9-7-2007

Colored Dissolved Organic Matter (CDOM) Workshop summary

Catherine A. Corbett
Charlotte Harbor National Estuary Program.

COLORED DISSOLVED ORGANIC MATTER (CDOM)

WORKSHOP SUMMARY

September 7, 2007 DRAFT

Hosted by the
Charlotte Harbor National Estuary Program

CHARLOTTE HARBOR
National Estuary Program

This document was written by Catherine A. Corbett, Charlotte Harbor National Estuary Program. Much of the text was taken directly from presentations and double-checked by presenters. Any errors or omissions are solely the responsibility of Catherine A. Corbett.

Acknowledgements

The Charlotte Harbor National Estuary Program would like to acknowledge the following individuals for their contributions to this workshop:

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Heidi Recksiek from the NOAA Coastal Services Center and the many presenters and participants without whom this workshop could not be successful.

Sponsorship for this workshop was essential for its success and in bringing researchers and managers together to discuss this important and timely topic. Accordingly, we thank the NOAA Coastal Services Center, Sanibel-Captiva Conservation Foundation, Estero Bay Buddies, Tampa Bay Estuary Program and Friends of the Charlotte Harbor Aquatic Preserves.

The Charlotte Harbor National Estuary Program is a partnership of citizens, elected officials, resource managers and commercial and recreational resource users working to improve the water quality and ecological integrity of the greater Charlotte Harbor watershed. A cooperative decision-making process is used within the program to address diverse resource management concerns in the 4,400 square mile study area. Many of these partners also financially support the Program, which, in turn, affords the Program opportunities to fund projects such as this. The entities that have financially supported the program include the following: U.S. Environmental Protection Agency; Southwest Florida Water Management District; South Florida Water Management District; Florida Department of Environmental Protection; Florida Coastal Zone Management Program; Peace River/Manasota Regional Water Supply Authority; Polk, Sarasota, Manatee, Lee, Charlotte, DeSoto and Hardee Counties; the Cities of Sanibel, Cape Coral, Fort Myers, Punta Gorda, North Port, Venice and Fort Myers Beach and the Southwest Florida Regional Planning Council.

Table of Contents

List of Acronyms and Abbreviations

a	absorption/absorption coefficient
C	Carbon
CDOM	Colored Dissolved Organic Matter
Chl	Chlorophyll
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CU	Copper
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
EEMS	Excitation-emission Matrix Spectroscopy
EMC	Event Mean Concentration
Fe	Iron
HAB	Harmful Algal Bloom
IOP	Inherent optical property
Kd or K	Light Extinction Coefficient
MAA	Mycosporine Amino Acid
N	Nitrogen
NEP	National Estuary Program
O_2	Oxygen gas
P	Phosphorous
PAR	Photosynthetically Active Radiation
PCU	Platinum Cobalt Units
POC	Particulate Organic Carbon
POM	Particulate Organic Matter
S	Spectral Slope
SFWMD	South Florida Water Management District
SWFWMD	Southwest Florida Water Management District
TOC	Total Organic Carbon
TOM	Total Organic Matter
TSM	Total Suspended Matter
UV	Ultraviolet
UVR	Ultraviolet radiation
v	frequency
λ	wavelength
$C_6H_{12}O_6$	Sugar

Executive Summary

Dissolved organic matter (or DOM) is the largest reservoir of organic carbon in the aquatic environment. Colored DOM (or CDOM) contributes to light absorption and may also fuel bacterial respiration while carrying large quantities of carbon, nitrogen, and phosphorous to estuaries, thereby indirectly contributing to eutrophication. In Charlotte Harbor, Florida, CDOM can account for the majority of light attenuation in the water column in some instances. CDOM is a key component of the Charlotte Harbor National Estuary Program (NEP) numeric water clarity targets along with turbidity and chlorophyll *a*; however, CDOM concentration and composition dynamics are not well understood. The Charlotte Harbor NEP hosted a 2-day technical exchange workshop on CDOM as an imperative first step in implementation of the program's numeric water quality targets to initiate a dialogue with local researchers and resource managers on the importance of CDOM dynamics and the roles it plays in estuaries.

The workshop was well-attended with over 70 participants each day and very informative to participants and Charlotte Harbor NEP staff. The workshop generated multiple conclusions that will affect research and monitoring in the Charlotte Harbor region in the future. First, the workshop participants agreed that CDOM composition variability is very important to better understand because it can affect seagrass and other benthic communities. Gathering CDOM composition as well as more robust concentration data can have implications for resource management and should be added to on-going local research and monitoring as soon as resources allow. The quality of light reaching seagrass communities is important and has been overlooked in the past. Lack of specific wavelengths of light energy may be the reason in some instances that seagrass restoration or maintenance activities have not been successful; thus, photosynthetically useful radiation should be added to on-going monitoring programs. In situ equipment with augmented discrete sampling are potential inexpensive methods in which to accomplish this objective. Previous literature and existing data may provide initial information to guide future research and monitoring. Researchers can start by first developing rough relationships with rainfall, flow, landuse, etc. and CDOM spectral characteristics.

Second, results from analyses of current CDOM data (i.e., color or PCU) demonstrate that CDOM concentrations are in general positively associated with flow up to the point in which a "washing out" effect occurs. Therefore, hydrologic alterations that increase flow, such as increased rainfall, will increase CDOM concentrations up to a point.

Third, a better understanding of the spatial-temporal variability of CDOM concentration and composition is needed before resource managers and others try to manage it. Managers need to be able to predict results from management strategies and activities for these strategies to be successful. Managers and researchers do not currently well understand nor are we studying CDOM sufficiently to be able to understand or predict changes or tie to landuse and management activities. Since agencies need to tie monitoring and research activities to resource management, we can tie CDOM research and monitoring to the spectral needs of seagrass in Charlotte Harbor to gain management agency support for research. The quality of light and spectral needs of seagrass is important for long-term seagrass preservation.

A CDOM working group should be created to coordinate research and monitoring as well as data sharing and the Charlotte Harbor NEP would be the appropriate entity to facilitate the working group. This working group can be part of the Charlotte Harbor NEP Water Quality Targets Working Group and could facilitate the creation of a centralized data depository to aid in better data sharing.

Introduction

Dissolved organic matter (or DOM) is the largest reservoir of organic carbon in the aquatic environment. Colored DOM (or CDOM) contributes to light absorption and may also fuel bacterial respiration while carrying large quantities of carbon, nitrogen, and phosphorous to estuaries, thereby indirectly contributing to eutrophication. In a recent article in *Estuaries and Coasts*, a study found that in one Danish estuary, landuse was found to have significant impacts on the quality and quantity of dissolved organic matter loadings to receiving waters (See Stedmon et al. 2006). Forested subbasins of the watershed contributed significant dissolved organic matter throughout the year, but especially during the rainy season. Areas characterized by agricultural landuse contributed a smaller, more constant flow of dissolved organic matter to the estuary throughout the year. The study found that while forested lands provide more dissolved organic matter than agriculture, the nutrients bound in this material may be less bio-available than those from agricultural lands. In Charlotte Harbor, Florida, CDOM can account for 13-66% of light attenuation in the water column (McPherson and Miller 1987; McPherson and Miller 1994; Dixon and Kirkpatrick 1999). CDOM is a key component of the Charlotte Harbor NEP numeric water clarity targets along with turbidity and chlorophyll *a*; however, CDOM concentration and composition dynamics are not well understood. The Charlotte Harbor NEP hosted a 2-day technical exchange workshop on CDOM as an imperative first step in implementation of the program's numeric water quality targets to initiate a dialogue with local researchers and resource managers on the importance of CDOM dynamics and the roles it plays in estuaries.

Analyses by PBS&J for the Florida Department of Environmental Protection on the Peace River Cumulative Impact Assessment found that CDOM concentrations in the Peace River have increased (2007). The study speculates that apparent increases in CDOM in the upper and middle Peace River are associated with declines in ground water discharges by mining and local springs while those in the lower river and upper Charlotte Harbor estuary correspond with increases in wet-season flow. Analyses by South Florida Water Management District (SFWMD) staff have found increases in CDOM concentrations in the Caloosahatchee River in the 1999-2003 period versus the 1985-1989 period (Doering et al. 2005). Thus, it is apparent that CDOM concentrations within the Charlotte Harbor watershed may be changing. One major goal of the Charlotte Harbor NEP for the workshop was to determine the causes of these changes and if the causes are a result of landuse changes or other anthropogenic impacts. Another goal of the workshop was to determine if the composition of CDOM and the quality of light reaching seagrass has changed also or if data exist to address this goal.

To this end, the Charlotte Harbor National Estuary Program hosted the technical exchange workshop to discuss and gain a better understanding of CDOM dynamics in the Lemon Bay, Charlotte Harbor and Estero Bay watersheds. The Charlotte Harbor NEP seeked to address the following at this workshop:

1. Can CDOM measurement methods help us better understand sources and sinks of CDOM? The composition of CDOM? Spatial and temporal variability in the composition of CDOM? The quality and quantity of subsurface irradiance in the region?

2. How do the current monitoring protocols in southwest Florida compare to other regions? Should the protocols in Charlotte Harbor be changed? If so, how?

3. Are CDOM concentrations changing in the region? If so, why?

4. How can we better understand, document and predict the causes of these changes?

5. What are the spatial-temporal chemical components of CDOM in the Charlotte Harbor region? Can we obtain this information using existing data or do we need specific research project(s) or monitoring programs to obtain this information? Could this information be used to develop management decisions aimed at protecting aquatic resources? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.

6. Can landuse models be improved to better estimate CDOM "event mean concentrations" (EMCs)? Would this analyte be an important addition to models for resource management in the southwest Florida region? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.

7. Should agencies be collecting additional information to better understand CDOM dynamics and landuse impacts on CDOM concentrations and composition? For landuse models? To quality of light reaching seagrass beds and impacting primary productivity? Can this information be added to current monitoring programs? If specific studies/new instrumentation are needed, brief description of these needs…

8. Can or should we add CDOM to our management strategies? How? Can we add "quality of light" to our water quality targets?

9. How do we better coordinate research and monitoring in the region? Can regional data be better managed and shared and on-going projects better coordinated?

This document attempts to summarize the major points from the workshop presentations and resulting discussions. The workshop was segmented into a series of sessions, each of which included a subset of the questions listed above for the participants and presenters to discuss. The workshop agenda and presentations are available from the Charlotte Harbor NEP.

Presentations

INTRODUCTION

COLORED DISSOLVED ORGANIC MATTER WORKSHOP INTRODUCTION

Catherine Corbett, Charlotte Harbor National Estuary Program

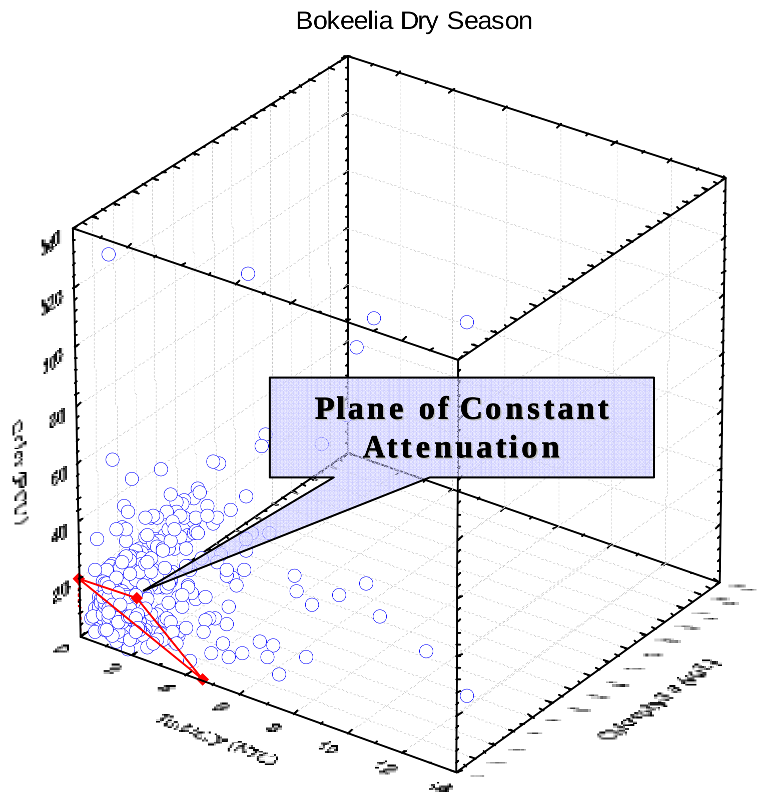
There has been rapid population increase and urbanization in the Charlotte Harbor watershed in recent past, and this trend is expected to continue. Water quality in some areas of the Charlotte Harbor region is degrading, and there is reason for concern for the long-term maintenance of essential fish habitat in region. Turner et al. (2006) found that seasonal hypoxia conditions in bottom waters of upper Charlotte Harbor started ca. 1950s. In 1980s FDNR reported Caloosahatchee reached nutrient loading limits (cited in Corbett et al. 2005). Seasonal chlorophyll *a* levels > 60-80 μg/l in the tidal Peace since monitoring began in 1976, while seasonal chlorophyll *a* levels > 20μg/l consistently observed in the tidal Peace and Myakka (cited in Corbett et al. 2005). These conditions are considered indicative of eutrophic to hypereutrophic conditions in some estuarine water quality classification systems (e.g., NOAA). In addition, multiple basins in the Charlotte Harbor watershed are impaired for nutrients and dissolved oxygen. Resource managers need to create scientifically defensible methods to stop the declining trends and protect the Charlotte Harbor watershed for future generations.

There are several methods in which resource managers may determine numeric water quality targets. These include amongst others accepting water quality standards or regulations as targets; establishing a baseline or historic conditions to which conditions should be maintained or restored; identifying an appropriate reference site and accepting its water quality conditions as a target or developing resource-based targets using the requirements of relevant living resources. In the Tampa Bay area, resource managers established the goal of restoring seagrass coverage to 95% of 1950's level, resulting in a restoration target of 12,350 more acres of seagrass. Water clarity in Tampa Bay is related to phytoplankton levels and chlorophyll *a* concentrations, and the focus of restoring 1950's level seagrass coverage is to reduce nitrogen loading to the bay. Reductions in nitrogen loadings from point sources resulted in a reduction in nitrogen loading and an increase in seagrass coverage between 1982-1996. Resource Managers in southern Indian River Lagoon have also established resource-based water quality targets using seagrass depth distribution to set water quality targets for salinity, color, turbidity, dissolved oxygen, pH and photosynthetically active radiation (PAR).

Components of Light Attenuation in Water Column:

$Kd = K_{Color} + K_{NaSS} + K_{chl\ a} + K_{water}$	**(Kirk 1983)**
$Kd = 0.014*color + 0.062*turbidity + 0.049*Chl\ a + 0.30$	**(McPherson and Miller 1994)**

To offset impacts from future development and maintain/restore water quality, the Charlotte Harbor NEP has used an optical model to establish numeric water quality targets for CDOM, turbidity and chlorophyll *a* specific to each estuarine segment that encompasses the greater Charlotte Harbor estuarine complex including Lemon and Estero Bays. The NEP determined percent-light-at-depth targets required to achieve seagrass maximum depth distribution in each segment and then applied an optical model which describes total light attenuation as the sum of three partial light attenuation components: CDOM, chlorophyll *a* and non-algal suspended solids.



This allowed us to back-calculate the contribution to total light attenuation by each component in terms of concentration intercepts (e.g. µg/L chlorophyll). Finally, seasonal water quality data for each estuary segment were plotted with the intercepts overlaid, producing a plane of constant attenuation given our percent-light-at-depth goal. Water quality data points located outside of the plane of constant attenuation identify times and locations when water quality did not meet NEP goals for that estuary segment. This plane allows the concentration for each component to assume any concentration between zero and its intercept; its value dependent on the concentrations of the other 2 components. These water quality targets will be used by resource managers and NEP partners to hold the line on water quality in the greater Charlotte Harbor estuary, especially those parameters influencing water clarity and seagrass coverage.

To implement these targets, the program and its partners will need to determine exceedance criteria for the optical model approach. The NEP proposes to manage for anthropogenically derived chlorophyll *a* and turbidity and to better understand landuse, climate and management impacts on CDOM as well as CDOM's impact on primary productivity, hypoxia and nutrient bioavailability. This workshop on CDOM is an imperative first step in that better understanding of CDOM and the implementation of the NEP water quality targets.

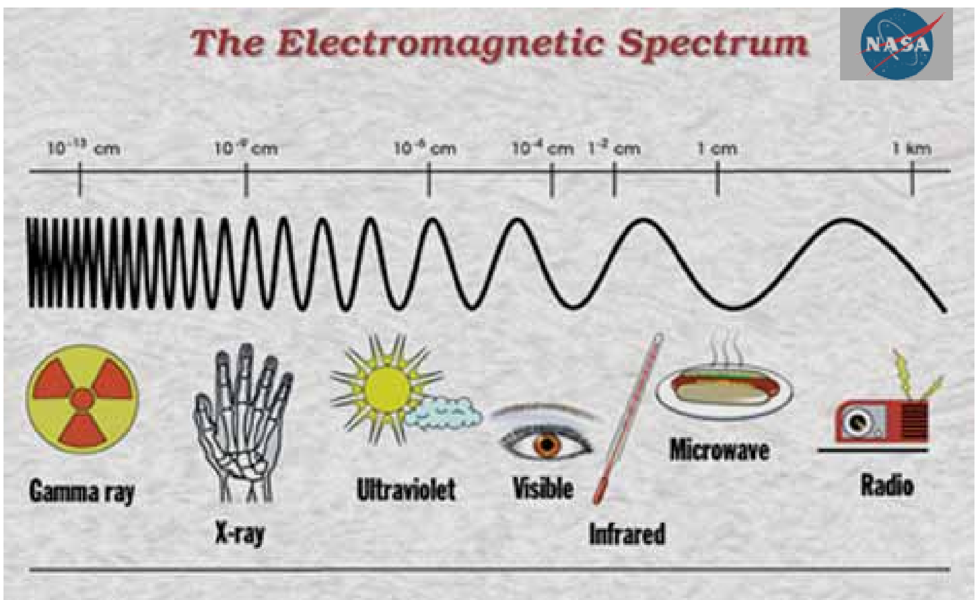
PHYSICAL PROPERTIES OF LIGHT IN THE WATER COLUMN

Chris Anastasiou, Florida Department of Environmental Protection

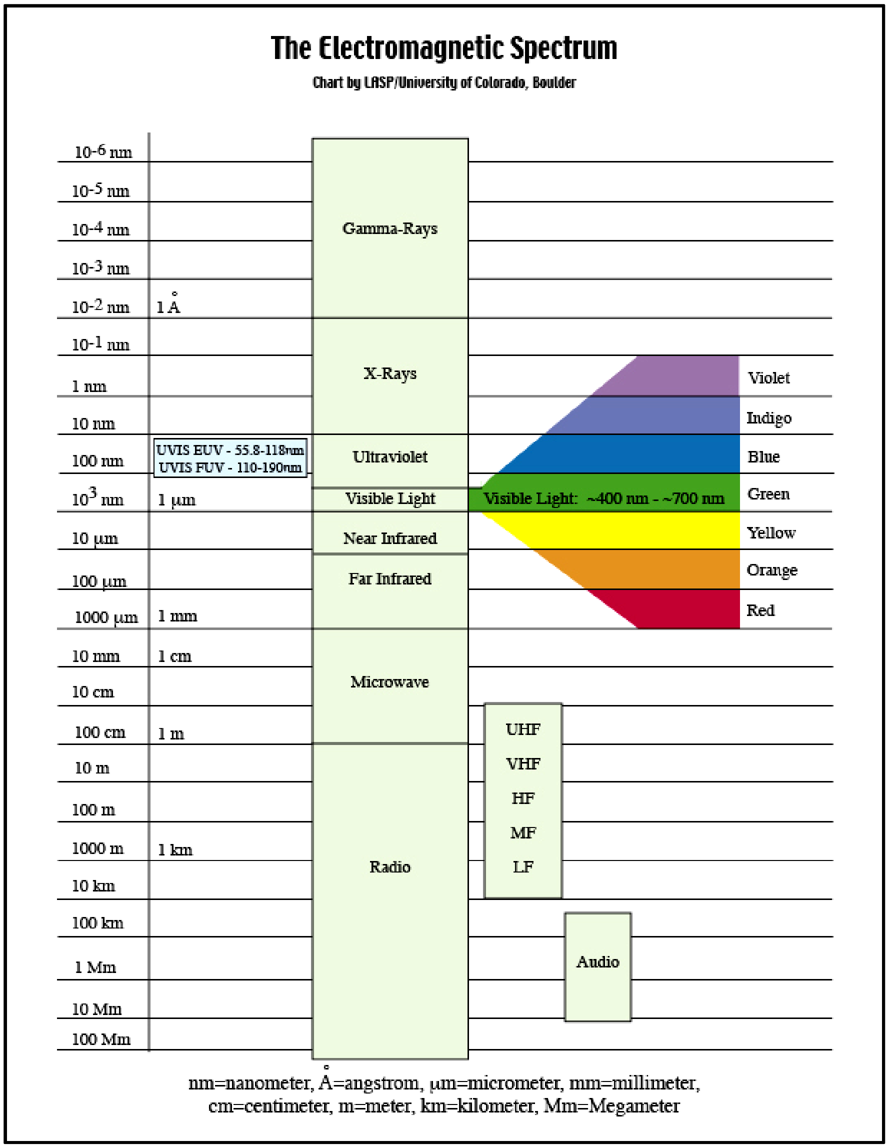
Light is unique in that it exhibits characteristics of both waves and particles. A photon is the fundamental "particle" of light. Every photon has a frequency (v) and a wavelength (λ):

$$\lambda = c/v$$

In the full summer sun 1.0 m^2 of a horizontal surface receives approximately 10^{21} quanta s^{-1} of visible light. The visible portion of the electromagenetic spectrum is very narrow (approx. 300nm – 800nm). With respect to human sight and plant photosynthesis, this is where the "action" is.

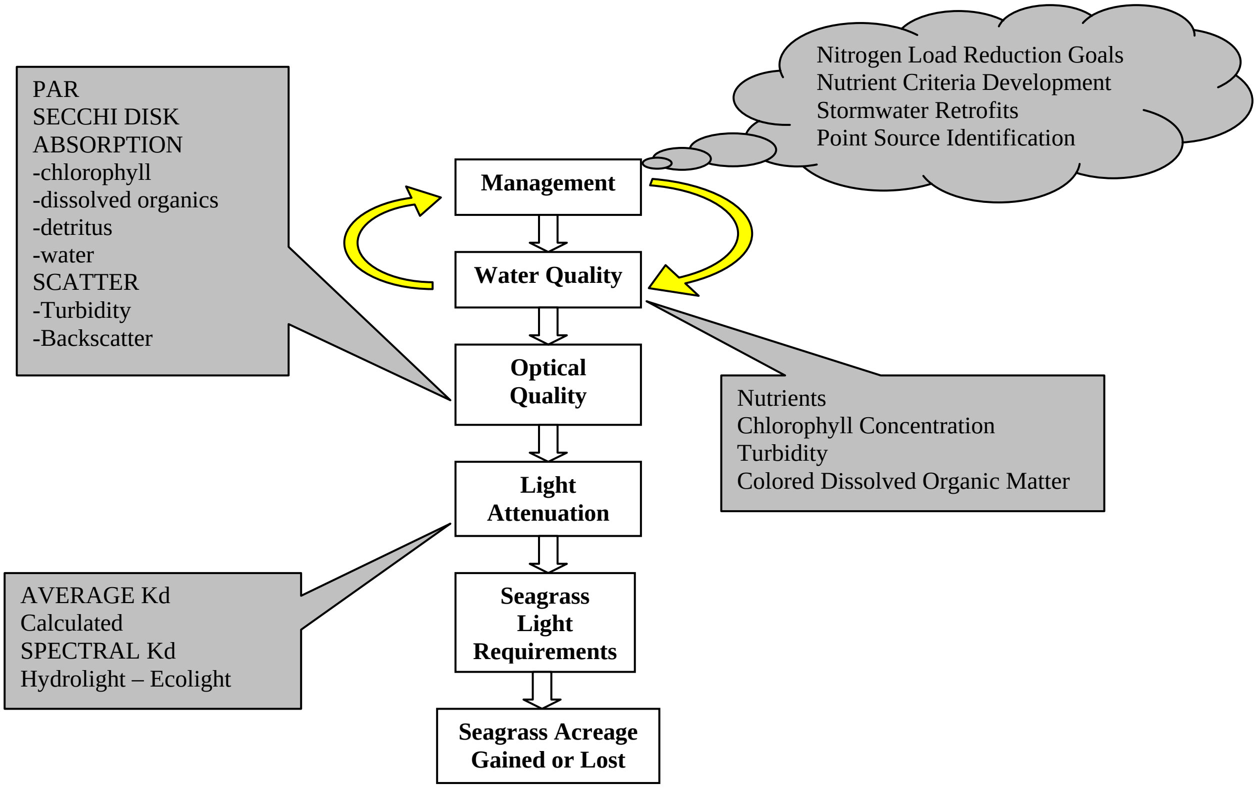


(provided by C. Anastasiou)



(provided by C. Anastasiou)

When light penetrates the water column, it can be either absorbed or scattered. Light attenuation is the loss of light with depth and is used to set minimum light requirements and maximum depth targets for managing seagrass sustainability and restoration. Water quality has direct impact on the quantity and quality of light penetrating the water column and reaching benthic habitat. Water quality in the context of light attenuation is related to chlorophyll, turbidity and CDOM. Understanding the relationship between these 3 parameters and light attenuation in the water column will have direct implications on the types of management strategies implemented to sustain healthy seagrass populations.

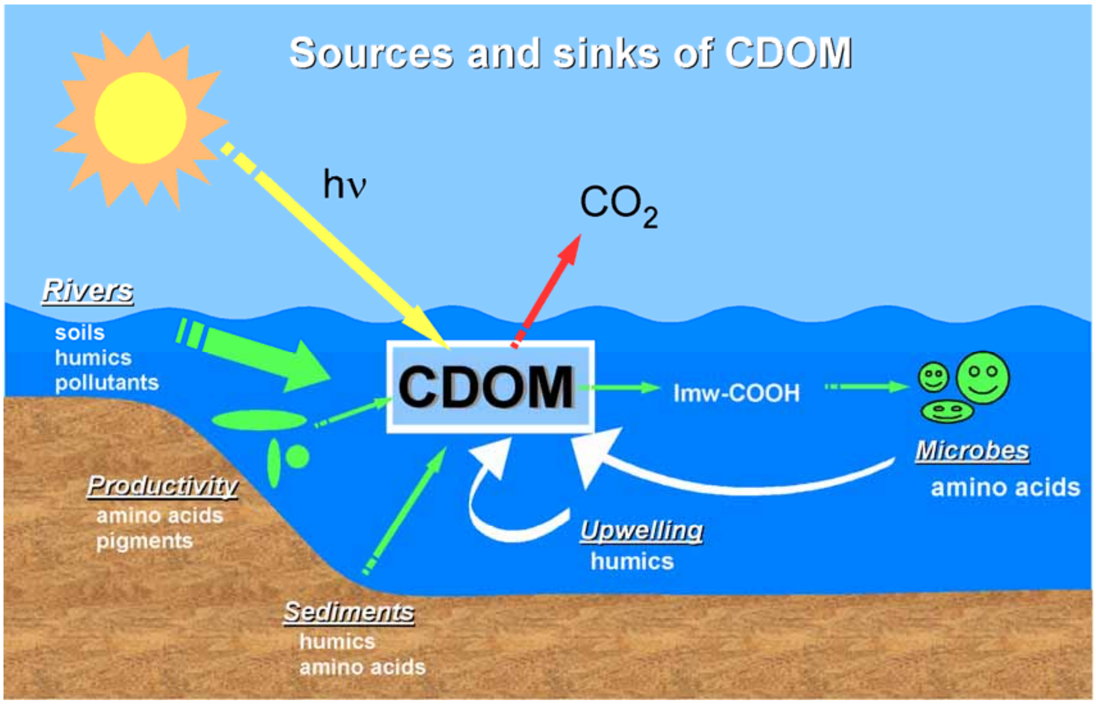


(provided by C. Anastasiou)

CDOM 101: Overview of Sources and Sinks, Spectral Properties and Measurements of CDOM

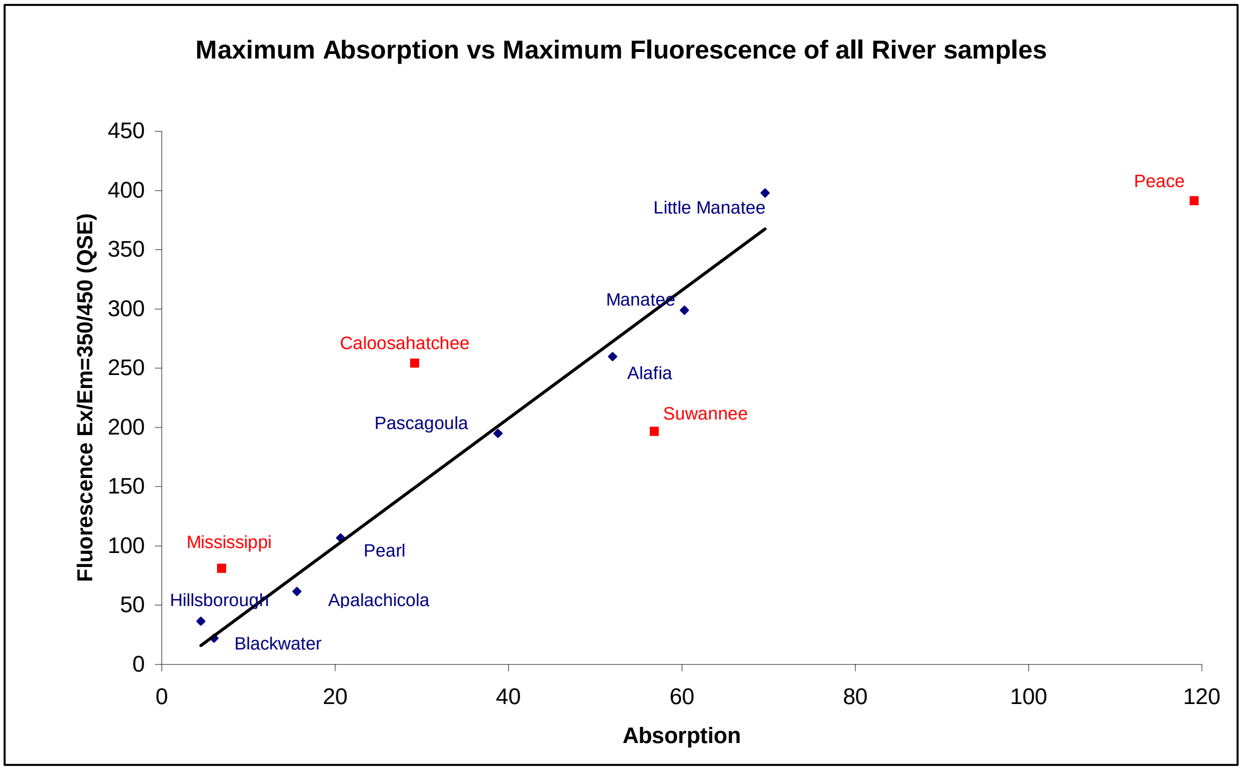
Paula Coble, University of South Florida

CDOM, is operationally defined as the component of total DOM that absorbs light over a broad range of visible (blue light) and UV wavelengths and is that part of the particle continuum within some pre-determined minimal diameter. Organic matter means that the material contains both carbon and hydrogen and is of biological origin. The term covers thousands of compounds. The chemical composition, origin, and dynamics of CDOM in aquatic systems are still poorly understood, namely in that the number and complexity of components that comprise organic matter is large and diverse as is the biological, physical, and chemical environment in which it is produced, transported and transformed. Sources of CDOM include rivers and groundwater, which carry CDOM primarily from soils, but coastal waters can also contain plankton and vascular aquatic plant-derived CDOM produced in rivers and estuaries. Other sources include anthropogenic compounds in runoff, sewage discharge and other effluents such as hydrocarbons and agricultural waste. Production by mangroves, seagrasses, marshes and tidal flats can be important on a small scale. In nearshore areas with strong river influence, mixing is the major factor controlling CDOM distribution, and an inverse linear relationship between CDOM and salinity is often observed. While other processes are impacting CDOM concentrations, physical factors dominate over the time scale of CDOM lifetimes within coastal waters. In the open ocean environment, however, *in situ* production is the primary source of CDOM. A number of studies have found that the lower trophic levels (primary producers, grazers, viruses, and bacteria) are important in production of CDOM in oceans, and in many locations CDOM is positively correlated with chlorophyll. Photobleaching is the dominant process for CDOM breakdown with microbial decomposition of lesser importance. Photodegradation from exposure to sunlight releases compounds used for growth of organisms, nitrogen and trace metals, although the major product is dissolved inorganic carbon.



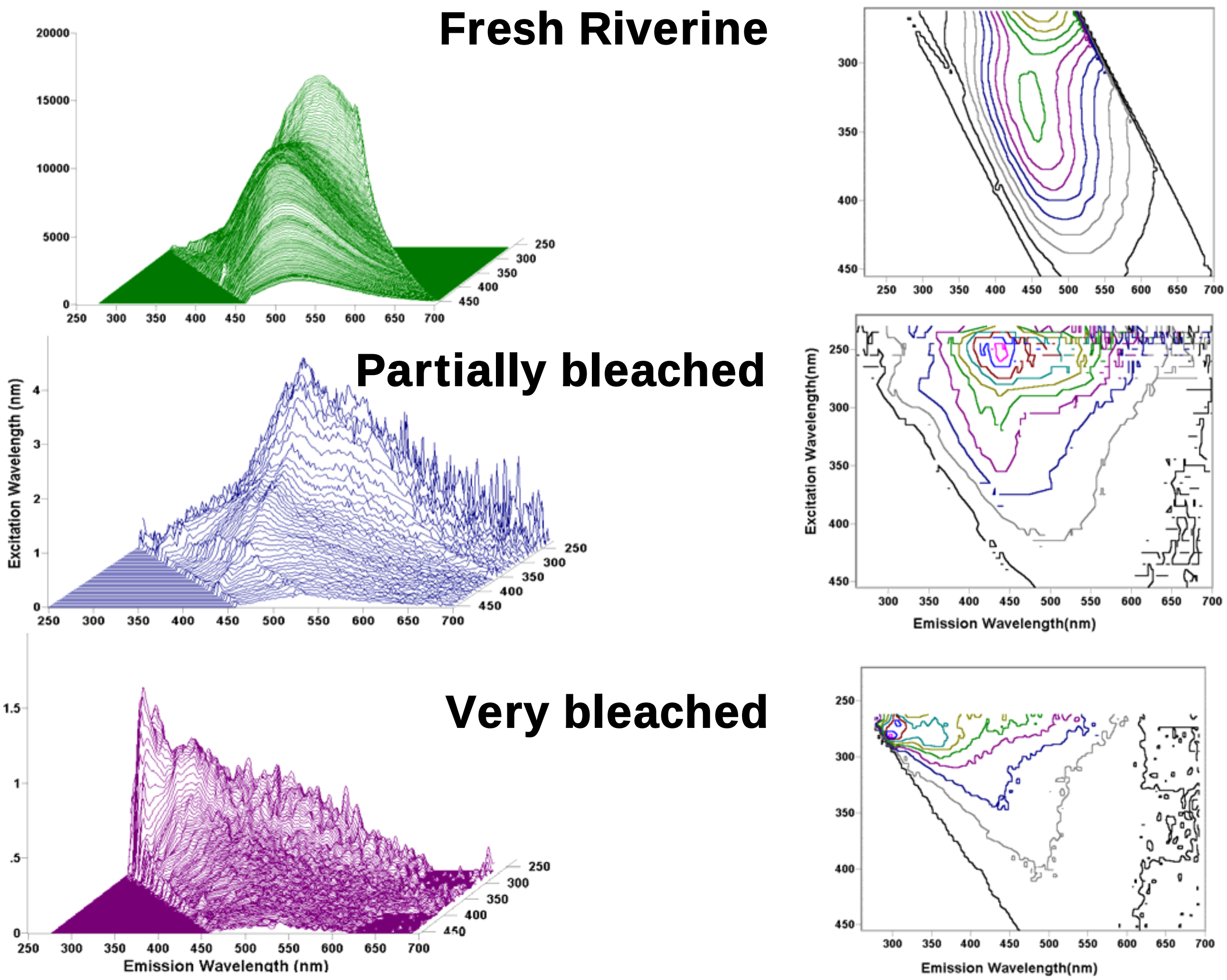
(provided by P. Coble)

CDOM can have different spectral properties depending on its origin. Both terrestrial and marine-derived CDOM have absorbance spectra that decrease exponentially toward longer wavelengths with no peaks; this lack of peaks supports the fact that CDOM is a complex mixture of compounds that have overlapping absorption spectra. The spectral slope of CDOM is often used to characterize CDOM composition and is an exponential function of the absorption coefficient versus wavelength. Differences in spectral slope can indicate the origin of CDOM. In general, lower spectral slopes indicate an origin of freshwater and coastal environments, and longer slopes indicate an origin within the marine environment. In addition, the absorbance spectrum of CDOM overlaps that of chlorophyll and can account for over 50% of the total absorption at 443 nm, the wavelength at which chlorophyll concentrations are most often measured. CDOM absorption can be several times that of chlorophyll.



