Preliminary water quality characterization of urban lakes using a state of the art optoelectronic technique

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Urban lakes are large water bodies that provide several ecosystem services in cities. Hence, urban lakes are highly vulnerable to human influences. The paper aimed to highlight spatial and temporal variability of dissolved organic matter in three urban lakes using a state of the art optoelectronic technique, and to establish a relationship between fluorescent dissolved organic matter and water quality parameters. Water quality was monitored using standard methods and fluorescence indices. The results present high relevance for improving water quality management in urban areas, which become a critical components in addressing urban resilience and sustainability.

(Received November 16, 2023; accepted November 24, 2023)

Keywords: Urban lakes, Fluorescence spectroscopy, Dissolved organic matter

1. Introduction

During the last decades, an increasing number of techniques have been developed with the aim to improve water quality characterization and monitoring of dissolved organic matter [1-2]. An advanced and innovative technique, fluorescence spectroscopy, which has been successfully used in different scientific fields, such as biology, medicine or chemistry, is a promising approach for the evaluation of aquatic organic compounds. Florescence spectroscopy, in the form of excitation-emission matrices, can be used to determine the concentration and composition of aquatic dissolved organic matter.

Fluorescence spectroscopy is a fast, high-sensitivity optoelectronic method that has several advantages: requires simple sample treatment procedures prior to analysis, does not use hazardous substances and can measure small quantities of sample. As the intensity and shape of the fluorescence spectra is given by the concentration and chemical composition of the dissolved organic matter, fluorescence spectroscopy can provide spectral fingerprints associated to different types of aquatic systems (rivers, lakes, seas). These fingerprints are influenced by physical and morphological features of the area where the water systems are located, and which are of great interest when it comes to a deeper understanding of ecosystems [3-9].

Fluorescent dissolved organic matter represents a heterogeneous mixture of poorly described compounds, which can include: proteins, pigments, lignin derived phenols, humic substances and hydrocarbons. Fluorescent dissolved organic matter is present in every aquatic system, influencing biogeochemical cycles in the water [1]. However, fluorescence signal is generally referred to as protein-like and humic-like, based on the similarity with standard solutions of protein and humic substances. The fluorescence of proteins is given mainly by two aromatic amino acids (tyrosine and tryptophan) and indicates the bacterial activity in the water samples [1]. The fluorescence of humic substances indicates the presence of organic matter from soils and sediments [10]. Fluorescence spectra with hydrocarbons signal indicates oil contamination of the sample [11-13]. Lignin derived phenols originate from natural human sources (e.g. industrial and household wastewaters, vegetation). The physical phenomenon of fluorescence can be described as the emission of light by molecules called fluorophores, excited by an external light source, with a preset wavelength, at a higher wavelength than the excitation radiation. Thus, fluorescence spectroscopy provides detailed information about the electronic transitions and interactions that occur in a molecular system, being able to provide valuable information regarding the state of a physical, chemical or biological system through the study of its photophysical properties [14-16]. It has been applied in previous studies for the characterization of seawater [2], freshwater [17] or coastal water [18], proving its versatility for characterization of organic matter from different types of aquatic systems. Along with fluorescence spectroscopy, researchers have utilized other optoelectronic techniques in order to determine the water quality parameters. One such method is ultraviolet-visible (UV-Vis) spectroscopy, which offers an effective means through which qualitative analysis and quantitative detection of contaminants from a water environment can be performed [19]. However, fluorescence spectroscopy provides greater sensitivity and selectivity in determining specific compounds compared to UV-Vis spectroscopy. In addition, fluorescence spectroscopy correlates well with standard water quality parameters, such as chemical oxygen demand, biochemical oxygen demand or total organic carbon [1].

Urban lakes are extensive water bodies that provide several ecosystem services in cities [20]. They reduce the impact of urban runoff [21], provide cultural services [22], supply cities with food and water [23] and help at adapting to climate change [24]. Due to their impact on the urban environment, several studies have been made to assess composition and characteristics of dissolved organic matter in lakes [3,5,25-32]. However, urban lakes are highly vulnerable to human influences, such as changes in lake surface, to water pumping, wastewater discharges [25,33]. Also, urban lakes connected to rivers can act as sinks or transformation media for pollutants and dissolved organic matter [26,34]. Thus, more studies are needed to understand the spatial and temporal changes of dissolved organic matter and its interaction with pollutants. Moreover, inconsistencies have been observed in relating pollutants to dissolved organic matter [32].

