Romanian Reports in Physics, Vol. 62, No. 1, P. 193–201, 2010

FLUORESCENCE EVALUATION OF ANTHROPOGENIC INFLUENCE ON RIVERS CROSSING SOFIA

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(Received May 19, 2009)

Abstract. Fluorescence spectroscopy was used to evaluate the anthropogenic influence on rivers crossing Sofia. Specific fluorescence fingerprints for different sampling locations on Dragalevska, Perlovska and Vladaiska rivers were compared. The increase in pollution downstream due to the continuous contribution of surface runoff and the presence of protein-like fluorescence peak coming from old surface runoff waters were shown. The fluorescence and biological indices were used to evaluate the relative fraction of microbial and humic substances in each river. Fluorescence recordings have proved that the major source of dissolved organic matter in the investigated rivers is allochtonous, specifically due to the release of old urban runoff.

Key words: fluorescence spectroscopy, surface runoff, anthropogenic influence, urban river.

1. INTRODUCTION

As the urban residences tend to increase, so does the effect they have on the natural ecosystems. Larger cities mean more houses, cars, factories, all of them leaving a mark on the environment and eventually on human health. The capital city of Bulgaria is a major town, crossed by several rivers, amongst which there are: Dragalevska, Perlovska and Vladaiska. The need to protect the environment leads to the need of better understanding the pollution sources, effects and treatment options. Standard chemical parameters for water quality are currently determined by local environmental agencies, but no data on urban runoff has been reported so far. Urban runoff originates from the human daily activity in the city and can be one of the most important factors affecting river water quality.

During the last years, fluorescence spectroscopy has been widely used in water studies as an alternate method for water quality tests, like biochemical oxygen demand (BOD) or chemical oxygen demand (COD), which are time and cost-consuming [1–4]. The fluorescence signal can be recorded as a fluorescence map, named excitation-emission matrix (EEM), which is obtained by collecting several emission spectra at different excitation wavelengths and assembling them into a two-dimensional image. This contour map symbolizes a fingerprint specific to different fluorophores present in a water body. The fluorescence maximum for an excitation wavelength / emission wavelength pair corresponds to a specific compound, its intensity being proportional with fluorophores concentration.

In natural aquatic systems, the commonly encountered fluorescent substances are the so-called humic-like and protein-like. The humic substances (specifically humic and fulvic acid) are derived from the breakdown of plant material and from soil, through geological activities [5], whilst the protein-like fraction (represented by tryptophan and tyrosine) is produced through microbial and algae activity [4, 6]. The fluorescence response of these fractions can be used as indicator of water quality and can establish by the specific fingerprint of water bodies the autochthonous or allocutions origin of organic matter. Fluorescence spectroscopy can provide valuable information about the characteristics of dissolved organic matter present in the water: hydrophobicity [8], aromaticity [9], anthropogenic inputs [10], and biological activity [11]. McKnight et al. [9] have discriminated microbial-derived humic substances from the terrestrially-derived fraction by calculating the fluorescence index (ratio between the emission intensity at 450 nm and at 500 nm, with excitation at 370 nm).

The aim of the present paper was to point out the anthropogenic impact, represented by the surface runoff released into some rivers crossing Sofia, using fluorescence spectroscopy. The specific fluorescent fingerprint of each sample was obtained using excitation-emission matrices. Dissolved organic matter has been characterized by calculating the fluorescence and biological indices in order to evaluate the relative fraction of microbial and humic substances in each river. These indices can help identify the source of dissolved organic matter in rivers.

2. DATA AND METHODS

Water samples were collected in September 2008, after one rainy day, along the course of three Bulgarian rivers, Dragalevska, Perlovska and Vladaiska, from 10 collection points for each river, at 0–0.5 m depth. The anthropogenic impact on these rivers is expected to originate mostly from surface runoff and not from household discharges, which are collected in the city sewerage. The sampling points were distributed from the entrance to the exit of the city, covering uninhabited and inhabited areas, as can be seen in Fig. 1, where 4 representative locations for each river and 2 locations, before and after water treatment station are indicated.

Dragalevska River (sampling points P10–P13) issues from Vitosha Mountain and crosses Sofia in the south-east part of the town. Perlovska River (sampling points P40–P43) traverses Sofia through the middle of the city from south to north-east direction, passing mostly through an inhabited area. Vladaiska River (P30–P33) from south-west to north-east part of the city and is tributary of Iskar River. It collects the runoff water from almost all parts of the town starting from the suburbs, before entering the town (P30) and it also collects some additional sewer channels in the north-east area of Sofia.