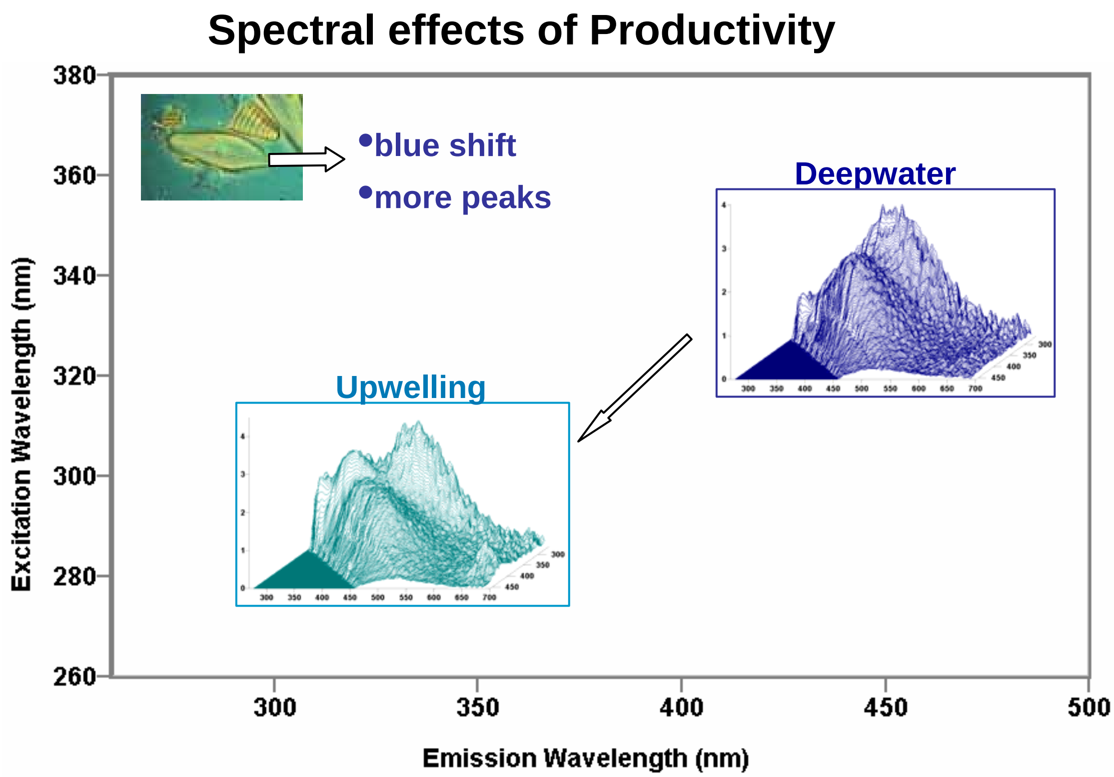
(provided by P. Coble)

Some CDOM is fluorescent, and fluorescence techniques have become important in measuring and understanding CDOM composition dynamics. Fluorescence techniques are more sensitive than absorption methods, and both excitation and emission spectra show greater detail and provide more information on chemical composition than do absorbance spectra. Excitation-emission matrix spectroscopy (EEMS) involves the collection of multiple emission spectra at a range of excitations that are then concatenated into a matrix. EEMS allows one to determine the source of CDOM based on which fluorophores are present and their relative concentrations. Terrestrial humics display excitation and emission maxima at longer wavelengths than do marine humics.



(provided by P. Coble)

EEMS also provides information on changes in CDOM resulting from mixing, biological degradation, biological production and photobleaching. 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. In coastal waters with salinities between 30 and 36 ppt, CDOM exhibits a shift toward the shorter wavelength excitation and emission maxima (blue-shift) of marine humics, and a similar blue shift in peak position can also be caused by photodegradation. Biological processes can result in production of new peaks during bloom periods. Several of these peaks have also been observed in wastewater and in streams receiving agricultural waste.



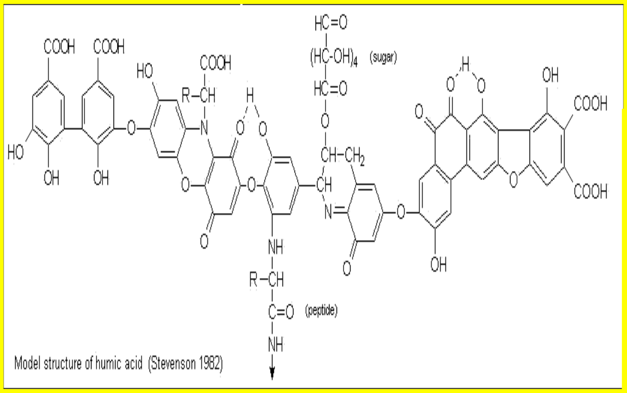
(provided by P. Coble)

While CDOM can have a large impact on photosynthetically active radiation and is therefore an important parameter in primary productivity, high concentrations of CDOM are important in protecting corals and other light-sensitive organisms from UV radiation.

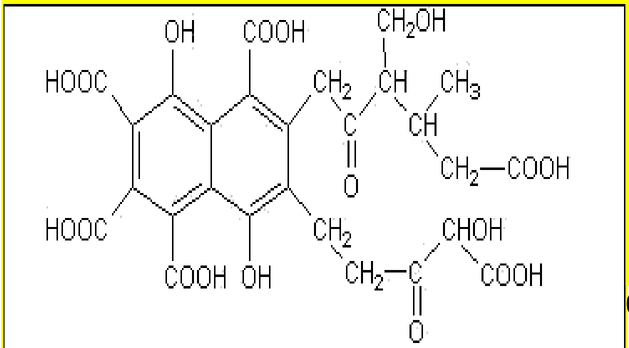
CDOM 102: GENERAL OVERVIEW OF CDOM CHEMISTRY AND METHODS OF BREAKDOWN

Chris Shank, University of Texas, Marine Sciences Institute

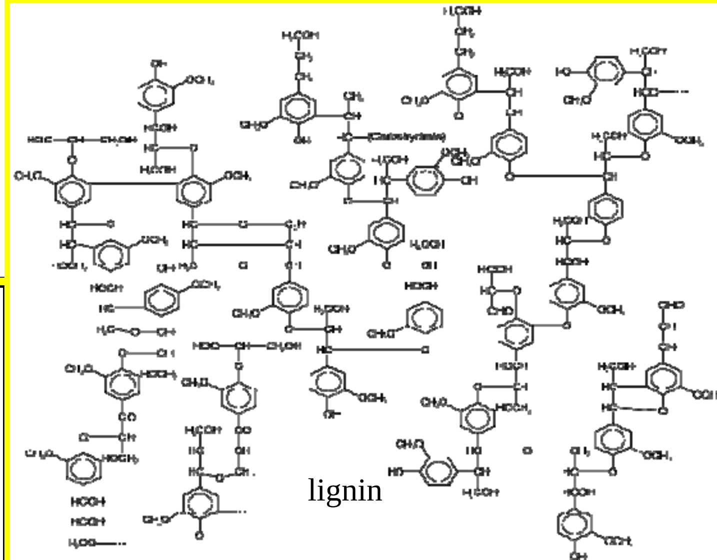
CDOM is derived from biodegraded terrestrial vegetation, phytoplankton exudates, seagrass leachates and other sources. CDOM chemical structure contains a variety of photoreactive functionalities, quinones, phenols, etc. and depends on origin, light exposure, microbial activity and other factors. CDOM's structural variability is responsible for the variable nature of CDOM's optical character and reactivity. Terrestrially-derived CDOM is generally more complex than marine CDOM and has a higher average molecular weight and lower spectral slope.



Model structure of humic acid (Stevenson 1982)

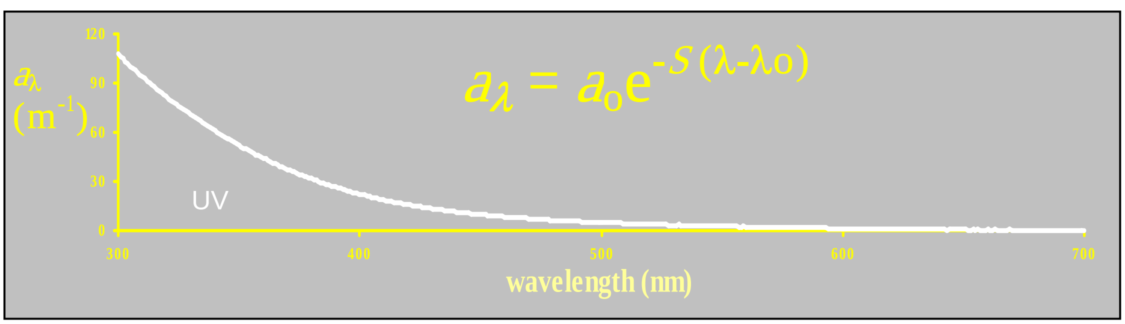


Model structure of fulvic acid by Buffle



(provided by C. Shank)

A CDOM absorbance scan allows one to determine from the absorption coefficients, an estimate of the quantity of CDOM, while the spectral slope coefficient (see above) is indicative of the source/size of the CDOM pool.



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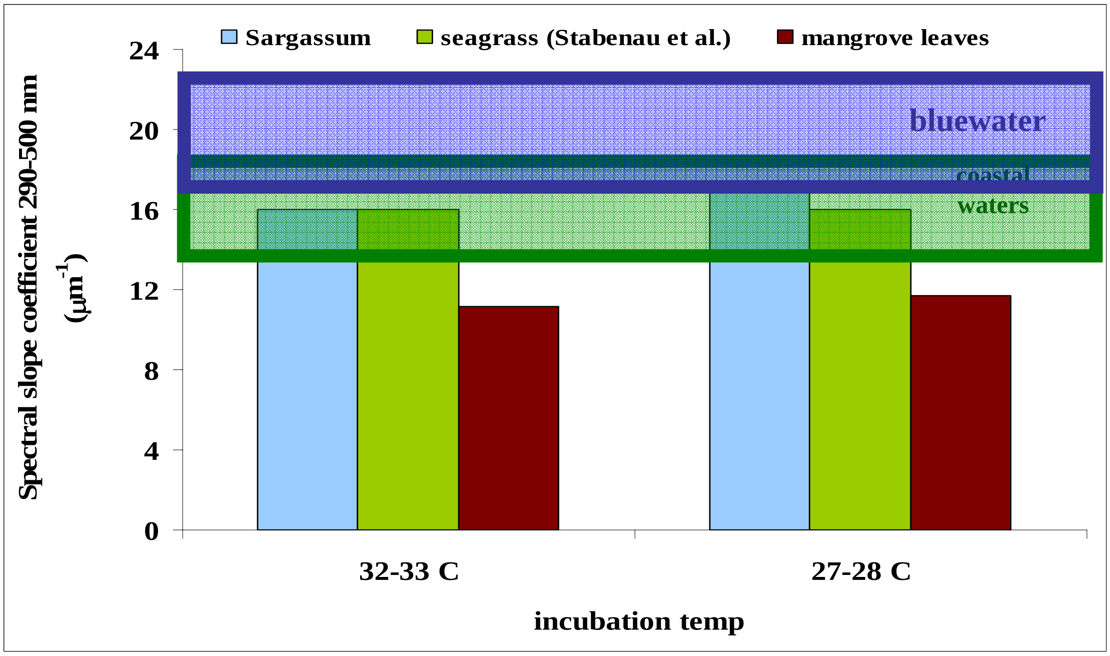
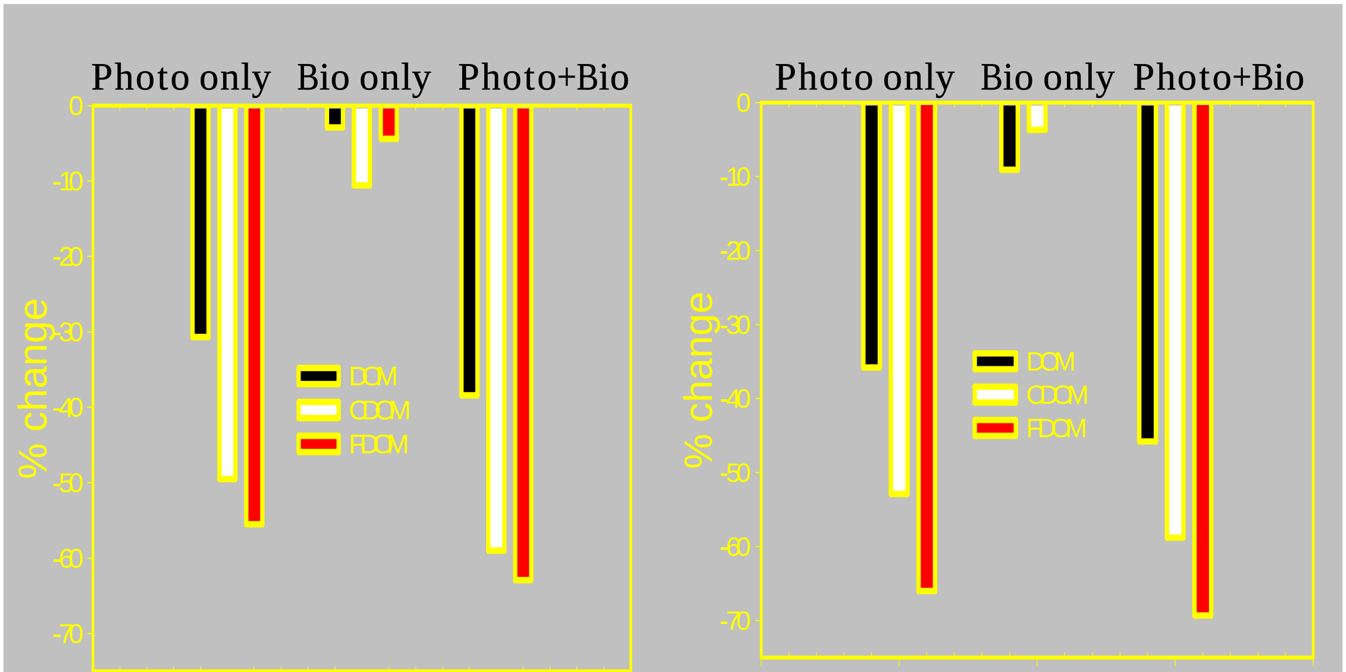
The spectral slope coefficients are much higher for CDOM produced by *Sargassum* and *Thalassia* (seagrass species) than from mangrove leaf litter:



(provided by C. Shank)

Most CDOM is relatively chemically unreactive in the absence of light, while in the presence of light, it has many important chemical reactions. CDOM strongly absorbs ultraviolet light (see above absorbance scan). UV has low wavelengths, and therefore has very high energy. Important chemical reactions involving CDOM include: 1) the production of bioavailable chemicals, 2) photo-mineralized to carbon monoxide (CO) and carbon dioxide (CO_2), 3) ammonium production and 4) alteration of metal species, such as iron and copper. CDOM photodegrades into biologically labile photoproducts, including low molecular weight acids and acetone, formaldehyde, acetaldehyde, glyoxal and others. CDOM is very important in the carbon cycle, as CDOM breakdown also releases CO and CO_2. The resulting microbial activity represents an important dissolved organic carbon (DOC) sink in the environment, and DOC photodegradation removes greater quantities of carbon than terrestrial DOC inputs in the oceanic DOC pool. CDOM with high nitrogen content is capable of adding significant ammonium quantities and is an important nutrient source in the absence of terrestrial sources of nitrogen. Finally, CDOM strongly binds trace metals such as copper (CU) and iron. CDOM binding buffers the concentration of toxic CU^{+2} ion; however, photodegradation of CDOM can release the CU^{+2}.

CDOM photobleaching equals the loss of chromophores and results in a decrease in the absorption coefficients and fluorescence. The rates of photobleaching are not necessarily the same for different wavelengths, and there is a significant fluorescence decrease in the terrestrial humic peak, for instance. Fluorescence excitation/emission maxima shift to shorter wavelengths following photobleaching. In addition, biodegradation of CDOM counteracts photodegradation effects on fluorescence; while biological degradation of DOC, CDOM and fluorescent DOM is stimulated by photodegradation. Iron and oxygen in the water column increase photobleaching rates.

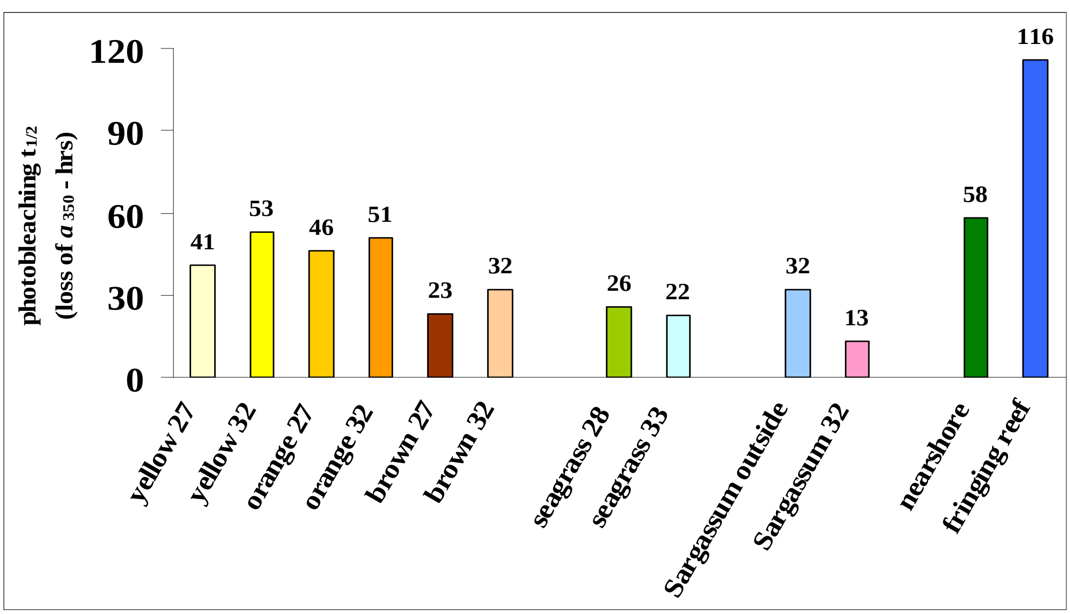


Irradiated 70 d with fluorescent lamps (mainly UV-A source)

Irradiated 38 h in Suntest CPS solar simulator (Xe arc)

(provided by C. Shank)

Changes in spectral slope (*S*) reflect changes to CDOM structure. Slopes increase following photobleaching and decrease in average molecular weight. CDOM photobleaching rates depend on the origin of CDOM. The half life ($t_{1/2}$) of blackwater rivers can be less than 20 hours.



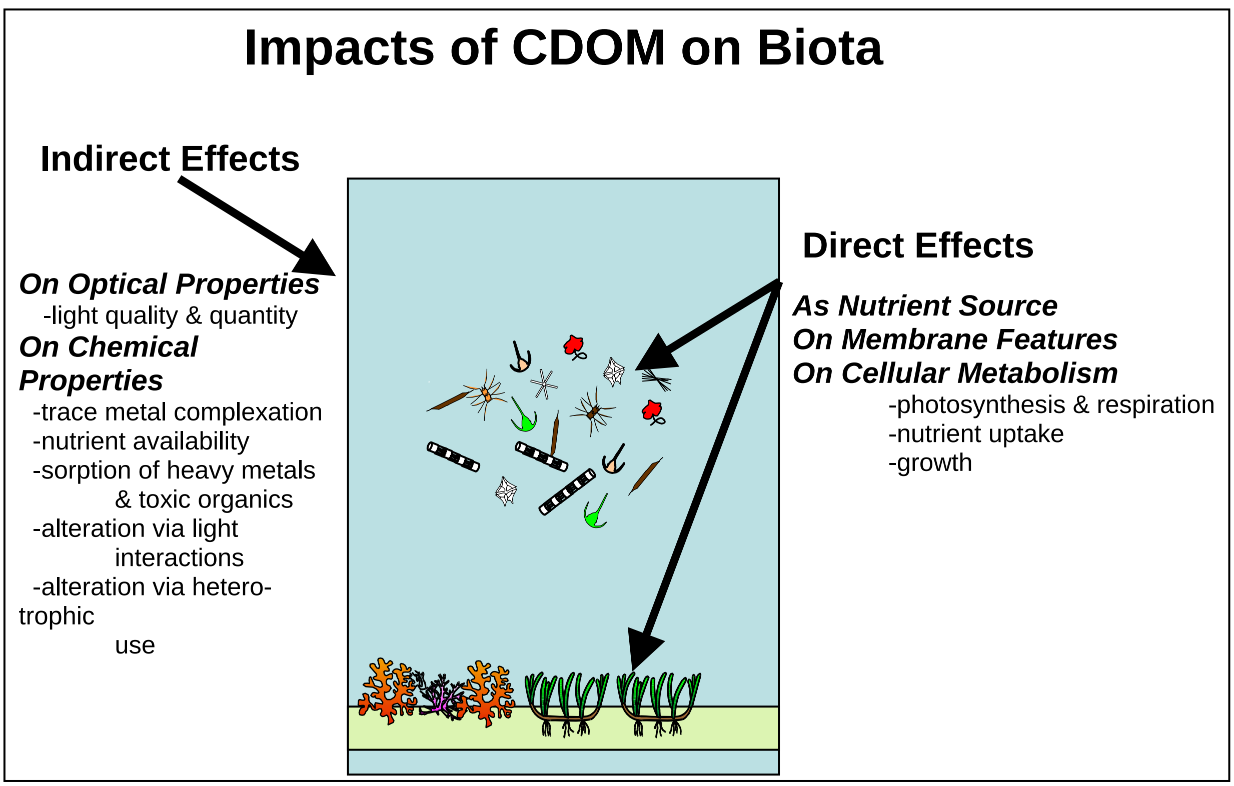
(provided by C. Shank)

CDOM 103: INDIRECT AND DIRECT BIOTIC LINKS WITH CDOM

Cynthia Heil, Florida Fish and Wildlife Research Institute

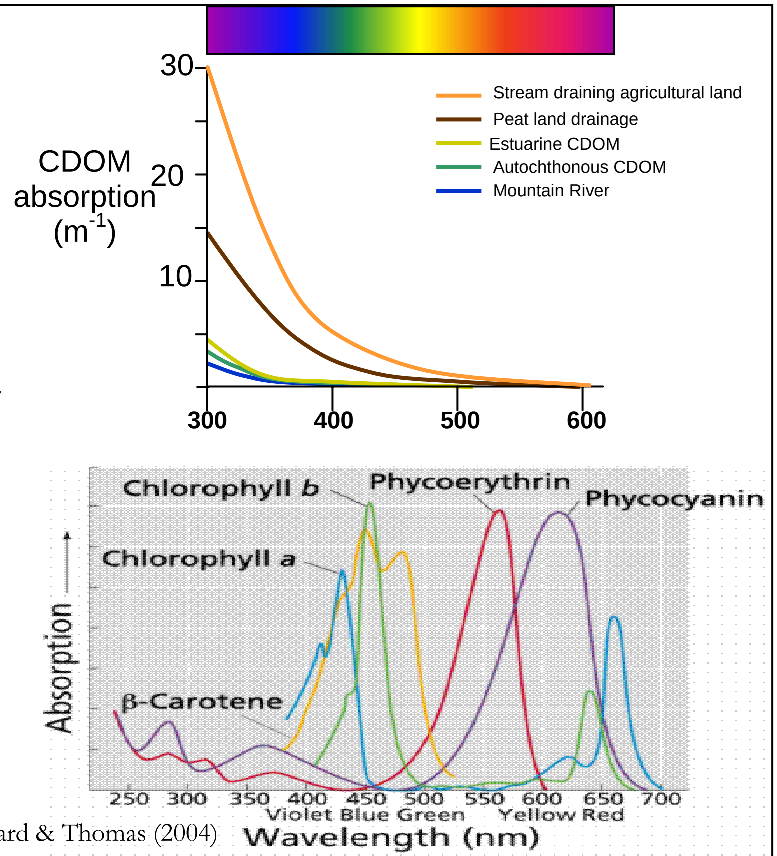
CDOM has many biological roles in aquatic systems. It is a regulator of light availability for primary producers: 1) affects spatial distribution (controlled by concentration, attenuation by particles, bathymetry of system) and 2) controls primary production by light availability. CDOM is a regulator of oxygen demand: process of CDOM degradation consumes oxygen gas (O_2). CDOM is a carrier of nutrients (C, N, P in both inorganic & organic forms) directly and via food webs (e.g., microbial loop), and it is a regulator of nutrient availability (N, P, Trace Metals). Many of these roles are directly influenced/modified by UV exposure and/or may influence the other roles.

Bacteria can utilize CDOM but prefer low molecular weight compounds; the larger compounds require considerable energy for breakdown, which may wasteful for the organism. Moran et al. (2000) estimated 4-11 % of CDOM directly utilized by bacteria with an increase to 58-59% after ultraviolet light exposure. There are 3 major factors that influence bacterial capacity for dissolved organic matter degradation: 1) suitability of DOM for degradation by bacterial enzymes, 2) DOM is originally degradable, but is transformed into nondegradable substances and 3) bacteria are limited by other factors rather than carbon availability (e.g., grazing, viral infections, N, P limitation).



(provided by C. Heil)

Influence of CDOM on Light Quantity and Light Quality

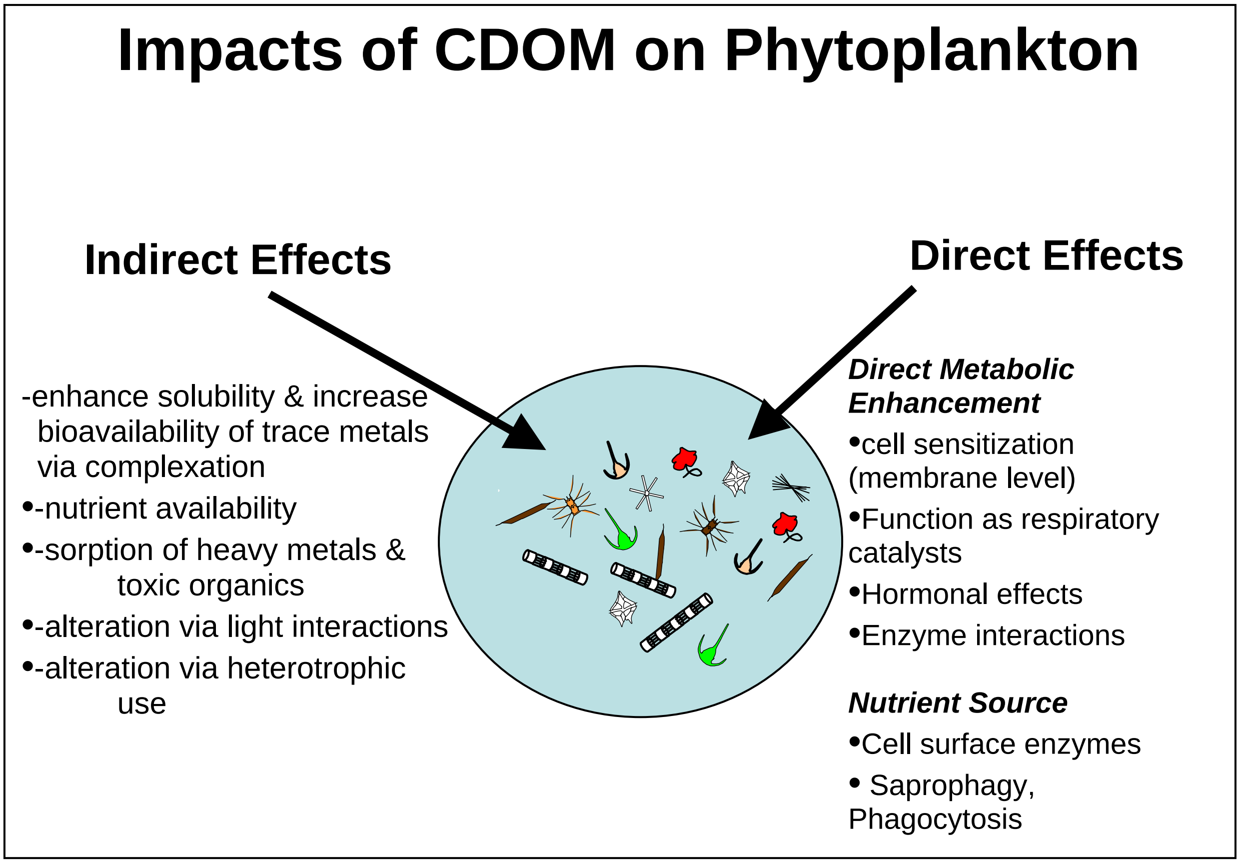


Top figure modified from Søndergaard & Thomas (2004)

(provided by C. Heil)

CDOM was traditionally thought of as a highly recalcitrant and refractory group of aquatic DOM. In the 1960's-70's biological conditioning experiments showed that additions of small concentrations of humic compounds stimulate growth of phytoplankton by increasing growth rates, nutrient uptake and carbon assimilation. In the 1980's with improved techniques for DOC & DON measurement, researchers recognized a microbial loop, with bacteria at the base of a DOM 'food web'. In the 1990-current with improved techniques to measure 'bioavailability', researchers have further refined the understanding of the microbial loop, with recognition that in many aquatic ecosystems bacterial DOM utilization is THE route of organic carbon turnover. Phytoplankton can directly use CDOM via biologically available photoproducts (e.g., nutrients suchas ammonium and phosphate and low molecular weight compounds such as acetate, propanal and pyruvate). Through saprophagy, phytoplankton can directly uptake CDOM and through phagotrophy, they can uptake particles. Through cell surface enzymes, phytoplankton can cleave molecules or compounds from CDOM for uptake. CDOM is also a source of dissolved organic and inorganic nitrogen.

CDOM photochemical interactions can have many impacts on biota. It can change rates of bacterial consumption via: 1) producing carbon photoproducts which can be bacterial substrates, 2) production of inorganic nutrients (esp. NH4+) and 3) alternation of refractory nature of remaining CDOM (eg. reduced avgerage molecular weight). The photobleaching of CDOM or loss of color can increase the quantity and depth of PAR and can act as a negative feedback to photochemistry. Finally, it can regulate nutrient availability (eg. diel P-humic-UV interactions).



(provided by C. Heil)

CDOM impacts on organisms are as complex as CDOM chemistry but are more poorly understood. There are direct and indirect impacts as well as optical, chemical and biological effects. CDOM impacts on organisms are influenced by many factors such as photochemistry and are subject to a variety of feedback loops. CDOM is important to understand and study because it regulates seagrass, bacteria and phytoplankton community composition in addition to physiology and ecology.

IMPORTANCE OF QUALITY OF LIGHT FOR SEAGRASS-PHYSIOLOGICAL IMPACTS ON DIFFERENT SEAGRASS SPECIES

Chris Anastasiou, Florida Department of Environmental Protection

Light is unique in that it exhibits characteristics of both waves and particles. A photon is the fundamental "particle" of light. Every photon has a frequency (v) and a wavelength (λ):

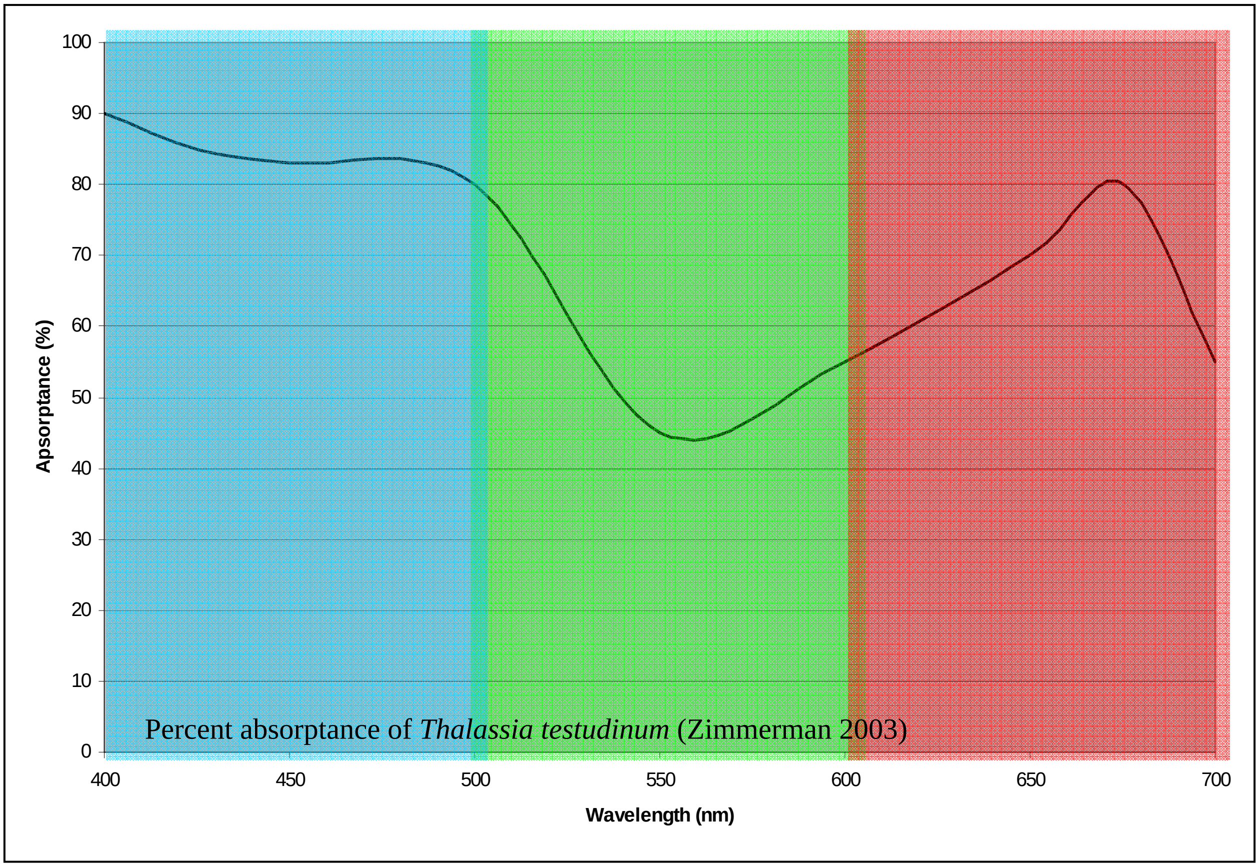
$$\lambda = c/v$$

In the full summer sun 1.0 m^2 of a horizontal surface receives approximately 10^{21} quanta s^{-1} of visible light. The visible portion of the electromagenetic spectrum is very narrow (approx. 300nm – 800nm), and with respect to human sight and plant photosynthesis, this is where the "action" is.

