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Methodology evaluation for remotely estimating water quality parameters in estuarine waters

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ABSTRACT

Water absorption signatures were measured from water samples placed in a 50 cm pathlength cylindrical cuvette. Quantitative analysis of chlorophyll-a and dissolved organic matter (DOM- humic acid, fulvic acid, or tannic acid) was conducted using second derivative spectra followed by computation of double inflection ratio (DIR) spectra for all possible combinations of bands (from 362-1115 nm with 252 channels). A specially designed instrument system is described which allows measurements of absorption of particulate and dissolved organic matter (chlorophyll-a and DOM) in a water sample. The ability of the system to allow measurement of absorption signatures and relating the data to observed or in-situ water reflectance signatures measured from a moving or in-situ platform is described. The methods demonstrate the value of high spectral resolution signatures to estimate concentrations of the water quality parameters and an analytical technique using optimal ambient correlation spectroscopy for selecting bands or channels for estimating concentrations directly from spectral absorption signatures.

1. INTRODUCTION

Remote sensing science is becoming widely used in the analysis of water quality parameters such as particulate matter (chlorophyll, seston) and dissolved organic matter (DOM). Quantifying these parameters is very valuable in the management of aquatic ecosystems. This is particularly important in coastal and estuarine aquatic systems such as those found along the coasts of Florida where levels of primary productivity often exceed those of manipulated croplands¹. An example is the current management of the Submerged Aquatic Vegetation (SAV) habitat in the Indian River Lagoon located on the east coast of central Florida. SAV habitats are important in providing shelter for various fishes and invertebrates and are a key component in the nutrient cycling of lagoon and estuarine systems in Florida¹. It has been shown that one of the biggest limiting factors in the growth and stability of SAV is the availability of photosynthetically active radiation (PAR) in the water column. PAR is usually reduced by high concentrations of particulate matter in fast flowing water areas as well as in low flow areas. The latter is probably the biggest factor in PAR loss due to low flushing rates and high levels of vegetative decomposition in the Lagoon system. The decomposition of this vegetation yields substances collectively known as humic substances². Specific entities of humic substances are fulvic acids and humic acids². Other DOM derived from vegetation such as bark or plant leaves and stems which can be found in lagoon and estuarine systems are tannins and lignins. Monitoring DOM concentration is therefore very important in the management of SAV beds. By following the trend of DOM concentrations over time at various locations one can use the data to determine the sources enabling a good management of excess DOM loading in the lagoon system. Remotely determining DOM by remote sensing systems or sensors may prove to be an effective tool in monitoring PAR's ability in reaching SAV beds as well as specific wavelengths or channels from 368-1115 nm that can be directly used for estimating DOM with good precision and accuracy.

The ability to spectrally recognize DOM in water is therefore important. However, it's spectral characteristic is also important in knowing when spectrally determining another indicator of water pollution such as

chlorophyll-a. Chlorophyll-a is a water quality parameter which has been widely measured remotely by the use of passive sensors (such as those found on the Coastal Zone Color Scanner) because of its role in the global carbon cycle as well as other biochemical cycles³. In deep ocean waters, chlorophyll measurements have been made, however, as one approaches coastal waters, the degradation of the signal for the channels used may occur due to the presence of DOM. This is because DOM absorbs light within the same spectral range as chlorophyll-a. This paper presents a method in which the spectral signature of chlorophyll-a may be discriminated from that of DOM by the combined use of a high sensitivity spectrograph, an absorption cuvette, and derivative spectroscopy.

2. METHODS

Two matching absorption tubes (one for a reference and one for the sample) were built using 50 cm Pyrex tubes fitted with optical grade lenses at both ends. A cylindrical casing was built as a chamber for these tubes. The inside of this casing was painted with a black absorbing paint. Baffles were added to prevent any forward scattering within this chamber. The chamber was fixed on an optical bench and fitted at one end with an SE590 high sensitivity solid state spectrograph with a 252 channel high radiometric sensitivity linear diode array and at the other end with an integrating sphere illuminated with a halogen light (figure 1). An opal lens was placed between the glass tube and the spectrograph so as to decrease the fraction of the photons being scattered outside of the viewing angle of the detector⁴ or spectrograph. This absorption system is now a commercially available instrument⁸ (Model CC-Abs-100b). Figure 25 shows 2 pictures at different angles of the absorption system.

