

**Modelling the light
absorption properties
of particulate matter
forming organic particles
suspended in seawater.
Part 1. Model description,
classification of organic
particles, and example
spectra of the light absorption
coefficient and the imaginary
part of the refractive index
of particulate matter for
phytoplankton cells and
phytoplankton-like particles***

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Abstract

Data on organic substances in the sea are applied to distinguish hypothetical chemical classes and physical types of suspended particulate organic matter (POM) in seawater. Spectra of the light absorption coefficients of particulate matter $a_{pm}(\lambda)$ and the imaginary refractive index $n'_p(\lambda)$, are assessed for some of these classes and types of POM in seawater, that is, for live phytoplankton cells and phytoplankton-like particles. The spectral characteristics of these coefficients are established and the probable ranges of variability of their absolute magnitudes defined on the basis of the mass-specific coefficients of light absorption by the various organic substances forming the particles. Also presented are mathematical relationships linking the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for the various chemical classes of POM with their physical parameters, such as the relative contents of organic matter, water, air or some other gas. This article is part of a bio-optical study undertaken by the authors, the objective of which is to implement remote sensing techniques in the investigation of Baltic ecosystems (Woźniak et al. 2004).

1. Introduction

This article is the first part of a study of the light absorption properties of the ‘unpacked’ (i.e. in solvent) matter of organic particles suspended in the sea. This research is part of our bio-optical studies, which are aiming towards the implementation of satellite teledetection methods in the investigation of Baltic ecosystems (Woźniak et al. 2004).

To describe the light absorption properties of such particles, the imaginary part $n'(\lambda)$ of the complex refractive index of light has been applied, which is also the non-dimensional absorption coefficient of the unpackaged matter of the particles¹. The index $n'(\lambda)$ is a practically useful quantity for calculating various optical properties of dispersible media, including the light absorption and scattering coefficients, and the volume scattering function obtained with the aid of electromagnetic theories, e.g. the Mie theory (Mie 1908, Bohren & Huffman 1983).

The theories underpinning the remote sensing of marine ecosystems are the modelled links between the inherent and apparent optical properties (IOPs and AOPs) of the upper sea layer and the concentration of various substances present in seawater (Dera 1995, 2003). So far, such models have usually been founded on a parameterisation of the optical properties of seawater based on the chlorophyll *a* concentration (C_a), the principal pigment in marine phytoplankton (e.g. Smith & Baker 1978, Morel 1988,

¹The relationship of the imaginary part of the absolute refractive index of light $n'(\lambda)$ of a particle and the universally applied Lambert light absorption coefficient of cellular matter (or in the more general case, particulate matter) a_{pm} is expressed by the following well-known equation: $n' = a_{pm}\lambda/4\pi$ (see eq. 7 in section 3.1) and will be discussed in Part 2 of the article covering this research.

Woźniak & Pelevin 1991, Woźniak et al. 1992, 2003). However, the efficiency of *remote sensing* algorithms based on this kind of model are fairly satisfactory only with respect to open oceanic waters (e.g. Ficek et al. 2003), classified by Morel & Prieur (1977) as case 1 waters. This is because the vast majority of optically significant admixtures in such waters originate from transformations of matter in the ecosystem stimulated by the primary production of phytoplankton, which in turn is correlated with the chlorophyll *a* concentration. Applying such a simple parameterisation based on a description of the optical properties of the sea (e.g. the remote sensing reflectance) and the chlorophyll *a* concentration in shelf and semi-enclosed seas (case 2 waters, such as the Baltic), will encumber the description with substantial errors and is all but useless for remote sensing purposes. Progress in remote sensing will therefore only be possible with the development of more complex, multi-component optical models of the sea. These must take into account the fact that in natural waters affected by terrestrial run-off, riverine waters etc., the concentrations of the three main groups of optically significant admixtures in seawater – coloured dissolved organic matter, phytoplankton, and other particulate matter – correlate poorly if at all with the chlorophyll concentration C_a . These substances consist in large part of allogenous components, arriving from without, and not produced ‘locally’ with the participation of phytoplankton. Moreover, this same group of substances may contain components with very different chemical properties, and thus also with different physical properties, including optical properties, which at the present moment are poorly understood (see e.g. Stramski et al. 2001).

A perusal of the relevant literature shows that of these three main groups of optically significant admixtures in seawater, the least understood as regards their optical properties are the particles of suspended matter in the sea, principally organic particles² (apart from phytoplankton), i.e. non-algal detrital particles, and mineral particles. Despite a sustained research effort, (e.g. Bowers et al. 1996, Bricaud et al. 1998, Babin et al. 2003, Babin & Stramski 2004, Stramski et al. 2004, Woźniak S.B. & Stramski 2004), our knowledge of these particles is still insufficient to produce a general description of their optical properties that could be applied in precision remote sensing algorithms for case 2 waters.

In order to achieve a better understanding of the optical nature of particulate matter in seawater, we need to examine their size distributions and complex refractive indices, (i.e. the real $n(\lambda)$ and imaginary $n'(\lambda)$ parts of the complex refractive index). As we have already mentioned, the latter

²Often described as POM (particulate organic matter).

are associated with light absorption by particulate (or cellular, in the case of plankton cells) matter ‘in solvent’, a_{pm} . By studying this absorption we can determine the values of $n'(\lambda)$ (see footnote 1). The particle size distributions and refractive indices can then be used to model various optical properties of the particles with the aid of relevant theories, such as the Mie theory.

There are several papers presenting certain generalisations regarding the size distributions of various types of particles (e.g. Bader 1970, Risović 1993, Stramski et al. 2001). But articles characterising the refractive indices $n(\lambda)$ and $n'(\lambda)$ are few in number, and most of those refer solely to mineral particles carried out to sea by rivers or wind (e.g. Kent et al. 1983, Woźniak S.B. & Stramski 2004, Babin & Stramski 2004). The least well understood are the spectra of $n(\lambda)$ and $n'(\lambda)$ for the non-living fraction of particulate organic matter (POM) in the sea, even though both refractive indices are generally well understood in the case of phytoplankton, i.e. the living fraction of POM (see e.g. Morel & Ahn 1990, Stramski 1999). In this paper we shall focus primarily on the spectra of the imaginary refractive indices $n'(\lambda)$ for this non-living fraction of POM, although the characteristics we shall be discussing by no means exclude live phytoplankton. In the published literature we have found just one mathematical formula representing the relative spectrum of $n'(\lambda)$ (relative to water) which, according to Stramski et al. (2001), applies to natural suspensions of organic matter in the sea³ and which were obtained on the basis of microspectrophotometric measurements of individual particles sampled in the Sargasso Sea by Iturriaga & Siegel (1989):

$$n'(\lambda) = 0.010658 \exp(-0.007186\lambda), \quad (1)$$

where the index $n'(\lambda)$ is dimensionless and the wavelength λ is expressed in [nm]. Obviously, expression (1) is not of a general nature: it merely describes the averaged spectra of $n'(\lambda)$ for a set of many different suspended organic particles different in origin, shape and size, and chemical structure in the quantitative proportions obtaining in the one basin studied by Iturriaga & Siegel (1989)⁴. Presumably, then, the indices $n'(\lambda)$ for the

³More often in the literature, however, we find the combined refractive indices for certain allogenous organic suspensions, e.g. possible oil-based pollutants such as dispersed oils, which are relatively easy to determine from laboratory measurements (see e.g. Otremba & Król 2001, Otremba & Piskozub 2004).

⁴As we were completing our manuscript a further paper by D. Stramski & S.B. Woźniak (2005) was accepted for publication in *Limnology and Oceanography*. This new paper presents in more detail the data underlying the exponential fit given originally by Stramski et al. (2001). The authors show that the eq. (1) is the average spectrum obtained from the set of 7 different spectral curves of $n'(\lambda)$ corresponding to detrital particles sampled at different depths (between 4 and 60 m) in the Sargasso Sea.

various types of particles of suspended matter and their configurations at different depths in different seas and under different conditions vary to a considerable extent.

The aim of Part 1 of this paper (Part 2 will follow shortly) is to carry out a preliminary assessment of the spectral diversity and the absolute scale of variability of the imaginary refractive indices $n'(\lambda)$ (hence, also of the light absorption coefficients) by various types of suspended POM, including phytoplankton. A further objective is to define the typical spectral characteristics of these indices for the probable sets of POMs occurring in seawaters.

At present, it is not possible to achieve these objectives by means of direct analyses and generalisations of relevant empirical data, simply because such data are unavailable: there is no suitable empirical material relating directly to the magnitudes of $n'(\lambda)$ for various particles of suspended organic matter in the sea. Our knowledge of the structures of these particles is also very scanty. In this paper, therefore, we have calculated the values of $n'(\lambda)$ indirectly, starting from known absorption properties – more specifically, from the mass-specific absorption coefficients – of various naturally occurring organic substances that can occur in seawater. We performed these calculations for model sets of marine organic particles, which we selected on the basis of theoretical speculations and rough assumptions for a first approximation of the problem, the principles of which we shall come to in due course.

In Part 1 of this paper we discuss the most important results of the first stage of the research efforts: (1) the differentiation of hypothetical, modelled chemical classes and physical types of POM in the sea on the basis of what we already know about organic substances occurring in the marine environment; (2) calculations of the light absorption coefficient of particulate matter $a_{pm}(\lambda)$ and the imaginary refractive index $n'_p(\lambda)$ for just a few examples of these chemical classes and physical types of modelled organic particles, namely, for cells of live oceanic phytoplankton and phytoplankton-like particles. A list of the symbols and acronyms used will be found in the Appendix.

