Chlorophyll and suspended sediment specific absorption coefficient in the sea.

Yu-Hwan Ahn* and Jeong-Eon Moon
Korea Ocean Research and Development Institute
Ocean Remote Sensing Lab.
yhahn@kordi.re.kr

Abstract

Absorption coefficient per mass unit of particles, specific absorption coefficient, is one of main parameters in developing algorithms for ocean color remote sensing. Specific absorption coefficient of chlorophyll (a^*_{ph}) and suspended sediment (SS) were analyzed by "wet filter technique" and "Kishino method" for data sets observed in the Yellow and Mediterranean Seas. A new data-recovering method for the filter technique was also developed using spectrum slopes. This method recovered the baseline of spectrum that was often missed in the Kishino method. High $a^*_{ph}(\lambda)$ values in the oligotrophic Mediterranean Sea and low values in the Yellow Sea were observed, spanning over the range of 0.02 to 0.12 m^2/mg, at the chlorophyll maximum absorption wavelength 440nm. The empirical relationship between a^*_{ph} and chlorophyll concentration was found to fit a power function, which was slightly different from that proposed by Bricaud *et al.* (1995). Absorption specific coefficients for suspended sediment (a^*_{ss}) didn't show any relationship with concentrations of suspended sediment. However, the average value of a^*_{ss} at 440nm was close to the specific absorption coefficient of soil (loess) measured by Ahn (1990). The more-pronounced variability of a^*_{ss} than a^*_{ph} perhaps can explain more wide range of size-distribution for SS, which were determined by their specific gravity and agitation of water mass in the sea surface.

1. Introduction

It is well known that absorption by phytoplankton plays a key role in determining the optical properties of case-I water. In case-II water, where waters are generally turbid, the suspended sediment (SS) is the major particles of water body. It will be meaningless in discussing case-II water without SS. In the analytical ocean color remote sensing algorithm, the final values extracted from the upwelling radiance are the absorption coefficients. These absorption coefficients should be converted to particle concentrations using their own specific absorption coefficients. Therefore, it's important to know the specific absorption coefficient (a^*), namely, light absorption per unit mass of particles, in the seawater in developing algorithms for ocean color remote sensing. Beside this, the specific absorption coefficient by phytoplankton is used for the modeling of quantum yield (Dubinsky et al., 1984; Morel, 1978) or for the primary production model.

Morel and Bricaud (1981) firstly developed the theoretical variation of a^* by cultured phytoplankton (ph). The variability of a^*_{ph} values are decreased with the increasing of phytoplankton size and intracellular pigment concentration with the same pigment concentration. It is called "package effect" or "discreteness effect". Until now, a^*_{ph} have been assumed as constant in optical model or in ocean color algorithms (Ahn, 1990), whatever the trophic levels of waters are. This assumption has brought certainly some error in the optical model. For example, Ahn(1990) presented an analytical ocean color model, from which the analyzed chlorophyll values clearly were small in high chlorophyll concentration region. It certainly would come from the constant a^*_{ph} value used in the model. These coefficients, however, are now known as varying for natural phytoplanktonic assemblages (Bricaud and Stramski, 1990). Recently, Bricuad *et al.* (1995) proposed a varying a^*_{ph} with chlorophyll concentration of seawaters using world wide gathered data. The result show that a^*_{ph} is greatly changed a lot along with trophic level of water or with the water types.

Yellow Sea has been recognized as representative case-II water. The name is originated from the watercolor. But Yellow Sea is now identified as Case-II water (Ahn *et al.*, 1997) even if in the limpid center of the sea. The optical properties of Yellow Sea are not clearly studied. We don't know yet specific absorption coefficient for phytoplankton for this region.. The specific absorption coefficient of SS is no more a parameter to be neglected. Withlock et al. (1985)

measured the optical properties SS in river water. In their work, the absorption spectrum form of SS could not be believed to be exact. Ahn (1990) studied the first optical properties of soils (loess) in seawater by spectrophotometry. At the present, as far as we know, the optical properties of SS in coastal water are not examined up to the rate of phytoplankton. We don't know yet if SS has the package effect or nor. The optical properties of SS are now become inevitable parameter not only for Case-II water study but also for ocean color algorithm development.

In order to measure the absorption of SS in the sea, filter technique is considered to be the most convenient method for the particles of sea, though there is some problem so-called "β-effect" (path length amplification effect; Kiefer and SooHo, 1982, Ahn, 1990) and frequently changing base-line value. β-effect is now solvable, but the missing base-line is still under problem. This base-line problem should be removed for correct measurement of absorption.

