An Empirical Algorithm using Derivative Difference for Estimating Chlorophyll-A in Case-II Water

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Abstract Water quality management includes measurement of quantity and quality. The abundance of phytoplankton in water body represents the physical condition and chemical constituents. As Chlorophyll-a exists in all types of phytoplankton, naturally the choice for water quality measurement is estimation of Chl-a concentration. The Chl-a concentration is estimated using various spectral reflectance algorithms such as single band regression, band ratio, three-band ratio, four-band ratio etc have been developed and is being used. Subsequently, the first order derivative ratio and second order derivative ratio methods are also used in some studies. Though such algorithms provide water quality measures, new algorithms are being introduced to improve estimation accuracy. In this paper, a new algorithm ‘Derivative Difference’ is proposed. It is based on the Chlorophyll concentration variation with shape of reflectance spectrum. The derivative data represents the slope of the reflectance data at different wavelength. The difference in derivative values at selected two different wavelengths were correlated with measured values to estimate Chl-a concentration. Obtained results were compared with the values obtained from band ratio method and derivative ratio methods. The algorithm is found to be better in some conditions.

Keywords Remote sensing; Chlorophyll-a; Derivative; Spectroradiometer; Hyperspectral

1. Introduction

The deterioration of water quality of inland water bodies is a serious ecological and social problem as they are the water resources for drinking, domestic, agricultural and industrial purposes. Management of quality of water bodies is essential to provide water to the ever increasing population and changing lifestyle. Water management activities usually include protecting water bodies from polluting elements, saving water and distributing it without wastage, i.e. managing the quality and quantity of water. While quantity management is maintaining capacity of water body by preventing encroachment and sedimentation, quality management is controlling the physical, chemical and bio-objects within the specified limit to enable usability of the water.

As the abundance of Chl-a content represents the physical and chemical characteristics of the water, Chlorophyll-a (Chl-a) concentration is a major indicator of eutrophic status and water quality (Moses et
al., 2009). In case of ocean water (Case-I), the reflectance is dominated by the chlorophyll and the variation of reflectance can be attributed to the Phytoplankton abundance variation only. In contrast, the reflectance of in-land water (Case-II) is considerably affected by the optical properties of inorganic suspended matter and Colored Dissolved Organic Matter (CDOM). Hence the algorithms with blue-green bands used in case-I water is not suitable to case-II water. As CDOM absorption and particulate scattering decrease with increase in wavelength and become negligible in Red-infrared region, Red and Near Infrared (NIR) spectral region is extensively used to estimate Chl-a in Case-II water (Yu et al., 2014). As the physical and chemical components vary from lake to lake, the spectral bands suitable to measure the Chl-a for a particular lake may not suit to another lake. For every lake, suitable spectral bands are to be selected by comparing the estimated values from spectral bands combinations with laboratory-measured values.

The conventional method of quantifying Chl-a measurement is collecting samples from different locations of water body and measuring the chlorophyll-a concentration using spectrophotometer. This method needs field sampling, usage of chemical etc, which are time consuming, so difficult to perform for large area water bodies. Measuring certain optical properties like reflectance in different wavelength provides the concentration of the chlorophyll instantly. The spectral reflectance methods are used to estimate Chl-a in Aerial, Satellite and in situ measurements. The aerial surveys collect the spectral reflectance of the water bodies of small area and study the relation between reflectance spectrum with the chlorophyll-a. The satellite remote sensing provides a near real time, large scale and spatially continuous data in fixed time frequency, at less cost.

Many algorithms are developed to estimate the abundance of these constituents in water bodies like ocean, coastal, lakes and rivers based on spectral reflectance. The Chl-a estimation algorithms can be divided into two different categories: (i) Multiband models in the forms of ratios of different band combinations which utilizes the absorption bands of Chl-a in the red and NIR spectral region (Ruddick et al., 2001); and (ii) algorithms that use the Chl-a fluorescence emission around 685 nm (Gower et al., 1999).