In Part 2 we shall present in detail our modelled classes of POM on the basis of the mass-specific light absorption coefficients known for the various components of this matter. We shall analyse the empirical material and evaluate the spectra of the imaginary refractive indices $n'(\lambda)$ for all the classes and types of POM differentiated here in Part 1 of the paper.

2. Selection and general characteristics of the POM covered by the model

2.1. Fundamental assumptions

In view of the complexity of the chemical and physical states of the matter making up the marine environment, the number of possible combinations of physical types and chemical structures of particles suspended in seawater is practically infinite. To distinguish model sets of suspended organic particles in such a way as to reflect the diversity of the particles occurring in various conditions in the sea would therefore seem to be an immensely difficult problem. These particles differ in numerous characteristics, both chemical and physical. The chemical diversity stems from the complexity of the substance forming the individual particles, the proportions of the components making up this substance, and the molecular structures created by these components. The diversity of their physical characteristics is principally the upshot of the differences in the states of matter making up the particles; it is thus due mainly to their mean density, which depends closely on the content of the solid substance of the particle, and also on the liquids (usually water) and gases (usually air) filling the cavities within it or adhering to its outer surface. This potentially vast complexity of particles suspended in the sea means that, for the purposes of modelling their light absorption capacity, we have had to make a number of assumptions in order to simplify their description. As a result, the description of the chemical and physical nature of the suspended organic matter in the sea can be expressed unequivocally by means of a small, finite set of base parameters. With these, we have been able to distinguish a series of model physical types and chemical classes of organic particles occurring in the sea.

As far as the structure of the suspended particles is concerned, the first assumption is that in the general case it is filled with an isotropically distributed mixture of matter consisting of three principal components radically different in their chemical and physical properties, and especially as regards their capacity to absorb light. These three components of organic particles are:

- 1) organic matter, consisting of one or more organic compounds (possibly with inorganic admixtures, apart from air and water), of which at least one is a strong absorber of UV⁵-VIS light;
- 2) water, or more specifically, liquid water, which is an 'average' or 'weak' absorber of UV-VIS light in comparison with the organic absorbers;

⁵The relevant UV wavelengths are $\lambda > 200$ nm, which may be present in daylight entering the sea.

- 3) gases (mainly air), whose absorption of UV-VIS light can be neglected, since it is very much less than the absorption of such light by the other components of the particle.

We further assume that the light absorption capacities (particularly the spectral mass-specific absorption coefficients) of these named principal components of particles are known, as are their fundamental physical properties, such as their densities in given thermodynamic conditions of the sea.

We will go on to show that, given the above assumptions, the resultant absorption coefficients and imaginary refractive indices of POM can be defined unequivocally by means of only three base parameters: the first one, which covers the chemical composition of the particle (1), and two of the three physical characteristics stated below (2-4). The base parameters that we have assumed to differentiate particles are thus the following:

- 1) the chemical content of the organic matter, and where relevant, inorganic admixtures filling empty spaces in suspended particles (apart from water, and air or other gases);
- 2) the relative water content v_w ;
- 3) the relative air content v_a ;
- 4) the relative organic matter content v_{OM} .

By these relative contents of water v_w , air v_a and organic matter v_{OM} we mean the volume ratios of these several components to the volume of the whole particle. These ratios also determine a particle's mean density and buoyancy.

In our further discussion, we shall consider these four (or three⁶) parameters of organic particles suspended in seawater in a simplified manner. Nevertheless, even if we focus only on this small number of distinguishing parameters, our classification of particles with respect to chemical and physical properties (including light absorption) will still be a rather complicated affair. In our later discussions we have limited ourselves to 26 distinct classes of model particle, differing in the chemical substance they are formed from. We define them briefly as the 26 chemical classes of model particles. Moreover, within these 26 classes, we have distinguished a series of particle types differing in their combination of the three physical parameters, i.e. the relative contents of water v_w , air v_a and organic matter v_{OM} . In short, these are the 3 principal physical types of particle

⁶From the obvious relationship between the relative contents of water - v_w , air - v_a , and organic matter - v_{OM} in the form $v_w + v_a + v_{OM} = 1$, we see that if we know two of these parameters, we can define the third unequivocally.

(including subtypes), which differ primarily in their mean density and thus in their buoyancy in the water (see Section 2.3, Fig. 1). We arrived at this classification after having analysed a small number of generalisations of empirical data and theoretical considerations, which we shall explain later. However, the available sets of empirical data are still not enough to carry out a clear division of POM in the sea. We are thus compelled to base our considerations on our general knowledge of the probability with which certain particles will appear and remain in the water, and also on what we know about their interaction with light in the sea, particularly about light absorption by particulate matter. This will become clear as we proceed with our description of the foundations of this classification.

2.2. Model chemical classes of suspended POM

Let us begin with a chemical classification of particle matter suspended in the sea. Since we are primarily interested in the light absorption capabilities of the components of the marine environment, our classification and its analysis will include only those suspended organic particles which are made up of substances strongly absorbing UV and VIS light, along with possible other organic or inorganic admixtures. We can assume that this will cover the majority of organic particles in seawaters. The light-absorbing molecules in them are various unsaturated organic compounds, among them, two groups of low- and medium-molecular weight nitrogen-containing compounds that are very strong UV absorbers, and four groups of medium- or high-molecular weight compounds absorbing UV and/or VIS. They are:

- 1) *amino acids and their derivatives*, including peptides and protein fragments (strong UV absorbers);
- 2) *purine and pyridine compounds*, including nucleic acid fragments (strong UV absorbers);
- 3) *natural proteins* (UV or VIS absorbers);
- 4) *plant pigments* (strong VIS absorbers);
- 5) *humus acids*, i.e. humic and fulvic acids and their mixtures (strong absorbers of UV and VIS);
- 6) *lignins* (UV and VIS absorbers; UV absorption particularly strong).

The first five of these six sets of absorbers are organic compounds produced during biochemical and biogeochemical reactions, and also in a variety of biological processes occurring in all natural terrestrial and marine ecosystems, and also in the bottom sediments (Hansell & Carlson 2002). We can therefore take it as read that all of them, be they of marine or terrestrial origin, are potential components of suspended particulate matter

in the sea, in various concentrations and various relative proportions. In open seawaters these are largely substances formed in the sea itself, that is, they are autogenous products of marine ecosystems. In shelf regions, particularly in river estuaries, they may also to some extent be allogeous substances (terrigenous). Wholly allogeous are the last of the six groups, the lignins, which are organic compounds produced only by the higher plants (trees), and are therefore terrigenous (Meyers-Schulte & Hedges 1986, Staniszewski et al. 2001). We can therefore expect them to occur in considerable amounts, also in the form of suspended particles, in the coastal waters of oceans and in enclosed seas, especially shallow ones like the Baltic (Nyquist 1979, Pempkowiak 1989, Grzybowski & Pempkowiak 2003).

With these premises in mind, and assuming further that every single suspended organic particle strongly absorbing UV-VIS radiation contains at least one of some of the substances from the above-mentioned six principal groups of absorbers (apart from non-absorbing components), we have attempted a chemical classification of these particles. We have made a further important assumption to simplify the subsequent analysis, namely, that particulate organic matter (POM) in the sea consists of the same organic compounds or their combinations occurring in the same proportions as in living animals and plants or as in dissolved organic matter (DOM) in seawater⁷. On this basis, we have identified 26 model classes of particles, which can be divided into the following three types depending on the quantity of organic components they contain:

- *single-component organic particles*⁸ containing (see Table 1a): (1) aromatic amino acids or protein fragments containing these amino acids, which are some of the strongest absorbers of UV, especially in the 200–300 nm range – these are *class A1* particles; (2) ‘mycosporine-like’ amino acids, UV absorbers in the 300–400 nm range – *class A2* particles; (3) natural proteins – *class A3* particles (e.g. natural mixture of single proteins and proteids); (4) phytoplankton pigments with a composition typical of oceanic phytoplankton – *class P1*

⁷This assumption appears to be largely justified by the fact that organic matter in the sea is formed by living organisms and the products of their metabolism and decay. POM in the sea thus consists of these organisms and the particles they produce, and also of other particles formed by the coagulation of dissolved matter. Of course, there may well be organic molecules in the sea other than those we are assuming to be present, with a different chemical composition, but we are unable to define what they are.

⁸The term ‘single-component matter’ is used conventionally and does not imply that this is a single chemical compound. In this paper, this term defines matter containing chemical compounds classified in the same group of compounds, e.g. in a particle containing class A1 compounds various aromatic amino acids, such as a mixture of tryptophan, tyrosine and phenylalanine, may occur simultaneously.