2. Methods and Data

In this research, optical measurements in the Yellow Sea were carried out in June and October (1997) cruise. The data set of Mediterranean Sea, measured during Pre-Eumeli in October 1989, was used to compare with the results of Yellow Sea as standard absorption spectrum and for the oligotrophic water. Suspended sediments are collected on 25mm GF/F filter. Filtering volume of seawater were varied with the particle concentration of seawater. Absorption coefficient of total particles, $a_{to}(\lambda)$, were measured with adapted spectrophotometer (Varian) using "wet filter technique" (Trüper and Yentsch, 1967). Absorption spectra of non algal material (mainly detritus and inorganic particles), $a_d(\lambda)$ or $a_{ss}(\lambda)$, were also determined experimentally by method of Kishino *et al.* (1985). Subsequently, the absorption spectra of living phytoplankton $a_{ph}(\lambda)$ were obtained by subtracting $a_d(\lambda)$ from $a_{to}(\lambda)$. Additionally, the shape of $a_{ss}(\lambda)$ spectrum was compared to $\tilde{a}_{soil}(\lambda)$(Ahn, 1990).

All absorption spectra were corrected for the β-effect by adopting value 2 regardless of wavelength (Ahn, 1990, Bricuad and Stramski, 1990). Chlorophyll-*a* specific absorption coefficients of phytoplankton $a^*_{ph}(\lambda)$ were finally obtained by dividing $a_{ph}(\lambda)$ by chlorophyll-*a* concentration(<chl>, unit is mg/m^3). The specific absorption coefficients of suspended sediment $a^*_{ss}(\lambda)$ were also obtained by dividing $a_d(\lambda)$ by SS concentration (g/m^3). We supposed here that the most part of nonalgal particle are originated from suspended sediment and mineral particles, because of strong tidal current of this coastal area and yellow sand deposition from China through atmospheric transport (This phenomenon can be seen easily by satellite images). Pigment concentrations were determined by spectrophotometry using the equation of Jeffrey and Humphery (1975) or by fluorometry.

As mentioned above, missing baseline during the absorption measurement was occurred frequently because measured sample filter can not be same with the reference filter in base-line measurement. This inevitable problem in using the filter technique is only can be removed when all used GF/F filter have same optical properties (absorption and scattering). We can easily imagine that the different optical properties of GF/F are caused by inhomogenous each filter paper's thickness. Figue 1 shows an error of absorption spectrum caused by missing baseline (a_{ss} values around 700nm are higher than a_{to}). Undoubtedly, a_{ph} value always must be lower than a_{to}. In figure 1, the baseline of a_{ss} moved upward in parallel with X axis. However, we could find out the moved baseline value by grace of consistency of a_{ss} slope; near IR band to blue band ratio, e.g, $a_{ss}(750)$: a_{ss} (400) was always same slope value (about 4.3). So the baseline deviations for SS, X_{ss}, were calculated as follows;

$$X_{ss} = \frac{4.3\ a_{ss}(400) - a_{ss}(750)}{4.3 - 1} \qquad (1)$$

In order to correct $a_{to}(\lambda)$, baseline for total absorption X_{to} was made so that $a_{to}(750)$ is 1.05 time greater than $a_{ss}(750)$ (Ahn, 1990).

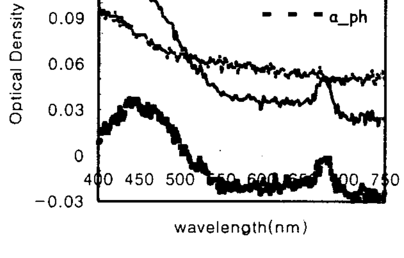

Figure 1. One example of changing baseline during absorption measurement by "wet filter technique"

3. Results & Discussions

The all spectrum of specific absorption coefficients of phytoplankton measured in Mediterranean Sea (MEDS) and Yellow Sea (YS) are shown in Figure 2.

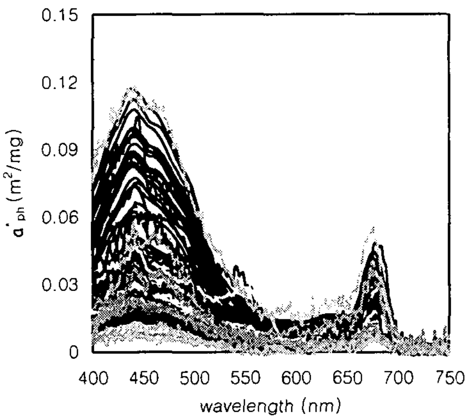

Figure 2. All specific absorption coefficients of natural phytoplankton population measured in the Mediterranean Sea and Yellow Sea.

