# Global POC concentrations from in-situ and satellite data

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#### ABSTRACT

During the last two decades significant contributions have been made to understanding regional and global distribution of chlorophyll in the ocean by developing algorithms from ocean-color products. Analogously, in this work empirical algorithms are developed to derive concentrations of particulate organic carbon (POC) from ocean color products. We combined vertical profiles of particulate beam attenuation coefficient at 660 nm (cp) collected on numerous cruises during World Ocean Circulation Experiment (WOCE), Joint Global Ocean Flux Study (JGOFS), South Atlantic Ventilation Experiment (SAVE), and other programs since the 1980's to create a global data base. Discrete samples of POC and synchronously measured  $c_p$  data collected in the Atlantic, Pacific, Indian and Southern oceans during JGOFS and other programs were used to make  $c_p$ :POC regressions to convert  $c_p$  data to POC values. During two programs satellite data were available when synchronous POC samples and c<sub>p</sub> profiles were obtained over several seasons. cp averaged over one attenuation depth in the South Pacific and northeast Gulf of Mexico was correlated with four synchronous ocean-color products. A good correlation was obtained with both normalized water-leaving radiance at 555 nm (L<sub>WN</sub>(555)) and diffuse attenuation coefficient at 490 nm  $(K_{490})$ . Using a combined  $K_{490}$ :  $c_p$  regression from the two areas, global maps of the estimated mean  $c_p$  were created and converted to mean POC concentration down to one attenuation depth for summer and winter seasons. Seasonal  $c_p$ , POC and chlorophyll distributions were used to map %CHL and  $c_p$ :CHL ratios within the one attenuation depth as a possible index of phytoplankton physiology.

KEYWORDS: Beam Attenuation, Light Transmission, Water Transparency, POC, WOCE, JGOFS, SeaWiFS. REGIONAL INDEX: World Ocean

#### 1. BACKGROUND and OBJECTIVES

One of the major goals of the Joint Global Ocean Flux Study (JGOFS) was to develop regional and global mass balances for carbon. Various aspects of carbon budgeting have been attempted for selected areas through shipboard sampling during JGOFS Process and Time-Series Programs (e.g. North Atlantic Bloom Experiment (NABE) – <u>Chipman et al., 1993</u>; Arabian Sea – <u>Lee et al. 1998</u>; Equatorial Pacific – <u>Walsh et al., 1995</u>; <u>Landry et al., 1997</u>; <u>Le Borgne et al., 2002</u>; Antarctic Polar Front Zone – <u>MacCready and Quay, 2001</u>; <u>Nelson et al., 2002</u>; Ross Sea - <u>Gardner et al. 2000a</u>; Hawaii Ocean Time-Series (HOT) – <u>Karl and Lukas, 1996</u>; Bermuda Atlantic Time Series (BATS) – <u>Steinberg et al., 2001</u>). To extend global coverage, the marine carbon dioxide survey linked up with the World Ocean Circulation Experiment (WOCE) (<u>Sabine et al., 2002</u>; Feely et al., 2004).

In order to make more complete carbon budgets it is necessary to know the magnitude and distribution of particulate organic carbon (POC) and dissolved organic carbon (DOC). POC can be measured through sample filtration and land-lab analysis, but it would be preferable to obtain continuous profiles of POC at the resolution of a CTD. Transmissometers, instruments that measure beam attenuation, c, due to water and particles can be interfaced with a CTD. The portion of c due to particles,  $c_p$ , is known to be linearly related to particle concentration (Zaneveld, 1973; Bartz et al., 1978; Gardner et al., 1985; Bishop, 1986; 1999; Spinrad, 1986; Pak et al., 1988). Morel (1988) suggested there was a nearly linear relationship between particle light scattering and POC. During the JGOFS and other studies of the last two decades we have also found a very good linear correlation between *in-situ*  $c_p$  and POC concentration in sea water in the North Atlantic (Gardner et al., 1993), Equatorial Pacific (Gardner et al., 1995), Arabian Sea (Gundersen et al., 1998); Ross Sea (Richardson et al., 1999; Gardner et al., 2000b) the Pacific Southern Ocean (Gardner et al., 2000b; Mishonov and Gardner, 2003a), HOT (Mishonov and Gardner, 2003a) and the Gulf of Mexico (Richardson et al., 2003). Linear correlations have also been found by others in the Equatorial and North Pacific (e.g. Claustre et al., 1999; Bishop et al. 1999; Bishop, 1999).

In order to extend our POC coverage to a global scale, we worked with other scientists to interface our transmissometers on many WOCE cruises. We archived the raw data and the JGOFS Synthesis and Modeling Program provided an opportunity to process and synthesize the  $c_p$  data and convert these measurements to POC. Like the marine carbon dioxide survey, these global measurements have not been synoptic, but they were collected simultaneously with hydrographic data extending through the full water column.

For more than two decades great effort has been expended to "sea-truth" satellite ocean color data via shipboard measurements to develop reliable algorithms to convert ocean color to chlorophyll-a concentrations (Morel and Prieur, 1977; Lewis et al., 1983; Morel, 1988;; Morel and Berthon, 1989; Sathyendranath and Platt, 1997; Hooker and McClain, 2000; Morel and Maritorena, 2001; Sathyendranath et al., 2001;). Those efforts are continually being refined, especially as new color sensors such as the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and Moderate-resolution Imaging Spectroradiometer (MODIS) have become available (e.g. Aiken et al., 1998; Evans et al., 2000; Sathyendranath et al., 2000; Del Castillo et al., 2001; Shifrin, 2001). These efforts are also driven by the desire to understand biological processes and led to the development of algorithms to predict photosynthetic rates from chlorophyll concentration (Behrenfeld and Falkowski, 1997) and other parameters (Behrenfeld et al., 2005).

In Case I waters, where the chlorophyll concentration is high relative to the scattering coefficient (Morel and Prieur, 1997), most particles and POC originate from biological processes and there is a general covariation between chlorophyll-*a* and POC (Legendre and Michaud, 1999), though detailed differences have been examined (Kitchen and Zaneveld, 1990). However, the mass of chlorophyll is small compared to bulk POC (1.5-4% for phytoplankton, Banse, 1977; Eppley et al., 1977; 1992), and because the bulk carbon to chlorophyll-*a* ratio can vary by 10-40 fold (Morel, 1988; Chung et al., 1996) as proportions of phytoplankton, bacteria and detritus change (El-Sayed and Taguchi, 1981; Smith et al., 1996; Gundersen et al., 2001), and as the ratio of chlorophyll to phytoplankton carbon changes (e.g. Geider et al., 1998), and the intracellular distribution of chlorophyll within cells change as a function of changing irradiance, temperature and

nutrients (Behrenfeld and Boss, 2003), it is extremely difficult to accurately estimate POC from chlorophyll concentrations measured either directly or by remote sensing. Efforts to measure or model complete carbon budgets (including export and remineralization) require more accurate data on POC concentration and distribution than can be derived from chlorophyll concentration. Thus, although there is general covariance between chlorophyll or POC concentrations and ocean color, it is desirable to develop algorithms to estimate POC concentrations directly from satellite ocean color products. Stramski et al. (1999), Loisel et al. (2001), Mishonov et al., (2003b), and Behrenfeld et al, (2005) have proposed ways to accomplish that goal. In this paper we develop algorithms for POC concentrations from satellite data, examine seasonal differences and discuss possible interpretations of the constructed global maps.

