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feature article

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Recent advances are making it possible for optical oceanographers to solve a host of pressing environmental problems.

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Light drives the physics, chemistry, and biology of the ocean. Without light in the ocean, life on Earth could not exist, nor would there be fuel for the heat engine that drives the ocean's currents and the atmosphere's circulation. Furthermore, light and sound are the two primary means available for probing the ocean. (See the article by Tom Sanford, Kathie Kelly, and David Farmer in PHYSICS TODAY, February 2011, page 24.)

Optical oceanography, which concerns all facets of light, its interactions with seawater, and its ultimate fate, is central to many important studies.[1,2] It is vital for addressing problems of photosynthesis, ecosystem dynamics, the health of the ocean, seawater clarity, underwater imaging, biogeochemical cycling, carbon budgets, upper-ocean thermodynamics, and climate change. The future of the ocean and its inhabitants will depend on our ability to learn how anthropogenic activity affects them.

Light interaction

How does light interact with seawater? The simplest optical interactions, which occur at the boundary of the atmosphere and ocean, are governed by Snell's law and the Fresnel equations. But even those straightforward geometrical-optics effects are complicated by surface roughness. Once light enters the ocean, it interacts with water molecules and with a great variety of other constituents, organic and inorganic. Accurately modeling those complex interactions requires radiative-transfer methods and accurate measurement of the many highly variable constituents and parameters in the water. It would be convenient to think of the ocean as simply a homogeneous body of water. But the ocean is in fact more like a stratified witches' brew, with many different solid and dissolved ingredients.

The interactions of light in the ocean involve many processes and feedback mechanisms. Consider phytoplankton, microscopic drifting algae that form the base of the ocean food chain by performing photosynthesis. They absorb light, take up CO_2, and release oxygen. They also fluoresce some of the light back into the ocean, and they can exhibit bioluminescence—light emission through chemical processes.

Phytoplankton vary in size, shape, and optical properties, and they contribute to the color of seawater. They affect the heating and stratification of the upper ocean through their interactions with light. And those processes in turn affect their growth environment. Anand Gnanadesikan and coworkers at Princeton University have recently suggested that phytoplankton may even affect the frequency of typhoons.[3] It had been suggested in 2004 that hurricanes, which increase the availability of plant nutrients in the upper layer, can stimulate phytoplankton blooms and thus accelerate the drawdown of CO_2 by the ocean.[4]

Why is the ocean blue?

Speculation about the blue color of the ocean, as seen from above, goes way back. Lord Rayleigh claimed it was simply reflection of the blue sky. The correct explanation required com-

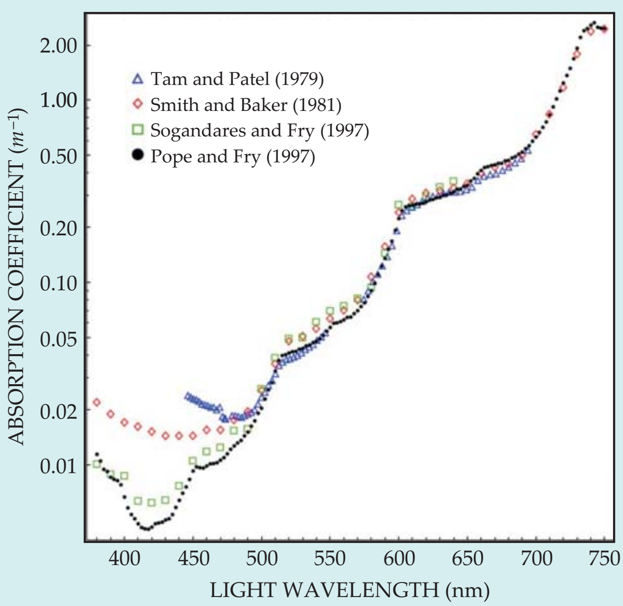

Figure 1. Various measurements of the absorption coefficient of light in pure water. Considerable discrepancy is evident near the absorption minimum at 420 nm in the blue region of the visual spectrum, where light can travel more than 100 meters with little absorption, making laboratory measurement difficult. The most accurate measurements near the minimum to date are by Edward Fry's group at Texas A&M University.[18]

bining the 19th-century ideas of Robert Bunsen, who felt that the color depended on light absorption by water, and Jacques-Louis Soret, who felt that the color was entirely due to scattering. C. V. Raman pointed out the importance of molecular scattering, and in 1923 Vasily Shuleikin combined those ideas to develop a complete explanation of the color of the sea.