Photosynthesis is the process by which plants, some bacteria, and some protists use light energy to produce sugar, which cellular respiration converts into ATP, the "fuel" used by all living things:

$$6H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2$$

Photosynthetic pigments (chlorophylls, carotenoids, and biliproteins) are molecules whose structures are such that they efficiently absorb light in the 400-700nm range (Kirk 1994). However, photosynthetic pigments do not absorb equally across the visible spectrum or across species.



Percent absorptance of *Thalassia testudinum* (Zimmerman 2003)

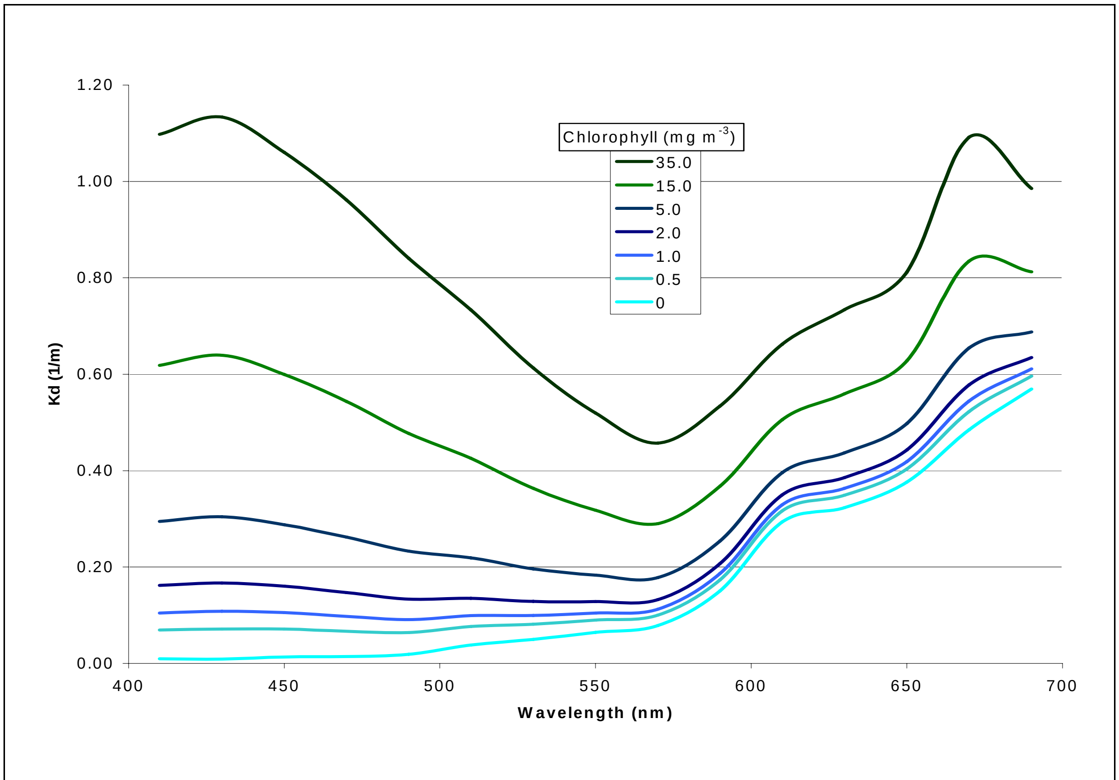
(provided by C. Anastasiou)

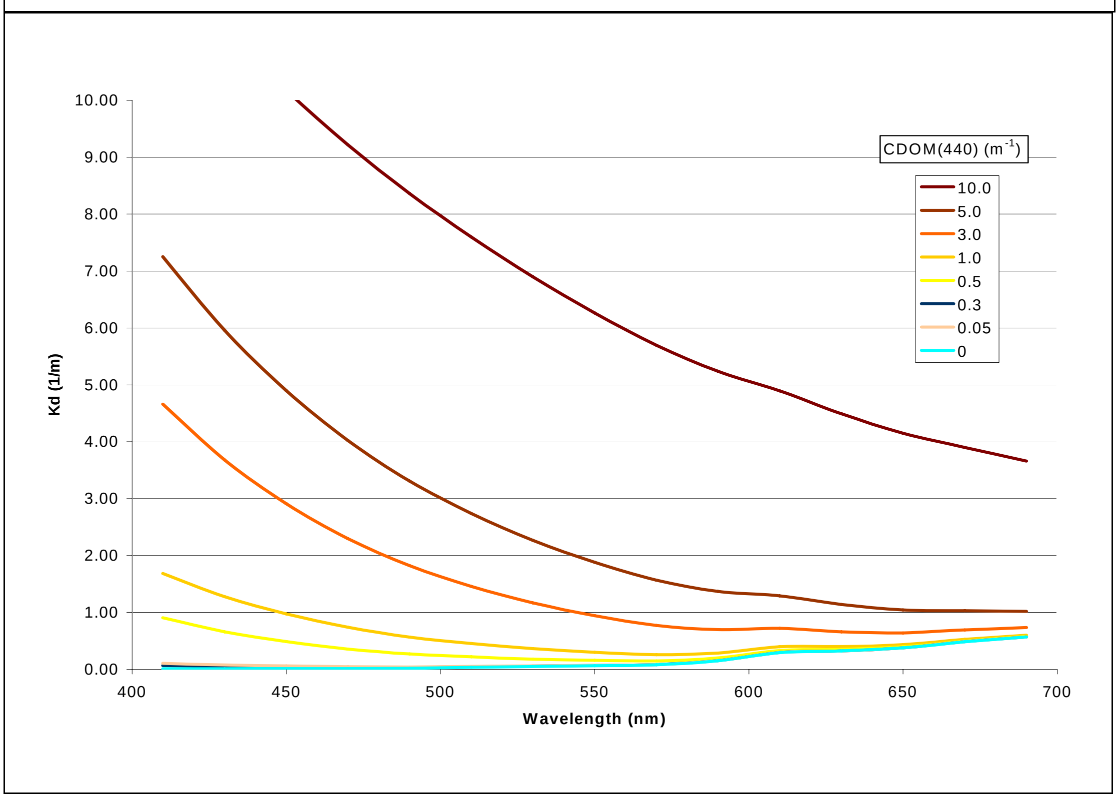
The most important basic principle of the interaction of light and matter: Both the physical properties of light and their biological effects depend strongly on wavelength and must be taken into account in any proposed simplification of light measurements (Keith J. McCree, 1973). Resource managers in the area measure water clarity via secchi disk depth and photosynthetically active radiation (PAR), which is determined by an instrument averaging all wavelengths of downwelling irradiance in the visible range (roughly 400-700 nm). However, it is the photosynthetically USEFUL radiation (PUR) that is important to the plants. Measuring PAR versus PUR can be thought of as the difference between measuring light quantity as opposed to light quality. To accurately measure PUR, on emust first define which wavelengths are most important relative to the species of interest. Water quality (chlorophyll, CDOM, turbidity) has a direct impact on both the quantity AND quality of light. Light is attenuated with depth via two mechanisms: absorption and scatter. The light attenuation coefficient can be broken down into its component parts or partial attenuation coefficients:

$$Kd = Kd(Chl) + Kd(Turbidity) + Kd(CDOM) + Kd(water)$$

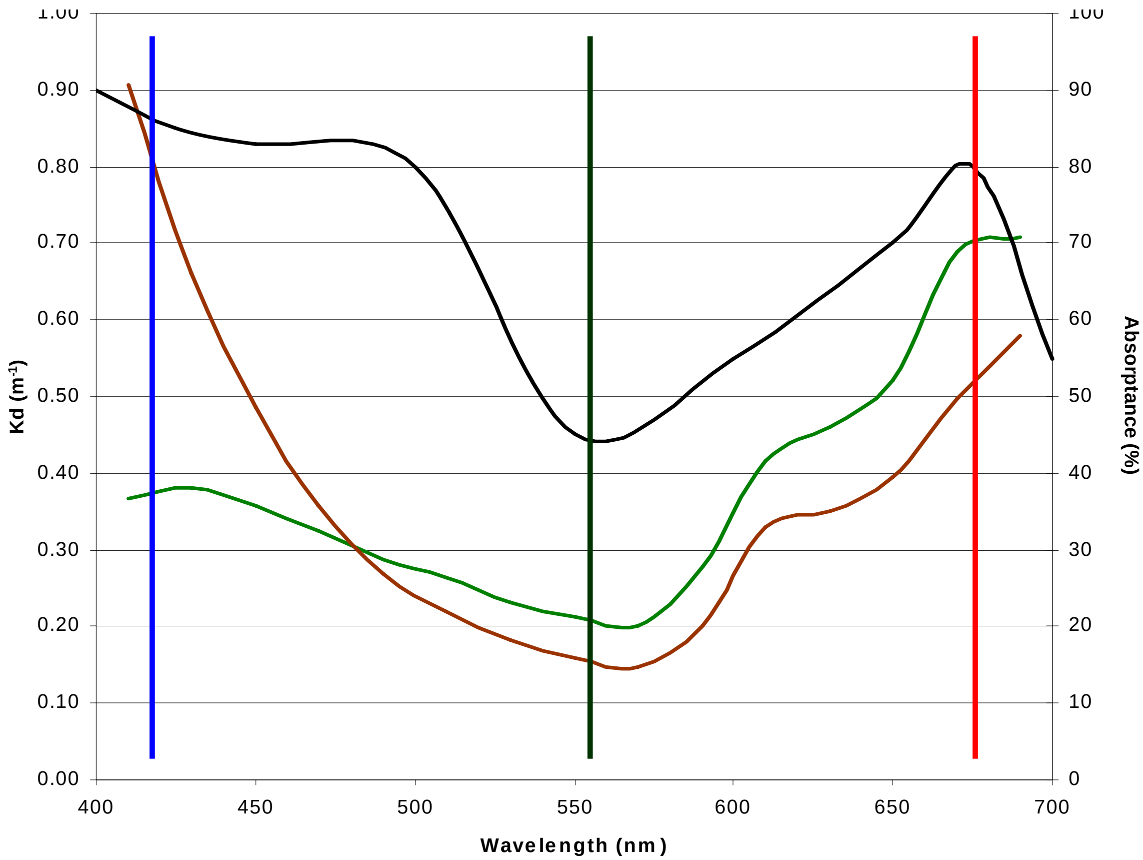
Light attenuation coefficients can be calculated using Beer's Law which states that light decreases with depth exponentially. When light is broken down into its component wavelengths, a spectral light attenuation coefficient can be calculated. The spectral shape of any given water parcel can be very different depending on the water quality even though the light extinction coefficient (Kd) is the same. For this reason, simply knowing the Kd doe snot provide insight as to the quality of light reaching the bottom. While PAR and Kd provide good bulk estimates of the light field in the water column, resource managers are limited in their ability to implement strategies to best protect and restore seagrass without knowing what wavelengths are penetrating to the bottom and what wavelengths are most important to the target seagrass species.

Thanks to new technology, it is now relatively simple and cost effective to measure light quality and is now being incorporated in seagrass management plans in systems like Charlotte Harbor and Tampa Bay. Another important step in this process is to accurately measure light utilization by seagrass and better understand the physiological responses of seagrass under different light conditions. .





(provided by C. Anastasiou)



	Chl = 7.0 mg m-3	CDOM = 0.5 m-1
Kd (Ave)	0.38	0.38
Kd(Blue)	0.34	0.54
Kd(Green)	0.23	0.18
Kd(red)	0.56	0.43

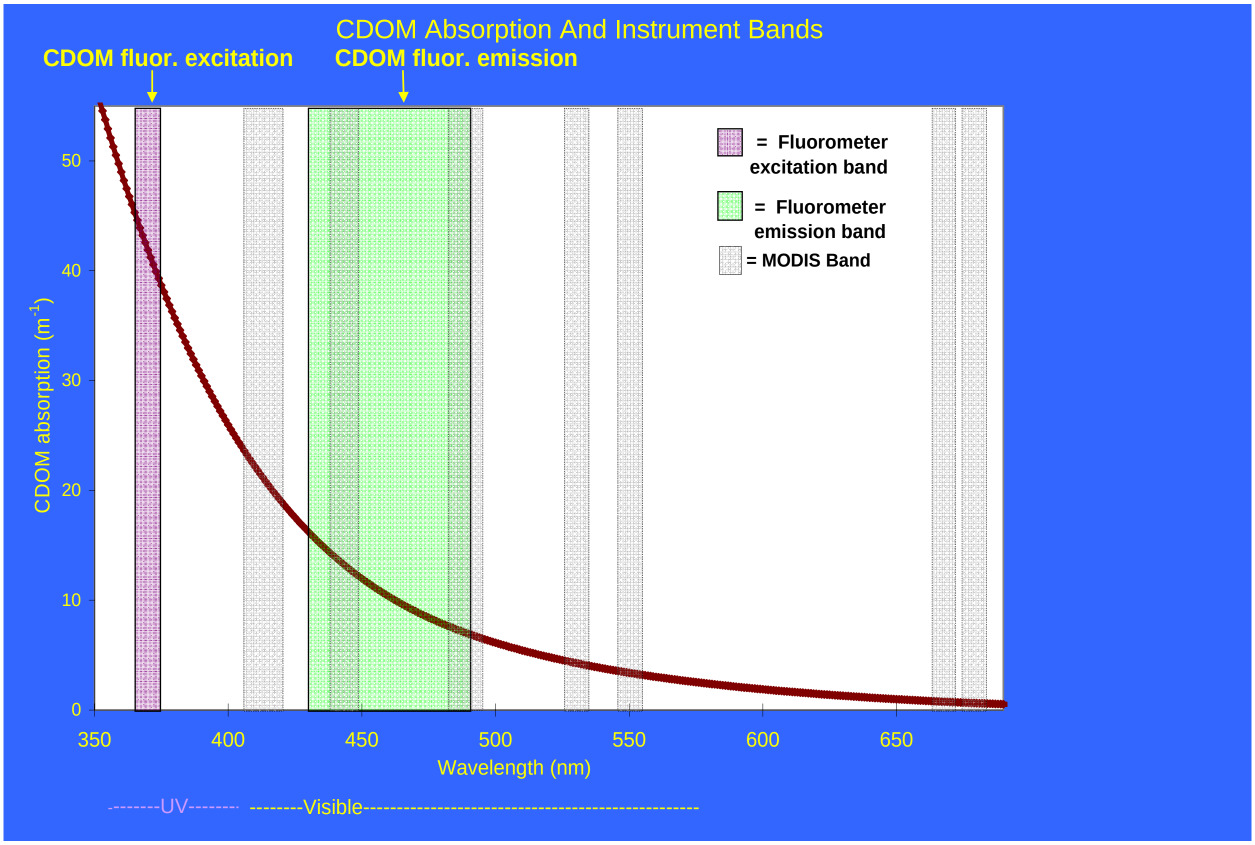
(provided by C. Anastasiou)

SESSION ONE: What are the different methods of measuring CDOM concentrations? How do these help us to better understand quality and quantity of light in the region? How do the current monitoring protocols in southwest FL compare to other regions? Should the protocols in Charlotte Harbor be changed?

TOOLS FOR OBSERVATION OF SYNOPTIC DISTRIBUTION OF CDOM-FLOW-THROUGH MEASUREMENTS

Kendall Carder, University of South Florida

CDOM concentrations are defined by absorption but measured *in situ* with fluorescence. Discrete samples are measured in a lab with a spectrophotometer by using the absorption at a reference wavelength and a spectral shape function to describe CDOM (e.g. $a_g(400)$ and exponential or hyperbolic slope). *In situ* CDOM fluorescence measurements are regressed to laboratory CDOM absorption spectra.

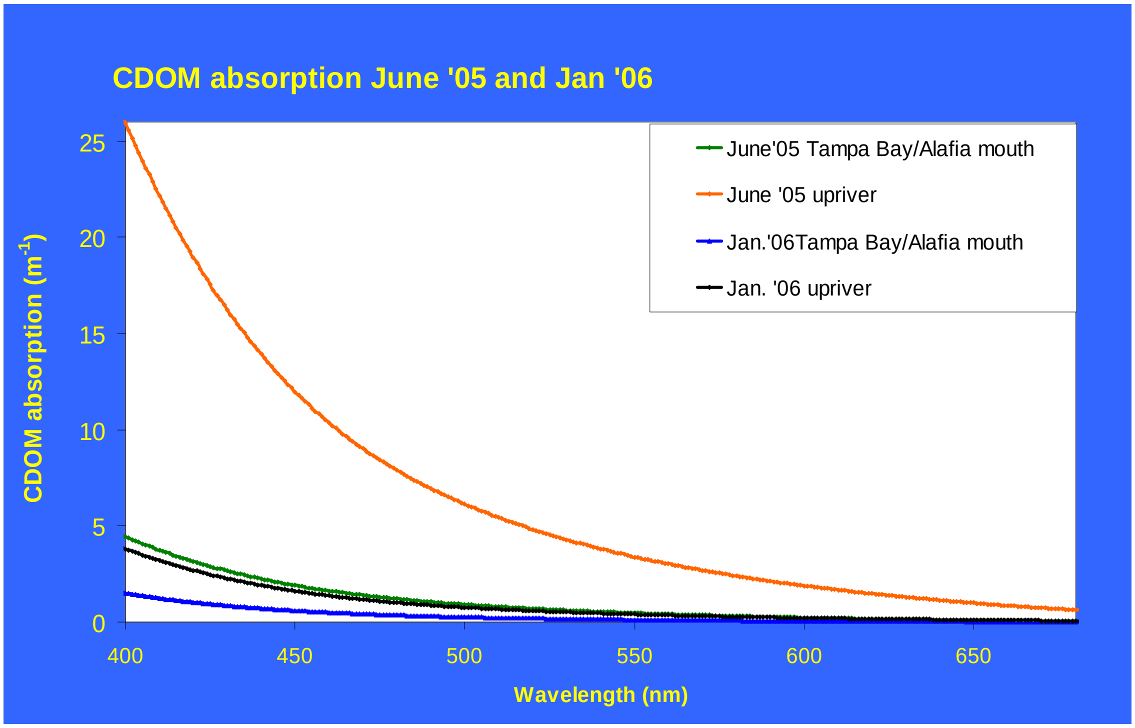


(provided by K. Carder)

CDOM is seasonally and spatially variable. In Florida estuaries CDOM co-varies inversely with salinity. CDOM has been linked to chlorophyll or other biomass concentrations, particulate material, nutrients, rainfall and land use. CDOM fluorescence to absorption relationship is usually at least as stable as chlorophyll *a* fluoresence relationships.


(provided by K. Carder)

Flow-through measurement systems allow researchers to obtain vertical, horizontal or temporal profiles. Vertical profiles are obtained from a vertical structure cast at one location, while temporal profiles are obtained at a stationary monitoring location over time (e.g., MARVIN, AMOS, etc). Horizontal profiles are obtained from a moving platform with fixed or variable depth intake. Example measurements available from flow through systems include amongst others: salinity, temperature, pressure, Beam transmission (blue and red light), CDOM fluorescence (inline and in-tank), chlorophyll *a* fluorescence (inline and in-tank), backscatter (blue and red light), GPS for location and time data and optional instruments (e.g., pH, IR turbidity). All data are logged to a laptop, and some data are stored at the instrument. The GPS data are merged on the logger at time of collection.



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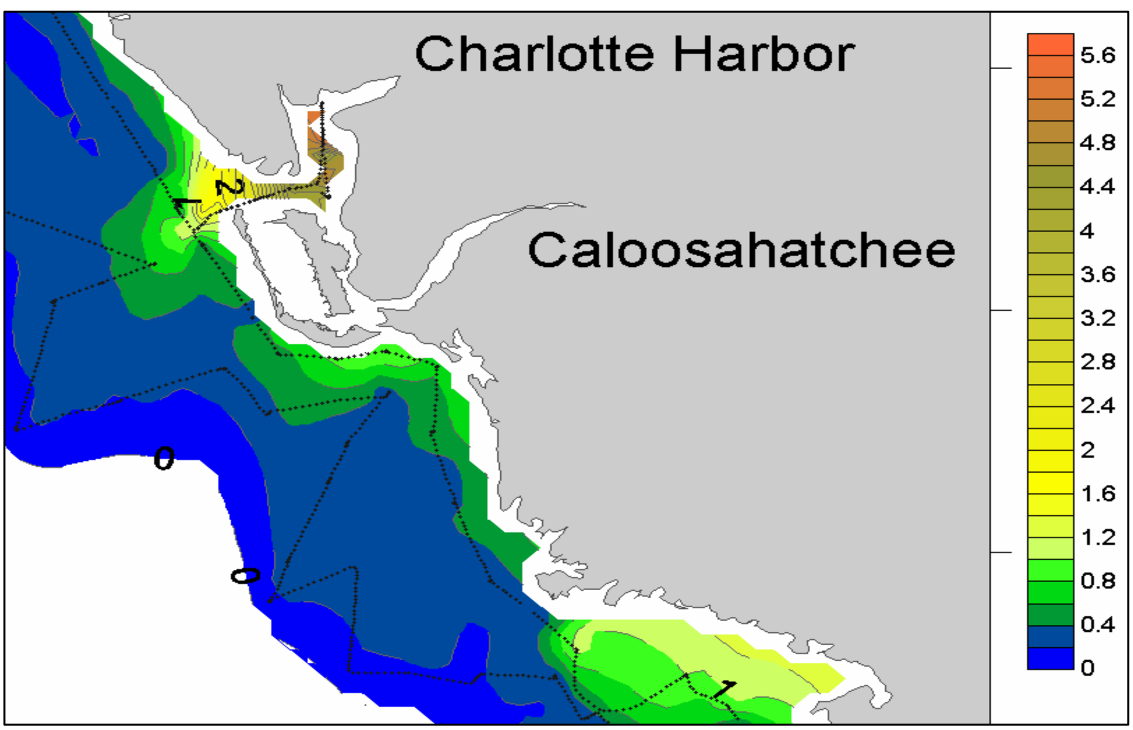
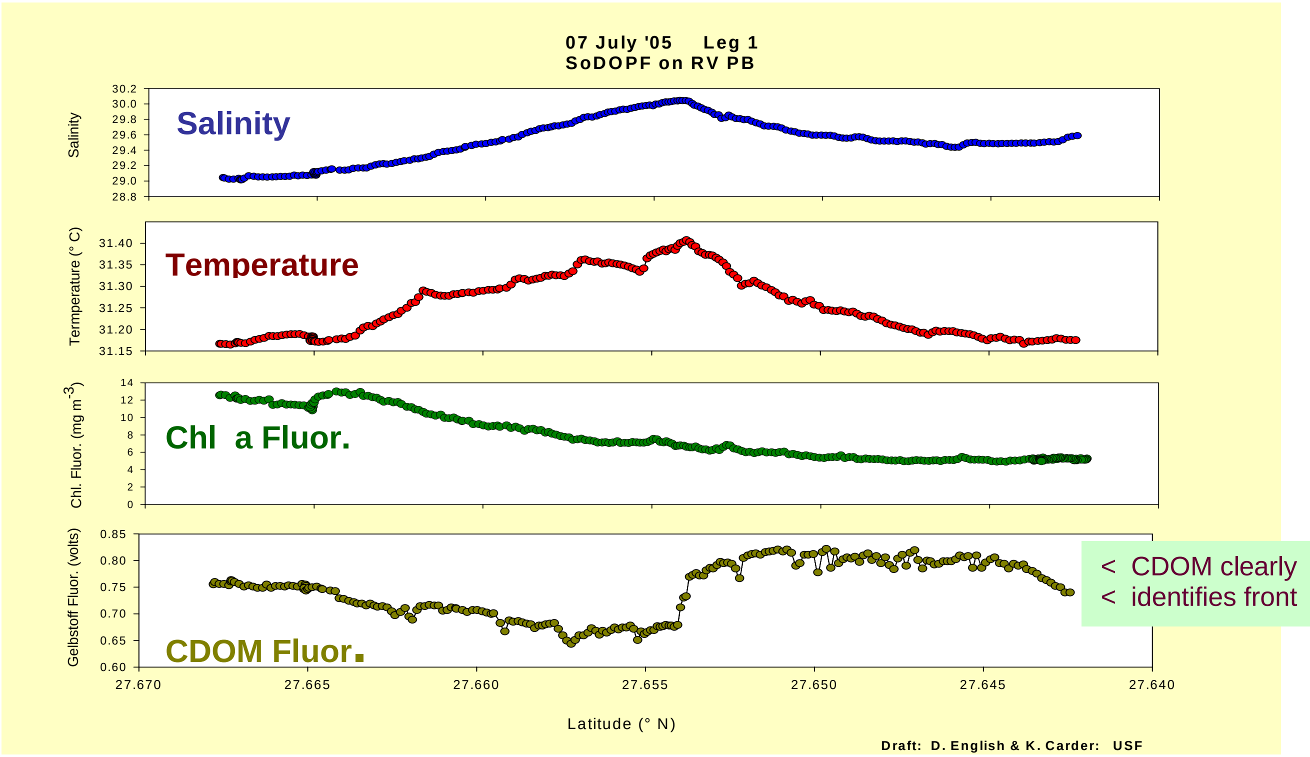


Example CDOM spatial distribution interpolated from flow-through data (a portion of a larger cruise track, October 2006) (provided by K. Carder)



Detecting Visible Fronts in Estuaries. Transect across a front between two different water types in Tampa Bay (provided by K. Carder)

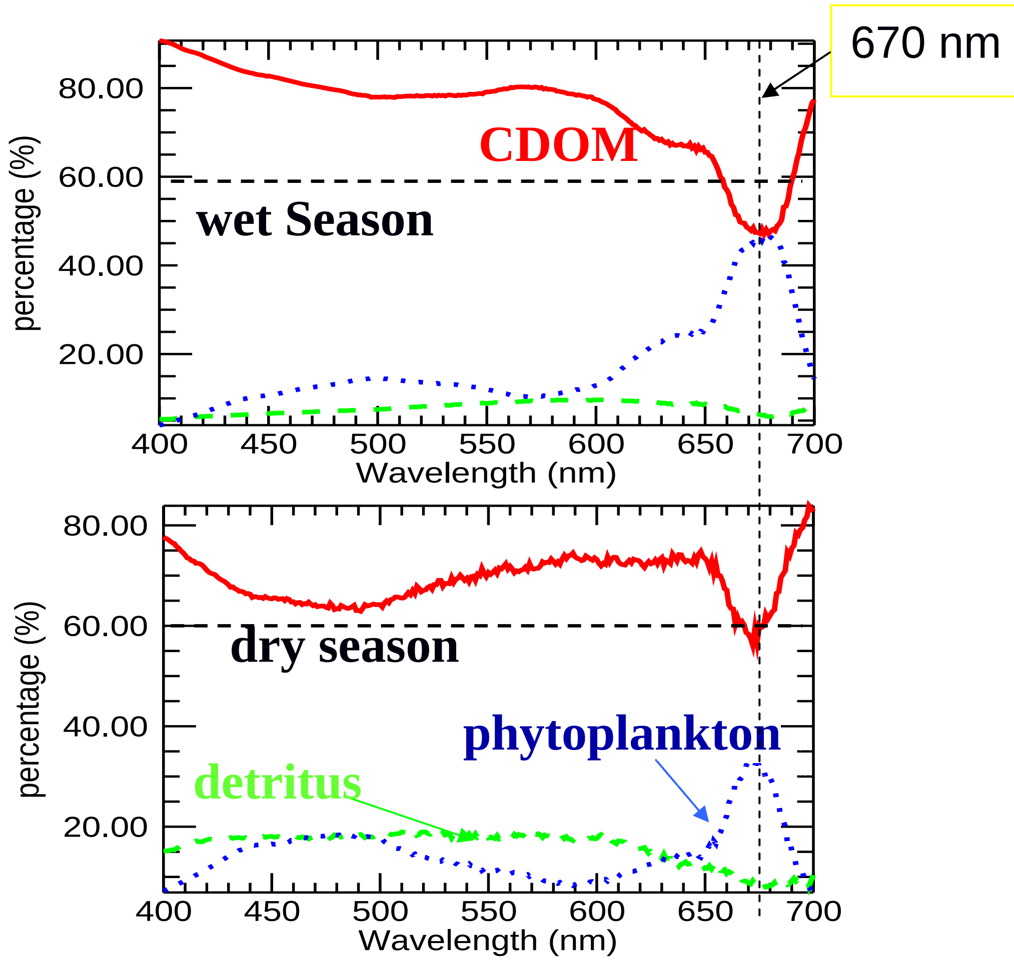
CDOM is an important element of multi-sensor detection and analysis systems because of various reasons. CDOM thresholds can be used to generate a warning/indicator flag, and CDOM is an optical indicator of salinity fronts. In situ CDOM can be combined with other bio-optical measurements not only to improve estimates of optical properties and the light field, but used in algorithms classifying waters with harmful algal blooms.CDOM can help constrain HAB algorithms, and CDOM estimates can improve the accuracy of in situ fluorometric chlorophyll *a* estimates in high CDOM waters such as Charlotte Harbor. For instance, flow through measurements documented false positive HAB results in Charlotte Harbor in the past due to high CDOM concentrations. Due to improved measurements and resulting algorithms, these false positive values in Charlotte Harbor have been removed.

TOOLS FOR OBSERVATION OF SYNOPTIC DISTRIBUTION OF CDOM—SATELLITE IMAGES, A CASE STUDY IN TAMPA BAY ESTUARY

Zhiqiang Chen, Frank Muller-Karger and Chuanmin Hu, University of South Florida

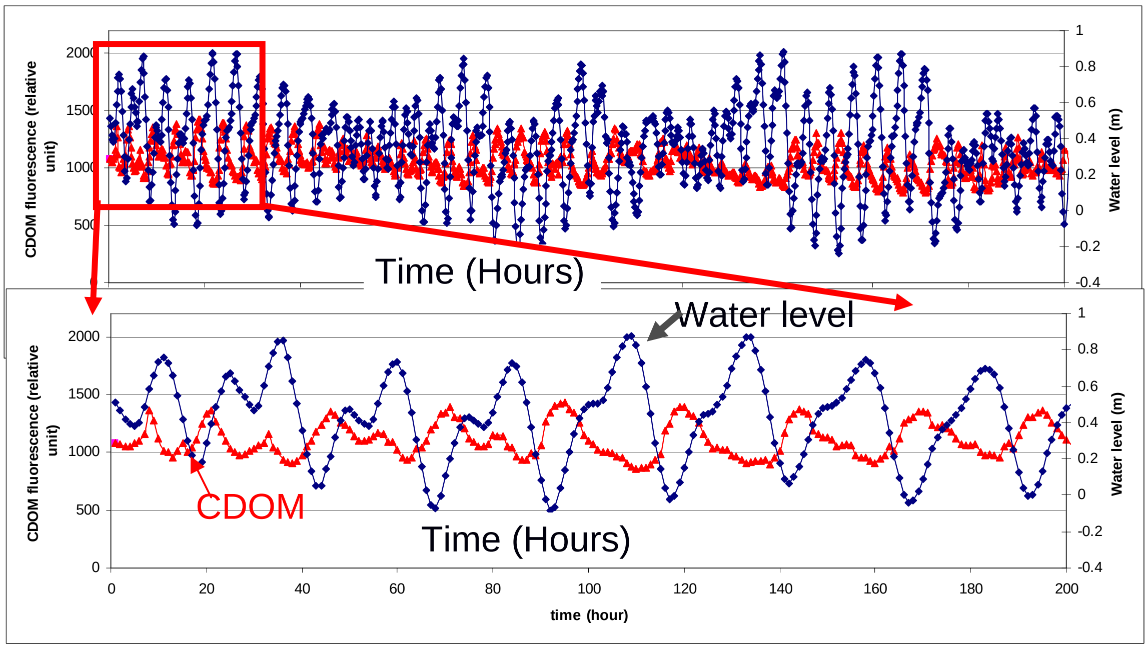
CDOM strongly absorbs light, particularly at UV and blue bands, and its absorption exponentially decreases with increasing wavelength. This absorption is a primary factor controlling water color in coastal and estuarine waters where high CDOM is often observed. It affects the quantity and quality of light available in estuarine ecosystems and the productivity of phytoplankton, seagrass and coral reefs.

Two methods have been used to characterize CDOM light absorption or concentration. Traditionally CDOM absorption is referred as to “color” in most water quality monitoring programs and is characterized using “PCU color [Platinum-Cobalt Units]”. Recently CDOM absorption is directly expressed (primarily outside of discrete monitoring programs, such as remote sensing community) as light adsorption coefficients at certain wavelengths. Generally, the absorption coefficients and PCU colors are closely correlated.



