The Global Distribution and Dynamics of Chromophoric Dissolved Organic Matter

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Abstract
Chromophoric dissolved organic matter (CDOM) is a ubiquitous component of the open ocean dissolved matter pool, and is important owing to its influence on the optical properties of the water column, its role in photochemistry and photobiology, and its utility as a tracer of deep ocean biogeochemical processes and circulation. In this review, we discuss the global distribution and dynamics of CDOM in the ocean, concentrating on developments in the past 10 years and restricting our discussion to open ocean and deep ocean (below the main thermocline) environments. CDOM has been demonstrated to exert primary control on ocean color by its absorption of light energy, which matches or exceeds that of phytoplankton pigments in most cases. This has important implications for assessing the ocean biosphere via ocean color–based remote sensing and the evaluation of ocean photochemical and photobiological processes. The general distribution of CDOM in the global ocean is controlled by a balance between production (primarily microbial remineralization of organic matter) and photolysis, with vertical ventilation circulation playing an important role in transporting CDOM to and from intermediate water masses. Significant decadal-scale fluctuations in the abundance of global surface ocean CDOM have been observed using remote sensing, indicating a potentially important role for CDOM in ocean-climate connections through its impact on photochemistry and photobiology.
INTRODUCTION

The Optical Nature of CDOM and Its Importance in the Global Ocean

Chromophoric dissolved organic matter (CDOM; also often referred to as gelbstoff or gelvin) is the fraction of DOM that interacts with solar radiation. CDOM compounds absorb light, and a fraction of them are also fluorescent. For the purposes of this review, we operationally define CDOM as material that passes through a submicron filter (usually 0.2–0.4 μm) and appreciably absorbs light in the solar radiation bands as found at the Earth’s surface (e.g., UVB, UVA, and visible light; 280–700 nm). This definition practically excludes much of the DOM pool, which spectroscopically absorbs shortwave UV radiation but does not interact with light in the natural environment (Fichot & Benner 2011). We further operationally define the quantity of CDOM by its Naperian absorption coefficient at a reference wavelength. Quantification of CDOM in terms of mass or carbon content is not currently possible, so obviously optical characterization of any nature is relative to the exact composition of CDOM, which likely varies in both time and space. Nevertheless, it is useful to compare the distribution of CDOM by way of its absorption coefficient, as this must at some level correlate with the quantity of chromophoric material present, following Beer’s law.

CDOM is ubiquitous in the marine environment. Measurable light absorption was observed in all open ocean samples collected by our group on US CO2/CLIVAR (Climate Variability and Predictability) Repeat Hydrography sections from the surface to the ocean floor (Nelson et al. 2007, 2010; Swan et al. 2009) and in samples collected by others (e.g., Kitidis et al. 2006, Yamashita & Tanoue 2008, Jørgensen et al. 2011). This suggests that a substantial component of oceanic CDOM is long lived and likely biologically refractory. Our time-series observations at the Bermuda Atlantic Time-Series Study (BATS) site in the western Sargasso Sea (Nelson et al. 1998, Nelson & Siegel 2002) and in a global study (Nelson et al. 2010) have also revealed no correlation between CDOM absorption and dissolved organic carbon (DOC) concentration, in contrast to studies conducted in coastal waters and the coastal transition zone (Mannino et al. 2008). This suggests that in carbon terms, CDOM represents a small part of the DOM pool in the open sea.

CDOM is spectroscopically unusual. The UV-visible absorption spectrum of CDOM samples (Figure 1) is typically smooth and declines with wavelength in an approximately exponential fashion (Bricaud et al. 1981). Discrete absorption peaks are typically not observed in the solar radiation bands, with some exceptions (e.g., dinoflagellate or Trichodesmium blooms; Vernet & Whitehead 1996, Subramaniam et al. 1999, Whitehead & Vernet 2000). Del Vecchio & Blough (2004) advanced a theory to explain the nature of the CDOM absorption spectrum in which rapid intramolecular redox reactions produce virtual pi-electron clouds that smooth out the spectrum. An implication of this is that CDOM fractionation (by, for example, ultrafiltration) may result in fractional absorption spectra that cannot be recombined to reproduce the original spectrum (Del Vecchio & Blough 2002; Goldstone et al. 2004; S.J. Goldberg & N.B. Nelson, unpublished data). This complicates the identification of CDOM components, but new methods to chemically characterize the DOM pool that may also apply to the CDOM fraction are evolving (see Measuring and Characterizing CDOM, below).

CDOM is most often characterized by features of its absorption spectra, in particular exponential parameters (S) that model the spectrum over a discrete wavelength interval such that

\[ a_{\text{cdom}}(\lambda) = a_{\text{cdom}}(\lambda_o)e^{-S(\lambda - \lambda_o)}, \]  

where \( a_{\text{cdom}} \) is the absorption coefficient (m\(^{-1}\)) at wavelength \( \lambda \) (nm) or reference wavelength \( \lambda_o \) (nm), and \( S \) is the exponential slope parameter (nm\(^{-1}\)). The value of \( S \) can be found by linear regression of log-transformed data (Bricaud et al. 1981) or by a nonlinear fit of an exponential
Figure 1

(a) Absorption spectra ($a_g$) of chromophoric dissolved organic matter (CDOM) from different environments. Absorption spectra were measured using a WPI UltraPath liquid waveguide spectrophotometer (Miller et al. 2002) following procedures developed by our group (Nelson et al. 2007, 2010). Observations are from a major river outflow (the Orinoco River in the Caribbean; 14°N, 66°W), North American continental shelf surface waters (40°N, 70°W), Indian Ocean abyssal waters (5,000-m depth; 17°S, 95°E), North Pacific main thermocline waters (1,000-m depth; 51°N, 152°W), and South Pacific subtropical surface waters (9°S, 151°W). Figure 4 shows the locations of these observations. (b) Estimates of the exponential slope parameter for each location using nonlinear fitting ($S_{	ext{nlf}}$) over the wavelength interval 320–400 nm (Nelson et al. 2007).

Figure 1 highlights the diversity of CDOM absorption spectra found in the open ocean environment. These samples were collected by the UCSB CDOM group on US CO2/CLIVAR Repeat Hydrography Project cruises (Feely et al. 2005), and their spectra were determined using a WPI UltraPath liquid waveguide spectrophotometer (D’Sa et al. 1999, Miller et al. 2002) following procedures developed by the UCSB CDOM group (Nelson et al. 2007, 2010; Swan et al. 2009; C.M. Swan, N.B. Nelson, D.A. Siegel & E.A. Fields, manuscript in review). The highest model to the data (Stedmon & Markager 2001, Twardowski et al. 2004). Values of $S$ depend strongly on the chosen wavelength interval and less strongly on the method used to find the parameter. Nonlinear fits are less biased to longer-wavelength data (a problem when using linear fits to log-transformed data). Nevertheless, $S$ values for CDOM absorption spectra in the visible and UVA wavebands are typically in the range of 0.015–0.03 nm$^{-1}$ for open ocean spectra (Bricaud et al. 1981; Nelson et al. 1998, 2004, 2007, 2010; C.M. Swan, N.B. Nelson, D.A. Siegel & E.A. Fields, manuscript in review).

