*Romanian Reports in Physics, Vol. 65, No. 3, P. 1092–1104, 2013*

*Dedicated to Professor Valentin I. Vlad's 70th Anniversary*

# SPATIAL CHARACTERIZATION OF URBAN LAKES

E.M. CARSTEA[1], C.I. IOJA[2], R. SAVASTRU[1], A. GAVRILIDIS[2]

[1]National Institute of R&D for Optoelectronics, Atomistilor 409, Magurele, 077125, Romania,
E-mail: frida@inoe.ro Email: rsavas@inoe.ro
[2]University of Bucharest, CERIS center, Bucharest, 010041, Romania,
E-mail: iojacristian@yahoo.com Email: athanasios_gavrilidis22@ yahoo.com

*Received June 27, 2013*

*Abstract*. Spectroscopic techniques have been intensely used in the past decades for the study of water quality. Lake water offers an indication of the health of a city, however little research has been done to evaluate the spatial distribution of dissolved organic matter (DOM), within an urban lake. This study presents the first spatial characterization of DOM, by the use of fluorescence spectroscopy, at large and small scales. Samples have been collected from a network of urban lakes, located on Colentina River, and from an enclosed urban lake, Tineretului Lake, Bucharest. Fluorescence analysis has revealed the presence of microbial DOM, at both experiments, highlighting the autochthonous nature of DOM. Allochthonous sources of DOM have also been detected, originating from Colentina River, at the lake network, and from surface runoff, at Tineretului Lake. In conclusion, fluorescence spectroscopy has identified effectively the varied spatial features of DOM at both experiments.

*Key words*: fluorescence spectroscopy, dissolved organic matter, urban lakes.

## 1. INTRODUCTION

In the past decades, spectroscopic methods have found several applications in environmental research. Fluorescence spectroscopy is especially used to evaluate water quality due to its advantages, like: sensitivity, short measurement time, almost no sample preparation and reduced sample quantities [1]. Numerous researchers have proved its effectiveness by studies on ground water [2], marine and estuarine waters [3, 4], rivers [5], lakes [6, 7], transitional waters river – marine [8, 9], sewage [10, 11] or oil fingerprinting [12].

Urban environments can contribute greatly to the contamination of lakes and rivers by sewage discharges, industrial effluents or nutrients runoff [13]. Urban lakes are especially under high risk because large quantities of pollutants lead to increased eutrophication, which affects wildlife habitat and population quality of life [13, 14]. According to Ravikumar et al. [15], lakes are "ecological barometers of the health of a city". Therefore, complex spatial and temporal evaluation of lake

water quality is needed. So far, characterization of temporal variation of lake dissolved organic matter (DOM) fluorescence has been intensely studied [16, 17]. Little research has been done on the spatial distribution of lake DOM. Mostofa et al. [16] have measured the fluorescence of DOM, in several samples collected from one side of Lake Biwa and downstream of rivers that flow into the lake, in the attempt to identify the allochthonous and autochthonous sources of DOM. Large spatial assessment has been made by Ghervase et al. [18], however the researchers have analyzed discrete samples from some urban rivers, not accounting for the changes within a lake.

This study aims to identify the spatial features of lake DOM, by fluorescence spectroscopy, at large and small scales. The large spatial scale analysis focuses on a network of lakes, artificially created on the course of a river, while the small scale experiment is concentrated on an enclosed artificial park lake; all lakes being located in Bucharest, Romania. Based on the authors knowledge this is the first such study on the spatial characterization of lake DOM.

## 2. METHODOLOGY

### 2.1. SITE DESCRIPTION AND SAMPLE COLLECTION

Water samples were collected within the period May – June 2011, for the large scale experiment, and in August – September 2011, for the small scale study. Water was sampled, from the epilimnion section, in plastic bottles, washed, prior to sampling in ultrasound bath and rinsed thoroughly with distilled water. The samples for the large scale experiment were taken from 9 urban lakes (Grivita, Baneasa, Herastrau, Floreasca, Tei, Plumbuita, Fundeni, Dobroesti and Pantelimon), situated on Colentina River, which crosses Bucharest from its North side (Fig. 1). The water quality of these lakes is influenced by anthropogenic activities located on the shores (especially by residential areas not connected to the sewage network and by small industrial units). Samples for the small scale experiment were collected from 36 points (31 points near the shore and 5 points on the center), from an artificial lake located in Tineretului Park, Bucharest. Tineretului Lake (Fig. 1) water is supplied by surface runoff, which influences the water quality. The characteristics of all lakes are presented in Table 1.

*Table 1*

Lakes characteristics [19]

| Lake | Area (ha) | Water volume (mil.cm) | Use | Water degradation sources |
|---|---|---|---|---|
| Grivita | 75.85 | 1.16 | Fishing, recreation | Unorganized waste landfill, vegetation |
| Baneasa | 40.00 | 0.62 | Fishing, irrigation, flooding mitigation, recreation | Residential area, unorganized waste landfill, vegetation |