In very clear, open waters with few particulates, called hydrosols, the ocean's optical properties depend primarily on the scattering and absorption properties of the water molecule itself. Let us first address absorption. One might think that the wavelength dependence of water's absorption coefficient—a sine qua non for calculating the ocean's intrinsic color as a function of depth—is known to high precision. But one would be wrong. Figure 1 shows the recent history of the absorption coefficient's measurement in pure water. The principal feature is the almost thousandfold rise from the absorption minimum at blue wavelengths to a maximum in the red.

The very little absorption on a scale of meters in the blue is why there have been such large discrepancies in the measurements at that end of the visible spectrum. The minimal absorption arises primarily from the vibration modes of the water molecule's O–H bonds. The fundamental vibrational modes occur at IR wavelengths near 3 µm. Therefore, absorption in the blue requires excitation of higher-lying states vibrating at high overtones of the fundamental. Because the density of such states is low, there's little absorption at blue wavelengths. It's remarkable that the intrinsic blue color of water is due primarily to molecular vibrations and not to direct electron interactions, which are the primary determinants of color in almost all other substances.

Scattering in water

The scattering of light in the ocean can be elastic (with no frequency shift of the incident radiation) or inelastic (frequency shifted). Both types are often called Rayleigh scattering. But Rayleigh certainly did not describe inelastic scattering in bulk liquids; that phenomenon was not understood before Rayleigh's death in 1919. (See the article by Andrew Young in PHYSICS TODAY, January 1982, page 42.)

The scattering of light in liquid water is primarily due to density fluctuations, which can be broken down into two different types, mechanical and thermal (see figure 2a). Mechanical disturbances create isentropic pressure fluctuations that propagate as phonons with the speed of sound in water. Light of incident frequency ω_0 scattered off such a phonon suffers a pair of frequency shifts to produce a so-called Mandelstam–Brillouin (MB) doublet, as shown in figure 2b. In the language of Raman scattering theory, the doublet's red- and blueshifted spectral lines are called, respectively, the Stokes and anti-Stokes lines. The weaker unshifted line in the spectrum of scattered light, discovered by Evgenii Gross in 1930, is due to scattering off nonpropagating, isobaric entropy fluctuations.[5]

Bragg scattering off phonon waves and Doppler shifts due to the motion of those waves, as shown in figure 2b, determine the MB frequency shifts $\omega = \omega_0 \pm \omega_{MB}$.

$$\omega_{MB}/\omega_0 = 2n \sin(\theta/2) v_s/c\,, \qquad (1)$$

where n, the refractive index of water, depends on ω_0, salinity, and temperature; θ is the scattering angle at which the scattered waves are observed; and v_s and c are, respectively, the speed of sound in the water and the speed of light in vacuum.

Note that there is no frequency shift in the forward direction, and that the maximum shift occurs at 180° backscattering. For pure water, the backscattering frequency shift is around 7.5 GHz, which is also the frequency of the sound waves producing the light scattering.