We can see a great variation of $a_{ph}(\lambda)$ values with the sampling sites. But spectral forms with the wavelength do not show big difference between spectra of MEDS and YS. We can only see big spectral difference, a boss of absorption in 450 – 480 nm in place of 440nm, in depth of 100m in the MEDS (not clearly displayed on the figure). The noise of signals, appeared on the spectrum of YS, could not smoothed because of too much noise. The variation of a^*_{ph} at the wavelength 440nm as function of <chl> are shown in Figure 3.

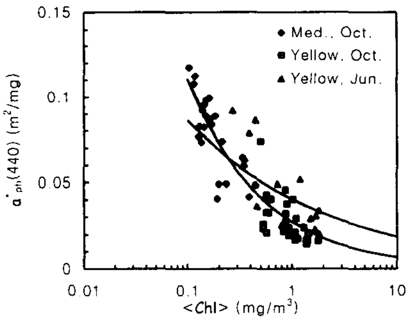

Figure 3. Variation of the chlorophyll-specific absorption coefficient of living phytoplankton as function of the chlorophyll-*a* concentration.

It is clear that $a^*_{ph}(440)$ value in MEDS are certainly greater than the values of YS. It means that a^*_{ph} decreases with the trophic level of water (decreasing from oligotrophic water to eutrophic water, spanning over the range of 0.02 to 0.12 m²/mg). If we approve that the size distribution of phytoplankton in MEDS is tinier than in the YS, then the package effect in two seas is clearly appeared. The regression curve obtained between $a^*_{ph}(\lambda)$ and <chl> by least square fit is displayed on the figure, another curve is that of proposed by Bricaud et al. (1995). Perhaps two different curves come from different size or species of phytoplankton in the sea. If we express $a^*_{ph}(440\lambda)$ value with <chl> function, the result is as follow;

$$a^*_{ph}(440) = 0.027 <chl>^{-0.612} \qquad (2)$$

The whole spectrum values, 400 – 750nm, $a^*_{ph}(\lambda)$ for phytoplankton at an arbitrary <chl> can be obtained multiplying $a^*_{ph}(440)$ from equation (2) to the normalized and averaged spectrum of MEDS and YS (see Table 1).

The all spectrum of specific absorption coefficients of suspended sediment measured in the YS are shown Figure 4.

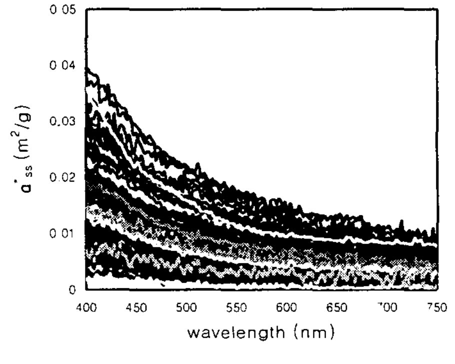

Figure 4. Suspended sediment specific absorption spectra as determined in theYellow Sea.

As previously stated, these figures were naturally corrected using baseline correction method. The general increase of $a_{ss}(\lambda)$ toward short wavelength is due to nonalgal material. If we suppose that spectral form is dependent on the wavelengths, the following expression was given (using normalized spectra at 440nm); $\tilde{a}_{ss}(\lambda) = 10^6 \lambda^{-2.34}$ where $\tilde{a}_{ss}(\lambda)$ is normalized absorption spectrum for SS , λ is wavelength in [nm]. The variation of a^*_{ss} at the wavelength 440nm as function of <SS> are shown in Figure 5. Over the

<SS> range, $a^*_{ss}(440)$ varied from 0.005 to 0.04 [m^2/g] (a^*_{ss} values in MEDS were not measured). But, the scattered points indicate nothing significance, like package effect. We couldn't find the reason why the values for a^*_{ss} are so variable and don't have a tendency. We believe that these widely scattered values are related to the variability of size distribution of suspended sediment state which is again linked to other physical environment parameters, such as specific gravity of particles, wind strength, stratification of water, tidal current, and water depth etc...

