# Pigments and photoacclimation processes

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# Chapter 4.4: Pigments and photoacclimation processes

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## Content of the chapter

This chapter reviews the nature of pigment variations in phytoplankton in response to changes in light regime (irradiance, spectral composition and daylength). These changes belonging to processes called acclimation and/or adaptation maximize the evolutionary fitness of a species, within the constraints set by the environmental conditions (Raven and Geider, 2003). In general, adaptation indicates long-term evolutionary outcome based on the genes a given species obtains (genetic adaptation) while acclimation denotes adjustments in response to variation in key-environmental variables (physiological acclimation).

Photo-acclimation corresponds to a mosaic of processes involving many cellular components and occurring over a broad range of time scales, from seconds to days. These processes, covering many physiological, biochemical, biophysical and biological changes, allow the optimization of cell activities, such as photosynthesis, respiration, growth and division when faced with changing irradiance (e.g., Herzig and Dubinsky, 1993; Anning et al., 2000; Raven and Geider, 2003). This is an important issue in phytoplankton ecology because of the fluctuating light environment experienced by pelagic algae, related to daylight variations together with the exponential decrease of light and the vertical – active or passive – movements of algae along the water column.

In order to cope with these never-ending fluctuations in light-regime, marine phytoplankton can adjust their pigment pool, which is mainly constituted by two functional categories, namely pigments used for light harvesting and for photoprotection. Many accessory pigments constituting the light-harvesting complexes are photosynthetically active i.e. they are able to transfer the energy absorbed from sunlight to the photosynthetic reaction centers (RC) of photosystems (PS) II and I. They are called light harvesting pigments and include the photosynthetic carotenoids. However, some carotenoids are not involved in photosynthesis and do not transfer the absorbed energy to the RC. These non-photosynthetically active carotenoids are also called photoprotective carotenoids (PPC).

The function and dynamics of long-term (hours-days) and short-term (minutes-hours) photo-acclimation are described in the following two sections (4.4.1 and 4.4.2, respectively). The long-term photo-acclimation response mainly consists in changes of structure and composition of the photosystems while the short-term photo-acclimation

process mainly concerns the xanthophyll cycle (XC) activation and the associated non-photochemical fluorescence quenching (NPQ). In the third section (4.4.3), the ecophysiological variability of XC and its use as a biological tracer in oceanographic studies is reported.

### 4.4.1. Long-term photoacclimation

In general, photoacclimation in a living cell is characterized by changes in the amount and ratios of light harvesting pigments and photoprotective carotenoids, in photosynthetic parameters, in enzymatic activities involved in photosynthesis and respiration, and finally, in cell volume and chemical composition (Falkowski and LaRoche, 1991). In this part, we will focus on changes in chloroplasts, light harvesting complexes, pigment composition and function.

#### 4.4.1.1. Chloroplast size, number, morphology and distribution

The different phytoplankton classes and pigment-groups show huge differences in chloroplast size, numbers, morphology and distribution (Kirk and Tilney-Bassett, 1978; Larkum and Vesk, 2003). The chloroplast number is species-specific and varies from 1 chloroplast per cell to more than 100. An example can be given from the diatom genus *Chaetoceros*, were some species only contain one, other 2, 6 or more than 10 chloroplasts per cell. The species-specific differences in chloroplast size (typically 0.2-2 $\mu$m in length) and morphology (shape and structure) in a given species is also affected as a function of light climate (irradiance, the spectral composition of irradiance and day length). Light-induced chloroplast changes in a given species will especially affect light harvesting and utilization (Raven and Geider, 2003), seen as changes in intracellular self-shading (the package effect, see chapter 4.3) and the optical signature from the chloroplast (colour, optical density, and *in vivo* fluorescence emission, Falkowski and Chen, 2003; Sakshaug and Johnsen, 2005; Johnsen and Sakshaug, 2007). Typically, low light (LL)-acclimated cells have chloroplasts evenly distributed in the cells (large light

harvesting surface), while high light (HL)-acclimated cells have condensed chloroplasts (small light absorbing surface, Blatt *et al*., 1981).

#### 4.4.1.2. Light harvesting complexes and thylakoid membranes

The majority of pigments in phytoplankton cells are situated inside the thylakoid membranes as discrete light harvesting complex, made up from pigment-protein complexes. The build-up of the different light harvesting complexes in the different phytoplankton classes is discussed in chapter 4.3. The light harvesting complexes in different phytoplankton classes differ in thylakoid membrane organization and in energy regulation mechanisms (Green *et al*., 2003). Most green algal thylakoids have both stacked and unstacked membrane regions, but often with the same PSI:PSII ratio in both regions (Bertos and Gibbs, 1998). In contrast, the chromophytes comprising Bacillariophyceae, Cryptophyceae, Dinopyceae, Pelagophyceae, Eustigmatophyceae, Chrysophyceae, Bolidophyceae, Pinguiophyceae, Raphidophyceae, Dictyochophyceae, haptophyta (comprising the two classes Coccolithophyceae and Pavlovophyceae) do not have lateral segregation of of PSII and PSI (Green *et al*., 2003). Lateral segregation of PSII and PSI in Rhodophyta and in most Chlorophyta is related to the ability of performing state transitions (see chapter 4.3).

The majority of chromophytes contain large light harvesting complexes associated with PSII where the fraction of light harvesting pigments and PPC is tuned as a response to light history. The fraction of pigment-specific absorption of light is highly dependent on the photo-acclimation status of algae and water colour (Johnsen *et al*., 1994; Schofield *et al*., 1996; Stolte *et al*., 2000; Johnsen and Sakshaug, 2007, Fig. 1). Generally HL-acclimated cells are characterized by low light harvesting pigment content and a corresponding high amount of PPC, and a corresponding inverse relationship for LL-acclimated cells (Johnsen *et al*., 1997; Stolte *et al*., 2000; Falkowski and Chen, 2003; Rodriguez *et al*., 2006). Isolated and functional light harvesting complexes (that are able to transfer light energy to acceptor chlorophyll *a*) differ in LL and HL-acclimated cells of a given species (Johnsen *et al*., 1994, 1997). For example, HL-acclimated dinoflagellates may have a significant amount of diadinoxanthin in the antenna (denoted chl*a*-chl*c*-

peridinin protein = ACP) that does not transfer light energy to chl*a*. This can be seen by using spectral absorption coefficients (indicating the total amount of light absorbed) and fluorescence excitation spectra (scaled at the red peak of chl*a* assuming 100% light energy transfer efficiency) indicating the fraction of light that is received by acceptor chl*a*. This analysis shows that ACP antennas from HL acclimated cells with high photoprotective caraotenoids (PPC, diadinoxanthin and diatoxanthin) relative to chl*a* (49%, w:w) have low relative light transfer efficiency at the absorption peaks of the PPCs at 490 (15-20%) and 460 nm (20-30%, Johnsen *et al*., 1997). In contrast, ACP antennas from LL-acclimated cells with 15% PPC relative to chl*a*, reach 70-80% relative light energy transfer efficiency at 490 and 460 nm. Johnsen *et al*. (1997) also showed that wavelengths from 550-700 nm, where PPCs do not absorb, have a close to 100% relative light energy transfer efficiency.

