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Classification of Spatial Variability of Water Quality using Absorption and Fluorescence Spectra: A Case Study on Beira Lake

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Abstract- Chlorophyll content of a water sample is used as an indirect estimate for the nutrient level of the sample. Optical spectroscopic techniques are widely used to estimate chlorophyll contents of water samples. However, in a complex environment such as an urban lake, there are many other pollutant constituents. Hence it is difficult to determine the pollutant level only by investigating the chlorophyll signatures. A study is carried out by collecting water samples from different spatial locations of Beira Lake, Colombo (29° 52' N, 77° 53' E, 0.0001 m above mean sea level) and fluorescence spectrum excited at 405 nm and absorption spectrum were obtained for each sample.

Despite spectral signatures of chlorophyll, spectral signatures of different polluted constituents were observed in both fluorescence and absorption spectra of the every sample. Obtained data set was compressed using singular value decomposition and used first two components which carry 62 % of information. It was found that the samples got into four clusters with cophenetic correlation coefficient of 0.76 when the compressed data set was clustered using K-means algorithm. Water samples from the locations near Gangarama Simamalakaya, near Sri Uttarananda Mawatha and near floating market shows highest polluted level. It is evident that in the absorption spectra also 775 nm peak were found which characteristics an infestation of green photosynthetic bacteria due to stagnation. Water quality of Beira Lake near Lake House clustered into two polluted levels. And highest absorption intensity and lowest fluorescence intensities of polluted constituents show in the upper part of the Lake where currently undergo the high construction of Lotus tower and the park. PH measurements of all the locations are in the range of 6.5-7.5 and its mean is 7.2±0.04.

Key Words: Beira Lake, Chlorophyll, Spectroscopy, Water quality.

1. INTRODUCTION

Water is an essential substance for life. The quality of water is rapidly diminishing, endangering the lives on Earth. Growth of population, revolution of industry and many other factors have caused the water pollution. Nutrient enrichment is one of the most significant and widespread water quality issues in the global environment [1]. This situation has been linked to several environmental concerns; including eutrophication, disturbances to ecosystems and changing decomposition rates [2]. Excessive plant growth caused by

nutrient enrichment from human activity is known as “Cultural Eutrophication” and is caused by various anthropogenic factors [3].

Nutrients are introduced into agricultural soils through application of inorganic fertilizers and animal manure the residues of which ultimately end up in water bodies. In addition, various nutrient loads are added to inland surface waters with sewage which are dumped to surface waters untreated [2]. Sri Lanka is one of the countries with very high usage of fertilizer [4]. Hence, there is a possibility of eutrophication of these reservoirs as a result of surface runoff of nutrients from agricultural fields as well as from commercial plantations. In addition domestic and commercial sewage contribute to the addition of nutrients to water bodies.

Due to high algal growth and related impairment of water quality, there have been many environmental and economic impacts [3]. One famous example is Beira Lake in Colombo where untreated urban sewage and runoff have caused eutrophication [5]. Famous Kandy Lake is threatened now due to algal blooms, foul smell and visual pollution [6]. There is nutrient enrichment and heavy algal growth in Kotte-Kolonnawa Marsh [7]. Similarly, in Vauniya Lake fishery production has been continuously declined due to eutrophication [8]. Moreover, pollution from algae are believed to have contributed to health problems such as Chronic Kidney Disease of Unknown aetiology (CKDU) in some parts of the country [9].

Globally, the scientists, decision makers and the general public have raised their concerns over management of eutrophication issue. Therefore, effective detection of water quality deterioration due to eutrophication is essential in order to control pollution of water and related problems. Phytoplankton level plays a major role in measuring level of nutrients in water sample.

Chlorophyll being a key component in algae is used as an indicator to detect the level of eutrophication. Both absorption and fluorescence measurements are widely used for detecting the algae levels especially by the Chlorophyll content (Chlorophyll a) of water [10]. Many methods that are being currently used to detect eutrophication are laboratory based using instruments including spectrophotometers [11]. Spectrophotometer is contained with a light source that is capable of emitting a range of wavelengths. It measures the reflectance or transmission properties of a material as a function of wavelength [11]. Fluorometer is another device used to detect fluorescence and its intensity and wavelength