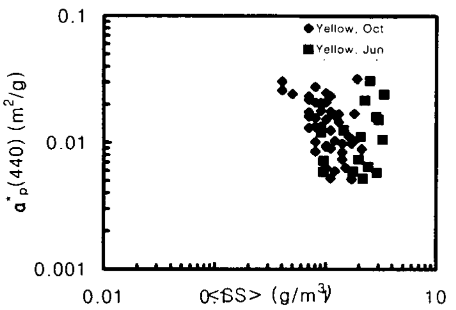

Figure 5. Variation of specific absorption coefficient of suspended sediment at 440nm as function of the <SS>

The comparison of normalized absorption spectra between $\tilde{a}_{ss}(\lambda)$ and $\tilde{a}_{soil}(\lambda)$ is displayed in Figure 6. The results show that two spectra are similar each other in terms of increasing absorption to the short wavelengths. The only difference is the slope of spectrum. $\tilde{a}_{soil}(\lambda)$, in particular in 400 – 550nm, has steeper slope than the $\tilde{a}_{ss}(\lambda)$.

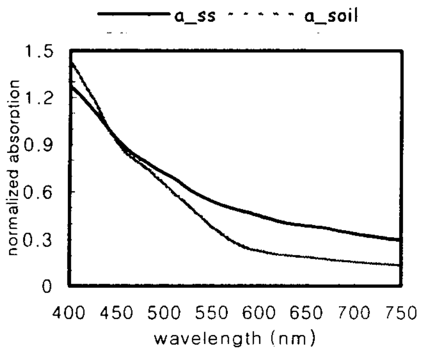

Figure 6. Comparison of normalized absorption spectra between suspended sediment and soil.

4. Conclusions

The specific absorption coefficient for phytoplankton observed in the Mediterranean and Yellow Sea remains large, probably due to the package effect caused by the relative cell size distributions. A reference spectrum of absorption form for natural phytoplankton populations was proposed and a certain relationship between a^*_{ph} and chlorophyll concentration ($a^*_{ph}(440) = 0.027 <chl>^{-0.612}$) was found. This relationship will improve the future ocean color algorithm. The specific absorption coefficients for SS are widely ranged, spanning over from 0.005 to 0.04m^2/g, without any relationship between a^*_{ss} and <SS>. Since there are still uncertainties on the specific absorption of SS, more studies are needed, especially in coastal waters.

The problem, in measurement of absorption coefficient for natural particles, of missing or changing baseline in using wet filter technique is also solved.

The inherent backscattering optical properties for natural phytoplankton and suspended sediments are not studied yet and need urgently for the coastal and Case-II water research.

References

Ahn Y. H, 1990. Optical properties of biogenous and mineral particles present in the ocean. Application: inversion of reflectance. *Thesis, Paris-VI university*. P 214.

Ahn Y. H., S. D. Hahn, S. Galleogos, R. Itturiga, Y. S. Suh, K. A. Jeon, 1997. The absorption and attenuation of light in the Yellow Sea. PICES 1997 annual meeting in PUSAN.

Bricaud A., M. Babin, A. Morel and H. Claustre, 1995. Variability in the chlorophyll-specific absorption coefficients of natural phytoplankton: Analysis and parameterization.

Bricaud, A. and D. Stramski, 1990. Spectral absorption coefficient of living phytoplankton and nonalgal biogenous matter: A comparison between the Peru upwelling area and Sargasso Sea. Limnol and Oceangr., 35, 562-582, 1990.

Dubinsky Z., T. Berman, and F. Schanz, 1984. Field experiments for *insitu* measurement of photosynthetic efficiency and quantum yield. J. Plankton. Res. 6:339-349.

Kishino M., M. Takahashi, N. Okami and S. Ichimura, 1985. Estimation of the spectral absorption coefficients of phytoplankton in the sea. Bull. Mar. Sc., 37, 634-642.

Kiefer D. A. and J. B. Soohoo, 1982. Spectral absorption by marine particles of coastal waters of Baja California. Limnol. Oceanogr., 27, 492-499.

Morel A., 1978. Available, usable and stored radiant energy in relation to marine photosynthesis. Deep-Sea Res., 25, 673-688.

Trüper H. G. and C. S. Yentsch, 1967. Use of glass fiber filters for the rapid preparation of in vivo absorption spectra of photosynthetic bacteria. . J. Bacteriol., 94, 1255-1256.

