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Correlation of dissolved organic matter fluorescence and several metals concentration in a freshwater system

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Abstract

Dissolved organic matter (DOM) strongly influences several ecosystem processes, including the reduction of solar radiation, control of nutrient availability, modification of contaminant toxicity, and energy cycling. Using fluorescence spectroscopy, one of the most important DOM features, metal binding affinity, has been characterized, due to its direct effect on aquatic ecosystems. This paper presents the analysis of the relationship between type and concentration of metal ions and DOM fluorescence for water sampled from Arges River. The results suggest that certain competitive complexation processes occur among metal ions and that iron and chromium ions have the most significant impact on DOM fluorescence.

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Keywords: fluorescence spectroscopy; dissolved organic matter; metal binding affinity; wastewater

1. Introduction

Dissolved organic matter (DOM), the ubiquitous fraction in soil and aquatic ecosystems, is a heterogeneous mixture of primarily complex compounds, being among the largest reservoirs of carbon on Earth. The dynamics and characteristics of DOM strongly influence a number of ecosystem processes, which include the reduction of solar radiation, control of nutrient availability, modification of contaminant toxicity, and material and energy cycling [1]. It comprises the decay products of animal and plant matter [2]. Due to the fact that some DOM components are intrinsically fluorescent, their

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fluorescence has been intensively used to characterize and detect contaminations in water systems. The fluorescent DOM fractions, which provide water quality information, are tryptophan-like and tyrosine-like (protein-like), indicators of microbial activity, and humic-like, derived from both allochthonous and autochthonous sources. The fluorescent signal is mostly recorded as excitation - emission matrix (EEM) which is formed by collecting a large number of emission spectra, within certain excitation and emission wavelength domain, and combining them into a two dimensional image. It has been shown that EEMs confer sensitivity and selectivity to the measurement [3, 4]. In figure 1, an EEM is exemplified containing the typical fluorophores found in DOM. The excitation/emission wavelength pairs, specific to each component are, as follows: T1 and T2 for tryptophan ($\lambda_{\text{excitation}} / \lambda_{\text{emission}}$: $\sim 280 / \sim 350$ nm for T1, and $\sim 225 / \sim 350$ nm, for T2), B for tyrosine ($\lambda_{\text{excitation}} / \lambda_{\text{emission}}$: $\sim 225 / \sim 305$ nm), A ($\lambda_{\text{excitation}} / \lambda_{\text{emission}}$: $\sim 225 / 400 - 500$ nm), and C ($\lambda_{\text{excitation}} / \lambda_{\text{emission}}$ = $300 - 350 / 400 - 500$ nm) for humic substances.

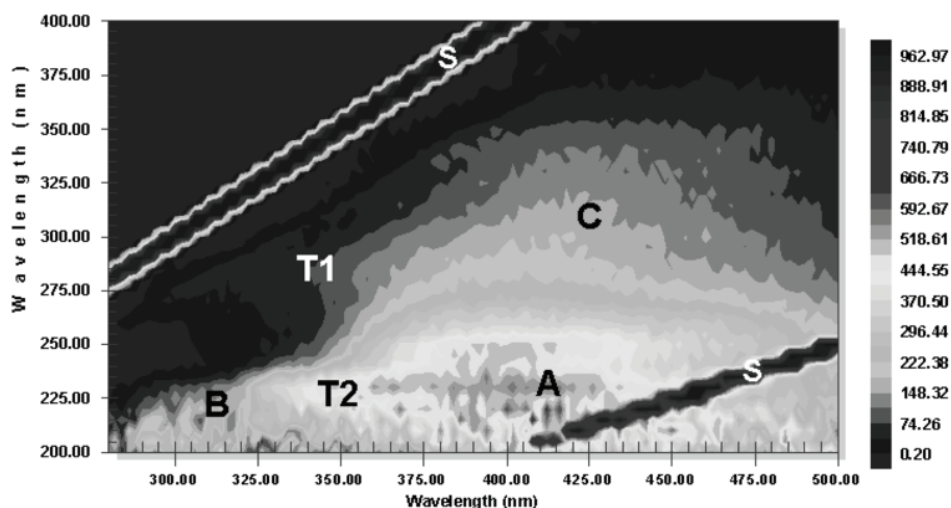


Fig. 1. Fluorescence excitation – emission matrix showing the DOM fractions: T and B -protein-like; A and C -humic-like. The excitation wavelength is represented on the ordinate, and the emission wavelength on the abscissa.

