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An Overview of Remote Sensing of Chlorophyll Fluorescence

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Abstract – Besides empirical algorithms with the blue-green ratio, the algorithms based on fluorescence are also important and valid methods for retrieving chlorophyll-a concentration in the ocean waters, especially for Case II waters and the sea with algal blooming. This study reviews the history of initial cognitions, investigations and detailed approaches towards chlorophyll fluorescence, and then introduces the biological mechanism of fluorescence remote sensing and main spectral characteristics such as the positive correlation between fluorescence and chlorophyll concentration, the red shift phenomena. Meanwhile, there exist many influence factors that increase complexity of fluorescence remote sensing, such as fluorescence quantum yield, physiological status of various algae, substances with related optical property in the ocean, atmospheric absorption etc. Based on these cognitions, scientists have found two ways to calculate the amount of fluorescence detected by ocean color sensors: fluorescence line height and reflectance ratio. These two ways are currently the foundation for retrieval of chlorophyll-a concentration in the ocean. As the in-situ measurements and synchronous satellite data are continuously being accumulated, the fluorescence remote sensing of chlorophyll-a concentration in Case II waters should be recognized more thoroughly and new algorithms could be expected.

Key words – chlorophyll-a, ocean color, fluorescence line height, reflectance ratio, MODIS, MERIS

1. Introduction

Oceanic satellite observations in the visible and near infrared bands allow the measurements of varieties of ocean color information, mainly including phytoplankton chlorophyll-a, yellow substance (*i.e.* CDOM: Colored Dissolved Organic Matter) and suspended sediments. Regarding to determination and retrieval of chlorophyll-a concentration, there is over 30 years of history, from the 1970's. Sensors of the first and second generations, Coastal Zone Color Sensor (CZCS) and Sea-viewing Wide Field-of-view Sensor (SeaWiFS), both adopt blue-green Ratio Algorithms. However, deriving from the Moderate Resolution Imaging Spectroradiometer (MODIS) and Medium Resolution Imaging Spectrometer (MERIS), the 3rd generation sensors have been exploring new algorithms based on *in vivo* chlorophyll fluorescence, which has become one of the main retrieval methods for chlorophyll-a concentration.

In oceanic Case 1 waters, there exist little yellow substance and suspended sediments; phytoplankton with its accompanying and covarying retinue of material of biological origin is the principal agent responsible for variations in optical properties of the water. For Case 1 waters, the phytoplankton chlorophyll-a concentration is not extremely high, accordingly the blue-green ratio algorithms have been confirmed to work well. Nevertheless, for coastal Case 2 waters with more yellow substance and increasing suspended matter, the non-phytoplankton matters play an important role in determining the optical properties of the water body. In the coastal waters, chlorophyll-a concentration is generally high due to eutrophic waters. For such eutrophic waters, the traditional blue-green ratio algorithms become less efficient, as the signal in the blue part of the optical spectrum drops

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below the limits of detection because of high absorption by algae. Contrarily, the Fluorescence-based Algorithms have been demonstrated to be most effective.

Maritorena and his colleagues indicated that the first measurement of passive fluorescence *in situ* was made in 1966 by Tyler and Smith (1970) in the San Vicente reservoir using the Scripps spectroradiometer (Maritorena *et al*. 2000). This signal, however, was not recognized as fluorescence. Further study by Morel and Pireur (1977) and Neville and Gower (1977) suggested that the observed enhancement of the diffuse reflectance near 685 nm should be from the *in vivo* fluorescence of chlorophyll-a induced by ambient sun and sky light. Neville and Gower (1977) confirmed that the height of the peak observed at 685 nm was strongly correlated with chlorophyll concentration by using spectral reflectance data observed in Saanich Inlet. Their investigation primarily demonstrated the possibility of using sun-induced fluorescence in reflectance spectra to determine chlorophyll concentration. Thereafter this idea has been assessed by different scientist groups (Gower and Borstad 1990; Fischer and Kronfeld 1990; Fischer and Schlüssel 1990; Letelier and Abbott 1996; Gower *et al*. 1999). On the 18th of December 1999, the first ocean color sensor equipped with several bands specifically designed to measure the solar-stimulated fluorescence, MODIS TERRA, was launched.

