Watercolors in the Coastal Zone

What Can We See?

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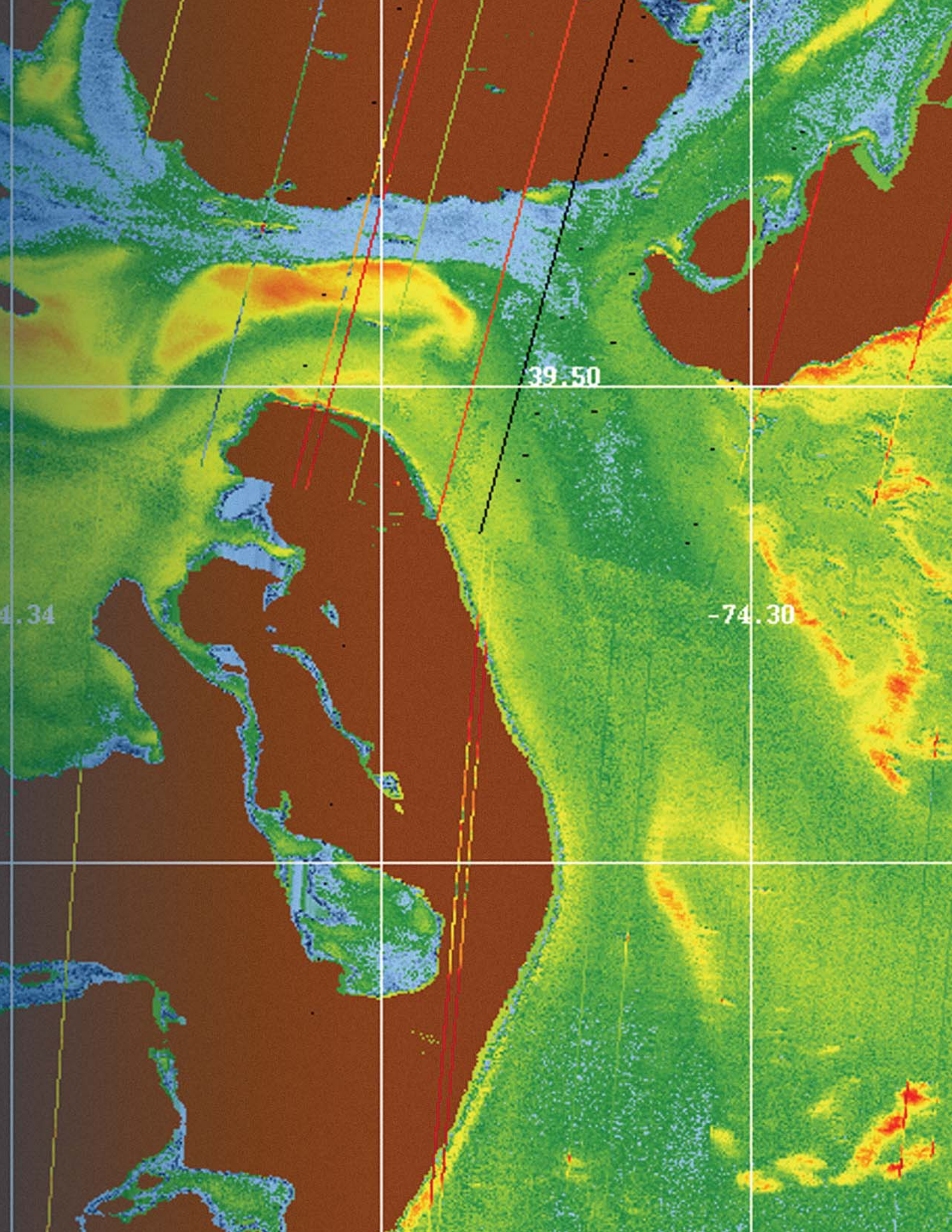
The Role of Optics in Oceanography

Hydrological optics has a rich history, playing a significant role in physical, chemical, and biological oceanography. The success over the last 30 years has provided oceanographers with a non-invasive means to study regional and global scale physical, chemical, and biological processes (Figure 1). The ability to map the color of the world's oceans has been used to estimate global ocean productivity (Longhurst et al., 1995; Platt and Sathyendranath, 1988; Sathyendranath et al., 1989; Behrenfeld and Falkowski, 1997), aid in understanding radiant heating processes (Ohlman et al., 2000), assist in delineating oceanic biotic provinces (Longhurst, 1998), and document regional shelf break frontal processes (Ryan et al., 1999a, 1999b). The scientific utility of mapping ocean color led to wide community support that has resulted in three generations of satellites launched by the United States, complemented by an international constellation of ocean color satellites from Europe, Japan, China, and India.