Table 1. List of chemical classes of model suspended organic particles in the sea
a – particles containing one organic component

Symbol	Name of class (kind of organic substance)	Composition and/or origin of organic substances in the suspended particle	Reference*
A1	Aromatic amino acids (protein fragments)	Mixture of compounds: tryptophan, tyrosine and phenylalanine in proportions by weight 1:1:1	(A)
A2	Mycosporine-like amino acids (MAAs)	Natural mixture of compounds: mycosporine-glycine, shinorine and mycosporine-glycine valine, typical of <i>Phaeocystis antarctica</i>	(1)
A3	Natural proteins	Mixture of various amino acids and proteids present in the sea, containing 7.5% by weight of aromatic amino acids	(2)
P1	Ocean phytoplankton pigments	Natural mixture of plant pigments typical of oceanic phytoplankton	(3)
P2	Baltic phytoplankton pigments	Natural mixture of plant pigments typical of Baltic phytoplankton	(4)
N	Purine and pyridine compounds	Mixture of the compounds: adenine, guanine and cytosine in proportions by weight 1:1:1	(A)
L	Lignins	Natural mixture of lignins isolated from Baltic waters	(5)

b – particles consisting of organic humic matter

Symbol	Name of class (kind of organic substance)	Composition and/or origin of organic substances in the suspended particle	Reference*
H1	Baltic humus	Natural mixture of various humus substances isolated from Baltic waters	(5)
H2	Atlantic coastal humus	Natural mixture of various humus substances isolated from Atlantic coastal waters	(6)
H3	Humus from inland waters	Natural mixture of various humus substances, typical of inland waters	(7)
H4	Marine humus	Natural mixture of various humus substances, typical of seawaters	(7)
H5	Sargasso Sea humus	Natural mixture of various humus substances isolated from Sargasso Sea waters	(6)

Table 1. (*continued*)**b** – particles consisting of organic humic matter (*continued*)

Symbol	Name of class (kind of organic substance)	Composition and/or origin of organic substances in the suspended particle	Reference*
H6, H7 and H8	Humus from the Gulf of Mexico	Mixtures of natural fulvic and humic acids isolated from waters of the central Gulf of Mexico in proportions by weight: –0:1 (H6); 1:0 (H7); 0.9:0.1 (H8)	(8)
H9	Fulvic acids from Mississippi estuarine waters	Natural mixture of various humus substances isolated from Mississippi estuarine waters in the Gulf of Mexico	(8)
H10	Soil humic acids	Natural humic acids isolated from the soil	(7)
H11	Soil fulvic acids	Natural fulvic acids isolated from the soil	(7)
H12	Humic acids from bottom sediments	Natural humic acids isolated from bottom sediments	(9)
H13	Fulvic acids from bottom sediments	Natural fulvic acids isolated from bottom sediments	(9)

c – multi-component particles of organic matter

Symbol	Name of class (kind of organic substance)	Composition and/or origin of organic substances in the suspended particle	Reference*
Ph1	Ocean phytoplankton and phytoplankton-like particles	Proteins (49%), chlorophyll <i>a</i> (1%) together with the accompanying set of pigments typical of oceanic phyto- plankton; the remaining organic matter does not absorb light (50%); note that slightly different proportions between proteins and pigments are also possible, but their overall content remains the same	(3) and (10)
Ph2	Baltic phytoplankton and phytoplankton-like particles	Proteins (49%), chlorophyll <i>a</i> (1%) together with the accompanying set of pigments typical of Baltic phyto- plankton; the remaining organic matter does not absorb light (50%); note that slightly different proportions between proteins and pigments are also possible, but their overall content remains the same	(4)

Table 1. (*continued*)**c** – multi-component particles of organic matter (*continued*)

Symbol	Name of class (kind of organic substance)	Composition and/or origin of organic substances in the suspended particle	Reference*
PhM	Polar phytoplankton and phytoplankton-like particles	Composition typical of <i>Phaeocystis antarctica</i>	(1)
Z	Zooplankton and zooplankton and/or nekton-like particles	Proteins (70%); the remaining organic matter does not absorb light (30%)	(11)
D1	Oceanic DOM-like particles	Proteins (1.2%), purine and pyridine compounds (0.3%), Sargasso Sea humus (10%); the remaining organic matter does not absorb light (88.5%)	(A)
D2	Baltic DOM-like particles	Proteins (8%), purine and pyridine compounds (2%), Baltic humus (55%), lignins (18%); the remaining organic matter does not absorb light (17%)	(A)

* References: (1) Moisan & Mitchell 2001; (2) Popov et al. 1979; (3) Woźniak et al. 1999; (4) Ficek et al. 2004; (5) Nyquist 1979; (6) Stuermer 1975; (7) Zepp & Schlotzhauer 1981; (8) Carder et al. 1989; (9) Hayase & Tsubota 1985; (10) Koblenz-Mishke & Vedernikov 1977; (11) Romankievich 1977; (A) The composition and/or origin of organic substances in a particle taken to be an assumption of on the basis of the author's own studies.

particles; (5) phytoplankton pigments with a composition typical of Baltic phytoplankton – *class P2* particles; (6) purine and pyridine compounds, and nucleic acid fragments – *class N* particles; (7) lignin fragments – *class L* particles;

- *particles containing organic humus matter*, which because of the complex nature of humus (cf. e.g. Aiken et al. 1985, Rashid 1985, Spitzky & Ittekkot 1986), can be classified both as quasi-single component matter and as multi-component matter. These particles contain: (1) humus substances originating from various marine basins – *class H1 to H9* particles, and (2) particles formed in soils and bottom sediments – *class H10 to H13* particles. The exact environmental origins of these substances are given in Table 1b;

- *multi-component organic particles*, including those with an organic composition (1) such as in phytoplankton or similar to that of phytoplankton in the oceans (we call these ‘oceanic phytoplankton and phytoplankton-like particles’) and the Baltic (‘Baltic phytoplankton and phytoplankton-like particles’) – *class Ph1* and *Ph2 particles*; (2) resembling that of phytoplankton species growing, for example, under elevated levels of UV (polar regions) and containing large amounts of mycosporine-like amino acids (MAAs) (polar phytoplankton and phytoplankton-like particles) – *class PhM* particles; (3) zooplankton and zooplankton and/or nekton-like particles – *class Z* particles; (4) oceanic DOM-like particles – *class D1* particles and Baltic DOM-like particles – *class D2* particles. As we have said, all these substances are strong UV and/or VIS absorbers. But it is as well to bear in mind that in all these cases, the particulate matter also contains weakly absorbing organic substances. The approximate proportions between the various components of this POM are given in Table 1c.

2.3. Model physical types of POM

Not only the organic content of suspended particles, but their physical characteristics, i.e. the relative contents of water – v_w , air – v_a and organic matter – v_{OM} (see section 2.1) affect the resultant (averaged) absorption properties and the imaginary refractive indices of particle matter. At the same time, these characteristics govern the probability that particles appear in the water and remain suspended there. This is due to the fact that for various combinations of these relative contents, the mean density ρ of the particles may differ, as may their relative buoyancy in the surrounding water, given by $b = (\rho_w - \rho)/\rho_w$. The mean density of a particle can be written as the sum

$$\rho = v_w \rho_w + v_a \rho_a + v_{OM} \rho_{OM}, \quad (2)$$

where ρ_w , ρ_a , and ρ_{OM} are the respective densities of water, air and dry organic matter.

Remembering that $v_w + v_a + v_{OM} = 1$, equation (2) can alternatively be written as the dependence of particle density ρ on the densities of the three components and any two of these relative contents.

It emerges from relationship (2) that a series of physically distinct types of suspended particle is possible – this is illustrated by the relevant ternary graphs in Fig. 1. These graphs were drawn for the following densities assumed for the various components: $\rho_w = 1000 \text{ kg m}^{-3}$, $\rho_a = 0 \text{ kg m}^{-3}$ and $\rho_{OM} = 1400 \text{ kg m}^{-3}$. This last value for dry organic matter is a typical one

and approaches the densities of pure forms of proteins and carbohydrates⁹, i.e. the compounds most commonly present in living organisms; at the same time it includes most of the strong organic absorbers of light. For the sake of accuracy, we should add that in some cases, POM could also be derived from lighter substances (also with a density less than that of water); most of these, however, are not strong UV-VIS absorbers. We shall not be looking at these cases in the present paper.

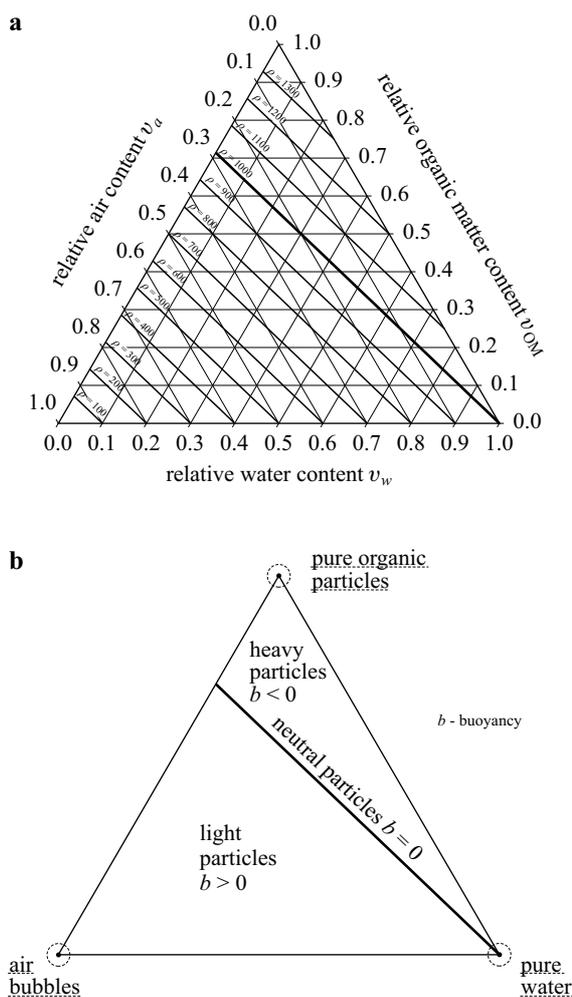


Fig. 1. Ternary graphs showing the relationships between the mean density ρ , or the relative buoyancy b , of model suspended particles and relative contents of water – v_w , air – v_a and organic matter – v_{OM} . (a) isolines of mean density of particles ρ [kg m⁻³] determined using eq. (2) for the following densities of the various components: water – $\rho_w = 1000$ kg m⁻³, air – $\rho_a = 0$ kg m⁻³ and organic matter $\rho_{OM} = 1400$ kg m⁻³; (b) the geometrical areas on these ternary graphs correspond to the various model physical types of suspended particles (explanation in the text)

The graph in Fig. 1a shows the model relationship between the densities of POM in the sea (in the form of isolines) and the simultaneous relative

⁹This is c. 1335 kg m⁻³ for proteins and c. 1530 kg m⁻³ for carbohydrates – after Morel & Ahn (1990).

contents of organic matter, water and air. Fig. 1b shows the areas of this relationship corresponding to particle densities greater or smaller than the density of water, and hence their negative or positive buoyancy. Thus, we can distinguish three principal model physical types of particle, differing fundamentally in their buoyancy b in the water. Let us call them:

- 1) *neutral (or free) particles*, with a zero buoyancy $b = 0$;
- 2) *heavy particles*, with a negative buoyancy $b < 0$;
- 3) *light particles*, with a positive buoyancy $b > 0$.