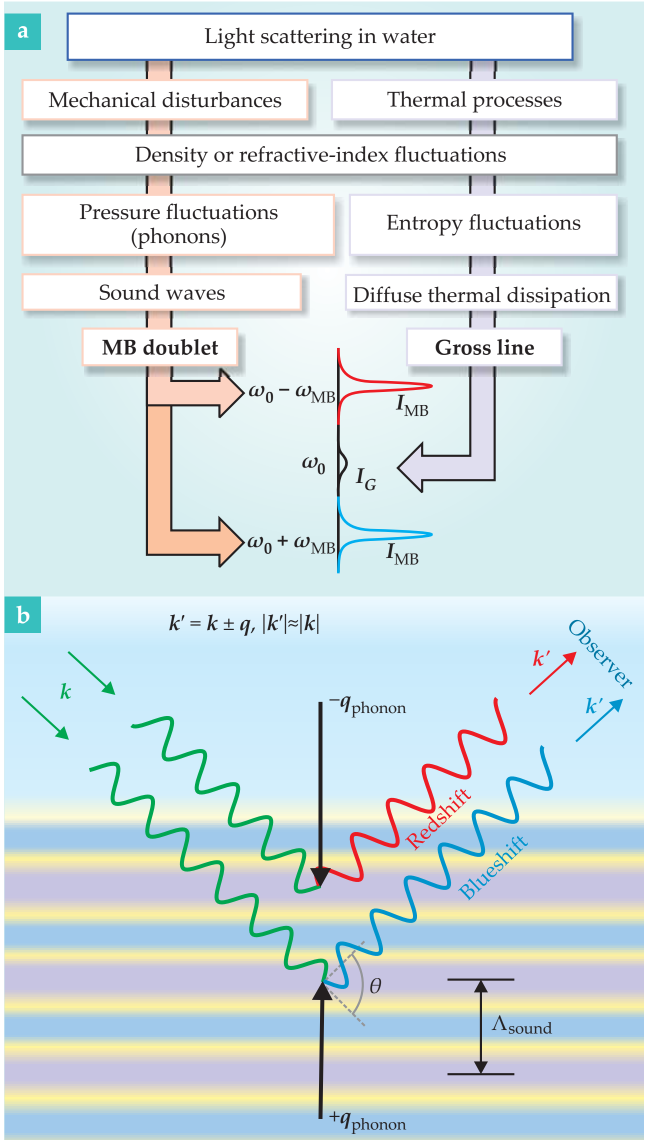

Figure 2. Light scattering in water by fluctuations in density or refractive index. **(a)** Mechanical disturbances generate phonons that scatter incident light of frequency ω_0 to produce a Mandelstam–Brillouin (MB) doublet of spectral lines shifted redward and blueward by ω_{MB}, given by equation 1 in the text. Thermally generated entropy fluctuations, by contrast, scatter light without shifting its frequency, resulting in the Gross line in the spectrum of scattered light. **(b)** One can derive equation 1 by imagining the Bragg scattering of incident photons of momentum **k** off phonon waves (shown as striations) of incident momentum ± **q**. Scattering off approximately approaching (+**q**) or receding (−**q**) wavefronts Doppler-shifts the photon, respectively, toward the blue or red. The wavefront orientation of the relevant phonons is deduced from the scattering angle θ at which the observer is looking.

The ratio of the intensity of the unshifted Gross line to the sum of the intensities of the MB doublet lines in the reflected-light spectrum is $(C_P/C_V) - 1$, where C_P and C_V are, respectively, the specific heats of water at constant pressure and constant volume. Because that ratio at 25 °C is only about 0.01, the spectrum of scattered light in pure water shows very little intensity at the unshifted wavelength; almost all the scattered light appears in the Stokes and anti-Stokes lines.