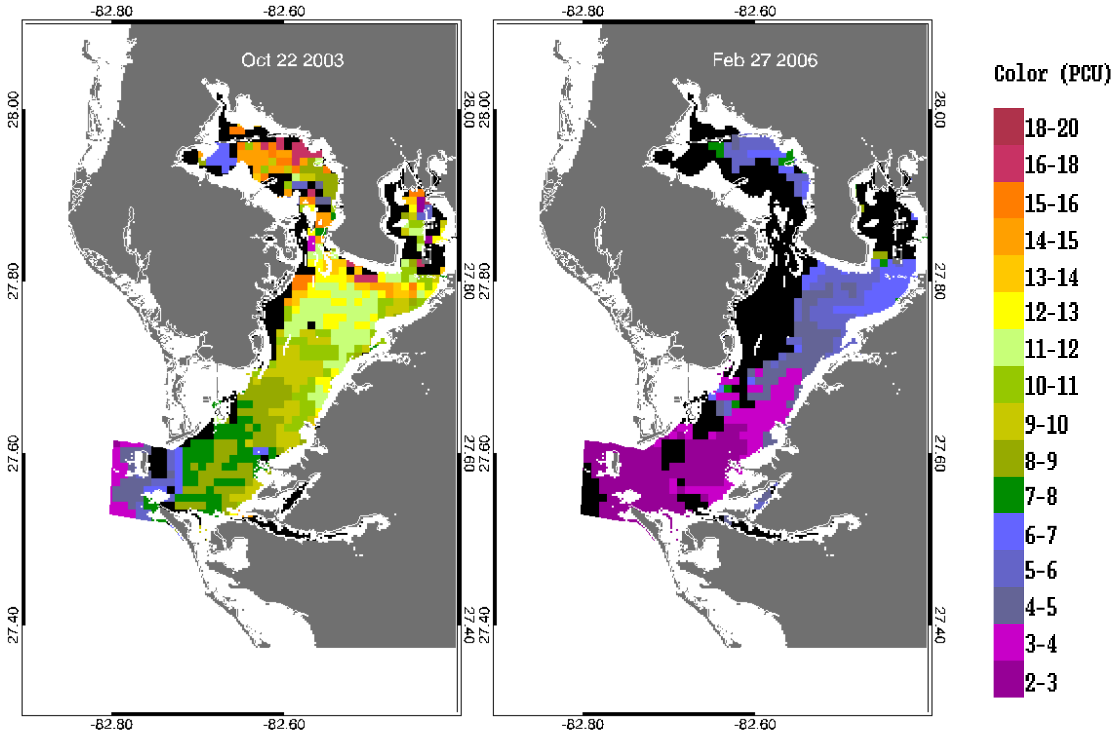
Absorption of light due to CDOM vs. total light absorption
(provided by Z. Chen, F. Muller-Karger and C. Hu)

In most water quality monitoring programs, PCU colors are measured on a monthly or quarterly basis at discrete sample stations. These methods are non-synoptic and provide relatively infrequent data for a fast changing coastal environment. In comparison remote sensing provides unprecedented capability to provide synoptic, frequent sampling of CDOM once a valid bio-optical algorithm is developed. We developed an algorithm to remotely sense CDOM concentration in Tampa Bay by comparing satellite spectral observations with concurrent (time window of less than 3 hours between satellite overpass and in situ sample time) color/CDOM concentrations from local monitoring programs. Results shows that satellite estimates are closely correlated with *in situ* PCU color (ranging 2-16) measurements (r^2 ~0.4, n=60), indicating satellites can estimate "PCU color" within reasonable accuracy for most of Tampa Bay. The relationship was further validated with other discrete samples than those used to develop the algorithm, and results showed a strong relationship between CDOM absorption at 400 nm and MODIS derived PCU color with r^2 of 0.96 (n=19). Previous efforts have used similar band ratios to estimate CDOM absorption in other coastal waters. From the derived relationship, a Tampa Bay CDOM time series was developed.

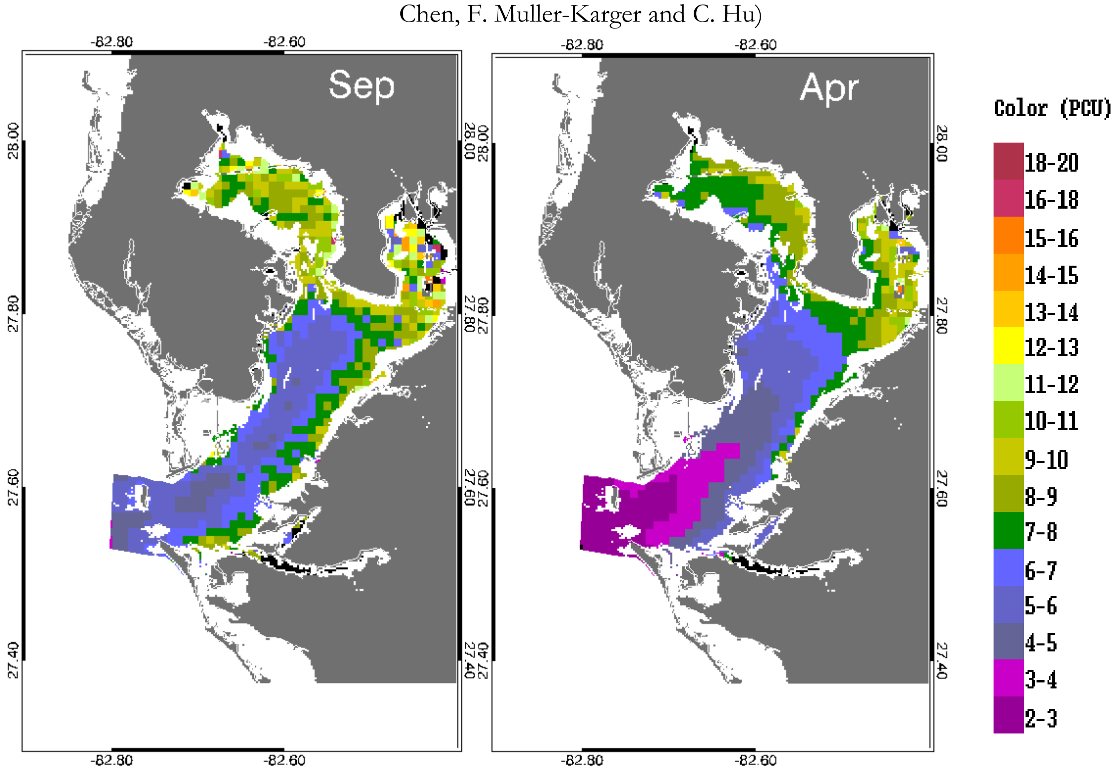


CDOM time series (Oct 31-Dec 13, 2005) (provided by Z. Chen, F. Muller-Karger and C. Hu)

A similar effort was tried for Charlotte Harbor but more *in situ* data and field work are needed for the Charlotte Harbor estuary. At present, a lack of data precludes the derivation of a more robust algorithm. However, the limited data and preliminary results from algorithm derivation suggest that there is more CDOM input into Charlotte Harbor than Tampa Bay which is consistent with those *in situ* measurements from these estuaries.



Sample Variation of daily MODIS "PCU Color" estimates in different seasons (provided by Z. Chen, F. Muller-Karger and C. Hu)



"4-year climatology" (2002-2006): Seasonal Variation of MODIS "PCU Color" estimates (provided by Z. Chen, F. Muller-Karger and C. Hu)

OVERVIEW OF THE CURRENT CDOM MONITORING AND LAB ANALYSES PROTOCOLS IN SOUTHWEST FLORIDA

Charles Kovach, Florida Department of Environmental Protection

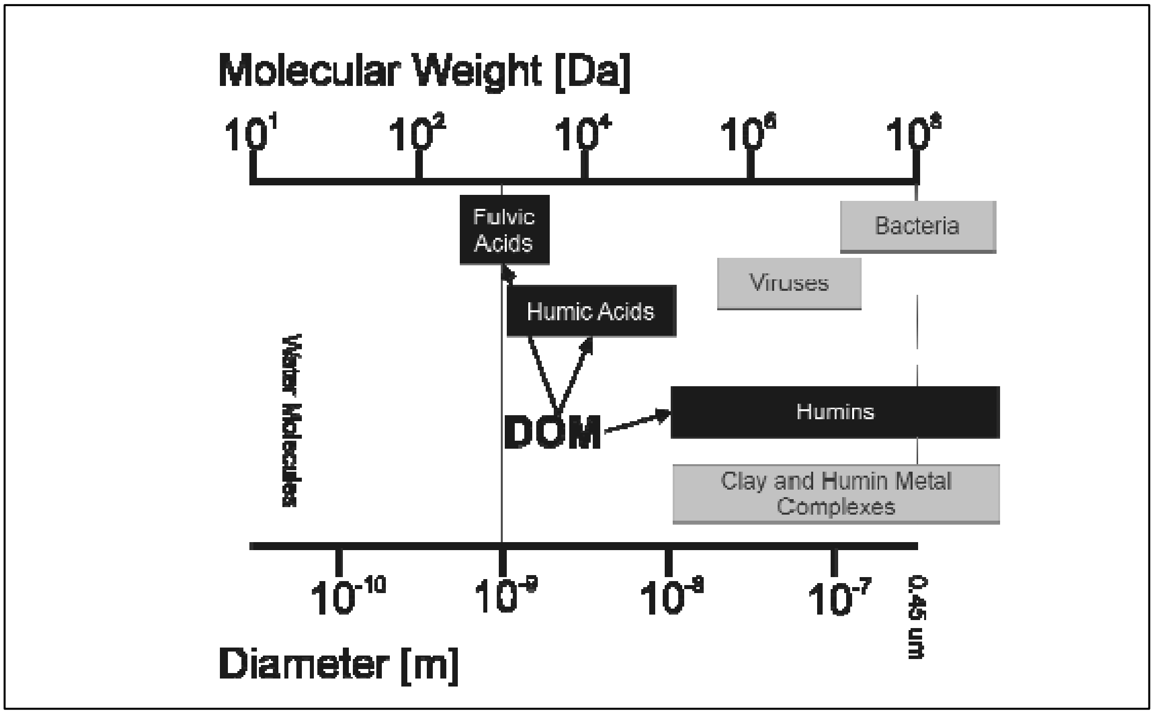
> *Please note that this presentation has many citations that were not included herein; please see the actual presentation for further detailed information on the subject matter described.*

Two main groups of aquatic organic matter exist: particulate and dissolved organic matter (DOM). DOM is operationally defined as the fraction which passes though a filter with a 0.45 μm pore size, while the particulate organic matter (POM) is that which remains on the filter as residue. This distinction between dissolved and particulate matter is arbitrary; the threshold value is chosen because it coincides with the shortest wavelength of the visible light: 400 nm. The DOM and POM combined give the Total Organic Matter (TOM). The main components of DOM are humic and fulvic acids and humin.

The concentration of each type of organic matter is cumbersome to determine directly because it involves the determination of numerous different compounds. Dissolved organic carbon (DOC) is commonly used as a substitute value for DOM and is included in many water monitoring programs. The estimation of DOM from DOC is based on the finding that approximately 60% of DOM consists of carbon, resulting in a positive linear relationship between DOM and DOC. Relationships between DOC and other water quality variables are in turn considered similar to those of DOM and the variables. The Total Organic Carbon (TOC) of a water sample is determined by the amount of carbon dioxide that is produced after combustion or strong oxidation (while removing inorganic carbonates). The DOC is determined in the same way as the TOC, but the water sample is filtered first through a 0.45 μm filter. Similar to TOM, POM and DOM, the organic carbon is expressed as TOC, POC and DOC.

Another method to estimate DOM concentration is based on a characteristic that is shared by the majority of the compounds that make up DOM: color. Some 60-80% of freshwater DOM consists of colored molecules, and this group is called CDOM. As with DOC, a positive linear relationship between DOM and CDOM is assumed. CDOM can be determined by optical measurements, such as a laboratory spectrometer. CDOM may also be accurately determined from remotely sensed data, which could be more cost-effective than traditional *in situ* methods and provide more spatial and temporal information. Laboratory size distribution measurements of CDOM have shown a size range of approximately 0.5 nm to 0.1 μm, a range well below the threshold value for dissolved material (0.45 μm) and the 0.22 μm filter pore size used for CDOM measurements in some Ocean Color protocols.

Particulate organic matter is comprised of zooplankton, phytoplankton and organic detritus. Inorganic particles generally consist of sand, silt and clay minerals or metal oxides. Clay minerals may be smaller than the 0.45 μm threshold value for particulate matter and thus end up in the dissolved fraction. DOM, viruses and bacteria encompass the dissolved matter. DOM consists of a broad range of organic compounds including colloids (see above). Viruses and bacteria in dissolved matter may be present in great numbers. The inherent optical properties of viruses and bacteria, although possibly significant, are not typically included in management strategies such as optical models, because there are few practical methods for separating them physically in natural waters. Their absorption and scattering may influence the measurements of beam attenuation and CDOM absorption nonetheless.



The main components of DOM are Humic and Fulvic acids and Humin (provided by C. Kovach)

Water color is resultant of the components within the water column and can be greatly influenced by CDOM. Previous work has found that a three-component model based on total chlorophyll (Chl), total suspended matter (TSM) and CDOM was required to successfully simulate ocean color. This three-component model is applied in most optical modeling studies and can be used in resource management strategies (e.g., Charlotte Harbor NEP water quality targets). Attention has recently shifted to CDOM as knowledge about the optical characteristics of Chl and TSM has accumulated. The influence of CDOM is mainly in the ultraviolet (UV) and blue regions of the spectrum, and an increase in CDOM has an effect mostly on the reflectance values in the blue and green light region of the spectrum. To discriminate between total Chl, TSM and CDOM, information is required of the total reflection in the green wavelength area (550-600 nm), of the total Chl absorption peak around 676 nm, of the reflection peak at 706 nm where only TSM is optically active and in the blue area (400-450 nm) where only CDOM is optically active.

Because optical properties of water quality compounds are used in optical models, the accuracy of the estimation of these properties is crucial for model performance. Past research has found that the measured CDOM absorptions used as input for bio-optical modeling were often a source of error. Measured CDOM absorption spectra need to be corrected (for systematic errors and random noise) by means of modeling. CDOM absorption is characterized by a strong absorption in the blue wavelength region, exponentially declining towards longer wavelengths. This exponential shape is thought to be the theoretical form of CDOM absorption, and measured CDOM absorption spectra are usually corrected by fitting an exponential function. The resulting exponential function, or modeled CDOM absorption, is then used within the optical model. The slope of the exponential function varies due to the differences in composition of CDOM material. It has been argued that a two-component exponential function may provide better results than the single currently used because CDOM is comprised of two groups of compounds (humic and fulvic acids) with differing properties (see presentation for studies using this approach).

CDOM is typically only determined optically, and therefore it is usually not possible to calculate a concentration-independent inherent optical property. Although it is possible to measure the concentration of DOC, such measurements are not performed routinely in optical remote sensing studies, and the relationship between the concentration of CDOM and the concentration of DOC varies considerably in literature. As an alternative, modeled CDOM absorption is often normalized at 440 nm in order to make it more or less independent of the concentration. The currently accepted way of estimating the CDOM absorption spectrum is by measuring the absorbance in a dual beam bench spectrometer of the filtered sample against a reference, which is usually distilled water. The absorbance is measured in a standard bench spectrometer, where light passes through a cuvette containing the filtered sample or reference. The difference in attenuation of light between a 10 cm cuvette filled with reference fluid and a cuvette with sample water gives the absorbance of the sample; the influence of the light source, the spectrometer and absorption and scattering by pure water is cancelled out.

Instead of measuring the attenuation of light passing through a cuvette, the attenuation of light in an integrating cavity may be measured. Such a device, called the Point-Source Integrating-Cavity Absorption Meter (PSICAM) holds a number of theoretical advantages over the cuvette method. A recent study found that CDOM was systematically underestimated by all inversion methods and concluded that the standard measurement of CDOM absorption overestimates the absorption curve. The study hypothesized that scattering and methods used to calculate absorption coefficients were to blame. Usually absorbance is determined by measuring the light attenuation by a filtered sample (compared to a reference such as pure water) in a cuvette, assuming that the scattering coefficient of the filtrate is negligible and using the relationship between attenuation (c), absorption (a) and scattering (b):

$$\boldsymbol{c = a + b}$$

Until recently, scattering was assumed to be negligible compared to absorption when measuring CDOM absorption of natural waters using the cuvette method, but this assumption is now being questioned. If there is any residual scattering it will, erratically, be added to the absorption coefficient. A crude correction for such residual scattering is to subtract the offset of the absorption spectrum at around 750 nm where it is assumed that the absorption is negligible. This will nonetheless lead to an underestimation if there is still significant absorption at that wavelength. Other ways to avoid absorption overestimation caused by scattering losses in a cuvette are given in recent literature (see presentation).

SESSION TWO: General overview of CDOM in Estero Bay, Charlotte Harbor and Lemon Bay and the tributaries to each, including impacts to quality and quantity of light reaching seagrass beds and influencing primary productivity. Are CDOM concentrations changing in the region? If so, why?

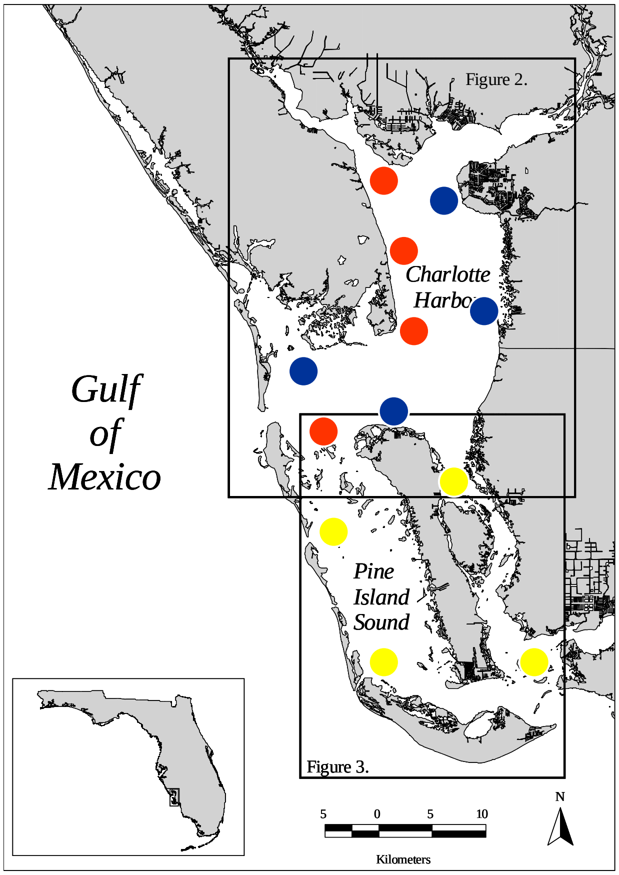
CAUSES OF LIGHT ATTENUATION WITH RESPECT TO SEAGRASSES IN UPPER AND LOWER CHARLOTTE HARBOR

L. Kellie Dixon, Gary J. Kirkpatrick, and Emily R. Hall, Mote Marine Laboratory

Little destruction of grasses has occurred in Charlotte Harbor, and while anthropogenic impacts appeared minor at the time of this study, nutrient loadings were expected to increase. Light limitation has been postulated and demonstrated as the major limiting factor and for grassbeds in Tampa Bay. Nutrient enrichment from point sources appears restricted to localized areas. Freshwater inflows to Charlotte Harbor are large, and during the wet season, salinity values across the Harbor can be severely depressed. Many regions may be at the extreme low end of an acceptable salinity range for seagrasses at times. High color values (and light attenuation) are associated with the freshwater discharges, which generally display a rapid onset and a persistent presence throughout the summer wet season. Grasses near the mouth of the Myakka and Peace Rivers experience combined effects of low light and low salinity.

SWFWMD and CHNEP funded a join tstudy in late 1990s to accomplish the following tasks: 1) Quantify light present at deep edge of seagrass, 2) Amount of light reduction from epiphytes on seagrass, 3) Relative importance of various attenuators on water column clarity and 4) Develop an Optical Model for water clarity, seagrasses. Two scalar PAR sensors were deployed, and a continuous record at deep edge was recorded. Seagrass response based upon shoot density, blade area per shoot and a leaf area index were measured. Epiphyte attenuation was measured as the suspension of scraped material placed in transparent dish that was matched to shoot area. Dish illuminated and a Li-COR sensor placed underneath. Water clarity parameters collected were color, turbidity, chlorophyll *a*, spectral absorption (CDOM). The study was tiered with 3 levels of monitoring:

- Blue=Level I (two continuous PAR sensors for a year, visited weekly for cleaning and monthly for collection of water quality and seagrass samples)
  PUN=T, COT=T, BOK=T. DEV=H
- Red=Level II (not instrumented but visited weekly for a year for the determination of attenuation coefficients, and monthly for water quality and seagrass samples)
  HOG=H, RAD=H, CAP=T, PAT=T
- Yellow=Level III (visited monthly for 6 months to determine water column attenuation coefficients and to collect water quality samples and seagrasses)
  MAT=H, PAS=T, SAN=H, BIG=H



Map of sampling stations
(provided by L. Dixon, G. Kirkpatrick, and E. Hall)

Results of the study demonstrated strong gradients in chlorophyll and CDOM from the mouths of the rivers down to Gasparilla Pass because of the freshwater inflow. Researchers found CDOM (ag440) values up to 13 m^{-1} and color up to 200 PCU, while chlorophyll concentrations were found as high as 143 mg/m^3. Mineral loads were found to be relatively low. Stations in the upper harbor experienced declines in seagrass response variables in comparison to the lower harbor stations, with declines typically produced by loss of blade area per shoot. Researchers found the following results when looking at epiphytic attenuation and the light available to plants:

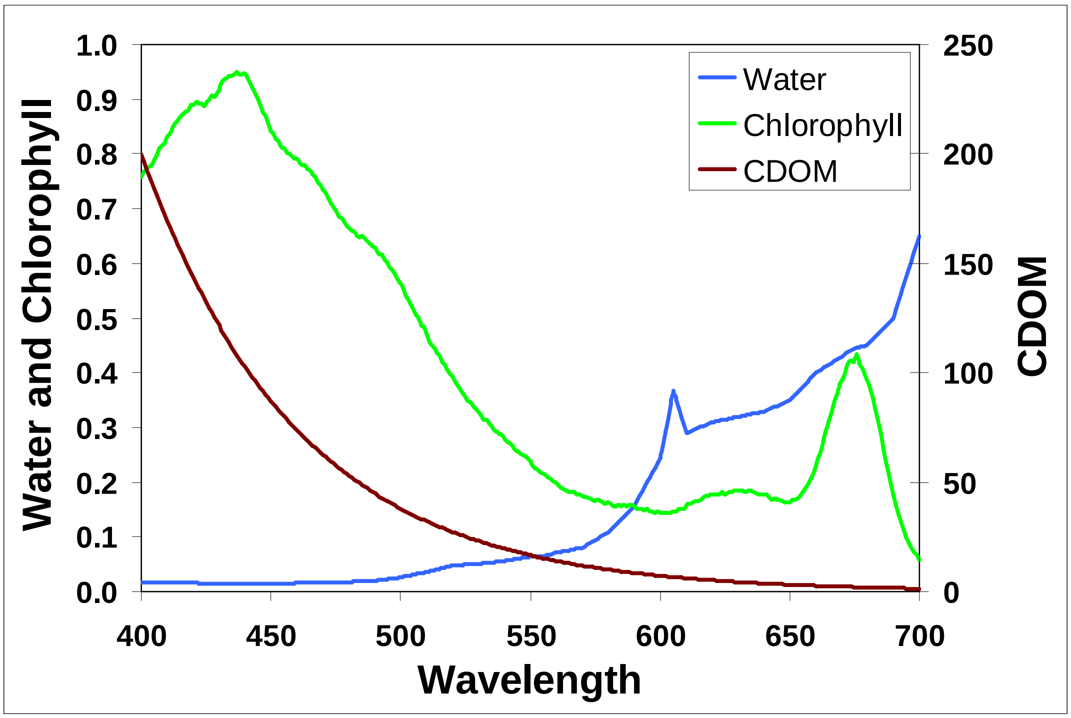
- Water column at deep edge
  - %PARw = 29% - 13%
- Available to plant
  - % PARp = 16% - 11%

Whereas %PARw is the immediately subsurface PAR reaching the maximum depth limits of seagrasses and %PARp equals the subsurface PAR after attenuation by epiphytic loads.

Researchers also developed an optical model with this study. Total absorption was partitioned into that attributable to: 1) water (a_w) using literature values, 2) phytoplankton (a_{ph}) specific to Charlotte Harbor communities, 3) dissolved color (a_{dc}), the exponential function of color and 4) detritus (a_d) from particulate absorption:

$$a_{total}=a_w+a_{ph}+a_{dc}+a_d$$

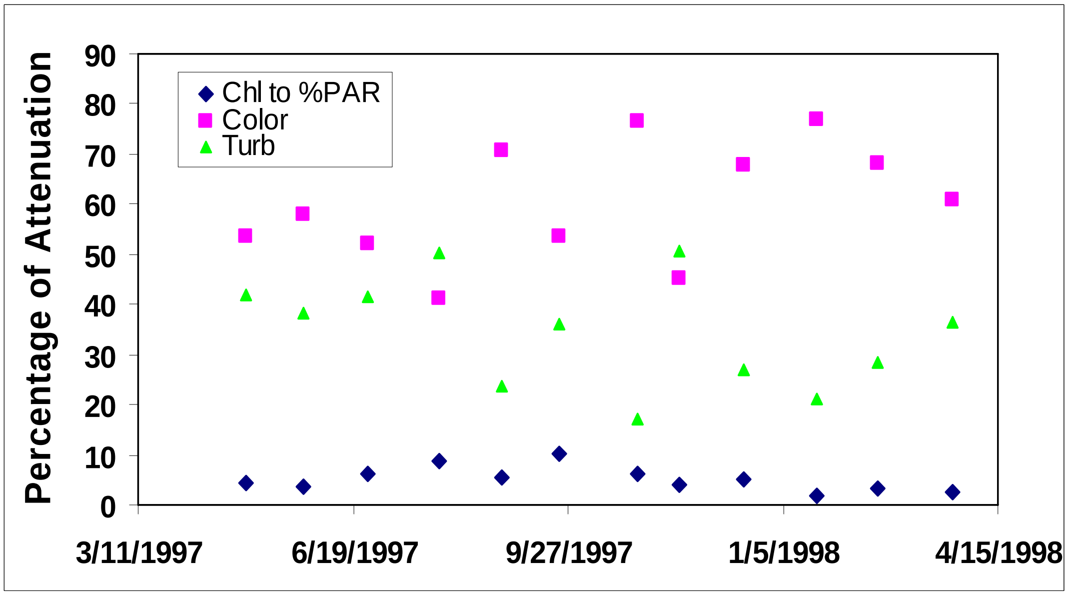
Chlorophyll-specific absorption [$a_{pl}(\lambda)$] was calculated for the model from the linear relationship between maximum absorption MA_{pl} and analytical chlorophyll concentrations. Absorption due to dissolved color appears as a negative exponential function of absorption at 440nm (g_{440}) and spectral slope (s_{dc}). Absorption due to detritus and other particulate material also represented as an exponential function of turbidity (NTU) and the absorption cross section of turbidity (σ_d). Further dependence on color, that may be attributed to type of particulates present. The scattering component demonstrated some spectral shape but was not as pronounced as those shown below. Researchers found that the scattering component was best described by turbidity (i.e., not total suspended solids).



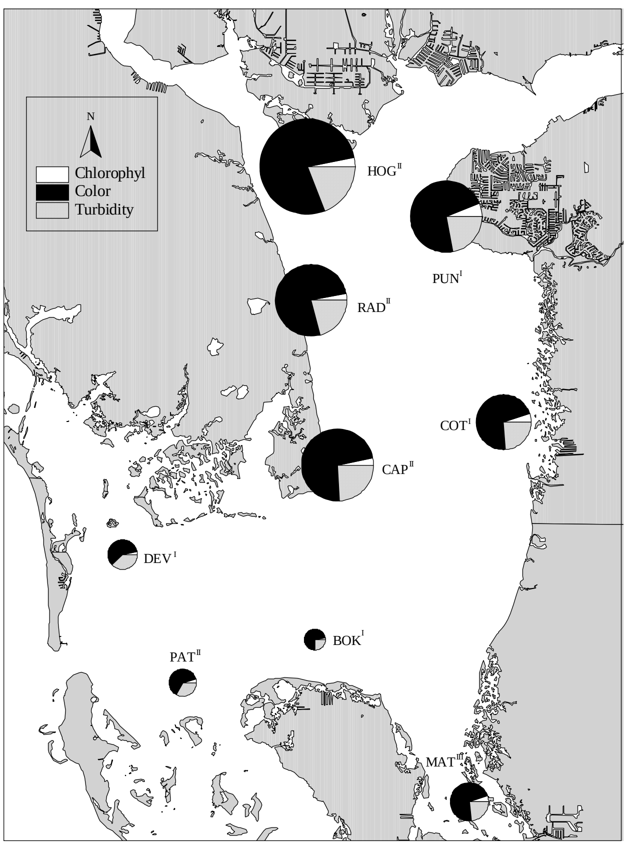
$a_t = a_w$, a_{ph} , (a_{dc} + ad) (provided by L. Dixon, G. Kirkpatrick, and E. Hall)

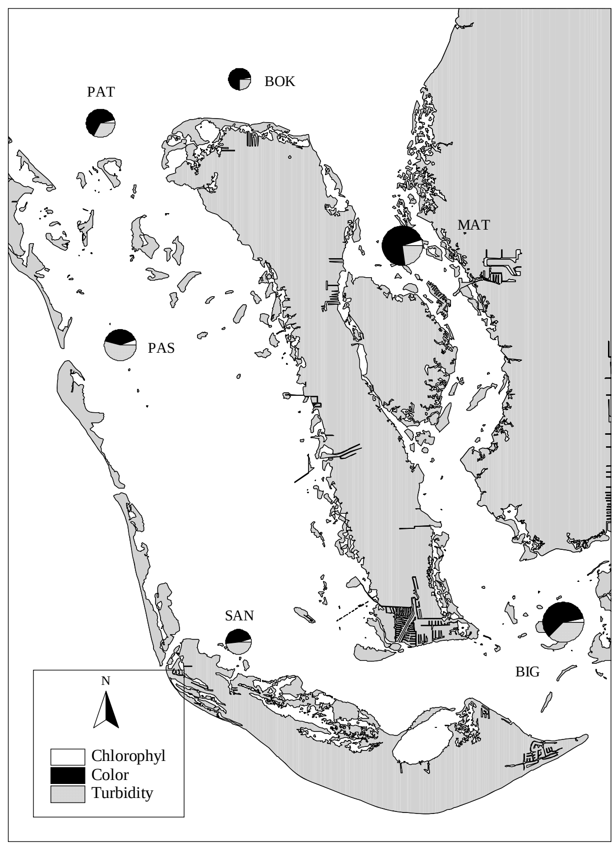
The developed optical model is spectrally sensitive (1nm) and includes color, turbidity, and chlorophyll to describe absorption and scattering. Wavelength-specific attenuation is integrated over 400-700nm (PAR).

The spectral character of the remaining light at depth is a function of water quality and absorption by chlorophyll *a* and other pigments controls photosynthesis. Photosynthetically Useable Radiation (PUR) is therefore important to measure rather than the entire spectrum alone to understand the light available to plants for photosynthesis. There is additional attenuation by epiphytes, and the spectral attenuation by epiphytes is assumed to look similar to chlorophyll. This attenuation is not presently included in the optical model.



Lower Charlotte Harbor (provided by L. Dixon, G. Kirkpatrick, and E. Hall)



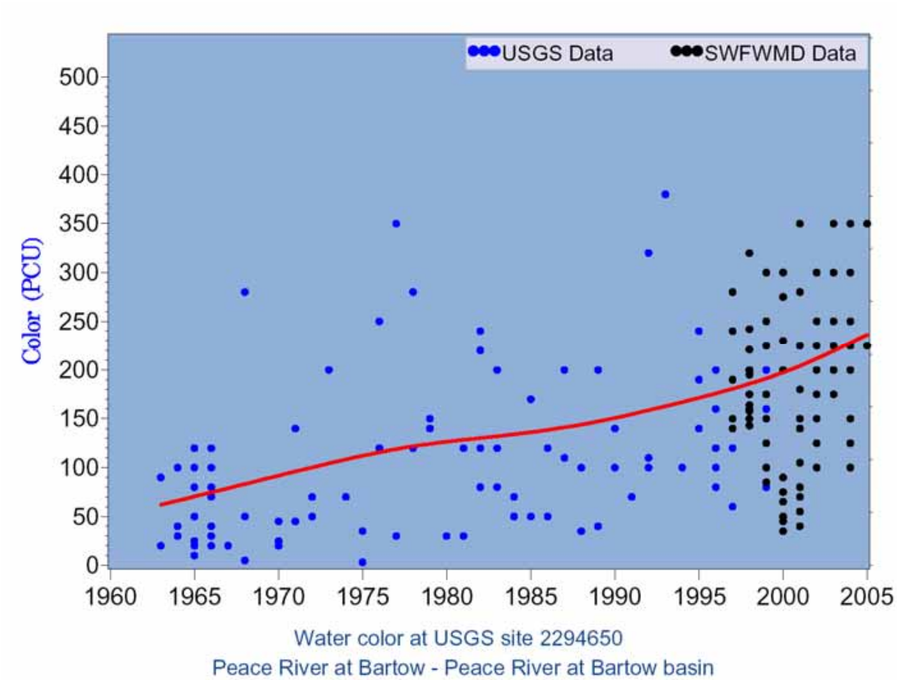


Relative attenuation of color, chlorophyll and turbidity. The diameter of circles is proportional to the annual adjusted attenuation coefficients (Kd Adj)
(provided by L. Dixon, G. Kirkpatrick, and E. Hall)

CHANGES IN LAND USE IN THE PEACE RIVER WATERSHED AND CDOM IN THE LOWER PEACE RIVER WATERSHED AND UPPER CHARLOTTE HARBOR

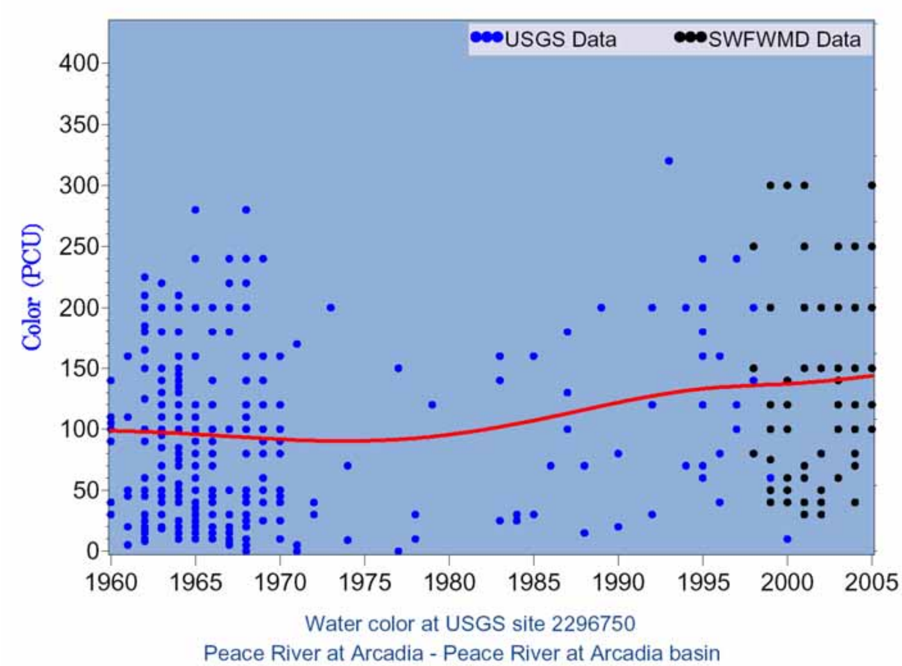
Ralph Montgomery, PBS&J and Sam Stone, PRMRWSA

By the 1940s, only 15% of the Peace River watershed had been developed or cleared: 60% was native uplands; 25% wetlands. By 1979, half of the native uplands had been cleared at a rate of 14 square miles (land sections) per year, and wetlands went from covering 25% of the watershed to 18%. By 1999, native uplands were reduced to 17% from 30%, and additional wetlands were also lost. Agriculture was the main developed landuse in the 1940s; mining and urban were still quite small. By 1979, however, cleared agricultural land was 40% of the watershed and mining and urban represented 5% of the landuse each. Cleared agricultural land comprised 44% of the watershed in 1999 with urban and mining representing about 10% of the watershed each. Thus, there have been major land use changes in the Peace River Watershed, and the largest of these changes pre-date most available water quality data (e.g., color).



