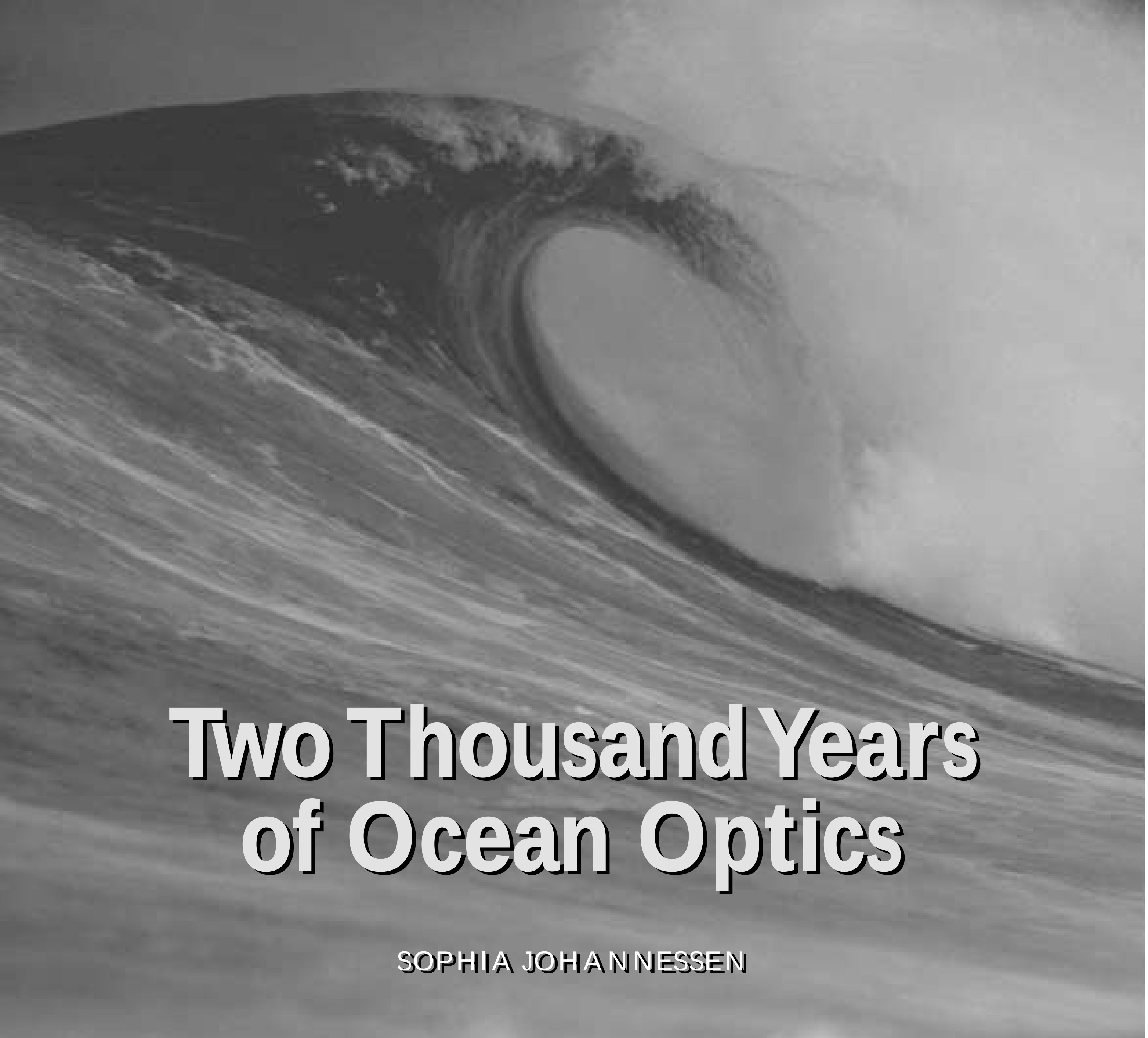

Two Thousand Years of Ocean Optics

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In the fourth century B.C., Aristotle noticed that seawater was blue and transparent, while river water was yellowish and murky. Scientists have spent the last 2,000 years trying to understand why. Although there was speculation for centuries, an empirical answer could not be derived until the penetration and color of light in the ocean could be measured. With the advent of useful instruments and techniques in the late 1800s and early 1900s, people began to make measurements that could explain Aristotle's observations. Throughout the twentieth century, improved methods have led to an increasingly detailed understanding of the physical, chemical, and biological processes controlling the distribution of light in the ocean. Our understanding of ocean color and transparency can be traced historically through the different approaches and motivations of some of the investigators.