# 2. STUDY AREAS

We have collected transmissometer data around the world since the early 1980's during JGOFS, WOCE, and other programs such as the South Atlantic Ventilation Experiment (SAVE), North East Gulf of Mexico (NEGOM; shelf and slope), and Coastal Mixing and Optics (CMO; the shelf south of Martha's Vineyard, USA). Our data base includes  $c_p$  measurements from 51 cruises, and there are POC measurements from JGOFS and other cruises at 8 different regions of the world (see Fig. 1), including numerous cruises at the Hawaii Ocean Time-Series (HOT) and Bermuda Atlantic Time Series (BATS) sites. Temporal distribution of the transmissometer data is charted on the insert in Fig. 1.

#### 3. METHODS

#### **3.1. Optical Data Base**

Our entire processed transmissometer data set consists of 7251 profiles and spans the period from 1983 to 2000. Our field measurements were made using one of 16 different 25cm path-length SeaTech transmissometers interfaced with a CTD rosette.

The SeaTech transmissometer measures beam attenuation in the red spectral band ( $\lambda = 660$  nm). Attenuation of the light beam across the transmissometer's 25cm path-

length (*r*) was obtained using the same procedure for all data making them comparable and uniform. In brief, the percent transmission (*Tr*) of light was measured and converted to beam attenuation coefficient (*c*) using the equation  $c = -r^{-1} \cdot \ln(Tr)$ . As explained by Pak et al. (1988), the beam attenuation coefficient can be described as the sum of attenuation due to particles (*c*<sub>p</sub>), water (*c*<sub>w</sub>), and colored dissolved organic matter (*c*<sub>CDOM</sub>):  $c=c_p+c_w+c_{CDOM}$ . According to several studies, *c*<sub>CDOM</sub> is small enough to be ignored in measurements at 660 nm in open waters (Bartz et al., 1978; Bricaud et al., 1981; Pak et al., 1988). Attenuation due to water *c*<sub>w</sub> is essentially constant for this instrument at a value of 0.364 m<sup>-1</sup>set at the factory.

The majority of original raw transmissometer data were acquired during both down and up casts of the CTD-rosette. The down-trace data usually are preferred because the optical sensor is less obstructed during descent. On the other hand, water bottles are nearly always tripped during the ascent, so it is essential to record transmissometer data at the time and depth of the bottle trip when water samples are used for  $c_p$  calibration. Having both down and up traces provides an opportunity to compare the two profiles to check for instrumental errors in the data and to use the up trace data. Temperature hysteresis can cause slight differences between down and up traces, especially in areas where temperature gradients are large (Gardner et al., 1985; Bishop, 1986), but compared to the  $c_p$  signal in surface waters, this effect is small.

The data processing procedure described below was applied uniformly to all data from WOCE and SAVE. HOT and BATS data were added for more temporal coverage but required more intensive processing, whereas JGOFS, NEGOM, and CMO data had been previously reduced and were in need of only minor corrections and final adjustments.

Raw-data files were processed with a customised software algorithm. Processing included (a) pressure checking and depth inversion filtering, (b) spike removal using two depth-dependent window filters and a  $c_p$  gradient check (single-point spikes were removed as they most likely represented individual large particles), (c) data averaging and reduction from the 30Hz recording frequency to 2 db pressure intervals centered at even numbers, (d) application of the instrument's calibration data using pre-cruise, cruise

and post-cruise calibration values, (e) removal of excessively noisy data, (f) profile smoothing by 5-point running average, and (h) determination of profile minimum.

Our basic assumption was that deep-waters are highly stable and constant in terms of hydro-optical characteristics. The minimum  $c_p$  value, its depth and the station bottom depth were plotted for each profile on every cruise. This allowed detection of any cruise-long decay in the light-emitting diode intensity, dirty windows or instrumental offsets. The cruise trend evaluation used the profile minimum  $c_p$  values only at open-ocean, deep-water stations.

Profile adjustments were made by shifting the entire profile so that the profile's minimum  $c_p$  value in deepwater (from the zone deeper than 750 m and more than 750 m above the seafloor) was set equal to the cruise's minimum. Shallow-water stations were adjusted only by the mean offset in deep-water stations of each cruise. <u>Gardner et al.</u>, (1985) used this method in modified ways during processing of the JGOFS transmissometer data and it seems widely applicable as long as data from deep water are available.

#### **3.2. POC Data**

All of the POC data in this paper came from rosette water bottle samples. Bulk water samples include all organic particles filtered that were greater than the nominal pore size of filters used (typically GF/F filters; 0.7  $\mu$ m), which includes heterotrophic bacteria, pico- nano- and microphytoplankton, microzooplankton, detritus, and may occasionally include some small mesozooplankton (Legendre and Michaud, 1999; Liu et al., 2005). Additionally there can be DOM absorbed on the filter (Menzel, 1967; Moran et al., 1999). POC sampling and processing were performed for all the data by several different investigators following a standard protocol (Knap et al., 1994, http://www.uib.no/jgofs/Publications/Report\_Series/JGOFS\_19.pdf). In general, during the cruises water collected at specific depths was drawn from Niskin bottles and filtered at low vacuum (0.25 atm) through a funnel setup onto 25 mm glass fiber filters (GF/F). None of the samples were pre-filtered to remove macrozooplankton other than the HOT samples (http://hahana.soest.hawaii.edu/hot/protocols/chap10.html). Filters were dried at

 $60^{\circ}$ C for 8 hours, wrapped with pre-combusted aluminum foil and stored in a sealed plastic bag. Onshore, filters were acidified to remove carbonates and analyzed by combustion with elemental analyzers according to JGOFS protocols (Knap et al., 1994; JGOFS, 1996), most often at the Bermuda Biological Research Station. The same methods were used to analyze some samples at Horn Point Marine Laboratory and the Virginia Institute of Marine Science. Filter blanks were pre-combusted filters taken to the field, but no filtered water was passed through the blanks, which could result in higher POC values, most notably at low concentrations (<4  $\mu$ M), due to adsorption of DOC and colloidal organic carbon onto filters (Moran et al., 1999; Gardner et al., 2003a).

