1997].

1.3. Case for Using Remote Sensing to Study the Calcium Carbonate Cycle

[6] Clearly, the ability to remotely map suspended CaCO₃ from space would provide new insights into the global carbonate cycle. In addition to its impact on atmospheric CO₂ on a variety of timescales, there are several reasons for using remote sensing to study suspended CaCO₃. The first reason is the impact of CaCO₃ producers on the upper ocean light field, especially during coccolithophore bloom events [Ackleson et al., 1988; Balch et al., 1989; Holligan et al.,

1993, 1983; Tyrell et al., 1999]. In typical nonbloom situations, backscattering of light by suspended coccoliths routinely accounts for 10-20% of all visible backscattered light from the sea [Balch et al., 1999]. This percentage can exceed 90% in coccolithophore blooms [Balch et al., 1991] when the concentration of calcite is much higher. The second reason for using remote sensing to study the global distribution of CaCO3 is that CaCO3 producers are well known for the production of dimethylsulfide (DMS) which has links to planetary albedo [Charlson et al., 1987; Shaw, 1983]. One coccolithophore species, Emiliania huxleyi, is a significant producer of dimethylsufide [Keller et al., 1989; Malin et al., 1993; Matrai and Keller, 1993]. A third reason for remotely studying the global marine CaCO₃ distribution is that our interpretation of the paleorecord in marine sediments hinges on what we know about the production and dissolution of CaCO₃ in the modern ocean. Understanding extant global distributions of PIC can aid in understanding paleopatterns of PIC deposition. Lastly, CaCO₃ serves as ballast for particulate organic matter, especially in the deep sea, where the relative abundance of CaCO₃ in particulate material becomes dominant. Recent work [Armstrong et al., 2002; Francois et al., 2002; Iglesias-Rodrigues et al., 2001] has focused on the dominant role of ballast minerals such as calcium carbonate as a carrier of organic carbon into the ocean interior. Understanding global PIC distributions through remote sensing will eventually allow better calculation of global export fluxes of carbon.

1.4. Optical Properties and Carbon Content of Coccoliths: The Heart of the Optical Algorithm

[7] Given the importance of suspended calcium carbonate to the global carbon cycle, a remote means to detect it is essential. Unlike phytoplankton pigments, which, when present, decrease the radiance in the blue but increase it only slightly in the green, coccolithophores increase the radiance uniformly in both the blue and green [Gordon et al., 1988]. Thus their remote study requires an understanding of the actual water-leaving radiance rather than just radiance ratios as in the case of pigments [Gordon and Morel, 1983]. Furthermore, the "flattening" of the reflectance spectrum in coccolithophore blooms implies that the standard ratio pigment algorithms [Gordon and Morel, 1983] will not provide correct pigment retrievals within the blooms [Balch et al., 1989]. A previous solution to this problem was to use a coccolithophore "flag" to check for regions of high coccolithophore abundance, whereupon the associated pigment concentrations could be flagged as suspect [Brown and Yoder, 1994].

[8] A fundamentally different remote sensing approach for the remote sensing of coccolithophores is to use individual water-leaving radiance values, not ratios, to resolve the interacting effects of coccolithophore calcite and chlorophyll in seawater. *Gordon et al.* [1988] developed a prototype model for explaining the dependence of the water-leaving radiance on the concentration of constituents in Case 1 waters. Briefly, the normalized water-leaving radiance is related to the absorption and scattering properties of the biogenic components of the water, phytoplankton and their associated detritus. This model provides the basis for extraction of the concentration of the

detached coccoliths, or the coccolith PIC concentration, based on water-leaving radiance measurements and known optical properties of calcium carbonate.

- [9] The calcite-specific backscattering cross section for coccolithophores is critical to the above optical PIC algorithm. This has been previously determined to be about 1.37 m² mol PIC⁻¹, based on lab and field studies [Balch et al., 1999]. Obviously, this property is related to the size, shape and mass of the calcite coccoliths [Gordon and Du, 2001]. It is important to point out that even within the species E. huxleyi, there can be variability in the PIC content of coccoliths, especially when comparing results from culture and field measurements [Paasche, 2002]. Such variance will invariably affect the coccolith- and PIC-specific backscattering cross sections, and, in turn, the accuracy of any optically derived PIC estimates. This variance exists because of assumptions about the numbers of coccoliths attached to each coccolithophore as well as effects of growth conditions on coccolith production. For example, PIC content per E. huxleyi coccolith has been estimated in many studies: 0.16 pg [Paasche, 1962], 0.45-0.5 pg for field measurements from a NE Atlantic bloom [Holligan et al., 1983], 0.2 pg for measurements of a Gulf of Maine bloom (see Balch [1991], but note correction [Balch, 1991]), 0.26 pg based on both field and culture measurements [Balch et al., 1992], 0.21 pg (P. M. Holligan, unpublished calcite measurements for the NE Atlantic bloom measurements as cited by Balch et al. [1992]), 0.47-1.05 pg for measurements from a North Atlantic bloom [Balch et al., 1996a; Fernández et al.,
- [10] The above observations suggest that field measurements of coccolith carbon content often are greater than measurements from cultures. Results from nonbloom measurements in the Equatorial Pacific [Balch and Kilpatrick, 1996] and Arabian Sea [Balch et al., 2000] certainly support this contention, as do observations of Paasche [2002]). We surmise that PIC present in other relatively rare, undocumented, calcite particles (e.g., other rare coccolithophores, foraminifera, and pteropod species, resuspended calcite particles or even fecal pellets containing coccoliths [Keller et al., 1992]) contribute to the elevated PIC coccolith content measured in the field.
- [11] More recent culture-based estimates of PIC per coccolith for *E. huxleyi* (based on Ca measurements from cell-free suspension) have shown values of about 0.2 pg PIC, consistent with previous culture measurements: 0.18–0.25 pg PIC for an Atlantic clone [*Paasche*, 1998, 1999], 0.20–0.23 pg for a clone from coastal Scandinavia [*Paasche*, 1999; *Paasche et al.*, 1996], 0.27 pg for a Mediterranean clone [*Paasche*, 1999]. X-ray analysis of individual coccoliths showed 0.201 pg PIC per coccolith [*Fagerbakke et al.*, 1994]. The above cell-free PIC estimates are reasonably close to the theoretical value of 0.276 pg estimated by *Young and Ziveri* [1999] using coccolith dimensions.
- [12] These observations suggest that the overall strategy for designing a radiance-based PIC algorithm clearly should be to incorporate the light scattering properties of *E. huxleyi*, consistent with (1) its large numerical abundance in the global ocean (including frequent mesoscale blooms) and (2) its relatively stable PIC coccolith content

- and an optical backscattering cross section for *E. huxleyi*-sized coccoliths that is orders of magnitude greater than for larger calcite-containing particles in the sea, such as foraminifera and pteropods [*Balch et al.*, 1996a]. This means that the bulk of calcite-related reflectance likely originates from small, *E. huxleyi*-sized coccoliths, not larger (and much less abundant) foraminfera and pteropods. While most historical literature supports a value of ~0.2 pg PIC per coccolith to convert coccolith concentration to PIC, it is likely that algorithm PIC estimates based on this conversion may be underestimates of the total PIC concentration since they nonetheless neglect rare, relatively large, suspended calcite particles.
- [13] In this paper, we present a formalized description of a two-band algorithm for the determination of the concentrations of detached coccoliths, suspended calcium carbonate and chlorophyll based on normalized water-leaving radiance at 440 and 550 nm. We present validation results for this optical algorithm based on shipboard measurements from a variety of environments. Next we calculate the overall accuracy of the satellite-based PIC estimates, assuming different time and space binning. We apply the two-band algorithm to water-leaving radiance data from MODIS/Terra (a 36-band satellite spectrometer designed to observe land, ocean and atmosphere) to produce global PIC maps. Last, we make some preliminary inferences about the expected global rates of calcite production based on limited observations from a few ocean regions of the turnover time of calcite coccoliths in the euphotic zone.

2. Methods

- [14] As described below, the two-band PIC algorithm is based on a semianalytic model of ocean color developed by *Gordon et al.* [1988] to explain the variation of water-leaving radiance with pigment concentration observed in radiance measurements of *Clark* [1981]. (Note that the pigment concentration (*C*) is defined as the sum of the concentrations of chlorophyll *a* and phaeophytin *a* measured fluorometrically.)
- [15] Field validation measurements used to test this algorithm were made in the Straits of Florida, Arabian Sea, North Atlantic (south of Iceland), and Gulf of Maine. We also include measurements associated with an experimental addition of Cretaceous chalk to surface seawater in the NW Atlantic (dubbed "Chalk-Ex," complete details to be published elsewhere). Most of the data, in fact, come from the Gulf of Maine, due to the proclivity of naturally occurring coccolithophore blooms in the region as well as the presence of our long-term sampling program aboard a passenger ferry, the M/S *Scotia Prince* [*Balch*, 2001; *Balch et al.*, 2004].
- [16] Shipboard validation consisted of parallel measurements of acid-labile backscattering (b_b') with a multiangle light-scattering photometer [Balch et al., 2000, 2001; Balch and Drapeau, 2004; Balch et al., 1999, 1996a] and PIC determinations [Balch et al., 1996a; Balch and Kilpatrick, 1996; Fernández et al., 1993] on sea water samples. We also validated the algorithm using measurements of upwelling radiance, sky radiance and downwelling irradiance at 443 and 555 nm, made with a Satlantic SAS system mounted on the above-mentioned ferry, using protocols

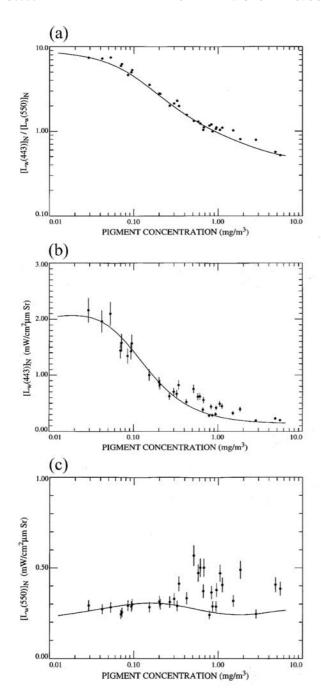


Figure 1. (a) Normalized water-leaving radiance ratio between 443 and 550 nm as a function of the pigment concentration. (b) Normalized water-leaving radiance at 443 nm as a function of the pigment concentration. (c) Normalized water-leaving radiance at 550 nm as a function of the pigment concentration. Data points are from *Clark* [1981], and the curve is the result of the semianalytic model [*Gordon et al.*, 1988]. The plankton-detritus scattering parameter in the model has been adjusted to provide the best fit to the *Clark* [1981] data for concentrations less than 0.3 mg m⁻³.

described by *Mueller et al.* [2003]. Briefly, the location of the radiance sensors on the bow of the ferry avoided any potential wake contamination in the upwelling radiance data. The upwelling (ocean) and downwelling (sky) radi-

ance sensors were always pointed 40° from nadir and zenith, respectively, and $90^{\circ}-120^{\circ}$ from the Sun's azimuth to minimize Sun glint. A downwelling irradiance sensor was located on the uppermost deck of the ship, away from any of the ship's superstructure, in order to achieve a full view of the sky. All data were sampled at 16 Hz and only the lowest 5% of the data were used, in order to eliminate highly reflective white caps. SAS-based PIC estimates are reported only if made under clear-sky conditions.

