Marine Optical Biogeochemistry: The Chemistry of Ocean Color

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1. Introduction

The composition and dynamics of colored dissolved organic matter (CDOM) in natural waters has been the subject of study for decades. However, renewed interest in CDOM properties and cycling in the ocean has been sparked by an increased need for understanding its distribution along with technological developments resulting in improved measurements. Early studies to characterize CDOM relied on extracting the material from water to obtain adequate amounts for chemical analyses, too often resulting in alteration of the natural materials. In the past 10 years, instrumentation and methodologies for assessing both concentration and chemical properties of CDOM using optical techniques without preconcentration have advanced rapidly. Development of instrumentation for continuous, underway, *in-situ* sampling and improvements in satellite sensors and algorithms have resulted in advances in our understanding of CDOM by increasing sampling densities and linking CDOM to other environmental parameters that influence its distribution.

CDOM has been the topic of several reviews since 2001. A review of CDOM optical properties, sources, sinks, and distribution in coastal regions by Blough and Del Vecchio[1] updates a previous review of the subject by Blough and Green[2] and includes an extensive compilation of observations of CDOM optical properties collected worldwide since 1981. A second review in that same volume by Nelson and Siegel[3] covers the topic of CDOM in open ocean areas. It includes discussion of CDOM chemical properties, methods, and implications for remote sensing applications, photochemistry, and photobiology. A third review with a focus on remote sensing applications in coastal areas by Del Castillo[4] includes an excellent summary of the chemical properties of CDOM, which give rise to its absorption and fluorescence characteristics. It also discusses CDOM within the context of ocean color, ocean optics, and development of empirical algorithms for separation of ocean color spectra into discrete components.

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This review will provide a general overview of the nature and importance of CDOM in marine waters and an update on new results regarding CDOM properties and dynamics with a focus on application to future global biogeochemical studies using optical techniques amenable to satellite remote sensing or ocean observing systems. One recent body of work covered herein is a collection of papers on the role of physical, chemical, and biological processes in controlling CDOM distributions in the ocean, which was published in 2004.[5] This volume was the outcome of a special session on the topic at the Ocean Sciences Meeting in Honolulu, Hawaii, in 2002. Many of these papers describe results collected during multicruise field studies conducted in the Gulf of Mexico.

The reader is referred to other articles in this issue that cover complementary topics related to CDOM in sediments (Burdige), cycling of organic carbon in the ocean (Mopper *et al.*), and spectroscopic studies of inorganic components of seawater (Johnson *et al.*).

1.1. What Is Colored Dissolved Organic Matter (CDOM)?

CDOM, also known as gelbstoff,[6] gilvin,[7] yellow substance, and chromophoric dissolved organic matter, is operationally defined as that component of total DOM that absorbs light over a broad range of visible and UV wavelengths. In order to best understand the interest in the study of CDOM, we need to consider separately the terms "color," "dissolved," and "organic matter". Beginning with the last of these, organic matter means that the material contains both carbon and hydrogen and is of biological origin. The term covers thousands of compounds but is used generically to indicate the entire pool of material or when composition of the sample has not been sufficiently characterized as to be named by specific compounds or compound classes. The chemical composition, origin, and dynamics of CDOM in aquatic systems are still poorly understood. This is not to say that these parameters are unknown but rather that the number and complexity of components that comprise organic matter in the ocean is large and diverse, as is the biological, physical, and chemical environment in which it is produced, transported, and transformed.

Next we examine "dissolved." While one might easily understand that this means the opposite of "particulate" or that the compounds are present as solutes in water, in actual practice "dissolved" is defined operationally by mechanical separation of water samples using filtration, centrifugation, or other techniques to remove particles larger than some minimal diameter. It is important to understand that particulate matter in the ocean is a continuum of sizes and that both organic matter and CDOM have some distribution across this continuum between truly dissolved and truly particulate.

Last, there is "colored". This refers to the optical properties of CDOM, which include a yellowish color (absorption of blue light) and blue fluorescence. It is the absorption of blue light that makes CDOM of interest to satellite remote sensing and ocean optics researchers and also provides an easily measured property for determining CDOM concentrations in the environment. The chemical characteristics responsible for the optical properties also impart high photochemical reactivity.

1.2. Why study CDOM?

In the past 10 years, the primary driver for the study of CDOM has been Satellite Oceanography. The launch of the Coastal Zone Color Scanner (CZCS) in 1978 ushered in a new era of oceanographic research. CZCS was primarily conceived of as a means for assessing global oceanic plant biomass. The several ocean color sensors that have followed CZCS have had added capabilities that permit estimates not only of temporal and spatial distributions of chlorophyll pigments but also of suspended sediments, dissolved and particulate organic carbon, and primary productivity.

As satellite ocean color sensors and data interpretation of their signals have improved, it has become increasingly important to understand distribution and dynamics of CDOM in order to make more accurate estimates of the other ocean color components. Ocean color signatures and derivation of chlorophyll concentrations are based on upwelling radiance of sunlight that has traveled through the atmosphere and through the water column and is reflected back to the satellite. The signal therefore is influenced by the concentrations of all absorbing constituents, including water, chlorophyll, detritus, CDOM, and other absorbing chemical species. The absorbance spectrum of CDOM overlaps that of chlorophyll and can account for 50% or more of total absorption at 443 nm, the wavelength at which chlorophyll concentrations are most often measured.[8] In many coastal areas, CDOM absorption is several times that of chlorophyll.

Estimates of the contribution of CDOM to total dissolved organic carbon (DOC) in the ocean have ranged from 20% to 70%,[9,10] with highest values in coastal regions, where river inputs are dominant, and values at the lower end of the range in open ocean areas. CDOM has proven to be a useful tracer not only for carbon but also as a proxy for mixing in a wide variety of environments. In most coastal areas and below the euphotic zone elsewhere in the oceans, CDOM displays conservative behavior on the time scale of physical mixing. Thus, CDOM has been used to trace inputs of rivers, distinguish between source waters of different origin, track distribution of river-borne pollutants,[11] and verify exchange of ballast water in ocean-going vessels.[12] It also provides a means of studying ocean surface circulation features, such as upwelling and eddies.[13] On continental margins, it has been used to refine budgets of both carbon and freshwater.[14] Spectral discrimination between natural and anthropogenic CDOM has been exploited to study human sewage,[11] agricultural waste, and polycyclic aromatic hydrocarbon (PAH) distribution in rivers and estuaries.[15] CDOM largely controls penetration of photosynthetically active radiation in coastal areas and is therefore an important parameter in coastal productivity. High levels of CDOM may also be important in protecting corals and other light-sensitive organisms from UV radiation.[16]

Last, CDOM plays a very important role in cycling carbon, trace elements, and trace gases of importance to biological activity and global climate. CDOM is highly photoreactive and is rapidly destroyed upon exposure to sunlight, producing dissolved inorganic carbon, smaller organic carbon compounds, hydroxyl radical, superoxide,[17] and many other species. CDOM serves as a photosensitizer to stimulate destruction and transformation of other organic compounds by sunlight, altering their bioavailability to microorganisms. CDOM also mediates redox reactions of some trace metals and influences air−sea exchange of trace gases.[18−23] Thus, the study of CDOM is truly interdisciplinary, with relevance

to ocean circulation; biogeochemistry of carbon, trace elements, and gases; ocean optics and remote sensing; photochemistry and photobiology; phytoplankton ecology and physiology; harmful algal bloom mitigation; and coral reef ecology.

1.3. Recent Developments

Several new measurement and data analysis techniques have contributed to advancing our understanding of marine CDOM. Recent application of principle component analysis (PCA) and parallel factor analysis (PARAFAC) have led to new insights on the sources and concentrations of fluorophore groups within bulk CDOM.[24,25] Improvements have also been made in optical sensor techniques and technologies that permit separation of an ever-increasing array of seawater constituents by virtue of their optical properties.[26] This in turn has led to an improved understanding of the effects of individual components of ocean color on remote sensing reflectance and development of improved algorithms for quantification of each component. Of particular importance to remote sensing of CDOM have been improvements in algorithms to correct for the presence of aerosols, which absorb 90% or more of the total water-leaving radiance.[27] Further advances in modeling, theory, calibration, spatial and temporal coverage of the oceans, and *in situ* instrumentation have improved accuracy of measurements as well as understanding of causal relations among seawater constituents of ocean color.[28] New capabilities for hyperspectral measurements, those that are made continuously across the visible portion of the EM spectrum (400−700 nm) with a spectral resolution of 10 nm,[29] are now possible not only for absorbance and fluorescence but also for backscattering measurements, with applications for deriving phytoplankton species information and particle composition. Last, there have been parallel advances in hyperspectral methods and improved ability to couple optical models to ecosystem models.[30] Inclusion of temporal, spatial, and chemical variability of CDOM into these models improves understanding of CDOM dynamics as well as of ecosystem dynamics.

2. The Nature of Colored Dissolved Organic Matter (CDOM)

2.1. Optical Properties

The optical properties of CDOM provide information on both the amount of material present and the chemical properties of the bulk sample, which undergo change due to chemical, biological, and physical processes. Parameters derived from optical properties include the spectral slope and fluorescence efficiency, which have proven to be of some value in remote sensing applications of ocean color.