#### 3.3. Beam $c_p$ and POC data base

Some POC data (Fig. 2) were obtained from geographically small locations: North Atlantic (NABE; <u>Gardner et al., 1993</u>), Equatorial Pacific (EqPac; <u>Gardner et al., 1995</u>; <u>Walsh et al., 1997</u>), Ross Sea (<u>Gardner et al., 2000a</u>), shelf south of Cape Cod, Massachusetts (CMO; <u>Gardner et al., 2001</u>) and NEGOM area (<u>Bernal, 2001</u>; <u>Richardson et al., 2003</u>) (see triangles on Fig.1). In other areas the geographic coverage was basinwide; Arabian Sea (<u>Gundersen et al., 1998</u>) and Antarctic Polar Front Zone (APFZ; <u>Gardner et al., 1999</u>). BATS (<u>Steinberg et al., 2001</u>; <u>Mishonov and Gardner, 2003a</u>) and HOT (<u>Hebel and Karl, 2001</u>; <u>Mishonov and Gardner, 2003a</u>) POC data were also added.

The simultaneously collected  $c_p$  and POC data were used to assess the  $c_p$ :POC relationship. The total of all simultaneous  $c_p$ :POC data available from JGOFS process studies and from our other projects consists of 2858 data pairs. In order to increase temporal and spatial coverage we added  $c_p$ :POC data collected at HOT (306 data pairs) and BATS (855 data pairs). The  $c_p$  data collected at these two sites have been re-analyzed and corrected (Mishonov and Gardner, 2003a). We also utilized seasonal data from the NEGOM project collected during 9 cruises over three years (440 data pairs, Bernal, 2001; Richardson et al., 2003), bringing the total data pool to 4459 pairs. All data were combined into a single composite plot (Fig. 3). Correlations statistics are in Table 1.

It should be noted that POC is calculated using  $c_p$  at 660 nm, and that most of the light attenuation and scattering are dominated by the 0.5-20  $\mu$ m fraction of the particle

size spectra, with a peak sensitivity around  $1 - 2 \mu m$  (<u>Stramski and Kiefer, 1991;</u> <u>Chung</u> et al., 1996, <u>1998</u>; <u>Boss et al., 2001</u>). This is the size fraction in which phytoplankton contribution is greatest. The dominant contribution to POC (in open ocean waters) has been demonstrated on multiple occasions to be phytoplankton (e.g., <u>Eppley et al., 1992</u>; <u>DuRand and Olson, 1996</u>; <u>Gundersen et al., 2001</u>; <u>Green et al., 2003</u>; <u>Green and Sosik, 2004</u>).

 $c_p$  and POC sections and maps compiled from all processed data have been generated and can be viewed on our project web-site at http://oceanography.tamu.edu/~pdgroup/SMP\_prj/DataDir/SMP-data.html (data locations shown in Fig. 1).  $c_p$  data merged with temperature, salinity and oxygen data and stored in Ocean Data View (Schlitzer, 2003) software format can also be downloaded.

#### 3.4. Satellite data

#### **3.4.1. SeaWiFS versus** *c*<sub>p</sub> regression

To compare *in-situ* data with remotely sensed optical parameters, values of  $c_p$  were averaged from vertical profiles down to one attenuation depth of the ocean, assuming that is the maximum depth from which a remotely sensed signal is radiated. One attenuation depth was calculated based on SeaWiFS-derived diffuse attenuation coefficient (K<sub>490</sub>) data using the formula  $z=1/K_{490}$  (Gordon and McCluney, 1975). This depth varied from 9 to 29 m in the APFZ area, and from 1 to 30 m in the NEGOM and SAVE areas.

Data for K<sub>490</sub>, normalized water leaving radiance at 555 nm L<sub>WN</sub>(555), chlorophyll concentration (CHL) and Integral Chlorophyll (I<sub>CK</sub>=CHL/K<sub>490</sub>), i.e. chlorophyll integrated in one attenuation depth (<u>Campbell et al., 1995</u>), were extracted from the SeaWiFS data archives (<u>http://daac.gsfc.nasa.gov/data/datapool/SEAWIFS/index.html</u>). To provide better satellite data coverage in a cloudy area such as the APFZ (and NEGOM in some seasons) we used 8-day SeaWiFS composites (Level 3, 9x9 km, i.e. 1x1 pixels, Reprocessing 4 data). The total data set (Table 2) consists of 580 data points: 140 for APFZ and 440 for

NEGOM. Calculations from the 330 data point from SAVE (<u>Mishonov et al., 2003b</u>) are also listed.

# 3.4.2. APFZ area:

For comparison with  $c_p$ , satellite data were averaged over the time-scale appropriate to each cruise (one to three 8-day mosaics). Expedition KIWI cruises 6 and 8 covered a small geographical area due to ice coverage and a focus on the Polar Front Zone. For KIWI-Process cruises (7 and 9) satellite data were averaged over the period of southbound and northbound transects of each of the cruises. Field data on  $c_p$  and POC were collected during different stages of the plankton bloom that developed in the vicinity of the Polar Front (~61°S) over a five month period. The dynamic character of the optical field in the vicinity of the Polar Front is illustrated in Fig. 4, where mosaics a) to f) show the variability of the K<sub>490</sub> field during successive 2-3 week periods (sampling station positions are also marked).

# 3.4.3. NEGOM area:

All nine cruises were 10-11 days long, so single 8-day SeaWiFS mosaics falling into that timeframe were compared with the field data, providing good data coverage with a relatively small area obstructed by clouds. The NEGOM program covered different seasons (spring, summer, fall) for three years, spanning different hydrologic conditions. Variations in the Mississippi River outflow, different locations of the loop current, and seasonal phytoplankton blooms resulted in significant variability of  $c_p$  and POC in the upper water column. This variability is also well represented in the K<sub>490</sub> field shown as a background in Fig. 5.

#### 3.4.4. Temporal changes in POC from satellite color products

Although biogeochemical process studies from ships in a single location provide the opportunity to monitor changes over time for a body of water, they are obviously limited in spatial coverage, as well as time (length of a cruise). Satellites provide far greater synoptic spatial coverage than is possible with shipboard, moored, or profiling measurements, so it is highly desirable to develop reliable algorithms for quantifying POC from satellite ocean color. It is necessary to sea-truth algorithms in as many regions and seasons as possible in order to assure their reliability. Basin-wide

hydrographic/carbon programs, like the CLImate VARiability (CLIVAR) Repeat Hydrography program, provide an unprecedented opportunity to simultaneously measure all components of the carbon system in a variety of oceanic conditions at a time when satellite ocean color data are available. Once algorithms are refined, they will provide a new tool to quantify POC in surface waters at any time and location that ocean color data are available. With simultaneous data on POC and chlorophyll concentrations we can make time-series measurements to follow the evolution of an event to quantify changes in concentration and percentage of these two important components. Time series of chlorophyll concentration already exist for some areas (e.g. <u>Kahru et al., 2004</u>). Time series data on concentrations of both chlorophyll and POC should provide even better constraints on the output of biogeochemical models than chlorophyll alone.