In the past decades, numerous studies have shown that these fluorophores can provide more information about the characteristics of DOM and the aquatic system. According to some studies, peak C fluorescence intensity correlates with total organic carbon [5], shows a linear relationship with aromaticity [6], relates with the molecular weight of organic fractions [7] and shows the degree of hydrophobicity [8]. Peak T presents a very strong correlation with the standard parameter biological oxygen demand (BOD). Some researchers [9, 10] even tested the possibility of using peak T fluorescence as a surrogate for the standard water quality parameter, BOD. The relationship between biological activity of aquatic plankton, along with algae metabolism rates, and peak T fluorescence intensity for different DOM types has also been observed [11]. Fluorescence spectroscopy has helped to identify some of the most important DOM features: temporal variability [12, 13], spatial variability [14, 15], transport in the environment and interaction with pollutants, complex formation capacity [16, 17].

Complex formation is an extremely important characteristic of DOM because it has direct effect on surface water, groundwater and soil quality. The availability of numerous metal ions to plants and microorganisms and their transport in the environment are highly dependent on the complex formation

process with DOM, specifically humic substances. Considering the continuous and increasing input of heavy metals to the environment [18] and the guidelines of the European Water Framework Directive and the US Environmental Protection Agency programs to improve the ecological health of water bodies and to regulate the quantity of heavy metals in the environment [19, 20], there is an urgent need to better understand the metal – DOM complex formation process in freshwater systems.

The ability of DOM to bind metals during transport through water or soil, and form stable, aqueous complexes with copper, nickel, zinc and other ions has been shown in numerous works [21, 22, 23, 24, 25]. However, most of these studies have been made on organic matter extracts and it is unclear how these processes interfere with fluorescence in samples collected from freshwater with multiple sources of pollution. Therefore, this paper aims to evaluate the relation between DOM fluorescence and metal ions type and concentration at raw samples collected from the Lower Basin of the Arges River, which receives pollutants from multiple sources. The potential impact of several metals with different binding strengths has been tested for both protein-like and humic-like components.

2. Methodology

The Arges River is located in the S-SE of Romania traveling through 5 counties, for 350 km, until it flows into the Danube. The entire Arges Basin stretches over an area of 12600 km², collecting the water from 20 tributaries. The water from the Arges River Basin is mostly used for drinking and agriculture [26] by the residential areas along the river, and for these reasons it is highly important to evaluate and improve the water quality.

Water has been sampled from 5 points, within the Lower Basin of the Arges River (Fig. 2), which collects different types of contaminants or is located near several sources of pollution:

- *Sabar* point, located on Sabar River, near industrial sites, agricultural lands and a solid waste disposal site;
- *Colibasi* point, located on Arges River, in an area with intense agricultural activities;
- *Hotarele* point, on Arges River downstream of Sabar River confluence, collecting mostly farm wastes;
- *Budesti* point, located on Dambovita River which crosses Bucharest and flows into the Arges River after Hotarele point, containing high quantities of untreated sewage;
- *Clatesti* point, on Arges River before it flows into the Danube and after the confluence with Dambovita River.

Various pollution sources have been identified along the river, like: farm wastes, agricultural and industrial activities, at sampling points Sabar, Colibasi, Hotarele and Clatesti. The most affected by anthropogenic activities is Budesti location (situated between Hotarele and Clatesti, on Dambovita River), where high amounts of untreated sewage, from the metropolitan Bucharest area, are transported.

