Reports

Spectra of Backscattered Light from the Sea Obtained from Aircraft as a Measure of Chlorophyll Concentration

Abstract. Spectra of sun and skylight backscattered from the sea were obtained from a low-flying aircraft and were compared with measurements of chlorophyll concentration made from shipboard at the same localities and at nearly the same times. Increasing amounts of chlorophyll were found to be associated with a relative decrease in the blue portion of the spectra and an increase in the green. Anomalies in the spectra show that factors other than chlorophyll also affect the water color in some instances; these factors include other biochromes, suspended sediment, surface reflection, polarization, and air light.

The penetration of daylight into the sea is of fundamental significance in the oceanic ecosystem because it controls the growth of the primary plant producers and the behavior patterns of many marine animals. Previous investigations have revealed great variation in the rates of light penetration due to differences in amounts and kinds of materials in the water. In addition, the spectral composition of the light beneath the surface is altered by differential absorption and scattering due to the water itself, and also to whatever dissolved and particulate matter (both living and nonliving) may be present (1). Because chlorophyll affects the spectrum in a characteristic way and because it is associated with living plants, spectral measurements of chlorophyll concentration may be used as an index of the amount of phytoplankton present. Regions with high phytoplankton abundance can support large populations of herbivores and of successive links in the animal food chain, many of which are of economic importance to man. Thus, abundant chlorophyll indicates the presence of a potentially productive area (2).

The spectral changes imposed on the downwelling daylight by natural waters and by the materials in them have been measured by lowering an upwarddirected spectrometer in a watertight case to various depths (3). The upwelling, or backscattered, light that can be measured by employing the spectrometer in the inverted position is found to have its spectrum similarly modified by its passage through the water. A portion of the backscattered light escapes upward through the surface, where it has been recorded by an inverted spectrometer suspended above the water from a ship and from aircraft (4). Allowance must be made for light reflected from the ocean surface



Fig. 1. Upwelling light as received at the indicated altitudes at Station S (Fig. 2) east of Cape Cod, 26 August 1968 between 1345 and 1512 hours, E.D.T.

itself or scattered by the stratum of air above the water.

The possibility thus exists that spectral measurements of backscattered light can be used to delineate water masses, to trace currents, and to determine the abundance of chlorophyll, pollutants, or other significant materials in the water. Because measurements from aircraft or spacecraft can be made over extensive areas much more rapidly than from ships, they are especially suited to the study of smallscale, rapidly varying distributions of oceanic properties (5). Tests of some of these possibilities are reported here for water masses of widely different known chlorophyll concentrations off the New England coast.

During the summers of 1967 and 1968, records of the spectrum of backscattered light from the ocean have been made from our research vessel *Crawford* and our C-54-Q research aircraft. The spectrometer used was designed by Peter White of TRW Systems, Inc., and described by L. A. Gore (6). R. C. Ramsey of TRW operated the instrument and took part in the reduction of the data and in the interpretation of the results.

The TRW spectrometer is an electrooptical sensor of the off-plane Ebert type with an RCA 7265 (S-20 response) photomultiplier. The spectral range is 400 to 700 nm with a spectral resolution of 5 to 7.5 nm, a scan time of 1.2 seconds, and a field of view of 3° by 0.5°. A continuous curve of the spectrum is provided by a Sanborn recorder for each scan. The spectrum of the incident light from the sun and sky was determined before and after each series of measurements by recording the light reflected from a horizontally placed Eastman Kodak "gray card" with a nonselective reflectivity of 18 percent. A series of tests was made to detect changes in the spectral distribution of incident light during the 3 hours before and after noon due to changes in the sun's altitude and to changes in sky conditions from clear to light cloudiness. Changes found were not great enough to affect significantly our investigation of the differences in backscattered light from the ocean. By taking advantage of the fact that light reflected from a plane surface at Brewster's angle (approximately 53° from vertical incidence for normal sea water) is plane polarized with its vibration plane perpendicular to the plane of incidence, we could reduce the light

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received as reflection from the water surface. We placed a polarizing filter, oriented at right angles to the major axis of polarization, over the receiving aperture of the spectrometer and tilted the instrument at Brewster's angle (directed away from the sun).

When we operated the spectrometer from our C-54-Q research aircraft, the signal that we wished to measure, namely, the spectrum of the light backscattered from beneath the sea surface, was sometimes difficult to detect because of interference from "noise" caused not only by surface reflection but also by "air light." Air light is light that has been scattered to the instrument by the air and by material in the air between the sea surface and the aircraft. As the altitude of observation increases, the area of the sea from which light can enter the instrument enlarges, reaching the dimensions of about 52 by 9 feet (16 by 3 m) at 1000 feet (305 m). Smaller irregularities in surface reflection or in the nature of the seawater will be averaged out. At the same time interference from air light will increase with altitude because of the greater path length through the atmosphere. The curves shown in Fig.

1 were taken at altitudes ranging from 600 to 10,000 feet (183 to 3048 m) over an area east of Cape Cod (Station S, Fig. 2), where the water was 200 m deep and the estimated chlorophyll content, although not measured at the time, was probably about 0.6 mg/m³. As altitude increased, the values for upwelling light received increased markedly and regularly in all parts of the spectrum. The remainder of the measurements reported here were made at an altitude of 1000 feet (305 m).