The purpose of this study was to highlight spatial and temporal variability of dissolved organic matter in urban lakes using a state of the art optoelectronic technique. In addition, the study aimed to establish a relationship between fluorescent dissolved organic matter and standard water quality parameters.

2. Experimental

2.1. Study area

Three urban lakes have been included in the study, from different locations across Romania (Fig. 1): Morii Lake (Bucharest), Ciurel Lake (Targu Jiu), and Portile de Fier I Lake (Orsova). Morii Lake is the largest reservoir in Bucharest, with an area of 246 ha. It is an anthropogenic dam lake built along the Dambovita River, being surrounded by a mixed functional and highly dynamic area (collective housings, unused industrial spaces, individual homes, floodable areas and abandoned land fields). It has a history of water quality monitoring and is easily accessible for different measurements. The 10 collection points used for this study are presented in Fig. 1.

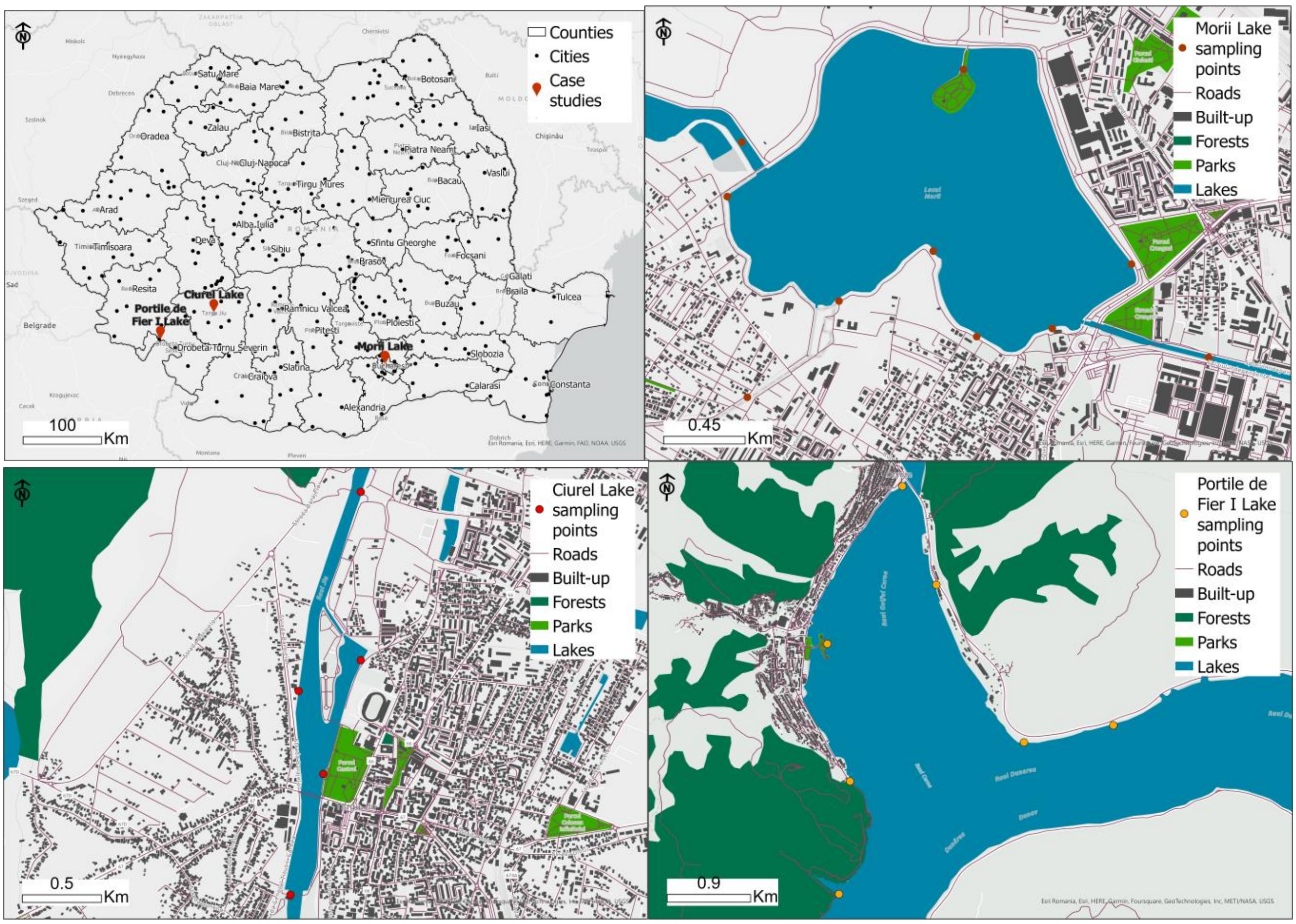

Fig. 1. Water quality monitoring network for the three case studies Morii Lake Ciurel Lake Portile de Fier I Lake (Esri Romania, Esri, HERE, Garmin Foursquare, GeoTechnologies, Inc, METI/NASA, USGS) (color online)

The sampling points were selected in order to identify the influence of Dambovita River, the input from the Arges channel, and green and constructed areas on lake water quality. Ciurel Lake is located along Jiu River and has an area of 56 ha. It is located in Targu Jiu, which is a city with average land use dynamics. Ciurel Lake is an anthropogenic lake and its right banks are covered by residential and industrial areas, while the left bank is covered by green spaces. The five sampling points are shown in Fig. 1. Portile de Fier I Lake is the largest lake in Romania, covering a surface of 25,300 ha, and is located along the Danube River, near Orsova city. The area has an average land use dynamics. The banks of Portile de Fier I Lake are characterized by constructed and forested lands. The sampling points from Portile de Fier I Lake are displayed in Fig. 1. Samples were collected in the spring and summer of 2017, using precleaned sample bottles, and were kept at 4° C prior to measurements.