The energy regulation mechanisms in the light harvesting complexes, that are different between phycobiliprotein, chl*c* and chl*b*-containing phytoplankton, are state transitions (e.g. phosphorylation and de-phosphorylation causing movement of light harvesting complexes in the PS II) and xanthophyll cycle caused by ΔpH (see section 4.4.2.). State transitions and the xanthophyll cycle affect the effective absorption cross section of PSII, $\sigma_{PSII}$, defined as the efficiency of absorbed quanta to drive a photochemical reaction in Ångstrom ($Å^2$ $quanta^{-1}$) indicating a quantum yield of charge separation (Falkowski and Chen, 2003).

In contrast, the spectrally integrated chl*a*-specific absorption coefficient (400-700 nm), $\bar{a}^*_{\varphi}$ (= optical cross section, units: $m^2$ mg $chla^{-1}$) indicates the total pigment-protein absorption by the cell. Both $\bar{a}^*_{\varphi}$ and $\sigma_{PSII}$ are spectrally dependent, inducing pigment-specific differences in photosynthetic efficiency as a function of wavelengths. Regarding PSII and photosynthesis, $\sigma_{PSII}$ can be determined for a single wavelength and extrapolated to other wavelengths from knowledge of the PSII-fluorescence excitation spectra (Johnsen *et al.*, 1997; Falkowski and Chen, 2003; Johnsen and Sakshaug, 2007). Changes in cross-sectional area of PSII and PSI due to re-association of mobile light harvesting complexes of the PS II (i.e. state transitions) contribute to <20% change in cross-section areas (Larkum, 2003). This indicates that it is the light harvesting complexes and their pigments that contribute to the major fraction of photo-acclimation in phytoplankton and

that state-transitions (which occur on a minute scale) only contribute to a small fraction in absorption cross-section changes (Larkum, 2003; Raven and Geider, 2003).

#### 4.4.1.3. Pigment composition and function

The high pigment diversity in light harvesting complexes, relative to the more conservative pigment composition in PSII and PSI, is responsible for the high pigment-group specific differences in light harvesting and utilization. In most bloom-forming phytoplankton, some light harvesting pigments are of high importance; these are the peridinin, prasinoxanthin, violaxanthin and the fucoxanthins (including acyl-oxy derivatives). From the ratios between photosynthetic pigments, distinct pigment-groups have been defined in the Prasinophyceae (e.g., Hooks *et al*., 1988; Egeland *et al*., 1995; Zingone *et al*., 2002) or in the haptophyta (e.g., Stolte *et al*., 2000; Zapata *et al*., 2004).

Generally, chl*a* is not an important pigment in light harvesting. Its major role is to receive light energy from donor pigments in light harvesting complex and it is one of the key molecules in the photochemical conversion of light energy to chemically bonded energy in the RC. Usually pigment data are normalized to chl*a* as biomass. Since cellular chl*a* content in a given species is highly light-regime dependent, the less variable Particulate Organic Carbon (POC) is a better biomass indicator (Johnsen and Sakshaug, 1993; Brunet *et al.*, 1996; Rodriguez *et al*., 2006). The interpretation of light harvesting pigments and PPC in HL and LL conditions is therefore highly dependent on biomass normalization (chl*a* *vs*. POC, Rodriguez *et al*., 2006; Johnsen and Sakshaug, 2007). The chl*a*:C ratio (w:w) is low in high light (and long day length) and high in low light. Thus, the chl*a*:C (w:w) ratio indicates the photo-acclimation status and is termed photo-acclimation index (Sakshaug *et al.*, 1997). The photo-acclimation index can be described as a function of absorbed quanta (Nielsen and Sakshaug, 1993). Averaged chl*a*:C ratios for HL- and LL-acclimated cells of 10 phytoplankton classes were 0.020 and 0.043, respectively (Johnsen and Sakshaug, 2007). Since chl*a* and light harvesting pigments co-vary (Johnsen *et al*., 1997; Rodriguez *et al*., 2006; Johnsen and Sakshaug, 2007), the variation in light harvesting pigments:C ratio will follow the corresponding variation in chl*a*:C ratio. In general, there are some common long-term photo-acclimation

characteristics. The faster the growth rate, the faster the acclimation process, since cells are dependent on rapid division to adjust to the key-environmental variables. Light history has also a relevant effect on the overall acclimative response of the cells (e.g., Anning *et al.*, 2000) and can be a determinant factor for the kinetic of some processes and pigment variations (Anning *et al.*, 2000; Dimier *et al*., 2007b).

### 4.4.2. The xanthophyll cycle and short term photoacclimation

#### 4.4.2.1. Role and regulation of the xanthophyll cycle

When chlorophyll (chl) *a* molecules of the light harvesting complexes antenna absorb light they enter a singlet-state excitation $^{1}$chl*a** from which energy is deactivated following several pathways. Most of the excitation energy is used to drive photochemistry, through charge separation within the reaction center of photosystems, with some associated leaks: reemission of the energy via chlorophyll fluorescence and heat. There is nevertheless a non-negligible part of the energy which can be dissipated through the 'triplet valve' thereby forming triplet-state excitation: chl*a* + light $\rightarrow$ $^{1}$chl*a** $\rightarrow$ $^{3}$chl*a**. This pathway depends on the lifetime of $^{1}$chl*a** which itself depends on the other deactivation pathways. When the light absorbed is in excess (i.e. under a high light exposure) and the ability of the photosynthetic machinery to use the excitation energy via photochemistry is at its maximum, the yield for chl*a* fluorescence increases and the probability of $^{3}$chl*a** formation increases. This situation is critical since $^{3}$chl*a** can react with oxygen ($O_2$) within the PS II reaction center, generating reactive $O_2$ species such as singlet $^{1}O_2$* which are very harmful for proteins, pigments and lipids and lead to a decrease in the rate of photosynthesis. Photosynthetic organisms are able to maintain a low steady-state of $^{3}$chl*a** generation through several rapid 'photoprotective' mechanisms which help to minimize the production of reactive oxygen species. Non-photochemical fluorescence quenching (NPQ) is believed to be the most important of these processes and the carotenoid xanthophylls play a central role in photoprotection, especially via the Xanthophyll Cycle (XC).

