Articles

Oceanic Primary Production: Estimation by Remote Sensing at Local and Regional Scales

Trevor Platt and Shubha Sathyendranath

Satellites provide the only avenue by which marine primary production can be studied at ocean-basin scales. With maps of chlorophyll distribution derived from remotely sensed data on ocean color as input, deduction of a suitable algorithm for primary production is a problem in applied plant physiology. An algorithm is proposed that combines a spectral and angular model of submarine light with a model of the spectral response of algal photosynthesis. To apply the algorithm at large horizontal scale, a dynamic biogeography is needed for the physiological rate parameters and the biological structure of the water column. Fieldwork to obtain this type of data should be undertaken so that the use of satellite data in modern biological oceanography may be optimized.

NE OF THE GOALS OF OCEANOGRAPHIC SCIENCE IS TO determine and understand on a global scale the processes controlling the time-varying fluxes of carbon and associated biogenic elements in the ocean (1). The major carbon flux in the ocean is that due to photosynthesis by phytoplankton. It has been estimated at about 5×10^{16} g of carbon per annum (2). Determination of carbon flux distribution on a global scale with conventional means is frustrated by the low cruising speed of research ships: the problem is one of extreme undersampling and inadequate spatial resolution. The only possible avenue to synoptic biological oceanography at this scale is to measure by satellite; such measurements can achieve the necessary coverage with acceptable spatial resolution on the surface (3). To characterize the ocean water column using satellite-based observations of its surface layer is certainly not ideal. But it is the only option available at these scales, now and into the foreseeable future. In this article we discuss a method for deriving an estimate of primary production from remotely sensed data on ocean color. We attempt to recover the primary production per unit area of sea surface, the quantity of greatest ecological interest.

The Surface Biomass Field

Phytoplankton biomass has been assessed by the Coastal Zone Color Scanner (CZCS), which operated between 1978 and 1986 (4). It provided enormous quantities of relevant data that are still being analyzed (4, 5). Sunlight incident on the ocean is modified in intensity and color according to the concentration of photosynthetic

T. Platt is a researcher in the Biological Oceanography Division, Bedford Institute of Oceanography, Box 1006, Dartmouth, Nova Scotia, Canada B2Y 4A2. S. Sathyendranath is a researcher at the National Institute of Oceanography, Dona Paula, 403 004 Goa, India, and a visiting professor in the Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J1.

pigments in the water (6). The optical signal reaching the CZCS contains information not just about the surface layer; it also contains contributions from layers deeper in the water column, albeit strongly damped by the attenuation between them and the surface. The damping is strong enough that contributions to the signal from deeper than one attenuation length are negligible. Algorithms are available (7) that convert the optical signal to give a chlorophyll concentration that is representative of the upper attenuation length (8). With these algorithms, maps can be produced that show the field of satellite-weighted chlorophyll concentration at ocean basin or even global scales. Such maps have already given useful insights into the ecological dynamics of the pelagic zone (9). In this article, we discuss how the maps of biomass can be converted into maps of water column production; we do not discuss details concerning the extraction of information on the biomass itself [but see references in (6, 7)].

The Local Algorithm for Primary Production

The determination of ocean primary production at regional or basin scales is a task that falls naturally into two parts: first, development of an algorithm for estimation of local water column production; and second, extrapolation of the local results to larger horizontal scales. We treat the construction of the local algorithm as a problem in basic physiology. The first-order factors controlling the rate of photosynthesis by phytoplankton are the flux of photons and the concentration of photosynthetic pigments available to absorb them. In the sea, available light is a strongly decreasing function of depth. We calculate the rate of photosynthesis at an arbitrary depth z and then integrate over depth to get the primary production of the water column. The dependence of photosynthetic rate on available light I is commonly written in the form

$$P^B = p(I; \alpha^B, P^B_{\rm m}) \tag{1}$$

where the superscript indicates normalization to the biomass, *B*, of photosynthetically competent pigments and α^B , P_m^B are parameters (10). At low light levels, the function *p* is a straight line of slope α^B . With increasing light, *p* begins to saturate and tends to an asymptotic value P_m^B (11). Given normalization to biomass, both of the first-order controls on primary production are combined in a single equation. A complication is that the photosynthetic pigments influence the intensity and quality of the submarine light field (12). We now examine the implementation of Eq. 1, using data from remote sensing.

ŀ

The irradiance field. Conventional satellite measurements of surface irradiance are not resolved with respect to either wavelength or angular distribution (13). Both the penetration of light underwater and its absorption by phytoplankton are sensitive to the angular and spectral composition of the irradiance field. Furthermore, the

photosynthetic response of phytoplankton is a function of wavelength. Ignoring wavelength and angular effects can lead to significant errors in the estimation of primary production (14). In developing the local algorithm, therefore, we obtain the light available at the sea surface (downwelling irradiance) by calculation (15).

At any depth z, irradiance, $I(z, \lambda, \theta)$, is partitioned into two components

$$I(z, \lambda, \theta) = I_{d}(z, \lambda, \theta_{d}) + I_{s}(z, \lambda, \theta_{s})$$
(2)

where λ is the wavelength, θ is the sun's zenith angle in water, subscript "s" refers to the diffuse (sky) component of sunlight, and subscript "d" refers to the direct component. With $I(0, \lambda, \theta)$ given, we need only the vertical attenuation coefficients to compute the irradiance at available at any depth. These are (16)

$$K_{\rm d}(z,\lambda) = [a(z,\lambda) + b_{\rm b}(z,\lambda)](\cos\theta_{\rm d})^{-1}$$
(3)

and

$$K_{\rm s}(z,\,\lambda) = [a(z,\,\lambda) + b_{\rm b}(z,\,\lambda)] \langle \cos\theta_{\rm s} \rangle^{-1} \tag{4}$$

where $a(z, \lambda)$ is the volume absorption coefficient and $b_b(z, \lambda)$ is the corresponding backscattering coefficient. The quantity $\langle \cos\theta_s \rangle$ is the mean value of $\cos\theta_s$ for the angular distribution of the diffuse light after refraction at the sea surface (17). The coefficient $a(z, \lambda)$ depends strongly on the concentration of phytoplankton pigments. Their (linear) contribution to $a(z, \lambda)$ is written as (18)

$$a_{c}(z, \lambda) = a_{c}^{*}(\lambda)C(z)$$
(5)

where $a_c^*(\lambda)$ is the specific absorption coefficient for the pigments and C(z) is the local concentration of pigments including their degradation products.

