

Spectroscopic and physico-chemical evaluation of lentic ecosystems from Bucharest City

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Abstract: Bucharest is one of largest cities in Romania and 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 area and characterized, for the first time by both physico-chemical parameters and spectroscopic methods. The standard quality indicators used are ascribed to general indicators (conductivity and pH), oxygen indicators (dissolved oxygen, chemical oxygen demand – COD) and nutrients (nitrates). The spectroscopic methods applied for the study of water quality were UV-Vis absorption and fluorescence spectroscopy. Various fluorescence indices were calculated as ratio between regions of the fluorescence maps. A good correlation was found between 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 purposes (industry, leisure, etc.). Bucharest is one of the largest cities in Romania, with a surface of 228 km² (only 6 % of which represent aquatic ecosystem) and a population of ~ 2 million people [1] and disposes of several semi-natural and artificial lakes (along Colentina River, in majority of urban parks and on the Dambovită River), arranged for different leisure activities and some of them even for bathing. Also, these lakes represent very important components in maintaining the territorial balance (including the attractiveness) of their locations [2].

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 are time-consuming investigations and are not available for field measurements.

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. Fluorescence spectroscopy has been efficiently used, during the last decade to determine and characterize water quality and dissolved organic matter (DOM) properties [3-5].

The objective of the present study was to describe the quality of several lakes from Bucharest city, based, for the first time, on the comparison of standard and fluorescence measurements. Special attention was paid to the relationship between fluorescence indices and physico-chemical parameters. The obtained results might help understand DOM behavior in lacustrine environments.

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**; Circului Lake– **P3**; Morarilor Lake – **P4**; National Parc Lake –**P5**; IOR Lake – **P6**; Carol Lake – **P7** and Tineretului Lake – **P8**.

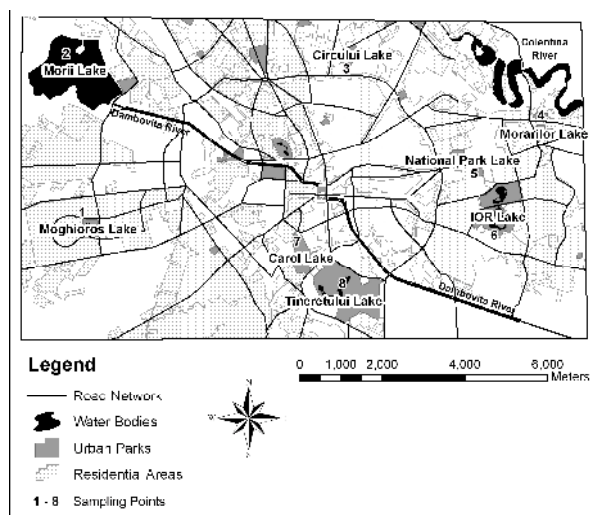


Fig. 1. Map with sampling location

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

- Reservoir (P2), on the Dambovitza River, with complex function (water flow regulation, assuring water supply in critical situation, and leisure activities);
- Anthropic (P1, P4, P5, P6), set up in cavity resulted after building rocks extraction;
- Semi-naturals (P3, P7, P8), which are superposed above natural lake bowl and modified for be adapted to urban morphology.

In Bucharest, after water supply, we identify two categories of lakes: with partial natural water supply (P3, P7 and P8) and predominant artificial water supply - groundwater sources with medium and high depth and water supply network (P1; P4; P5; P6).

After the bowl characteristics, Bucharest lakes 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.

Table 1. Water degradation sources for Bucharest lakes

Lake	Water degradation sources
P1	Pluvial waters
P2	Dwelling situated on the lake border non connected to sewage network
P3	Pluvial waters, vegetation, sediments from lake bottom, aquatic birds
P4	Pluvial waters, vegetation
P5	Pluvial waters, vegetation
P6	Pluvial waters, vegetation, sediments from lake bottom, restaurants, aquatic birds
P7	Vegetation, aquatic birds, restaurants, pluvial waters
P8	Sediments from lake bottom, vegetation, birds, restaurants, pluvial waters

2.2 Physico-chemical measurements

Sampling campaign was realized between May and June 2010, with similar climatic and hydrological condition. The following indicators were monitored: water temperature (electronic thermometer, with an error $\pm 0.1^\circ\text{C}$), 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-naphthol)-ethylenediamine for nitrate), chemical oxygen demand (USEPA 410.4 through oxidizable organic compounds 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 Cl G) (Table 2).