The xanthophyll cycle involves the enzymatic de-epoxidation/epoxidation of acetylenic xanthophylls, synthesized from β-carotene (Lohr and Wilhelm, 2001), as a function of of absorbed quanta. There are two groups of organisms, which can be defined on the basis of the pigments involved in the XC (Table II). A first group includes as the main XC the two-step de-epoxidation of violaxanthin (Vx) into zeaxanthin (Zx) via antheraxanthin (Ax). A second group includes the one step de-epoxidation of diadinoxanthin (Dd) into diatoxanthin (Dt), Dt showing the same degree of de-epoxidation Zx. A third group includes the phyla in which there is no XC but an accumulation of Zx directly from β-carotene under high light exposure (a few species of red macroalgae show a XC (Raven and Geider, 2003). Within group 1, some prasinophytes have been shown to be unable to convert Vx further than Ax (Goss *et al.*, 1998) and some green macroalgae have no XC (Raven and Geider, 2003). In addition, a second XC, which is not always minor, has been reported in several plant species and in the green microalga *Chlamydomonas* involving the de-epoxidation of lutein-epoxide into lutein under certain circumstances like prolonged high light stress (Rascher and Nedbal, 2006). Additionally, in the green macroalga *Caulerpa*, a secondary XC involving conversion between lutein and siphonaxanthin (biosynthetically related to siphonein) has been reported (Raniello *et al.*, 2006). Within the second group, there are also some phyla showing a second XC. They include some Heterokontophyta (Bacillariophyceae, Chrysophyceae, Xanthophyceae), Haptophyta and Dinophyta, showing the Vx-cycle under prolonged high light stress (Lohr and Wilhelm, 2001). It is still unclear whether the temporary accumulation of Zx under high light conditions is only an unavoidable consequence of the properties of the XC or if it has a real physiological significance by increasing the photoprotective ability of the chloroplast. Interestingly, for an unknown reason, among the Heterokontophytes, some very close phyla evolved towards the Vx-cycle as the main XC (the brown algae) while others (like the diatoms) evolved towards the Dd-cycle.

The regulation and operation of the XC (Fig. 2) has been described in details earlier, especially for the Vx-cycle (Latowski *et al.*, 2004). The de-epoxidation/epoxidation events are ensured by two enzymes, a Vx de-epoxidase (VDE) and a Zx epoxidase (ZEP) which are part of the few (in contrast to animals) lipocalin proteins known in plants. VDE

is localized on the lumen side and can bind/unbind to the thlyakoid membrane as a function of the lumenal pH, its optimal pH activity being around 5-6. ZEP is localized on the stroma side; its pH optimum is 7.5. In addition, VDE needs the acid form of ascorbate as a co-factor and ZEP needs NADPH, $H^+$ and oxygen. The operation of the XC results in the competition of the activity of these two enzymes as a function of the built-up of the transthylakoid proton gradient, which is driven by the irradiance-dependent photosynthetic electron transport rate and subsequent change in lumenal and stromal pH. In summary, when the irradiance is moderate to high, the lumenal pH drops down to values between 4.5 - 6.5. When the irradiance decreases to darkness, the de-epoxidation becomes weaker and finally stops, while the reverse epoxidation reaction, which is ten times slower, becomes dominant (note that ZEP is also active under high light). Hence, the accumulation of the photoprotective de-epoxidized xanthophylls Zx and Dt under an excess of light is dependent on the activity of the two enzymes which indirectly depends (via the change in pH and availability of the co-factors) on the irradiance. In the organisms displaying the Dd-cycle, a similar mechanism has been described with some special features. The Dd de-epoxidase (DDE) has been shown to be able to de-epoxidize Dd as well as Vx, which has been used as an explanation for the presence of the two XC in several phyla (Jakob *et al.*, 2001). Nevertheless, two genes have recently been found in the genome of the diatom *Phaeodactylum tricornutum* that encode for two homologues of the VDE ('VDE-like' genes) in addition to the gene coding for DDE (A. Gruber, pers. com.). In contrast to VDE, DDE pH optimum is shifted towards higher pH and is active even at pH values about 7 (Jakob *et al*., 2001). Consequently, Dd de-epoxidation can already be triggered by a weak lumen acidification induced by, for example, chlororespiration (Jakob *et al.*, 1999). It also means that the Dd de-epoxidation already occurs for lower light intensities and shorter illumination times than the Vx de-epoxidation. Additionally, a recent study (Grouneva *et al.*, 2006) showed that DDE requires much lower ascorbate concentration than VDE to be fully effective. Finally, DDE requires a lower concentration of lipids MGDG (monogalactosyldiacylglycerol) to drive efficient de-epoxidation meaning that higher Dd amounts can be converted under high light (Goss *et al.*, 2005). Regarding the analogue of ZEP, the Dd epoxidase also shows an interesting characteristic: it is inactivated under excess light, which completely

switches the equilibrium of the XC towards Dt accumulation (Goss *et al.*, 2006). All together these special features of the Dd-cycle explain the surprising efficiency and rapidity of accumulation of Dt in large amounts (Lavaud *et al.*, 2002a; Lavaud *et al.*, 2004). Finally, in diatoms, a species-dependent *de novo* synthesis of Dt under prolonged high light stress allows the cells to increase their capacity for photoprotection (Lavaud *et al.*, 2004).

4.4.2.2.The xanthophyll cycle and non photochemical quenching

The NPQ process takes place into the light harvesting complexes of the PS II and its role is to dissipate as heat or reallocate part of the excitation energy before it reaches the reaction center when the light has been absorbed in excess during a light exposure which exceeds the ability of the photosynthetic machinery to use all the energy for photochemistry. NPQ reduces the lifetime of $^{1}$chl*a** and, as a consequence, the quantum yield of chl*a* fluorescence as well as the quantum yield of photochemistry. NPQ can be divided into three components: qE, the energy-dependent quenching which is regulated by the build up of a transthylakoid ΔpH and the operation of the XC; qT, the state-transition quenching which allows reallocation of part of the energy absorbed from the PS II to the PS I; qI, the photoinhibitory quenching. Here, we will focus on the qE component. qE has been investigated up to both molecular (down to few Å) and gene levels, especially in higher plants and green microalgae (Cogdell, 2006; Jung and Niyogi, 2006), far less in other eukaryotic algae and cyanobacteria.