Fluorescence algorithms have huge advantages in retrieval of phytoplankton chlorophyll-a concentration in Case 2 waters and red tide areas. Firstly, the fluorescence signal, when present, is uniquely attributed by chlorophyll-a so that it is unlikely to be confused with anything else, such as yellow substance or suspended matters. Secondly, the atmospheric influence in the red part of the spectrum is smaller than in the blue-green, so fluorescence algorithms need only a simple atmospheric correction. Thirdly, absorption-based signals are a decreasing function of chlorophyll-a, whereas fluorescence contrastively increases with it; as a result, for eutrophic waters with extremely high chlorophyll-a concentration, blue light signal drops below the limits of detection; whereas, fluorescence signal is still powerful to probe.

2. Mechanisms and Characteristics

In the view of bio-optical mechanisms, *in vivo* chlorophyll fluorescence is an important physiological process which always concurs with photosynthesis of phytoplankton. There are two photosystems in the phytoplankton chloroplast: Photosystem I (PS I) and Photosystem II (PS II). In environmental temperature, chlorophyll fluorescence mostly comes from PS II. After light harvesting complex (LHC) of PS II captures light energy needed for photosynthesis, absorption of light quantum induces the transition of the pigment molecule into an excited state. From peripheral antenna complexes, excitation is efficiently transferred into core antenna complexes near to photosynthetic reaction centers, where it can be used in the primary photochemical reaction of photosynthesis. But a small fraction of these excitations are reemitted as fluorescence or thermal dissipation while they migrate in the core antenna complex to the reaction center. That is to say, a portion of the absorbed energy is used in photosynthesis; another portion is dissipated as heat, while the remainder, which usually occupies less than 5% of the absorbed energy, is re-emitted as fluorescence.

In the view of spectral characteristics, *in vivo* chlorophyll fluorescence is a sort of light emission phenomenon occurring in the reflectance spectrum near 685 nm, stimulated by ambient visible light covering wavelengths from 400 nm to 700 nm. It has been discovered that *in vivo* fluorescence accords reasonably well with a Gaussian distribution with a width at half-maximum of 25 nm centered and normalized to 685 nm (Mobley 1994), and the fluorescence maximal height customarily shows obvious positive correlation with chlorophyll-a concentration. Furthermore, the increase of the peak height is accompanied with a shift in its position towards the longer wavelength, generally characterized as “red shift”. For sea areas with chlorophyll-a concentration less than 3 mg/m^{-3}, the fluorescence was observed near 683 nm; when the concentration increases to 10 mg/m^{-3}, the peak position would be at 685 nm. If there are blooms of phytoplankton or HABs (harmful algal blooms), the red shift would be more evident. It would shift to 715 nm for the concentration more than 100 mg/m^{-3}. The velocity of red shift was examined by Gitelson (1992). For a variety of phytoplankton species, the distances of “red shift” are distinctly different (Zhao *et al*. 2004b).

3. Influence Factors

The ocean algae absorb ambient natural light, and then emit fluorescence into environmental waters. The emitted

fluorescence transfers through ocean and atmosphere to satellite sensors. There exist many materials in the ocean and atmosphere which have influence on the fluorescence signal. In addition, the essential physiological complexity of algae and variability of *in vivo* fluorescence increase many problems for remote sensing of chlorophyll fluorescence.

Quantum yield

Chlorophyll fluorescence quantum yield, sometimes called chlorophyll fluorescence efficiency, is defined as the number of emitted photons emitted divided by the number of photons absorbed by chlorophyll-a. The quantum yield of fluorescence *in vivo* is highly variable depending on the conditions of observation, the physiological status of the algae and the species observed. The observation done by Gordon (1979) showed that quantum yield of fluorescence varies ranging from 0.002 to 0.02. Maritorena *et al.* (2000) measured the vertical quantum yield profiles in the tropical central Pacific Ocean, which were strongly structured with maximal values (5-6%) values at depth, whereas the fluorescence quantum yield in the near-surface waters was approximately equal to 0.001. Besides, in fact, the quantum yield is known to undergo diel variations (Loftus and Seliger 1975; Abbott *et al*. 1982): The increase in quantum yield at the beginning and end of the "day" is part of the photoadaptive process. The mid-day depression is still under study, but it is probably related to photoadaptation of the reaction centers.