From the physical point of view we can also distinguish ‘dry’ particles, containing no water, but only two components – organic matter and air. Their geometric position on Fig. 1 is the left-hand axis of the graph. In one extreme case, such particles may be free of air: they are single-component particles consisting solely of organic matter (on Fig. 1 they are situated in the upper apex of the triangle), and in another extreme case, the particles may simply be bubbles of air (Fig. 1 – lower left apex). Yet other particles may be gas-free, consisting of the two components of organic matter and water. Their geometric position on Fig. 1 is on the right-hand axis of the graph. Apart from these two-component particles (or single-component particles in extreme cases) we can also have particles made up of all three components – organic matter, gas and water. Their place on Fig. 1 is the entire area of the triangle.

In this classification we could also take a further parameter into account – the relative inorganic matter content of a particle. However, we have neglected this on the assumption that it is relatively small in marine POM and affects light absorption to only a slight extent. The particle matter we are writing about here may consist of *living plankton cells and bacteria, detrital cellular matter* and other organic matter.

In view of the obvious diversity and numbers of possible physical types of suspended particles, our analysis of the absorption properties of such particle matter is restricted mainly to selected examples among the three physical types of particle mentioned below. In making this choice we have tried to take into consideration the kinds of particles that are likely to occur most commonly in the sea.

Two of these types refer to particles with neutral buoyancy and one to particles with negative buoyancy:

- a) neutral (free)¹⁰ dry particles, that is, particles with a mean density ρ approximately the same as that of the surrounding seawater, whose

¹⁰i.e. of neutral or practically neutral buoyancy.

organic matter does not contain water-filled cavities, but may contain air- or gas-filled spaces; together with these latter, the particle achieves neutral buoyancy;

- b) neutral (free) wet particles, that is, particles with a mean density ρ approximately the same as that of the surrounding seawater, but differing from the dry particles in that they contain water-filled spaces and together with that water and possibly air achieve neutral buoyancy. Theoretically, their relative water content can vary from 0% to 100%; in the extreme cases, the particle would become a *water particle* ($v_w = 1$), or a free, dry particle ($v_w = 0$);
- c) pure heavy particles (pure organic particles), from the upper apex of the triangle in Fig. 1. Devoid of air- or water-filled spaces, they have a decidedly negative buoyancy, so in the absence of other forces acting on them in the water, they will sink.

The first two of these types of particle (free dry and free wet) are freely suspended in the water, since the forces of gravity and upthrust acting on them in opposite directions balance each other out. This probably applies to the majority of large particles suspended in seawater (of the order of 100 μm , but not only), since large particles with distinctly negative or positive buoyancies gradually sink or rise up to the surface¹¹. If in certain situations such particles are produced in the sea, they are likely to remain in suspension for a far shorter time than free particles. On the other hand, most heavy organic particles in the sea are probably small ones (of the order of 1–10 μm , and also smaller colloids), consisting of pure or almost pure organic matter. Their dimensions must be appropriately small, because only then can their rate of sinking be very slow, of the order of 1 to 100 m per year (see, e.g. Dera 2003). It has to be said, however, that small organic particles, lighter than water, can also occur in the water, with an equally slow rate of rise to the surface. These may be tiny particles of heavy organic matter adhering to larger gas bubbles.

¹¹But the rate of free fall of particles in the sea is small, e.g. that of organic particles with a mean density of 1100 kg m^{-3} and diameter 1 μm is only c. $4 \times 10^{-8} \text{ m s}^{-1}$, and with a diameter of 100 μm is c. $4 \times 10^{-4} \text{ m s}^{-1}$; obviously, this assumes that the particles are not carried along by currents or other turbulent movements of the water and are not subject to any other processes. Generally speaking, however, this assumption does not hold in the sea: particles are at the mercy of the water's movements, they coagulate, dissolve in the water or clump together in large aggregates following their consumption by marine organisms (see e.g. Dera 2003).

3. Example results: spectra of the light absorption coefficient and the imaginary part of the refractive index of particulate matter for phytoplankton cells and phytoplankton-like particles

The methodology of calculating the light absorption coefficient of the particle matter $a_{pm}(\lambda)$ and the imaginary part of refractive index $n'_p(\lambda)$, along with the full set of input data and the results of the computations of these coefficients for the model organic particles distinguished here, will be presented in Part 2 of this paper, which we hope to publish in the next issue of *Oceanologia*. Here we shall just give an example of such calculations in order to illustrate the influence of the chemical composition of the organic particle and its aqueous and gaseous admixtures on the spectra and the absolute values of the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ of that particle. The example of these input data and results of calculations refers here to oceanic phytoplankton cells and to phytoplankton-like particles (see class *Ph1* in Table 1c), and is presented in the form of plots in Figs 2–6 and in Tables 2 and 3. By ‘phytoplankton-like particles’ we mean particles whose organic matter content is the same as that in live phytoplankton cells, and which come into being as a result of their death or their sustaining damage, or a series of natural physical processes such as fragmentation, coagulation, hydration or dehydration, and aeration or de-aeration. The plots on Figs 2–6 illustrate, among other things, the effect of the diverse pigment content of phytoplankton (determined by the trophic type of sea and the irradiance) and also the various possible relative contents of other organic matter, water and gas on the natural range of variability of $a_{pm}(\lambda)$ and $n'_p(\lambda)$. These plots characterise the absorption properties of the material of this large set of phytoplankton cells and phytoplankton-like particles.

3.1. Input data and an outline of the calculations

The input data for the calculations of the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for phytoplankton cells and phytoplankton like particles include:

- 1) the set of chlorophyll-specific coefficients of light absorption by phytoplankton pigments in the ‘in solvent’ state. This set covered the widest possible range of naturally occurring specific absorption coefficients $a^*_{pl,S}(\lambda)$, (see the solid lines on Fig. 2a). The spectra of these coefficients were defined with the aid of our earlier statistical models of photo- and chromatic acclimation and of light absorption by phytoplankton (Woźniak et al. 2000, 2003, Majchrowski et al. 2000), which made use of a variety of possible pigment combinations. The quantitative composition of these pigments and the factors

determining it, such as the underwater irradiance and the trophic type of waters, are given in the caption to Fig. 2.

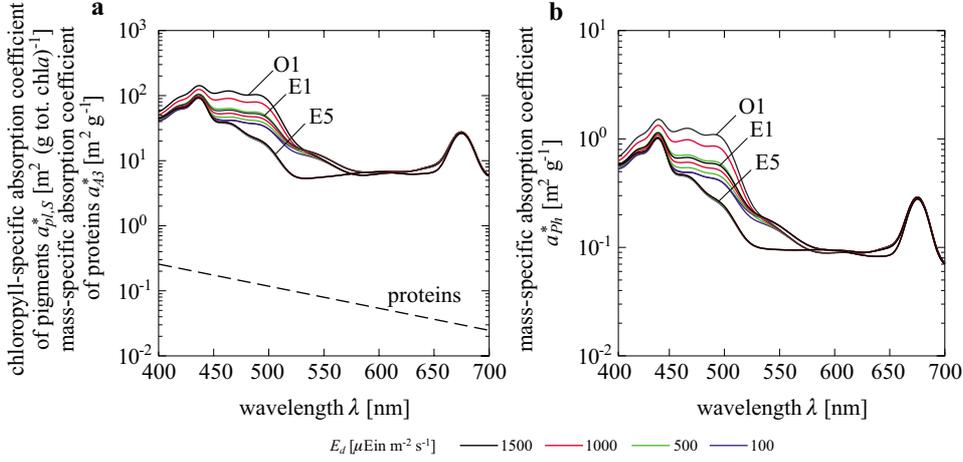


Fig. 2. Absorption spectra providing the input data for the calculations: (a) *solid lines* – the set of spectra of chlorophyll-specific coefficients of light absorption by phytoplankton pigments in the ‘in solvent’ state $a_{pl,S}^*(\lambda)$, characteristic of different trophic types of sea (O1 – superoligotrophic, i.e. with a chlorophyll *a* concentration C_a [mg tot. chl a m⁻³] in the range 0.02–0.05, E1 – eutrophic with C_a in the range 1.0–2.0, and E5 with C_a in the range 20–50) and for different irradiance conditions (the underwater PAR irradiance values (400–700 nm) E_d [μ Ein m⁻² s⁻¹] are given in the Figure; in the case of type E5, the curves for the different irradiances overlap). These spectra were determined on the basis of statistical models of photo- and chromatic acclimation and of light absorption by phytoplankton (after Woźniak et al. 2000, 2003, Majchrowski et al. 2000), for various possible sets of phytoplankton pigments (including diametrically different ones), determined by the trophic type and the magnitude of the underwater irradiance. The quantitative comparisons of these pigments characterise the ratio of the contents of chlorophyll *b* (C_b), chlorophyll *c* (C_c), photosynthetic carotenoids (C_{PSC}) and photoprotecting carotenoids (C_{PPC}) to chlorophyll *a*, which for the cases analysed here are given in Table 2; *dashed line* – the approximate spectrum of the mass-specific coefficient of light absorption by a mixture of natural proteins (see eq. (3)); (b) spectra of the mass-specific coefficients of light absorption referring to the whole of the organic matter contained in phytoplankton cells $a_{Ph}^*(\lambda)$, calculated from equation (4) for the same cases as in Fig. 2a

- 2) the spectrum of the mass-specific coefficients of light absorption for mixtures of natural proteins $a_{A3}^*(\lambda)$, which can be described by the approximate relationship which we derived for VIS light¹²:

¹²The complete formula approximating the spectra of the mass-specific absorption of light in the 200–700 nm wavelength range for most proteins, which we based on the

$$a_{A3}^*(\lambda) = 0.94 \exp(-0.00768(\lambda - 220)), \quad (3)$$

where $a_{A3}^*(\lambda)$ is expressed in $[\text{m}^2 \text{g}^{-1}]$ and λ in $[\text{nm}]$.