The first correlation between qE and the accumulation of de-epoxidized xanthophylls under high light was observed in higher plants and green microalgae (see Demmig-Adams, 1990). Later it was also reported in diatoms and dinoflagellates (Sakshaug *et al.*, 1987; Demers *et al.*, 1991; Olaizola and Yamamoto, 1994), Chrysophyceae (or chrysophyta) and euglenophyta (Lichtlé *et al.*, 1995; Casper-Lindley and Bjorkman, 1998), red algae (Ritz *et al.*, 1999) and more recently in cyanobacteria (Bailey *et al.*, 2005) and picoplanktonic chlorophyta (Dimier *et al.*, 2007b). A linear relationship between the operation of the XC, and the subsequent accumulation of zeaxanthin (Zx), antheraxanthin (Ax) and diatoxanthin (Dt), the development of qE and the quenching of

chl*a* fluorescence has been described in detail earlier (Gilmore and Yamamoto, 1991; Lavaud *et al.*, 2002a). The model for the qE mechanism is well understood in higher plants and green microalgae (Holt *et al.*, 2004; Horton *et al.*, 2005; Cogdell, 2006). In summary, it implies a feed-back reaction from the linear electron transport via the built-up of a transthylakoid ΔpH and subsequent acidification of the lumen of the thylakoid: the higher the irradiance, the higher the electron transport and coupled translocation of protons, the higher the accumulation of protons into the lumen. This acidification has two consequences: the protonation of specific sites of a special light harvesting complexes protein identified as PsbS in higher plants and the activation of VDE for synthesis of Zx. Both events enable the light harvesting complexes antenna to switch from a light-harvesting to a dissipative mode where excess excitation energy is converted into heat while chl*a* fluorescence is quenched.

The other group in which the qE mechanism and its relationship with the XC has been investigated in details are the diatoms (Olaizola *et al.*, 1994; Lavaud *et al.*, 2002a). qE can be up to 4-5 times higher in diatoms than in plants (Lavaud *et al.*, 2002a; Ruban *et al.*, 2004), making it the most important rapid photoprotective process. It has been argued that this is due to the absence of state-transitions in diatoms (Owens, 1986). Other differences have been listed earlier in detail (Wilhelm *et al.*, 2006). They include a different light harvesting complexes organization (Büchel, 2003; Guglielmi *et al.*, 2005) and especially the absence of PsbS, a different localization of the xanthophylls within the light harvesting complexes (Lavaud *et al.*, 2003; Beer *et al.*, 2006), a capacity for accumulating large amounts of xanthophylls and a different composition and regulation of the XC. Additionally, qE appears to be more tightly associated with the XC and the accumulation of Dt than in plants with Zx (Lavaud *et al.*, 2002a) so that both the transthylakoid ΔpH and XC have a strong role in finely regulating qE (Lavaud *et al.*, 2002b; Ruban *et al.*, 2004; Goss *et al.*, 2006). Part of the qE process in diatoms remains to be elucidated, however recent advances (Lavaud and Kroth 2006) contributed to the development of a first mechanistic model (Goss *et al.*, 2006).

The red algae and cyanobacteria have extrinsic light harvesting complexes system (i.e. phycobilisomes) and also show a qE process even though the amplitude is weak. The same remark holds true for *Prochlorococcus* and its intrinsic Pcb antenna system (Bailey

*et al.*, 2005). qE in these organisms does not depend on a XC but on high light dependent Zx accumulation. Actually a XC has been observed in some species of red algae, but no link with qE has been reported (Ursi *et al.*, 2003). In cyanobacteria, the process is believed to be a thermo-optic mechanism driven by blue light and taking place in the phycobilisomes where it involves a special carotenoid-binding protein and the pigments Zx and/or myxoxanthophyll (Cadoret *et al*., 2004; Wilson *et al*., 2006). It has been argued that qE in cyanobacteria would serve to adjust the energy transfer within the phycobilisomes of an already acclimated system to environmental stress(es) (high light, iron deficiency), but would not serve to cope with rapid fluctuations of irradiance as in higher plants and eukaryotic algae.

### 4.4.3. The xanthophyll cycle and the ecological properties of phytoplankton

#### 4.4.3.1. Ecophysiology and environmental modulation of the XC

There are striking peculiarities of the algal XC activity with respect to terrestrial plants, including a high degree of variation in structure and activity of the XC among phytoplankton belonging to different taxa (Casper-Lindley and Bjorkman, 1998; Lavaud *et al*., 2004, Masojidek *et al*., 1999, 2004; Wilhelm *et al*., 2006). In addition, the XC activity depends on the physiological and nutritional state of the algae (Latasa and Berdalet, 1994; Staehr *et al*., 2002). This diversity may affect the survival and the growth of species under high light and therefore their competitive ability, affecting the patterns of algal succession in phytoplankton community (Demers *et al.*, 1991; Lavaud *et al*., 2004). As an example of this, the XC and qE were shown to be involved in seasonal succession of diatoms in estuaries (Serodio *et al.*, 2005), while a high qE appears to contribute to the domination of some diatom species in aquatic habitats where the light environment fluctuates strongly (Mitrovic *et al*., 2003). Claustre *et al*. (1994) suggested than the higher content of Dd per unit of chl*a* in diatoms confers an adaptive advantage in allowing a fast acclimation along sharp gradients of light. Resuspension of benthic diatoms could also be tracked from a 12 h periodicity in Dd/chl*a* at a coastal station in the English Channel (Brunet and Lizon, 2003), and altogether, these *in situ* data support the

observation of an increased Dd content in diatoms exposed to fluctuating high light (Lavaud *et al*., 2002a).

It has been hypothesized that the habitat characteristics account for the observed differences in photoacclimative responses between species, including the long term variations in cellular chl*a* content (Sakshaug *et al*., 1987), or the potential activity and efficiency of XC (Lavaud *et al*., 2004; Lavaud *et al*., 2007; Dimier *et al*., 2007b, 2009a, b). As an example, strains isolated from estuaries show a higher (2.5 to 5 times) and faster qE than strains isolated from the open ocean or from coastal ecosystems (Lavaud *et al*., 2007). The difference in photoprotection ability between open ocean and coastal *Thalassiosira* species may also be due to an adaptation to low or high iron concentrations, respectively (Strzepek and Harrison, 2004).