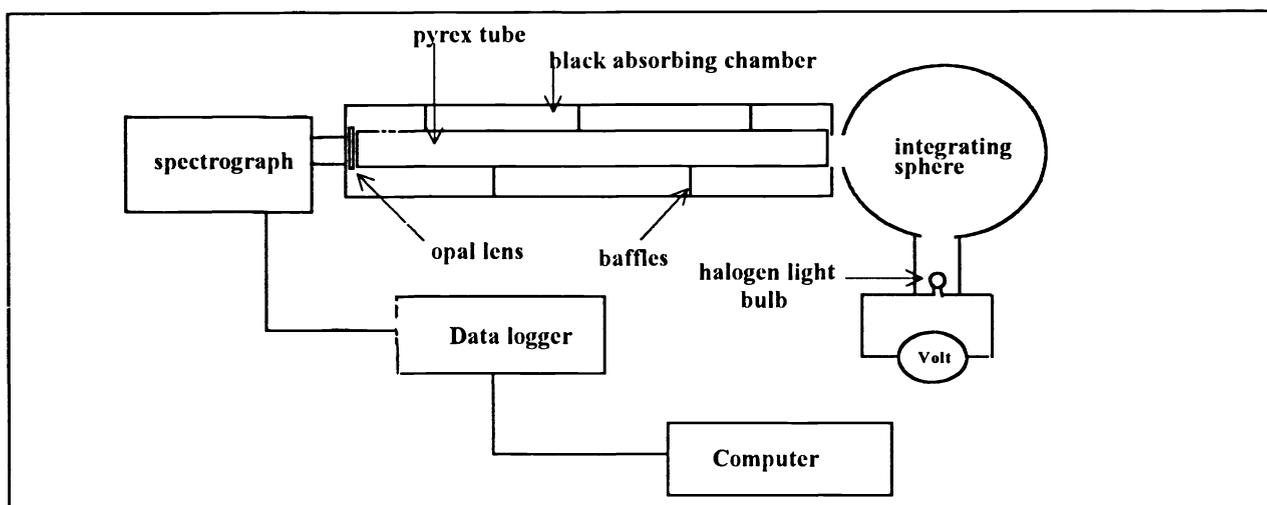


Fig. 1 Diagram of experimental instrument system setup

The use of 2 tubes allows the time between the reference and sample measurements to be reduced to approximately 1-2 minutes. It was experimentally determined that for this particular setup, slight changes in the light level occurred over a period of 10 minutes or more, even with a regulated power supply. This is approximately the time it takes to empty and refill the glass tube. This time delay leads to an upward or downward shift of the overall spectral signature for triplicate samples. To correct for any spectral irregularities between both tubes, a corrective ratio was calculated by scanning both tubes filled with D.I. water and calculating their ratio across the spectrum. These wavelength dependent ratios were then used to eliminate any influences of these tubes on samples scanned thereafter.

The reference tube was filled with D.I. water (unless otherwise noted) allowing one to normalize samples scanned to pure water. For each sample, triplicate scans were made and averaged. The mean spectral

signature of the sample was derived from 10 spectral scans taken at less than 1 second intervals. The resulting mean spectral signature was then used to calculate the absorption coefficient from:

$$a_s = 2.3 (\log (I_0/I_s)) / L \tag{1}$$

where a_s is the absorption coefficient (m^{-1}), 2.3 is the conversion from a \log_{10} to a natural \log , I_0 is the transmitted light through the reference tube ($W/m^2 \cdot sr$), I_s is the transmitted light of the sample through the sample tube ($W/m^2 \cdot sr$), and L (m) is the pathlength of the tubes which is 0.5 meters.

Absorption coefficients were obtained for humic acid, fulvic acid, tannic acid, and chlorophyll-a standard reference materials diluted in water to varying concentrations (Table 1). Absorption coefficients were also obtained for samples which combined both chlorophyll-a and humic acid (Table 2). Both humic acid and fulvic acid standards were collected from the Suwannee River located at the boarder between the state of Georgia and the state of Florida and prepared by the auspices of the International Humic Substances Society (IHSS) in Golden Colorado. The tannic acid was purchased from Sigma Corporation and was derived from the species *cutynus* and the species *coriaria* both of the genus *rhus*. Chlorophyll-a was also purchased from Sigma Corporation and was derived from spinach. Samples of lagoon water were also scanned to compare their spectral shapes to those of the standards.

samples	concentrations
humic acid (in mg/l)	200, 100, 50, 25, 12, 1
fulvic acid (in mg/l)	200, 100, 50, 25, 1, 0.05
tannic acid (in g/l)	10, 5, 1, 0.5
chlorophyll-a (in $\mu g/l$)	100, 75, 50, 20, 10, 1

Table 1. Concentrations at which samples where scanned.

chl-a concentrations ($\mu g/l$)	Concentrations of humic acid				
	100	50	25	1	0.5
80	x	x	x	x	x
40	x	x	x	x	x
20	x	x	x	x	x
10	n/a	n/a	x	x	x
1	x	x	x	x	x

Table 2. Mixtures of chlorophyll-a and humic acid at varying concentrations utilized for this study.

Optimal Passive Ambient Correlation Spectroscopy, OPACS^{5,7}, was used to compute inflection signatures (2nd derivative estimator) from the calculated absorption coefficients for the water quality parameters studied. The derivative estimator is calculated as follows:

$$I(\lambda)_{\text{sample } m,i,n} = a(\lambda)_{\text{sample } i}^2 / (a(\lambda)_{\text{sample } (i-n)} * a(\lambda)_{\text{sample } (i+m)}) \tag{2}$$

where $I(\lambda)_{\text{sample}}$ is the inflection estimator centered at band i for the sample calculated from it's absorption coefficient. $a(\lambda)_{\text{sample}}$ is the absorption coefficient of the sample. M and n are forward and backward operators,

respectively. OPACS computes each possible combination of m, i, n between 368 and 1200 nm. For every I calculated, a linear regression is performed based on the following model⁵:

$$C_{\text{sample}} = y_{\text{int}} + s * I(\lambda)_{\text{sample}} \quad (3)$$

where C_{sample} is the concentration of the sample, y_{int} is the y-intercept, and s is the slope of the model. The 3 bands which give the maximum correlation coefficient are then defined as the optimum bands after conducting the analysis for all combinations of i, m, n 's from 368 to 1115 nm for the 252 channel diode array sensor. A double inflection ratio⁵ (DIR) is used to "optically clean up" the spectrum by calculating the ratio between the optimum bands of a parameter being monitored, $I(\lambda)$, to that which we want to discriminate, $I'(\lambda)$. The DIR⁵ is calculated as follows:

$$\text{DIR} = I(\lambda) / I'(\lambda) \quad (4)$$

Fluorometric analysis of chlorophyll-a was also accomplished using a Turner Design fluorometer model 10-0001. Both chlorophyll-a diluted in deionized (D.I.) water and chlorophyll-a mixed with varying concentrations of humic acids were made. These analyses were made to indicate the degree to which these materials fluoresce and may contribute to chlorophyll-a fluorescence.