The spectrum of this coefficient is illustrated by the dashed line on Fig. 2a.

Table 2. The sets of phytoplankton pigment ratios C_i/C_a for different trophic types of waters (defined by corresponding values of C_a) and at different irradiance conditions E_d used in the calculations, the results of which are shown in Figs 2 to 4

Trophic type	Total chlorophyll <i>a</i> concentration C_a [mg tot. chl <i>a</i> m^{-3}]	Pigment ratio C_i/C_a	Irradiance conditions			
			$E_d = 100$ $\mu\text{Ein m}^{-2} \text{s}^{-1}$	$E_d = 500$ $\mu\text{Ein m}^{-2} \text{s}^{-1}$	$E_d = 1000$ $\mu\text{Ein m}^{-2} \text{s}^{-1}$	$E_d = 1500$ $\mu\text{Ein m}^{-2} \text{s}^{-1}$
O1	0.035	C_{PPC}/C_a	0.239	0.4917	0.8073	1.123
O1	0.035	C_b/C_a	0.1173	0.1173	0.1173	0.1173
O1	0.035	C_c/C_a	0.1226	0.1226	0.1226	0.1226
O1	0.035	C_{PSC}/C_a	0.4325	0.4325	0.4325	0.4325
E1	1.5	C_{PPC}/C_a	0.1915	0.2536	0.3312	0.4089
E1	1.5	C_b/C_a	0.1047	0.1047	0.1047	0.1047
E1	1.5	C_c/C_a	0.1736	0.1736	0.1736	0.1736
E1	1.5	C_{PSC}/C_a	0.52	0.52	0.52	0.52
E5	35	C_{PPC}/C_a	0.1776	0.1841	0.1923	0.2004
E5	35	C_b/C_a	0.044	0.044	0.044	0.044
E5	35	C_c/C_a	0.2318	0.2318	0.2318	0.2318
E5	35	C_{PSC}/C_a	0.1057	0.1057	0.1057	0.1057

In the first stage of calculations, the spectra of $a_{pl,S}^*(\lambda)$ and $a_{A3}^*(\lambda)$ were used as input data for estimating the spectral mass-specific coefficients of light absorption $a_{Ph}^*(\lambda)$ of the entire organic matter of the phytoplankton cells or phytoplankton-like particles. To simplify things, it was assumed that about half of this organic matter consisted of substances with a negligible light absorption, while the other half consisted of two groups of compounds – various proteins, and chlorophyll together with its accessory pigments. It was also assumed that the weight ratio of proteins and accessory pigments

statistical analysis of a set of over a dozen empirical absorption spectra of various forms of protein, will be presented in Part 2. This formula also takes account of the occurrence of aromatic amino acids in quantities typical of those obtaining in seawaters.

to chlorophyll *a* was 49:1¹³. Given these assumptions, the spectra of the coefficients $a_{Ph}^*(\lambda)$ for all the sets of pigments analysed here were determined from the formula:

$$a_{Ph}^*(\lambda) = 0.01a_{pl,S}^*(\lambda) + (0.49 - 0.01\Sigma C_{acc}/C_a)a_{A3}^*(\lambda), \quad (4)$$

where C_{acc}/C_a is the ratio of the accessory pigment content to the chlorophyll *a* content in the cell. The spectra described by equation (4) are illustrated on Fig. 2b.

The next and main stage in our calculations was to determine in turn: (1) spectra of the light absorption coefficient of the particle material $a_{pm}(\lambda)$, i.e. for all the matter in the organic particle, including the water and air trapped in it, and (2) spectra of the absolute imaginary refractive index $n_p'(\lambda)$ of these particles. For this purpose we used the following approximate relationships of the coefficients $a_{pm}(\lambda)$, expressed as functions that will be discussed in detail in Part 2 of the paper:

– the function of the intracellular concentration of organic matter C_{OM} , for the case of phytoplankton, whose cells we here treat as neutral particles ($\rho = \rho_w$) or as heavy particles with densities not greatly exceeding that of water ($\rho \cong \rho_w$):

$$a_{pm} = a_w \left(1 - \frac{C_{OM}}{\rho_w}\right) + a_{Ph}^* C_{OM}; \quad (5)$$

– the function of any two of the three relative contents of air v_a , water v_w and organic matter v_{OM} for phytoplankton-like particles, that is, for the general case of particles of any density:

$$a_{pm} = a_w v_w + a_{pm,dry} (1 - v_a - v_w), \quad (6a)$$

$$a_{pm,dry} = a_{Ph}^* \rho_{OM}, \quad (6b)$$

where $a_{pm,dry}(\lambda)$ represents the spectra of the light absorption coefficient of the particulate matter $a_{pm}(\lambda)$ for particles containing only dry organic matter; $a_w(\lambda)$ represents the spectra of the light absorption coefficient of

¹³The investigations of various authors (see e.g. Koblentz-Mishke & Vedernikov (1977) and Kirk (1994) and the papers cited there) indicate that in fact both of the mass ratios assumed here (absorbing substances to non-absorbing substances, and proteins to chlorophyll *a*) differ. This applies in particular to chlorophyll, whose content in the total mass of organic matter depends on both the species of phytoplankton and its conditions for growth, and can vary from fractions of one per cent to several per cent. Nevertheless, in our estimation, the proportions we have assumed here are close to the average values, although the modelled values do very occasionally overestimate the real ratios between the contents of the various groups of organic compounds contained in cells under natural conditions. We can thus assume that these discrepancies do not seriously affect the estimates and plots of the spectral coefficients $a_{Ph}^*(\lambda)$ (or of $a_{pm}(\lambda)$ or $n_p'(\lambda)$) of phytoplankton and phytoplankton-like particles, typical of the conditions generally obtaining in the World Ocean.

pure water (in our calculations we took the value of this coefficient as given by Pope & Fry 1997); C_{OM} – the intracellular concentration of the organic matter of the phytoplankton.

Finally, for determining the value of the absolute imaginary refractive index $n'_p(\lambda)$ of both types of particle, the relationship between the index $n'_p(\lambda)$ and the coefficient of light absorption $a_{pm}(\lambda)$ was used (Born & Wolf 1968, van de Hulst 1981):

$$n'_p(\lambda) = \frac{a_{pm}(\lambda)\lambda}{4\pi}. \quad (7)$$

As can be seen from equations (5)–(7), determining typical values and the range of differentiation of the spectral coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for the particles under scrutiny here requires a knowledge *inter alia* of the natural concentrations of the organic matter they contain C_{OM} for phytoplankton cells, and the relative contents of air v_a , water v_w , and organic matter v_{OM} for phytoplankton-like particles.

The results of numerous studies (e.g. Mullin et al. 1966, Verity et al. 1992, Stramski 1999, Stramski et al. 2002, DuRand et al. 2002) show that the intracellular concentration of organic carbon (making up about half the mass of all the organic matter) in naturally-occurring phytoplankton cells can take a wide range of values – from low ones of c. 20 kg m^{-3} (occasionally 10 kg m^{-3}) to extremely high ones of c. 500 kg m^{-3} . In view of this, we performed our calculations of the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for phytoplankton for two extreme concentrations of intracellular organic matter C_{OM} , namely, 50 kg m^{-3} as the lower boundary, and 1000 kg m^{-3} as the upper one¹⁴. On the other hand, the calculations for the phytoplankton-like particles were carried out for various possible combinations of relative contents v_a , v_w , v_{OM} , from anhydrous (dry) and gas-free particles (dry organic matter), to particles practically devoid of any organic matter. We also assumed that the density of the dry organic matter filling these particles takes some value intermediate between the densities of proteins and carbohydrates, roughly equal to $\rho_{\text{OM}} = 1400 \text{ kg m}^{-3}$ (see footnote 9).