Few papers have investigated the XC in microalgae other than diatoms (e.g., Casper-Lindley and Bjorkman, 1998; Moisan *et al*., 1998; Evens *et al*., 2001; Harris *et al*., 2005), limiting the value of comparative ecological and/or evolutionary interpretations within phytoplankton. Some recent studies have focused on picoplanktonic species such as cyanobacteria (Cadoret *et al*., 2004; Bailey *et al*., 2005; Wilson *et al*., 2006) or picoeukaryotes (Dimier *et al*., 2007a, 2009a, b). Despite the caution needed when generalizing results from single strains, there seems to be an effect of small size on the reactivity of the XC when compared to larger cells (Dimier *et al*., 2009a). On the other hand, picoeukaryotes are also able to adopt an alternative photoprotective strategy, by rapidly modifying their chl*a* content (~ less than one hour, Brunet *et al*., 2006, 2007).

The “light history” of the cell, which is the sum of past light variations experienced by the cell, is a key factor to consider when interpreting the dynamics of photoresponses (e.g. Moisan *et al*., 1998; Anning *et al*., 2000; Lavaud *et al*., 2002a). Although this aspect is very difficult, if not impossible, to assess for natural populations, evidences from cultures point to a major role of past light experience on the mode and the kinetics of light-induced reactions. As an example, previous acclimation to high or medium irradiance strongly influences the short-term photoprotective response to a further increase in irradiance, when compared to cells acclimated to lower light (Casper-Lindley and Bjorkman, 1998; Moisan *et al*., 1998; Dimier *et al*., 2007b).

In general, the physiological condition of algal cells has a strong influence on the functioning of the XC. Several authors have observed an increase in the XCP content with no parallel change in light conditions in stressed phytoplankton (e.g. Latasa and Berdalet, 1994; Brunet *et al*., 1996; Staehr *et al*., 2002). An increase of Dt has also been observed in diatoms exposed to toxic polyunsaturated aldehydes (Casotti *et al*., 2005), while inhibition of Dt epoxidation has been caused by Cd (Bertrand *et al*., 2001). These responses might be interpreted as related to the potential antioxidant role of Dt, as it has been hypothesized for zeaxanthin in higher plants (Strzalka *et al*., 2003).

4.4.3.2. The xanthophyll cycle and UV radiation

Depletion of the stratospheric ozone layer has resulted in increased UV-B radiation (280-320 nm) which can penetrate down to 30 meters in ocean waters (1% irradiance depth for 305 nm, Tedetti and Sempéré, 2006) and can potentially damage aquatic organisms, notably phytoplankton (e.g. Vincent and Roy, 1993). Two of the major targets of UV damage in phytoplankton are the photosystem (PS) II reaction centre complex and the carbon-fixing enzyme Rubisco (cf. review by Vincent and Neale, 2000). This damage to both the light and dark reactions of photosynthesis will reduce photochemical use of light energy and thus increase excess light energy, favoring the formation of dangerous reactive oxygen species (ROS) within the cell. Thus mechanisms that can protect against excess light energy, such as the xanthophyll cycle, should be solicited. Indeed, a number of studies from recent years have shown a stimulation of the xanthophyll cycle when algae were exposed to enhanced UV-B under field or light-simulated environment (including realistic levels of photosynthetically active radiation, PAR, and UV-A: 320-400 nm). These studies covered a range of algal groups, including diatoms (Goss *et al.*, 1999; Zudaire and Roy, 2001), dinoflagellates (with clear intra-specific, strain-related differences: Laurion and Roy, 2009), haptophytes (Döhler and Haas, 1995; Buma *et al.*, 2000), eustigmatophytes (Sobrino *et al.*, 2005), natural phytoplankton (Döhler and Hagmeier, 1997), and green macroalgae (Choo *et al.*, 2005). In most of these cases, an increase of the de-epoxidized pigment (diatoxanthin or zeaxanthin) was observed, while the epoxidized parent (diadinoxanthin or violaxanthin) decreased, and this correlated with

a decrease in photochemical efficiency (Fv/Fm) and an increase in non-photochemical quenching (NPQ) (cf. Goss *et al.*, 1999). In one study, both diadinoxanthin and diatoxanthin increased, which may be attributed to the longer duration of the experiment (4 days, Buma *et al.*, 2000). Sobrino *et al*. (2005) determined the biological weighting function (BWF, or action spectrum) for xanthophyll de-epoxidation induced by UV radiation (in the presence of realistic PAR levels), showing that both increased irradiance and inclusion of lower wavelengths in the UV range led to more extensive de-epoxidation. The BWF was similar in shape to the BWF for UV inhibition of photosynthesis, but with a 22-fold lower effectiveness. These results indicate that for the species used by Sobrino *et al.* (2005), stimulation of the xanthophyll cycle occurred upon UV exposure, but this was not sufficient to fully prevent UV inhibition of photosynthesis. Therefore, although xanthophyll de-epoxidation is affected by UV radiation, its main function is related to protection from excess PAR (Sobrino *et al*., 2005).

A second group of studies have reported no effect on the concentration of xanthophyll pigments upon exposure to UV radiation, although information on the level of de-epoxidation was not always available. These studies included work on diatoms (Buma *et al.*, 1996) including benthic species from oyster ponds (Rech *et al.*, 2005) and the Antarctic *Chaetoceros brevis* (Van de Poll *et al.*, 2005), green algae (Lütz *et al.*, 1997; Roleda *et al*., 2009), Antarctic ice phytoplankton (Schofield *et al.* 1995), a toxic dinoflagellate (Evens *et al.*, 2001) and coastal phytoplankton communities exposed to enhanced UV-B in floating mesocosms (Mohovic *et al.*, 2006; Roy *et al.*, 2006). The lack of response was attributed to factors such as interspecific differences, the production of UV-absorbing mucilage, or greater effects of PAR and UV-A. The physiological condition of the cells influenced this response, with a stimulation of the XC when condition declined (Mohovic *et al*., 2006). The detection of UV-B induced effects on photoprotective pigments in other studies was caused by a non realistic spectral balance, according to Van de Poll *et al.* (2005). This, however, does not apply to all cases (e.g. Sobrino *et al.*, 2005).