distribution of emission spectrum, after excitation by a certain spectrum of light [12]. But they are time consuming and usually require an experienced, efficient analyst to generate consistently accurate and reproducible results. A less expensive field-type optical instrument which has a fixed optical configuration can be more easily used in the field [10]. Although the scientific investigation arena today is filled with various systems, tools and instruments to assess water quality they all have failed to present a product which is affordable to the relevant institutes/ communities of a developing country like Sri Lanka [13]. It is possible to estimate concentration of chlorophyll in a liquid sample with the use of laser diode and Light Emitting Diode (LED) based absorption and fluorescence signals and it is low cost and low time consuming [14]. Since urban polluted water regions often contain suspended solids and dissolved organic matter (which interferes the existence of chlorophyll), light absorbed or fluoresce from a body of water represents a weighted spectra of contributions from water, suspended solids, and chlorophyll[15]. It has found that fluorescence signatures and absorption signatures of Chlorophyll could be interfere with various constituents in polluted water. Cyanobacteria lies in the range of 680-850 nm [16], Bacteriophage fluoresce in the range of 400-480 nm and vegetative bacteria in the range of 400-500 nm [17] when excited at 405 nm. Also Diesel fluoresces in the range of 350-430 nm. Absorption signatures of Peridinin could be found around 483 nm.

The purpose of this study is to judge the possibility of identifying pollutant sources by studying co-relation between the spatial locations of the sample obtained and the similar spectroscopic fingerprints.

2. MATERIALS AND METHODS

2.1 Sample collection

Samples were collected from different locations of Beira Lake (near Lake House, near Gangarama temple and near floating market) during south western rain season from 10.00a.m.to3.00 p.m. (see Fig. 3(a)). Water samples were collected in to black covered 100 ml bottles within the depth of 30-40 cm from the surface of the water bed and with a gap of 200 m in between. All the samples were stored at 5 ± 3 °C.

2.2 Acquisition of spectra and PH values

PH values of water samples were measured using the meter YSI model 63 with the resolution of 0.01. The absorption and fluorescence spectra were obtained using a custom made set up. A tungsten halogen lamp (Osram, 25 W and 12 V) was used as the light source for obtaining the absorption spectra and a blue laser diode lasing at 405 nm together with a long-pass optical filter having cut-off wavelength at 435 nm was used for obtaining fluorescence spectra obtained the light passed through a sample at 90° angle. Oceanoptics Flame spectrometer with 25 μm aperture was used for the measurements. A block diagram of the system is shown in Fig. 1. In the case of absorption spectra, the white reference was taken in the radiation of tungsten halogen lamp and the dark reference was taken covering the spectrometer slit with a black paper.

2.3 Data pre-processing and compression

Absorption spectra were normalized based on white and dark references, while Fluorescence spectra were normalized by the scattered 405 nm peak of emission spectra. PH measurements were normalized dividing by its highest value. Both normalized spectral data were combined all together with PH measurements. After generalizing spectra by single value decomposition, most significant principle components were reconstructed and constructed a Dendrogram using Euclidian distance of observations to identify what the appropriate number of clusters and to examine how well clusters are merged. Finally obtained k means unsupervised clusters.

3. RESULTS AND DISCUSSION

Fluorescence and Absorption spectra of Beira Lake consisted of many optical signatures. Averaged fluorescence and absorption spectrums were plotted (Fig. 1).

According to Fig. 1(a), two broad fluorescence peaks could be seen. One happened to be fluorescence signatures of Chlorophyll 680 nm and 735 nm and the other could see near 550 nm. 550nm broad peak could occur because of various constituents in polluted water [15]. Also Raman scattering at 469 nm could be also see. And Fig. 1(b) has shown a significant narrow peak near 662 nm, which occurs because of