The transparency of the ocean

Although Aristotle suggested in the fourth century B.C. that suspended particles might explain why river water was less clear than ocean water, his insights were not pursued for centuries. However, in the mid-1800s people began to measure ocean light penetration out of curiosity. A rough estimate of ocean transparency required only an object to submerge and a string to retrieve it.

In 1815, Captain Kotzebue made the first recorded ocean measurement. Kotzebue lowered a piece of red material into the ocean and measured the depth at which it disappeared. The first optical expedition was then mounted a few years later on board the *Coquille*, during which Captain Duperrée lowered a white plate into the water at a number of stations.

Michael Faraday used a similar technique in 1855 in the Thames River in England. He reported to the local newspaper that he had torn up pieces of white card and dropped them into the river in several locations. When the cards sank edge-first, he noted that the lower edge of the card disappeared before the upper edge was even below the surface of the water. He gave these findings as graphic evidence of the turbid pollution of the river.

Also in the mid-1800s, Father Angelo Secchi became interested in the physics of the Sun and sunlight's effect on Earth. Secchi, an Italian Jesuit priest, made major advances in stellar spectroscopy and geophysics under the patronage of Pope Pius IX. During this period, he published a combined total of 700 articles and books. In 1865, Secchi focused on sunlight penetration through seawater. He argued that none of the previously collected light penetration depth data was useful. Since earlier scientists had not reported the solar elevation or the degree of cloudiness, it was impossible to generalize from their observations.

That same year, Secchi made systematic measurements of light penetration on board the *Immacolata Concezione*. He used several different iron disks (the largest being 3.73 m in diameter) covered with white-varnished sail material. At each station, Secchi made replicate measurements of light penetration and simultaneously measured the solar zenith angle with a sextant. The measurements were then converted into equivalent depths for vertically incident sunlight.

Secchi noted that the depth measured using the disk method was not the depth of light extinction. On the contrary, light had to travel twice the depth of the submerged object to return to the observer's eye. In addition, since the disk disappeared when the only colors of light left to reflect off it were the same color as the surrounding ocean, he noted that light must travel even further into the ocean than twice the disk depth. Based on these conclusions, Secchi speculated that blue and purple light could penetrate to great depths. For his contributions, Secchi's name was eventually given to light penetration measurement disks used by generations of oceanographers.

In 1922, V. E. Shelford and F. W. Gail adapted a Kunz gas-filled photoelectric cell to measure light penetration off the west coast of the United States in Puget Sound. H. H. Poole and W. R. G. Atkins modified the Shelford and Gail design for use in the rougher waters of the English Channel near Plymouth. In 1925 and 1926, they carried out a number of experiments and introduced some innovations still used in optical measurements in the 1990s. These innovations included using an amplified telephone to detect unbalanced current, and attaching a diffuser over the photoelectric cell to simplify path-length calculations. In addition, Poole and Atkins corrected depth measurements for changes in surface light intensity by using a surface reference radiometer. With such techniques available, it became possible to quantify the effect of light on photosynthesis—a link that previously had been made only qualitatively.