Absorption measurements were also made on lagoon water and ocean water. Samples were taken from two stations in the Indian River Lagoon. The first sample was taken at the mouth of the Eau Gallie River and the second sample was taken south of the Banana River in a canal. The Eau Gallie River receives most of its water from land runoff. The Banana River gets most of its water from runoff and direct precipitation. One sample was collected from the Atlantic ocean near shore at Melbourne Beach. Scans of the whole water sample (i.e. lagoon water not filtered) were taken using deionized water in the reference. The ocean water sample and the lagoon filtrate were also scanned using deionized water as a reference.

3. RESULTS

Various tests were performed on the cylindrical absorption cuvette to determine reliability in reproducing scans from the same sample. The system is sensitive to very small variations in the light source intensity as expected. This problem was corrected by using two tubes (one for reference and one for sample) and scanning both tubes in the instrument system as soon as possible (1-2 minutes). The error from the variation in light source using this method was experimentally determined to be less than 1%.

The absorption tube was also very sensitive to "water streaks" left on the tube after being filled with a sample or reference water than wiped. This variation in streaking patterns on the outside wall of the tube leads to a variation in the optical property of the tube. This was the biggest potential in error. So extreme care was used in preventing water marks or streaking.

Another source of error was found when using certain types of water which had a tendency to create small bubbles (less than 0.5 mm) along the tube walls. This was due to the transferring process of the sample from the sample bottle to the tube in which a funnel was used. These bubbles could only be seen when the light was on and observed at either ends of the tube. This gave off a "constellation" like pattern of shiny specs along the inner wall of the tube. Like the streaks left after wiping the tube, the small bubbles altered the optical properties of the tube walls and thus the calculated absorption signatures. This problem was remedied by changing the method of filling. A 50 ml syringe was used to fill the tube. This not only minimized the formation of bubbles but also made for a cleaner transfer

making it unnecessary to wipe the tube. By changing the above procedures, the source of relative errors were decreased to less than 4% for triplicate scans. In this experiment, triplicate scans consist of repeating the following procedures 3 times:

1. Filling the sample tube with a syringe
2. Placing the tube in the environmental chamber
3. Conducting 10 scans of the sample at 1 second intervals across the spectrum
4. Average the 10 scans then calculating absorption coefficients from the resulting mean spectrum
5. Emptying out the sample from the tube

The above procedure gave us 3 absorption values for each band for one sample. These 3 absorption scans were than averaged.

Once the scans were made of humic acids, fulvic acids, tannic acids, and chlorophyll-a at various concentrations, a regression analysis was made of absorption values (dependent values) versus concentrations of the standard reference material (independent values). Figures 2 through 8 show the plots of absorption coefficients versus wavelength as well as the pearson correlations coefficients (r) at each wavelength.