Before reaching the treatment station, all three rivers join in one common river. City wastewater is released into this river (P50), all contributions being collected by the treatment station. The treated water flows into Iskar River (P51), which reaches Danube after passing of the north-west part of the country.

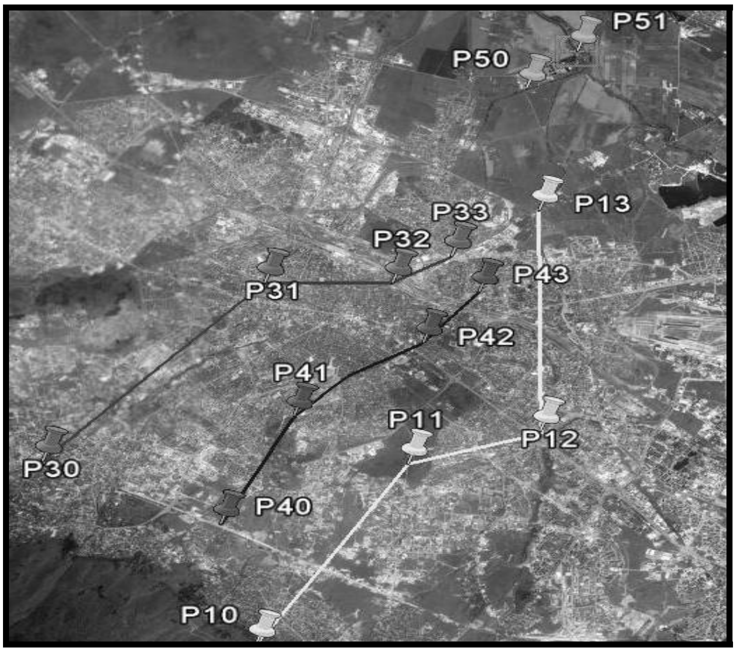


Fig. 1 – Sampling locations along the rivers crossing Sofia.

The samples were stored in glass bottles at 4 ºC for 2 days before they were analyzed. The samples were filtered (0.8 μm pore size filter) before measurements were made. Fluorescence spectra were recorded using a FLS 920 Edinburgh Instruments spectrometer equipped with a Xenon flash lamp, using 10 mm quartz cells. The excitation wavelength was set between 240–400 nm and the emission in the 250–700 nm wavelength range. The excitation and emission slits were 4 nm and the integration time was 0.2 s.

Physical parameters pH and conductivity were also measured using a pH/mV/Ion/Temp – meter and pH/mV/Cond/Sol/Temp – meter Laser Laboratories, respectively.

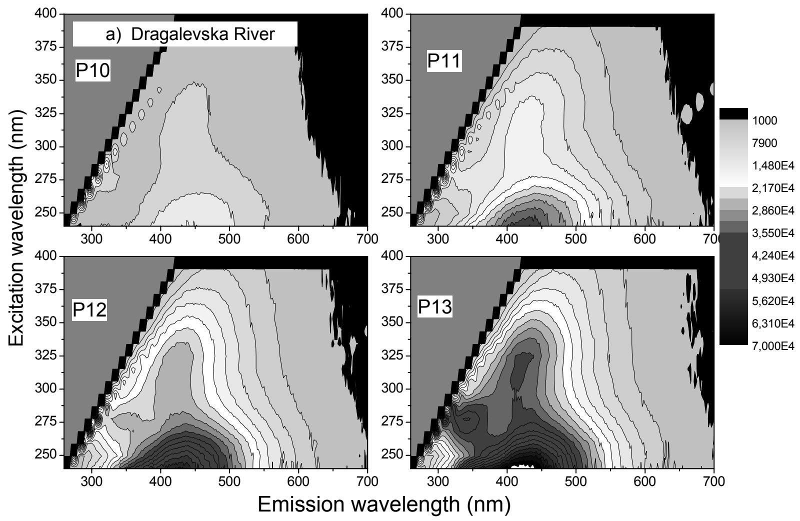
4. RESULTS AND DISCUSSION

All samples investigated had pH values between 6 and 7, which are normal values for river water. The conductivity recordings were between 80 and 890 μS/cm, higher values being registered for the most polluted water (P50), before the water treatment station.

Fluorescence excitation-emission matrices recorded for water sampled at four locations on each river are shown in Fig. 2. All data are presented in quadrant form as follows: the left-up corner represents the samples from the river water before its entrance to Sofia; in the right-up corner is the second sample, collected from the river water in the first third of its stream in the frames of the town; left-down shows the third sample, from the river water in the last third of its stream in the frames of the town and finally, the right-down represents the forth sample, which is from the river water after the exit of the river from Sofia area. For comparison purpose, all maps were normalized at the same fluorescence intensity value.