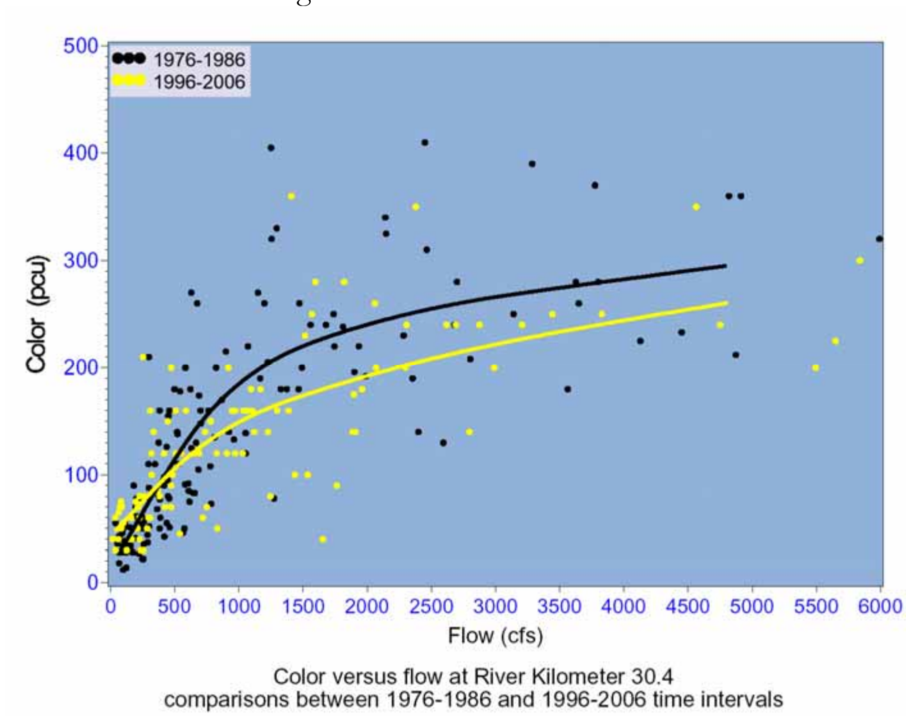
(provided by R. Montgomery and S. Stone)

Color appears to be increasing in the upper Peace River basin since the mid 1960s (see above graph). Color also appears to be increasing at the lower Peace River monitoring station since the 1960s (see graph below).

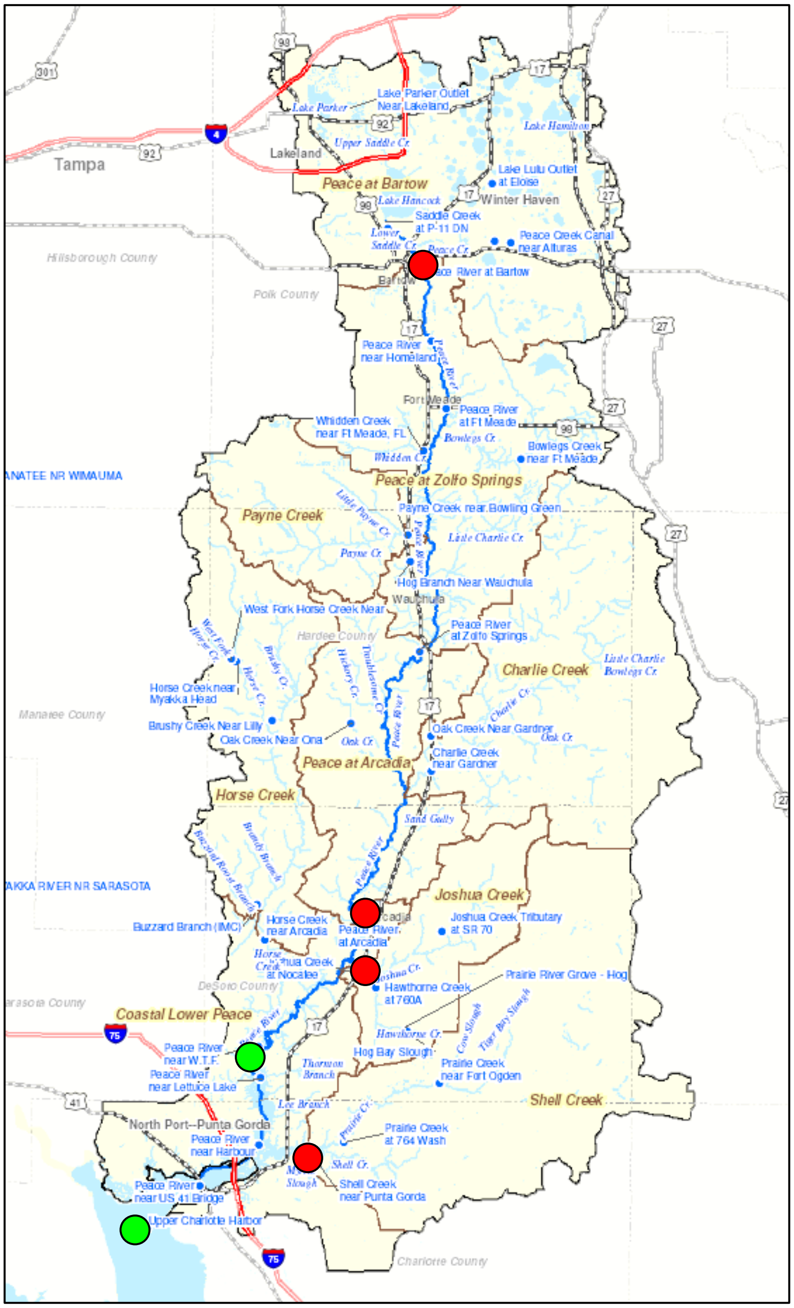


(provided by R. Montgomery and S. Stone)

These changes in color concentrations are associated with changes in flow conditions and are not a result of landuse change.



(provided by R. Montgomery and S. Stone)



Water Quality Stations in the Peace River:

- Peace River at Bartow
- Peace River at Arcadia
- Joshua Creek at Nocatee
- Shell Creek near Punta Gorda
- Lower Peace River
- Upper Charlotte Harbor

(provided by R. Montgomery and S. Stone)

Apparent increases in color in the upper and middle watershed are associated with declines in groundwater discharges by mining and local springs. Apparent recent increases in color in the lower river and upper Charlotte Harbor estuary correspond with increases in wet-season flow.

The following table lists average and median seasonal flow in the tidal Peace River and water color at 2 stations in the Peace estuary for different time periods.

Period	Season	Flow in cfs (Peace River at Arcadia + Horse & Joshua Creeks)		Water Color (pcu) at River Kilometer -2.4		Water Color (pcu) at River Kilometer 30.4	
		Median	Mean	Median	Mean	Median	Mean
1976-1986	Nov-Feb	363	689	28	26	87	106
	Mar-May	260	708	23	36	74	98
	Jun-Oct	643	1426	40	62	180	186
1996-2006	Nov-Feb	406	1220	28	42	90	111
	Mar-May	213	776	25	32	70	91
	Jun-Oct	1111	2369	60	88	200	207

(provided by R. Montgomery and S. Stone)

However, long-term changes in water quality characteristics such as orthophosphate and silica levels may be related to recent changes in landuse.

FLOW, SOURCE AND CDOM IN THE CALOOSAHATCHEE RIVER AND ESTUARY

Peter Doering, South Florida Water Management District

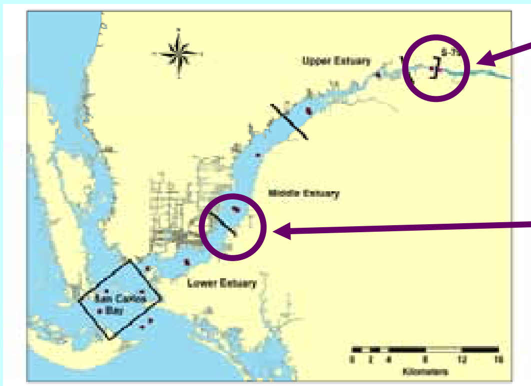
The Caloosahatchee Estuary is located on the southwest coast of Florida. The estuary extends from the Franklin Lock (S-79) to Shell Point where it empties into San Carlos Bay. The Caloosahatchee River, which runs from Lake Okeechobee to the Franklin Lock, is the major source of freshwater to the estuary. The Caloosahatchee River itself has two sources major sources of water: the Caloosahatchee River Watershed and Lake Okeechobee. On average, about half comes from the Lake and about half from the watershed. The short term variability is quite large, so that on a month-to-month basis the % derived from either source can vary from 0 to 100%.

CDOM can dominate the appearance of this system. The data herein measures CDOM as Color. This presentation includes data from just two areas of the estuary. The first is S-79, where we have a continuous bimonthly sampling that has been going on since 1982. And this has been augmented by sampling from a couple of other programs. The second is the mid estuarine region, which has been sampled discontinuously since 1985. The sampling has occurred in three time periods: 1985-89, 1994-1996, 1999-present. Also sampling has occurred at two different stations, these are about 300 yards apart.

Lastly, when we consider mixing behavior, we will be looking at data from all these stations pictured here. These were sampled 24 times during 2000, 2001 and 2003 by Harvey Harper from Environmental Research and Design, Inc.

Data Sources

CDOM measured as Color against a Pt-Co standard



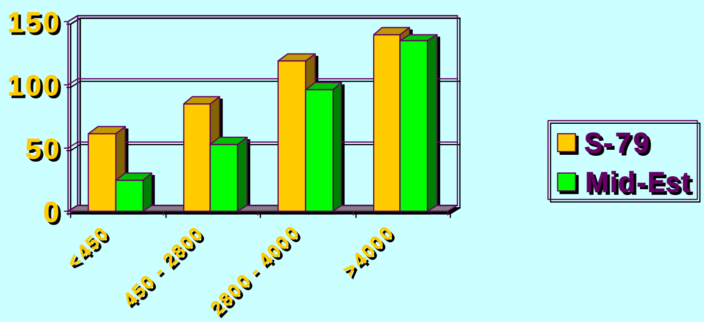
- S-79
  - CR: 1982-present
  - CAL: 1994-96
  - CESWQ: 1999-present
- Mid Estuary
  - CES06-CAL07: 1985-89, 1999-present
  - CAL08: 1994-96

(provided by P. Doering)

The graphic below shows the mean concentration of color at S-79 and in the middle estuary as a function of discharge at S-79. The discharge at S-79 is the average daily discharge that occurred for the 30-days prior to sampling.

Color Increases as Discharge at S-79 Increases

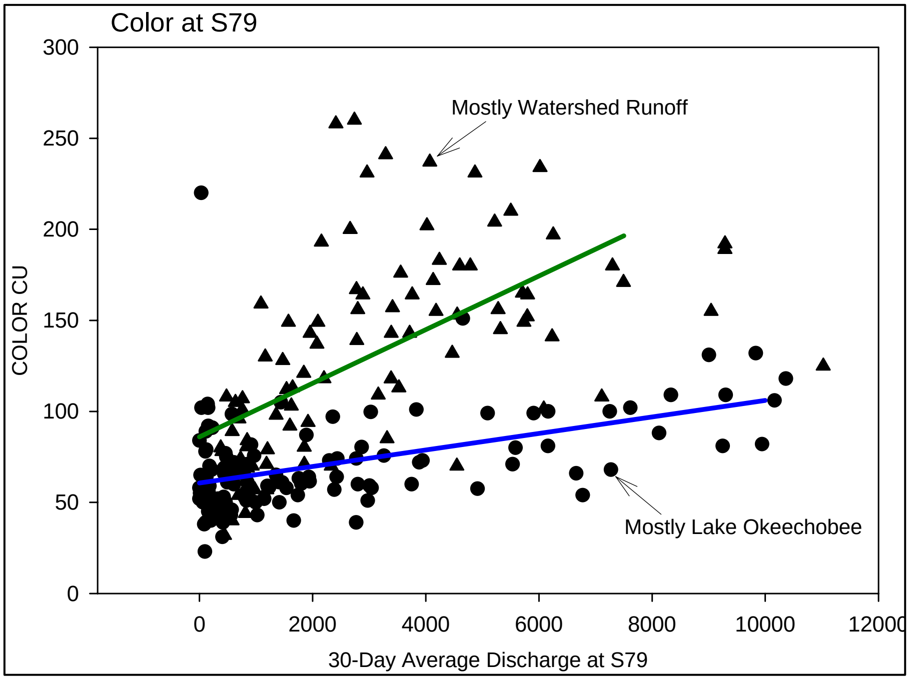
Color CU



30-day Average Discharge at S-79 (cfs class)

(provided by P. Doering)

At both S-79 and the Middle estuary, the concentration of color increases with discharge. At each site, these increases are statistically significant. For example, all these yellow bars are statistically different from each other.

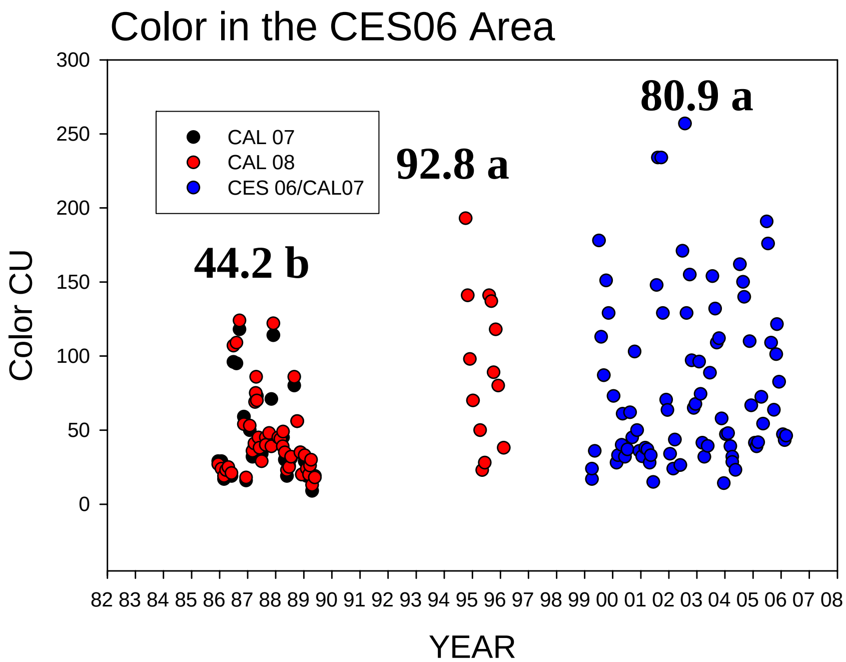


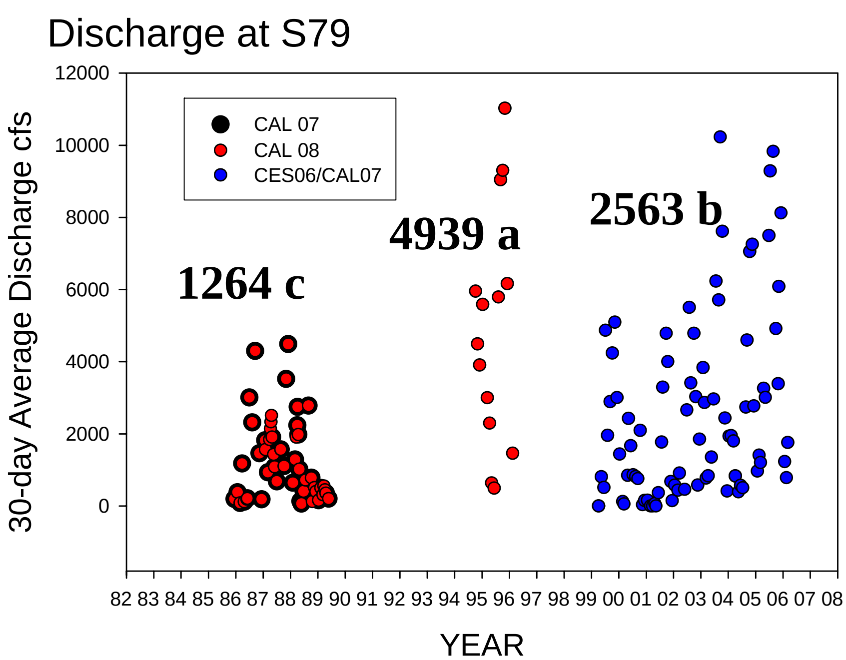
(provided by P. Doering)

The above graphic shows the concentration of color at S-79 as function of the average discharge at S-79 for the 30 days prior to sampling. As discharge increases the concentration also increases, but there is one relationship when most of the runoff (>50%) is from the watershed and another when most of the runoff (>50%) is from the lake. When most of the water at S-79 is coming from the watershed, the concentration increases faster per unit increase in discharge than when most of the water is coming from the Lake. The slopes of these two lines are statistically different. The same effect is evident in the Mid-estuary. The concentration of color increases as a function of discharge, but at a faster rate if most of the discharge is from the watershed. The lines have different slopes so they must intersect somewhere. Thus, we should not expect the difference in source to produce a difference in concentration of color at all discharges.

At low flows, the concentration of color does not depend on source of water while at higher flows, it generally does, with one exception. The concentration of color increases faster if the primary source of discharge is the watershed rather than Lake Okeechobee.

There has been no long-term change in the concentration of color at S-79 that was detectible with the Kendall tau or Spearman's rank correlation coefficient, although there was an apparent low point in the late 1980's and early nineties. In the Middle estuary, there has not been continuous sampling over the long-term. Thus, the three periods shown here were compared using the Kruskill-Wallis non-parametric one –way analysis of variance. This analysis detected significant differences between periods, and these were further examined using the Wilcoxon two sample test (just a two test using ranks). Results show that the earliest period has a lower concentration then the two later ones. On the bottom is the 30-day average discharge during the 3 sampling periods, and the flows are all different from each other. The pattern of flow differences follows the concentration differences. So whether the differences in concentration is seen between sampling periods is a true trend or due to flow differences needs further investigation.

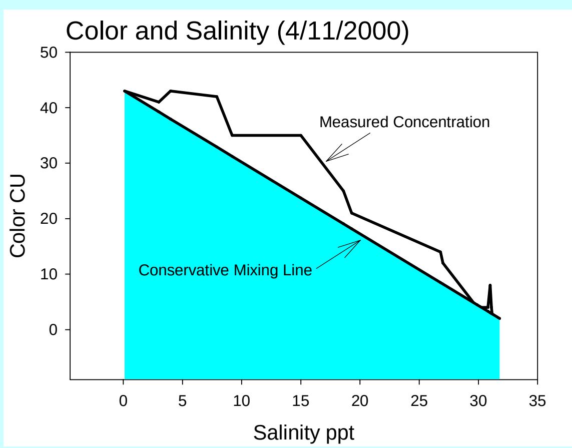


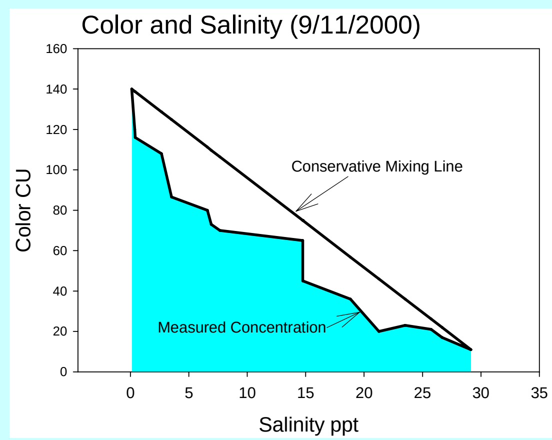


(provided by P. Doering)

The data used to evaluate the apparent mixing behavior of CDOM in the estuary come from a three year study conducted by ERD in which they made 24 synoptic surveys from S-79 to the Gulf of Mexico. It is important to define the term "apparent mixing behavior". Salinity versus property plots, constructed from field measurements, assume that a straight line results only from the mixing of one freshwater endmember and one saltwater endmember. Deviations from this conservative mixing line are caused by *in situ* production, addition from external sources, consumption in the water column or loss to the sediments. Conservative mixing can only be confirmed by laboratory experiments. If production is balanced by an equivalent loss, a straight line may still result and the constituent only appears to behave conservatively. Similarly, fluctuations in endmember concentration that occur on time scales shorter than the hydraulic residence time of the system can result in "apparent deviations" from the conservative mixing line, even if the constituent is behaving conservatively. Qualitative examination of the mixing diagrams suggested that 4 were apparently conservative, 14 suggested apparent removal and 6 suggested addition. We calculated the % added or removed as follows:

More Quantitatively:

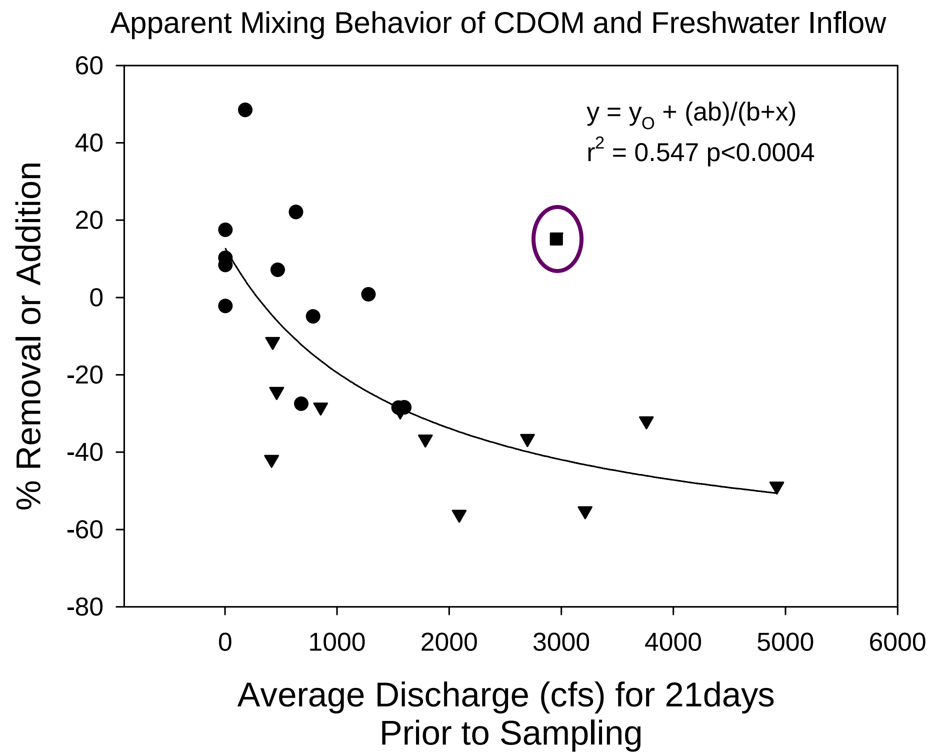




% Removed or Added = **(Area Under Measured Mixing Line - Area Under Conservative Mixing Line) / Area Under Conservative Mixing Line**

(provided by P. Doering)

The results can be described as a function of flow at S-79, using an equation of the form below. One point was left out, but if it is included, the results are still statistically significant. At low flows, addition is likely, and at higher flows, removal is more common. After about 2000 cfs, removal appears to level off. Therefore, the apparent mixing behavior of CDOM can be nonconservative with addition or removal related to the rate of discharge at S-79. Laboratory mixing experiments are required to confirm non-conservative behavior of color in the Caloosahatchee.



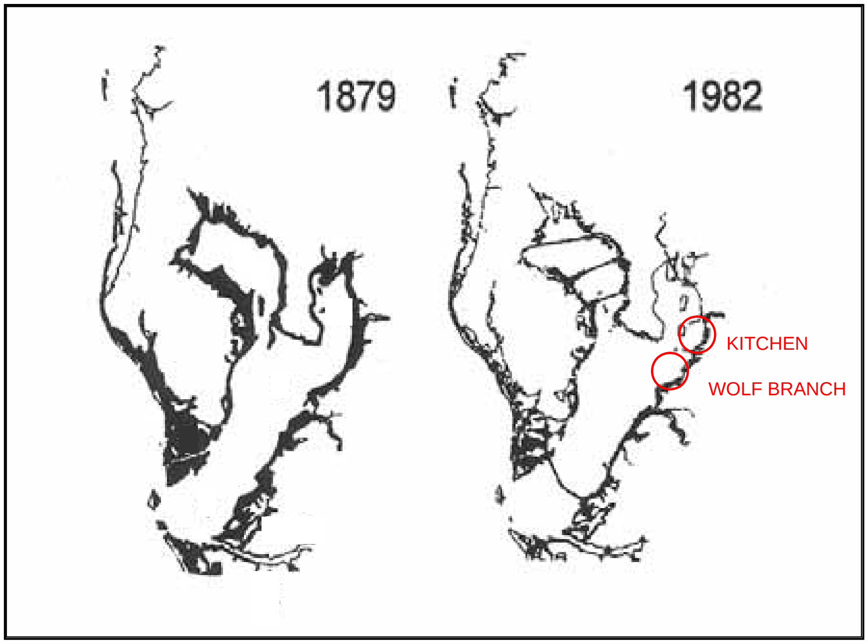
(provided by P. Doering)

SESSION THREE: What are the spatial-temporal components of CDOM in the Charlotte Harbor region? Can we obtain this information using existing data or do we need specific research project(s) or monitoring programs to obtain this information? Can landuse models be improved to better estimate CDOM "event mean concentrations" (EMCs)? Would this analyte be an important addition to models for resource management in the southwest Florida region? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.

NEAR-SHORE WATER QUALITY AND SEAGRASS RELATIONSHIPS IN THE UPPER PORTIONS OF TAMPA BAY

Roger Johansson, City of Tampa

Robin Lewis and others have estimated that historically, the entire shallow shelf around Tampa Bay was covered by submerged seagrass. The seagrass meadows are shown as the black areas in the graphic below. By 1982, major losses had occurred specifically in the upper bay as a result of eutrophication. Virtually all seagrass had been lost from Hillsborough Bay by this time. ~~This discussion~~ focuses on two areas on the eastern shore of the bay, the Kitchen in Hillsborough Bay and Wolf Branch in Middle Tampa Bay. These areas have seen some recent limited recovery of seagrass. However, much of the historic coverage is still missing.



(provided by R. Johansson)

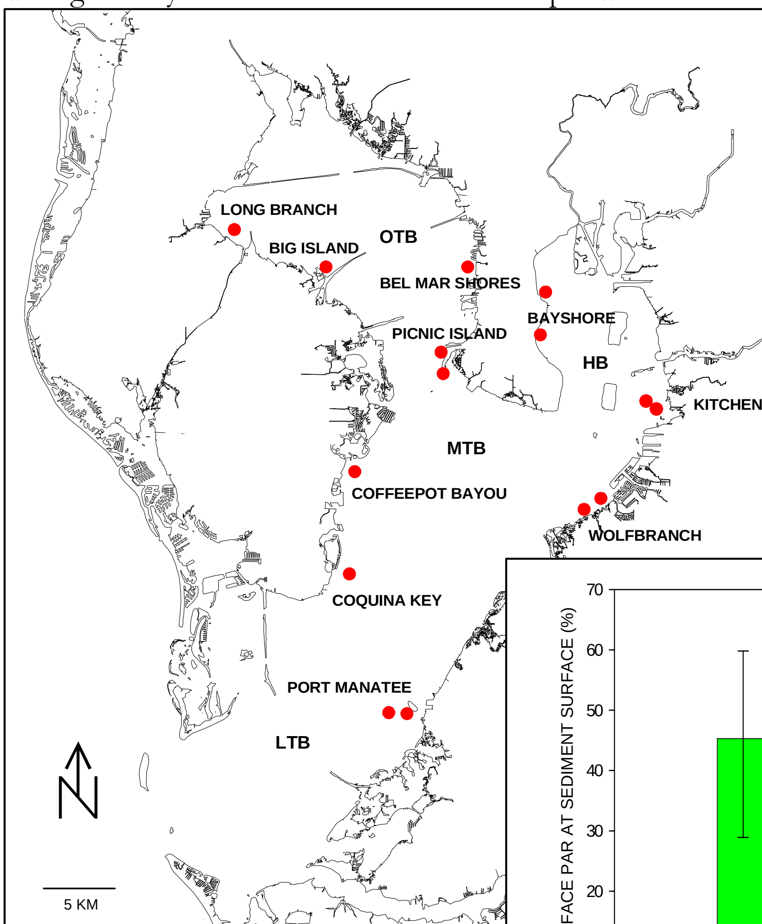
As a result of large nitrogen loading reductions from primarily point sources in the late 1970's and early 1980's, eutrophic conditions were reduced and water clarity increased. With increased water clarity, shallow seagrasses, primarily Halodule, started to colonize shallow areas. We looked at the seagrass expansion in the Kitchen in greater detail, and results demonstrated that coverage initially increased very fast and peaked in the 1997-99 period at approximately 40ha. Since then, coverage has been somewhat less, but relatively stable.

Thus, over the last decade there has been no sustained seagrass increase in the Kitchen. A striking feature of the Kitchen meadow is the remarkable stability of the deep edge. It appears that some invisible force is holding the meadow back from extending into deeper waters. After noticing the lack of expansion we wanted to know if light availability limited the expansion into deeper waters. At the time when we asked this question in 2000, we did not have any water quality or light information in the shallow area of the Kitchen, but we had PAR sensor measurements from two routinely monitored water quality stations in the deeper waters outside the Kitchen. A several year twice monthly record showed that the offshore PAR light attenuation coefficient Kd(PAR) was about -1.4m-1.

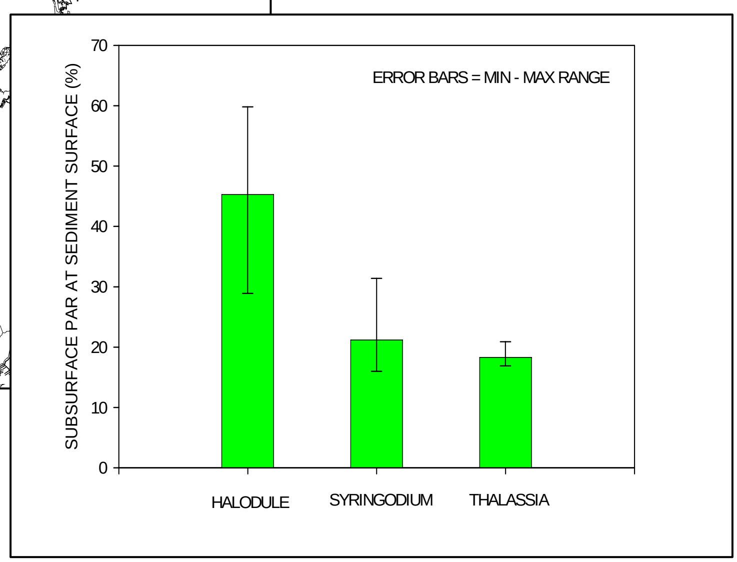
We also had high resolution DGPS bathymetry from a permanent seagrass transect and seagrass distribution along the transect. Using this information we calculated that the deep edge at -0.5m MTL received approximately 50 % of just below surface incident radiation. This level is much higher than what the literature reports to be required for sustained seagrass growth and should not limit seagrass expansion to deeper water. We then had to ask ourselves a second question: was the deep light information not representative of shallow conditions?

We did the same calculations for the Wolf Branch area in Middle Tampa Bay. This area is very similar to the Kitchen in that ~~is~~ has a shallow temporally stable deep edge of the near-shore Halodule meadow. Also both areas are adjacent to substantial mangrove and salt marshes. ~~And~~ both areas appear to have relatively high persistent CDOM levels that are present even during dry periods. We used the same method to calculate light availability at the stable near-shore meadow as we did in the Kitchen and found that this edge also received very high levels based on offshore light attenuation measurements. These light levels should not limit seagrass expansion into deeper areas.

In addition to the two study areas discussed, we also estimated light availability, based on deep water light information, at the deep stable edges of numerous seagrass meadows throughout Tampa Bay. We included Thalassia and Syringodium in this effort. The result of this study in 1999 and 2000 shows that the shallow Halodule meadows receive much higher light levels than the other two species. The Thalassia and Syringodium beds we measured were generally located offshore in much deeper water than the Halodule beds.



Light Availability at the Deep Edge of Tampa Bay Seagrass Meadows (1999-2000)



(provided by R. Johansson)

In 2005 we initiated a shallow water quality and light availability study of the shallow area in the Kitchen. With this ongoing study we aim to gain a better understanding of the shallow water light climate in terms of both quantity and perhaps most importantly the quality of the light available for seagrass growth. It is difficult nonetheless to measure the water column light climate directly in shallow waters using conventional monitoring tools. The Secchi Disk method gives a measure of water clarity, but the disk is most often visible on the bottom and does not provide ~~any~~ useful information. PAR sensors ~~provides~~ light attenuation coefficients, but because the sensors need to be vertically separated, this method is not very useful in water depths less than a minimum of 1m for areas with water clarity similar to Tampa Bay.

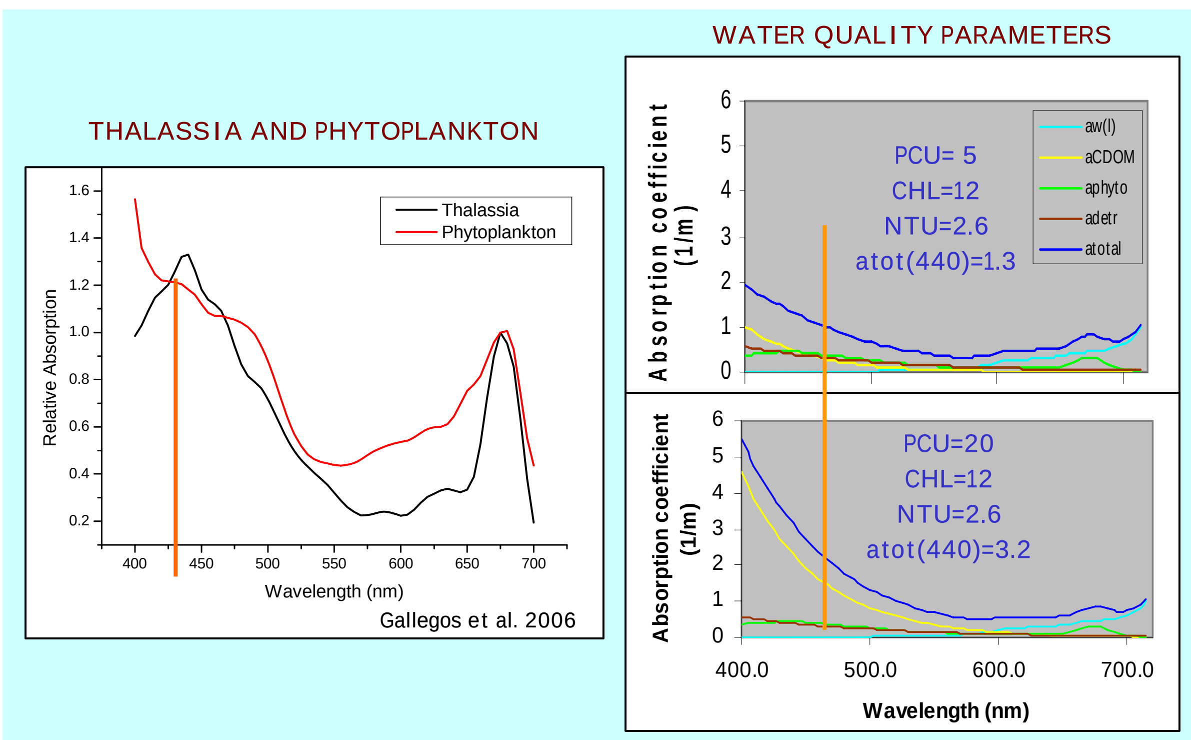
The light climate in shallow areas can be determined through the use optical models. These models use measured concentrations of the three important water quality parameters: chlorophyll, turbidity and CDOM to estimate subsurface light conditions. The model results in this effort are derived from an optical model developed by Dr. Charles Gallegos that he kindly provided to us. His model calculates total Kd(PAR) from the three water column parameters, but it can also estimate the contribution of each parameter to the total Kd. His optical spreadsheet model has been applied in numerous estuarine studies and has been described in many peer reviewed journal articles.

