Chlorophylls and their Degradation in Nature

Khan M. G. Mostofa, Cong-qiang Liu, Xiangliang Pan, Davide Vione, Kazuhide Hayakawa, Takahito Yoshioka and Gennady G. Komissarov

1 Introduction

Phytoplankton are responsible for approximately 40–50 % of the total primary production on Earth. They contribute to controlling the total CO_2 concentration and pH of the ocean, which together with physical processes (e.g. solar energy input, sea–air heat exchanges, upwelling of subsurface waters and mixed layer thickness) dictates the air-to-sea CO_2 gas exchanges (Longhurst et al. 1995; Field et al. 1998; Takahashi et al. 2002; Falkowski et al. 2004). The global net primary production from phytoplankton is 45–50 Gt C year^{-1}, whilst from land plants

K. M. G. Mostofa (✉) · C. Q. Liu
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,
Chinese Academy of Sciences, Guiyang 550002, China
e-mail: mostofa@vip.gyig.ac.cn

X. L Pan
Xinjiang Key Laboratory of Water Cycle and Utilization in Arid Zone, Xinjiang
Institute of Ecology and Geography, Chinese Academy of Sciences, Urumqi 830011,
People Republic of China

D. Vione
Dipartimento di Chimica, University of Turin,-I 10125 Turin, Italy

Centro Interdipartimentale NatRisk, I-10095 Grugliasco, (TO), Italy

K. Hayakawa
Lake Biwa Environmental Research Institute, Shiga Prefecture, Ohtsu 520-0806, Japan

T. Yoshioka
Field Science Education and Research Center, Kyoto University, Kitashirakawa Oiwake-cho,
Sakyo-ku, Kyoto 606-8502, Japan

G. G. Komissarov
Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117977, Russia

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it is of 45–68 Gt C year^{-1} and from coastal vegetation it is of 1.9 Gt C year^{-1} (Longhurst et al. 1995; Box 2004; Haberl et al. 2007).

Since the development of techniques for Chl *a* detection in water in the decade of 1930 and 1940s (Harvey 1934, 1939), a number of research works has been published to develop analytical methodologies (Richards and Thompson 1952; Parsons and Strickland 1963; Jeffrey and Humphrey 1975), to elucidate Chl *a* origin (Fennel and Boss 2003; Letelier et al. 2004; Huisman et al. 2006) and to understand its photoinduced degradation into various pheopigments (Welschmeyer and Lorenzen 1985; Barlow et al. 1993; Stephens et al. 1997). An additional issue is the production of autochthonous DOM by photoinduced degradation of Chl *a* or phytoplankton biomass, under both photoinduced and microbial (bacterial) metabolism/assimilation/respiration (Kirchman et al. 1991, 1995; Tranvik 1993; Nelson et al. 1998, 2004; Hart et al. 2000; Parlanti et al. 2000; Carrillo et al. 2002; Rochelle-Newall and Fisher 2002; Nieto-Cid et al. 2006; Mostofa et al. 2009; Zhang et al. 2009).

The spatial variability of the net primary productivity over the globe is substantially high, varying from about 1,000 g C m^{-2} for evergreen tropical rain forests to less than 30 g C m^{-2} for deserts (Scurlock et al. 1999). On the other hand, chlorophyll *a* (Chl *a*) concentrations vary from 0.0 to 2,080 μg L^{-1} in a variety of natural waters. Such a variability in Chl *a* concentration can produce either a surface/subsurface Chl *a* maximum (SCM) or a deep Chl *a* maximum (DCM) in natural waters (Huisman et al. 1999, 2006; Riley et al. 1949; Bainbridge 1957; Steele and Yentsch 1960; Anderson 1969; Derenbach et al. 1979; Dortch 1987; Viličić et al. 1989; Bjørnsen and Nielsen 1991; Donaghay et al. 1992; Huisman and Weissing 1995; Djurfeldt 1994; Gentien et al. 1995; Odate and Furuya 1998; Dekshenieks et al. 2001; Franks and Jaffe 2001; Klausmeier and Litchman 2001; Diehl 2002; Rines et al. 2002; Yoshiyama and Nakajima 2002; Arístegui Ruiz et al. 2003; Hodges and Rudnick 2004; Matondkar et al. 2005; Weston et al. 2005; Lund-Hansen et al. 2006; Beckmann and Hense 2007; Hense and Beckmann 2008; Hopkinson and Barbeau 2008; Whitehouse et al. 2008; Yoshiyama et al. 2009; Lu et al. 2010; Martin et al. 2010; Ryabov et al. 2010; Velo-Suárez et al. 2010).

The high variation in Chl *a* content is generally used as a universal signature of cyanobacteria (algae), or of phytoplankton bloom or eutrophication in a variety of waters (Fielding and Seiderer 1991; Ondrusek et al. 1991; Williams and Claustre 1991; Millie et al. 1993; Jeffrey et al. 1999; Bianchi et al. 1993, 2002, Blanco et al. 2008; Kasprzak et al. 2008). Variations in Chl *a* concentrations or primary production is entirely dependent on various environmental factors in natural waters, which have been extensively discussed before (see also chapter "Photosynthesis in Nature: A New Look").

It has been found that Chl *a* bound to phytoplankton can be degraded by photoinduced and microbial processes, thereby producing a number of pigments and colourless organic compounds in natural waters (Welschmeyer and Lorenzen 1985; Barlow et al. 1993; Stephens et al. 1997; Zhang et al. 2009; Bianchi et al. 2002; Schulte-Elte et al. 1979; Falkowski and Sucher 1981; Pietta et al. 1981; Mantoura and Llewellyn 1983; Keely and Maxwell 1991; Nelson 1993; Sun et al. 1993; Rontani et al. 1995, 1998, 2003, 2011; Rontani and Marchand 2000; Yacobi et al. 1996; Cuny et al.

1999; Marchand and Rontani 2001; Rontani 2001; Lemaire et al. 2002; Rontani and Volkman 2003; Marchand et al. 2005; Christodoulou et al. 2009; Christodoulou et al. 2010). Chl can also be degraded in higher plants, which for instance causes the colour change in leaves from green to yellow or red that is naturally observed in autumn. However, degradation can also occur as a consequence of cell death caused by external factors, such as injuries due to low or high temperature, pathogen attack, as well as phenomena taking place during various phases of the life cycle of plants (Hendry et al. 1987; Takamiya et al. 2000). Conversion of Chls to pheophytins can take place during discolouration of green vegetable upon processing by several chemicals, photoinduced or enzymatic reactions including simultaneous actions of enzymes, weak acids or changes in pH, oxygen, light and heat (Blair and Ayres 1943; Gupte et al. 1964; Hayakawa and Timbers 1977; Minguez-Mosquera et al. 1989; Mangos and Berger 1997; Koca et al. 2007). Moreover, the key PSII degradation reactions of Chls are photooxidation, involving attack of singlet oxygen or $HO^{\bullet}$ via H_2O_2, and enzymatic degradation (Takamiya et al. 2000; Brown et al. 1991; Hörtensteiner 2006; Kräutler and Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011; Gálvez et al. 1988).

This chapter will give an overview of the various kinds of Chl, their properties, functions, and techniques for their precise determination. It extensively discusses the distribution of Chl *a* providing information about SCM and DCM depths, the formation mechanisms of such maxima as well as the changes of Chl *a* concentrations in a variety of natural waters, under both field and experimental conditions. It also discusses the degradation and degradation mechanisms of Chl *a* bound to aquatic microorganisms and higher plants, as well as the modifications taking place during food processing. Finally, an explanation will be provided of how Chl *a* acts as a universal signature of phytoplankton bloom, and of the possible actions to be adopted for the management of eutrophication by controlling primary production or Chl *a*.

2 Chlorophylls (Pigments) in Phytoplankton

Photosynthetic organisms can collect light energy with their light-harvesting systems that are composed of core and peripheral antenna complexes (Green and Durnford 1996). Core antenna complexes of oxygen-evolving photosynthetic organisms have Chl *a* as pigment. In contrast peripheral antenna complexes, particularly for photosystem II (PSII), have various pigments depending on the group of photosynthetic organisms. They are Chl *b*, Chl *c* (made up of c_1, c_2 and c_3), Chl *d*, phycobilins, fucoxanthin, zeaxanthin (carotenoids), echinenone, peridinin, and so on (Bianchi et al. 2002; Woodward et al. 1960, 1990; Dougherty et al. 1966; Fleming 1967; Wu and Rebeiz 1985; Jeffrey and Wright 1987; Verne-Mismer et al. 1988, 1990; Fookes and Jeffrey 1989; Rowan 1989; Grossman et al. 1995; Miyashita et al. 1996, 1997; Motilva 2008).

Chl *b* is detected in various forms such as: divinyl Chl *b*, with two vinyl groups at R_1 and R_2 positions; monovinyl Chl *b*, with vinyl at R_1 and ethyl at

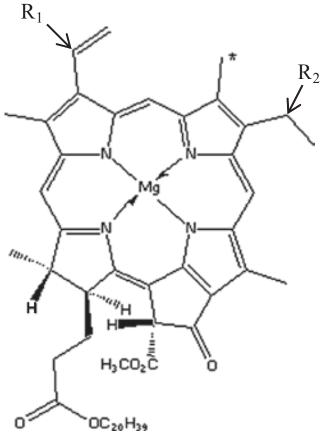


Fig. 1 Molecular structure of chlorophyll *a* and chlorophyll *b* with some medication. *Data source* Clarke et al. (1976)

R_2, and meso-Chl *b* with two ethyl groups at R_1 and R_2 (Fig. 1) (Clarke et al. 1976). Moreover, Chl *c* composed of a 17-acrylic side-chain has been isolated from two Moroccan oil shales of Cretaceous age (Verne-Mismer et al. 1988). Petroporphyrins, showing both a free C-7 position and a C-13 to C-17 substitution pattern typical of Chl *c* fossils, have been isolated from two Cretaceous Moroccan oil shales and may arise from a still unknown Chl, 7-formylchlorophyll *c* or Chl c_3 (Verne-Mismer et al. 1990). Chl c_3, isolated from a microalga, has tentatively been identified as 7-demethyl-7-methoxycarbonyl chlorophyll (Fookes and Jeffrey 1989). Chl c_2, isolated from the coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae), is present in approximately equal proportions as Chl c_3. It has absorption maxima at 447, 579 and 628 nm, whilst no Chl c_1 has been detected (Jeffrey and Wright 1987). Cells of the new prokaryote have an absorption maximum in the red region (714–718 nm) due to Chl *d* absorption, but they do not show any characteristic absorption peak of Chl *a* at around 680 nm (Miyashita et al. 1997). Chl *f* is [2-formyl]-chlorophyll *a* ($C_{55}H_{70}O_6N_4Mg$), and its in vitro absorption (706 nm) and fluorescence (722 nm) maxima are red-shifted compared to all other Chls from oxygenic phototrophs (Chen et al. 2010).

Uncoupled Chls in PSII of cyanobacteria or phytoplankton and red algae can absorb at shorter wavelength, e.g. 670 nm (close to their site energy), whilst electronically coupled chlorins (the central cofactors) or Chl dimers can absorb between 676 and 684 nm (Zhang et al. 2009; Telfer et al. 1990; Durrant et al. 1995; Renger and Marcus 2002). Formation of Chl dimers and their light-induced excitations are extensively discussed in the photosynthesis chapter "Photosynthesis in Nature: A New Look". Upon 440-nm excitation of Chl *a* bound to *Synechocystis* cells, a typical PSII fluorescence at 685 nm has been observed both at room temperature and at 77 K (Satoh et al. 2001). Two additional fluorescence components have been detected at 695 and 722 nm, whilst no fluorescence peak for Chl *b* has been observed in these cyanobacteria (Satoh et al. 2001). Red shifts are commonly observed in in vitro Chl *a* systems, including thin films, monolayers and colloidal dispersions used as models for the in vivo systems (Katz et al. 1991). Red shifts generally occur when electron releases follow the easiest way in the functional groups bound to the component system (see also chapters "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters" and "Fluorescent Dissolved Organic Matter in Natural Waters") (Mostofa et al. 2009; Senesi 1990). Chl *b* found in chlorophytes and prochlorophytes can absorb sunlight at around 470 nm (highest peak) and 650 nm (small peak) (Satoh et al. 2001). The Chl *c* isolated from *Peridinium gatunense* showed two peaks at 448–449 and 634–635 nm (Yacobi et al. 1996).

All pigments can bind to their specific proteins to form pigment-protein complexes (Cogdell et al. 1996; Pearlstein 1996). Complexation can provide the easiest way of electron release, as depicted in other chapters (see "Photosynthesis in Nature: A New Look" and "Complexation of Dissolved Organic Matter with Trace Metal ions in Natural Waters"). The Chl *b* content of the light-harvesting complex (LHC) of PSII in higher plants is highly preserved, approximately between 45 and 50 % or in the approximate ratio of 3:1 of Chl *a* to Chl *b* (Anderson 1986; von Elbe and Schwartz 1996). Conversely, the contents of Chl *b* in cyanobacteria are variable and relatively low (1.4–10.6 % or more) (Bianchi et al. 2002; Satoh et al. 2001). Experimental and other observation have shown that Chl *a* molecules can bind to LHC of PSII at Chl *b* binding sites (Thornber and Highkin 1974; Terao and Katoh 1989; Murray and Kohorn 1991; Paulsen et al. 1993; Polle et al. 2000). Correspondingly, Chl *b* is vital for the stability of LHC of PSII in the thylakoid membrane (Murray and Kohorn 1991; Bellemare et al. 1982). The core antenna complexes of chlorophytes have Chl *a* and do not bind Chl *b*, despite its presence (Satoh et al. 2001; Anderson et al. 1978).

2.1 Properties and Functions of Chlorophyll

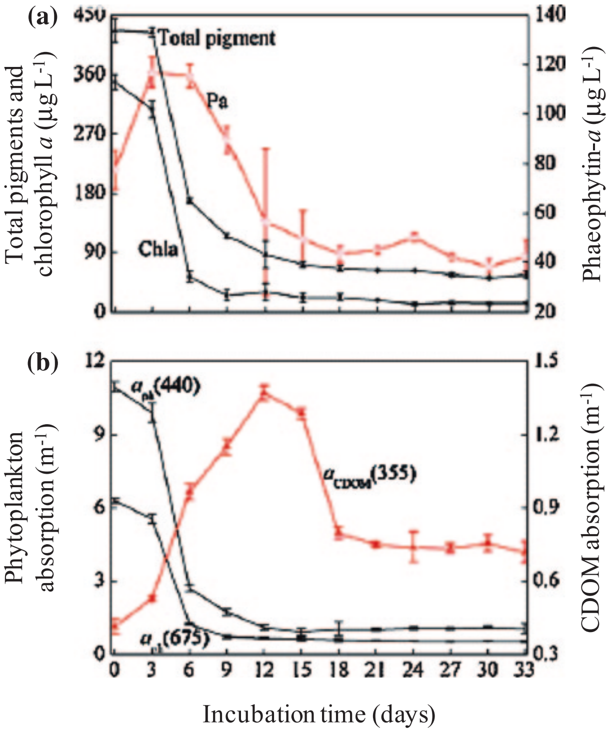
Chlorophyll (Chl) *a* has a methyl group at the C-3 carbon (molecular formula $C_{55}H_{72}MgN_4O_5$), while Chl *b* has the same chemical structure as Chl *a* but with a –CH_3 group replaced by a –CHO one, providing the molecular formula $C_{55}H_{70}MgN_4O_6$ (Fig. 1) (Clarke et al. 1976). The correct gross structure of Chl has been suggested at first by Fischer (Fischer and Wenderoth 1940) and verified in a synthesis by Woodward (Woodward et al. 1960; Woodward 1961). The relative configuration of the methyl and propionic ester groups on the D ring in the structure was shown to be *trans* by Ficken and his colleagues (Ficken et al. 1956). The stereochemistry and absolute configuration of the phytyl group is $2'$-*trans*-$7'R,11'R$, as discovered in 1959 (Burrell et al. 1959; Crabbe et al. 1959). The relative configuration at C_{10} is such that the methoxycarbonyl group is *trans* to the propionic ester side chain on C_7 (Closs et al. 1963; Wolf et al. 1967). In addition to their structural differences, Chl *a* is observed to be thermally less stable than Chl *b* (Buckle and Edwards 1970; Lajollo et al. 1971; Schwartz and von Elbe 1983; Canjura et al. 1991; Schwartz and Lorenzo 1991).