Table 2. Physico-chemical parameters

	Dissolved oxygen mg/l	Oxygen saturation %n	pH	Conductivity $\mu\text{S}/\text{cm}^2$	COD mg/l	Nitrite mg/l
P1	8.56	82	7.53	543	11.50	0.00
P2	7.68	74	7.39	413	19.00	0.00
P3	6.33	68	7.57	763	34.25	0.00
P4	4.17	52	7.89	603	27.00	0.00
P5	5.25	56	7.42	691	14.00	0.22
P6	7.83	83	7.82	981	25.60	0.06
P7	7.34	75	7.70	1270	39.60	0.02
P8	9.27	96	7.78	1309	26.13	0.43

pH measurements indicate neutral values for all lake water samples, with relatively low variations. The lowest pH value was recorded for the P2 sample (7.39) while the other lakes had pH ranging from 7.42 to 7.89. This situation is determined by the supplying water quality. 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 .

High values of oxygen indicators appear in

P3, P6, P7 and P8 lakes, where COD values were higher 25 mg O₂/l. Organic loading does not have a direct influence over the dissolved oxygen value for eutrophic lakes, due to the photosynthesis process.

Nutrients values were high in P8, P5, P3 and P6, where water is included in very bad ecological category.

The lowest conductivity values were recorded for samples P1 (543 µS/cm²) and P2 (413 µS/cm²), while the highest values were found for P6 (981 µS/cm²), P7 (1270 µS/cm²) and P8 (1309 µS/cm²) samples. The high values appear in unenclosed and eutrophic lakes, with degradation sources situated in their borders (restaurants, groundwater infiltration).

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 than P6 and P7 samples.

2.3 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 [3, 6]. 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 describes peaks that are ascribed to amino acids, mainly tryptophan and tyrosine.

Fluorescence spectroscopy was applied in the form of EEM, recorded with FL-920 Edinburgh Instruments spectrofluorimeter equipped with a 450 W 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 interference from concentration errors, such as inner-filter effect. All samples had low absorbance values (<0.1) and did not need to be diluted.

A review of EEMs for eight lakes (P1-P8) with the excitation wavelengths plotted on the y-axis and emission wavelengths on the x-axis is illustrated in fig. 2. The EEM map of a clean river water sample (P9) is also presented, as comparison. The EEMs of lakes are described mainly by the emission bands of protein-like fluorophores, in the emission range 320-340 nm, at excitation wavelengths of 230-280 nm, with one or two peaks corresponding to tyrosine or tryptophan. The fluorescence signal of the humic substances was recorded in the emission domain of 380-440 nm, with excitation between 240-250 nm and 310-370 nm. As noted in other studies [7], clean river samples exhibit only the humic-like substances, which is observed at P9 sample, 230-280 nm excitation wavelengths and emission between 440 and 450 nm. 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.

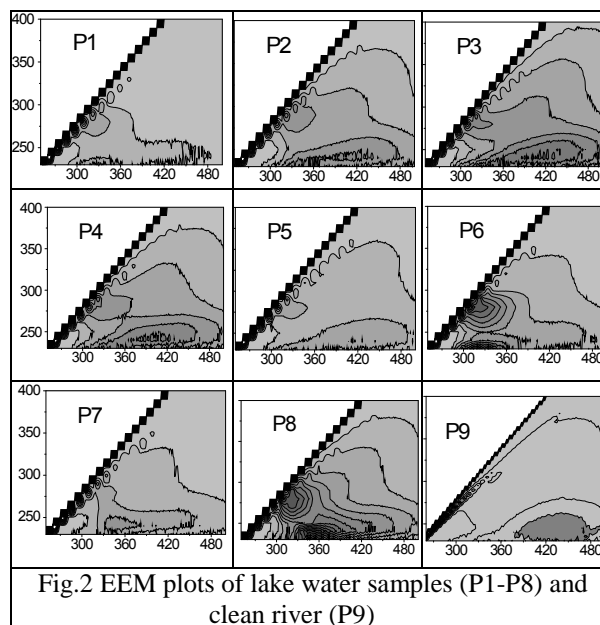


Fig.2 EEM plots of lake water samples (P1-P8) and clean river (P9)

The maps show little variations in the location of peak intensities and overall shapes between the eight lakes. The dissimilarities in the fluorescence behavior consist mostly in intensities of the major peaks. As representative for all our matrices, following ex/em pairs were chosen: 240/400 nm;

280/330 nm that is related to microbial derived components; for humic-like constituents the relevant ex/em pairs were: 310/390 nm that corresponds to recent production of humic substances and 350/440 nm for “old” organic matter. In Fig.3 the relative percentage for these representative peaks are presented. For 240 nm excitation wavelength, emission can occur for both protein-like (ex/em=240/350p) and humic-like components (ex/em=240/400h).