The utility of remote sensing results from algorithms that use satellite-measured reflectance to estimate the concentration of biogeochemically significant constituents. These algorithms were developed for optically "simple" waters where the optical properties of the ocean are largely defined by phytoplankton and water molecules (Figure 2; see article by Mobley et al., this issue). The spectral properties of water (Figure 2b) and phytoplankton are distinct. Increasing the concentration of phytoplankton (Figure 2c) in a volume of water selectively absorbs blue wavelengths of light, effectively "greening" the water reflectance in a predictable fashion. This "greening" allows empirical relationships to be derived that estimate chlorophyll a concentrations from the reflectance ratio of blue-to-green wavelengths of light. Many times, however, the optical signature of the ocean reflects the presence of materials other than phytoplankton and water molecules. The resulting complexity can directly influence the interpretation of what you "see" using satellite reflectance signals. A good example is the usually optically simple, high nutrient-low chlorophyll zones (HNLC). It has been proposed that deposition of atmospheric dust is a significant factor regulating overall productivity in HNLC zones (Martin, 1990; Prospero and Nees, 1986). Yet, if present in significant concentrations, the optical signature of the dust can compromise the empirical satellite algorithms (Moulin et al., 2001). The presence of significant submicron dust particles, which can remain in the water column for months (Claustre et al., 2002), influences the relative reflectance of the blue and green wavelengths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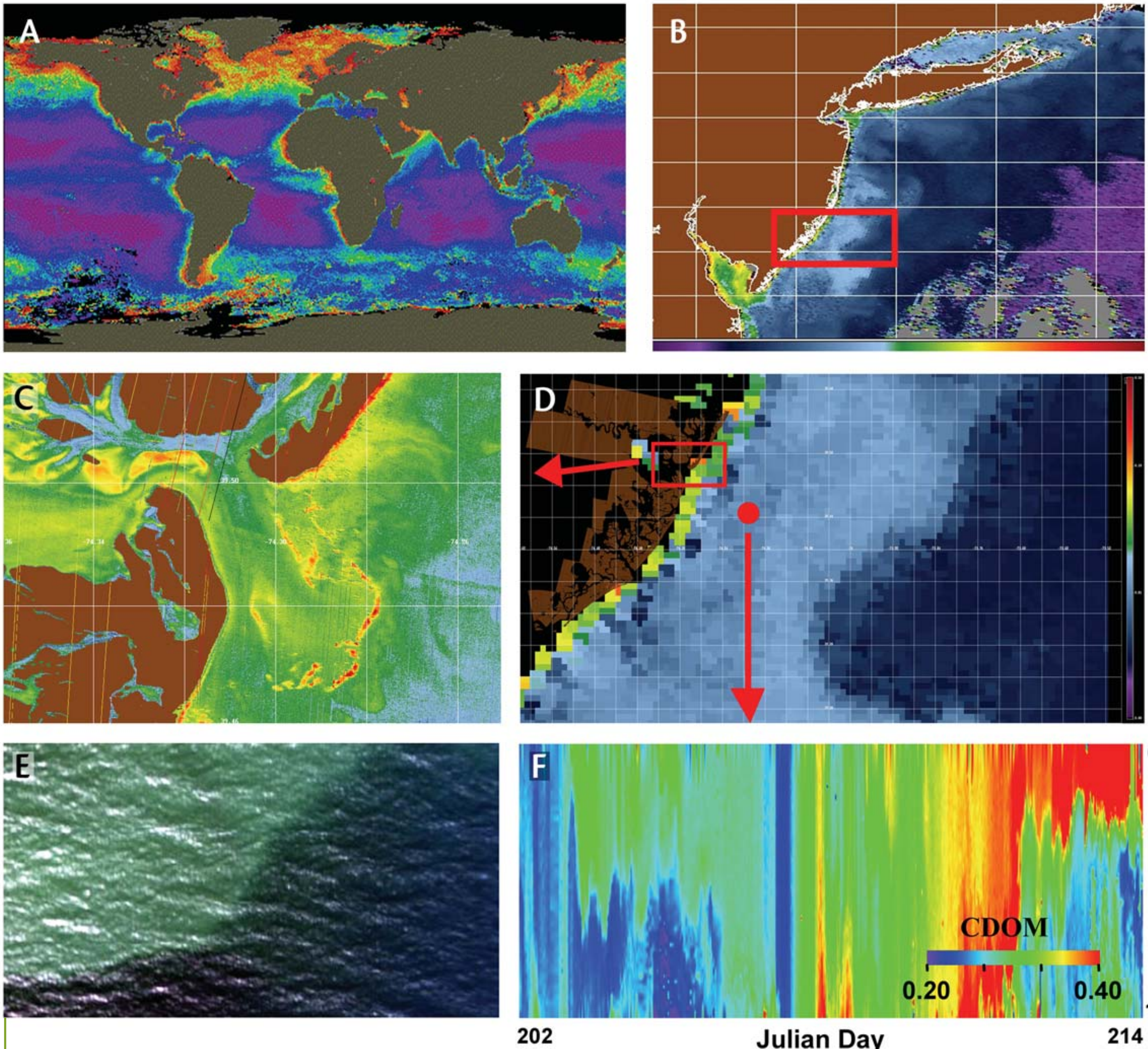