Functions of Chls and their degradation products can be discriminated as follows: (i) Chl is an efficient visible-light photosensitizer and a key component required for the absorption of sunlight. It is essential for the occurrence of photosynthesis as it is involved into the initiation of electron release in aquatic microorganisms and higher plants (see also chapter "Photosynthesis in Nature: A New Look") (Hörtensteiner and Kräutler 2011; Foote 1976; Kimball 1979; Knox and Dodge 1985). Under specific conditions (e.g. high light conditions, high temperature, drought and so on) Chl can significantly produce reactive oxygen species (ROS) such as singlet oxygen ($^1O_2$), superoxide radical anion ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2) and $HO^\bullet$ (see chapter "Photosynthesis in Nature: A New Look"). In turn, these species can degrade Chl and cause cell death (Rontani 2001; Hörtensteiner and Kräutler 2011; Marshall et al. 2002; Oda et al. 1998). ROS also play a role during senescence of photosynthetic cells or fruit ripening. Strong light gradients cause unbalanced excitation of the two photosystems and reduce photosynthetic efficiency (Dietzel et al. 2011). (ii) According to the Treibs hypothesis, petroporphyrins can originate from Chl (Treibs 1936; Liang et al. 1993). (iii) Chl, some of its synthetic analogues, metal complexes of porphyrins and phthalocyanines are all photoactive. As key components bound to organisms they can cause production of H_2O_2 in vivo under light, in aqueous solutions saturated with dioxygen (Hong et al. 1987; Bazanov et al. 1999; Premkumar and Ramaraj 1999; Lobanov et al. 2008). (iv) Chls, the pigments responsible for green color in fruits and vegetables, are highly susceptible to degradation during processing. This can result into changes from bright green to olive brown or other colors, during storage and processing in the agriculture and food industry (Schwartz and von Elbe 1983; Sweeney and Martin 1961). Color, the major quality attribute of vegetables and fruits, is a key factor in the commercial value of food to the consumer and can be highly affected by Chl breakdown as an important catabolic process of leaf senescence and fruit ripening (Takamiya et al. 2000; Hörtensteiner and Kräutler 2011; Schwartz and von Elbe 1983; Steet and Tong 1996). (v) The colorless "nonfluorescent Chl catabolites (NCC)" found in ripening fruits (e.g. apples and pears) can act as antioxidants, in a similar way as bilirubin (Moser et al. 2009; Stocker et al. 1987; Barañano et al. 2002). It has been shown that the rates of formation of hydroperoxides of linoleic acid in the presence of NCC is significantly reduced. The observed effect is a function of time and of the concentration of the added antioxidants. Moreover, the (concentration-dependent) peroxy radical scavenging effect of NCC is only slightly inferior to that of bilirubin (Moser et al. 2009; Stocker et al. 1987; Müller et al. 2007). (vi) Chl *a* is generally used to estimate the primary biomass production or the phytoplankton/cyanobacterial biomass or bloom in natural waters. In contrast, carotenoids and the degradation intermediates xanthophylls could be effective biomarkers of different classes of phytoplankton (Fielding and Seiderer 1991; Ondrusek et al. 1991; Williams and Claustre 1991; Millie et al. 1993; Jeffrey et al. 1999; Bianchi et al. 1993, 2002; Kasprzak et al. 2008). Therefore, Chl *a* and its degradation products could be useful indicators of the fate and composition of phytoplankton species and of transformation and degradation of phytoplanktonic carbon. As a key characteristic of phototrophic organisms, they can be used as a criterion in the classification of autotrophic bacteria and cyanobacteria or algae (Williams and Claustre 1991; Marchand et al. 2005; Rowan 1989; Liang et al. 1993; Downs and Lorenzen 1985; Trüper 1987; Volkman et al. 1988; Vaulot et al. 1990; Veldhuis and Kraay 1990; Wilhelm et al. 1991; Brunet et al. 1992; Head and Horne 1993; Soma et al. 1993). Similarly, phaeopigments (Chl degradation products) represent the dominant form of plant pigments in marine sediments (Brown et al. 1991; Baker and Louda 1983; Furlong and Carpenter 1988; Leavitt and Carpenter 1990; Bianchi and Findlay 1991; Bianchi et al. 1993; Jeffrey et al. 1997). Chl *b* is used as a biomarker for chlorophytes (Bianchi et al. 2002). (vii) Primary production (e.g. algae) is substantially high in ice bed (0.1–1,000 $\mu g\ L^{-1}$) and can provide food resources for organisms in higher trophic levels, in seasons and regions where the water-column biological production is low or negligible (Palmisano et al. 1985; Garrison et al. 1986; Wheeler et al. 1996; Mock and Gradinger 1999; Lizotte 2001). (viii) The specific Chl *a* content per unit of phytoplankton biomass is typically decreased with increasing phytoplankton standing stocks, and with Chl *a* concentration in natural waters and also in laboratory cultures of certain species (Kasprzak et al. 2008; Desortová 1981; Shlgren 1983; Wojciechowska 1989; Watson et al. 1992; Talling 1993; Chow-Fraser et al. 1994; Schmid et al. 1998; Felip and Catalan 2000; Sandu et al. 2003; Kiss et al. 2006). Such a trend might reflect several phenomena such as: degradation of Chl *a* bound in phytoplankton; lake trophic status; phytoplankton community structure; size frequency distribution of algal cells; and seasonal shifts within the plankton community (Bianchi et al. 2002; Bursche 1961; Nusch and Palme 1975; Harris 1986; Watson and McCauley 1988; Arnott and Vanni 1993; Fu et al. 2010; Mostofa KMG et al. unpublished data). (ix) Chloropigments (Chl *a* and carotenoids) and their degradation products could be important determinants of UV and PAR attenuation in natural waters, due to their efficient radiation absorption (see also chapter "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters") (Zhang et al. 2009; Devlin et al. 2009; Zhang and Qin 2007; Dupouy et al. 2010; Zhang et al. 2007). (x) The ultimate degradation products of Chls and pigments are colorless (Zhang et al. 2009; Marchand et al. 2005; Mostofa K et al. unpublished data; Wakeham and Lee 1993; Mostofa K et al. unpublished data; Meyers 1997). They may contribute to autochthonous DOM and, therefore, to DOM dynamics in natural waters. Lipids, one of the three major classes of organic matter in algal material, are often used as biomarkers because of their lower labilility compared to proteins and carbohydrates (Mostofa et al. 2009; Sun et al. 2002; Wakeham 1995; Volkman 1986).

2.2 Determination of Chls and Other Pigments

For the measurement of Chls, and particularly of Chl *a*, Chl *b* and Chl *c*, various absorption peaks have been used. Absorption peaks have small variations depending on the phytoplankton species (Goedheer 1970; Prezelin 1981; Aguirre-Gomez

Fig. 2 Changes in the (**a**) mean concentrations of total pigment, chlorophyll *a* and Phaeophytin-*a* (*P*a); and (**b**) phytoplankton pigment absorption at the Chl *a* absorption maxima at 440 and 675 nm and CDOM absorption at 355 nm during the degradation experiment period (0–33 days). *Error bar* indicates the means and standard deviations (n = 3). *Data source* Zhang et al. (2009)



et al. 2001; Pérez et al. 2007). For Chl *a*, peaks that are often used are those at 412–425, 435–455, 618–623 and 662–675 nm, respectively (Zhang et al. 2009; Goedheer 1970; Prezelin 1981; Aguirre-Gomez et al. 2001; Pérez et al. 2007). The in vivo absorption spectra of the brown alga *Laminaria digitata* have Chl *a* peaks at 418, 437, 618 and 673 nm. Moreover, absorption peaks of *Glenodinium* sp. occur at 419, 437, 618 and 675 nm, and absorption peaks (average) of three different groups of algae are located at 412, 435, 623 and 675 nm (Goedheer 1970; Prezelin 1981; Hoepffner and Sathyendranath 1991). The structural configuration of PSI and PSII in the reaction center shows that they may have two wavelength positions: uncoupled Chls can absorb at 670 nm (close to their site energy), and electronically coupled chlorins (the central cofactors) or Chl dimers can absorb between 676 and 684 nm (see also chapter "Photosynthesis in Nature: A New Look") (Telfer et al. 1990; Durrant et al. 1995; Renger and Marcus 2002).

Microbial degradation experiments show that absorbance of Chl *a* in the shorter wavelength region (~440 nm) disappears relatively faster compared to the longer wavelength region (~675 nm). Therefore, only the 675 nm absorption peak remains visible in the suspension if degradation time is long enough (Fig. 2; see also chapter "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters") (Zhang et al. 2009). Absorption peaks in the shorter wavelength region are generally accounted for by various substances such as proteins, amino acids and other organic components bound to PSI and PSII. These compounds are all susceptible to undergo microbial decompositon (see chapters "Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters, "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters", "Fluorescent Dissolved Organic Matter in Natural Waters"). On the other hand, Chls that absorb radiation in the longer wavelength region are susceptible to undergo photochemical decomposition (see chapters "Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters", "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters", "Fluorescent Dissolved Organic Matter in Natural Waters"). Absorbance in the longer wavelength regions (>600 nm) is generally linked to the easiest way of electron release from the functional groups bound to the parent molecule. Chl molecules are thus responsible for the absorption peaks located at $\lambda > 600$ nm. Interestingly, longer wavelength absorption peaks (>600 nm) are often observed for some functional groups that are present in terrestrial humic substances (fulvic and humic acids) in riverine ecosystems (see chapter "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters"). Therefore, changes in functional groups or molecules bound to PSI and PSII, which take place through either photoinduced or microbial processes, may affect the absorption peaks. Note that peaks appearing in the green region (500–600 nm) are small compared to those located in the blue (<500 nm) and red (>600 nm) regions (Aguirre-Gomez et al. 2001).

Considering the previously reported findings, the following suggestions can be followed for Chl determination: First, measurement of Chl *a* should be conducted only at a single wavelength, not at several ones. The most suitable is at around 665–675 nm, and absence of light should be ensured during sample processing and measuring. Second, Chl *b* should be measured only at around 643–650 nm. In earlier studies, the measurement of Chl *b* has been carried out using its absorption peaks at 465–470 or 483, 585–595 and 643–650 nm, but only the latter provides sufficiently accurate results (Satoh et al. 2001; Aguirre-Gomez et al. 2001; Bidigare et al. 1989; Millie et al. 1997). Some differences in absorption wavelengths in Chl *b* can be caused by the occurrence of various forms of this Chl, as mentioned before. The third issue is that Chl *c* should be detected at 630–639 nm, although earlier studies have adopted absorption peaks at 465–470, 589, and 630–639 nm (Bidigare et al. 1989; Millie et al. 1995, 1997). The many absorption peaks used in earlier studies, in particular at short wavelengths, should not be adopted for the measurement of any Chl molecule. The reason is that absorbance at shorter wavelengths has been observed for other pigments that could interfere with Chl determination, such as hycoerythrin (detected at 543–550 and 566–568 nm) (Payri et al. 2001; Smith and Alberte 1994); phycoerythrocyanin (~550 nm and ~575 nm) (Millie et al. 2002); phycocyanin (625–630 nm) (Payri et al. 2001; Millie et al. 2002); fucoxanthin (521–531 nm) (Bidigare et al. 1989); and different carotenoids (490–495 nm) (Millie et al. 1997; Owens et al. 1987). Furthermore, CDOM absorbs radiation in lower wavelength regions (250–500 nm) because of the functional groups present in allochthonous and autochthonous organic substances (see chapter "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters").

3 Distribution of Chlorophyll (Chl *a*)

Chl *a* concentrations are significantly varied in the water column, where a given set of parameters may lead to either a surface or a subsurface Chl *a* maximum (SCM), or to a deep Chl *a* maximum (DCM) (Huisman et al. 2006; Riley et al. 1949; Bainbridge 1957; Steele and Yentsch 1960; Anderson 1969; Derenbach et al. 1979; Dortch 1987; Viličić et al. 1989; Bjørnsen and Nielsen 1991; Donaghay et al. 1992; Huisman and Weissing 1995; Djurfeldt 1994; Gentien et al. 1995; Odate and Furuya 1998; Huisman et al. 1999; Dekshenieks et al. 2001; Franks and Jaffe 2001; Klausmeier and Litchman 2001; Diehl 2002; Rines et al. 2002; Yoshiyama and Nakajima 2002; Arístegui Ruiz et al. 2003; Hodges and Rudnick 2004; Matondkar et al. 2005; Weston et al. 2005; Lund-Hansen et al. 2006; Beckmann and Hense 2007; Hense and Beckmann 2008; Hopkinson and Barbeau 2008; Whitehouse et al. 2008; Yoshiyama et al. 2009; Lu et al. 2010; Martin et al. 2010; Ryabov et al. 2010; Velo-Suárez et al. 2010). The location of the maximum is entirely determined by the environmental conditions. The cited studies have shown that SCM and DCM of phytoplankton can occur in a variety of conditions in lake and marine waters. They can range in the vertical dimension from centimeters to a few meters, and have been observed to extend horizontally for kilometers.

3.1 Surface or Subsurface Chl a Maximum

The surface or subsurface Chl *a* maximum (SCM) is detected in the surface layer, which varies in different waters and may range between 0–25 m in lakes and 0–30 m or more in seawater (Fig. 3a; Table 1) (Fu et al. 2010; Mostofa K et al. unpublished data; Apollonio 1980; Vicente and Miracle 1984; Kimor et al. 1987; Pedros-Alio et al. 1987; Millán-Núñez et al. 1996; Gomes et al. 2000; Guildford and Hecky 2000; Li and Harrison 2001; Echevin et al. 2004; Koné et al. 2005; Camacho 2006; Ediger et al. 2006; Parab et al. 2006; Roy et al. 2006; Satoh et al. 2006; Sawatzky et al. 2006; Yacobi 2006; Norrbin et al. 2009; Xiu et al. 2009; Zhu et al. 2009; Hamilton et al. 2010). According to these studies, SCM can be defined as a zone of maximum photosynthetic activity that shows the highest Chl *a* contents. It occurs in the upper surface layer of the euphotic zone in the presence of strong light, high DOM contents and nutrients, and under high temperature as well as low or high turbulence. It is a remarkable feature of highly turbid water in the surface layer of stagnant natural waters, particularly in lakes and oceans. High variation with depth of SCM in seawater is presumably caused by an increase of the surface-water mixing zone, due to strong wind and wave compared

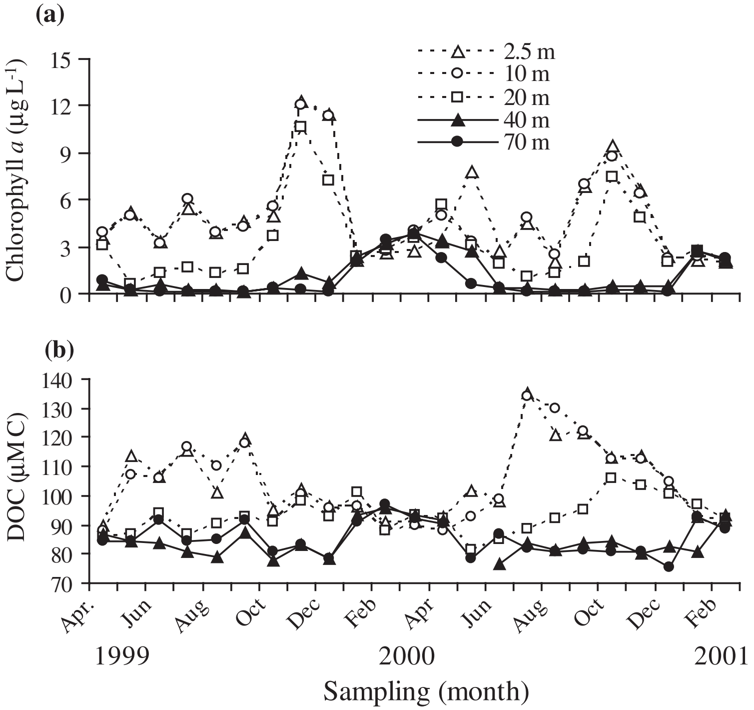


Fig. 3 Vertical changes in the chlorophyll *a* (**a**) and dissolved organic carbon (DOC) concentrations (**b**) in monthly collected samples from Lake Biwa and *Error bars* indicate the standard deviation *Data source* Mostofa et al. (2005), Mostofa KMG et al. (unpublished data)

to conditions in lakes. An upper-surface mixed layer commonly occurs in lakes and oceans, due to mechanical perturbation of surface waters (e.g. by wind, waves and storms) (Deuser 1987; Venrick 1993; Law et al. 2003; Moum et al. 1989; Brainerd and Gregg 1995). It is characterized by strong turbulent mixing, up to a depth of approximately 30–200 m or more. Note that few studies have reported the occurrence of DCM (or subsurface Chl a maximum) at a depth of 5–25 m or more (Table 1) (Parab et al. 2006; Sawatzky et al. 2006; Xiu et al. 2009; Hamilton et al. 2010; Fee 1976; Sommaruga and Augustin 2006). Considering the surface mixing zone of the water column, it might be supposed to have a similar meaning as the surface Chl *a* maximum (SCM). A high content of Chl *a* at a depth of 5–15 m may be due to the occurrence of strong photoinduced degradation of Chl *a* in the upper surface layer, e.g. at 0–4 m depth. Note that subsurface Chl *a* maxima have been considered as DCM in several earlier studies, while in this chapter a similar meaning (SCM) is adopted for the subsurface Chl *a* maximum (at e.g. 5–15 m depth) and for the surface Chl *a* maximum (0–30 m depth). SCM should thus be well differentiated from DCM to avoid any confusion. Such a rationalization could be useful to avoid confusion between SCM and DCM in future studies.

Table 1 Variation in chlorophyll *a* concentrations along with pH, water temperature and dissolved organic carbon (DOC) concentrations in a variety of natural waters