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absorption values were found in neritic (North American continental shelf) and offshore river
plume (Orinoco input to the central Caribbean) waters, and the lowest values were found in the
subtropics. The spectral shapes also vary, with those of the coastal and river CDOM being the
closest to exponential. Samples from the deep ocean (Indian Ocean abyssal and North Pacific main
thermocline waters) and the bleached South Pacific subtropical surface waters exhibit inflection
points and only roughly approximate exponentials over discrete wavelength intervals. Figure 1b
shows the exponential slope parameter for each sample location as estimated using nonlinear fit-
tting (S_{\text{nlf}}) over the wavelength interval 320–400 nm (Nelson et al. 2007). The lowest S_{\text{nlf}} values
(indicating the flattest spectra) were found in the coastal samples, and the highest values were
found in bleached surface waters of the subtropical gyres.

CDOM is the most important factor controlling UV and visible light penetration into the open
ocean (see below), which makes it a critical factor influencing photobiology as well as ocean color-
based remote sensing (Nelson & Siegel 2002; Siegel et al. 2002, 2005a,b). It can play an indirect
role in climate-related biogeochemistry, particularly via the carbon and sulfur cycles (Mopper &
Kieber 2002). Absorption of light by CDOM controls UV radiation penetration into the ocean
(Fichot et al. 2008), which has an impact on phytoplankton and bacterial productivity (Smith et al.
1992, Hernnd et al. 1993). CDOM also sensitizes the photoproduction of CO_2, CO, H_2O_2, and
et al. 2007, Zafrirou et al. 2008, Reader & Miller 2011) and is a photosensitizer in the photolysis
of DMS (dimethyl sulfdie) (Toole et al. 2003, 2008; Bouillon & Miller 2004). And because of its
impact on the underwater light field, CDOM can influence the accuracy of global satellite-based
measurements of ocean chlorophyll and primary productivity (Siegel et al. 2005b; D.A. Siegel,

Measuring and Characterizing CDOM

Determining the chemical composition of open ocean CDOM is subject to the same problems
encountered while analyzing DOC, with the added complication that CDOM is likely a small
fraction of the total DOM pool. Known contributors to the chromophore (and fluorophore)
pool include aromatic amino acids (Yamashita & Tanoue 2003, 2008), lignin phenols, and ill-
defined humic substances that are operationally characterized by their absorption and fluorescence
properties (Coble 1996).

Techniques used to characterize DOM, including nuclear magnetic resonance (NMR) and
ultra-high-resolution mass spectroscopy (Kujawinski et al. 2004, 2009; Repeta et al. 2004), do not
differentiate between chromophoric and nonchromophoric fractions. Concentration and fraction-
ation methods used to assess DOM are all selective, meaning that the recovery of CDOM is difficult
to determine because of the disruption of the absorption spectrum by fractionation processes (Del
and electrodialysis may provide nonselective DOM concentration in the near future (Ouellet et al.
2008, Young & Ingall 2010, Chen et al. 2011), but for the moment the chemical composition
of CDOM is likely to remain unknown. Spectroscopic analyses, including UV-visible absorption
spectroscopy and fluorescence spectroscopy, remain the main useful techniques for analyzing the
origin and composition of CDOM. The methodology for spectroscopic analysis of CDOM was
recently reviewed by Nelson & Coble (2010).

Characterization of CDOM through UV-visible spectroscopy primarily uses the absorption
coefficient as an index of CDOM abundance (Nelson et al. 2010), or the spectral slope parameter
(Equation 1) as it correlates to chemical composition parameters. Spectral slopes measured in
the “solar” wavelength region (~300–700 nm) have been shown in many studies to increase in
response to the bleaching of CDOM and have been observed to decrease with increasing water mass age in the deep ocean (Nelson et al. 2007), hinting at changes in CDOM composition driven by bleaching or production. Spectral slopes measured at wavelengths shorter than those of solar radiation have been quantitatively linked to DOC abundance (Fichot & Benner 2011) and molecular weight distribution (Helms et al. 2008). It is important to note that these relationships have been developed for coastal areas with strong CDOM and DOM gradients, and are not likely applicable to open ocean areas unaffected by terrestrial input on annual timescales.

Fluorescence spectroscopy, in particular the excitation-emission matrix (EEM) technique (Coble 1996), is also used to characterize CDOM in terms of its composition and origin. Typically, spectra are normalized to the fluorescence of a known concentration of quinine sulfate. In the EEM technique, a number of fluorescence emission scans at different excitation wavelengths are compiled into a matrix, which can then be visualized as a three-dimensional surface (Figure 2). Regions of the matrix can be assigned to various classes of compounds, in particular the amino acids. A powerful new technique, parallel factor analysis (Stedmon & Bro 2008), is now coming into common use to analyze EEM data. This technique decomposes the variability in a number of EEM spectra into components (similarly to empirical orthogonal function analysis). The components may then be correlated to other environmental variables. Jørgensen et al. (2011) decomposed a data set consisting of samples collected around the globe into seven components: one representing the aromatic amino acids and six others representing various humic materials. Correlating results such as this to concentrations of particular biogeochemicals may be the next step forward in the analysis of marine CDOM.

**CDOM Is the Dominant Source of Light Absorption in the Oceans**

The importance of CDOM to the optical properties of seawater can be demonstrated by comparing its spectrum, $a_g(\lambda)$, with the total absorption coefficient spectrum, $a_t(\lambda)$, which quantifies the loss of photons along a path due to photobiological work or to heat (e.g., Mobley 2004). The absorption coefficient spectrum is an inherent optical property, and as such it can be modeled as a sum of components that contribute to $a_t(\lambda)$. Typically, $a_t(\lambda)$ is partitioned into components due to pure seawater, $a_w(\lambda)$; living phytoplankton, $a_{ph}(\lambda)$; nonphytoplankton or detrital particulates, $a_d(\lambda)$; and CDOM, $a_g(\lambda)$:

$$a_t(\lambda) = a_w(\lambda) + a_{ph}(\lambda) + a_d(\lambda) + a_g(\lambda).$$

The seawater absorption coefficient spectrum is generally assumed to be constant (Pope & Fry 1997, Morel et al. 2010), although weak temperature dependence in the red and near-infrared regions has been observed (Pegau & Zaneveld 1993). The phytoplankton absorption spectrum, $a_{ph}(\lambda)$, quantifies losses of radiant energy by phytoplankton pigments, and its shape largely reflects the cellular chlorophyll $a$ and ancillary pigment concentrations, modified by cellular packaging effects, that are associated with the members of the phytoplankton community (e.g., Kishino et al. 1985, Mitchell & Kiefer 1988, Nelson et al. 1993, Bricaud et al. 1995, Ciotti et al. 2002). The detrital absorption spectrum, $a_d(\lambda)$, accounts for the light absorption of all nonpigmented particles, which may include zooplankton, bacteria, and actual detrital particles (e.g., Kishino et al. 1985, Iurriaga & Siegel 1989, Morel & Ahn 1991, Nelson & Robertson 1993, Stramski & Kiefer 1998). Detrital absorption spectra are nearly featureless, typically showing a declining spectrum with increasing wavelength (e.g., Roeser et al. 1989).