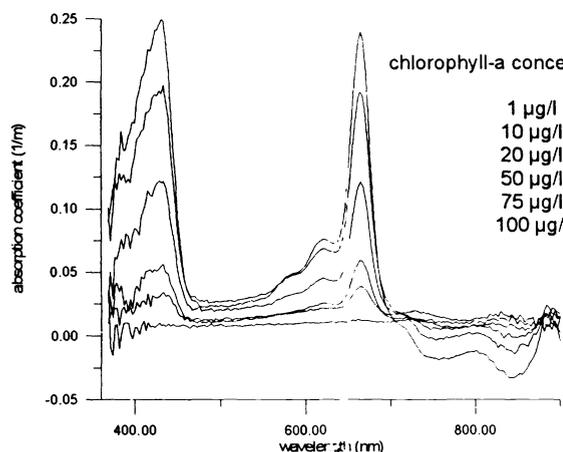


Fig.2 Absorption spectra of chlorophyll-a

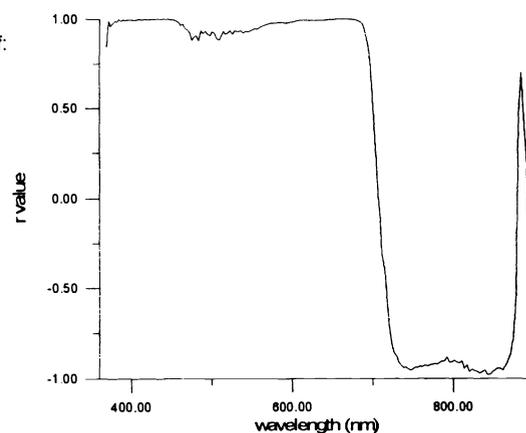


Fig.3 Correlation value for chl-a versus absorption coefficient

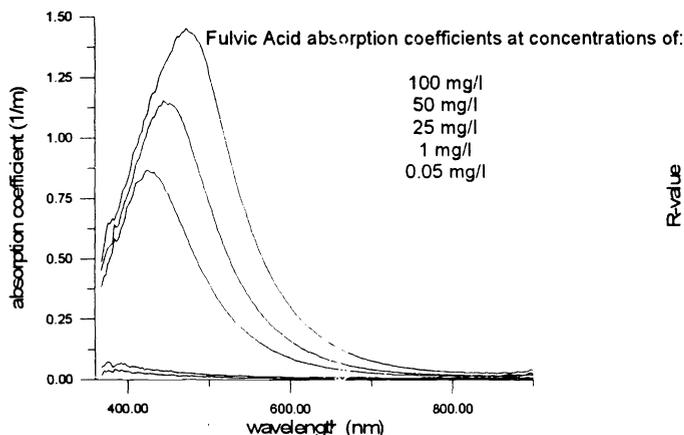


Fig.4 Absorption spectra of fulvic acid

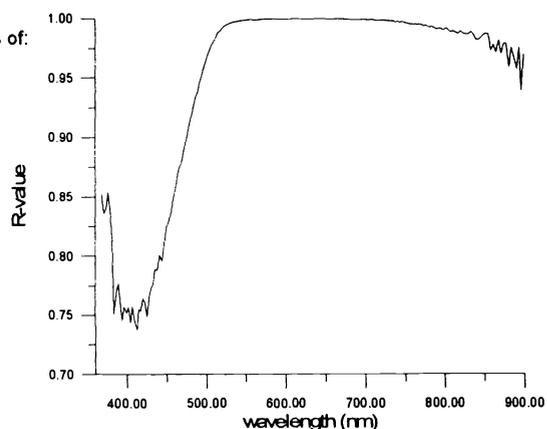


Fig.5 Correlation value of fulvic acid concentration versus absorption coefficient

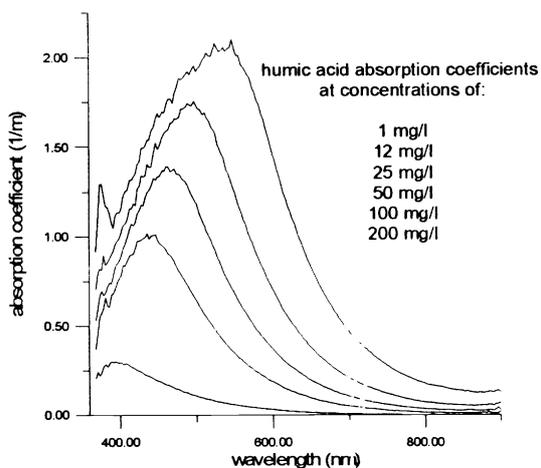


Fig.6 Absorption spectra of humic acid

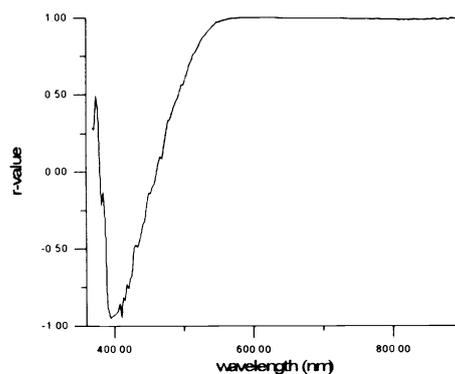


Fig.7 Correlation value for humic acid concentration versus absorption coefficient

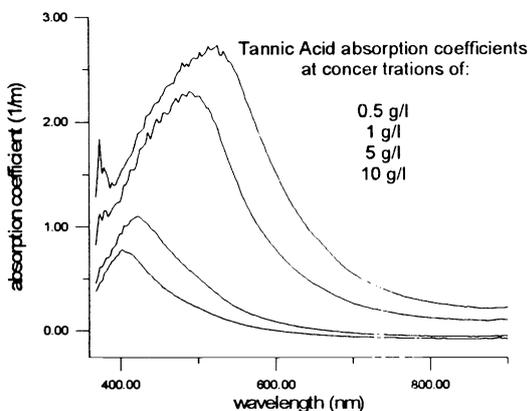


Fig.8 Absorption spectra of tannic acid

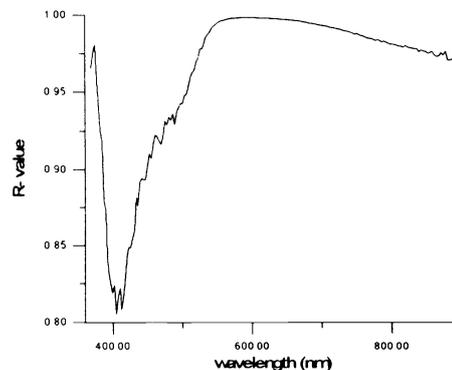


Fig.9 Correlation value for tannic acid concentration versus absorption coefficient

Now, the absorption coefficient of the sample water type can be related to the absorption of the water quality constituent, or:

$$a_s = a_{ss} * c_s \tag{5}$$

where, a_s is the absorption coefficient of the sample (1/m), a_{ss} is the specific absorption coefficient of the sample (m^2/mg), and c_s is the concentration of the sample (mg/m^3). The regression analysis as described above was made setting the intercept to 0. This enables one to create a model of the form:

$$y = a * x \tag{6}$$

where the y is thus set as being the absorption coefficient value, x is set as being the concentration value and a is the specific absorption coefficient - specific to a water quality constituent. The slope of the regression model (in this case a_{λ}) was plotted for each sample. Figures 10 to 13 represent the spectral signatures of the calculated specific absorption coefficients.

