RT&A, Special Issue № 3 (66)
Volume 17, January 2022

FAST METHODOLOGY (WARNING TOOLS) FOR TRACKING CHANGES OF THE AQUATIC ORGANIC MATERIAL

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Abstract

Increasing dissolved organic matter (DOC) in aquatic ecosystems can lead to disturb the balance, deterioration of the water quality, and a more expensive water purification process. As a significant part of the aquatic DOC, organic adsorbing compunds (OACs, amphiphilic/hidrophobic type), can impact on the both abiotic and biotic elements. In this study it was demonstrated that the no—expensive methodology can be used for the fast monitoring/evaluating water quality with respect to the content and the surface activity (i.e. hydrophobicity) of the DOC. This includes measurement of the total adsorption efect of OACs at the mercury electrode by electrochemical methods. The concept has been applied to rivers from the agricultural district (Sava and Lonja), and from the highly protected area (Krka as a part of National Park) as well as to the marine lake ecosystem (Rogoznica Lake).

Keywords: dissolved organic carbon, surface activity, organic adsorbing compunds, hydrophobicity, natural waters

I. Introduction

The widespread problem of water pollution is endangering aquatic ecosystem health, and ultimately can affect the human health [1]. One of the threats against good water quality is increasing content of dissolved organic carbon (DOC) in freshwaters into different regions around the world [2]. Some studies have been reported that there is link between climate change and increasing content of the DOC [2]. Organic matter (OM) transport to water bodies can lead to disturbance of the balance in the aquatic ecosystem and to deterioration of the water quality, giving a more complex and expensive water purification process [2,3]. Besides natural organic matter (NOM, originating from terrestrial sources or produced *in situ*), distinct classes of hydrophobic pollutions (e.g. peticides, biphenyls and polycyclic aromatic hydrocarbons) resulting from human activity (particularly in agriculture and industry) can be present in natural aquatic systems [4].

Due its different origins and complex composition, the various types of DOC have appreciably distinct physico-chemical properties including its surface activity (SA). One way of characterizing DOC quality is determination of the surface activity as a bulk parameter by electrochemical method, i.e. measurement of the total adsorption effect of the organic adsorbing compounds (OACs, amphiphilic or hydrophobic type) at the mercury electrode. Such measurement usually is expressed as an equivalent adsorption effect of a certain amount (mg dm^{-3}) of model surfactant the nonionic polyoxy ethylene-t-octylphenol, Triton–X–100 [5—12]. These classes compounds are the most reactive part of the DOC because they tend to adsorb at different natural phase boundaries in aqatic environments and on that way they can impact on the both abiotic and biotic elements/processes [4, 8─12]. Therefore, the SA of DOC is directly related to its hydrophobic/hydrophilic properties, in other words to its quality and reactivity.

Here we will look which information about aquatic organic material can be obtained from the analysis of the surface activity of DOC in the natural water samples using methodology that has been developed within the group at the Ruđer Bošković Institute in Zagreb, Croatia [5─12].

II. Methodology

Natural samples were collected from the two different water areas: (1) Sava and Lonja rivers in the agriculture area (45.5194° N 16.5314° E, Posavina region), and the karst Krka River as a part of the highly protected area (43.8666° N, 15.9725° E), the Krka National Park); (2) the small (10 276 m^2) and shallow (maximum depth, 15 m) marine lake ecosystem (43°32′ N, 15° 58′ E) Rogoznica Lake, Dalmatia. Rogoznica Lake can be taken as typical representative for highly stratified and euxinic marine environment on the Adriatic, i.e. Mediterranean cost [8─9]. After sample filtration through 0.7 μm Millipore filter, DOC was determined by the high–temperature catalytic oxidation (HTCO) by the accreditated method according to HRN EN ISO/IEC 17025:2017 on the TOC-5000 Model, Shimadzu, Japan. SA was determined on the basis of capacity current measurements using a.c. voltammetry in *out of phase* mode as already described [5 ─12]. Electrochemical measurements were performed on an μ-Autolab analyser (Eco Chemie, Utrecht, the Netherlands) connected to a 663 VA Stand multimode system (Metrohm, Herisau, Switzerland) equipped with a static mercury drop working electrode (SMDE). The reference electrode was an Ag/AgCl (3 M KCl). A platinum electrode served as the auxiliary electrode. The SA was expressed as equivalent in mg L^{-1} to a model substance, of Triton-X-100. The detection limit was 0.01 mg L^{-1} equivalent of T-X-100, with LOQ of 0.03 mg L^{-1}.

III. Results and discussion

Figure 1 show graphical characterisation of DOC in samples of investigated waters. This approach can be used to describe the quality of OM in terms of hydrophobicity/hydrophilicity. It is based on comparison of the correlation of SA/DOC values obtained in samples with those of the model substances selected as being main classes of OACs in natural waters. More hydrophobic model substances have higher SA/DOC values [5,8,11].