The first group of algorithms are based on multispectral imaging. In this group, many algorithms have been developed using Red and NIR region spectral bands to estimate Chl-a concentration in eutrophic and turbid case II waters (Huang et al., 2014; Han et al., 2014). It covers single band, band ratio model (Hoge et al., 1987), three band models (Sathyendranath et al., 1989; Chen et al., 2013; Duan et al., 2010a, Tian et al., 2014), four band model (Le et al., 2009), five band model (Gohin et al., 2002), normalised differential chlorophyll index (NDCI) (Mishra and Mishra, 2012) etc. Some band ratio algorithms developed for the Chlorophyll estimation in terrestrial vegetation have also demonstrated in estimating Chl-a in water (Dall’Demo et al., 2003). As multispectral imageries are collected with less number of wide spectral bands, they cannot reflect minute variations like intensity variation in particular wavelength, intensity maximum shifting from wavelength to wavelength. As their output is integrated reflectance, change in reflectance with respect to narrow spectral bands is submerged in wider band.

The second group of algorithms are mainly based on Hyperspectral data, which provides almost continuous spectral measurements with hundreds of narrow spectral bands. They are: peak position near 700 nm (Gitelson, 1992); peak magnitude above baseline; area above baseline; first order derivative (Rundquist et al., 1996), second order derivative (Shi et al., 2007) and derivative ratio model (Tsai and Philpot, 1998) etc. Artificial neural network based algorithm (Chauhan et al., 2005), spectral decomposition method (Zhang et al., 2014), weighted algorithm (Yi, 2013), Spectral Vector Machine (SVM) based model (Sun et al., 2009) and three-band reflectance difference model (Duan et al., 2010b) are also used to estimate the chlorophyll-a concentration.

In this paper, a new algorithm called Derivative difference is introduced to estimate the Chl-a in Case-II water. The effectiveness of this algorithm in case-II water bodies is demonstrated using spectroradiometer data.
2. Materials and Methods

2.1. Methods

Among many factors affect the reflectance values of water, atmospheric absorption, CDOM, Organic Substance Sediments (OSS) are important. When we calculate the derivative values from reflectance, the effect of slowly changing factors with respect to wavelength such as atmosphere and CDOM are eliminated (Philpot, 1991). The derivative values provide the slope of reflective spectrum. These derivative values and derivative ratio values are used to estimate chlorophyll in many studies.

In the present study, as a new measure, the difference of derivative values at two different wavelengths has been used to estimate the chlorophyll-a. Obtained results are compared with the estimated values from both band ratio and derivative ratio methods. The estimated values obtained using this algorithm using spectroradiometer data were verified with measured values as well. Method, study area and results are described in following sections.

2.2. Study Area

The study area selected for this purpose is the Halasuru Lake, which is located at the heart of Bangalore city, India spread over the latitudes of 12° 58’ 41” N and 12° 59’ 15” N and longitudes of 77° 36’ 57” E and 77° 37’ 22” E, respectively. The area of the lake is approximately 125 Acres and is 930 m above the sea level. The depth of the lake varies from 3 m to 15 m and average depth of the lake is 5m. The main source of water to this lake is rainwater. It also receives direct industrial and domestic wastewaters from the surrounding area after aerated. The increased settlements near the lake is the cause for the pollution of the Lake. The satellite view of Halasuru Lake is shown in Figure 1.

2.3. In-situ Reflectance Measurement using Spectroradiometer

In-situ measurements were carried out with spectro-radiometer at different locations of the lake. Sacchi disk measurement was also carried out to measure the Sacchi depth to avoid bathymetry
radiation. The depth of lake at sample collection locations was much more than the Sacchi depth. The specular reflection from the water was avoided by carrying out the fieldwork between 9.30 AM and 11.00 AM local time. The locations of sample collection in Halasuru Lake are marked and shown in Figure 1.