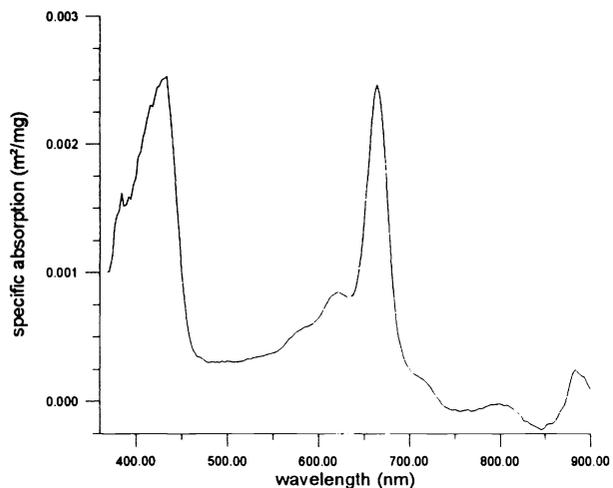


Fig.10 Specific absorption spectra of chlorophyll-a.

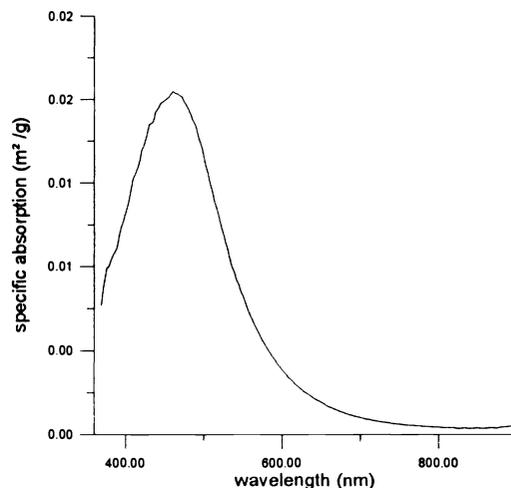


Fig.11 Specific absorption spectra of fulvic acid.

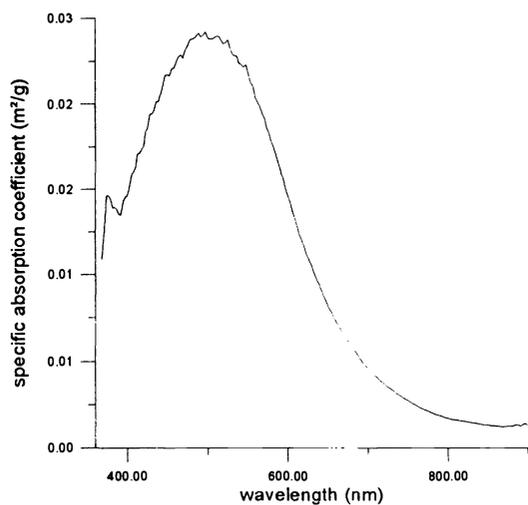


Fig.12 Specific absorption spectra of humic acid.

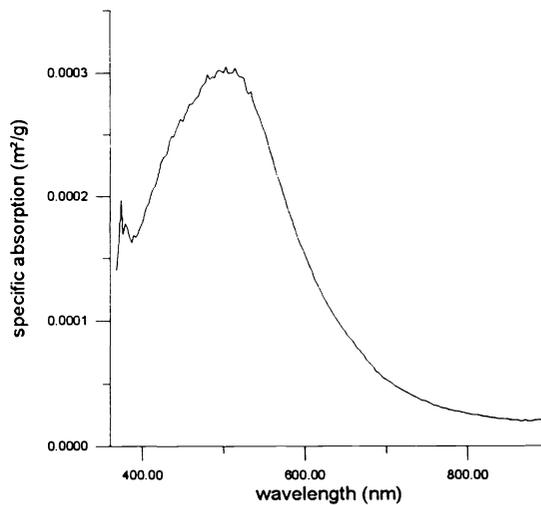


Fig.13 Specific absorption spectra of tannic acid.

For chlorophyll-a, a regression analysis was made between fluorometric readings and concentrations. Figure 14 shows this regression.

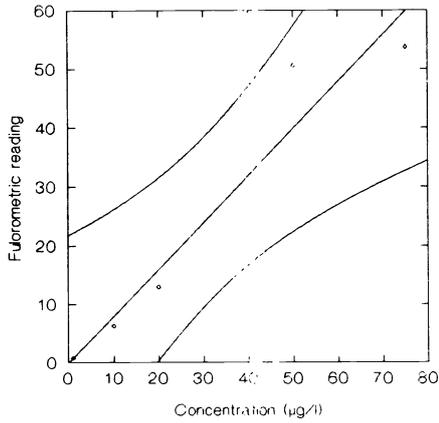


Fig. 14 Regression line of concentration on fluorometric readings of chlorophyll-a with 95% confidence intervals

For the samples of chlorophyll-a mixed with humic acid, a second derivative analysis using OPACS was used to determine the 3 optimum wavelengths which can be used to discriminate chlorophyll-a concentrations from those of humic acids. Figures 15 through 22 show plots of absorption for varying concentrations of chlorophyll-a mixed in with varying humic acid concentrations at each wavelength. The figures on the right side represent their respective regression analysis of fluorometric readings on concentration as well as the 95% confidence intervals. As expected, the fluorometric readings for chlorophyll-a mixed with the DOM component has a lower signal to noise component. Table 3 give the results of the OPACS analysis.