Suspended matter

Fischer and Kronfeld (1990) simulated the effects of suspended matter on the fluorescence using radiation transfer model. Scattering of suspended matter will cause decrease in the incoming irradiance and modification of the radiances. Nevertheless, Gower and his colleague (Gower *et al*. 1999) hold that the suspended matters do little affect to the relative fluorescence height above the baseline, in despite of the increase of reflection spectrum caused by them.

Yellow substance

Because the yellow substance in Case 2 water strongly absorbs the incident radiation mainly in the blue part of the visible spectrum, this affects the fluorescence by reducing the amount of available irradiance available which may be absorbed by chlorophyll-a. Fischer and Kronfeld (1990) and Gower *et al*. (1999) found that fluorescence line height was almost changeless, because the baseline height also experienced a decrease along with the fluorescence peak.

Penetration depth

The upward radiance reaching the water surface is a mixture of radiances from different depths and depends on the optical properties of components in waters and pure ocean water. Gordon and McCluney (1975) defined "penetration depth" or called "signal depth" as that depth above which 90% of the water-leaving radiance originates. It is expressed as

$$Z_{90} = \frac{2.3}{k_t} \quad (1)$$

where k_t is the total diffuse attenuation coefficient. For a clear ocean, the highest penetration of radiation is the blue light at 445 nm, where Z_{90} is 52.86 m. Reversely, for the fluorescence wavelength the penetration depth is only 1.96 m and becomes smaller with increasing amount of suspended sediments and yellow substance. Since ocean waters intensely attenuate algae fluorescence, the fluorescence signals only feed back the information of chlorophyll-a in the subsurface waters at depth less than 2 m.

Azimuth angle

The emission of the sun-induced chlorophyll fluorescence is assumed to be isotropic, but becomes anisotropic due to its extinction in ocean water and the transmission through the ocean surface. The fluorescence has its highest value around the nadir angle, and reduces with increase of the azimuth angle.

Solar elevation

The solar elevation plays an important role in modifying chlorophyll fluorescence, since extinction processes throughout the atmosphere and reflection at the water surface both decrease the incoming radiation, and indirectly decrease the fluorescence signal. Although theoretically, the solar elevation is not able to modify the relationship between fluorescence peak height and chlorophyll-a concentration, in practice, over-low fluorescence signals certainly influence the precision of retrieval algorithms.

Atmospheric absorption

Aside from the effects within ocean waters, there is also absorption by gases in the atmosphere. Scattering effects are most pronounced at shorter wavelengths, but the fluorescence line is located in the region of the spectrum where there are several narrow absorption bands. Particularly, there are two oxygen absorption bands at 687 and 760 nm as well as a water vapor absorption band at 730 nm. Therefore, the satellite sensor bands for detecting chlorophyll fluorescence are designed to avoid these atmospheric absorption bands. Especially, the fluorescence band on satellite sensor is acknowledged to be designed on the left of 685 nm, as fluorescence peak is close to the oxygen absorption band at 687 nm (Pan *et al.* 1989).

4. Principles

At present, there are two algorithms used to research and test the relationship between fluorescence signal and chlorophyll-a concentration, generally denoted as "fluorescence line height" and "reflectance ratio".

Fluorescence line height

In 1977, Neville and Gower (1977) detected *in vivo* fluorescence signal in Saanich Inlet by using an airborne multichannel spectrometer, and first brought forward an assumption of using fluorescence line height (FLH) to determine chlorophyll-a concentration. Afterwards Gower (1980) again demonstrated the possibility of using a shipborne spectroradiometer. Pan *et al.* (1989) first discussed the atmospheric effect on phytoplankton fluorescence, and proposed two suits of reasonable band combinations for fluorescence remote sensing to successfully avoid the atmospheric influence. In 1990, Fischer and co-workers (Fischer and Kronfeld 1990; Fischer and Schlüssel 1990) made several studies of oceanic and atmospheric effects on fluorescence line height, such as phytoplankton taxonomy, physiological status, chlorophyll absorption, fluorescence quantum yield, solar zenith angle, yellow substance, suspended matter and atmospheric composition. Gower *et al.* (1999) and Hoge *et al.* (2003) respectively validated FLH algorithms of MERIS and MODIS sensors. Despite their both finding a linear relation between fluorescence line height and chlorophyll-a concentration, Gower *et al.* (1999, 2003) believed that a nonlinear function must be expected for concentrations above about 5 mg/m^{-3}. It is first shown by Zhao *et al.* (2004b) that the functions are different for various algae species. Hu *et al.* (2005) presented the first application of the MODIS FLH data for detecting and tracing of HABs. As suggested by Letelier and Abbott (1996), the dominant source of uncertainty in fluorescence-based algorithms is in the physiological processes of the phytoplankton themselves. Accordingly, it is proposed that the FLH algorithm should be corrected from the algae physiological variability (Babin *et al.* 1996; Fell *et al.* 2002; Huot *et al.* 2005).