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Streams and rivers								
Streams ($n = 9$)	–	–	0.0–12.7	–	–	–	–	Gao et al. (2004)
Temperate streams (USA)	–	–	0.4–170	–	–	–	–	van Nieuwenhuyse and Jones (1996)
Ozark Streams (USA)	–	–	0.5–44.6	–	–	–	–	Lohman and Jones (1999)
Chalk stream (UK)	–	–	0.5–17.0	–	–	–	–	Palmer-Felgate et al. (2008)
La Trobe River Streams (Victoria, Australia)	–	–	~<65	–	–	–	–	Chessman (1985)
Streams and Rivers (USA)	–	–	1.0–97.0	–	–	–	–	Royer et al. (2008)
Streams and Rivers (Illinois, USA)	–	6.0–27.0	~00.0–18.0	–	–	–	–	Morgan et al. (2006)
Streams and Rivers (Paraná River basin: Argentina, Brazil and Paraguay)	6.74–7.78	11.7–21.5	0.14–216	–	–	–	–	Devercelli and Peruchet (2008)
Red River and its basin (USA)	–	–	0.1–263	–	–	–	–	Longing and Haggard (2010)
Rideau River (Ontario, Canada)	–	–	<27	–	–	–	–	Basu and Pick (1997)
Yukon River (Canada)	7.4–7.9	–	0.20–5.07	–	–	508–2835	–	Guéguen et al. (2006)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*			DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	Chl *a* and depth in SCM and DCM (μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
River Avon (Warwickshire, UK)	–	–	~<100	–	–	–	–	Foster et al. (1997)
River Alne (Warwickshire, UK)	–	–	~<280	–	–	–	–	Foster et al. (1997)
River Arrow (Warwickshire, UK)	–	–	~<240	–	–	–	–	Foster et al. (1997)[a]
Jacupiranguinha and Pariquera-Açu Rivers	–	–	1.4–12.0	–	–	–	–	Calijuri et al. (2008)
Lakes and reservoirs								
Lake Hongfeng (Southwest China)	–	7.0–31.0	2.7–47.8 (0–8 m)	1.4–32.7 (10–25 m)	43.6–47.8; SCM (4–5 m)	170–250	134–237	Fu et al. (2010)
Lake Baihua (Southwest China)	–	6.5–25	4.1–65.5 (0–8 m)	1.4–41.0 (10–25 m)	58.7–65.5; SCM (0–2 m)	169–330	157–303	Fu et al. (2010)
Subtropical and urban shallow Lakes (Wuhan, China)	6.8–9.1	3.7–31.6	2.1–189.8	–	–	–	–	Lv et al. (2011)
Lakes (38 Chinese lakes)	7.31–9.73 (8.67 ± 0.43)	13.3–28.3 (23.2 ± 2.69	0.01–133.22	–	–	–	–	Zhang et al. (2007)
Lakes (3 Chinese lakes)	–	16.5–16.7 (mean)	0.85 ± 0.17–9.67 ± 2.25	–	–	–	–	Pan et al. (2009)
Lake Taihu (China)	–	5.0–30.0	~5.0–30.0	–	–	–	–	James et al. (2009)[a], Liu et al. (2011)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion	Hypolimnion		Epilimnion	Hypolimnion	
			(µg L^{-1})		(µg L^{-1}; m)	(µM C)		
Lake Baiyangdian (China)	–	–	0.0–66.93	–	–	–	–	Wang et al. (2012)
Lake Biwa: (Japan)	–	–	0.5–12.3 (0–20 m)	0.1–3.9 (40–80 m)	9.4–12.3; SCM (2.5–10 m)	81.5–135.1	75.6–96.9	Mostofa et al. (unpublished data)
Lake Kizaki (Japan)	7.68–9.55	8.40–21.49	15.3–82.1 (2 m)	–	–	–	–	Yoshioka (1997)
Lakes (Japan)	–	–	0.2–189	–	–	–	–	Aizaki et al. (1981)
Lake Baikal (Russia)	–	0-17.9 (s)	0.5–5.8	–	<5.8; SCM (~10 m)	–	–	Satoh et al. (2006)[a], Yuma et al. (2006)
Lake Baikal (Southern Basin) during late winter	–	0.40–0.84 (average)	0.67–2.0 (0–25 m)	–	–	–	–	Straškrábová et al. (2005)
Lake Victoria (Africa)	–	–	~15–110	–	–	–	–	Silsbe et al. (2006)[a]
Lake Victoria (Africa)	–	–	4.7–78.5	–	–	–	–	Guildford and Hecky (2000)
Lake Tanganyika (Africa)	–	23–37 (surface layer)	0.1–4.5	–	–	–	–	Yuma et al. (2006)
Lake Malawi (Africa)	–	–	0.03–18.7	–	–	–	–	Guildford and Hecky (2000)
Lakes (16 shallow Danish lakes)	–	–	33–276	–	–	–	–	Windolf et al. (1996)
Lakes (Lake Ånnsjön, Erken and Balaton, Sweden)	7.3–8.4	6–11.3	1.2–10 (1 m)	–	–	–	–	Kahlert (2002)
Lakes (Stechlin, Kleiner Väter, Großer Väter, Tiefwaren & Feldberger Haus)	–	–	0.7–175.9	–	–	–	–	Kasprzak et al. (2008)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl a		Chl a and depth in SCM and DCM	DOC		Reference
			Epilimnion (µg L^{-1})	Hypolimnion	(µg L^{-1}; m)	Epilimnion (µM C)	Hypolimnion	
Lakes (Förchensee, Brunnensee, Klostersee, Langbürgenersee, Thalersee, Bansee)	–	–	0.2–53.4	–	–	–	–	Striebel et al. (2008)
Lake Krankesjön (Sweden)	–	–	10–60 (0–2 m)	–	–	–	–	Blindow et al. (2006)
Lake Börringesjön (Sweden)	–	–	60–145 (0–2 m)	–	–	–	–	Blindow et al. (2006)
Lake La Caldera (Southern Spain)	–	1.2–12.4	0.14–2.85	–	–	42	–	Carrillo et al. (2002)
Lake Cisó (Spain)	–	–	<850	–	850; SCM or DCM? (1.0–1.5 m)	–	–	Pedros-Alio et al. (1987)
Lake Arcas (Spain)	–	–	<298	–	298; SCM or DCM? (8-9 m)	–	–	Camacho (1997)
Lake El Tobar (Spain)	–	–	< 90	–	90; SCM or DCM? (11–12 m)	–	–	Miracle et al. (1993); Camacho (2006)
Lake La Cruz (Spain)	–	–	<25	–	25; SCM or DCM? (10–12 m)	–	–	Rojo and Miracle (1987), Dasí and Miracle (1991)
Lake La Parra (Spain)	–	–	<15	–	15; SCM or DCM? (9 m)	–	–	Camacho et al. (2003)
Lake Lagunillo del Tejo (Spain)	–	–	<15	–	15; SCM or DCM? (4–11 m)	–	–	Vicente and Miracle (1984)
Lakes (26 lakes in Austria, Italy and Spain)	–	–	0.3–7.97	–	–	–	–	Laurion et al. (2002)
Amazon flood plain lakes (shallow lakes, 1–3 m)	–	–	8.2–89.2	–	–	–	–	de Moraes Novo et al. (2006)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl a		Chl a and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Lakes (New Zealand, n = 11)	–	–	0.39–4.38	–	–	25-833	–	Rae et al. (2001)
Lake Taupo (New Zealand)	–	11.1–20.6 (s); 10.6–11.1 (b)	0.75 (annual mean)	–	~3–6; SCM/DCM? (~10, 40–85 m)	–	–	Hamilton et al. (2010)[a]
Lake Rotoma (New Zealand)	–	11.2–22.1 (s); 10.7-12.6 (b)	0.93 (annual mean)	–	~2–8; SCM/DCM? (~ 10-20, 75 m)	–	–	Hamilton et al. (2010)[a]
Lake Tarawera (New Zealand)	–	11.0–21.7 (s); 10.9–11.7 (b)	1.26 (annual mean)	–	~1–5.8; SCM/DCM? (~10–25; 25–30 m)	–	–	Hamilton et al. (2010)[a]
Lake Rotoiti (New Zealand)	–	11.1–22.0 (s); 10.7–13.5 (b)	8.7 (annual mean)	–	~10-30; SCM/DCM? (~0–10, 50–90 m)	–	–	Hamilton et al. (2010)[a]
Lake Superior (USA)	–	–	0.57–1.3	–	–	110-119	–	Biddanda et al. (2001), Guildford and Hecky (2000)
Lake Superior (USA)	–	6.0-18.0	0.10–1.82 (0–80 m)	–	<1.82; DCM (23–35 m)	–	–	Barbiero and Tuchman (2004)
Lake Michigan (USA)	–	~3.0–24.0	~0.5–8.0 (0–70 m)	–	<~4: SCM? (15 m) or <~8.0: DCM (25–70 m)	–	–	Fahnenstiel and Scavia (1987)[a]
Lake Josephine (USA)	–	–	11.57	–	–	545	–	Biddanda et al. (2001)
Lake Johanna (USA)	–	–	20.2	–	–	484	–	Biddanda et al. (2001)
Lake Eagle (USA)	–	–	25.16	–	–	643	–	Biddanda et al. (2001)
Lake Medicine (USA)	–	–	40.49	–	–	615	–	Biddanda et al. (2001)
Lake Christmas (USA)	–	–	1.37	–	–	551	–	Biddanda et al. (2001)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*	Hypolimnion	Chl *a* and depth in SCM and DCM	DOC	Hypolimnion	Reference
			Epilimnion (μg L^{-1})		(μg L^{-1}; m)	Epilimnion (μM C)		
Lake Turtle (USA)	–	–	2.47	–	–	600	–	Biddanda et al. (2001)
Lake Minnetonka (USA)	–	–	3.35	–	–	712	–	Biddanda et al. (2001)
Lake Round (USA)	–	–	8.74	–	–	537	–	Biddanda et al. (2001)
Lake Owasso (USA)	–	–	4.25	–	–	695	–	Biddanda et al. (2001)
Lake Mitchell (USA)	–	–	52.7	–	–	784	–	Biddanda et al. (2001)
Lake Okeechobee (USA)	–	14.8–30.2 (monthly mean)	10.0–60.0	–	–	–	–	James et al. (2009)[a]
Lake Tahoe (USA)	–	~5.0–16.0	0.2–0.9 (0–100 m)	–	~0.9; DCM (40–60 m)	–	–	Winder et al. (2009)[a]
Lake Tahoe (USA)	–	~4–14	~0.1–0.7 (0–500 m)	–	~0.3–0.7; DCM (100, 320, 350 m)	–	–	Kiefer et al. (1972)[a]
Florida Lakes (n = 438)	–	–	2–265	–	–	–	–	Bachmann et al. (2003)
Yellow Belly Lake (USA)	–	~3–17 (4–9 at DCM)	0.7–3 (0–20 m)	–	~2–3; SCM? (~8–15 m)	–	–	Sawatzky et al. (2006)
Redfish Lake (USA)	–	–	<4.8	–	2.2–4.8; DCM (~18–35 m)	–	–	Gross et al. (1997)[a]
Lakes of the Experimental Lakes Area, northwestern Ontario (Canada)	–	4.0–20.0	~1.0–327 (0–15 m)	–	311; SCM or DCM ? (5–7 m)	–	–	Fee (1976)
Quebec lakes (n = 8), Canada	–	–	1.5–6.9 (0.5–1.0 m)	–	–	233-625	–	McCallister and Del Giorgio (2008)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Lakes (small sizes in Northwestern Ontario)	–	–	0.3–7.9	–	–	–	–	Guildford and Hecky (2000)
Lakes (large sizes in Northwestern Ontario)	–	–	0.7–18.1	–	–	–	–	Guildford and Hecky (2000)
Alpine lake (Gossenköllesee)	–	–	0.3–8.5 (0–9 m)	–	8.5; DCM? (9 m)	10-54.	–	Sommaruga and Augustin (2006)
High Arctic Lake (Canada)	~7.0–8.2	~1.0–8.45	0.03–0.23	–	–	–	–	Antoniades et al. (2009)
Atazar Reservoir (Spain)	–	–	<22	–	< 22; SCM Or DCM (0–10 m)	–	–	Almodovar et al. (2004)
La Concepción Reservoir (Spain)			<58		<58; SCM Or DCM? (8–10 m)			Gálvez et al. (1988)
Forata Reservoir (Spain)			<15		15; SCM or DCM? (8 m)			Dasí et al. (1998)
Taechung Reservoir (South Korea)	–	–	2–173	–	–	–	–	An and Park (2002)
Stanford Reservoir (UK)	–	–	~0.0–919	–	–	–	–	Foster et al. (1997)[a]
Lower Bittel Reservoir (UK)	–	–	~<120	–	–	–	–	Foster et al. (1997)[a]
Draycote Reservoir (UK)	–	–	<200	–	–	–	–	Foster et al. (1997)[a]
Gorky Reservoir (Russia)	7.8–8.2	19.7–21.9	5.9–28.0	–	–	–	–	Mineeva et al. (2008)
Cheboksary Reservoir (Russia)	7.6–8.4	19.9–24.0	4.2–72.4	–	–	–	–	Mineeva et al. (2008)
Cheboksary Reservoir (Russia)	–	11.0–24.0	6.6 ± 0.7–239.8 ± 68.2	–	–	–	–	Mineeva and Abramova (2009)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Upper Volga Chain of Reservoirs (Russia)	–	–	0.4–54.5	–	–	–	–	Sigareva and Pyrina (2006)
Estuaries								
Upper reach, Pearl River Estuary (China)	–	–	15.5–40.0	–	–	199–473	–	He et al. (2010)
Lower reach, Pearl River Estuary (China)	–	–	1.5–9.3	–	–	84–161	–	He et al. (2010)
Mixing zone, Pearl River Estuary (China)	–	–	1.2–14.6	–	–	165–278	–	He et al. (2010)
Changjiang (Yangtze River) Estuary (China)	–	18.0 (mean)	0.4–11.0	–	11.0; SCM (surface)	–	–	Zhu et al. (2009)
Patuxent River Estuary, USA	7.6–8.2	0.0–28.6	3.7–33.3	–	–	–	–	Stross and Stottlemyer (1965)
Rhine Estuary (Germany, Italy, Austria, Switzerland, France, Netherlands)	–	–	0.5–5.1	–	–	142–258	–	Abril et al. (2002)
Gironde Estuary	–	–	0.3–3.5	–	–	92–208	–	Abril et al. (2002)
Thames Estuary	–	–	1.5–5.1	–	–	217–417	–	Abril et al. (2002)
Elbe Estuary	–	–	3.2–8.9	–	–	258–367	–	Abril et al. (2002)
Ems Estuary	–	–	4.5–5.4	–	–	425–592	–	Abril et al. (2002)
Sado Estuary	–	–	1.6–13.8	–	–	300–525	–	Abril et al. (2002)
Douro Estuary	–	–	2.0–5.0	–	–	158–208	–	Abril et al. (2002)
Loire Estuary	–	–	5.1–60	–	–	200–292	–	Abril et al. (2002)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion	Hypolimnion		Epilimnion	Hypolimnion	
			(μg L^{-1})		(μg L^{-1}; m)	(μM C)		
Scheldt Estuary	–	–	1.2–220	–	–	183–517	–	Abril et al. (2002)
European Estuaries (n = 9)	–	–	0.2–220	–	–	–	–	Lemaire et al. (2002)
Estuaries: Chesapeake Bay	–	–	9–77.4 (surface)	–	–	–	–	Gitelson et al. (2007)
Delaware Estuary	–	–	15–60	–	–	–	–	Pennock (1985)
The Exe Estuary SPA	–	–	>101	–	–	–	–	Langston et al. (2003)
North Carolina estuaries (n = 6)	–	–	0–184	–	–	–	–	Mallin (1994)
Neuse River Estuary	–	~10.0–30.0	~0.0–80	–	–	–	–	Gaulke et al. (2010)
Estuary, Bedford Basin (Canada)	–	–	0.58–18.02	–	–	–	–	Craig et al. (2012)
Temperate Estuaries (n = 7)	–	–	4.0–23.0	–	–	–	–	Hauxwell et al. (2003)
Coastal and open oceans								
Yellow Sea (Southern region)	–	~9.0–20.0	0.06–152	–	–	–	–	Li et al. (2007)
East China Sea	–	15–24.0	~0.06–3.2 (3–70 m)	–	–	–	–	Hung et al. (2000), Gong et al. (2000)
East China Sea surrounding Cheju Island	–	12.0–28	0.08–4.14	–	–	–	–	Kim et al. (2009)
Subtropical coastal waters (Hong Kong)	–	15.0–30.6	0.6–14.5 (0.0–10 m)	–	–	–	–	Chen et al. (2011)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Bay of Bengal, Inshore to offshore waters (Bangladesh-India)	–	–	0.1–2.5 (0–250 m)	–	2.5: SCM (0-10 m); 0.5-0.8: DCM (60-80 m)	–	–	Gomes et al. (2000)[a]
Southwest coastal waters (India)	–	23.8–27.8	0.04–8.3 (0–45 m)	–	8.3; SCM (5 m)	–	–	Roy et al. (2006)
Concepción Bay (Chile)	–	–	1.0–25	–	–	–	–	Gonzalez et al. (1989), Ahumada et al. (1991)
Mejillones Bay (Chile)	–	–	1.0–35	–	–	–	–	Iriarte and González (2004)
Inner Sea of Chiloé and austral fjord (Chile)	–	–	0.1–40	–	–	–	–	Dellarossa (1998), Pizarro et al. (2000)
Coastal waters, Inner Sea of Chiloé (Chile)	–	~10.0–17.0	0.0–32	–	–	–	–	Iriarte et al. (2007)
Upwelling seawaters of northern Chile	–	14.4–22.1	0.2–16.8	–	–	–	–	Morales et al. (1996)
The Kattegat, shallow marginal sea	–	~14.7	1.27–2.98	–	–	–	–	Carstensen et al. (2004)
Chesapeake Bay (USA)	–	–	0.2–23.3	–	–	100–341	–	Rochelle-Newall and Fisher (2002)
Scotian Shelf	–	–	0.5–5.6	–	–	–	–	Guildford and Hecky (2000)
Continental Slope	–	–	00.01–1.1	–	–	–	–	Guildford and Hecky (2000)
Southwest Florida Shelf (Shark River: Sts 26-30)	–	–	3.66–4.57	–	–	391–671	–	Clark et al. (2004)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl a	Hypolimnion	Chl a and depth in SCM and DCM	DOC Epilimnion (μM C)	Hypolimnion	Reference
			Epilimnion (μg L^{-1})		(μg L^{-1}; m)			
Southwest Florida Shelf (Caloosahatchee River: Sts 51-55)	–	–	4.41–11.60	–	–	419–1425	–	Clark et al. (2004)
Southwest Florida Shelf (Charlotte Harbor/ Peace River: Sts 62-68)	–	–	0.97–15.54	–	–	165–966	–	Clark et al. (2004)
Southwest Florida Shelf (Gulf of Mexico: St 73)	–	–	0.38	–	–	146	–	Clark et al. (2004)
California Current System, seawater	–	~12–22	0.06–15.23 (mean)	–	<7.33; SCM (0–11 m)	–	–	Millán-Núñez et al. (1996)[a]
California Current System, seawater	–	~12–22	0.06–15.23 (mean)	–	~1.17–6.45; DCM (31–78 m)	–	–	Millán-Núñez et al. (1996)*
Scotia Sea (near South Georgia)	–	–	0.06–14.6	–	–	–	–	Holm-Hansen et al. (2004)
Gulf of St. Lawrence (Canada)	–	–	0.13–10.88	–	–	–	–	Doyon et al. (2000)
Gulf of Mexico (North-central location)	–	21.1–32.0	0.7–5.9 ± 1.5 (~<20 m)	–	–	–	–	Grippo et al. (2010)
Bohai Sea at station (38.1 N, 119.5E)	–	~24.7–25.6	~1–2 (~0–20 m)	–	~1.9; SCM or DCM? (5–6 m)	–	–	Xiu et al. (2009)
Sargasso Sea	–	–	0.03–0.5	–	–	–	–	Guildford and Hecky (2000)
Baltic Sea	–	12.0–24.0	1.0–12.5	–	–	–	–	Seppälä et al. (2007)
Bering Sea (Southeast region)	–	1.5–10.5	0.40–4.45 (4–30 m)	–	–	–	–	Olson and Strom (2002)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion (μg L^{-1})	Hypolimnion	(μg L^{-1}; m)	Epilimnion (μM C)	Hypolimnion	
Alboran Sea (North-western region) or W-Mediterranean)	–	14.0–18.0	0.4 ± 0.3–148 ± 63.1 (0–200 m)	–	–	–	–	Reul et al. (2005)
Arabian Sea	–	~ 20–30	~ 0.0–2.1	–	–	–	–	Kinkade et al. (2001)
Arabian Sea (Eastern region)	–	20.6–29.4	0.17–2,080	–	7.52; SCM or DCM? (~10–15 m)	–	–	Parab et al. (2006)
Black Sea (Southwestern region)	–	~8.0–18.05	0.0–1.7	–	~1.7; SCM (0–15 m)	–	–	Ediger et al. (2006)[a]
Eastern North Pacific marine water	–	~11–28	~0.1–0.31	–	~ < 0.33–1.0; DCM (~60–75 m)	–	–	Hopkinson and Barbeau (2008)[a]
Central Atlantic Ocean	–	–	0.02–0.88	–	0.23–0.88; DCM (50–139 m)	–	–	Planas et al. (1999)
Atlantic subtropical gyres	–	–	0.06 ± 0.01–0.09 ± 0.01 (surface)	–	0.29 ± 0.01–0.34 ± 0.02; DCM (93 ± 3–119 ± 4 m)	–	–	Pérez et al. (2006)
Atlantic Ocean	–	–	0.1–4.0	–	–	–	–	Gibb et al. (2000)
Atlantic Ocean	–	13.8–27.3 (mean)	0.13–0.96 (mean)	–	–	–	–	Calbet et al. (2009)
North Atlantic Ocean	–	–	0.0–17.0	–	<17; SCM (0.0-30 m); DCM (40-100 m)	–	–	Li and Harrison (2001)[a]
North Atlantic Sub-tropical Gyral East province	–	–	~ 0.0–0.6	–	<0.6; DCM (80-110 m)	–	–	Li and Harrison (2001)[a]
North Pacific Subtropical Gyre	–	–	<0.12–1.08	–	0.12–1.08; DCM (100-136 m)	–	–	Letelier et al. (2004)
Western equatorial Pacific Ocean	–	–	0.1–0.4	–	0.4; DCM (74–96 m)	–	–	Mackey et al. (1995)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a* Epilimnion (μg L^{-1})	Hypolimnion	Chl *a* and depth in SCM and DCM (μg L^{-1}; m)	DOC Epilimnion (μM C)	Hypolimnion	Reference
Pacific Ocean (North-west region)	–	2.4-14.8	0.37–17.0	–	–	–	–	Isada et al. (2010)
Pacific Ocean (western subarctic region)	–	~3.0–8.0	~ 0.1–30 (0–200 m)	–	–	–	–	Sasaoka et al. (2002)[a]
Arctic and Antarctic ice waters								
Barents and Greenland Sea ice (Arctic Ocean)	–	–	<86 (ice)	–	–	–	–	Mock and Gradinger (1999)
Dumbell Bay, Arctic Ocean	–	(−)1.7 to (+)1.9	0.5–8.2 (1–25 m)	–	8.2; SCM (5 m)	–	–	Apollonio (1980)
Arctic coastal waters (Summer and Winter)	–	(−)1.8 ± 0 to (+)4.1 ± 1.3	0.06 ± 0.01–0.48 ± 0.11 (2 m)	–	–	–	–	Cottrell and Kirchman (2009)
Barents Sea (Arctic Ocean)	–	–	<0.11–2.27	–	<2.27; SCM? (2.5–32 m)	–	–	Norrbin et al. (2009)
Central Arctic Ocean	–	–	0.1–297 (ice)	0.1–5.2 (water)	–	70-208	–	Wheeler et al. (1996)
Arctic Ocean	–	–	0.2–7.8	–	–	–	–	Guildford and Hecky (2000)
South Shetland Islands (Antarctica)	–	0.0–2.4	<0.6–4.0 (<70 m)	–	–	–	–	Hewes et al. (2009)
Gerlache and south Bransfield Straits (Antarctic Peninsula)	–	–	~<25 (0–70 m)	–	–	–	–	Varela et al. (2002)
Coastal seawater ice, Antarctic Ocean	–	(−)2 to (+)1.0	0.45–4.03 (surface)	–	–	–	–	Verlencar et al. (1990)