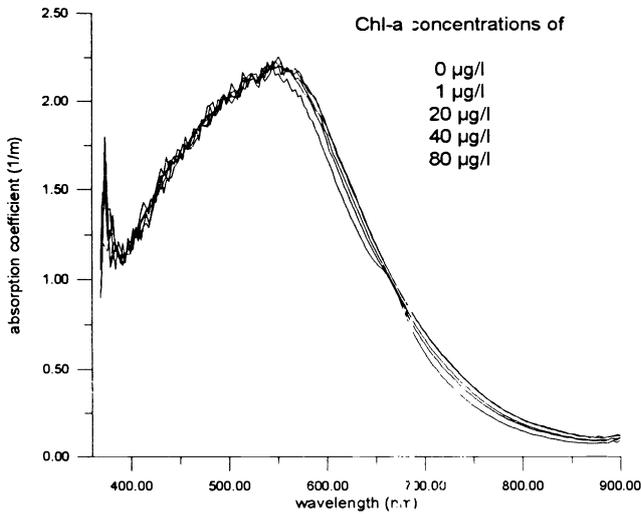


Fig.15 Chlorophyll-a in 50mg/l of humic acid

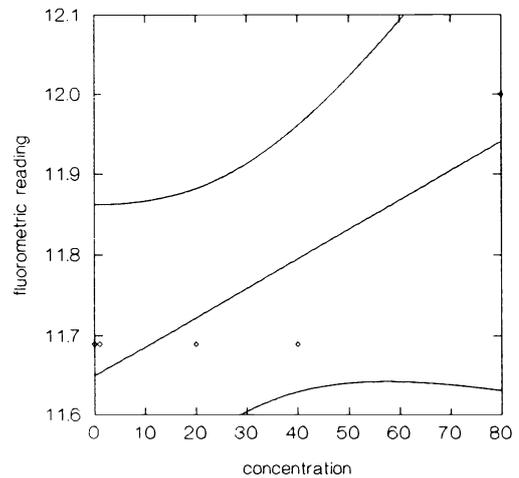


Fig. 16 Chlorophyll-a in 50 mg/l of humic acid

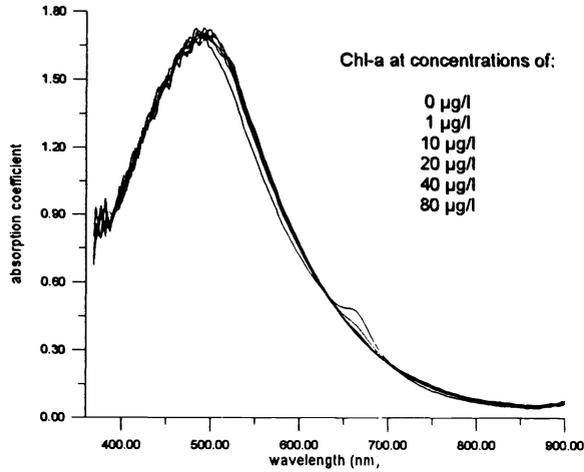


Fig. 17 Chlorophyll-a in 25 mg/l of humic acid

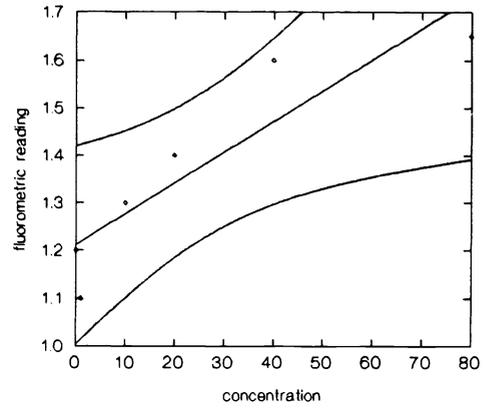


Fig. 18 Chlorophyll-a in 25 mg/l of humic acid

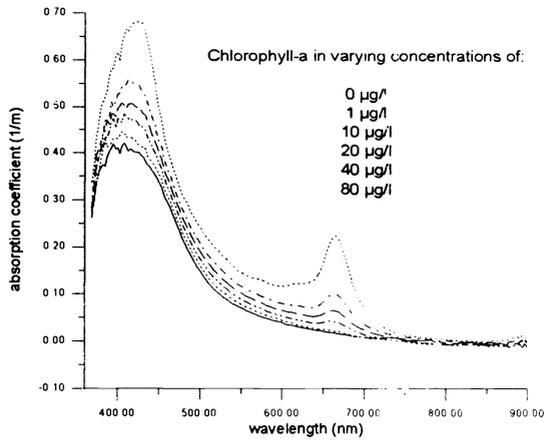


Fig.19 Chlorophyll-a in 1 mg/l of humic acid

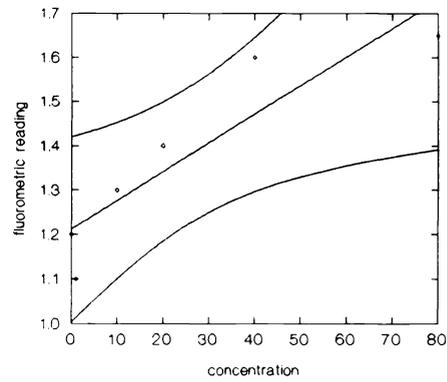


Fig.20 Chlorophyll-a in 1 mg/l of humic acid

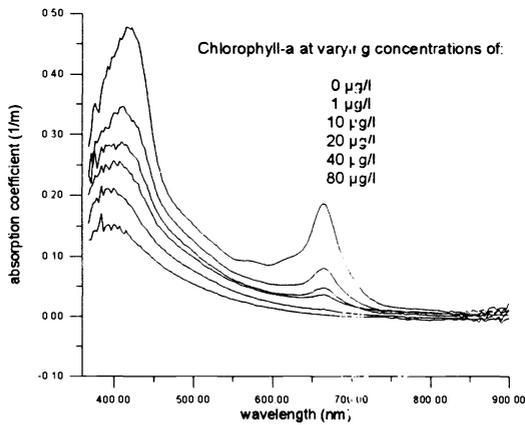


Fig.21 Chlorophyll-a in 0.5 mg/l of humic acid

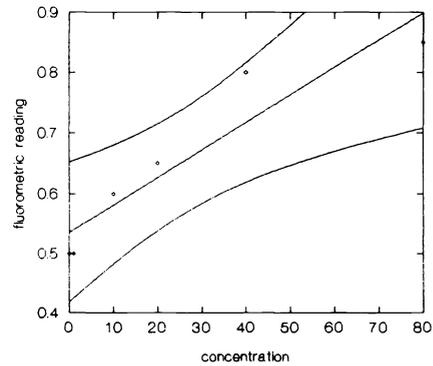


Fig.22 Chlorophyll-a in 0.5 mg/l of humic acid

Constituent	Forward band m	Center band i	Backward band n	R value
chlorophyll-a	717.4 nm	676.0 nm	649.6	0.88
humic acid	422.8 nm	399.5 nm	371.0 nm	-0.94
fulvic acid	732.3 nm	527.9 nm	500.0 nm	1
tannic acid	447.0 nm	441.4 nm	428.0 nm	0.97

Table 3 OPACS' analysis results on 4 water quality parameters. These results represent the 3 bands for the best I in equation (2)

Constituent	Forward band m	Center band i	Backward band n	R value
chlorophyll-a in the presence of humic acid	480.5 nm	430.6 nm	371 nm	0.75

Table 4 OPACS' analysis results on chlorophyll-a in the presence of humic acid. These bands are determined based on the best DIR calculated. This procedure results in an "optical cleanup" for the presence of DOM-humic acid.

The following graphs are the absorption spectra of the 3 water samples collected in the Lagoon and on the Atlantic coast. Note the similarity between figure 24 and figures 19 and 21.

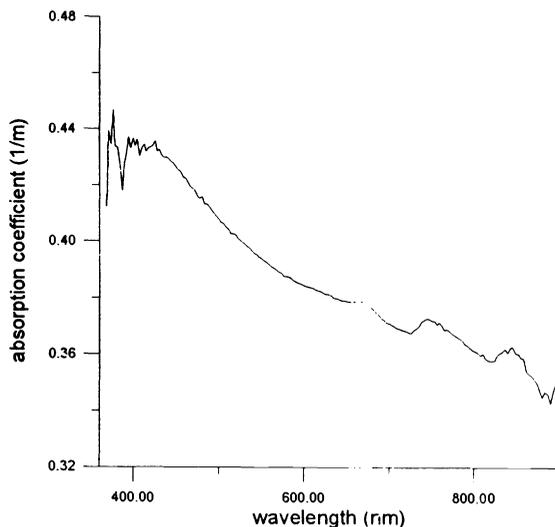


Fig. 23 Absorption spectra of coastal water

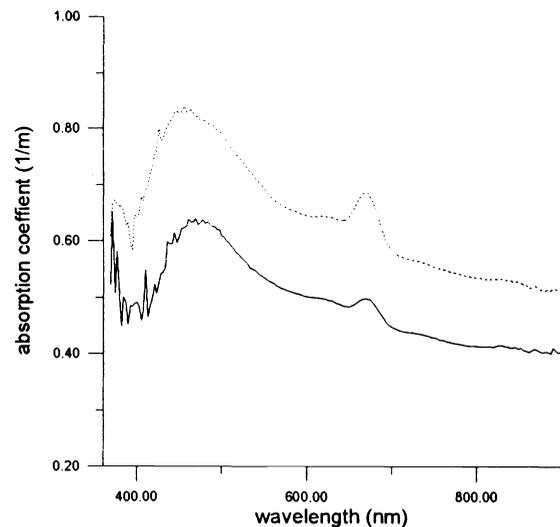


Fig.24 Absorption spectra of Indian Harbor (dashed line) and Eau Gallie river (solid line)

4. DISCUSSION