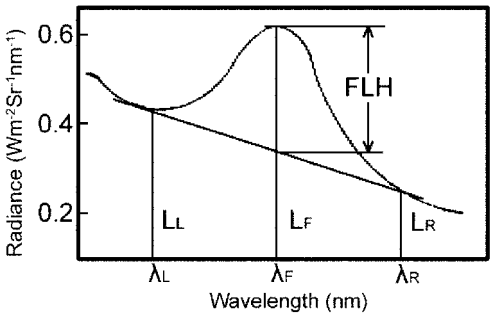

Fig. 1. The principle of fluorescence line height, where λ_F, λ_L, λ_R are respectively the center wavelengths of fluorescence band and two baseline bands. L_F, L_L, L_R are respectively the radiances of fluorescence band and two baseline bands.

It is simple to estimate FLH as shown in Fig. 1. A baseline is first formed by a linear interpolation of two baseline bands, and then subtracted from radiance of fluorescence band to obtain the FLH. So the expression of FLH can be calculated as follows.

$$FLH = L_F - \left[L_R + \frac{\lambda_R - \lambda_F}{\lambda_R - \lambda_L}(L_L - L_R) \right] \quad (2)$$

where λ_F, λ_L, λ_R are respectively the center wavelengths of fluorescence band and two baseline bands. L_F, L_L, L_R are respectively the radiances of fluorescence band and two baseline bands. Although Gower and Borstad (1987) suggested that a curved baseline might perform better, eventually the simple linear model is developed and likely to be little different from the former one.

There indeed exists a linear relationship between FLH and chlorophyll concentration in oligotrophic waters; nevertheless the intercept and slope of regression equation are variable in different dataset. The FLH does not only vary with variation in the chlorophyll-a pigment concentration, but is also affected by photoinhibition, phytoplankton species, and physiological states (Kiefer 1973; Falkowski and Kiefer 1985; Campbell *et al.* 1998).

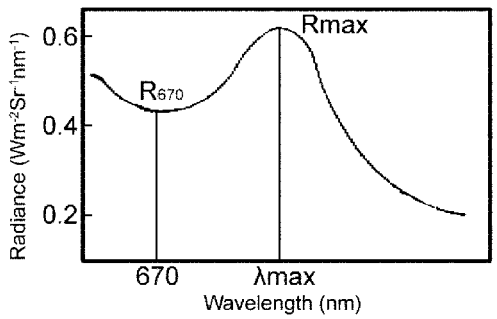

Fig. 2. The principle of reflectance ratio.

In mesotrophic and eutrophic waters, a nonlinear expression performs better. As Gower *et al.* (2005) said, because an increasing fraction of fluorescence signals is partly absorbed by algae itself, so an increase in phytoplankton concentration does not lead to a proportional increase in signal. Both the stimulating short-wave solar irradiance and the emitted fluorescence at 685 nm are partly absorbed. So the water leaving radiation decreases as 1/a, where "a" is the total absorption at 683 nm. And they suggested the relation is as follows

$$FLH = k + \frac{b*[Chla]}{1 + a*[Chla]} \quad (3)$$

where [Chla] denotes chlorophyll-a concentration, k is a negative offset, the factor "b" depends on the sun elevation angle, fluorescence quantum yield and vertical distribution of the phytoplankton, and instrument band placing (Gower and King 2003).

