

Urban Water Absorbance to Predict Chlorophyll a and Turbidity

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Abstract. This study aimed to use water absorbance in the range of 200-900 nm to predict the turbidity and chlorophyll a concentration (Chl-a) in urban water. Six kinds of water samples were artificially prepared in this study: spirulina samples (S), chlorella vulgaris samples (C), turbidity samples (T), mixed water samples of S-T, C-T, and S-C. The correlation analysis results showed that the turbidity had a strong correlations with the absorbance at most of the wavelengths, and linear models were built to predict turbidity for each type of water samples, the R_v^2 of each specific model was higher than 0.981, and the overall R_v^2 reached to 0.955. For Chl-a prediction, SVM method had better accuracies ($R_v^2 > 0.986$) for the algae water samples than those ($R_v^2 < 0.826$) for the turbidity mixed samples. In order to improve Chl-a prediction accuracy for turbidity mixed samples, LS-SVM method was used to estimate Chl-a ($R_v^2 > 0.987$), which was increased by 31.1% comparing to the corresponding SVM method. Furthermore, the R_v^2 of the overall Chl-a decoupled model for both S-T and C-T also reached to 0.915. The results showed that the absorbance of unprocessed water samples had great potential to predict Chl-a fast and accurately.

Introduction

Water quality has directed influence on the appearance and functions of urban landscape water which mainly includes natural lakes, artificial lakes, reservoirs, and rivers in the urban area. Most of the urban waters are shallow, small in size, and enclosed or half-enclosed, which makes the maintenance of higher water quality even harder. The parameters of urban water quality with greatest concern are algae amount per unit/ (algae density) and turbidity.

Chlorophyll a (Chl-a) is widely used for evaluate the algae density of water, and spectral absorbance is popularly used for Chl-a estimation. Absorption spectrum of algae represents the competitive ability for light, and also can be used to distinguish different types of algae and concentration. The relationship between the absorption spectrum of algae and the concentration of Chl-a was significant: the absorption spectrum of algae increased gradually with the increasement of Chl-a concentration [1]. In the study of the absorption spectrum of cyanobacteria chlorophyll in polluted waters, the difference between the absorbance value at 436 nm and 664.5 nm could be used to predict the Chl-a concentration [2].

Turbidity refers to the degree of obstruction when the light through the water suspended solids, and one of most commonly used methods to detect this parameter is spectrophotometric method. The absorbance of series turbidity standard suspensions were measured, and then the turbidity standard curves for different types of suspensions could be established [3, 4, 5, 6].

Various algorithms have been developed for estimating Chl-a concentration in waters. The three-band algorithm and four-band algorithm based on spectral reflectance of water were often employed to estimate Chl-a concentration [7, 8, 9, 10, 11]. In order to better reduce the effects of suspended particles absorption and backscattering, researchers have also done many studies. For example, the

unmixing hyperspectral imagery based on support vector nonlinear approximating regression and the Gaussian parameters of Chl-a and suspended sediment based on spectral decomposition were proposed to estimated Chl-a [12,13]. Moreover, the researchers used hyperion data to estimate Chl-a and total suspended solid (TSS) based on the bio-optical model, and then assessed the degree of the Gard lake's eutrophication [14]. For Shitoukoumen Reservoir, the chlorophyll prediction model based on Landsat-TM image data was established by using GA-PLS method [15].

Tremendous effects have been contributed to predict water chlorophyll content and other major parameters in different water body from spectral reflectance, but the prediction accuracies seldom reached a high level due to the outdoor and open style in the measurement of spectral reflectance. In this research, instead of reflectance, absorbance which can be measured from a relative close environment was suggested to fast and accurately predict Chl-a and turbidity.

Materials and Methods

Cultivation or Configuration of Water Samples

(1) Single-factor water samples

Single-factor water sample means the water sample has only one kind of alga or suspension. To simplify the experiment, two most commonly known algae in urban waters were considered in this research: spirulina and chlorella vulgaris. Those two algae were artificially cultivated in laboratory. Two 20 L experimental water tank were placed beside the window where had sufficient natural light, the temperature held 18-25°C. The algae seeds were put into those two tanks respectively, and grew for 15 days with supplemental oxygen. Then the spirulina and chlorella vulgaris water samples were acquired to 1) measure Chl-a concentration, 2) dilute to get more water samples with different concentration to measure the absorbance.

The Chl-a concentration of the original water samples was determined by acetone-spectrophotometry with Formula (1).

$$Chl-a = \begin{bmatrix} 11.85 \times (A_{664} - A_{750}) \\ -1.54 \times (A_{647} - A_{750}) \\ -0.08 \times (A_{630} - A_{750}) \end{bmatrix} \times V_1 / (V_2 \times \delta) \quad (1)$$

Where *Chl-a* represents Chl-a concentration in water sample (µg/L); A_{664} , A_{647} , A_{630} and A_{750} are the absorbance of the extracts at the wavelength of 664 nm, 647 nm, 630 nm and 750 nm, respectively. V_1 is the volume of the acetone extract (mL); V_2 is the volume of the suction sample (L); δ is the cuvette optical path (cm).