The position of the principal fluorophores typically observed in rivers and wastewaters [1–5] can be identified from the recorded matrices. The spectra show the presence of humic like substances in the 400–480 nm domaine and the protein-like components in the range of 300–360 nm.

The fluorescence fingerprints for Dragalevska evidence the urban influence by presenting higher fluorescence intensity of P12 and P13 samples in comparison with samples P10 and P11, which are collected before and right after the entrance to the city, in a green, uninhabited area, without pollution sources. The major contribution of urban region is brought by surface runoff waters which are directly



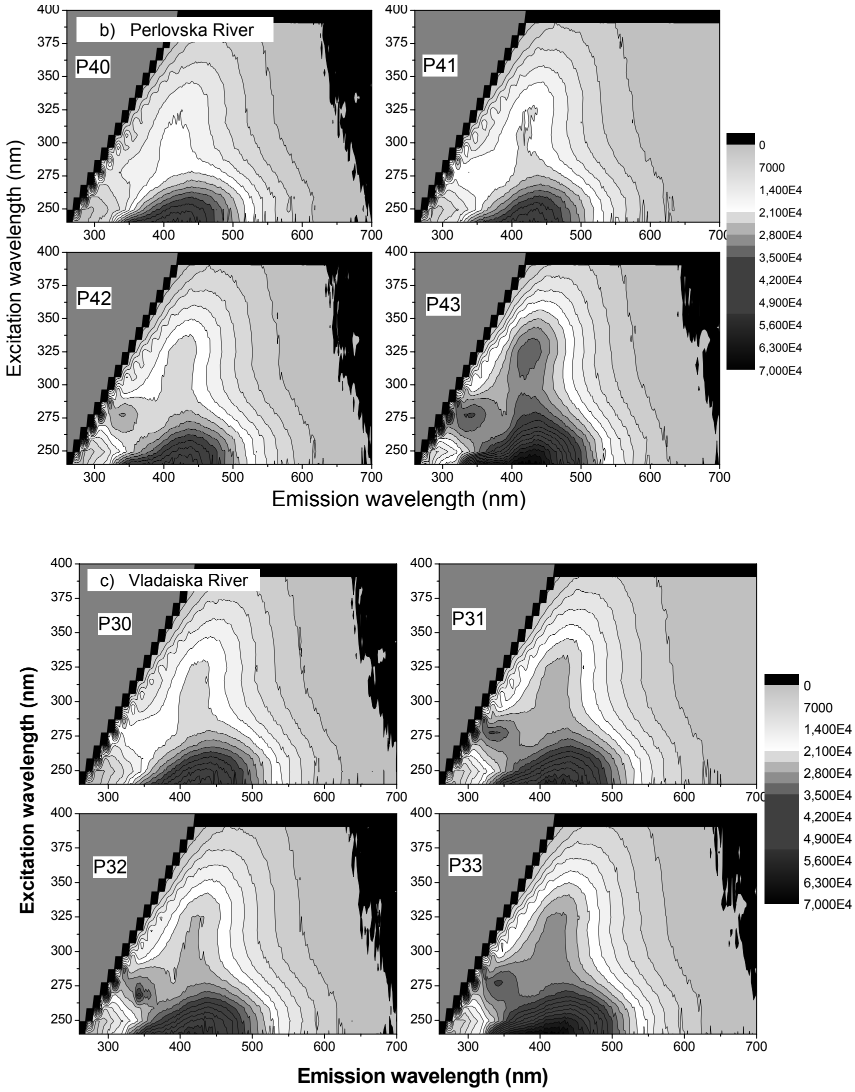
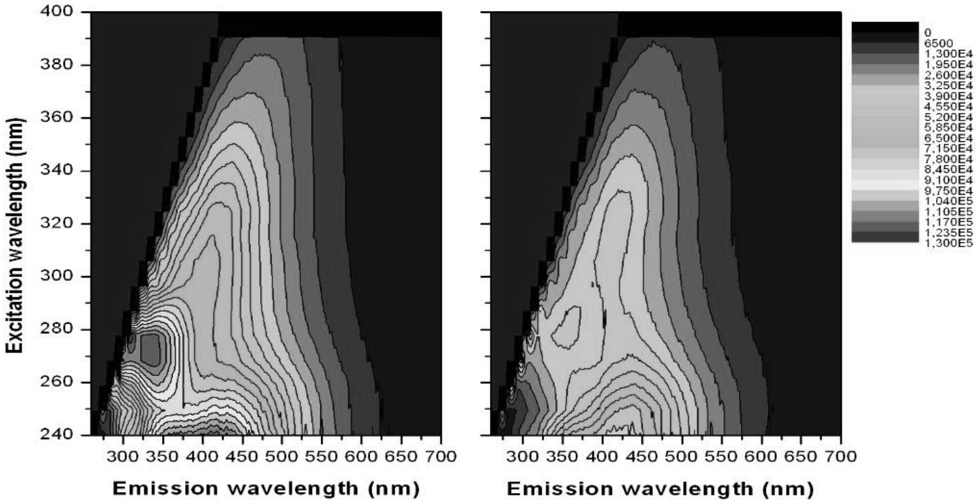