Reflectance ratio

For the reflectance peak around 685 nm observed by Neville and Gower (1977), some scientists had different comprehension initially. They regarded it as a minimum on the combined absorption curve of algae and water for high chlorophyll values, and the reflectance ratio, or "normalized reflectance", was considerably correlated with chlorophyll-a concentration in mesotrophic and eutrophic waters (Vasikov and Kopelevich 1982; Vos *et al.* 1986; Kishino *et al.* 1986; Gitelson and Kondrat'ev 1991; Mittenzwey *et al.* 1991, 1992; Gitelson 1992, 1993; Yacobi *et al.* 1995, Gitelson *et al.* 1996, 2000). Moreover, Gitelson (1992, 1993) first investigated the "red shift" of *in vivo* fluorescence peak, and noticed that the speed of "red shift" is likely to be invariable (approximately equal to 0.268 nm/mg Chla m^{-3}) with concentration increasing. The regression equation was found as follows

$$\text{Peak position} = 683.51 + (0.268 \pm 0.0075)\ [Chl]$$

with correlation R^2 higher than 0.93. Zhao *et al.* (2005a, 2005b) studied the reflectance ratio algorithms for various algae species, and suggested that the speeds of "red shift" should be different from each other.

The reflectance ratio algorithms have been embodied into several forms; a simple ratio $R_{maxred}/R670$ or $R_{maxred}/R560$ was customarily used as a predictor of chlorophyll concentration, as follows

$$\text{Reflectance Ratio} = R_{maxred}/R_{560} \quad (4)$$

$$\text{or Reflectance Ratio} = R_{maxred}/R_{560} \quad (5)$$

where R_{maxred} is the reflectance at fluorescence peak around 685 nm in red or near infrared part of spectrum, sometimes replaced by R_{700} or R_{705}. The ratio algorithms quantify the chlorophyll fluorescence signal by normalizing it to the reflection peak and absorption trough of chlorophyll-a found respectively near 560 nm and 670 nm, so the ratio is also called as "normalized reflectance" by Gitelson (1992) or "normalized fluorescence height" by Zhao *et al.* (2005a, 2005b). In addition, some complex forms were once proposed and tested such as

$$\text{Reflectance Ratio} = (R_{560}-R_{700})/(R_{560}-R_{700}) \quad (6)$$
(Gitelson and Keydan 1990);

$$\text{Reflectance Ratio} = (R_{705}-R_{670})/R_{550} \quad (7)$$
(Mittenzwey *et al.* 1991);

$$\text{Reflectance Ratio} = (R_{705}-R_{670})/(R_{550}-R_{670}) \quad (8)$$
(Mittenzwey *et al.* 1991);

$$\text{Reflectance Ratio} = (R_{705}-R_{670})/(R_{550}-R_{760}) \quad (9)$$
(Mittenzwey *et al.* 1991),

the most popular forms have ever been the two simple ones.

Indeed, the reflectance ratio algorithms are valid for high chlorophyll concentration, whereas it seems impossible to apply the ratio to oligotrophic waters. As said by Mittenzwey *et al.* (1992), the uncertainty of the chlorophyll concentration determined based on the basis of these reflectance ratios grows for lower values of concentration, especially for [Chla] < 10 μg/L.

Table 1. The comparison of sensor fluorescence bands, where NEΔL is Noise equivalent radiance, PFT is Proto Flight Test, EMT is Engineering Model Test, and SPC is Specification. (IOCCG report 2 1999)

Sensors		The Left Baseline Band (λ_L)	The Fluorescence Peak Band (λ_F)	The Right Baseline Band (λ_R)
BandCenter (nm)	MODIS	665.1	676.7	746.4
	MERIS	665	681.25	709
	GLI	666.7	679.9	710.5
	GOCI	660	680	745
BandWidth (nm)	MODIS	10	10	10
	MERIS	10	7.5	9
	GLI	10	10	10
	GOCI	20	10	20
NEΔL ($Wm^{-2}sr^{-1}\mu m^{-1}$)	MODIS	0.008	0.007	0.009
	MERIS	0.013	0.014	0.011
	GLI	0.015	0.014	0.012
	GOCI	0.032	0.031	0.020
Signal/Noise Ratio	MODIS(PFT)	1163	1265	1077
	MERIS(PFT)	708	589	631
	GLI(EMT)	863	853	826
	GOCI(SPC)	1010	870	860

5. Application on Sensors

Presently, all of the third generation ocean color sensors, including MODIS, MERIS and GLI, are equipped with fluorescence bands specifically designed. Additionally, the first geosynchronous ocean color sensor scheduled for launch in 2008 by Korea, the Geostationary Ocean Color Imager (GOCI), will also carry three fluorescence bands as similar as MODIS's bands.

