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EVALUATION OF THE ANTHROPOGENIC IMPACT ON THE WATER QUALITY OF DAMBOVITA RIVER

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ABSTRACT

The river Dambovita, which crosses Bucharest city, is characterized by two superposed artificial riverbeds: the lower part, under Dambovita river floor, which is a channel containing sewage from the city and the upper part, which is cleaner and combines with the lower part when exiting Bucharest. This study aims to evaluate the anthropogenic impact on the water quality of the upper canal. Samples were collected from 10 points along the sector, during two sampling campaigns, between January and February 2015. These points were chosen based on the ease of access, the environmental characteristics and any possible human influence. Physico-chemical parameters were measured: the concentration and saturation of dissolved oxygen, temperature, pressure, pH, turbidity, conductivity, amount of ammonium, phosphorus and nitrates. In addition, fluorescence spectroscopy method was used to determine the presence and types of organic substances in water samples. The results showed significant differences between the urban sector of Dambovita and the final sampling point, situated downstream of the Glina wastewater treatment plant. Fluorescence measurements showed that the quantity of humic substances had a continuous increase along the sector. Regarding the microbial fraction, fluorescence spectroscopy revealed a sudden increase at the sample collected from the entrance of the river in Bucharest and at Glina sewage effluent discharge point. Fluorescence results evidenced the anthropogenic impact on the water quality of Dambovita River. In conclusion, the quality of Dambovita waters varies across space and time, depending on human influence affecting the areas from where samples were taken and also reflecting a temporal variation, with a drop in quality during January, caused by weather conditions that lead to the concentration and stagnation of pollutants.

Keywords: water quality, fluorescence spectroscopy, dissolved organic matter, Dambovita River.

1 INTRODUCTION

The importance of Dambovita River, as a hydrographic artery, stems from the possibilities of using its waters for various purposes and also from the need to establish a detailed research program on the physical and chemical state of water and its polluting factors, including the solutions that can combat the decreasing quality of water. Dambovita River has undergone numerous changes, which have led to the creation of an entirely artificial water course in the sector that passes through Bucharest. This specific sector of Dambovita River has a unique hydro-technical structure, which is represented by two superposed artificial riverbeds: the upper part collects the clean waters from Morii Lake, built to attenuate the floods and to store water for different uses, while the canal underneath accumulates all the wastewater from the city.

The problem of pollution affecting Dambovita when passing through Bucharest, has been investigated by various authors (e.g. Morcotet et al. 2011; Cocos 1998) and by specialized institutions from numerous perspectives, including water resources management, with the goal of improving quality of life and achieving a sustainable development (Order no. 161/2006 approving the Norms concerning the classification of surface waters quality to establish ecological status of water bodies).

Hydrochemistry research and methods for assessing water quality represented a starting point for this study, and we included both older works, studies and synthesis, as a theoretical foundation, and recent research, valuable in terms of methodology both for Romania – Ioja (2008) and at an international level: Meratnia et al. (2000), Debels et al. (2005), Boyacioglu (2006), Said et al. (2007).

This study aims to create an inventory of data on water quality and to carry out a quantitative and qualitative analysis, at spatial and temporal scale. The quantitative evaluation will include the measurement of the concentration of dissolved oxygen, temperature, pressure, pH, turbidity, conductivity and the amount of ammonium, phosphorus and nitrates. The qualitative component involves the use fluorescence spectroscopy to assess the character of dissolved organic matter fractions and the type of organic pollution. The present research is part of recent trends involving the study of water quality in rivers that cross major urban areas, serving the goal of better understanding the temporal and spatial evolution of relevant parameters and the economic or environmental significance of exceeding certain quality limits.

2 STUDY AREA

Samples were collected along a sector of Dambovita River that crosses Bucharest, and involved a field study on a distance of ~ 21 kilometers, from the entrance in a lake reservoir (Morii Lake) until the effluent discharge point at Glina wastewater treatment plant (Fig. 1). The details regarding the sampling points locations and the potential sources of contamination are presented in Table 1.