Results of analyses comparing the shallow and deep water stations show seasonal differences in chlorophyll concentrations but no statistical difference in annual concentrations between 2005 and 2006. There was no seasonal nor annual difference for turbidity concentrations in either year. In contrast to both chlorophyll and turbidity, there was a consistent gradient of decreasing levels of CDOM from near-shore to offshore. For both years, waters above the seagrass edge had statistically higher levels of CDOM than levels at the deep areas. Both 2005 and 2006 were relatively dry years with low overall CDOM levels in the bay during the wet period. The results suggest that the shallow areas are chronically impacted by relatively high CDOM levels and that the locally elevated levels occur independent of wet season bay-wide CDOM enrichment.

When inputting collected water quality data into the optical model, results show that estimated light attenuation (total Kd(PAR)) is virtually the same at the shallow stations and just slightly lower (better light penetration) in the deep reference area. The percent light reaching the sediment varies with depth and Kd. Based on the shallow water quality at the edge of the meadow, the edge receives near 60 % of the incident PAR radiation. This value is slightly higher than what was estimated from the earlier estimates using deep water quality. This suggests that in terms of PAR estimates it may not make much difference if shallow or deep information is used, at least for this area. However the relative importance of the three water quality parameters in affecting PAR differs. CDOM appears to be the most important parameter affecting PAR light attenuation at the most near-shore stations, and chlorophyll appears to be least important. Turbidity is most important at the deep reference station. Because each of the three parameters affects light availability differently, it follows that the optical quality of the light is not the same in the shallow and deep areas.

CDOM is a strong absorber of light in the blue region of the visible spectrum, and the high energy blue light is very important for photosynthesis. Therefore, the higher CDOM levels found in the shallow area of the Kitchen may reduce the important high energy fraction of PAR light reaching the seagrass meadow and affect the quality of light availability. This loss would not be fully accounted for by the broad-band Kd(PAR) estimates of light availability. To compensate for these losses, broad-band light availability may have to be much higher for sustained seagrass growth in areas with chronic CDOM influence than other areas in Tampa Bay.

Finally, it is not only the optical properties of the water column that determines what light is available for photosynthesis, but the seagrass themselves have specific abilities to utilize the available light. The graph to the left below shows the absorbance spectrum for Thalassia. Thalassia has two important peaks of absorption in the PAR spectrum, the greatest near 440nm in the blue region and the other near 675nm in the red region. The figures to the right show the PAR absorption spectra for two water quality scenarios based on the shallow Kitchen data. In both scenarios chlorophyll and turbidity have been set constant as the averages for the two years. There are two CDOM concentrations: 5 and 20 PCU, which approximates minimum and maximum levels during the study. Results show that this relatively small variation in CDOM concentrations cause significant differences in the amount of light that is available for Thalassia at 440nm. The two graphs show that increasing CDOM levels from 5 to 20 PCU causes a 15% increase in light absorption of the important high energy light.



(provided by R. Johansson)

The Kitchen study ~~shows~~ that CDOM levels are consistently higher in waters above the near-shore grass beds compared to areas further offshore. Chlorophyll and turbidity show less consistent trends with distance from shore. The optical quality of light available for near-shore and offshore seagrass meadows may be different because of spatially different water quality. As a result, near-shore and offshore seagrass meadows may require different actions for protection and restoration. Seagrass light requirements based on photosynthetically usable radiation (PUR), which take into account spectrum-weighted energy requirements of seagrass, may provide better comparisons of light availability for areas with a wide range of water quality conditions.

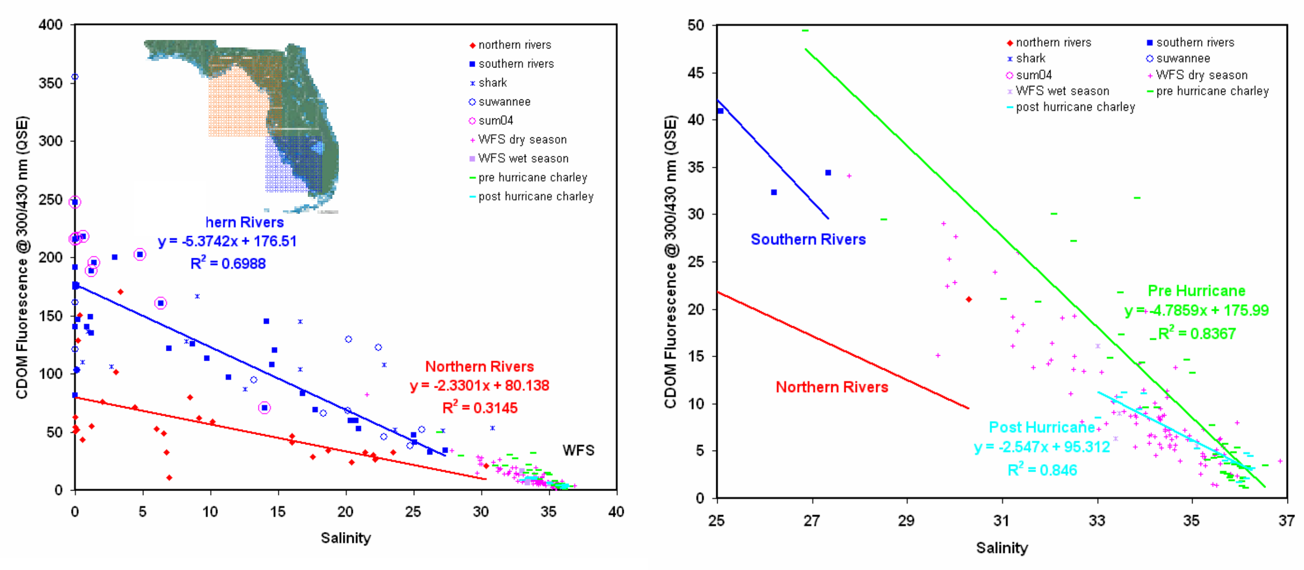
TEMPORAL AND SPATIAL VARIABILITY OF CDOM OPTICAL PROPERTIES

Robyn Conmy, University of South Florida

This work focuses on CDOM optical properties along the West Florida Shelf with emphasis on water mass tracking, characterizing estuarine plumes, determination of variability of inherent optical properties (IOPs), a need to better understand the CDOM pool and improving remote sensing products. To understand CDOM in the coastal ocean, additional information is needed about estuarine/riverine endmembers and the biogeochemical processes that control its variability. Changing scales (both temporal and spatial) can bring new questions/concerns, such as the response time of CDOM, interaction with bottom sediments, particles/turbidity, sediment type, estuarine circulation/tides and anthropogenic influences.

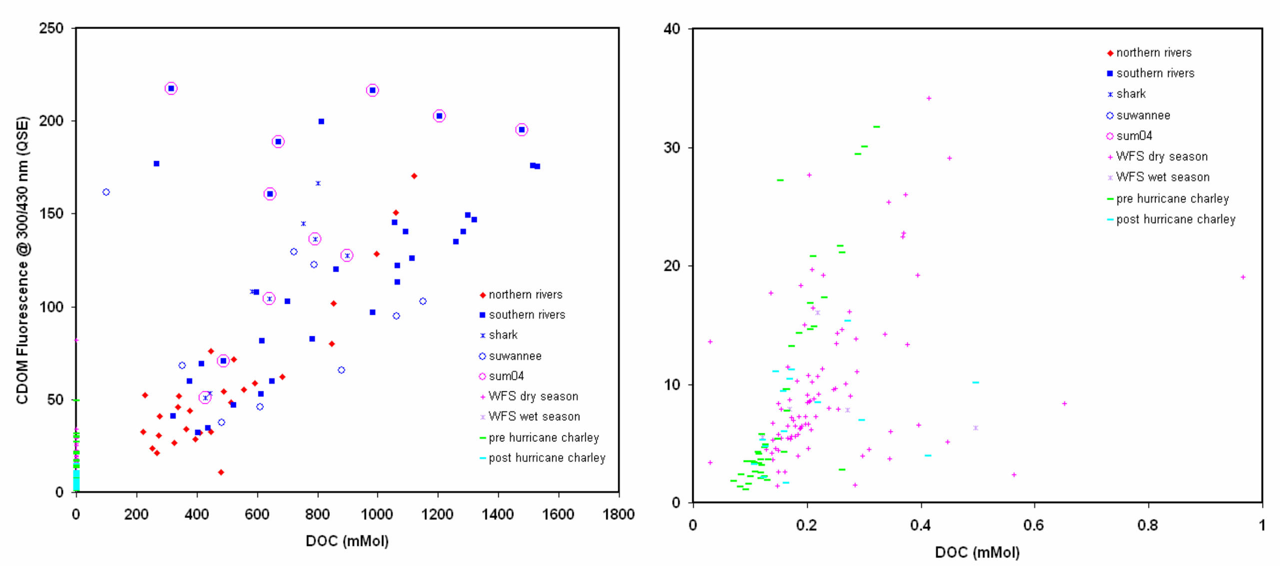
The work measures CDOM by discrete sampling methods for absorption spectroscopy and fluorescence spectroscopy [3D high-resolution excitation emission matrix spectroscopy (EEMS)] as well as continuous in situ fluorescence measurements that increases the spatial-temporal resolution [single channel (WetStar) and multichannel (WetLabs Inc SAFIre)]. IOPs that are measured are driven by quantity and composition issues, such as fluorescence intensity, absorption coefficients and spectral changes (e.g., positions of maxima, fluorescence efficiencies, fluorescence ratios, spectral slopes).

The following graphs demonstrate CDOM quantities for northern versus southern Florida rivers as well as before and after hurricane Charley. The data in blue represent measurements taken from southern rivers, while the data in red represent measurements taken from northern rivers. The data in green in the graph at right represent data from the Peace River prior to August 13, 2004, while those in light blue represent those data gathered subsequently. The graphs demonstrate that there is spatial variability in CDOM quantities amongst rivers along the west coast of Florida and temporal variability within a single river. Other measurements in this work show the spatial and temporal distribution of CDOM quantities within the Charlotte Harbor estuary (see presentation). The in situ measurements require correction for turbidity and/or self-shading effects within the estuary.



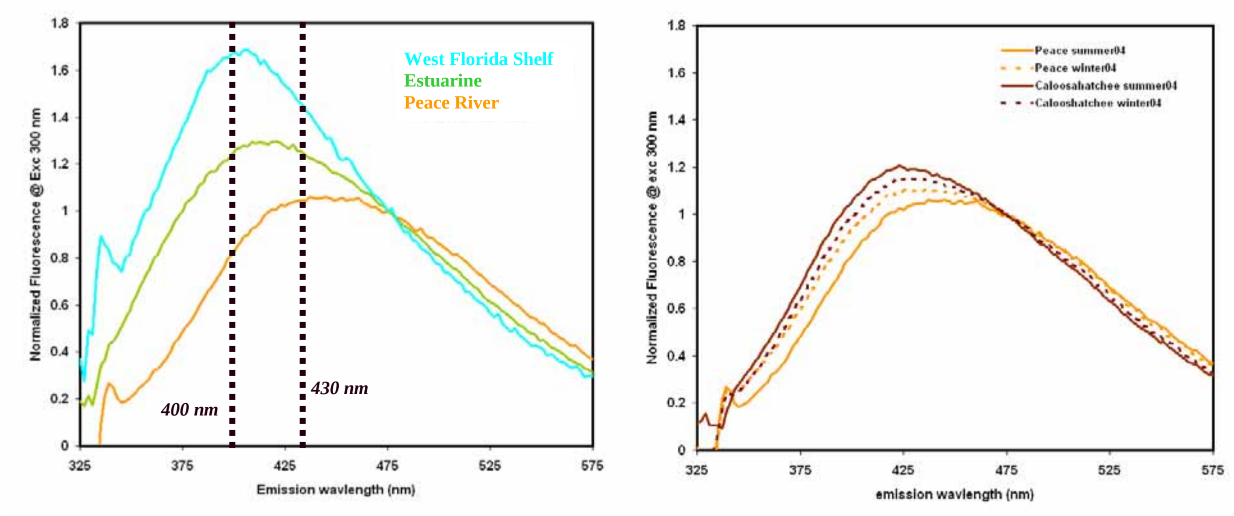
(provided by R. Conmy)

In Charlotte Harbor, there is a strong correlation with CDOM and DOC, with the exception of post hurricane conditions. Thus, there is a potential of using CDOM as an optical proxy for DOC.

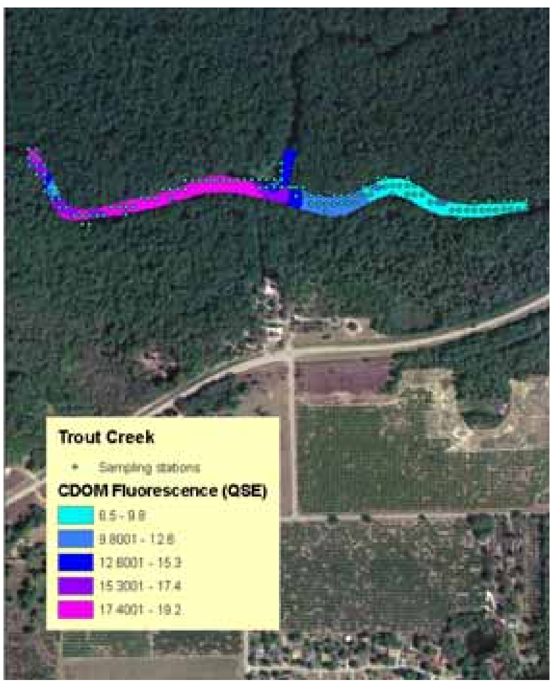


CDOM fluorescence and absorbance. Note the x-axis scales differ in the 2 graphs. (provided by R. Conmy)

The composition of CDOM also shows temporal and spatial variability. There are spectral changes, such as the positions of maxima shift; the position is related to chemical composition. When maxima are blue-shifted (i.e., towards shorter wavelengths), the CDOM has a more composition, whereas red-shifted maxima (towards longer λ), there are fresher organics and a more riverine composition. The spectral shape differs spatially and temporally as well:



(provided by R. Conmy)



Researchers can use fluorescence ratios to determine sources, but which fluorescence pair and the location within the matrix may be regionally dependent. On-going work in the Hillsborough River with specialized equipment has given high spatial resolution mapping of CDOM fluorescence.

(provided by R. Conmy)

From this work and other research, scientists know that coarse sampling practices are inadequate for determining CDOM variability in estuaries and streams and that single channel measurements only tell us 'how much?', but says nothing about composition, age or behavior in environment. CDOM fluorescence can be an optical proxy for DOC and in situ fluorescence is a quick, cheap, yet sensitive measurement of organic matter. Turbidity correction essential for in situ sensors, and large multi-year datasets exist through management agencies that can help explain trends researchers see.

Future directions for this work include the following:

- Investigate robustness of wavelength ratios
  - Is there a better ratio for tracking?

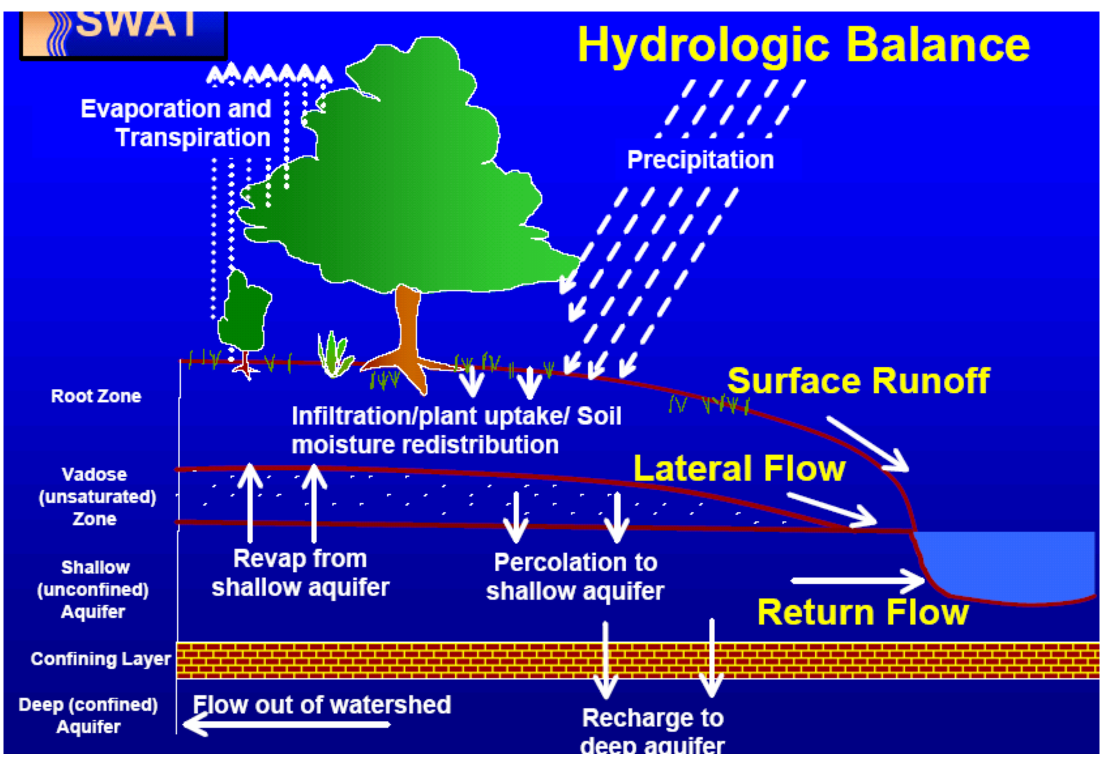
- Are the relationships universal?
  - Seasonality?
  - Regional dependence?
- Could this method work with 2 single-channel fluorometers that draw less power and can be deployed on monitoring platforms?

- Characterization of CDOM signatures besides surficial waters in estuaries
  - Groundwater, sediments, sea grasses, phytoplankton
- Incorporating EEMS into Parafac model
- Use GIS to answer questions about CDOM variability.

EXAMINATION OF THE SPATIAL RELATIONSHIP OF SOILS, LANDUSE AND SLOPES TO FLORESCENCE DATA IN SELECTED WATERSHEDS: AN INTEGRATED ANALYSIS WITH GIS

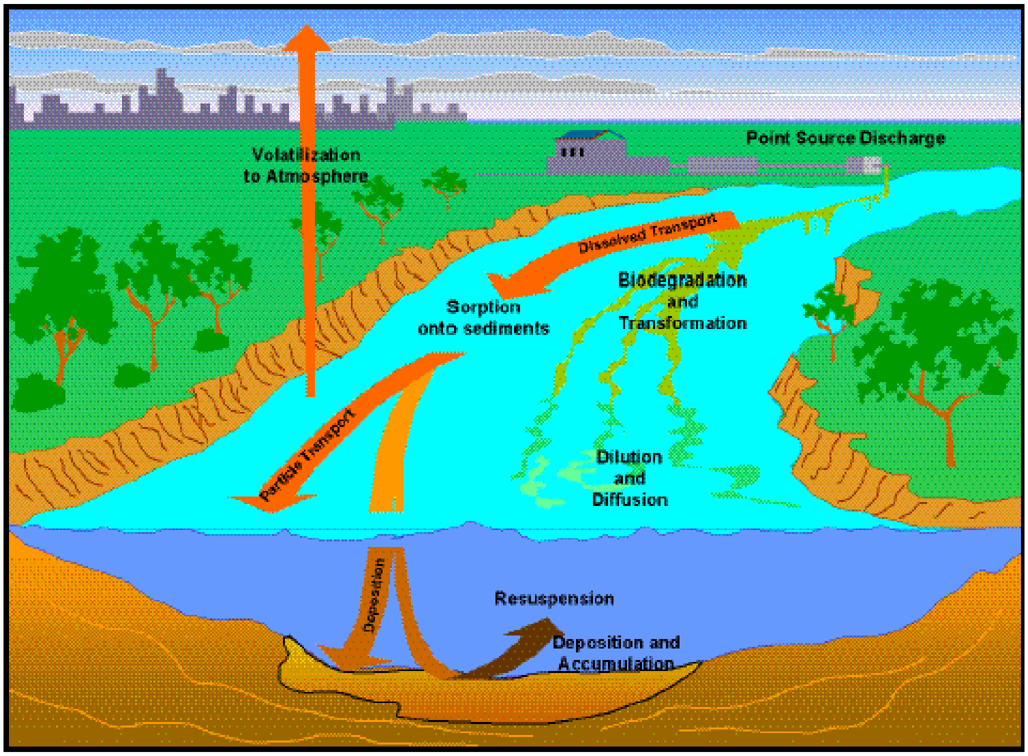
Barnali Dixon, University of South Florida

The objectives of this work are to determine if there are relationships between landuse, slopes and/or secondary soil properties that explain the levels of fluorescence in selected streams using the Soil Water Assessment Tool (SWAT) and GIS. Watersheds were divided into 2 groups: Southern Rivers, including the Manatee River and Charlie Creek/Peace River, (Group A) and Northern Rivers, including the Hillsborough and Alafia (Group B). GIS data such as elevation, hydrology, transportation, soils, geology and other landuse were incorporated into the SWAT model for each group of watersheds. Landscape processes modeled by SWAT include the following:



(provided by B. Dixon)

In-stream processes modeled by SWAT include those depicted below:



(provided by B. Dixon)

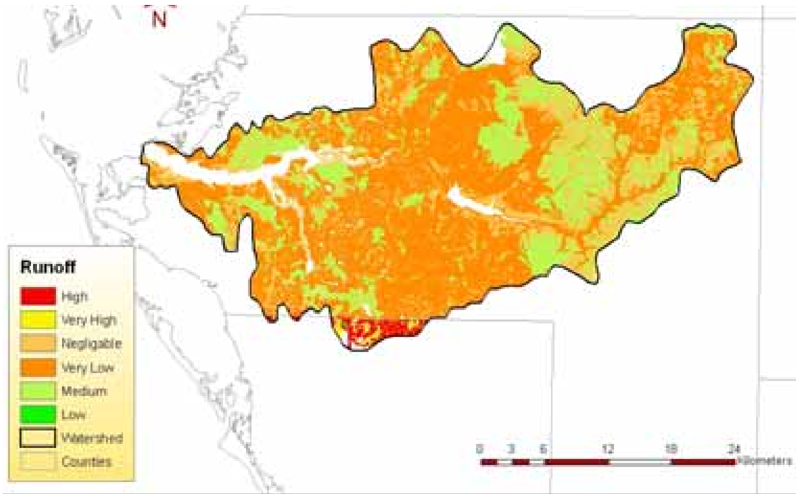
SWAT model components include:

- ✓ Weather
- ✓ surface runoff*
- ✓ Return flow
- ✓ Percolation and leaching
- ✓ ET*
- ✓ Transmission losses*
- ✓ Pond and reservoir storage*
- ✓ Crop growth and irrigation*
- ✓ Groundwater flow
- ✓ Reach routing
- ✓ Nutrient and pesticide loading *

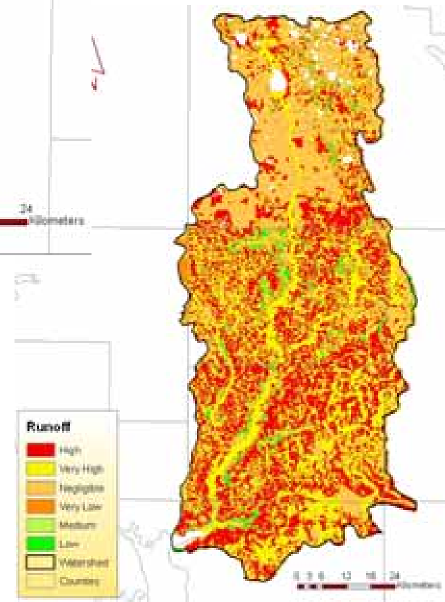
* *can be derived directly or indirectly from remote sensing*

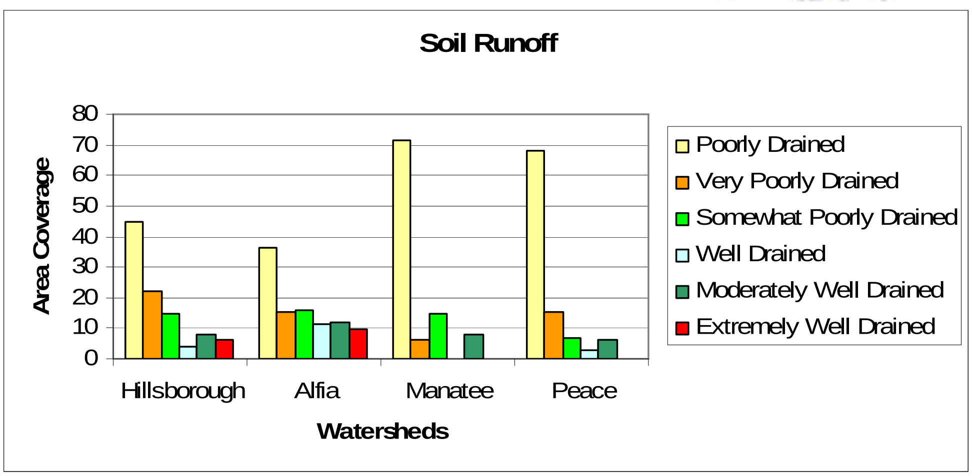
and the objective is to predict the effect of management decisions on water, sediment, nutrient and pesticide yields with reasonable accuracy on large watersheds. The model quantifies the impact of changes in management practices, climate, vegetation, landuse etc. on water quality or other variables over large spatial scales. Basins are subdivided into hydrologic response units (HURs) to account for differences in soils, landuse, crops, topography, weather, etc, and then subdivided into grid cells. Basins of several thousand square miles can be studied, and soil profile can be divided into 10 layers to account for permeability and horizons. Results of this study have shown that there are distinct flow and sediment characteristics between the Northern and Southern rivers, and that this should be applied to other rivers for more robust analyses.

Some example results from exploratory GIS analysis include the following graphs:

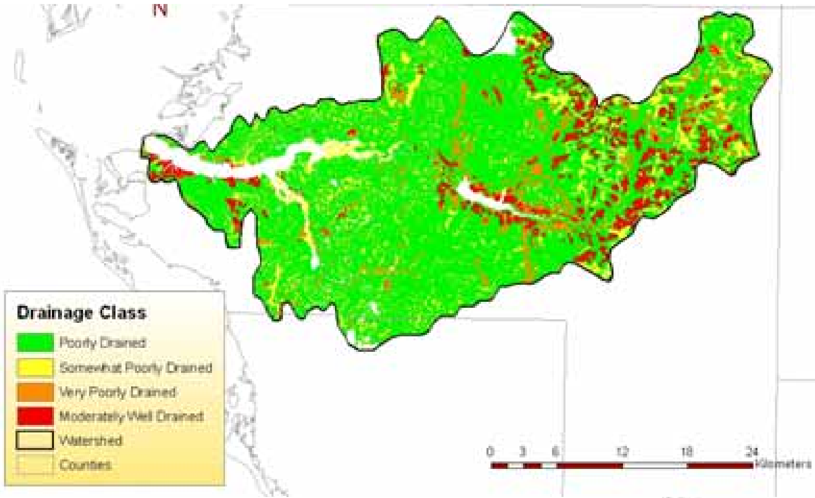


Soil Runoff Potential: Group A

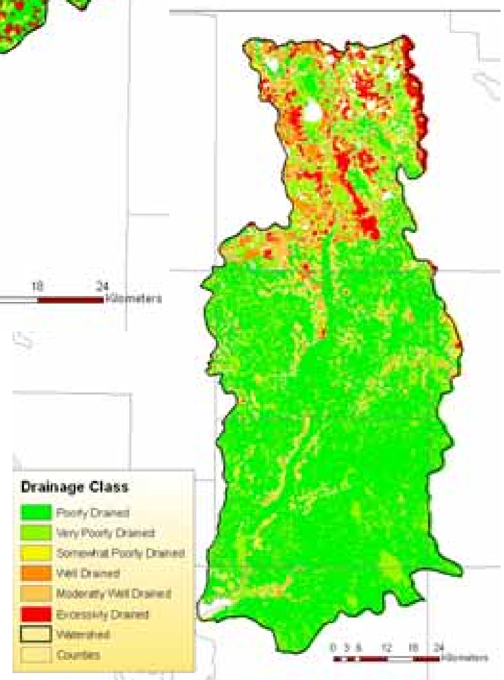


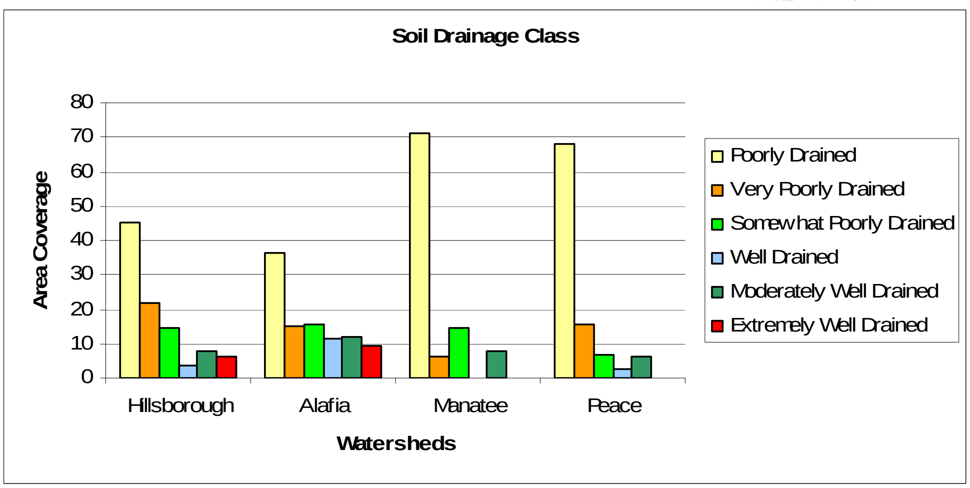


(provided by B. Dixon)

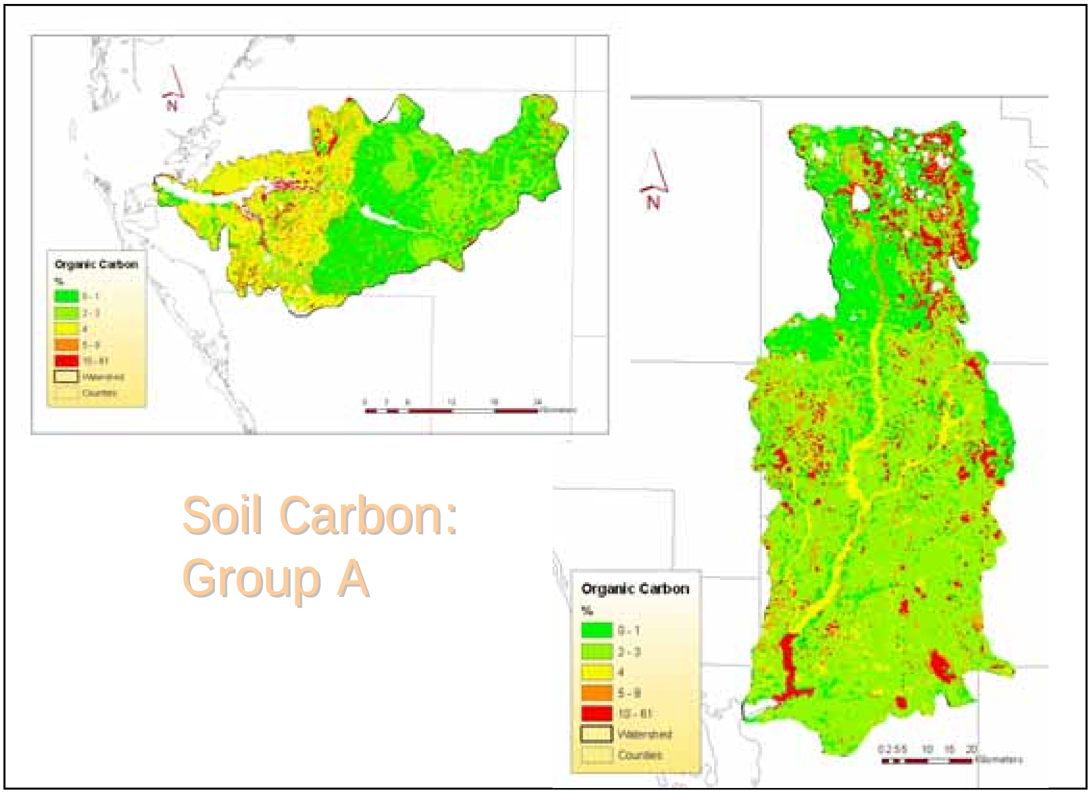


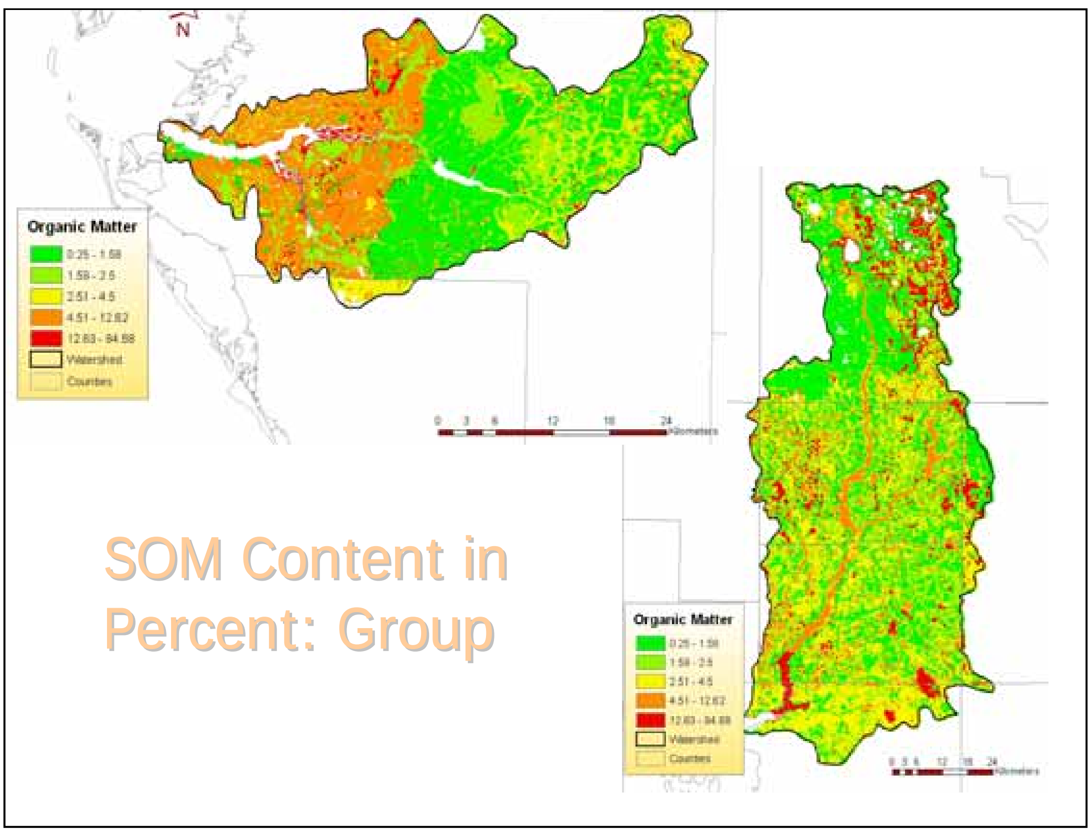
Soil Drainage Class: Group A





(provided by B. Dixon)



