Running Title: CDOM In the Open Ocean

Chromophoric DOM in the Open Ocean

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I. Introduction

Recent research has shown that the optically active fraction of dissolved organic matter (chromophoric DOM, or CDOM, also called "gelbstoff" or "gilvin") plays a major role in determining underwater light availability in the open ocean (Siegel *et al.*, 1995; Siegel and Michaels, 1996; Vodacek *et al.*, 1997; Nelson *et al.*, 1998; Blough and Del Vecchio, this volume). We define the open ocean as the part of the global ocean where coastal runoff and riverine input are negligible on annual time scales. Furthermore, these aforementioned studies have suggested that significant variability in CDOM concentrations occur on the seasonal to interannual time scales in the upper water column. This 'picture' of open ocean CDOM differs from the traditional view where light absorption by CDOM was thought to be minor and that CDOM variability was not significant on annual time scales. The change in our perception of CDOM dynamics is important because CDOM can play a direct or indirect role in climate related biogeochemical cycles, particularly the carbon and sulfur cycles (Mopper and Kieber, this volume). Absorption of light by CDOM controls ultraviolet radiation penetration into the ocean, which has an impact upon phytoplankton and bacterial productivity. CDOM is also a primary reactant in the photoproduction of CO_2, CO, H_2O_2 and OCS and is a photosensitizer in the photolysis of DMS. Because of its impact upon the underwater light field, CDOM can influence the accuracy of global satellite-based measurements of ocean chlorophyll and primary productivity. The purpose of the present chapter is to present recent results of CDOM dynamics in the open sea and to introduce a new synthesis of the factors regulating the global CDOM distribution.

A. A Short History of CDOM Research in the Open Ocean

Optical oceanographers working in the Baltic Sea first related CDOM concentrations to the observed freshwater fraction or salinity of a water mass (e.g., Kalle, 1938; Jerlov, 1953; 1976; Højerslev, 1982). These observations, as well as recent ones (e.g., Blough *et al.* 1993; Vodacek *et al.* 1997; Del Castillo *et al.* 1999; Ferrari, 2000), demonstrated that, as the salinity approaches oceanic values, inferences of CDOM concentration decrease to nearly undetectable levels (Blough and Del Vecchio, this volume). This suggests that the source of oceanic CDOM is terrestrial runoff and that oceanic CDOM concentrations can be used as a tracer for terrestrial DOC. On the other hand, organic geochemists have shown that open ocean DOM contains only small amounts of organic molecular markers for materials of terrestrial origin (cf., Meyers-Schulte and Hedges, 1986; Hedges *et al.*, 1997; Opsahl and Benner, 1997), and that processes in sediments release CDOM into the water column (e.g., Chen 1999). These results imply that open ocean concentrations of colored dissolved organic matter are derived from the long-term (multi-year) breakdown products of marine productivity, as has also been proposed (e.g., Kalle, 1966; Bricaud *et al.* 1981; Hedges *et al.*, 1997). Together, these results suggest that CDOM distributions in coastal regions will be strongly affected by land-ocean interactions; whereas in the open ocean, CDOM concentrations will reflect local creation and destruction processes.

Theoretical and practical use of satellite ocean color data was enhanced by the “bio-optical” assumption which relates upper ocean optical properties to the concentration of the phytoplankton pigment, chlorophyll *a* (e.g., Smith and Baker 1978). These studies classified the ocean into a "Case I" ocean where optical properties covary with chlorophyll concentrations in a predictable manner (Morel 1988) and "Case II" waters

where the influence of CDOM, detrital particulate absorption and/or particulate scattering destroys this simple correlation. The "Case I" assumption is useful as it allows the development of simple empirical algorithms relating ocean color and phytoplankton biomass (Morel, 1988; O'Reilly *et al.*, 1998; Morel and Maritorena, 2001). For Case I waters, the contribution of CDOM and detrital absorption is assumed to be small which has inhibited CDOM research away from coasts and estuaries. Results of recent open ocean CDOM studies suggest that there is decoupling of the optical signatures of CDOM and phytoplankton biomass (Siegel and Michaels 1996, Vodacek *et al.* 1997, Nelson *et al.* 1998) on the seasonal scale in the open ocean. These results highlight limitations in simple ocean color algorithms that use chlorophyll concentration as the only index of water optical properties. On the other hand, the lack of correspondence between CDOM and phytoplankton absorption leads to the possibility of using ocean color data to quantify CDOM as well as the chlorophyll concentration (Roesler and Perry, 1995; Garver and Siegel 1997; Carder *et al.* 1999; Hoge and Lyon, 1996; Maritorena *et al.* submitted). Efforts to apply these techniques on a global scale with the goal of obtaining a better understanding of the role of CDOM in biogeochemical cycling and ocean ecology are underway (Siegel *et al.*, submitted).

Other on-going efforts in CDOM – related research include an assessment of photochemical transformations of DOM on its biological lability and upon carbon cycle in a general sense (e.g. Kieber *et al.* 1989; Moran and Zepp, 1997; Mopper *et al.* 1991, Miller and Zepp, 1995; Mopper and Kieber, this volume). These studies have been mostly focused upon the transformations of terrestrial CDOM in estuarine and coastal

waters but many of the processes involved are relevant to the open ocean. Only recently have detailed studies investigated the roles of photochemical transformations of DOM on food web interactions and the open ocean biogeochemistry.

II. Characterization of CDOM

A. An Operational Definition of CDOM

A complete characterization of open ocean CDOM is complicated, as it requires the understanding of the optical and chemical factors that comprise CDOM. Compounding this is the few open ocean observations of CDOM dynamics. Like all DOM, the definition of CDOM is the manifestation of procedure used to separate a water sample into "particulate" and "dissolved" fractions. Hence, the definition of CDOM is strictly operational. Typically, CDOM is defined as organic substances which absorb UV or visible light that have been passed through a submicron filter. In some cases combusted GF/F glass fiber filters (effective pore size 0.7 μm) are used but in most cases preconditioned 0.2 μm polycarbonate Nuclepore filters or mixed-ester Millipore filter cartridges are used to separate the dissolved and particulate fractions. Depending on the method the dissolved fraction may include, for example, viruses and colloids as well as truly dissolved materials (e.g., Shifrin, 1988). Concentration and isolation of CDOM from the bulk pool in fresh or coastal waters has been accomplished by using XAD ion-exchange resins, which take advantage of the hydrophobic and acid nature of humic materials (e.g. Carder *et al*., 1989). These techniques have allowed characterization of the humic and fulvic acids in seawater, but it is unlikely that open ocean CDOM is composed

entirely of water-soluble organic acids (Harvey and Boran, 1985). Other techniques used have included C-18 liquid chromatography (Coble *et al.,* 1990) and ultrafiltration (Mopper *et al.,* 1996) but these have not yet been widely used to study CDOM in the open ocean. Therefore, CDOM in oceanic systems is usually assessed by its optical activity; either by its absorption or fluorescence properties.

B. Optical Properties of CDOM

The absorption of light by water, suspended material (phytoplankton and other particles including nonliving detritus), and CDOM control the propagation of solar radiation through the water column (e.g., Jerlov, 1976; Shifrin, 1988; Kirk, 1994a; Mobley, 1994). Of these four absorbing components, water absorbs visible light primarily in the red and yellow portion of the spectrum and light of these colors is attenuated rapidly within the water column. Phytoplankton absorb light mostly in the blue and blue-green regions of the spectrum, with a secondary absorption peak in the red, giving rise to the green to golden color of most phytoplankton. CDOM absorbs primarily ultraviolet and blue light, and is also fluorescent. Natural waters containing large amounts of CDOM appear yellowish in color, thus the terms “gelbstoff” (Kalle, 1938), “yellow substance” (Shifrin, 1988) and “gilvin” (Kirk, 1994a).

Despite the fact that CDOM is a mixture of chromophores, absorption spectra of CDOM are typically featureless in the visible (400-700 nm) and UV-A (320-400 nm) portion of the spectrum, declining exponentially with wavelength (Fig. 1). Because of this, CDOM spectra are usually parameterized as an exponential function with a single slope parameter, S, (Bricaud *et al.*, 1981), or

$$a_g(\lambda) = a_g(\lambda_o)e^{-S(\lambda-\lambda_o)} \quad (1)$$

where $a_g(\lambda)$ is the absorption coefficient of CDOM at wavelength λ (m^{-1}), λ_o is a reference wavelength, and S is the exponential slope parameter (nm^{-1}). At shorter wavelengths (< 320 nm), the CDOM absorption spectrum has features which do not allow the exponential approximation to apply. Values of S found in the literature range typically from 0.014 to more than 0.025 nm^{-1}, but these results are difficult to compare because of the various wavelength ranges and curve fitting techniques used to compute S (Bricaud *et al.*, 1981; Carder *et al.*, 1989; Green and Blough 1994, Blough and Del Vecchio, this volume). Higher values of S are typically found where and when CDOM absorption is fairly small. Particulate detrital absorption spectra usually decrease uniformly with wavelength in a manner similar to CDOM (e.g., Roesler *et al.*, 1989; Iturriaga and Siegel, 1989). Typical slope parameters for particulate detrital absorption are noticeably smaller than those found for CDOM.

It seems likely that the parameter S reflects relative proportions of the various chromophores found within the CDOM pool. Several investigators have suggested that the value of S can be used as an indicator of the origin or history of a given CDOM water sample. For example, Carder *et al.*, (1989) diagnosed variations in the S parameter for CDOM in Gulf of Mexico in terms of the relative proportion of humic and fulvic acids in a water sample. Blough *et al.* (1993), Nelson *et al.* (1998) and Whitehead *et al.* (2000) attributed certain changes in S to selective bleaching of CDOM components by solar

radiation. Nelson and coworkers (unpubl. data) have also diagnosed S in Sargasso Sea CDOM as reflecting the relative contribution of newly created, biologically semi-labile CDOM vs. older, more refractory CDOM. Clearly, the interpretation of S parameter variations remains an open question and one that may eventually provide important information about the state and/or history of the CDOM pool.