The relative contributions of CDOM and the other absorption components can be assessed by normalizing each component by the total absorption spectrum, $a_t(\lambda)$, at the same wavelength. **Figure 3** shows the estimated mean relative contribution of each component (and the envelope
Figure 2
Fluorescence excitation-emission matrix for an open ocean sample of Southern Ocean surface waters. In this sample, the fluorescence is dominated by humic materials of different origins (regions A and C, thought to represent terrestrial humics, and region M, thought to represent marine-derived humics), but little protein-derived fluorescence is present (region T, thought to represent aromatic amino acids) (Coble 2007); these peak regions are subject to wavelength shifts. The W represents the excitation-emission pair of a commonly used CDOM fluorometer (the WET Labs WETStar). White areas are masked due to first- and second-order Rayleigh and Raman scattering (as these data were collected using a single monochromator instrument). Abbreviation: QSE, quinine sulfate equivalent.

assessing the 95% confidence interval for each mean estimate) using a consistent, global, open ocean, in situ data set of component absorption spectra from the surface ocean; Figure 4 shows the locations of the samples used to construct this figure and Figure 1. For wavelengths less than ~440 nm, CDOM is by far the most important factor regulating total absorption in the upper layers of the open ocean. Nearly 50% of the total light absorption at 400 nm and more than 70% of the total light absorption at 300 nm are due to CDOM. Clearly, CDOM dominates light absorption throughout the blue and especially in the UV spectral regions of the open ocean.

The other absorption components make a much smaller contribution to the total light absorption budget in the surface ocean. Phytoplankton absorption never dominates the open ocean spectral light absorption budget, and its contribution is only equal to that of CDOM absorption for wavelengths greater than 450 nm (Figure 3). Above 450 nm, seawater itself dominates light absorption.
Figure 3
Estimated mean relative contributions of CDOM and other components to the total (nonwater) light absorption at wavelengths of 300–600 nm, based on averages of spectra collected at the surface on sections shown in Figure 4. Shaded areas represent the 95% confidence intervals for these estimates. Data are from Nelson et al. (1998, 2010) and Swan et al. (2009).

absorption. Further, absorption by inanimate detrital particulates makes a small contribution [<12% of $a_\lambda$] throughout the visible spectrum. Only in areas with substantial terrigenous inputs will detrital absorption contribute much to the $a_\lambda$ budget (e.g., Babin 2003, Bélanger et al. 2008). For wavelengths less than 400 nm, phytoplankton, detrital particles, and seawater contribute similar amounts to $a_\lambda$ (<20% each). Thus, CDOM dominates surface ocean light absorption spectra throughout the global ocean and should be considered independently when satellite ocean color reflectance observations are used to understand global changes in ocean phytoplankton distributions (D.A. Siegel, M.J. Behrenfeld, S. Maritorena, C.R. McClain, D. Antoine, et al., manuscript in review).

The Chemical Nature of CDOM
Little is known about the compounds or structures that make up autochthonous CDOM in the open ocean. State-of-the-art techniques for studying the composition of natural organic matter, including NMR and ultra-high-resolution mass spectroscopy, have been applied to the study of oceanic CDOM in a few cases, but for the most part the problem of discriminating between chromophoric and nonchromophoric DOM has not been resolved (see Measuring and Characterizing CDOM, above). Most studies have focused on the fate of terrestrial DOM and have not addressed the problem of autochthonous DOM.

Unambiguously terrestrial lignin phenols (fluorophores from higher-plant decomposition) must be present in oceanic CDOM at low concentrations (Hernes & Benner 2003), and terrestrial humic and fulvic acids are present in the coastal transition zone (Hedges et al. 1997,
Carder et al. 1989). Spectrofluorometric analysis (see Measuring and Characterizing CDOM) has identified aromatic amino acids as a portion of the CDOM pool in the surface ocean that declines with depth (Murphy et al. 2008, Yamashita & Tanoue 2008, Jørgensen et al. 2011), implying a local surface origin. And in some specific conditions, blooms of dinoflagellates (Whitehead & Vernet 2000), Sargassum spp. (Shank et al. 2010), and Trichodesmium spp. (Steinberg et al. 2004) can contribute significant amounts of mycosporine-like amino acids (MAAs) to the CDOM pool. MAAs are amino acid derivatives that are found in a wide variety of taxa and serve a photoprotective function by absorbing UV radiation in the 300–350-nm range (Banaszak & Trench 2001, Moisan & Mitchell 2001). However, the absorption peaks that signify the presence of MAAs are largely absent in the global, open ocean CDOM absorption spectrum data set collected by our group (Nelson et al. 2010), suggesting that conditions where MAAs accumulate in CDOM are rare. One study suggested that halogen-substituted aromatics similar to polychlorinated biphenyls may be a significant contributor to CDOM (Repeta et al. 2004), but similar results have not been reported elsewhere.

Most of the remaining CDOM is loosely classified as marine humic material, but it is not certain that it is similar to terrestrial humic and fulvic acids. In terms of fluorescent material, distinct regions of the excitation-emission matrix (see Measuring and Characterizing CDOM) have been assigned to marine humics (Kalle 1966, Coble 1996). Similar fluorescence characteristics are taken
to suggest some similarity in structure to terrestrial humics, but the processes by which these may form in the ocean are not well understood.

GLOBAL DISTRIBUTION AND PATTERNS OF CDOM

The global surface ocean distribution of CDOM can be assessed using modern satellite ocean color algorithms (e.g., Lee et al. 2002; Maritorena et al. 2002, 2010; Siegel et al. 2002, 2005a; Johannessen 2003; Morel & Gentili 2009; Bricaud et al. 2011). Here, we apply the Garver-Siegel-Maritorena bio-optical model to partition the satellite-determined reflectance spectra into components for phytoplankton absorption or phytoplankton chlorophyll concentrations, CDOM and detrital particulate absorption, and particulate backscattering \( b_{bp}(440) \) coefficients (e.g., Garver & Siegel 1997, Maritorena et al. 2002). Alternative bio-optical models give largely similar results (Lee et al. 2002, Morel & Gentili 2009, Bricaud et al. 2011). Relevant to this discussion are the retrievals of CDOM and detrital particulate absorption at 440 nm; this combined quantity is often referred to as colored detrital material (CDM). As addressed above, detrital particulates typically make a small contribution in the global open ocean relative to CDOM. Analysis of the in situ data set used to construct Figure 3 shows the mean ratio of \( a_g(440) \) to \( a_g(440) + a_{det}(440) \) to be 12\% (95\% confidence interval for the mean = 0.9\%). Thus, these satellite determinations of CDM are largely accounting for CDOM variations (e.g., Siegel et al. 2002, 2005a; Nelson et al. 2010).