2.1.1. Absorbance

Both terrestrial and marine CDOM have absorbance spectra that increase exponentially toward shorter wavelengths, with no discernible peaks. This lack of features fits the explanation that CDOM is a complex mixture of compounds that have overlapping absorption spectra, with no single compound dominating. The smoothness of the absorption spectrum at wavelengths greater than 350 nm may also result from intramolecular electronic interactions.[31]

Bricaud *et al.*[32] first proposed a wavelength-independent formulation of an exponential fit of the spectral dependence of CDOM absorption, with the intent of establishing that measurements in the UV region could be extrapolated to the visible with sufficient accuracy to be more reliable for open ocean samples. This is the equation now in general use to calculate CDOM spectral slope, *S*, which is also widely used in remote sensing applications. The equation is

$$a(\lambda) = a(\lambda_0)\, e^{-S(\lambda-\lambda_0)}$$

where $a(\lambda)$ is the absorption coefficient at wavelength λ, $a(\lambda_0)$ is the absorption coefficient at a reference wavelength, and S is the spectral slope parameter. The absorption coefficient is calculated as $2.303A/l$, where A is the absorbance ($\log I_0/I$), l is the path length (in meters), and 2.303 converts between $\log_{10}$ and natural log. The log transformed absorption coefficient *versus* wavelength takes on a linear shape for most natural water samples, especially between 400 and 700 nm; however, spectral slope calculations are dependent on the wavelength range used in calculations[33,34] and whether linear or nonlinear fitting methods are used. In a recent comparison of fitting methods, Twardowski *et al.*[35] found that a hyperbolic model outperformed the single-exponential model. However it is still important to report the spectral range over which *S* is calculated due to loss of signal at longer wavelengths and increased steepness in the spectrum at shorter wavelengths, which may be accentuated by photobleaching transformations. A recent compilation of spectral slope observations, including range of wavelengths over which calculations were made, can be found in previous reviews.[1,35]

Differences in *S* have been proposed as indicative of CDOM origin, with generally lower slopes in freshwater and coastal environments than in marine environments.[1,26] While some of this change is likely due to increasing importance of marine humics and new biological CDOM, much is also due to photobleaching.[36] Figure 1 shows typical results for changes in CDOM spectral slope as a result of mixing and photobleaching in coastal waters.[37] Data were collected in the Gulf of Mexico over the same region during 2 years, one during moderate drought conditions (2001) and one during severe drought conditions (2000). Spectral slopes for salinity less than 25 are low and fairly constant. Even though mixing is obviously occurring, the amount of CDOM in the freshwater is high enough to dominate the optical signature. Slopes increase rapidly at salinities greater than 30, as concentration of marine humics begins to reach those of the diluted freshwater CDOM. Samples collected during 2000 show a sharper increase at intermediate salinities, indicative of photobleaching caused by low river discharge, higher solar radiation, and increased stratification of the water column. Changes in CDOM emission maxima for this same data set are shown in Figure 1B. The inflection point in this curve is at the same salinity, with the 2000 data again showing a sharper increase and inflection at a lower salinity, 27 *versus* 32. Similar relationships have been observed in other regions;[1] however, Figure 1A shows less scatter in the salinity mixing curve because *S* was calculated over the UVC portion of the spectrum. This region is more sensitive to effects of photobleaching and may provide better information regarding chemical composition of CDOM than the longer wavelength range typically used in remote sensing algorithms.

The greatest value of using *S* is in remote sensing applications, where sensor bands are finite and CDOM

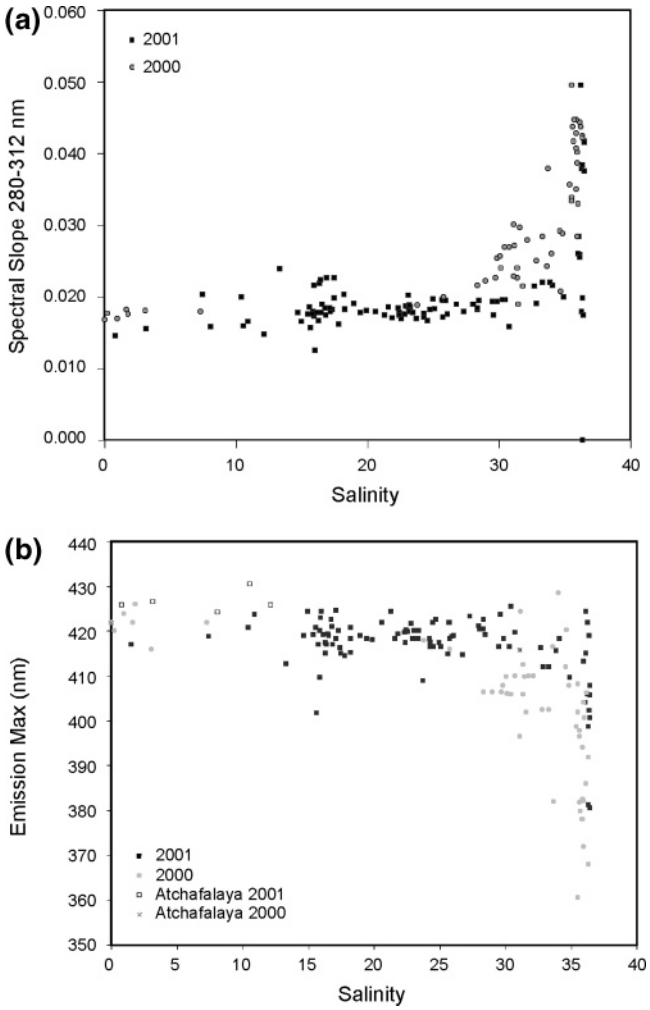

Figure 1. Data from two cruises during the summers of 2000 and 2001 to the Gulf of Mexico south of the Mississippi River: (a) spectral slope calculated using linear regression for wavelengths between 280 and 312 nm *versus* salinity; (b) position of fluorescence emission maximum *versus* salinity.

contributes to absorbance in the chlorophyll channel. Greatest accuracy for CDOM concentration and composition is achieved at the shorter visible wavelength bands (280−400 nm), but corrections to chlorophyll algorithms require conversion to CDOM absorption (a_{CDOM}) at 443 nm. An understanding of how *S* varies is thus important in accurate chlorophyll concentration retrievals, but our understanding of processes controlling *S* is still limited. At this point, the most accurate chlorophyll and CDOM algorithms rely on choosing the best values of *S* based on season, CDOM concentration, or some other parameter that strongly influences corrections for a given region.[4]

2.1.2. Fluorescence

The natural fluorescence properties of seawater were recognized as early as 1949 and attributed to the presence of CDOM.[6] Kalle also was first to recognize the potential of these properties to trace freshwater inputs in coastal areas.[6,38] Fluorescent DOM (FDOM) is colored, but not all CDOM is fluorescent. This is evidenced by the fact that absorption spectra show a featureless increase in intensity with decreasing wavelength between 200 and 700 nm, whereas excitation spectra show one or more discrete peaks, most commonly around 250 and 350 nm. In most cases, the two pools show a linear relationship,[39,40] although globally there is a 3-fold variation in absorption to fluorescence ratios.[1] Variability is much smaller within a given geographical area, and the ratio has been used to derive absorption coefficients from more sensitive fluorescence measurements. This ratio is constant on the West Florida Shelf even when freshwater endmember sources have widely different CDOM concentrations; however, interannual differences reflecting variability in river discharge can be important.[37] Fresh terrestrial and deep marine waters have the highest fluorescence efficiencies, with a decrease in values offshore as exposure to photodegradation increases.[1]

Fluorescence techniques are more sensitive than absorption spectroscopy and both excitation and emission spectra show greater detail and provide more information as to chemical composition than do absorbance spectra. Collection of hyperspectral fluorescence data has been shown to provide an enormous benefit over collection of individual spectra, and two techniques have been employed. Excitation−emission matrix spectroscopy (EEMS) involves collection of multiple emission spectra at a range of excitations, which are concatenated into a matrix (Figure 2).[41] Synchronous scanning (SS) involves increasing both excitation and emission wavelengths simultaneously to produce a single scan.[42] Although less time-consuming, SS provides less information and is more difficult to interpret.

The use of EEMS permits discrimination of CDOM sources based on which fluorophores are present and their relative concentrations. Eight general types of fluorescence peaks have been identified in natural waters.[43] These groups include humic-like, protein-like, and pigment-like fluorescence.[43−46] Terrestrial humic-like materials display excitation and emission maxima at longer wavelengths than do marine humic-like materials, as would be predicted from their more aromatic chemical nature and presumed higher molecular weight. Table 1 summarizes fluorescence properties of fluorophores identified to date.[25,43,47−49]

EEMS also provides information on changes in CDOM resulting from mixing, biological degradation, biological production, and photobleaching that occur in the environment. Mixing between water masses has the primary effect of dilution, but shifts in excitation and emission maxima can result when the water masses with different CDOM composition have comparable concentrations of CDOM.[50,51] Thus, at salinities between 30 and 36, CDOM in coastal areas begins to exhibit a shift toward the shorter wavelength excitation and emission maxima (blue-shift) of marine humics.[33,43,45] A blue shift in peak position can also be caused by photodegradation.[33,43,45] Biological processes can result in production of new peaks during bloom periods, especially peaks T, B, and P. The marine-humic peaks M and N are also associated with high biological activity.[43,45] Several of these peaks have also been observed in wastewater and in streams receiving agricultural waste.[11]

2.1.3. Remote Sensing of CDOM

Remote sensing applications are more concerned with determining concentrations of ocean color constituents accurately in all areas of the ocean. Historically, these studies were focused solely on accurate determination of chlorophyll *a* (Chl *a*) concentrations and non-chlorophyll constituents were treated as signal "contamination". However, more recently the goal has been to derive as many biogeochemical properties as possible from optical data. (See Twardowski[26]