Specifications

The detailed specifications of the four sensors are listed in Table 1. The fluorescence bands on all these sensors are designed according to fluorescence line height algorithms, so designed three bands are respectively the left baseline band (λ_L), the fluorescence peak band (λ_F) and the right baseline band (λ_R) respectively. In Table 1, it is shown that the bandwidths are similar to each other, and MERIS is a little better; MODIS has advantages in capabilities of instrumentation, such as noise equivalent radiance (NEΔL) and signal to noise ratio (SNR).

The most crucial difference of all specifications is the bandcenter, that is, the position of bands. For the fluorescence peak band, 676.7 nm band on MODIS is the farthest from the actual fluorescence peak position to avoid the influence of oxygen absorption band at 687 nm by the greatest extent; on the contrary, 681.25 nm band on MERIS is most close to 685 nm in order to answer to more fluorescence signal. Gower *et al*. (2004) have shown that MODIS is responding to only 57% of fluorescence information, and MERIS can obtain 78%. For the right baseline band, 746.4 nm band on MODIS and 745 nm band on GOCI are set at the right of water vapor absorption band at 730 nm; by contrast, 709 nm band on MERIS and 710 nm band on GLI are designed at its left. Though over approach to the fluorescence peak band would reduce the sensitivity of FLH, Gower *et al*. (2003) noticed that 709 nm band is able to detect blooms of phytoplankton. Compared with MODIS and GLI using lab and in situ data, MERIS is more reasonable in band designation as figured by Zhao *et al*. (2004a).

Sensitivity analysis

Based on Equation (2) and assuming that noise is independent between bands, the Signal to Noise Ratio (SNR) of the baseline may be calculated as:

$$\frac{1}{SNR_{Baseline}} = \frac{1}{SNR_R} + \left(\frac{1}{SNR_L} - \frac{1}{SNR_R}\right) (\lambda_R - \lambda_F) / (\lambda_R - \lambda_L) \quad (10)$$

Where SNR_R denotes the Signal to Noise Ratio (SNR) of the right band, and SNR_L denotes the Signal to Noise Ratio (SNR) of the left band. The SNR of FLH is

Table 2. The SNR of baseline and FLH, PFT is Proto Flight Test, EMT is Engineering Model Test, and SPC is Specification.

Sensors	SNR_L	SNR_F	SNR_R	$SNR_{Baseline}$	SNR_{FLH}
MODIS (PFT)	1163	1265	1077	1150	602
MERIS (PFT)	708	589	631	677	315
GLI (EMT)	863	853	826	852	426
GOCI (SPC)	1010	870	860	970	459

calculated as

$$\frac{1}{SNR_{FLH}} = \frac{1}{SNR_F} + \frac{1}{SNR_{Baseline}} \quad (11)$$

From the specification of Table 2, the SNR of every sensor is figured, and the results are also shown in Table 2, where we can see that the SNR of MODIS is the best of all, $SNR_{Baseline}$=1150, and SNR_{FLH}=602.

Fischer and Schlüssel (1990) estimated that upward radiances at λ=685 nm at the top of the atmosphere (TOA) range from 8 to 20 Wm^{-2} sr^{-1} μm^{-1} for realistic atmospheric turbidity variations and a solar zenith distance of Θs=50.7°, while the lower radiance of this range corresponds to an atmospheric turbidity factor of 0.5 (88 km horizontal visibility), the upper value corresponds to a turbidity factor of 10 (6 km horizontal visibility). A similar value at λ=676.7 nm is calculated by Letelier and Abbott (1996) using LOWTRAN. The upwelling radiance at TOA is 9.05 Wm^{-2} sr^{-1} μm^{-1} with a horizontal visibility of 50 km, a solar zenith angle of 60°. Then we can obtain the Minimum Signal of Detection (MSD) of MODIS, based on the SNR of MODIS FLH and the TOA radiance at λ=676.7 nm:

$$MSD_{MODIS} = \frac{Radiance_{TOA}}{SNR_{MODIS\ FLH}} = \frac{9.05\,Wm^{-2}sr^{-1}\mu m^{-1}}{602}$$

$$0.015\,Wm^{-2}sr^{-1}\mu m^{-1} \quad (12)$$

Compared with MODIS, the MSD of others is higher. Moreover, under higher turbidity, the MSD heightens and the sensitivity of FLH algorithms decreases.