Hyperspectral reflectance was measured using Analytical Spectral Devices, Field spec Pro spectroradiometer with a spectral resolution of one nm and the spectral range from 350 nm to 1800 nm. During the measurement, the instrument was held 0.6 m above the water surface manually, 0.5 m away from the boat and the probe was directed vertically down towards water. During the measurement at each location, sampling of the radiance was carried out for 25 times and the final output is produced after averaging these values. Five such outputs were collected at each location. The radiance plots from those outputs from same locations were compared and the datasets with large errors were rejected. Good data sets were averaged to generate final radiance data. This procedure was followed for measurement of water radiance and reference plate (Lambertian reflector) radiance as well. When radiance of reference plate was measured, the reference plate was kept parallel to the water surface in sun light and the measurement probe was held normal to the surface. The Longitude and Latitude of sample collection location were recorded from a GPS system output.

The remote sensing reflectance spectra $R_{rs}(\lambda)$, were calculated as (Rundquist 1996; Han, 1997).

$$R_{rs}(\lambda)_{\text{meas}} = \frac{L_w(\lambda)}{L_{cal}(\lambda)} \times R_{cal}(\lambda) \times 100 \ldots (1)$$

Where $L_w(\lambda)$ water leaving radiance, $L_{cal}(\lambda)$ scattered by reference plate and $R_{cal}(\lambda)$ reflectance of reference panel. At each sampling location, both water leaving radiance and reference radiance were measured without time gap.

2.4. Laboratory Measurements

Water samples were collected at a depth of 10 to 15 cm below the surface immediately after the reflectance measurements. Chl-a in the water was measured using the laboratory method (Jeffrey and Humbrey, 1975; Arar, 1997).

3. Analysis

3.1. Reflectance Spectra Analysis

As the reflectance variation due to Chl-a concentration is found to be between 350 to 800 nm and the absorption of radiation by water is more beyond 800 nm, hence spectroradiometer data with wavelength between 350 and 800 nm was selected for study. The spectral reflectance of the samples collected from different locations is shown in Figure 2.

The reflectance spectra magnitudes in the region of 350 to 450 nm are low due to the high absorption of water in this region. The maximum absorption is seen at 440 nm. The reflectance spectra show a clear reflectance peak in the green region between 550 nm and 570 nm. After 570 nm the reflectance comes down steadily up to 630 nm and at 640 nm, an inflection is observed. The red absorption is peak around 670 nm. This is due to the combined effect of absorption of chlorophyll and water. After this, the reflection steadily increases up to the region around 705 nm (NIR) and this high reflectance is due to the fluorescence of chlorophyll-a (Neville and Gower, 1997). After this, the reflection decreases to the lowest level due to the absorption of water. Also, around 760 nm a small peak is seen in reflection spectra.
3.2. Reflectance Band Ratio Methods

As the reflectivity in the NIR region $R_{\text{NIR}}$ is due to the fluoresence of chlorophyll and is directly proportional to chlorophyll contents and the dip in reflectance in Red region $R_{\text{Red}}$ is due to the absorption of Chl-a, and inversely proportional to reflectance in Red region, the Ratio $R_{\text{NIR}}/R_{\text{Red}}$ will be directly proportional to the chlorophyll concentration. Hence, the ratio of NIR to Red reflectance will represent the chlorophyll-a concentration.

Table 1: Top ten-correlation values obtained using the reflectance band ratio method

|   | WL$_1$ | WL$_2$ | $R^*$  |
|---|--------|--------|--------|
| 1 | 637    | 705    | 0.9042 |
| 2 | 637    | 703    | 0.9025 |
| 3 | 638    | 705    | 0.9017 |
| 4 | 637    | 702    | 0.9002 |
| 5 | 623    | 705    | 0.8995 |
| 6 | 637    | 706    | 0.8993 |
| 7 | 638    | 703    | 0.8981 |
| 8 | 629    | 709    | 0.8979 |
| 9 | 637    | 701    | 0.897  |
| 10| 643    | 704    | 0.8957 |