*Table 1 (continued)*

| | | | | |
|---|---|---|---|---|
| Herastrau | 77.00 | 2.39 | Fishing, irrigation, flooding mitigation, recreation | Vegetation, pesticides from parks treatments |
| Floreasca | 70.00 | 1.62 | Fishing, flooding mitigation, recreation | Unorganized waste landfill, vegetation |
| Tei | 80.00 | 2.00 | Fishing, flooding mitigation, recreation | Residential area, waste landfill, vegetation, pesticides from parks treatments |
| Plumbuita | 44.00 | 0.90 | Fishing, irrigation, flooding mitigation, recreation | Residential area, unorganized waste landfill, vegetation, pesticides from parks treatments |
| Fundeni | 88.00 | 0.85 | Fishing, irrigation, flooding mitigation, recreation | Residential area, unorganized waste landfill, vegetation, fisheries |
| Pantelimon | 260.00 | 12.30 | Fishing, irrigation, flooding mitigation, recreation, industrial water supply | Residential area, unorganized waste landfill, vegetation, fisheries |
| Tineretului | 13.50 | 0.20 | Recreation | Vegetation, pesticides from parks treatments |

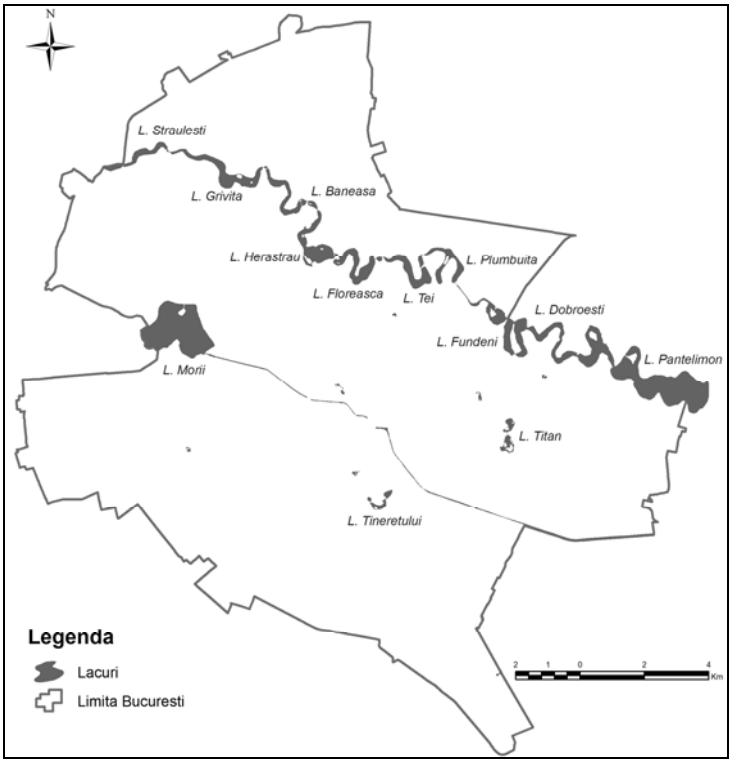



Fig. 1 – Location of the lakes analyzed in this study: from left to right representing the urban lake network on Colentina River – Grivita, Baneasa, Herastrau, Floreasca, Tei, Plumbuita, Fundeni, Dobroesti and Pantelimon; the enclosed urban lake – Tineretului. The black filled areas represent the lakes and the black border line indicate Bucharest City limits.

### 2.2. FLUORESCENCE SPECTROSCOPY MEASUREMENTS AND STANDARD ANALYSES

The fluorescence signal of DOM was measured as excitation – emission matrix (EEM), which represents a color coded fluorescence map consisting of several fluorescence emission spectra recorded within a given spectral domain. The fluorescence maxima can be identified by analyzing the excitation wavelength / emission wavelength pairs. The following parameters were used for recording the EEMs: excitation wavelength domain 230–400 nm, emission wavelength range 250–500 nm with steps of 5 and 2 nm, respectively, slits of 4 nm and integration time 0.200 s. The water Raman peak was recorded before every set of measurements in order to check the instrument stability.

Chlorophyll a (Chl a) was measured by fluorescence spectroscopy, recording emission spectra at 420 nm excitation wavelength, within the emission wavelength domain of 440–800 nm, step of 2 nm. All samples were analyzed within 24 h from collection and were filtered with a 0.8 μm Millipore filter to remove particulate matter. Conductivity (EC) and pH were monitored using Consort C352 multiparameter analyzer.

## 3. RESULTS AND DISCUSSION

Fluorescence analysis and standard parameters for the large and small scale experiments are presented in Table 2 and Table 3, respectively. The standard parameter pH, indicated that water samples presented values within, or close to, the normal range [20]. Considering that pH values were close to the neutral value and were similar between the lake network (large scale) and Tineretului Lake (small scale) it was assumed that pH had no effect on the fluorescence spectroscopy measurements. EC showed clear differences between the lake network and Tineretului lake, with higher values for Tineretului Lake samples, indicating a higher amount of dissolved ions but also less external water inputs, compared to lake network.

The protein-like and humic-like fractions of DOM were detected in the fluorescence spectra of both experiments, large and small spatial scales. Fluorescence maxima were identified with the peak-picking method and the nomenclature given by Coble [3]. Peaks T and B, indicating tryptophan and tyrosine, representing the protein-like fraction, were detected within the regions: peak T – excitation wavelength domain 230–240 nm, emission wavelength range 325–345 nm; peak B – excitation wavelength domain 230 – 240 nm, emission wavelength range 300–310 nm. Peaks A and C, designating the humic substances (humic and fulvic acids), were observed in the regions: peak A – excitation wavelength domain 230–250 nm, emission wavelength range 405–430 nm; peak C – excitation wavelength domain 300–350 nm, emission wavelength range 410–435 nm.