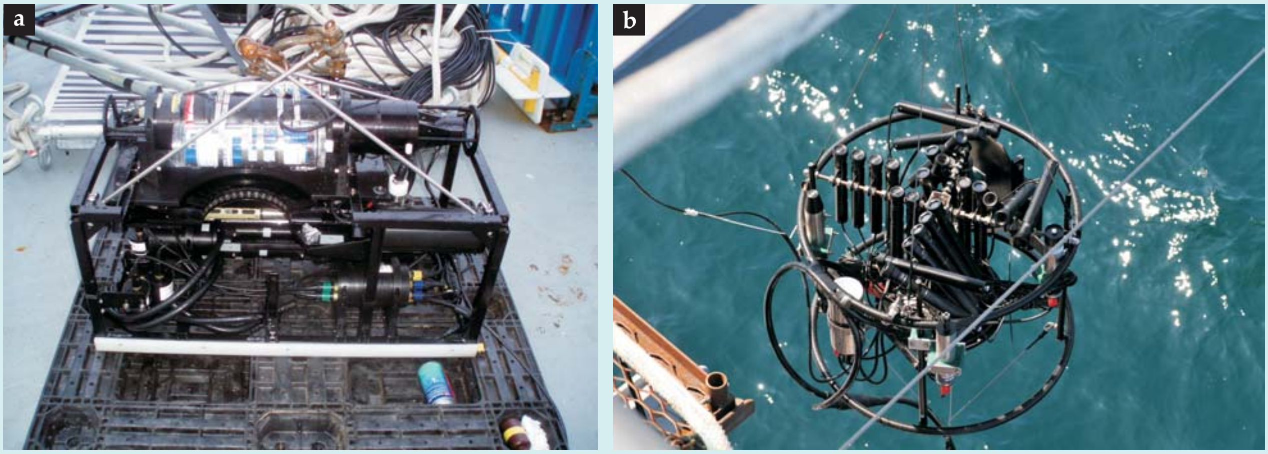

Figure 3. (a) The Multi-Angle Scattering and Optical Transmission (MASCOT) detector built and deployed by Michael Twardowski measures light-absorption and light-scattering properties and bubble-size distributions of ocean water at different locations and depths. (Photo by Michael Twardowski.) **(b) Optical system** used by a group from the Scripps Institution of Oceanography for measuring rapid light fluctuations that occur naturally just below the ocean's surface. (Photo by Dariusz Stramski.)

That result has enormous consequences for improving image quality in the ocean, because light scattered from hydrosols or underwater objects experiences no frequency shift.

Another inelastic process in water is Raman scattering, where vibrations of the water molecule modulate the liquid's polarizability and thus give rise to both Stokes and anti-Stokes Raman shifts of the incident light. There's always a competition between Raman scattering off single water molecules and off polymeric stacks of water molecules held together by hydrogen bonds. The resulting equilibrium is very temperature sensitive, and it can alter the shape of the Raman band. That effect has been exploited for measuring depth profiles of water temperature with light-detection-and-ranging (lidar) systems.[6]

Although the Raman scattering coefficient is about the same as the MB scattering coefficient, there are important differences between the two processes. Used together, they provide a powerful tool for remotely monitoring the sound speed, temperature, and salinity in the ocean as a function of depth. Like Rayleigh scattering in the atmosphere, both processes have a roughly λ^{-4} dependence on wavelength, which contributes to the ocean's blue color, as it does to the blue sky. With minimum absorption near 420 nm, in some very clear, clean locations, most notably near Easter Island in the South Pacific Gyre, the water appears almost purple.[7]

It's useful to define two classes of water's optical properties: Inherent optical properties (IOPs), which characterize spectral scattering and absorption independent of the directional structure of the ambient light field, can be measured in the lab. Apparent optical properties (AOPs), on the other hand, depend on the light field and can be measured only in situ. Radiometric quantities include the radiance L, defined as the light power impinging on an underwater detector per unit area, frequency, and acceptance solid angle. It depends, of course, on the detector's underwater position and the direction it's pointing, and on the Sun's position. (Irradiance is the integral of radiance over some specified solid angle—for example, the entire downward hemisphere.) To predict radiance and irradiance for comparison with measurements one uses radiative-transfer models that take account of all the things that can happen to a photon on the way from the Sun to the detector, using the IOPs as inputs.

Radiance and irradiance thus computed and compared with measurements are often used for determining AOPs. For example, the spectral diffuse-attenuation coefficient at a given optical wavelength is defined as the negative of the vertical gradient of downward irradiance.[1] In natural ocean water, many factors modify optical properties, and hence the apparent color. They include dissolved organic matter, which preferentially absorbs in the UV, thus shifting the water's color toward green and red. That shift is often very evident in puddles or areas of standing water in which leaves are decaying.

In areas of sediment runoff, large particles dominate the scattering, decreasing the wavelength dependence of the backscattering. When that effect combines with dissolved organic material, the water acquires a brownish tinge. Phytoplankton contain chlorophyll, which absorbs light in the blue and red. Thus an increase in phytoplankton concentration causes the ratio of blue to green reflection from the ocean to decrease, creating greenish hues. In shallow water, reflection from the sea floor can also have a profound effect on the sea's apparent color. That effect can be exploited in shallow waters for bathymetry—determining sea-floor depth.

Observational methods and strategies

Optical oceanography relies heavily on field data sets—needed for discovering new phenomena and developing models. Some of the earliest ocean measurements of light were done with a Secchi disk, named after the 19th-century priest and astronomer Pietro Angelo Secchi, who also did oceanographic studies aboard the papal yacht *L'Immacolata Concezione*. The white disk, about the size of a dinner plate, is lowered slowly in the sea until, at the so-called Secchi depth, it can no longer be seen from above the surface. So simple a measurement turns out to be amazingly stable from observer to observer, and it can be linked to modern global-scale optical and biological data.[8]

One objective of Britain's 1872–76 HMS *Challenger* expedition, which essentially initiated oceanography as a science, was to carry out worldwide measurements of light penetration into the sea. Soon thereafter, color-based comparators invented by Swiss investigator François-Alphonse Forel were used to define water masses by their color. Toward the end of World War II, electronic radiometers began being used for oceanic optical measurements. Those instruments, like the present generation of optical instruments, had to withstand shock during deployment and recovery, high pressure, temperature variations, corrosion, and fouling by marine organisms.