Samples have been collected during 3 campaigns in February, June and October, to account for seasonal changes. Detailed information about the sampling locations and protocol is provided by Pfeiffer et al. [27]. Fluorescence measurements were performed using the FLS-920 Edinburgh Instruments spectrofluorimeter, equipped with a 450 W Xenon lamp and double monochromators, for excitation and emission. Fluorescence excitation – emission matrices (EEMs) were recorded utilizing the following parameters: excitation wavelength range from 230 to 400 nm at 5 nm intervals, emission wavelength domain from 250 to 500 nm at 1 nm intervals. Metal concentrations have been determined using the Perkin Elmer Flame-AAS 3030 B, for the following metal ions: Fe²⁺, Ni²⁺, Ca²⁺, Zn²⁺, Cr²⁺, Mn²⁺, Mg²⁺.

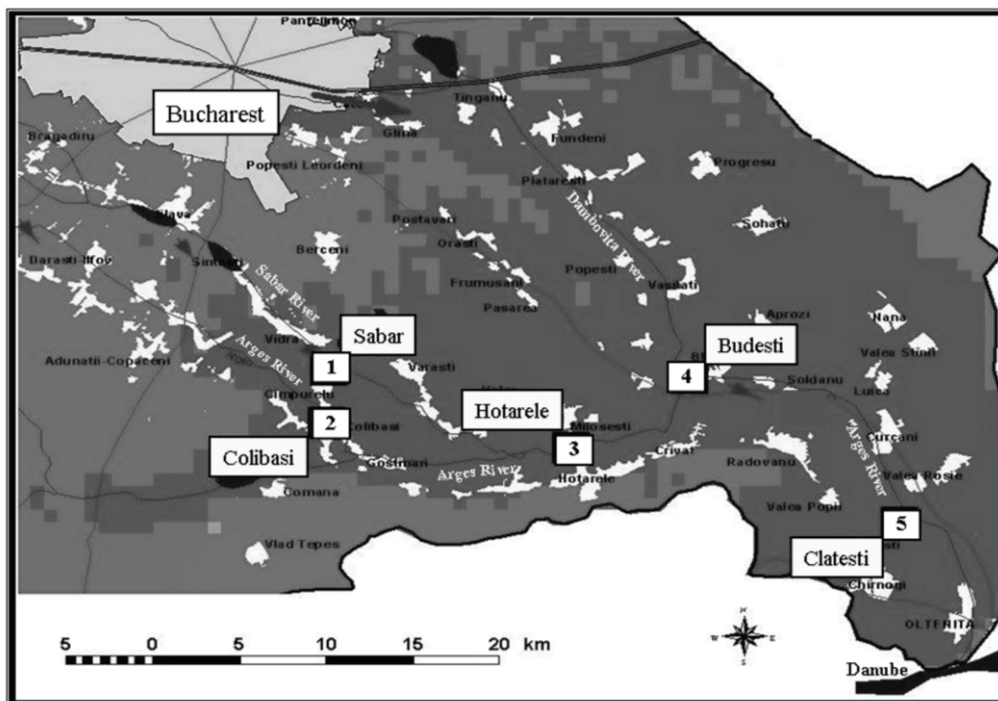


Fig.2. Map of the Lower Arges Basin with the 5 sampling points: 1 – Sabar point, located on Sabar River; 2 – Colibasi point, located on Arges River; 3 – Hotarele point, on Arges River downstream of Sabar River confluence; 4 – Budesti point, located on Dambovitza River; 5 – Clatesti point, on Arges River before it flows into the Danube and after the confluence with Dambovitza River.

3. Results and discussions

Seven metals have been chosen, based on the binding strength classification given by Schnitzer and Skinner [28] and Wu et al. [29]: $Fe^{2+} > Ni^{2+} > Ca^{2+} > Zn^{2+}$, $Cr^{2+} > Mn^{2+} > Mg^{2+}$ ions. Figure 3 (a - g; arranged in the order of their binding strength) shows the concentration of each metal plotted with the humic-like and protein-like fluorescence intensity, for samples collected in three different seasons. Thus, the specific DOM components can be better evaluated according to seasonal variability.