## 3.1. LARGE SPATIAL SCALE CHARACTERIZATION – LAKE NETWORK

Fluorescence analysis of lake network samples revealed higher values for peaks T and B, compared to peaks A and C, suggesting a microbial character of DOM. The fluorescence values and indices calculated for each peak, are presented in Table 2. The highest peak T value was recorded at Baneasa P3 sample and the lowest at Herastrau P6 sample. Moreover, Herastrau P6 sample showed the lowest peak B, while the highest peak B was registered at Herastrau P8 sample. The humic substances maxima, A and C, presented the lowest values at P11 sample, from Floreasca Lake, and the highest at the last sample, P26 from Pantelimon Lake, at the end of the urban lake network.

These results indicated a different spatial distribution of DOM components between the lakes and even between the samples from the same lake. The spatial variation of fluorescence values are presented in Fig. 2. Peak T fluorescence showed high values, at Grivita and Baneasa Lakes, which slowly decreased at Herastrau Lake samples. Fluorescence intensity increased again towards the exit of Herastrau Lake until sample P13 from Tei Lake, where low fluorescence values were recorded, increasing again at Plumbuita Lake. This is followed by low fluorescence intensity starting with the entrance to Fundeni Lake and a slight increase towards Pantelimon Lake.

*Table 2*

Fluorescence and standard measurements for the lakes network

| **Samples** | | **Fluorescence intensity (a.u.)** | | | | **$C_{em}$* (nm)** | **Fluorescence indices** | | | **Chl a (a.u.)** | **pH** | **EC** (µS/cm)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Nr.** | **Location** | **T** | **B** | **A** | **C** | | **T/C** | **HIX** | **BIX** | | | |
| **P1** | **Grivita** | 95920 | 62450 | 43550 | 19290 | 416 | 4.97 | 1.4 | 0.88 | 16600 | 8.31 | 354 |
| **P2** | **Baneasa** | 103600 | 55080 | 51560 | 24470 | 433 | 4.23 | 1.86 | 0.76 | 12660 | 8.51 | 347 |
| **P3** | | 124900 | 61540 | 52310 | 22880 | 434 | 5.46 | 2.44 | 0.79 | 16270 | 6.7 | 348 |
| **P4** | **Herastrau** | 83050 | 60100 | 39310 | 19120 | 412 | 4.34 | 0.65 | 0.89 | 16580 | 8.85 | 377 |
| **P5** | | 76390 | 51140 | 38080 | 19750 | 410 | 3.87 | 0.69 | 1.09 | 15390 | 8.57 | 360 |
| **P6** | | 32490 | 18860 | 36370 | 17790 | 410 | 1.83 | 1.01 | 0.83 | 13770 | 8.86 | 266 |
| **P7** | | 68860 | 55030 | 38010 | 18500 | 411 | 3.72 | 0.52 | 0.92 | 14060 | 6.89 | 372 |
| **P8** | | 67610 | 105000 | 38750 | 18240 | 413 | 3.71 | 0.55 | 0.92 | 13290 | 8.5 | 246 |
| **P9** | **Floreasca** | 80550 | 48560 | 36380 | 17960 | 412 | 4.48 | 0.61 | 0.92 | 13500 | 8.81 | 374 |
| **P10** | | 77480 | 53610 | 36890 | 17310 | 410 | 4.48 | 0.57 | 0.95 | - | 8.9 | 377 |
| **P11** | | 74250 | 55340 | 35320 | 16950 | 416 | 4.38 | 0.69 | 0.93 | 12310 | 8.81 | 218 |
| **P12** | **Tei** | 76060 | 52700 | 50340 | 25010 | 410 | 3.04 | 0.59 | 0.97 | 4818 | 6.5 | 409 |
| **P13** | | 45160 | 26170 | 39360 | 19690 | 411 | 2.29 | 0.38 | 0.9 | 5266 | 7.28 | 422 |
| **P14** | | 46500 | 34720 | 39570 | 19620 | 412 | 2.37 | 0.4 | 0.92 | 5093 | 7.94 | 400 |

*Table 2 (continued)*

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **P15** | **Plumbuita** | 40980 | 29260 | 38810 | 19530 | 410 | 2.1 | 0.38 | 0.9 | 5045 | 7.74 | 411 |
| **P16** | | 120400 | 84860 | 43970 | 22680 | 410 | 5.31 | 0.92 | 0.97 | 25460 | 7.54 | 487 |
| **P17** | | 75270 | 49240 | 43520 | 21890 | 413 | 3.44 | 0.62 | 0.92 | 8970 | 8.75 | 432 |
| **P18** | | 46850 | 35250 | 40850 | 20200 | 413 | 2.32 | 0.42 | 0.91 | 7518 | 8.15 | 418 |
| **P19** | **Fundeni** | 60500 | 36950 | 43760 | 21270 | 413 | 2.84 | 0.49 | 0.92 | 13160 | 8.15 | 450 |
| **P20** | | 48310 | 29550 | 43650 | 21490 | 413 | 2.25 | 0.41 | 0.92 | 9406 | 7.61 | 452 |
| **P21** | | 60840 | 42120 | 42730 | 21170 | 413 | 2.87 | 0.49 | 0.94 | 14250 | 8.63 | 458 |
| **P22** | **Dobroesti** | 52330 | 33910 | 45050 | 21770 | 411 | 2.4 | 0.43 | 0.93 | 9337 | 7.34 | 475 |
| **P23** | | 81440 | 45140 | 44390 | 22810 | 411 | 3.57 | 0.5 | 0.89 | 12440 | 8.66 | 493 |
| **P24** | **Pantelimon** | 64160 | 37190 | 48430 | 24470 | 411 | 2.62 | 0.44 | 0.92 | 10990 | 8.65 | 478 |
| **P25** | | 70520 | 45360 | 47850 | 23790 | 412 | 2.96 | 0.52 | 0.91 | 29160 | 8.65 | 518 |
| **P26** | | 62350 | 41780 | 57260 | 29490 | 410 | 2.11 | 0.4 | 0.84 | 6886 | 8.16 | 555 |