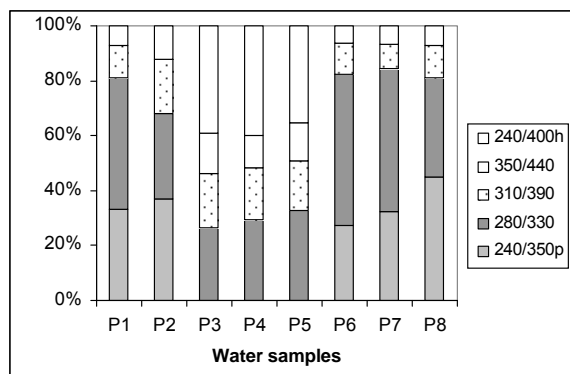


Fig. 3 Fluorescence fractions corresponding to protein-like and humic-like components

As can be seen in fig. 3 the most important contribution for all lakes originates from the microbial loading and a smaller input comes from the humic-like substances. At excitation wavelength of 240 nm, an intense emission was noticed at 350 nm for sample P8, and likewise for samples P6 and P7, but with lower intensities. This maximum can be explained by the water degradation sources, amongst which there are restaurant discharges and birds populations. For samples P2 - P5, high intensities of the humic substances were signaled for both ex/em = 240/440 nm and 350/440 nm, probably due to the contribution from pluvial water, lake shores and vegetation.

2.4 Fluorescence indices

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 [8] which is able to estimate the degree of DOM maturation, the biological index, BIX [9], dedicated to characterize the autochthonous inputs, the fluorescence index (FI), denoting DOM origin [10] and the T/C ratio [11], for the balance of

tryptophan and humic substances. The values of these indices are summarized in Table 3.

Table 3. Fluorescence indices

	HIX	BIX	FI	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	1.8	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	0.8	1.31	1.37	4.31

The humification index, indicator of the content of humified materials, was calculated using the formula first introduced by Zsolnay [8]: $HIX = \sum F_{435 \rightarrow 480} / \sum F_{300 \rightarrow 345}$, when excited with 254 nm wavelength. Although the chosen excitation wavelength does not give the maximum fluorescence intensity of any fluorophore band, it 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 a ratio of fluorescence intensity F_{380} / F_{430} at 310 nm excitation wavelength. This ratio is related to the recent autochthonous production of humic substances.

HIX and BIX values for lake water samples were plotted in fig.4. 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 [10]. All samples had BIX values between 0.91 and 1.37, denoting that lake waters are characterized by predominantly autochthonous origin of DOM and organic matter freshly released into water [10]. 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) [7]. 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, and are correlated with the

lowest dissolved O₂ and oxygen saturation levels (Table 2). The humic substances are “older”, originated from bottom sediments and vegetation, with no recent production of humic-like material.

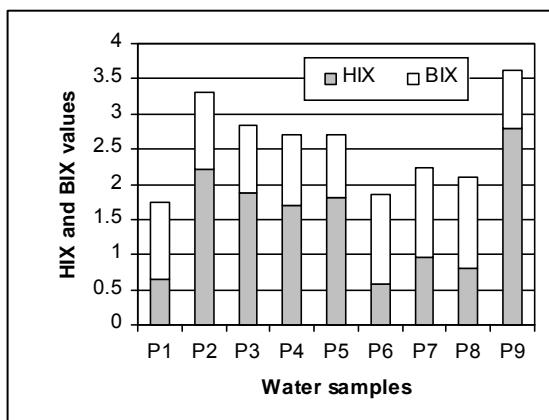


Fig.4. HIX and BIX indices for lake water samples

The index FI, as the ratio of the fluorescence intensity recorded at 450 and 500 nm, for excitation wavelength of 370 nm, discriminates between allochthonous and autochthonous organic matter origin. All samples had FI values around 1.18-1.39, suggesting a mixture of allochthonous and autochthonous organic matter based on classification made by McKnight [10]. This is in agreement with the fact that all lakes are influenced both by internal and external sources, such vegetation, bird populations and decay of terrestrial plant material and subsequent leaching of partial decomposition products.

Finally, the T/C ratio which is similar to HIX was calculated as the maximum recorded signal of tryptophan (ex/em in the domains 270-280/320-350 nm) and humic-like substances (ex/em range 330-350/420-480 nm). The values of T/C ratio divide the lakes in two categories, with more (4.31 - 7.30) or less (1.81 - 2.77) microbial contribution. High protein-like components for P1, P6 and P8 samples are the results of birth presence and run-off from the lake shores. P3 and P5 samples present less microbial contamination, probably influenced by the fact that the water level of these lakes is adjusted using water from the public distribution system.

Eutrophication is directly connected with a phytoplankton bloom, represented in the fluorescence analysis by the presence of chlorophyll (fig. 5). Chlorophyll signal was recorded at 680 nm emission, when excited with 420 nm wavelength. High chlorophyll concentrations were found in P3, P4, P6, P7 and P8 samples which correlated well with the values

of COD obtained for these samples (Table 2). The high COD values are given by the fact the putrefaction cells of the phytoplankton are oxygen consumers, using this element for the decomposition processes.