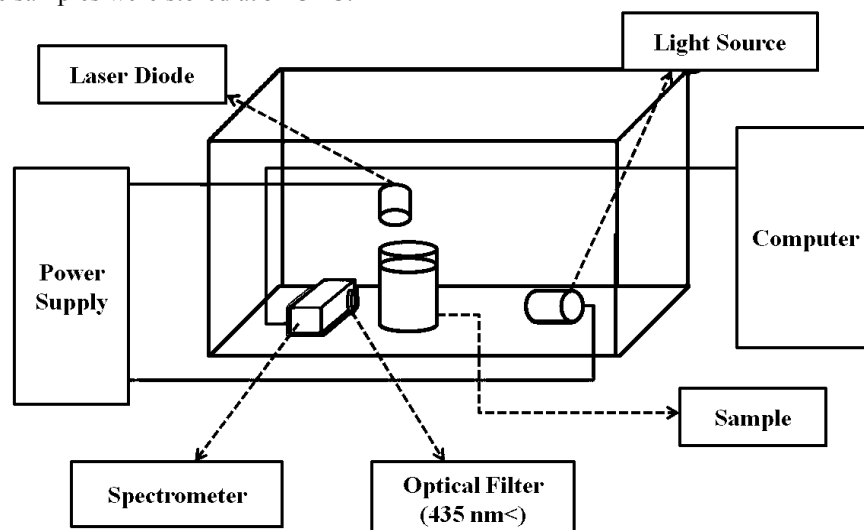


Fig. 1: Experimental set up

the Chlorophyll-a absorption and a slight lump near 642 nm which occurs because of the Chlorophyll-b absorption. Green pigment absorption of broad peak around 500 nm also could see and weighted spectrum could occur because of various constituents in polluted water [15].

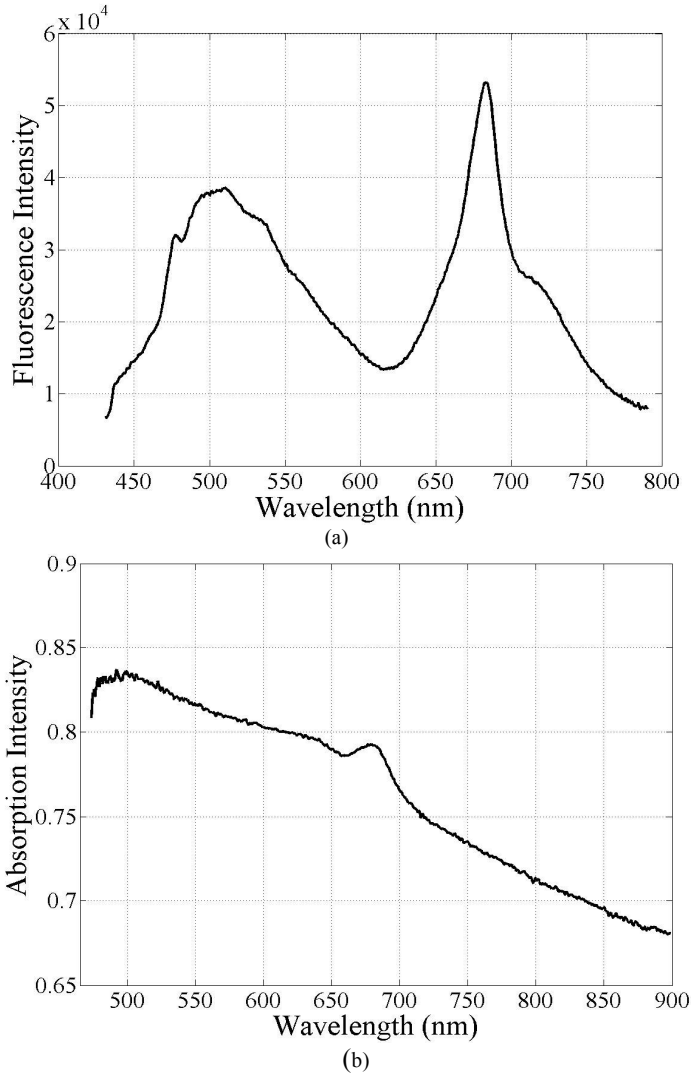


Fig. 2: Fluorescence spectrum (a) and Absorption spectrum (b) of Beira Lake water sample