For the tannic, humic, and fulvic acids, a shift occurs towards higher wavelengths in the spectrum as the concentrations of these samples increase. This is probably due to the scattering effect encountered for these high concentrations. However, good correlation seems to exist at certain wavelengths in the spectrum for each sample. Furthermore, from the OPACS' analysis, it appears feasible to discriminate between these various water components by objectively selecting different bands.

For chlorophyll-a, good correlation exists between concentrations at the peak centered at around 670 nm. The spectral shape of chlorophyll-a is very similar to that of Yentsch's pad and tube method⁶. Another interesting phenomena is the apparent fluorescence that occurs beyond 700 nm.

A consistent linear relation occurs at specified wavelengths between the absorption coefficients of chlorophyll-a and humic acid at varying concentrations. However, at concentrations of humic acids above 25 mg/l (which is common in Florida lagoons and wetlands²), the spectral peak of chlorophyll-a is no longer observed. The chlorophyll-a peak seems to occur near 665 nm. This indicates that DOM does not shift this peak towards the red. Only at concentrations of humic acid of less than 1 mg/l can the influence of the chlorophyll-a peak near 425 be seen on the mixture. From the calculated optimal double inflection ratio (DIR), the best correlation between DIR and concentrations of chlorophyll was selected at bands centered around 430.6 nm. This spectral region would seem to be suitable in waters with low concentrations of DOM, however, if DOM concentrations were relatively high, the blue region of the spectrum would no longer be suitable. Inputs of the chlorophyll-a/humic acid mixture where humic acid concentrations were low indicated good correlation near the blue region of the spectrum. However, if higher concentrations of humic acids were used in a sample, then the region around 670 nm would probably have yielded the best correlation.