[*] Peak C emission wavelength; [**] Electrical conductivity

The high peak T fluorescence intensity was attributed to the presence of major bacterial matter. According to the study of Stanescu [20], made on some of the lakes from the network, fecal coliforms, intestinal enterococci and Escherichia Coli were found in all the assessed lakes. As shown by Elliott et al. [21], fluorescence spectroscopy is capable to detect different types of bacteria, which are reflected in the intense peak T. The spatial variation of peak T might be explained by the process of accumulation of the microbial load, in the low water volume lakes, and dilution into the high volume lakes, Herastrau, Tei and Pantelimon (Table 1), determined by the Colentina River water flow (max. 3 m/s).

Peak B showed the same accumulation / dilution trend, with the exception of Herastrau P8 sample. According to some unpublished research of the authors, peak B could be associated with bird waste and thus it could indicate the agglomeration of bird populations on one part of Herastrau Lake, near P8 sampling point. The accumulation process was better observed at the Plumbuita P16 sample, which was collected from a "tail" of the lake that had poor water flow towards other lakes, promoting a high degree of organic matter build-up.

The trend of accumulation / dilution for the humic-like fluorescence, peaks A and C, was not similar to that seen at the protein-like fraction. The minor fluorescence intensity increase, as shown in Fig. 2, coincided with the samples collected from points with natural embankments, P2, P22, P23, P25 and P26, or with construction waste found on the lake shore, P2, P12 and P20. This could have lead to an allochthonous rise in the quantity of humic substances. Therefore, in the case of the lake network, humic substances had mainly an allochthonous source, while the protein-like fraction represented an autochthonous production, reflected in the accumulation effect observed at some lakes. Mostofa et al. [16] stated that

spatial and temporal effects of the autochthonous and allochthonous input of DOM determine the variation of DOM, confirming the aforementioned results.

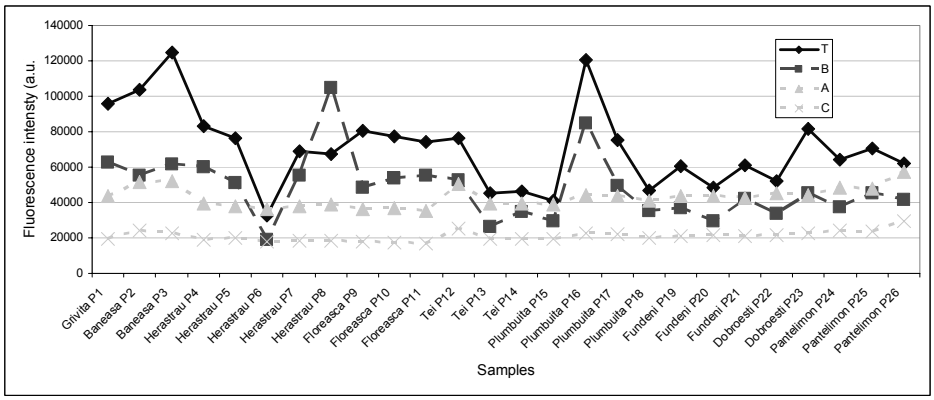



Fig. 2 – Spatial variation of fluorescence intensity for peaks A and C – humic substances and peaks T and B – protein-like fraction.

The source and nature of DOM can be better assessed by evaluating various fluorescence parameters: the ratio between the fluorescence intensity of peaks T and C, the emission wavelength of peak C ($C_{em}$), humification index (HIX) and biological index (BIX) (Table 2). The $T/C$ ratio, indicating DOM aromaticity [5], showed high values at samples with very intense peak T and low values at the samples with reduced fluorescence intensity for both peak C and T. The results suggested that peak T fluorescence intensity represented the influencing factor in DOM variation for the lake network samples. Thus, DOM, in all samples, had a tendency towards a microbial character.

Peak C alone could also reveal the source of DOM by analyzing the emission wavelength of the peak. Mostofa et al. [16] observed that $C_{em}$ decreased starting with the upstream samples to the samples taken from the lake. In the present study, the first 3 samples, from Grivita and Baneasa Lakes, showed high peak C emission wavelength, which was followed by a sudden shift towards low wavelengths. The first 3 samples might have still contained the organic matter from Colentina River. Several studies [5, 7, 22] had shown that riverine DOM is mostly allochthonous, thus the humic substances from the first 3 samples could have been of an allochthonous origin, but microbially reprocessed in Herastrau Lake. $C_{em}$ could also indicate the presence of hydrophobic DOM, when the peak wavelength is seen within 400 – 420 nm, and of hydrophilic DOM, if peak wavelength is within 430 – 450 nm [23]. Samples P2 and P3, with allochthonous DOM, were classified as hydrophilic, whereas the other samples presented a hydrophobic character. The observations of Carstea et al. [5] that riverine DOM was mostly hydrophobic confirmed that the humic substances, from the lake network samples, had an allochthonous source. Therefore, the lake network water contained a major fraction

of microbial DOM, resulted principally from an autochthonous production, and a humic component, originated from an allochthonous source, specifically from Colentina River.