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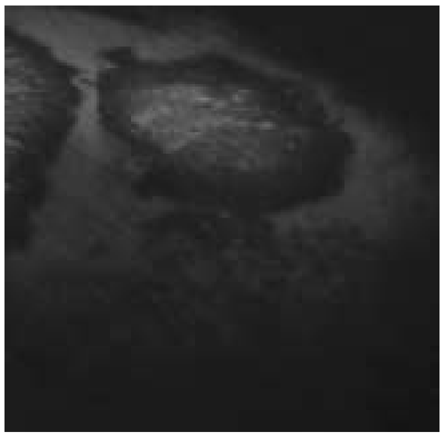

In 1933, Penelope Jenkin made measurements that linked photosynthesis with ocean light penetration for the first time. At the time, marine plant photosynthesis was of considerable interest to people who wanted to understand the productivity of the sea. The International Council for the Exploration of the Sea (ICES) was formed in 1902 to carry out research benefiting the fisheries of the member states. Britain had directed much of its share of the ICES money to the Plymouth Laboratory for studies of productivity in the English Channel and in the North Sea. In 1921, W. R. G. Atkins was appointed as a physiologist at the Plymouth Laboratory. It was Atkins who suggested that Jenkin undertake the simultaneous measurement of light and photosynthesis in the English Channel.

In 1933, Jenkin also began to measure light and photosynthesis together. Teamed with Atkins and Poole aboard the Marine Biological Association's steam trawler *Salpo*, Jenkin hoped to show that light controlled marine plant photosynthetic rates. While Jenkin performed photosynthesis experiments, Atkins and Poole measured light in the water using a photocell with colored filters. The team hoped that light measurements could be used as a proxy for the much more time-consuming measurements of photosynthesis.

During the cruise, Jenkin exposed diatoms to light at different depths in the water. She then measured the light and oxygen production at those depths. Jenkin used a monospecific culture of *Coscinodiscus excentricus*—a centric diatom that she had collected from the English Channel in the early spring. She placed six bottles containing the cultured diatom at each depth. Three clear glass bottles were open to light incident from all directions, two bottles were entirely blackened except on one side, and one bottle was totally dark. Jenkin placed the bottles into wire baskets attached to a fixed cable for a number of hours.

Light energy was measured as the sum of all illumination from 380 to 720 nm. The ultraviolet and infrared portions of the spectrum were excluded, as Jenkin felt that their influence would be minimal. The dark bottle at each depth was included as a correction for respiration, which was thought to be constant, regardless of the level of incident light. In order to obtain total production numbers, Jenkin added the oxygen loss in the dark bottle to the oxygen increase measured in the light bottles.

From these experiments, Jenkin concluded that photosynthesis depended strongly on available light. In addition, she noted that oxygen production increased with increasing incident daylight. Although it was already known that chlorophyll readily absorbed red light, Jenkin reported that red light could not limit photosynthesis. Her conclusion was based on the finding that red light was attenuated quickly with depth, while the rate of oxygen production decreased proportionately with total energy.

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Jenkin found that both total light energy and photosynthesis decreased exponentially with depth. Yet near the ocean's surface, photosynthesis did appear to be somewhat inhibited. Since the inhibition was less noticeable in the partially blackened bottle and more noticeable during the midday irradiation, Jenkin concluded that intense light must itself be the limiting factor. Due to the general increase in oxygen production with increasing incident light, the depth of maximum oxygen production was about 5 m below the water surface.

Jenkin also calculated a compensation depth at which photosynthesis exactly balanced respiration over 24 hours. Based on these findings, she produced a plot of "photosynthesis vs. irradiance"—a model so effective that it is still used commonly in the 1990s. In addition to being the first experiment to combine measurements of photosynthesis with simultaneous measurements of light, Jenkin's light and dark bottle procedure is still used to determine the rate of primary production.

In 1935, Hans Pettersson felt that the Poole and Atkins photoelectric method described earlier, though quantitative, was rather complicated and unwieldy because it required an external amplifier to make the tiny currents strong enough to measure. Recognizing that submarine daylight was essential to primary production in the ocean, Pettersson invented a more accurate measure of ocean penetration.

Pettersson placed a cuprous oxide cell in a submarine actinometer that he had constructed with colleagues. He used the actinometer to measure light from above and scattered light from below. Although the cuprous oxide cells he used had a number of problems (such as losing sensitivity after exposure to intense light), Pettersson obtained continuous records of submarine daylight at various depths for a year, including some measurements made beneath a 20 cm sheet of ice.