The model described above is a clear sky model that does not include the effect of clouds (15). To correct for clouds we use a simple model for total shortwave radiation that incorporates data on total cloud cover (19). In the absence of information on cloud types, a mean albedo of 0.5 is assigned to the clouds (20). The simple model accounts for the reduction in total intensity and the possible increase in the diffuse component because of cloud albedo, but it does not account for spectral changes.

The primary production model. With the irradiance model described above, the rate of photosynthesis at any depth z is given by an equation of the form (17)

$$P(z) = \Pi(z) \{1 + [\Pi(z)/P_{\rm m}(z)]^2\}^{1/2}$$
(6)

where

$$\Pi(z) = B(z) \left[\sec \theta_{d} \int \alpha^{B}(z, \lambda) \ I_{d}(z, \lambda, \theta_{d}) \ d\lambda + \langle \cos \theta \rangle^{-1} \int \alpha^{B}(z, \lambda) \ I_{s}(z, \lambda) \ d\lambda \right]$$
(7)

and

$$I(z, \lambda, \theta) = I_{d}(z - \Delta z, \lambda, \theta_{d})e^{-K_{d}(z,\lambda)\Delta z} + I_{s}(z - \Delta z, \lambda, \theta_{s})e^{-K_{s}(z,\lambda)\Delta z}$$
(8)

If we assume that $I_s(z, \lambda)$ is independent of θ within the cone of refraction at a flat sea surface (21), we can simplify Eq. 7 to

$$\Pi(z) = \int \alpha(z, \lambda) \{ I_d(z, \lambda, \theta_d) \sec \theta_d + 1.20 I_s(z, \lambda) \} d\lambda$$
 (9)

The integrals are taken over the entire photosynthetically active range (PAR, 400 to 700 nm). The function $\alpha(\lambda)$, which appears under the integral over λ weighted by the wavelength distribution of the available light, is the photosynthetic action spectrum (22). It is now accessible to routine measurement at sea (23). For the data available, $\alpha(\lambda)$ appears to have a common shape in a variety of oceanographic regimes (24). The amplitude, however, is variable.

With this formalism, the water column production can be com-

puted if the necessary variables and parameters are known. At particular oceanographic stations, these quantities are all accessible to routine measurement (17), such that the formalism can be tested. We obtained a nearly one-to-one correspondence between observed and computed water column production for data from a diversity of oceanographic regions (Fig. 1).

The biomass profile. One of the fundamental limitations of remotely sensed data on ocean color is that information on the vertical structure of the pigment field, B(z), is lacking. It would not matter if B(z) were nearly uniform, but in many instances this is not the case. The existence of a peak in the pigment profile, the "deep chlorophyll maximum" (DCM), is widespread over much of the ocean (25). The DCM is typically located within the photic zone but deeper than one attenuation length, and is therefore invisible to the sensor on the satellite. Thus a significant proportion of the biomass is out of range of the detector. However, the exponential decay of light with depth limits the photosynthesis of this undetectable biomass. Because the depth of the DCM changes seasonally as the water stratifies, the interpretation of the remotely sensed signal might have to be changed on the same time scale. Does the presence of a DCM invalidate the estimation of water column primary production by remote sensing?

To study this question, we have used a generalized biomass profile (26) that represents well a wide variety of stereotypic cases:

$$B(z) = B_0 + \frac{h}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{(z-z_m)^2}{2\sigma^2}\right]$$
(10)

Here, B_0 is the background or baseline pigment concentration, z_m is the depth of the chlorophyll maximum, σ defines the breadth of the peak, and *h* determines the total biomass above the background (27).



Fig. 1. Goodness of fit (17) of local algorithm for water column primary production compared against measured water column production. Note that the fit is not a descriptive hindcast: the axes show quite independent measures. The abscissa refers to in situ measurements. The ordinate depends on photosynthesis parameters measured by the incubator method on the same stations. Input to local algorithm is a chlorophyll profile constructed from measurements made on acetone-extracted samples. Linear fit has slope not significantly different from unity and intercept not significantly different from unity and intercept not significantly different sequere meter per day. Data from cruises of CSS *Hudson* by the Biological Oceanography Division of the Bedford Institute of Oceanography.

SCIENCE, VOL. 241

The height of the peak above the baseline is given by $h/[\sigma(2\pi)^{1/2}]$. Using this profile in Eq. 10, we have explored the consequences of variations in the depth, amplitude, and thickness of the DCM for the estimation of primary production (14, 26). Results (Fig. 2) indicate that, whereas the error in the estimate of production is modest when the DCM lies near the base of the photic zone, the error can be considerable when the maximum lies near the surface. The error can be computed and corrected if the shape parameters for the biomass profile are known.

Extension of the Local Production to Large Horizontal Scale

We must specify two parameters for the photosynthesis light curve and four parameters for the biomass profile to compute water column production using the local algorithm (28). However, given also the satellite-weighted chlorophyll, the biomass profile is overspecified. This redundancy can be turned to advantage as follows. We have characterized the biomass profile by the depth of the DCM, z_m , its thickness σ , and the dimensionless factor, ρ , equal to the ratio of the peak height of the DCM to the background biomass

$$\rho = h/[(2\pi)^{1/2}\sigma B_0]$$

Using a model of spectral reflectance for nonuniform biomass distribution (29), we next establish a relation between the blue to green reflectance ratio (7) and the sum of peak height and back-ground. We can then easily solve for the parameters h and B_0 (30). Thus, given an estimate of satellite-weighted chlorophyll or the blue to green ratio, we can modify the local algorithm such that only three properties of the biomass profile in addition to the two photosynthesis parameters need to be specified.