[17] MODIS/Terra data used in the validation activities were sampled at 1 km resolution. Data for global images were used at 36 km resolution. Version 4.1 of the MODIS processing software was used to process the data. MODIS processed data are assigned a product quality level ranging from 0 (best) to 3 (worst). The quality of the MODIS level 2 products for the coccolith concentration, the PIC concentration and pigment concentration in the presence of coccoliths, depend directly on the quality of the input data (normalized water-leaving radiance at 443 nm and 551 nm). Therefore these three products have been assigned the quality level of the input data. Moreover, if the calculated PIC concentration was ≤ 0 or ≥ 1000 mg PIC m⁻³ (exceeding the highest level ever observed in a bloom) then the quality level for the coccolith/PIC products and coccolithophore pigment concentration was assigned a quality level of 3 (worst). For the results reported here, we required that the input data, as well as the resultant calcite products, all had quality flags set to zero (highest quality).

3. Results

3.1. Moderate-Resolution Imaging Spectroradiometer (MODIS) Two-Band Algorithm for Coccoliths and Suspended Calcite

[18] Using the data of Clark [1981], the Gordon et al. [1988] semianalytic radiance model successfully explained the dependence of the blue-green water-leaving radiance ratio on the pigment concentration (Figure 1a). It actually fits the ratio data better over the full range of pigment concentration than the power law fits usually used in the analysis of remotely sensed ocean color data [e.g., see Gordon and Morel, 1983]. It was also moderately successful at relating the actual radiances themselves to the pigment concentration. Figures 1b and 1c compare the computed and observed relationship between $[L_w(443)]_N$, $[L_w(550)]_N$ and pigment concentration (C) for the same data shown in Figure 1a. In the figures, the plankton-detritus scattering parameter was adjusted to provide the best fit for C < 0.3 mg m^{-3} . The resulting value of this parameter was well within the range generally found for Case 1 waters [Gordon and Morel, 1983]. Also, the "noise" in the relationship for C > 0.3 mg m⁻³ appears to be due to the natural variation in the backscattering of plankton and detritus, as it is consistent with the noise observed in the scattering-chlorophyll relationship for Case 1 waters [Gordon and Morel, 1983]. It was straightforward to introduce detached coccoliths from coccolithophores into the model by simply including their contribution to the backscattering.

[19] By direct measurement of detached coccoliths in the Gulf of Maine, *Balch et al.* [1991] showed that at 436

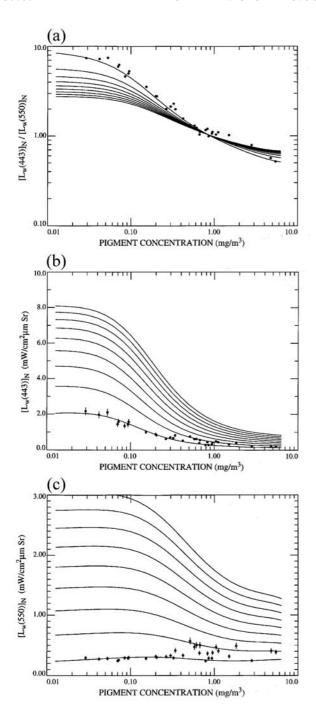


Figure 2. Results of the semianalytic model [Gordon et al., 1988] with increasing coccolith concentration (C_{cc}), plotted along with data points from Clark [1981]. (a) Normalized water-leaving radiance ratio between 443 and 550 nm as a function of the pigment concentration. Curved lines are for different values of C_{cc} , increasing from 0 to 200×10^6 coccoliths L^{-1} , in steps of 25×10^6 coccoliths L^{-1} (the higher coccolith concentrations yield the "flatter" curves). (b) Normalized water-leaving radiance at 443 nm as a function of the pigment concentration. (c) Normalized water-leaving radiance at 550 nm as a function of the pigment concentration. For both Figures 2b and 2c, curved lines are for different values of C_{cc} from 0 to 200×10^6 coccoliths L^{-1} , increasing in steps of 25×10^6 coccoliths L^{-1} , from bottom to top.

and 546 nm the backscattering coefficient, $b_b(\lambda)$, of the detached coccoliths was approximated by

$$b_b(\lambda) = A(\lambda)C_{cc},\tag{2}$$

where C_{cc} was the concentration of detached coccoliths, A (436) = 1.5×10^{-13} m² coccolith⁻¹, and $A(546) = 1.1 \times 10^{-13}$ m² coccolith⁻¹. On the basis of these measurements the spectral variation of $b_b(\lambda)$ was best described by equation (3):

$$b_b \propto \lambda^{-1.35}. (3)$$

Figures 2a-2c provide the radiance ratio, $[L_w(443)]_N$ $[L_w(550)]_N$ as functions of C and C_{cc} , as derived from the radiance model. Figure 2a shows that if the blue-green ratio were applied to ocean color data without regard for the presence of coccoliths considerable error would be present in the retrieved pigment concentration. For example, if the measured ratio was 4 and C_{cc} was 75 × 10⁶ coccoliths L⁻¹, C would be approximately 0.05 mg m⁻³ but if coccoliths were ignored, the retrieved value of C would be closer to 0.11 mg m^{-3} . Examination of Figures 2b and 2c shows that, while the coccolith concentration exerts a strong influence on both $[L_w(443)]_N$, C still has a large influence on $[L_w(443)]_N$ but only a moderate influence on $[L_w(550)]_N$. This suggests that it should be possible to separate, with reasonable accuracy, C and C_{CC} in measurements of $[L_w(443)]_N$ and $[L_w(550)]_N$. The two-band algorithm simply consists of inverting the semianalytic model to derive C and C_{cc} from measurements of $[L_w(443)]_N$ and $[L_w(550)]_N$. This is accomplished with the aid of a lookup table that is graphically represented in Figure 3. Examination of Figure 2b suggests that the natural variation in phytoplankton backscattering for $C < 10 \text{ mg m}^{-3}$ corresponds to 0 to 25 \times 10⁶ coccoliths L⁻¹. Thus given accurate values of $[L_w(\lambda)]_N$ there will always be an uncertainty in Values of $L_w(\lambda)_{JN}$ under win almost 5 L^{-1} . Figure 3 suggests that the sensitivity of the radiances to C_{cc} falls by about a factor of 2 from low to high C. Note, Figure 3 provides a simultaneous method for deriving both C_{cc} (or the equivalent PIC concentration assuming the coccoliths are from E. huxleyi) and C in coccolithophore blooms; however, the sensitivity when the pigment concentration is >2 mg m⁻³ is poor.

3.2. Influence of Atmospheric Correction on the Accuracy of the Two-Band Algorithm

[20] As the two-band PIC algorithm uses absolute values of the water-leaving radiances, it is more susceptible to error in atmospheric correction than algorithms employing radiance ratios. Thus atmospheric correction could be an important source of error, over and above the inherent error in the algorithm due to natural variability in calcite particles in the sea. The atmospheric correction algorithm [Gordon and Wang, 1994; Gordon, 1997] uses near infrared (NIR) spectral bands to assess the atmospheric interference based on the observation that $[L_w(\lambda)]_N$ is usually negligibly small in the NIR. The algorithm has an inherent error of ± 0.002 and ± 0.0005 in normalized water-leaving reflectance at 443 and 550 nm, respectively. (Normalized water-leaving reflectance $[\rho_w(\lambda)]_N$ is related

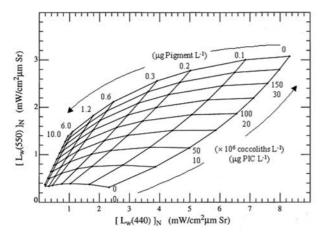


Figure 3. Graphic representation of the lookup table used to estimate the coccolith concentration and the pigment concentration from $[L_w(443)]_N$ and $[L_w(550)]_N$. The lines with the steeper slopes are lines of constant pigment concentration specified in units of μg pigment L^{-1} (written along the top curve on the figure). The lines with more gentle slopes are lines of constant coccolith concentration. The concentration is written along the rightmost curve of constant pigment either in units of 10^6 coccoliths L^{-1} (upper numbers) or after conversion to particulate inorganic carbon (PIC) in units of μg PIC L^{-1} (lower numbers). The natural variability of phytoplankton-detritus backscattering approximately corresponds to the separation between adjacent C_{cc} isopleths.

to $[L_w(\lambda)]_N$ through $[\rho_w(\lambda)]_N = \pi [L_w(\lambda)]_N/F_0(\lambda)$, where F_0 is the extraterrestrial solar irradiance.) However, with increasing coccolith concentration, there will be a nonnegligible $[L_w(\lambda)]_N$ in the NIR, and this will lead to additional error in atmospheric correction: the NIR $[L_w(\lambda)]_N$ will be interpreted by the algorithm as a contribution from the atmosphere. Thus we examine the influence of atmospheric correction errors for both low (negligible $[L_w(\lambda)]_N$ in the NIR) and high (significant $[L_w(\lambda)]_N$ in the NIR) coccolith concentrations.

- [21] For low coccolith concentrations and the Sun near the zenith, the errors in atmospheric correction described above correspond to uncertainties of ± 0.12 and ± 0.03 mW cm⁻² m⁻¹ Sr⁻¹ in $[L_w(\lambda)]_N$ at 443 and 550, respectively. It should be noted that by the nature of the atmospheric correction algorithm, these errors will have the same sign, i.e., both will be positive or negative. For a coccolith concentration of 15×10^6 coccoliths L⁻¹, the error in C_{cc} will be approximately $\pm 2 \times 10^6$ coccoliths L⁻¹ for C near 0.2 mg m⁻³ and approximately $\pm 1 \times 10^6$ coccoliths L⁻¹ for C near 1 mg m⁻³. Thus for low C_{cc} the atmospheric correction–induced error in C_{cc} is negligible compared to that induced by the natural variability in plankton-detritus backscattering. The error induced in C however, is quite large for C > about 1 mg m⁻³.
- [22] To assess the influence of atmospheric correction errors at high C_{cc} , we need to estimate $[\rho_w(\lambda)]_N$ in the NIR. As the absorption coefficient of water is very large in the NIR, the pigment concentration is almost irrelevant in predicting the reflectance, so $[\rho_w(\lambda)]_N \cong b_b(\lambda)/6a_w(\lambda)$,

Table 1a. Error in Retrieved $[L_w(\lambda)]_N$ Due to Coccolith-Induced Water-Leaving Reflectance in the Near-Infrared (NIR)

C_{cc} , coccoliths L^{-1}	$\Delta [L_w(443)]_N$, mW/cm ² μ Sr	$\Delta [L_w(550)]_N$, mW/cm ² μ Sr
100×10^6 200×10^6	-0.066 -0.155	-0.057 -0.115

where $a_w(\lambda)$ is the absorption coefficient of water. For $C_{cc} = 100 \times 10^6$ coccoliths L⁻¹, this gives $[\rho_w(765)]_N \cong$ 0.00045, and $[\rho_w(865)]_N \cong 0.00022$, and doubling C_{cc} will simply double these values. These reflectances will be interpreted by the correction algorithm as an addition to the reflectance of aerosols $\rho_A(\lambda)$. Typical values of $\rho_A(\lambda)$ in a clean maritime atmosphere are ~0.01 with little dependence on wavelength. The correction algorithm uses the aerosol reflectances at 765 and 865 nm to assess the spectral variation $\rho_A(\lambda)$ in the NIR and then uses aerosol models to extrapolate this into the visible. Following the approximate single scattering development provided by Gordon [1997], $\rho_A(\lambda) = \exp[a \ (865 - \lambda)] \rho_A(865)$, where the parameter a is found by setting λ to 765 nm. Adding the NIR reflectance contribution from the coccoliths to the true $\rho_A(\lambda)$ for a clean maritime atmosphere, i.e., 0.01, determining the apparent a, and computing the apparent $\rho_A(443)$ and $\rho_A(550)$, we arrive at the error in $[L_w(443)]_N$ and $[L_w(443)]_N$ provided in Table 1a. The error induced in the retrieved C_{cc} by the coccolith-induced NIR waterleaving reflectance can be determined by picking a point (C_{cc},C) on Figure 3, adding $\Delta[L_w(443)]_N$ and $\Delta[L_w(550)]_N$ to the normalized water-leaving radiances at the point and determining the change in C_{cc} and C. The resulting change in C_{cc} for both low and high pigment concentration is provided in Table 1b. This suggests that the error induced by NIR coccolith reflectance is also negligible compared to the natural variability in plankton-detritus scattering.