Figure 4 shows the mean surface distribution of CDOM and detrital particulate absorption at 443 nm (CDM) from the SeaWiFS (Sea-Viewing Wide Field-of-View Sensor) satellite mission using the Garver-Siegel-Maritorena ocean color model (GSM-01) (e.g., Garver & Siegel 1997; Maritorena et al. 2002, 2010; Siegel et al. 2002, 2005a). Variations in satellite-derived CDM illustrate a largely oceanic pattern, with low values in the subtropical gyres and higher values in the subpolar oceans and regions of persistent upwelling (equatorial divergence, eastern boundary currents, etc.). CDM values in the Northern Hemisphere subpolar oceans are often >0.1 m\(^{-1}\), contrasting with the very low values (≤0.01 m\(^{-1}\)) found in the subtropical gyres. These patterns largely reflect those found from in situ surface observations of CDOM in the global ocean (e.g., Kitidis et al. 2006; Nelson et al. 2007, 2010; Swan et al. 2009; Yamashita & Tanoue 2009; Ortega-Retuerta et al. 2010). Further, there is a hemispheric asymmetry in global CDM distributions, with those in the high northern latitudes being considerably higher than those in the Southern Ocean (Figure 4). Deviations from the largely oceanic CDM patterns can be seen where known rivers (such as the Amazon, Congo, Orinoco, and Yangtze Rivers) discharge into the ocean.

Figure 5 shows the depth-latitude dependence of the global CDOM distribution compiled from meridional sections taken from the three global basins; Figure 4 highlights the profiles used to construct these sections, with the CDOM values quantified as the absorption coefficients of the dissolved materials at 325 nm. The field surveys encompass all three ocean basins, transecting the subtropics (where satellite-retrieved surface CDOM values are low) and the tropics and high latitudes (where CDOM is elevated at the surface).

Field observations of the CDOM distribution in surface waters (<100 m) for the three ocean basins (Figure 5) are consistent with satellite-retrieved observations of CDM (Figure 4). Again, higher near-surface CDOM values are found in the subarctic North Atlantic and Pacific, lower abundances are found in the subtropical gyres, and intermediate values are found in equatorial upwelling regions and the Southern Ocean (Figure 5). Extremely low values \( a_g(325) < 0.005 \text{ m}^{-1} \) are found in the subtropical South Pacific (Figure 5a) (Swan et al. 2009). The low values, characteristic of the subtropical gyres, often extend deeper than 1,000 m and are found in every basin. Again, the contrast is greater in the South Pacific (Figure 5b) and the South Indian (Figure 5c) Oceans, and lesser in the North Pacific (Figure 5a) and the subtropical gyres of the North Atlantic (Figure 5b). Further, subsurface relative CDOM minima corresponding to
subtropical mode waters are observed in the North Atlantic and the subantarctic mode waters of the South Pacific and South Indian Oceans (Figure 5). This demonstrates the importance of ocean ventilation processes for the meridional-depth CDOM distribution (Nelson et al. 2007, 2010; Swan et al. 2009).

The most prominent features in the meridional-depth CDOM distributions are the high values \([a_g(325) \geq 0.2 \text{ m}^{-1}]\) found in the main thermocline waters of the North Pacific and North Indian Oceans (Figure 5a,b), which approach those found in the surface waters offshore of the Amazon and Orinoco Rivers (e.g., Nelson et al. 2007, 2010). Interestingly, the meridional-depth CDOM pattern found in both the North Pacific and Indian Oceans is not found in the North Atlantic basins (Figure 5). This feature is indicative of the timescale associated with the production of long-lived CDOM, and is described in greater detail below. CDOM values for depths greater than 2,000 m decrease to something approaching a global deep ocean mean value of \([a_g(325)]\) between 0.12 and 0.17 \(\text{m}^{-1}\) (Figure 5).

Latitudinal-depth CDOM patterns correspond to a remarkable degree with determinations of the apparent oxygen utilization (AOU) throughout the Pacific and Indian Oceans, but not in the Atlantic Ocean (Figure 5a–c). [AOU is defined as the difference between the dissolved oxygen concentration that would be expected at saturation and the measured dissolved oxygen concentration; high values imply high rates of dissolved oxygen consumption by remineralization processes (e.g., Keeling et al. 2010).] In fact, a statistical comparison shows that AOU values explain 75% of the CDOM variance in the Pacific and Indian Ocean basins \((n = 2,593)\), whereas AOU and CDOM are not related in the Atlantic basin \((R^2 = 0.01, n = 1,607; \text{Figure 6})\). The strong relationship between CDOM and AOU in the Pacific and Indian Ocean basins indicates that as organic matter is oxidized, a chromophoric by-product is produced. This pattern has been observed previously in the Pacific (e.g., Hayase & Shinozuka 1995; Yamashita et al. 2007; Yamashita & Tanoue 2008, 2009; Swan et al. 2009); however, it is not global, as CDOM and AOU observations from the Atlantic are uncorrelated (Figure 6). The strong relationship between CDOM and AOU in the main thermocline waters of the Pacific and Indian Oceans is thought to be caused by the remineralization of the sinking flux of organic matter in these waters and the extreme length of time (~900 years; Matsumoto 2007) since ventilation of the deep water masses of the Pacific and Indian Ocean basins (e.g., Nelson et al. 2010).

There is a complete lack of relationship between open ocean observations of CDOM abundance [again as \(a_g(325)\)] and DOC concentrations (Figure 7). This contrasts with observations made in the near-coastal environments (see below). Both CDOM and DOC vary by more than a factor of two throughout the open ocean, but no simple relationship has been found between them either as a function of depth (Figure 7) or when isolated by an ocean basin (see Nelson et al. 2010, table 1). DOC concentrations show a clear depth dependence, with values decreasing into the deep ocean (Hansell 2013). In contrast, CDOM shows only hints of depletion in surface waters, consistent with the reduced CDOM values found in the upper layers of the subtropical gyres (Figure 5).

The lack of correspondence between CDOM and DOC provides important information about the contribution that CDOM makes to the total DOM pool. Figure 7 shows that CDOM can vary by factor of two independent of changes in DOC concentration. This implies that CDOM is a small part of the open ocean’s total DOC pool, as has been discussed elsewhere (Siegel & Michaels 1996; stubborn.)
Figure 6
Scatter plot of CDOM abundance (as absorption coefficient ($a_g$) at 325 nm) versus apparent oxygen utilization (AOU) in samples from the sections shown in Figure 5. The blue points are the CDOM and AOU values of samples taken from the Atlantic Ocean; the red points are those of samples taken from the Pacific and Indian Oceans.

Nelson et al. 1998, 2010; Nelson & Siegel 2002). This contrasts with coastal regions, where land-ocean interactions supply high-CDOM/DOC waters to the oceans and correspondence between CDOM and DOC concentration is often observed (see below). Investigators have been unable to determine the contribution that CDOM makes to the total DOC pool in open ocean environments, as this requires the carbon content of CDOM to be known. In the coastal regions, local CDOM-DOC relationships can be developed and used to infer DOC fluxes to the ocean (Mannino et al. 2008), but these are dependent on the source waters for the DOM and do not necessarily reflect the fraction of DOC that is chromophoric.