C. Chemical Composition of CDOM

The compounds which make up CDOM in the open sea remain largely undefined. The polysaccharides which are known make up much of the total DOM in ocean systems (e.g., Benner et al., 1992; Aluwihare *et al.*, 1997) are not known to be optically active at visible wavelengths. Thus much of the DOM produced by excretion from phytoplankton or net community production (e.g., Biersmith and Benner, 1998; Hansell and Carlson, 1998; Aluwihare and Repeta, 1999) must be altered before becoming part of the CDOM pool. Terrestrial-origin CDOM which is introduced to the coastal ocean by rivers and runoff is composed largely of humic and fulvic acids (Harvey and Boran, 1985; Carder *et al.,* 1989). These are organic acid polymers derived from the breakdown of higher plant matter (Opsahl and Benner, 1998) by microbes in soil or sediments. These compounds resist degradation by microbes and solar radiation and may make up an unknown portion of the 'background' level of CDOM observed in the open sea (e.g., Nelson *et al.* 1998). However, terrestrial DOM is thought to make up less than 5% of the total DOM in the open ocean (Opsahl and Benner, 1997). Humic and fulvic acids in the open ocean are distinct from terrestrial humic material, and may result from the reaction of fatty acids released by phytoplankton (Harvey and Boran, 1985). Additional contributors to the

CDOM pool may include amino acids and peptides, nucleic acids and bases, urea, and other low molecular weight compounds. These substances are generally very dilute in concentration in the water column as phytoplankton and bacteria readily utilize them. A significant fraction of the high molecular weight (> 1000D) dissolved organic matter in the open ocean is thought to consist of polysaccharides (Benner *et al.,* 1992). Nitrogen-15 nuclear magnetic resonance (NMR) analyses of dissolved organic nitrogen (DON) from the central North Pacific suggests that amide compounds, proteins or chitinous compounds (from the breakdown of zooplankton exoskeletons), account for the majority of DON in the water column (McCarthy *et al.,* 1997). These N-15 NMR analyses suggest melanoidins (e.g., compounds formed from peptides and sugars by the Maillard reaction; Kalle, 1966) are a much smaller fraction of the total DON pool. Chitins and melanoidins are also optically active, and are probably less readily consumed by bacteria and phytoplankton than the smaller compounds. Direct release of UV-absorbing compounds (mycosporine-like amino acids) into the water column by some phytoplankton has been demonstrated (Vernet and Whitehead, 1996, Whitehead and Vernet, 2000). These compounds may also contribute chromophores to the CDOM pool.

Another way to assess the composition of CDOM is in terms of its “lability,” or its biological reactivity. This is typically assessed in terms of the ability of the microbial community to consume the DOM in question. "Labile” DOM is consumed rapidly and does not necessarily appear in the water column, “refractory” DOM has a long lifetime and is resistant to microbial consumption, while “semi-labile” DOM can be consumed but over a longer time period (Carlson *et al.,* 1994; Carlson and Ducklow, 1996). The

paradigm describing the formation of refractory humic materials from particulate organic material in the terrestrial environment involves microbial degradation of biopolymers into low molecular weight compounds, which subsequently undergo condensation reactions to form more refractory geopolymers (e.g., Rashid, 1985). This process implies a decrease in lability with an increase in molecular weight. Irradiation of refractory CDOM is thought to yield reactive low molecular weight compounds which are more labile, and thus encouraging to microbial growth (e.g., Lindell *et al.,* 1995; Bushaw *et al*., 1996; Moran and Zepp, 1997; Anderson and Williams, 1999). On the other hand some studies have indicated that irradiation of CDOM does not necessarily result in increased lability, and that some lower molecular weight compounds are actually less reactive than their larger precursors (Tranvik and Kokalj, 1998). The impact of solar irradiation on the chemical and biological properties of CDOM in the open sea remains an important ongoing research question.

As will be described in more detail below, the time series record at the Bermuda Atlantic Time-series Study (BATS) shows a near-inverse relationship between CDOM and DOC concentrations (Siegel and Michaels, 1996; Nelson *et al.,* 1998). For example, summertime depletions in DOC concentrations observed in the seasonal thermocline co-occur with local increases in CDOM absorption. A similar lack of correspondence is seen in the summer time mixed layer. This complete lack of correlation between DOC and CDOM indicates that they are regulated by very different processes. Further, as large relative changes in CDOM seem to have no impact upon the DOC concentration (cf. Fig. 8), this result suggests on a mass basis that CDOM comprises a small fraction of the total

DOM pool (e.g., Siegel and Michaels, 1996). These observations will be further explored later in this chapter.

D. Methods for Quantifying CDOM

At this time, CDOM is distinguishable from total DOM only by its optical activity. The standard method for estimating the absorption spectrum of CDOM involves measuring the optical density of filtered seawater samples relative to highly purified fresh water in 10 cm quartz-windowed cuvettes, using a conventional spectrophotometer (Green and Blough, 1994; Vodacek *et al*., 1997; Nelson *et al.*, 1998). There are two drawbacks to this methodology in open ocean systems: first, many water purification systems do not produce sufficiently CDOM-free water, and second, conventional spectrophotometers do not have sufficient sensitivity to detect the slight absorption which occurs over a 10 cm path of open-ocean water (e.g., Mitchell *et al.,* 2000). High-quality laboratory spectrophotometers can detect CDOM absorption in 10 cm cells down to approximately 0.05 m^{-1} (range 0.03 - 0.07 m^{-1}) which is near the average absorption coefficient of CDOM at 400 nm in the Sargasso Sea (Kirk, 1994a; Nelson *et al.,* 1998). Absorption at longer wavelengths can be estimated by extrapolation from valid measurements using the exponential approximation (Eq. 1), but of course it is difficult to assess the accuracy of this technique. A possible method for overcoming the limitations of conventional spectrophotometry involves using custom long-path cells (Bricaud *et al.,* 1981) or capillary optical waveguide cuvettes (D'Sa *et al.,* 1999) but to date these instruments are not in routine use except in a few laboratories. Even if these advanced techniques were to become popular, a 1m pathlength will not enable CDOM

measurements throughout the visible spectrum in open ocean seawater unless photometric accuracy also increases dramatically. Thus objective measurements of CDOM light absorption in the open sea will remain difficult to obtain.

An *in situ* method for measuring CDOM absorption was developed by Twardowski *et al.,* (1999) using paired WETLabs AC-9 absorption meters. This instrument is comprised of a 'shiny tube' absorption instrument (Zaneveld *et al.,* 1992) which measures the total absorption coefficient (i.e. the sum of water, dissolved material, and particulate absorption coefficient) and a transmissometer, which measures the beam attenuation coefficient (sum of absorption and scattering coefficients) at 9 discrete visible-light wavelengths in a flow-through 0.25m tube. CDOM absorption coefficient can be estimated from two AC-9 instruments by placing an in-line filter on the incoming water line of one of the instruments to capture particles larger than 0.2 μm and to subtract off the signal from an unfiltered instrument. The principal advantages of this technique over standard laboratory spectrophotometry of discrete samples is that high-resolution profiles can be measured (Twardowski *et al.,* 1999) and the increased sensitivity due to the longer pathlength of the AC-9 optics makes routine measurements to ca. 550 nm in open ocean waters possible.

An unknown fraction of the absorbing chromophores which make up CDOM are also fluorescent (often termed FDOM). In coastal and continental shelf waters, empirical relationships have been developed between FDOM fluorescence and absorption of CDOM using UV excitation and blue emission (e.g., Hoge *et al.,* 1995; Ferrari and Tassan 1991; Vodacek et al 1995, Chen, 1999) but these seem to be specific to the

composition of CDOM and are not universal. This limits the utility of FDOM measurements for assessment of CDOM dynamics. Decoupling between CDOM absorption and FDOM fluorescence decrease with salinity was noted by Kalle (1966), who attributed the decoupling to mixing of fresh water CDOM with material of offshore origin, and by Vodacek *et al*. (1997) who attributed the decoupling to selective bleaching of selected chromophores. On the other hand, deep-ocean profiles of FDOM (measured with single excitation and emission bands) provide clues as to the deep-ocean distribution of CDOM (Chen and Bada, 1992; Hayase and Shinozuka, 1995; Determann *et al.,* 1996; Karabashev, 1999; section III.B).

Patterns of fluorescent chromophore distribution can be elucidated using synchronous fluorescence spectroscopy (Ferrari and Mingazzini, 1995) and excitation-emission matrix spectroscopy (Coble, 1996). To date these techniques have mostly been used in coastal waters and in the coastal transition zone. Fluorescent "fingerprints" have been used to discriminate between terrestrial sources of fluorescent CDOM and between coastal and offshore-origin CDOM, as well as different oceanic water masses (Coble *et al*., 1990; Coble *et al.,* 1998; Del Castillo *et al.,* 1999, 2000). These results highlight the diversity of the compounds which make up CDOM. As with absorption spectroscopy, the use of fluorescence spectroscopy to characterize open ocean CDOM is limited by low ambient concentration. The exponential decrease of absorption with wavelength still limits the amount of information that can be gained from visible wavelengths.

Another important set of methods for estimating CDOM light absorption rely on its known impact on the underwater light field. We will refer to these methods hereafter as

inversion methods. Inversion methods for CDOM can be based upon determinations of the vertical attenuation of downwelling spectral irradiance or upon the reflected light spectrum. The latter approach may be applied using satellite ocean color data sets enabling global distributions to be assessed. The former method provides a more direct measure of the absorption properties of the water column with fewer corrections for backscattering and geometric issues. Obviously, these inverse methods are not filtering seawater and the operational designation of CDOM from other optically similar absorbing materials cannot be made. The difficulty is that the optical properties for detrital particles and CDOM are similar enough that inverse methods can only provide a determination of their combined effects (Carder *et al.,* 1989; 1999; Siegel and Michaels, 1996; Garver and Siegel, 1997). As we will see below, the contribution of detrital particles on a global scale is small. We will refer to the combined absorption due to CDOM and detrital particles as "colored detrital materials" or CDM, which highlights its origin as a recycled material.

The decrease of spectral irradiance with depth can be used to compute the diffuse attenuation coefficient spectrum, $K_d(\lambda)$,which is to first order a function of absorption (Kirk, 1994a; Mobley, 1994). In the open ocean, the diffuse attenuation coefficient spectrum is generally computed over depth intervals up to 10 meters, thereby overcoming the limited pathlength problem found in the laboratory. Siegel *et al.* (1995) and Siegel and Michaels (1996) partitioned $K_d(\lambda)$ determinations into components for water, phytoplankton and colored dissolved and detrital materials. This partitioning took advantage of the fact that the optical properties of phytoplankton are distinct from those

of CDM (Fig. 1). This work assumed fixed values for the spectral CDM slope parameter and the chlorophyll-specific absorption coefficient spectrum for phytoplankton which enabled the time-depth variability of CDM at the BATS site to be assessed (Siegel and Michaels, 1996).

A host of investigators have developed semi-analytical models to differentiate CDM from chlorophyll absorption using remote sensing reflectance spectrum computed from *in situ* radiometric data (Roesler and Perry, 1996; Garver and Siegel, 1997; Hoge and Lyon, 1996; Carder *et al.,* 1999; Maritorena *et al.,* submitted). These models can be applied to global ocean color imagery, such as from the SeaWiFS sensor. A globally optimized version of the Garver and Siegel (1997), known as the UCSB (University of California, Santa Barbara) inverse ocean color model, has been used to provide the first assessment of global near-surface CDM distribution (Section IV). The UCSB ocean color model is based upon four basic assumptions: 1) an analytical relationship between the ocean color spectrum and the inherent optical properties (i.e. the absorption and backscattering coefficients) is known, 2) pure seawater optical properties are known, 3) a small number of dissolved and particulate constituents contribute to variations in absorption and backscattering coefficient and 4) the spectral shapes of these dissolved and/or particulate constituents are assumed to be constant or at least can be parameterized. The application of these assumptions results in an analytical model for ocean color as measured by a remote sensing instrument, with only the magnitudes of the constituent values to be determined. This problem is then solved for the unknown magnitudes (including CDM absorption) by solving the resulting nonlinear least-squares problem. A description of the

model may be found in Garver and Siegel (1997) and its global optimization in Maritorena *et al.* (submitted), respectively. Global results of this method applied to SeaWiFS ocean color imagery are discussed below (from Siegel *et al*. submitted).