Discrimination between DOM sources could be better achieved by the fluorescence indices, HIX and BIX, as proven by Huguet et al. [24]. HIX was calculated as the ratio between the fluorescence intensity in the emission wavelength region 300–345 nm and the region 435–480 nm, at excitation wavelength 254 nm. BIX was calculated as the fluorescence intensity at 380 nm divided by the intensity at 430 nm, with excitation wavelength at 310 nm. HIX was introduced by Zsolnay [25] to evaluate the degree of DOM humification in soil samples. It was later applied by Huguet et al. [24] to identify different sources of DOM, in water samples. The researchers proved that values < 4 indicated bacterial DOM, while values above 4 indicated a decreasing microbial fraction to an entirely humified DOM. In the current study, all samples presented HIX values below 4, suggesting that DOM had a microbial character, i.e. an autochthonous origin.

The other parameter, BIX, was developed by Huguet et al. [24] to identify the autochthonous input, in water samples. In the present study, BIX separated the data in 2 groups, based on the classification of Huguet et al. [24]: 0.8–1 indicating strong autochthonous character and >1 showing DOM of bacterial origin. According to Huguet et al. [24] the first group also contained, along with bacterial matter, a minor humic component. BIX identified the slight humic input, at the first samples, P1 – P4, and at the last sample from the lake network, Pantelimon P26, which based on the fluorescence intensity of peaks A and C (Table 2), accumulated more humic matter compared to the samples taken from the middle of the lake network. The other parameters, HIX, $T/C$ ratio and $C_{em}$, were not able to identify the minor humic input at sample P26. Consequently, parameter BIX was the most effective tool in distinguishing the sources of DOM in lakes with both allochthonous and autochthonous input.

Different spatial distribution was also detected at Chl a, as it showed varied results for the samples taken from the lake network (Table 2). Starting with sample Grivita P1 to Floreasca P11, Chl a presented a continuous, slow decrease, followed by a sudden decrease at Tei P12 sample, continuing with highly variable values until Pantelimon P26. The sunlight exposure, at the sampling sites, could be responsible for the changes in Chl a fluorescence intensity. No or poor correlation was seen between the fluorescence intensity of Chl a and DOM fluorescence (correlation coefficients with peak T → 0.55; B → 0.45; A → 0.02; C → –0.03). The lack of correlation could also be explained by sunlight exposure. Generally, epilimnion DOM is greatly influenced by sunlight, transforming the diagenetically fresher DOM into less biologically available DOM [26]. On the other hand, Miller and Moran [27] proved that a large refractory DOM fraction could become available for biological uptake after exposure to sunlight. Considering these facts, it would be difficult to establish a correlation between the fluorescence of DOM and Chl a.

## 3.2. COMPARISON WITH SMALL SCALE SPATIAL CHARACTERIZATION – TINERETULUI LAKE

Fluorescence data of the Tineretului Lake samples displayed a certain level of variation for all peaks (Table 3); however, in a lower degree compared to the lake network samples. The standard deviation of Tineretului Lake fluorescence values was: peak T – 7489 a.u.; B – 4962 a.u.; A – 2706 a.u.; C – 610 a.u., while for the lake network spectra: peak T – 22757 a.u.; B – 18162 a.u.; A – 5624 a.u.; C – 2892 a.u.. Therefore, due to the influence of Colentina River, the lake network presented a higher spatial variation, compared to the enclosed Tineretului Lake.

The spatial distribution of Tineretului Lake fluorescence peaks is illustrated in Fig. 3. The fluorescence values indicated high quantities of protein-like fraction, peaks T and B, at the samples collected from points where debris was accumulated. In the upper part of the lake, a restaurant was located coinciding with the point where the highest protein-like fluorescence values were recorded. This fact showed that organic waste could potentially be released into the lake, from the restaurant, as reflected by the high peak T, or bird populations could gather around the area in search for food, as seen in the high peak B.

Peak A showed generally low fluorescence intensity, in only 10 points more terrestrial humic matter being detected. These points could be attributed to locations with surface runoff input. Peak C presented higher variability, compared to peak A, especially at the samples that also displayed high fluorescence intensity of peaks T and B. According to Ishii and Boyer [28], peak C corresponded to microbially reprocessed humic substances. This fact suggested that Tineretului Lake contained large quantities of humic substances, reprocessed by the bacterial load. This was also observed at the lake network, but only at the first three samples where significant quantities of humic substances were released, from Colentina River, which were microbially reprocessed starting with sample P4, in Herastrau Lake. The other lake network samples did not present microbial reprocessing of humic substances due to water recirculation, within lakes, which allowed less time for this process.

