Evaluation of lentic ecosystems from Bucharest City

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Abstract: Bucharest is the capital city and also one of the largest cities in Romania. It disposes of natural and artificial lakes, arranged for different leisure activities and some of them even for bathing. Monitoring and maintaining the quality of lentic ecosystems is important from both an economical and environmental point of view. Several lake water samples were collected from Bucharest city area. The water quality of these lakes was evaluated using, for the first time, fluorescence spectroscopy together with standard indicators (conductivity and pH, oxygen indicators, like dissolved oxygen – DO and chemical oxygen demand – COD and nutrients, specifically nitrates and nitrites). The anthropic influence on the lentic ecosystems was evidenced by the presence of high quantities of ammonia, a clear sign of uncontrolled wastewater spills from the residential settlements on the lake borders. From the fluorescence measurements, various indices were calculated as ratio between regions of the fluorescence maps. A good correlation was found between some of these indices and the standard parameters, thus suggesting that fluorescence spectroscopy might be a potential tool in the monitoring of the lake water quality.

Key-Words: lakes, fluorescence spectroscopy, water quality, chlorophyll, humification, chemical oxygen demand

1 Introduction

Water is the essential element of life; it is found everywhere, from the ground to the sky and in all living things. Human communities use water not only for survival, but also in economical and recreational purposes. Urban water bodies are important due to the large scale of potential external pollutants they are subjected to and their role in the functioning of the metropolitan ecosystems. That is why they have been a topic of particular interest for researchers, trying to understand, model and control the fate and quality of these systems [1-4]. Bucharest is one of the largest cities in Romania, with a surface of 228 km^2 (of which only 6 % represent aquatic ecosystems) and a population of ~ 2 million people [5]. The city disposes of several semi-natural and artificial lakes, arranged for different leisure activities, some of them even for bathing. Also, these lakes represent very important components in maintaining the territorial balance (including the attractiveness) of their locations [6].

Therefore, assessing, monitoring and maintaining the quality of lakes ecosystems of Bucharest city is important from both an economical and environmental point of view. Commonly, for this goal, physico-chemical parameters are recorded, like temperature, turbidity, pH, conductivity, nutrient load, chemical oxygen demand (COD) etc. Some of these investigations are time-consuming and expensive analysis and are not available for field measurements, whereas optically-based measurements allow rapid, low cost, *in situ* analysis.

Fluorescence spectroscopy has been efficiently used, during the last decade to determine and characterize water quality through the dissolved organic matter (DOM) properties and pollution analysis [7, 8]. It was found to be highly suitable for all kinds of water types, from river and lakes to sea, ocean and even glacier water. Although it is not yet standardized, fluorescence spectroscopy can be used as a correlated method with some standard parameters, in order to give a rapid, qualitative evaluation of the state of health of water samples. Its main advantages are rapid measuring time, low sample quantities, *in situ* availability.

The objective of the present study was to describe the quality of several lakes from Bucharest city area, based, for the first time, on the comparison of standard and fluorescence measurements. Special attention was paid to the relationship between various fluorescence indices, like the humification index and the biological index, and physico-chemical parameters. The obtained results might help understand DOM behavior in lacustrine environments and aid in the proper maintenance protocol of these systems.

2 Methods

2.1 Spatial distribution of lakes

For the present study several lakes within Bucharest city area, were chosen. A map with the sampling locations is presented in fig. 1: Moghioros Lake, hereafter named **P1**, Morii Lake – **P2,** both of them located in the western part of the city; Circului Lake– **P3**, in the northern area; Morarilor Lake – **P4**, National Park Lake – **P5** and IOR Lake – **P6** which are located in the eastern part of Bucharest; Carol Lake – **P7** and Tineretului Lake – **P8** in the south-center region of the city.

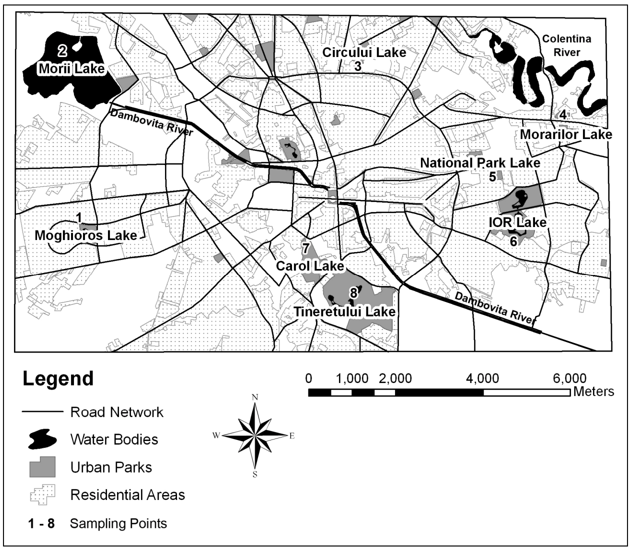


Fig. 1 Map with sampling locations

According to their origin, these lakes can be divided in three main categories:

- Reservoir (P2), on the Dambovita River, with complex function (water flow regulation, assuring water supply in critical situations and leisure activities);
- Anthropic (P1, P4, P5, P6), set up in the cavities resulted after building rocks extraction;
- Semi-naturals (P3, P7, P8), which are superposed above natural lake bowls and modified so as to best fit the urban morphology.