Table 1. Normalized (at 440nm) and averaged specific absorption spectra values for natural living phytoplankton population and suspended sediment sampled in the Yellow Sea and Mediterranean Sea

λ	$\tilde{a}_{ph}$	$\tilde{a}_{ss}$
400.0	0.593778	1.272867
402.5	0.617820	1.259259
405.0	0.645593	1.244945
407.5	0.677194	1.230361
410.0	0.710259	1.215832
412.5	0.744925	1.200669
415.0	0.777787	1.183933
417.5	0.806042	1.167045
420.0	0.831168	1.149416
422.5	0.853916	1.132597
425.0	0.877137	1.115169
427.5	0.902648	1.097129
430.0	0.929163	1.078542
432.5	0.954567	1.059004
435.0	0.975205	1.039226
437.5	0.990774	1.019656
440.0	1.000000	1.000000
442.5	1.001615	0.981282
445.0	0.994737	0.963825
447.5	0.982399	0.947677
450.0	0.968712	0.931641
452.5	0.953549	0.915966
455.0	0.939764	0.900231
457.5	0.929351	0.885226
460.0	0.922175	0.870755
462.5	0.913160	0.858226
465.0	0.903132	0.846598
467.5	0.891431	0.835860
470.0	0.877571	0.825791
472.5	0.860106	0.815772
475.0	0.843054	0.806527
477.5	0.826546	0.798019
480.0	0.809545	0.788928
482.5	0.789638	0.779051
485.0	0.766554	0.768671
487.5	0.744561	.759082
490.0	0.722728	0.749723
492.5	0.698878	0.741374
495.0	0.670172	0.732992
497.5	0.634416	0.724412
500.0	0.593860	0.715963
502.5	0.551694	0.707842
505.0	0.507075	0.699933
507.5	0.464933	0.691954
510.0	0.425498	0.682932
512.5	0.394169	0.673179
515.0	0.366420	0.662582
517.5	0.341342	0.651087
520.0	0.319851	0.639421
522.5	0.301228	0.627605
525.0	0.284899	0.616348
527.5	0.269215	0.606454
530.0	0.255188	0.597725
532.5	0.241400	0.589321
535.0	0.228790	0.581500
537.5	0.217245	0.574459
540.0	0.206869	0.567570
542.5	0.197818	0.560614
545.0	0.189608	0.553680
547.5	0.180978	0.546535
550.0	0.172120	0.539525
552.5	0.162745	0.532864
555.0	0.153015	0.526633
557.5	0.143788	0.520657
560.0	0.135507	0.514643
562.5	0.128627	0.509288
565.0	0.122889	0.504397
567.5	0.118507	0.499942
570.0	0.115411	0.495529
572.5	0.113610	0.491167
575.0	0.112685	0.487040
577.5	0.112229	0.483167
580.0	0.112679	0.479332
582.5	0.113464	0.475525
585.0	0.114544	0.471797
587.5	0.116214	0.468108
590.0	0.117576	0.464490
592.5	0.118637	0.460715
595.0	0.119299	0.456729
597.5	0.118761	0.452668
600.0	0.117509	0.448684
602.5	0.115949	0.444670
605.0	0.115146	0.440588
607.5	0.115538	0.436595
610.0	0.117490	0.432422
612.5	0.121102	0.427968
615.0	0.125184	0.423787
617.5	0.129446	0.419863
620.0	0.133829	0.415781
622.5	0.137587	0.412007
625.0	0.140928	0.408699
627.5	0.144319	0.405657
630.0	0.147511	0.403178
632.5	0.150599	0.401089
635.0	0.153377	0.399118
637.5	0.155665	0.397007
640.0	0.157454	0.394853
642.5	0.158505	0.392657
645.0	0.159645	0.390580
647.5	0.161706	0.388574
650.0	0.164499	0.386706
652.5	0.170053	0.384914
655.0	0.180373	0.383382
657.5	0.197615	0.382253
660.0	0.224774	0.380800
662.5	0.262879	0.378706
665.0	0.310416	0.376658
667.5	0.357891	0.374750
670.0	0.393810	0.372577
672.5	0.416901	0.369850
675.0	0.426233	0.366125
677.5	0.418471	0.362026
680.0	0.393442	0.358421
682.5	0.353310	0.355739
685.0	0.297222	0.353171
687.5	0.228741	0.350534
690.0	0.167611	0.347866
692.5	0.126272	0.345148
695.0	0.095548	0.342173
697.5	0.071640	0.339259
700.0	0.054387	0.336292
702.5	0.043306	0.333546
705.0	0.035406	0.331166
707.5	0.030288	0.328894
710.0	0.026502	0.326994
712.5	0.023196	0.325483
715.0	0.020629	0.323846
717.5	0.019035	0.321958
720.0	0.018023	0.320072
722.5	0.017180	0.318014
725.0	0.016340	0.315776
727.5	0.015739	0.313637
730.0	0.015236	0.311570
732.5	0.014838	0.309623
735.0	0.014444	0.307719
737.5	0.014131	0.305651
740.0	0.013781	0.303721
742.5	0.013159	0.302270
745.0	0.012905	0.301156
747.5	0.012826	0.299962
750.0	0.012668	0.298362