In order to obtain water samples of different algae concentrations, the original water samples were further diluted based on a certain concentration gradient to obtain spirulina and chlorella vulgaris water samples. All the spirulina and chlorella vulgaris water samples were listed in Table 1. C_1 and C_2 represent the Chl-a concentration of their original water samples, respectively.

Table 1 Spirulina water samples and Chlorella vulgaris water samples with different concentrations after dilution process

Spirulina water samples	Relative concentration	Absolute concentration [$\mu\text{g/L}$]	Chlorella vulgaris water samples	Relative concentration	Absolute concentration [$\mu\text{g/L}$]
S0	C ₁	635.672	C0	C ₂	466.707
S1	0.900C ₁	572.105	C1	0.900C ₂	420.036
S2	0.810C ₁	514.894	C2	0.810C ₂	378.033
S3	0.729C ₁	463.409	C3	0.729C ₂	340.229
S4	0.656C ₁	417.064	C4	0.656C ₂	306.207
S5	0.590C ₁	375.358	C5	0.590C ₂	275.586
S6	0.472C ₁	300.286	C6	0.472C ₂	220.469
S7	0.378C ₁	240.229	C7	0.378C ₂	176.375
S8	0.323C ₁	192.183	C8	0.323C ₂	141.099
S9	0.211C ₁	134.528			
S10	0.127C ₁	80.717			
S11	0.063C ₁	40.359			

Another important kind of one-factor water samples was the samples with different turbidity. Formazine suspension was used to simulate the water turbidity. The suspension was configured by following the polymer formazine turbidity standard (SL 88-2012), which is a water industry standards of China. In the experiment, 5.00 mL of hydrazine sulfate and 5.00 mL of hexamethylenetetramine solution were uniformly mixed in a volumetric flask, and then held at 25 ± 3 °C for 24 h. The mixed solution was further diluted by adding pure water to the mark line position of 100 mL. This solution was mixed thoroughly to get the standard stock solution which had turbidity of 400 NTU. The standard turbidity suspension of 400 NTU was further diluted several times to obtain water samples with turbidity of 5, 10, 20, 40, 80, 100, 160, 200, 280 and 400 NTU, which was recorded as T0-T9.

(2) Two-factor water samples

In order to deeply analyze the absorbance prediction ability in more complicated water samples, three mixed water samples with 2 components were further configured, named two-factor water samples: S-T water samples (70 sample in total) which were cross mixed from spirulina (S5-S11) and turbidity (T0-T9) samples at a 1:1 ratio; C-T water samples (80 sample in total) which were cross mixed from chlorella vulgaris (C0-C7) and turbidity (T0-T9) samples at a 1:1 ratio; S-C water samples (11 sample in total) which were mixed from spirulina samples with concentrations range of 0-317.835 $\mu\text{g/L}$ (with an interval of 31.784 $\mu\text{g/L}$) and chlorella vulgaris samples with concentrations range of 233.355-0 $\mu\text{g/L}$ (with an interval of 23.336 $\mu\text{g/L}$).

Spectral Absorbance Measurement

Different water samples were thoroughly mixed before transferring to quartz cells for their measurement of spectral absorbance. The optical length of the quartz cell was 1 cm. The absorbance of each water sample was measured by Shimadzu UV-VIS spectrophotometer UV-2600 with a spectral interval of 0.5 nm, and the spectral range was 200-900 nm.

Methods

The correlations between absorbance and different components were firstly analyzed, and sensitive wavelengths were selected, and then the selected bands were denoised with wavelet transform method, 2 abnormal samples were removed. Cross-validation was used to build and evaluate the prediction models for each group of water samples. Linear models were built to predict turbidity for each group of samples which included turbidity because of the strong correlation between turbidity and absorbance found at the sensitive wavelength. Then, SVM method was further adopted to estimate Chl-a concentration for each group of samples. In order to improve the Chl-a prediction

accuracy for turbidity mixed samples, LS-SVM method was used by adding the predicted turbidity from previous linear model as the input variable.

Results and Discussion

Correlations between Spectral Absorbance and Chl-a&turbidity

The correlations between absorbance and each component in both single-factor and two-factor water samples were analyzed, the results are shown in Fig.1 and Fig.2. Fig.1 represents the correlations between the single factor and absorbance in the single-factor samples, and Fig.2 is the correlations between Chl-a/turbidity and the absorbance in the two-factor samples.