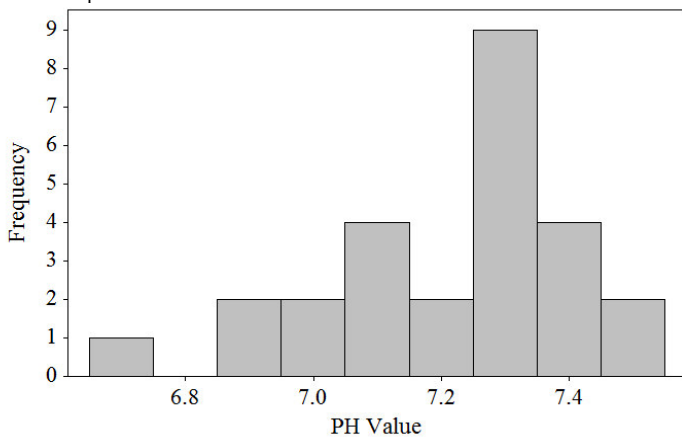


Fig. 3: Histogram of PH values of water samples from different locations

PH measurements of each sample were plotted against their corresponding sample number (Fig. 3). As all the samples

are in the range of 6.5-7.5, Beira Lake polluted water is in neutral conditions. Mean PH value is 7.2 ± 0.02 .

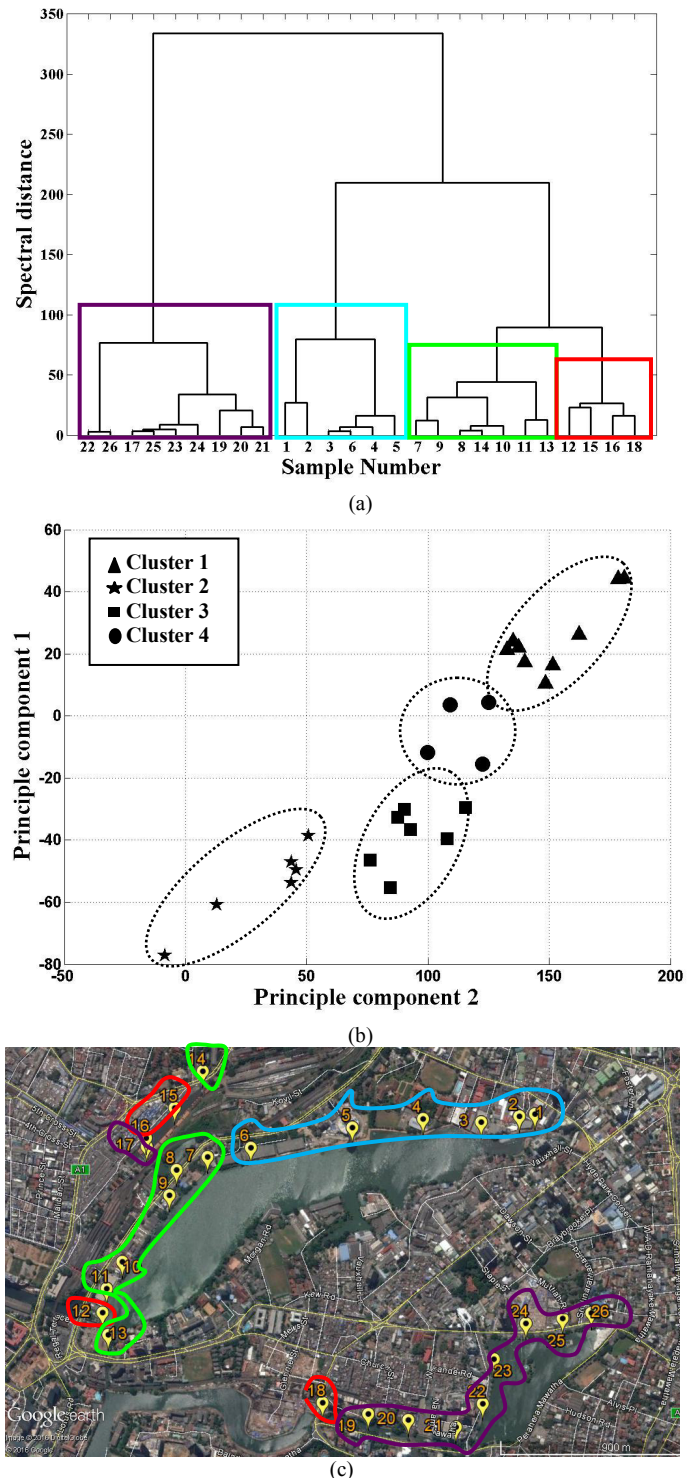


Fig. 4: Dendrogram (a) and K-Means clustering (b) of different locations, Four clusters marked on Beira Lake Google map (c)

Data were reconstructed using the method singular value decomposition. Significance of first 3 principle components was reconstructed as they are high in value. Dendrogram of the similar, optical featured geographic locations was given in Fig. 4 (a) with a cophenetic correlation coefficient of 0.76. The similarity of reconstructed spectrums was analysed and clustered in to four (Fig. 4 (b)). Finally clustered similar, optical featured geographic locations were mapped (Fig. 4(c)).