(continued)

Table 1 (continued)

Sampling	pH	Water temperature (°C)	Chl *a*		Chl *a* and depth in SCM and DCM	DOC		Reference
			Epilimnion	Hypolimnion		Epilimnion	Hypolimnion	
			(μg L^{-1})		(μg L^{-1}; m)	(μM C)		
Oceanic seawater, Antarctic Ocean	–	(−)2 to (+)0.5	0.19–0.43 (surface)	–	–	–	–	Verlencar et al. (1990)
Antarctica ice seawater (control and light perturbation experiment)	–	–	3.54 ± 1.00–111 ± 30	–	–	–	–	Palmisano et al. (1985)
Southern Ocean (Antarctic marine waters)	–	(−) (0.3 to 1.4)	~0.87–30.0 (experimental growth)	–	–	–	–	Spies (1987)
Southern Ocean (Antarctic marine waters)	–	–	10.0–50.0 (experimental growth)	–	–	–	–	Sakshaug and Holm-Hansen (1986)

SCM surface Chlorophyll *a* maximum; *DCM* deep chlorophyll *a* maximum; *S* surface tempertaure; *b* bottom temperature; *?* remark either SCM or DCM which reasonably formed in water column

[a] Some data used approximately which are taken from the graphs of the related paper

SCM is often observed in coastal seawater and subsequently decreases in the offshore direction, whereas DCM is increased along the offshore direction with its enhanced depth (Millán-Núñez et al. 1996; Hayward et al. 1995; Maranón et al. 2004). Chl *a* values are quite high in SCM in coastal seawater, and decrease much more rapidly in the offshore direction (Millán-Núñez et al. 1996; Echevin et al. 2004). The occurrence of SCM in coastal seawater is possibly responsible for the high contents of DOM and nutrients, which is a general phenomenon in coastal environments. High contents of DOM can protect surface waters against sunlight exposure (Laurion et al. 2000; Hayakawa and Sugiyama 2008), and the photoproducts generated from photoinduced degradation of DOM and POM can enhance photosynthesis. The consequence is SCM formation in surface waters. For similar reasons, SCM is limited at the epilimnion (~0–5 m) in Lake Kinneret, Lake Hongfeng (4–5 m), Lake Baihua (0–2 m); Lake Biwa (2.5–10 m) and Lake Baikal (~0–30 m, with a peak at 10 m). DOC concentrations are quite higher (258–485 μM C) in Lake Kinneret compared to Lake Hongfeng (134–250 μM C at 0–25 m), Lake Baihua (157–330 μM C at 0–25 m), Lake Biwa (76–135 μM C at 0–80 m), and Lake Baikal (88–142 at 0–1,620 m) (Table 1) (Fu et al. 2010; Mostofa KMG et al. unpublished data; Satoh et al. 2006; Yacobi 2006; Berman et al. 1995; Yoshioka et al. 2002, 2007; Annual Report 2004; Sugiyama et al. 2004; Yuma et al. 2006; Mostofa et al. 2005). The overall penetration depth in Lake Kinneret was on average 1.77 m, and the uppermost layer is supposed to be representative of the entire euphotic zone (Yacobi 2006). Therefore, it is suggested that DOM and mechanical perturbation of surface waters (e.g., by wind, waves and storms), which also depends on the depth and size of the water ecosystem (particularly for lakes), are the two key factors for SCM formation.

Lakes having high water temperature (WT) often exhibit the SCM in the epilimnion, such as Lake Hongfeng (10.9–47.8 μg L^{-1} at 4–5 m and 15.3–31.0 °C), Lake Baihua (15.0–65.5 μg L^{-1} at 0–2 m and 15.3–31.0 °C), Lake Biwa (2.0–12.3 μg L^{-1} at 2.5–10 m and 11.6–28.7 °C), Lake Kinneret (95 % of Chl *a* at 0–5 m and 15–30 °C), Lake Baikal (0.7–5.8 μg L^{-1} at 0–30 m and 16.5–17.9 °C); Lake Malawi (0.03–18.7 μg L^{-1} at upper mixing layer and ~40 °C); Lake Victoria (4.7–78.5 μg L^{-1} at upper mixing layer and 25–29 °C) and Lakes of Experimental Lakes Area (<311–327 μg L^{-1} at 5–7 m and 4–20 °C) (Table 1) (Fu et al. 2010; Mostofa K et al. unpublished data; Guildford and Hecky 2000; Satoh et al. 2006; Yacobi 2006; Fee 1976; Berman et al. 1995; Mostofa et al. 2005). Therefore, high contents of DOM in surface water under high WT, driven by strong sunlight, can photochemically decompose DOM and POM to produce high amounts of DIC, CO_2, and H_2O_2. These species are directly linked with occurrence of high photosynthesis and high primary production. Moreover, in mesocosm experiments it has been observed that increasing DOM concentrations from ~10 mg C. L^{-1} to ~20 mg C. L^{-1} had a negative effect on total phytoplankton growth. The most likely explanation is the reduction of irradiance because of radiation absorption by DOM (Klug 2002).

DOC concentrations are relatively low in the offshore direction, which may afford easy penetration of sunlight (UVR) that can reach the deeper layers. This issue may increase the photosynthetic layer depth in the water column, i.e. increase the DCM depth. A significant contribution to Chl *a* may come from phytoplankton in deeper layers, in the case of a low-DOC lake water when UV attenuation increases with Chl *a* concentrations (Laurion et al. 2000). Moreover, the mixing depth can play an important role in SCM or DCM formation in lakes or oceans. A low mixing depth can often induce SCM formation, whilst high mixing depth can cause DCM formation. For example, SCM formation (~0–15 m) occurs when mixed-layer depth is low (3–15 m), whilst DCM formation (~65 m) takes place when the mixed-layer depth is high (e.g. 33 m in East China Sea) (Hung et al. 2000).

The Chl *a* concentrations in Lake Biwa are several times (~15–24) higher at the epilimnion (0–10 m), compared to those of deeper layers (40 and 70 m) during the summer stratification period (Mostofa KMG et al. unpublished data). SCM is often observed during autumn, e.g. November in 1999 and October in 2000 at the epilimnion. Chl concentration largely fluctuates and it is lower during the summer stratification period compared to early spring and autumn seasons (Fig. 3a) (Mostofa KMG et al. unpublished data). The low Chl *a* contents in SCM and its fluctuation during the summer stratification period is presumably caused by photodegradation induced by strong sunlight, coupled with high WT (maximum 28.7 °C). However, an early bloom in 2000 compared to 1999 was probably caused by a longer summer period. WT was 26.8 to 21.9 °C during September–October in 1999, which is lower compared to 2000 (WT: 23.6 to 19.5 °C at the same time).

Moreover, reduction of water clarity through eutrophication can cause a shift in phytoplankton distributions, from a DCM in spring or summer to a SCM within the surface mixed layer. This may happen when the depth of the euphotic zone is consistently shallower than the depth of the surface mixed layer (Hamilton et al. 2010). Such a SCM, which is susceptible to occur because of high primary production in spring or summer, is initially caused by the photoinduced generation of photoproducts in waters. Simultaneously, the decrease of primary production because of photoinduced degradation does not predominantly occur during that period. Therefore, the new primary production may prevail over photoinduced degradation processes. The DOM that is generated as a consequence of the high primary production can substantially absorb sunlight and cause the depth of the euphotic zone to be shallow.

These results may suggest that two important phenomena account for the occurrence of SCM and DCM in natural waters: First, waters with high contents of DOM and POM can have intense solar radiation in the surface layer. In contrast, photoproducts (DIC, CO_2, H_2O_2, and so on) are generated photochemically under high WT (caused by strong sunlight) from DOM and POM. They are responsible for the occurrence of high photosynthesis, with the consequence that high primary production can form SCM in surface waters. The second phenomenon is that water with low contents of DOM and POM lets sunlight to penetrate in the deeper water layer. Photoinduced or microbial products (DIC, CO_2, H_2O_2, nutrients, and so on) are generated from DOM and POM and are responsible for occurrence of photosynthesis. As a consequence, enhanced primary production at depth can produce DCM in deep water. The two described phenomena are extensively discussed in the next sections.

3.1.1 Mechanism of SCM Formation

SCM is driven by sunlight and it is formed during the summer stratification period in waters with high contents of DOM and POM and high temperature. High contents of DOM (of both allochthonous and autochthonous origin) and POM (e.g. algae) along with Chl *a* or phytoplankton, together with incident light wavelengths or solar zenith angle are the main limiting factors for sunlight in the surface layer (see also chapter "Colored and Chromophoric Dissolved Organic Matter (CDOM) in Natural Waters" for detailed description) (Laurion et al. 2000; Hayakawa and Sugiyama 2008; Markager and Vincent 2000; Belzile et al. 2002; Shank et al. 2005; Zhao et al. 2009). High contents of DOM and POM are thus responsible for having most of the sunlight intensity in the upper surface layer. Therefore, most of the photoinduced degradation processes would occur in the surface layers or in epilimnion. OM including DOM and POM is one of the key factors that can produce nutrients (NO_3^-, NH_4^+ and PO_4^{3-}) and various photo- and microbial products (H_2O_2, CO_2, DIC, LMW DOM, and so on) (see also chapters "Dissolved Organic Matter in Natural Waters , Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters ", "Photosynthesis in Nature: A New Look" and "Impacts of Global Warming on Biogeochemical Cycles in Natural Waters") (Zepp et al. 1987; Palenik et al. 1987; Palenik and Morel 1988; Cooper and Lean 1992; Miller and Zepp 1995; Bushaw et al. 1996; Graneli et al. 1996, 1998; Miller and Moran 1997; Sarthou et al. 1997; Gao and Zepp 1998; Jørgensen et al. 1998; Bertilsson et al. 1999; Bertilsson and Tranvik 2000; Anesio and Granéli 2003; Scully et al. 2003; Obernosterer and Benner 2004; Ma and Green 2004; Croot et al. 2005; Molot et al. 2005; Johannessen et al. 2007; Kujawinski et al. 2009; Mostofa and Sakugawa 2009; Finlay et al. 2009; Stets et al. 2009; Jiao et al. 2010; Liu et al. 2010; Lohrenz et al. 2010; Omar et al. 2010; White et al. 2010; Zepp et al. 2011; Borges et al. 2008). All these species can influence photosynthesis directly and indirectly in waters.

Photoinduced degradation of DOM and POM (e.g. degradation of phytoplankton) can be described as follows:

$$\begin{aligned}\text{DOM} + \text{POM} + h\upsilon \rightarrow\ & H_2O_2 + CO_2 + \text{DIC} + \text{LOW DOM} + NO_3^- \\ & + NO_2^- + PO_4^{3-} + \text{autochthonous DOM} + \text{others}\end{aligned} \tag{3.1}$$

where DIC is usually defined as the sum of an equilibrium mixture of dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}.

Microbial degradation of DOM and POM is as follows:

$$\begin{aligned}\text{DOM} + \text{POM} + \text{microbes} \rightarrow\ & H_2O_2 + CO_2 + \text{DIC} + \text{LOW DOM} + NO_3^- \\ & + PO_4^{3-} + \text{autochthonous DOM} + \text{others}\end{aligned} \tag{3.2}$$

The mechanism behind the formation of SCM might be that H_2O_2, photogenerated intracellularly in a photosynthetic cell or extracellularly from DOM and POM in surface waters can induce photosynthesis in the presence of CO_2 or DIC (dissolved CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}). Dependence of photosynthesis by aquatic microorganisms on OM (DOM and POM) is extensively documented in the literature (see

Sect. 5.5, chapter “Photosynthesis in Nature: A New Look”). It has recently been shown that dissolved O_2 is significantly related to benthic or sestonic Chl concentration (Heiskary and Markus 2003; Miltner 2010). Moreover, a 10 mg L^{-1} difference between daytime and nighttime dissolved O_2 concentrations was observed at an enriched site, where benthic Chl *a* levels exceeded 500 mg m^{-2} (Sabater et al. 2000). Variation in dissolved O_2 concentration forced by algal respiration is an important link between increasing nutrients and decreasing biological quality, as shown in a study of medium to large rivers (Heiskary and Markus 2003). These findings are consistent with the hypothesis that photoinduced formation of H_2O_2 from dissolved O_2 may be involved in SCM formation or primary production. Correspondingly, when cyanobacterial blooms are accumulated as scums in surface waters, prolonged exposure to UV radiation can cause enhanced carotenoid production, which can subsequently increase Chl *a*-specific photosynthetic production of O_2 (Jeffrey et al. 1997).

3.2 *Deep Chl* a *Maximum*

The Deep Chl *a* maximum (DCM) is a well-known phenomenon occurring in the presence of maximal Chl *a* contents in the deeper layer of the euphotic zone of the water column (Table 1) (Fennel and Boss 2003; Letelier et al. 2004; Huisman et al. 2006; Steele and Yentsch 1960; Anderson 1969; Klausmeier and Litchman 2001; Hodges and Rudnick 2004; Beckmann and Hense 2007; Hense and Beckmann 2008; Ryabov et al. 2010; Pérez et al. 2007; Gomes et al. 2000; Camacho 2006; Sawatzky et al. 2006; Fee 1976; Kiefer et al. 1972; Cullen 1982; Moll and Stoermer 1982; Abbott et al. 1984; Pick et al. 1984; Steinhart et al. 1994; Varela et al. 1994; Budy et al. 1995; Ediger and Yilmaz 1996; Gross et al. 1997; Goericke and Welschmeyer 1998; Marañón et al. 2000; Wurtsbaugh et al. 2001; Cuny et al. 2002; Pérez et al. 2002; Tittel et al. 2003; Barbiero and Tuchman 2004; Chapin et al. 2004; Holm-Hansen and Hewes 2004; Park et al. 2004; Ghai et al. 2010; Johnson et al. 2010; Harrison and Smith 2011; Mellard et al. 2011). According to these studies, DCM can be defined as a zone of maximum photosynthetic activity with highest Chl *a* contents. It is usually a region lacking a pronounced density gradient, generally occurring in or below the thermocline (the metalimnion). It is a stable and common feature occurring in the presence of sufficient light and nutrients under low temperature and low turbulence, and it is a remarkable characteristic of clear water with low nutrients in the deep layer, particularly in lakes and oceans. The DCM is a stable feature in tropical waters whilst it is a seasonal phenomenon in the Mediterranean and other temperate waters, following seasonal changes in incident light intensity and nutrient conditions (Letelier et al. 2004; Huisman et al. 2006; Ghai et al. 2010). The DCM is found to vary from 20 to 350 m in lakes and from 30 to 139 m in oceans (Table 1).

DCM is entirely different in Lake Superior and Lake Michigan. It is observed in the upper hypolimnion at a depth of 23–35 m in Lake Superior, whilst its depth in Lake Michigan changes seasonally. Depth varies from 15 to 30 m during early thermal stratification primarily in June, to 25–50 m by mid-stratification in July, and finally reaches 40–70 m in August (Barbiero and Tuchman 2004; Moll et al. 1984; Fahnenstiel and Scavia 1987). It has been shown that WT is relatively higher (3–24 °C) in Lake Michigan than in Lake Superior (6–18 °C), and high WT along with DOM contents may affect the DCM depth variation in Lake Michigan. Redfish Lake and other Sawtooth Valley (Idaho) lakes had DCM with mean Chl *a* peaks reaching 240–1,000 % of the mean epilimnetic Chl *a* concentrations. The DCM can be present at low light levels and account for 36.72 % of the lake primary production (Gross et al. 1997). The Sawtooth Valley lakes have DCM Chl values that can be up to 10 times higher in the metalimnia and hypolimnia than in the epilimnia (Steinhart et al. 1994; Budy et al. 1995). The DCM in the Sawtooth Valley lakes are located at depths where the light levels are near or below 1 % of surface light (Gross et al. 1997).

Seasonal changes in mixing and light intensity can produce a seasonal reset of Chl distributions, which can alter the DCM or SCM formation and ablation as a regime shift (Hense and Beckmann 2008; Hamilton et al. 2010; Abbott et al. 1984; Vincent 1983; Vincent et al. 1984; Marshall and Peters 1989; Bayley et al. 2007; Carpenter et al. 2003). Three different ‘regimes’ can occur during the seasonal occurrence of a DCM in Lake Tahoe, with transitions alternatively controlled by diffusion, nutrient supply and light (Abbott et al. 1984). Seasonal changes of DCM in the water column can depend on the depth of light penetration, which can largely affect DCM depth during the summer stratification period (Hamilton et al. 2010). Seasonal variations in the water-column attenuation coefficient of the photosynthetically available radiation (PAR) can shift the 1 % sea-surface PAR depth from approximately 105 m in winter to 121 m in summer, in the North Pacific Subtropical Gyre (Letelier et al. 2004). Such a seasonal depth shift of isolumes (constant daily integrated photon flux strata) can also be increased to 31 m due to the added effect of changes in sea-surface PAR (Letelier et al. 2004). Such a discrepancy can induce a significant deepening of the DCM during the summer period, with a concomitant increase in Chl *a* (Letelier et al. 2004).

The DCM phytoplankton contains higher amounts of phosphorus than for the epilimnion, which is likely caused by the rapid photochemical degradation of SCM phytoplankton in epilimnion. Nutrient-rich DCM might be useful as a food source for grazers, including deep-living calanoid copepods that may have a substantial impact on total lake phytoplankton productivity (Barbiero and Tuchman 2004; Moll et al. 1984). The DCM also releases the new DOM and nutrients in the hypolimnion under microbial assimilation (Rochelle-Newall and Fisher 2002; Maurin et al. 1997; Yamashita and Tanoue 2008). Phytoplankton from DCM do not show marked differences from epilimnetic communities in taxonomy or nutrient status, but can exhibit substantially higher photosynthetic impairment under UVR exposure (Harrison and Smith 2011). This suggests that epilimnetic phytoplankton can be acclimated to in situ light conditions in a spectrally-specific manner, and that ultraviolet-A radiation may be a stronger stressor than ultraviolet-B or photosynthetically active radiation in the mixed layers of lakes (Harrison and Smith 2011). DCM has varying characteristics that suggest multiple processes contributing to its formation and maintenance in lakes and oceans (Anderson 1969; Steele 1964; Hobson and Lorenzen 1972).

3.2.1 Mechanism of DCM Formation

It has been shown that DCM is generally developed in clear water at low temperature. The main effect of these conditions result is the penetraton of radiation into deep water, in which case photosynthesis can enhance the primary production and produce the DCM in deeper water. The mechanism behind DCM formation is presumably that H_2O_2 and HCO_3^- produced in the DCM water layer are susceptible to take part in phytoplankton photosynthesis. It has been shown that DIC (dissolved CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}) is mostly produced from particulate organic matter (POM: e.g. algae or cyanobacteria) and DOM microbiologically in natural waters as well as under in situ experiments (Ma and Green 2004; Finlay et al. 2009; Stets et al. 2009; Jiao et al. 2010). Correspondingly, most H_2O_2 can be produced either from algae (cyanobacteria or phytoplankton or biota) or from DOM, by several biological or photochemical processes (see also chapter "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters" for more references and description) (Palenik et al. 1987; Palenik and Morel 1988; Cooper and Lean 1992; Sarthou et al. 1997; Croot et al. 2005; Mostofa and Sakugawa 2009; Zepp et al. 1987; Angel et al. 1999; Wentworth et al. 2000; Wentworth et al. 2001; Moreno 2012; Moffett and Zafiriou 1990). Such processes are: (i) extracellular phenomena, (ii) biological processes such as glycolate oxidation during photorespiration, (iii) enzymatic reduction of oxygen at the cell surface, and (iv) microbial degradation of DOM under dark incubation. Most phytoplankton cells have the enzyme superoxide dismutase (SOD), which can catalyse the conversion of superoxide to H_2O_2. This is one of the many biological reactions that produce H_2O_2 in seawater (Croot et al. 2005).