Fig.2 – EEM matrices of the four sampling points for:
a) Dragalevska, b) Perlovska, and c) Vladaiska rivers.

discharged into the rivers. In P12 and P13, sampled after the river passes through an inhabited zone, the tryptophan-like fluorescence peak can be observed. In our opinion this fluorescence is generated by old surface runoff waters and by accumulation of old water inputs, respectively. Old surface runoff waters correspond to runoff water stored in street, storm drain and sewer networks.

The same peaks can be observed in the spectra of Perlovska (Fig. 2b) and Vladaiska (Fig. 2c) rivers, but because of the fact that the sampling locations are from inhabited areas, the protein contribution is high from the beginning (P40, P30 respectively) and it increases as the rivers cross the city (P43, P33 respectively). Vladaiska River covers the longest distance through the city, thus being subjected to the urban impact more than the other two rivers. This influence is reflected in the fluorescence maps by the high protein-like intensities.

Figure 3 shows the excitation-emission maps, normalized at the highest fluorescence intensity value, for samples before (P50) and after (P51) water treatment plant. Because the water reaching the treatment station contains wastewater discharges from the entire city, the EEM map shows a higher intensity of tryptophan peak (excitation 270 nm /emission 340 nm) in comparison with humic substances (emission 400-480 nm). The fluorescence EEM for P50 sample represents a specific fingerprint for sewage wastewater. The cleaning procedures applied in the treatment plant reduce the microbial fraction in the water, which can be seen in the representative EEM map of sample P51. The intensity of humic acid fluorescence also significantly decreases in comparison with the water samples before purification procedures applied.



a) b)

Fig. 3 – Comparison between water samples: a) before, and b) after cleaning station.

The surface runoff influence, after a rain event, on all three rivers is shown in Figs. 4a and b. To monitor the microbial distribution along the rivers, the fluorescence intensity of amino acids (340 nm) obtained under excitation at 280 nm was recorded Fig. 4a). It presents the evolution in 4 collection points of the protein-like fluorescent component, normalized with respect to the Raman peak at 310 nm. For all rivers the effect is cumulative – downstream the organic contamination increases, as well as the fluorescence intensity of the protein-like maximum, correlating with the content of microbial pollutants in the water samples, consequence of the allochthonous input with old surface runoff.

Figure 4b shows the fluorescence intensity of humic – like component (emission at 440 nm), normalized with respect to the Raman peak (310 nm) of each sample. For Perlovska and Vladaiska rivers no significant changes have been observed in the fluorescence emission intensity. In the case of Dragalevska River some changes can be noted, but they depend on the local environment of the sample collection points and do not correlate with the position in the stream of the river itself. Significant part of its stream in the frames of the town is mainly in its natural river-bed, therefore the observed increase of the humic substances fluorescence could be related also to the structure of the river banks as additive to the urban sources.

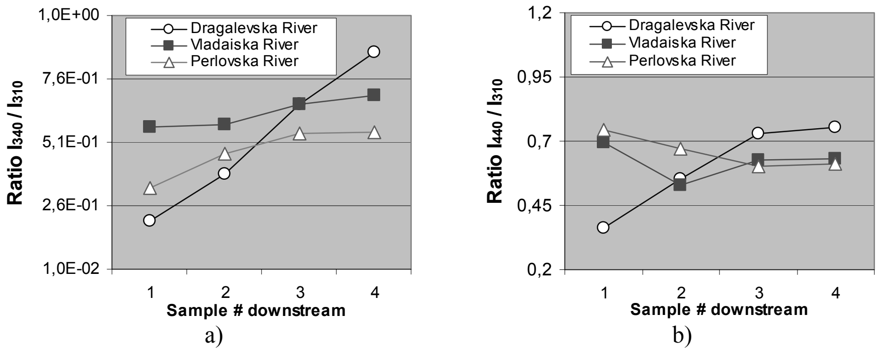


Fig. 4 – Graphical representation of normalized to Raman peak of:
a) protein-like, and b) humic-like fluorescence for the three river systems.