3.2. The results of our calculations

All the spectra of the light absorption coefficients $a_{pm}(\lambda)$ and of the absolute imaginary refractive index $n'_p(\lambda)$ of the entire intracellular material

¹⁴In the light of our earlier assumption that chlorophyll makes up 1% of the mass of the intracellular organic matter in phytoplankton, the assumption of these extreme values of C_{OM} is equivalent to assuming that the natural differentiation in intracellular chlorophyll concentrations lies approximately between c. 0.5 and 10 kg m^{-3} ; this is in agreement with the results of empirical studies (see e.g. DuRand et al. (2002) and the references cited there).

in the phytoplankton are shown in Fig. 3. They were calculated for extreme intracellular organic matter concentrations C_{OM} and for different pigment compositions determined by the trophic type of the waters and the ambient irradiance. The figure shows that the differences in the spectra affect both the absolute values of the absorption coefficients and their shapes. This differentiation in absolute values, which may be twenty-fold and more for individual light wavelengths, is primarily the consequence of the similar, natural differentiation of the intracellular organic matter concentration C_{OM} . This differentiation is also due to the various pigment compositions, particularly in the medium- and short-wave VIS range, i.e. for $\lambda < 570$ nm. It is greatest for light with a wavelength around 500 nm and, as the distributions of the spectra of $a_{pm}(\lambda)$ in Fig. 3a and the spectra of $n'_p(\lambda)$ in Fig. 3b show, the values of the coefficients can vary around fourfold for the same concentrations C_{OM} . The pigment composition in phytoplankton thus affects the values of both these coefficients to a lesser extent, but is nevertheless the principal factor responsible for the differentiation of their spectral features, especially in the Soret band region and the middle part of the visible spectrum. Hence, at fixed concentrations C_{OM} , the corresponding coefficients $a_{pm}(\lambda)$ (Fig. 3a) and $n'_p(\lambda)$ (Fig. 3b) in the aforementioned spectral intervals are highest for oligotrophic waters, especially in their surface layers, i.e. for phytoplankton rich in various plant

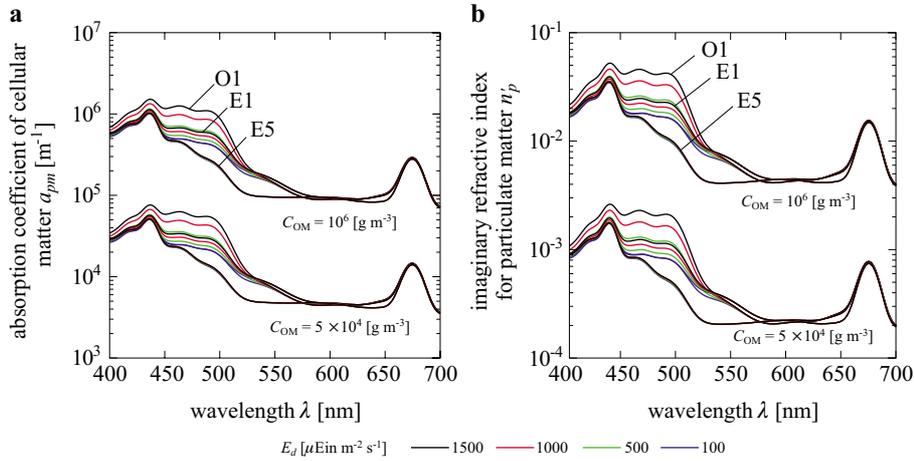


Fig. 3. Model spectra of light absorption by cellular matter $a_{pm}(\lambda)$ (a), and of the imaginary parts of the absolute refractive index of light $n'_p(\lambda)$ for phytoplankton, calculated for different trophic types of waters and different irradiance conditions (see the caption to Fig. 2a) (b), assuming extremely high and extremely low intracellular concentrations of organic matter C_{OM}

pigments¹⁵ (see the O1 curves for the irradiance of $1500 \mu\text{Ein m}^{-2} \text{s}^{-1}$ on those plots). They diminish in value with the trophicity of the water, reaching the lowest values in eutrophic seas, in which the phytoplankton contains smaller amounts of accessory pigments. In contrast, we can see from the plots in Fig. 3 that the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ are no longer dependent on the pigment composition in the long-wave part of the visible spectrum. This is an obvious consequence of the fact that most accessory pigments (except some forms of biliprotenoids) do not absorb light from this spectral range, the only absorbers here being the chlorophylls (especially chlorophyll *a*).

The other group of suspended particles, whose coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ have been calculated here, are the phytoplankton-like particles, which are the remains of phytoplankton cells broken up by purely physical processes (Figs 4 and 5 illustrate the results of these calculations). Assuming a physical mechanism for the formation of these particles from live cells, we also conjectured that the chemical composition of the organic matter in these particles is identical with that in live phytoplankton cells. But they probably differ from phytoplankton only in their relative contents of water and gases, which in this case can take very different values. Thus, as expected, the shapes of the spectra of absorption and of the imaginary refractive index $a_{pm}(\lambda)$ and $n'_p(\lambda)$ are in most of the graphs¹⁶ identical with that of phytoplankton containing the same sets of pigments. Quite different, however, are the absolute values and the diversity of $a_{pm}(\lambda)$ and $n'_p(\lambda)$. As we have already shown, these values for phytoplankton for fixed wavelengths differ by not much more than one order of magnitude (only 20 times), but in the case of phytoplankton-like particles the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ characteristic of them can, theoretically, take values differing by many orders of magnitude. The largest values of $a_{pm,dry}(\lambda)$ are typical of pure organic particles, i.e. dry ($v_w = 0$) and also air-free ($v_a = 0$); in other words, they are composed exclusively of dry organic matter ($v_{OM} = 1$). This is illustrated by the continuous-line spectra in Figs 4a and 4b. The values of the coefficients $a_{pm,dry}(\lambda)$ there are 1.4 times greater than the maximum

¹⁵Owing to the high level of irradiance in the water under these conditions (see, for instance, our papers on photo- and chromatic acclimation in phytoplankton, e.g. Majchrowski & Ostrowska (1999, 2000), Woźniak et al. (2003)), there are large quantities of accessory photo-protecting pigments (various carotenoids), strong absorbers of light in this spectral range, besides chlorophyll and other accessory photosynthetic pigments.

¹⁶The only exceptions here are the spectra of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for the hypothetical case of such particles with very high water contents, containing only trace amounts of organic material (see Fig. 5a, the spectrum in the lower part of the plot), which will be discussed in due course.

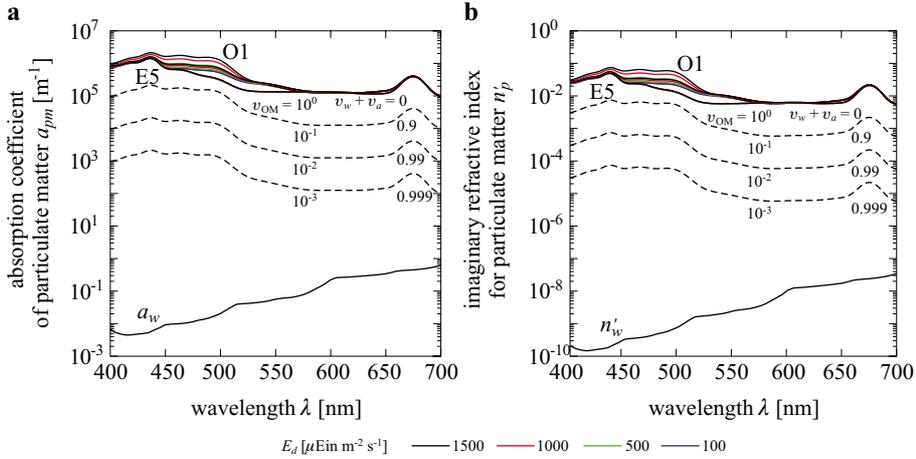


Fig. 4. Model spectra (a) of light absorption by particle material $a_{pm}(\lambda)$, and (b) of the imaginary parts of the absolute refractive index of light $n'_p(\lambda)$ for phytoplankton-like particles, calculated for various possible combinations of pairs of the following parameters: v_{OM} (relative organic matter content) and $(v_w + v_a)$ (sum of the relative contents of water and air); *solid lines* – in the upper parts of the graphs – spectra of $a_{pm,dry}(\lambda)$ and $n'_{p,dry}(\lambda)$, that is, of the highest possible values of coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$, characteristic of suspensions made up of dry organic matter (i.e. $v_{OM} = 1$ and $(v_w + v_a) = 0$), calculated for various compositions of pigments occurring in different trophic types of waters and for different irradiance conditions (see the caption to Fig. 2a); *dashed lines* – spectra of these coefficients for one single pigment composition (the one for the highest solid lines), calculated for the other combinations of parameters v_{OM} and $(v_w + v_a)$; *solid lines* – in the lower parts of the graphs – spectra of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for water particles (i.e. pure water)

values for phytoplankton cells¹⁷. As the relative contents of water and air v_w and v_a increase, and so, as the relative organic matter content v_{OM} in these phytoplankton-like particles falls, their coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ also decrease. The example spectra of these coefficients in Figs 4a and 4b (the dashed lines) illustrate this.

Over a wide range of variability of the relative organic matter content v_{OM} (from the largest $v_{OM} = 1$ to small v_{OM} of the order of 10^{-5} , which is equivalent to $v_w + v_a = 0.99999$), the values of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ are practically proportional to v_{OM} and do not display any obvious dependence on the water content of the particle, which, formally, there should be

¹⁷This factor of 1.4 emerges from the assumption in our calculations that the density of dry organic matter $\rho_{OM} = 1400 \text{ kg m}^{-3}$, i.e. is 1.4 times greater than the maximum intracellular concentration of organic matter in phytoplankton cells $C_{OM} = 1000 \text{ kg m}^{-3}$ assumed in the calculations.

according to formula (6a). This can be explained by the fact that the amount of light absorbed by the organic matter (even though there is not much of it) is very much greater than that absorbed by the water. Obviously, this is because the mass-specific absorption coefficients of visible light for water are many orders of magnitude smaller than the corresponding coefficients for the organic substances we are analysing here. The light absorption by the water contained in the phytoplankton-like particles may therefore dominate the resultant absorption by these particles for extremely low values of v_{OM} . This is illustrated by the graphs in Fig. 5a, which show some spectra of the imaginary refractive index $n'_p(\lambda)$. They have been calculated for the case of two-component particles (organic-water, without air) for various proportions of the relative water content v_w and the relative organic matter content v_{OM} over the whole range of their possible values, that is from 0 to 1. As is evident from Fig. 5a, when v_{OM} in the particle is less than 10^{-5} (i.e. the water content $v_w > 0.99999$), values of n'_p are no longer proportional to v_{OM} (the spectral plots are bunched). Moreover, when the value of v_{OM} approaches zero, these imaginary refractive indices diminish to a finite limiting value, which is in fact the imaginary refractive index for water n'_w . According to this regularity, the spectra of the light absorption $a_w(\lambda)$ and those of the imaginary refractive index $n'_w(\lambda)$ for water set the lower limits to the range of possible differentiation of $a_{cm}(\lambda)$ and $n'_p(\lambda)$ as presented in Fig. 5a for two-component particles containing organic matter and water but not air.