The differences in the composition of the OM between rivers Sava, Lonja and Krka are clearly visible (Fig. 1). Low DOC concentration in the Krka River indicate an extremely clean and noneutrophic water system. Concerning the OM type in the Krka River, the poor surface activity of DOC measured at the hydrophobic surface of the mercury electrode, suggest its highly hydrophilic character [6]. Taking into account that Krka is karst river, it is no surprise that has the lower content of fulvic material. In the Sava River, DOC and SA values are twice high than in the Krka River, and data for SA/DOC ratio are grouped around fulvic acid line, pointing to the more hydrophobic nature of the studied OM. A relative high SA/DOC ratio was detected in the Lonja River as a consequence of the fact that this river receives water from the main melioration channel close to sampling location (45.5194° N 16.5314° E) [5]. The hydrophilic OM, similar to polysaccharide─xanthane and saturated fatty acid types predominate in the Lonja River waters. Detected compounds can be considered as indicators of the degradation processes.

The seasonal variability of OM properties was observed in the marine environment of Rogoznica Lake (Figure 1). It can be seen that the type of OM significantly vary from season to season with more hydrophobic material recorded in summertime.

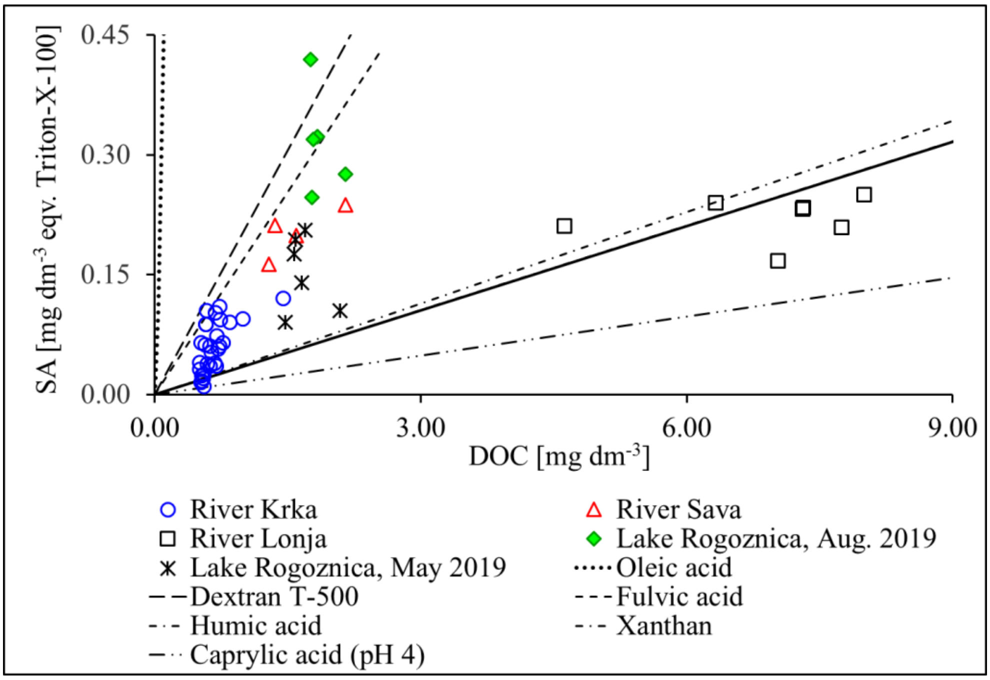

Figure 1: *Correlation of SA/DOC in samples collected: (a) in the rivers from the agricultural district, Sava (Central Posavina) and Lonja River (Lonja field), in period 2017─2019; (b) in the River Krka (part of the National Park Krka), in 2012 [6]; (c) along the depth profile (0─12 m) of Rogoznica Lake (highly stratified and euxinic marine lake in Dalmatia) in 2019. Lines correspond to model substances [5,8]*

By using an integral method that include the measurement of the DOC concentrations and determination of its surface activity by electrochemical method, it was possible to reveal qualitative properties based on the hydrophobic/hydrophilic nature of OM in different aquatic systems. However, the varibility of DOC concentrations is not so pronounced in Rogoznica Lake in the investigated period, implaying on the importance for monitoring of the nature/reactivity of the OM, especially in the small water bodies as isolated water systems. Due to morphological characteristics and relatively small volume, these systems react rapidly to external pressures, and biogeochemical signal of such processes can be several times multiplied with respect to the larger water areas such are open sea and the ocean [6,8,9].

IV. Conclusions

Considering that the changes in the composition of OM can have implications for water quality and ecosystem health, the rapid method described above is very useful as early warning tool for detection quality and tracking the organic matter dynamics in marine and fresh waters. It is important to emphasise that the rough differentiation of DOC into hydrophobic/hydrophilic type is only a first step in OM characterisation. For detail analyses, electrochemical measurement needs to be combined with other more selective methods such as spectrophotometry and chromatography.

Acknowledgments. This work is supported by the project "Marine Rogoznica Lake as a model for ecosystem functioning in the changing environment" (MARRES, IP-2018-01-1717).

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