We suggest that, for a given region of the ocean, in a given season,



Fig. 2. Relative error in estimation of primary production when satelliteweighted chlorophyll concentration is assumed to extend throughout photic zone. The results are of a sensitivity analysis carried out around a typical profile with the following parameters (see Eq. 10): h = 18.8 mg m⁻²; $z_m = 0$ m; $B_0 = 0.1$ mg m⁻³; and $\sigma = 5$ m. (A) Effect of variations in h; (B) effect of variations in σ ; (C) effect of variations in z_m ; and (D) effect of variations in B_0 . The errors, rather than being most acute in the presence of a DCM, are highest when the chlorophyll maximum occurs at the surface.

Table 1. The mean daily production rate and standard error (in brackets) for different regions in milligrams of carbon per square meter per day. The percent value below each entry is the relative contribution of that region to the total daily production in its latitudinal zone.

Region	Mean daily production rate		
	Shelf	Slope	Oceanic
Subtropical	1630 (172)	302 (18)	236 (4)
	19%	12%	69%
Equatorial	16600 (1770)*	821 (40)	528 (5)
	18%	10%	72%
Transitional	1220 (52)	440 (10)	325 (3)
	35%	14%	51%

*Equatorial shelf estimates probably are unreliable because of the small number of data points there, limitations of CZCS algorithms in coastal and high chlorophyll water, and limitation of equation used to compute light absorption by phytoplankton at pigment concentrations greater than 10 mg m⁻³.

the shape of the vertical profile of pigment biomass is stable and can be characterized by quasi-constant values of the parameters ρ , σ , and $z_{\rm m}$ (Fig. 3). Of course, this assumption is an idealization, but there is considerable evidence that it is a good one (31). We further assume that the parameters of the photosynthesis light curve are similarly stable by region and season, and the evidence for this assumption is good in those regions for which there are data (32). We are proposing that, from consideration of the biological structure of the water column and the physiological rate parameters of the phytoplankton, the ocean can be partitioned into a small set of regions. The procedure would be similar to the partitioning of continents or oceans into biogeographic provinces according to taxonomic criteria, except that the boundaries of the regions and the magnitudes of the characteristic parameters in the regions could change with season. We might call this partition a "dynamic biogeography." The challenge is to find the minimum set of regions that will permit adequate description of ocean production. A data base needs to be assembled to archive these large-scale properties of the pelagic ecosystem. It would be refined progressively as the resolution of the observations improves in time and space. We propose that this data base of slowly varying properties be combined with remotely sensed data on the more rapidly varying quantity (pigment biomass) to produce maps of water column primary production. For the present, the archival data are sufficient to illustrate a plausible approach to estimation of oceanic primary production at large horizontal scales.

Recommended Protocol

We illustrate the approach by estimating the primary production for the Atlantic Ocean between 20°S and 50°N for the month of September 1979, using the monthly composite image released by NASA (3). We first partitioned the basin into representative regions to which the parameters will be assigned. We recognize three depth zones (shelf, slope, and oceanic) and three latitudinal zones (equatorial, subtropical, and transitional) for a total of nine regions. An accurate estimate of the parameters for the oceanic depth zone is most important because it occupies more than 90% of the surface area of the ocean (2). Estimating production for latitudes higher than 50°N would require inclusion of subarctic and Arctic zones. The crucial boundary between the subtropical and the transition zones, which varies seasonally, is best fixed by inspection of the satellite image of the biomass field. For simplicity, we assumed that all boundaries between latitudinal zones are parallel to the equator. In each of the nine regions, we assigned values for the parameters of the biomass profile and photosynthesis (Fig. 4 and Table 1), on the

basis of data in our archive. These were not always strictly suitable with respect to season, but will suffice for demonstration.

Data on mean cloud cover for September were obtained from a climatological atlas (33) and combined with the clear sky irradiance generated from the model to produce the forcing irradiance. We used a spatial grid with 1° by 1° resolution. At each of some 3800 grid points, the forcing irradiance, satellite chlorophyll, and parameters characteristic of the region were substituted into the local algorithm to calculate primary production. Wavelength resolution was 5 nm; the integration step for depth was 1 m. Water column primary production was calculated at half-hour intervals in simulated time and integrated over time to yield a result expressed as a daily rate (Fig. 4).

New Production

Primary production in the ocean can be partitioned into two components: the regenerated production, P_r , and the new production, P_n (34). Regenerated production uses material that has been recycled in the photic zone for its nitrogen source, and it therefore depends only on processes internal to the zone. New production is fueled by nitrogen supplied from outside the photic zone. In the open ocean, the dominant source of extra photic zone nitrogen is the vertical flux from below (35). New production therefore depends on the coupling between the photic zone and the rest of the water column, and the ratio $f = P_n/(P_n + P_r)$ is a measure of the degree of this coupling. Regenerated production may be thought of as that component of the total primary production required to satisfy the



Fig. 3. The generalized chlorophyll profile. Fit of generalized profile to data from (**A**) Celtic Sea in May and (**B**) New England seamounts in June. Also shown is the stability of the profile (**C**) in time (fitted profiles from data collected during a 4-week period in Celtic Sea in spring); and (**D**) in space (fitted profiles from along a transect some 1000 km long east through New England seamounts). Profiles in (C) and (D) normalized to common amplitude. Celtic Sea data from cruise of RSS *Charles Darwin* by National Environmental Research Council (United Kingdom); New England seamounts mount data from cruise of CSS *Hudson* by Biological Oceanography Division of Bedford Institute of Oceanography.

metabolic demands of the pelagic ecosystem. New production is what is left after these requirements have been satisfied; it is the residual component that is accessible to measures of change in the bulk properties of the water column (36).

We need to know P_n as well as total primary production P_T because P_n is the exportable component of primary production; it is the force behind the "biological pump" that transports CO₂ from the atmosphere to the deep water (37). Thus, in discussions of the possible role of the pelagic biota in modulating the greenhouse effect, the relevant ecological flux is P_n .

The difficulty of estimating P_n with satellite oceanography is that it has no electromagnetic signature that can be exploited for development of a suitable remote-sensing procedure. In global terms, the data base on the *f*-ratio is weak. We are obliged to resort to indirect methods. The approach of choice would appear to be to archive data on *f*-ratio in a diversity of oceanographic environments, as for the parameters of the local production algorithm, and apply them to the corresponding estimates of primary production, P_T , to obtain P_n . The disadvantage of this method is that it ignores the importance of episodic events. Aperiodic inputs of nutrients associated with the passage of atmospheric disturbances are thought to account for a considerable portion of the annual new production in the open ocean: nitrogen-limited systems will be characterized by a positive covariance between primary production and the *f*-ratio (38).