3.3. First Order Derivative Values

The derivative values are calculated using following equation:

$$R'_{\lambda n} = \frac{R_{\lambda n+1} - R_{\lambda n-1}}{\lambda_{(n+1)}-\lambda_{(n-1)}} \ldots (2)$$

Where $R_{\lambda n+1}$, $R_{\lambda n-1}$ are the reflectance at $\lambda n+1$ and $\lambda n-1$. These values provide the change in reflection with respect to small change in wavelength (1 or 2 nm).
The derivative values of reflectance spectrums are correlated with measured chlorophyll values to estimate Chlorophyll-a (Huang et al., 2010). In this study, the derivative values are smoothened to reduce the noise and correlated with Chl-a values. The maximum correlation value 0.69 was found at wavelength of 678 nm. Smoothening was done with linear running mean filter with different window size. Following figure shows the derivative values smoothened by different window sizes.

The maximum correlation value was achieved at 356 nm with 1 x 3 window smoothening. Many bands have shown better correlation in 678, 676nm range and 550-552 range. The R^2 values are varying with the smoothening window size.

**Table 2: Top ten correlation values obtained using derivative values**

| Not smoothened | Smoothened with 1 x 3 windows | Smoothened with 1 x 5 windows | Smoothened with 1 x 7 windows |
|----------------|-------------------------------|-------------------------------|-------------------------------|
| WI (nm) | R^2 | WI (nm) | R^2 | WI (nm) | R^2 | WI (nm) | R^2 |
| 1 | 678 | 0.69 | 356 | 0.70 | 350 | 0.66 | 678 | 0.64 |
| 2 | 612 | 0.63 | 678 | 0.66 | 637 | 0.64 | 677 | 0.61 |
| 3 | 392 | 0.62 | 392 | 0.63 | 678 | 0.64 | 383 | 0.59 |
| 4 | 385 | 0.61 | 677 | 0.62 | 677 | 0.62 | 679 | 0.58 |
| 5 | 552 | 0.60 | 679 | 0.61 | 679 | 0.61 | 544 | 0.57 |
| 6 | 460 | 0.59 | 545 | 0.59 | 392 | 0.59 | 545 | 0.56 |
| 7 | 545 | 0.58 | 546 | 0.58 | 545 | 0.58 | 676 | 0.55 |
| 8 | 680 | 0.57 | 552 | 0.57 | 421 | 0.58 | 543 | 0.55 |
| 9 | 551 | 0.57 | 680 | 0.57 | 544 | 0.57 | 550 | 0.54 |
| 10 | 624 | 0.56 | 551 | 0.56 | 546 | 0.56 | 551 | 0.54 |

3.4. The First Order Derivative Ratio Method

The derivative ratio method combines the benefits of the ratio and derivative methods. In this method the ratio of first derivative at two different wavelengths is correlated with measured values of chlorophyll-a.

The ratio of first derivative can be computed as:

\[ P_{\lambda_1, \lambda_2} = \frac{R'_{\lambda_1, \lambda_2}}{R'_{\lambda_2, \lambda_1}} \] (3)

Where, \( R'_{\lambda_1, \lambda_2} = \frac{\lambda_{\lambda_1} - \lambda_{\lambda_2}}{\lambda_{\lambda_2} - \lambda_{\lambda_1}} \)
**Figure 4**: Correlation between first order derivative values and measured Chl-a values at different wavelengths: A—without smoothening; B, C & D are smoothened with 1 x 3, 1 x 5 and 1 x 7 window running linear mean filter.

**Figure 5**: The correlation of ratio of first order derivative values with measured Chl-values at different wavelengths: A—without smoothening; B, C & D are smoothened with 3, 5 and 7 window running average algorithm.