III. Observed CDOM dynamics

A. Impact of CDOM on the Underwater Light Field

An analysis of the component light absorption budget provides valuable insights into the relative importance of CDOM to light availability and ocean color. The total absorption coefficient spectrum, $a(\lambda)$, may be partitioned into components due to seawater, $a_w(\lambda)$, phytoplankton, $a_{ph}(\lambda)$, CDOM, $a_g(\lambda)$, and detrital particles, $a_{det}(\lambda)$, or

$$a(\lambda) = a_w(\lambda) + a_{ph}(\lambda) + a_g(\lambda) + a_{det}(\lambda) \quad (2)$$

where $a_w(\lambda)$ is assumed to be a known constant (Smith and Baker, 1981; Pope and Fry, 1997). As described previously, the spectral shapes of CDOM [$a_g(\lambda)$] and detrital particulate [$a_{det}(\lambda)$] absorption are similar. Hence, inverse methods cannot *yet* differentiate between these two signals. Available spectroscopic observations from the surface waters of many sites from around the world suggest that non-water absorption is dominated by CDOM . For example, surface layer observations from the Sargasso Sea show that CDOM and detrital particulate absorption comprises 72% (15% s.d.; n=143) of the non-water absorption at 440 nm while detrital particles contribute only 9% (9% s.d.; n=143) of this total (Nelson *et al*., 1998 with additional data). Analyses using a global data set of surface component absorption observations show that on the average 57.0%

(16.4% s.d., N=1365) of the non-water absorption at 440 nm is due to CDOM and detrital particles while 17.8% (14.0% s.d., N=1365) of this absorption is due to detrital particles (Siegel *et al.,* unpubl. data). Further, there is a general trend that as chlorophyll levels increases, the contribution made by CDOM and detritus decreases. At a chlorophyll concentration of ~0.5 mg m^{-3} the influence of phytoplankton and CDOM absorption are about the same. A disproportionate fraction of this global data set is coastal (the data set mean chlorophyll concentration is 1.45 mg m^{-3} compared with mean values from SeaWiFS 0.36 mg m^{-3}). Hence, it is expected that the actual contribution of detrital particles on a global scale will be much smaller than the factors cited previously. In summary, CDOM absorption dominates the total absorption budget over most of the open ocean (chlorophyll concentrations less than 0.5 mg m^{-3}) and detrital particles will make a small contribution to the CDOM absorption signal determined from inversion methods (Siegel *et al.,* manuscript to be submitted).

B. Local Sources and Sinks of CDOM

Geochemical evidence demonstrating that terrestrial-origin DOM is a small fraction of total DOM (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1998) as well as field results which show large seasonal time scale variations in CDOM highlight the importance of local biological processes on open ocean CDOM. Local sources and sinks in the open sea may include not only production and consumption of CDOM due to biological processes, but also upwelling and convective export. At this point in time, it is clear that much of the open ocean CDOM is cycled by local processes although neither details of the nature of these processes (i.e. microbial, phytoplankton exudation,

photochemical bleaching, etc.) nor their variability in space and time has been established.

The first multi-year time series of CDOM measurements in the open sea was made in the subtropical Sargasso Sea near Bermuda at the BATS site (Nelson *et al.,* 1998). Optical measurements made at BATS by the Bermuda Bio-Optics Project (Siegel *et al.,* 1995) revealed a seasonal pattern in spectral light availability that was interpreted as seasonal variability in CDOM and/or particulate detritus absorption (Siegel and Michaels, 1996). The hypothesized seasonal variability of CDOM was confirmed using spectroscopic data and showed that particulate detritus was a small contributor to the signal (Nelson *et al.,* 1998). A well mixed water column and roughly homogenous distribution of CDOM in the winter months changes each year to a distinct surface minimum – subsurface maximum pattern during the summer (Fig. 2). In fact the divergence between the surface minimum and subsurface maximum tends to increase over the course of the summer while phytoplankton productivity remains low (Nelson *et al.,* 1998). The pattern is repeated on an annual basis as winter mixing homogenizes the water column. This is seen clearly in the relation between mixed layer depth and the depth-time distributions of CDOM (here shown as $a_g(325)$) presented in Fig. 3. The observed seasonal CDOM cycle at BATS suggests a number of possible local sources and sinks.

Processes which potentially produce CDOM *in situ* include release or excretion by organisms and lysis of cells by viruses. In the Sargasso Sea, during the annual spring phytoplankton bloom, there is a slight increase in CDOM near the surface, which rapidly

decreases with the onset of stratification (Fig. 3). This suggests the possibility that phytoplankton release CDOM during active growth, as DOM release by growing phytoplankton is well known and CDOM by growing phytoplankton has been shown to occur in a coastal dinoflagellate (Vernet and Whitehead, 1996, Whitehead and Vernet, 2000). However, the subsurface production of CDOM during the summer occurs mostly between 50 and 100m (Fig. 2), which is typically shallower than the deep chlorophyll maximum layer (90-120m) and is not at a depth of either elevated phytoplankton pigment biomass or primary productivity. The 50-100m depth range supports the highest biomass and productivity of bacteria in the upper water column (e.g., Carlson *et al.*, 1996), suggesting that the microbial community may be the source of the "new" summertime CDOM (Nelson *et al.,* 1998).

Subsurface maxima in fluorescent CDOM have been observed in the open Pacific over similar depth regions (Chen and Bada, 1992; Hayase and Shinozuka, 1995). In these studies FDOM concentration was closely related to inorganic nutrient distribution and apparent oxygen utilization, suggesting a link between microbial remineralization and FDOM.

The assertion of a link between remineralization and CDOM or FDOM production is strengthened by results of microbial culture experiments using natural populations of bacteria growing in the dark, in seawater amended with organic and inorganic substrates (Nelson *et al.*, 1998; Nelson, Carlson, and Steinberg, unpubl. data). In these experiments CDOM light absorption increased in cultures with actively growing bacteria but decreased almost to the initial value over a period of days after the bacterial growth rate

went to zero, indicating both production and consumption of CDOM by microbes (Fig. 4). In other experiments (not shown) up to 10% of the CDOM produced during the experiment remained for up to 90 days, indicating that this process does produce CDOM which is refractory enough to resist consumption within the water column.

Mechanisms for CDOM production as a consequence of bacterial production are unclear. The action of microbial extracellular enzymes on DOM is one possibility (e.g., Martinez *et al.,* 1996). Reaction products that are not immediately assimilated by the bacteria may rejoin the DOM pool. Some reactions result in optically active products where the reactants are not optically active. The Maillard (1913) reaction between sugars and peptides is an example of such a reaction, although this particular reaction is not known to result from bacterial exoenzyme activity. Release of capsular material or exopolysaccharides by bacteria may also contribute to the CDOM pool. The impact of viral lysis *in situ* is also difficult to estimate, but it has been proposed that virus abundance is proportional to bacterial cell density (e.g., Guixa-Boixereu *et al.,* 1999). However, culture experiments (e.g., Fig. 4) suggest that if viral lysis is the process which releases CDOM from bacterial cells, the rate of lysis is proportional to bacterial productivity and not cell density.

Disappearance of new CDOM from the dark culture experiments suggests that the majority of newly produced CDOM is labile (i.e. consumable by bacteria) and a small portion (ca. 10% or less) is more refractory. Hence, microbial processes are also a sink for CDOM. It is clear, however, that a large sink for CDOM in the open ocean is solar bleaching (Siegel and Michaels, 1996; Nelson *et al.,* 1998; Siegel *et al.*, submitted).

Sunlight-mediated CDOM bleaching has been well documented in culture and in the field (Mopper *et al.,* 1991; Kouassi and Zika, 1992, Vodacek *et al.,* 1997; Nelson *et al.,* 1998; Andrews *et al.,* 2000; Whitehead *et al.*, 2000). The CDOM surface minimum found in the Sargasso Sea in the summer is thought to be caused by elevated bleaching rates due to CDOM being trapped near the surface during stratification (Siegel and Michaels, 1996; Nelson *et al.,* 1998).

The seasonal scale Sargasso Sea CDOM observations (Figs. 2 and 3) have been explained using a simple model of depth-dependent bleaching (decreasing exponentially with depth) and CDOM production proportional to specific bacterial production (Nelson *et al.,* 1998). The model yielded scale estimates for the turnover time of CDOM in the Sargasso Sea due to bleaching of approximately 90 days, and turnover time for production of 125-300 days. Estimated bleaching rates were consistent with apparent quantum yields for CDOM bleaching in the published literature (e.g., Kouassi and Zika, 1992; Whitehead *et al.,* 2000) when diurnal variations in irradiance were taken into account (Nelson unpubl. data). Extrapolation of this estimated bleaching rate over a deepening mixed layer (Nelson *et al.,* 1998) was sufficient to explain the summer-winter decrease in CDOM (e.g., Fig. 2) if it is assumed that the rate of photobleaching at the surface remains constant. This may not be the case as during the fall, as irradiance decreases and the mixed layer depth deepens. Hence it is possible that both bleaching and microbial consumption play important roles in drawing down CDOM in the Sargasso Sea.

In summary, it is clear that CDOM has an important if not dominant role in prescribing light availability in the open ocean. The influence of CDOM will be even more important in the predicting availability of ultraviolet light which is critical for many photochemical reactions. A host of biological and photochemical processes are regulating the concentration of CDOM in the water column. The exact nature of these has yet to be fully documented and this appears to be a very exciting avenue for future research.

IV. Global CDOM distribution patterns

A. Global Distribution of CDM Absorption From SeaWiFS

The UCSB inverse model is used with SeaWiFS determinations of water leaving radiance to provide global fields of CDOM and detrital particles (Fig. 5). Again, the absorption coefficient due to both CDOM and detrital particles is determined using our inverse modeling approach (i.e., CDM) although detrital particulate absorption should be small relative to CDOM in the open ocean (see above). End-to-end errors in the application of the UCSB ocean color model to SeaWiFS water leaving radiance determinations are assessed by comparing satellite retrieved values of CDM with near-simultaneous (within 4 day) field determinations of CDOM and detrital particulate absorption. This rough match-up data set shows that the satellite retrievals predict 64.3% of the variance (N=523) in the field observed CDM determinations with a near-perfect one-to-one line (Siegel *et al*., submitted). Hence, the preliminary satellite-derived CDM

distribution presented here should reflect the actual distribution of CDOM and detrital particles with a rather high degree of fidelity.