Since those early measurements of light penetration, there has been an explosion of work on the subject. Today, more precise silicon diodes have replaced photocells for light detection, and instruments are more streamlined and accurate than those of the 1930s. However, the same optical properties—irradiance, scattering, and absorption—are still measured. And the goal remains the same: to relate remotely sensed properties to the physical, chemical and biological states of the ocean.

In the late 1800s, J. Aitken went to the Mediterranean Sea to determine why the water was so blue and why the water color varied from one place to another.

Absorption studies in transparency

It is important to note that absorbance affects transparency: any light that is absorbed is unavailable to be scattered. In 1936, William Powell and George Clarke discovered that absorbance near the surface of the ocean was significant to transparency. They quantified light reflection off the surface of the ocean to determine the varying "surface loss" estimates by reflection. They found that reflection depended strongly on the angle of the Sun and the state of the sea. Furthermore, the proportion of light reflected back from the surface could vary from 3 to 9% while the Sun was more than 30 degrees above the horizon. They attributed the 60% "surface losses" reported by previous scientists to absorption by a particularly opaque layer of water just beneath the surface.

Using both a transparency meter and a Tyndall meter to measure scattering, the Danish researcher Nils Jerlov determined the relative influence of dissolved and particulate matter on transparency. In 1953, he related scattering to particulate absorbance. Jerlov then determined dissolved absorbance by difference: he subtracted absorbance by particles alone from absorbance by particles and dissolved matter combined.

The euphotic zone is the surface layer of the ocean, where there is enough light for phytoplankton to live. Phytoplankton are the microscopic (and sometimes large, but for optical purposes only the little ones are important)plants that live (and usually float) in the ocean. The euphotic zone is sometimes defined as the depth at which only 1% of the light incident at the surface remains. It traps light and heat, and much of the biological activity of the ocean is concentrated in that zone.

It is now relatively easy to measure irradiance throughout and below the euphotic zone, either in discrete bandwidths or over an integrated range of visible wavelengths. However, the topic still has some appeal. In 1986, Rudolf Preisendorfer published a review paper that described how to make quantitative measurements using a Secchi disk. In this paper, Preisendorfer coded the "ten laws of the Secchi disk" into mathematical form. Although he did not recommend using a Secchi disk where more precise, electronic measurements were appropriate, Preisendorfer noted that there was a long record of Secchi disk measurements available for comparison in long-term studies. In 1988, a team led by Marlon Lewis and Charles Yentsch used the Secchi depth measurement database to calculate mean transparency fields in the ocean. From variations in mean transparency, they were able to identify areas of major upwelling and show temporal variation in fronts of new production.

The color of the ocean

Certainly, people besides Aristotle must have noticed before the nineteenth century that the ocean was not the same color everywhere or all the time. By the early seventeenth century, people evidently recognized that the color of the ocean was affected by its components. Shakespeare's Macbeth lamented that if he tried to wash his bloodstained hands in the ocean they would "the multitudinous seas incarnadine."

But other than an occasional reference to the sea's turning to blood, references to the cause of ocean color are scarce before the work of J. Aitken in the late 1800s. Aitken went to the Mediterranean Sea to determine why the water was so blue and why the water color varied from one place to another. He wanted to know whether particles or impurities in the Mediterranean Sea determined its color, or whether the absorbance of red was responsible. Without any complicated equipment, he tested the absorbance hypothesis in several ways.

Aitken initially looked at submerged white objects through a glass-ended tube. He also submerged several colored objects, including oranges and lemons, and observed their underwater color. All the results, including the apparent unripening of the fruit, showed that the water preferentially transmitted blue and absorbed red. Aitken also determined that color brightness depended on the size and color of suspended particles.

To be sure that the red absorption was not due to any impurity, Aitken condensed water into several containers made of different materials. He wanted to be sure that

The Mediterranean Sea off the coast of Cyprus.

the resulting water always looked blue. It did, and Aitken was quite satisfied with the result. He commented: "The addition of impurities to water seems generally to change its color from blue to green or yellow… No attempt was made to find out what the discoloring substances in water are. The task would evidently be an endless one, and of little value." Other scientists disagreed with Aitken's assessment of the value of further inquiry into this matter. As a result, research into the cause of ocean color did not end in 1882 (as will be discussed in later sections of this article).

