biological processes of phytoplankton that lives in cleaner waters upstream. In terms of water quality classes, the three above mentioned compounds could be found to fall within each and every class at the 10 sampling points.

3.1 Fluorescence characterization of organic matter

Examples of fluorescence EEMs sampled on Dambovita River are presented in Fig. 5. Fluorescence spectra of environmental samples generally reveal the presence of 5 peaks, which correspond to different fractions of organic matter. The peaks are located in the following excitation and emission wavelength ranges: peak T- $\lambda_{ex}/\lambda_{em}$: *260-280/325-350 nm*, peak B- $\lambda_{ex}/\lambda_{em}$: *240-250/300-310 nm*, peak A- $\lambda_{ex}/\lambda_{em}$: *240-260/420-460 nm*, peak C- $\lambda_{ex}/\lambda_{em}$: *310-350/400-500 nm* and peak M- $\lambda_{ex}/\lambda_{em}$: *310 - 320/380–420 nm.* Peaks T and B (protein-like) are associated with living and dead cellular material and their exudates, and indicate microbial activity. These peaks present high fluorescence intensity when phenolic or indolic compounds are found in the water sample. Peaks A, C and M (humic-like) are attributed to organic matter formed by terrestrial, microbial and chemical processes. Usually, these three peaks display high fluorescence intensity when humic substances are present in the sample (Carstea et al. 2014).