2.2. Methods

2.2.1. Ancillary measurements

The following water quality parameters have been measured: temperature, pH, dissolved oxygen, nitrites, phosphates, phosphorus and chemical oxygen demand. Water temperature and pH were measured in situ with a C6030 multiparameter (Consort, Belgium) and dissolved oxygen with a HI9146 multiparameter (Hanna Instruments, USA). Nitrites were measured using a CECIL 1100 (UK) spectrophotometer. Chemical oxygen demand was determined using a standard titration method (SR ISO 6060-96).

2.2.2 Fluorescence measurements

Fluorescence excitation-emission matrices were recorded with an Edinburgh Instruments FLS920 spectrofluorimeter using the following parameters: excitation wavelength range 250-370 nm, 30 nm step, emission wavelength range 270-500 nm, 1 nm step and 0.2 s integration time. For each sample, three fluorescence matrices were registered, the values of the fluorescence peaks representing the average of the 3 measurements.

The fluorescence spectra were processed using the peak-picking method, as described by Coble et al. [10]. Fiver major peaks were determined: peak T ($\lambda_{exciattion}/\lambda_{emission}$ 225 (280) / 350 nm), peak B ($\lambda_{exciattion}/\lambda_{emission}$ 225 (280) / 305 nm), peak A ($\lambda_{exciattion}/\lambda_{emission}$ 225 / 400-500 nm), peak M ($\lambda_{exciattion}/\lambda_{emission}$ 310-320 / 380-420 nm) and peak C ($\lambda_{exciattion}/\lambda_{emission}$ 300-350 / 400-500 nm) [10]. Peaks T and B are associated with living or dead cellular matter and their byproducts, indicating the presence of microbial activity within the tested aquatic systems as well as matter derived from different anthropogenic activities [35-36]. The amino acid standards (tryptophan and tyrosine) fluoresce in the optical region of peaks T and B, thus being generically referred to as tryptophan-like and tyrosine-like. Peaks A, C and M are associated with humic-like matter, from autochthonous (peak M) and allochthonous sources (peaks A and C). [37].