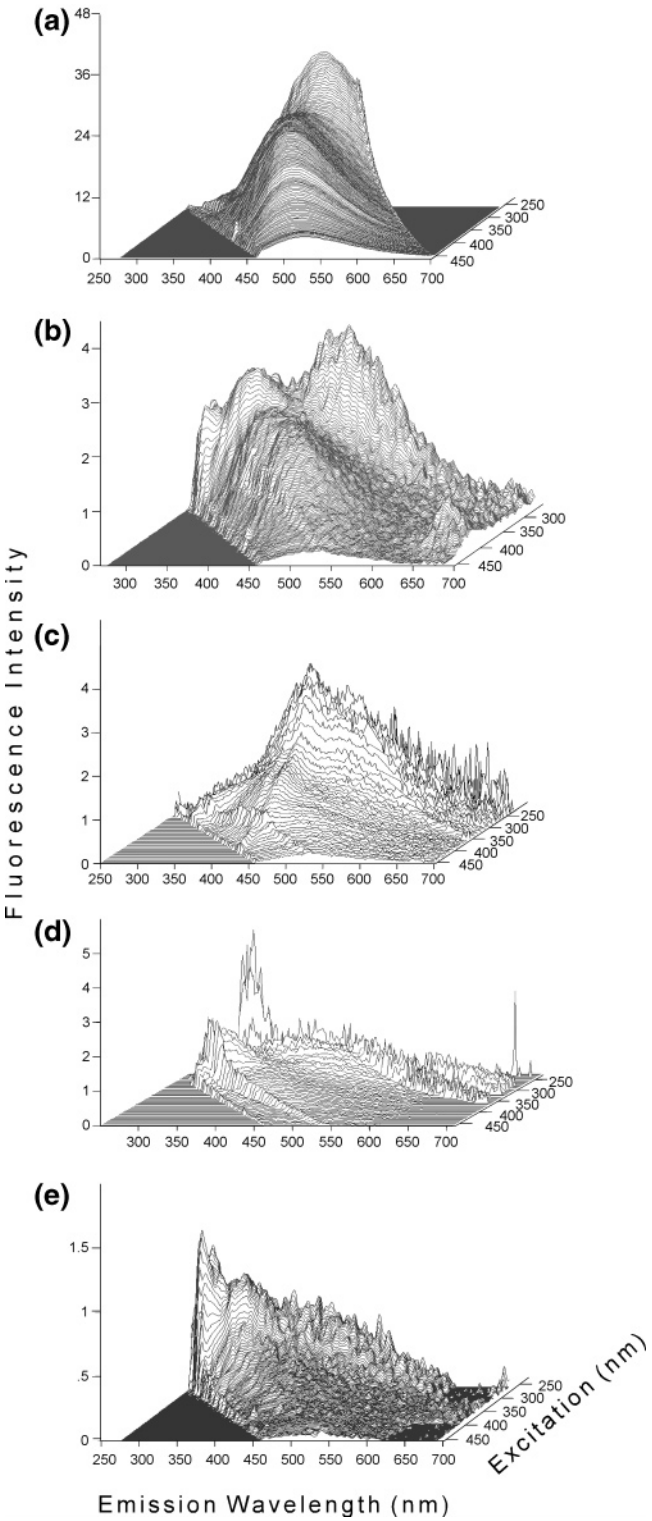

Figure 2. Three-dimensional excitation−emission spectra for samples from a variety of environments showing type spectra for (a) rivers, (b) new marine productivity, (c, d) partially photobleached samples, and (e) fully photobleached samples. The vertical axis is fluorescence in QSE for all except panel a, which is in relative fluorescence intensity.

for a summary of properties derived to date.) Empirical and semianalytical algorithms have been developed to determine CDOM concentrations from ocean color data for the purpose of studying distribution and dynamics of CDOM itself, or as a proxy for surface ocean features.[4] Discussion in this section will be confined to an explanation of how this approach differs from laboratory and field studies and focus on what can be learned about CDOM using remotely sensed ocean color.

The most important difference between in-water and remote sensing approaches is that satellites cannot discriminate between dissolved and particulate materials. For the purpose of geochemical studies, CDOM is operationally defined as the fraction of dissolved organic matter that absorbs light between 280 and 700 nm. Partitioning between dissolved and particulate is most commonly achieved by filtration using filters that retain particles larger than 0.2−0.8 μm, the nominal size of GF/F glass fiber filters. Filtration can be difficult or impossible in some *in situ* applications and impossible using satellite sensors.

Ocean color is measured as remote-sensing reflectance (R_{RS}), which depends on absorption and backscatter of all constituents in the water, including phytoplankton, detritus, dissolved materials such as CDOM, and the water itself. Backscatter is dependent on particle size, phytoplankton species, particle mineralogy, detritus composition, and particle concentration over all size ranges that influence optical properties. Colloids are an especially important but poorly studied component of R_{RS}. Our level of understanding ocean optics is such that there is a need for additional field and laboratory studies that detail hyperspectral backscatter and absorption of all these components in the same water sample.[52]

The presence of CDOM has a large effect on R_{RS} spectra. Del Castillo[4] presents R_{RS} model results that illustrate how spectra change even for water samples that have the same *S* values and suggests that coastal regions can be divided into two groups, those where CDOM absorption changes only due to dilution and those where both absorption intensity and optical properties change. The former are usually found at salinities less than 30, while the latter are found at higher salinities.

Gregg and Casey[53] recently evaluated the SeaWiFS chlorophyll data set over both regional and global scales using comparison with *in situ* chlorophyll data. They attributed the largest errors to CDOM and absorbing atmospheric aerosols, which caused substantial errors in six of the twelve major basins. Excessive CDOM was found in areas influenced by tropical rivers, as well as in the Baltic Sea, the Mediterranean/Black Sea, and the Antarctic. In contrast, the South Atlantic and the entire Pacific Ocean seemed to be minimally influenced by CDOM contamination.

In addition to absorption and *S* for CDOM, absorption and scattering by colored particulate organic matter is also a factor of varying importance in R_{RS}. While studies using water samples are able to differentiate between CDOM and particulate colored organic matter, satellite studies cannot, and the combined pool has been called colored detrital matter or CDM. Absorption by colored particles in coastal regions has been implicated in altering spectral slope at wavelengths between 412 and 450 nm. Less steep spectral slopes have been observed when there is a higher percentage of detrital CDOM in unfiltered samples.[54] Balch *et al.*[55] observed sharp changes in spectral slope across frontal boundaries and after heavy rains in the Gulf of Maine, which they attributed to changes in particle concentrations.

The spectral slope of CDM is also influenced by its chemical composition. Babin *et al.*[56] measured *S* for nonalgal particles in a variety of European coastal waters and found that values sorted into two groups. Samples in the low group

Table 1.

component	peak name[43]	Ex/Em	peak number[25,49]	source[25,49]	peak[47,48]
tyrosine-like, protein-like	B	275/305	8	autochthonous	γ
tryptophan-like, protein-like	T	275/340	7	autochthonous	δ
unknown	N	280/370			
UVC humic-like	A	260/400−460	4	fulvic acid, autochthonous, terrestrial	α'
UVC humic-like	A	260/400−460	1	humic, terrestrial, allochthonous	α'
UVC humic-like	A	260/400−460	3	humic, terrestrial, allochthonous	α'
UVA marine humic-like	M	290−310/370−410	6	anthropogenic from wastewater and agriculture	β
UVA humic-like	C	320−360/420−460	5	terrestrial, anthropogenic, agriculture	α
pigment-like	P	398/660			
UVA humic-like		250 (385)/504	2	fulvic acid, terrestrial, autochthonous	

approached values for pure mineral particles of 0.011 nm^{-1} previously reported by Bowers and Binding.[57] Samples with values in the high group, 0.0128 nm^{-1}, were from areas where particles had a high organic content.

In a study of the St John's River in Florida, where CDOM concentrations are very high ($a_{440} = 6-30\ m^{-1}$), a significant CDOM signal was also found in the colloidal pool.[58] Fine particulate absorption increased logarithmically with log CDOM concentration. Overall, the effects of high colloidal CDOM at high CDOM concentrations had greater effect on scattering than on estimates of CDOM by absorbance.

High concentrations of particles also have negligible impact on CDOM measured as fluorescence. Belzile *et al.*[59] found that filtration changed FDOM intensities by <4% in a variety of coastal environments but the relationship between A_{370} and fluorescence was unaffected.

In open ocean areas, detrital CDOM is very low; therefore most of the CDM signal is due to CDOM. However, CDOM in colloidal form (<0.2 μm) may be a major source of backscattering in both the open ocean[52] and coastal seas. It has been estimated that 67% of DOC and CDOM coming out of the Yukon River into the Bering Sea is in the colloidal size range.[60] Data are insufficient at this time to generalize to other coastal areas.

Separation of backscatter into constituents is still in the very early stages of understanding, and there are likewise few studies in which absorbance and scatter are measured on multiple size classes. There is a clear need for addition of multiple particle types to measurement suites as well as models. However, advances in these areas hold promise for improved understanding of both dissolved and detrital carbon distribution and carbon cycling.

2.2. Chemical Properties

CDOM has yet to be fully chemically characterized. Parallels have been drawn between CDOM composition and the structure of humic and fulvic acids found in soils[61−67] and transported via rivers to lakes and oceans as aquatic humic substance. Humic substance ranges from yellow to brown in color, and therefore this pool, which is defined by extraction procedures, clearly contains part of the pool defined as CDOM. However, not all humic components are colored, and not all CDOM is isolated using humic substance extraction techniques. To the extent that chemical properties of humics are consistent with the optical properties of CDOM and *vice versa*, compositional studies can provide insight into the chemical properties of CDOM.

In coastal areas where terrestrial carbon dominates the dissolved carbon pool, CDOM does contain a large fraction of soil humic substances. However, it is also now well-established that marine CDOM, although still predominantly humic-like in nature, has a distinctly different origin and different chemical structure.[62,64,68,69] Marine humics are less aromatic, have lower C/N ratios, and contain more carboxylic groups and sugars than do terrestrial humics. This agrees well with the observations that marine humics have a blue-shifted fluorescence relative to terrestrial humics.

Many compounds, including lignins, phenols, and other plant degradation products have been proposed to contribute to marine and terrestrial humic substances, and many of these exhibit CDOM-like absorbance and fluorescence properties. In the past, much debate was focused on humic substance formation theories, some arguing the material originated with major plant biochemicals that proceeded along a degradative pathway to form humics.[70] The other school argued that sugars, amino acids, and other small molecules polymerized in the ocean to form CDOM, perhaps in the presence of UV radiation.[65,71] Recent results suggest that aspects of both pathways may produce CDOM in the ocean.

Among the nonhumic components of marine CDOM are pigment-like components[43] and amino acid or protein-like components.[43−46,72] These components are not observed in all samples but rather seem to show some relationship to elevated biological activity. It is also unclear whether these are truly dissolved or result from disruption of phytoplankton cells during filtration, but the presence of both protein-like and pigment-like components in marine CDOM provides evidence for its production in the ocean.

Protein-like fluorescence has been observed in many past studies; however only recently has a strong link between protein concentrations and protein fluorescence been documented. Tyrosine-like fluorescence was observed at all stations and all depths on transect from Ise Bay, Japan, across Kuroshio Current into the North Pacific Ocean.[73] A tryptophan-like fluorescence was observed as a distinct peak only in surface waters from the bay and coastal regions. Concentrations of these amino acids and of the amino acid-like fluorophores decreased with distance from the bay and with depth. Amino acid fluorescence intensities showed strong correlation with measured concentrations of the corresponding amino acid, as well as with total hydrolyzable amino acids (THAA) throughout the study area. When data were separated by region, no significant correlation was found in the ocean samples. However, a relationship in the open ocean may have been concealed by the presence of background fluorescence in these samples. Taken as a whole, these results suggest that the THAA are present as small peptides and not as protein molecules. Observation of discrete fluorescence of tyrosine, which is not visible in proteins containing tryptophan and is likewise suppressed when complexed with humic material, suggests that the amino acids and THAA are associated with nonhumic-containing CDOM.