To first order, the global pattern of CDM absorption estimated from SeaWiFS ocean color imagery mimics the major gyre systems and other large-scale circulation features of the world ocean (Fig. 5; Siegel *et al.,* submitted). High values of CDM light absorption are found within regions of persistent large-scale upwelling (e.g., subarctic gyres, equatorial divergences, eastern boundary currents, etc.) while low values are observed for regions characterized by large-scale downwelling (e.g., subtropical gyres, western equatorial Pacific warm pool). The basin-scale CDM distribution appears similar in many ways to global distributions of chlorophyll concentration or primary production. This suggests that the same local processes that create regions of high phytoplankton biomass are regulating the near-surface CDM distributions. However, a robust statistical relationship is not found between retrieved CDM and chlorophyll concentrations (r^2 = 0.34) suggesting that these factors vary independently. When evaluated at high spatial resolution, riverine inputs can be discerned in the CDM distribution although these effects are localized. However, it is apparent that inputs of terrestrial materials are not the first order controls on the basin-scale CDM distribution (Fig. 5).

The fraction of blue light absorption regulated by CDM can be quantified using its contribution of non-water absorption at 440 nm (which we refer to as %CDM, for percent contribution of CDM to non-water absorption coefficient). On a global basis, the mean value of %CDM is 51.1%. This points again to a dominant role for CDOM and detritus in the absorption of blue light. The spatial distribution of %CDM shows a broad

minimum in the tropical ocean where %CDM retrievals are approximately 45 %. Towards the poles, values of %CDM increase dramatically (Fig. 5).

The %CDM contributions also differ among the major ocean basins. Mean determinations of %CDM are higher for the Atlantic and Indian Oceans than for the Pacific Ocean. For example, the mean value of %CDM is 52.5% (s.d. 10.7%) for the North Atlantic subtropical gyre whereas it is 45.8% (s.d. 9.3%) for the North Pacific subtropical gyre (Table 2). The mean value of %CDM for the tropical Pacific Ocean is smaller than the other basins (mean = 43.2% s.d. = 6.6%). These inter-basin variations suggest regional differences in the processes that produce mixed layer concentrations of CDOM.

B. Temporal Variability of the Global CDM Distribution

Significant temporal changes in CDOM and detritus (CDM) light absorption and %CDM contribution are also observed in zonally averaged latitude-time distributions of both (determined for 440 nm, Siegel et al., submitted). At latitude 30ºN, seasonal changes in zonally averaged CDM retrievals vary by more than a factor of five, from ~0.005 m^{-1} to more than 0.03 m^{-1}. Seasonal cycles are apparent throughout the subtropical gyres as CDM light absorption is reduced in the local summer and increased in the winter. Similar changes, though not as striking, are found throughout the record including the tropics. In general, CDM light absorption estimates are larger for the northern hemisphere subpolar region (north of 45ºN) compared with the southern subpolar hemisphere (south of 45ºS). The lowest CDM estimates are found in the

southern hemisphere mid-latitudes due to the large extent of the South Pacific subtropical gyre.

The character of seasonal changes is similar between sites within the North Atlantic and North Pacific subtropical gyres although their amplitudes are very different (Figs. 7a and 7b). Near Bermuda, CDM estimates increase by more than a factor of two (Fig. 6a) whereas observations from near the Hawaiian Islands show weaker, though still significant seasonal patterns (Fig. 6b). The satellite observed mean value of %CDM off Bermuda is approximately 55% which consistent with the spectrophotometric results presented previously while the %CDM values off Hawaii are considerably lower (approximately 42%). The lower amplitude of the seasonal cycle off Hawaii mirrors lower seasonal changes in primary production and chlorophyll a concentrations observed for this site north of Hawaii compared with the Sargasso Sea off Bermuda (Siegel *et al.*, 2001).

Large intraseasonal changes are also observed. For example, a large pulse in CDM light absorption was observed during the summer of 1998 in the equatorial Pacific Ocean (0° 155°W) in response to the transition from El Niño to La Nina conditions (Fig. 6c). After this transition, retrieved CDM values increased by a factor of roughly 50% compared with the El Niño period before the transition. This result indicates that the onset of equatorial upwelling brings CDOM-rich subsurface waters towards the surface. Sustained equatorial upwelling after this event produces the increased levels of %CDM observed.

C. Controls on the Global CDM Distribution

If CDOM is a long-lived product of the degradation of organic matter and photo-bleaching is its primary sink, then it is logical to assume that open ocean CDOM will be consistently depleted in stratified surface waters and enriched below. This pattern of increased CDOM absorption below the mixed layer is observed within the Sargasso Sea during the summer when the water column stability is high (Fig. 3). Increased CDOM values with depth have been also observed from the Arabian Sea and Equatorial Pacific (Pegau, 1996; Del Castillo *et al.,* 2000) and in vertical distributions of CDOM fluorescence from the world ocean (Chen and Bada, 1992; Hayase and Shinozuka, 1995; Determann *et al.,* 1996; Karabashev, 1999). Hence, it appears likely that elevated CDOM concentrations will occur at depth and that this pattern may be found throughout the global ocean (although it is apparent that more observations are required).

The meridional trend in incident solar irradiance provides additional information about controls on the global CDOM distribution. Rates of CDOM photo-bleaching should decrease towards the poles in proportion to reduced incident light levels (e.g., Kouassi and Zika 1992). Further, annual mean mixed layer depths are in general deeper towards the poles. The combination of deep mixed layers and reduced light doses suggest that integrated light doses for photo-bleaching will be much less in the high latitude oceans compared with the tropics and subtropics. This should result in CDOM concentrations that increase towards the poles. This pattern is clearly observed in the global CDM distribution where CDM retrievals increase dramatically towards the poles (Fig. 5). This general meridional trend in the global CDM distribution points to photo-

bleaching as the proximate control on near-surface, open ocean CDOM concentrations (Chen and Bada, 1992).

Superimposed on the global-scale meridional CDOM increase with latitude, the global CDM distribution shows patterns spatially consistent with the major ocean gyres and boundary currents (Fig. 5). This indicates that vertical transport of the "deep" reservoir of CDOM within these large-scale current regimes should be a significant external *net* source of "new" CDOM to the surface ocean. Vertical transports can be due to Ekman pumping driving large-scale vertical motions in the major gyres and equatorial zones of the world ocean, vertical advection created by the presence of a coastal boundary (i.e. coastal or shelf break upwelling), as well as convective and small-scale turbulent mixing creating diapycnal transports. An excellent example of the role of upwelling can be seen in CDM distribution sampled in the equatorial Pacific during the relaxation of the 1998 El Niño (Figs. 6c and 6d). Passive (convective) export may also be a sink for surface ocean CDOM in temperate and subtropical areas where there is a large seasonal variation in mixed layer depth. Convective export has been shown to be a significant factor in export of DOM from the surface waters of the Sargasso Sea (Carlson *et al.,* 1994; Hansell and Carlson, 2001), which would logically return some CDOM to deeper waters as well. This is the case observed off Bermuda (Fig. 3) and is likely to be the dominant process at higher latitudes. At present, it is unclear what the partitioning is between local (i.e. remineralization) vs. terrestrial sources for the deep-ocean reservoir of CDOM.

A cartoon illustrating the linkage between CDOM production, photo-bleaching and vertical transport processes on near-surface abundances of CDOM is shown in Fig. 7. A host of biological processes have been implicated in the production of CDOM. These include phytoplankton release, products of zooplankton grazing, bacterial release, and viral interactions. Production of CDOM is likely to occur throughout the water column; however, the photo-bleaching of near-surface CDOM makes it difficult to view this production from a time course of CDOM stocks (hence, the dashed arrow in Fig. 7). The net transport of "deep" CDOM into surface layers therefore is the important factor in regulating the global CDOM distribution (Fig. 7). This suggests that the use of CDOM in conjunction with its bleaching rate (on the seasonal time scale) may be an effective tracer for evaluating the residence time for surface water masses, which would be useful for evaluating global circulation models of the ocean.

V. Relationship between DOM and CDOM in the open ocean

Because a significant fraction of terrestrial-origin DOM appears to be optically active humic material, instances of correlation between DOC concentration and CDOM light absorption is expected. Estimates of the mass ratio of CDOM carbon to DOC based on these assumptions range from 0.1% to 4% (Shifrin, 1988). At first glance it would also appear that, as there often is in coastal regions (e.g. Vodacek et al., 1995; Ferrari, 2000), there should be a strong relationship between DOC concentration and CDOM absorption coefficient in the open sea. This stems from the supposition that new CDOM production results from either phytoplankton productivity or microbial reprocessing of DOM, which is also a by-product of phytoplankton growth. This presumed correlation turns out not to

be present, possibly in part due to the temporal decoupling of the different processes, and in part due to the differences in the processes which regulate CDOM and DOM.

In the subtropical Sargasso Sea, no correlation exists between DOC and CDOM in the upper water column (Fig. 8; Nelson *et al.,* 1998). This appears to be a result of the summertime bleaching of the surface CDOM (Fig. 2), which does not have a noticeable impact upon the concentration of DOC (Fig. 3). Thus, most open-ocean surface DOM appears to be colorless and thus not subject to bleaching (e.g., Siegel and Michaels, 1996). Further, microbial activity and convective export is relatively low in the tropics and central gyres, the concentration of DOC increases as one travels away from the source areas (Hansell *et al.,* 1997). This leads to the curious postulate that CDOM absorption and DOC concentrations in the open sea will vary *inversely* over large spatial scales. This is in direct conflict with coastal regions where CDOM is removed with distance from the coast, leading to a positive correlation with DOC. This unusual inverse pattern is consistent with the present synthesis of global DOC concentrations as prepared by Hansell and coworkers (Fig. 5C, Hansell et al. 1997; Hansell, this volume). The global DOC distribution shows neither global scale meridional patterns nor gyre-scale patterns consistent with the CDM distribution (Fig. 5). This suggests that the basic mechanisms driving the surface DOC distribution are fundamentally different from those driving the CDOM distribution (i.e., the net vertical transport of subsurface CDOM).

VI. Implications for Photochemistry and Photobiology

Many marine processes require CDOM as a reactant or use CDOM as protection from harmful UV radiation. Hence, open ocean CDOM concentrations have an important role

in marine photochemical and photobiological processes. For example, the photochemical production of dissolved inorganic carbon (DIC) from DOM is thought to occur primarily through the cleaving of organic acids found in CDOM (Miller and Zepp, 1995). Globally integrated DOM to DIC conversion rate estimates are highly uncertain, ranging from 0.1 to 12 Tg C per year (D. Siegel, UCSB, unpubl. results; S. Johannesen, Dalhousie Univ., unpubl. data). The upper end of these global rate estimates is many times greater than the global air-sea flux of CO_2 and nearly equal to the new production rate (Takahashi *et al.,* 1997; Falkowski *et al.,* 1998). Similarly, it is important to understand the role of UV radiation on phytoplankton photosynthesis. Hence, it is imperative to improve our ability to estimate photochemical and photobiological rates on a global scale. It is clear from the field and remote sensing evidence presented here that open ocean CDOM distributions vary significantly in both space and time. These factors must be taken into account when estimating the rates of many processes involving the interaction between solar energy and the ocean environment (Mopper and Kieber, this volume).