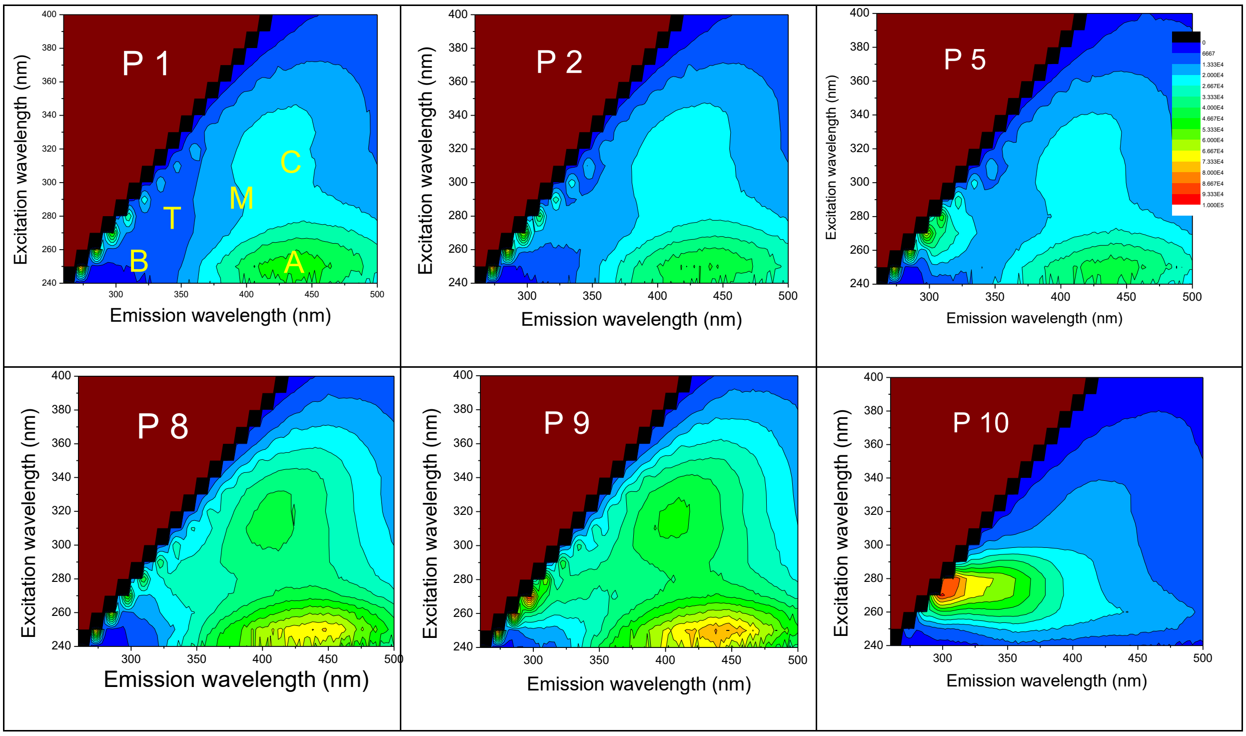

Figure 5. Examples of fluorescence excitation-emission matrices

The fluorescence spectra revealed the predominance of humic-like peaks, A, C and M, over the protein-like fluorescence, at the samples collected before Bucharest main residential area (P1-P3). The intensity of peaks T and B increased at samples towards Bucharest city centre (P4 and P5), indicating a greater quantity of microbial components and a higher anthropogenic activity compared to upstream samples. A slight decrease in intensity of all peaks was observed at samples P6 and P7 (Fig. 5), potentially due to dilution of Dambovita River with surface runoff. It may be assumed that a larger coverage of pavement produces a greater quantity of surface runoff that leaches into the river compared to unpaved areas near the river banks, as seen at sample P4 and P5. Starting with sample P8, the fluorescence intensity, especially for peak T increased and reached a maximum at sample P10, which was collected after the release of wastewater effluents. Peak T fluorescence is dominant at P10 sample due to the high quantity of microbial matter (proteins, peptides, amino acids), lignin degradation products or aromatic hydrocarbons that are generally found in the composition of treated and untreated sewage (Carstea et al. 2016). As reviewed by Carstea et al. (2016), peak T may be used to track domestic wastewater contamination in surface water, as this component is prevalent at anthropogenically impacted samples. Overall, fluorescence spectra evidenced that samples P1-P4, P6 and P7 showed similar characteristics: low protein contribution, more humic material, indicating that the water presented almost no organic contamination. Samples P5, P8 and P9 showed both humic and protein-like content, and a possible contribution from hydrocarbons especially for sample P5, indicating a mild anthropogenic impact. Sample P10 collected from a much polluted area (after Glina wastewater treatment plant) with unpleasant odor, had predominant peak T fluorescence, revealing a substantial influence from anthropogenic activities (Fig. 6).

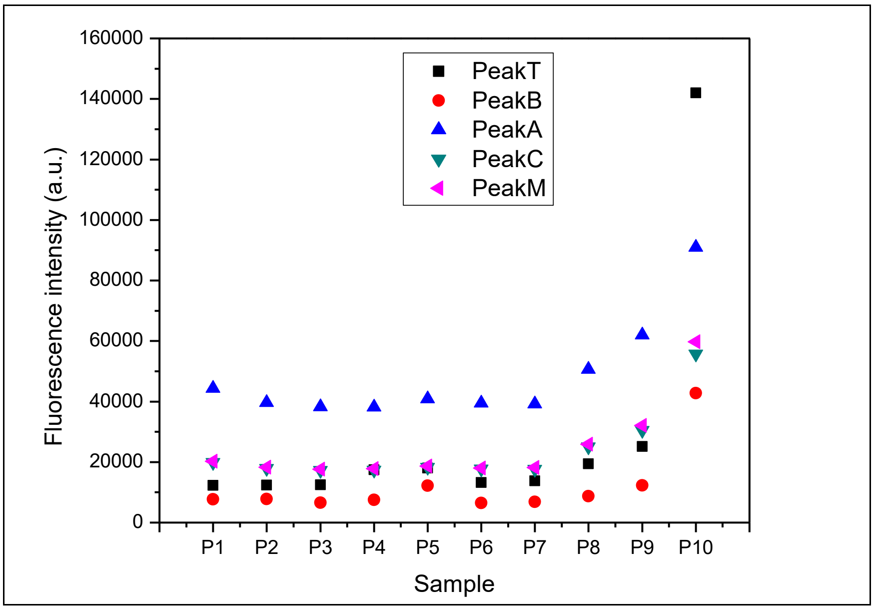

Figure 6. Spatial variation of the fluorescence peaks

The temporal analysis of results showed that higher values for all fluorescence peaks were recorded in January compared to February (Table 3). The difference in the quantity of organic matter between the two months was probably caused by the weather conditions that lead to the concentration and stagnation of pollutants. The fluorescence intensity values for the spatial and temporal analysis displayed inverse correlation with dissolved oxygen. The inverse correlation is expected since a low dissolved oxygen value indicates poor water quality, while the opposite rule is typical for fluorescence intensity. Excellent negative correlation was obtained for peaks T and B (-0.95 and -0.92), very good negative correlation with peaks C and M (-0.89 and -0.88) and good negative correlation with peak A (-0.79). Also, fluorescence values presented excellent correlation with turbidity. The following correlation coefficients were obtained: peak T (0.98), peak B (0.96), peak C (0.93), peak M (0.92), and peak A (0.83).