# 4. RESULTS

# 4.1. c<sub>p</sub>:POC Regressions by Region

The large data set of  $c_p$  and POC allows us to assess relationships between  $c_p$  and POC in different regions over different seasons. In Fig. 2 all data, collected under a wide variety of physical and geographical conditions, are presented as  $c_p$  versus POC scatter plots. For comparability plots are shown on the same relative X-Y scale but with different ranges so that regression slopes can be visually compared. Since beam  $c_p$  is a function of particle size, shape and index of refraction (Zaneveld, 1973; Twardowski et al., 2001), it is reasonable to expect the beam  $c_p$  to POC relation to vary regionally and temporally during the cycle of a bloom and spatially as regimes with different community structures are encountered with plankton of different composition (organic, siliceous, carbonate) and size spectra.

Based on more than 7000  $c_p$  profiles, there is little variability in structure of the  $c_p$  profiles below 200-300 m except near some continental margins and close to the sea floor. In regions of resuspended sediments, beam  $c_p$  should be regressed against total particulate matter concentration (PMC), which still yields a linear correlation, but with a different slope (Spinrad et al., 1983; Gardner et al., 1985; Gardner, 1989; Gundersen et

<u>al., 1998;</u> <u>Gardner et al., 2000b</u>). Analysis of the near-bottom beam attenuation data is not in the scope of this work.

Slopes of the Model II  $c_p$ :POC linear regressions for regional data sets appear to be relatively close, especially within a given oceanic region (Fig. 2). Parameters of these regressions are shown in Table 1. The major exception is the Ross Sea regression – its slope is twice that for NABE or NEGOM. The larger slope might be due to a difference in the physiology and composition of plankton produced in this regional ecosystem during the intensive phytoplankton blooms (Smith et al., 2000). While we have documented some seasonal and spatial fluctuations in the  $c_p$ :POC relationship (e.g. <u>Gundersen et al., 1998</u>), the year-round data collected in the Arabian Sea, HOT, and BATS show the annual variations to be small. Therefore, for this large-scale analysis we have combined all data (excluding the Ross Sea) to produce a single global  $c_p$ :POC ratio (Fig. 3). <u>Bishop (1999)</u> advocated this approach, although some regional and seasonal variations obviously exist.

The resulting data set consists of 3465 data pairs (excluding 994 Ross Sea pairs), which were assembled into one data pool and a general regression between  $c_p$  and POC was constructed. Fig. 3 shows the global property-property plot with the Model II regression line (parameters of this regression are shown in the last column of the Table 1). Obviously a general combined regression is a compromise: from Fig. 3 it is clear that in the Pacific this regression will underestimate values of POC (blue crosses), while in the Atlantic POC values will be slightly overestimated (red diamonds). For the Indian Ocean this regression is a good fit (green triangles), although all Indian Ocean data were collected in the Arabian Sea.

#### 4.2. SeaWiFS products versus c<sub>p</sub> regression

<u>Mishonov et al., (2003b)</u> used shipboard  $c_p$  data collected in the South Atlantic in 1987-89 regressed against four SeaWiFS data products seasonally averaged for 1997-2002 because no synchronous satellite data were available. Despite the decade gap between data sets, there was a reasonable correlation between  $c_p$  and  $L_{WN}(555)$  (r=0.882) and K<sub>490</sub> (r=0.800) using an exponential regression when Case II waters were eliminated. In this paper we used only <u>synchronous</u> data sets of  $c_p$ , POC, and SeaWiFSderived ocean color products collected during the APFZ and NEGOM programs to derive empirical algorithms. In addition to  $L_{WN(555)}$  and  $K_{490}$ , comparisons were made with CHL and  $I_{CK}$ =CHL/K<sub>490</sub>. The four SeaWiFS data products were plotted versus mean  $c_p$  (Fig. 6) and several types of regression fits were calculated and evaluated for all data products. The log-log equations provide the highest correlation between variables. Two parameters,  $K_{490}$  and  $L_{WN}(555)$  produced very good relationships in both regions, but  $K_{490}$  produced somewhat less scatter and a higher overall correlation than  $L_{WN}(555)$  and was selected for further use. The resulting equation is

 $c_{\rm p} = \text{EXP}(1.124*\text{LN}(\text{K}_{490}) + 1.361).$ 

The comparable relationship for SAVE data is

 $c_{\rm p} = \text{EXP}(1.476*\text{LN}(\text{K}_{490}) + 2.560).$ 

Parameters of each regression are presented in Table 2. Maps were made and evaluated independently using both  $K_{490}$  and  $L_{WN}(555)$ , but the maps and figures in this paper are only from  $K_{490}$  data using synchronous APFZ and NEGOM data.

It is encouraging, that regressions based on *in-situ* and seasonally averaged SeaWiFS data collected ten years later match well with regressions based on synchronously collected data for two of the parameters tested (Fig. 6). This is most likely due to the fact that the five-month average of  $K_{490}$  and  $L_{WN}(555)$  done by Mishonov et al., (2003b) indicated that about 80% of the area had a standard deviation of less that 20% over a five year period.

#### 4.3. Global POC distribution from SeaWiFS products.

To produce global seasonal maps of POC, SeaWiFS  $K_{490}$  data were averaged over a 5-year period (1997-2002) for summer (May-Aug) and winter (Dec.-March) seasons (maps not shown). Using the  $c_p:K_{490}$  regression (Table 2, Fig. 6b) the  $K_{490}$  field was converted to a global map of  $c_p$  (not shown). Finally, the  $c_p$  field was converted to POC for summer (Fig. 7b) and winter (Fig. 8b) seasons using the global  $c_p:POC$  regression (Table 1, Fig. 3). POC was recalculated in units of mg m<sup>-3</sup> rather than  $\mu$ M m<sup>-3</sup> for consistency with SeaWiFS-derived chlorophyll concentration data.

# 4.4. POC predicted versus POC measured

In order to estimate the reliability of the global  $K_{490}$ : $c_p$ :POC transformation we plotted the predicted POC values (from  $K_{490}:c_p:POC$ ) for APFZ and NEGOM against the synchronously measured POC values from filters (Fig. 9). This was done using both the global regression and the regional regression for both areas. For NEGOM the fit is better overall than for APFZ, but the values are generally overestimated. This is most notable at low concentrations where measured values are as low as 2 µM, while the minimum predicted values are about 3  $\mu$ M. In the APFZ, minimum measured and predicted values are both about 3 µM, but the higher predicted POC values are underestimated significantly by the global regression, which is also a known problem with chlorophyll algorithms for high latitudes (Kahru and Mitchell, 1999; Stramska et al., 2003). This could be due partially to the effects of low solar zenith angle on remotely sensed signals for high latitude areas. Another reason could be a statistical influence since there are nearly three times as many NEGOM data points as APFZ points used for the regression calculation and the difference in slopes (Table 2) reduce the predicted APFZ POC values - this is an expected drawback of using a global algorithm. This issue could possibly be improved by incorporating more data or switching to regional regressions. The regional regressions give better results, decreasing the values in NEGOM and increasing the values in APFZ, but using regional algorithms creates discontinuities at the regional boundaries. Using  $L_{WN}(555)$  instead of  $K_{490}$  provided higher maximum values of POC, but the scatter was greater in the correlation with POC.