The humification index (HIX) indicates the degree of humification and was calculated using the following formula:

$$HIX = \frac{\sum(F_{435} - F_{480})}{\sum(F_{300} - F_{345})}$$

where $F_{300} – F_{345}$ and $F_{435} – F_{480}$ represent the fluorescence intensities in the mentioned wavelength ranges, with the excitation wavelength set at 254 nm [18]. The biological index (BIX) shows the biological activity in water samples. BIX was calculated as the ratio between the fluorescence intensities registered at 380 nm and 430 nm respectively, at an excitation wavelength of 310 nm [18]. The F_{450}/F_{500} index represents the ratio between the fluorescence intensities at an excitation wavelength of 370 nm and emission wavelengths of 450 nm and 500 nm respectively. It offers a separation between sources of organic matter (autochthonous or allochthonous). To determine the predominance of fluorescent dissolved organic matter the ratio between fluorescence intensity peak T and peak C (T/C) was also calculated.

2.2.3 Statistical analysis

The statistical analysis was performed using PAST v3.0 software and the Real Statistics Resource Pack in Microsoft Excel (https://www.real-statistics.com/free-download/). The distribution of the data is significantly non-normal (Shapiro Wilk test, W=0.77–0.98, $p < 0.001$) and thus, Kendall's Tau correlation coefficient was determined between fluorescence data and standard water quality parameters, on 43 samples.

3. Results and discussions

3.1. Ancillary measurements

The temporal variability of the ancillary measurements are shown in Table 1. Values for pH varied between 6.5 and 8.4. Phosphorus and phosphate did not show any temporal or spatial tendencies. The highest value for phosphorus was 7.9 mg/L, while for phosphate 0.92 mg/L, both recorded at Morii Lake samples. The average values for phosphorus were higher at Morii Lake compared to the other lakes, and the average concentration of phosphate was higher at Ciurel Lake. These high levels are potentially generated by the input from agricultural practices along Dambovita and Jiu Rivers. Dissolved oxygen varied between 2.8 and 9.5 mg/L. The lowest concentrations were recorded for Morii Lake and the highest at Portile de Fier I Lake, in spring, and Ciurel Lake, in summer. The low values, at Morii Lake were recorded at the Arges channel inlet, potentially driven by pollutants originating from agricultural and domestic sources. The highest concentration of nitrites was 0.4 mg/L, recorded at Morii Lake, in spring. Most of the samples located near the inlet of Dambovita River and Arges channel presented concentrations above the recommended value of 0.03 mg/L [38]. In summer, however, the average concentration of nitrites was substantially higher at Ciurel and Portile de Fier I Lakes, compared to Morii Lake.

The highest concentration of chemical oxygen demand was 37 mg/L, recorded in spring at Morii Lake samples. Influences were observed from Dambovita River and Arges channel due to agricultural practices and release of organic matter from sewage discharges.

Table 1. Average values for standard water quality parameters for Morii, Ciurel and Portile de Fier I Lakes

	Spring			Summer		
	Morii	Ciurel	PFI	Morii	Ciurel	PFI
pH	7.53	7.06	7.63	7.81	6.86	7.64
SD	0.66	0.09	0.16	0.45	0.31	0.35
CV (%)	8.76	1.22	2.15	5.80	4.56	4.59
Median	7.80	7.07	7.65	7.70	6.70	7.80
DO (mg/L)	6.43	6.58	8.99	3.98	4.54	4.47
SD	1.40	1.80	0.48	0.40	1.03	0.39
CV (%)	21.69	27.34	5.39	10.04	22.66	8.83
Median	5.80	6.10	9.10	4.00	4.70	4.50
Nitrite (mg/L)	0.11	0.07	0.07	0.03	0.11	0.10
SD	0.13	0.03	0.02	0.01	0.05	0.02
CV (%)	112.99	33.92	29.96	42.97	43.47	23.56
Median	0.06	0.06	0.08	0.03	0.10	0.10
Phosphorus (mg/L)	2.71	0.58	0.70	0.43	0.26	0.22
SD	3.22	0.31	0.12	0.52	0.24	0.13
CV (%)	118.91	53.70	16.50	120.62	92.63	59.27
Median	1.30	0.60	0.70	0.10	0.20	0.20
Phosphate (mg/L)	0.19	0.25	0.08	0.29	0.88	0.09
SD	0.24	0.30	0.06	0.31	0.97	0.09
CV (%)	127.00	118.30	71.44	108.19	109.38	98.76
Median	0.07	0.13	0.06	0.19	0.82	0.08
COD (mg/L)	23.22	12.80	9.71	16.80	17.80	9.00
SD	7.97	8.98	3.09	11.06	7.01	5.77
CV(%)	34.33	70.18	31.85	65.85	39.41	64.15
Median	23.00	13.00	10.00	16.00	19.00	8.00

