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The trophic status of various oceanic provinces as revealed by phytoplankton pigment signatures

Abstract—For various oceanic regimes, a pigment biomarker approach is used to investigate the relationship between the biomass and taxonomic composition of autotrophic communities. It is demonstrated that chlorophyll standing stocks are linearly related to the diatom (fucoxanthin) and dinoflagellate (peridinin) contents; other phytoplankton diagnostic pigments do not present any significant correlation with chlorophyll standing stocks. A pigment ratio, F_p, is proposed as an estimator of the proportion of new producers' biomass in a phytoplankton community. The variation of the F_p-ratio with chlorophyll *a* biomass and (modeled) primary production rates suggests strong similarities between F_p and the *f*-ratio (new production : total production).

In the ocean, large phytoplankton species are associated with eutrophic areas, whereas small cells dominate in the oligotrophic provinces (Malone 1980; Chisholm 1992). In autotrophic communities, a relationship between the species composition and the size of the standing stock is therefore implicit (Bienfang and Zieman 1992; Dugdale and Wilkerson 1992). Quantifying such a relationship is essential in the context of particulate organic flux studies, because the fluxes not only depend on the production and biomass levels but also on the composition of the autotrophic communities (especially the size of organisms) (Michaels and Silver 1988). Nevertheless, this relationship has not been properly established because the wide range in phytoplankton size (0.2–200 μm) prevents the use of a single method for complete characterization (qualitative and quantitative) of a phytoplankton assemblage. Different techniques like microscopy (micro- and nanophytoplankton) and flow cytometry (nano- and picophytoplankton) must be combined and conversion factors applied in order to derive biomass estimates (on a carbon or biovolume basis) from cell number determination (e.g. Li et al. 1992). These procedures inevitably generate uncertainties. In contrast, the global estimation of phytoplankton biomass based on pigment biomarkers avoids most of these approximations. HPLC analysis (e.g. Mantoura and Llewellyn 1983) provides a detailed description of a phytoplankton assemblage over the whole size range by determining the concentration of Chl *a* ("normal" chlorophyll *a* + divinyl-chlorophyll *a*), the universal index of phytoplankton biomass, and various accessory pigments, most of which are specific to various taxonomic groups. In this comparative study of different oceanic systems (oligotrophic, mesotrophic, and eutrophic areas in the North Atlantic, frontal conditions in the Mediterranean Sea), I examine the relationship between the abundance of the areal Chl *a* biomass (ranging from 20 up to 200 mg Chl *a* m^{-2}) and its composition, as inferred from the 0–200-m integrated concentration of seven specific diagnostic pigments (Table 1).

Data were acquired during three JGOFS-France cruises. Eumeli 3 (September–October 1991) and Eumeli 4 (May–June 1992) were conducted in the northeastern tropical Atlantic at three sites with eutrophic (20°30′N, 18°30′W), mesotrophic (18°30′N, 21°00′W), and oligotrophic conditions (21°00′N, 31°00′W). Almofront 1 (April–May 1991) was conducted in the Alboran Sea (36°N, 2°W) in the frontal zone formed by the interaction of the Atlantic and Mediterranean waters (Prieur et al. 1993; Claustre et al. 1994). Pigment analyses were performed either at sea (Eumeli 3 and Almofront 1) or in the laboratory (samples of Eumeli 4 were stored in liquid nitrogen); the procedures have been described by Williams and Claustre (1991) and Claustre et al. (1994). The identification of pigments was achieved by online diode array spectroscopic detection (Waters 991) on selected samples. Detectors were calibrated using pigment standards provided by R. Bidigare. Particular identification and quantitation of prochlorophyte pigments, di-