A last group of studies have shown that UV can inhibit the xanthophyll cycle, generally causing a decrease in the diatoxanthin concentration. Pfündel *et al.* (1992) showed that UV-B (280-320 nm) could inhibit the enzyme violaxanthin deepoxidase in

isolated pea chloroplasts, preventing the transformation of antheraxanthin into the de-epoxidized zeaxanthin. UV-A and UV-B damage to the xanthophyll cycle was observed in cultures of the haptophytes *Pavlova* spp. (Döhler and Lohmann, 1995), the chlorophyte *Dunaliella tertiolecta* (Döhler *et al.* 1997), and of three marine diatoms (Lohmann *et al.*, 1998), including the Antarctic diatom *Chaetoceros brevis* (Janknegt *et al*., 2008). Mewes and Richter (2002) reported a UV-B-dependent decrease in diatoxanthin in cultured diatoms caused by an increase in the epoxidation reaction transforming diatoxanthin into diadinoxanthin. The stimulation of DEP by UV-B may be related to the loss of the pH gradient across the thylakoid membrane which could reduce the affinity of diatoxanthin to its binding site, making it more accessible to DEP. A UV-B-induced loss of the de-epoxidized pigment was also observed in studies by Garde and Cailliau (2000) on the haptophyte *E. huxleyi* and on green macroalgae (*Ulva lactuca*) exposed to natural sunlight with selective exclusion of UV radiation using screening foils (Bischof *et al.*, 2002, 2003). The diminished activity (or reversal) of the xanthophyll cycle has also been attributed to enhanced production of ROS (Lichtenthaler, 1998) which can reduce the relative content of diatoxanthin in cells of the marine, near-bottom diatom *Cylindrotheca closterium* subjected to enhanced UV-B during simulated emersion (Rijstenbil, 2005). This decrease in diatoxanthin was related to UV-A more than to UV-B, and increased salinity exacerbated this reaction. Bischof *et al*. (2003) also related the reduction in xanthophyll cycle activity to increased production of ROS. Hence both direct (cellular UV targets) and indirect (ROS-related) UV effects can damage the xanthophyll cycle and reduce the diatoxanthin content.

Apparently contradictory conclusions can thus be reached from these recent studies, with the enzyme-mediated xanthophyll cycle being either a potential UVR target or a mechanism stimulated by it. However, detailed examination of the spectral and irradiance conditions reveals that most of the phytoplankton studies reporting a stimulation of the xanthophyll cycle were done under a spectral balance (PAR:UV-A:UV-B) relatively close to that found in nature, with relatively low UV-B levels, while studies reporting inhibition of the xanthophyll cycle were often done under more damaging spectral conditions, sometimes with low PAR levels, no UV-A, and with total UV-B dose often higher than 10 $kJ.m^{-2}$. While these studies are useful to unravel the mechanisms of UV

damage to the xanthophyll cycle, they are less useful to predict effects under natural environmental conditions. Interestingly, there are a few cases where UV-B damage to the xanthophyll cycle has been observed under ecologically-relevant conditions (natural sunlight and high PAR irradiances). These include studies on partly or fully sessile organisms such as benthic diatoms (Rijstenbil, 2005) and macroalgae (e.g. Bischof *et al.*, 2002). Epilithon and other sessile organisms may be more sensitive to UV radiation than free-floating phytoplankton perhaps because they are unable to physically avoid UV stress (Bothwell *et al.*, 1994; Vinebrooke and Leavitt, 1999). Increased oxidative damage could also affect the response of the xanthophyll cycle to UV stress (Bischof *et al.*, 2002; Rijstenbil, 2005). Conceivably, organisms where antioxidant levels are low and oxidative stress is high could show UV damage to the xanthophyll cycle (see Fig. 3). Acclimation may also explain some of the variability in responses of the xanthophyll cycle to UV exposure, with different photoprotection mechanisms alternating through time (Zudaire and Roy, 2001). Lastly, the range of responses to environmental UV radiation is quite large in phytoplankton (Neale *et al.*, 1998), accounting for the variability in size, physiological condition and prior light history. One example of this is the different UV responses observed before, during, and after a bloom of diatoms inside a mesocosm, where the amount of diatoxanthin retained after 24h of surface exposure was related to the fraction of inactive PSII reaction centres and was influenced by nitrate limitation (Bouchard *et al.*, 2008). Hence there is not a unique response of the xanthophyll cycle to UV radiation and understanding the overall stress condition of the cells would help elucidate these responses.

4.4.3.3. The XC and the dynamics of water masses

Several studies have investigated marine ecosystems at different time scales with the aim of characterizing the algal responses to the surrounding light environment through the analysis of the XCPs (e.g. Brunet *et al*., 1993; Moline, 1998; Brunet *et al*., 2003; Fujiki *et al*., 2003; Muller and Wasmund, 2003 for coastal sites, Claustre *et al*., 1994; Brunet *et al*., 2003 for frontal systems, Bidigare *et al*., 1987; Olaizola *et al*., 1992; Kashino *et al*., 2002; Brunet *et al*., 2006, 2007 for offshore areas).

*In situ* studies have used different indicators of the photoprotective state of the cells: (Dd + Dt)/chl*a*, Dd/chl*a*, Dt/chl*a* or also Dt/(Dt + Dd). For any of these, when Dd is included in the numerator, it implies a long-term process (Bidigare *et al*., 1987), because Dd reacts at much longer time scales than Dt (Lavaud *et al*., 2002a; Dimier *et al*., 2007b). Instead, Dt is formed at very short time scales, and it represents a clear indicator of fast activation of photoprotection. The DES (de-epoxidation state) index (Dt/(Dt+Dd) ratio) is often more useful than the ratio Dt/chl*a* to infer the photoprotective state of a natural phytoplankton community, since the normalization by chl*a* may introduce a bias due to the natural variability of chl*a* related to the physiological state and the light history of cells. In addition, dividing by chl*a* may be misleading if chl*a* includes algal biomass with no XC (e.g., cyanobacteria) or with the other XC (Vx-cycle in chlorophytes).

Time is a key factor affecting algal physiology. On a yearly scale, photoprotection in terms of any of the above mentioned indices appears to be directly correlated with the daylength and the seasonal increase in total irradiance (Brunet *et al*., 1993; Moline, 1998; Fujiki *et al*., 2003). On a diel scale, Dt/chl*a* and Dt/(Dd+Dt) increase during the daytime and peak around noon (Brunet *et al*., 1993), while (Dd+Dt)/chl*a* peaks later, due to the longer reactivity time scales of Dd (Moline, 1998). A highly significant relationship with irradiance is generally obtained, with sinusoidal variations of Dt/chl*a* in the upper layer (Brunet *et al*., 2008).