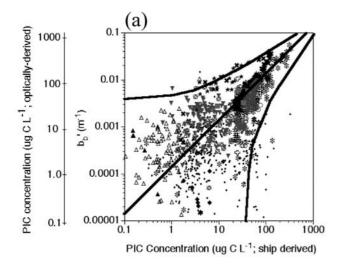
3.3. Validation Results

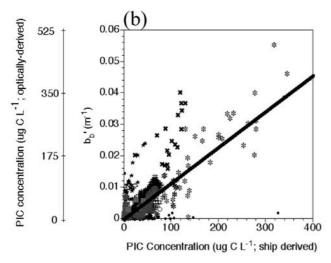
[23] When ship and satellite validation data were plotted using log axes (which highlights errors at low PIC concentration (Figure 4a)) and linear axes (which better shows the high PIC concentration results from blooms (Figure 4b)), the statistics showed an overall RMS error of 28 μ gPIC L⁻¹ for 1 kilometer pixel data on any given day. It was possible that the variance about the lines in Figures 4a and 4b, particularly at low PIC concentrations, arose from other non-PIC, nonorganic particles such as biogenic silica. Using only the satellite-derived validation data plotted (i.e., not including ship radiance data), the RMS error was reduced by about a factor of two (to \sim 15 μ gPIC L⁻¹ (Figure 4c)). This may indicate that the satellite-derived radiances are more accurate than the ship-derived radiances (which might

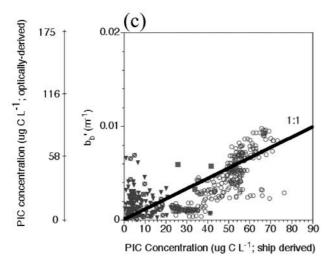
Table 1b. Error in Retrieved C_{cc} Due to Coccolith-Induced Water-Leaving Reflectance in the NIR

C, mg/m ³	C_{cc} , coccoliths L ⁻¹	ΔC_{cc} , %
0.07	100×10^{6}	-4.2
1.2	100×10^{6}	-6.4
0.07	200×10^{6}	-5.3
1.4	200×10^{6}	-5.4

be expected, given errors in azimuthal and nadir viewing geometries due to ship roll). The causes of the above RMS error may have resulted from a mismatch in the background, noncalcite, b_b value assumed in the algorithm versus that present in the field. For example, it can be seen in the 2002 Gulf of Maine bloom satellite results (designated with open circles in Figure 4c) retrievals where the satellite-derived







PIC values approached zero while the ship-derived values were about 30 ug C L⁻¹. Such "blank" bias varied for the other field data sets in Figure 4c, with data falling above and below the 1:1 regression line. Another potential source of variability between ship and satellite measurements might have been due to errors in atmospheric correction.

- [24] Even with the increased accuracy associated with using just the satellite-derived PIC estimate, it is difficult using 1 km daily data to accurately derive background oceanic PIC concentrations from satellite since the average global PIC concentration is $\sim 2~\mu g PIC~L^{-1}$, less than the RMS error about the line in Figure 4c.
- [25] The solution to the above problem, that the background PIC concentration is less than the standard deviation of the technique used to measure it, is to bin the satellite data in space and time, the sample size could be made sufficiently large that the standard errors were then significantly reduced. This is shown in the table of standard errors for the PIC algorithm (Table 2) where, at spatial scales of 4.6 km and time binning of 8 days, the standard errors of the PIC estimates were $\sim\!1.2~\mu gPIC~L^{-1}$, slightly less than the average global PIC concentration. For data binned over 36 km and 30 days, the standard error was 0.08 $\mu gPIC~L^{-1}$, 1/16 of the average PIC concentration in the global ocean.

Figure 4. (a) Plot of optically derived PIC concentration versus ship-measured values (based on inductively coupled plasma atomic absorption spectrometry measurements of particulate material). The y axis includes an extra scale with the intermediate acid-labile backscattering value (b'_b) used to optically estimate PIC. Conversion of b'_b to PIC assumes 1.37 m² mol PIC⁻¹ = 1.14 × 10⁻⁴ m² [mg PIC]⁻¹. The data sets used to make this plot were 1991 Iceland coccolithophore bloom (asterisks), Arabian Sea 1995 (open triangles), Straits of Florida 1995 (solid triangles), flow cytometer analysis of sorted coccoliths (solid stars), Gulf of Maine Ferry 1998–2001 (solid dots), Chalk-Ex ship measurements November 2001 (black crosses), Moderate-Resolution Imaging Spectroradiometer (MODIS) Gulf of Maine 2000–2001 (shaded squares with white cross within), Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Gulf of Maine 1998-2001 (solid inverted triangles), Gulf of Maine coccolithophore bloom ship measurements (open crosses, pound symbols), Gulf of Maine July 2002 coccolithophore bloom MODIS measurements (open circles), and Chalk-Ex MODIS measurements November 2001 (solid shaded squares). There are both satellite and ship data shown in this plot. The two bold, black, curved lines that enclose the data distribution were drawn by eye. The bold straight line is the least squares linear fit to the data, with the standard error given in parentheses $[b'_b(0.0033) = 1.145E-4]$ $(1.576E-6) \times PIC$; $r^2 = 0.60$; n = 1783; RMS error in PIC concentration = 28.56 ug PIC L⁻¹; P < 0.001]. (b) Same as Figure 4a, but using linear axes instead of log axes. The complete statistics for the plot are the same as in Figure 4a. (c) Same as Figures 4a and 4b, except only satellite-derived PIC data are shown. The bold straight line is the 1:1 line for PIC. The equation describing the best least squares linear fit to the data is $[b'_b = 9.665\text{E}-5 \times \text{PIC}; r^2 = 0.55; n = 463;$ RMS error in PIC concentration = 14.9 ug PIC L^{-1} ; P <0.001].

Table 2. Standard Error Estimates for Remote Particulate Inorganic Carbon (PIC) Measurements Binned at Different Timescales and Space Scales^a

		Spatial Res	olution, km	
Time Bins, days	1	4.63	36	111.2
1	14.90	3.218	0.414	0.134
8	5.632	1.216	0.156	0.051
30	2.720	0.588	0.076	0.024
365	0.780	0.168	0.022	0.007

^aPIC measurements are in μg PIC L^{-1} . The 111.2 km spatial scale is equivalent to 1 degree of latitude. Bold values show binning, which provides a standard error less than globally averaged PIC of \sim 2 μg PIC L^{-1} .

Space/time binning clearly allowed more confidence in interpreting global images of surface PIC.

4. Discussion

4.1. Potential Interactions From Other Suspended Minerals

[26] A potential source of error, not considered in the PIC algorithm, was the presence of other suspended minerals in the water, such as large concentrations of diatom silica (opal). The data used to make the two-band PIC algorithm were from the field, and indeed contained diatoms and their associated opal silica. Thus some degree of "opal contamination" is already inherent in the algorithm, which likely contributed to its overall error budget (but also we implicitly compensated for the presence of this mineral since it occurs naturally in the same seawater that the original algorithm was derived from). Nonetheless, it is well known that there are regions of the ocean that can have high concentrations of diatoms (e.g., Southern Ocean [Brzezinski et al., 2001]). In the Bering Sea, some regions of high scattering, once thought to be caused by coccolithophores, have been shown

to be resuspended diatom frustrules from the sea floor [Broerse et al., 2003]. Thus the issue is to define the error in the PIC algorithm when the opal:PIC ratio in surface waters was different from that used in the original algorithm development. In other words, we need to define how robust the PIC algorithm was under typical and atypical oceanic concentrations of biogenic silica.

[27] A first-order estimate of the error from suspended silica can be made quite easily. Brzezinski et al. [2001] observed concentrations of 12–16 µmol of biogenic silica per liter in intense diatom blooms in the Southern Ocean. In our laboratory, we have measured the mass-specific backscattering coefficient of suspended diatom frustules $(0.624 \text{ m}^2 \text{ (mol Si)}^{-1})$ [Broerse et al., 2003]. Thus the amount of Si observed by Brzezinski would contribute 7.5×10^{-3} to 10×10^{-3} m⁻¹ of backscattering over and above that due to POC- or PIC-containing particles. This quantity of biogenic silica in a diatom bloom indeed could cause significant error in the PIC determination. However, more typical biogenic silica concentrations (1– 3 μ mol L⁻¹) would only produce additional backscattering of 0.62×10^{-3} to 1.87×10^{-3} m⁻¹; such quantities likely are already "built into" the current PIC algorithm. In short, the extent of error due to biogenic silica cannot be estimated until radiometric data sets become available that would allow the partitioning of variance between opal and calcium carbonate.

4.2. Recent Observations of Global Particulate Inorganic Carbon (PIC)

[28] The launch of MODIS/Terra and MODIS/Aqua, along with the above-described validation results, have allowed the first opportunities to map global PIC with definable errors (Table 2). We have assembled version 4.1 MODIS/Terra data from 2002 into images of seasonal

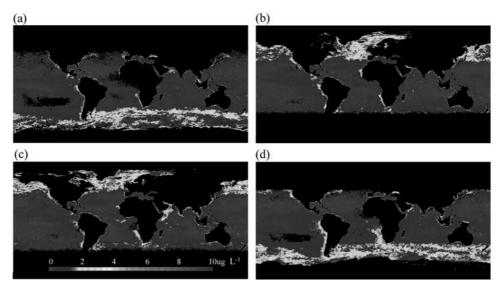


Figure 5. Global composite images of suspended PIC concentration calculated from MODIS/Terra data using two-band calcite algorithm. See text for other details of how the data were processed. The color scale is highlighted in Figure 5c. These data were binned into 36 km and 90 day averages, and thus the standard error will be $<0.08~\mu gPIC~L^{-1}$ (see Table 2), well below the average seawater concentration of $\sim 2~\mu gPIC~L^{-1}$. (a) January–March. (b) April–June. (c) July–September. (d) October–December. See color version of this figure at back of this issue.

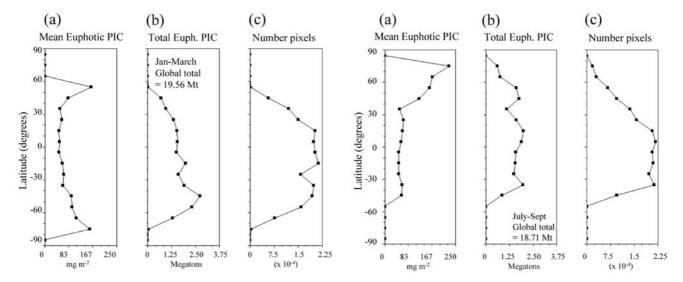


Figure 6. Statistics for 2002 PIC estimates as a function of latitude between January and March. (a) Mean PIC integrated over the euphotic zone. (b) Total euphotic zone PIC, integrated aerially in each latitudinal band. (c) Number of pixels analyzed in each latitudinal band. See text for details.

average PIC (Figure 5). There were some striking features in these data. From October to March (including Austral spring and summer), there were large regions of the Polar Convergence Zone and subpolar front that appear to have relatively high concentrations of PIC. Note, the peak concentration shown in Figure 5 is 10 μ g PIC L⁻¹, which, by no means should be considered a discolored coccolithophore bloom, but still is significantly higher than typical values seen in the central ocean gyres. From April to September (including Northern Hemisphere spring and summer) the Bering Sea, North Atlantic and Barents Sea showed high concentrations of PIC. The

Figure 8. Statistics for PIC estimates as a function of latitude between July and September 2002. All else is identical to Figure 6.