Considering the type of water supply, Bucharest lakes can be grouped in two categories: ones with partial natural water supply (P3, P7 and P8) and others with predominant artificial water supply - groundwater sources with medium and high depth and water supply network (P1; P4; P5; P6). After the bowl characteristics, they are enclosed (P1, P4, P5), partial enclosed (P6, P7) and unenclosed (P3, P8). The unenclosed lakes have big environmental problems due to sediment loading with organic matter.

The major sources that influence water quality in the analyzed lakes from Bucharest city are listed in Table 1. The most common degradation source of lakes derives from the surface runoff leading all ground impurities into the lakes. Another important problem is posed by the overgrowing of the vegetation and the fauna found in these systems, which determined the eutrophication. Some of these lakes are also subjected to important uncontrolled household and restaurant discharges, seriously impacting the state of health of the lentic ecosystems.

Table 1. Water degradation sources for Bucharest lakes

Lake	Water degradation sources
P1	Water enriched with organic and inorganic matter from the slope
P2	Dwellings situated on the lake borders non connected to the sewage network
P3	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, vegetation
P4	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, vegetation
P5	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, vegetation
P6	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, restaurants, vegetation
P7	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, restaurants, vegetation
P8	Water enriched with organic and inorganic matter from the slope, organic matter accumulated in the sediments, restaurants, vegetation

2.2 Sampling

Sampling campaign was performed between May and June 2010, a period with similar climatic and hydrological conditions. The water samples were collected in sterile plastic bottles from the surface layer, at approximately 30 cm. immediately after collection, they were measured *in*-situ for some of the physico-chemical parameters and afterwards transported to the laboratory, where the rest of the measurements were performed in the same day.

2.3 Physico-chemical measurements

The following standard indicators were monitored: water temperature (electronic thermometer, with an error ±0.1ºC), dissolved oxygen (HANNA HI 9145 oxygen meter), pH, conductivity (conductivity and pH meter Consort C352), turbidity (ORION turbidimeter), transparency (Secchi disk), nitrogen compounds (spectrophotometer with sulphanilamide and N-(1-naphtol)-ethylenediamine for nitrate), chemical oxygen demand (USEPA 410.4 through oxidizable organic compounds to reduce dichromate ion to the chromic ion) and free chlorine (adaptation of the EPA 330.5 and Standard Methods for Examination of Water and Wastewater 4500 CI G).

2.4 Spectroscopic measurements

As a modern and rapid method for water characterization, fluorescence spectroscopy has been advanced by the use of tri-dimensional excitation–emission matrix (EEM) spectroscopy, which measures emission spectra across a range of excitation wavelengths, resulting in a landscape surface defined by the fluorescence intensity at pairs of excitation and emission wavelengths [7, 9]. The resulting map represents a fingerprint specific for each aquatic system. The visual "peak-picking" method indicates that the fluorescence of water samples EEMs is given by the DOM found in water, which is composed of two major categories of fluorophores: humic-like and protein-like substances. Humic-like fluorescence is attributed to the presence of humic, fulvic and "marine" humic-like acids, accounting for 40-60% of the organic matter, while the protein-like fluorescence is given by the amino acids, mainly tryptophan and tyrosine.

Fluorescence spectroscopy was applied in the form of EEM, recorded with FLS-920 Edinburgh Instruments spectrofluorimeter equipped with a 450W Xenon lamp and double monochromators, for both excitation and emission. The excitation was set in the wavelength domain of 230-400 nm, with 10 nm step and the emission in the spectral range of 250-500 nm, with 1 nm step, integration time 0.2 s.

Before fluorescence analysis, the absorbance of the samples was measured with Perkin-Elmer spectrometer, in the wavelength domain of 200-500 nm, in order to avoid any concentration errors, such as the inner-filter effect. All samples had absorbance values lower than 0.1 and did not need to be diluted.

3 Results and Discussion

The most important physico-chemical parameters measured are listed in Table 2. pH measurements indicated neutral values for all lakes, with relatively low variations. The lowest value was recorded for the P2 sample (7.39), probably determined by the addition of chlorine-treated water from the distribution network, while the other lakes had pH ranging from 7.42 to 7.89. For P6 and P8 the increase of pH value is influenced by the direct interaction between water and sediments that contain high concentration of $CaCO_3$.