During the first decade of the 1900s, both Germany and Norway conducted experiments related to the spring diatom bloom. In 1904, this research led Franz Schütt, a botanist in Kiel, to comment that the color of the water was determined by its physical structure and the physiology of the organisms living in it. Schütt's colleague Victor Henson, along with other Kiel scientists, noticed that phytoplankton, in high concentrations, turned the water green (although a detailed absorbance spectrum had to wait until Yentsch's work in 1960).

In the 1920s and 1930s, the realization that phytoplankton did not absorb all colors equally drove efforts to determine the attenuation rates of different colors of light through seawater. Sir Isaac Newton published results in 1686 showing that white light was made up of all the colors of the rainbow, and that individual colors could be separated from the rest by refraction. This information, coupled with the work by James Clerk Maxwell and Heinrich Hertz on the wave theory of light in the late 1800s, allowed scientists to design experiments that used selective cutoff filters to measure penetration of light of different colors through the ocean.

The photocells used in the 1920s and 1930s to measure sunlight penetration of the ocean were also useful for measuring the penetration of different colors of light. In 1926, Victor Shelford and J. Kunz used photoelectric cells covered with plates of colored glass to measure the penetration of red, yellow, blue, and green light through the ocean. In order to collect light incident at a wider range of angles, they used a hemisphere-shaped filter to cover the top of the photocell. After the attenuation due to pure water had been subtracted, Shelford and Kunz discovered that something absorbed the short wavelengths of light, leaving green and yellow at depth.

C. Utterback and J. Boyle (1933) and R. Oster and George Clarke (1935) also made measurements of red, blue and green light penetration in situ with similar results. Their efforts were apparently the earliest recorded measurements of absorbance by colored dissolved organic matter in the ocean (CDOM). CDOM, called "yellow substance" by W.V. Burt in 1958 (see below), is one of the most biogeochemically significant constituents of seawater.

CDOM is now known to absorb most of the UV radiation that enters the ocean. It protects phytoplankton and other organisms from intense UV radiation, and reacts photochemically to form a variety of ecologically and chemically important products.

Narrow bandwidth filters that measured light in precisely defined wavebands eventually replaced the older, broadband filters used by researchers in the 1930s. However, J. Tyler pointed out a problem associated with these new filters in 1959. Seawater acts as a strong monochromator. Eventually seawater absorbs short and long wavelengths, leaving a narrow band of light centered on 510 nm. Tyler believed that many of the narrow band filters let in too much stray light from other wavelengths. As a result, once the water had filtered out all the light at the wavelength to be measured, the detector would still measure a significant amount of 510-nm light. The leakage might only be a small percentage of the total measured light at the surface, but it could be 100% of the signal at depth. Such waveband leakage is still a problem for ocean optical measurements. The narrow band filters, which have proved too valuable to discard, are still in use today.

In 1958, W. V. Burt measured light penetration through seawater in 13 wavebands over a range of 400-800 nm and at depths of 1170 m. Although he did not specify the depth used to measure any of the wavelengths, he noted that transmission increased with increasing wavelength. He attributed the rapid attenuation of short wavelengths to a high concentration of "yellow substance," which presumably absorbed the blue and violet light. This finding was another example of the early measurement of the biogeochemically important colored dissolved organic matter in seawater.

Absorption studies in color

Laboratory studies of absorption complemented the field measurements of Shelford, Kunz, and Burt. In 1926, E. O. Hurlburt measured visible radiation absorption with three open ocean water samples using a monochromator in the laboratory. Although the spectral resolution of Hurlburt's measurement is unclear in his report, he is credited with making the first direct measurements of light absorption by seawater.

Hurlburt observed that if sunlight passed through an atmosphere that contained the equivalent of 40 meters of water (salt or fresh), the resulting, selectively attenuated light spectrum coincided exactly with the sensitivity curve of the human eye. From this observation, Hurlburt speculated that our eyes developed their sensitivity at a time when the atmosphere contained much more water vapor than it does today.