Meticulous analysis of the dependence of the average absorption properties of the whole material contained in phytoplankton-like particles (see footnote 18) on their physical properties has shown that the aforementioned restriction also applies to three-component particles (i.e. also containing air), that is, to all neutral (free-floating) particles ($\rho = \rho_w$), all heavy particles ($\rho > \rho_w$) and most possible light particles ($\rho < \rho_w$). This restriction is inapplicable only to the highly improbable cases of two-component gas-water particles (including single-component air bubbles but excluding hypothetical single-component water particles) and to particles with extremely low organic contents or extremely low densities¹⁸. In such

¹⁸Starting from equations (2), (6) and (7), and assuming that the absorption coefficients and density of air are equal to zero and that $v_w + v_a + v_{\text{OM}} = 1$, we can write the dependence of a_{pm}/a_w (or n'_p/n'_w) on the mean density of a particle ρ and on the relative organic matter content v_{OM} in the form: a_{pm}/a_w (or n'_p/n'_w) = $\rho/\rho_w - v_{\text{OM}}(\rho_{\text{OM}}/\rho_w + a_{pm,dry}/a_w)$. It emerges from this relationship that when $a_{pm,dry} > a_w$ (e.g. $a_{pm,dry}/a_w = 10^{-7}$) and $\rho_{\text{OM}} > \rho_w$, (e.g. $\rho_{\text{OM}}/\rho_w = 1.4$), that is, under the conditions that are satisfied by the model particles analysed here, the above-mentioned ratios of absorption coefficients and imaginary refractive indices take values less than unity (i.e. $a_{pm} < a_w$ or $n'_p < n'_w$) solely with respect to light

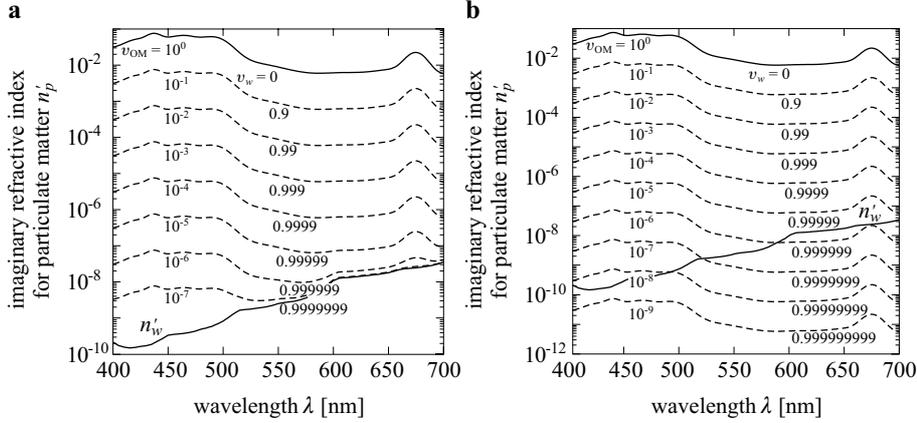


Fig. 5. Model spectra of the imaginary parts of the absolute refractive index of light $n'_p(\lambda)$ for phytoplankton-like particles, calculated for (a) two-component, organic-water particles (i.e. air-free, $v_a = 0$) with various possible combinations of v_{OM} (relative organic matter content) and v_w (relative content of water); (b) two-component, organic-gas particles (i.e. dry, water-free, $v_w = 0$) with various possible combinations of v_{OM} (relative organic matter content) and v_a (relative content of air); *solid lines* – in the upper parts of the graphs – spectra of $n'_{p,dry}(\lambda)$, that is, the highest possible values of $n'_p(\lambda)$, characteristic of suspensions of dry organic matter (i.e. $v_{OM} = 1$ and $(v_w + v_a) = 0$), calculated for one pigment composition (the one for the highest solid lines in Figs 2–4); *dashed lines* – the spectra of these coefficients for the same composition, calculated for the other combinations of v_{OM} and v_w (a), and v_{OM} and v_a (b); *solid lines* – in the lower parts of the graphs – spectra of the absolute refractive index of light for water particles (i.e. pure water)

cases, as the organic content diminishes ($v_{OM} \rightarrow 0$), the values of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ can decrease infinitely and reach values below the boundary values of $a_w(\lambda)$ and $n'_w(\lambda)$. This situation is illustrated in Fig. 5b for two-component, organic-gas particles. But since the occurrence of such particles in sea water is very unlikely, it seems justified to assume that the lower boundaries of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for intraparticulate material in the vast majority of suspended organic particles are set by the limiting values of $a_w(\lambda)$ and $n'_w(\lambda)$ characteristic of pure water.

Selected results of model calculations of the properties of the particle material in model phytoplankton cells and phytoplankton-like particles are compared in the plots in Fig. 6 and Table 3 (numerical data). There we give

particles with very low values of v_{OM} , defined by the following approximate inequality: $v_{OM} < 10^{-7}(\rho_w - \rho)/\rho_w$. For example, such values of v_{OM} defined on the basis of the above inequality are: $v_{OM} < 10^{-7}$ for $\rho = 0.01 \rho_w$, $v_{OM} < 0.5 \cdot 10^{-7}$ for $\rho = 0.5 \rho_w$, $v_{OM} < 10^{-8}$ for $\rho = 0.9 \rho_w$ and $v_{OM} < 10^{-9}$ for $\rho = 0.99 \rho_w$.

the very highest and very lowest values from the set of all calculated spectra of the imaginary part of the absolute refractive index $n'_p(\lambda)$ for both groups of particles (curves 2, 3 and 4, plus the spectrum of $n'_w(\lambda)$). Fig. 6 and Table 3 therefore illustrate the probable natural ranges of differentiation of the index $n'_p(\lambda)$ characteristic of phytoplankton cells (the area between curves 3 and 4) and for phytoplankton-like particles in the World Ocean (the area between curve 2 and the spectrum of $n'_w(\lambda)$). In addition, Fig. 6 and Table 3 (see curve 1) also show the independently calculated¹⁹ spectrum of $n'_p(\lambda)$ for model particles consisting solely of dry organic matter, that is, made up of nothing but phytoplankton pigments, in the proportions typical of phytoplankton with the highest values of $a_{pl,S}^*(\lambda)$, (that is, as in Fig. 2a for curve O1 at an irradiance of $E_d = 1500 \mu\text{Ein m}^{-2} \text{s}^{-1}$). Such hypothetical particles, which are, for instance, chloroplast fragments that may form when dead algae cells break up, are some of the strongest absorbers of visible light among the various possible particles produced by the physical fragmentation of cells. We can thus assume that the area between curve 1 and the spectrum of $n'_w(\lambda)$ in Fig. 6 illustrates the range of natural differentiation in the World Ocean of the imaginary refractive indices for all particles originating from plankton cells.

3.3. Discussion and summary of results

As we can see from the data in Fig. 6 and in Table 3 (also Figs 3 to 5), the absorption properties of the particle material in phytoplankton cells and phytoplankton-like particles are subject to considerable differentiation with respect not only to the spectral structure of the coefficients $a_{pm}(\lambda)$ and the index $n'_p(\lambda)$, but also to their absolute values. This differentiation is at its most evident in the short- and medium-wave interval of the visible spectrum ($< 570 \text{ nm}$) for $a_{pm}(\lambda)$ and $n'_p(\lambda)$. This is mainly due to the differentiation in the phytoplankton pigment content, which in turn is governed primarily by the trophicity and ambient irradiance of the seawaters in question. However, the various pigment contents do not directly cause any significant differentiation in the absolute values of $a_{pm}(\lambda)$ and $n'_p(\lambda)$, since this differentiation depends largely on the intracellular concentration of organic matter in the case of phytoplankton cells, or on the relative contents of air and/or water in the case of phytoplankton-like particles.

¹⁹According to equations (5) and (7), by substituting $a_{Ph}^*(\lambda)$ with the corresponding mass-specific absorption coefficient of light by all phytoplankton pigments $a_{pig,S}^*(\lambda)$, determined on the basis of $a_{pl,S}^*(\lambda)$ from the relationship: $a_{pig,S}^*(\lambda) = (C_a/\Sigma C)a_{pl,S}^*(\lambda)$, where $C_a/\Sigma C$ denotes the ratio of the chlorophyll *a* content to the total content of all phytoplankton pigments.