The chemical oxygen demand represents the capacity of a water body to consume oxygen for the decomposition of organic matter or for oxidation of inorganic substances and it is a measure of the degree of water pollution with organic matter [10, 11]. High values of oxygen indicators appeared in P3, P6, P7 and P8 lakes, where COD values were higher than 25 mg O_2/l. Organic loading does not have a direct influence over the dissolved oxygen value for eutrophic lakes, due to the photosynthesis process.

Nitrates values were high in P8, P6, P5 and P4, where water is included in bad ecological category. Nitrite concentrations were under the detection limit for P1-P4 locations, while the highest content was measured for samples P5 and P8, up to 20 times greater that P6 and P7 samples.

The lowest conductivity values were recorded for samples P1 (543 $\mu S/cm^2$) and P2 (413 $\mu S/cm^2$), while the highest values were found for P6 (981$\mu S/cm^2$), P7 (1270 $\mu S/cm^2$) and P8 (1309$\mu S/cm^2$) samples. The higher values were registered in unenclosed and eutrophic lakes, with degradation sources situated in their borders (restaurants, groundwater infiltration).

Also, relief morphometry influences the lake water quality, because large quantities of organic and inorganic matter come from the slope. This situation is characteristic for P3, P6, P7 and P8 lakes.

Table 2. Physico-chemical parameters

	P1	P2	P3	P4	P5	P6	P7	P8
Dissolved oxygen (mg/l)	8.56	7.68	6.33	4.17	5.25	7.83	7.34	9.27
Oxygen saturation (%)	82	74	68	52	56	83	75	96
pH	7.53	7.39	7.57	7.89	7.42	7.82	7.70	7.78
Conductivity (µS/cm^2)	543	413	763	603	691	981	1270	1309
COD	11.50	19.00	34.25	27.0	14.00	25.60	39.60	26.13
Nitrite (mg/l)	0.00	0.00	0.00	0.00	0.22	0.06	0.02	0.43
Nitrate (mg/l)	-	-	0.89	14.84	20.73	9.39	-	26.17
Ammonia (mg/l)	0.03	5.41	5.71	0.03	0.00	3.05	1.67	2.28

After the general quality indicators values, the water quality can be very good (I), good (II), medium (III), bad (IV) and very bad (V). The first quality class encompasses water used for drinking, in the food industry, agriculture, swimming pools, while the last quality class includes water that is unfit for use and constitutes a threat to public health [12].

Table 3. General water quality

	P1	P2	P3	P4	P5	P6	P7	P8
Dissolved O_2	II	II	III	IV	IV	II	II	I
Nitrate	-	-	I	V	V	IV	-	V
Nitrite	I	I	I	I	III	III	II	V
Ammonia	I	V	V	I	I	IV	IV	IV
COD	II	II	III	III	III	III	III	III
O_2 saturation	II	II	III	III	III	II	II	I
General quality	I	II	III	III	III	IV	IV	IV

The general water quality of the chosen lentic systems from Bucharest metropolitan area, described by the dissolved O_2, nitrate, nitrite, ammonia, COD and oxygen saturation (Table 3), indicates that P1 and P2 lakes have the best water quality amongst all investigated lakes. The P3, P4 and P5 lakes have medium water quality, mostly given by the poor level of oxygen indicators (oxygen saturation, COD and dissolved O_2). P6, P7 (fig. 2) and P8 samples are ascribed to the worst water quality category, especially due to large quantities of ammonia input and high values of chemical oxygen demand.

Fig. 2 Degradation sources on P7 lake – vegetation and restaurants

A review of the fluorescence recordings of the eight lakes (P1-P8), in the form of EEMs, with the excitation wavelengths plotted on the y-axis and emission wavelengths on the x-axis is illustrated in fig. 3. The EEM map of a clean river water sample (P9) is also presented, as comparison. All matrices presented in the figure are normalized at the same intensity scale. The EEMs of lakes are described by the emission bands of protein-like fraction, in the range 320-340 nm, at excitation wavelengths of 230-280 nm, with one or two peaks corresponding to tryptophan. The presence of both tryptophan maxima in all lakes samples is, probably, based on the static nature of these water bodies.

The humic substances were detected in all eight spectra, in the emission domain of 380-440 nm, with excitation between 240-250 nm and 310-370 nm. The maximum which appears at lower excitation wavelength is due to the presence of humic acid and the one at longer excitation wavelength is attributed to the fulvic acid.

The P9 sample is characterized just by the presence of humic-like substances, for 230-280 nm excitation wavelengths and emission between 440 and 450 nm, as was noticed in [13]. No obvious contribution of the microbial-derived fluorophores was detected, because the flowing nature of rivers does not allow them to develop any significant bacterial activity, which is highly probable in the case of lakes.