In 1927, Hurlburt went on to determine absorption coefficients for UV radiation in seawater. He reported that UV was attenuated more quickly than visible radiation through both seawater and fresh water. Magnesium chloride and calcium sulphate contributed significantly to the absorption of UV, while the other salts absorbed little. Speculating further about the ancient Earth, Hurlburt commented that it seemed unlikely that the atmosphere and ocean would be transparent to the most intense parts of the solar spectrum (the visible portion) by coincidence. He suggested that visible radiation might have effectively burned its way through whatever chromophores had originally absorbed it. Although Hurlburt's ideas about ancient Earth have never been verified, they remain interesting speculations.

By the late 1950s, it was widely accepted that the blue color of the open ocean was due to the scattering of the shortest light wavelengths and the absorption of the longest light wavelengths.

Following Hurlburt, George Clarke and Henry James at the Plymouth Laboratory made light absorption measurements in seawater in 1938. The two hoped to discover the percentage of light attenuation in seawater attributed to suspended particles and dissolved components, termed "color." Using a monochromator with a one-meter sample path length, Clarke and James measured the absorption of different seawater components from a number of locations over a range of 365 to 800 nm. They filtered their water through both coarse and fine filters and compared the colors of the filtrates. Since the filtered seawater samples had almost the same absorption as distilled water in that region of the spectrum, they determined that particles were responsible for almost all of the absorption at longer wavelengths (473 to 800 nm). In contrast, they found that blue and ultraviolet radiation was absorbed strongly by something in solution.

Clarke and James speculated that this unknown, UV-absorbing material might have come from the disintegration of phytoplankton. In order to compare the transparency of seawater in situ to that measured in the laboratory, they deployed a submarine photometer while collecting their samples. Clarke and James hoped to find that laboratory absorbance measurements would provide a convenient proxy for in situ light attenuation. Unfortunately, their preservation method changed the sample color too much for such comparisons to be practical.

By the late 1950s, it was widely accepted that the blue color of the open ocean was due to the scattering of the shortest light wavelengths and the absorption of the longest light wavelengths. It was also accepted that inshore waters turned green due to the influence of dissolved organic matter. However, although it was known that phytoplankton were affected by the color of incident light, the effect of phytoplankton on ocean color was not clear.

In 1960, for the first time, it became possible to quantify precisely the contribution of phytoplankton to spectral attenuation. Charles Yentsch published a spectrum of particulate phytoplankton absorbance. He determined that phytoplankton absorbance shifted the reflectance of water from blue to green because of its strong absorption at 443 nm. Yentsch also noted that most of the colored material seemed to be contained in cells that did not pass through a 5-mm filter. This filter size was much larger than pore sizes generally used today, but it helped to standardize the measurement of phytoplankton absorbance.

In 1981, Annick Bricaud and colleagues at the Université Pierre et Marie Curie (France) reported that dissolved organic matter might affect ocean color in much the same way as phytoplankton did in a different spectrum region. Bricaud's team presented absorbance spectra that showed that dissolved organic matter absorbed UV strongly, and visible radiation less so. This demonstration marked the first time absorbance spectrum was described as an exponential decay with wavelength—an insight that has proved useful to subsequent optical and chemical oceanographers.

Bricaud's team found that the log-linearized spectral slope did not vary greatly. Therefore, if one knew the absorbance at one wavelength, one could apply an average slope to calculate the absorbance of all the other wavelengths over the UV and visible spectrum.

Since that time, however, a number of scientists have disputed the claim that the slope of the log-linearized absorbance spectrum of colored dissolved organic matter is constant. There have subsequently been many attempts to characterize the changes in the slope with respect to location, season, and salinity. So far, there has been no consensus. Often researchers still use the single slope calculated by Bricaud in models.

An Illustration of the SeaStar spacecraft, which carries the SeaWiFS sensor (left). A SeaWiFS image of the Caribbean Sea (above).