Namibian upwelling region, off of West Africa, showed dramatic increases in PIC concentration between October and December (Figure 5d).

[29] Given the seasonal images in Figure 5, we integrated the total surface PIC over the euphotic zone, within 10° latitudinal bands (Figures 6–9; Tables 3 and 4). First, the depth of the euphotic zone was estimated using satellite-derived chlorophyll concentration; the MODIS product "chlor-a2" was used as input to the algorithm for calculation of the average K_{par} over the euphotic zone to the 1% light depth [Morel, 1988, equation (5)]. We then made the first-order assumption, admittedly over simplified but still reasonable based on field PIC results in non-bloom conditions, that the concentration of PIC was vertically uniform over the euphotic zone.

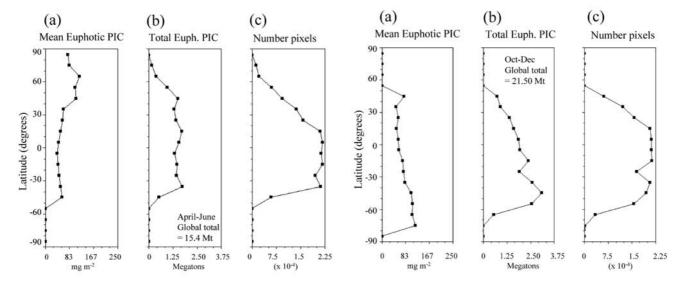


Figure 7. Statistics for PIC estimates as a function of latitude between April and June 2002. All else is identical to Figure 6.

Figure 9. Statistics for PIC estimates as a function of latitude between October and December 2002. All else is identical to Figure 6.

Table 3. Total Euphotic Zone PIC as a Function of Season in 2002, Estimated From the Surface to the 1% Light Level^a

								Midpo	int of 1	0° Lati	tudinal								All
	85	75	65	55	45	35	25	15	5	-5	-15	-25	-35	-45	-55	-65	-75	-85	
Jan-Feb	0.00	0.00	0.00	0.03	0.71	0.95	1.35	1.54	1.56	1.51	1.98	1.60	1.92	2.74	2.32	1.30	0.04	0.00	19.56
Mar-Jun	0.00	0.14	0.37	0.95	1.51	1.31	1.42	1.70	1.55	1.33	1.45	1.43	1.72	0.52	0.00	0.00	0.00	0.00	15.40
Jul-Sep	0.00	0.61	0.75	1.60	1.75	1.11	1.60	1.97	1.89	1.58	1.56	1.47	1.97	0.85	0.00	0.00	0.00	0.00	18.71
Oct-Dec	0.00	0.00	0.00	0.00	0.72	0.91	1.38	1.61	1.85	1.93	2.40	1.92	2.59	3.08	2.56	0.55	0.01	0.00	21.50

^aValues given in 10° latitude increments (in megatons of carbon). These same data are graphed in Figures 6b, 7b, 8b, and 9b. Values of 0.00 represent regions with no satellite radiance estimates available, mostly due to low Sun angle at high latitudes.

[30] Equation (25) of Morel [1988] (POC = 90 $C^{0.57}$) provided a means to estimate surface POC (mg m⁻³) based on the mean remotely sensed pigment concentration, C. The pigment data used to generate Morel's [1988] relationship were sampled from a variety of environments ranging from oligotrophic to eutrophic regions (n = 409), spanning over three orders of magnitude of pigment concentration. Moreover, this relationship reasonably provided a range in the carbon:chlorophyll ratio of 1000 in the most oligotrophic environments to 25 in eutrophic environments, which is the typical range of field observations [Eppley et al., 1977; Geider, 1987; Steele and Baird, 1962]. In order to integrate the POC values to the base of the euphotic zone, we assumed a constant POC concentration with depth. We caution that this only provides a first-order estimate of euphotic POC since there is well known vertical heterogeneity in phytoplankton biomass over the euphotic zone [Cullen, 1990].

[31] Seasonal global totals of euphotic PIC (within all latitudes visible to the satellite) ranged from 15.4-21.5 Mt PIC (Figures 6-9). Moreover, the results demonstrated two global patterns of PIC distribution over the year. The first pattern prevailed between October and March, when about 69% of the PIC was in the Southern Hemisphere. During the period between April and September, the pattern shifted hemispheres, but not symmetrically; about 59% of the PIC was in the Northern Hemisphere during this period. It is clear from the images (Figure 5) that the bands with elevated PIC in the Southern Hemisphere represented a large fraction of the total global euphotic PIC. About 40% of the global PIC was found south of 30°S between October and March compared to the April to September period in the Northern Hemisphere (in which \sim 29% of the PIC was found north of 30°N). Unfortunately, as of this writing, few shipboard data exist that could be used to validate these regions of elevated PIC in the Southern Convergence Zone.

4.3. Regional Analysis of PIC Distributions

[32] To provide more quantitative regional estimates of the global PIC standing stock, we used the biogeographic provinces described by *Longhurst* [1998] and calculated the average surface PIC concentration and its variance within each province over a season (Table 5). Owing to the high PIC concentrations observed in the Black Sea and Persian Gulf, we added separate provinces to *Longhurst*'s [1998] original list. The Caspian Sea is not included in our budget calculations due to its isolation from the global ocean. The Chesapeake Bay province listed by *Longhurst* [1998] also is not included here due to its small size. To aid in global estimates, we also generated a table of average integrated euphotic zone PIC concentration (calculated as described

above) and its standard deviation within each biogeochemical province (Table 6).

[33] Tabular budgets of surface PIC concentration demonstrate some striking trends. The seasonal average PIC concentration (Table 5) for all provinces was 2 μ g PIC L⁻¹ (which varied from $1.9-2.2 \mu g PIC L^{-1}$). Clearly, the PIC concentrations within the Trades biome were consistently the lowest, regardless of season, averaging 0.66-0.81 μg PIC L⁻¹. Northern polar biomes (including boreal polar, Atlantic Arctic, Atlantic Subarctic, North Pacific Epicontinental) consistently showed above average PIC concentrations, at least when they were visible to the MODIS sensor between April and September. Northern polar PIC concentrations were highest between July and September 2002. The Atlantic Subarctic province, within the polar biome, showed $2-3 \times$ the global average PIC concentration during those months, fully consistent with previous observations of mesoscale coccolithophore blooms in these areas [Balch et al., 1992, 1996a, 1996b; Brown and Yoder, 1994; Fernández et al., 1993; Holligan et al., 1993]. Southern polar biomes, when visible to MODIS/Terra between October and March, showed PIC concentrations slightly lower than the Northern Hemisphere polar biome. There are few validation measurements from this region to confirm these MODIS estimates. Coastal provinces had the greatest PIC concentrations of all the biomes, averaging between 2.5 to 3.8 μ g PIC L⁻¹, depending on the season. As might be expected, the variance in PIC concentration was greatest over space and time in the coastal provinces.

[34] Specific provinces that had above average PIC concentrations, in at least one 3 month period, were: boreal polar, Atlantic arctic, Atlantic subarctic, North Pacific epicontinental, Black Sea, Pacific subarctic gyres (east and west), northeast Atlantic Shelves, Canary coastal, Guianas coastal, northwest Atlantic shelves, southwest Atlantic shelves, Benguela Current Coastal, Persian Gulf, east India Coastal, west India Coastal, Australia west, Alaska downwelling coastal, China Sea Coastal and New Zealand Coastal. The observations of coastal shelf coccolithophore blooms are consistent with historical remote sensing observations from a number of these areas such

Table 4. Percentage of Total Global, Euphotic PIC Poleward of 30° Latitude or the Equator as a Function of Season in 2002

	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec
% PIC N of 30°N	8.65	27.80	31.07	7.57
% PIC S of 30°S	42.55	14.59	15.08	40.88
% PIC N Hemisphere	31.39	58.07	60.30	30.10
% PIC S Hemisphere	68.61	41.93	39.70	69.90

Table 5. Surface PIC Aerially Integrated Within the Biogeochemical Provinces Defined by Longhurst [1998]^a