PFI – Portile de Fier I; DO – dissolved oxygen; COD – chemical oxygen demand; SD – standard deviation; CV – coefficient of variation

3.2. Fluorescence spectroscopy

The highest quantity of protein-like organic matter was recorded at Morii Lake (Fig. 2), potentially due to the input of agricultural and municipal wastes, as shown in previous studies [39]. The highest values for peaks B and T were observed at the samples collected from locations that favor accumulation of waste on the water surface. Morii Lake samples also had the highest COD concentrations (Table 1). Significant correlations were observed between peaks B and T, and COD (Table 2).

The lowest concentration of protein-like matter was found at Ciurel Lake water samples, which were collected from points located near the Jiu River flow into the lake. Ciurel Lake samples also presented the highest values for the humic-like peaks (Fig. 2), in particular, for the sample located at the exit of the lake towards Jiu River, where high quantities of humic substances accumulate. Peaks A, C and M displayed significant negative correlation with dissolved oxygen (Table 2). Also, significant correlation was found between peaks A and C, and phosphate, which indicated that an increase in humic-like organic matter, potentially caused by soil erosion, may lead to the deterioration of aquatic conditions. Portile de Fier I Lake contained relatively stable fluorescent dissolved organic matter, displaying no significant spatial variation (Fig. 2).