The P2, P3, P4, P6 and P8 samples have similar shapes, showing the presence of both the protein and the humic-like fractions of DOM. Amongst these, P6 and P8 have a more pronounced contribution from the tryptophan maxima than the others. On the other hand, samples P1, P7 and P5 have common features, being characterized by lower intensities of the DOM fractions. P5 sample resembles also the clean river sample, P9, with low microbial content, probably indicating a more ventilated system.

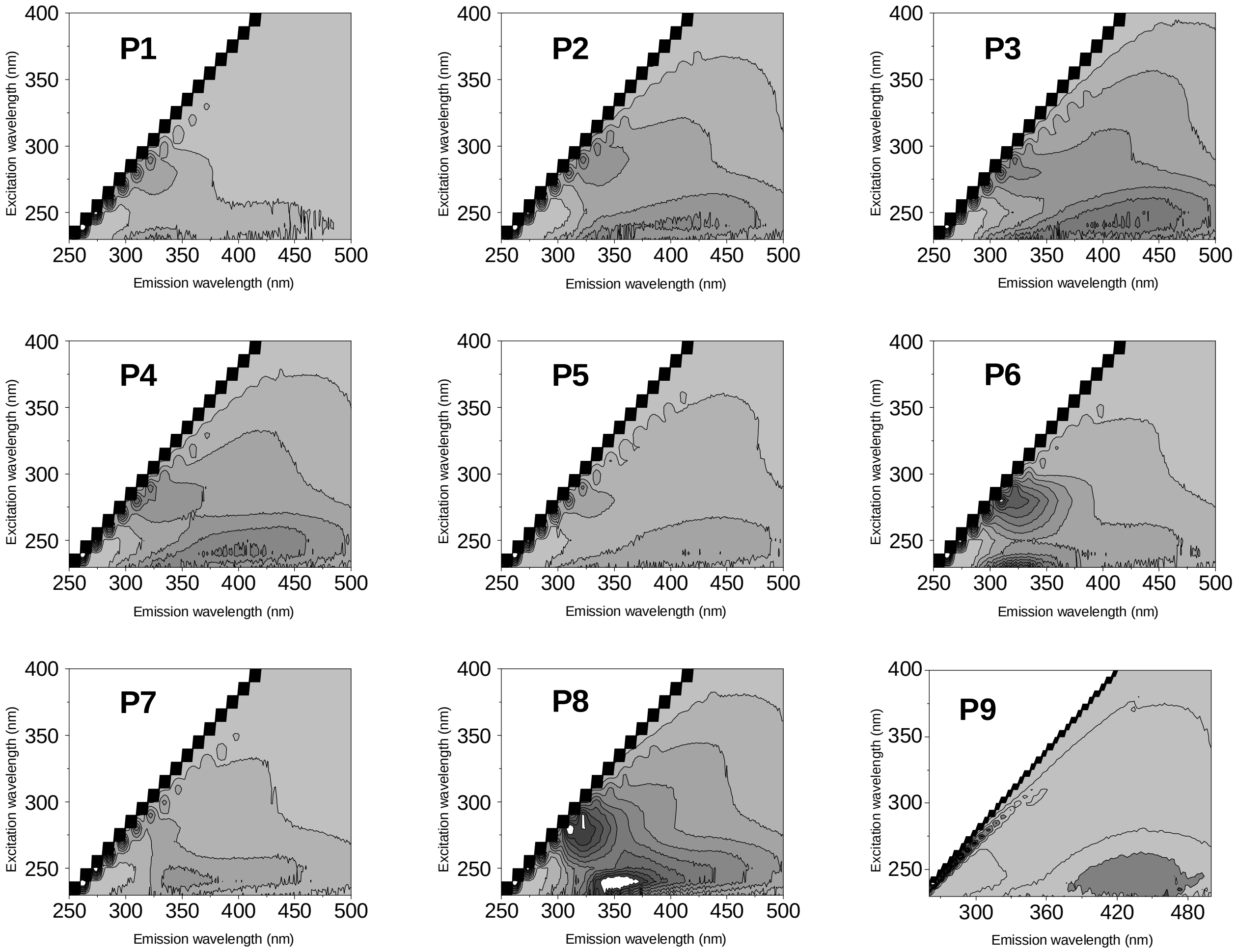
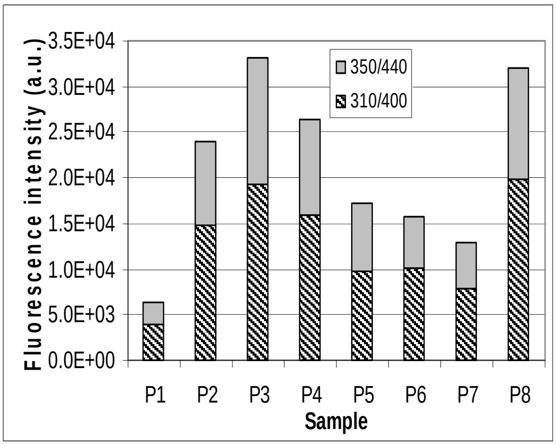