Figure 1. The time and space scale variability in ocean color. (A) An annual global chlorophyll *a* map measured using SeaWIFS (from http://seawifs.gsfc.nasa.gov/SEAWIFS.html). (B) Backscattering measured in summer 2001 in the Mid-Atlantic Bight using SeaWIFS. (C) An enlarged section in panel B focusing on the backscattering signal derived from the SeaWIFS observations; the satellite's 1-kilometer pixel is clearly visible and illustrates the features in the coastal ocean that are poorly resolved. It should be noted that some of newer ocean-color satellites have spatial resolutions down to 250 km. Ocean-color satellites with 30-meter resolution are proposed. (D) An enlargement from panel C showing backscatter measured by aircraft. Note the features clearly visible in the aircraft imagery that are missed with the standard 1-km pixels in the satellite imagery. (E) The visible image viewed by aircraft, with resolution on the order of tens of meters, showing the dramatic color change associated with crossing an upwelling front in the Mid-Atlantic Bight. The visible "greening" of the water is associated with enhanced blue light absorption. This color shift underlies empirical algorithms for ocean color remote sensing. (F) Time series of CDOM absorption, estimated from inverting bulk absorption measured with an ac-9 mounted on the Long term Ecosystem Observatory (LEO) electro-optic fiber optic cabled seafloor node (Oliver et al., 2004). Rapid changes in CDOM concentration are associated with the passage of storms and a large plume of Hudson River water.

of light and can result in an overestimate of chlorophyll a by a factor of two to three using standard ocean color satellite algorithms (Claustre et al., 2002). Therefore, when interpreting ocean-color imagery, one must ask whether the iron-rich dust leads to a true increase in phytoplankton or whether the perceived color change reflects the dust itself. The interpretation of ocean-color imagery is even more difficult in optically complex waters where many different optically significant constituents influence remote-sensing reflectance.

The Optical Complexity of Coastal Waters

Coastal waters are very often optically complex. In nearshore continental shelf waters, organic detritus and Colored Dissolved Organic Matter (CDOM) are often present in quantities sufficient to obscure the plant biomass signal because they influence the blue-to-green reflectance ratio (Figure 2b). Additionally, the presence of highly scattering inorganic particles and photons reflected off the seafloor (see *Limnology and Oceanography*, 48: 323-585, Figure 2d) can complicate the quantitative interpretation of the satellite imagery. Coastal waters are also characterized by numerous distinct frontal boundaries. Large changes in the *in situ* concentration of optically active constituents are often observed across these frontal boundaries (Figure 1). The spatial variability of these frontal features is often on scales of kilometers to meters (Figure 1D) and is difficult to resolve with a standard 1-km satellite pixel. How this spatial variability within a pixel influences the observed satellite signal is an open question (see Bissett et al., this issue).