As can be seen from Fig.1: a) For single-factor samples, the correlation between absorbance and turbidity remained stable throughout the measured spectral range, and the correlation coefficient (R) was close to 1; b) the absorbance of chlorella vulgaris water samples also had a stable and significant correlation with Chl-a except for the wavelengths near 232 nm, and the maximum correlation coefficient (0.999) was obtained at 240 nm; c) the correlation curve of spirulina water samples absorbance and Chl-a concentration fluctuated greatly in 200-500 nm, and gradually stabilized within the range of 650-900 nm, and the highest R was reached at 237.5 nm, which was 0.996.

Fig.2 shows that: a) For the mixed water samples, such as S-T and C-T samples, Chl-a had completely opposite correlation trends with absorbance, comparing to the correlation trends between turbidity and absorbance; b) the wavelength around 237 nm is the maximum correlation of Chl-a and absorbance, but also the minimum correlation between turbidity and absorbance; c) the R of turbidity and absorbance at 680 nm was above 0.98; d) for the most range of the waveband, the correlations between Chl-a and absorbance were not significant, the R was less than 0.2.

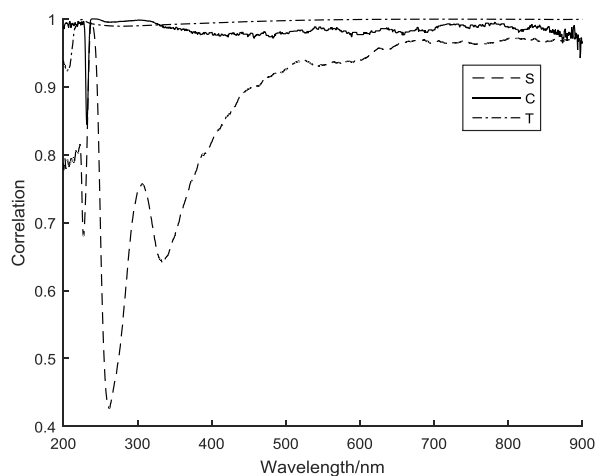


Fig. 1 Correlation analysis of different factors and absorbance in single-factor water samples

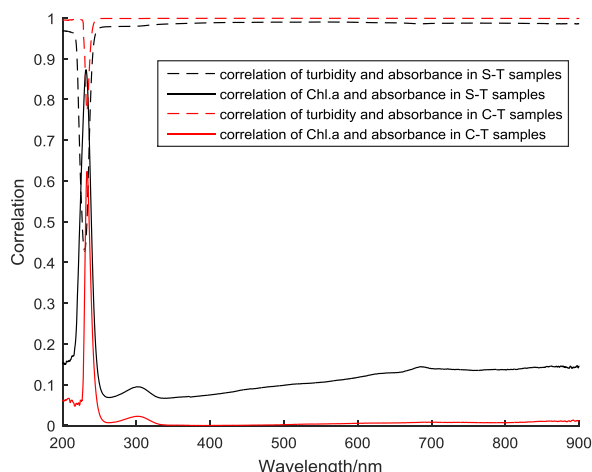


Fig. 2 Correlation analysis of different factors and absorbance in two-factor water samples

The band near 675 nm was characteristic absorption peak of Chl-a, and had a significant relationship with other bands [16]. Based on the turbidity standard curve, there was an obvious linear relationship between turbidity and spectral absorbance at 680 nm. Therefore, 680 nm was selected as one of the sensitive band. The other band was 237 nm, at which the correlation changed greatly, such as the R was only 0.750 in the S-T samples, while the R was up to 0.993 in the T samples.

Different Predictions Models

(1) Turbidity prediction models

In order to simplify the turbidity prediction model, only linear models at 680 nm were built to predict turbidity for each sample type. The linear regression models are shown in Table 2, where y is the turbidity of different water sample types, and x is the absorbance of different water sample types. As can be seen in Table 2, different models were acquired for different type of water sample, the R_v^2 of them were higher than 0.981, but different models would also bring troubles in application, so an overall model (last column) for all type of the water samples was also built, and the R_v^2 reached to 0.955, showed a good potential for further application.

Table 2 Linear regression models to predict turbidity

Samples	Sample numbers	Validation method	Turbidity model	R_v^2	RMSE	p -value
T	10	three-fold cross-validation	$y=285.534x+1.360$	0.999	3.026	0
S-T	70	seven-fold cross-validation	$y=272.256x-33.129$	0.981	7.978	0
C-T	78	six-fold cross-validation	$y=262.411x-5.079$	0.997	2.458	0
T&S-T&C-T	158	three-fold cross-validation	$y=260.3792x-15.398$	0.955	14.255	0

(2) Chl-a prediction model

Firstly, SVM method was used to predict the Chl-a concentration for different water sample types, and the prediction models were listed in Table 3. As can be seen from the Table 3, for algae water samples, the R_v^2 of the Chl-a model was greater than 0.98. But when the water samples contained algae and suspended solid, the R_v^2 was reduced to 0.753 and 0.826. This also showed that the addition of turbidity has a significant impact on the Chl-a concentration in the absorbance, suggesting a coupling relationship between Chl-a concentration and turbidity was existed.