Comparisons of our predicted POC values at low concentrations can also be made at HOT and BATS, although the long-term averaging of our data and coarse plotting grid make it difficult to resolve details at those sites. <u>Hebel and Karl, (2001)</u> plotted POC data from 1989-1997 indicating that surface values were between 2-4  $\mu$ M. Values at BATS are similar, so the predicted POC values may be 1-2  $\mu$ M high, which is consistent with findings of <u>Moran et al., (1999)</u>. The JGOFS EqPac POC data at 140° W from 12°S to 12°N yielded bottle POC values between 3-5  $\mu$ M, which is comparable to values in figures 7 and 8.

# 4.5. POC, c<sub>p</sub> and Chlorophyll.

For comparison of POC and  $c_p$  with chlorophyll we compiled seasonal 5-year (1997-2002) averaged global maps from SeaWiFS CHL data for the same period (Figs. 7a and 8a). A bulk carbon:chlorophyll ratio could be obtained by simple division of the data in Figs. 7 and 8 a and b, but this could be confused with the typical carbon:chlorophyll ratios used in analyzing phytoplankton (Geider et al., 1998). Mishonov et al., (2003b) mapped CHL as a percent of POC ((CHL:POC)\*100) to look at spatial variations in the carbon:chlorophyll relationship, and we have made similar maps here (Figs. 7c and 8c). Behrenfeld and Boss (2003) argued that  $c_p$  is a better proxy for phytoplankton biomass than for POC. They suggested a parameter of  $c_p$  normalized to chlorophyll concentration,  $c_p$ :CHL, or  $c_p^*$  with units of m<sup>2</sup> mgCHL<sup>-1</sup>. Following this suggestion we have taken the  $c_p$  fields used to derive Figs. 7b and 8b and divided them by the matching spatial chlorophyll data (Figs. 7a and 8a) to produce summer and winter maps of  $c_p^*$  (Fig. 10). This relationship bypasses any conversion to POC.

#### 5. DISCUSSION:

A major goal of the oceanographic community is to develop regional and global mass balances for carbon in order to understand the role of the ocean as a source and sink for atmospheric  $CO_2$  because of its impact on earth's climate. To better understand and predict cycling of carbon and associated elements in the ocean, we must better understand the distribution and cycling of a very mobile component of the carbon cycle – particulate organic carbon (POC).  $CO_2$  and dissolved organic carbon (DOC) in the surface ocean are converted to POC through biological processes. While  $CO_2$  and DOC move with the water, POC can settle through the water, across isopycnals, scavenging or aggregating other particles and transporting carbon and associated elements to deeper waters where they enter the sediments, or, more likely, are remineralized. Because carbon is the primary "currency" used in energy budgets of biogeochemical processes in the ocean, it is

essential to quantify local and global carbon abundance. Although particulate organic carbon is a small component of the total carbon budget, it is a dominant component of primary production, which creates particles that can sink and transport carbon to deep waters. <u>Deuser et al. (1983)</u> also demonstrated that the flux of non-biogenic particles from the sea surface is controlled by biological processes related to POC flux. As ocean observing systems develop, we need data on  $c_p$ :POC and other bio-optical relationships in more places during different seasons to determine the temporal and spatial variability of these parameters so they can be applied more confidently to the data collected from ships, moored and autonomous sensors. The utility and importance of this capability was elegantly demonstrated in the North and South Pacific by <u>Bishop et al. (2002, 2004</u>).

To improve biogeochemical and ecosystem models (e.g. <u>Geider et al., 1998;</u> <u>Christian at al., 2002; Schlitzer, 2002, Hood et al., 2003; Jackson and Burd, 2002</u>), it is necessary to obtain more accurate POC data than can be obtained from estimates based on chlorophyll concentrations (<u>Legendre and Michaud, 1999</u>). In this paper we have presented a new empirical algorithm to estimate POC concentrations from ocean color products. As a demonstration of its application we averaged all ocean data over five years (1997-2002) for two seasons (Figs. 7-8; May-August and December-March). Such averaging results in the smoothing of small-scale details and interannual variability, but we chose this path to examine large-scale trends in this summary of global distributions.

Regarding the distribution of chlorophyll as a percentage of POC (Fig. 7c and 8c), chlorophyll percentage is susceptible both to changes of pigment/carbon within the phytoplankton (<u>Banse, 1977; Eppley et al., 1977; 1992; Geider et al., 1998</u>) and changes in composition of the different carbon pools relative to phytoplankton pigment (<u>El-Sayed and Taguchi, 1981; Smith et al., 1996; Gundersen et al., 2001</u>). The % chlorophyll contours of 1.0 and 0.2 are equivalent to C:CHL ratios of 100 and 500 respectively.

<u>Behrenfeld and Boss, (2003</u>) argued that  $c_p^*$  is an optical index of phytoplankton physiology in surface waters. They cited several observations where changes in  $c_p^*$  with depth were consistent with expected changes in photoacclimation, or changes in growth irradiance, which cause changes in intracellular chlorophyll concentrations that have been observed as a function of depth (<u>Kitchen and Zaneveld, 1990</u>; <u>Mitchell and Kiefer, 1988</u>; Mitchell and Holm-Hansen, 1991; Fennel and Boss, 2003). Behrenfeld and Boss, (2003) also argued that if the  $c_p^*$  and photoacclimation relationship holds in the vertical dimension it could also hold in the horizontal and temporal dimensions as well. They noted that  $c_p$  is largely insensitive to changes in intracellular chlorophyll concentration, so changes in  $c_p^*$  could be an indication of changes in the physiological state of phytoplankton cells due to changes in irradiation, nutrients and temporal variability in the combined effects of cellular chlorophyll, incident light and growth rate of the plankton at that location. Using existing data from HOT, BATS, NABE and EqPac, they found a first-order correlation between  $c_p^*$  and chlorophyll-normalized photosynthetic rate,  $P_{opt}^{b}$ . Behrenfeld et al., (2005) went on to show that  $c_p^*$  could be used with other parameters not only to look at phytoplankton physiology from space, but also to calculate carbon-based net primary production.