Today's optical instruments are being used to investigate how light interacts with seawater for a variety of purposes: to determine IOPs and AOPs, particle size distributions, chemical concentrations, and resident organisms.[2] To such ends, the instruments measure the absorption, scattering, and total attenuation of light. They utilize either ambient sunlight or artificial light to quantify the optical medium and the light field itself.

In the past decade, newly developed ocean instruments using linear variable filters and spectrometers have increased spectral resolution by almost an order of magnitude—to a few nanometers in the visible. This so-called hyperspectral resolution makes possible improved identification and quantification of assemblages of phytoplankton and dissolved matter. It also provides detailed bathymetric data critical for addressing a host of practical and research problems.[9]

RaDyO

A fundamental IOP is the volume scattering function, which describes the angular scattering pattern of light. Such measurements are difficult because they span a large dynamic range; variations with angle span several orders of magnitude. But the past few years have seen much progress. As one example, during the 2008–09 Radiance in a Dynamic Ocean (RaDyO, pronounced "radio") program conducted off California and Hawaii, oceanographer Michael Twardowski (WET Labs, Narragansett, Rhode Island) and colleagues deployed a newly developed instrument package, shown in figure 3a, capable of absorption measurements at several wavelengths and scattering measurements at 17 different angles. Data from such instruments provide essential inputs for radiative-transfer models. Twardowski's instrument has also been used to measure bubble-size distributions (ranging from submicron to a few hundred microns), complementing bubble measurements done with acoustic-resonator systems.

Until recently, few studies have been devoted to the nature and potential effects of high-frequency light fluctuations within 10 meters of the ocean's surface. Such fluctuations arise from intense sunlight focused and defocused by waves. As part of the RaDyO experiment, Dariusz Stramski and coworkers at the Scripps Institution of Oceanography in La Jolla, California, deployed an instrument suite comprising several irradiance and radiance sensors that can measure light fluctuations on time scales from milliseconds to minutes (see figure 3b). Stramski and company showed that instantaneous light pulses exceeding 10 times the average irradiance occur near the surface. The implications of such bursts for heating and photosynthesis remain to be explored.

Virtually all of the IOPs and light-field characteristics can be derived from the radiance distribution—that is, the measurements of radiance at all angles.[1] During the RaDyO program, advances were made in the accomplishment of such demanding measurements by Marlon Lewis (Dalhousie University, Halifax, Nova Scotia), one of us (Voss), and coworkers. Lewis's ship-deployed instrument measured the radiance distribution as a function of depth and time with an angular resolution of less than 1° over a dynamic range of a million. Cameras were also developed for measuring polarized spectral-radiance distributions in the water and above the surface at five different wavelengths. Voss and coworkers found that near the surface under clear skies, the polarization of the light field was dominated by refracted skylight. At depths below 20 m, the polarization was due mostly to light scattering by the water itself.

Polarization is enormously important to many sea creatures. Some use polarized light as a compass, much in the same way honeybees do. Squid use polarized light to see the phytoplankton on which they feed. It's also conjectured to be important for the ability of squid and other cephalopods (octopus and cuttlefish) to camouflage themselves.[10] (See figure 4.)

Modeling of the surface and subsurface light field requires inputs of high spatial and temporal resolution. One needs to know the topography of the surface and its wind-dependent condition—roughness, breaking waves, whitecaps, or foam. Optical measurements of waves down to millimeter scales were carried out by several groups during RaDyO. They used lidar, IR, and polarimetric video cameras—some of them stereographic. Chemical and physical data were also collected in the surface microlayer down to 1 mm. The light field in that microlayer affects surface tension and photochemical transformations.[11]

Calculating radiative transfer

To model complex, rapidly time-varying features in the ocean, one must confront the time-dependent radiative-transfer (RT) equation that seeks to describe energy transfer by electromagnetic radiation in media. Models have to couple the atmosphere to the ocean across a time-varying interface consisting of waves whose structural detail ranges from millimeters to meters. And the waves can be nonlinear.