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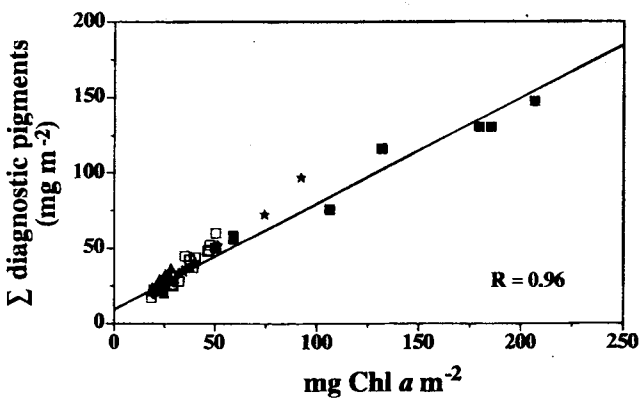

Fig. 1. Relationship between the Chl *a* concentration (normal chlorophyll *a* + divinyl-chlorophyll *a*, in mg m^{-2}, integrated from 0 to 200 m) and the sum of the concentration of seven diagnostic pigments (fucoxanthin, peridinin, 19′-HF, 19′-BF, zeaxanthin, "Chl *b*," alloxanthin; *see Table 1*) for various oceanic areas. Atlantic eutrophic site—■; Atlantic mesotrophic site—□; Atlantic oligotrophic site—▲; typical Mediterranean sites—◆; Mediterranean frontal area—★. The regression line is: Σ diagnostic pigments = 0.70Chl *a* + 10.83.

vinyl-chlorophyll *a* and divinyl-chlorophyll *b*, have been described by Morel et al. (1993).

The relationship between the sum of water-column-integrated concentrations (0–200 m) of all diagnostic pigments and integrated Chl *a* is presented in Fig. 1. The linear regression is highly significant ($P < 0.001$), which allows the accumulated concentration of these diagnostic pigments to be used as an estimator of the overall phytoplankton biomass. The positive value of the intercept at the origin supports the observation that phytoplanktonic cells from oligotrophic waters with a low Chl *a* content and a pronounced deep chlorophyll maximum generally contain more accessory pigments per unit Chl *a* than cells from eutrophic areas (Gieskes et al. 1988).

Figure 2 shows that changes in fucoxanthin and, to a lesser extent, peridinin are tightly coupled to changes in Chl *a* standing stocks. The other accessory pigments, however, are invariable with changes in Chl *a* concentration. When stations with Chl *a* levels >50 mg m^{-2} are not considered (since they may explain most of the variance), the above observations remain the same. Therefore, significant increases in Chl *a* standing stocks appear to be linked mainly to increases in diatom and dinoflagellate populations, which corroborates previous studies reporting increase of the average phytoplankton size with increasing biomass (Malone 1980; Chisholm 1992). Moreover, the observed linear relationship between the fucoxanthin and peridinin pigments and Chl *a* standing stocks is of great importance in understanding the fluxes of oceanic particulate material. The fate of large diatoms and dinoflagellates indeed differs from that of other phytoplankters; they may sink as fast-sedimenting particles, such as copepod fecal pellets or even ungrazed aggregates (Smetacek 1985; Fowler and Knauer 1986). Consequently, particulate organic fluxes possibly increase in a nonlinear fashion with increasing chlorophyll (and therefore diatom) standing stocks.

High Chl *a* standing stocks in the ocean are generally considered to result from nitrate consumption by phytoplankton and hence serve as evidence for new production (Eppley 1992). Consequently, diatoms and dinoflagellates, the main contributors to elevated Chl *a* standing stocks (Fig. 2), can be identified as the main contributors to new production, which corroborates recent evidence of a large phytoplankton new-production scheme (Michaels and Silver 1988; Dugdale and Wilkerson 1992;

Table 1. Diagnostic accessory pigments used to characterize the main phytoplankton groups in the ocean.