6. Problems and Resolutions

It has been 30 years since the hypothesis of determination of the chlorophyll-a concentration using *in vivo* fluorescence was first presented by Neville and Gower (1977). Meanwhile, many remote sensing scientists, oceanographers, biologists and phytoplankton physiologists have been making great contributions to remote sensing of *in vivo* fluorescence, and fluorescence-based algorithms have become important ways for coastal Case 2 waters and HABs regions. However, because of complex physiological mechanisms and particular spectral characteristics, there still exist some problems in satellite remote sensing.

Quantum yield

As discussed in the algorithm theoretical basis document of MODIS (Abbott and Letelier 1999), there are three processes that would affect measurements of FLH. The first is the absorption properties of the atmosphere. In particular, these intense absorptions at red and near-infrared part of spectrum significantly influence the shape of the fluorescence peak such that it deviates from a pure Gaussian curve. By designing sensor bands reasonably, the influence may be basically avoided. The second process involves the performance of the instruments themselves, including bandwidth, noise equivalent radiance and SNR etc, which may be further improved. The final process is physiological change in the phytoplankton which may result in variability in FLH. This can be troublesome if we try to estimate chlorophyll concentrations from FLH as the amount of fluorescence per unit chlorophyll is not constant. The amount of fluorescence will vary as a function of the quantum yield of fluorescence, which may vary with the species and physiological state of the algae, thus increase the uncertainty of algorithms.

The quantum yield of sun-induced fluorescence *in vivo* defined by remote sensing scientists is the ratio of photons fluoresced by chlorophyll-a over the whole fluorescence region and the photons absorbed by all cellular pigments (Huot *et al*. 2005). Others have referred to this as the apparent quantum yield of chlorophyll fluorescence. As mentioned above, there are three competitive and mutually exclusive processes to transform or transfer absorbed energy: fluorescence, photosynthesis and heat dissipation. Decrease of the fluorescence quantum yield due to the photosynthetic processes is called “photochemical quenching”, and non-photochemical processes, mainly

including heat dissipation, reducing the quantum yield of fluorescence is referred to as "non-photochemical quenching". Largely owing to the presence of photochemical quenching and non-photochemical quenching, fluorescence quantum yield becomes variable. So our focus for algorithm evolution should be to utilize variability in fluorescence quantum yield to improve the estimates of chlorophyll-a concentration.

However, the crucial problem is that the quantum yield of sun-induced fluorescence is highly changeable and, furthermore, can't be measured directly. The first exact relationship was presented by Babin *et al*. (1996) to estimate fluorescence quantum yield using *in situ* measurements as follows

$$L_f(0) = E_{PAR}(0)[Chla]\bar{a}^*_{ph}Q^*_a(685)\varphi_f\frac{1}{4\pi}\frac{1}{[K_{PAR}+\kappa(685)]} \quad (13)$$

where φ_f is the quantum yield of fluorescence, $L_f(0)$ is the radiance in upward vertical direction due to fluorescence, $E_{PAR}(0)$ is scalar irradiance at surface, K_{PAR} is the vertical attenuation coefficient for $E_{PAR}(z)$, $\kappa(685)$ is the vertical attenuation coefficient at 685 nm, [Chla] is chlorophyll-a concentration, $\bar{a}^*_{ph}$ is the mean chlorophyll-specific absorption coefficient of phytoplankton, and $Q^*_a(685)$ is a dimensionless factor accounting for intracellular reabsorption of fluorescence within the emission spectral band (centered on 685 nm).

The CFE (chlorophyll fluorescence efficiency) products provided by MODIS can be considered as a coarse evaluation of fluorescence quantum yield, calculated by adding a constant radiance (FLH_{min}) to the FLH value and then normalizing by the radiance absorbed by phytoplankton in the upper ocean ($ARP_{radiance}$).

$$CFE = \frac{FLH + FLH_{min}}{ARP_{radiance}} \quad (14)$$

In 2005, Huot *et al*. (2005) presented a more accurate estimation of fluorescence quantum yield basing on the equation (13) derived by Babin *et al*. (1996). Through a global view of fluorescence quantum yield, the algorithm may obtain a higher precision.

Low signal

As a result of photosynthesis and heat dissipation, the quantum yield of *in vivo* fluorescence is very small, generally less than 5%. That is to say, for low value of chlorophyll-a concentration, the fluorescence signal is extremely weak; so much as the estimate of FLH is negative. Overly low fluorescence signal brings us a new problem; the fluorescence-based algorithms may be inapplicable in oligotrophic environments and open oceanic waters, which have low content of phytoplankton. Therefore, there should be a detection limit for ensuring the precision and quality of the FLH algorithm.