Fig.3 EEM plots of lake water samples (P1-P8) and clean river (P9)

The fact that lakes with different geo-physical attributes have resembling fluorescence spectra indicates that the fluorescence response is not directly influenced by the geo-physical characteristics (type of water source, origin, bowl). Their spectral response is more likely given by the combination of degradation sources to which each system is subjected. The maps show little variations in the location of peaks between the eight lakes. The dissimilarities in the fluorescence behavior consist mostly in intensities of the major peaks. As representative for all our matrices, several ex/em pairs were chosen and their intensities are presented in fig. 4. For the microbially-derived components the 240/355 nm and 280/330 nm pairs were chosen. For the humic-like constituents the relevant ex/em pairs were: 310/400 nm that is representative for the recent production of humic substances and while 350/440 nm, for “old” organic matter. As can be seen from fig. 3, the recent production of humic substances is low as compared with the “old” organic matter.

The most important contribution for all lakes originates from the microbial loading and a lesser input comes from the humic-like substances. The largest amount of DOM, especially protein-like (at excitation wavelength of 240 nm, and emission at 350 nm) can be found in P8 sample, which also fits in the worst general quality standard. This fluorescence maximum can be explained by the water degradation sources, amongst which there are restaurant discharges and birds populations. The large microbially-derived input associates with the fact that P8 has also the highest level of oxygen saturation, conductivity, nitrates concentration and also a very large chemical oxygen demand.

At the other end, there is P1 sample, which shows the lowest DOM concentration, of both protein and humic-like components and fits in the best general quality class. This sample has one of the lowest conductivity, COD and nutrients values.



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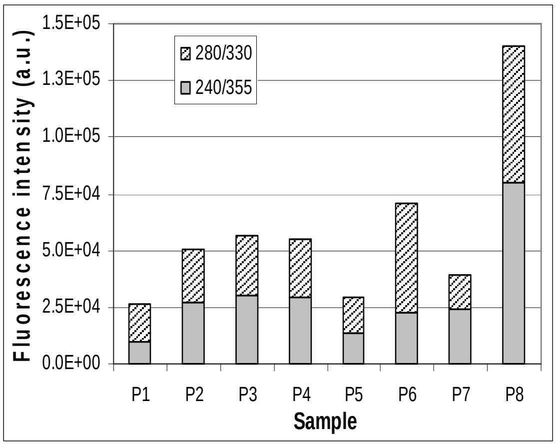


b)

Fig. 4 Fluorescence intensities of a) humic-like and b) protein-like components

Various fluorescence intensity ratios can be used to infer the relative contributions from autochthonous and allochthonous sources in lake ecosystems, to distinguish between humic substances and protein-like compounds. For this purpose, some fluorescence indices were used: humification index, HIX [14] which is able to estimate the degree of DOM maturation, the biological index, BIX [15], dedicated to characterize the autochthonous inputs, the f_{500}/f_{450} index, denoting DOM origin [16] and the T/C ratio [17], for the balance of tryptophan and humic substances.

The values of these indices for the eight lake water samples are summarized in Table 4.

Table 4. Fluorescence indices

	HIX	BIX	f_{500}/f_{450}	T/C
P1	0.64	1.11	1.29	5.89
P2	2.21	1.1	1.25	2.55
P3	1.87	0.96	1.25	1.81
P4	1.69	1.01	1.27	2.30
P5	1.80	0.91	1.18	1.97
P6	0.59	1.26	1.37	7.30
P7	0.97	1.27	1.39	2.77
P8	0.80	1.31	1.37	4.31

The humification index, indicator of the content of humified materials, was calculated using the following formula: $HIX = \sum F_{435\rightarrow 480} / \sum F_{300\rightarrow 345}$, for excitation with 254 nm wavelength. The humification index gives qualitative details about the water samples and the degree of DOM maturation.

The biological index, BIX, can give information about the organic matter source and it was calculated as ratio of fluorescence emission intensity $BIX = F_{380} / F_{430}$ when excited with 310 nm wavelength. This ratio is related to the recent autochthonous production of humic substances.

All four fluorescence indices that were calculated for the lake water samples are plotted in fig.5. HIX values for all investigated samples were in the range of 0.59 - 2.11, indicating the presence of bacterial organic matter, of autochthonous origin and less DOM humification degree. All samples had BIX values between 0.91 and 1.37, denoting that lakes are characterized by predominantly autochthonous origin of DOM and organic matter freshly released into water [14]. This is easy to understand, considering that the major water degradation sources of these lakes come from run-off, vegetation and aquatic bird populations. The lake samples all had lower HIX and higher BIX values than those obtained for other aquatic systems (sewage impacted river, canal and pond) [8]. In contrast, the river sample (P9) shows high value for HIX and low value for BIX in comparison with lakes P1-P8, denoting that this sample is characterized by a larger fraction of humic-like substances as compared to the protein-like component.