One possible approach to estimate P_n is to look for negative local anomalies in the surface temperature field as evidence of upwelling of cold, nutrient-bearing water. These would be interpreted as evidence for local enhancement of the *f*-ratio. In certain cases, strong empirical correlations between surface temperature and nutrients have been found (39), as have empirical algorithms for estimating *f*ratio from nitrate (38). It might be possible to relate the frequency of perturbation of local nitrate supply to the scale of the physical forcing as determined by indices accessible to remote sensing.

Second-Order Factors

Although the response of algal photosynthesis to light and biomass has been well described with models (10), mathematical description of its response to second-order factors such as temperature, nutrients, and species composition has proved a more elusive goal. Chlorophyll and light account for such a high proportion of the variance in primary production that the influence of secondorder factors is often obscured. First-order factors can be difficult to control when studying the second-order ones in the field. Perhaps the relevant physiology is poorly understood.

In the case of temperature, the response of photosynthesis parameters to transient changes in temperature is often difficult to distinguish from adaptations of photosynthetic performance on longer time scales (40), especially when these adaptations are accompanied by shifts in species composition. For short-term response, the assimilation number, P_m^B , is sensitive to temperature, whereas α is not (41). The appropriate algorithm to correct P_m^B for short-term temperature changes could be constructed easily, but it would be specific to particular oceanic regimes (42). Arctic phytoplankton respond differently to temperature than do equatorial phytoplankton.

Regarding nutrients, explaining much of the variance of primary production of natural phytoplankton assemblages with mathematical models in which nutrient concentration is the independent variable has proved difficult. Perhaps the analytical methods that have been used to measure nutrients were too insensitive to yield data that were suitable to allow the development of adequate models. Nitrate provides a good example: the recent introduction of the chemiluminescent method (43) has revolutionized our understanding of the dynamics of nitrate in the pelagic zone. There is now direct evidence for the vertical input of nitrate pulses into the photic zone caused by passage of storms and the subsequent utilization of this nitrate by phytoplankton (44). The concentrations of nitrate involved are low enough that they were undetectable by previous chemical methods. Nutrient concentration is a static quantity and does not necessarily provide information about either the rate of supply or the rate of utilization. Except in a few cases (45), models that included physical processes such as wind stress and vertical mixing as sources of nutrient supply have been unsuccessful for describing the primary production of natural populations. Integrating shipboard observations of phytoplankton physiology with those on physical forcing has been difficult.

Species composition and size distribution of the phytoplankton community are known to affect primary production (46). Existing algorithms for interpretation of ocean color images can tell us nothing about size distribution. In particular cases, such as during coccolithophorid blooms (47), the species assemblage may have a distinct spectral signature. But in general, with only three channels available for chlorophyll retrieval on sensors such as the CZCS, our ability to discriminate among broad taxonomic groups is limited.

In view of these uncertainties, to include second-order factors explicitly in the primary production algorithm is premature. This approach is not to deny the importance of nutrients for phytoplankton growth: with the protocol that we suggest, their influence would be manifested implicitly through the average values of the photosynthesis parameters chosen as representative of each ocean type. The prospect for large-scale modeling of second-order factors is not good even without the additional problem of assimilation of satellite data. However, satellite data should be of great help in improving our insight into the scales of forcing.

Alternatives for the Local Algorithm

Empirical regression models. Early in the search for ways to extract information on primary production from ocean color images, simple regression models of measured production on satellite-derived chlorophyll concentration were tried (48). Such models can explain significant portions of the variance in local primary production, but they do not have the basis in physiology that would support their extrapolation to studies at global scales. Separate regressions would have to be established for an unknown number of water types to construct an estimate for global production. A local regression model might perform better at the station and season for which it was developed than our algorithm because the regression coefficients would contain information on the structure of the local biomass profile and on the photosynthesis parameters (26). The advantage of adopting a physiological approach is that when such empirical coefficients are available for a particular time and place, they can be given a direct physiological interpretation. Conversely, if particular physiological information is available for a given region, it can be assimilated immediately into the local algorithm in a way that would not be possible for simple regression models. In short, physiological models offer more promise for future refinement than do regression models lacking biological structure. The algorithm presented above is offered as a first step in this direction, to show what can be done with the data available now, and to suggest how it might be improved in the future.

Fig. 4. Estimation of water column primary production in the month of September for the Atlantic Ocean between 20°S and 50°N. (A) Relative cloud cover for September (33). Darker color indicates greater cloud cover. Range is from 30 to 80%. (B) Biogeographic regions in which physiological parameters and shape of chlorophyll profile are taken to be constant. Depth zones are: shelf (0 to 200 m); slope (200 to 2000 m); and oceanic (>2000 m). Note that oceanic zone occupies the largest fraction of the surface area. Latitudinal zones are: subtropical in green (20°S to 10°S and 10°N to 37°N); equatorial in blue (10°S to 10°N); and transitional in red (37° to 50°N). (C) The monthly composite, satel-lite-weighted chlorophyll field for September 1979 (NASA) used as input, logarithmic scale. Purple is lowest chlorophyll, yellow highest. Gray areas are blocks for which no data are available. (D) Derived field for water column primary production, logarithmic scale (range 100 to 1000 mg of carbon per square meter per day). Blue is lowest production, orange highest. Production estimates



smoothed across boundaries between latitudinal zones. Derived rates are in Table 1. A possible explanation for the east-west asymmetry in primary production of the equatorial zone is the deepening of the thermocline from

Linearized model. The physiological model expressed in Eq. 6 was presented first in a linearized approximation (49). Water column production divided by water column biomass was related linearly to surface irradiance I_0 through a coefficient ψ that has the same dimensions as α . The value of ψ is remarkably constant across the spectrum of regions that have been examined. If the linear assumptions are strictly applicable, it can be shown that ψ is directly proportional to α . The realized value of ψ in particular applications will be influenced by the shape of the local biomass profile. The errors introduced by the assumptions of a linear photosynthesis model and a vertically homogeneous biomass profile can be calculated from the exact solution and expressed as a function of the dimensionless surface irradiance $I_{0\alpha}/P_{m}$ (50). Because removal of the bias involves some knowledge of the shape of the biomass profile and because the linear model is insensitive to the spectral and angular distributions of irradiance, we preferred to work with the local algorithm discussed above. However, for exploratory investigations, and where only relatively crude measurements of irradiance are available, the linear model remains useful.