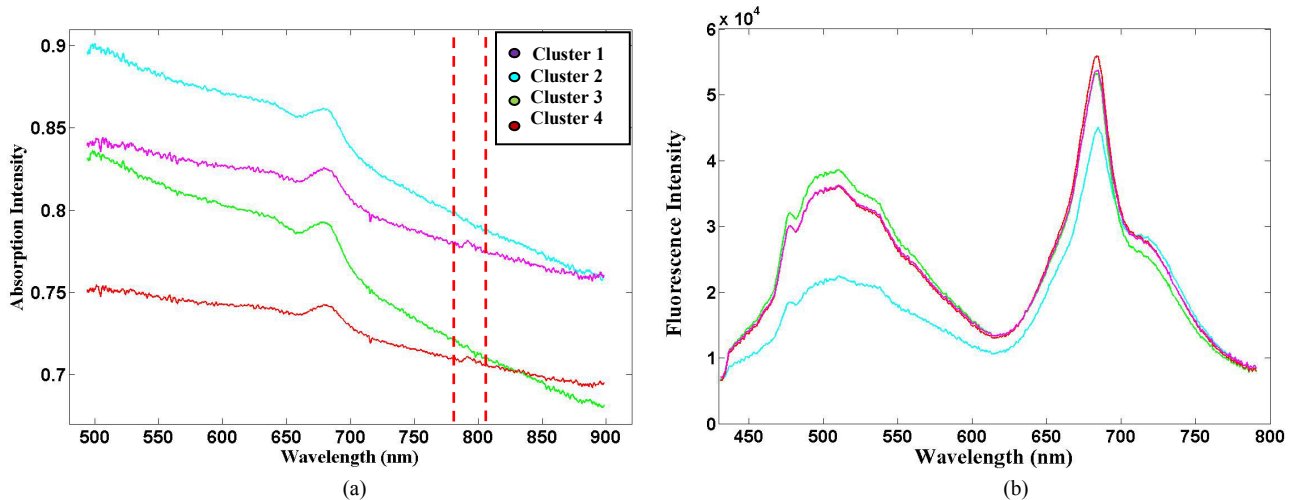


Fig. 5: Averaged Fluorescence spectra (a) and averaged Absorption spectra (b) of each cluster