The possible existence of separate humic and protein fractions is also suggested by the results of Boehme and Wells.[74] Their analysis of the colloidal fraction in the estuary of the Damariscotta River, Maine, shows that the smallest fraction (1−5 μm) has protein-like character, whereas the larger sizes have humic-like character. Fluorescence of the humic-like material is increasingly red-shifted in larger size fractions.

While much of the recent effort regarding CDOM research has centered on optical measurement, several recent chemical studies have provided new insight regarding CDOM composition. Parlanti *et al.*[75] combined high-performance liquid chromatography (HPLC) with subsequent excitation−emission matrix spectroscopy (EEMS) and capillary electrophoresis (CE) analyses to the separation and characterization of marine and freshwater CDOM. While they were only partially successful in separating chromophore groups, they did show that CE adds information useful for discriminating between sources.

New insights on the effects of photoirradiation and protozoan grazers on composition of aquatic fulvic acids were obtained using electrospray ionization (ESI) combined with Fourier transform ion cyclotron resonance mass spectrometer (FT−ICR MS) analysis.[76] Photobleaching of Suwanee River fulvic acid was not found to produce new compounds but rather a preferential loss of compounds with high double bond equivalent and low oxygen content. It is possible that new compounds produced by photooxidation were not detectable using this technique due to low molecular weight or charge properties. Protozoans grazing on bacteria produced new compounds and degraded some of the compounds produced by the bacteria.

In another study employing photooxidation to probe CDOM composition, evidence obtained suggests that the CDOM absorption spectrum arises from a continuum of coupled states, which undergo intramolecular charge-transfer interactions between aromatic polymers, rather than from the summation of multiple individual compound absorption spectra.[77] Species that would be predicted to exhibit these properties include lignin, polyphenols, tannins, and melanins.

The last study applied HPLC to analysis of water samples from three marine sites. Samples from the North Pacific were found to have three major compounds and more than 90 minor compounds.[78] The major compounds were identified as 2,4-dichlorobenzoic acid and several tetrachlorobiphenyl carboxylic acids. Coastal waters from Woods Hole, MA, also had high concentrations of tetrachlorobiphenyl carboxylic acids, superimposed on a high background peak from unresolved humic substances. The sample from Bermuda was more like that from the open ocean, but some humics were still present. Concentrations of these polychlorinated biphenyl (PCB) compounds ranged from 1 to 10 μg/L, which would account for a minimum of 2% of total CDOM absorption. The evidence suggests that these PCBs are most likely natural products rather than anthropogenic, because the estimated concentration in the ocean is more than 2 orders of magnitude higher than the oceanic man-made inventory.

3. Distribution of CDOM

3.1. Sources

The patterns of CDOM distribution are controlled by the balance between sources and sinks (Figure 3). Primary sources are rivers and groundwater near coastlines, which

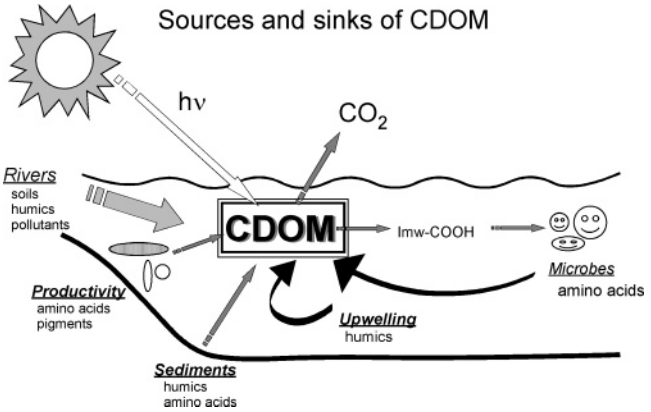

Figure 3. Schematic of sources and sinks of CDOM to the ocean.

carry CDOM primarily from soils, but coastal waters can also contain plankton-derived CDOM produced in rivers and estuaries, as well as anthropogenic compounds from runoff, sewage discharge, and other effluents. Production by marshes and tidal flats,[79] as well as input of porewaters during sediment resuspension events,[80] can also be locally important. In nearshore areas with strong river influence, mixing is the major factor controlling CDOM distribution and conservative behavior, that is, an inverse linear relationship between CDOM and salinity is often observed. While other processes are undoubtedly adding and destroying CDOM, as evidenced by scattered observations of nonconservative behavior, physical factors dominate over the time scale of CDOM lifetimes in coastal surface waters.

Multiple freshwater sources within the same outflow region have been attributed to variation in mixing and distribution subsequent to discharge from the river mouth. Hitchcock *et al.*[81] studied CDOM in the Mississippi River plume using Lagrangian drifters and a profiling system. CDOM was conservative throughout the study region, although at least three distinct water masses were evident. The fresh plume of river water was mixed with two different subsurface, high salinity, low CDOM water masses in different regions of the study area. A fourth water mass with low salinity and lower CDOM than the plume may also have been important. They estimated the residence time of the freshwater parcels in the plume based on satellite data and river discharge data to be 5.5 days, which, in contrast to published values of CDOM degradation rates of weeks to a month, supported dilution as the controlling factor in CDOM distributions on the Louisiana shelf.

Recent studies also continue to demonstrate that factors other than mixing control CDOM distributions in some areas. Nonconservative behavior of CDOM fluorescence and DOC was observed in the St. Mary's River estuary. Losses in the region of salinity less than 10 were attributed to flocculation, while increases in DOC and appearance of amino acid-like peaks in the lower estuary may be from biological production in saltmarshes and coastal waters.[82]

Away from river-dominated margins and in open ocean areas, *in situ* biological production is the primary source of CDOM. Numerous field studies have implicated all the lower trophic groups (primary producers, grazers, viruses, and bacteria) in production of CDOM, and in many locations a positive correlation has been found between CDOM and chlorophyll. Although primary production is the ultimate source of all fixed carbon in the open ocean, phytoplankton have not been definitively shown to be a primary source of

CDOM. Processes that release or recycle phytoplankton cell contents, such as sloppy feeding by grazers, viral lysis, excretion of metabolites by bacteria and zooplankton, or exudation of mucus and other extracellular secretions, likely play a major role in production of CDOM.

In one of the more comprehensive laboratory studies of CDOM sources, Rochelle-Newall and Fisher[83] concluded that phytoplankton are not an important direct source of CDOM, as not even sonication of 11 cultures resulted in direct production. However, bacteria were implicated in production of CDOM from noncolored algal precursors.

Increased CDOM concentrations have been reported in association with harmful algal blooms of the dinoflagellate *Karenia brevis*[84] and the brown tide organism *Aureococcus anophagefferens*.[85] In the latter study, there was also an increase in a protein-like signal in the colloidal (0.2−0.7 μm) fraction at the height of the bloom. Since these were field studies, bacteria and zooplankton were undoubtedly present, but their role in CDOM production cannot be assessed.

Steinberg *et al.*[86] observed CDOM production by zooplankton, protozoans, and a colonial cyanobacterium during incubation experiments. Excretion was likely the major process responsible for zooplankton CDOM, since incubations were made in filtered seawater and dissolution from fecal pellets did not produce measurable amounts of CDOM. The absorbance spectra of CDOM produced by each group of organisms were markedly different. Crustacea (copepods, euphausiids, amphipods) CDOM had an absorbance maximum at 250−275 nm, similar to that of nitrogenous waste products such as amino acids and urea. CDOM from salps (pelagic tunicates) showed a peak at 295−298 nm, possibly from the mucus slime produced by these organisms. The spectrum of CDOM from a gelatinous polychaete worm (alciopid) showed one peak at 270 nm and a second broader peak at 425 nm with a shoulder at 375 nm. These worms are known to produce a yellow slime, which would be consistent with this spectrum. Colonial radiolaria also produced CDOM, with an absorbance maximum at 300 nm.

This same study[86] also found production of CDOM from colonial cyanobacteria species of genus *Trichodesmium* with absorbance maxima at 325 and 360 nm, similar to spectra of mycosporine-like amino acids (MAAs). Similar absorbance spectra have previously been reported from *Lingulodinium polyedrum*,[87,88] a red-tide-forming dinoflagellate, as well as from water-soluble *Trichodesmium* pigments.[89] MAAs are thought to be produced by a variety of marine organisms to provide UV protection.[90]

Bacteria, not phytoplankton, may be responsible for new CDOM production in the Sargasso Sea based on (1) lack of correlation between chlorophyll concentrations and CDOM concentrations, (2) a lag between the main phytoplankton bloom and peak in CDOM concentration, and (3) correlation between depth profiles of CDOM and bacterial abundance.[91] Recent incubation experiments with Sargasso seawater demonstrated both production and consumption by bacteria. Estimates of bacterial contribution of new CDOM to the total CDOM pool ranged from 12% in winter to over 50% in autumn.[92]

A similar lag in CDOM increase after phytoplankton blooms has also been observed in a coastal region, where CDOM dominates total water column absorbance except during the spring bloom.[93] Again, this would seem to suggest that remineralization by microbes is responsible for CDOM production.

A recent paper by Hu *et al.*[94] shows a connection between chlorophyll and CDOM based on analyses of 5 years of daily high-resolution sea-viewing wide field-of-view sensor (SeaWiFS) images of ocean color for the central North Atlantic Ocean, including the Sargasso Sea. CDOM maxima were shown to lag pigment maxima by 2−4 weeks. The synoptic coverage and long time series provide strong evidence that chlorophyll and CDOM are not correlated but that the source of oceanic CDOM is almost certainly the result of phytoplankton degradation.

Another open ocean environment where autochthonous production of CDOM is locally important is coral reefs. High reef productivity and remineralization in the shallow waters of Bahamas Banks produces new CDOM. Boss and Zaneveld[95] found that near-bottom concentrations of CDOM were higher over reef sediments than over adjacent sand sediments. The CDOM in the water column is concentrated by evaporation and the resulting high salinity, high CDOM water mass is carried into adjacent Exuma Sound where its fate varies diurnally.[96] During warm days, solar heating of the water mass can be sufficient to cause it to remain at the surface, where it is observed as high CDOM plumes in satellite ocean color images. During the night when cooler water temperatures prevail, the high CDOM plume sinks to intermediate depths in the sound, where it can persist as a subsurface maximum at the base of the mixed layer for distances of tens of kilometers. Intensified input of CDOM to local oligotrophic waters was observed following wind events. This study provides valuable insights into CDOM distribution in the oceans, specifically the formation of subsurface layers where density differences can impart stability and location below the surface imparts protection from photodegradation of chromophores. The CDOM also may protect corals from damaging UV radiation.[97]

CDOM is present in porewaters of other sediment types, and both humic-like and protein-like fluorophores have been detected using EEMS.[45,98−100] Diffusion, bio-irrigation and resuspension from organic-rich sediments may serve as a locally important source of CDOM.[80,98−100]

3.2. Sinks

Photobleaching is the dominant process for CDOM removal from natural waters,[101] with microbial decomposition of lesser importance.[102,103] Destruction of CDOM by exposure to sunlight releases compounds used for growth of organisms,[104] as well as nitrogen and trace metals, although the major product is dissolved inorganic carbon (see reviews by Moran and Zepp[105] and Mopper and Kieber[106]).