Figure 1. Location of sample collecting points

Table 1. Details of sampling points

Sample name	*Details of sampling points*
P1	Land use: Mixed area with scattered houses and natural green spaces prone to flooding, on the right, and open fields and scattered houses on the left side of the river. Possible sources of contamination: riverine vegetation and agricultural runoff from upstream areas
P2	Land use: on the left - dump sites, no houses and fallow vegetation and on the right – households from Dudu village. Possible sources of contamination - Dudu Village storm drain
P3	Land use: open field, fallow vegetation and scattered houses in the distance. Possible sources of contamination: village wastewater
P4	Land use: Residential area, open fields, greenhouses. Possible sources of contamination: Dambovita Swimming pool, arable land and dump sites.
P5	Land use: residential, commercial and industrial areas. Possible contamination sources: heavy traffic, households, commercial waste, rain that travel across CET Grozavesti
P6	Land use: green areas (Izvor Park upstream), residential, administrative and commercial area. Possible sources of contamination: heavy traffic, passers-by, wastewater
P7	Land use: residential area, agriculture, commercial spaces (warehouses). Possible sources of pollution: wastewater, agricultural drain water
P8	Land use: Agriculture (especially greenhouses), Industrial Area (CET Sud), Green areas and wetlands (Vacaresti ”Delta”), open fields. Possible Sources of contamination: industrial waste, wastewater, agricultural waste (greenhouses), traffic
P9	Land occupied by deposits of building materials, Agricultural area, open field and commercial area. Possible contamination sources: industrial waste, city storm drain, agricultural waste
P10	Sources of contamination: industrial wastes, agricultural wastes, all the water coming from Dambovita River underground water canal, containing all wastewater collected on the river’s way through Bucharest

3 RESULTS AND DISCUSSIONS

For all 10 points, the physical and chemical parameters of water were determined: dissolved oxygen [mg/l and C%], water temperature at the moment when the sample was collected [°C], pH, conductivity [µS], turbidity [mg/l] by using EPA 180 methods, and also the amounts of ammonium, phosphorus and nitrates found in the water [mg/l]. Some values are presented in Table 2.

Table 2. Physico chemical parameters

	Dissolved Oxygen (mg/l)		*Conductivity (µS)*		*Turbidity (mg/l)*	
	Jan	***Feb***	***Jan***	***Feb***	***Jan***	***Feb***
P1	3.30	2.50	465.00	602.00	11.5	5.1
P2	3.60	3.30	499.00	547.00	6.35	3.72
P3	3.40	3.60	566.00	515.00	11.6	4.82
P4	3.70	3.50	495.00	467.00	6.87	4.4
P5	3.90	3.50	710.00	460.00	4.25	3.89
P6	3.80	3.60	559.00	461.00	4.35	4.29
P7	3.70	3.30	725.00	478.00	4.19	3.76
P8	3.80	3.40	365.00	486.00	4.43	3.54
P9	**3.80**	**2.30**	459.00	750.00	10.3	7.43
P10	***1.10***	***0.20***	525.00	699.00	266	31.5

For the sampling points situated upstream of Glina, the dissolved oxygen in the samples was included into the 4th class of quality (poor water quality), and at the last point downstream of Glina, the water sample was found to belong to the last category (Class 5 – degraded water that cannot be used and is harmful to humans and to aquatic organisms). The dissolved oxygen presented low values for sample P7 and the first sampling point (P1) and very low values at the sample downstream of the Glina wastewater treatment plant (P10). The concentration of dissolved oxygen is illustrated in Fig.2 for the samples collected in January 2015.

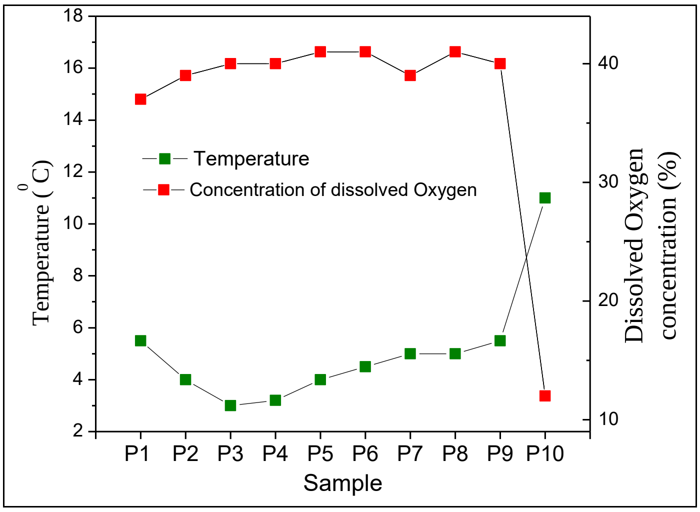

Figure 2. Correlation between water temperature and concentration of dissolved oxygen

In addition, it was possible to establish an inversely proportional relation between these two physical parameters, thus illustrating the importance of this relation of dependency and the increase of one parameter (temperature) when the other one decreases, causing damage to the aquatic environment, which depends on the presence of dissolved oxygen. We took notice of the water samples collected at Glina (P10), where water temperature was above 10 degrees Celsius at the moment when they were collected, and dissolved oxygen was less than 10%.