Efforts to decipher this complex coastal optical soup often use *in situ* measurements to characterize observed reflectance spectra. This has become much easier in recent years due to advances in instrumentation that measure the *in situ* inherent optical properties [absorption (a), backscattered (b_b), and attenuation (c), note c – a = scattering (b)] (Figure 3). One such effort, the Hyperspectral Coupled Ocean Dynamics Experiment (HyCODE), has integrated these instruments into an ocean observatory (Glenn and Schofield, 2003; Schofield et al., 2003), enabling bio-optical adaptive sampling of the Mid-Atlantic Bight (Schofield et al., 2003). Given the desire to develop coastal remote-sensing applications, HyCODE focused on a wide range of optical issues that are highlighted in this issue of *Oceanography*. As an introduction to those efforts, this manuscript reviews some of the major optically active constituents that underlie the spectral variability of remote-sensing reflectance in coastal waters.

Understanding the spectral variability in ocean-color reflectance is key to using remote-sensing approaches, so our first need is to understand what underlies reflectance. Remote-sensing reflectance is the above-water ocean color and is defined as the ratio of the upward flux of light to downward flux of light incident on the ocean surface. Atmospheric effects aside (which represent ~95 percent of the actual satellite signal), reflectance is a function of both the spectral backward scattered light [$b_b(\lambda)$] and spectral absorption [$a(\lambda)$] within the water column. The relationship between spectral reflectance [$R(\lambda)$] and the inherent optical properties can reasonably be described as

$$R(\lambda) = G \frac{b_b(\lambda)}{a(\lambda) + b_b(\lambda)} \qquad (1)$$

where G is a relatively constant parameter dependent on the angular distribution of the light field and the volume scattering coefficient (Gordon, 1975; Morel and Prieur, 1977). Given that the magnitude of the inherent optical properties represents the linear combination of all optically active constituents, the color of the reflected light integrates the spectral absorption and backscattering properties for all the materials present. For example, in coastal waters the total absorption might be described by the absorption of phytoplankton, detritus, sediment, water, and CDOM. The net effect is that the first-order factor determining the spectral shape and total amount of reflectance is the concentration of absorbing and scattering constituents present; however, it should be emphasized that the absorption and scattering efficiencies of different constituents vary dramatically due to their specific molecular properties. For ocean-color remote sensing, backscatter is a source of photons from the ocean to the satellite. Backscattered light is a small proportion of the total scattered light, and the relative amount of backscattered light is dependent on the type and size of the material present in the ocean. In contrast, absorption is a sink for photons. Absorption is very high in aquatic systems due to H_2O molecules that are extremely effective at absorbing red light and phytoplankton that are effective at absorbing blue light. The net result is that reflectance signal over the ocean is low (Figures 2f and 2g offer an opportunity to compare the scales of reflectance for terrestrial leaves versus that of coastal waters).

This presents the remote-sensing engineer the difficult task of designing sensitive sensors that will not become saturated if the signal is high, such as is the case on a windy day when white caps and the presence of air bubbles can lead to enhanced light scatter. The available satellites have varying degrees of spectral resolution ranging from five spectral bands to hyperspectral systems (often designed for terrestrial remote sensing,<http://eo1.gsfc.nasa.gov/miscPages/home.html>, the degree with which these systems have utility for ocean applications is an open area of research). Increased spectral