Many methods are available for solving the static one-dimensional RT equation for either the atmosphere or the

Figure 4. An octopus of the common species *Octopus vulgaris* reacts to the approach of a diver by completely changing its camouflage within two seconds. Initially camouflaged to match the mottled greenish color, pattern, texture, and reflective intensity of the surrounding algae, it quickly changes to match the white sea floor. (Adapted from ref. 10.)

Figure 5. R/P *FLIP*, a floating research platform operated by the Scripps Institution of Oceanography, is an extraordinarily stable platform for the deployment of multiple research instruments at sea. It's a towable sea-going vessel 108 meters long that becomes the tall, stable tower shown in the photo when its aft ballast compartments are flooded to flip the vessel bow up. (Photo by Kyla Buckingham.)

ocean.[12] But the number of methods becomes quite small when total coupling is required. Modelers are faced with time-varying patterns requiring resolution down to a thousandth of a second. That's in addition to the range of relevant spatial structures. So 3D, time-dependent models are mandatory. Recently, a group at Texas A&M University led by one of us (Kattawar) and an MIT group led by Richard Yue have independently developed 3D Monte Carlo simulation models for treating that daunting problem. Many of the RaDyO measurements include polarization data. So the models had to handle the vector RT equation; solving the scalar RT equations almost always gives incorrect results, with the magnitude of the error depending strongly on the degree of polarization of the light field.

The IOPs needed for performing the requisite RT calculations are the volume-scattering function (involving a matrix if polarization is taken into account), the single-scattering probability, and the total beam-extinction coefficient. The computational methods developed by the MIT and Texas A&M groups have yielded very good agreement with many of the RaDyO measurements.[13] Linear dimensions in RT calculations are usually given in terms of a dimensionless "optical depth,"—the actual length divided by the characteristic extinction length for light in a given environment.

Remote color sensing

Satellite-based remote observation of ocean color has made major contributions to oceanography. The variation of color with chlorophyll concentration provides remote-sensing techniques for estimating biomass. The first ocean color satellite instrument, the experimental Coastal Zone Color Scanner, was flown aboard a National Oceanic and Atmospheric Administration satellite in 1979. With pioneering data from the CZCS, algorithms were developed for turning measured radiance into the relevant biogeophysical quantities.[14] The CZCS experiment was remarkably successful, and the instrument continued to make measurements aboard the satellite for eight years. Its name notwithstanding, the CZCS was most useful in the open ocean, where color is determined by fewer factors than in coastal zones. In the open ocean, chlorophyll concentration is the primary determinant.

Coastal zones, complicated by sediment runoff, dissolved organic matter, and shallow-water effects, require more spectral information than could be provided by the four visible-light bands of the CZCS. Later generations of color sensors with advanced spectral capabilities, flown by US, European, Indian, and Japanese space agencies, have advanced the remote monitoring of the ocean. Applications range from local issues such as fisheries and harmful algal blooms in the coastal regions to climate issues and the cycling of carbon in the global ocean environment.[2]

Oceanographers have to measure many variables in a complex, inhomogeneous medium in an ever-changing environment. To that end they have to deploy their instruments aboard a dazzling variety of specialized platforms, ranging from orbiting satellites and airplanes to twin-hulled catamarans, undersea vehicles, and R/P (for research platform) *FLIP*, a very stable floating instrument platform that comes into temporary existence when the 108-meter-long vessel is flipped over so that its bow rises straight up, as shown in figure 5. A video by University of Rhode Island oceanographer Helen Czerski that illustrates several ocean optical measurements made from various platforms during the RaDyO program is available on YouTube.[15]

Visibility and imaging

The study of visibility in the ocean, and the associated problem of seeing underwater objects, was one of the earliest applications of ocean optics. Water is, of course, denser than air, and it generally harbors more particulates. In the ocean, maximum imaging distances are highly variable, ranging from centimeters in dirty water to more than 100 m in very clear water.

In the ocean, scattering by particulates and by the water itself affects image quality in many ways. A quantitative measure of the visibility of an object is the contrast, C, given by

$$C\,(r) \equiv \{L_o(r) - L_b(r)\}/L_b(r), \qquad (2)$$

where r is the distance of the object from the observer, and L_o and L_b are the radiances of the object and its background. With that definition, we have the "inherent contrast" at $r = 0$, the "apparent contrast" at r, and the "contrast transmittance," which propagates the inherent contrast to the apparent contrast.