The concentration of several pollutants impacted upon the variation of pH, which is sensitive to fluctuations when the surface of the water is covered by a layer of ice, and temperatures oscillate diurnally. For this reason, although the increase was not alarming (max pH of 7.18 at the Grozavesti wharf, compared to maximum admitted concentrations between 6.5 and 9.5), it marked an increase in the water's alkalinity in

January, accompanied by more homogenous values for conductivity (The minimum value for January was 25 µs, and the maximum was 365 µs, compared to 875 µs and 286 µs in December, a month characterized by thermal inversions and potential stagnation of pollutants). Furthermore, January holds the record for the number of points (9 out of 10) where pH values did not exceed the maximum legal limits. The inverse proportionality between conductivity and the dissolved oxygen (Fig.3), can be explained by the increase of dissolved oxygen that takes place when polluting substances that cause turbidity are eliminated from water.

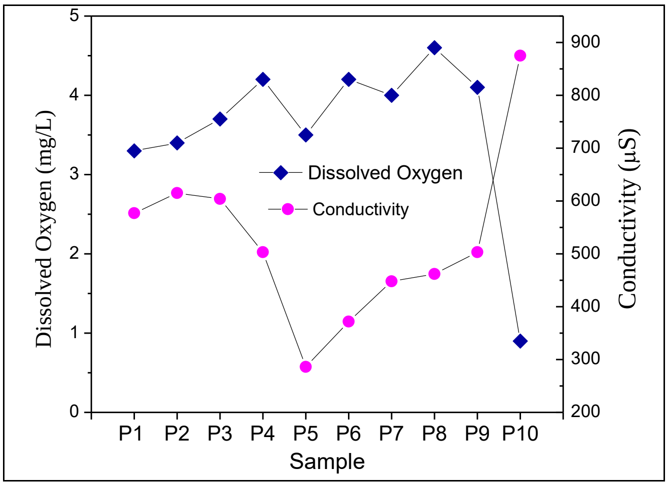

Figure 3. Correlation between conductivity and dissolved oxygen

The observations on pollution sources, the analysis of land use near Dambovita, the possible connections to the sewage network and weather conditions during sampling, all become reference points for interpreting the values taken by the water quality parameters. Thus, the results indicate an increase in temperature, conductivity, ammonium content, turbidity and phosphorus as water moves closer to the Glina sampling point, coinciding with a drop in the concentration and saturation of dissolved oxygen, water pressure and nitrate content. In the context of increased conductivity and an accumulation of pollutants in the water, turbidity also rises (Fig. 4).

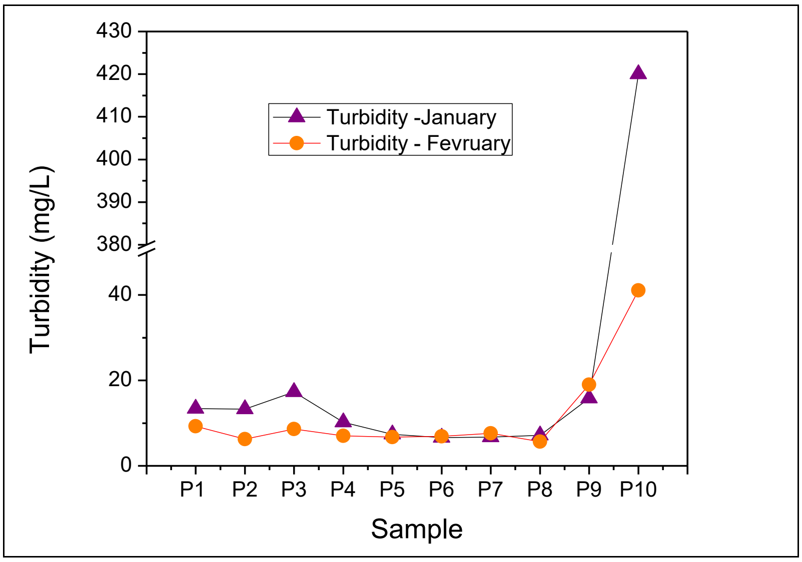

Figure 4. Turbidity variation chart

The amount of organic and inorganic matter carried by water exhibited a sharp increase towards the final sampling point at Glina, from a value of less than 190mg/l in samples taken upstream all the way to 420mg/l downstream of Glina. The analyzed organic compounds, the amounts of phosphorus, nitrates and ammonium, were found to fall within two general intervals, in accordance with their water interaction properties and their ability to react with other organic and inorganic compounds. On the one hand, mineral phosphorus and ammonium increase as we move closer to Glina, due to high biochemical intake in the context of exothermal and anaerobic reactions and of the water nutrient saturation. On the other hand, the amount of nitrates registered the lowest values at Glina, since this compound is already used up by the 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).