Fluorescence. In the development of the local algorithm for primary production, we have exploited the change in spectral reflectance of light from the sun induced by absorption and scattering due to phytoplankton, but we have not made use of any electromagnetic effect associated with photosynthesis itself. After absorbing a photon, the photosynthetic apparatus has several channels available for de-excitation, including fluorescence (51). The fluorescence emission peak is at 685 nm, a wavelength for which seawater is strongly absorbing. However, solar-stimulated fluorescence by phytoplankton can be detected from ships down to at least 80 m (52). Furthermore, with the Fluorescence Line Imager (FLI), a highresolution sensor developed specifically to monitor this emission, high-altitude aircraft can be used to map the distribution of ocean chlorophyll. The signal-to-noise ratio of the conventional imager is just sufficient for monitoring ocean fluorescence from the top of the atmosphere, that is, from satellites, in chlorophyll-rich waters (53).

The exciting possibility therefore is that photosynthesis itself may be indexed directly from remotely sensed data. In the most simplistic analysis one would ascribe a linear dependence on light absorbed to both photosynthesis P and fluorescence F such that, at a particular depth, $P/F = \phi_p/\phi_f$, where ϕ_p is the quantum yield of photosynthesis and ϕ_f is the quantum yield of fluorescence (54). A corollary is that $\alpha = (\phi_p/\phi_f)\partial F/\partial I$. At discrete depths there is already evidence that α is correlated with fluorescence efficiency (55). Thus, at least in principle, one can envisage future determination of one of the key photosynthesis parameters from remote sensing. This would be a great advance over what we have available at present for spatial resolution of a rate parameter. The resulting data could be assimilated directly into the local algorithm for primary production.

Discussion of Errors

Accuracy. Because parameters determined by the ¹⁴C method are used in the local algorithm, it will be of no use for addressing the question of the validity of the ¹⁴C method in local applications (56). However, at the regional scale, because of the rich information supplied on the horizontal structure of the biomass field, estimates of regional primary production should be of superior accuracy to those scaled up from a small number of shipboard observations at discrete stations. Because production is generally calculated as specific production multiplied by biomass, the more information supplied about the biomass field, the more reliable the result at the extrapolated scale.

model that we use accounts for change in light intensity due to clouds, but not in light quality. A further complication is that areas of persistent cloud cover yield only limited CZCS data. Spatial or temporal averages of the biomass field are therefore weighted more strongly by those areas that are persistently cloud-free. Areas of strong upwelling, usually highly productive, are often obscured by fog. In such cases, underweighting their contribution to the regional coverage could lead to serious bias.

Precision. The agreement between the local algorithm and field data shown in Fig. 1 was obtained with biomass data collected by ship (17). In a remote-sensing application, the precision of the biomass estimate will not be better than a factor of 2 (57), setting an upper limit to the precision of a local estimate of primary production. On a regional scale, the complex of errors on the profile and the photosynthesis parameters and errors in the irradiance and its correction for cloud cover and their nonlinear interactions make assigning a figure to the precision of the result difficult at this stage (26).

New production. In calculating new production, the error in the f-ratio has to be included in addition to the errors of total production. The sources of systematic error have been discussed for local estimates (58). Because f and $P_{\rm T}$ covary, inaccuracies can be expected if a constant and uniform value of f is adopted for a given region. In other words, a weighted integral at the regional scale must be calculated (38):

$$P_{n}^{\text{region}} = \iint_{\text{region}} f(x, y) P_{T}(x, y) dx \, dy \tag{11}$$

Similar-weighted integration should be performed for the integrals over time to calculate values representative of the seasonal or longer time scale. Such values integrated over time and space,

$$\iiint_{\text{region}} f(x, y, t) P_{\text{T}}(x, y, t) dx \, dy \, dt \tag{12}$$

are suitable estimates of P_n to compare with regional new production calculated from seasonal changes of bulk properties of the water column (36, 59).

Implications for Oceanographic Programs

For emerging programs such as JGOFS and IGBP (International Geosphere-Biosphere Program) (1), which will rely on remote sensing of the large-scale distribution of primary production in the ocean, the following conclusions can be drawn. The most useful field activity to aid in assimilation of ocean color data would be, in a broad range of oceanographic regimes, (i) to establish the typical shape of the biomass profile and its seasonal variation expressed in terms of the dimensionless properties of the generalized profile; (ii) to catalog the optical properties including their wavelength dependence; and (iii) to measure the frequency distributions of the photosynthesis parameters and their seasonal variation. For estimates of new production, the magnitude and variation of the *f*-ratio in stable and disturbed conditions should be assessed in the same range of oceanographic regimes (60). This suite of measurements, invaluable to improve our ability to assimilate ocean color data, is also of fundamental importance to the aims of JGOFS. All of the relevant quantities are observable by routine methods. In terms of allocation of shipboard effort, higher priority should be given to detailed study of vertical structure, which is required to support the physiological models, at the expense of proliferation of surface observations, which can be recovered from satellites (in the case of biomass) or from satellites and calculation (in the case of irradiance).

For ecological modeling, models should be constructed for which The occurrence of clouds is a source of systematic error. The light the state variable is the primary production of the water column, that is, a flux per unit area. Remote sensing cannot yet give information on the depth distribution of either biomass or production. Another important area of ecological modeling is food web analysis. Because the f-ratio depends on the flow structure of the pelagic food web and how it is perturbed by transients (61), this kind of modeling is required to support the estimation of new production given estimates of total primary production.

Calculation of ocean primary production at large horizontal scale is already a reality: it has been demonstrated with reference to the existing data base on ocean color. By the time data become available in 1991 from the new SeaWiFS (4) ocean-color sensor on the Landsat-6 spacecraft, application of a protocol such as the one outlined here should be able to produce global scale maps of ocean production in quasi-real time.