Significant loss of CDOM due to photobleaching has been shown for surface waters of the Mid-Atlantic Bight during summer stratification, along with an increase in S and decrease in a_{CDOM}/DOC ratios.[31] The study suggests that autochthonous CDOM is a minor portion of total CDOM and that CDOM sources and sinks are distinct from those of DOC.

Three recent studies have compared the relative importance of bacterial *versus* photochemical processes on CDOM composition and concentration. In a study of long-term fate of CDOM, Vahatalo and Wetzel[107] found that 96% of CDOM from freshwater was destroyed by solar radiation. Decomposition of CDOM in dark incubations took 70 times longer than during exposure to sunlight.

Obernosterer and Benner[108] compared long-term decomposition of phytoplankton cultures, lake water, and water

from a blackwater river from both photomineralization and bacterial mineralization. Both processes decreased a_{350} and DOC in the blackwater river and the lake samples, with an increase in spectral slope as well. Terrigenous DOM was more susceptible to photodegradation than biodegradation. The phytoplankton DOM showed a much higher susceptibility to biodegradation than did the other two sources of DOM. The phytoplankton DOM showed decrease in a_{350} from photomineralization, but DOC only decreased in response to biomineralization. All types of DOM had some component that was resistant to both photodegradation and biodegradation, varying from 20% for the terrestrial material to 65% for lake water. This finding may be partially explained by the constant exposure of surface water in the lake to both processes, allowing destruction of reactive DOM while resistant DOM slowly accumulates.

Stedmon and Markager[109] studied the composition of CDOM produced by phytoplankton in large bag experiments. They found that microbial activity both produced and destroyed fresh autochthonous DOM from algae. Norwegian fjord water was enriched with nitrogen and phosphorus to create a bloom. Some bags also received silicate to stimulate diatom growth. After 7 days, bags were forced into nutrient limitation. Seven unique components were produced, all of which were similar to those previously identified in natural water samples. Two of the components were protein-like, and five were humic-like. Subsequent photochemical and microbial degradation was somewhat dependent on phytoplankton nutrient status. The five humic fractions were produced by microbial degradation of phytoplankton DOM and were readily removed by photodegradation. Two protein-like fractions were produced during exponential growth of algae and were degraded both photochemically and microbially.

Taken as a whole, these studies suggest that CDOM production and degradation is not well-described by bulk optical properties, but rather the chromophore pools can respond differentially. Production by different types of animals appears to be compound specific and may also depend on source of carbon. CDOM source and history of exposure to sunlight may also influence results from photobleaching studies. More studies of processes on multiple CDOM components will be needed to explain apparent discrepancies in results.

Photobleaching of CDOM decreases absorption coefficients, permitting increased light penetration and increasing euphotic zone depths in the water column. Along with decreased absorbance, there is an increase in *S*, decrease in fluorescence intensity, and blue shift in position of fluorescence maxima. EEMs from blue water, open ocean surface waters of the central North Pacific and Indian Oceans, show total removal of the C humic-like peak.[44,43] Numerous spectra have also been collected from transitional waters where photobleaching was in progress but not yet complete.[24] Typical EEMs from various water types are shown in Figure 2, and excitation spectra are shown in Figure 4. Evidence that EEM fingerprints for oligotrophic surface waters are caused by photobleaching come indirectly from high temperature and salinity of samples, as well as from PCA analysis. What is striking about the partially bleached spectra is the change in shape of the emission spectra from Gaussian in fresh CDOM, both marine and riverine, to flat and pointed in photobleached samples. With increased age, fluorescence intensity continues to decrease and the maximum continues to shift toward shorter wavelength, until the peak position resides at Ex/Em = 275/305,375 nm.[33] This is consistent with what is known of the action spectrum for CDOM solar bleaching and spectral distribution of solar radiation at the surface of the ocean that only compounds absorbing below 300 nm could survive prolonged exposure in surface waters. The EEMs are also consistent with spectral alterations expected from light-induced reactions that reduce the extent of π-electron system of humics, elimination of functional groups, and reduction in molecular weight.

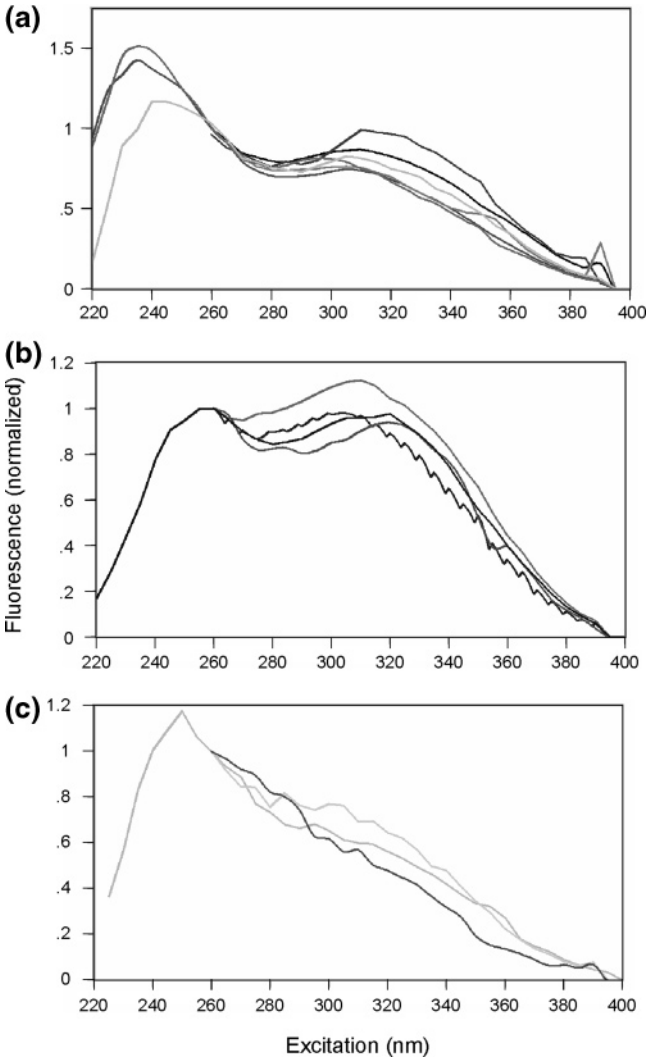

Figure 4. Normalized excitation spectra for samples from various environments showing effects of increased photobleaching from top (rivers) to bottom (oligotrophic ocean). Sample sites include (a) Amazon, Columbia, Suwanee, Hillsborough, Alafia, and Manatee Rivers, (b) coastal samples from the Gulf of Mexico, the Mississippi River plume, the Orinoco River plume, and the Arabian Sea, and (c) oligotrophic samples from the Gulf of Mexico, North Atlantic Ocean, and Arabian Sea.

3.3. Coastal Ocean

River plumes undergo dilution with seawater as they move away from the shore. However, the buoyancy of the plume and very high CDOM concentrations can contribute to persistence such that plumes from large rivers can be discernible many kilometers from the coast. Muller-Karger *et al.*[97] cite several examples where the influence of rivers on ocean color is visible in satellite imagery and has

application to the study of ocean circulation, assessment of terrestrial inputs to coral reef ecology, and other coastal management issues.

Hu *et al.*[14] described temporal patterns of Amazon and Orinoco River plume dispersal in the North Atlantic over a 5 year period using sea-viewing wide field-of view sensor (SeaWiFS) for ocean color data and salinity profiling autonomous Lagrangian current explorer (S-PALACE) floats that collected *in situ* hydrographic data. They were able to determine that low salinity patches observed as far as 2000 km away from the mouths of these rivers originated from river flow, not from coastal upwelling as had been previously proposed. The color signature of the plumes was dominated by CDOM, in contrast to oceanic waters adjacent to the plume where chlorophyll dominated ocean color. Maximum extent of the plumes was observed in July and showed a lag time of about 30 days after maximum discharge rate. In this region, CDOM was a better indicator of water of river origin than was chlorophyll. They also found that satellite detection of CDOM was useful for budgeting freshwater inputs from rivers and their areal extent, as well as in mass balance calculations for salt and carbon.

Under special conditions, even smaller rivers can impact oceanic regions. Kudela and Chavez[110] observed that during heavy El Nino rains in southern California, riverine CDOM spread up to 300 km offshore, not something seen in typical upwelling dominated years.

In a study of the highly industrialized Pearl River estuary, Hong *et al.*[111] observed that most of ocean color signature was due to CDOM, not chlorophyll. Furthermore, the protein-like peak dominated over humic-like peaks, which was interpreted as an indication that anthropogenic DOM makes a significant contribution to the carbon pool in this system. Callahan *et al.*[112] found conservative mixing of both CDOM and DOC in Pearl River Estuary; however the ratio of CDOM/DOC decreased with salinity, mostly due to loss of CDOM.

Arctic rivers have high concentrations of DOC, but few studies of CDOM have been done until recently. Terrestrial CDOM dominates the western Artic Ocean, which receives 10% of global river discharge.[113] In the Yukon River, DOC concentrations decreased from the time of ice breakup through summer, but CDOM/DOC increased during that same period.[114] This indicates that soil-derived carbon dominated the system during summer. One possible explanation is that extraction efficiencies of humic materials from soils were increased due to warm summer temperatures.

Amon *et al.*[115] used *in situ* fluorescence as a proxy for distribution and concentration of terrigenous DOM in Nordic Seas for the purpose of refining estimates of carbon export into Atlantic Ocean. They found that 20−50% of the annual river discharge is exported. They also observed a subsurface fluorescence maximum in the East Greenland Current and suggested that Asian rivers are the main source of signal. There was little alteration of fluorescent properties during multiyear transport of water across Arctic Basin from source rivers and likewise indiscernible evidence of photochemical alteration. Evidence of new marine production of CDOM was found in the appearance of protein-like fluorescence in marine samples from Greenland Sea and Fram Strait.