DYNAMICS OF CDOM IN THE GLOBAL OCEAN

Sources and Sinks

Early in the study of ocean optics, it was assumed that most CDOM entered the ocean as terrestrial humic materials via rivers and runoff (Kalle 1938, Jerlov 1953). Even then, it was recognized that
Figure 7
Scatter plot of CDOM abundance [as absorption coefficient ($a_g$) at 325 nm] versus dissolved organic carbon (DOC) concentration in samples from the sections shown in Figure 5 (1,267 total points). The color of each data point represents the depth at which that sample was taken.

An autochthonous component to CDOM was present, as could be inferred by fluorescence in a particular waveband increasing in an offshore transect (Kalle 1966). Remote sensing and field studies have since demonstrated that terrestrial-origin CDOM is mostly removed in the coastal zone (e.g., Mannino et al. 2008) and that the autochthonous production of CDOM dominates the surface ocean signal in the subtropics (e.g., Nelson et al. 1998). Further, some early assumptions in ocean optics theory held that CDOM was a direct result of primary production and would thus be well correlated with (for example) chlorophyll concentration (e.g., Smith & Baker 1978, Morel & Maritorena 2001). Although direct production of CDOM components by phytoplankton is known in certain species (e.g., Vernet & Whitehead 1996, Moisan & Mitchell 2001, Steinberg et al. 2004), Nelson et al. (1998) demonstrated the temporal and spatial separation of CDOM and chlorophyll concentrations in the Sargasso Sea, suggesting that microbial degradation of organic matter is responsible for the majority of autochthonous CDOM production.

Sediments in coastal regions and on the continental shelf may be significant local sources of CDOM (e.g., Chen & Gardner 2004), but deep ocean profiles do not show elevated CDOM near
the bottom (Nelson et al. 2007, 2010), suggesting that deep sea sediments are not a significant source. However, a recent study detected significantly elevated amounts of CDOM in hydrothermal vent fluids (Yang et al. 2012), which may also be a local or long-term source of CDOM to the deep sea.

Analysis of CDOM spectra on cross-shelf transects by UV-visible spectroscopy (e.g., Vodacek et al. 1997, Blough & Del Vecchio 2002, Twardowski & Donaghay 2002, Mannino et al. 2008) and fluorescence spectroscopy (e.g., Ferrari & Dowell 1998, Del Castillo et al. 2001, Conny et al. 2004, Coble 2007) has shown that terrestrial DOM rapidly declines across the continental shelves owing to precipitation, mixing, and photolysis (Hedges et al. 1997, Coble 2007). With the exception of large river plumes (e.g., Siegel et al. 2002, Del Vecchio & Subramaniam 2004, Salisbury et al. 2011), terrestrial CDOM does not appear to influence open ocean surface waters on an annual timescale, but it may be present as a persistent background (Nelson et al. 1998, Herbes & Benner 2003).

Like most DOM in the ocean (Hansell 2002, 2013), CDOM is produced primarily as a by-product of microbial metabolism, degrading the fruits of primary productivity (Yentsch & Reichert 1962, Nelson et al. 2004). The primary evidence for this comes from experiments using mesocosms (Rochelle-Newall et al. 1999, Ortega-Retuerta et al. 2009), microbial culture experiments (Nelson et al. 2004), and field data (Nelson et al. 1998). Zooplankton (Steinberg et al. 2004), Trichodesmium spp. (Subramaniam et al. 1999, Steinberg et al. 2004), dinoflagellates (Vernet & Whitehead 1996, Whitehead & Vernet 2000), and macroalgae (Hulatt et al. 2009, Shank et al. 2010) can release CDOM in significant amounts.

CDOM exists along a continuum of lability (Carlson 2002) that describes its sensitivity to microbial degradation and photolysis. Culture studies of microbial CDOM production (Nelson et al. 2004) have highlighted the production of a labile CDOM fraction, which is rapidly degraded by microbes and is not necessarily detectable in the water column. We thus refer to the production of less labile CDOM as net production of CDOM, as we can detect its presence and accumulation.

The main sink of semilabile or refractory CDOM in the ocean is presumed to be solar bleaching. We avoid the use of terms such as photooxidation to describe this process, as it does not always result in (for example) release of CO$_2$. Although photochemical production of CO$_2$ and consumption of oxygen are thought to be significant (Andrews et al. 2000, Johannessen & Miller 2001, Clark et al. 2004), significant bleaching can occur in the surface waters without a significant change in DOC (Nelson et al. 1998; P. Neale & M. Tzortziou, personal communication). Studies of bleaching have focused mainly on terrestrial-origin CDOM (Del Vecchio & Blough 2004, Goldstone et al. 2004), but some have considered open ocean seawater (Kouassi & Zika 1992, Swan et al. 2012). It is generally assumed that CDOM bleaching rate (i.e., the change in absorption coefficient at a discrete wavelength per unit time) is a linear function of light absorption, modulated by an action spectrum that takes into account off-wavelength effects of exposure.

Superficial evidence for bleaching controlling global CDOM abundance in surface waters is abundant. CDOM is generally depleted in the surface ocean away from large sources such as terrestrial runoff, or areas of intense blooms or upwelling (Figure 4). CDOM levels are at a minimum in the subtropics (Figure 4), where shallow mixed layers and high surface irradiance levels result in significant bleaching (Siegel et al. 2002), and are higher in areas of upwelling, high productivity, and/or decreased irradiance (Siegel et al. 2005a).

**Surface Ocean Processes**

Hints of the mechanisms controlling CDOM levels in the upper ocean can be seen in the seasonal patterns observed at the BATS site in the western Sargasso Sea (e.g., Nelson et al. 1998, Steinberg...
Figure 8

Time-depth contours of (a) monthly mean CDOM abundance [as absorption coefficient \( \alpha_g \) at 325 nm] and (b) chlorophyll concentration from the Bermuda Atlantic Time-Series Study (BATS) site in the western Sargasso Sea (e.g., Nelson et al. 1998, Siegel et al. 2001). Monthly mean values were constructed from bottle observations between April 1994 and July 2010. The white lines represent the mean mixed-layer depths calculated using a density criterion of 0.2 kg m\(^{-3}\) (Siegel et al. 2001).

et al. 2001). Figure 8 shows the monthly mean patterns of CDOM abundance and chlorophyll concentration calculated over 16 years of roughly monthly observations at the BATS site. The CDOM seasonal cycle can be illustrated in three parts: (a) the formation of a subsurface CDOM maximum just below the mixed layer during the summer, (b) a substantial decrease of CDOM in the surface mixed layer during the summer and continuing into fall, and (c) a homogenization of CDOM abundances during convective mixing in later winter, which effectively repeats the seasonal cycle (Figure 8a). The summer subsurface CDOM maximum lies several tens of meters shallower than the chlorophyll maximum (Figure 8b) and is thought to be created as a by-product of the net heterotrophic recycling of organic carbon in the lower euphotic zone (Nelson et al. 1998, 2004; Siegel et al. 2002; Steinberg et al. 2004) (see discussion below). There are also hints of increased CDOM levels at the BATS site in April following the demise of the spring bloom, again possibly related to heterotrophic processes (Nelson et al. 2004, Steinberg et al. 2004).