Fluorescence index (FI) defined as the fluorescence intensity ratio 450 nm/500 nm, excitation at 370 nm, is a tool in identifying the humic matter origin [9]. All samples indicate that most of the humic substances are terrestrially derived (fluorescence index in the range of 1.21–1.56), denoting an allochthonous input from surface runoff waters released into the rivers. The FI values obtained are comparable with the work of McKnight et al. [9]. For Dragalevska River a linear increase of FI from 1.2 to 1.4 is observed, as the river flows downstream, due to natural degradation processes of vegetation. For Perlovska and Vladaiska rivers the FI varied unevenly, related to more random discharge from different kinds of urban sources.

The accumulation of runoff water into the drain pipes facilitates the development of bacterial flora, this water being released into the river after rain. To evaluate the impact of old surface runoff (water stored in street, storm drain and sewer networks) to the river water quality, the ratio between the microbial and humic fractions, as biological index (BIX), was applied. The biological index was introduced by Huguet et al. [12] to evaluate the origin of dissolved organic matter from marine samples, calculating the ratio between the fluorescence emission intensity at 380 nm and 430 nm, excitation at 310 nm. As marine samples present different fluorescence characteristics, this specific index cannot be applied to all types of water systems, therefore we adapted BIX in order to evaluate surface runoff impact on rivers. The biological index in our case was obtained as the ratio between fluorescence emission maximum in the range of 300 – 345 nm and of 425 – 480 nm. The excitation wavelength was chosen at 250 nm, taking into account that it excites both protein-like and humic-like substances typically found in river waters. All samples measured in our study, as can be seen in Fig. 5, have BIX values lower than 0.5, denoting an allochthonous nature, according with values of about 0.6 obtained in [12]. For Dragalevska the linear increase of biological index denotes an increase of microbial component due to anthropogenic influence by new and old runoff flushed from the urban storm sewerage system.

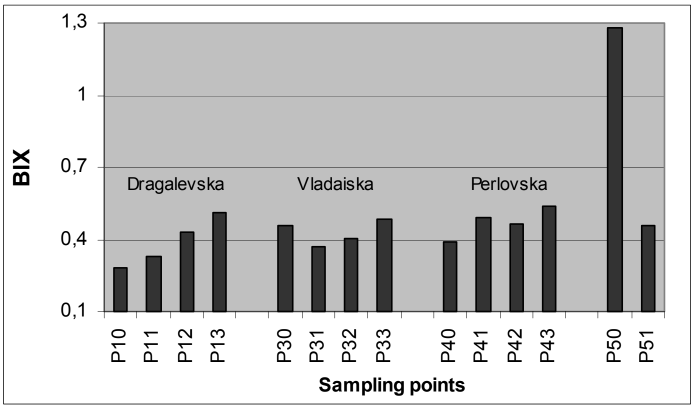


Fig. 5 – Biological index for different sampling location.

Different results have been obtained for Perlovska and Vladaiska rivers, which indicate a random contribution of humic substances (plant matter and soil leaching) and microbial (old and new runoff flow) determined by local urbanized catchments along the rivers.

The effect of water treatment station is evidenced by a significant decrease of biological index value after cleaning station, which implies an important decrease of the microbial component.

4. CONCLUSIONS

Fluorescence spectroscopy, in the form of excitation-emission matrices, and related indices have been used in order to evidence the surface runoff influence on the quality of urban rivers crossing Sofia.

Fluorescence index values indicated that most of the humic substances are terrestrially derived, pointing out the allochthonous input from surface runoff waters released into the rivers. The biological index, obtained as the ratio between fluorescence emission maximum in the range of 300–345 nm and of 425–480 nm, excitation wavelength at 250 nm was applied for the first time to evaluate the surface runoff impact on rivers. The biological index highlighted the contribution of old water accumulated in the storm drains to the urban rivers, due to the increase of the microbial component in the water.

Based on the resulting EEM maps it can be concluded that fluorescence can rapidly and accurately identify the degree and origin of dissolved organic matter in urban rivers. Knowing the level and sources of river pollution, it can be easier to control the water treatment processes, thus improving the health of humans and ecosystems.

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