REFERENCES AND NOTES

- T. F. Malone and J. G. Roederer, Eds., *Global Change* (Cambridge Univ. Press, New York, 1985); P. G. Brewer, K. Bruland, R. W. Eppley, J. J. McCarthy, *Eos* 67, 827 (1986); Canada, France, Germany, Holland, United Kingdom, and the United States all have national programs in the Joint Global Ocean Flux Study (JGOFS).
- J. H. Martin et al., Deep Sea Res. 34, 267 (1987)
- 3. W. E. Esaias, G. C. Feldman, C. R. McClain, J. A. Elrod, Eos 67, 835 (1986). See also W. A. Hovis et al., Science 212, 60 (1980).
- 4 E. S. Putnam, Ed., System Concept for Wide-Field-of-View Observations of Ocean Phenomena from Space, Report of the SeaWiFS (Sea-viewing, Wide-Field-of-View
- Phenomena from Space, Report of the SeaWiPS (Sea-Viewing, Wide-Field-of-View Sensor) Working Group (NASA, Greenbelt, MD, 1987).
 5. European Space Agency (ESA), ESA Rep. BR-20 (1983).
 6. H. R. Gordon and W. R. McCluney, Appl. Opt. 14, 413 (1975). For a sensor viewing the sea at wavelength λ, 90% of the signal received from the water arises from above the "penetration depth," defined as z₉₀ = 1/K(λ), where K(λ) is the diffuse attenuation coefficient in water for light at that wavelength. Attenuation length is the inverse of K. The activities is the inverse of K. The activities in the inverse of K. The activities in the inverse of K. length is the inverse of K. The satellite signal therefore contains practically no information from depths greater than one attenuation length. The magnitude of z_{90} depends on wavelength and on the optical properties of the water at that wavelength, which are in turn determined by the amount and nature of the particulate and dissolved material in the water. Even above the penetration depth, the signal is heavily weighted toward the surface because of the exponential decay of light as it travels down to a particular depth and back to the surface after scattering. The phytoplankton concentration that the satellite "sees" is expressed as a weighted mean to account for this effect, with the weighting factor decreasing exponentially with depth. See H. R. Gordon and D. K. Clark, *Appl. Opt.* **19**, **3428** (1980); H. R. Gordon and A. Y. Morel, *Remote Assessment of Ocean Color for* Interpretation of Satellite Visible Imagery: A Review (Springer-Verlag, New York, 1983); S. Sathyendranath and A. Morel, in Remote Sensing Applications in Marine Science and Technology, A. P. Cracknell, Ed. (Reidel, Dordrecht, 1983), pp. 323-357; S. Sathyendranath, Can. Bull. Fish. Aquat. Sci. 214, 561 (1986). Chlorophyll retrieval algorithms depend on changes in the spectral reflectance of seawater with changing pigment concentration.
- The most commonly used algorithms employ ratios of reflectances at two wavelengths. If we denote reflectance by R, these algorithms are of the form $C_{\rm s} = A_{\rm I} [R(\lambda_1)/R(\lambda_2)]^{A_2}$, where $C_{\rm s}$ is the satellite-weighted pigment concentration and A_1 and A_2 are constants determined empirically. For the CZCS, the wavelength pairs used (λ_1 and λ_2) are 440 and 550 nm (for $C_s < 1.5 \text{ mg m}^{-3}$), and 520 and 550 nm (for $C_s > 1.5 \text{ mg m}^{-3}$). These reflectance ratios are commonly referred to as blue to green ratios; see (4–6).
- The photic zone, defined typically as the zone within which the light is reduced to 1% of its surface value, extends over some 4.6 attenuation lengths. This is the illuminated zone, where the primary production takes place
- Multinated Zole, where the primary production tacks place.
 K. Banse and C. R. McClain, Mar. Ecol. Prog. Ser. 34, 201 (1986); O. Brown et al., Science 229, 163 (1986); G. C. Feldman, Eos 67, 106 (1986); M. R. Abbott and P.
 M. Zion, J. Geophys. Res. 92, 1745 (1987); J. A. Yoder et al., Limnol. Oceanogr. 32, 929 (1987); J. J. Walsh et al., Deep Sea Res. 34, 675 (1987).
 T. Platt, K. L. Denman, A. D. Jassby, in The Sea: Ideas and Observations on Progress in the Octor of the Sea P. D. Colliberation of Laboration of the Sea Program of the Sea P. Colliberation of the
- 10. the Study of the Seas, E. D. Goldberg et al., Eds. (Wiley, New York, 1977), vol. VI, pp. 807–856.
 11. In this treatment we have ignored the effect of photoinhibition of photosynthesis.
 12. S. Sathyendranath and T. Platt, J. Geophys. Res., in press.
 13. C. Gautier and K. B. Katsaros, *ibid.* 89, 11,779 (1984).

- 14. S. Sathyendranath et al., in preparation. For computations with a clear sky model, errors in estimated production could be as high as 17% if the incident light spectra are assumed to be neutral.
- R. E. Bird, Sol. Energy 32, 461 (1984).
 See (14). Equations 3 and 4 neglect multiple scattering effects.
- S. Sathyendranath and T. Platt, in preparation.
- 18. The coefficients a and b_b can be expressed as a sum of contributions from individual components. There is always a constant contribution from pure seawater. For open ocean waters, phytoplankton and associated covarying material may be considered the single major variable component. In coastal waters, contributions from other sources (mainly suspended sediments and dissolved organic matter) may be far from negligible. Our computations are for the open ocean case. We have computed

 $a_{c}(\lambda)$ using the method of L. Prieur and S. Sathyendranath, Limnol. Oceanogr. 26, 671 (1981). The backscattering by pure seawater is computed according to A Morel, in Optical Aspects of Oceanography, N. G. Jerlov and E. S. Nielsen, Eds. (Academic Press, London, 1974), pp. 1–24. Scattering by phytoplankton is computed according to A. Morel, *Boundary-Layer Meteorol.* 18, 177 (1980). We assumed that the backscattering by phytoplankton is 0.5% of their scattering coefficient and that its spectral form is complementary to the absorption spectrum.