$P_{\lambda mn}$ is the ratio of first derivative, $R'_{\lambda m}$ is the derivative at $\lambda_m$ and $R''_{\lambda mn}$ is the derivative at $\lambda_m$. Computation of derivative, derivative ratio and regression between derivative ratio and the Chl-values were implemented in software. The correlation was calculated for all possible band combinations and results are presented in the Figure 5.
### Table 3: Top ten-correlation values obtained using derivative ratio values

|                | Not smoothened | Smoothened with 1 x 3 values | Smoothened with 1 x 5 values | Smoothened with 1 x 7 values |
|----------------|----------------|------------------------------|------------------------------|------------------------------|
|                | B1   | B2   | R²  | B1   | B2   | R²  | B1   | B2   | R²  | B1   | B2   | R²  |
| 1              | 460  | 473  | 0.9122 | 612  | 714  | 0.8925 | 421  | 460  | 0.9386 | 421  | 544  | 0.9667 |
| 2              | 460  | 486  | 0.8938 | 653  | 699  | 0.8885 | 356  | 376  | 0.9183 | 421  | 545  | 0.9645 |
| 3              | 612  | 715  | 0.8849 | 422  | 482  | 0.8823 | 421  | 539  | 0.8962 | 421  | 527  | 0.959  |
| 4              | 356  | 700  | 0.8778 | 356  | 796  | 0.8724 | 421  | 540  | 0.8923 | 420  | 545  | 0.959  |
| 5              | 356  | 703  | 0.8778 | 356  | 732  | 0.8506 | 653  | 696  | 0.8866 | 421  | 525  | 0.9559 |
| 6              | 612  | 683  | 0.8684 | 356  | 733  | 0.8481 | 421  | 611  | 0.8864 | 421  | 546  | 0.9553 |
| 7              | 356  | 649  | 0.8608 | 421  | 482  | 0.8398 | 421  | 749  | 0.8808 | 420  | 535  | 0.9495 |
| 8              | 356  | 758  | 0.8573 | 539  | 710  | 0.8374 | 421  | 543  | 0.8748 | 420  | 538  | 0.9487 |
| 9              | 356  | 720  | 0.8562 | 421  | 651  | 0.8323 | 355  | 615  | 0.8742 | 421  | 459  | 0.9399 |
| 10             | 666  | 735  | 0.8501 | 356  | 652  | 0.8317 | 421  | 546  | 0.8742 | 421  | 547  | 0.937  |

The high correlation was found with the wavelengths of 460 nm and 473 nm.

### 3.5. The Second Order Derivative Method

The higher order derivative methods for spectral analysis is proposed by Philpot (1991). The second order derivative values were used for chlorophyll estimation in many studies (Shi, 2007). The ratio of Second derivative is computed as

$$P_{\lambda m} = \frac{R_{\lambda m}^n}{R_{\lambda n}^m} \ldots (4)$$

Where, $R_{\lambda n}^m = \frac{R_{\lambda n}^{(n-1)} - R_{\lambda n}^{(n+1)}}{\lambda_n^{(n+1)} - \lambda_n^{(n-1)}}$

$P_{\lambda m}$ is the ratio of second derivative, $R_{\lambda n}^n$ is the second derivative at $\lambda n$ and $R_{\lambda m}^m$ is the second derivative at $\lambda m$. As the second order derivative values have noise and spikes, smoothening is recommended to get better results.

![Second order derivative data](image)
**Figure 7:** Correlation between second order derivative values and measured Chl-a values at different wavelengths: A - without smoothening; B, C & D are smoothened with 1 x 3, 1 x 5 and 1 x 7 window running linear mean filter