A. Photochemistry and the Carbon and Sulfur Cycles

Photochemical decomposition of CDOM by sunlight results in the production of various atmospheric trace gases, including carbon dioxide, carbon monoxide and carbonyl sulfide (e.g., Valentine and Zepp, 1993; Erickson, 1989; Miller and Zepp, 1995). CDOM is also implicated in the cycling of organic sulfur compounds including the photolysis of dimethyl sulfide (Shooter and Brimblecombe, 1999; Kieber *et al.* 1996) and the photoproduction of carbonyl sulfide (Doney *et al.,* 1995; Preiswerk and Najjar, 2000). Details of the major photochemical reactions related to CDOM and their

biogeochemical implications have been reviewed elsewhere (Blough, 1997; Mopper and Kieber, this volume). We here discuss some aspects of the problem which are specifically related to the properties of CDOM, particularly in the open ocean.

Quantum yield spectra for photochemical reactions tend to decline exponentially with wavelength, as do CDOM absorption spectra. Irradiance spectra, conversely, increase dramatically with wavelength in the UV (Kirk 1994), which typically leads to a peak in the production spectrum in the UV-A (320-400nm) range. In this waveband CDOM dominates absorption of light in the open sea (Kirk, 1994a,b; Siegel *et al.,* 1995; Nelson *et al.,* 1998; Siegel *et al.,* in prep, Fig. 5B). Available light in the water column at a temperate or subtropical site varies about 50% over the course of a year (Siegel *et al.,* 1995), tropical sites much less, and high-latitude sites much greater (Kirk, 1994a). Temporal variability in CDOM concentration in many open ocean areas around the globe is proportionally similar or greater than that of the light field (Nelson *et al.,* 1998; Fig. 2; Fig. 3). Thus, available light energy for photochemical reactions is a function of astronomical and meteorological factors (e.g., latitude, daylength and clouds), and of the amount of CDOM in the water column (Kirk, 1994a,b), in which light availability and CDOM concentration play approximately an equal part.

CDOM has a compound effect on photochemical reaction rates: first by being a reactant or intermediary in the photochemical reaction, and second by being a major light-absorbing component. Increasing the amount of CDOM will not only increase the absorbed quanta (assuming the incident irradiance is similar), but will shift the depth distribution of production closer to the surface. For example, model estimates of CO

production rate profiles in the Sargasso Sea have an e-folding depth of approximately 14m in the spring, and 25m in the summer (N. Nelson, O. Zafiriou, H. Xie, R. Najjar unpubl. data). This is significant in terms of the overall biogeochemical cycling of species in which air-sea gas exchange plays an important part (e.g., Doney *et al.,* 1995; Preiswerk and Najjar, 2000).

The quantum yield itself may be a function of the chemical composition (or 'quality') of the CDOM, and may be different for 'fresh' or 'aged' CDOM, and different still for CDOM of terrestrial origin. For example, there appears to be significant differences between CO quantum yields calculated for U.S. estuarine, coastal and open ocean sites (Valentine and Zepp 1983, O. Zafiriou and W. Wang pers. commun. 2000, L. Ziolkowski pers. commun. 2001). However for the open ocean, the impact of CDOM quality on photochemical quantum yields may be small. Measurements of spectral quantum yields for CO production made on a long gyre-to-gyre transect across the equatorial Pacific (thereby sampling bleached, 'aged' CDOM and freshly upwelled CDOM) suggest that such variability may be small (O. Zafiriou and W. Wang pers. commun. 2000). Nevertheless, it is clear that the variability of CDOM light absorption over ocean basins and in time is significant in terms of global photochemical reaction rates.

B. Photoinhibition of photosynthesis and microbial growth

Light absorption by CDOM is the major factor controlling the penetration of ultraviolet radiation (both UV-A and UV-B) into the open ocean (e.g., Fig. 1). This in turn implies that CDOM concentration controls the amount of UV-mediated inhibition of biological production and growth. UV radiation is implicated in photoinhibition of

photosynthesis (Smith *et al.,* 1980, 1992; Cullen *et al.,* 1992; Smith and Cullen, 1995) and in inhibition of microbial growth (Herndl *et al.,* 1993).

Like photochemical quantum yield spectra, 'biological weighting functions' for photoinhibition and microbial mortality typically decline exponentially with wavelength (Smith and Baker, 1979; Cullen *et al.,* 1992; Boucher and Prézelin, 1996). Unlike photochemical reactions however, these biological processes are complicated by factors such as dynamic repair of damaged cells (Lesser *et al.,* 1994), turbulent mixing in a steep light gradient altering exposure(Scully *et al.,* 1998), and relatively long time constants for the onset of photoinhibition (Neale and Richerson, 1987). It is less certain that CDOM concentration will be clearly inversely related to photoinhibition processes. On the other hand, measured photosynthetic rates (Smith *et al.,* 1980) and microbial cell counts (Carlson and Ducklow, 1996) in stratified (hence bleached) ocean waters do show surface minima, as if photoinhibitory processes are acting on the populations. This pattern is less often observed in mixed (possibly more CDOM-rich) waters (Arrigo and Brown, 1996). Smith and Baker (1979) demonstrated that the vertical attenuation of the DNA-damage dose (convolution of downwelling irradiance with the action spectrum of Setlow (1974)) was approximated by the diffuse attenuation coefficient for irradiance at 305 nm. At this wavelength, light absorption (and therefore the diffuse attenuation coefficient) is dominated by CDOM, therefore a change in CDOM will have a nearly proportional impact upon the biologically effective dose. This may explain the release of UV-A absorbing compounds by some phytoplankton (Vernet and Whitehead, 1996, Whitehead and Vernet, 2000). Estimates of the global distribution of CDOM in this context will add

to our understanding of the global impact of UV radiation on primary productivity, microbial populations, and DOM cycling, especially in the context of ozone depletion.

VII. Needs for Future Advances

Many of the problems faced in the study of CDOM in the open ocean are common to the study of the larger DOM pool. Sources, sinks, reactivity, and chemical composition are only starting to become known. An additional complication is that only a small fraction of the total DOM is optically active, and a technique for separating the two has not been developed. Yet CDOM is the largest factor controlling the penetration of UV and (blue) visible light into the water column, and there is compelling evidence that CDOM plays an important role in biogeochemical carbon and sulfur cycles and in microbial ecology. Hence increased understanding of the properties and dynamics of CDOM is in order. Some broad areas of study include:

- Origin and chemical composition of CDOM
- Relationship between biological lability and photo-lability
- Rates of formation of CDOM and its global distribution
- Determination of the lability of CDOM and its relation to DOM lability
- Impact of bleaching on CDOM lability and photochemical reactivity
- Role of chemical composition of CDOM on photochemical reactions
- The ultimate role of CDOM in biogeochemical cycles

The origin of open-ocean CDOM has not been clarified by recent investigations. It has been clearly demonstrated that local sources and sinks can account for annual fluctuations but the flux terms are not well enough constrained to rule out the possibility that the "background" or deep-ocean CDOM may have a significant terrestrial component. To determine the contribution of terrestrial components to the CDOM pool requires that terrestrial biomarkers be quantified in CDOM separately from the entire DOM pool. As mentioned previously, the chemical makeup of open ocean CDOM is less-well understood than terrestrial CDOM, as are the processes which give rise to it. It may well be that the paradigm for terrestrial humic matter formation (microbial digestion and alteration of biopolymers, followed by biological or abiological condensation reactions) does not apply to marine CDOM. This remains to be explored.

Variations in the composition of CDOM can influence its reactivity (both in terms of photochemical and biological lability) and by this its role in biogeochemistry and ecology. But at present no feasible method exists of assessing the CDOM separately from the bulk pool of DOM without making limiting assumptions about the chemical nature of the open ocean CDOM.

The process by which 'refractory' CDOM accumulates in the deep ocean also may have interesting oceanographic applications. The annual pattern of CDOM distribution in the Sargasso Sea is superimposed upon a background of CDOM 'concentration' (as absorption coefficient) which makes up 50-100% of the total (Nelson *et al.,* 1998). In fact this background CDOM appears to have significant changes in concentration in the Sargasso Sea on the multi-year time scale (Nelson unpubl. data) which may suggest it can

be used as a tracer of intermediate water masses outcropping at the surface. This in turn would be useful for assessing the rate subsurface water mass renewal. It is by no means certain that this 'background' CDOM is the same material that is produced and destroyed on an annual basis in the upper water column, as it can be spectroscopically distinct from newly produced CDOM (Nelson and Carlson, unpubl. data). Some of this background material may also be attributable to 'residual' terrestrial-origin DOM, as the ratio of land end-member absorption coefficient (e.g. Blough and Del Vecchio, this volume) to open ocean 'background' end-member absorption coefficient (e.g., Fig. 2) is similar to the range of estimates for the fractional contribution of terrestrial biomarkers to open ocean DOM (ca. 5%, Meyers-Schulte and Hedges 1986, Opsahl and Benner 1997). On the other hand, clear evidence exists for the production of FDOM as a consequence of microbial remineralization in the thermocline (Chen and Bada, 1992; Hayase and Shinozuka, 1995) which could also account for the deep reservoir of CDOM. Understanding the formation of refractory CDOM and its properties seems to be an important if far-off goal.

Along those lines, assessing the biological and photochemical properties of different 'types' of CDOM is also in order. The 'background' CDOM found in intermediate or deep water masses may be more or less labile than newly produced CDOM or material that has been bleached in surface waters. The possible difference in lability may have an impact upon the growth of the microbial community. The photochemical reactivity of the different pools of CDOM may also differ. The issue of "quality" of CDOM remains an open question.

The role of CDOM in biogeochemical cycles relevant to the climate is also a relatively untouched field. To date no ecosystem GCM models have incorporated marine boundary layer photochemistry, although by some estimates these fluxes of inorganic carbon and sulfur gases may be climatically significant. This may prove worthy of research as global assessments of photochemical reaction rates become available for incorporation (e.g. Erickson, 1989; Doney *et al.,* 1995; Preiswerk and Najjar, 2000).