The summer decrease in CDOM is caused by photobleaching due to the intense integrated light doses found in the shallow mixed layers at the BATS site (e.g., Nelson et al. 1998, Swan et al. 2012). Nearly half of the spring CDOM levels in the surface mixed layer are removed from spring to late fall by photobleaching (changing the absorption coefficient from 0.13 to 0.08 m\(^{-1}\); Figure 8). The cycle is repeated as winter mixing homogenizes the upper-ocean CDOM levels (Figure 8). Beyond the BATS site, photobleaching of CDOM appears to be the proximate control on global surface ocean CDOM concentrations (Siegel et al. 2002, 2005a; Nelson et al. 2007, 2010; Swan et al. 2009, 2012).

The impact of the coupled processes of heterotrophic production, photobleaching, and convective mixing creates seasonal patterns in surface ocean CDOM levels where a spring increase is followed by an intense reduction in the summer, which then lasts until winter mixing
reestablishes moderate levels. Thus, when viewed from space, seasonal CDOM patterns look similar to those of phytoplankton chlorophyll concentration (Figure 8). At the BATS site, a strong spring bloom from January to April is followed by a substantial decrease in the surface mixed layer, with a subsurface maximum at ∼90 m. The summer decreases are created by the photoacclimation of cellular chlorophyll concentration to the high light doses (Steinberg et al. 2001, Behrenfeld et al. 2002). The resulting surface patterns in CDOM and chlorophyll concentration look similar, although the causal mechanisms are different (Siegel et al. 2005a).

Further, the timescales associated with the creation and destruction of upper-ocean CDOM at the BATS site (and as inferred from remote sensing determinations elsewhere) are on the order of 100 days (Nelson et al. 1998, 2007; Siegel et al. 2002; Swan et al. 2009). These are much shorter than the centennial scale inferred from the deep ocean surveys discussed above. Hence, there is a continuum of CDOM reactivity and lability that must be considered. Microbial culture experiments and investigations of CDOM production by other heterotrophs and Trichodesmium spp. (e.g., Nelson et al. 2004, Steinberg et al. 2004, Biers et al. 2007) have demonstrated rapid production or release of CDOM that far exceeds the timescales of observed surface ocean CDOM increases. The microbial culture experiments of Nelson et al. (2004) also demonstrated rapid CDOM decline in culture, suggesting that there is a labile fraction of CDOM that turns over on a short (∼10-day) timescale (see also Biers et al. 2007). The growth of microbes on zooplankton excreta in culture also results in transient decreases of CDOM (C.A. Carlson & S.J. Goldberg, unpublished data, personal communication).

These results imply the existence of a semilabile CDOM fraction produced near the surface that escapes microbial degradation or solar bleaching long enough to be transported downward by mixing or subduction. This is apparent in the local CDOM minima visible in subtropical and subpolar mode waters between the euphotic zone and the main thermocline (Figure 5). In the subtropics, these waters carry the low-CDOM signature of the late autumn below the seasonal thermocline (Nelson et al. 2007). It also appears that remineralization processes result in a relatively rapid CDOM increase in the subtropical mode water of the North Atlantic (Nelson et al. 2007). Because microbial activity in this layer is still high (Carlson et al. 2010, Lomas et al. 2010), increases in CDOM must belong to the long-lived, semilabile fraction. It appears that in the Atlantic the CDOM mixes with the permanent thermocline waters and may be ventilated near the equator by equatorial upwelling (Figure 4). In the Pacific, the subantarctic mode water mixes with the Pacific Deep Water mass and is advected through the Indonesian straits, returning to surface waters in the Indian Ocean.

Jørgensen et al. (2011) analyzed a global-scale set of fluorescence matrix data (see Measuring and Characterizing CDOM, above) and found that fluorescence components related to aromatic amino acids declined rapidly in the top kilometer of the water column (i.e., above the main thermocline). This may suggest that the majority of autochthonous CDOM produced in surface waters is recycled, so the main pathway for CDOM to reach the deep ocean is ventilation in the deep and bottom water formation areas (see below).

Swan et al. (2012) investigated the photochemical lability of CDOM from samples collected around the global ocean in a controlled laboratory setting. Only samples from previously bleached South Pacific waters with extremely low CDOM levels failed to produce measurable bleaching when exposed to irradiance that simulated 10 days of solar exposure at the surface in subtropical latitudes. This implies the presence of a bleaching-refractory component in the CDOM pool at very low concentrations and/or the continuous replenishment of bleaching-labile CDOM related to remineralization processes near the surface.

Swan et al. (2012) found that bleaching efficiencies (when nonzero) had a range of a factor of two under similar irradiance conditions, suggesting that diversity in CDOM composition has a
significant effect on bleaching on the global scale. The estimated bleaching rate parameters were correlated with the spectral slope parameter and with the initial N:P ratio of the macronutrient concentrations of the samples. This suggests that both the light history and the biogeochemical origin of the CDOM play a role in determining its photochemical lability. Hence, a global model of CDOM dynamics must include variable photochemical lability in this important sink term.

Interestingly, Swan et al. (2012) also observed the photoproduction of a blue-light-absorbing component in selected samples. A single Gaussian absorption peak centered near 440 nm appeared over time in irradiated 0.2-μm-filtered samples from high-nutrient, low-chlorophyll (HNLC) regions, but not in samples taken in regions where macronutrient concentration ratios were near Redfield values. UV absorption coefficients for the HNLC samples declined in a way similar to those in CDOM samples collected in nutrient-depleted areas. A link to photochemically active nitrate was suggested and experimentally tested, as significant nitrate was present. This peak was not observed in field samples from HNLC areas, suggesting that the material, if produced under natural conditions, is labile and in fact long-term irradiation. Further, Swan et al. (2012) showed that the absorption feature at 440 nm would be photobleached under continued irradiation. This result could be an observation of the formation of a microbially labile intermediate from refractory or semilabile DOM, as has been suggested is an important process supporting the surface microbial community (Kieber et al. 1989, Moran & Zepp 1997).

Deep Ocean Processes

In the deep ocean, CDOM abundance increases with depth in the main thermocline in every ocean basin (Figure 5) (see also Chen & Bada 1992, Omori et al. 2011). There is also a strong correlation between deep ocean CDOM and AOU in the Pacific and Indian Ocean basins, which has been interpreted as the remineralization of sinking particles resulting in new CDOM production (Yamashita & Tanoue 2009, Nelson et al. 2010). However, this correlation is weak or absent in the Atlantic (Figure 8) (see also Jørgensen et al. 2011), which suggests a significant role for mixing and general circulation in determining the deep ocean CDOM abundance (Nelson et al. 2007, 2010). In the Atlantic, formation of intermediate and deep waters in relatively high-CDOM areas (Figure 5) and rapid overturning carries a high-CDOM/low-AOU signal to depth (see also Del Castillo et al. 2011, Jørgensen et al. 2011), obscuring the CDOM-AOU correlation that is present in the northern Pacific and Indian Ocean basins, which do not ventilate in the same way (Schmitz 1996). In the Pacific and Indian sectors of the Southern Ocean, rapid ventilation carries a low-CDOM/low-AOU signal to intermediate and deep waters owing to low surface concentrations (Nelson et al. 2010).