Diagnostic pigment	References	Phytoplankton group
Fucoxanthin	Jeffrey 1980	Diatoms
Peridinin	Jeffrey 1980	Dinoflagellates
19′-HF and 19′-BF*	Wright and Jeffrey 1987	Nanoflagellates†
Chlorophyll *b*‡	Jeffrey 1980	Green flagellates
Alloxanthin	Gieskes and Kraay 1983	Cryptophytes
Zeaxanthin	Guillard et al. 1985	Cyanobacteria
Zeaxanthin, divinyl-chlorophyll *b*‡	Goericke and Repeta 1992	Prochlorophytes§

* 19′-HF: 19′-hexanoyloxyfucoxanthin; 19′-BF: 19′-butanoyloxyfucoxanthin.
† The term nanoflagellates refers essentially to chrysophytes and prymnesiophytes which are characterized by 19′-BF and 19′-HF, respectively.
‡ Chlorophyll *b* and divinyl-chlorophyll *b* are regrouped as "Chl *b*" in this study as they coelute on reverse-phase HPLC.
§ Zeaxanthin is an accessory pigment in surface prochlorophytes while divinyl-chlorophyll *b* is an accessory pigment in deeper populations (Morel et al. 1993).

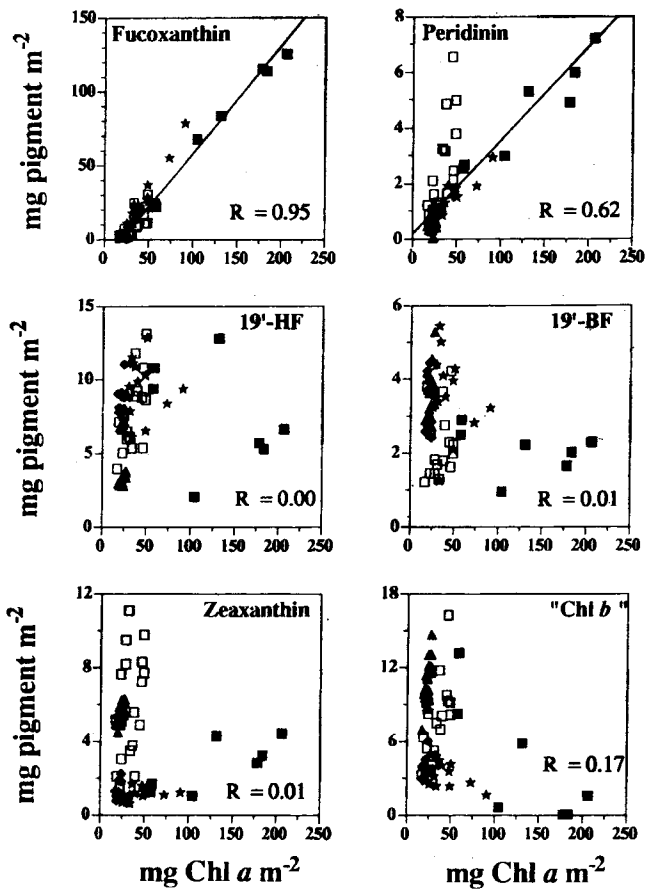

Fig. 2. Relationship between the Chl *a* concentration (normal chlorophyll *a* + divinyl-chlorophyll *a*, in mg m^{-2}, integrated from 0 to 200 m) and the concentration of each diagnostic pigment (*see Table 1*) for various oceanic areas. Symbols as in Fig. 1. The regression line for fucoxanthin is: Σ fucoxanthin = 0.72 ΣChl *a* − 13.40. The regression line for peridinin is: Σ peridinin = 0.04 Σ Chl *a* + 0.18.