**Table 4:** The high correlation values with second order derivative values

| Not smoothened | Smoothened with 3 windows | Smoothened with 5 windows | Smoothened with 7 windows |
|----------------|----------------------------|----------------------------|----------------------------|
| Wl (nm) | R² | Wl (nm) | R² | Wl (nm) | R² | Wl (nm) | R² |
| 1    | 654 | 0.6327 | 778 | 0.7312 | 565 | 0.752 | 457 | 0.7434 |
| 2    | 354 | 0.5963 | 354 | 0.7145 | 384 | 0.6561 | 560 | 0.6757 |
| 3    | 562 | 0.5246 | 561 | 0.5892 | 457 | 0.6402 | 481 | 0.6054 |
| 4    | 390 | 0.5243 | 385 | 0.5756 | 482 | 0.6276 | 561 | 0.5985 |
| 5    | 622 | 0.4892 | 715 | 0.5721 | 458 | 0.6064 | 478 | 0.5985 |
| 6    | 635 | 0.4750 | 390 | 0.5172 | 560 | 0.5887 | 421 | 0.5475 |
| 7    | 597 | 0.471 | 357 | 0.4966 | 545 | 0.5454 | 624 | 0.5423 |
| 8    | 372 | 0.4609 | 356 | 0.4952 | 353 | 0.5451 | 383 | 0.5335 |
| 9    | 458 | 0.4595 | 755 | 0.4683 | 568 | 0.5355 | 383 | 0.5027 |
| 10   | 624 | 0.4529 | 512 | 0.4614 | 389 | 0.5255 | 477 | 0.5012 |

**3.6. The Second Order Derivative Ratio Method**

The second order ratio method is used to estimate the chl-a Concentration.

The ratio of Second derivative is computed as $P_{\lambda mn} = R^\prime_{\lambda mn}/R^\prime_{\lambda n}$ \(\cdots (5)\)
Where, $R^\prime_{\lambda mn} = \frac{R_{\lambda(n+1)}-R_{\lambda(n-1)}}{\lambda(n+1)-\lambda(n-1)}$

$P_{\lambda mn}$ is the ratio of second derivative, $R^\prime_{\lambda n}$ is the second derivative at $\lambda n$ and $R^\prime_{\lambda m}$ is the second derivative at $\lambda m$.

**Figure 8:** The correlation between ratio of second order derivative values and measured Chl-a values at different wavelengths: A - without smoothing; B, C & D are smoothed with 3, 5 and 7 window running average algorithm

**Table 5:** High ten-correlation values obtained using second order derivative ratio values

| 2\text{nd} rat | Not smoothened | Smoothened with 1 \times 3 values | Smoothened with 1 \times 5 values | Smoothened with 1 \times 7 values |
|---------------|----------------|----------------------------------|----------------------------------|----------------------------------|
|               | WL₁ | WL₂ | R²   | WL₁ | WL₂ | R²   | WL₁ | WL₂ | R²   | WL₁ | WL₂ | R²   |
| 1             | 377 | 413 | 0.8675 | 708 | 735 | 0.8892 | 354 | 519 | 0.9314 | 681 | 709 | 0.9172 |
| 2             | 704 | 735 | 0.8578 | 355 | 501 | 0.8668 | 354 | 771 | 0.9160 | 399 | 647 | 0.8778 |
| 3             | 355 | 708 | 0.8490 | 355 | 562 | 0.8647 | 616 | 622 | 0.8997 | 447 | 500 | 0.8603 |
| 4             | 355 | 655 | 0.8328 | 355 | 677 | 0.8625 | 354 | 687 | 0.8953 | 681 | 708 | 0.8554 |
| 5             | 357 | 597 | 0.8325 | 355 | 628 | 0.8625 | 354 | 722 | 0.8953 | 447 | 500 | 0.8603 |
| 6             | 357 | 662 | 0.8286 | 355 | 712 | 0.8348 | 354 | 553 | 0.8819 | 353 | 545 | 0.8336 |
| 7             | 355 | 691 | 0.8277 | 355 | 704 | 0.8317 | 354 | 445 | 0.8765 | 556 | 696 | 0.8328 |
| 8             | 355 | 505 | 0.8219 | 386 | 527 | 0.8277 | 354 | 561 | 0.8757 | 497 | 616 | 0.8314 |
| 9             | 355 | 683 | 0.8098 | 355 | 734 | 0.8185 | 354 | 742 | 0.8696 | 458 | 553 | 0.831 |
| 10            | 424 | 577 | 0.8089 | 355 | 707 | 0.8181 | 459 | 562 | 0.8440 | 458 | 561 | 0.8301 |
3.7. Derivative Difference Method

In this study, a new algorithm called Derivative Difference method is introduced to estimate Chlorophyll-a. In this algorithm the difference between derivative values at different wavelengths were correlated with the measured Chl-a values.