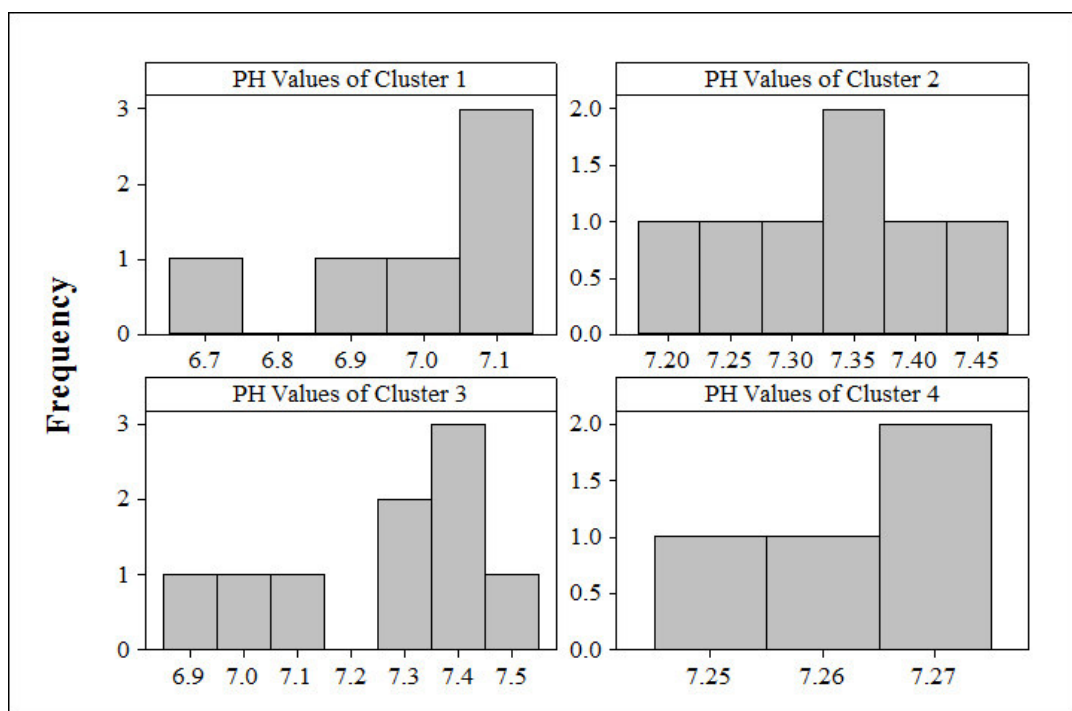


Fig. 6: Histogram of PH values of different samples according to their clusters

Cluster number three has locations of the least human influence due to the restricted access of the area. The area which has clustered as two, currently undergo the high construction of Lotus tower and the park. And it is the only area where Beira Lake is directly connected with slums. So the percentage of detergents, vegetable extractions and swage concentrations could be higher. Cluster number one area is mainly the surrounding of Gangarama Simamalakaya and the side of Sri Uttaranda Mawatha, where main roads are located in the sides of the Beira Lake, but unlike in floating market, with lack of influence of urbanization. Thus Location number 17 at floating market which is away from the Pettha main road, also clustered in cluster number two. While Location number 18 in the joint of two main roads (Justice Akbar Mawatha and Sri Uttaranda Mawatha) clustered with Location number 15 and 16 at floating market. Location number 12 at the Lake house vehicle park also clustered with those. The flowing of water in those locations is much lesser.

So their similarity could be the higher concentration of Chlorophyll and the high thickness in colour green.

Averaged fluorescence spectrums and averaged absorption spectrums were plotted for each cluster (Fig. 5). Although spectra were distinguished clearly, cluster number two and three shows a similar pattern of variation with the wavelength, but absorption intensity of cluster two is higher than cluster three and fluorescence intensity of cluster two is less than cluster three. This could be resulted due to the higher human activities near cluster two than cluster three. Cluster number one and four shows a similar pattern of variation with the wavelength, but absorption intensity of cluster four is higher than cluster one and fluorescence intensity of cluster four is less than cluster one. This could be resulted due to the long period exposure of sun light and higher attempt of photosynthesis, which wear off the Chlorophyll amount.

An absorption peak near 775 nm could be seen in averaged spectra of cluster one and four (Fig. 5(a)).

“Candidatus Chlorothrixhalophila”, a hyper saline-tolerant photosynthetic bacterium absorbs energy at 459, 629, and 761 nm at room temperature and at room temperature, it fluoresces at 760 and 870 nm when excited at 440 nm [18]. Also the absorbance and fluorescence spectra of “Ca. Chlorothrixhalophila” seemed to have properties similar to photosynthetic properties of both phyla of green photosynthetic bacteria when they were compared to the photosynthetic characteristics of Chlorobium tepidum and Chloroflexus aurantiacus [18].

PH values of cluster four are alike and near 7.2, while all the PH values of cluster two are below 7.2. 67 % of PH values of cluster one and 72 % of PH values of cluster three are below 7.2 (Fig. 6).

4. CONCLUSION

In this study it was found that Beira Lake polluted water shows fluorescence signatures of Chlorophyll 680 nm and 735 nm and 550nm broad peak which could occur because of various constituents in polluted water and shows absorption signatures of narrow peak near 662 nm, which occurs because of the Chlorophyll-a absorption, a peak near 642 nm which occurs because of the Chlorophyll-b absorption and broad peak around 500 nm which could occur because of green colour of water and various constituents in polluted water.

Beira Lake could be clustered into four with a cophenetic correlation coefficient of 0.76. Cluster one from the locations near Gangarama Simamalakaya, near Sri Uttarananda Mawatha and near floating market shows highest polluted level. And the absorption peak near 775 nm of those places shows an infestation of green photosynthetic bacteria due to stagnation. Highest absorption intensity and lowest fluorescence intensities of polluted constituents show in the upper part of the Lake where currently undergo the high construction of Lotus tower and the park. Thus Beira Lake near Lake House shows two polluted levels. PH measurements of all the locations are in the range of 6.5-7.5.

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