		Pixels	0	0 0	501	18530	685	508	686 7715	1978	329	3034	087	2116	5646	9584	1386	21359	31728	5360	3314	3048	12847	1/87	12400	10281	5941	9444	6340	13	465	484	811	728	1310	677	2568	321 125	2325	502	546 1966
Average		PIC:POC	NA	Υ Z	0.032	0.045	0.039	0.017	0.026	0.036	0.086	0.016	0.033	0.027	0.021	0.020	0.034	0.037	0.040	0.027	0.020	0.028	0.040	0.051	0.031	0.019	0.024	0.024	0.023	0.130	0.045	0.034	0.085	0.037	0.059	0.057	0.042	0.036	0.025	0.060	0.050
-Dec A	SD,	mg/m ³	0.00	00.0	1.14	0.47	0.94	0.21	1.32	5.15	2.04	0.33	0.40	1.95	0.30	0.18	0.77	0.36	0.02	3.40	0.30	0.31	0.66	6.53	0.25	0.20	0.24	0.39	1.47	5.19	2.42	1.22	9.10 3.01	2.09	2.36	2.11	2.30	7.97	0.93	5.64	6.51 2.14
Oct	Surf. PIC,	mg/m ³	0.00	00.0	1.83	1.77	1.61	0.65	1.02	1.22	6.17	0.47	1.51	1.02	0.78	0.40	1.65	0.80	1.04	0.66	0.62	0.97	1.12	1. // 0.60	0.70	0.40	0.67	0.75	0.32	6.28	2.38	1.73	88.4	1.55	5.17	4.13	1.59	9.29	1.33	3.45	3.50 1.63
	Tot. PIC,	Mt	0.0000	0.0000	0.0010	0.0257	0.0007	0.0004	0.0008	0.0029	0.0023	0.0018	0.0008	0.0028	0.0052	0.0053	0.0028	0.0237	0.0202	0.0051	0.0032	0.0045	0.0197	0.007	0.0121	0.0058	0900.0	0.0108	0.0076	0.0001	0.0015	0.0013	0.0060	0.0016	0.0067	0.0044	0.0056	0.0008	0.0046	0.0025	0.0028
		Pixels	7123	3208	4420	0	0	3608	966	2106	350	3558	3292	2497	6157	9839	1370	25571	5189	5514	3535	2981	12893	28/2	12407	10586	5929	9385	6317	738	485	429	96/	720	278	752	2567	328 126	2032	586	443 1976
Average		PIC:POC	0.064	0.058	0.050	NA	NA	0.043	0.027	0.033	0.181	0.021	0.079	0.030	0.033	0.026	0.030	0.021	0.023	0.032	0.019	0.022	0.024	0.043	0.020	0.026	0.025	0.019	0.024	0.050	0.032	0.032	0.061	0.071	0.111	0.040	0.041	0.035	0.036	0.079	0.064
Sep Ave	SD,	ng/m³ I	2.05	1.12 2.40	1.15	0.00	0.00	1.10	0.60	0.13	2.75	0.19	1.05	0.72	0.58	0.10	1.74	0.27	0.67	3.05	0.35	0.42	0.38	5.45	0.27	0.15	0.30	0.34	1.72	1.57	1.59	1.09	2 80	2.62	96.9	1.23	3.17	2.37	1.84	6.47	8.57 4.47
Jul-	Surf. PIC,	ng/m³ r	4.12	3.54	3.29	0.00	0.00	2.34	0.84	0.50	12.96	0.55	4.18 50	1.05	1.03	0.46	1.36	0.55	0.93	0.76	99.0	0.94	0.75	1.58	0.61	0.54	0.73	0.64	0.96	4.40	1.75	1.65	3.82	1.79	6.94	2.61	1.82	3.64	2.35	4.32	5.32 2.95
	Tot. PIC,	Mt	.0167	01111	.0130	0000	0000	.0083	00010	.0016	.0051	.0024	0000	.0034	.0075	.0064	.0023	0.0194	0046	.0061	0.0036	.0043	.0133	0113	01105	0800	.0065	0092	0088	.0027	.0011	.0011	0046	00018	.0021	.0027	.0064	9000	.0071	.0037	0.0035 0.0082
		Pixels	_		_	_	_	_	_	_	_	_		_	_		_		_	_	_	_	_	_	_	_	_	_	_	_	_		_	_	_				_	_	540 (1965 (
rage		PIC:POC I																																							0.052 0.047
-Jun Average	SD,	g/m³ Pl	1.34).47	.35	00.0	00.0	1.03	1.33	7.71	69:1	17	70	.94	.57	0.20	.20).23 45	.45	3.11).28).22).21	5.50).22	.16	69.).23	52	2.74	2.71	1.72	5.18 0.08	06.1	1.30	1.25	2.37	2.36	1.24	5.40	7.85 3.09
Apr-	Surf.	ıg/m³ m				_	_		_	_	•				_	_					_	_				_	_														3.75
	Tot. S PIC, I	=									(1																_														0.0030
		Pixels	_	0 0	_	_	_	_	_	_	_	_	_	_	_	_	_		_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_	_		_	_	_	542 0 1961 0
rage		PIC:POC I	NA	0.000 N A	0.029				0.035				0.017					0.032						0.034				0.019					0.07					0.036			0.055 0.041
Jan-Mar Average	SD,	m	0.00	0.00	0.99	0.78	98.0	3.42	2.60	1.01	1.43	0.50	0.26	2.31	0.24	0.20	0.28	0.27	0.07	3.60	0.56	0.19	0.32	24.65	0.17	0.26	0.31	0.28	2.13	9.12	2.90	1.08	/8./	1.50	1.58	2.52	1.81	2.34	1.30	4.75	7.96 2.16
Jan-	Surf. PIC,	~		0.00	1.56	1.85	2.56	1.73	1./1	1.10	6.07	0.62	0.65	1.11	0.67	0.40	0.65	0.57	1.51	0.68	0.53	0.49	0.64	1.90	0.53	4.0	0.64	09.0	0.40	19.00	2.76	1.35	4.49 84.4	1.19	3.69	2.85	1.28	1.82	1.23	2.43	4.33 1.38
	Tot. PIC,			0.0000	0.0008	0.0354	9600.0	0.0017	0.0011	0.0028	0.0024	0.0023	0.0004	0.0030	0.0041	0.0054	0.0011	0.0158	0.0223	0.0050	0.0021	0.0013	0.0112	0.00 /9	0.0092	0.0060	0.0057	0.0087	0.0039		0.0018	0.0005	0.0054	0.0012	0.0048	0.0031	0.0045	0.0008	0.0042	0.0022	0.0035 0.0038
		Biome		polar 0					westerlies 0				westerlies 0						westerlies 0			trades 0		trades 0					trades 0		coastal 0		coastal 0		_			coastal 0 coastal 0			coastal 0 coastal 0
		Bic	bc	od g	3 8	, bd	bd	west	West	west	west	west	west	west	west	west	west	west	WCSL	tra	tra	tra	tra	tra	tra	tra	tra	tra	ura fra	200	200	200	303	300	200	200	200	8 8	c05	200	₀₀
Surface PIC		Province	Boreal Polar	Atl Arctic	N Pac Epicontinental	Antarctic	Austral Polar	N Atl Drift(WWDR)	Gulf Stream N A41 Subtree Gras (M)	Mediterranean Sea	Black Sea	N Atl Subtrop Gyre (E)	Pac Subarctic Gyres (E)	Kuroshio Current	N Pac Polar Front	N Pac Subtrop Gyre	Tasman Sea	S Pac Subtrop Gyre	Subantarctic	N Atl Trop Gyre	W Trop Atl	East Trop Atl	S Atl Gyre	Caribbean Indian Mongoon Games	Indian S Subtrop Gyre	N Pac Trop Gyre	N Pac Eq Countercurrent	Pac Eq Divergence	w Fac warm Fool Archinelagic Deen Basins	NE Atl Shelves	Canary Coastal (EACB)	Guinea Current Coastal	Guianas Coastal	Brazil Current Coastal	SW Atl Shelves	Benguela Current Coastal	E Africa Coastal	Ked Sea Persian Gulf	NW Arabian Upwelling	E India Coastal	W India Coastal Australia West

PIC:POC Dec Average 0.00300.0005 0.3460 0.00650.0053 9800°C 0.0031 0.05 18750 84327 90896 0.05 Sep Average .68 0.81 0.0010 0.0019 0.0074 0.0012 0.0007 0.0045 0.0038 0.3290 0.00250.053 0.094 09860 14586 9826 91515 PIC:POC 0.00 .022 0.0320.036 0.05 Apr-Jun Average 1.04 0.94 0.88 2.73 80 0.0047 0.00420.00200.0064 0.0008 0.0005 0.0300.1000.0011 0.27710.08038307 87026 31767 95911 PIC:POC 0.026 0.040 0.033 Jan-Mar Average .03 66.1 0.0028 0.0049 0.0093 0.0008 0.3175 0.046 0.1170.0025 0.0080 0.0021 0.0004 coastal coastal coastal coastal coastal coastal coastal Alaska Downwelling Coastal California Upwelling Coastal Surface PIC Centr American Coastal Fable 5. (continued) East Australian Coastal New Zealand Coastal China Sea Coastal Inclassified Westerlies Summary Coastal **Irades** Sunda Polar

785 1867 498 2532 751 1110 324 **23281**4

99014 90306

0.029 0.036

), (3) standard deviation of the average PIC (mg m⁻³), (4) PIC:POC ratio (where PIC was taken from the average value in the second column of each 3 month period and POC was taken from the same column of Table 7), and (5) the total number of pixels available for the analysis. Any values of 0.00 in the first three columns of the polar biome for each 3 month period represent regions where no satellite radiance data were available, mainly due to low Sun angle. At the bottom of the table the global statistics are provided as well as statistics for each of the four biomes. total PIC for each province for (1) Results are given of 2002. period o made for each 3 month essentially, the total PIC found in the top meter of the water column, aerially integrated over the province), (2) average surface PIC (mg m have been Calculations Trades, and Coastal. Westerlies, respective biome: Polar, into their ^aProvinces are grouped

as the northwest Atlantic shelves [Ackleson et al., 1994; Balch, 2004; Balch et al., 1991; Keller et al., 1992; Matrai and Keller, 1993; Townsend et al., 1994], the northeast Atlantic shelves [Berge, 1962; Birkenes and Braarud, 1952; Brown and Yoder, 1994; Brussaard et al., 1996; Buitenhuis et al., 1996; Burkill et al., 2002; Garcia-Soto et al., 1995; GREPMA, 1981; Head et al., 1998; Holligan et al., 1983; Malin et al., 1993; Samtleben and Bickert, 1990; Van der Wal et al., 1995; Wal et al., 1995], Australian coastal [Blackburn and Cresswell, 1993], Alaska downwelling and North Pacific Epicontinental [Kai et al., 1999; Lavrentyev et al., 2001; Napp and Hunt, 2001; Stockwell et al., 2000; Takahashi et al., 1995; Broerse et al., 2003], Black Sea [Cokacar, 2001], the southwest Atlantic shelves [Gayoso, 1995], and Pacific subarctic gyres [Fukushima and Ishizaka, 1993; Takahashi et al., 1995].

[35] Satellite-derived PIC concentrations can be checked for consistency using independent ship measurements from the same area. Note, however, this approach only allows for a gross comparison of the PIC levels since the ship and satellite observations, while measured in the same season, were made in different years. Satellite-derived values of $0.64 \pm 0.34 \,\mu g$ PIC L⁻¹ were observed in the Pacific equatorial divergence province during July-September 2002 (Table 5). These were lower than the average shipboard value of 2.52 (±0.58) μg PIC L⁻¹ described by Balch and Kilpatrick [1996] for the period between August and September 1992, between 5°N and 5°S along 140°W, top 10 m only (n = 17; note one anomalously high surface value of 15 μ g PIC L⁻¹ at 2°N was not included in this average). Satellite-derived PIC values from the NW Arabian upwelling province were estimated to be $2.35 \pm$ 1.84 μg PIC L⁻¹ during August–September 2002 (Table 5). During July and August 1995, the average PIC measured by *Balch et al.* [2000] in the Arabian Sea was 2.38 \pm 2.14 μg PIC L⁻¹ [see *Balch et al.*, 2000, Table 1], not significantly different from the satellite-derived value. During October and November 1995, average PIC concentrations measured by Balch et al. [2000] were 1.62 \pm 2.03 μ g PIC L⁻¹, also not significantly different from the satellite-derived values between October and December 2002 (1.33 \pm 0.93 μ g PIC L⁻¹ (Table 5)).

[36] A different view of the PIC budget can be seen in the table of PIC concentrations integrated over the euphotic zone, and aerially over each province (Table 6). The average integrated concentrations of PIC approximately mirrored the trends in surface concentration described above (but not exclusively). Aerially integrating over the various biomes, the majority of the euphotic standing stock of calcium carbonate (70-77%) occurred in the combined Westerlies and Trades biomes. This is consistent with results suggesting that low-latitude, nonbloom coccolithophores are responsible for large export ratios of CaCO₃: organic matter [Sarmiento et al., 2002]. While the polar biomes had the highest concentrations of PIC, they only contributed 7-12% of the total PIC and the coastal biomes contributed ~15%. Note, however, these polar values are likely underestimates during the fall and winter months of each hemisphere, since no satellite-derived radiance estimates are possible due to low Sun angle. Provinces that contributed over 0.5 Mt of PIC (greater than \sim 2% of the global total PIC) for at least one 3 month

Table 6. Euphotic Zone PIC Aerially Integrated Within the Biogeochemical Provinces Defined by Longhurst [1998]^a