The lowest BIX values were recorded for P3, P4 and P5 samples, which also had the lowest dissolved O_2 and oxygen saturation levels. The humic substances are “older”, originated from bottom sediments and vegetation, with no recent production of humic-like material.

The f_{500}/f_{450} values (1.18-1.39) and the T/C index (4.31-7.30) suggested high protein-like components of predominantly allochthonous origin. The lake water degradation is principally due to the presence of bird communities and run-off from the lake shores. For P3 and P7 samples, in which the water level is adjusted using water from the public distribution system, a lower microbial contamination (1.81-2.77) was detected, probably due to a larger chlorine input.

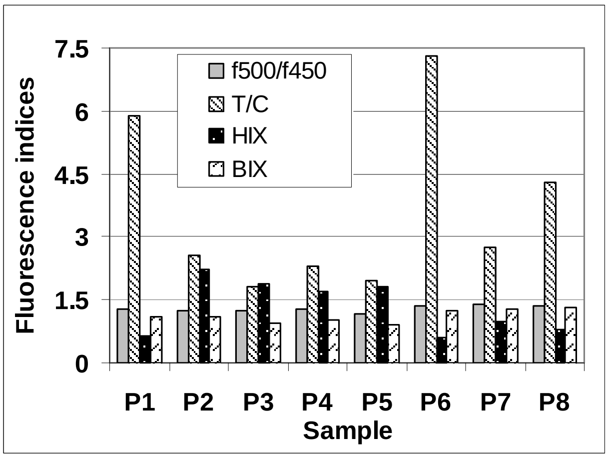


Fig. 5 Calculated fluorescence indices for lake water samples

Eutrophication is one of the problems affecting the lakes in plain areas of Romania; many of them are eutrophic, as a result of nutrients input from different anthropic sources [18]. Fig. 6 illustrated one of the lakes which are most affected by eutrophication, P8.

Fig. 6 Eutrophication in P8 lake

Eutrophication is directly connected with a phytoplankton bloom, represented in the fluorescence analysis by the presence of chlorophyll-a (fig. 7). Chlorophyll-a signal was recorded at 680 nm emission, when excited with 420 nm wavelength. The highest concentrations were found in P3, P4, P6, P7 and P8 samples.

The eutrophication level of Bucharest lakes is influenced by the morfometric characteristics (depth, bowl structure), meteorological conditions, human intervention (water supply, wastewaters discharge and aquatic vegetation management), other intake (e.g. runoff) and the nutrients concentration. In Bucharest, the eutrophic lakes are frequently characterized by high slopes on the borders, aquatic birds' communities (P3, P6, P7, P8), high level of organic matters in sediments (P8, P3) and degradation sources on the border (P2, P6, P7, P8).

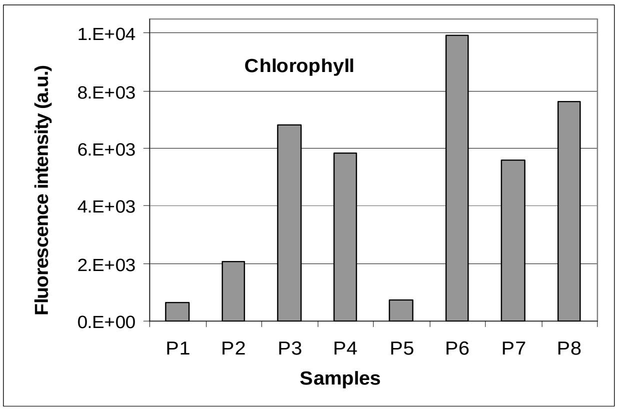


Fig. 7 Chlorophyll-a distribution

The chlorophyll-a concentration derived from the fluorescence spectra was well correlated with the values of COD (Table 2), as illustrated in fig. 8. The correlation coefficient (approximately 0.69) is easy to understand, considering that high COD values are given by the fact the putrefaction cells of the phytoplankton are oxygen consumers, using this element for the decomposition processes. Therefore, higher chlorophyll values involve more decomposition processes and higher demand for oxygen.

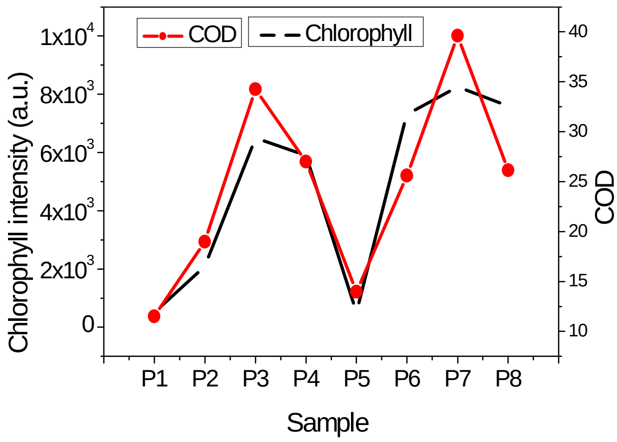


Fig. 8 Correlation between chlorophyll-a content and COD

In order to evaluate the ability of fluorescence to be used as an alternate method for the standard chemical analyses, the degree of correlation between the fluorescence indices and the chemical parameters was calculated.