Difference of First Order Derivative

The difference of first order derivative can be computed as

\[ P'_{\lambda mn} = R'_{\lambda mn} - R'_{\lambda m} \ldots (6) \]

Where, \( P'_{\lambda mn} \) is the Difference of first order derivative, \( R'_{\lambda mn} \) is the derivative at \( \lambda n \) and \( R'_{\lambda m} \) is the derivative at \( \lambda m \).

Difference of Second Order Derivative

The difference of Second order derivative can be computed as

\[ P''_{\lambda mn} = R''_{\lambda mn} - R''_{\lambda m} \ldots (7) \]

Where, \( P''_{\lambda mn} \) is the difference of second order derivative, \( R''_{\lambda mn} \) is the second order derivative at \( \lambda n \) and \( R''_{\lambda m} \) is the second order derivative at \( \lambda m \).

This method was used on raw data, first order derivative data and second order derivative data, individually. The results are tabulated and shown below in Table 6-8.

Table 6: High ten-correlation values obtained using difference method on raw data

|          | Not smoothened | Smoothened with 1 x 3 values | Smoothened with 1 x 5 values | Smoothened with 1 x 7 values |
|----------|----------------|-------------------------------|-----------------------------|-------------------------------|
|          | WL1 WL2 R'     | WL1 WL2 R'                  | WL1 WL2 R'                 | WL1 WL2 R'                  |
| 1        | 650 693 0.8167 | 650 693 0.8111              | 650 693 0.8064             | 650 693 0.8057              |
| 2        | 651 693 0.8066 | 651 693 0.8053              | 651 693 0.8043             | 648 694 0.8001              |
| 3        | 355 359 0.8032 | 632 694 0.8005              | 646 693 0.8005             | 651 693 0.7976              |
| 4        | 646 694 0.7989 | 652 693 0.7942              | 652 693 0.7875             | 645 693 0.7901              |
| 5        | 650 694 0.7901 | 642 694 0.7882              | 633 394 0.7875             | 649 694 0.7888              |
| 6        | 647 693 0.7885 | 650 694 0.7866              | 645 693 0.7859             | 630 695 0.7868              |
| 7        | 652 693 0.7850 | 634 694 0.7809              | 650 694 0.7878             | 628 693 0.7813              |
| 8        | 633 694 0.7834 | 631 695 0.7799              | 641 694 0.7813             | 652 693 0.7806              |
| 9        | 639 695 0.7829 | 645 693 0.7792              | 637 694 0.7726             | 653 692 0.7802              |
| 10       | 642 694 0.7816 | 631 693 0.7681              | 632 695 0.7718             | 650 694 0.7783              |
It is to be noted from Tables 1

Table 7: High ten-correlation values obtained using difference method on first order derivative data

| Table 7 |
|---------|

| Not smoothened | Smoothened with 1 x 3 values | Smoothened with 1 x 5 values | Smoothened with 1 x 7 values |
|---------------|-------------------------------|-------------------------------|-------------------------------|
| WL1 WL2 R²    | WL1 WL2 R²                   | WL1 WL2 R²                   | WL1 WL2 R²                   |
| 1 422 611 0.9266 | 475 482 0.9397              | 648 672 0.9283              | 379 677 0.9052              |
| 2 425 430 0.9222 | 422 612 0.9199              | 610 671 0.8934              | 379 678 0.8904              |
| 3 392 401 0.9101 | 436 624 0.9122              | 611 671 0.8898              | 610 671 0.8752              |
| 4 428 678 0.9021 | 648 671 0.8949              | 356 379 0.8774              | 375 678 0.8591              |
| 5 624 678 0.8936 | 648 673 0.8898              | 648 673 0.8752              | 613 671 0.8529              |
| 6 399 545 0.8921 | 610 672 0.8815              | 376 678 0.8748              | 612 671 0.8527              |
| 7 666 736 0.8797 | 648 673 0.8780              | 611 672 0.8744              | 609 670 0.8512              |
| 8 476 624 0.8683 | 612 671 0.8709              | 609 671 0.8712              | 611 671 0.8477              |
| 9 385 625 0.8527 | 498 681 0.8573              | 421 749 0.8647              | 613 670 0.8462              |
| 10 356 732 0.8517 | 356 615 0.8569              | 427 678 0.8591              | 426 678 0.8440              |