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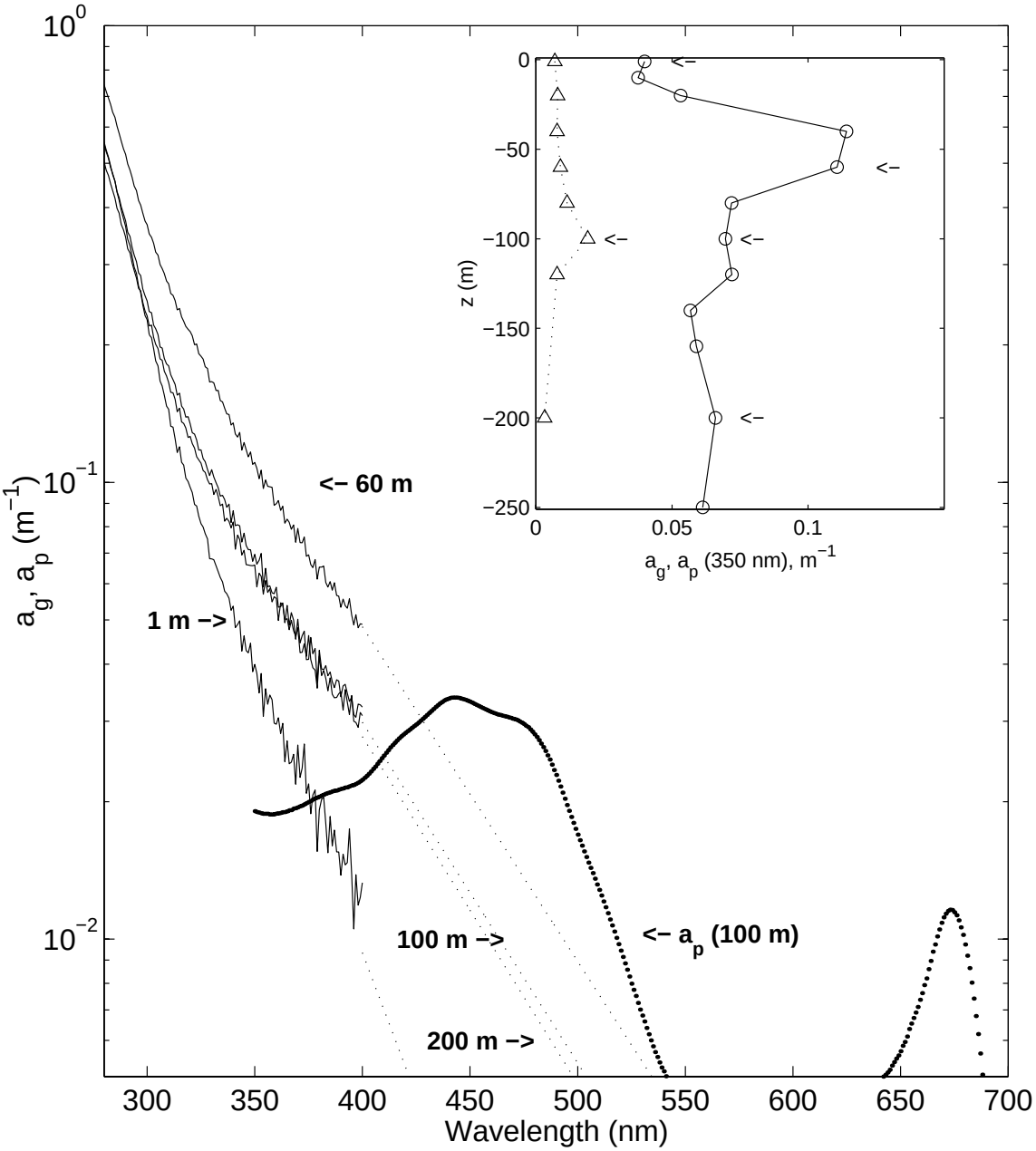

Figure 1: Absorption spectra of CDOM and particulate matter from the Sargasso Sea, July 1999. Thin solid lines: CDOM absorption spectra from 1, 60, 100, and 200m (see inset for vertical profile of CDOM absorption at 350 nm, [o]). Fine dotted lines are extrapolations from exponential curve fits using the 325-380 nm range as a basis. Heavy line is the absorption spectrum of particulate material (mostly phytoplankton) from 100m. The higher exponential slope in the surface CDOM spectrum is visible, as are non log-linear features in the spectra at wavelengths below 320 nm. Inset: Vertical profile of CDOM absorption coefficient (o) and particulate matter (△) at 350 nm. Arrows show the depths of collection of the different spectra shown in the main figure.

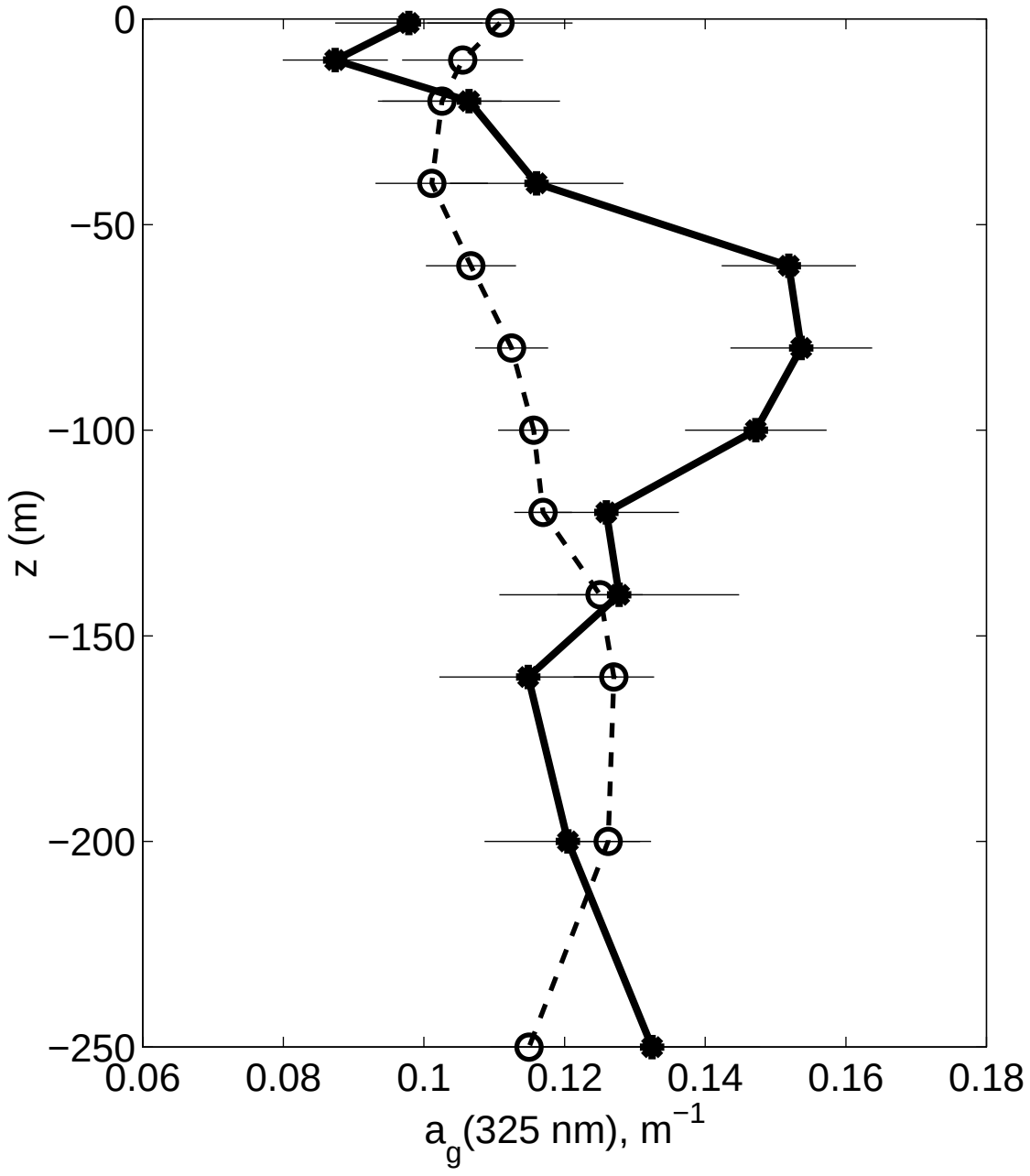

Figure 2: Seasonal averages of light absorption by CDOM (a_g) at 325 nm, 1994-1999 (Nelson and Carlson unpubl. data). Horizontal bars are standard deviation / mean. Open circles are winter averages (Dec-Feb) and closed circles are summer averages (Jun-Aug). The winter average profile has features which result from interannual variability in mixed-layer depth. The summer profile reflects the combined effects of sunlight-mediated bleaching of CDOM near the surface and subsurface production of CDOM.

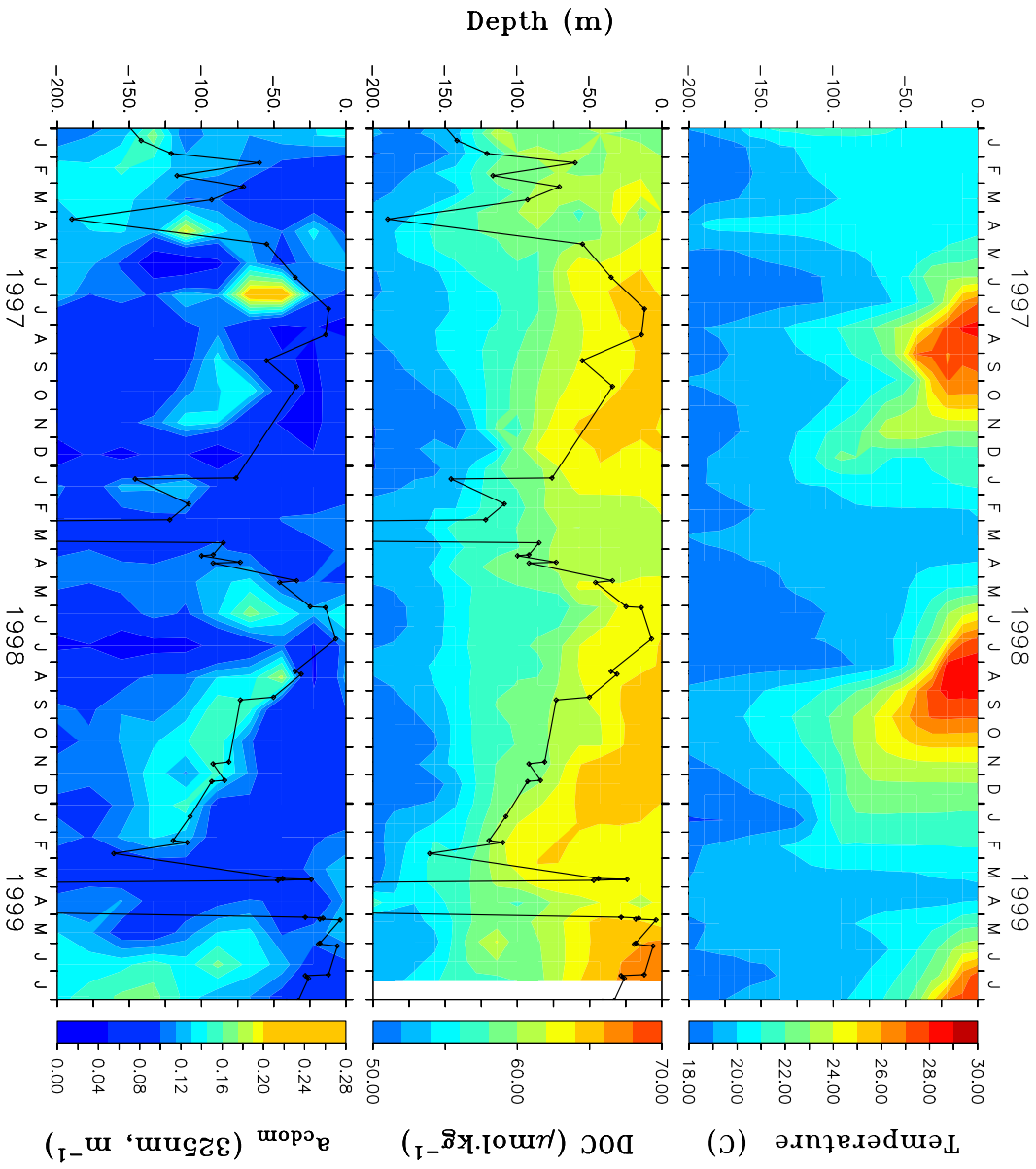

Figure 3: Time-depth contours of temperature (ºC, top panel) dissolved organic carbon concentration (µmol kg^{-1}, middle panel) and the absorption coefficient of CDOM at 325 nm (m^{-1}, bottom panel) at the BATS site in the Sargasso Sea (31º40'N, 64º10'W). The mixed layer depth (solid black line) is overlaid on the bottom two panels.