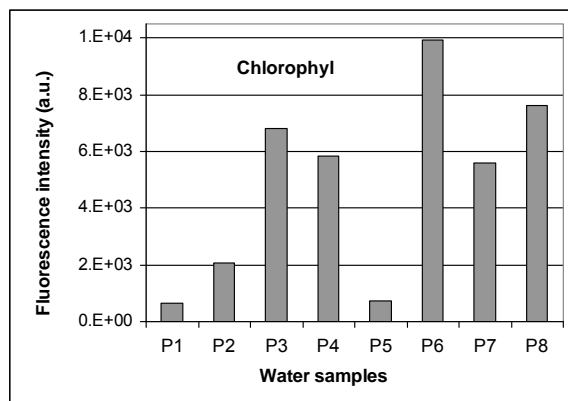


Fig.5. Chlorophyll distribution lakes

Eutrophication level of Bucharest lakes is influenced by the morfometric characteristics (depth, bowl structure), meteorological condition, human intervention (water supply, wastewaters discharge, water vegetation mown), other intake (e.g. runoff) and the nutrients concentration. In Bucharest, the eutrophic lakes are frequently where are high slope (P3, P6, P7, P8), aquatic birds communities (P3, P6, P7, P8), direct contact water-sediments (P8, P3) and degradation sources on the border (P2, P6, P7, P8).

3 Conclusions

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

An important microbial content was found in all lakes coming from 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, of autochthonous origin, with very low DOM humification degree, of predominantly autochthonous origin. The FI values in the range of 1.18-1.39 denoted a mixture of allochthonous and autochthonous DOM sources. The T/C index suggested high protein-like components (4.31 - 7.30) in lakes with degradation sources due to birds' presence

and run-off from the lake shores. For lakes in which water level is adjusted using water from the public distribution system, a lower microbial contamination (1.81 - 2.77) was detected.

The chlorophyll values determined by fluorescence spectroscopy matched very well with the COD.

The study results indicate that fluorescence spectroscopy fairly evaluated the health state of several lakes from Bucharest city. According to the measurements performed, there are no obvious differences between lake type (natural or anthropogenic), the only differences being derived from the surrounding ecosystems, the flora, fauna and leisure activities that are available for each lake. Fluorescence spectroscopy appears to be suitable for the evaluation and monitoring of the health of water systems, providing the opportunity for real-time, *in situ* qualitative monitoring of the quality of water systems.

Acknowledgement

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References:

- [1] Ioja, C., *Methods for environmental quality assessment in Bucharest metropolitan area*, University of Bucharest Press, Bucharest
- [2] Ioja, C., Patroescu, M., Nita, M., Rozyłowicz, L., Vanau, G., Ioja, A., Onose, D. Categories of residential spaces by their accessibility to urban parks - indicator of sustainability in human settlements case study: Bucharest, *WSEAS Transactions on Environment and Development*, 2010, pag. 32-44
- [3] Coble P.G., Characterisation of marine and terrestrial dissolved organic matter in seawater using excitation emission matrix spectroscopy, *Marine Chemistry*, **51** (1996), 325-346
- [4] Hudson N., Baker A., Reynolds D., Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review, *River Research and Applications*, **23** (2007), 631-649.
- [5] Pfeiffer E., Pavelescu G., Baker A., Roman C., Ioja C., Savastru D., Pollution analysis on the Arges River using fluorescence spectroscopy, *Journal of Optoelectronics and Advance Materials*, **10** (6) (2008), 1489 – 1494
- [6] Sierra M.M.D., Giovanela M., Parlanti E. Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques, *Chemosphere* **58** (2005), pp. 715-733.
- [7] Cârstea, E.M., Ghervase, L., Pavelescu, G., Savastru, D., Assessment of the anthropogenic impact on water systems by fluorescence spectroscopy, *Environmental Engineering and Management Journal*, **8** (2009), No.6, pp.1321-1326
- [8] Zsolnay, Á., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F., Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying, *Chemosphere* **38**, (1999), pp.45-50
- [9] Huguet, L. Vacher, S. Relexans, S. Saubusse, J.M. Froidefond, E. Parlanti, Properties of fluorescent dissolved organic matter in the Gironde Estuary, *Organic Geochemistry* **40**, (2009) pp. 706-719
- [10] McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, *Limnol. Oceanogr.* **46**, (2001), pp. 38-48
- [11] Baker, A., Fluorescence excitation-emission matrix characterisation of some sewage impacted rivers. *Environmental Science and Technology*, **35**, (2001), pp.948-953