In a field study, dark production of H_2O_2 was highest at 40–60 m depth and the corresponding DCM was detected at 90 m. The finding suggests that photosynthesis, which causes the DCM may reduce the dark production of H_2O_2 at 90 m depth (Palenik and Morel 1988). Simultaneously, the increase in pigment production caused by phytoplankton under the low-light conditions of the DCM layer (Steele 1964; Hobson and Lorenzen 1972; Kiefer et al. 1976) may lead to high contents of H_2O_2 and contribute to DCM formation. Note that pigments made up of Chls can rapidly absorb light energy upon irradiation. Radiation absorption can excite an electron to form the superoxide radical anion ($O_2^{\bullet-}$) and then H_2O_2 (see chapters "Photosynthesis in Nature: A New Look" and "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters"). The H_2O_2 concentration increase at the depth of the Chl maximum is possibly due to biological production (Croot et al. 2005). The formation of H_2O_2 by phytoplankton in the DCM layer can be supported by the observation that *Chattonella marina*, a harmful algal bloom species, is capable of producing reactive oxygen species (ROS) including $O_2^{\bullet-}$, H_2O_2, and $HO^\bullet$ at levels 100 times higher than those produced by most algae (Marshall et al. 2002; Oda et al. 1998). ROS are often produced as by-products of various metabolic pathways localized in mitochondria, chloroplasts, and peroxisomes (see also chapter "Photosynthesis in Nature: A New Look") (Apel and Hirt 2004). The presence of the cyanobacterium *Microcystis* sp. can produce a buildup of apoptosis-inducing ROS in the competing dinoflagellate *Peridinium gatunense* (Vardi et al. 2002). A distinct H_2O_2 maximum at depth in the Southern Ocean can correspond to a DCM, which also suggest a significant biological source of H_2O_2 (Sarthou et al. 1997; Croot et al. 2005). The decay of H_2O_2 apparently follows first-order kinetics (Petasne and Zika 1997; Yuan and Shiller 2001) and is biologically mediated by small microorganisms (Petasne and Zika 1997).

Filtration of seawater to remove the biota typically produces a dramatic reduction in the decay rate of H_2O_2 (Moffett and Zafiriou 1990; Petasne and Zika 1997; Fujiwara et al. 1993), whilst the amount of colloidal material influences the decay rate (Yuan and Shiller 2001). H_2O_2 may be concentrated by particulate organic matter or small fungi through rapid transpiration (Komissarov 1994, 1995, 2003). The decay process of H_2O_2 can be explained in two ways: one is the uptake possible of H_2O_2 by microorganisms during photosynthesis, the other is the decomposition of H_2O_2 by catalases and peroxidases bound to microorganisms. Catalases and peroxidase can enzymatically activate H_2O_2 to detoxify it to H_2O (see also chapter "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters") (Moffett and Zafiriou 1990). Moreover, conversion of H_2O_2 to H_2O by catalases and peroxidases could play a key role in photosynthesis and needs further study to clarify the possible links. Note that dark reduction of CO_2 may take place because of the electrons that are released by organic molecules and sulfide (Jagannathan and Golbeck 2009). Some important phenomena relevant to this context are extensively discussed in the photosynthesis chapter ("Photosynthesis in Nature: A New Look").

3.3 Changes in the Chl *a* Concentrations in Natural Waters

Chl *a* concentrations undergo significant variations in the water column, which can be seasonal, spatial and temporal depending on various factors that characterize water (Bianchi et al. 2002; Sommaruga and Augustin 2006; Biggs 2000; de Moraes Novo et al. 2006; Duan and Bianchi 2006; Lewis et al. 2010).

Streams and Rivers

Chl *a* concentrations range from 0.0 to 280 $\mu g\ L^{-1}$ in streams and rivers (Table 1) (Miltner 2010; Chessman 1985; Lohman and Jones 1999; van Nieuwenhuyse and Jones 1996; Basu and Pick 1997; Gao et al. 2004; Guéguen et al. 2006; Morgan et al. 2006; Devercelli and Peruchet 2008; Palmer-Felgate et al. 2008; Royer et al. 2008; Longing and Haggard 2010; Calijuri et al. 2008). The highest Chl *a* concentrations in freshwater riverine ecosystems are in the order of <280 $\mu g\ L^{-1}$ in River Alne (Warwickshire, UK); <263 $\mu g\ L^{-1}$ in Red River and its basin (USA); <240 $\mu g\ L^{-1}$ in River Arrow (Warwickshire, UK); <216 $\mu g\ L^{-1}$ in Paraná River basin (South America); <170 $\mu g\ L^{-1}$ in temperate streams (USA); <100 $\mu g\ L^{-1}$

in River Avon (Warwickshire, UK); <97 μg L^{-1} in streams and rivers (USA); <65 μg L^{-1} in La Trobe River Streams (Victoria, Australia); <44.6 μg L^{-1} in Ozark Streams (Missouri, USA); <27 μg L^{-1} in Rideau River (Ontario, Canada); <18.0 μg L^{-1} in sStreams and rivers (Illinois, USA); <17 μg L^{-1} in Chalk stream (UK); and 0.0–12.7 μg L^{-1} in other studied systems (Table 1).

Chl *a* mostly results from in-channel production rather than from tributary or outside inputs. Chl *a* concentrations in the Pearl River are high only during summer low-flow periods and are often controlled by temperature and by CDOM concentration (Duan and Bianchi 2006). Lower phytoplankton biomass (dominated by chlorophytes) in the Pearl River is likely linked with intense shading by CDOM and lower availability of nutrient inputs (Duan and Bianchi 2006). High concentrations of Chl *a* (0.4–170 μg L^{-1}) are strongly correlated with high contents of phosphorus (5–1,030 μg L^{-1}) in temperate streams (van Nieuwenhuyse and Jones 1996). Chl *a* concentrations in the lower Mississippi River are high in summer low-flow periods and also during interims of winter and spring. They are not coupled with physical variables or nutrients, likely due to a combination of in situ production and inputs from reservoirs, navigation locks and oxbow lakes in the upper Mississippi River and Missouri River (Duan and Bianchi 2006). The high, diatom-dominated phytoplankton biomass in the lower Mississippi River is likely the result of decreasing total suspended solids (because of increased damming in the watershed) and increasing nutrients (due to enhanced agricultural runoff) over the past few decades (Duan and Bianchi 2006).

Lakes and Reservoirs

Chl *a* concentrations are significantly variable, from 0.01 to 850 μg L^{-1} in a variety of lakes (Table 1) (Carrillo et al. 2002; Kasprzak et al. 2008; Fu et al. 2010; Mostofa KMG et al. unpublished data; Vicente and Miracle 1984; Pedros-Alio et al. 1987; Guildford and Hecky 2000; Camacho 2006; Satoh et al. 2006; Sawatzky et al. 2006; Hamilton et al. 2010; Fee 1976; Sommaruga and Augustin 2006; Yuma et al. 2006; Kiefer et al. 1972; Gross et al. 1997; Barbiero and Tuchman 2004; Fahnenstiel and Scavia 1987; de Moraes Novo et al. 2006; Aizaki et al. 1981; Rojo and Miracle 1987; Dasí and Miracle 1991; Miracle et al. 1993; Windolf et al. 1996; Camacho 1997; Yoshioka 1997; Biddanda et al. 2001; Kahlert 2002; Laurion et al. 2002; Bachmann et al. 2003; Camacho et al. 2003; Straškrábová et al. 2005; Blindow et al. 2006; Silsbe et al. 2006; McCallister and del Giorgio 2008; Striebel et al. 2008; Antoniades et al. 2009; James et al. 2009; Pan et al. 2009; Winder et al. 2009; Lv et al. 2011; Wang et al. 2012; Liu et al. 2011; Zhang et al. 2007; Rae et al. 2001). These studies demonstrate that the highest detected Chl *a* concentrations can be ordered as follows: <850 μg L^{-1} in Lake Cisó (Spain); <327 μg L^{-1} in lakes of the Experimental Lakes Area (northwestern Ontario, Canada); <298 μg L^{-1} in Lake Arcas (Spain); <276 μg L^{-1} in several shallow Danish lakes; <265 μg L^{-1} in numerous Florida Lakes; <189.8 μg L^{-1} in Subtropical and urban shallow Lakes (Wuhan, China); <189 μg L^{-1} in several lakes in Japan; <175.9 μg

L^{-1} in several lakes in Germany; <145 μg L^{-1} in Lake Börringesjön (Sweden); <133.22 μg L^{-1} in several Chinese lakes; <~110 μg L^{-1} in Lake Victoria; <90 μg L^{-1} in Lake El Tobar (Spain); <89.2 μg L^{-1} in Amazon flood plain lakes (shallow lakes: 1–3 m depth); <82.1 μg L^{-1} in Lake Kizaki (Japan); <66.93 μg L^{-1} in Lake Baiyangdian (China); <65.5 μg L^{-1} in Lake Hongfeng and Lake Baihua (China); <60 μg L^{-1} in Lake Okeechobee (USA) and Lake Krankesjön (Sweden); 53.4 μg L^{-1} in Lake Bansee (Germany); 52.7 μg L^{-1} in Lake Mitchell (USA); 40.49 μg L^{-1} in Lake Medicine (Canada); <30 μg L^{-1} in Lake Taihu (China); 26.9 μg L^{-1} in Lake Thalersee (Germany); 25.16 μg L^{-1} in Lake Eagle (Canada); <25 μg L^{-1} in Lake La Cruz (Spain); 20.2 μg L^{-1} in Lake Johanna; <18.7 μg L^{-1} in Lake Malawi (Africa); <18.1 μg L^{-1} in large Northwestern Ontario lakes; <15 μg L^{-1} in Lake La Parra and Lake Lagunillo del Tejo (Spain); <12.3 μg L^{-1} in Lake Biwa (Japan); 11.57 μg L^{-1} in Lake Josephine (USA); 0.03–10.0 μg L^{-1} in other lakes studied including relatively low Chl *a* concentrations in some famous lakes such as in Lake Superior (<0.73 μg L^{-1}); Lake Michigan (< ~ 8.0 μg L^{-1}), Lake Baikal (<5.8 μg L^{-1}) and Lake Tanganyika (<4.5 μg L^{-1}) (Table 1).

In Lake Biwa, Chl *a* concentration ranged from 2.1 to 12.3 μg L^{-1} in the upper epilimnion (2.5 and 10 m), from 0.5 to 10.7 μg L^{-1} in the deeper epilimnion (20 m), and from 0.1 to 3.3 μg L^{-1} in the hypolimnion (40 and 70 m) during the summer stratification period (Fig. 3a) (Mostofa KMG et al. unpublished data). From January to March, Chl *a* (2.0–4.0 μg L^{-1}) was almost uniformly distributed throughout the entire water column, due to vertical mixing during the overturn period (Fig. 3a) (Mostofa et al. 2005).

The summer maximum of *Microcystis* biomass in Lake Taihu peaked at 112.0 mg L^{-1} in August 1998, which accounted for 94.5 % of the total phytoplankton biomass. In contrast, Chl *a* concentrations varied from approximately 5–30 μg L^{-1} (Table 1) (James et al. 2009; Liu et al. 2011). It has also been shown that the annual cycles of WT showed a regular summer peak each year in lake Taihu, in accordance with fluctuations in *Microcystis* biomass. WT reached almost up to 30 °C during summer and declined to 5 °C by January (Liu et al. 2011). However, WT is relatively high (14.5–30.2 °C) in Lake Okeechobee (USA) that showed substantially high contents of Chl *a* (10–60 μg L^{-1}, Table 1) (James et al. 2009).

In two eutrophic lakes, e.g. Lake Hongfeng and Baihua (Southwestern China), Chl *a* concentration showed the highest level (44–66 μg L^{-1}) in the epilimnion (0–6 m) in July, during the summer stratification period (Fu et al. 2010). WT and DOC concentrations for these two lake waters were 25–31 °C and 134–330 μM C, respectively. Similarly, in the warm monomictic Lake Kinneret (Israel) Chl *a* concentrations exhibited a maximum at the epilimnion (0–5 m) during the spring season (April–May) (Yacobi 2006; Berman et al. 1995). WT and lake DOC concentrations were 15–30 °C and 258–485 μM C, respectively (Yacobi 2006; Annual Report 2004). On the other hand, in water of monomictic Lake Biwa Chl *a* maximum was observed in the epilimnion during the autumn season: November 1999 (12.3 μg L^{-1}) and October 2000 (9.4 μg L^{-1}) (Mostofa KMG et al. unpublished data). Moreover, WT and DOC concentrations were 17.0–19.5 °C and 76–135 μM C, respectively (Mostofa et al. 2005; Mostofa KMG et al. unpublished data).

Chl *a* concentrations are greatly variable, ranging from 0.01 to 133.22 μg L^{-1} in 38 Chinese lakes. Most of them are mesotrophic (TN = 0.31–2.30 mg L^{-1}; TP = 0.01–0.11 mg L^{-1}), five lakes are oligotrophic (TN < 0.31 mg L^{-1}; TP < 0.01 mg L^{-1}), and another four lakes are eutrophic (TN > 2.30 mg L^{-1}; TP > 0.11 mg L^{-1}) with algal blooms during the summer period (Zhang et al. 2007). The TN:TP ratio ranged from 2:1 to 253:1 for all 38 lakes (Zhang et al. 2007). Chl *a* concentrations significantly varied (10–145 μg L^{-1}) in two Swedish lakes. In Lake Börringesjön the highest concentration (145 μg L^{-1}) has been found in September, when light attenuation ranged from 4.61 to 7.81 m^{-1} (Blindow et al. 2006). Chl *a* concentrations were low (0.3–1.2 μg L^{-1}) in an alpine lake during the ice-cover period, but after ice-break the values increased particularly in the deep layers. The maximum was observed at 9 m depth (8.5 μg L^{-1}), whilst DOC concentrations in the water column ranged from 10 to 54 μM C (Sommaruga and Augustin 2006). Chl *a* concentrations were also very low (0.14–2.85 μg L^{-1}) in lake water with low WT (1.2–12.4 °C) and low DOC concentrations (such as ~42 μM C) (Carrillo et al. 2002). In Bohai Sea the vertical distribution of Chl *a* and water temperature at depth 0–20 m was approximately 1–2 μg L^{-1} and 24.7–25.6 °C. The diffuse attenuation coefficient increased with depth, producing a DCM at around 5–6 m depth (Xiu et al. 2009). High temperature and other factors suggest that this low variation of Chl *a* (1–2 μg L^{-1}) might be caused by high photoinduced decomposition of Chl *a* in the surface layer (0–5 m). This result is not accounted for by DCM, rather it can be considered as SCM or mixed layer depth.

On the other hand, Chl *a* concentrations in reservoirs are substantially high, ranging from approximately 0.0–919 μg L^{-1} (Gálvez et al. 1988; Foster et al. 1997; Dasí et al. 1998; An and Park 2002; Almodovar et al. 2004; Sigareva and Pyrina 2006; Mineeva et al. 2008; Mineeva and Abramova 2009). The highest Chl *a* concentrations were detected in several UK reservoirs, such as <120–919 μg L^{-1}; Chl *a* was then found at <54.5–239.8 ± 68.2 μg L^{-1} in several Russia's reservoirs and <173 μg L^{-1} in Taechung Reservoir (South Korea) (Table 1). The Chl *a* concentrations in Gorky Reservoir varied from 6.3 to 28.0 μg L^{-1} in both right and left banks, and from 5.9 to 20.6 μg L^{-1} in riverbed with variation of water temperature (WT) from 19.7 to 21.9 °C. In Cheboksary reservoir, Chl *a* concentrations were 4.2–72.4 and 6.6 ± 0.7 - 239.8 ± 68.2 μg L^{-1}, respectively, with variation of WT from 11.0 to 24.0 °C (Table 1) (Mineeva et al. 2008; Mineeva and Abremova 2009). The peak Chl *a* levels in Stanford reservoir exceeded 916 μg L^{-1} in June and July, but they remained below 25 μg L^{-1} for the remainder of the sampling period (Foster et al. 1997).

Estuaries

The Chl *a* concentrations are quite high (0.0–220 μg L^{-1}) in estuaries (Table 1) (Lemaire et al. 2002; Zhu et al. 2009; Stross and Stottlemyer 1965; Pennock 1985; Abril et al. 2002; Hauxwell et al. 2003; Langston et al. 2003; Gitelson et al. 2007; He et al. 2010; Craig et al. 2012; Mallin 1994; Gaulke et al. 2010). The highest Chl *a* concentrations are <220 μg L^{-1} in European estuaries; <184 μg L^{-1} in North Carolina estuaries; >101 μg L^{-1} in the Exe Estuary SPA; <80 μg L^{-1} in Neuse River Estuary; <77.4 μg L^{-1} in estuaries of Chesapeake Bay; <60 μg

L^{-1} in Delaware and Loire Estuaries; <40.0 μg L^{-1} in Pearl River Estuary; <33.3 μg L^{-1} in Patuxent River Estuary; <23.0 μg L^{-1} in several temperate estuaries; <18.02 μg L^{-1} in estuary of Bedford Basin, Canada; <13.8 μg L^{-1} in Sado Estuary; <11.0 μg L^{-1} in Changjiang (Yangtze River) Estuary; <8.9 μg L^{-1} in Elbe Estuary; and 0.3–5.4 μg L^{-1} in all other estuaries studied (Table 1). Such high contents of Chl *a* in estuaries are indicative of highly productive waters, which might be cause by several factors: (i) Estuarine waters contain high contents of DOM, such as 84–525 μM C, which are mostly originated from terrestrial DOM along with the autochthonous DOM and land-derived nutrients (Table 1; see also in chapter "Dissolved Organic Matter in Natural Waters") (Hauxwell et al. 2003; Monbet 1992). Water with high contents of DOM can significantly enhance primary production in estuaries, along with factors that have been discussed previously (see also chapter "Photosynthesis in Nature: A New Look"). (ii) Tidally-driven resuspension along with other associated processes (e.g. tidal mixing, current velocity, light penetration, and sediment resuspension) can influence the variability of suspended particulate matter in estuaries (Monbet 1992; Nichols and Biggs 1985; Allen et al. 1980; Schubel 1971). Estuaries with a low tidal range have maximum suspended sediment load, on the order of 100–200 mg L^{-1}. In contrast, systems with high tidal ranges have sediment concentrations of about 1,000–10,000 mg L^{-1} (Nichols and Biggs 1985). Comparative data analysis from 40 microtidal and macrotidal estuaries shows that mean annual Chl *a* levels are significantly lower in systems with high tidal energy (Monbet 1992). In contrast, nitrogen concentrations are equal to nitrogen levels in the microtidal systems (Monbet 1992). The mechanism behind these phenomena is presumably that strong tidal wave along with strong wind mixing can produce high concentrations of H_2O_2, DIC, nutrients, and so on. These species can be produced either photochemically or microbially from DOM and POM, and can strongly influence photosynthesis and primary production as discussed in an earlier chapter (see "Photosynthesis in Nature: A New Look").