Phytoplankton is continuously subject to variations in environmental parameters caused by passive displacement due to water mass dynamics, mixing or sinking (Lewis *et al*., 1984a), or to active displacement due to cell migration. Within a certain time range, mixing triggers short-term photoacclimative responses (MacIntyre *et al*., 2000), which can be traced and used to monitor physical processes such as upwelling, downwelling, or water mass properties such as transparency.

In the case of rapid mixing, the cells may experience light variations faster than their ability to photoacclimate, while in the case of slow mixing, cells may have the time to acclimate to the average light level (Fig. 4). Indeed, the acclimation rates depend on which parameter is considered, since some responses may require seconds or minutes to be activated (e.g. chl*a* fluorescence or the XC), while others (e.g., chl*a* content, absorption capacity, photosynthetic parameters) require much longer times (MacIntyre *et*

*al*., 2000; Brunet *et al*., 2003). The vertical distribution of fast-reacting photodependent parameters (e.g. XC or fluorescence) generally presents a decrease from the very surface to the bottom of the upper mixed layer, as expected from their role in high irradiance protection (Welschmeyer and Hoepffner, 1986; Olaizola *et al*., 1992; Claustre *et al*., 1994; Moline, 1998; Brunet *et al*., 2003, 2006, 2007). However, at times, in actively mixed water columns, homogeneous profiles of XCP have been observed, due to mixing velocities higher than photoacclimation reaction times (Brunet *et al*., 1993).

Other examples of relationships between physical forcing and algal response come from the use of XCP (e.g. Claustre *et al*., 1994; Brunet *et al*., 2003), cell autofluorescence measured by flow cytometry (Dusenberry, 2000) or variable fluorescence (Oliver *et al*., 2003). Many of these authors have used the kinetics of phytoplankton photoresponses to estimate mixing velocities. As an example, Claustre *et al*. (1994), Brunet *et al*. (2003, 2008) estimated, in two different areas of the Mediterranean Sea, vertical mixing velocities between $5\ 10^{-4}$ and $7\ 10^{-4}$ $m.sec^{-1}$, which are realistic values for the areas investigated (see also Falkowki, 1983; Dusenberry, 2000). Thompson *et al.* (2007) found significant differences in vertical mixing velocities ($5\ 10^{-3}$ *vs*. $8\ 10^{-3}$ $m.sec^{-1}$) using XCP distribution between two strongly dynamics eddies in the South-eastern Indian ocean.

The value of these investigations lies in that mixing rates are very difficult parameters to measure directly. From their results on XCP dynamics, Brunet *et al*. (2003; 2008) compared the percentage variations of different photodependent parameters at the surface or the bottom of the mixed layer and were able to establish a decreasing hierarchy in velocity of photodependent indicators. From the inferred kinetic coefficients, a threshold value of 4% $h^{-1}$ was estimated as the value below which photoacclimation reactions were not significant with respect to the physical dynamics. From this, the vertical eddy diffusivity at the time of sampling could be estimated to be $1.75\ 10^{-2}$ $m^2\ sec^{-1}$ (Brunet *et al*., 2003), calculated according to Lewis *et al*. (1984b) and Cullen and Lewis (1988). This example shows how the analysis of the vertical profiles of photo-dependent parameters may provide valuable insights into the effects of hydrodynamism on algal physiology.

In order to use pigments to infer physical properties and dynamics of water masses, knowledge of the kinetics of changes in photo-physiological parameters is needed. These

can be retrieved from laboratory (e.g., Falkowski, 1983) or *in situ*-simulated experiments using natural phytoplankton communities incubated under natural light (deck incubations), subjected to shifts in light intensities. The latter may provide useful terms of comparison to interpret *in situ* observations, but the appropriate sampling pace must be chosen to obtain statistically sound data (Claustre *et al*., 1994; Brunet *et al.*, 2003). During the incubations, the photoacclimative dynamics is generally described by a first-order kinetic equation, from which the kinetic coefficient K is retrieved (Falkowski, 1983; Claustre *et al*., 1994). Alternatively, the use of a logistic model allows the consideration of hysteresis, i.e. the influence of the light experienced by the cell before the sampling (light history) which may have a crucial role in the cell response, modulating its kinetics according to the sign of the light change (Cullen and Lewis, 1988). This model has been successfully applied by Cullen and Lewis (1988) and Dusenberry (2000) but remains to be tested on XCP dynamics.

In general, caution must be adopted when using photoprotective pigments as markers of phytoplankton dynamics in the water column. First, the approach presented is only valid for algae using Dt and Dd in the xanthophyll cycle and not for those using violaxanthin and zeaxanthin. This is because zeaxanthin is also part of the constitutive antenna system of prokaryotic algae. Second, it is recommended to use Dt – not Dd - as a tracer of short-term photoacclimation, while the ratio Dd/chl*a* is a good alternative when long-term photoacclimation processes are considered, due to the different kinetics of transformation inside the XC. Indeed, it is recommended to use Dt/(Dd+Dt) as an indicator of the de-epoxidation state (DES), excluding any normalization by chl*a*.

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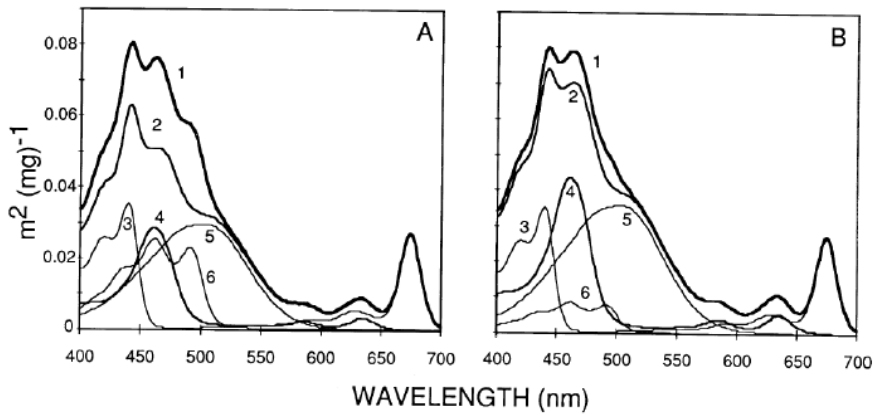
**Table I : List of abbreviations used in this chapter**

| | | |
|---|---|---|
| PPC | : | Photoprotective carotenoids |
| ACP | : | Chl*a*-chl*c*-peridinin protein |
| XCP | : | Xanthophyll-cycling pigments |
| XC | : | Xanthophyll-cycle |
| DDE | : | Diadinoxanthin de-epoxidase |
| ZEP | : | Zeaxanthin epoxidase |
| VDE | : | Violaxanthin de-epoxidase |
| NPQ | : | Non-photochemical fluorescence quenching |
| DEP | : | Diadinoxanthin epoxidase |
| DES | : | De-epoxidation state |
| RC | : | Photosynthetic reaction centers |
| PS | : | Photosystems |