The protein-like fluorescence intensity is slightly higher during the summer, due to the fact that elevated temperatures create the perfect environment for bacteria to proliferate, especially at Budesti location. As for the humic substances, higher quantities are found in autumn because of litter that leaches or degrades in the river and because of higher frequency and quantity of precipitation, which amplify the geological activities. Metal concentrations depend on the type and location of the pollution source and time of release into the aquatic system. For this reason, there have been such variations in values, even at the same location. As an example, high quantities of iron ions have been detected in autumn for Colibasi location, but considerably lower values in winter and summer.

According to the classification given by Schnitzer and Skinner [28] and Wu et al. [29], iron ions have the highest binding strength, among the other tested metals, and, as can be seen in Fig. 3a, their concentration is inversely proportional to DOM fluorescence values. Based on Lu and Jaffe [30]

hypothesis that metal ions bind preferentially to certain fluorophores, the iron ions seem to have a greater effect on protein-like components than on humic-like. The process of binding is also affected by the concentration of the metal. As mentioned by Reynolds and Ahmad [31], metal binding is more effective at concentrations lower than 1 mg/L. In this case, iron ions present almost the same effect at both lower and higher concentrations.

Next on the binding strength scale [28, 29] are nickel ions (Fig. 3b), which show inversely proportional values to fluorescence data, but only on February samples. During the other seasons, a consistency between fluorescence values and metal ions concentration can be observed. Similar behavior can be seen at zinc (Fig. 3d) and manganese (Fig. 3f) ions. This trend should have been observed at chromium ions as well, which based on Wu et al. [29] study should have the same binding strength as zinc ions. But, unlike zinc ions, chromium ions seem to have a significant impact on DOM fluorescence. However, the behavior of Ni^{2+} , Zn^{2+} and Mn^{2+} can probably be explained by competitive complexation between them.

The fact that in February and June lower quantities of both Fe^{2+} and Cr^{2+} ions have been detected, may lead to the speculation that due to the almost total lack of those two ions, the others have had the possibility to form metal - DOM complexes. Since this is only a supposition, further analysis is needed in order to draw a solid conclusion.

Apart from the above mentioned factors, like metal concentrations and competitive complexation, the complex formation processes can be affected by the presence of other specific ions. Fu et al. [32] noticed that calcium ions induce an increase in fluorescence by adding them to an already formed metal - DOM complex. In the present case, Ca^{2+} concentration shows very little variation (Fig. 3c), but the values are quite high leading to the assumption that it might have interfered in the process of complex formation. Fu et al. [29] have also shown that Mg^{2+} has little effect on metal-DOM complexes. This is confirmed by our results (Fig. 3g), showing neither an inversely nor a directly proportional relation to DOM fluorescence. However, the present study is limited to only one freshwater system, multiple systems being needed in order to test complex formation processes and competitive complexation in several environmental conditions.

Although, the reaction of DOM with two certain metals has been studied, the behavior of three or more metals in interaction with DOM can be very difficult to predict, specifically when dealing with samples without previous treatment or extraction. Given the complex pool of compounds that water contains and the various sources of pollution, the analysis of fluorescence must be made with caution. Hence, it is needed to emphasize the importance to test water samples for as many metal ions as possible. Also, it is recommended to take into account the probable reactions, between DOM and metals.

4. Conclusions

The study on the Lower Basin of the Arges River has shown that the influence of metals on DOM fluorescence is difficult to predict, especially when dealing with multiple metal ions present in the same sample and several sources of pollution. It has been observed that iron and chromium ions have higher impact on DOM fluorescence, influencing the protein-like fraction, compared to the other studied metals. A certain competitive complexation has been seen at nickel, zinc and manganese ions, while manganese ions have had no observable influence on DOM fluorescence. Also, metal ions concentrations lower than 1 mg/L, have a greater impact on DOM fluorescence compared to higher concentrations. Considering the number of processes that occur at DOM-metal interaction and the complex nature of the water, it is strongly recommended to test water samples for metal ions and evaluate the interference with fluorescence.