Coastal and Open Oceanic Environments

The Chl *a* concentrations undergo higher variations, from 0.02 to 2080 μg L^{-1} in the waters of coastal and open oceans compared to those of lakes and estuaries (Table 1) (Letelier et al. 2004; Rochelle-Newall and Fisher 2002; Hopkinson and Barbeau 2008; Wheeler et al. 1996; Millán-Núñez et al. 1996; Gomes et al. 2000; Guildford and Hecky 2000; Li and Harrison 2001; Ediger et al. 2006; Parab et al. 2006; Roy et al. 2006; Norrbin et al. 2009; Xiu et al. 2009; Hung et al. 2000; Ahumada et al. 1991; Morales et al. 1996; Dellarossa 1998; Planas et al. 1999; Doyon et al. 2000; Gibb et al. 2000; Gong et al. 2000; Pizarro et al. 2000; Kinkade et al. 2001; Olson and Strom 2002; Sasaoka et al. 2002; Carstensen et al. 2004; Clark et al. 2004; Reul et al. 2005; Holm-Hansen et al. 2004; Pérez et al. 2006; Iriarte et al. 2007; Li et al. 2007; Seppälä et al. 2007; Calbet et al. 2009; Kim et al.

2009; Grippo et al. 2010; Isada et al. 2010; Chen et al. 2011; Iriarte and González 2004; Gonzalez et al. 1989; Mackey et al. 1995). Detected Chl *a* concentrations are as high as 2080 μg L^{-1} in Arabian Sea, <152 μg L^{-1} in Yellow Sea, <148 ± 63.1 μg L^{-1} in north-western Alboran Sea or W-Mediterranean (0–200 m depth), <40 μg L^{-1} in Chiloé and austral fjord (Chile), <35 μg L^{-1} in Concepción and Mejillones Bay (Chile), <30 μg L^{-1} in western subarctic waters of the Pacific Ocean (0–200 m depth), <23.3 μg L^{-1} in Chesapeake Bay (USA), <17 μg L^{-1} in Northwest Pacific Ocean, <17 μg L^{-1} in North Atlantic Ocean, <16.8 μg L^{-1} in upwelling seawater of northern Chile, <15.54 μg L^{-1} in Southwest Florida Shelf, <15.23 μg L^{-1} in California Current System, <14.6 μg L^{-1} in Scotia Sea (near South Georgia), <14.5 μg L^{-1} in Subtropical coastal waters (Hong Kong: 0–10 m depth), <12.5 μg L^{-1} in Baltic Sea, <11.6 μg L^{-1} in Southwest Florida Shelf (Caloosahatchee River: Sts 51–55), <10.88 μg L^{-1} in Gulf of St. Lawrence (Canada), <8.3 μg L^{-1} in Southwest coastal waters (India), and 0.0–4.45 μg L^{-1} in rest of the coastal and other oceans (Table 1). Very low values have been found in Southeast Bering Sea (4.45 μg L^{-1}), Atlantic Ocean (<4.0 μg L^{-1}) and East China Sea (<4.14 μg L^{-1}) (Table 1).

Extremely high Chl *a* concentrations at the surface of eastern Arabian Sea (the highest ever observed in natural water) are responsible for the surface growth of *Trichodesmium* spp. (Parab et al. 2006). This effect is probably linked to high water temperature (20.6–29.4 °C) (Parab et al. 2006) and relatively high DOC contents, varying from 80 to 300 μM C (Menzel 1964; Dileep Kumar et al. 1990; Breves et al. 2003). High contents of Chl *a* in Yellow seawater are also presumably caused by the occurrence of high contents of DOM (129–268 μM C) (Xia et al. 2010) and relatively high water temperature (9–20 °C) (Li et al. 2007) driven by solar irradiance. High contents of Chl *a* are generally detected in coastal seawaters, probably due to high terrestrial input of DOM and POM. Both DOM and POM can produce DIC, CO_2 and H_2O_2 upon photoinduced or microbial respiration/degradation, which are responsible for high photosynthesis and high primary production (see chapter "Photosynthesis in Nature: A New Look" for detailed mechanisms).

In the Baltic Sea, the Chl *a* concentrations are highest in the water column during the spring bloom in late April and during the cyanobacterial bloom in August, which are the two major bloom events (Bianchi et al. 2002). In contrast Chl *a* concentration is low during the summer period, despite the extensive development of cyanobacterial surface blooms (Bianchi et al. 2002). The contents of Chl *a* vary from 0.3 to 13.5 nmol L^{-1}, whilst those of Chl *b* vary from 0.05 to 0.92 nmol L^{-1} (Bianchi et al. 2002). Chl *a* is approximately 15 times higher than Chl *b* in the Baltic Sea.

The observed, relatively low concentrations of Chl *a* in oceanic environments are presumably due to several facts: (i) Low contents of DOM and POM, particularly in open Oceanic environments, may cause the occurrence of low contents of CO_2, DIC, H_2O_2, nutrients, and so on. They are responsible for low photosynthesis and low primary production, as extensively discussed in the photosynthesis chapter (see chapter "Photosynthesis in Nature: A New Look"). In contrast, high contents of organic matter (DOM and POM) in coastal waters are responsible for the higher observed contents of Chl *a* compared to the open ocean (Clark et al. 2004). It is generally known that DOM and POM (e.g. phytoplankton) can release NO_3^- and PO_4^{3-}, by either photoinduced or microbial assimilation/respiration in waters (see chapters "Dissolved Organic Matter in Natural Waters, Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters" and "Photosynthesis in Nature: A New Look").

(ii) Strong wind and wave mixing along with the solar (UV and PAR) radiation may degrade Chl *a*, DNA or biomolecules bound to PSI and PSII of microorganisms. The effect would be more marked in the open ocean compared to coastal waters. This issue would be supported by the observation that UV-B radiation (280–315 nm) can inhibit photosynthetic carbon fixation by tropical phytoplankton assemblages in coastal to pelagic surface seawaters (Li et al. 2011). The inhibition of photosynthesis by UV-A (315–400 nm) increases from coastal to offshore waters (Li et al. 2011). It has also been shown that UV-B inhibits photosynthesis by up to 27 % and UV-A by up to 29 % (Li et al. 2011). In East China Sea, lower concentration of Chl *a* (0.06–0.07 $\mu g\ L^{-1}$: Kuroshio sites) has been detected in the open ocean, with high water temperature (23.9–24.0 °C) and low NO_3^- ($<0.1\ \mu M$), than in coastal seawater (0.43–2.44 $\mu g\ L^{-1}$) (Hung et al. 2000). The latter had low temperature (16.3–18.9 °C) and high NO_3^- (<0.4–$6.0\ \mu M$) (Hung et al. 2000).

Similarly and interestingly, Chl *a* concentrations are largely variable (0.06–1,000 $\mu g\ L^{-1}$) and substantially high (occasionally $>1{,}000\ \mu g\ L^{-1}$) in ice-covered Antarctic and Arctic Oceans (Table 1) (Palmisano et al. 1985; Garrison et al. 1986; Wheeler et al. 1996; Mock and Gradinger 1999; Apollonio 1980; Guildford and Hecky 2000; Norrbin et al. 2009; Sakshaug and Holm-Hansen 1986; Spies 1987; Verlencar et al. 1990; Varela et al. 2002; Cottrell and Kirchman 2009; Hewes et al. 2009). The highest Chl *a* concentrations, reaching values higher than 1,000 $\mu g\ L^{-1}$, have been detected in bottom-ice communities of Antarctica Ocean. Otherwise, Chl *a* is largely variable: it reached $<297\ \mu g\ L^{-1}$ in the ice undersurface; <5.2 in the water column of central Arctic Ocean; $<86\ \mu g\ L^{-1}$ in Barents and Greenland Sea ice (Arctic Ocean); $<25\ \mu g\ L^{-1}$ in Gerlache and south Bransfield Straits (Antarctic Peninsula); $<8.2\ \mu g\ L^{-1}$ in Dumbell Bay (Arctic Ocean); $<4.03\ \mu g\ L^{-1}$ in ocean seawater (Antarctic Ocean); $<4.0\ \mu g\ L^{-1}$ in South Shetland Islands (Antarctica), 0.10–2.27 in other ice seawater; and finally $111 \pm 30\ \mu g\ L^{-1}$ in incubation experimental studies using Antarctic ice seawater (Table 1).

It has been shown that Chl *a* varies significantly, from 0.1 to 297 $\mu g\ L^{-1}$ in ice undersurface and from 0.1 to 5.2 $\mu g\ L^{-1}$ in the water column (Wheeler et al. 1996). The values of Chl *a* can increase in the range of the potential phytoplankton standing stock (25–50 $\mu g\ L^{-1}$) in Antarctic marine waters, Southern Ocean (Sakshaug and Holm-Hansen 1986; Spies 1987). Similarly, Chl *a* contents in bottom ice communities reach 300–400 mg m^{-2} (Steemann-Nielsen 1962; Palmisano and Sullivan 1983). Such numerous algal communities are presumably the consequence of several phenomena: (i) Algal growth may be prolonged due to low temperature and low solar irradiance, which are unable to form $O_2^{\bullet -}$ and subsequently H_2O_2 or $HO^{\bullet}$. This phenomenon can protect algal cells from death, allowing high primary production caused by accumulation of algal species in the ice bed. Interestingly, observation of a series of ice age classes indicated that older ice has higher concentrations of particulate organic carbon, Chl and algal cells (Gleitz and Thomas 1993). Substantial increases have been observed for the abundance of *Chaetoceros neogracile, F. cylindrus,* and *Nitzschia lecointei,* implying growth of these algae (Gleitz and Thomas 1993). The abundance of other species (*F. kerguelensis, Dactyliosolen*) decreased with the age of the sea ice, implying that they can possibly accumulate in ice but are selected against over time (Gleitz and Thomas 1993). Correspondingly, algal pigment signatures in sea ice also suggest that older ice is more diatom-dominated (Lizotte et al. 1998). Lower concentrations of Chl *a*, which have been observed in a light perturbation experiment (3.54 ± 1.00 to 14.2 ± 12.4 $\mu g\ L^{-1}$) compared to the control experiment (5.21 ± 2.33 to 111 ± 30 $\mu g\ L^{-1}$) in Antarctica ice seawater (Palmisano et al. 1985) can also support the above phenomena. The occurrence of more elevated concentrations of dissolved O_2 in Arctic and Antarctic Oceans compared to tropical and subtropical waters (Codispoti and Christensen 1985; Falkner et al. 2005; Garcia et al. 2005; Schmittner et al. 2007; Araoye 2009; Abowei 2010; Keeling et al. 2010) are also responsible for the rapid formation of H_2O_2 under low irradiance. These phenomena can support high photosynthesis in seawater ice. (ii) The occurrence of the ozone hole, and a corresponding increase in UV-B exposure, can cause unequivocal increase of direct or indirect oxidative damage, either directly or indirectly through formation of ROS. It has been shown that the latter can alter biomolecules (lipids, DNA, amino acids, proteins, Chls) and can affect photosynthetic efficiency, reproduction and development in Antarctic marine organisms (see also chapter "Photosynthesis in Nature: A New Look") (Bidigare 1989; Smith et al. 1992; Arrigo 1994; Lesser et al. 2001, 2004; Lesser and Barry 2003; Karentz et al. 2004; Leu et al. 2007; Lister et al. 2010; Cullen and Neale 1997). The effects of the ozone hole and of the corresponding UV-B exposure is largely mitigated by sea ice coverage, in the case of aquatic organisms that live beneath the ice cover (Moreno 2012; Karentz et al. 2004; Lister et al. 2010; Tremblay et al. 2006; Perovich 1993; Trodahl and Buckley 1989). (iii) Intracellular and extracellular production of H_2O_2 from algae (or phytoplankton species) can take place under light conditions in the ice layer (see also chapter "Photosynthesis in Nature: A New Look") (Hong et al. 1987; Bazanov et al. 1999; Premkumar and Ramaraj 1999; Lobanov et al. 2008; Palenik et al. 1987; Palenik and Morel 1988; Komissarov 2003), and could enhance photosynthesis. A further enhancement effect could be caused by relatively high amounts of DIC, H_2O_2 and nutrients produced from DOM and POM, either by microbial or photoinduced processes in Arctic and Antarctic Oceans.

Photosynthesis could rapidly occur under low irradiance conditions in the presence of large amounts of algae (or phytoplankton), and if H_2O_2, DIC and nutrients are available. It has been shown that nutrient concentrations (e.g. nitrate) are considerably high (2–12 μM) in the Arctic Ocean (Tremblay et al. 2006). In the Antarctic Ocean, Chl *a* concentrations in coastal surface seawater ice are high (0.45–4.03 $\mu g\ L^{-1}$), and at the same time there are low contents of NH_4^+ (0.05–2.21 μM), NO_3^- (7.82–23.1 μM), and PO_4^{3-} (0.60–3.0 μM) compared to those of oceanic offshore waters (Table 1) (Verlencar et al. 1990). In contrast, Chl *a* concentrations are relatively low (0.19–0.43 μg L^{-1}) in the presence of rather elevated amounts of NH_4^+ (0.14–1.36 μM), NO_3^- (22.55–29.50 μM), and PO_4^{3-} (1.71–2.35 μM), even in the presence of similar water temperatures (Table 1) (Verlencar et al. 1990). This result can imply that nutrients have limited influence on photosynthesis in offshore seawater. A more important effect could be that high contents of algae (or phytoplankton species) in coastal Antarctic seawater ice can absorb irradiance by Chl *a* bound to PSI and PSII. A possible consequence would be intracellular or extracellular H_2O_2 formation, which could directly affect photosynthesis. This effect could be more important in coastal seawater ice than in offshore oceanic seawater ice. The covariation of dissolved nitrate and phosphate maintained by ocean circulation (Weber and Deutsch 2010) might be a factor that affects photosynthesis in offshore regions. However, future studies will be required to provide evidence for this mechanism.

4 Factors Controlling Chl *a* in Natural Waters

There are a numbers of environmental factors that substantially influence Chl *a* concentrations or primary production in natural waters. The key factors affecting photosynthetic and respiratory activities can be detected based on the growth and development of organisms. They are: (i) seasonal variation in sunlight and UV radiation, which affect photosynthesis; (ii) occurrence of CO_2 forms; (iii) variation in temperature; (iv) effects of water stress (drought) and precipitation/rainfall; (v) effects of the amount and nature of DOM and POM; (vi) variation in nutrient contents; (vii) variation in trace metal ions; (viii) effect of salinity or salt stress; (ix) effects of toxic pollutants on aquatic microorganisms; (x) effect of size-fractionated phytoplankton; (xi) effects of global warming. These factors are similar to those affecting primary production or cyanobacterial bloom, which the exception of the effect of global warming (see chapter "Photosynthesis in Nature: A New Look" and "Impacts of Global Warming on Biogeochemical Cycles in Natural Waters").

4.1 Effects of Global Warming

Global warming can affect the heat budget and other physical processes of a water body, and can subsequently alter the stratification and mixed layer depths (Huisman et al. 2006; Schindler 1997; Magnuson et al. 1997). Such changes, along with global warming-induced changes in the seasonal light cycle, can alter the seasonal patterns of Chl contents (or primary production), phytoplankton composition and nutrient concentrations in SCM and DCM (Huisman et al. 2006; Walsby et al. 1997; O'Reilly et al. 2003; Verburg et al. 2003; Baulch et al. 2005; Fu et al. 2007; Jöhnk et al. 2008; Castle and Rodgers 2009; Davis et al. 2009; Paerl and Huisman 2009). Correspondingly, an extension of the summer season due to global warming may prolong the photochemical processes, with high production of photoproducts, pH alteration, and microbial food web stimulation (Baulch et al. 2005; Morris and Hargreaves 1997; Cooke et al. 2006; Malkin et al. 2008). These issues can result into high photosynthesis, thereby enhancing phytoplankton productivity in lakes and oceans. These phenomena will particularly affect the Arctic and Antarctic regions.

Climate models predict that global warming will increase the stability of the vertical stratification in large parts of lakes and oceans (Huisman et al. 2006; Sarmiento et al. 1998, 2004; Bopp et al. 2001, 2005; Schmittner 2005). This will subsequently reduce vertical mixing and suppress the upward flux of nutrients, leading to a decrease in primary production. However, increased stability of the water column might also increase the photochemical degradation of DOM, and cause high photosynthesis via high temperature and longer summer season. Reduced vertical mixing can generate oscillations and chaos in phytoplankton biomass, size and species composition of DCM (Huisman et al. 2006; Barbiero and Tuchman 2004; Winder et al. 2009). These perturbations are generated by the difference in timescale between the sinking flux of phytoplankton and the upward flux of nutrients. Increasing background light attenuation can increase light limitation, shifting phytoplankton towards the surface and generally decreasing DCM depth and total biomass, particularly in the mixed layer (Mellard et al. 2011). Climate warming may promote the growth of toxic, rather than non-toxic, phytoplankton populations (Davis et al. 2009). Therefore, changes induced by global warming can significantly impact the SCM, DCM, species composition, nutrients dynamics, and carbon cycle. This issue is also extensively discussed in other chapters (see chapters "Photosynthesis in Nature: A New Look" and "Impacts of Global Warming on Biogeochemical Cycles in Natural Waters").

5 Degradation of Chl

It has been shown that terrestrial plants adapt their annual life cycles of growth, reproduction and senescence to the annual climate cycle with period of one year. In contrast, phytoplankton biomass can turn over around 100 times each year as a result of fast growth and equally fast consumption by grazers (Calbet and Landry 2004; Behrenfeld et al. 2006; Winder and Cloern 2010). Therefore, the significance of the degradation of Chl *a* bound to higher plants and aquatic microorganisms shows characteristic differences.

5.1 Degradation of Chl a in Aquatic Microorganisms

Chl *a* bound to phytoplankton or cyanobacteria can be degraded by both photoinduced and microbial degradation processes and can produce chlorophyllide *a*, pheophorbide *a*, pheophytin *a*, and pyropheophytin *a* in aqueous media

(Welschmeyer and Lorenzen 1985; Stephens et al. 1997; Zhang et al. 2009; Bianchi et al. 2002; Schulte-Elte et al. 1979; Falkowski and Sucher 1981; Pietta et al. 1981; Mantoura and Llewellyn 1983; Keely and Maxwell 1991; Nelson 1993; Sun et al. 1993; Rontani et al. 1995; Rontani et al. 1998, 2003, 2011; Rontani and Marchand 2000; Yacobi et al. 1996; Cuny et al. 1999; Marchand and Rontani 2001; Rontani 2001; Lemaire et al. 2002; Rontani and Volkman 2003; Marchand et al. 2005; Christodoulou et al. 2009; Christodoulou et al. 2010; Rontani et al. 2000). Photosynthetically active radiation (PAR, 400–700 nm) and UV radiation (UV-B: 280–315 nm and UV-A: 315–400 nm) are responsible for the degradation of Chls, of PSI, and of PSII bound to phytoplankton species, either directly or through photoinduced generation of ROS in the natural environment (see also chapter "Photosynthesis in Nature: A New Look") (Schulte-Elte et al. 1979; Nelson 1993; Rontani et al. 1995; Nelson and Wakeham 1989; Rontani et al. 1994; Sinha and Häder 2002; Häder and Sinha 2005; Rath and Adhikary 2007; Gao et al. 2008; Pattanaik et al. 2008; Jiang and Qiu 2011). It has also been shown that the degradation rates of Chl *a* bound to algae are several times higher than those of sediment TOC or of algae themselves (Leavitt and Carpenter 1990; Westrich and Berner 1984; Garber 1984; Henrichs and Doyle 1986). The photodegradation of different lipid compounds in killed cells of *Phaeodactylum tricornutum* and *Dunaliella* sp. shows that Chl phytyl chain is degraded to 6,10,14-trimethylpentadecan-2-one and 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol, sterols to 5α- and 6α/6β-hydroxysterols, carotenoids to loliolide and *iso*-loliolide, and unsaturated fatty acids to C_7–$C_{11}\omega$-oxocarboxylic and α,ω-dicarboxylic acids (Rontani et al. 1998). After elimination of insufficiently specific photoproducts, the compounds 3-methylidene-7,11,15-trimethylhexadecan-1,2-diol, 5α- and 6α/6β-hydroxysterols, C_7–$C_{11}\omega$-oxocarboxylic and α, ω-dicarboxylic acids (with C_9 as the most abundant species) have been selected to constitute a "pool" of useful indicators of photooxidative alteration of phytoplankton (Rontani et al. 1998).