Much of the theory and experimental work on image transmission in the ocean was developed by the Scripps Visibility Laboratory in La Jolla, California, starting in the 1940s.[16] In general, the contrast of a relatively large object is reduced by scattering of ambient light in the medium between the viewer and the object, causing what's known as veiling, or path-radiance. The ambient light increases equally the apparent radiance from the object and the background, thus effectively reducing the object's apparent contrast. For large objects, that's often the limiting factor for visibility.

For longer distances or smaller objects, small-angle forward scattering of light reflected from the object can cause images to blur, which reduces the contrast between light and dark portions of the object and, along its edges, between object and background. In water, small-angle scattering is a large portion of the total scattering of light by particles. The resultant blurring can be quantified by means of the point-spread function (PSF) often used to characterize the limits of imaging devices such as telescopes. In the early 1970s, Willard Wells at Tetra Tech Inc in Pasadena, California, pioneered the use of PSFs to enhance underwater imaging, and such work has continued to yield new techniques for better imaging. Related research has sought to understand the different methods by which aquatic animals camouflage themselves against predation (see figure 4).

Methods intended to improve imaging in the water work either to reduce the effects of the veiling backscattered light or to reduce the blurring effect of forward scattering. One can, for example, illuminate the underwater object with a polarized light source, cover the camera's lens with a polaroid filter, and then time-gate both source and camera so as to minimize the recording of light not directly reflected off the object.[17]

To compensate for the blurring effect of forward scattering, imagers have recently revisited time-varying intensity (TVI), an approach first used at the Scripps Visibility Lab. The technique, currently being investigated by groups at the Naval Air Systems Command and elsewhere, uses a laser line-scan illumination source close to the object. Rather than being a conventional multipixel imaging device, the TVI imager is a single-pixel detector synchronized to the scanning of the source. In that way, forward scattering between the object and the detector does not degrade the image. (The limiting factor is blurring between the illumination source and the object.) Recent work on TVI systems has demonstrated the possibility of underwater imaging at optical depths of 25—that is, 25 times the distance in which the medium attenuates the direct radiance by a factor of *e*.

With regard to the purposeful avoidance of imaging, groups at the Marine Biological Laboratory (Woods Hole, Massachusetts) and elsewhere are studying the ability of cephalopods and some fish to camouflage themselves. As shown in figure 4, such a creature can, in response to a changed background, very quickly change its skin's spectral reflectance, patterning, texture, and even the polarization of the light reflected from its skin. Current work strives to understand the structures in the skin that can do all that, and how the animal determines the best camouflage strategy.

Toward the future

With relatively modest spectral resolution, researchers have begun to quantify near-surface constituents in the ocean such as chlorophyll, dissolved organic and detrital materials, and even particle-size distributions. Data from instruments with significantly higher spectral resolution, deployed in situ or carried aboard space- and aircraft, are now yielding improved mapping of shallow ocean depths and the plants growing there and are even distinguishing between classes of phytoplankton. New multidirectional measurements of light on short time and space scales will allow oceanographers to better characterize the ambient light and its interactions in the ocean.

Fluorescence techniques are making it possible to extract detailed information about phytoplankton and oil spills. Active sensing with lasers has great potential for revealing information about the physiological states of phytoplankton. Pulsed narrowband lasers will let us exploit MB and Raman scattering to probe vast regions of the ocean for salinity, temperature, and sound speed as a function of depth. Femtosecond laser pulses with intensities high enough to affect material properties of the medium may someday be used for hyperspectral remote sensing. Adaptive optics, which astronomers use so effectively to combat atmospheric distortion, may well be applicable for reducing the effect of waves and turbulence on imaging in the ocean. Much new information can also be garnered by exploiting polarized light.

The next generation of optical oceanographers has much to accomplish. The potential number of ocean variables that could be measured optically is great. Multidisciplinary, multiplatform sampling of the ocean has already demonstrated its effectiveness. Still, no truly concurrent measurements have been accomplished over the space and time scales relevant to most problems. Future oceanographers will be able to capitalize on multiscale observing systems and on powerful computer systems that can handle integrative data-assimilation models. But they will need to be well versed in traditional subdisciplines, with ocean optics at the nexus, as were the first oceanographers aboard HMS *Challenger* a century and a half ago.

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