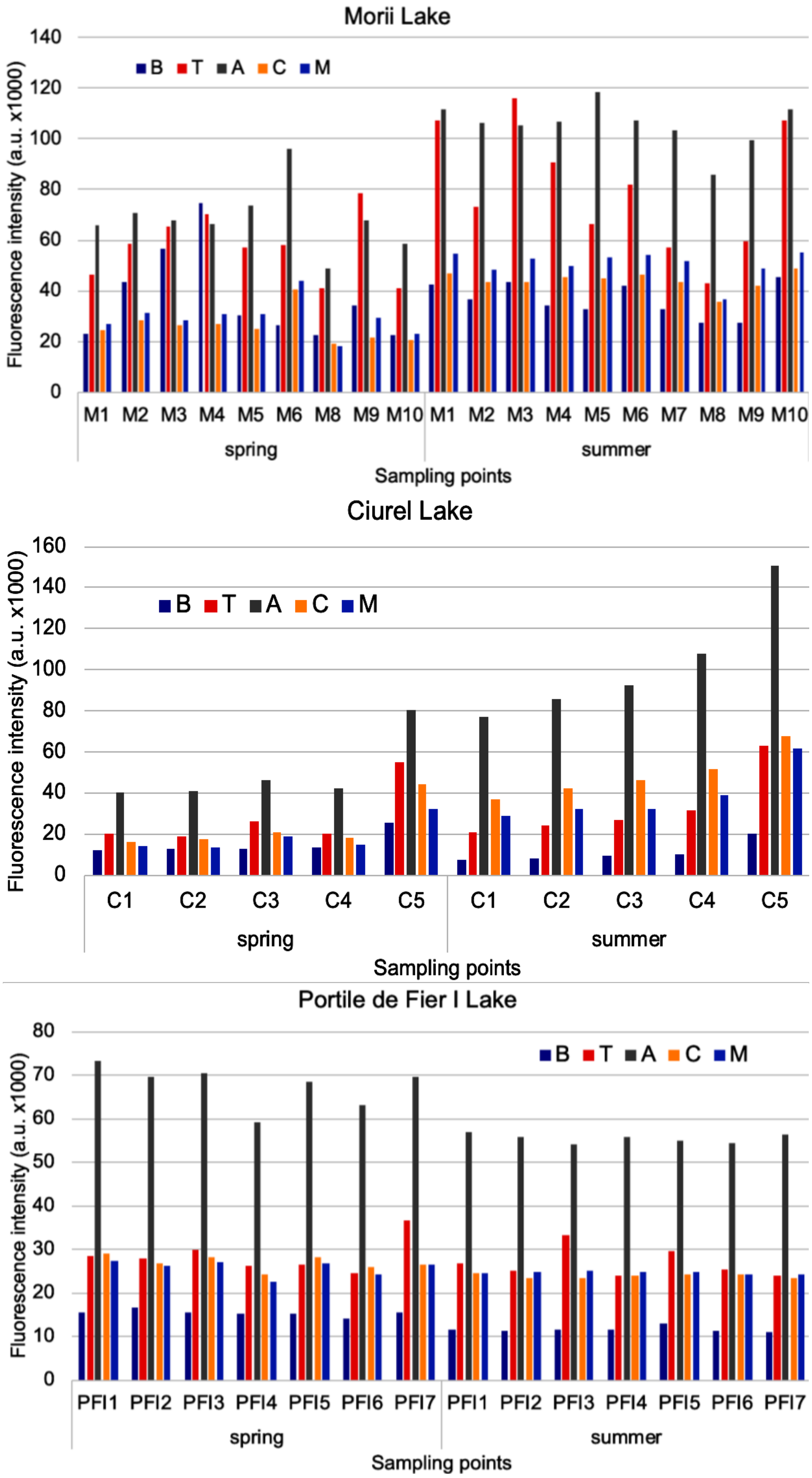

Fig. 2. Temporal and spatial evolution of the fluorescent signal of organic matter for the samples collected from: Morii Lake (up); Ciurel Lake (middle); Portile de Fier I Lake (down) (color online)

Seasonal differences were observed in the quantity of fluorescent dissolved organic matter. Morii and Ciurel Lakes contained higher concentrations of fluorescent dissolved organic matter in summer compared to spring. On the contrary, Portile de Fier I Lake contained less allochthonous humic-like fluorescence in summer compared to spring. This was potentially caused by the increased discharge from Danube River tributaries in spring [40], which can bring high quantities of terrestrial, allochthonous dissolved organic matter, reflected in high peak A fluorescence. The rest of the fluorescence peaks displayed no substantial changes from spring to summer, at the Portile de Fier I Lake.

Table 2. Statistically significant correlations between standard water quality parameters and fluorescence peaks.(red – p<0.001; blue – p <0.01; black - <0.05)

	pH	DO (mg/L)	Phosphorus (mg/L)	Phosphate (mg/L)	COD (mg/L)
B (a.u.)			0.35		0.48
T (a.u.)	0.41	-0.36			0.53
A (a.u.)		-0.48		0.46	
C (a.u.)		-0.54		0.53	
M (a.u.)		-0.56			0.35
HIX	-0.43			0.34	
BIX	0.56				

DO – dissolved oxygen; COD – chemical oxygen demand; HIX – humification index; BIX – biological index

Fluorescence indices can provide a thorough analysis of dissolved organic matter properties. Fig. 3 shows the values obtained for HIX, BIX, F450/F500 and T/C. The highest HIX values (6.17-6.96) were determined for the summer samples, collected from Ciurel Lake. According to Huguet et al. [18], HIX values higher than 6 indicate the presence of dissolved organic matter with an important humic character and a weak recent autochthonous component. The rest of the samples from Morii and Portile de Fier I Lakes, collected in spring and summer, and Ciurel Lake, collected in spring, showed HIX values below 4, indicating a biological or aquatic bacterial origin of the organic matter. Also, most samples presented high BIX values, above 0.8 (Fig. 3), which is generally found at samples containing organic matter with a strong autochthonous character and of biological or bacterial origin [18]. As shown by HIX values, Ciurel Lake summer samples contained samples with a mixture of autochthonous and allochthonous organic matter. These results have shown that Ciurel Lake received high quantities of allochthonous organic matter, potentially due to increased river flow and accumulation in lake water. The F450/F500 index did not display substantial variation between samples (Fig. 3).