3.4. Open Ocean

Open ocean areas away from the influence of rivers and coastal waters have historically been under-sampled for CDOM. The surface waters of central ocean gyres have the lowest concentrations of CDOM due to the long residence time of water above the mixed layer and prolonged exposure to solar radiation. Concentrations of CDOM in these areas have been reported to be between 0.0684 and 0.1108 m^{-1} ($a_{325\ nm}$) on the NW Australian Shelf (Coble and Conmy, unpublished) and between 0.05 and 0.075 m^{-1} ($a_{325\ nm}$) for the North Atlantic.[116] Below the surface, CDOM increases monotonically with depth.[38,117−120] Values reported for deep-water in the North Atlantic ranged from 0.125 to 0.2 m^{-1}.[116]

Subsurface fluorescence maxima have been reported from the Pacific Ocean,[121,122] where association with nutrient maxima and apparent oxygen utilization minimum suggest remineralization as the source of CDOM. Depth profiles of CDOM (Ex/Em = 320−390/475−530) and flavin (Ex/Em = 450/525) fluorescence collected in the Black Sea, the world's largest anoxic basin, also showed DOM fluorescence increasing with depth, with a sharp increase below the base of the surface mixed layer and well below the depth of the chlorophyll maximum. Subsequent EEMS analysis of samples from the Black Sea confirmed the humic-like nature of the CDOM.[41] Since salinity increases with depth in the Black Sea, *in situ* production from organic matter decomposition rather than river input was the likely source of CDOM.

Early results using EEMs and a towed profiling system in the Arabian Sea showed that upwelling of subsurface waters is a source in these regions, as is remineralization of phytoplankton.[43] Results of long-term time series in the Sargasso Sea have shown seasonal patterns of CDOM distribution and concentration in the upper water column associated also with remineralization of the annual phytoplankton bloom.[91]

In an overview paper on results of bio-optical studies of the JGOFS (Joint Global Ocean Flux Studies) equatorial Pacific studies, Bricaud *et al.*[123] review past observations of oceanic CDOM. They point out the scarcity of open ocean CDOM measurements and that the relationship of CDOM to other bio-optical parameters is largely unknown. CDOM absorption contributes ~50% of total absorption at 440 nm in surface waters of the equatorial Pacific and 100% below the chlorophyll maximum. They conclude that there is a critical need for systematic measurements of CDOM to enhance bio-optical modeling efforts in the ocean and recommend that future survey efforts include CDOM absorption wavelengths for filtered and unfiltered sampling.

The first global maps of CDOM distribution using SEAWIFS published by Siegel *et al.*[8] showed seasonal and spatial variability in both CDOM concentration and relative contribution of CDOM to total nonwater absorbance at 440 nm. CDOM contributed 50% or more of nonwater absorbance over large areas of the Pacific Ocean in both winter and summer, despite extremely low CDOM concentrations of less than 0.01 m^{-1}. Two additional conclusions from this analysis were that (1) even though CDOM distributions mimicked chlorophyll distribution on the global basin scale, there was no statistically significant correlation, indicating that the two are decoupled and (2) terrestrial inputs of CDOM were not the primary factor determining global distributions.

Results from CLIVAR, the most extensive field study to date that included measurement of CDOM concentrations, are still in preparation, but preliminary results indicate that CDOM remineralization may be less important than water mass mixing and circulation in the North Atlantic Ocean.[116] Measurements of CDOM absorption coefficients on water

samples were also found to agree well with previous estimates from ocean color.

Despite low oceanic concentrations, satellite measurements of CDOM can be useful in studying circulation patterns in the open ocean. Hoge and Lyons[13] found that CDOM was up to ten times more effective in identifying eddies in Middle Atlantic Bight Region than was sea surface temperature data. Warm core rings and cold core rings showed only a 5% contrast relative to temperature of the surrounding water mass whereas elevated and depressed CDOM core rings showed 45−65% contrast. This CDOM signal is especially valuable for analysis of Gulf Stream eddies during the summer season when temperatures are high and contrast is low. They suggest using CDOM as general procedure to get a better view of physical dynamics of the surface ocean in other areas.

4. New Insights into the Dynamics of CDOM

The past 5 years have seen publication of results from several studies where high spatial or temporal resolution have advanced our understanding of CDOM dynamics. In addition to satellite ocean color observations, these include time-series results from the Bermuda Atlantic Time-series Study (BATS) site and repeated frequent field studies in the Gulf of Mexico. Increased spatial and temporal resolution has also been achieved using *in situ* towed profiling systems in the Mississippi Delta region and in a New England estuary. Last, multichannel instruments have provided increased spectral resolution that permits discrimination of CDOM sources and composition. These results are useful in a larger context for the insights provided on circulation in the coastal areas where the studies have been conducted.

4.1. Increased Spatial and Temporal Resolution

4.1.1. Sargasso Sea

One of the first studies to document the importance of CDOM in the open ocean came from the JGOFS BATS site, which is located 75 km south-east of Bermuda, near 31°50′ N, 64°10′ W. Cruises have been conducted approximately 16−20 times per year since October 1988, but optical observations using a profiling spectroradiometer did not begin until January 1992 as part of the Bermuda Bio-Optics Program (BBOP). Results from 2 years of observations, published by Siegel and Michaels in 1996,[124] showed for the first time that CDOM, or CDM, could play a significant role in light attenuation even in clear, open ocean waters. Furthermore, unlike previous assumptions of CDOM variability in this type of environment (case I waters), the study showed temporal and spatial variations in CDM that were significantly different from those of algal pigment concentrations. These observations were only made possible because of the repeated, long-term sampling program, and they caused the research community to reassess optical water mass classifications.

The Siegel and Michaels[124] conclusions were based on in-water estimates of attenuation coefficients and could not determine whether CDOM or CDM was responsible. A later study established that CDM did not make a significant contribution to light attenuation and that colored organic matter was predominantly in the dissolved fraction.[125] This study went on to propose that three processes were controlling CDOM distributions at BATS: photobleaching caused decreases in the surface layer during summer months, microbial decomposition of phytoplankton organic matter was responsible for the production of CDOM during spring and summer, and winter mixing removed stratification and homogenized concentrations prior to the start of a new cycle.

Again, the availability of a 2-year time series added validation to these hypotheses of a seasonal cycle for CDOM uncoupled from chlorophyll. Furthermore, the ongoing nature of BATS permitted subsequent hypotheses to be tested within the framework of well-studied system.

4.1.2. Gulf of Mexico

In the Gulf of Mexico, multiple projects to study CDOM over a 10 year period have provided the first generalized picture of the influence of terrestrial inputs in this large coastal sea. One of the world's largest rivers, the Mississippi, is a major contributor to the freshwater budget of the Gulf. The plume is visible from satellites as elevated Chl *a* concentrations,[126−128] but it also contains elevated concentrations of CDOM. The differences in composition of the rivers entering the Gulf of Mexico, including their organic matter components, are sufficient to permit source discrimination between rivers and between discharges of different age from the same river.

During the summer, especially in years of high rainfall and river discharge, fragments of the freshwater plume have been observed 1000−2000 km away from the source.[129] In extreme years, such as 1993 when river discharge reached a 63 year maximum, water from the Mississippi was observed to extend beyond the Florida Keys[130] and into the Gulf Stream off the east coast of Florida.[131] Discrete observations and ship surveys across these patches in the past have collected what appear to be anomalous values in the absence of satellite data.

One large discharge event occurred in 1998,[126] during a 3-year program to study the NE Gulf of Mexico (NEGOM). Field studies conducted quarterly covered the area between the 10 and 1000 m isobaths from the Mississippi River to Tampa Bay.[128] At the same time, the ecology of harmful algal blooms (ECOHAB) project was being conducted on the West Florida Shelf (WFS) between Tampa Bay and the Caloosahatchee River with monthly surveys to ∼150 km offshore.[127] Both projects collected underway data for chlorophyll and CDOM fluorescence, along with temperature and salinity. SeaWiFS ocean color imagery of Chl *a* concentrations (see Figure 3 in Del Castillo *et al.*[127] and Figure 5 in Hu *et al.*[128]) captured the development and areal extent of the plume, which was sampled by both field studies. The ratio at $a_{443\ nm}$ for CDOM/Chl *a* in flow-through data collected during the NEGOM cruise averaged 2.5:1.[132] The SeaWiFS imagery was not corrected for CDOM contamination; therefore, much of the ocean color signature in the figures cited above is due to CDOM, not chlorophyll. Additional evidence for identification of the Mississippi plume off the WFS came from CDOM/Chl *a* ratios, which were much lower in the plume than in plumes of local rivers, and from CDOM emission ratios collected using the multispectral SAFIre (spectral absorption and fluorescence instrument) fluorometer. Water in the Mississippi River plume had high ratios of long wavelength fluorescence (430/540 nm) and a lower ratio of short wavelength fluorescence (375/400 nm), both characteristic of freshwater CDOM and significantly different from adjacent Gulf of Mexico surface waters.[127]

A second event in the summer of 2004, captured by MODIS imagery, showed the presence of Mississippi River

plume water in the South Atlantic Bight off the coast of Georgia.[129] CDOM concentrations in the plume by the time it had reached the Florida Straits were less than predicted from salinity based on previous observations, and this was attributed to photobleaching in the estimated 1 month since the plume entered the Gulf of Mexico. This study highlights the potential longevity of surface manifestation of the Mississippi River when entrained in the Loop Current−Florida current−Gulf Stream system, as well as the influence of the Mississippi River throughout the region.

In addition to the CDOM/Chl *a* ratio, other parameters used to distinguish between riverine sources in the Gulf of Mexico include CDOM/salinity and CDOM/DOC. The most robust and well-documented is the CDOM/salinity relationship for the Mississippi River and rivers of the WFS region.[37,128,133] Figure 5 shows the FDOM to salinity relationship for samples collected over several years in the Gulf of Mexico. The slopes of regression lines vary from 1 to over 8, with highest values in the Shark River, which drains the Everglades. Fluorescence of CDOM in the Mississippi River endmember over several years remains constant at about 50 quinine sulfate equivalents (QSE).[37,81,134] High values for the Atchafalaya River, a distributary of the Mississippi, were observed in 2000, but values were similar to those of the Mississippi in 2001.[37] Values for the Mississippi River are low in comparison to the CDOM fluorescence of rivers on the WFS (Tampa Bay rivers, Peace, Caloosahatchee). These differences in CDOM/salinity are large enough to easily identify occasional intrusions of Mississippi River water in the region.