Interpretation of remotely sensed data

Since the mid-1900s, scientists have interpreted optical variations as indications of physical, chemical, and biological processes in the ocean. Based on these interpretations, scientists began applying that knowledge to remotely sensed data. The earliest remote sensing data was collected by airplane. In 1954, C. Cox and Walter Munk took aerial photographs of the sea's surface while a ship below them measured wind speed. They calculated statistics of the surface glitter using the photographs, and compared them to the actual state of the sea at the time they were taken. From this relationship, Cox and Munk found that glitter could be used as a proxy for sea surface slope and wind speed.

Ocean color remote sensing on a global scale became possible with the advent of artificial satellites that carried light reflectance sensors. With the beginning of the American National Aeronautics and Space Administration (NASA) program in 1958, people were able to see photographs of the entire Earth for the first time. Patterns were visible in the clouds, and in 1964 NASA launched Nimbus 1—the first weather satellite to take cloud cover photographs relating to local weather. A succession of weather satellites followed, each with more advanced sensors.

In 1978, NASA launched Nimbus 7, a weather satellite that carried the Coastal Zone Color Scanner (CZCS). CZCS measured the reflectance of different light wavelengths from the ocean's surface, making remote sensing of ocean color possible. Now that weather prediction is possible on a local scale, NASA wants to predict long-term trends in climate change and to find patterns that will help to predict sudden changes in weather. Ocean color, as earlier research has shown, reflects the physical, chemical, and biological conditions of the ocean. As a result, it is a natural parameter to study in relation to climate change.

In 1981, R. Austin and T. Petzold at Scripps Institute of Oceanography (California) published empirical relationships that related the reflectance ratio at two visible wavelengths measured by CZCS to the in situ light attenuation at an intermediate wavelength. At the same time, Howard Gordon, an influential optical oceanographer based at the University of Miami, published atmospheric correction algorithms. These algorithms, when used with Austin and Petzold's empirical relationships, allowed the calculation of chlorophyll concentration in surface waters. Gordon also tested a chlorophyll retrieval algorithm that did not use the reflectance ratio method. This algorithm predicted chlorophyll concentrations to within 30% of the in situ value.

In 1988, Trevor Platt and Shubha Sathyendranath at the Bedford Institute of Oceanography (Nova Scotia) created another algorithm for global scale estimation of chlorophyll concentration. Making this link between ocean color and remote sensing was essential for global calculations of primary production by phytoplankton. Although the CZCS satellite was no longer operational at this time, the model was intended for use with a satellite to be launched later. Platt and Sathyendranath also proposed that there should be large-scale field studies to ground-truth the algorithm.

By the late 1980s, it had become apparent that the errors in the chlorophyll estimates were not improving. Something was interfering with the estimates made from reflectance data. In 1989, Ken Carder at the University of South Florida showed that the CZCS algorithms often made chlorophyll concentrations too high in areas where there was a large concentration of colored dissolved organic matter. Carder's team pointed out that earlier assumptions (such as the premise that dissolved organic matter absorption at 443 nm was low and that it co-varied with chlorophyll) were incorrect in many places. They suggested that these errors could account for the incorrect chlorophyll estimates.

In 1995, Dave Siegal and Anthony Michaels at the Bermuda Biological Station agreed. They calculated that in some areas colored dissolved organic matter could account for up to 60% of the observed absorption. Algorithms for quantifying dissolved organic matter absorption from remote reflectance measurements are still being developed. The Sea-viewing, Wide-Field-of-View Sensor (SeaWiFS) sensor on the SeaStar satellite, launched in August 1997, will provide more data for testing and improving calculated relationships.

Conclusion

Since the mid-1800s, the study of light in the ocean has been driven largely by interest in the controls on primary production. More recently, the focus has shifted to the prediction of local weather and global climate change. Today, we seem to have convincing explanations for most of the variations in the color and transparency of the ocean. As Aitken concluded in 1882, color is determined by absorption, and the intensity of color by scattering. Both scattering and absorption affect transparency. Phytoplankton, dissolved organic matter, detritus, and water itself all contribute to the color of seawater. We can even plot the spectral effect of each component on ocean color. The discovery of the causes of ocean color and transparency required the development of a number of instruments and the curiosity and techniques to use them. Remote sensing now allows us to apply the ocean process knowledge we have gained on a global scale, and to approach answers to Aristotle's two thousand-year-old questions.

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