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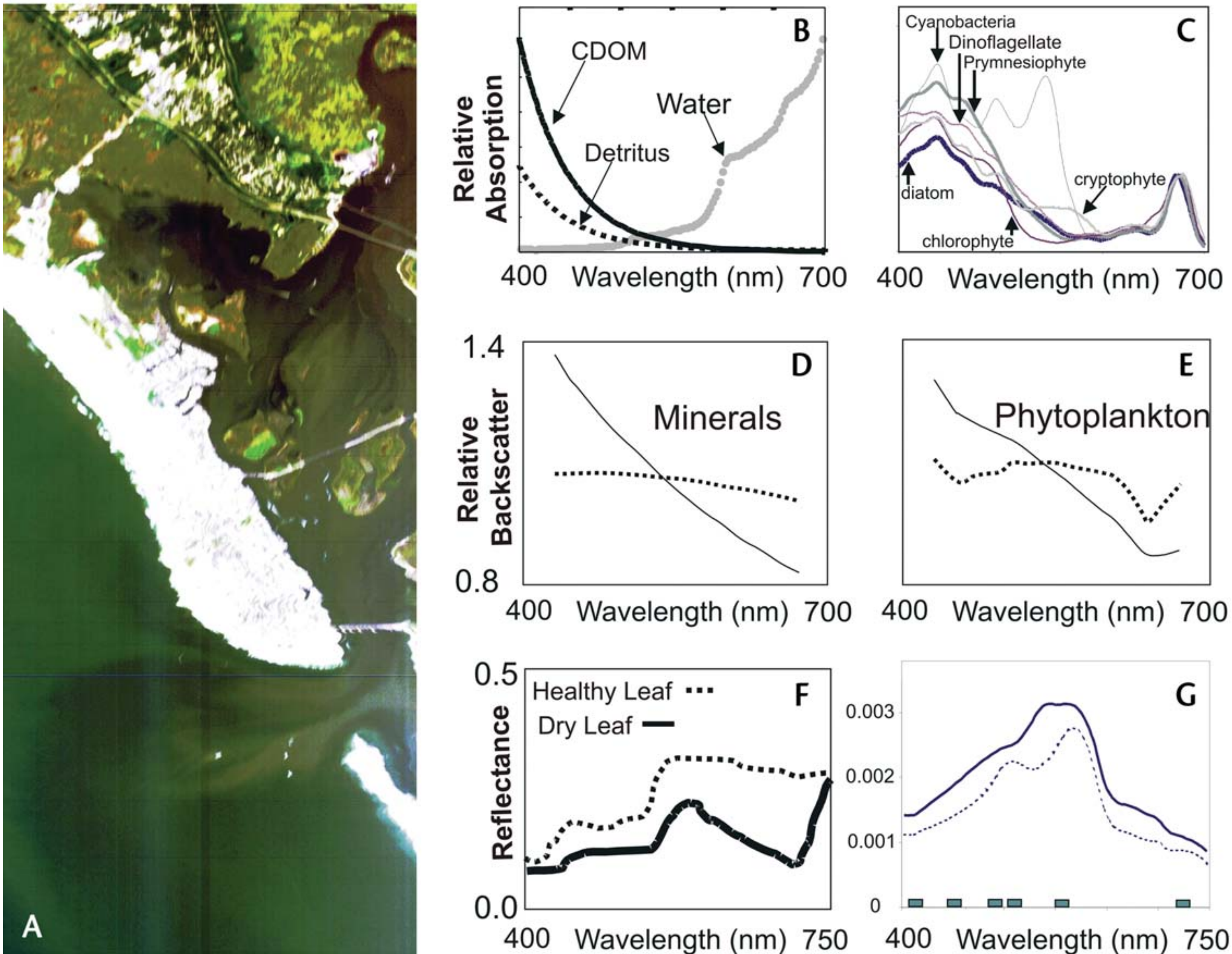

Figure 2. Spectral signatures that dominate reflectance in coastal zones. (A) A visible image taken from an aircraft spanning nearshore coastal waters over an urbanized area into an estuary in New Jersey. The letters illustrate different optical zones in which different optical constituents dominate the reflectance perceived from the aircraft. (B) The relative spectral absorption of water, colored dissolved organic matter (CDOM), and detritus. Absorption of water in the red wavelengths is orders of magnitude higher than CDOM and detrital particles. (C) Relative absorption of different phytoplankton species (Johnsen et al., 1994) illustrating spectral variability due to different phytoplankton pigments. (D) Relative spectral backscattering associated with inorganic particles (redrawn from Babin et al., 2003) for different particle sizes with a constant refractive index. (E) Relative spectral backscattering associated with phytoplankton (redrawn from Babin et al., 2003) for two different particle sizes with a constant refractive index. (F) Reflectance spectra for a healthy and dry leaf. Note scale for the y-axis. (G) Reflectance for nearshore and offshore waters of the Mid-Atlantic Bight. Columns along the x-axis indicate the spectral bands measured by SeaWIFS.

resolution expands the potential to improve approaches that can invert the measured reflectance into its constituent components, which have distinct absorption and scattering properties.