Irradiation of killed non-axenic cells of *Emiliania huxleyi* (Prymnesiophyceae) under PAR and UV radiation can degrade most of the unsaturated lipid components, such as Chls, unsaturated fatty acids and brassicasterol (Christodoulou et al. 2010). Exposure to UV radiation can also induce photosensitized stereomutation (cis–trans isomerization) of the double bonds of some lipids (e.g. monounsaturated fatty acids and Chl phytyl side-chain) and of some of their oxidation products. These processes yield (after reduction) some compounds (e.g. 9-hydroxyoctadec-cis-10-enoic and 10-hydroxyoctadeccis-8-enoic acids arising from oleic acid oxidation and 11-hydroxyoctadec-cis-12-enoic and 12-hydroxyoctadec-cis-10-enoic acids arising from cis-vaccenic acid oxidation), which are sufficiently specific to act as tracers of UV-induced in situ photodegradation (Christodoulou et al. 2010). The abiotic degradation processes can act on most of the unsaturated lipid components of senescent phytoplankton, such as sterols, unsaturated fatty acids, Chl phytyl side-chain, carotenoids, alkenones and alkenes (Rontani et al. 1998; Rontani 2001, 2008; Christodoulou et al. 2010). In phytodetritus, the visible light-dependent degradation rates are 3–4 times higher for the Chl tetrapyrrolic structure than for the phytyl side-chain (Cuny et al. 1999; Cuny and Rontani 1999).

Planktonic lipids are more susceptible to biodegradation than terrestrial lipids. Moreover, biodegradation is more intense in sinking particulate organic matter (POM) than in suspended POM (Rontani et al. 2011). Simultaneously, there would be efficient transfer of singlet oxygen from suspended and senescent phytoplankton cells to associated bacteria, with subsequent inhibition of heterotrophic degradation (Rontani et al. 2011). The in vitro enzymatic degradation of Chl *a* in several species of marine phytoplankton can produce chlorophyllide *a*, pheophorbide *a*, pheophytin *a*, and pyropheophytin *a* (Owens and Falkowskit 1982). In some species, Chl *a* can be degraded to products that do not absorb visible light. It has also been observed that losses of phytol and Mg^{2+} are catalysed by chlorophyllase and by a magnesium-releasing enzyme, respectively. Both enzymes are activated by cell disintegration (Owens and Falkowskit 1982). Phaeophytin *a*, pyrophaeophytin *a*, phaeophorbide *a*, and pyrophaeophorbide *a* are the phaeopigments found in largest amount in both sediments and water column (Furlong and Carpenter 1988). Tetrapyrrole derivatives of chloropigments (phaeopigments) are formed as a result of bacterial or autolytic cell lysis, and of metazoan grazing activities (Welschmeyer and Lorenzen 1985; Sanger and Gorham 1970; Shuman and Lorenzen 1975; Bianchi et al. 1988, 1991). Further degradation may produce several colorless organic substances (Brown et al. 1991; Westrich and Berner 1984; Henrichs and Doyle 1986).

From the differences between anoxic and oxic decomposition in incubation experiments, together with naturally observed concentration profiles, it can be inferred that Chl *a* in natural sediments can be degraded during the oscillation between oxic and anoxic conditions caused by physical and biological mixing processes (Ming-Yi et al. 1993). Oscillation experiments (oxic vs. anoxic and anoxic vs. oxic) also suggest that the activity of aerobic organisms may be an important factor that affects Chl *a* degradation (Ming-Yi et al. 1993). Examination of the effects of meiofauna on Chl *a* degradation under oxic conditions, implies that microorganisms may play a stronger role in Chl *a* degradation than meiofauna (Ming-Yi et al. 1993). The relative temperature independence of anoxic degradation and temperature dependence of oxic degradation suggest that anoxic degradation may be largely controlled by chemical factors, while oxic degradation may be more strongly controlled by biophysical and biochemical processes (Ming-Yi et al. 1993).

It is shown that the maximum DOM production lags in time relative to Chl *a* concentration in surface waters, whilst Chl *a* concentrations were relatively low and fluctuated during the summer stratification period in Lake Biwa (Fig. 3a and b) (Zhang et al. 2009; Mostofa KMG et al. unpublished data; Mostofa et al. 2005; Sasaki et al. 2005; Hanamachi et al. 2008). The summertime fluctuation of Chl *a* is possibly linked to its photoinduced degradation, which can contribute to the DOC increase in the surface water of Lake Biwa (Fig. 3a and b) (Mostofa KMG et al. unpublished data; Mostofa et al. 2005). The release of DOM from algae or phytoplankton might be one of the key causes for the decrease of Chl *a* or of the primary production in the surface layer, during the summer season. It is shown that both 'labile' and 'refractory' fractions of DOM are produced during phytoplankton or algal biomass degradation. However, the 'labile' fraction of organic matter, such as glucose, is rapidly decomposed within a few days and the 'refractory' fraction is decomposed more slowly (Mostofa et al. 2009; Zhang et al. 2009; Mostofa KMG et al. 2008; Ogawa et al. 2001).

Low concentrations of Chl *a* during the summer stratification period in upper surface waters might be the effect of photoinduced degradation of Chl *a* by sunlight. Degradation of Chl *a* presumably involves two facts. First of all, cyanobacteria can generate internally reactive oxygen species (ROS) such as superoxide radical anion (O_2^-), hydrogen peroxide (H_2O_2) and hydroxyl radical ($HO^•$) in PSII, which can all be involved into cells decomposition (see chapter "Photosynthesis in Nature: A New Look" for a detailed description). The second fact is the photoinduced generation of ROS from DOM (of both allochthonous and autochthonous origin), NO_2^- and NO_3^- (see also chapters "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters" and "Photoinduced Generation of Hydroxyl Radical in Natural Waters"). These ROS can decompose Chl *a* that is found outside the cells (see chapter "Photosynthesis in Nature: A New Look"). H_2O_2 involvement can be justified by the observation that autoxidation is substantially enhanced in the presence of a peroxide or hydroperoxide initiator (Fossey et al. 1996; Wilson et al. 2000; Kwan and Voelker 2003). Dissolved O_2 is substantially varied (from 6.0 to 12.0 mg L^{-1}) in a variety of surface waters, whereas the saturated dissolved O_2 concentration in pure water is 7.5 mg L^{-1} at 30 °C (Falkner et al. 2005; Garcia et al. 2005; Schmittner et al. 2007; Araoye 2009; Abowei 2010; Keeling et al. 2010; Hatcher 1987). High contents are generally found at low temperature, particularly in the Arctic and Antarctic Oceans. Such high contents of dissolved O_2 prompt the rapid absorption of electrons released from either chromophoric DOM (CDOM) or POM (e.g. phytoplankton or algae) upon light illumination, which enhances production of $O_2^{•-}$ and H_2O_2. Dissolved O_2 in water is the ultimate electron acceptor upon illumination by light, forming $O_2^{•-}$ that is a long-suspected first intermediate in photoinduced reactions that take place in natural surface waters (Baxter and Carey 1983; Bielski et al. 1985; Petasne and Zika 1987; Micinski et al. 1993). The involvement of dissolved O_2 in H_2O_2 production can be justified by the experimental observation that 5–40 % of the oxygen produced by photosynthetically active organisms can be fixed through photochemical reactions in natural waters (Laane et al. 1985).

Experimental studies show that H_2O_2 can affect cyanobacteria at concentration values that are 10 times lower than for green algae and diatoms. Strong light-dependent toxicity can enhance the difference, for which reason H_2O_2 can act as a limiting factor for cyanobacterial growth (Drábková et al. 2007). H_2O_2 concentrations of approximately 2–8 μM, which are produced during light exposure of aquatic macrophyte leachates or DOM, can inhibit microbial growth or bacterial carbon production (Farjalla et al. 2001; Anesio et al. 2005). The addition of 0.1 μM H_2O_2 to humic lake water can inhibit BCP by as much as 40 % (Xenopoulos and Bird 1997). Photobleaching and CO_2 production in irradiated waters can be significantly decreased upon addition of ROS scavengers, whilst post-irradiation bacterial growth in samples containing a ROS scavenger can be significantly increased Scully et al. (2003). The decrease of ROS activity (CO_2 production) can likely cause an accumulation of bioavailable DOM and enhance microbial processes (Scully et al. 2003). Chl *a* is more susceptible to photochemical decomposition than zeaxanthin in the epilimnion, because zeaxanthin is generally a more stable compound. It is photo-resistant and is found in higher contents than Chl *a* during the summer period (Bianchi et al. 2002; Rowan 1989, 2000). Photoresistance of carotenoids such as zeaxanthin and *ß*, *ß*-carotene involves quenching of singlet oxygen, which prevents photooxidation reactions (Rowan 1989; Jeffrey et al. 1997).

5.2 Degradation of Chl a *in Higher Plants*

Degradation of Chl can have two visible effects on plant leaves (Hendry et al. 1987; Takamiya et al. 2000; Matile et al. 1996; Amir-Shapira et al. 1987; Merzlyak et al. 1999; Park et al. 2007; Pruzinská et al. 2005; Zimmermann and Zentgraf 2005; Kratsch and Wise 2000; Karuppanapandian et al. 2011; Hillman et al. 1994). The first is the colour change from green to yellow or red, which naturally occurs during the season change in autumn and is the most conspicuous and rapid event. The second is cell death caused by external factors, such as injuries sustained by low or high temperature, pathogen attack during various phases of the life cycle of plants, and so on. It has been estimated that approximately 1.2 billion tons of Chl is degraded globally each year (Hendry et al. 1987). The conversions of Chl to chlorophyllide and of pheophytin to pheophorbide in coleslaw, cucumbers and brined olives are the result of chlorophyllase activity (Heaton et al. 1996). Chl *a* in crude extracts of *Chenopodium album* (white goose foot) in the dark can produce chlorophyllide *a*, pheophorbide *a*, 13^2-hydroxychlorophyllide *a* and pyropheophorbide *a*, the increase of which is accompanied by a concomitant decrease in levels of Chl *a* (Shioi et al. 1991). Chl *a* is degraded in a crude extract of *C. album* via enzymatically catalyzed reactions (Shioi et al. 1991).

Chl of detached rice leaves undergoes an initial long lag that lasts for one whole day, after which it is rapidly degraded in the second and third days during experiments conducted under total darkness at 30 °C (Okada et al. 1992). Light only has a weak protecting effect on soluble proteins, and ribulose-1,5-bisphosphate carboxylase/oxygenase rapidly disappeared under illumination with weak white light (Okada et al. 1992). In an in vitro system of extracted broccoli florets, Chl *a* is degraded initially to chlorophyllide *a* or 13^2-hydroxychlorophyll *a*. Subsequently, chlorophyllide *a* is degraded to pyrophaeophorbide *a* through 13^2-hydroxychlorophyll *a* (Yamauchi et al. 1997). Finally, 13^2-hydroxychlorophyll *a* and pyrophaeophorbide *a* can be degraded to colourless, low molecular weight compounds.

5.3 Degradation of Chl During Food Processing

It is well-known that blanching can inactivate chlorophyllase and enzymes, producing a subsequent decrease in the photosynthetic capacity that is responsible for senescence and rapid loss of green colour. The discolouration of green vegetable during processing is caused by conversion of Chls to pheophytins, which is also influenced by pH (Blair and Ayres 1943; Gupte et al. 1964; Minguez-Mosquera et al. 1989; Koca et al. 2007). Chl degradation reactions can be caused by several chemical, photoinduced or enzymatic processes, including simultaneous actions of enzymes, weak acids or pH changes, oxygen, light and heat. Such processes can lead to the formation of a large number of degradation products (Hayakawa and Timbers 1977; Koca et al. 2007). Major chemical degradation processes are pheophytinization, epimerization, pyrolysis, as well as hydroxylation, oxidation or photoinduced oxidation (Mangos and Berger 1997).

The green colour of vegetables can be altered to an olive green under mild acidic conditions, whereas hydrogen ions can transform Chls to their corresponding pheophytins by substitution of the magnesium ion in the porphyrin ring (Minguez-Mosquera et al. 1989; Gold and Weckel 1958; Gunawan and Barringer 2000). Preferential degradation of Chl *b* in the degreening of ‘Satsuma’ mandarin (*Citrus unshiu* Marc.) is found in ethylene-treated fruits and in fruits ripening on the tree. In contrast, Chl *a* is predominantly degraded in non-treated fruits (Keishi 1979). Methyl jasmonate and ethylene can markedly enhance the mRNA levels and chlorophyllase activity, which presumably accelerates leaf senescence and fruit ripening (Drazkiewicz 1994; Smart 1994; Creelman and Mullet 1997; Jacob-Wilk et al. 1999; Tsuchiya et al. 1999). Stimulatory effects by methyl jasmonate and ethylene also indicate that chlorophyllases are key enzymes for senescence or ripening.

5.4 Mechanism for Degradation of Chl

The key PSII reactions of Chls are photooxidation, involving attack of $^1O_2$, $HO^\bullet$ or H_2O_2, and enzymatic degradation (see also chapter “Photosynthesis in Nature: A New Look”) (Takamiya et al. 2000; Brown et al. 1991; Gossauer and Engel 1996; Hörtensteiner 2006; Kräutler and Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011). The processes occurring under high irradiance or UV light and high temperature have been documented in the photosynthesis chapter (see chapter “Photosynthesis in Nature: A New Look”). Three Chl catabolic enzymes, such as chlorophyllase, pheophorbide *a* oxygenase, and red Chl catabolite reductase (RCCR) are susceptible to play key roles into Chl degradation, either during leaf senescence and fruit ripening or in response to pathogens and wounding (Hörtensteiner 2006; Hörtensteiner and Kräutler 2011; Kariola et al. 2005; Azoulay Shemer et al. 2008).

The mechanism responsible for the degreening of plants and the degradation of Chl involves enzymatic reactions in two phases, through several chain reactions (Fig. 4) (Takamiya et al. 2000; Hörtensteiner 2006; Kräutler and Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011). In the first phase, Chl degradation is caused by the removal of the phytol tail (dephytylation) and of the central Mg atom (magnesium dechelatase). Dephytylation occurs first by

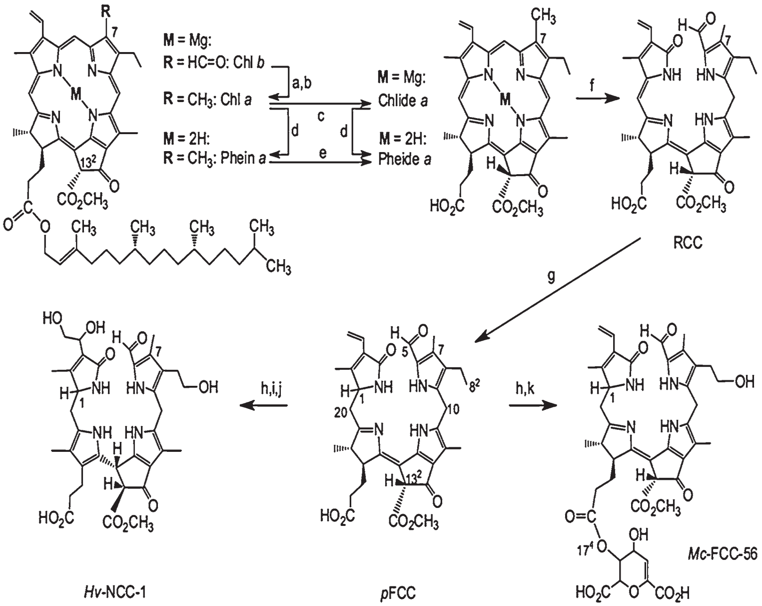


Fig. 4 Representative structural outline of major catabolites delineating the main paths of chlorophyll breakdown in higher plants (Kräutler and Hörtensteiner 2006; Moser et al. 2009): Chls are degraded in the chloroplast by enzyme-catalyzed processes via pheophorbide (Pheide) *a* and the red chlorophyll catabolite (RCC) to give primary fluorescent chlorophyll catabolites (*p*FCC, or its C1-epimer, epipFCC). The relevant enzymes involved in this part are: (**a**) Chl *b* reductase; (**b**) 7-hydroxymethyl Chl reductase; (**c**) chlorophyllase (CLH);)**d**) 85magnesium dechelatase; (**e**) pheophytinase (PPH); (**f**) Pheide *a* oxygenase (PAO); (**g**) RCC reductase (RCCR). *p*FCCs are modified further by unidentified hydroxylating enzymes (**h**, **i**). When carrying a free propionic acid group, FCCs are transported into the vacuole, where they are suggested to isomerize by a spontaneous, acid catalyzed reaction (**j**) to the corresponding nonfluorescent chlorophyll catabolites (NCCs), such as Hv-NCC-1 (the main tetrapyrrolic catabolite found in senescent leaves of barley, Hordeum vulgare). Else, they are esterified by unknown enzymes at the propionic acid group (**k**) to give 'persistent' hypermodified FCCs, such as Mc-FCC-56 (the main FCC in peels of ripe bananas, Musa acuminata, cavendish cultivar). Relevant atom numbering is specified *Data source* Hörtensteiner and Kräutler (2011)

hydrolysis of a phytol residue in ring IV, catalyzed by the enzyme chlorophyllase that converts Chl to phytol and chlorophyllide (Drazkiewicz 1994; Jacob-Wilk et al. 1999; Tsuchiya et al. 1999; Willstätter and Stoll 1913; Trebitsh et al. 1993; Schelbert et al. 2009). The 'Mg dechelatase' subsequently occurs in chlorophyllide, by displacement with 2 H^+ (dechelation) that produces pheophorbide. The latter is subsequently cleaved by an oxygenase enzyme and converted into red Chl catabolite (RCC). Subsequent reduction can produce colorless primary fluorescent Chl catabolite (*p*FCC). The in vivo and in vitro accumulation of pheopigments during Chl degradation in algae and higher plants suggests the presence of a 'magnesium dechelatase' enzyme (Owens and Falkowskit 1982; Shioi et al.

1991; Janave 1997; Maeda et al. 1998; Ziegler et al. 1988). Pheophorbide *a* oxygenase is thought to catalyze the reaction that produces RCC in various leaves and fruits (Fig. 4) (Hörtensteiner 2006; Kräutler et al. 1997; Mühlecker et al. 1997; Hörtensteiner et al. 1998). Pheophytinase, a chloroplast-located and senescence-induced hydrolase that is widely distributed in algae and land plants can also specifically dephytylate the Mg-free Chl pigment, pheophytin (phein), yielding pheophorbide (Schelbert et al. 2009).