Table 8: High ten-correlation values obtained using difference method on second order derivative data

| Table 8 |

| Not smoothened | Smoothened with 1 x 3 values | Smoothened with 1 x 5 values | Smoothened with 1 x 7 values |
|---------------|-------------------------------|-------------------------------|-------------------------------|
| WL1 WL2 R²    | WL1 WL2 R²                   | WL1 WL2 R²                   | WL1 WL2 R²                   |
| 1 517 705 0.8836 | 512 562 0.9434              | 354 366 0.9628              | 433 566 0.8510              |
| 2 509 563 0.846  | 355 396 0.8707              | 354 397 0.9226              | 467 561 0.8420              |
| 3 609 691 0.8259 | 355 397 0.856              | 372 605 0.9101              | 422 616 0.8347              |
| 4 600 716 0.8199 | 355 385 0.8435              | 354 603 0.9071              | 562 778 0.8265              |
| 5 655 789 0.8174 | 505 562 0.8361              | 354 604 0.8974              | 458 562 0.8237              |
| 6 633 655 0.816  | 562 636 0.8225              | 354 604 0.8919              | 458 553 0.8226              |
| 7 459 655 0.815  | 513 623 0.8183              | 616 622 0.8879              | 601 640 0.8201              |
| 8 373 417 0.8147 | 386 626 0.8016              | 562 779 0.8776              | 458 482 0.8194              |
| 9 517 704 0.8141 | 355 456 0.7944              | 354 596 0.8770              | 459 561 0.8190              |
| 10 598 779 0.8104 | 562 779 0.7937             | 459 546 0.8739              | 353 545 0.8131              |

Table 9 compiles the effectiveness of the derivative difference methods w.r.t to derivative ratio and band ratio methods.

Table 9: Comparison of the derivative difference results with derivative ratio and band ratio

| Without Smoothening | Smoothened with 1 x 3 window | Smoothened with 1 x 5 window | Smoothened with 1 x 7 window |
|---------------------|------------------------------|------------------------------|------------------------------|
| Raw data Band Ratio | 0.9042                      | 0.8987                      | 0.8945                      |
| Raw data Band Difference | 0.8167                  | 0.8111                      | 0.8064                      |
| 1st order derivative ratio | 0.9122                  | 0.9139                      | 0.9386                      |
| 1st order Derivative Difference | 0.9266                | 0.9397                      | 0.9283                      |
| 2nd order Derivative Ratio | 0.8808                  | 0.8945                      | 0.9314                      |
| 2nd order Derivative Difference | 0.8836                  | 0.9434                      | 0.9628                      |
| 4. Conclusion |

Chlorophyll concentration was estimated with band ratio, derivative ratio and derivative difference methods. The suitable wavelength sets vary slightly with smoothening window size. From Table 9, it is found the 1 x 5 window provides better correlation values. It is noticed that while proposed band difference method provided a poor correlation with raw data, it provides improved high correlation results with derivative data. The results of proposed difference method on derivative data has provided highest determination coefficient uniformly in 1st order and 2nd order derivative difference methods. It is to be noted from Tables 1-8, the correlation coefficients due to band ratio and derivative methods
are poorer and mostly effective for a narrow range of wavelengths; on the other hand the correlation coefficients due to derivative difference methods provide very good measure across all wavelength bands.

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