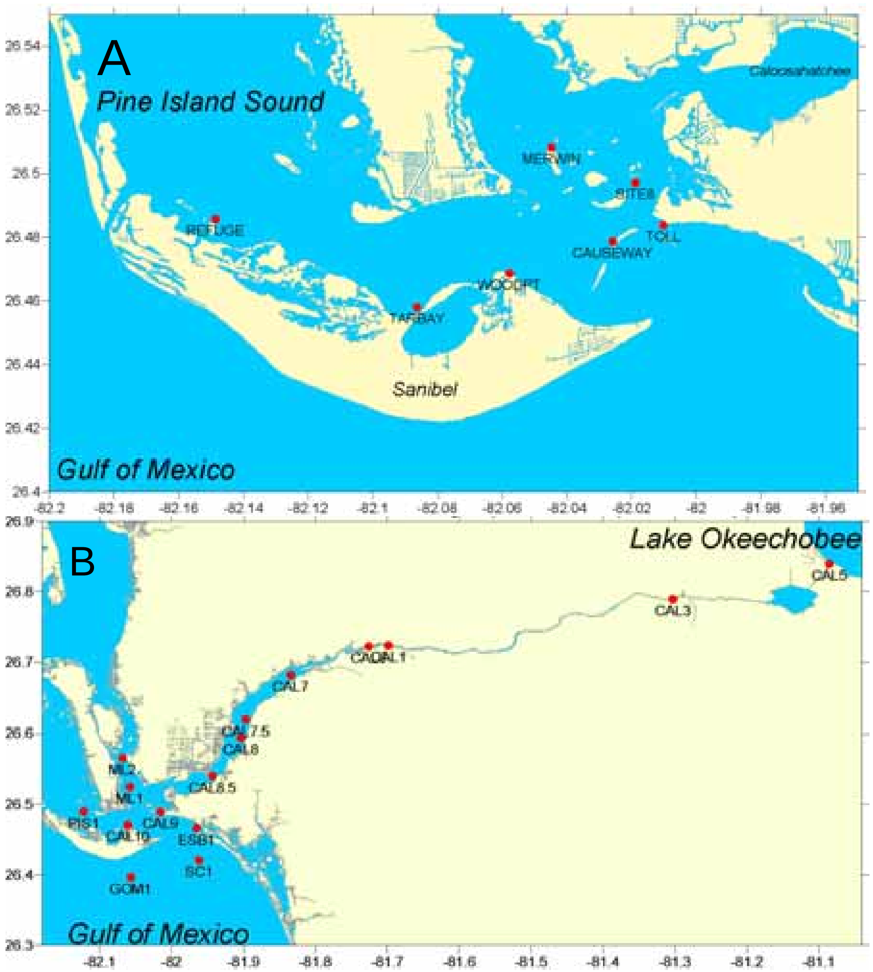


Soil Carbon and Organic Matter Content (provided by B. Dixon)

LANDUSE, CDOM, AND LIGHT ATTENUATION ALONG THE RIVER-ESTUARY-OCEAN INTERFACE

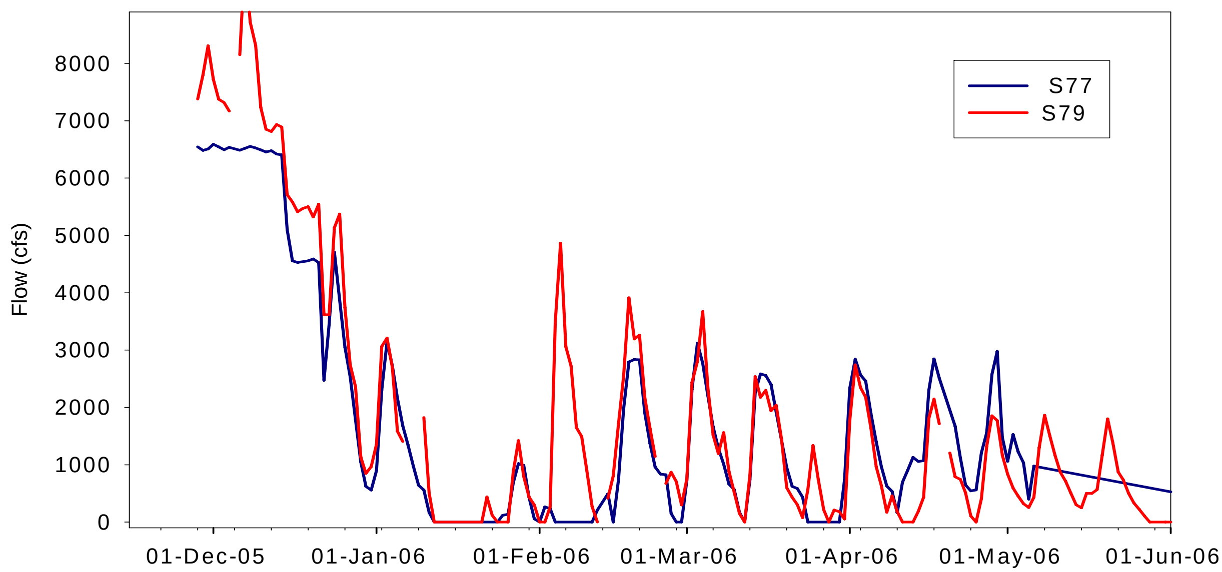
Eric Milbrandt, Sanibel-Captiva Conservation Foundation, Marine Laboratory

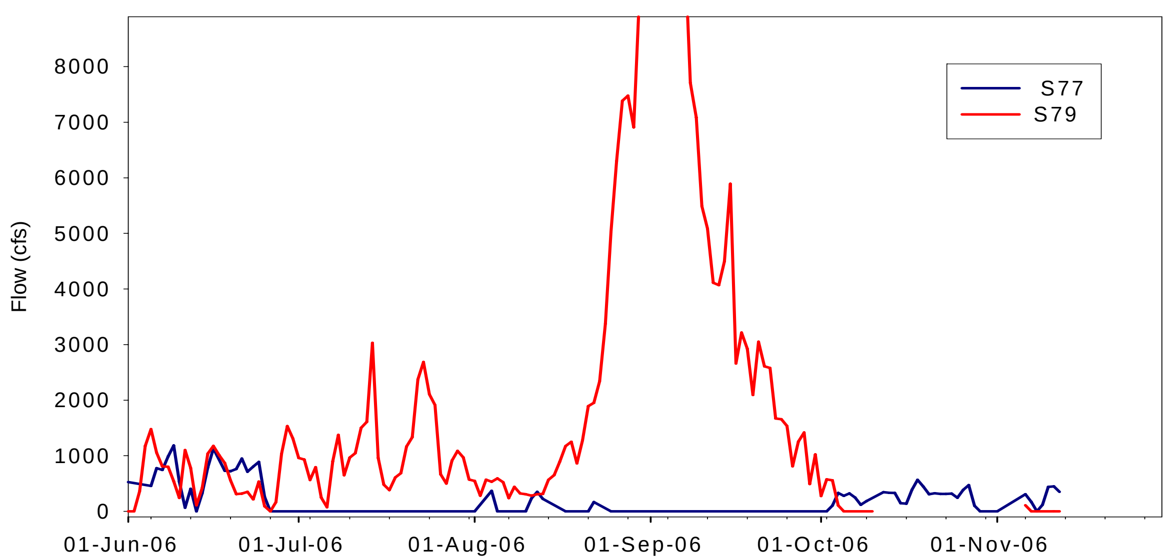
The objective of this study is to investigate the linkages between freshwater discharges (Lake Okeechobee, basin) and optical properties along the river-estuary-ocean continuum, to determine whether discharge conditions are harmful to seagrass and compare CDOM and DOM chemistries from watershed sources to the main stem of the Caloosahatchee. Sampling stations for CDOM, ESI mass spectrometry and light extinction coefficients were situated along the route of the Caloosahatchee River into San Carlos Bay. Seagrass growth rates, total suspended solids (TSS), chlorophyll a and CDOM absorption coefficients were measured.



(provided by E. Milbrandt)

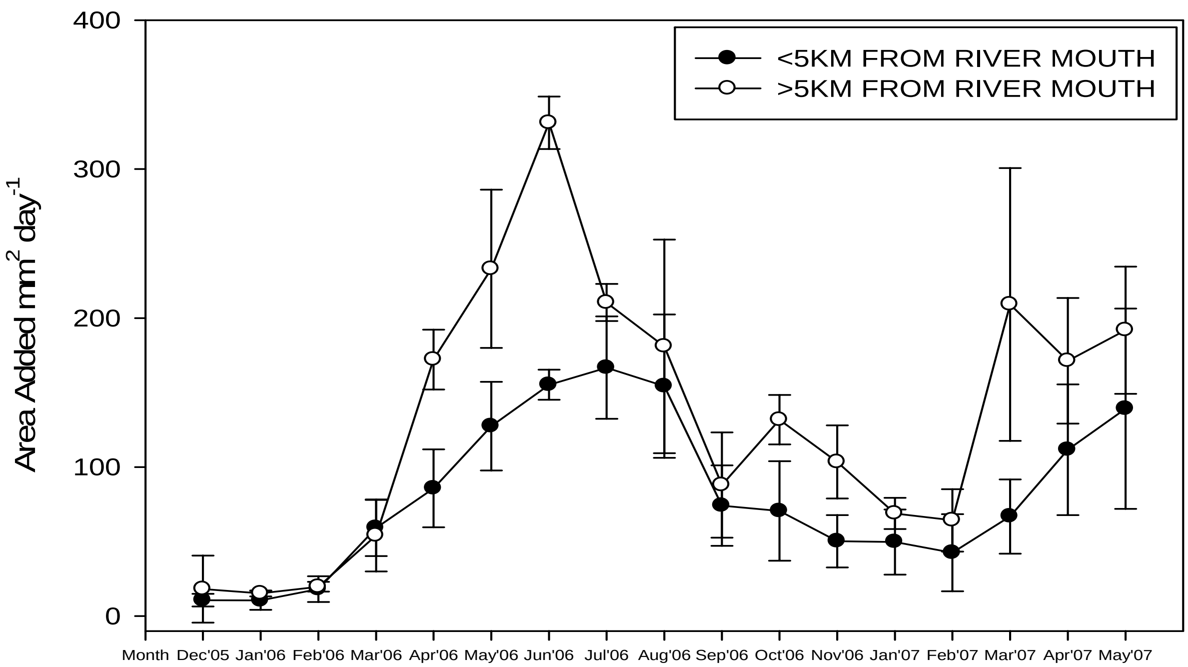
During the experiment, there were large releases from both the freshwater basin east of the Franklin Locks (S-79) and Lake Okeechobee (S-77). Thus, researchers could compare water quality conditions in the river resulting from lake and basin releases to those conditions of basin releases (see graphics below).

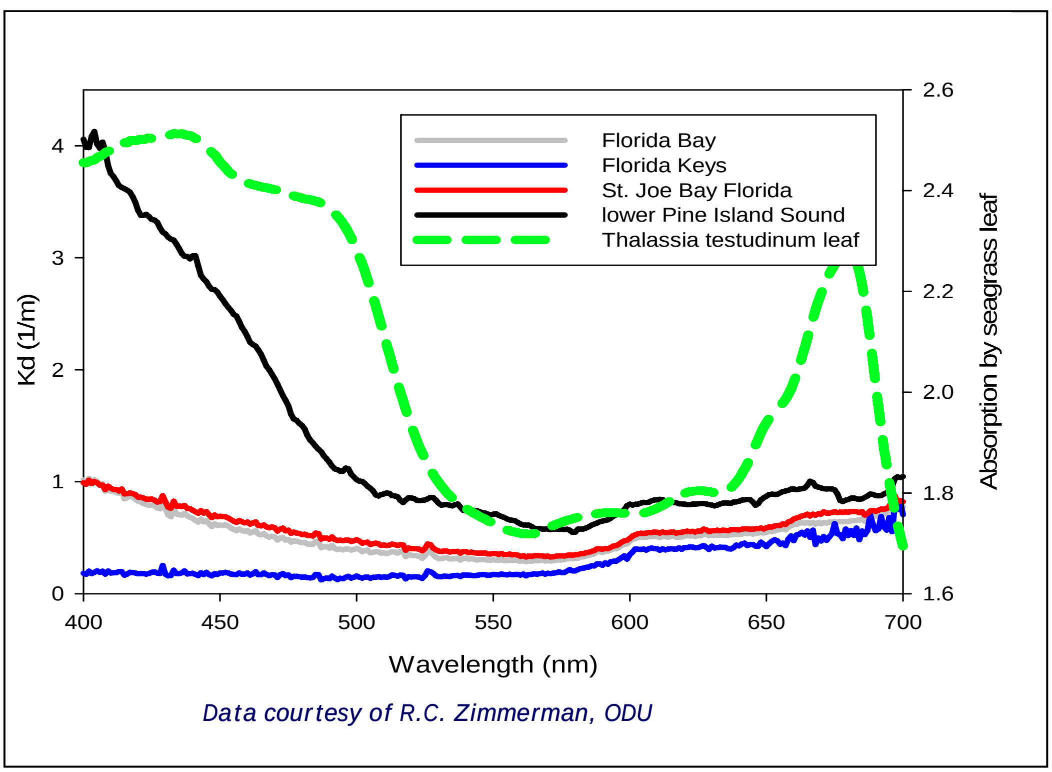




(provided by E. Milbrandt)

Results of the research demonstrated that growth rates of seagrass were significantly lower near the source of freshwater discharges; however it was unclear whether light limitation or salinity was responsible for the differences in growth rates. Results also demonstrated spectral light attenuation demonstrated high blue light attenuation in the Caloosahatchee estuary. The shorter wavelengths within the blue light region are very important for seagrass growth.





(provided by E. Milbrandt)

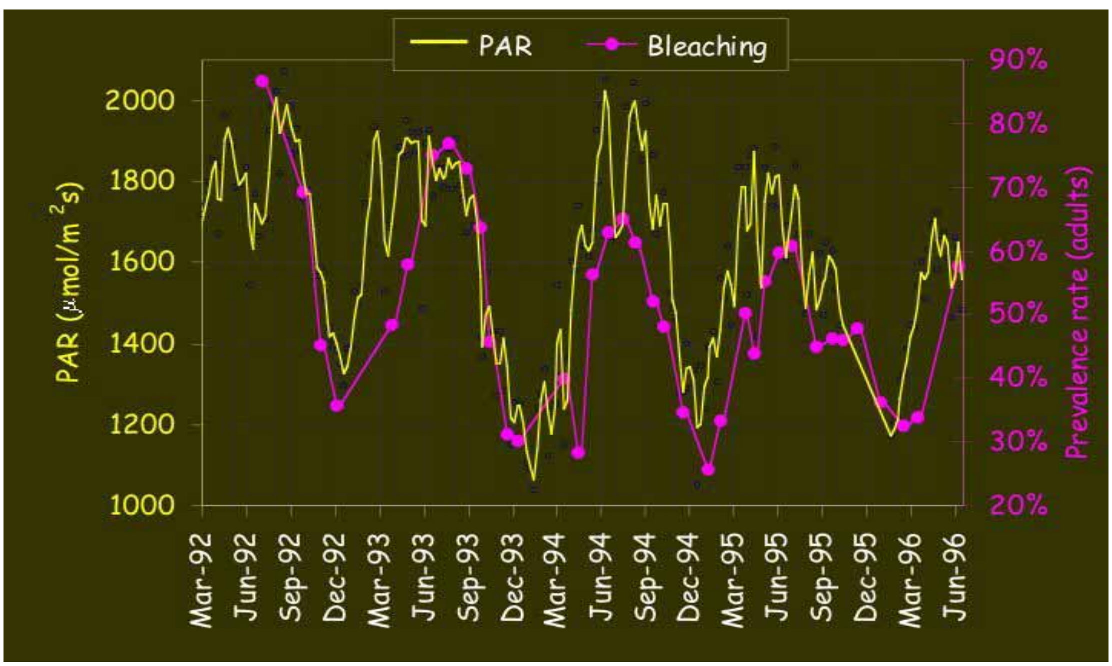
TSS was a reasonably good indicator of the geographic extent of Lake discharges, and CDOM was a higher contributor (66%) to blue light attenuation. CDOM dilutes along the route from Lake Okeechobee to the estuary as predicted by conservative mixing. The conservative mixing slope was similar for basin and Lake discharges but differed from discharges associated with Tropical Storm Ernesto. Preliminary DOM characterization with mass spectrometry suggests seasonality in the main stem of the river-estuary and significant photobleaching from watershed sources.

SESSION FOUR: Should agencies be collecting additional information to better understand CDOM dynamics and landuse impacts on CDOM concentrations and composition? For landuse models? To quality of light reaching seagrass beds and impacting primary productivity? Can this information be added to current monitoring programs?

ULTRAVIOLET RADIATION AND COLORED DISSOLVED ORGANIC MATERIAL IN THE FLORIDA KEYS: CAN SOLAR IRRADIANCE PROVIDE CLUES TO MANAGING CORAL REEFS?

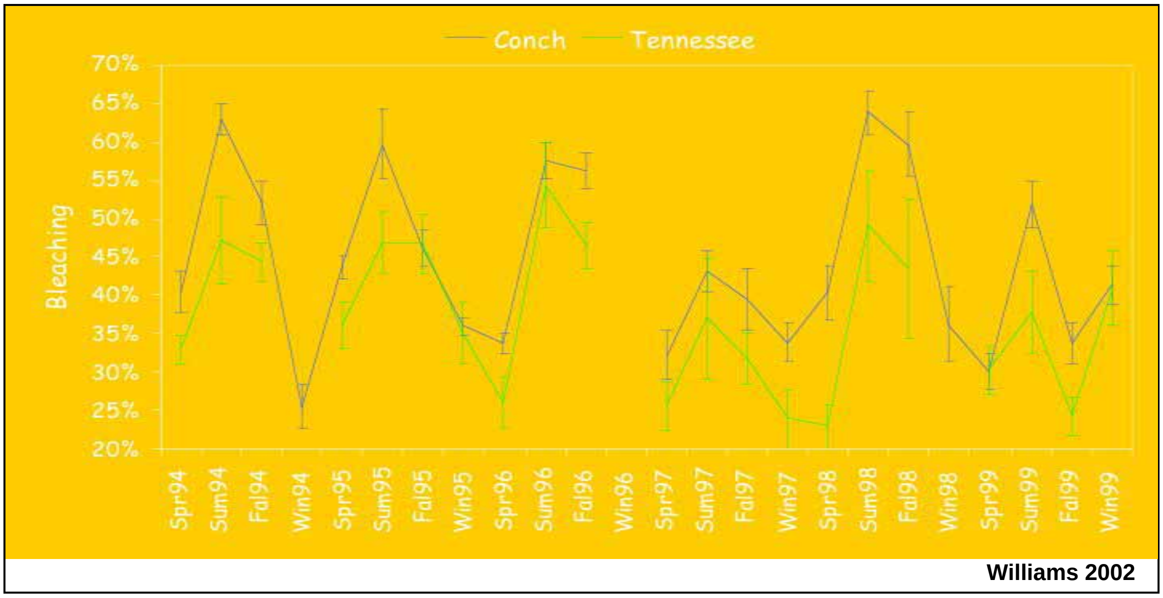
Lore Ayoub, Paula Coble and Pamela Hallock-Muller, University of South Florida

Absorption due to CDOM steadily decreases from the mangrove canals in John Pennekamp Park to the reef tract to offshore blue water. Water plumes with higher CDOM flow over the inshore reefs near mangrove hammock or intact shorline, as well as reefs near CDOM-rich Florida Bay outflows. Data from the late 1990's show that foraminifera bleaching in the Keys is in sync with the PAR seasonal cycle.



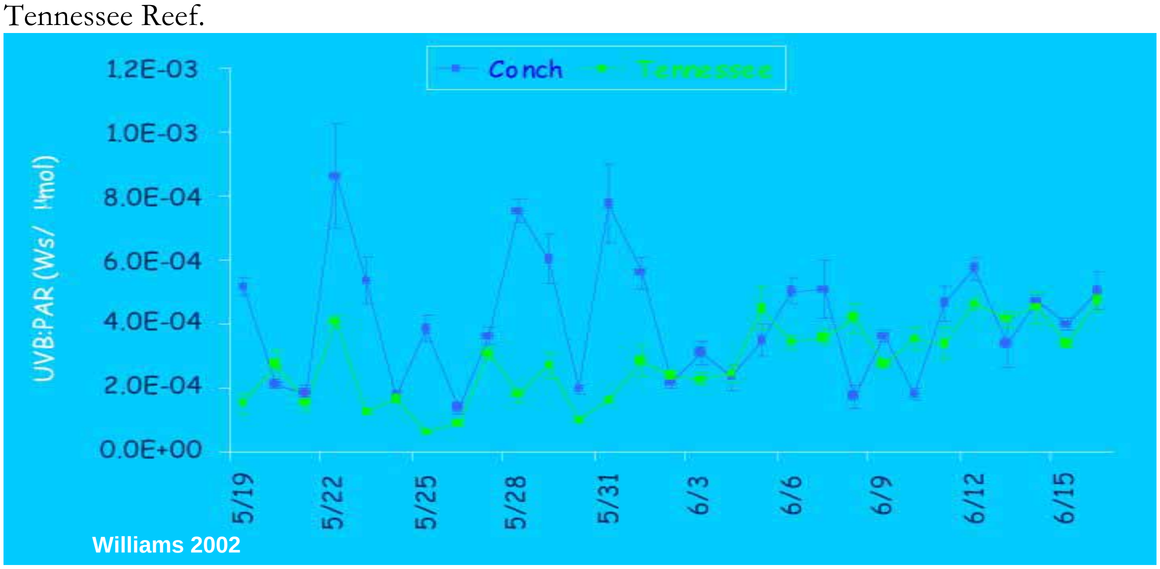
(provided by L. Ayoub, P. Coble and P. Hallock-Muller)

In addition, bleaching is consistently higher at the lower CDOM Conch Reef than the Tennessee Reef.



(provided by L. Ayoub, P. Coble and P. Hallock-Muller)

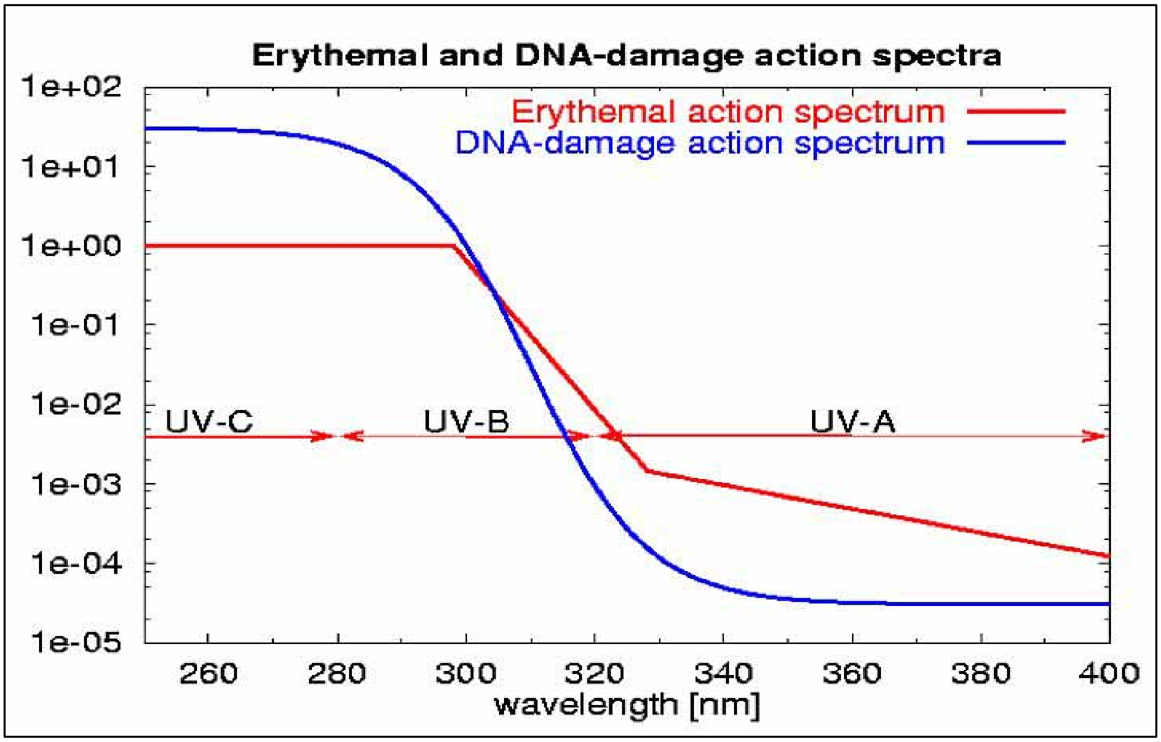
At the same time, the ratio of ultraviolet B radiation to PAR is higher at Conch than Tennessee Reef.



(provided by L. Ayoub, P. Coble and P. Hallock-Muller)

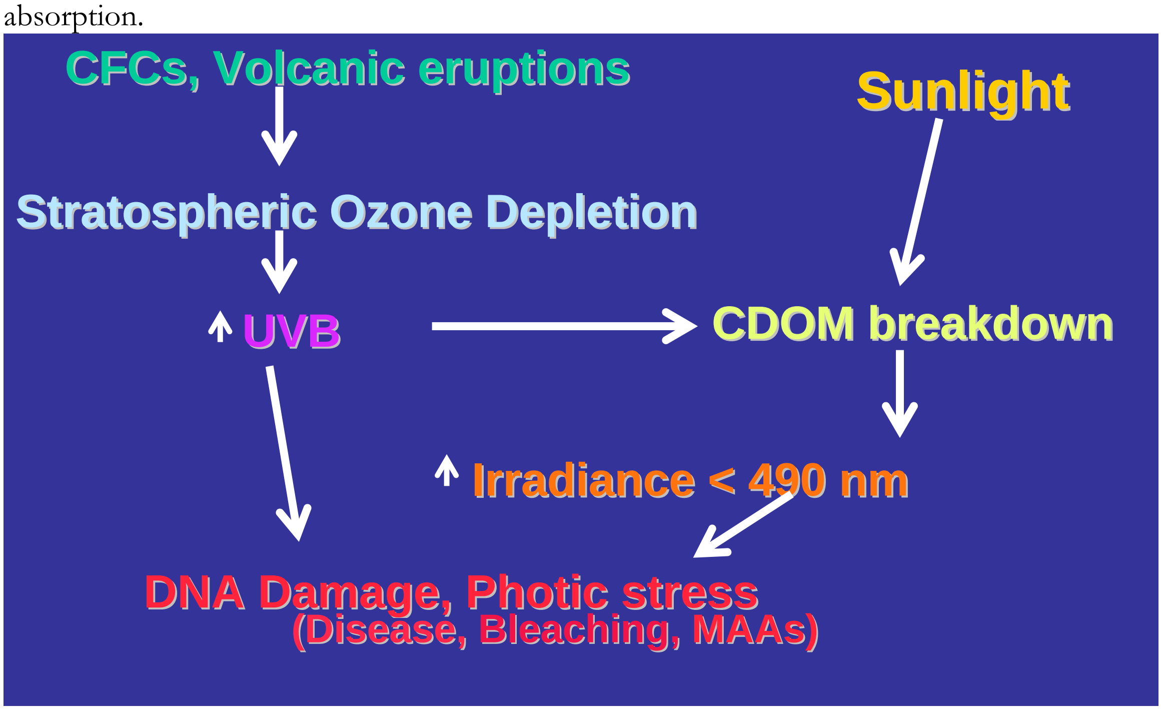
Data from SeaWiFS demonstrate that CDOM concentrations are higher at Florida Bay outflow areas (e.g., Tennessee Reef). Also, there is a greater lesion recovery rate for corals near intact mangrove shorelines than developed shorelines (see presentation).

Action spectra describe the relative effect of energy at different wavelengths in producing a certain biological or chemical response. Photic stress is depended on the wavelengths of light energy. DNA damage, for instance, is prevalent when an organism is exposed to ultraviolet radiation. CDOM absorbs strongly in the ultraviolet region; therefore providing a photoprotective barrier for benthic organisms against ultraviolet radiation.



(provided by L. Ayoub, P. Coble and P. Hallock-Muller)

Exposure to UV radiation can induce UV-absorbing substances such as Mycosporine Amino Acids (MAAs). This work demonstrates that higher coral cover and lower rates of decline in cover co-occur with relatively high absorption due to CDOM. Relative MAA expression is greater on reefs which experience consistently lower and/or more variable CDOM absorption.



(provided by L. Ayoub, P. Coble and P. Hallock-Muller)

CDOM contribution to attenuation of UV radiation is much higher than that of particulates (>0.7 um), and irradiance reaching the benthos is higher in reefs near developed shoreline than reefs near intact shorelines. The spectral slope of absorbance between 280-312 nm was more variable and higher (an indicator of photic stress) near developed shorelines than intact. Relative MAA expression was lower at intact shoreline-associated reefs and negatively correlated with CDOM absorbance.

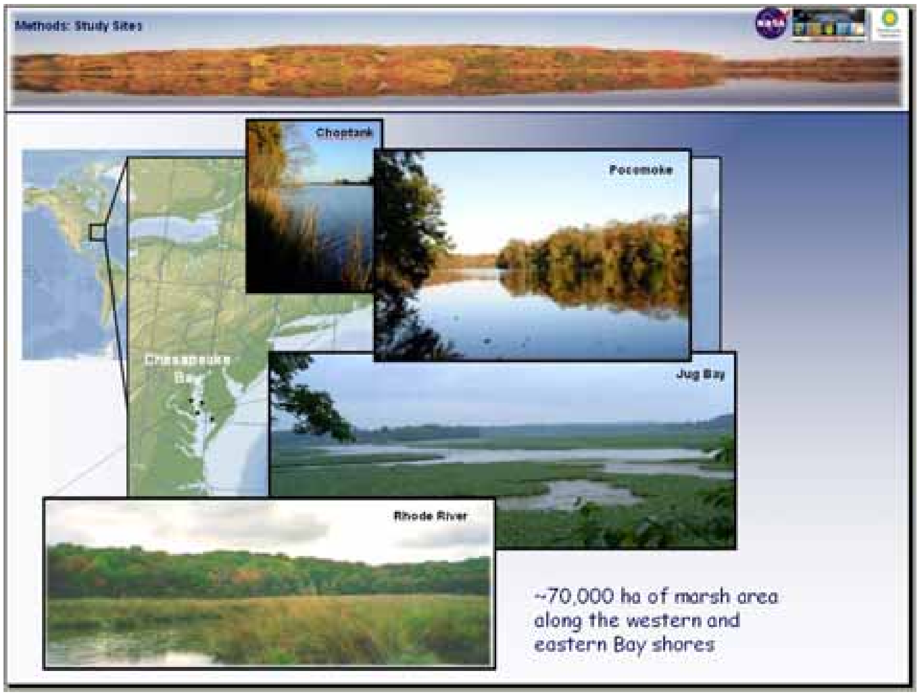
In summary, Florida Keys reefs with consistent sources of CDOM have higher coral lesion recovery rates, lower rates of bleaching in foraminifera, and lower rates of decline in coral cover. CDOM provides a photoprotective barrier to UVR for benthic biota on coral reefs. Mangroves and wetlands should be preserved as important sources of CDOM to coral reefs.

EXPORT OF OPTICALLY AND COMPOSITIONALLY DISTINCTIVE DOM FROM TIDAL MARSHES IN THE CHESAPEAKE BAY AND EFFECTS OF SOLAR EXPOSURE ON ITS SPECTRAL CHARACTERISTICS

Maria Tzortziou, NASA Goddard Space Flight Center- ESSIC/University of Maryland Smithsonian Institution

Dissolved organic matter (DOM) plays a key role in a broad range of processes and climate-related biogeochemical cycles in aquatic ecosystems, affecting carbon dynamics, nutrient availability, microbial growth and ecosystem productivity. The colored fraction of DOM, CDOM, is one of the key water constituents determining the underwater UV-visible light field, affecting ocean color and aquatic photochemistry.