According to McKnight et al. [41] values closer to 1.9 indicate that dissolved organic matter has autochthonous, microbial sources, while values closer to 1.3 indicate terrestrial and soil sources. Most of the lake samples, in this case, presented F450/F500 values close to 1.3, the highest values being recorded for a Morii Lake summer sample (F450/F500=1.57) and a Ciurel Lake spring sample (F450/F500=1.57). However, the F450/F500 values are slightly higher compared to estuary samples [18], but are considerably lower than the values reported by McKnight et al. [41] for lake and river samples. The differences are potentially given by the specific conditions of the aquatic systems and the difference in organic matter input from the tributary rivers.

The ratio between peaks T and C shows the dominance of the protein-like versus humic-like fractions in a sample. The highest T/C values were obtained for Morii Lake samples (Fig. 3), substantially higher compared to Ciurel and Portile de Fier I Lakes. At Morii Lake, higher overall values were determined in spring compared to summer. The dominance of the protein-like fraction showed the considerable influence from the release of domestic wastewater in Dambovita River, upstream the lake. Also, a recent study found a relationship between the urban fabric and protein-like fluorescence, in urban lakes, linking constructed areas and open waste dumps to high protein-like matter. The lowest T/C values were determined at Ciurel Lake summer samples, which evidenced the dominance of humic substances, potentially from allochthonous and autochthonous sources. According to Felgate et al. [42], fluorescent dissolved organic matter increases as forested land is changed to agricultural land. Humic substances, in particular, accumulate downstream the river [42], which could explain the humic dominance of Ciurel Lake samples, also considering the agricultural practices along Jiu River. At Portile de Fier I Lake, the T/C values were relatively similar across the lake, and between spring and summer, with an average value of 1.09, indicating that the samples contained a mixture of protein-like and humic-like fractions.

Lakes			HIX	BIX	F450/500	T/C
Morii	spring	M1	1.88	0.95	1.33	1.90
		M2	1.19	0.80	1.35	2.06
		M3	0.99	0.94	1.42	2.47
		M4	0.83	1.04	1.28	2.61
		M5	1.46	1.08	1.41	2.31
		M6	2.66	0.92	1.47	1.44
		M8	1.41	0.84	1.33	2.12
		M9	1.09	1.00	1.41	3.68
		M10	1.91	1.06	1.37	1.99
	summer	M1	1.37	1.06	1.47	2.28
		M2	1.84	0.93	1.29	1.68
		M3	1.77	1.16	1.40	2.67
		M4	2.47	1.01	1.49	1.99
		M5	2.03	1.04	1.38	1.48
		M6	1.62	1.08	1.24	1.77
		M7	2.40	0.99	1.30	1.31
		M8	2.59	0.86	1.57	1.20
		M9	2.38	1.06	1.40	1.43
		M10	1.31	0.97	1.29	2.21
Ciurel	spring	C1	2.44	0.78	1.29	1.26
		C2	2.67	0.81	1.22	1.09
		C3	2.27	0.82	1.30	1.26
		C4	2.58	0.86	1.28	1.11
		C5	2.33	0.77	1.57	1.25
	summer	C1	6.96	0.79	1.25	0.55
		C2	6.79	0.76	1.29	0.57
		C3	6.17	0.66	1.32	0.58
		C4	6.38	0.75	1.27	0.61
		C5	4.39	0.91	1.41	0.93
Portile de Fier I	spring	PFI1	3.57	0.87	1.30	0.98
		PFI2	3.48	0.83	1.31	1.05
		PFI3	3.27	0.82	1.30	1.06
		PFI4	3.00	0.79	1.23	1.08
		PFI5	3.46	0.86	1.32	0.94
		PFI6	3.21	0.97	1.11	0.94
		PFI7	2.63	1.01	1.28	1.38
	summer	PFI1	3.81	0.92	1.46	1.08
		PFI2	3.49	0.96	1.33	1.07
		PFI3	2.38	1.00	1.34	1.42
		PFI4	3.39	0.91	1.40	1.01
		PFI5	2.62	0.95	1.32	1.23
		PFI6	3.28	0.91	1.39	1.04
		PFI7	3.38	0.95	1.32	1.02

Fig. 3. Fluorescence indices for the samples collected from Morii, Ciurel and Portile de Fier Lakes

Peak C emission wavelength generally indicates the hydrophilic or hydrophobic nature of the fluorescent dissolved organic matter. Samples that present a peak C emission at wavelengths between 400 nm and 420 nm potentially contain relatively more hydrophobic organic matter compared to samples that have a peak C emission wavelength between 430 nm and 450 nm. The highest peak C wavelengths were recorded for Ciurel Lake (Fig. 4), indicating that the organic matter present in these samples may contain predominantly aliphatic carbon and nitrogen-based compounds, such as carboxylic acids, carbohydrates and proteins, which are associated with the hydrophilic fraction of dissolved organic matter [43].