#### 5.1. Regional observations

<u>Mishonov et al. (2003b)</u> created maps of POC concentration for the North and South Atlantic using satellite data averaged over just one month, yielding much finer detail than is seen in our 5-year averages over four summer or winter months (Figs. 7 and 8). Weekly or daily maps would reveal even greater detail, but the likelihood of complete areal coverage decreases because of cloud cover. In examining these global maps each reader is likely to focus on geographic regions of their interest to look for specific features; we comment here on some general observations. Note that scales for CHL and POC are linear at the low end, yet this lower range covers approximately 80-90% of the ocean area. Scales are non-linear at the upper end and were chosen to best portray features in the areas of high gradients, which cover <10% of the ocean. The % CHL scale in Figures 7c and 8c is linear only to 0.4%, which covers the majority of the ocean. Areas with >2% CHL are rare outside of coastal regions. The  $c_p^*$  scale in Figure 10 is linear only in the lower range, with low values indicating a greater abundance of chlorophyll per phytoplankton cell than at large values of  $c_p^*$ . Thus the shelf areas and regions of higher productivity have lower  $c_p^*$  values than the oligotrophic gyres. Both our  $c_p$  and CHL maps are parameters derived from ocean color products, but they still match quite well with the in-situ measurements of  $c_p$  and chlorophyll that <u>Behrenfeld and Boss</u>, (2003) used in their analysis of  $c_p^*$ . For instance  $c_p^*$  ranged between 0.14 and 1.6 at HOT over several years, 0.08 to 1.42 at BATS over several years, 0.25 to 0.84 at NABE over two months, and 0.22 to 0.7 at EqPac during parts of a year. They did not provide data from any shelf regions. The 5-yr averages of our maps do not allow one to visualize temporal variations, but one could apply the algorithms to estimate temporal changes.

Northern polar regions: There are clear seasonal differences in both chlorophyll and POC. However, even in winter, POC concentrations appear high off of Alaska, around the British Isles, the Yellow Sea-East China Sea, and the Java Sea. Some of the high values may result from the presence of Case II waters where river runoff and resuspension of bottom sediments in shallow waters give a false signal of high POC. It is also likely that some regions have already experienced a spring bloom by late March, so the "winter" average is not entirely one of low productivity. The  $c_p^*$  values in the northern hemisphere summer are lower (higher productivity) over a much larger region than the austral summer values of the Southern Ocean.

South Atlantic and Southern Ocean: In general the Southern Ocean is an area of high nutrients and relatively low chlorophyll during austral summer. However, there is evidence that the algorithms for chlorophyll concentration based on SeaWiFS data are as much as a factor of two low (Kahru and Mitchell, 1999; Stramska et al., 2003). Chlorophyll values increase significantly in austral summer, especially in the Argentine Basin, Falkland Plateau and along the margin of Antarctica. The elevated chlorophyll in the Argentine basin coincides with a region of high surface eddy kinetic energy (Cheney et al., 1983; Garraffo et al., 1992; Richardson et al., 1993) that is probably mixing nutrients up into the mixed layer. POC concentrations are highly elevated through most of the Southern Ocean in Dec-March, but there are large patches where POC and chlorophyll are not high over that four-month period. The %CHL and  $c_p^*$  values in the Southern Ocean exhibit less summer-winter variation than either chlorophyll or POC except along the ice edge or continental margin (once the ice has melted) and in the South Atlantic sector.

The tongue of low  $c_{p}^{*}$ , high POC and high CHL water starting at South Africa and extending eastward in the Indian Ocean sector of the Southern Ocean is noteworthy, especially during the austral summer (Figs. 7c, 8c, 10). The position of that tongue coincides well with the area of the retroflection of the Agulhas Current extending eastward along ~48-52°S. This is a region where drifting buoys revealed persistent eddies moving eastward along that gradient (Pazan and Niiler, 2004). Perhaps the eddies mix up enough useful nutrients to fuel a sustained low level of primary production. The area of high chlorophyll (0.5 mg m<sup>-3</sup>; Fig 8c) at 50°S and 70°E in the middle of that eastwardextending tongue coincides with the Kerguelen islands, which provide a source of iron and cause island upwelling, thus enhancing productivity in their vicinity. Between South Africa and the Kerguelen Islands and Plateau are the Agulhas Plateau (~2300m), Prince Edward Island and the Crozet Plateau and Islands. The circumpolar current moving through and around these obstacles probably causes upwelling all along this line. Similarly, both chlorophyll and POC concentrations are elevated especially in austral summer in the vicinity and downstream of the South Sandwich Islands east of the Drake Passage.

Coastal regions: Productivity is elevated in coastal regions during both seasons based on the low  $c_p^*$  values, but further evaluation is needed to determine the degree to which Case II waters are influencing the values.

Oligotrophic central gyres of all oceans: The areal extent of low %CHL, high  $c_p^*$  values (low productivity, Figs. 7c, 8c, 10) in the central gyres of all oceans increases in area and intensity during each hemisphere's "summer". This probably results from summer stratification and lower amounts of nutrients. It is still possible that subsurface chlorophyll maxima exist below these apparently oligotrophic regions as was documented in the Arabian Sea (Gundersen et al., 1998).

Equatorial Pacific: during the May-August period (Fig. 7), the tongue of elevated POC and CHL values are much more constrained along the equator than during December-March (Fig. 8), suggesting more constrained upwelling along the equator. From Dec-March, CHL abundance along the equator is less pronounced west of  $120^{\circ}$ W and the region of lower  $c_{p}$ \* values is slightly broader than in May-Aug.

Seasonal upwelling areas along the west-coast of Africa: The upwelling off of Namibia and off-shore of the Congo River is high in CHL, POC, and %CHL during both summer and winter seasons and exhibit low  $c_p^*$  values, suggesting high productivity.

# 5.2. Areal coverage by concentration and hemisphere

Histograms of the area of the ocean covered by different POC concentrations (Fig. 11) are divided by hemisphere and season and are based on total area of the ocean. The sums of the histograms are less than 100% and vary by season primarily because of ice cover. Contours and sums are in divisions of 12 for easy conversion to  $\mu$ M (12 mg m<sup>-3</sup> = 1  $\mu$ mole l<sup>-1</sup> or 1  $\mu$ M). About 80% of the ocean has surface concentrations of less than 72 mg m<sup>-3</sup> during May-August and about 70% of the ocean is less than 72 mg m<sup>-3</sup> in December-April. A doubling of the area covered by concentrations of 72-96 mg m<sup>-3</sup> occurs in the southern hemisphere during the summer with only a slight increase in that area with that concentration in the northern hemisphere. Note that the area covered by the lowest concentration bin (<48 mg m<sup>-3</sup>) increases from winter to summer in the southern hemisphere because of an increase in the oligotrophic area of the central gyres (Figs. 7b and 8b), perhaps as a result of stratification and prior utilization of nutrients.