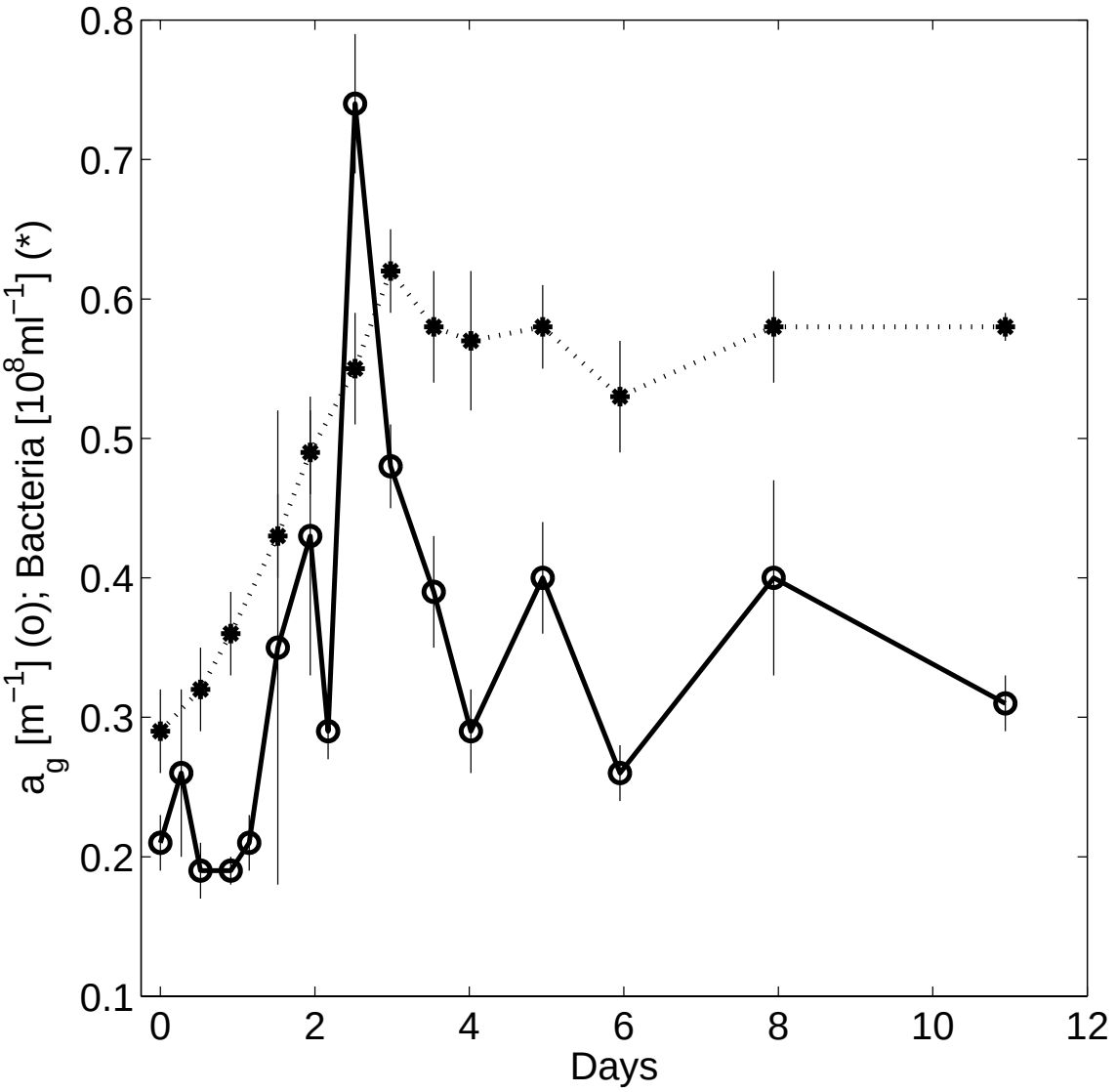

Figure 4: Time course of a microbial culture experiment using filtered seawater collected in the Sargasso Sea in late winter – early spring 1996 and incubated in the dark (Nelson and Carlson unpubl. data). Asterisks (*) are direct counts of acridine orange stained bacteria using fluorescence microscopy (units are 10^8 cells l^{-1}). Open circles (o) are absorption coefficient of CDOM at 300 nm (units are m^{-1}). Vertical bars are standard deviation of replicate samples. In this experiment CDOM was measured for 43 days after the beginning of the experiment: after that time the CDOM absorption coefficient was 0.33 m^{-1}.

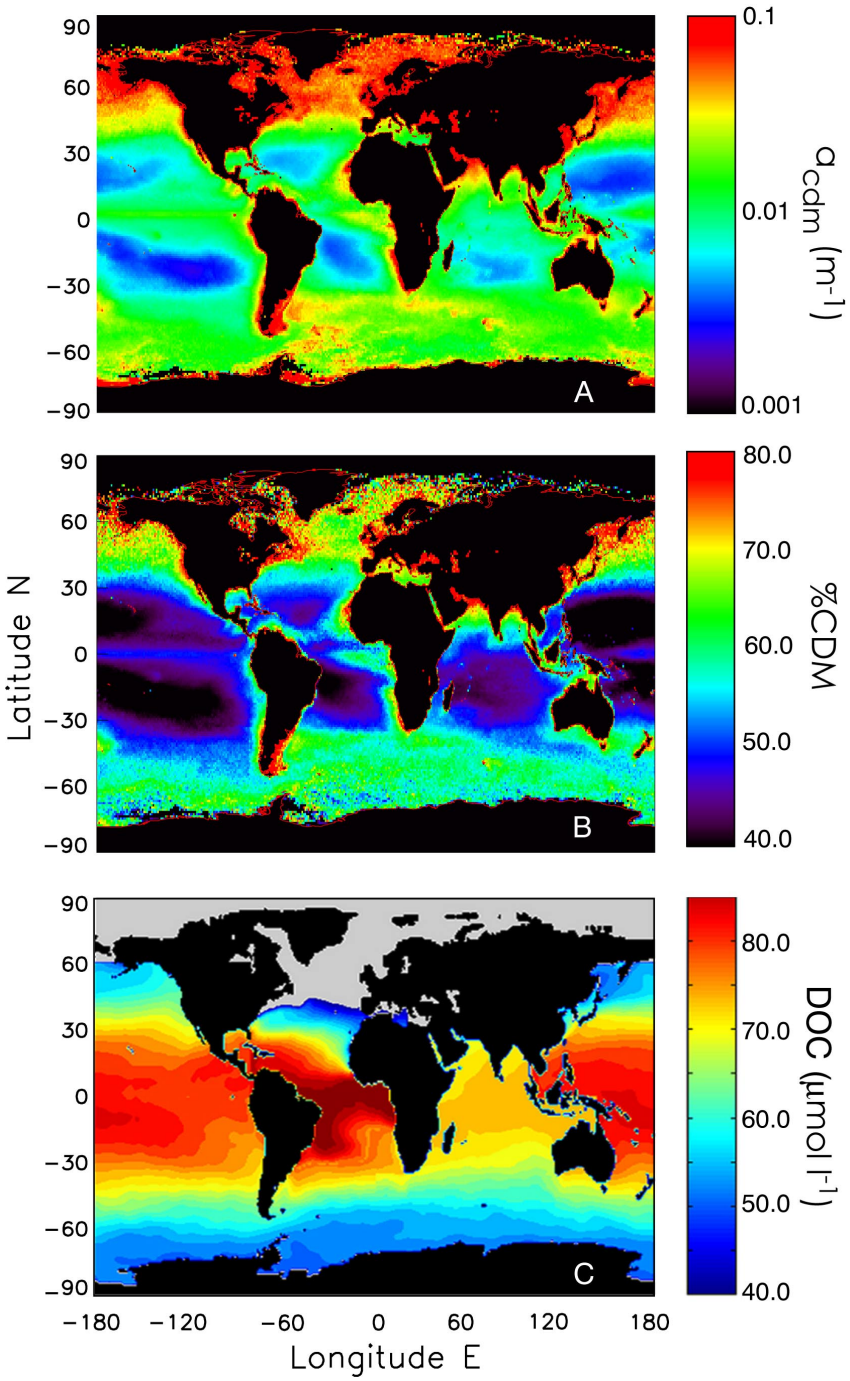

Figure 5: Global distribution of A) absorption coefficient of CDM at 443 nm (ensemble mean estimates using data from Sep. 1997 to Jun. 2000), B) the % contribution of CDM to total non-water light absorption based on SeaWiFS observations of ocean color spectra (Siegel *et al.*, submitted), and C) Global surface ocean DOC distribution (µmol l^{-1}) inferred from global surveys of DOC and empirical relationships between DOC and sea surface temperature (D. Hansell, pers. commun. 2000, Siegel et al., submitted). Central gyre regions where DOC accumulates are typically regions of lower CDM concentration (Fig. 5), as increased stratification leads to increased bleaching of CDM. (Panel C courtesy of D. Hansell and C. Pequignet)