Given the desire to invert bulk reflectance into its constituent components, the ocean optics community has focused on defining the scattering and absorption properties of the compounds that dominate ocean color. This is often accomplished by collecting discrete and *in situ* measurements. The first efforts have focused on characterizing the relative importance of the dissolved and particulate constituents, including phytoplankton, detritus, and sediments, which dominate the particulate material; and CDOM, small bacteria, colloidal material, and viruses, which dominate the dissolved phases.

What Gives Coastal Water its Color?

CDOM refers to organic matter that can nominally pass through a 0.2 micron filter and can be detected optically, as not all organic compounds absorb light. High concentrations of CDOM decrease light reflectance dramatically because its spectral absorption can be high (Figure 2b). CDOM is often predominantly composed of humic and fulvic acids, but can also include small colloidal material. Generally, CDOM's largest impact is on absorption, but some colloidal material can contribute to the backscattering of light. CDOM sources include cellular exudation/lysis/defecation (Kalle, 1966; Bricaud et al., 1981; Guixa-Boixeru et al., 1999), resuspension from sediments (Chen, 1999; Komada et al., 2002) and humic/fulvic acids from rivers and terrestrial watersheds (Blough et al., 1993; Vodacek et al., 1997). Satellite algorithms for CDOM absorption are being developed and offer in the near future the possibility of mapping CDOM concentration. These algorithms are based on empirical models that relate CDOM absorption to the ratio of green to red wavelengths of reflectance.

Absorption properties can also be used to describe CDOM composition. Spectral absorption of CDOM decreases exponentially with increasing wavelength (Figure 2b). A low CDOM slope is generally interpreted as freshly produced material, which is then degraded through either photo-oxidation (Mopper et al., 1991; Kouassi and Zika, 1992; Nelson et al., 1998) or microbial activity (Whitehead, 1996). Spectral slope increases as the material is chemically modified (Rashid, 1985), and over monthly time scales, CDOM becomes increasingly refractory (Nelson et al., 1998). Mechanistic interpretation of the age and source of CDOM from the spectral slope is difficult due to the complexity of the degradation process, which is described by at least two rate constants that span days to weeks (Twardowski and Donaghay, 2002). Despite these uncertainties, CDOM slope has been effectively associated with specific water masses in the Baltic Sea (Højerslev et al., 1996), Gulf of Mexico (Carder et al., 1989), Caribbean (Blough et al., 1993), Mid-Atlantic Bight (Vodacek et al., 1997), and Sargasso Sea (Nelson et al., 1998). Developing methods to characterize CDOM composition from space does not exist, but as the spectral resolution of satellite systems increases, the ocean optics community will undoubtedly explore the potential for new algorithms.

Depending on the filter, some organic particles are often included in the CDOM fraction. The most notable particles are viruses and bacteria. Viruses are very small (~ 100 nm) and are not believed to contribute significantly to the overall absorption and scattering of light. Bacteria are also abundant in the water column and contribute significantly to the overall scattering properties (Morel and Ahn, 1990) in clear ocean waters, where the contributions of other larger particles such as phytoplankton and sediment are small. These bacteria also play a disproportionately large role in remote-sensing reflectance due to the relative increase in backscattered to total scattered light associated with small particles.

Particles are an important component influencing the reflectance of the ocean. Phytoplankton represent a dominant absorbing constituent in most of the world's oceans (see below). However, in nearshore waters, the presence of resuspended sediments can be significant. Inorganic sediment sources can be resuspended from storms, deposited from airborne dust, produced biologically (Balch et al., 1991), and be transported into coastal waters from rivers. Inorganic particles have high scattering efficiency and thus significantly increase the light emanating from the ocean interior when present in significant concentrations (Figure 2d, note the bright reflectance of urbanized areas in Figure 2a).