- G. W. Paltridge and C. M. R. Platt, Radiative Processes in Meteorology and Climatology 19. (Elsevier, Amsterdam, 1976). We have adopted the method from chapter 6 of this book
- 20. The cloud albedo values listed in (19) vary from 0.35 to 0.6, depending on cloud
- 21. This is not a restrictive assumption. It gives $\langle \cos\theta_s \rangle = 0.83$. Assumption of a cardioid distribution would change its value to 0.85. In the model, we assume that $\langle \cos \theta_s \rangle$ is independent of depth.

- (cost_b) is independent of depth.
 22. L. N. M. Duysens, in *Photobiology of Microorganisms*, P. Halldal, Ed. (Wiley-Interscience, London, 1970), pp. 1–16.
 23. M. R. Lewis et al., J. Phycol. 21, 310 (1985).
 24. M. R. Lewis et al., *Limnol. Oceanogr.* 30, 794 (1985); M. R. Lewis et al., *Can. Bull. Fish. Aquat. Sci.* 214, 235 (1986); R. E. Warnock, unpublished data. In the model, therefore, the spectral shape of α^B(λ) is held constant.
 25. L. U. Warn *Can. L. Eich. Acust. Sci.* 29, 701 (1982).
- J. J. Cullen, Can. J. Fish. Aquat. Sci. 39, 791 (1982). 25.
- T. Platt et al., Deep Sea Res. 35, 855 (1988).
- 27. The parameters of the biomass profile have the following units: B_0 , milligrams per cubic meter; z_m , meters; σ , meters; and h, milligrams per meter squared.
- 28. As a first approximation, we assume that the photosynthesis parameters are uniform with depth, an assumption that can be relaxed if there is information to the contrary. In a stably stratified ocean, α and $P_{\rm m}$ will adjust with depth through the process of photoadaptation; T. Platt et al., Deep Sea Res. 10, 1159 (1982); K. L. Denman and A. E. Gargett, J. Mar. Res. 46, 77 (1988). Destabilization, for example, through wind mixing, results in a more uniform distribution of photosyn-thetic properties with depth; M. R. Lewis *et al.*, *Nature* **311**, 49 (1984). S. Sathyendranath and T. Platt, in preparation. The commonly used relationship is between the blue to green ratio and the
- satellite-weighted surface concentration.
- Such stability is behind the concept of "Typical Tropical Structure"; A. Herbland, Oceanogr. Tropic. 18, 295 (1983). R. T. Barber, unpublished data, found an exceptionally stable biomass profile along a 12,000-km transect in the South Pacific. A. R. Longhurst and W. G. Harrison, unpublished manuscript, provide a 31. W. G. Harrison and T. Platt, *Polar Biol.* 5, 153 (1986). Open ocean areas are
- 32. particularly lacking in archive data of the parameters. The JGOFS North Atlantic Pilot Program (1989) will follow the northward movement of the spring phyto-
- Plankton bloom along 20°W.
 W. F. McDonald, Ed., Atlas of Climatic Charts of the Oceans (U.S. Weather Bureau, Washington, DC, 1938).
- R. C. Dugdale and J. J. Goering, Limnol. Oceanogr. 12, 196 (1967); R. W. Eppley and B. W. Peterson, Nature 282, 677 (1979); T. Platt and W. G. Harrison, *ibid.* 318, 55 (1985). When the components P_n and P_r are distinguished, their sum $P_{\rm T}(\equiv P_{\rm n} + P_{\rm r})$ is commonly labeled with a subscript.
- 35.
- T. Platt et al., in preparation. W. J. Jenkins, Nature **300**, 246 (1982) 36.
- 37. B. Moore III and B. Bolin, Oceanus 29, 9 (1986)
- 38 T. Platt and W. G. Harrison, Nature 318, 55 (1985)
- D. Kamykowski and S.-J. Zentara, Deep Sea Res. 33, 89 (1986); D. Kamykowski, 39. W. K. W. Li, in *Primary Productivity in the Sea*, P. G. Falkowski, Ed. (Plenum, New
- 40. York, 1980), pp. 259–280. T. Platt and A. D. Jassby, *J. Phycol.* **12**, 421 (1976).
- W. K. W. Li et al., Mar. Ecol. Prog. Ser. 17, 237 (1984); J. C. Smith and T. Platt, ibid. 25, 31 (1985); W. K. W. Li, Deep Sea Res. 32, 1381 (1985).

- C. Garside, Mar. Chem. 11, 159 (1982).
 R. W. Eppley and E. H. Renger, Deep Sea Res., in press.
 D. F. Winter et al., Mar. Biol. 29, 139 (1975); B. M. Jamart et al., Deep Sea Res. 24, 753 (1976); J. Plankton Res. 1, 267 (1979)
- I. Morris, Ed., The Physiological Ecology of Phytoplankton (Blackwell, Oxford, 1980).
 P. Holligan et al., Nature 304, 339 (1983).
- 48. R. C. Smith et al., Mar. Biol. 66, 281 (1982); R. W. Eppley et al., J. Plankton Res. 7, 57 (1985).
- 49. T. Platt, Deep Sea Res. 33, 149 (1986). In this early model, Platt assumed that P is linear in I for all I and that B, α^B, and P^B_m are all independent of depth. See also J. W. Campbell and J. E. O'Reilly, Cont. Shelf Res. 8, 179 (1988).
- The photoadaptation parameter $I_k \equiv P_m/\alpha$, is roughly the light intensity at which saturation sets in. It is a useful scale for normalization of I_0 . The dimensionless light
- $I* \equiv I_0/I_k$ varies from about 0 to 10 in natural conditions. Govindjee, J. Amesz, D. C. Fork, Eds., Light Emission by Plants and Bacteria (Academic Press, Orlando, 1986). 51.
- 52. B. J. Topliss, Oceanologica Acta 8, 263 (1985). The depth accessible by laser from an aircraft is much smaller. A maximum depth of 4 m has been reported by C. S. Yentsch and C. M. Yentsch, Oceanogr. Mar. Biol. Ann. Rev. 22, 55 (1984).
- J. F. R. Gower and G. Borstad, in *Oceanography from Space*, J. F. R. Gower, Ed. (Plenum, New York, 1981), pp. 329–338. R. F. Davis and C. R. Booth, *Eos* **68**, 1694 (1987); P. Stegmann, *ibid.*, p. 1694; D. 53.
- 55.
- A. Kiefer and W. S. Chamberlin, *ibid.*, p. 1694 (1987); P. Stegmann, *ibid.*, p. 1694; D. A. Kiefer and W. S. Chamberlin, *ibid.*, p. 1694.
 B. J. Topliss and T. Platt, *Deep Sea Res.* 33, 849 (1986).
 B. J. Peterson, *Annu. Rev. Ecol. Syst.* 11, 369 (1980); P. J. LeB. Williams et al., *Nature* 305, 49 (1983). 56.
- 57. H. R. Gordon et al., Appl. Opt. 22, 20 (1983).