Ventilation of high-CDOM surface waters in the North Atlantic Deep Water presumably carries a terrestrial CDOM signal to the deep ocean, as inferred from the presence of lignin phenols at depth (Hernes & Benner 2003). This may represent a portion of the refractory CDOM pool in the deep ocean. The fluorescence analysis of Jørgensen et al. (2011) (see Measuring and Characterizing CDOM, above) revealed the presence of humic materials that increased within the main thermocline as protein-like materials declined above the main thermocline. The origin of these humic materials can include some terrestrial input via the North Atlantic Deep Water, but there must be production of “new” CDOM within the ocean interior. From fluorescence analysis (Yamashita & Tanoue 2008, Jørgensen et al. 2011), we can infer that protein-like materials do not constitute a large part of the net CDOM production below the thermocline. Jørgensen et al. (2011) also inferred diversity in humic-like CDOM from different locations, linking one fluorescing component to terrestrial lignin-like materials and others to autochthonous production.
Observations and inferences concerning CDOM circulation in the global ocean can thus be synthesized into the conceptual model shown in Figure 9. These graphs are analogous to the sections in Figure 5. Here, the gradients in CDOM concentration and overturning fluxes that control the distribution of CDOM throughout the deep sea are clearly shown. In the North Atlantic, rapid overturning of higher concentrations of CDOM is contrasted with ventilation of lower CDOM concentrations from the Southern Ocean in the Pacific and Indian Ocean sections. In the North Pacific, the lack of rapid ventilation allows CDOM to accumulate below the thermocline.

SYNTHESIS

CDOM and the Dirty Bathtub Ring

Open ocean concentrations of CDOM are difficult to estimate owing to their inherently low signal levels compared with inland and estuarine waters (see Measuring and Characterizing CDOM, above). In fact, the earliest systematic CDOM observations showed that CDOM level is a strong function of the observed freshwater fraction or its salinity (Kalle 1938, Jerlov 1953, Højerslev 1982). An example from the Baltic Sea (Jerlov 1953) showed that the CDOM distribution [measured as $a_g(380)$] decreases dramatically as oceanic salinities are approached (Figure 10a). Here, values of $a_g(380)$ decreased from values of $>1$ m$^{-1}$ for salinities less than 5 ppt to $\leq 0.1$ m$^{-1}$ for salinities of $\sim 34$ ppt—roughly typical values for the North Sea (e.g., Janssen et al. 1999). This result suggests a terrestrial source for CDOM in the ocean.

Recent observations support this near-linear trend in CDOM versus salinity in terrestrially affected waters, as CDOM and/or CDOM proxies decrease to nearly undetectable levels as the salinity approaches oceanic values (e.g., Blough et al. 1993; Vodacek et al. 1995, 1997; DeGrandpre et al. 1996; Del Castillo et al. 1999; Del Vecchio & Blough 2004, 2006; Del Vecchio & Subramaniam 2004; Hu et al. 2004; Del Castillo & Miller 2008; Palacios et al. 2009; Salisbury et al. 2011). CDOM signals decrease linearly with increasing salinity if the mixing of offshore and terrestrial end-member water masses is the only process affecting CDOM. Deviations from this mixing line indicate the presence of CDOM sources or sinks in the marginal oceans as well as the possibility of temporal/spatial heterogeneity in terrestrial CDOM origins (e.g., Del Vecchio & Blough 2004, 2006). As described above, a variety of processes are possible, including the photodegradation of CDOM, temporally and spatially dependent variations in CDOM river discharges, and in situ production.

Figure 10b shows the dependence of CDOM [here $a_g(355)$] as a function of salinity on a transect from Delaware Bay into the Mid-Atlantic Bight during September 1998 (Del Vecchio & Blough 2006). The CDOM-salinity relationship deviates from a linear relationship, illustrating the importance of both net CDOM production (deviations above the mixing line for salinities between roughly 8 and 28 ppt) and net CDOM destruction (for salinities $\geq 30$ ppt). This is particularly apparent for surface water masses compared with deeper ones, suggesting the importance of photodegradation reducing CDOM from the linear mixing line (Figure 10b inset). Note also the strong deviations from the two-end-member mixing model in the Baltic Sea example (Figure 10a). Importantly, statistics for the linear fits between CDOM and salinity appear to vary temporally (at least seasonally) and regionally (Del Vecchio & Blough 2006, Mannino et al. 2008, and many others).

In these terrestrially influenced waters, strong relationships are often observed between CDOM and DOC; however, these relationships are also variable among regions and in time and space within a given region. For example, Mannino et al. (2008) found strong intraregional relationships between CDOM [as $a_g(355)$] and DOC from the Chesapeake Bay into the Mid-Atlantic Bight on
Figure 9
Box model of CDOM dynamics in the (a) Atlantic and (b) Pacific and Indian Oceans. Colors indicate CDOM abundance [as absorption coefficient ($\alpha_{(325)}$) at 325 nm]. Straight arrows indicate fluxes, and curved arrows indicate local production due to particle flux remineralization. Contrast the high ventilation rate in the high-latitude Atlantic and South Pacific with the lack of ventilation in the North Pacific and North Indian Ocean, and their associated impacts on subsurface CDOM concentration. Abbreviations: AAIW, Antarctic Intermediate Water; NADW, North Atlantic Deep Water; AABW, Antarctic Bottom Water.
Figure 10
Examples of the relationship between CDOM absorption coefficient ($a_g$) and salinity in terrestrially influenced coastal regions. (a) Observed relationship between $a_g$ at 380 nm and salinity in the Baltic Sea (adapted from Jerlov 1955). (b) Observed relationship between $a_g$ at 355 nm and salinity in the Delaware Bay (adapted from Del Vecchio & Blough 2006) The inset shows an expanded view of the data between 26 and 38 ppt salinity. In both cases, the CDOM values decreased to background levels as the salinity approached oceanic values (~36 ppt).

individual cruises. However, the regression slopes for the CDOM-DOC relationships vary by a function of nearly two from cruise to cruise (Mannino et al. 2008, figure 2) owing primarily to differences in the source waters among the cruise time frames. This makes the determination of DOC from the remote assessment of CDOM in coastal waters difficult, and field data are required to provide regional and (hopefully) seasonal relationships between the two variables (e.g., Vodacek et al. 1997, Mannino et al. 2008).

These results indicate that CDOM concentrations for regions with substantial terrestrial influences will be regulated to first order by land-ocean interactions. This is seen in the relationships between CDOM and salinity (Figure 10) as well as in observed relationships between CDOM and DOC from terrestrially affected waters. For open ocean environments, CDOM distributions reflect local processes, and the influences of land-ocean interactions are not obvious. Hints of autochthonous net CDOM production can be found in the nonlinearities in the mixing line for CDOM and salinity shown in Figure 10. Clearly, we need to assess where the boundary lies between regions where autochthonous versus allochthonous processes dominate CDOM distributions.