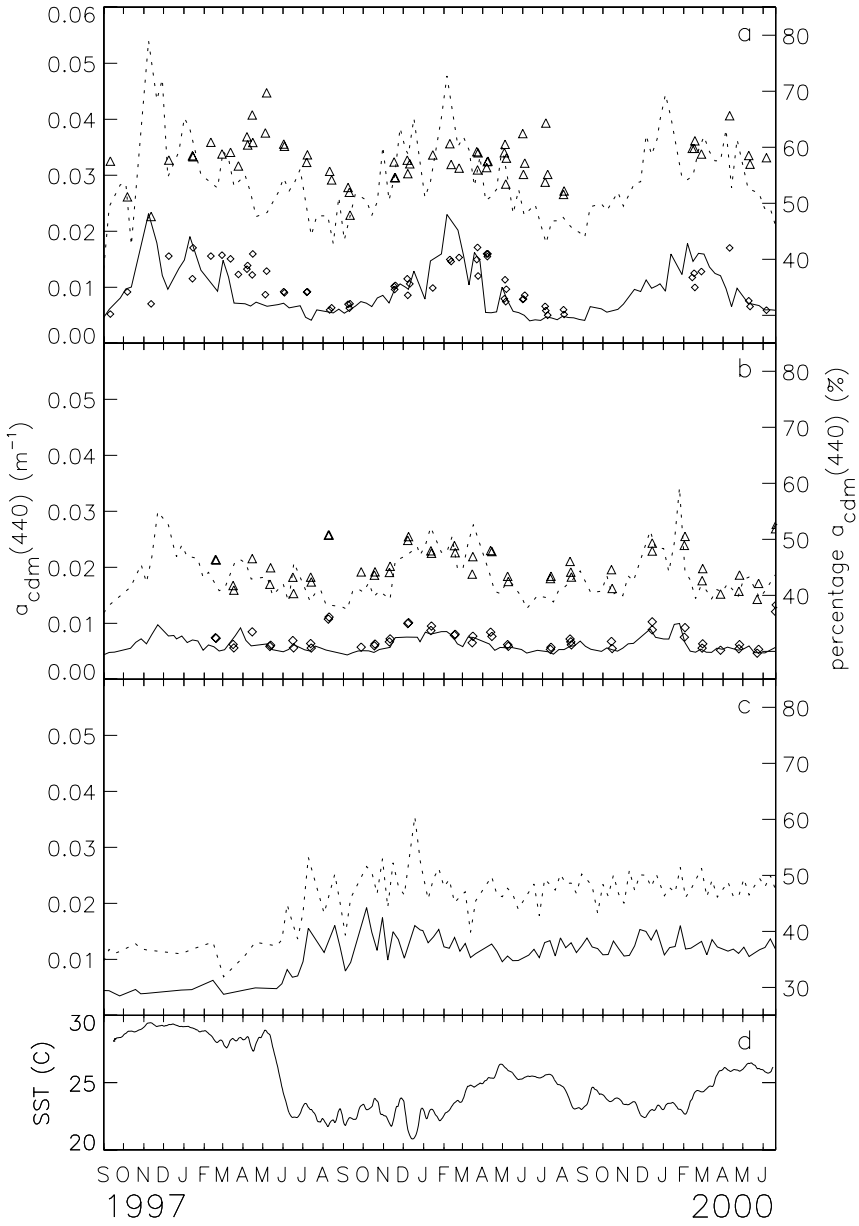

Figure 6: Time series of CDM absorption coefficient (black - left axis) and %CDM (dotted - right axis) for sites in a) the Sargasso Sea off Bermuda (BATS), b) the subtropical Pacific ocean near Hawaii (HOT) and c) the eastern equatorial Pacific ocean (0° 155°W). The time series of sea surface temperature (SST, ºC) from the TOGA/TAO mooring at 0° 155°W is shown in panel d. In panels a and b, *in situ* radiometer observations (symbols) are also plotted (Siegel et al., submitted). The field observations were collected and analyzed following the SeaWiFS *in situ* data protocols (Mueller and Austin, 1995) and the UCSB ocean color algorithm was applied.

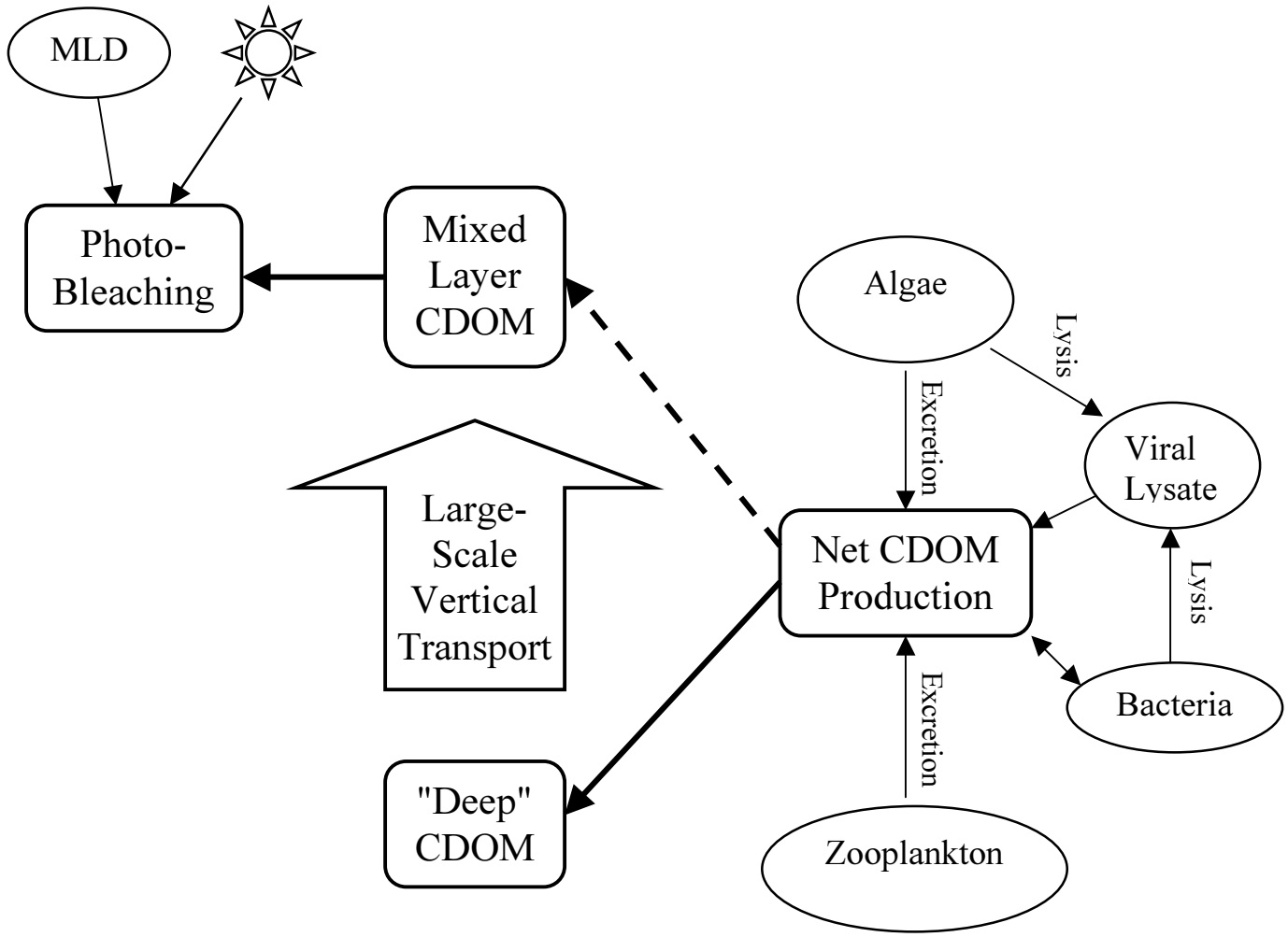

Figure 7: Hypothesized interactions regulating mixed layer concentrations of CDOM in the open ocean. Possible sources of CDOM production (excretion by organisms, lysis) contribute to either (or both) the deep CDOM reservoir or the mixed layer CDOM, where the major sink is photobleaching (as controlled by irradiance and mixed layer depth, or MLD). Production and consumption of CDOM by microbes in the mixed layer is indicated by the double-headed arrow. The dashed line connecting "Net CDOM Production" and "Mixed Layer CDOM" indicates that this flux is presumed but not usually observed, as bleaching can occur quickly.

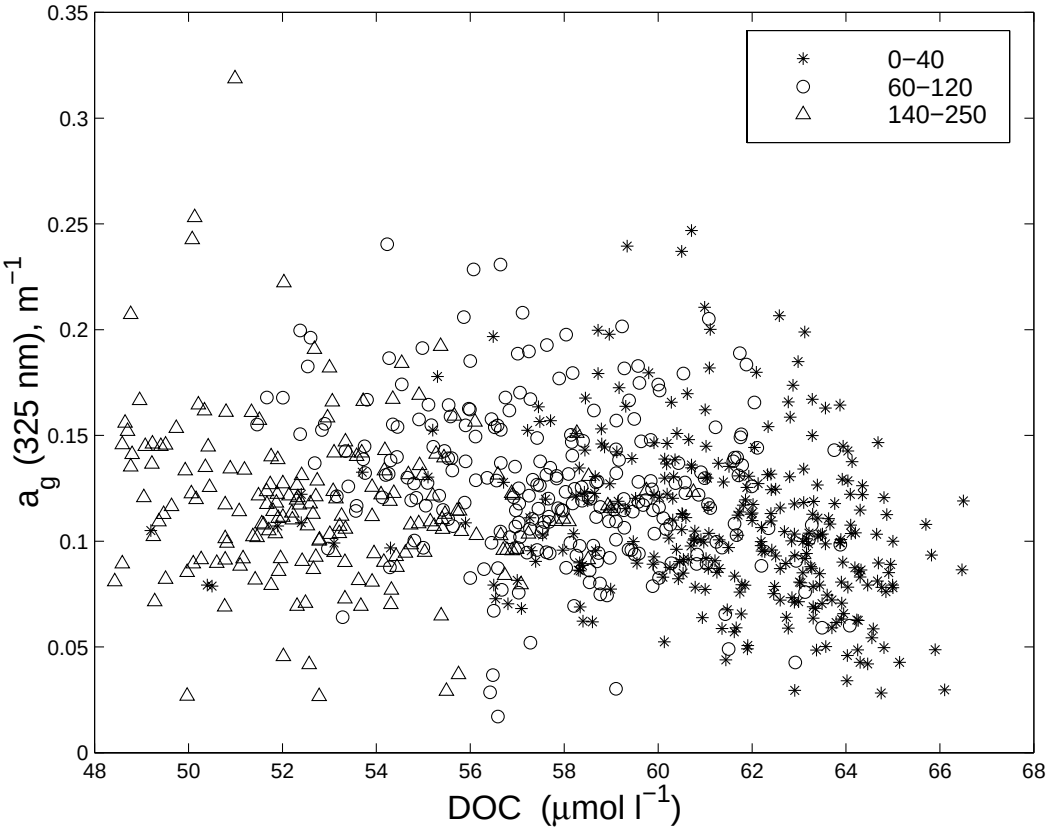

Figure 8: Scatter plot comparison of DOC concentration (µmol l^{-1}) with CDOM absorption [a_g(325 nm), m^{-1}] from samples taken on BATS cruises in the Sargasso Sea (e.g., Fig. 3) from spring of 1994 through the end of 2000. DOC and CDOM samples were taken on the same or adjacent days. (*): 0-40 m samples. (0): 60-120m samples. (x): 140-250 m samples.