*Table 3*

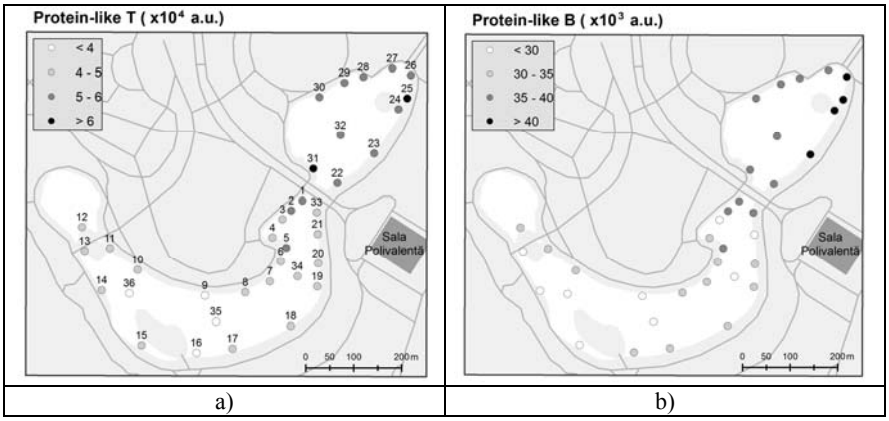
Fluorescence and standard measurements for Tineretului lake

| **Samples** | **Fluorescence intensity (a.u.)** | | | | **$C_{em}$*** | **Fluorescence indices** | | | **Chl a** | **pH** | **EC**** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **T** | **B** | **A** | **C** | **(nm)** | **T/C** | **HIX** | **BIX** | **(a.u.)** | | **(µS/cm)** |
| **LT1** | 59920 | 39480 | 21620 | 7489 | 414 | 8 | 1.45 | 0.95 | 8848 | 7.51 | 962 |
| **LT2** | 51190 | 37020 | 19510 | 6775 | 420 | 7.56 | 1.5 | 1.06 | 6515 | 7.05 | 964 |
| **LT3** | 48590 | 28130 | 21300 | 6624 | 412 | 7.34 | 1.42 | 1.09 | 6151 | 7.41 | 974 |
| **LT4** | 47900 | 34140 | 19430 | 9006 | 440 | 5.32 | 1.18 | 0.82 | 6208 | 7.44 | 926 |

*Table 3 (continued)*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **LT5** | 58760 | 38630 | 18210 | 6881 | 412 | 8.54 | 1.39 | 1.04 | 6657 | 7.66 | 967 |
| **LT6** | 44540 | 33360 | 18870 | 7084 | 410 | 6.29 | 1.4 | 1.01 | 6199 | 7.96 | 982 |
| **LT7** | 45600 | 32440 | 22620 | 6666 | 406 | 6.84 | 1.31 | 1.06 | 6273 | 7.93 | 958 |
| **LT8** | 42200 | 32900 | 21390 | 6254 | 402 | 6.75 | 1.58 | 1.16 | 6489 | 7.83 | 988 |
| **LT9** | 38350 | 27690 | 17300 | 6277 | 410 | 6.11 | 1.38 | 1.08 | 6313 | 7.84 | 990 |
| **LT10** | 45690 | 30550 | 16300 | 5919 | 404 | 7.72 | 1.7 | 1.13 | 5086 | 7.83 | 987 |
| **LT11** | 42620 | 30660 | 17490 | 5776 | 412 | 7.38 | 1.37 | 1.03 | 6542 | 8.02 | 961 |
| **LT12** | 42680 | 30800 | 19020 | 6461 | 408 | 6.61 | 1.34 | 1 | 6150 | 8.1 | 994 |
| **LT13** | 44450 | 27970 | 16610 | 6209 | 440 | 7.16 | 1.38 | 0.97 | 7911 | 7.88 | 988 |
| **LT14** | 40140 | 28660 | 17260 | 6704 | 436 | 5.99 | 1.44 | 0.92 | 8112 | 8.12 | 987 |
| **LT15** | 44180 | 26700 | 17730 | 6403 | 416 | 6.9 | 1.37 | 0.98 | 8023 | 8.08 | 964 |
| **LT16** | 38440 | 31960 | 16430 | 6898 | 440 | 5.57 | 1.23 | 0.94 | 5830 | 8 | 966 |
| **LT17** | 46220 | 33830 | 17140 | 6080 | 408 | 7.6 | 1.46 | 1.07 | 7436 | 8.07 | 962 |
| **LT18** | 48510 | 32800 | 21470 | 6385 | 404 | 7.6 | 1.49 | 1.04 | 7732 | 8.05 | 954 |
| **LT19** | 45990 | 32710 | 17230 | 6134 | 408 | 7.5 | 1.65 | 1.09 | 6719 | 8.1 | 960 |
| **LT20** | 45670 | 33730 | 20220 | 6074 | 404 | 7.52 | 1.44 | 1.08 | 7219 | 8.01 | 956 |
| **LT21** | 46110 | 29030 | 19280 | 6177 | 408 | 7.46 | 1.41 | 1.06 | 7587 | 8.1 | 953 |
| **LT22** | 54210 | 37790 | 20060 | 6390 | 402 | 8.48 | 1.7 | 1.15 | 8960 | 8.2 | 930 |
| **LT23** | 50240 | 41250 | 18410 | 6461 | 402 | 7.78 | 1.58 | 1.12 | 8124 | 8.12 | 935 |
| **LT24** | 54020 | 42720 | 18650 | 7131 | 408 | 7.58 | 1.54 | 1.02 | 6974 | 8.21 | 930 |
| **LT25** | 70690 | 41870 | 25200 | 7095 | 402 | 9.96 | 1.57 | 1.11 | 7227 | 8.24 | 922 |
| **LT26** | 52290 | 41980 | 18760 | 6785 | 414 | 7.71 | 1.51 | 0.99 | 9750 | 8.17 | 934 |
| **LT27** | 51950 | 37060 | 24210 | 7348 | 440 | 7.07 | 1.39 | 0.96 | 7740 | 8.25 | 929 |
| **LT28** | 50730 | 37600 | 19880 | 7254 | 438 | 6.99 | 1.29 | 0.97 | 7197 | 8.22 | 928 |
| **LT29** | 57940 | 35330 | 17030 | 6375 | 406 | 9.09 | 1.49 | 1.05 | 8734 | 7.66 | 920 |
| **LT30** | 52630 | 37300 | 19820 | 6359 | 408 | 8.28 | 1.52 | 1.02 | 8972 | 8.17 | 932 |
| **LT31** | 64890 | 39530 | 29380 | 7536 | 402 | 8.61 | 1.61 | 1.1 | 7870 | 8.11 | 937 |
| **LT32** | 50570 | 39480 | 17830 | 6776 | 402 | 7.46 | 1.78 | 1.16 | 14360 | 8.06 | 953 |
| **LT33** | 47630 | 36620 | 17740 | 6762 | 402 | 7.04 | 1.75 | 1.16 | 12560 | 8.17 | 943 |
| **LT34** | 41010 | 24620 | 18010 | 6901 | 402 | 5.94 | 1.46 | 1.2 | 13070 | 8.17 | 935 |
| **LT35** | 37080 | 28230 | 17580 | 6642 | 402 | 5.58 | 1.43 | 1.17 | 11500 | 7.94 | 977 |
| **LT36** | 39020 | 27120 | 19390 | 7700 | 404 | 5.07 | 1.02 | 1.16 | 10910 | 7.98 | 987 |