Table 3. Fluorescence intensity and indices for samples collected from Dambovita River

Sample	Fluorescence intensity (a.u.)									
	T		B		A		C		M	
	Jan	Feb	**Jan**	**Feb**	Jan	Feb	Jan	Feb	Jan	Feb
P1	13930	10670	8193	7214	51330	37440	25630	14160	26010	14480
P2	14000	10800	7875	7663	43410	35860	22210	13540	22510	14140
P3	14940	10050	7877	5245	44680	31820	21950	12600	22390	12960
P4	22860	11950	8887	6072	42670	33760	21040	13670	21540	14080
P5	24340	11750	18070	6404	45570	36300	23160	13430	23650	13770
P6	15190	11270	6782	6136	44700	34220	22080	13280	22560	13530
P7	15520	12070	7552	6158	43060	35310	21730	13580	22430	14010
P8	27650	11190	11260	6097	67240	34020	36850	13150	38160	13530
P9	28870	21350	14990	9542	65570	58440	36920	24080	38720	25350
P10	197900	86140	47580	38010	75920	106100	58040	53420	60350	59100

Fluorescence indices were calculated in order to obtain additional information on the characteristics of organic matter fractions. Table 4 presents the values for the humification index (HIX), biological index (BIX), fluorescence index (F450/500) and the ratio between peaks T and C (T/C). The fluorescence indices were calculated based on the equations provided by Huguet et al. (2009). HIX was introduced by Zsolnay et al. (1999) and describes the degree of maturation/humification of organic matter, while BIX represents an indicator of autochthonous biological activity in water samples (Huguet et al. 2009).

Table 4. Fluorescence indices

Sample	Fluorescence indices							
	HIX		BIX		$F_{450/500}$		T/C	
	Jan	Feb	Jan	Feb	Jan	Feb	Jan	Feb
P1	4.32	3.17	0.81	0.87	1.32	1.30	0.54	0.75
P2	3.56	2.91	0.85	0.89	1.34	1.35	0.63	0.80
P3	3.55	3.47	0.86	0.89	1.35	1.25	0.68	0.80
P4	2.67	3.26	0.87	0.91	1.36	1.39	1.09	0.87
P5	2.10	3.21	0.88	0.90	1.39	1.31	1.05	0.87
P6	3.77	3.28	0.87	0.91	1.37	1.31	0.69	0.85
P7	3.48	3.12	0.88	0.91	1.36	1.39	0.71	0.89
P8	3.44	3.22	0.95	0.90	1.49	1.36	0.75	0.85
P9	2.73	3.16	0.98	0.99	1.46	1.40	0.78	0.89
P10	0.71	1.51	0.98	1.12	1.28	1.51	3.41	1.61

According to the classifications for HIX given by Huguet et al. (2009), all samples with the exception of P1, contain organic matter with biological or aquatic bacterial origin. Sample P1 presents a weak humic character and an important recent autochthonous component. BIX provided similar results; however, it separated better between P10 and the other samples. P10 was the only sample that presented organic matter of biological or bacterial origin, while the other samples were classified as containing organic matter of strong autochthonous component. F450/500 was introduced by McKnight et al. (2001) and helps discriminate between the sources of organic matter. Values above 1.3 indicate microbial sources, while values below suggest a terrestrial source. The parameter shows that most samples contain organic matter of mixed sources. Nevertheless, the highest value was calculated for sample P10, collected in February, indicating the anthropogenic impact from the sewage discharge at that sampling point. The last parameter, T/C, can be used to identify the preponderance of organic matter fractions. As seen in Table 4, sample P10 contains a substantially higher quantity of protein-like matter compared to the other samples. This shows the significant impact of anthropogenic activities on the quality of Dambovita River.

CONCLUSIONS

The weather conditions, and particularly the freezing of the river water, influenced the physical and chemical parameters. A significant part of the pollution sources (most of them industrial and agricultural in nature) were identified, and the substantial difference between the values measured at Glina and the values observed upstream were highlighted. Chemical compounds exhibited different values, depending on the pollution sources. The amount of phosphorus and ammonia increased as the sampling point approached Glina, while nitrates decreased.

With regards to fluorescence spectroscopy, humic compounds dominated the upstream samples, up to P7 sampling point. In the sector between P7 and upstream of Vacaresti Lake, humic acids dominated the samples, with a weak presence of protein-like substances. Then, before passing through the Glina treatment station, the water samples contained, in roughly equal proportions, protein-like and humic compounds. Downstream of Glina, the microbial element became the most important.

According to the Order no. 161/2006, the quality of water found in the 10 sampling points differed from one location to another for every parameter, and fitted into one of the 5 water quality classes established by the Order. The methods for determining the quality of water are complementary and confirm the link between organic substances found in water and the values of physical and chemical parameters. Because of the nature of the data on water quality for Dambovita, we believe that this study will bring significant advances in the level of knowledge on this subject, updating and completing the issue of water quality management (the AGIR Bulletins, the hydrological protection plans for the city of Bucharest drafted by the Mayor’s Office and ANAR, the analysis bulletins and the yearbooks compiled by the Argeş-Vedea Basin Management Authority etc.).

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