The fluorometric measurements of these samples give most likely poor correlation between concentrations of humic acid mixtures and concentrations of chlorophyll-a for fluorometric readings (figures 16, 18, 20 and 22). This is most likely due to the quenching effect of the humic acid.

The absorption spectra of the Lagoon water samples have the same chlorophyll-a peak (around 667 nm) as the chlorophyll-a standard peak (figure 2). Also, the broad band associated with the DOM is also present in the water sample. The absorption spectra of the ocean water also seems to indicate the presence of DOM because of the higher absorption in the blue region of the band.

This optical system (CC-Abs-100b) and the OPACS methodology is suitable to estimate and compare absorption coefficients of water samples. The resulting data can be directly related to irradiance reflectance measured above the water surface. This is because the same instrument can be used in both measurements, therefore preventing any errors due to the difference in instruments or the sensors. This allows for true comparisons between in-situ water reflectance measured and reported by Bostater (EOS/SPIE in the symposium) and the absorption coefficients measured and reported here.

5. CONCLUSION

The use of the cylindrical cuvette based system (BHS CC-Abs-100b) absorption tube combined with the OPACS technique show that chlorophyll-a concentrations can passively be determined in waters with relatively moderate DOM concentrations. Future studies will involve collecting reflectance data above the water surface, quantifying various water quality parameters such as chlorophyll-a and DOM, and testing different derivative algorithms. Also, future studies will compare the spectral signature between absorption and backscatter (above water reflectance) allowing us to test models with reflectance data. These combined techniques, in the long run, will help to provide the optimum bands to be used on remote sensing platforms.

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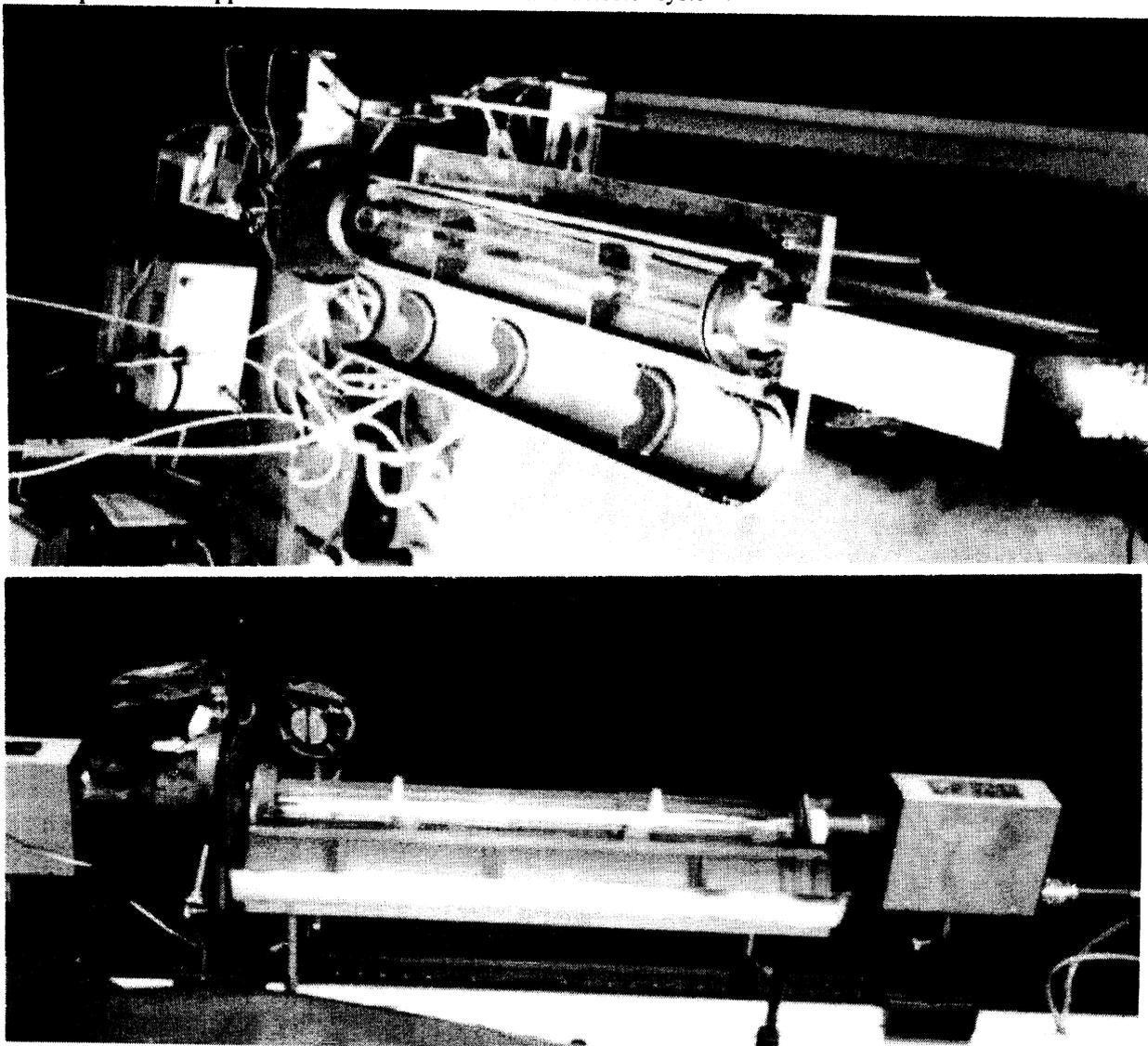


Fig. 25 Two pictures of the absorption system at different viewing angles