The humification index could be correlated only with the turbidity (fig. 9), with a correlation coefficient (r^2) of approximately 0.62. The relationship between the two is probably due to the fact that higher turbidity values are connected with a larger content of humified dissolved organic matter.

On the other hand, the biological index was best correlated with pH (r^2~0.67) and conductivity (r^2~0.73), as illustrated in fig. 10a. Conductivity is a pollution indicator, which could denote a microbial loading and thus correlate with the biological index. pH values can also be influenced by the type of pollution within a specific water system.

Just like BIX, the f_{500}/f_{450} index showed the strongest correlation with the pH (r^2~0.65) and conductivity (r^2~0.78), shown in fig. 10b. The elevated conductivity values correlated with the higher f_{500}/f_{450} values, both representatives for allochthonous organic matter of terrestrial origin, mostly from lakeshore leaching.

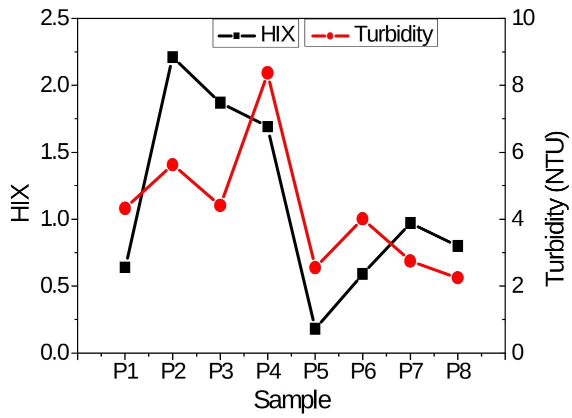
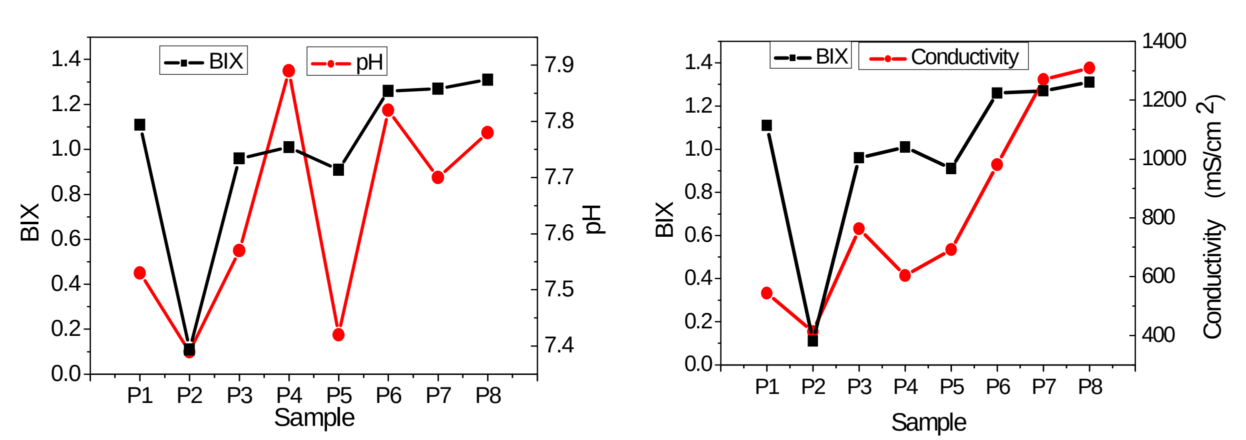


Fig. 9 Correlation between HIX and turbidity

The T/C index showed similar trend with the oxygen indicators, both dissolved oxygen (r^2~0.62) and oxygen saturation level (r^2~0.65), as can be seen in fig. 10c.