The critical issue is to assess what fraction of the world’s oceans have their CDOM dynamics dominated by terrestrial inputs of CDOM—the “dirty bathtub ring” noted by Stommel and others (as cited in Briscoe 1993). Salinity is a key variable to follow, although it is not completely clear how to calculate this fractional area of coverage from salinity observations alone. The recent availability of satellite salinity observations from the Aquarius mission (http://aquarius.nasa.gov) may be very
useful for addressing this issue. Suffice it to say that the region of allochthonous dominance of CDOM dynamics must be a very small fraction of the global ocean, although additional research is needed to quantify this.

**CDOM and Its Changes on Decadal Timescales**

How is CDOM changing on interannual to decadal timescales? Results from the SeaWiFS satellite mission provide a window into these changes. Figure 11 shows monthly anomalies for CDM calculated using the GSM-01 bio-optical model for three global aggregates: the cool Northern Hemisphere ocean (mean sea surface temperature (SST) < 15°C); the warm, permanently stratified ocean (mean SST > 15°C); and the cool Southern Hemisphere ocean (mean SST < 15°C). The choice to use the mean 15°C SST isotherm to define global aggregates follows previous work (e.g., Behrenfeld et al. 2006; D.A. Siegel, M.J. Behrenfeld, S. Maritorena, C.R. McClain, D. Antoine, et al., manuscript in review).

All three global aggregates exhibit strong interannual patterns, with the 1998–1999 El Niño–La Niña transition from warm to cool SST values (and from low to high CDM levels) most clearly seen in the warm ocean aggregate. The statistical correlation between monthly anomalies of SST and CDM in the warm ocean aggregate is highly significant (R = 0.76), indicating the strong interactions between the physical environmental changes and seasonal- to decadal-scale surface ocean CDOM dynamics. Correspondence between SST and CDM is found for the other global aggregate regions as well, but with less statistical significance (R values are −0.30 for the cool Northern Hemisphere ocean and insignificant for the cool Southern Hemisphere ocean). Covariation of CDM with SST is not necessarily indicative of direct SST effects on ocean CDOM dynamics; instead, SST is more likely a proxy for changes in physical ocean conditions, where anomalously warm SSTs are associated with decreasing mixed-layer depth, suppressed surface nutrient input, and higher average light exposure for the near-surface mixed layer, which in turn influence CDM retrievals.

The SeaWiFS record can also be used to document secular trends in CDM retrievals over the past 13 years. For all three global aggregates, highly significant increasing SST trends have been observed during the SeaWiFS period (Figure 11). These trends vary from 0.015°C year⁻¹ in the warm ocean, to 0.029°C year⁻¹ in the cool Southern Hemisphere ocean, to 0.035°C year⁻¹ in the cool Northern Hemisphere ocean. At the same time, statistically significant decreasing SST trends have been found for CDM in both the warm ocean (−0.31% year⁻¹) and cool Northern Hemisphere ocean (−0.56% year⁻¹), whereas insignificant trends have been found in the cool Southern Hemisphere ocean.

The tight inverse coupling of CDM and SST suggests that increasing surface stratification is leading to decreased surface CDOM concentrations, as happens seasonally in midlatitude waters (Nelson et al. 1998, Siegel et al. 2002). What are the implications of declining CDOM in surface waters—which may continue into the future—for the ocean biogeochemical environment?

One consequence is related to the retrieval of ocean chlorophyll content from ocean color remote sensing data. Empirical models of ocean color using the bio-optical assumption (e.g., Morel & Maritorena 2001) imply a consistent relationship between chlorophyll and CDOM light absorption. Increasing stratification may lead to decreases in phytoplankton production as well as CDOM (Behrenfeld et al. 2006), but because the processes differ, the relationships required by the bio-optical assumption may change. This will directly impact the ability of researchers to develop consistent and accurate long-term assessments of the ocean biosphere (Natl. Res. Counc. 2011). Accurate assessments of all ocean color products must explicitly include assessment of CDOM as an independent variable in bio-optical models while its relationship with phytoplankton absorption is likely changing in time.
A reduction in surface CDOM abundance will also lower the photochemical potential for photoreaction sensitization, assuming surface solar irradiance does not change complementarily. This may reduce the production of CO and CO$_2$ through photochemistry and reduce the photolysis of DMS (Toole et al. 2008), which may lead to a small negative effect on greenhouse gas concentration and a small enhancement of sulfate aerosol production. This would be partially counteracted by reduced OCS production (Cutter et al. 2004). Changes in CDOM abundance will also have
significant impacts on atmospheric composition and chemistry through CDOM’s connections to the production of acetaldehyde (Millet et al. 2010) and other reactive gases and aerosols (e.g., Zepp et al. 2007).

Decreased CDOM will also result in increased UV penetration and greater UV fluxes deeper into the oceans. This will likely have a significant negative effect on both primary and secondary productivity rates (e.g., Jokiel & York 1984, Smith et al. 1992, Herndl et al. 1993). Further increased fluxes of UV will increase DMSP (dimethylsulfoniopropionate) concentrations in phytoplankton and water column DMS concentrations at open ocean sites (Sunda et al. 2002, Toole & Siegel 2004). The magnitude and interactions of these impacts are not easy to predict; suffice it to say that CDOM directly or indirectly affects many significant biogeochemical processes, and trends in overall CDOM abundance cannot help but have an impact.

**SUMMARY POINTS**

1. CDOM is ubiquitous in the ocean environment and controls UV and visible solar radiation penetration in the surface ocean.
2. CDOM is a small fraction of the total DOM pool in the open ocean, as changes in CDOM abundance are often unrelated to changes in DOC concentrations.
3. Heterotrophic processes are responsible for the majority of net CDOM production at the surface and in the deep ocean.
4. CDOM abundance in surface waters is controlled by a balance between production, solar bleaching, and mixed-layer dynamics.
5. CDOM abundance in the deep sea is controlled by a balance between in situ production and meridional overturning circulation.
6. Global ocean CDOM abundance varies on timescales related to climate oscillators and can have significant connections to climate-related biogeochemical processes.

**FUTURE ISSUES**

1. Understanding the distribution and optical properties of CDOM will contribute to significant improvement in ocean color remote sensing products, including the important climate data record of phytoplankton chlorophyll biomass.
2. The next generation of satellite ocean color sensors must be designed to characterize CDOM and its spectral dependence, which will likely require making new measurements in the UV spectral region.
3. Spectroscopic and chemical characterization techniques now being employed to study terrestrially derived organic matter will be increasingly used to characterize the origin and transformation processes of CDOM in the open ocean.
4. The boundary of the “dirty bathtub ring” between regions where terrestrially derived CDOM versus oceanic CDOM dominate needs to be delineated more clearly.
5. Atmosphere and climate connections to surface ocean CDOM can be addressed by modeling or remote sensing analysis.
DISCLOSURE STATEMENT
The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED


Lomas MW, Steinberg DK, Dickey T, Carlson CA, Nelson NB, et al. 2010. Increased ocean carbon export in the Sargasso Sea linked to climate variability is countered by its enhanced mesopelagic attenuation. *Biogeosciences* 7:57–70


**RELATED RESOURCES**

The Ocean Optics Web Book ([http://www.oceanopticsbook.info](http://www.oceanopticsbook.info)) is an excellent resource for understanding the interactions between CDOM and the underwater light environment.
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Errata

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