* Peak C emission wavelength; ** Electrical conductivity




a) b)

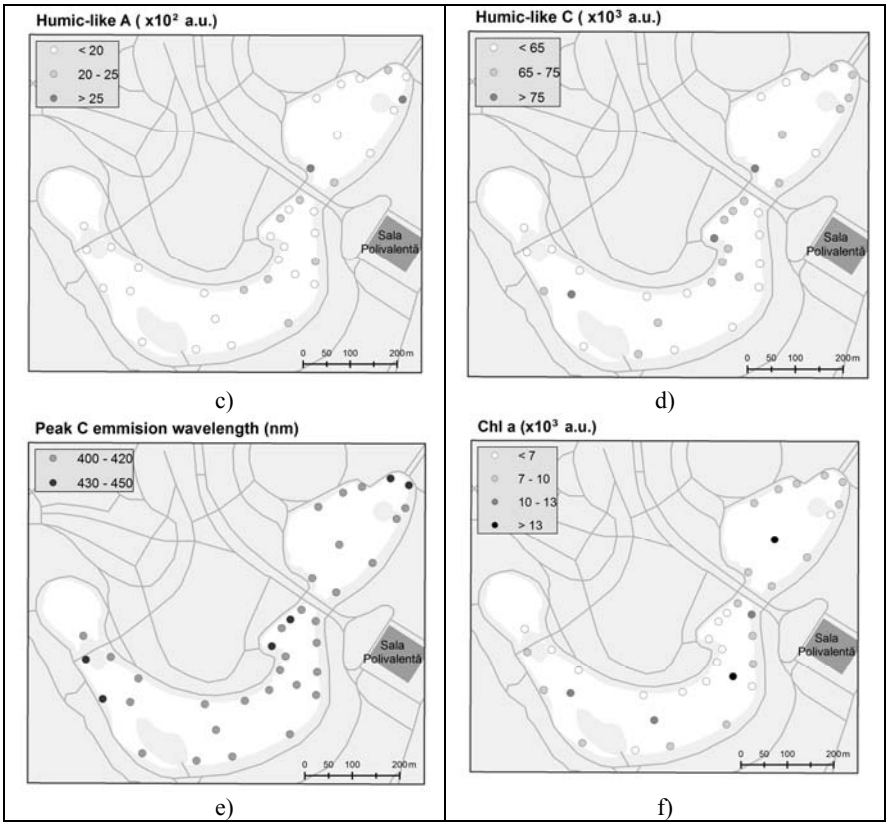



Fig. 3 – Spatial characterization of Tineretului lake: protein-like fluorescence peak T (a) and peak B (b); humic-like fluorescence peak A (c) and peak C (d); emission wavelength of peak C (e); Chl a fluorescence (f)**.**

As in the case of lake network, peak C emission wavelength identified 2 sources of DOM, at Tineretului Lake. High $C_{em}$ were seen at the points where debris accumulated from surface runoff, which indicated a minor allochthonous source of DOM. The fluorescence indices, *T*/*C* ratio, HIX and BIX, showed a significant microbial fraction, with only a few points that presented values associated with minor humic input, which belonged to surface runoff. These results were different from the lake network, where the humic, allochthonous input was observed along the flow of Colentina River through the lakes, evidencing the impact of the river.

Chl a spatial characterization seemed more relevant in the case of Tineretului Lake, compared to the lake network evaluation. High fluorescence intensity was recorded at samples collected from the areas with vegetation waste or sunlight exposure. The water sampled from the middle of Tineretului Lake showed the highest fluorescence intensity due to prolonged sunlight exposure. These results

indicated that Chl a fluorescence could be used to identify the areas where DOM could be subjected to photochemical processes.

In conclusion, fluorescence spectra were able to identify the minor humic input from Colentina River, at the lake network, and from surface runoff at Tineretului Lake, although both types of lakes had predominantly microbial DOM. Also, the large spatial scale experiment showed that DOM varies between lakes, but the small scale analysis evidenced the DOM variation within lake.