The white lines in Figs 7b and 8b are the divisions used by <u>Behrenfeld and Falkowski (1997)</u> in calculating primary productivity by ocean, and are used here to calculate the integrated POC stock in different oceans (Table 3). The Arctic is the region  $>60^{\circ}$ N and the Southern ocean is  $>50^{\circ}$ S. Table 3 also provides the average annual POC concentration by ocean area. The Atlantic, Pacific and Indian oceans have mean standing stocks of 1.3-1.4 g m<sup>-2</sup> in the first attenuation depth of the ocean. The accuracy of the data are insufficient to distinguish differences between these three oceans. The values for the Arctic (0.4 g m<sup>-2</sup>) and Southern Ocean (0.8 g m<sup>-2</sup>) are much smaller, but the algorithm underestimates POC at high latitudes, and overestimates POC in oligotrophic regions, thus making the differences between polar and temperate oceans less certain than the values appear.

Along several WOCE lines in the Pacific we calculated the total POC to the depth when POC reached background levels (based on beam  $c_p$  profiles) and determined that the POC in the first attenuation depth is only 20-40% of the total POC down to background levels (<u>Gardner et al., 2003b</u>). This means that the standing stock of POC in the upper ocean could be 2.5 to 5 times larger than calculated in Table 3. Deep chlorophyll and POC maxima are not sensed by satellites (<u>Gundersen et al., 1998</u>). Although algorithms have been developed to account for deep chlorophyll maxima (<u>Morel, 1988; Sathyendranath et al., 2001</u>), such algorithms remain to be developed for POC.

#### 5.3. Integrated Stock and Residence Time of POC

In estimating the average concentration of POC in the surface attenuation depth of the ocean we can also integrate POC over that depth and obtain a standing stock of POC at each location and calculate contributions by ocean and season. The total global mass of carbon in the first attenuation depth is estimated from our data to be 0.40 Pg C in summer and 0.42 Pg C in winter (Table 3) (Gardner et al., 2003b). If we know the rate of input (primary production) or output (export plus remineralization), we can calculate a residence time of POC in surface waters. Behrenfeld and Falkowski (1997) estimated the global annual primary phytoplankton production of POC to be 43.5 Pg C yr<sup>-1</sup>. Our estimate for the average annual mass of POC in the upper attenuation depth of the ocean from five years (1997-2002) of SeaWiFS data is 0.43 Pg C (Table 3), yielding a residence time of 3.6 days. Najar et al. (2003) estimated the annual export of POC to be 12 Pg C yr<sup>-1</sup>. Exclusive of remineralization, this yields an approximate residence time of 13 days, which is close to the 18 days (range 8-43 days) estimated at the HOT area in the Pacific (Karl et al., 1996) and 15 days estimated by Eppley et al. (1992) in the same region.

As noted earlier, the POC in the first attenuation depth is 20-40% of the total POC down to background levels (<u>Gardner et al., 2003b</u>). This suggests that the residence time of POC in the upper ocean is 5 to 2.5 times longer than the time based on one attenuation depth. Calculations of POC stock have been made for each ocean (Table 3), and the residence time in different oceans ranges from 3-5 days for one attenuation depth, but 7-12 days if this represents only 40% of the total POC in surface waters and 14-25 days if this represents only 20% of the POC in surface waters. Based on export data of <u>Najar et</u>

<u>al. (2003)</u> the residence time would be 33 days (40%) to 67 days (20%). These preliminary results need further refinement.

#### 5.4. Future Applications

Algorithms for POC from ocean color can be used to make time-series estimates. <u>Doney et al. (2004)</u> point out that this type of data is useful beyond the constraint of model output for spatial distributions and concentrations, citing the example of <u>McClain</u> <u>et al. (1990)</u> where moored current measurements could be used to estimate mass budget values for temporal rate of change, horizontal advective and diffusive fluxes, etc. Such data could be assimilated into numerical models like those of <u>Friedrichs (2002)</u> to optimize model parameters such as growth, mortality and grazing rates to improve our understanding of biological processes and oceanic systems <u>Doney et al. (2004)</u>.

The ocean observatories initiatives (e.g. Integrated Ocean Observing System (IOOS), Ocean Observatories Initiative (OOI), Ocean Research Interactive Observatories Networks (ORION)) require that *in-situ* proxies be created/refined to obtain biogeochemical parameters from relatively easy measurements such as those available with optical devices. Our results are directly applicable to these programs because they provide algorithms to determine POC in the vicinity of these sampling platforms using *in-situ* optical measurements and enable others to extrapolate the local results to regional or global scales using remotely sensed satellite data.

#### 6. CONCLUSIONS

POC concentration can be effectively estimated from beam attenuation data through linear regression of simultaneously collected data. Using ocean color data collected simultaneously with beam attenuation and POC data in two areas, an empirical relationship between  $c_p$  in the surface one attenuation depth of the ocean and K<sub>490</sub> was developed. A five-year average of K<sub>490</sub> during summer and winter seasons was converted to  $c_p$  and then to POC using a combined  $c_p$ :POC regression. Thus it is possible to predict both POC and chlorophyll concentrations from ocean color products to assess spatial and temporal variations. If  $c_p$  is a better proxy for phytoplankton biomass than POC as suggested by <u>Behrenfeld and Boss, (2003)</u>, maps of  $c_p^*$  provide information about the physiological state of phytoplankton communities, and with other data, predict net primary production <u>Behrenfeld et al., (2005)</u>.

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MOD II -	Regions										
params.	NABE	CMO- 96	NEGoM	HOT corr.	EqPac	BATS corr.	Ross Sea	APFZ	Arabian Sea	All data (no RS)*	
Slope	25.3	32.2	27.6	46.6	46.0	35.8	52.6	33.5	39.3	31.7	
Intercept	0.276	0.374	-0.457	0.381	0.420	0.494	1.902	3.064	-0.388	0.785	
SD Slope	0.610	2.399	0.737	1.439	0.975	0.709	0.592	0.609	0.707	0.275	
SD Intercept	0.178	0.943	0.218	0.042	0.078	0.032	0.304	0.125	0.078	0.048	
n	165	88	440	305	224	855	994	659	726	3462	
$\mathbb{R}^2$	0.904	0.513	0.685	0.710	0.899	0.664	0.874	0.781	0.766	0.739	

Table 1. Parameters of the Model II linear regression for different regions of the World Ocean: Beam attenuation due to particles ( $c_p$ , 1/m) vs POC ( $\mu$ M) concentration.

\* No Ross Sea data used in global fit.

Table 2. Regression between synchronous  $c_p$  and SeaWiFS data products observed in Northeast Gulf of Mexico (NEGoM, 440 data points) and Antarctic Polar Front Zone (APFZ, 140 data points). Non-synchronous regression parameters from the South Atlantic Ventilation Experiment (SAVE, 330 data points adopted from Mishonov et al., 2003) are shown for comparison.

Equation:  $c_p = \text{EXP}(\text{Slope*LN}(\text{Product}) + \text{Intercept})$ . Combined – combined regression using APFZ and NEGOM data sets.