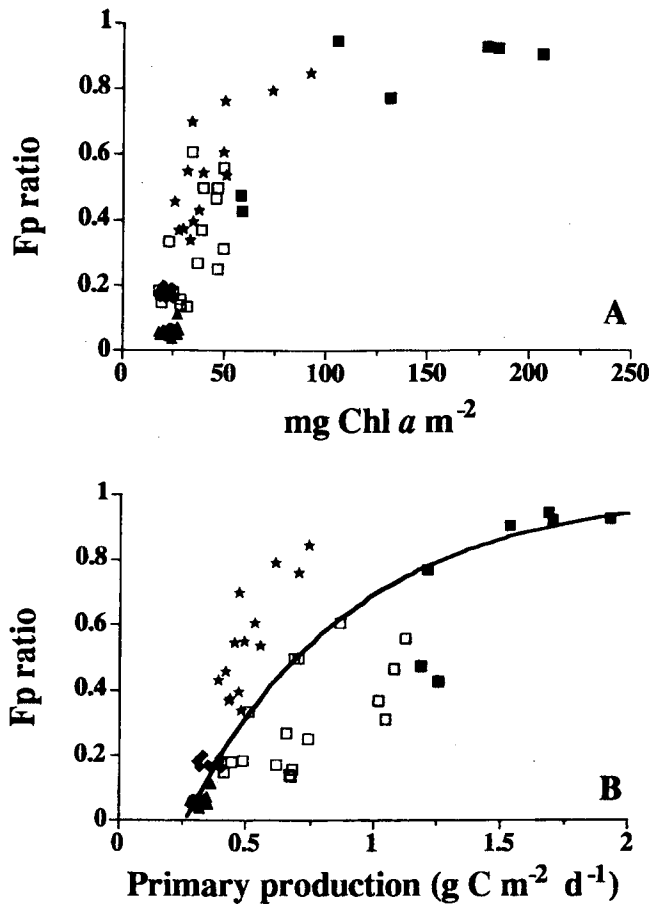

Fig. 3. A. Relationship between the Chl *a* concentration (normal chlorophyll *a* + divinyl-chlorophyll *a*, in mg m^{-2}, integrated from 0 to 200 m) and the F_p-ratio (*see text*) for various oceanic areas. Symbols as in Fig. 1. B. Comparison between the integrated primary production (P) and the F_p-ratio. Primary production was computed according to the relation described by Morel and Berthon (1989): $P = (1/39)\mathrm{Chl}_{eu}\mathrm{PAR}(0^+)\psi^*$, where Chl_{eu} (mg m^{-2}) is the chlorophyll content in the euphotic zone (computed from each profile down to the 1% level, Morel and Berthon 1989), PAR(0^+) (J m^{-2} d^{-1}) is the surface irradiance, and ψ^* [m^2 (mg Chl *a*)$^{-1}$] is the cross-section for photosynthesis per unit of areal chlorophyll biomass. The 1/39 factor expresses that the fixation of 1 mg of carbon is equivalent to an energy storage of 39 J. The values of PAR(0^+) and ψ^* are given elsewhere (Morel and André 1991; Berthon, 1992). The relation for the steady state line, $F_p = 1 - [\exp - 1.6 \times (\Sigma\ P - 0.27)]$, has been fitted solely on data corresponding to North Atlantic and Mediterranean oligotrophic conditions and to North Atlantic eutrophic conditions (except for two stations investigated 1 week before the other five, which present noticeable deviation according to an expected pattern). Symbols as in Fig. 1.

Goldman 1993). In contrast, cyanobacteria, prochlorophytes, and small flagellates are believed to be most likely involved in systems dominated by regenerated production. These observations do not imply that these small species are unable to use nitrates, which would be contradictory to many laboratory studies of successful monospecific culture growth on nitrate (e.g. Verity et al. 1992); it simply means that in a natural phytoplankton community, diatoms and(or) dinoflagellates are the taxa most suited to take rapid advantage of nitrate availability (Fogg 1991), whereas small algae are most adapted to survive in impoverished environments.