Table 3 Chl-a model established by SVM method

Samples	Sample numbers	Validation method	predictor	R_v^2	RMSE	<i>p</i> -value
S	12	three-fold cross-validation	Chl-S	0.993	0.254	0.016
C	9	three-fold cross-validation	Chl-C	0.991	0.460	0.021
S-T	70	seven-fold cross-validation	Chl-S	0.753	0.185	0.001
C-T	78	six-fold cross-validation	Chl-C	0.826	0.201	0.002
S-C	11	three-fold cross-validation	Chl-S	0.986	0.235	0.006
			Chl-C	0.986	0.153	0.005
			total Chl-a	0.988	0.150	0.003

There was no obvious absorption peak in the visible region for T-mixed samples comparing to T-excluded samples, but the peak was obvious in the ultraviolet region the reason for this could be the high turbidity [17]. In order to further study the influence of turbidity on Chl-a concentration, SVM model for S water samples was directly used in S-T water samples to predict its Chl-a concentration. A data set which had same Chl-a concentration (20.179 $\mu\text{g/L}$) but different turbidity were selected out to compare their measured Chl-a and predicted Chl-a values, and it found that the turbidity led to an increase in the Chl-a prediction. The effects of turbidity on the chlorophyll absorbance included two aspects, one is the suspended solid can absorb some of the light, and the other is the suspended solid can reflect back the light which could also reduce the light at the receive end. The absorb ability of turbidity is nearly a linear trend as shown in Table 2. Therefore, the influence of turbidity was positively correlated with the chlorophyll concentration. In order to further improve the Chl-a prediction accuracy for turbidity mixed samples, LS-SVM method was used to build Chl-a decoupled models by adding the predicted turbidity which calculated from the previous linear model as the input variable. The models were shown in the Table 4.

Table 4 The Chl-a decoupled models with LS-SVM method for mixed water samples with turbidity

Samples	Sample	Validation method	predictorr	R_v^2	RMSE	<i>p</i> -value
S-T	70	seven-fold cross-validation	Chl-a	0.987	5.643	0
C-T	78	six-fold cross-validation	Chl-a	0.993	3.684	0
S-T&C-T	148	four-fold cross-validation	Chl-a	0.915	15.625	0

Comparing the Chl-a prediction models in Table 3 and 4, it can be seen that the R_v^2 of Chl-a decoupled model for S-T and C-T reached to 0.987 and 0.993, which were increased by 31.1% and 20.2%, respectively. The results indicated that the decoupled models had greater potential to predict Chl-a concentration. And another overall decoupled model for both S-T and C-T was also built to try to predict Chl-a concentration for unknown water type.

Conclusions

In this study, 6 types of water samples were artificially prepared in this study: spirulina samples (S), chlorella vulgaris samples (C), turbidity samples (T) and three mixed water samples of S-T, C-T, S-C. Efforts were made to predict Chl-a concentration and turbidity from water absorbance. The correlations between absorbance and Chl-a & turbidity were firstly analyzed, and then the sensitive

bands were selected. Linear, SVM and LS-SVM method were adopted to build prediction models for turbidity and Chl-a concentration. The main findings were summarized as follows:

1) Whether in the single-factor water samples, or in two-factor water samples, turbidity always had a great correlation with water absorbance. Linear models were built for both specific type of water samples and all the water samples, the R_v^2 of specific model was higher than 0.981 and the overall R_v^2 was reached to 0.955.

2) For algae water samples, Chl-a concentration had relative lower correlation with absorbance, therefore, SVM method was used for Chl-a prediction, and the R_v^2 were higher than 0.986.

3) In the mixed water samples containing both algae and suspended solids, the accuracies of SVM model ($R_v^2 < 0.826$) were lower than the algae water samples because of the interaction effect between Chl-a and turbidity, so LS-SVM method was used to build Chl-a decoupled models by adding the predicted turbidity as the input variables. The R_v^2 of the decoupled model reached to 0.987 and 0.993 for turbidity mixed water samples, which were increased by 31.1% and 20.2% comparing to the corresponding SVM method. Furthermore, the R_v^2 of the overall decoupled model for unknown water type also reached to 0.915, indicating an good potential for application.

The results showed that the absorbance of unprocessed water samples had great potential to predict Chl-a fast and accurately. But more efforts should be done to consider more water types which include more components, such as S-C-T, and more universe model should be further explored to apply in natural urban water with unknown components.

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