Para-				SeaWiFS data products									
meters	•	CHL				<u>K49</u>	<u> </u>		<sub>VN</sub> (555)			IC <sub>K</sub>	
Region	NE GoM	APFZ	SAVE	NE GoM	APFZ	Com- bined	SAVE	NE GoM	APFZ	SAVE	NE GoM	APFZ	SAVE
								1.388					
Inter- cept	-1.228	-0.306	-1.013	1.254	3.856	1.361	2.560	-0.636	-0.186	0.601	-3.730	-5.068	-3.018
KMS	0.131	0.090	0.002	0.150	0.107	0.100	0.040	0.249 0.455	0.090	0.048	0.047 0.850	0.080	0.084

Table 3. Regional POC stock ( $g*10^{13}$ ) integrated down to one attenuation depth (based on  $K_{490}$ ). Annual average POC ( $gm^{-2}$ ) is the regional stock divided by regional area.

Annual (60 mo avg)	Summer (20 mo avg)	Winter (20 mo avg)	Annual averag POC g m <sup>-2</sup>		
0.73	0.56	0.20	0.4		
9.82	9.54	9.41	1.3		
5.76	5.53	5.37	1.2		
4.07	4.01	4.04	1.3		
7.52	7.39	7.44	1.4		
19.15	18.99	18.98	1.4		
9.89	9.79	9.71	1.3		
4.47	4.40	4.38	1.4		
5.42	5.39	5.33	1.3		
9.26	9.20	9.27	1.4		
2.34	2.32	2.24	1.4		
6.91	6.88	6.93	1.4		
5.61	3.94	5.52	0.8		
42.83	40.43	41.54	1.2		
	(60 mo avg) 0.73 9.82 5.76 4.07 7.52 19.15 9.89 4.47 5.42 9.26 2.34 6.91 5.61	(60 mo avg)         (20 mo avg)           0.73         0.56           9.82         9.54           5.76         5.53           4.07         4.01           7.52         7.39           19.15         18.99           9.89         9.79           4.47         4.40           5.42         5.39           9.26         9.20           2.34         2.32           6.91         6.88           5.61         3.94	(60 mo avg)(20 mo avg)(20 mo avg)0.730.560.209.829.549.415.765.535.374.074.014.047.527.397.4419.1518.9918.989.899.799.714.474.404.385.425.395.339.269.209.272.342.322.246.916.886.935.613.945.52		

# **Figure Captions**

**Figure 1.** Transmissometer stations and sites where POC was measured simultaneously (triangles). Insert: temporal distribution of the transmissometer data: # profiles per year.

**Figure 2.** Regressions between POC and Beam  $c_p$  acquired in different regions:

- a) North Atlantic Bloom Experiment (NABE), modified from Gardner et al. (1993).
- b) Coastal Optics and Mixing experiment, 1996 (CMO-96), modified from Gardner et al. (2001)
- c) North-East Gulf of Mexico (NEGOM), modified from Richardson et al. (2003).
- d) Hawaii Time Series (HOT), corrected data from HOT archives, modified from Mishonov et al. (2003a).
- e) Equatorial Pacific (EqPac) JGOFS, RV *Th.Thomson* cruise TT012. Beam  $c_p$  from Gardner et al. (1995); Chung et al. (1996; 1998); POC from JGOFS data base.
- f) Bermuda Atlantic Time Series (BATS), corrected data from BATS archives, modified from Mishonov et al. (2003a).
- g) Ross Sea AESOPS, RV *N.B.Palmer* cruises NBP 96-3, NBP 96-8, NBP 97-1, NBP 97-3, NBP 97-8, & NBP 98-2. Modified from Gardner et al. (2000a).
- h) Antarctic Polar Front Zone (APFZ), RV *R.Revelle* cruises KIWI-6, 7, 8, & 9.
   Modified from Morrison et al. (2001); Gardner et al. (2000b).
- Arabian Sea JGOFS, RV *Th.Thomson* cruises TN043, TN045, TN049 and TN054. Modified from Gundersen et al. (1998).

**Figure 3.** Global POC – Beam  $c_p$  regression calculated on all available data collected in Indian ( $\nabla$ ), Atlantic ( $\diamond$ ) and Pacific (+) Oceans. See Table 1, "All data" for regression parameters.

**Figure 4.** SeaWiFS diffuse attenuation coefficient at 490 nm data averaged over cruise time-span for different KIWI cruises/legs in Antarctic Polar Front Zone (APFZ) area. Dots along cruise tracks denote station positions. See text for details.

**Figure 5.** SeaWiFS diffuse attenuation coefficient at 490 nm data averaged over cruise time-span for different NEGOM cruises in the Northeast Gulf of Mexico. Dots along cruise tracks denote station positions. See text for details.

**Figure 6.** Regressions between Beam  $c_p$  and four SeaWiFS products calculated with simultaneously collected data: APFZ ( $\nabla$ ) and NEGOM (+), modified from Richardson et al. (2003); and seasonally averaged data: SAVE ( $\diamond$ ), modified from Mishonov et al. (2003b): (a) SeaWiFS chlorophyll, CHL; (b) SeaWiFS diffuse attenuation coefficient at 490 nm, K<sub>490</sub>; (c) SeaWiFS normalized water-leaving radiance at 555 nm, L<sub>WN</sub>(555); (d) SeaWiFS chlorophyll integrated over one attenuation depth, I<sub>CK</sub>. The regression used for global maps in Figs. 8 and 9 is the solid gray line in b), which is a composite of the  $c_p$ :K<sub>490</sub> data collected at APFZ and NEGOM.

**Figure 7.** Global distribution for summer season (1997-2002, May-Aug, 20 months) of: (a) SeaWiFS CHL (mg m<sup>-3</sup>, level 3, reprocessing 4 data); (b) average POC (mg m<sup>-3</sup>) over one attenuation depth calculated from  $K_{490}:c_p:POC$ ; (c) CHL as a % of POC. White lines in b) mark boundaries separating ocean basins as used by Behrenfeld and Falkowski (1977) and in Table 3.

**Figure 8.** Global distribution for winter season (1997-2002, Dec-Mar, 20 months) of: (a) SeaWiFS CHL (mg m<sup>-3</sup>, level 3, reprocessing 4 data); (b) average POC (mg m<sup>-3</sup>) over one attenuation depth calculated from  $K_{490}:c_p:POC$ ; (c) CHL as a % of POC. White lines in b) mark boundaries separating ocean basins as used by Behrenfeld and Falkowski (1977) and in Table 3.

Figure 9. Predicted POC versus measured POC concentration ( $\mu$ M) for (a) APFZ area; (b) NEGOM area.

**Figure 10.** Global distribution for a) summer and b) winter season (1997-2002, Dec-Mar, 20 months) of:  $c_p$ :CHL, m<sup>2</sup> mgCHL<sup>-1</sup> ( $c_p^*$  of Behrenfeld and Boss, 2003)

**Figure 11.** Histogram of the percent of the total ocean area covered by five ranges of POC concentration in the Northern Hemisphere (a) and Southern Hemisphere (b) in May-August and December-April.