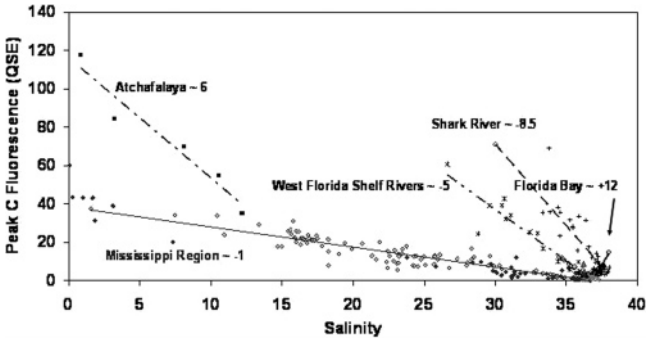

Figure 5. The relationship between CDOM fluorescence of peak C and salinity in the eastern Gulf of Mexico: (◇) Mississippi River; (■) Atchafalaya River in 2001; (∗) WFS rivers, (+) Shark River. Numbers following the river names indicate slopes of the linear regressions. Note that the mixing line for the southernmost section of the West Florida Shelf shows a steep positive slope due to evaporation combined with CDOM production.

Variability in the Chl *a*:CDM ratios presented in Del Castillo *et al.*[127] range from a high of 0.5 for Tampa Bay to 0.08 for the Mississippi plume in the WFS region. While helping in water mass identification, these results also highlight the difficulty in application of fixed algorithms for chlorophyll estimated from satellite images in the area.

The relationships between CDOM and DOC also show large differences between the Mississippi River and the rivers of the WFS. Although the Mississippi River has low fluorescence and relatively low DOC concentration at zero salinity near its mouth, it has a the most fluorescent DOC in the region, with the slope of the linear regression between 0.116 and 0.301 QSE/μM.[135,136] Maximum DOC values for rivers on the WFS range as high as 10 000 mM and maximum fluorescence values as high as 400 QSE have been measured, but FDOM/DOC regression slopes range from 0.080 to 0.005 QSE/μM.[136] An explanation for the differences in the relationship has not been proposed, but the difference itself is an additional factor for freshwater source discrimination.

Similar results for mixing relationships have also been reported south of the ECOHAB region on the southwest Florida shelf.[133] Fluorescence of CDOM showed a strong negative correlation with salinity and strong positive correlation with DOC and a_{300}. Chl *a* and pCO_2 also showed a strong negative correlation with salinity, indicating the influence of terrestrial inputs in the area. Distinct gradients in riverine concentrations of pCO_2 were found to aid in river source discrimination.

The fact that the Mississippi plume can be visible at large distances from its source implies a certain degree of conservative behavior of CDOM in the plume as it mixes with seawater. However, high-resolution studies have found evidence of transformation and small short-term variability in endmember concentrations. Chen *et al.*[134,135] used a towed continuous profiling system to provide high spatial resolution from surface to near bottom depths along sections on the Louisiana shelf. They identified high levels of CDOM in thin layers within the pycnocline off the mouth of the Mississippi River not correlated with elevated chlorophyll. The CDOM in these peaks showed no correlation with salinity and appeared to have been formed *in situ*. Three distinct CDOM/salinity mixing curves were identified for the same region in June 2000, suggesting variability in freshwater endmembers, perhaps as a function of season.[134,135] Although evidence of photobleaching and new biological production was found, physical mixing was the dominant process controlling CDOM concentrations.

During the same time period, Conmy *et al.*[37] analyzed CDOM fluorescence spectra and found seasonal and spatial variability in ratios of peak A and C as well as in the spectral shape of normalized fluorescence spectra. Fluorescence spectral properties were used to distinguish three water masses in the Louisiana Bight over the 2-year study period and to map distributions of different waters masses in the region. One of the water masses identified was marine with blue-shifted fluorescence and high A/C ratios (2.7−4.0), one was from the Mississippi River and Atchafalaya in 2000 with red-shifted fluorescence and low A/C ratios (1.7−1.8), and a third was from the Atchafalaya in 2001, which showed intermediate values of A/C and fluorescence peak position. Spatial distribution of these water masses agreed well with salinity distributions, providing independent confirmation of water sources. Differences in CDOM properties between the 2 years were attributed to differences in discharge rates, with 2000 being an extreme drought year. Examination of detailed fluorescence spectra indicated that differences between Mississippi and marine CDOM were due to photobleaching, not new production.

Several high CDOM features have been observed in the WFS region. Elevated CDOM concentrations on the WFS between the Everglades and the Florida Keys were first reported in 2002 and labeled "black water"[137−139] due to the appearance of the water being described as very dark by fishermen. These patches are also visible as dark areas in true color satellite imagery. The feature appears to be the result of local river discharge combined with a minimum in particle backscatter. Samples collected during these events,

which have recurred several times since 2002, fall on the historically observed CDOM/salinity mixing line (Figure 5).

The following year a dark water plume was observed in this same general region.[140] Satellite imagery indicated that the water contained bloom concentrations of the red-tide organism *Karenia brevis*. This bloom appeared to originate with nutrient input from high river discharge in the Charlotte Harbor, Florida, region following a period of high rainfall. As the plume aged and was carried toward the Dry Tortugas in the Florida Keys, CDOM concentrations became an increasingly larger percentage of the absorption, while chlorophyll and inorganic nutrients decreased to negligible levels. Additional observations of these dark water events are needed to understand their origin and relationship to nutrients, river discharge, water quality, harmful algal blooms, and other associated phenomena.

Last, two recent studies of the molecular mass of CDOM on the southwest Florida Shelf provide additional confirmation of strong terrestrial inputs. Molecular masses of CDOM measured by absorbance and fluorescence were compared in one study.[141] Higher molecular mass of CDOM was associated with increased freshwater flow on the SW Florida shelf. Fluorophores had consistently lower molecular mass than did chromophores in the same samples.

A second study used solid-phase extraction combined with ESI continuous flowing ion trap mass spectrometry (cf-MS) to study distribution in the same region.[142] This technique also showed decrease in molecular mass with increased salinity. They found that the best correlation between fluorescence and organic carbon was in the highly colored rivers draining the Florida Everglades. They also observed a bimodal distribution of molecular mass in all rivers studied.

4.1.3. Estuaries

The distribution of CDOM in estuaries has generally been observed to be conservative, with CDOM concentrations decreasing as salinity increases. This reflects the dominance of riverine CDOM in the system. Exceptions have been found and attributed to local production in saltmarshes and mud flats that fringe the estuary. Traditional sampling strategies often fail to convincingly demonstrate nonlinearity due to inadequate spatial or temporal resolution. Deployment of continuous underway systems can provide new insights into estuarine CDOM dynamics.

In one such study, Gardner *et al.*[143] collected profiles in a small New England estuary and found that freshwater endmember varied over time scales of hours (Figure 6). They also found that conservative mixing did not hold. In addition to variations in the freshwater endmember CDOM on a time scale of hours, there was also a source of CDOM in the mid estuary attributable to new production by marshes. This new production showed seasonal variability, with a maximum in late summer and no production in winter. More studies of the detailed seasonal and spatial dynamics of CDOM in estuaries would greatly enhance understanding of carbon exchange between terrestrial and marine systems.

4.2. Increased Spectral Resolution

Multispectral *in situ* fluorometers have been used to assess CDOM composition in several recent studies. Some examples of data and results from surface waters in the Gulf of Mexico region have been discussed above. In coastal waters off New England, Conmy *et al.*[144] collected a time series of depth profiles for Chl *a* and CDOM fluorescence

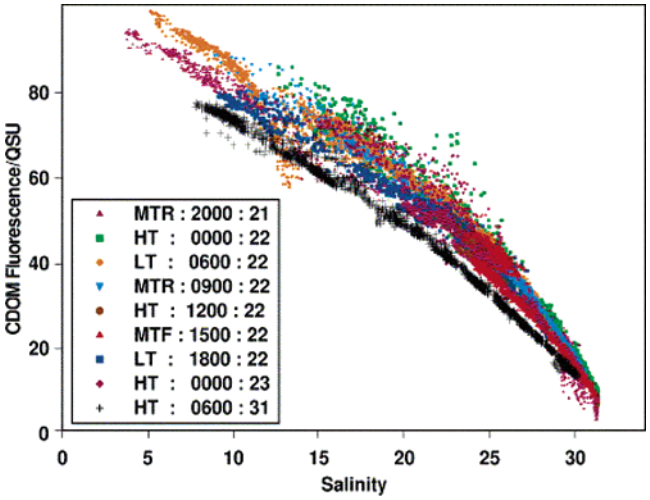

Figure 6. Distinct CDOM−salinity mixing curves from Neponset River Estuary collected over 2 days (colored) compared with one curve from data collected 1 week later (black). LT = low tide; MTR = mid-tide rising; HT = high tide; MTF = mid-tide falling. Reprinted from ref 143, Copyright 2005, with permission from Elsevier.

at six excitation wavelengths and eight emission wavelengths using the SAFIre. During the first 5 days of the 2-week study, CDOM concentrations were low, with blue-shifted humic-like fluorescence (higher emission ratio of 400:490 nm at excitation 265 nm) (Figure 7). These fluorescence properties

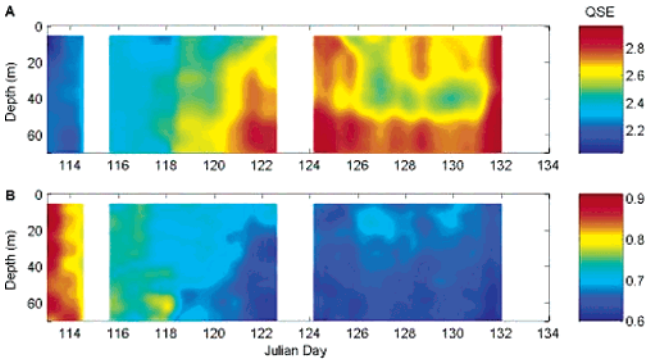

Figure 7. Time series of CDOM fluorescence (top) and CDOM emission ratio at 400:490 nm from excitation at 265 nm (bottom) collected in the coastal North Atlantic during the CM&O experiment. Reprinted from ref 144, Copyright 2004, with permission from Elsevier.

are typical of marine sources or of photobleached riverine CDOM. Surface temperatures increased and salinity decreased during the second half of the study. CDOM concentrations increased, and fluorescence maxima became more red-shifted, indicative of a freshwater source.