23 SEPTEMBER 1988

- 58. W. G. Harrison et al., J. Plankton Res. 9, 235 (1987).
- 59. W. J. Jenkins, Nature 331, 521 (1988)
- 60. A particularly important comparison will be between the subtropical zone, where nutrient input is believed to be episodic, and the equatorial zone, where the nutrient supply is more persistent through upwelling. To do the integrations over
- time, the variance at seasonal and shorter time scales must be known.
 A. F. Vezina and T. Platt, Can. J. Fish. Aquat. Sci. 44, 198 (1987).
 F. C. Fuglister, Atlantic Ocean Atlas (Woods Hole Oceanographic Institution, Woods Hole, MA, 1960).
- 63. F. E. Muller-Karger, C. R. Mclain, P. L. Richardson, Nature 333, 56 (1988).
- This work was supported by a grant-in-aid from the Department of Ocean Development (New Delhi) to the National Institute of Oceanography (Goa). Collaboration was facilitated by the award of a Natural Science and Engineering Research Council (NSERC) of Canada International Scientific Exchange Award to S.S. Further NSERC support through an operating grant to T.P. is gratefully acknowledged. We thank N. Kuring and C. Caverhill for help with computations and R. T. Barber, W. G. Harrison, E. P. W. Horne, M. R. Lewis, and A. R. Longhurst for useful comments.

Fractal Reaction Kinetics

RAOUL KOPELMAN

Classical reaction kinetics has been found to be unsatisfactory when the reactants are spatially constrained on the microscopic level by either walls, phase boundaries, or force fields. Recently discovered theories of heterogeneous reaction kinetics have dramatic consequences, such as fractal orders for elementary reactions, self-ordering and self-unmixing of reactants, and rate coefficients with temporal "memories." The new theories were needed to explain the results of experiments and supercomputer simulations of reactions that were confined to low dimensions or fractal dimensions or both. Among the practical examples of "fractal-like kinetics" are chemical reactions in pores of membranes, excitation trapping in molecular aggregates, exciton fusion in composite materials, and charge recombination in colloids and clouds.

MONG THE MOST IMPORTANT CHEMICAL REACTIONS ARE those called "heterogeneous." These reactions take place at interfaces of different phases, for example, gas-solid or liquid-solid boundaries, and include reactions such as industrial surface-catalysis and electrode reactions, as well as many bioenzymatic and membrane reactions and some geochemical and atmospheric reactions. In addition, there are many heterogeneous "nonchemical" reactions: in solid-state physics there are electron-hole, soliton-antisoliton, and exciton-exciton "recombinations," as well as the aggregation of excitations, defects, and so forth. Charge and excitation recombination, as well as excitation quenching, are also found in biological systems, such as photosynthetic units.

The most universally found instruction in chemical synthesis is to "stir well." However, convective stirring cannot always be achieved for reactions in or on media that are solid, viscous, porous, or otherwise structured. In the absence of convective stirring, there is still diffusive stirring, which is called "self-stirring." However, under dimensional constraints (surface reactions) or topological constraints (solid-state reactions), self-stirring may be highly inefficient. Fractal spaces such as percolation clusters are ideal testing grounds for "understirred" reaction kinetics. However, a reaction medium does not have to be a geometrical fractal in order to exhibit fractal kinetics. The drastic and unexpected consequences of such "fractallike reaction kinetics" are described below.

Classical Kinetics

Classical, homogeneous chemical kinetics will be briefly reviewed so as to introduce the terminology of fractal kinetics. We limit ourselves to elementary (single-step) bimolecular (pairwise) reactions, as these are by far the most important and prevalent chemical (and nonchemical) reactions. For a single-reactant bimolecular reaction.

$$A + A \rightarrow \text{products}$$
 (1)

as well as for a two-reactant bimolecular reaction,

$$A + B \rightarrow \text{products}$$
 (2)

one has second-order reaction rates, that is, all of the concentration dependence of the reaction can be expressed either as

$$Rate = K[A]^2 \quad (A + A \to A) \tag{3}$$

or as

$$Rate = K[A][B] \quad (A + B \to 0) \tag{4}$$

where [A] is the reactant concentration (or density) of A and K is the rate constant (not to be confused here with the equilibrium constant). Note that K is independent of time. Equations 3 and 4 are valid for both "batch" and "steady-state" conditions. In the batch case, the system is prepared instantaneously (at time t = 0), and the reaction rate is given by

$$Rate = -d[A]/dt = -d[B]/dt$$
(5)

that is, the disappearance of reactant concentration per unit time. Substituting Eq. 5 into Eq. 3 or 4 gives a differential rate equation:

$$-d[\mathbf{A}]/dt = K[\mathbf{A}]^2 \quad (\mathbf{A} + \mathbf{A} \to \mathbf{A})$$
(3a)

Its solution (the integrated rate equation) is:

$$[\mathbf{A}]^{-1} - [\mathbf{A}_0]^{-1} = Kt \tag{6}$$

where $[A_0]$ is the initial concentration (at t = 0). Similarly

$$-d[\mathbf{A}]/dt = K[\mathbf{A}][\mathbf{B}] \quad (\mathbf{A} + \mathbf{B} \to \mathbf{0})$$
(4a)

If [A] = [B], Eq. 6 is also the solution of Eq. 4a.

The author is professor of chemistry at the Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.