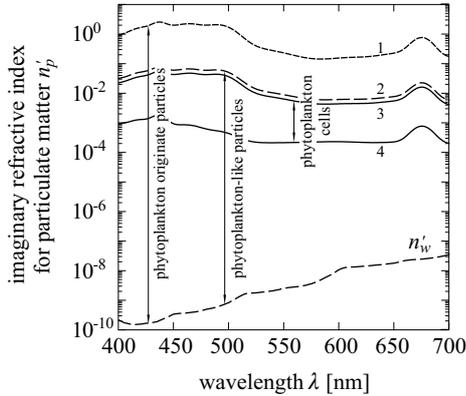


Fig. 6. Comparison of the probable ranges of natural differentiation of the most common spectra of the imaginary parts of the absolute refractive index of light for oceanic phytoplankton cells (area between curves 3 and 4) and their associated phytoplankton-like particles (area between curves 2 and n'_w) and phytoplankton generic particles (area between curves 1 and n'_w). The various curves present model spectra of this index for: *curve 1* – particles containing dry organic matter composed only of phytoplankton with a composition typical of the highest irradiances and of oligotrophic waters O1; *curve 2* – particles containing dry organic matter composed of all the organic substances in phytoplankton with a composition typical of the highest irradiances and of oligotrophic waters O1; *curve 3* – phytoplankton cells with the highest possible intracellular concentrations of organic matter ($C_{OM} = 10^6 \text{ g m}^{-3}$) with a composition typical of the highest irradiances and of oligotrophic waters O1; *curve 4* – phytoplankton cells with the lowest possible intracellular concentrations of organic matter ($C_{OM} = 5 \times 10^4 \text{ g m}^{-3}$) with a composition typical of eutrophic waters E5; n'_w – for water particles (i.e. pure water)

These model analyses have shown that the natural diversity in the absolute values of $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for phytoplankton cell material is greater than one order of magnitude – it is a factor of more than 20. This result of our model calculations appears to be corroborated by empirical data. So, for example, the n'_p data set for various systematic units of phytoplankton presented by Stramski et al. (2001) coincides very well with the range of variability of this index, here illustrated in Fig. 6 (the area between curves 3 and 4). But this is not a large difference in comparison with the differences in the absorption characteristics for phytoplankton-like particles, that is, particles containing organic matter similar to that in the phytoplankton from which they are derived. As a result of hydration and aeration, and also the reverse processes of dehydration and de-aeration in dead plankton cells, the suspended particles formed from them have a far wider range of absorption properties than live phytoplankton. Expressed

Table 3. Values of the imaginary part of the absolute refractive index of visible light of selected wavelengths for selected particle cases 1–4 and n'_w ; explanations below the table

Particle	Imaginary part of the refractive index n' for wavelength λ (nm)						
case	400	440	480	500	520	540	560
1	8.95E-01	2.41E+00	1.95E+00	1.64E+00	4.84E-01	2.69E-01	1.83E-01
2	3.05E-02	7.18E-02	5.80E-02	4.90E-02	1.64E-02	1.00E-02	7.35E-03
3	2.18E-02	5.13E-02	4.14E-02	3.50E-02	1.17E-02	7.17E-03	5.25E-03
4	9.01E-04	1.63E-03	5.98E-04	4.24E-04	2.29E-04	2.06E-04	2.11E-04
n'_w	2.11E-10	2.22E-10	4.85E-10	8.12E-10	1.69E-09	2.04E-09	2.76E-09
Particle	Imaginary part of the refractive index n' for wavelength λ (nm)						
case	580	600	620	640	660	675	700
1	1.40E-01	1.51E-01	1.63E-01	1.95E-01	3.35E-01	7.43E-01	1.67E-01
2	5.91E-03	5.98E-03	6.13E-03	6.84E-03	1.06E-02	2.19E-02	5.63E-03
3	4.22E-03	4.27E-03	4.38E-03	4.88E-03	7.56E-03	1.56E-02	4.02E-03
4	2.20E-04	2.23E-04	2.13E-04	2.11E-04	3.29E-04	7.51E-04	1.95E-04
n'_w	4.14E-09	1.06E-08	1.36E-08	1.58E-08	2.15E-08	2.41E-08	3.48E-08

The separate values of this index refer to various types of particle – **case 1:** particles containing dry organic matter consisting solely of phytoplankton pigments with a composition typical of the highest irradiances and oligotrophic waters O1; **case 2:** particles containing dry organic matter consisting of all the organic substances in phytoplankton with a composition typical of the highest irradiances and oligotrophic waters O1; **case 3:** phytoplankton cells with the highest possible intracellular concentrations of organic matter ($C_{OM} = 10^6 \text{ g m}^{-3}$) with a composition typical of the highest irradiances and oligotrophic waters O1; **case 4:** phytoplankton cells with the lowest possible intracellular concentrations of organic matter ($C_{OM} = 5 \times 10^4 \text{ g m}^{-3}$) with a composition typical of eutrophic waters E5; **case n'_w** for ‘water particles’.

by the index n'_p , these properties vary over a range of about 8 orders of magnitude for blue light 420 nm and by about 5 orders for red light 650 nm (see the area between curve 2 and the spectrum of $n'_w(\lambda)$ in Fig. 6).

As a result of cell break-up, phytoplankton may also be a source of suspended particles with an organic matter content different from those considered earlier. Thus it is that among the particles derived from phytoplankton there may be some containing organic matter that absorb light more strongly than the natural mixture of organic compounds found in live phytoplankton. Such particles may contain, for example, chloroplast fragments composed of pigments. The upshot is that the range of differentiation of the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ is further extended (especially their absolute values) by almost two orders of magnitude (see

the area between curve 1 and the spectrum of $n'_w(\lambda)$ in Fig. 6). The range of differentiation of these coefficients for any particles originating from phytoplankton is thus c. 10 orders of magnitude for blue light 420 nm and c. 7 orders of magnitude for red light 650 nm.

4. Concluding remarks

The classification of POM in Part 1 of this paper is a first attempt at systematising the model description of sets of organic particles that play a significant role in the absorption of light in the sea. Formally, this classification reduces to a simplified, two-index parameterisation of the particle sets, that is, with respect to two characteristics: the chemical composition of the organic matter in the particles, and their physical properties as expressed by the various probable combinations of three parameters, i.e. their relative contents of water, air and organic matter. This parameterisation constitutes the basis of our calculations and analyses of the spectral, mass-specific, light absorption coefficients of particle matter and its spectra of absolute, imaginary refractive indices for sets of POM in the sea. We shall present the results of these calculations in the second part of this paper, to be published in the next issue of *Oceanologia*. In this first part, we have calculated and presented only examples of the spectra of the coefficients $a_{pm}(\lambda)$ and $n'_p(\lambda)$ for the matter in phytoplankton cells and in particles originating from phytoplankton. A List of symbols and abbreviations denoting the physical quantities used in this paper will be found in the Appendix.

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Appendix

List of the symbols and abbreviations denoting the physical quantities used in this paper

Symbol	Denotes	Units
a	absorption coefficient	m^{-1}
a_{pm}	absorption coefficient of particulate (or cellular) matter	m^{-1}
$a_{pm,dry}$	absorption coefficient of dry particulate (or cellular) organic matter	m^{-1}
a_w	absorption coefficient of pure seawater	m^{-1}
a^*	mass-specific absorption coefficient	$\text{m}^2 \text{g}^{-1}$
a^*_{A3}	mass-specific absorption coefficient of natural proteins	$\text{m}^2 \text{g}^{-1}$
a^*_{Ph}	mass-specific absorption coefficient of the entire organic matter of phytoplankton cells or phytoplankton-like particles	$\text{m}^2 \text{g}^{-1}$
$a^*_{pig,S}$	mass-specific absorption coefficient of all phytoplankton pigments	$\text{m}^2 \text{g}^{-1}$
$a^*_{pl,S}$	chlorophyll-specific absorption coefficient of phytoplankton pigments in the 'in solvent' state	$\text{m}^{-2} (\text{g tot. chl } a)^{-1}$
AOPs	apparent optical properties	
b	relative buoyancy	dimensionless
C_a	total chlorophylls a concentration	$\text{mg tot. chl } a \text{ m}^{-3}$
C_{acc}	total accessory pigment concentration	mg pigment m^{-3}
$C_b, C_c,$	concentrations of chlorophylls b , chlorophylls c ,	mg pigment m^{-3}
C_{PPC}, C_{PSC}	photoprotecting carotenoids, photosynthetic carotenoids	
C_i	concentrations of the i -th pigment	mg pigment m^{-3}
C_{OM}	average intraparticulate (intracellular) concentration of organic matter	g m^{-3}
C_w	average intraparticulate (intracellular) concentration of water	g m^{-3}
DOM	dissolved organic matter	
E_d	downward irradiance	$\mu\text{Ein m}^{-2} \text{s}^{-1}$
E1	eutrophic waters with total chlorophyll concentration C_a about $1.5 \text{ mg tot. chl } a \text{ m}^{-3}$	
E5	eutrophic waters with total chlorophyll concentration C_a about $35 \text{ mg tot. chl } a \text{ m}^{-3}$	
IOPs	inherent optical properties	
MAAs	mycosporine-like amino acids	

Appendix

List of the symbols and abbreviations denoting the physical quantities used in this paper (*continued*)

Symbol	Denotes	Units
n	real part of the absolute or relative complex refractive index	dimensionless
n'	imaginary part of the absolute or relative complex refractive index (non-dimensional absorption coefficient)	dimensionless
n'_p	imaginary part of the absolute or relative complex index of light refraction for particulate matter (non-dimensional absorption coefficient)	dimensionless
$n'_{p,dry}$	imaginary part of the absolute or relative complex index of light refraction for dry organic matter	dimensionless
n'_w	imaginary part of the refractive index for water	dimensionless
O1	oligotrophic waters with total chlorophyll concentration C_a about 0.035 mg tot. chl $a \text{ m}^{-3}$	
PAR	photosynthetically available radiation	
POM	particulate organic matter	
UV	ultraviolet light	
VIS	visible light	
v_a	relative air content	dimensionless
v_{OM}	relative organic matter content	dimensionless
v_w	relative water content	dimensionless
λ	wavelength of light	nm
ρ	average density of a particle	g m^{-3} or kg m^{-3}
ρ_a	density of air (other gas)	g m^{-3} or kg m^{-3}
ρ_{OM}	density of dry organic matter	g m^{-3} or kg m^{-3}
ρ_w	density of pure seawater	g m^{-3} or kg m^{-3}