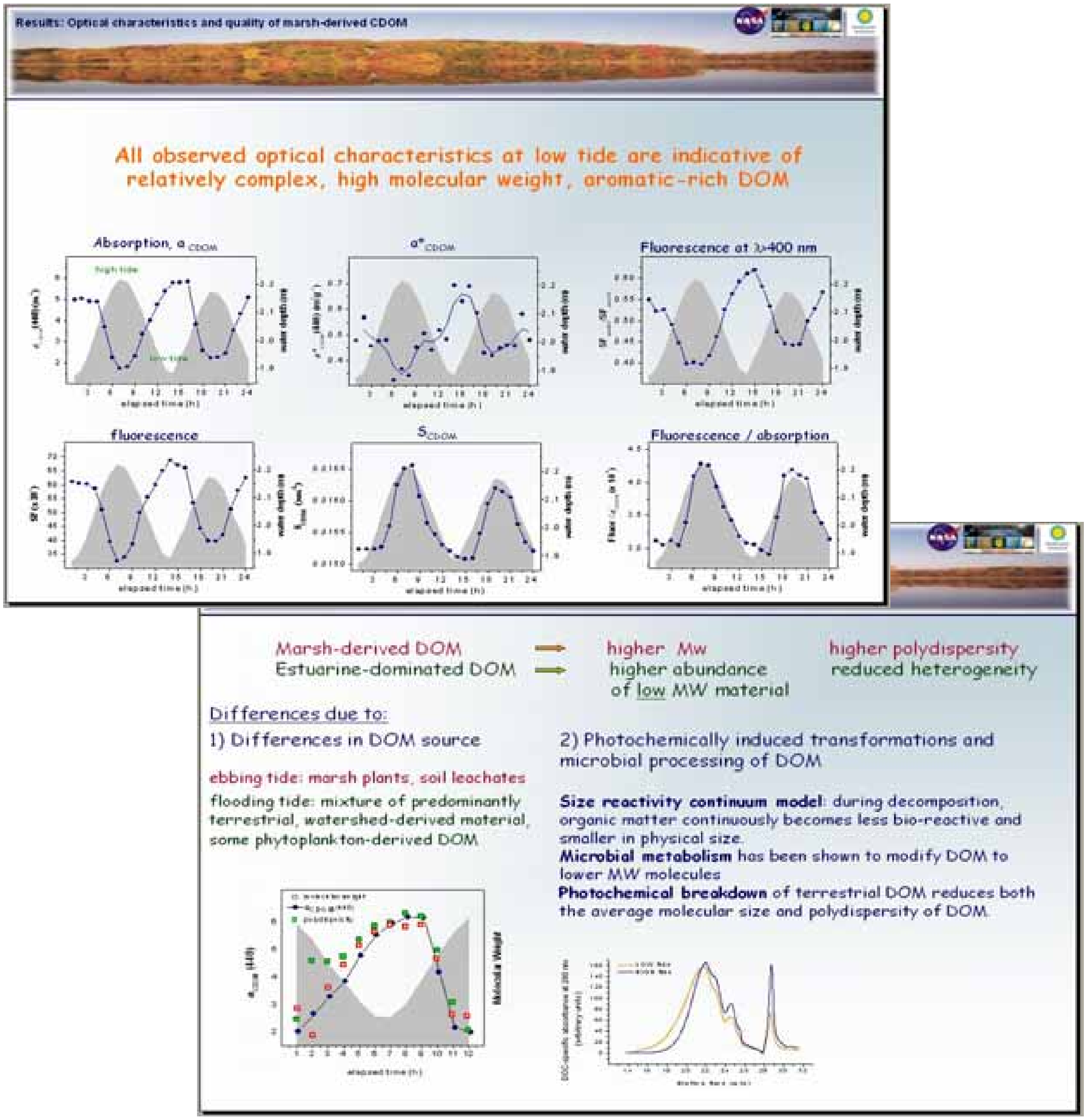
Estuarine and coastal margin ecosystems are hot spots of DOM cycling because of intense physical and biological activity. This study in the Chesapeake Bay focused on the role of coastal tidal marshes as a source of dissolved organic carbon (DOC) and CDOM for adjacent estuarine waters. Brackish and freshwater tidal marsh systems cover a large area (about 70,000 ha) along the western and eastern Bay shores, potentially playing an important role in the complex biogeochemical processes, optics and exchanges taking place in these highly dynamic environments.



(provided by M. Tzortziou)

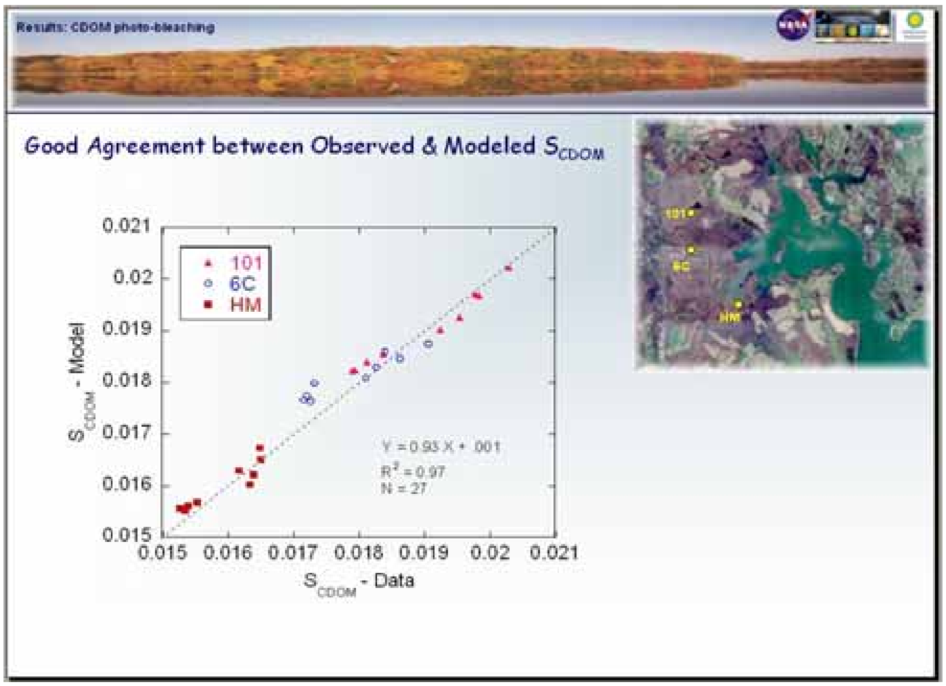
Measurements of DOM tidal exchange in the Rhode River marshes of the Chesapeake Bay showed a net DOC export from the marshes to the estuary during seasons of both low and high marsh plant biomass. Optical analysis demonstrated that, in addition to contributing to the carbon budgets, the marshes had a strong influence on the estuary's CDOM dynamics. Marsh-exported CDOM had optical properties that were consistently and markedly different from those of CDOM in the adjacent estuary: (i) considerably stronger absorption, (ii) larger DOC-specific absorption, (iii) lower exponential spectral slope, S_{CDOM}, (iv) larger fluorescence signal, (v) lower fluorescence per unit absorbance, and (vi) higher fluorescence at wavelengths > 400 nm. These optical characteristics are indicative of relatively complex, high molecular weight, aromatic-rich DOM, which was confirmed by results of molecular weight distribution analysis.

Photochemical and microbial processes both play critical roles in regulating the residence time and cycling of DOM. CDOM derived from the tidal marshes and watershed surrounding the Rhode River was strongly photoreactive and, thus, highly susceptible to photochemical transformation. Photo-bleaching experiments were performed to examine the effects of solar exposure on the photochemical degradation and optical quality of this material.



(provided by M. Tzortziou)

Considerable loss of colored DOM was measured in all samples collected from the Rhode River watershed edge upon exposure to the full spectrum of natural sunlight. Consistent with changes in fluorescence emission, absorption loss upon exposure to different portions of the solar spectrum (i.e. different long-pass cut-off filters) occurred across the entire spectrum but the wavelength of maximum photobleaching decreased as the cut-off wavelength of the filter decreased. These results illustrated that solar exposure can cause either an increase or a decrease in the CDOM absorption spectral slope depending on the spectral quality of irradiation and, thus, on the parameters that affect the spectral characteristics of the light to which CDOM is exposed (e.g. atmospheric composition, latitude, season, water depth, water composition). A simple, predictive, spectral model of CDOM photobleaching was developed that successfully predicted the effects of solar exposure on estuarine CDOM optical quality. The model can be integrated into more general models of DOM environmental dynamics and carbon cycling.



(provided by M. Tzortziou)

Discussions

This section attempts to summarize the group discussions within each session. During each session a facilitator posed a series of questions to workshop participants and took notes of the responses. The participant recommendations are listed underneath the posed questions. On several occasions, such as Session 1, one or more questions may have been combined if it was convenient to do so.

The questions listed herein were paired with the presentations above for the same session. Presentations were designed to inform participants of existing science and knowledge and then “kick off” the participant discussion.

SESSION ONE:

1) Can any of the mentioned CDOM measurement methods help us better understand sources and sinks of CDOM? The composition of CDOM? Spatial and temporal variability in the composition of CDOM? The quality and quantity of subsurface irradiance in the region?
2) How do the current monitoring protocols in southwest Florida compare to other regions? Should the protocols in Charlotte Harbor be changed? If so, how?
    - Current monitoring is flawed:
        - Lab analysis includes absorbance at X nm or color wheel from discrete samples taken 1x per month at Y number of sites (usually fixed)—
        - agencies use plastic bottles (introduces contaminants via hydrocarbons)—
        - entities do not obtain spectral slope
        - also entities add scattering component which will interfere with obtaining accurate spectral slope (particles between 0.2 and .45 microns)
    - Improvements in monitoring could include the following:
        - flow through measurements
        - Satellite/remote sensing to better understand CDOM variability
        - In situ sampling at key locations
        - Absorbance measurements at shorter wavelengths will get better DOC estimates (@250 nm at 1 cm cell)
        - Agencies can measure at >2 wavelengths to extrapolate spectral slope—the more, the better
        - Obtain spectral shape of endmembers (e.g., river, groundwater, Gulf of Mexico) repeatedly over time at 1st (then perhaps don't need so robust and can measure fewer wavelengths for just slope)
    - Considerations for better understanding CDOM composition and concentrations variability:
        - Need to develop a relationship between color wheel and absorbance/spectral slope
        - Getting spectral slope and shape, may allow us to better understand absorbance at wavelengths important to seagrass
        - Measure fluorescence at 2 wavelengths—have 2 channels (chl a & CDOM fluorescence and turbidity) (convert backscattering to turbidity) with cheaper equipment & take discrete samples with equipment maintenance periods
            - 350 and 400 nm are 2 important wavelengths
            - Find spectral shape of end members before determining 2 CDOM fluorescence wavelengths to measure
            - Ecotriplets (2 CDOM fluorescence channels—3rd becomes a turbidity measurement) and chl a fluorometer additionally covers the entire suite

    - Need to add temporal component and repeated measurements to determine CDOM sources
    - Measure CDOM and water quality at shallower areas
    - Design sampling around seasons and flow changes
    - In situ sampling technology is getting better and cheaper—gives temporal variability and if multiple sites can also give spatial variability
    - Hindcasting spectral slope using new & old data to determine changes from historic conditions is possible

- **Consensus with workshop participants in that CDOM composition variability is important to understand because it can affect seagrass and other benthic communities. Gathering CDOM composition as well as more robust concentration data are important for resource management and should be added to on-going local research and monitoring as soon as resources allow. In situ equipment with augmented discrete sampling are potential inexpensive methods.**

SESSION TWO:

1) Are CDOM concentrations changing in the region? If so, why?
    - Changes in residence times and flows confound question—research is finding that CDOM concentrations increase concomitant to flow increases in the Peace and Caloosahatchee Rivers
    - Higher CDOM concentrations arising from hydrologic changes that augment flows and increase discharge; this relationship is generally found in other systems
    - At high flows, CDOM concentrations start to level off in Peace River; is this due to a flushing effect?
    - Terrestrial source material get "washed off"—flushed (example of tea bag)
    - Are humans having an effect on CDOM concentrations or is it more related to climate changes?
    - Slopes for CDOM and flow regressions can be different because of different sources/endmembers
    - 2 endmembers in the Caloosahatchee—basin and Lake Okeechobee; we don't know enough about freshwater endmember variability

- **Consensus with workshop participants is that CDOM concentrations are in general positively associated with flow up to the point in which a "washing out" effect occurs. Therefore, hydrologic alterations that increase flow, such as increased rainfall or increases in Lake Okeechobee and basin releases in the Caloosahatchee River watershed, will increase CDOM concentrations up to a point. Thus, increasing trends in CDOM concentrations in the Peace and Caloosahatchee Rivers may be resultant of increases in flow and not specifically a result of landuse changes. Although it follows that landuse changes that lead to increases in flow**

may in turn lead to increases in CDOM concentrations given sufficient source material, CDOM concentrations have not been directly tied to landuse type nor has this issue been well researched yet.

2) How can we better understand, document and predict the causes of these changes?

- It will be very expensive and timely to try to determine the suite of chemicals that make up the CDOM pool in this region
    - Need a group of folks to review existing datasets to determine what can be done/determined with existing data
    - More empirical data are needed; researchers can use existing data to create rough relationships; start with a literature review; should attempt side by side comparisons of different datasets and different variables
- We need to evaluate rainfall and CDOM relationships
- Distributed system of sampling sites
- Are there measures of resuspended/recycled CDOM sources? Takes a long time for freshwater CDOM to break down and become biologically available; CDOM derived from aquatic resources (e.g., seagrass, macroalgae) has a different spectral shape than riverine & marine CDOM sources
- Perhaps we should concentrate on understanding the duration and timing of "CDOM events" or low light availability periods—the timing and duration could be altered with hydrologic changes—we can start here
- Do large water retention facilities allow CDOM to accumulate and photobleach? Or do a number of smaller facilities work better (surface to volume ratio) for allowing photodegradation?
    - Shallow systems allowing exposure to UV and well-flushed systems may allow photodegradation and less accumulation; however, there is a concern that such systems may cause other water quality problems
- There is a difference of old versus new CDOM for quality of light reaching seagrass and for bioavailability of nutrients
    - New CDOM can be broken down faster/easier than older CDOM
- Do we know enough to manage CDOM or are we being presumptive?

- **Consensus with workshop participants is that understanding the entire suite of chemicals in the local CDOM pool will be expensive and difficult. Previous literature and existing data may provide initial information to guide future research and monitoring that will respond to emerging resource management questions. Grad students and others can start by first developing rough relationships with rainfall, flow, landuse, etc. and CDOM spectral characteristics.**

SESSION THREE:

1) What are the spatial-temporal chemical components of CDOM in the Charlotte Harbor region? Can we obtain this information using existing data or do we need specific

research project(s) or monitoring programs to obtain this information? Would information on the spatial-temporal components be used to develop management decisions aimed at protecting aquatic resources? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.

- Landuse change is important to understand to predict CDOM variability; impacts on soil, types of soil and runoff
- Hydric soils are important to study as they may be a source for CDOM; less well drained soils whereby water pools and allows CDOM to accumulate
- Chemistry of CDOM, breakdown etc would be very useful
    - It will be very expensive and timely to try to determine the suite of chemicals that make up the CDOM pool in this region
- Understanding the differences between nearshore and offshore CDOM concentrations and components are useful for seagrass management strategies and to relate sources and sinks with management activities; better understanding of these differences needs different monitoring programs to gather these data
- Utilize vertical profiling systems because impacts of water column stratification
- Data analyses should incorporate rainfall and runoff
- Utilization of EEMs is useful and link the results to landuse models
- Is CDOM something we need to manage is the 1st question before we ask whether we need to understand the spatial-temporal components.
    - For water management decisions, CDOM pool might be important for seagrass management strategies
    - Can we manage color other than by hydrologic changes and is it worth spending money for this issue?
    - Managing something requires one to explain an issue/strategy to citizens. CDOM concentration has been important and is easier to convey importance to citizens; composition may be more difficult
    - In management, we need to be able to predict what will happen to aquatic resources. For this reason CDOM pool may be important. Cannot make a reasonable prediction without knowing what is happening with CDOM.
    - Need to better link CDOM concentration, composition to the aquatic resource one is trying to protect
    - In some areas, finding seagrass restoration strategies are not working as well as thought, might need to look elsewhere such as CDOM for reasons behind this
- CDOM is at times a good thing (i.e., photoprotective barrier against UV radiation); it seems this discussion is leading towards managing/controlling CDOM like it is bad or unnatural
- We cannot predict CDOM yet so how can we presume to manage it? We need to study CDOM and link rainfall and hydrologic changes to duration of "CDOM events" to help us understand and therefore better predict CDOM variability

- Common data depository is necessary for data sharing; coordination of efforts
  - Common methods on measuring CDOM and data sharing; need to better understand anthropogenic inputs
  - Build relationships between different datasets so that existing data can be used
  - Centralized databases need to allow different formats, metadata etc
  - There is a standard GIS database; may be able to incorporate lab data; units in PCUs versus absorbance can all be incorporated into this database; query for type of data you need
  - Can agree on common QA/QC standards, metadata needed etc.
  - FLUORONET (UK group) has a website that offers regular training on methods on fluorescence technologies—possible training for southwest Florida?
- **Consensus with workshop participants in that CDOM composition variability is important to understand because it can affect seagrass and other benthic communities. Participants quickly discussed whether managing CDOM is a good idea and if the questions arising from trying to manage CDOM should drive future research. Consensus was not yet reached on this issue (see Session 4, question 2 below). Participants did agree that a centralized data depository, better data sharing and coordination of efforts are needed and listed some suggestions.**

2) Can landuse models be improved to better estimate CDOM "event mean concentrations" (EMCs)? Would this analyte be an important addition to models for resource management in the southwest Florida region? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.

- With more research and more coordination between sampling/analyses entities, the integration of multiple data sources and a central coordinating entity, it may be possible to predict CDOM
  - a CDOM working group is a good start
- Can CDOM be converted to mass? Isn't this necessary to do for a landuse model?
  - In literature there may be a fulvic/humic standard that can be used to relate to landuse
  - High molecular weight versus low molecular weight materials absorb differently, so converting CDOM to mass may be problematic and not very useful
- Standards may not be useful since CDOM chemistry is complex and variable
- Is it possible to use rainfall, soils, slope, landuse data to predict CDOM concentrations? Components?
- Models may not be able to predict or incorporate a CDOM concentration or its components, but perhaps the model can produce an indicator, index or scale—can predict vulnerability, for instance

- Content of CDOM can be important because there may be something about it that limits light for seagrass, etc.
- If CDOM is conservative, we can model with flow; can simulate CDOM concentrations with flow rates;
- High CDOM may be natural background and due to this it may be more critical to manage for nutrients and turbidity during those times when there are high CDOM concentrations—CDOM happens
- Managing CDOM may be in part a question of managing turbidity
- CDOM can be providing photoprotective properties for seagrass beds—there may be a happy medium where there is just right CDOM concentrations—other areas are too much or too little—spatial variability can be key

- **Consensus with workshop participants in that a CDOM working group should be created and that the Charlotte Harbor NEP would be the appropriate coordinating entity for the working group. This working group can be part of the Charlotte Harbor NEP Water Quality Targets Working Group**

SESSION FOUR:

1) Should agencies be collecting additional information to better understand CDOM dynamics and landuse impacts on CDOM concentrations and composition? For landuse models? To quality of light reaching seagrass beds and impacting primary productivity? Can this information be added to current monitoring programs? Are they willing? Next steps…
    - We should learn more about SWAT
    - FDEP is establishing 3 in situ continuous CDOM, turbidity and chlorophyll *a* monitoring stations at seagrass transects (East Wall, West Wall and Cape Haze) and coordinating with SCCF's work in southern Charlotte Harbor
        - USF and FDEP also trying to add flow-through and SAFIRE sampling to determine spatial variability
        - FDEP could pull discrete samples in the bottom waters of upper Charlotte Harbor
        - USF working with these FDEP efforts and hope to use satellite images/calibrate algorithms
            - These results can be used to determine daily or more frequent water quality conditions and hindcast conditions
    - Data management & sharing for in situ equipment that gather LOTs of data
        - Can be efficient and collect data to catch specific conditions
        - CHEC website
    - Need financial support for data analyses
    - Data comparability; folks can start moving forward with up-to-date technology
    - Funding is an issue; we need to find sources of financial support (e.g., Oceans Council, Monitoring Council; GoMA)

- SWFWMD might add hyperspectral mapping in 2007 seagrass maps if FDEP can provide funding
- We should create a conceptual diagram to make CDOM resonate with citizen and policy makers
- FWRI efforts related to CDOM, fluorescence etc work in southwest Florida can be related to landuse and CDOM; however, this funding must be tied to red tide
- Research by CDOM/Water Quality targets working group on CDOM role with cations, water temperature, optical properties, protection from UV damage, juvenile fish habitat, etc.
- Light limitation causes nutrient uptake further down in system (outer estuaries) when CDOM diluted, degraded
- Need study on microbial and phytoplankton primary production in Charlotte Harbor

- **Consensus that more research and monitoring is needed on CDOM and that possibly the CDOM/Water Quality Targets Working Group could coordinate efforts.**

2) Can or should we add CDOM to our management strategies? How? Can we add "quality of light" to our water quality targets?
    - Collecting information doesn't necessarily mean you are managing; needs to be much more background information gathered and understood about CDOM before trying to manage/control it
    - Understanding spatial-temporal variability of CDOM, including role with flow and hydrologic changes, is important before trying to restore/develop management strategies
    - Agencies cannot monitor/gather data just for monitoring sake—need to have management implications—or agencies won't spend limited funds—has to tie monitoring to resource
    - Seagrass light quantity targets may not be working because they do not encompass quality of light—CDOM is important for the quality of light question—possibly why seagrass recovery not as great as expected
        - Can determine 5 seagrass species' spectral needs and provide those through site-specific management strategies (not just CDOM but chl a, water and turbidity components)
        - Need to look at wavelengths/spectral need of 3 main seagrass species; then add study of CDOM spectral properties in the areas where restoration/maintenance activities occur—add more sophisticated sampling via a ripple effect based upon questions emanating from each study
    - Landuse changes can impact organic matter and therefore composition and concentrations of CDOM but we do not have historic (past 1970s) CDOM concentrations much less composition/spectral slope-shape
        - Perhaps can tie vegetation cover to CDOM and hindcast (use existing data)

    - Moving towards using satellite images for daily/hourly water quality data in estuaries but need to calibrate algorithms with local data and bottom types
    - Salinity stress confounding factor with CDOM
    - Might be able to tie salinity data and changes to CDOM concentration changes—use existing data to hindcast changes
    - Need to use word "study" not "monitoring"; "monitoring" is scary
- **Consensus with workshop participants that a better understanding of the spatial-temporal variability of CDOM concentration and composition is needed before resource managers and others should try to manage it. We need to be able to predict results from management strategies and activities; we do not understand nor are we currently studying CDOM well enough to be able to understand or predict changes and tie to landuse or management activities. Can tie CDOM research and monitoring to spectral needs of seagrass in Charlotte Harbor to gain management agency support for research—spectral needs is important for long-term seagrass preservation.**

3) How do we better coordinate research and monitoring in the region? Can regional data be better managed and shared and on-going projects better coordinated?
    - CDOM working group
    - Centralized database
    - Integrated Coastal Ocean Observing Systems
    - FL Ocean Council, Gulf of Mexico Alliance
    - GAME—FWRI (Harry Norris' group)
    - Water Management District's SWIM Programs
    - Email distribution list (Frank Muller-Karger offered to provide)

Conclusions

The workshop was well-attended with over 70 participants each day and very informative to participants and Charlotte Harbor NEP staff. All attendees surveyed informally responded that they learned something from the workshop, while some said it was the best Charlotte Harbor NEP workshop/conference to date.

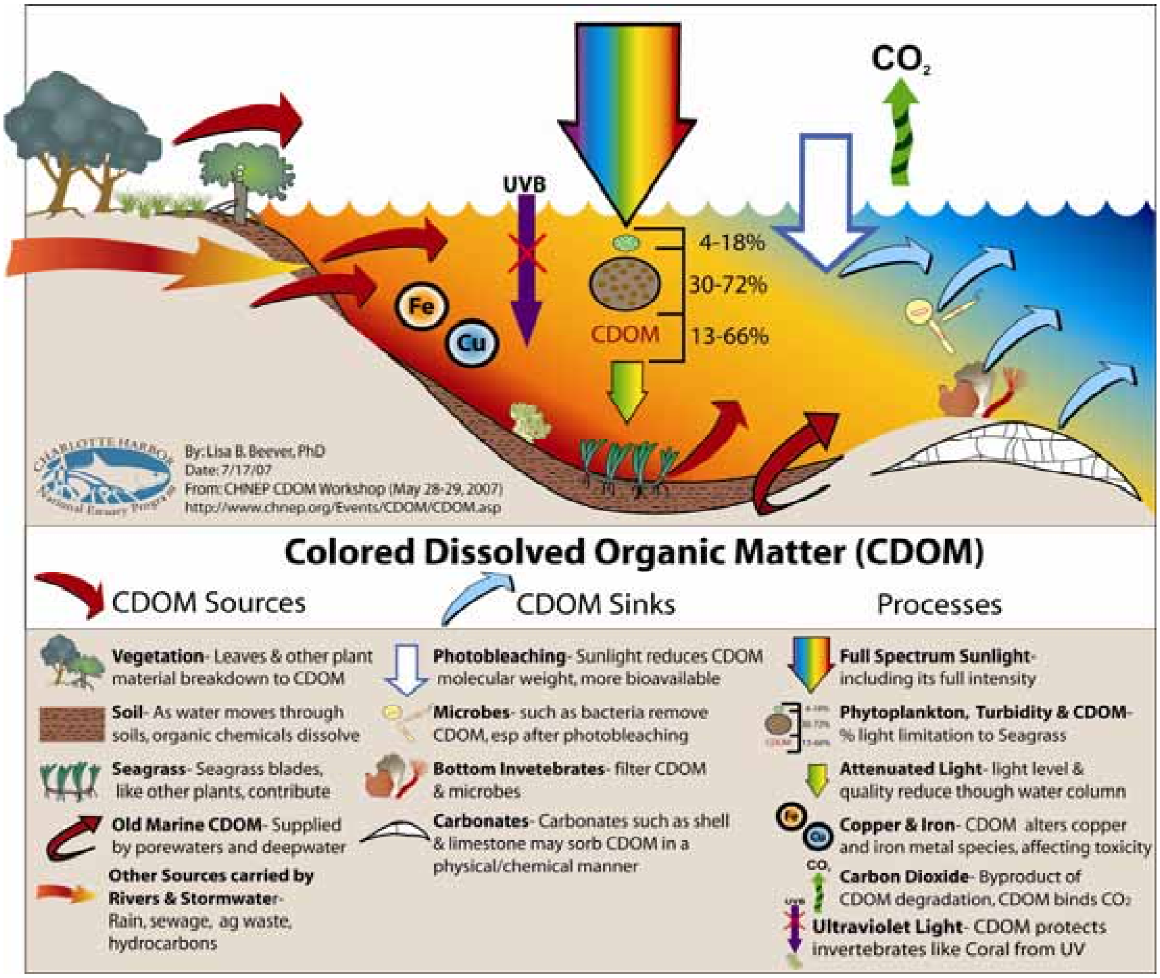
The workshop generated multiple conclusions that will affect research and monitoring in the Charlotte Harbor region in the future. First, the workshop participants agreed that CDOM composition variability is very important to better understand because it can affect seagrass and other benthic communities. Gathering CDOM composition as well as more robust concentration data can have implications for resource management and should be added to on-going local research and monitoring as soon as resources allow. The quality of light reaching seagrass communities is important and has been overlooked in the past. Lack of specific wavelengths of light energy may be the reason in some instances that seagrass restoration or maintenance activities have not been successful; thus, photosynthetically useful radiation should be added to on-going monitoring programs. In situ equipment with augmented discrete sampling are potential inexpensive methods in which to accomplish this objective. Understanding the entire suite of chemicals in the local CDOM pool will be expensive and difficult, however. Previous literature and existing data may provide initial information to guide future research and monitoring. Researchers can start by first developing rough relationships with rainfall, flow, landuse, etc. and CDOM spectral characteristics.

Second, results from analyses of current CDOM data (i.e., color or PCU) demonstrate that CDOM concentrations are in general positively associated with flow up to the point in which a "washing out" effect occurs. Therefore, hydrologic alterations that increase flow, such as increased rainfall or increases in Lake Okeechobee and basin releases in the Caloosahatchee River watershed, will increase CDOM concentrations up to a point. Analyses showing increasing trends in CDOM concentrations in the Peace and Caloosahatchee Rivers suggest that these trends may be a result of increases in flow and not specifically a result of landuse changes. Although it follows that landuse changes that lead to increases in flow may in turn lead to increases in CDOM concentrations given sufficient source material, CDOM concentrations have not been directly tied to landuse type nor has this issue been well researched yet.

Third, a better understanding of the spatial-temporal variability of CDOM concentration and composition is needed before resource managers and others try to manage it. Managers need to be able to predict results from management strategies and activities for these strategies to be successful. Managers and researchers do not currently well understand nor are we studying CDOM sufficiently to be able to understand or predict changes or tie to landuse and management activities. Since agencies need to tie monitoring and research activities to resource management, we can tie CDOM research and monitoring to the spectral needs of seagrass in Charlotte Harbor to gain management agency support for research. The quality of light and spectral needs of seagrass is important for long-term seagrass preservation.

Fourth, a CDOM working group should be created to coordinate research and monitoring as well as data sharing and the Charlotte Harbor NEP would be the appropriate entity to facilitate the working group. This working group can be part of the Charlotte Harbor NEP Water Quality Targets Working Group and could facilitate the creation of a centralized data depository to aid in better data sharing. A first step in this Working Group is to create an email distribution list in which members can discuss issues and ideas, and the University of South Florida staff offered to create a CDOM listserve.

Finally, the Charlotte Harbor NEP staff offered to create a CDOM conceptual model to distribute. The CDOM conceptual model would be helpful in succinctly translating CDOM issues to citizens and policy-makers. The CDOM conceptual model was constructed by Charlotte Harbor NEP staff with the aid of Drs. Chris Shank and Paula Coble and is included below:



(provided by L. Beever)

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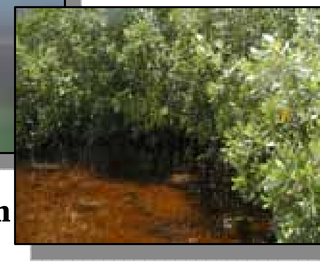
Appendix A

COLORED DISSOLVED ORGANIC MATTER WORKSHOP

AGENDA



Tuesday, May 29 MORNING

8:30	MORNING RECEPTION
9:00	Welcome and Opening Remarks **Catherine Corbett, Charlotte Harbor National Estuary Program** **Heidi Recksiek, NOAA Coastal Services Center**
9:15	Physical Properties of Light in the Water Column **Chris Anastasiou, Florida Department of Environmental Protection**
9:25	CDOM 101: Overview of Sources and Sinks, Spectral Properties and Measurements of CDOM. **Paula Coble, University of South Florida**
9:50	CDOM 102: General Overview of CDOM Chemistry and Methods of Breakdown. **Chris Shank, University of Texas, Marine Sciences Institute**
10:15	BREAK
10:40	CDOM 103: Indirect and Direct Biotic Links with CDOM. **Cynthia Heil, Florida Fish and Wildlife Research Institute**
11:10	Importance of Quality of Light for Seagrass-Physiological Impacts on Different Seagrass Species **Chris Anastasiou, Florida Department of Environmental Protection**
11:30	Questions and Answers
12:00	LUNCH

Tuesday, May 29 AFTERNOON

SESSION ONE: What are the different methods of measuring CDOM concentrations? How do these help us to better understand quality and quantity of light in the region? How do the current monitoring protocols in southwest FL compare to other regions? Should the protocols in Charlotte Harbor be changed?
Moderator: Frank Muller-Karger, University of South Florida

1:00	Tools for Observation of Synoptic Distribution of CDOM-Flow-Through Measurements **Kendall Carder, University of South Florida**

1:15 Tools for Observation of Synoptic Distribution of CDOM—Satellite Images, a case study in Tampa Bay estuary
Zhiqiang Chen, Frank Muller-Karger and Chuanmin Hu, University of South Florida

1:30 Overview of the Current CDOM Monitoring and Lab Analyses Protocols in Southwest Florida
Charles Kovach, Florida Department of Environmental Protection

1:45 Facilitated Session—Can any of these measurements help us better understand sources and sinks of CDOM? The composition of CDOM? Spatial and temporal variability in composition of CDOM? Should the protocols of measuring CDOM concentrations in southwest Florida be changed? If so, how?

2:20 BREAK

SESSION TWO: General overview of CDOM in Estero Bay, Charlotte Harbor and Lemon Bay and the tributaries to each, including impacts to quality and quantity of light reaching seagrass beds and influencing primary productivity. Are CDOM concentrations changing in the region? If so, why?
Moderator: Peter Doering, South Florida Water Management District

2:45 Causes of Light Attenuation with Respect to Seagrasses in Upper and Lower Charlotte Harbor
L. Kellie Dixon, Gary J. Kirkpatrick, and Emily R. Hall*, Mote Marine Laboratory

3:00 Changes in Land Use in the Peace River Watershed and CDOM in the Lower Peace River Watershed and Upper Charlotte Harbor

Ralph Montgomery*, PBS&J and Sam Stone, PRMRWSA

3:15 Flow, Source and CDOM in the Caloosahatchee River and Estuary
Peter Doering, South Florida Water Management District

3:30 Facilitated Session—Are CDOM concentrations changing in Charlotte Harbor? If so, why?

4:30 Summary of Next Day Activities
Catherine Corbett, Charlotte Harbor National Estuary Program
Heidi Recksiek, NOAA Coastal Services Center

5:00 POSTERS AND CONFERENCE SOCIAL

CDOM Workshop Agenda

Wednesday, May 30 MORNING

8:30 MORNING RECEPTION

9:00 Opening Remarks
Catherine Corbett, Charlotte Harbor National Estuary Program
Heidi Recksiek, NOAA Coastal Services Center

SESSION THREE: What are the spatial-temporal components of CDOM in the Charlotte Harbor region? Can we obtain this information using existing data or do we need specific research project(s) or monitoring programs to obtain this information? Can landuse models be improved to better estimate CDOM "event mean concentrations" (EMCs)? Would this analyte be an important addition to models for resource management in the southwest Florida region? If specific studies/new instrumentation are needed, a brief description of these needs should be determined.
Moderator: Paula Coble, University of South Florida

9:10 Near-shore Water Quality and Seagrass Relationships in the Upper Portions of Tampa Bay
Roger Johansson, City of Tampa

9:30 Temporal and Spatial Variability of CDOM Optical Properties
Robyn Conmy, University of South Florida

9:50 Examination of the Spatial Relationship of Soils, Landuse and Slopes to Florescence Data in Selected Watersheds: An integrated analysis with GIS
Barnali Dixon, University of South Florida

10:10 Landuse, CDOM, and Light Attenuation along the River-Estuary-Ocean Interface
Eric Milbrandt, Sanibel-Captiva Conservation Foundation, Marine Laboratory

10:30 BREAK

SESSION THREE *Continued*

11:00 Facilitated Session—What are the spatial-temporal components of CDOM in Lemon Bay, Charlotte Harbor and Estero Bay? Can we obtain this information using existing data or do we need specific research project(s) or monitoring programs to obtain this information? If specific studies/new instrumentation are needed, brief description of these needs…

12:00 LUNCH

CDOM Workshop Agenda

Wednesday, May 30 AFTERNOON

Session Four: Should agencies be collecting additional information to better understand CDOM dynamics and landuse impacts on CDOM concentrations and composition? For landuse models? To quality of light reaching seagrass beds and impacting primary productivity? Can this information be added to current monitoring programs?

Moderator: Judy Ott, Florida Department of Environmental Protection

1:00	Photoprotective Benefits of CDOM in Inshore Environments **Lore Ayoub, Paula Coble and Pamela Hallock-Muller, University of South Florida**
1:20	Export of Optically and Compositionally Distinctive DOM from Tidal Marshes in the Chesapeake Bay and Effects of Solar Exposure on its Spectral Characteristics **Maria Tzortziou, NASA Goddard Space Flight Center- ESSIC/University of Maryland Smithsonian Institution**
1:40	Facilitated Session-- Should agencies be collecting additional information to better understand CDOM dynamics and landuse impacts on CDOM concentrations and composition? For landuse models? To quality of light reaching seagrass beds and impacting primary productivity? Can this information be added to current monitoring or research programs? If specific studies/new instrumentation are needed, brief description of these needs…
2:40	Break
3:00	Facilitated Session— Can or should we add CDOM to our management strategies? How? Can we add “quality of light” to our water quality targets? How can data be better managed and shared? Remaining questions.
4:45	Workshop Wrap Up **Catherine Corbett, Charlotte Harbor National Estuary Program** **Heidi Recksiek, NOAA Coastal Services Center**
5:00	Closing Remarks **Lisa B. Beever, Charlotte Harbor National Estuary Program**