**Table II**. Distribution of the major photosynthetic phyla according to the nature of their main xanthophyll cycle (XC). Group 3 shows no XC but accumulation of ZX under an excess of light. H stands for Heterokontophyta. Some phyla, indicated by *, have a secondary XC (see the text). VX, violaxanthin; AX, antheraxanthin; ZX, zeaxanthin; DD, diadinoxanthin, DT, diatoxanthin.

| **Group 1** | **Group 2** | **Group 3** |
|---|---|---|
| **VX/AX/ZX** | **DD/DT** | **No XC but ZX accumulation** |
| Embryophyta * | Bacillariophyceae* (H) | Cyanophyta |
| Pteridophyta | Xanthophyceae* (H) | Rhodophyta (most species) |
| Bryophyta | Haptophyta * | Glaucocystophyta |
| Chlorophyta * | Dinophyta* | Cryptophyta |
| Phaeophyceae (H) | Raphidophyta | Chlorophyta (some species) |
| Eustigmatophyceae (H) | Euglenophyta | |
| Chrysophyceae* (H) | | |
| Rhodophyta (some species) | | |

# List of Figures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m2 (mg)-1
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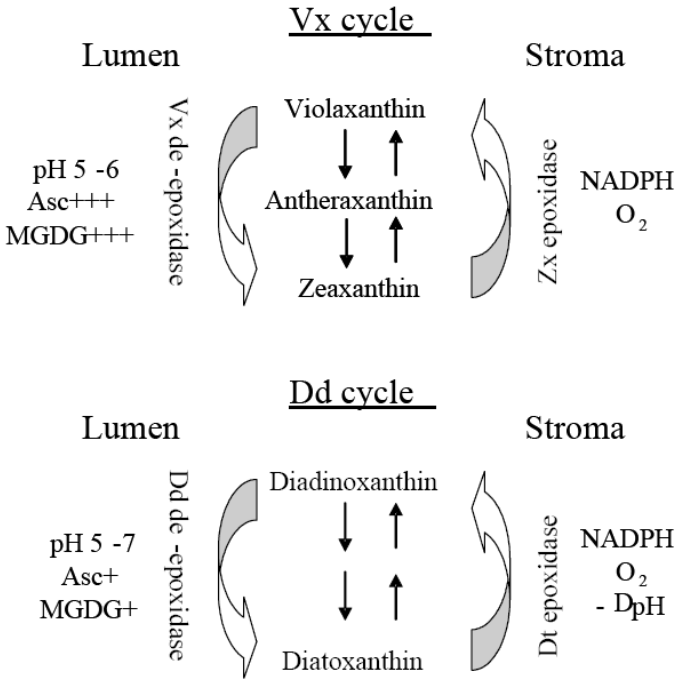
WAVELENGTH (nm)

**Fig. 1**


Vx cycle
Lumen
Stroma
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Asc+++
MGDG+++
Vx de -epoxidase
Violaxanthin
Antheraxanthin
Zeaxanthin
Zx epoxidase
NADPH
O2
Dd cycle
Lumen
Stroma
pH 5 -7
Asc+
MGDG+
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Diadinoxanthin
Diatoxanthin
Dt epoxidase
NADPH
O2
- DpH

**Fig. 2**

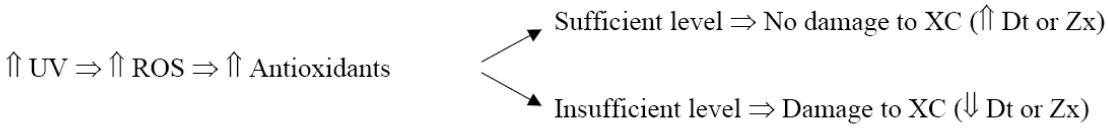
⇑ UV ⇒ ⇑ ROS ⇒ ⇑ Antioxidants
Sufficient level ⇒ No damage to XC (⇑ Dt or Zx)
Insufficient level ⇒ Damage to XC (⇓ Dt or Zx)

**Fig. 3**

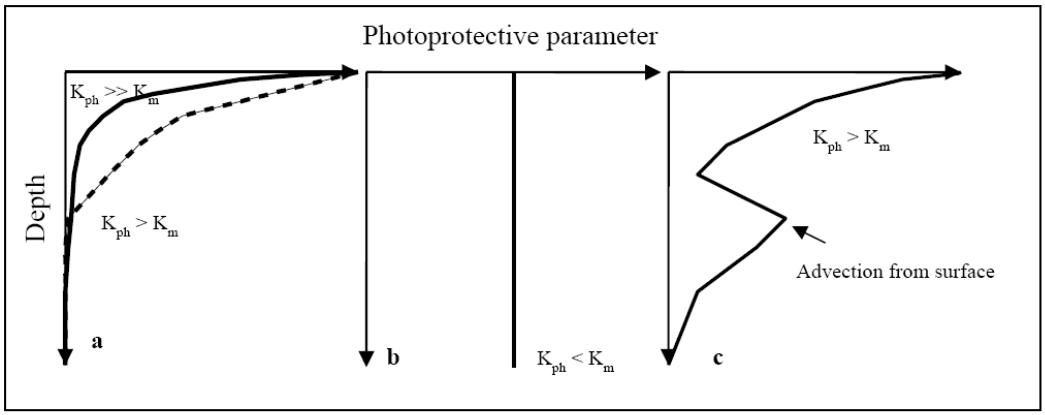
Photoprotective parameter
Depth
$K_{ph} >> K_m$
$K_{ph} > K_m$
a
b
$K_{ph} < K_m$
c
$K_{ph} > K_m$
Advection from surface

**Fig. 4**