## 4. CONCLUSIONS

Complex spatial characterization, at small and large scale, of urban lake DOM was performed. This was the first study of DOM spatial evaluation, by fluorescence spectroscopy, on a lake network, which was compared to an enclosed urban lake. The study proved that the fluorescence technique was able to identify the varied sources of DOM, in both experiments. In each case, DOM derived mainly from autochthonous production, however allochthonous inputs from Colentina River and from surface runoff were detected, at the lake network and Tineretului Lake, respectively. BIX was more effective in identifying DOM sources compared to HIX, $C_{em}$ or $T/C$ ratio, which revealed only the major input of humic substances.

DOM from lake network samples also suffered changes caused by Colentina River flow. Fluorescence analyses showed that organic matter accumulated at the low volume lakes, being subsequently diluted into large volume lakes. Accumulation of DOM could generate a high degree of eutrophication with potential serious consequences on lakes ecological health.

Chl a spatial characterization was more relevant in the case of Tineretului Lake, compared to the lake network evaluation, showing high fluorescence intensity at samples collected from the areas with vegetation waste or sunlight exposure. Chl a fluorescence could be used to identify the areas where DOM could be subjected to photochemical processes.

This study proved that particular lake areas, with high accumulation of DOM, from both allochthonous and autochthonous sources, required extensive water quality management to improve and preserve the ecological state.

***Acknowledgements***.This study was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number PN-II-PT-PCCA-2011-3.2-0084.

## REFERENCES

1. N. Hudson, A. Baker, D. Reynolds, River Res. Appl., **23**, 631–649 (2007).
2. M. Mudarra, B. Andreo, A. Baker, Sci. Total Environ., **409**, 3448–62 (2011).

3. P. G. Coble, Marine Chemistry, **51**, 325–346 (1996).
4. R. G. M. Spencer, B. A. Pellerin, B. A. Bergamaschi, B. D. Downing, T. E. C. Kraus, D. R. Smart, R. A. Dahlgren, P. J. Hernes, Hydrol. Process, **21**, 3181–3189 (2007).
5. E. M. Carstea, A. Baker, I. Boomer, G. Pavelescu, Hydrol. Process, **23**, 1937–1946 (2009).
6. B. Hua, K. Veum, J. Yang, J. Jones, B. Deng, Environ, Monit, Assess., **161**, 71–81 (2010).
7. L. Ghervase E. M. Carstea, G. Pavelescu, E. Borisova, A. Daskalova, Rom. Rep. Phys., **62**, 193–201 (2010).
8. J. Boehme, P. Coble, R. Conmy, A. Stovall-Leonard, Mar Chem, **89**, 3–14 (2004).
9. K. Murphy, C. A. Stedmon, D. Waite, G. Ruiz, Mar. Chem., **108**, 40–58 (2008).
10. E. Pfeiffer, G. Pavelescu, A. Baker, C. Roman, C. Ioja, D. Savastru, J Optoelectron. Adv. Mat., **10**, 1489–1494 (2008).
11. N. Hudson, A. Baker, D. Ward, D. M. Reynolds, C. Brunsdon, C. Carliell-Marquet, S. Browning, Sci. Total. Environ., **391**, 149–158 (2008).
12. J. B. C. Budgen, C. W. Yeung, P. E. Kepkay, K. Lee, Mar. Pollut. Bull., **56**, 677–685 (2008).
13. C. Bernes, S. R Carpenter, A. Gardmark, P. Larsson, L. Persson, C. Skov, E. Van Donk, Environmental Evidence, **2**, 1-8 (2013).
14. F. Cui, B. Yuan, Y. Wang, Procedia Environmental Sciences, **10**, 2525–2532 (2011).
15. P. Ravikumar, M. A. Mehmood, R. K. Somashekar, Appl. Water Sci., **3**, 247–261 (2013).
16. K. M. G. Mostofa, T. Yoshioka, E. Konohira, E. Tanoue, K. Hayakawa, M. Takahashi, Limnology, **6**, 101–115 (2005).
17. N. Fujitake, K. Tsuda, S. Aso, H. Kodama, M. Maruo, K. Yonebayashi, Limnology, **13**, 45–53 (2012).
18. L. Ghervase, C. Ioja, E. M. Carstea, D. Savastru, Environ Eng Manag J, **11**, 567–571 (2012).
19. *** http://www.alpa.ro/
20. S. V. Stanescu, Ecoterra, **27**, 53–56 (2011).
21. S. Elliott, J.R. Lead, A. Baker, Water Res., **40**, 2075–2083 (2006).
22. A. Baker, R. Inverarity, M. E. Charlton, S. Richmond, Environ. Pollut., **124**, 57–70 (2003).
23. A. Baker, E. Tipping, S. A. Thacker, D. Gondar, Chemosphere, **73**, 1765–1772 (2008).
24. A. Huguet, L. Vacher, S. Relexans, S. Saubusse, J. M. Froidefond, E. Parlanti, Org. Geochem., **40**, 706–719 (2009).
25, A. Zsolnay, E. Baigar, M. Jimenez, B. Steinweg, F. Saccomandi, Chemosphere, **38**, 45–50 (1999).
26. D. N. Kothawala, E. von Wachenfeldt, B. Koehler, L. J. Tranvik, Sci. Total Environ., **433**, 238–246 (2012),
27. W. L. Miller, M. A. Moran, Limnol. Oceanogr., **42**, 1317–1324 (1997).
28. S. K. L. Ishii, T. H. Boyer, Environ. Sci. Technol., **46**, 2006−2017 (2012).