In the context above, we discussed that MSD of MODIS at TOA is 0.015 Wm^{-2} sr^{-1} μm^{-1}, with a horizontal visibility of 50 km, a solar zenith angle of 60°. To convert MSD into Minimum Chlorophyll of Detection (MCD), we should account for atmospheric attenuation, transmission through the air/sea interface, and variability in the fluorescence quantum yield. The algorithm theoretical basis document of MODIS (Abbott and Letelier 1999) suggested that, for a typical mid-latitude oceanic atmosphere, the radiative transfer of the sea surface fluorescence signal measured at λ=676.7 nm to the TOA is close to 80%. Increasing the ocean atmospheric aerosol content from a turbidity factor of 0.5 (visibility=90 km) to a factor of 10 (visibility=6 km) decreases the absolute atmospheric transfer of the fluorescence signal by less than 30%. Variations in the atmospheric water vapor content also affect the recovery of the TOA fluorescence signal by less than 20%. We believe that 30% is a conservative estimate of the loss of the fluorescence signal through the atmosphere. Then the MSD at sea surface detectable by MODIS becomes 0.021 Wm^{-2} $sr^{-1}\mu m^{-1}$. When the fluorescence signal crosses the air/sea interface, the loss due to refraction and reflectance is 45.7% (the Fresnel reflectance index and refractive index respectively is approximately equal to 0.025 and 1.34 according to NASA optical protocols), consequently, the MSD under the sea surface detectable by MODIS is 0.039 Wm^{-2} $sr^{-1}\mu m^{-1}$. Fischer and Kronfeld (1990) calculated a conversion factor of 0.05Wm^{-2} $sr^{-1}\mu m^{-1}$ per mg chlorophyll for light saturated photosynthetic conditions. Then the Minimum Chlorophyll of Detection (MCD) is estimated to be around 0.78 mg/cm^3, and increases with atmospheric turbidity ascending.

Red shift

The third problem is the "red shift" of fluorescence peak position with chlorophyll-a concentration increasing. In eutrophic environments and HABs waters, the fluorescence peak would entirely deviate from the fluorescence peak

Table 3. A modified MERIS band-set according to Gower *et al.* (2003)

Start(nm)	End(nm)	Center(nm)	Width(nm)	New/Existing
650	660	655	10	New band
660	670	665	10	Existing band
670	677.5	673.75	7.5	New band
677.5	685	681.25	7.5	Existing band
685	695	690	10	New band
695	703.75	699.375	8.75	New band
703.75	713.75	708.75	10	Existing band
713.5	723.5	718.5	10	New band

band, and the FLH algorithm would be inoperative and useless as well. For this phenomenon, MERIS has obvious advantages compared to MODIS and others. All the fluorescence peak bands are designed at the left of the true fluorescence peak around 685 nm, avoiding the atmospheric influence, but the one of MERIS at 681.25 nm is closer, and will be valid at higher concentration. Furthermore, the right baseline band of MERIS is set at 709 nm; Gower *et al.* (2003) suggested that this band may be used to detect the shifted fluorescence peak with the concentration above 100 mg/m^{-3}; they produced a similar FLH, using 681 nm and 753 nm band as baseline, then abstracted by 709 nm band, named as "Maximum Chlorophyll Index (MCI)", and demonstrated that MCI could provide considerable sensitivity.

Besides, ESA has accepted a proposal (A.O. No.612) for measurements of biomass and phytoplankton bloom in the spectral range 650 to 720 nm using a modified MERIS band-set. The band-set would include the spectral bands listed in Table 3. There are five new bands, which plus three existing bands will provide contiguous coverage of the wavelength range 650 to 723.5 nm with a resolution of 7.5 to 10 nm (Gower *et al.* 2003). The modified MERIS band-set will be available in observation of red shift and remote sensing of phytoplankton bloom waters.

7. Summary

Although present study on fluorescence should be taken as exploratory research partly owing to these problems discussed above, the approaches using in vivo fluorescence to detect algae pigment concentration have been used successfully in many local areas, and should be considered as a new direction for development. Along with further improvement of instruments, accumulation of *in situ* data and advancement of algorithms, *in vivo* fluorescence is certain to play a more important role in ocean color remote sensing.

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