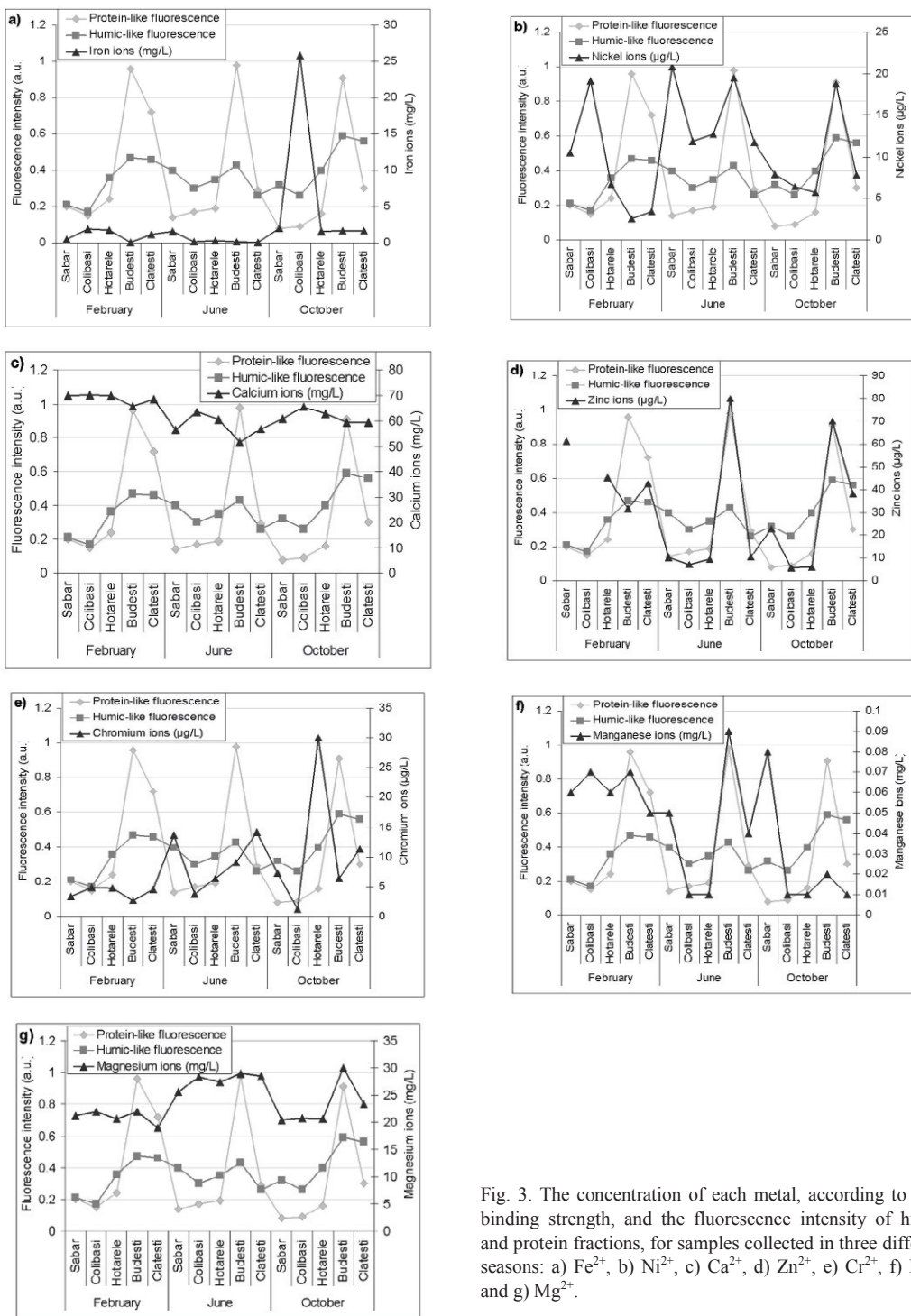


Fig. 3. The concentration of each metal, according to their binding strength, and the fluorescence intensity of humic and protein fractions, for samples collected in three different seasons: a) Fe^{2+} , b) Ni^{2+} , c) Ca^{2+} , d) Zn^{2+} , e) Cr^{2+} , f) Mn^{2+} and g) Mg^{2+} .

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