Representative spectral measurements obtained over water with high chlorophyll content (about 4 mg/m³, Buzzards Bay), with low chlorophyll content (about 0.3 mg/m³, north of the Gulf Stream), and with very low chlorophyll content (less than 0.1 mg/ m³, Sargasso Sea) are presented in Fig. 3. The values for the backscattered light from these areas have been calculated as percentages of the incident light. The curves display characteristic differences in shape. For the water with high chlorophyll content the backscattered light rose from values mostly about 2.2 percent of the incident light in the blue region of the spectrum to about 2.5 percent in the



Fig. 2. The flight of the aircraft after leaving Nantucket on 27 August 1968 and the location of Stations A to E. Station S was occupied on 26 August. Representative temperatures measured from the aircraft flying at 305 m are shown to the left or below the flight path; representative chlorophyll concentrations in milligrams per cubic meter measured from the surface ship are shown to the right or above the flight path.

green, and then dropped to about 0.3 percent in the red. For water with low chlorophyll content the values were higher in the blue, dropped rapidly to much lower values in the green, and continued to drop in the red. Where chlorophyll content was very low, the backscattering was higher at all wavelengths shorter than 500 nm and reached a maximum of 7 percent at 400 nm.

On 27 August 1968 a more extensive survey of the changes in backscattered light from contrasting bodies of water was conducted during a flight from Buzzards Bay and Nantucket Sound to a point in the Sargasso Sea south of the Gulf Stream, then north on a 556-km transect that crossed successively the Gulf Stream, the slope water, a transition zone, Georges Bank, Georges Shoals, and the southern part of the Gulf of Maine, and returned via Cape Cod Bay (Fig. 2). Records of the spectrum were taken at frequent intervals with the TRW spectrometer, and a continuous trace of surface temperature was obtained by P. M. Saunders by means of a Barnes infrared radiometer. A continuous record of the temperature and the chlorophyll concentration of the surface water was obtained from the R.V. Crawford by means of a thermistor and a continuous-flow Turner fluorometer (7). Water for this purpose was drawn from an intake valve through the hull of the vessel 2 m below the surface. Analysis of these data shows that the surface temperature and the surface chlorophyll of the slope water, the Bank water, and the Gulf of Maine are statistically differentiated to a highly significant degree. We also have evidence from a previous study (8) that surface chlorophyll values may be useful as an index of biological productivity. During four cruises in the Atlantic and Pacific, one of us (C.J.L.) collected 91 samples, which covered a range of surface chlorophyll concentrations from 0.04 to 28.3 mg/m³. Analysis showed highly significant correlations with measurements of the total chlorophyll in the euphotic zone and with the primary productivity of the phytoplankton in the waters studied. Temperature values obtained from the aircraft agreed closely with values obtained from the ship (see Fig. 2). Owing to the relative sterility of warm Gulf Stream water, the lower chlorophyll measurements tend to be associated with higher sea temperatures.

A comparison of the spectra of the backscattered light as a percentage of



Fig. 3. Data from the high and low chlorophyll curves plotted as percentage of the incident light and compared with data taken on the same day from an area with very low chlorophyll concentration south of the Gulf Stream.



Fig. 4. Spectra of backscattered light measured from the aircraft at 305 m on 27 August 1968 at the following stations (Fig. 2) and times (all E.D.T.): Station A, 1238 hours; Station B, 1421 hours; Station C, 1428.5 hours; Station D, 1445 hours; Station E, 1315 hours. The spectrometer with polarizing filter was mounted at 53° tilt and directed away from the sun. Concentrations of chlorophyll a were measured from shipboard as follows: on 27 August, Station A, 1238 hours; on 28 August, Station B, 0600 hours; Station C, 0730 hours: Station D, 1230 hours.

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the incident light at five localities along the flight path of 27 August is presented in Fig. 4. Simultaneous measurements from the aircraft and the ship were made in the slope water at Station B. The ship's observations at Stations C, D, and E were not made until the following day, but the range of chlorophyll values was so great that the differences among the stations can be relied upon for the present comparison. Time did not permit the ship to reach the locality of the aircraft's observation at Station A in the Sargasso Sea south of the Gulf Stream, but the chlorophyll content of the water there was almost certainly lower than in the slope water north of the Stream. Along the entire transect the shape of the spectral curves changed progressively as chlorophyll values increased from south to north. The percentage of backscattered light diminished markedly in the blue region and increased relatively in the green region, with an indication of an inflection point at about 515 nm and with little change in the red region. This result agrees satisfactorily with the calculated values for the effect of increasing amounts of chlorophyll on ocean color presented by Ramsey (9). The change in shape with increasing chlorophyll is reflected in decreased mean slope of the spectra. Anomalies in the shape and amplitude of these spectra. and of some taken on other occasions, make it evident that other factors play a role that merits further investigation.

Our investigation shows that large differences occur in the spectra of the light backscattered from the ocean and that they can be recorded from aircraft. In the present instance, the slopes of the spectra correlate quite closely with differences in chlorophyll concentration. The discrepancies are believed to be due to difference in time within paired observations, to differences in surface reflection, to scattered air light, and to the presence in the water of material other than chlorophyll that affected the light selectively. If such interference can be eliminated, or identified and allowed for, spectrometric procedures from aircraft (and perhaps from satellites) will be of great value in the rapid investigation of oceanic conditions, including conditions important for biological productivity.

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Acidic Mine Drainage:

The Rate-Determining Step

Abstract. The rate-determining step in the oxidation of iron pyrite and the formation of acidity in streams associated with coal and copper mines is the oxidation of ferrous iron. Effective pollution abatement necessitates controlling this reaction.

The oxidation of iron pyrite (FeS_2) and the release of acidity into waters draining through coal mines (1) can be represented by the following reaction sequence (2).

Initiator reaction:

$$\operatorname{FeS}_{2}(s) \xrightarrow{(+ O_{2})} F^{2+} + S$$
-compound (1)

Propagation cycle:

 $(1 \ 0)$

$$Fe^{3+} + FeS_2(s) \longrightarrow Fe^{3+} + SO_4^{-2} \quad (3)$$

Fe²⁺ is released in the initiator reaction either by simple dissociation of the iron pyrite or by oxidation of the