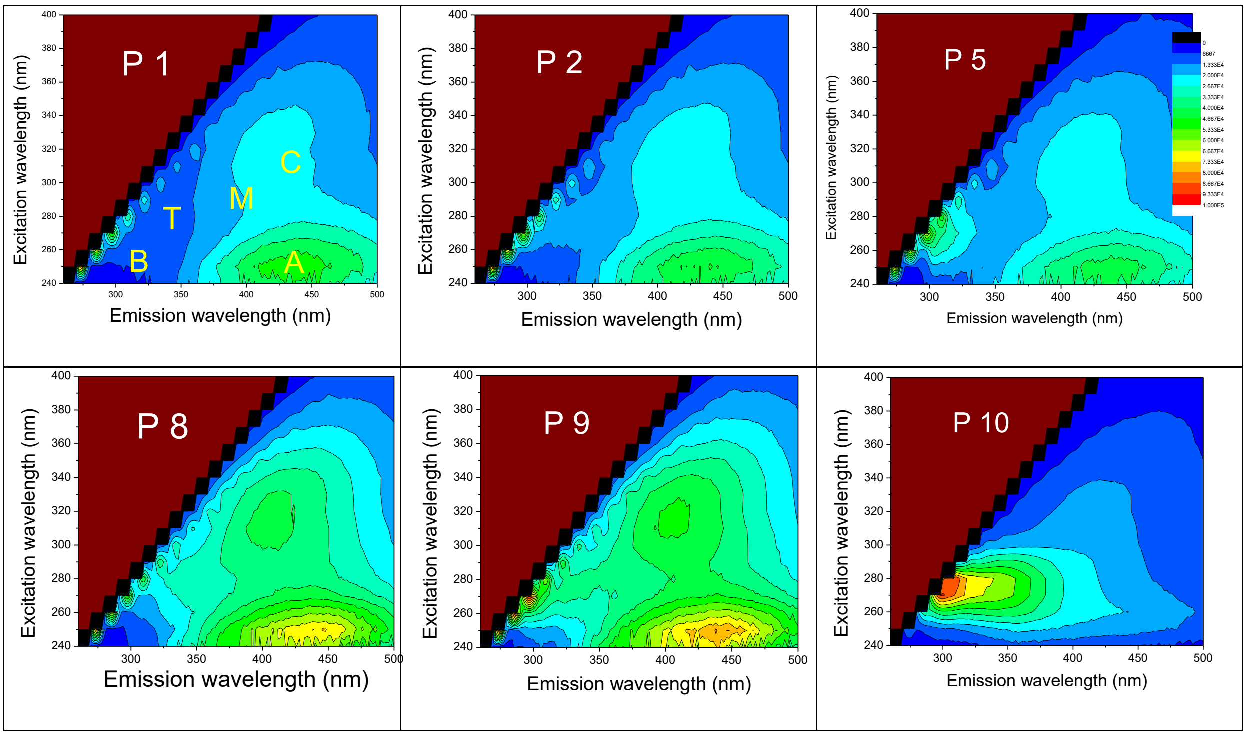

Figure 5. Examples of fluorescence excitation-emission matrices

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).

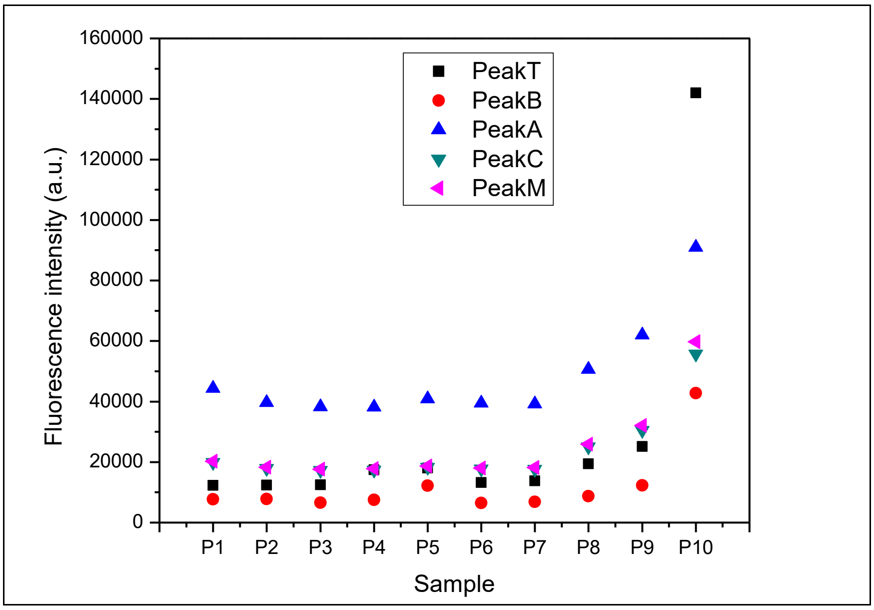

Figure 6. Spatial variation of the fluorescence peaks

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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