Individual diagnostic pigments : Chl *a* ratios have been used to characterize the floristic composition of phytoplankton (Bidigare et al. 1990). Here, I propose to use a single pigment index to identify the trophic status of an ecological province. This index, F_p, is defined as the ratio of the integrated concentration of fucoxanthin and peridinin to the sum of the integrated concentration of diagnostic pigments

of all taxa that may be present in a phytoplankton community:

$$F_p = (\Sigma \text{ fucoxanthin} + \Sigma \text{ peridinin}) \times (\Sigma \text{ fucoxanthin} + \Sigma \text{ peridinin} + \Sigma \text{ 19′-HF} + \Sigma \text{ 19′-BF} + \Sigma \text{ zeaxanthin} + \Sigma \text{ "Chl } b\text{"} + \Sigma \text{ alloxanthin})^{-1}.$$

This index can be considered as the biomass ratio of phytoplankton involved in new production over total phytoplankton. The nonlinear relationship between the F_p-ratio and the Chl *a* content (Fig. 3A) resembles the relation between the *f*-ratio (new production : total production) and the primary production rates (Eppley and Peterson 1979). The F_p values remain stable for typical oceanic areas (Fig. 3A), namely the North Atlantic (0.06±0.01) and Mediterranean (0.18±0.01) oligotrophic regimes, as well as for eutrophic conditions (0.76±0.22). These values are comparable with *f*-ratio estimates of 0.05 for the typical oligotrophic conditions of the central North Pacific (Eppley and Peterson 1979), of 0.21 for Mediterranean waters (Dugdale and Wilkerson 1992), and of 0.80 for typical upwelling conditions (Dugdale and Wilkerson 1992). The oceanic systems concerned here are in relative steady state: oligotrophic provinces are mainly regulated by their regenerative capacity, while upwelling regimes are regularly enriched by nutrients. For such situations (representative of the largest part of the world's oceans) standing stocks and fluxes are at equilibrium. Therefore, although the F_p- and the *f*-ratios do not derive from the same concepts, both indices can be compared for such well-defined oceanic conditions.

In contrast to the steady state regimes, a large F_p-ratio variability is observed (Fig. 3A) in the North Atlantic mesotrophic regime (0.15–0.60) as well as in the Mediterranean frontal area (0.35–0.85). When primary production rates are derived from Chl *a* standing stocks (Fig. 3B), some order appears in this variability. Compared to the curve representative of steady state regimes (typical oligotrophic and upwelling conditions) and with respect to their production levels, the frontal system appears dominated by phytoplankton involved in new production while the converse applies for mesotrophic conditions. Frontal and mesotrophic situations, in contrast to typical oligotrophic and eutrophic steady state systems, present characteristics of transient regimes. The diatom-dominated ecosystem associated with the frontal area is restricted to a 30-km-wide band permanently enriched in nutrients (Prieur et al. 1993), so that the observed system may rather look like a bloom at its beginning. On the other hand, the phytoplankton community recorded at the mesotrophic site (mostly cyanobacteria, prochlorophytes, and flagellates) results from the evolution of an autotrophic biomass, initially produced in an upwelling area and advected along a 300-km-long filament (Van Camp et al. 1991). This mesotrophic regime looks like a declining bloom, where regenerated substrates become available for the growth of a typical community. For these unsteady conditions, where biomass and fluxes may be strongly uncorrelated, both *f*- and F_p-ratios may not be of equal significance. Nevertheless, high variability of the *f*-ratio was reported for stations with an intermediate level of production (Eppley and Peterson 1979, their figure 2b), as observed in this study for the F_p-ratio (Fig. 3B).

The F_p pigment index presented here is derived from the demonstration that variations in chlorophyll standing stocks on a global scale are mainly due to diatom and, to a lesser extent, dinoflagellate variations. The direct relationship between F_p- and *f*-ratios remains to be established. Acquisition of *f*-ratio data is laborious, and thus the data are still extremely limited in time and space (Eppley 1993). Therefore the F_p-ratio may be an alternate tool in identifying the trophic status of many oceanic regimes.

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