Phytoplankton represent a major absorbing constituent in the world's oceans due to the presence of photosynthetic and non-photosynthetic pigments. The absorption variability associated with the diversity of phytoplankton pigmentation impacts the blue and green light reflectance (Figure 2c). In coastal waters, all major spectral classes of phytoplankton (chlorophyll *c*-containing, phycobilin-containing, and chlorophyll *b*-containing) are often present. Because phytoplankton must harvest light for photosynthesis and light is rapidly attenuated with depth in the ocean, phytoplankton have evolved an extensive array of accessory carotenoids. This attenuation is easily observed in the field where filtered material from ocean water is most often brown due to high concentrations of accessory carotenoids. This brown color contrasts with the bright green we observe in terrestrial plants where the chlorophylls dominate absorption characteristics. The diversity in pigment absorption signatures is tantalizing because it might permit discrimination of different phytoplankton groups based on their optical properties. While promising, one difficulty is the low spectral resolution available from *in situ* and remote sensing. When hyperspectral information is available, pattern recognition and derivative analyses have proven most effective at discriminating phytoplankton taxa using discrete data (see Chang et al., this issue; also Schofield et al., 1999; Kirkpatrick et al., 2000; Millie et al., 2002); however, this capability has yet to be robustly achieved using presently available remote-sensing techniques. This remains an active area of research.

Phytoplankton contribute significantly to the total scattering of the light. Total scattering is, to first order, regulated by biomass; however, the efficiency with which individual phytoplankton cells contribute to scattering can vary with phytoplankton size and refractive index. Some of the changes in refractive indices are due to phenotypic features, such as internal air pockets (Subramaniam et al., 1999) or minerogenic armor (Iglesias-Rodriguez et al., 2002), or the physiological state of the cell (Stramski, and Reynolds, 1993; Reynolds et al., 1997). For remote-sensing applications, phytoplankton have a high scattering signal, but generally only a small proportion is backscattered, therefore phytoplankton absorption dominates their contribution to reflectance.

Figure 3. Some examples of now-robust off-the-shelf optical technology during the HyCODE effort that are currently available to oceanographers. (A) A Webb glider (http://www.webbresearch.com/slocum.htm) outfitted with an attenuation meter and two backscattering sensors embedded in the belly of the autonomous vehicle. (B) Another Webb glider outfitted with a 2-wavelength backscatter sensor and a fluorometer. (C) A robotic-profiling optical mooring outfitted with absorption-attenuations meters (Wetlabs, Inc.), bioluminescence bathyphotometers, forward-scattering sensors (Sequoia Instruments), and backscatter sensors (HOBI labs and Wetlabs, Inc.). (D) A biplane, one of the world's slowest, outfitted with a hyperspectral, remote-sensing reflectance sensor. The slow speed is ideal for allowing detailed calibration studies. (E) A radiometer (Satlantic) outfitted with a copper shutter. The copper shutters have been demonstrated to be highly effective at minimizing biofouling problems. (F) An optical mooring being deployed by the Ocean Physics Laboratory. (G) Living the dream in the COOL room (Glenn and Schofield, 2003) where scientists can sit and drink coffee while all the data are delivered in near real-time. This capability allows for adaptive sampling (Schofield et al., 2003).

Detrital particles represent nonliving organic matter including fecal pellets, cell fragments, large colloids, and marine snow. An exponentially decreasing slope describes detrital spectral absorption, but the slope is typically less steep than for CDOM (Figure 2b). The relative backscatter of detritus can be high compared to that of phytoplankton (Stramski and Kiefer, 1991), but of all the optical constituents, detrital particles remain relatively understudied. This lack of information is problematic in coastal-water studies where detrital absorption can represent up to 30 percent of the blue light absorption signal (Schofield et al., In press).

Where Do We Go From Here?

Coastal waters are complex, but recent advances in optical instrumentation allow the oceanographer to decipher this complex soup, as highlighted in the other manuscripts in this issue. Optical data allow ocean-observing networks to serve the needs of chemists and biologists by providing data over ecologically relevant scales. It is our hope that the wider community will adopt these measurements and approaches so that one day they become as standard as a Conductivity-Temperature-Depth (CTD) sensor in the oceanographer's tool box.

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