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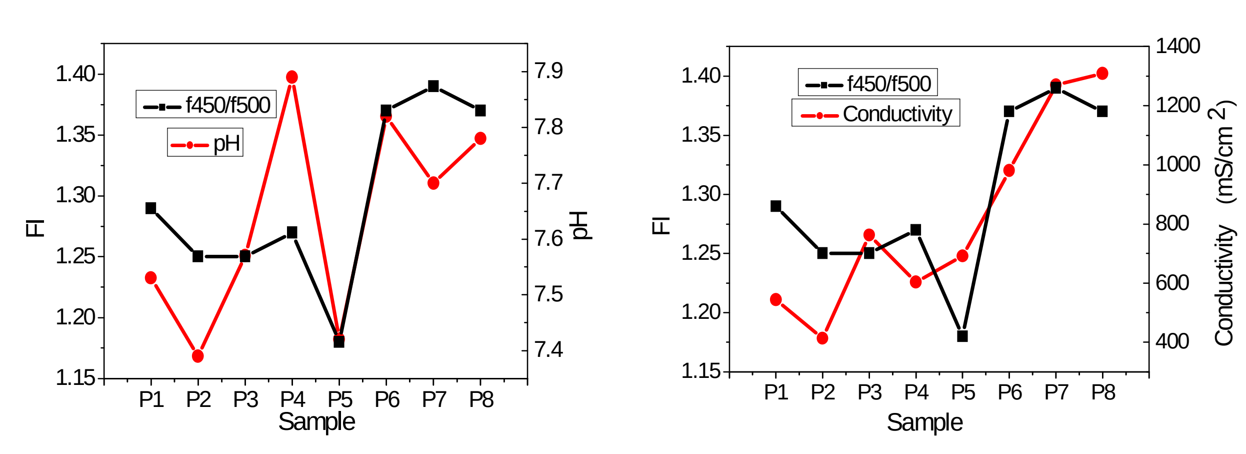

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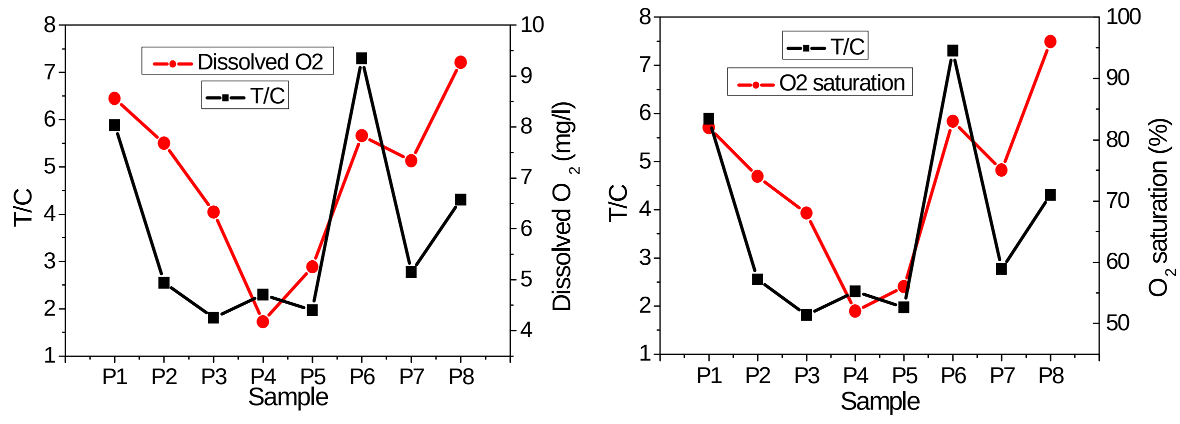

c)

Fig. 10. Correlation between fluorescence indices and standard water parameters

The correlation coefficients between the fluorescence indices and the standard water parameters values point out the ability of fluorescence spectroscopy in the rapid and low cost qualitative assessment of the lentic systems.

4 Conclusions

Fluorescence spectroscopy and standard physico-chemical parameters analysis put in evidence the characteristics of some lakes from Bucharest city, whose quality is directly influenced by the surrounding environment's features.

An important microbial content was found in all lakes coming from the external water degradation sources, amongst which there are restaurant discharges and birds populations. Humification index values (between 0.59 and 2.21) and biological index values (0.91-1.37) indicated the presence of bacterial organic matter, with very low DOM humification degree.

The f_{500}/f_{450} values (1.18-1.39) and the T/C index (4.31-7.30) suggested high protein-like components of predominantly allochthonous origin. The lake water degradation is principally due to the presence of bird communities and run-off from the lake shores. For two lakes, in which the water level is adjusted using water from the public distribution system, a lower microbial contamination (1.81-2.77) was detected, probably due to a larger chlorine input.

The chlorophyll-a values determined by fluorescence spectroscopy matched very well with the COD and denoted stronger eutrophication of some lakes.

The obtained results show that fluorescence spectroscopy fairly evaluated the health state of several lakes from Bucharest city. According to the measurements performed, it appears that lake water quality is not directly influenced by the geological characteristics (type of lake, origin, bowl), but more likely by the flora, fauna and the combination of anthropogenic degradation sources to which each lentic system is directly subjected to.

The correlation between the fluorescence indices and various standard physico-chemical parameters indicates that fluorescence spectroscopy appears to be suitable for the evaluation and monitoring of the health of water systems thus providing the opportunity for real-time, *in situ*, qualitative assessment of the quality of lentic systems.

These results are very important in order to promote the implementation of the actions of Local Environmental Action Plan and the Sustainable Development Strategy [19].

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