*		,)				•		4	1									
Int. PIC Over Euphotic Zone	Zone			Jan-Mar				A	Apr–Jun]		J	lul-Sep		ĺ			Oct-Dec		Ī
		Tot. PIC.		Avg Int. PIC.	SD.		Tot. PIC.	Ī	Avg nt. PIC.	SD.		Tot. PIC.	П	Avg nt. PIC.	SD.		Tot. PIC.		Avg int. PIC.	SD.	
Province	Biome		% Total	mg/m^2	mg/m^2	Pixels	Mt %	o Total	, "			Mt %	Total		ng/m ²	Pixels	Mt 9	% Total	mg/m^2	mg/m^2	Pixels
Boreal Polar	polar	0.000	0.00	0.00	0.00	0 0	0.115	0.75		37.03	2606 ().662	3.54		70.05	7123	0.000	0.00	0.00	0.00	0 0
Atl Subarctic	polar	0.000	0.00	0.00	0.00	0	0.277	1.80			_				86.67	3208	0.000	0.00	0.00	0.00	0
N Pac Epicontinental	polar	0.037	0.19	67.95	39.08	491	0.379	2.46			_				35.83	4420	0.043	0.20	77.61	41.00	501
Antarctic		1.988	10.17	104.02	30.24	25137	0.000	0.00							0.00	0 0	1.493	6.95	102.92	22.16	18530
Austral Folar N Afl Driff(WWDR)	potar westerlies	0.085	1.90 0.43	102.07 87.03	122.79	923	0.000	0.00							37.27	3608	0.041	0.19	39.41	45.39	508
Gulf Stream		0.048	0.24	73.74	90.51	554	0.059	0.38			_				27.54	966	0.043	0.20	53.74	52.55	989
N Atl Subtrop Gyre (W)	westerlies	0.192	86.0	37.82	18.95	3902	0.328	2.14			_				16.49	4622	0.204	0.95	35.72	13.59	4415
Mediterranean Sea		0.152	0.78	59.84	43.51	2074	0.154	1.00			_ `				22.69	2106	0.174	0.81	71.82	67.83	1978
Black Sea N Atl Subtron Gvre (F)	westerlies	0.082	0.42	210.41 40.24	47.44 22.37	349 2891	0.347	2.26 2.24							80.32	3558	0.087	0.40	255.65 34.81	02.42 15.86	3034
Pac Subarctic Gyres (E)		0.023	0.12	38.24	14.57	584	0.238	1.55			_				45.77	3292	0.040	0.19	79.93	19.47	473
Pac Subarctic Gyres (W)		0.044	0.22	45.62	21.63	906	0.162	1.06			_				41.67	2133	0.072	0.33	09.79	17.75	982
Kuroshio Current		0.150	0.77	55.57	67.75	2084	0.216	1.41			_				26.64	2497	0.156	0.72	56.73	68.92	2116
N Pac Polar Front	westerlies	0.237	1.21	39.09	13.79	5125	0.498	3.24			_ `				26.83	6157	0.319	1.49	48.05	16.05	5646
IN Fac Subtrop Cyre Tasman Sea		0.0350	0.38	59.44 44.63	12.48	1384	0.033	0.58			_				67.08	1370	0.343	0.65	83.21	30.63	1386
S Pac Subtrop Gyre		1.633	8.36	59.32	29.48	19687	1.591	10.35		(1					16.50	25571	2.148	66.6	72.19	30.06	21359
S Subtrop Convergence	westerlies	1.347	68.9	78.49	27.00	14724	0.703	4.58			_				28.88	13039	1.598	7.43	92.68	26.40	14790
Subantarctic	westerlies	2.959	15.14	95.27	29.49	31157	0.155	1.01			_				21.62	5189	3.334	15.50	105.57	24.78	31728
N Atl Trop Gyre	trades	0.344	1.76	47.38	135.15	5024	0.445	2.89			_				101.43	5514	0.339	1.58	43.81	113.76	5360
W Trop Atl		0.157	0.80	40.17	22.39	2564	0.206	1.34			_				16.12	3535	0.226	1.05	44.78	17.27	3314
East Trop Atl		0.099	0.51	37.00	15.34	1758	0.172	1.12			_				18.23	2981	0.294	1.37	63.27	17.91	3048
S Atl Gyre		1.115	5.71	63.91	26.65	12750	0.798	5.19			_ `				16.28	12893	1.512	7.03	85.99	35.74	12847
Caribbean Indian Monegon Gyrnes	trades	0.578	1.94 2.75	71.55	10.05	7/87	0.288	1.8/							21.74	C/ 87 10284	0.559	1.6/	80.99	163.41	1/8/1
Indian S Subtrop Gyre		0.997	5.10	57.99	17.54	12392	0.743	48.4 48.4		, (_				13.61	12407	1.076	5.00	62.54	14.20	12400
N Pac Trop Gyre		0.551	2.82	40.67	21.12	9584	0.704	4.58			_				14.32	10586	0.547	2.55	37.74	15.63	10281
N Pac Eq Countercurrent	trades	0.381	1.95	42.66	12.67	5918	0.444	2.89			_				14.07	5929	0.466	2.17	51.95	13.09	5941
Pac Eq Divergence		0.598	3.06	41.33	14.88	9489	0.528	3.43			_				18.14	9385	0.762	3.54	52.85	21.38	9444
W Pac Warm Pool	trades	0.592	3.03	48.14	22.00	8099	0.544	3.54			_				16.53	8190	0.608	2.83	48.89	14.04	8190
Archiperagic Deep Basins NE Atl Shelves	coastal	0.0220	0.33		282.83	95	0.434	20.7			_				20.44 45.53	738	0.323	0.02	252.20	46.20 181 41	13
Canary Coastal (EACB)	coastal	0.059	0.30		79.97	480	0.063	0.41			_				45.42	485	0.065	0.30	104.73	85.82	465
Guinea Current Coastal	coastal	0.020	0.10		31.21	242	0.049	0.32			_				46.17	429	0.058	0.27	78.48	42.22	484
Guianas Coastal	coastal	0.188	96.0		212.66	796	0.139	0.90			_				181.30	798	0.217	1.01	176.37	248.78	811
NW Atl Shelves		0.207	1.06	154.34	179.90	1152	0.180	1.17			_ `				132.59	1898	0.163	0.76	121.47	123.35	1150
Brazii Current Coastai	coastal	0.001	0.51	117.37	49.07	1211	0.075	0.47			_			`	84.24	0778	0.078	0.30	173.56	16.71	1210
SWK Att Silcives Benonela Current Coastal	coastal	0.102	0.70	94 63	49.74	783	0.010	0.07			_			•	35.83	757	0.220	0.78	155.74	56.10	779
E Africa Coastal	coastal	0.246	1.26	69.69	49.41	2565	0.228	1.49			_				96.93	2567	0.298	1.39	84.39	71.31	2568
Red Sea	coastal	0.037	0.19		85.57	318	0.034	0.22			_				67.27	328	0.037	0.17	80.05	99.79	321
Persian Gulf	coastal	0.051	0.26	_	220.31	124	0.024	0.16			_				77.05	126	0.057	0.26	332.59	259.81	125
NW Arabian Upwelling F India Coastal	coastal	0.169	0.86	49.05	34.83	2322	0.153	0.99							47.83	2032	0.218	1.01	63.22	30.41	2325
E IIIuia Coastal W India Coastal	coastal	0.074	0.30	129.03	183 79	542	0.030	0.58			_				08.50	269 443	0.092	0.45	119 37	170 12	502 546
Australia West	coastal	0.210	1.07	76.53	79.26	1961	0.269	1.75			_			•	175.72	1976	0.252	1.17	91.47	95.96	1966

3281

69.07 11.91 96806 56.64 18.699 0.034 0.059 09860 91515 Avg Int. PIC 111.89 51.63 38307 87026 31767 95911 01.21 31.85 41.01 66.04 00.00 9.546 0.026 .408 0.104 coastal coastal coastal coastal coastal coasta coasta Int. PIC Over Euphotic Zone Alaska Downwelling Coastal California Upwelling Coastal [able 6. (continued) Centr American Coastal New Zealand Coasta Australian Coastal China Sea Coastal Jnclassified Westerlies Summary Coastal Frades Polar

Results are given for each province for (1) total euphotic zone PIC (essentially, the total PIC found above the 1% light depth of the water column, aerially integrated over the province), (2) average integrated PIC (mg The algorithm used to estimate POC is described in the text m⁻²), (3) standard deviation of the average PIC (mg m⁻²), and (4) the total number of pixels available for the analysis. Any values of 0.00 in the first three columns of the polar biome for each 3 month period regions where no satellite radiance data were available, mainly due to low Sun angle. At the bottom of the table the global statistics are provided as well as statistics for each of the four biomes. Calculations have been made for each 3 month period of 2002. into their respective biome: Polar, Westerlies, Trades, and Coastal. regions where no satellite grouped ^aProvinces are

period, were boreal polar, Atlantic subarctic, North Pacific epicontinental, Antarctic, Austral Polar, North Atlantic drift, Black Sea, Pacific subarctic gyres (east and west), North Pacific polar front, North Pacific subtropical gyre, South Pacific subtropical gyre, south subtropical convergence, subantarctic, South Atlantic gyre, Indian Monsoon gyres, Indian subtropical gyre, North Pacific tropical gyre, Pacific Equatorial divergence, West Pacific warm pool, and Archipelagic deep basins. Not a single coastal province contributed more than 0.5 Mt PIC in any 3 month period.

[37] We summarize the POC budget as well, in order to support our estimates of the PIC:POC ratios globally. As with the PIC concentrations, the polar POC estimates are likely underestimates due to the fact that remote sensing is limited during winter and fall months of either hemisphere. Average surface POC concentrations were $\sim 40-52$ mg m⁻³, with highest average global POC from April to June (mean for all biomes = 52.1 mg m^{-3} ; SD = 26.05 (Table 7)). Provinces with POC concentrations >80 mg m⁻³ (which is $\sim 1.5-2 \times$ the mean) for at least one 3 month period of the year were Atlantic subarctic, Black Sea, northeast Atlantic shelves, northwest Atlantic shelves, southwest Atlantic shelves, Persian Gulf, Alaska downwelling, and west India coastal waters. As expected, lowest POC concentrations were consistently seen in the subtropical and tropical gyre systems of the Trades and Westerlies biomes. Our results nonetheless demonstrated that the Westerlies and Trades biomes accounted for 80-82% of global POC, even greater than the percentage of global PIC that comes from those same biomes. Polar regimes accounted for only 4.7-8.5% of the global POC, less than the fraction of total global PIC that is produced in the same region (Table 7). Coastal biomes supplied 11.8-13.9% of the global POC. Interestingly, the period from January to March and October to December had the highest global concentrations of POC (699 and 682 Mt, respectively, as opposed to 631 and 647 Mt during April-June and July-September (Table 8)).

[38] The PIC:POC ratio was estimated from the data shown in Tables 5 and 7 (note, because of how the PIC calculations were made, the ratios are identical whether they are based on surface or euphotic integrated estimates; thus, results are only shown in Table 5). The global average PIC:POC ratio varied from 0.041 (April-June) to 0.051 (July-September). Such values are highly consistent with average global export ratios estimated by Sarmiento et al. [2002] based on a biogeochemical transport box model of the top 100 m, using measurements of the vertical gradients of potential alkalinity and nitrate. The reader should note that our PIC:POC estimates would not be expected to match PIC:POC export ratios at 100 m. This is mainly because there can be mineralization of both components between the surface optical depth (the top few meters visible to MODIS/Terra [Gordon and McCluney, 1975]) and the 100 m depth horizon used by Sarmiento et al. [2002]. Nonetheless, their area-weighted global mean export ratio (0.056 ± 0.004; based on ocean chemistry) was strikingly close to our average global value of 0.047 ± 0.004 for all seasons, based on MODIS water-leaving radiance measurements.

Table 7. Surface POC Aerially Integrated Within the Biogeochemical Provinces Defined by Longhurst [1998]^a