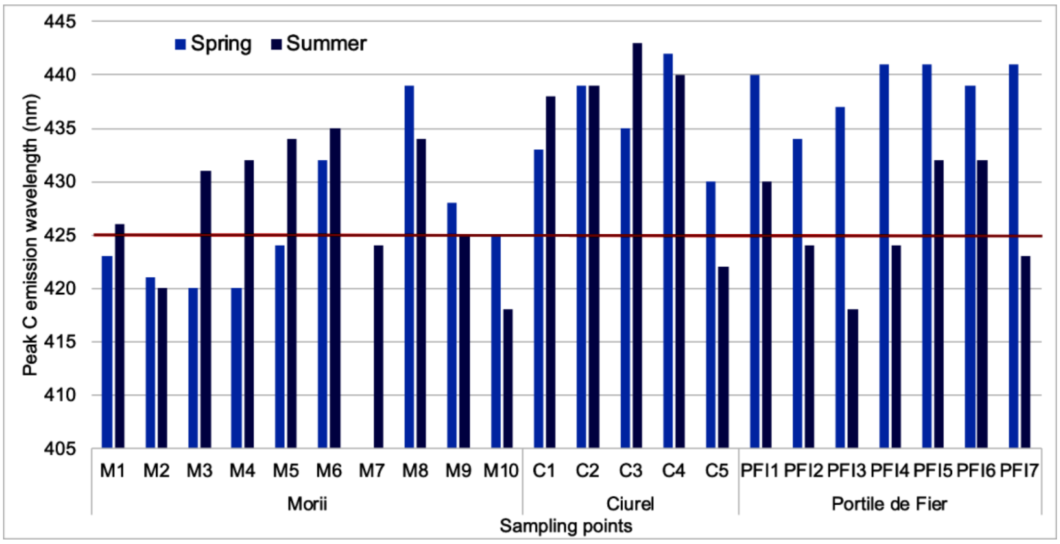

Fig. 4. Temporal and spatial evolution of the emission wavelength of peak C

Differences were observed between spring and summer samples in peak C emission wavelength. The organic matter from Morii Lake samples turned relatively hydrophilic from spring to summer. On the contrary, at the Portile de Fier Lake, organic matter transitioned from hydrophilic, in spring, to hydrophobic in summer. At Ciurel Lake, organic matter might have potentially been in a more stable state compared to the other lakes, as peak C emission wavelength did not change substantially from spring to summer.

4. Conclusions

In order to determine the water quality parameters of urban lakes with unique characteristics, fluorescence spectroscopy, a state of the art and advanced analysis method was used and its efficiency has been proven. Morii Lake presented the highest concentration of protein-like matter, Ciurel Lake samples showed a humic-like dominance, in summer in particular, while Portile de Fier I Lake contained a mixture of humic and protein-like fractions. Results showed that a dynamic urban environment influences lake water quality and the properties of fluorescent dissolved organic matter. Also, agricultural practices and the input from river tributaries may increase the humic-like matter in lentic systems.

In this context, this preliminary study could be considered as being the foundation for further more extensive studies on the temporal and spatial evolution of water quality parameters in urban lakes. The ability of fluorescence spectroscopy as an advanced optoelectronic method to provide comprehensive data about the state of the water quality is an important factor in creating the premises of urban lakes water management.

Acknowledgements

The authors acknowledge the support of the Romanian Ministry of European Investment and Projects, the Ministry of Research, Innovation and Digitalization, and CNCS – UEFISCDI, through the following projects: 18PFE/30.12.2021; PN-III-P4-PCE-2021-0585 (78/2022); 8/1.2.1 PTI ap.2/17.02.2023; Core Program OPTRONICA VII PN23 05 (11N/2023).

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