In the second phase, *p*FCC-modifying reactions produce FCCs that are imported into the vacuole by a primary active transport process. FCCs are further converted to nonfluorescent Chl catabolites (NCCs) by an acid-catalyzed isomerization, taking place inside the vacuole (Fig. 4) (Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011; Hinder et al. 1996; Kräutler 2003; Christ et al. 2012). Transfer of catabolites from senescent chloroplasts to the vacuole is mediated by primary activated transport processes (Hörtensteiner and Kräutler 2011). Note that the vacuole is a membrane-bound organelle within the cell cytoplasm. It occurs in plant cells and other microorganisms and can store water, salts, minerals, nutrients, proteins, pigments and enzymes. It is involved in growth, protection, waste disposal and structural support and tends to be very large in mature plant cells. Degradation products and enzymes involved in the described reactions have been identified in leaves and fruits (Hörtensteiner and Kräutler 2011; Hörtensteiner et al. 1995, 1998; Hinder et al. 1996; Christ et al. 2012; Kräutler et al. 1991; Matile et al. 1992; Ginsburg and Matile 1993; Mühlecker and Kräutler 1996; Matile et al. 1999).

A process that is closely coupled with the oxygenase reaction is a reduction of the δ-methine bridge of the RCC by a stromal enzyme, termed RCC reductase (RCCR). The reaction yields colorless fluorescent products (Fig. 4) (Hörtensteiner 2006; Rodoni et al. 1997; Wüthrich et al. 2000; Oberhuber and Kräutler 2002; Oberhuber et al. 2008). RCCR has been purified and cloned recently in barley and *Arabidopsis* (Wüthrich et al. 2000).

Spectroscopic analysis shows that *p*FCC has been identified from senescent leaves of various plants (Matile et al. 1996; Mühlecker et al. 1997, 2000; Kräutler and Matile 1999). The *p*FCC is converted to FCCs by several modifications depending on the plants, such as demethylation and hydroxylation (Hörtensteiner 2006; Hörtensteiner and Kräutler 2011; Matile et al. 1992). Modified FCCs are transported to the central vacuole by ATP-dependent translocator(s) in the tonoplast. They are non-enzymatically converted to NCCs by rearrangement of double bonds, in the pyrrole IV ring and adjacent g-methine bridge (Fig. 4) (Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011; Hinder et al. 1996; Kräutler 2003; Christ et al. 2012; Matile et al. 1999). The *p*FCC and all fluorescent Chl catabolites have the same absorption spectrum, with a major peak at around 320 nm and a shoulder at around 360 nm (Takamiya et al. 2000). In contrast, NCCs have an absorption maximum at 316 nm with no shoulder (Takamiya et al. 2000). Finally, three degradation products of monopyrrole derivatives such as hematinic acid, methyl ethyl maleimide and methyl vinyl maleimide aldehyde have been detected in senescent leaves and cotyledons of barley, spinach, pea and cucumber (Suzuki and Shioi 1999).

Senescent mes16 mutants exhibit a strong UV-excitable fluorescence, which is due to accumulation of FCCs. This derives, at least in part, from the fact that FCC isomerization to the respective NCC in the presence of an intact C132-carboxymethylester is slower than with a free carboxylic acid group (Christ et al. 2012; Oberhuber et al. 2008). The most likely reason is differences in the vacuolar pH, which determine the rate of FCC-to-NCC isomerization. Therefore, whether a plant can accumulate FCCs or NCCs might depend on the presence/absence of O13^4-demethylation and/or on the vacuolar pH (Christ et al. 2012). Accumulation of 'hypermodified' FCCs (*h*FCCs) in ripening bananas (*Musa acuminata*, Cavendish cultivar) can indicate a new role of Chl catabolites. Moreover, *h*FCCs are a group of unprecedented FCC-esters, and their accumulation in the peels of ripening bananas is rationalized by the corresponding deactivation of the natural, acid-induced (FCC-to-NCC) isomerization (Moser et al. 2008). Such isomerization occurs rapidly in weakly acidic solution (at pH 4.9) and at ambient temperature in aqueous solution. It also occurs in the vacuoles of senescent leaves, in senescent leaves of banana plants and of the peace lily (*Spathiphyllum wallisii*) (Matile et al. 1988; Matile 1997; Oberhuber et al. 2003; Moser et al. 2009; Banala et al. 2010; Kräutler et al. 2010). The *h*FCCs are esterified at the C17-propionic acid side chain, but they are not isomerized to NCCs in some senescing leaves and in ripening banana fruits (Moser et al. 2009; Banala et al. 2010; Kräutler et al. 2010).

The conversion of FCCs to NCCs in vacuole is partly due to either Fenton-type or photo-Fenton type reactions that can generate the $HO^\bullet$, a strong oxidizing agent. This issue is supported by the observation of hydroxylated NCC products or of products with OH-containing other functional groups in place of CH_3 (R_1 or R_3 positions) (Moser et al. 2009; Hörtensteiner and Kräutler 2011; Müller et al. 2007; Pruzinská et al. 2005; Christ et al. 2012; Kräutler et al. 1991; Mühlecker and Kräutler 1996; Oberhuber et al. 2003; Kräutler et al. 1992; Curty and Engel 1996; Berghold et al. 2004; Berghold et al. 2006). Further evidence is the occurrence of the reactions under acidic conditions (pH 4.9), which is vital for obtaining sufficiently high efficiency of Fenton or photo-Fenton reactions. Note that Fenton reaction occurs in an aqueous solution of H_2O_2 and ferrous or ferric salts, which can produce $HO^\bullet$ (see also 'Photoinduced Generation of Hydroxyl Radical in Natural Waters") (Fenton 1894; Barb et al. 1951; Zepp et al. 1992; Kwan and Voelker 2002). The efficiency of the Fenton reaction is highest at pH 3, whilst the photo-Fenton process takes place in the presence of light. The occurrence of various salts, minerals, proteins, FCCs, water and so on in vacuole may favor such type of reactions. The reduction of the rate of formation of hydroperoxides of linoleic acid (induced by H_2O_2) in the presence of NCC may also support the occurrence of such reactions in vacuole (Moser et al. 2009; Müller et al. 2007). High production rates of H_2O_2 in vacuole can be due either to light-sensitive FCCs or from the complexes of FCCs with metal ions present in vacuole. Upon irradiation, such compounds yield electrons (e^-) that can subsequently produce superoxide radical anions ($O_2^{\bullet -}$), H_2O_2, and finally $HO^\bullet$ from H_2O_2. The latter process can take place by either direct photodissociation ($H_2O_2 + h\upsilon \rightarrow HO^\bullet$) or upon Fenton and photo-Fenton reactions. Such processes are discussed in detail in other chapters (see chapters "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters", Photoinduced Generation of Hydroxyl Radical in Natural Waters", and "Complexation of Dissolved Organic Matter with Trace Metal ions in Natural Waters"). The transformation of FCCs to NCCs can be depicted shortly as below (Eqs. 5.1–5.4):

$$\mathrm{FCCs} + h\upsilon \rightarrow \mathrm{FCCs}^{+} + e^{-} \tag{5.1}$$

$$e^{-} + O_2 \rightarrow O_2^{\bullet -} \tag{5.2}$$

$$O_2^{\bullet -} + 2H^{+} \rightarrow H_2O_2 \rightarrow HO^{\bullet} \tag{5.3}$$

$$\mathrm{FCC}^{+} + HO^{\bullet} \rightarrow \mathrm{FCC} - OH \rightarrow \mathrm{NCC} - OH \tag{5.4}$$

where FCCs upon illumination by light are excited and produce e^{-}, (Eq. 5.1) which then reacts with aqueous dissolved oxygen to generate $O_2^{\bullet -}$ (Eq. 5.2). $O_2^{\bullet -}$ then produces H_2O_2 and subsequently $HO^{\bullet}$ upon several pathways as mentioned earlier (Eq. 5.3). The $HO^{\bullet}$ radical can then react with FCC^{+} to convert it into FCCs-OH and then into NCCs-OH (Eq. 5.4). Organic peroxides (ROOH) are produced either by similar processes or by breakdown of other organic components. They can generate the organic peroxide radical ($RO^{\bullet}$) and give NCC-OR. These reactions are extensively discussed in earlier chapters (see chapters "Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters and Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters"). Such a mechanism can also be supported by the observation that Chl degradation of chloroplast lysate or leaf extracts can be induced by intrinsic (per)oxidation with phenolic compounds and H_2O_2, and by lipoxygenation with linolenic acid ('oxidative Chl bleaching') (Janave 1997; Johnson-Flanagan and Spencer 1996; Adachi et al. 1999). Similarly, peroxidase or oxidase activity rise in parallel to the degreening of seeds or cotyledons in some plants (Johnson-Flanagan and Spencer 1996; Adachi et al. 1999). Therefore, $HO^{\bullet}$ or $RO^{\bullet}$ may play a significant role in the transformation of FCCs to NCCs in vacuole. Chl breakdown is a prerequisite to detoxify potentially phototoxic pigments within the vacuoles, to allow the remobilization of nitrogen from Chl-binding proteins that takes place during senescence (Hörtensteiner 2006).

On othe other hand, Chl *b* is degraded to chlorophyllide *b* by chlorophyllase, then chlorophyllide *b* is converted to chlorophyllide *a* by 'Chl *b* reductase' (Schelbert et al. 2009; Ito et al. 1996; Folly and Engel 1999; Scheumann et al. 1999; Tanaka and Tanaka 2006; Rüdiger 2003). The further degradation of chlorophyllide *a* proceeds in similar ways as mentioned before.

6 Chl Acting as Universal Signature of Cyanobacteria (Algae) or Phytoplankton Dynamics

Chl *a* concentrations are very variable in waters, ranging from 0.0 to 280 $\mu g\ L^{-1}$ in streams and rivers, 0.01–850 $\mu g\ L^{-1}$ in lakes, 0.0–919 $\mu g\ L^{-1}$ in reservoirs, 0.0–220 $\mu g\ L^{-1}$ in estuaries, 0.0–2080 $\mu g\ L^{-1}$ in coastal and marine waters, and 0.06–1,000 $\mu g\ L^{-1}$ in ice-covered Arctic and Antarctic Oceans (Table 1). Changes in Chl *a* concentrations reflect the occurrence and features of microorganisms present in natural waters. Therefore, Chl *a* can be used to estimate the primary production or the cyanobacterial (algal) bloom in a variety of waters (Fielding and Seiderer 1991; Ondrusek et al. 1991; Williams and Claustre 1991; Millie et al. 1993; Jeffrey et al. 1999; Bianchi et al. 1993, 2002; Kasprzak et al. 2008). Chl *a* concentration is a predictor of phytoplankton biomass across a broad trophic gradient of lakes, ranging from oligotrophic to highly eutrophic. It is also the most generally used indicator of eutrophication (Blanco et al. 2008; Kasprzak et al. 2008). Concentrations of Chl *a* depend on the fractional contributions of three phytoplankton size classes (micro-, nano- and picoplankton), whereas small cells dominate at low Chl *a* concentrations and large cells at high Chl *a* concentrations (Sathyendranath et al. 2001; Brewin et al. 2010).

The specific Chl *a* content per unit of phytoplankton biomass typically decreases with an increase of phytoplankton standing stocks in filed and experimental observations (Zhang et al. 2009; Kasprzak et al. 2008; Desortová 1981; Shlgren 1983; Wojciechowska 1989; Watson et al. 1992; Talling 1993; Chow-Fraser et al. 1994; Schmid et al. 1998; Felip and Catalan 2000; Sandu et al. 2003; Kiss et al. 2006). The decreases in Chl *a* content per unit of phytoplankton biomass presumably involves two facts: First, Chl *a* bound to microorganisms is the individual component that can be rapidly degraded by either photoinduced or microbial processes (Zhang et al. 2009; Takamiya et al. 2000; Hörtensteiner 2006; Kräutler and Hörtensteiner 2006; Moser et al. 2009; Hörtensteiner and Kräutler 2011). Second, the release of autochthonous DOM from phytoplankton biomass, by either photoinduced or microbial assimilation/respiration (see also chapter "Dissolved Organic Matter in Natural Waters") (Parlanti et al. 2000; Mostofa et al. 2009; Mostofa et al. 2009; Zhang et al. 2009) may affect the decrease in the total content of Chl *a* in phytoplankton standing stocks. In addition, Chl *a* concentrations are substantially affected by the occurrence of phytoplankton species or of size-fractionated phytoplankton, which undergoes seasonal variations in different waters (Bianchi et al. 2002; Satoh et al. 2001; Goedheer 1970; Prezelin 1981; Aguirre-Gomez et al. 2001; Pérez et al. 2007; Hoepffner and Sathyendranath 1991; Parab et al. 2006; Huang et al. 2004, 2005; Buchanan et al. 2005; Qiu et al. 2010). Micro- and nano-Chl *a* are both higher than pico-Chl *a*, but pico-Chl *a* can reach 40 % of total Chl *a* in Wanshan islands in summer (Huang et al. 2005). Micro- and nano-Chl *a* in Pearl River Estuary (South China Sea) generally account for 60 % of total Chl *a*, and pico-Chl *a* account for 20 % of total Chl *a* in most samples (Qiu et al. 2010). In September, picophytoplankton is dominant except for the estuary head, where nano-phytoplankton is predominant. Pico-Chl *a* in far offshore samples accounts for 69 and 75 % of total Chl *a* (Qiu et al. 2010). Picophytoplankton typically accounts for less than 10 % of the total phytoplankton biomass during winter and early spring in Chesapeake Bay. However, it can often contribute to more than 50 % of total phytoplankton biomass in summer and early autumn, particularly in mesohaline and polyhaline waters (Buchanan et al. 2005). Variations in Chl *a* concentrations among phytoplankton species and changes in Chl *a* concentrations per unit of phytoplankton biomass are caused by environmental factors, but Chl *a* is the only parameter that allows precise and rapid determination of phytoplankton biomass or primary production in natural waters.

6.1 Possible Mechanisms For the Management of Eutrophication by Control of Primary Production

Most present studies try to correlate Chl *a* with nutrients, in order to regulate Chl *a*, primary production or photosynthesis by controlling nutrients or by other measures of flood disturbance frequency or of days available for accrual (Biggs 1985, 1995, 2000; Biggs et al. 1998, 1999; Lohman et al. 1992; Welch and Lindell 1992; Chapra 1997; Dodds et al. 1998; Chetelat et al. 1999; Huszar et al. 2006). Nutrients, particularly NO_3^- and PO_4^{3-} are produced mostly by DOM and POM (e.g. phytoplankton species or algae or cyanobacteria), via photoinduced or microbial respiration and degradation. This issue strongly suggests that regulating Chl *a* is vital for the control of DOM and POM in aquatic environments. DOM and POM are in fact the sources of all reactants such as CO_2, DIC, H_2O_2, nutrients and autochthonous DOM, which are responsible for photosynthesis and, therefore, for the primary production of Chl *a* (see chapters “Photosynthesis in Nature: A New Look” and “Impacts of Global Warming on Biogeochemical Cycles in Natural Waters”). DOM and POM along with global warming can lead to excess primary production and to photosynthesis, as shown in chapter “Impacts of Global Warming on Biogeochemical Cycles in Natural Waters”. A conceptual model of primary production enhancement and three important steps for remediation, to control algal blooms are extensively discussed in Sects. 5 and 5.1 of chapter “Impacts of Global Warming on Biogeochemical Cycles in Natural Waters”. The same measures can be adopted to control photosynthesis and, therefore, to limit primary production or Chl *a* concentration. This activity can reduce eutrophication in natural waters.

7 Scope of the Future Research

DOM along with POM (e.g., algae or phytoplankton) can play an important role in the formation of SCM and DCM. The mechanism behind SCM and DCM formation may pave the way for future research. Formation of H_2O_2 in DCM layer by phytoplankton might be important, and distribution of H_2O_2 as well as its formation from the existing phytoplankton in DCM could be interesting to understand the mechanism of DCM formation. Almost all of previous studies dealt with nutrients (total nitrogen, NO_3^- or NH_4^+, and total phosphate or PO_4^{3-}), but they have some problems. First, DOM and POM can release nutrients in natural waters by photoinduced or microbial respiration or degradation. Therefore, release and uptake of nutrients during photosynthesis has limited importance in waters with high contents of DOM and POM or high contents of nutrients. Second, waters with high contents of DOM and POM can produce DIC, CO_2, H_2O_2 and so on, which are directly linked to photosynthesis and, therefore, to primary production (see chapter “Photosynthesis in Nature: A New Look”). Therefore, DOM and POM should be more directly linked to Chl *a* than nutrients are. Important research needs can thus be listed as follows: (i) Investigation on the relationship between Chl *a* and DOM and POM in a variety of waters, with high and low DOM contents; (ii) Investigation on phytoplankton photosynthesis along with measurement of Chl *a*, DIC, CO_2, H_2O_2 and dissolved O_2. Note that H_2O_2 is photochemically produced from dissolved O_2 (see chapter "Photosynthesis in Nature: A New Look"). Recently, significant correlation has been found between dissolved O_2 and benthic or sestonic Chl concentration (Heiskary and Markus 2003; Miltner 2010), possibly due to H_2O_2 generation from dissolved O_2 followed by in algal production. (iii) New model studies are required, dealing with the mechanism of SCM and DCM formation and elucidating the role of organic matter (DOM and POM), solar radiation, photoinduced formation of DIC, CO_2 and H_2O_2, and water temperature. Note that solar radiation and water temperature are vital for the photoinduced generation of H_2O_2, DIC, CO_2 and nutrients from DOM and POM (see chapter "Photosynthesis in Nature: A New Look"). (iv) Investigation on photosynthesis in natural waters, with and without addition of phytoplankton/algae/cyanobacteria (POM) Such a study could elucidate the effect and role of POM on the photosynthesis, allowing a distinction between photosynthetic processes conducted by DOM and POM. (v) Study of changes of dissolved O_2 concentration along with those of H_2O_2 and Chl *a*. (vi) Elucidation of the role and contribution of H_2O_2, produced either intramolecularly or extracellularly on photosynthesis, in aquatic phytoplankton and higher plants.

8 Nomenclature

CDOM	Chromophoric dissolved organic matter
Chl	Chlorophyll
Chls	Chlorophylls
DCM	Deep chlorophyll *a* maximum
DIC	Dissolved inorganic carbon (dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-})
DOM	Dissolved organic matter
FDOM	Fluorescent dissolved organic matter
H_2O_2	Hydrogen peroxide
NCC	Nonfluorescent chlorophyll catabolites
$^1O_2$	Singlet oxygen
O_2^-	Super oxide anion radical
$HO^\bullet$	Hydroxyl radical
OM	Organic matter
*P*fcc	Primary fluorescent chlorophyll catabolite
POM	Particulate organic matter
RCC	Red chlorophyll catabolite
RCCR	Red Chl catabolite reductase
ROS	Reactive oxygen species
SCM	Surface or subsurface chlorophyll *a* maximum
WT	Water temperature

Problems

(1) List the various kinds of Chl found in organisms
(2) Explain shortly the Chl *a* functions.
(3) How does the surface or subsurface Chl *a* maximum (SCM) differ from the deep Chl *a* maximum (DCM)?
(4) Explain the mechanisms of SCM and DCM formation in the water column.
(5) How does global warming affect SCM or DCM?
(6) Explain the mechanism of Chl *a* degradation
(7) How does Chl act as universal signature of cyanobacteria (algae) or phytoplankton biomass?
(8) Explain possible actions for the management of eutrophication by controlling primary production (Chl *a*).

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