Surface POC			Jan.–Mar	ır			Apr-Jun	n			Jul-S	-Sep			Oct-Dec)ec	
Province	Biome	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m ³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m ³	Pixels
Boreal Polar	polar	0.0000		0.00	0	0.1150	78.39	13.79	2786	0.2705	64.46	13.04	7360	0.0000	0.00	0.00	0
Atl Arctic	polar	0.0000	30.52	0.00		0.2210	70.59	9.94	4997	0.1914	60.77	8.01	4997	0.0000	0.00	0.00	0
Atl Subarctic N Pac Enicontinental	polar	0.0000	0.00 54 63	0.00	0	0.1750	87.75 92.31	16.63	322 / 403 1	0.1360	65.16 65.41	7.69 8.37	3228 4426	0.0000	0.00	0.00	0 808
Antarctic	polar	0.7814	38.41	6.00	26816	0.0000	0.00	0.00	0	0.0000	0.00	0.00	0	0.5807	39.67	4.53	18713
Austral Polar	polar	0.2238	57.12	10.55	6370	0.0000	0.00	0.00	0	0.0000	0.00	0.00	0	0.0194	40.97	4.02	719
N Atl Drift(WWDR)	westerlies	0.0730	34.95	5.12	2004	0.2353	66.15	7.89	3612	0.1921	54.03	6.74	3609	0.0506	38.24	2.15	1239
Gulf Stream	westerlies	0.0556	48.78	10.11	227	0.0626	53.86	10.83	966	0.0359	30.95	4.4 4.4	966	0.0450	38.87	5.28	994
N Atl Subtrop Gyre (W)	westerlies	0.1711	28.63	5.61	4622	0.1572	26.30	8.98	4622	0.1137	19.02	2.15	4622	0.1426	23.85	3.80	4622
Mediterranean Sea Black Sea	westerlies	0.1093	86.21	6/./ 14 54	351	0.0038	83.63 83.63	7.03 16.01	353	0.0089	71.60	6.71	351	0.0875	71.59	8.59	343
N Atl Subtrop Gyre (E)	westerlies	0.1499	33.79	5.48	3559	0.2001	45.11	16.08	3559	0.1159	26.12	5.26	3559	0.1263	28.47	4.30	3559
Pac Subarctic Gyres (E)	westerlies	0.0607	38.89	2.58	1518	0.1850	56.90	9.73	3371	0.1674	52.81	5.77	3293	0.0307	45.50	3.07	638
Pac Subarctic Gyres (W)	westerlies	0.0846	41.61	3.59	1942	0.1399	64.48	11.23	2105	0.1326	60.01	8.14	2139	0.0629	48.01	5.21	1218
Kuroshio Current	westerlies	0.1360	42.33	12.51	2504	0.1722	53.36	19.93	2517	0.1106	34.41	9.53	2506	0.1215	37.98	9.37	2493
N Pac Polar Front	westerlies	0.2986	40.80	4.87	6214	0.3139	43.82	8.47	0809	0.2301	31.67	5.54	6169	0.2678	36.63	4.55	6207
N Fac Subtrop Gyre	westerlies	0.2915	21.11	6.94	9839	0.0786	20.65	0.35	9839	0.2450	C/./I	1.6/	1204	0.2725	19.74	3.70	1200
Lasillali Sca S Pac Subtrop Gyre	westerlies	0.0329	17.84	6.23	75907	0.0700	73.67	7.27	25890	0.0707	25.50	6 95	75809	0.7695	71.57	4.04	25743
S Subtrop Convergence	westerlies	0.6278	36.41	11.53	14792	0.6245	42.78	7.14	12363	0.6229	37.20	5.02	14328	0.7104	41.21	7.56	14790
Subantarctic	westerlies	1.2271	39.05	7.87	31554	0.1568	43.90	5.50	3162	0.3122	34.62	3.77	8232	1.3404	42.44	6.33	31734
N Atl Trop Gyre	trades	0.1904	23.60	9.56	5577	0.2137	26.55	15.71	5562	0.1923	23.92	9.77	5557	0.1947	24.13	8.27	5578
W Trop Atl	trades	0.1469	27.26	5.16	3539	0.1874	34.79	7.35	3537	0.1879	34.87	7.96	3539	0.1645	30.52	4.45	3539
East Trop Atl	trades	0.1632	32.34	11.72	3309	0.1965	38.15	10.91	3379	0.2157	42.93	6.67	3295	0.1797	34.87	6.77	3380
S Atl Gyre	trades	0.3581	19.87	6.63	13146	0.5134	28.49	7.84	13146	0.5675	31.86	7.82	13005	0.4965	27.81	11.01	13032
Caribbean	trades	0.1456	35.00	17.07	2891	0.1329	31.98	15.70	2887	0.1338	32.18	14.39	2889	0.1438	34.58	13.86	2891
Indian Monsoon Gyres	trades	0.4192	26.83	0.00	10301	0.4631	29.65	4.0	10298	0.5492	35.17	8.3/	10295	0.4651	29.77	5.00	10298
Indian S Subtrop Gyre	trades	0.3051	17.73	5.47	12407	0.464/	27.00	5.34 1 8 1	1240/	0.5194	30.18 20.47	4.93 55 C	1240/	0.38/6	22.52	4.79 70	1240/
N Pac Ed Countercurrent	trades	0.2979	33.16	10.20	5948	0.3182	35.42	13.75	5948	0.2643	29.48	7.76	5934	0.2509	27.93	7.96	5947
Pac Eq Divergence	trades	0.4560	31.48	4.84	9492	0.5156	35.59	5.17	9492	0.4967	34.66	5.37	9387	0.4414	30.62	5.50	9444
W Pac Warm Pool	trades	0.2483	19.96	5.52	8188	0.2732	21.95	5.45	8191	0.2686	21.58	4.48	8191	0.2624	21.08	3.91	8191
Archipelagic Deep Basins	trades	0.2509	27.07	15.44	6348	0.2896	31.25	11.64	6347	0.3276	35.39	10.07	6340	0.2674	28.82	11.21	6356
NE Atl Shelves	coastal	0.0086	75.77	32 01	503	0.0848	130.27	18.50	501	0.05/8	88.37	17.50	800	0.0012	48.44 53.33	9.17	501
Guinea Current Coastal	coastal	0.0462	57.43	22.72	531	0.0605	60.87	21.35	655	0.0360	51.21	12.92	462	0.0503	51.40	15.47	645
Guianas Coastal	coastal	0.0744	59.59	63.03	823	0.0933	73.71	71.01	834	0.0795	62.92	61.17	833	0.0732	57.45	58.78	840
NW Atl Shelves	coastal	0.1089	64.92	20.52	1469	0.1754	82.83	22.73	1908	0.1226	57.81	16.87	1911	0.0849	56.77	17.10	1289
Brazil Current Coastal	coastal	0.0387	38.71	23.11	730	0.0425	42.61	15.50	727	0.0431	43.29	17.65	726	0.0420	42.08	25.12	728
SW Atl Shelves	coastal	0.1208	92.42	28.17	1315	0.0104	75.07	12.32	122	0.0238	62.72	13.01	347	0.1137	87.05	25.11	1315
Benguela Current Coastal	coastal	0.0778	72.05	48.78	783	0.0847	78.39	31.23	783	0.0695	66.03	18.15	764	0.0778	72.32	25.58	08/2
E Amea Coastal	coastal	0.1229	50.27	21.00	220	0.1018	45.81	16.29	243	0.13/0	20.73	11.91	240	0.1324	27.43	14.19	242
Red Sca Persian Gulf	coastal	0.0171	100.21	12.56	125	0.0203	86.25	9.33	125	0.0111	64.49	7.84	126	0.0131	75.94	8.43	126
NW Arabian Upwelling	coastal	0.2196	63.37	20.17	2337	0.1576	45.59	21.66	2331	0.2079	65.31	19.78	2141	0.1808	52.16	14.98	2337
E India Coastal	coastal	0.0571	58.91	49.50	662	0.0541	57.63	44.01	640	0.0482	54.70	29.39	601	0.0562	57.57	47.16	999
W India Coastal	coastal	0.0663	78.54	52.77	575	0.0597	71.60	51.30	267	0.0563	82.55	38.51	460	0.0590	69.85	40.80	575
Australia West	coastal	0.0942	34.04	14.26	1978	0.1295	46.80	13.49	1976	0.1281	46.23	11.40	1979	0.1019	36.89	11.59	1974

Table 7. (continued)

Surface POC			JanMar	ſar			Apr-Jun	u.			Jul-Sep	də			Oct-Dec)ec	
Province	Biome	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m ³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m ³	Pixels	Tot. POC, Mt	Avg. Surf. POC, mg/m ³	SD, mg/m ³	Pixels
Alaska Downwelling Coastal	coastal	9000.0	54.01	6.22	11	0.0572	117.35	13.99	695	0.0378	78.91	68.9	559	0.0000	0.00	0.00	0
California Upwelling Coastal	coastal	0.1266	47.13	19.62	2144	0.1477	57.40	30.78	2070	0.1225	45.16	19.78	2172	0.1040	42.39	13.48	1914
Centr American Coastal	coastal	0.0784	67.08	27.84	794	0.0749	64.55	26.84	789	0.0528	45.90	18.62	782	0.0584	50.27	19.41	790
Chile	coastal	0.1486	08.09	28.69	1891	0.1437	69.33	26.52	1522	0.1100	56.62	15.48	1469	0.1442	59.66	19.91	1874
China Sea Coastal	coastal	0.0553	79.13	29.15	518	0.0446	63.73	24.00	519	0.0352	50.27	13.55	520	0.0418	59.92	20.07	517
Sunda	coastal	0.1606	41.80	17.69	2531	0.1600	41.27	14.91	2554	0.1596	41.38	13.06	2541	0.1498	38.71	12.85	2549
East Australian Coastal	coastal	0.0260	25.14	7.09	754	0.0355	34.32	7.52	753	0.0380	36.62	6.65	754	0.0305	29.41	9.50	755
New Zealand Coastal	coastal	0.0563	46.67	9.51	1112	0.0253	55.27	80.9	396	0.0361	44.69	5.46	721	0.0632	52.48	9.93	1110
Unclassified		0.0136	30.61	24.31	360	0.0154	37.74	37.86	318	0.0149	34.70	28.70	337	0.0123	29.31	15.57	327
Summary		10.1730	43.66	21.56	260007	10.2363	52.13	26.05	213132	9.9558	44.15	18.76	224813	6.9977	39.59	18.56	243205
Polar		1.052	50.05	8.95	33970	0.847	82.26	12.03	15041	0.857	64.70	9.28	20011	0.638	45.64	4.90	20040
Westerlies		4.014	38.92	7.40	109301	3.582	46.95	9.84	81983	3.369	37.85	5.40	99688	4.137	38.42	5.52	106931
Trades		3.313	26.37	8.44	91768	3.890	30.21	9.10	91744	4.028	31.06	7.76	91433	3.572	27.83	7.13	91688
Coastal		1.780	88.65	25.58	24607	1.902	66.87	24.71	24046	1.687	55.76	17.95	24066	1.638	51.31	19.81	24219

^aProvinces are grouped into their respective biome: Polar, Westerlies, Trades, and Coastal. Calculations have been made for each 3 month period of 2002. The algorithm used to derive POC concentrations was according to Morel [1988] and is described in the text. Results are given for each province for (1) total POC (essentially, the total POC found in the top meter of the water column, aerially integrated over the province), (2) average surface POC (mg m⁻³), (3) standard deviation of the average POC (mg m⁻³), and (4) the total number of pixels available for the analysis. Any values of 0.00 in the first three columns of the polar biome for each 3 month period represent regions where no satellite radiance data were available, mainly due to low Sun angle. At the bottom of the table global statistics are provided as well as statistics for each of the four

Table 8. Euphotic Zone POC Aerially Integrated Within the Biogeochemical Provinces Defined by Longhurst [1998]^a