4.3. Improved Data Analysis Techniques

EEM spectroscopy is a powerful hyperspectral tool, but identification of peaks and their quantification is imprecise and subjective without more rigorous analysis. Multivariate analysis techniques that have been used to detect changes in CDOM using 2D and 3D fluorescence data[145,146] showed that both principal component analysis (PCA) and partial least-squares regression (PLS) were useful in distinguishing water mass origin in the Baltic Sea.

In a more comprehensive study, Boehme *et al.*[24] applied PCA to EEMs from a large dataset collected over a period of several years in the Gulf of Mexico between the Mississippi Delta and the Caloosahatchee River in Ft. Myers, FL. The presence of at least two different marine transitional endmembers were identified, one highly influenced by the Mississippi River and the other arising from West Florida Shelf waters. Photobleached samples were also distinguished from other water types.

Another perhaps more powerful tool is parallel factor analysis (PARAFAC), which has the capability to resolve EEMs into individual fluorescent groups and provide estimates of relative concentrations of each component. In the initial demonstration of the technique, Stedmon *et al.*[25] identified five components of bulk fluorescence, four of which were humic-like and the fifth appeared to be a combination of peak N, formerly associated with new marine production, and peak T, similar to tryptophan fluorescence. Unlike the previous scheme for peak identification, in which humic-like peaks generally displayed two excitation peaks, some of the components identified by PARAFAC were best modeled with a single excitation peak and preliminary evidence supported that all five components varied independently of each other.

In a subsequent study, Stedmon and Markager[109] identified eight fluorophore components in a watershed that included forested, agricultural, and wastewater environments. They found that water from agricultural sites showed strong similarity to marine samples, particularly with regard to blue-shifted fluorescence previously recognized from seawater samples.[43,45,147] The similarities between marine and agricultural CDOM fluorescence have previously been observed by Her[148] and may be more an indication of new biological production of CDOM than a distinction between freshwater and marine humics. Stedmon and Markager[149] went on to conduct an analysis of covariability among fluorescent components to determine which components have similar controlling factors. The two terrestrial humic components (1 and 2) were found to covary but had different production rates. Production rates were also found to vary seasonally in the lake outflow and estuary samples. Photodegradation during summer, when residence times were high, had a greater effect on component 2 than on component 1. The two protein-like fluorophores showed a constant association across all DOM types and also covaried with the humic- and fulvic-like components (1−4), suggesting that the tyrosine and tryptophan in these waters are linked to degradation of terrestrial CDOM. These two amino acid-like components have previously been thought to be produced autochthonously. This more recent study would suggest that in watersheds, biological or chemical processes producing protein-like fluorescence may depend on presence of an allochthonous precursor. Analysis of covariability between fluorescent components and environmental parameters identified for the first time that temperature influenced both concentration and composition of fluorophores.

Kowalczuk *et al.*[150] took the somewhat simpler approach for peak-fitting by integrating discrete areas within EEMs corresponding to fluorophores A, C, T, and M to determine relative concentrations in the Baltic Sea. They found a high correlation between a_{375} and total fluorescence, as well as between a_{375} and all individual peaks. Similar relationships were found for humic peaks, but peak T showed relatively lower intensities at high a_{375}, and the relative proportion of T/total fluorescence increased from 2% to 5% across the range of CDOM concentrations measured. The explanation of the increased importance of peak T from estuarine to marine environments seems to be its resistance to degradation rather than from new production by biological or photochemical processes, since there was no increase in the absolute value of T across salinity gradient. Fluorophore T may be more protected from sunlight since its absorbance maximum is below 300 nm.

5. CDOM versus Dissolved Organic Carbon (DOC)

The ease of measuring CDOM fluorescence has made it attractive as a proxy for DOC concentration, which is more difficult to measure and does not yet have an *in situ* measurement technique. However, reports in the literature of a positive correlation between these two properties appear to hold only in areas where mixing between rivers and seawater control distribution of both CDOM and DOC.[1] It is now thought that CDOM is a small fraction of the total DOC pool, partially based on the large intercept in plots of CDOM *versus* DOC (see Figure 7 in Blough *et al.*[151]), which are interpreted to signify an uncolored background concentration of DOC in ocean surface waters where all colored organic matter has been lost to photobleaching or microbial degradation. In open ocean areas or coastal areas away from terrestrial influence, a relationship is not generally observed (see Figure 8 in Nelson and Siegel[3]). Depth profiles show DOC concentrations highest at the surface, especially during high productivity. CDOM concentrations may be high following a burst in productivity, but over most of the open ocean CDOM is extremely low in surface waters due to photobleaching. Below the euphotic zone, CDOM concentrations generally increase, while DOC concentrations decrease.[152] The overall consensus is that the processes that produce and control these two pools of organic matter are decoupled over most of the ocean and the relationship between them is more likely to exhibit a negative than a positive correlation. Nevertheless, the strong, if variable, relationship in coastal waters is still highly valuable in studies of nearshore carbon cycling because of the ability of satellites to capture daily, synoptic distributions and because these are the regions of highest DOC concentrations.[4]

One interesting note on this subject is the variation in what measurement is used to determine CDOM concentrations when comparisons are made to DOC concentration. In the reviews cited above, the various parameters are normalized fluorescence from excitation at 355 nm,[1] absorption coefficient at 325 nm,[3] and absorption coefficient at 412 nm.[4] EEMS shows large changes in CDOM composition from freshwater to open ocean environments (Figures 1 and 4). Many studies have found strong correlation between fluorescence and absorbance of CDOM, but there has been no systematic assessment of which of these CDOM measurements should or does best correlate with DOC concentration. These procedural differences may, in fact, contribute to the disparity in literature reports of correlations. Absorbance at 254 nm is a generally accepted parameter for measurement of carbon-containing compounds in HPLC procedures; however historically this wavelength has not been used in the ocean because measurements in this part of the spectrum are impracticable for remote sensing applications. Certainly, given the range in fluorescence properties reported for CDOM, one might expect that the wavelength at which best

correlations are obtained might also vary with DOC composition. One recent paper does mention that a_{340} was the most optimal optical parameter for correlation with DOC concentration in the River Tyne catchment and estuary;[11] however absorbance measurements were not made at other wavelengths and the only other optical parameter measured was spectral fluorescence.

Figure 8 shows a comparison of correlations between DOC

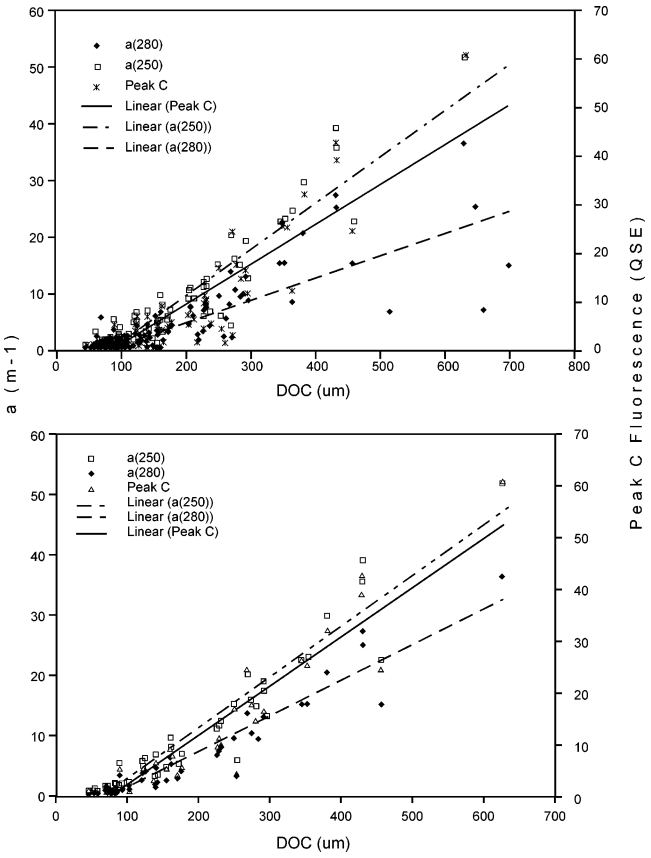

Figure 8. A comparison of the relationship between DOC concentration and CDOM optical properties for the WFS region during 2001: (a) compilation of five cruises during summer and fall; (b) data from the cruise in September, which showed highest correlations.

and several CDOM optical signals for data collected during several cruises to the WFS during summer and fall 2001. The best correlation was for the shortest wavelength absorption measured, at 250 nm, with a correlation coefficient of $r^2 = 0.8862$. The second was for a_{280} at $r^2 = 0.7909$. Third best was for fluorescence of peak C at $r^2 = 0.6944$. Absorption coefficients at longer wavelengths showed increasingly poor correlations. Also shown in Figure 8 are data from the cruise that had the highest correlations between DOC and CDOM optical parameters. These samples were collected on the southern end of the WFS during September 2001. The order from best to worst correlation was unchanged with $r^2 = 0.9259$, 0.9152, and 0.9034, respectively. These data show some seasonal variability, in this case most likely due to changes in river discharge rates; however the analysis also illustrates the value of further investigation of relationships between DOC and the full range of CDOM optical properties rather than using a single, arbitrary parameter. The ideal solution would be some compromise between meaningful optical information pertaining to DOC and practical considerations of what is possible via satellite sensors.

6. Unresolved Questions and Future Directions

This review presents many significant advances in CDOM research over the past few years; however there are still unresolved questions and unmet capabilities that need attention in the coming years. It is clear that implementation of new observing systems including new ocean color sensors and ocean observing systems (e.g., ORION, IOOS) will drive much of the future collection of data. Therefore, the pace at which CDOM research advances will be very much contingent upon our ability to improve sensitivity and specificity of sensors deployable on these platforms.

The second area for future research involves further development of some of the derived parameters of interest for global studies. Some of these products include photooxidation potential, which determines rate of production of photoproducts and CDOM degradation rates, optical measurement of DOC concentration, and CDOM mass-specific absorption coefficient.

Last, improvements are needed in linking spectral characterization to chemical characterization. Unique spectral signatures for rivers, upwelling, and biological production would go a long way toward permitting estimates of DOC production rates and rates of CDOM transformation.

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