, (C)	t			;)			•	,		1	,									
Int. POC Over Euphotic Zone	Zone		_	Jan-Mar				A	Apr-Jun					Jul-Sep					Oct-Dec		
		Int. POC.		Avg. Int. POC.	SD.		Int. POC.	П	Avg.	SD.		Int. POC.		Avg. Int. POC.	SD.		Int. POC.		Avg. Int. POC.	SD.	
Province	Biome		% Total	mg/m ² 1	7	Pixels	Mt %	Total	mg/m² 1	ng/m ² I	ixels	Mt 9	6 Total	mg/m ² ,	mg/m^2	Pixels	Mt	% Total	mg/m ²	mg/m^2	Pixels
Boreal Polar	polar	0.000	0.00	0.00	0.00	0	4.158	99.0	2834.36	362.72	2786	11.269	1.74	2685.57	318.29	7360	0.000	0.00	0.00	0.00	0
Atl Subarctic	polar	0.007	00.0	0.007	00.0							8.3/9	0.85	2660.96	309.57	3228	0.000	00.0	00.0	00.0	0 0
N Pac Epicontinental	polar	2.202	0.31		195.71							0.705	1.65	2706.74	187.26	4426	1.764	0.26	2604.19	112.39	809
Antarctic	polar	47.352	6.77		141.38							0.000	0.00	0.00	0.00	0	34.552	5.07	2360.06	140.46	18713
Austral Polar		10.075	1.44		146.14							0.000	0.00	0.00	0.00	0	1.125	0.17	2375.89	151.20	719
N Atl Drift(WWDR)	westerlies	4.754	0.68		110.42							9.122	1.41	2566.18	107.90	3609	3.101	0.45	2341.62	42.36	1239
Gulf Stream N A41 Subtrop Gyre (W)	westerlies	2.830 12 824	1 83	2487.38	67.651 87.03							2.555 1 499	0.39	1924 04	37.47 37.44 44.42	4627	2.718	0.40	2343.24	04.92 44.08	4627
Mediterranean Sea	westerlies	6.226	0.89		92.36							5.475	0.85	2103.04	80.70	2130	5.839	0.86	2248.71	98.74	2124
Black Sea	westerlies	1.152	0.16		130.01							1.097	0.17	2786.85	79.51	351	1.072	0.16	2784.57	103.67	343
N Atl Subtrop Gyre (E)	westerlies	9.991	1.43		104.81							9.279	1.43	2091.20	83.51	3559	9.523	1.40	2146.32	65.90	3559
Pac Subarctic Gyres (E)	westerlies	3.671	0.52		58.68							8.097	1.25	2553.92	105.87	3293	1.660	0.24	2457.34	58.64	638
Fac Subarctic Gyres (W)	westerlies	4.8/1	0.70	2395.83	91.57							5.846	0.90	2645.96	123.38	2139	3.265	0.48	2492.00	91.94	2402
N Pac Polar Front	westernes	7.000	7.40		75.751							6.057	7.48	22,6427	75.06	6169	16870	2.47	2300.40	20.601	6202
N Pac Subtrop Gyre	westerlies	27.011	3.86		117.82							6.083	4.03	1889.33	55.73	9839	26.764	3.92	1938.64	53.97	9839
Tasman Sea	westerlies	3.725	0.53		88.35							4.139	0.64	2456.94	95.75	1384	4.223	0.62	2499.88	60.37	1388
S Pac Subtrop Gyre		67.186	9.61		243.41	-				• •	•	74.457	11.50	2076.38	187.99	25809	70.358	10.32	1967.25	224.94	25743
S Subtrop Convergence	westerlies	39.157	5.60		176.10							88.827	00.9	2318.79	111.65	14328	40.987	6.01	2377.68	130.35	14790
Subantarctic	westerlies	73.553	10.52		175.85						` '	20.520	3.17	2275.31	85.27	8232	75.861	11.13	2402.09	155.44	31734
N Atl Trop Gyre	trades	16.325	2.33		200.95							6.331	2.52	2031.45	202.93	5557	16.488	2.42	2043.22	179.40	5578
W Trop Atl	trades	11.463	1.64		91.26							2.253	1.89	2273.42	136.64	3539	11.837	1.74	2196.31	84.31	3539
East Trop Atl	trades	11.165	1.60		197.42							2.099	1.87	2407.98	153.17	3295	11.728	1.72	2275.68	120.60	3380
S Atl Gyre	trades	34.728	4.97		149.06							9.309	6.07	2206.85	150.14	13005	37.503	5.50	2100.67	199.98	13032
Carlobean Indian Mongoon Garage	trades	37 007	1.54	2240.13	14.81	•					•	9.134	1.41	2202.00	142.64	10205	37.046	1.57	270.72	100.86	10208
Indian S Subtrop Gyre	trades	32.411	4.63		123.46							37.615	5.81	2185.97	122.26	12407	34.590	5.07	2010.21	121.07	12407
N Pac Trop Gyre	trades	29.898	4.27		117.78							9.321	4.53	1966.22	106.70	10594	29.711	4.36	1986.46	101.01	10625
N Pac Eq Countercurrent	trades	20.063	2.87		174.36							9.406	3.00	2165.19	154.10	5934	19.134	2.81	2130.06	158.90	5947
Pac Eq Divergence	trades	32.087	4.59		87.95	` '					•	32.590	5.03	2274.51	100.38	9387	31.639	4.64	2195.06	113.87	9444
W Pac Warm Pool	trades	24.151	3.45		155.11	. , ,					. , .	24.767	3.83	1989.97	121.80	8191	24.634	3.61	1979.25	106.55	8191
Archipelagic Deep Basins	trades	19.379	2.77		270.60	•					•	1.084	3.26	2277.89	176.77	6340	19.907	2.92	2145.13	206.43	6356
NE Au Snelves Canary Coastal (FACB)	coastal	0.527	0.05	2793.14	129.12							1.907	0.29	2910.39	355.80	800 490	0.000	0.01	2484.89	339 31	501 501
Guinea Current Coastal	coastal	2.080	0.30		268.46							1.775	0.27	2525.54	170.32	462	2.468	0.36	2522.80	191.04	645
Guianas Coastal	coastal	3.076	0.44		572.99							3.205	0.50	2536.05	527.53	833	3.140	0.46	2464.00	524.20	840
NW Atl Shelves	coastal	4.485	0.64		254.01							5.470	0.84	2580.15	207.92	1911	3.855	0.57	2577.25	212.70	1289
Brazil Current Coastal	coastal	2.265	0.32		228.12							2.358	0.36	2368.91	231.98	726	2.300	0.34	2304.64	245.52	728
SW Atl Shelves	coastal	3.844	0.55		316.87							1.013	0.16	2668.73	181.73	347	3.789	0.56	2900.22	316.48	1315
Benguela Current Coastal	coastal	2.8/4	0.41	2661.00	506.24							2.849	4.0-	2/0/2	246.10	7569	2.971	4.0	2762.49	288.90	08/
Dad San	coastal	1.00.7	1.12		20.772							1 1 2 0	1.32	2423.24	20.0/1	240	0.112	0.19	24.32	100.21	240
Ned Sea Persian Gulf	coastal	0.523	0.07		106.92							0.466	0.07	2705.66	97.06	126	0.488	0.07	2832.25	85.84	342 126
NW Arabian Upwelling	coastal	9.243	1.32		193.04							8.579	1.33	2695.33	197.42	2141	8.788	1.29	2535.68	152.04	2337
E India Coastal	coastal	2.448	0.35		416.26			0.38	522.44			2.231	0.34	2531.68	289.60	601	2.456	0.36	2517.41	395.78	999
W India Coastal	coastal	2.317	0.33		432.23			0.35	2680.41			1.938	0.30	2844.00	351.56	460	2.275	0.33	2693.67	346.93	575
Australia West	coastal	6.187	0.88	2235.10	288.35			80.1	457.30			808.9	1.05	2457.28	241.62	1979	6.355	0.93	2299.92	257.84	1974

99.62 134.68 648.06 369.83 611.67 547.11 128.84 124.33 Total 224813 99688 91433 226.69 48.69 193.83 24.81 198.27 188.21 Total 240.267 289.488 0.942 24046 15041 81983 555.00 21 Avg. Int. POC, 591.12 2407.60 2424.35 2169.73 Total 83.229 109301 91768 24607 522.24 260007 360 25.54 1 61.07 60.32 58.39 127.81 491.30 061.66307.69 084.30 458 43 % Total 8.53 281.983 99.380 274.006 0.948 59.630 2.967 coasta coastal coastal coastal coastal Int. POC Over Euphotic Zone Alaska Downwelling Coastal California Upwelling Coastal entr American Coastal [able 8. (continued) East Australian Coastal New Zealand Coastal China Sea Coastal Inclassified Westerlies Summary Coastal **Frades** Chile Polar

zone POC (essentially, the total POC found above the 1% light depth of the water column, aerially integrated over the province), (2) average integrated POC (mg m⁻²), (3) standard deviation of the average POC (mg m⁻²), and (4) the total number of pixels available for the analysis. Any values of 0.00 in the first three columns of the polar biome for each 3 month period represent regions where no satellite radiance data were available, mainly due to low Sun angle. At the bottom of the table the global statistics are provided as well as statistics for each of the four biomes. province for (1) total euphotic Results are given for each Calculations have been made for each 3 month period of 2002. Trades, and Coastal. respective biome: Polar, Westerlies, grouped into their ^aProvinces are

Note, while these PIC:POC and export ratios are consistent, they are both considerably less than the often-used value of 0.25 (see *Sarmiento et al.* [2002] for further discussion about this discrepancy).

[39] Sarmiento et al. [2002] further found their predicted export ratios to be everywhere less than 0.1. This was not true in our case; the highest PIC:POC ratios that we observed (exceeding 0.1 (see Table 5)) were observed in the Black Sea, NE Atlantic shelves, SW Atlantic shelves, Persian Gulf and China Sea Coastal provinces. All Northern Hemisphere polar provinces had PIC:POC ratios >0.05 from July to September. Other provinces with PIC:POC ratios >0.05 for at least one 3 month period were North Atlantic Drift, Black Sea, northeast Atlantic Shelves, Guianas coastal, northwest Atlantic shelves, southwest Atlantic shelves, Benguela Current coastal, Persian Gulf, east India Coastal, west India coastal, Australia West, China Sea coastal, and New Zealand coastal provinces. Regions where our PIC:POC ratios were less than the export ratios of Sarmiento et al. [2002] were in the Equatorial regions of the Pacific, Atlantic and Indian Oceans. Moreover, we found higher values of PIC:POC in the North Atlantic subarctic gyre (summer values of 0.093 (Table 5)), compared to export ratios of 0.023 ± 0.02 [Sarmiento et al., 2002]. The reason for this disparity is not immediately obvious, unless calcite dissolution in the top 100 m is responsible for remineralizing a larger proportion of the PIC than POC [Milliman et al., 1999]. Given the frequent blooms in the North Atlantic subarctic gyre, higher PIC concentrations (Tables 5 and 6) and higher PIC:POC ratios clearly would be expected.

[40] Another cross check of the above PIC estimates is to estimate the rate of global PIC turnover in the sea by dividing the average global, MODIS-derived PIC value (18.8 Mt PIC \pm 2.56) by the typical annual global calcification rate of \sim 1 Gt PIC yr⁻¹ [Archer and Maier-Reimer, 1994; Archer, 1997; Milliman et al., 1999; Morse and Mackenzie, 1990; Wollast, 1994] which gives a quotient of 0.0188 years (= 6.86 days). This value is reasonably consistent with the average turnover time of PIC particles based on direct shipboard measurements of ¹⁴C calcification, combined with atomic absorption analyses of PIC standing stock. For example, in the equatorial Pacific, the PIC turnover time typically was \sim 6.5 days (\pm 3.5 days) [Balch and Kilpatrick, 1996] while in the Arabian Sea, the mean turnover time was \sim 13 days (\pm 6 days), depending on season [Balch et al., 2000]. While these observations reveal internal consistencies between PIC standing stock and field measurements of PIC turnover, one must remember that the turnover time of PIC particles can be highly variable due to factors such as growth and grazing. Moreover, there are few field observations of PIC turnover available to constrain global models of the calcium carbonate cycle. Verification of the global PIC estimates must await further in situ validation measurements from ship. Specifically, the large PIC-rich features observed by the MODIS sensors in the southern ocean, must be verified, as they have a large effect on the total global PIC standing stock.

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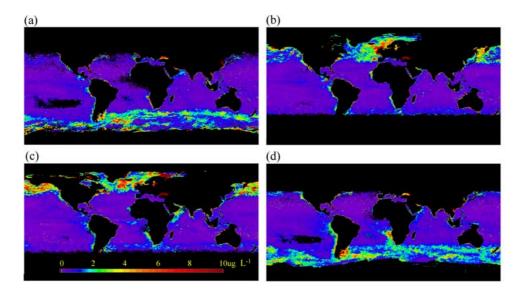


Figure 5. Global composite images of suspended PIC concentration calculated from MODIS/Terra data using two-band calcite algorithm. See text for other details of how the data were processed. The color scale is highlighted in Figure 5c. These data were binned into 36 km and 90 day averages, and thus the standard error will be <0.08 μ gPIC L⁻¹ (see Table 2), well below the average seawater concentration of \sim 2 μ gPIC L⁻¹. (a) January–March. (b) April–June. (c) July–September. (d) October–December.