

COMPARISON BETWEEN THE CHARACTERISTICS OF DISSOLVED ORGANIC MATTER AND NITRATE CONTENT IN AN URBAN RIVER

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Materia organică acvatică își schimbă constant caracteristicile în urma interacției cu diverși compuși care intră în sistemul acvatic prin infiltrarea în sol, prin aportul apelor pluviale sau poluare. Asemenea procese complexe duc la formarea nitraților. Pentru a determina cantitatea de nitrați și corelarea acesteia cu materia organică s-a realizat un experiment de monitorizare continuă a unui râu urban. În acest studiu s-au efectuat măsuratori de fluorescență ale materiei organice și măsuratori ale parametrilor fizico-chimici. Apele pluviale au avut un impact puternic asupra calității apei determinând după fiecare precipitație cantități mari de nitrați și materie organică.

Aquatic organic matter is constantly changing its characteristics under the interaction with different components which enter the water body through soil leaching, surface runoff or pollution. Complex processes also lead to the formation of nitrate. In order to determine the quantity of nitrate and the correlation with dissolved organic matter a continuous monitoring experiment of an urban river has been performed. This study has been conducted by measuring the fluorescence of organic matter and physiochemical parameters. Surface runoff had a great impact on the river water quality triggering after each precipitation event high quantities of nitrate and organic matter.

Keywords: dissolved organic matter, fluorescence spectroscopy, nitrate, urban river.

1. Introduction

Urban rivers are complex aquatic ecosystems with constant anthropogenic influence. Dissolved organic matter, the ubiquitous fraction in water systems, interacts continuously with compounds which enter the water body through soil leaching, surface runoff and point-source pollution. The types and sources of

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contamination are well documented [1-3] but extended research is needed for the understanding of pollutants interaction with the aquatic ecosystem natural components. Also, new in situ measurement techniques need to be developed for rapid contamination evaluation.

During the last decades, fluorescence spectroscopy has received much attention into the scientific world because of its ability to find numerous applications in environmental issues. The method proved to be very efficient in determining and characterizing the water quality and organic matter content [4-6]. In fact, many researchers [7, 8] suggest using fluorescence spectroscopy as a surrogate technique for conventional water quality parameters. Fluorescence spectroscopy is a rapid and sensitive technique requiring only small quantities of sample, without any preparation.

The common fluorophores found in water samples collected from urban rivers are protein-like and humic-like. Protein-like fraction indicates the microbial and algal activity while the humic-like component shows the quantity of degraded plant material present in the river. Both fractions present large fluorescence excitation and emission domains, as can be seen in Fig. 1. The fluorescence map, named excitation-emission matrix (EEM), is obtained by collecting a certain number of emission spectra at different excitation wavelengths and assembling them into a two dimensional image.

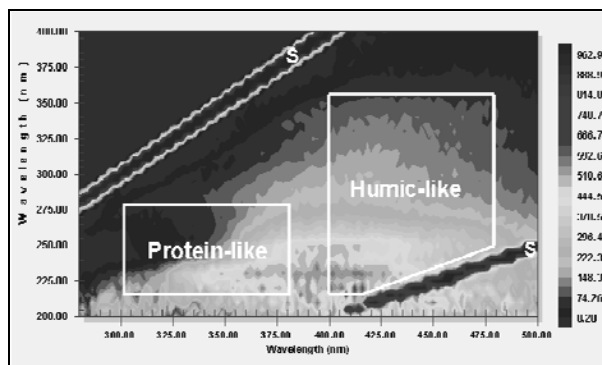


Fig. 1. Excitation-emission matrix presenting the two common fluorescent fractions (protein-like and humic-like) of an urban river sample. S – Scattered light.

Along with organic matter fluorescence, nitrate is also a very efficient water quality parameter. The large number of sources (run-off from agricultural land, animal manure, sewage, atmospheric deposition, etc) indicates a major contribution to eutrophication in a river system [9]. The study of Baker and Inverarity [9] shows a strong correlation (0.87) between the protein-like fluorescence and nitrate using the nitrate data as proxy for the identification of dissolved organic matter source.

In this study, a daily scale monitoring experiment of an urban river water quality has been performed. The objective was to determine the behavior of organic matter in comparison with nitrate under the influence of precipitation. Therefore, dissolved organic matter was measured using fluorescence spectroscopy and nitrate using a conventional method. In parallel, other water quality parameters had been determined: pH, conductivity, phosphate and ammonia, total organic carbon.

2. Experimental technique

The experiment took place in November 2007 on an urban river (Bournbrook River) from Birmingham, UK. For two weeks, water samples were collected every hour with an ISCO autosampler. All samples were measured within 24h from collection and no pre-analysis treatment was applied. For measurements, the following equipment was used: nitrate, phosphate and ammonia with three separate colorimeters (Hanna Instr.), total organic carbon with a Shimadzu TOC-Vcpn analyzer, the precipitation amount with a tipping bucket rain gauge, conductivity and pH with the Ultrameter II, Myron Co., portable instrument.

The fluorescence signal was recorded with a Varian Cary Eclipse spectrofluorometer. Instrument settings were: integration time of 0.0125 s, excitation wavelength range 200-400 nm with a step of 5 nm, emission wavelength range 280-500 nm, with steps of 2 nm and excitation and emission slit widths 5 nm. The sample chamber was kept at a constant temperature of 20°C by using a Peltier temperature controller.

3. Results and discussion

The experiment was characterized by periods of precipitation with quantities from 0.2 to 2.2 mm. Mainly, there were two periods of precipitation: the first in November 8 – 13, with short daily rains, and the second lasted two days November 18 and 19, with continuous precipitation (large quantities of rain and snow). The daily distribution and the quantity of precipitation are presented in Fig. 2.

Results show a significant response after every precipitation event with an increase in the quantity of nitrate, phosphate and organic matter. All samples presented a pH between 6.5 and 7.5 with no influence from rain. Conductivity values increased only after large quantities of precipitation. Total organic carbon presented the same behavior as organic matter. Values between 0-1.03 mg/L were registered for ammonia and no trend or relationship with the other components and rain had been observed.

Nitrate quantities were lower than the European Community [10] limit due to the fact that the major contribution to the urban system comes from surface runoff and storm sewers. In the days with no precipitation the nitrate quantity did not exceed 3 mg/L, while the precipitation periods larger quantities of nitrate were triggered. The results for nitrate quantities in relation with precipitation are presented in Fig. 2.

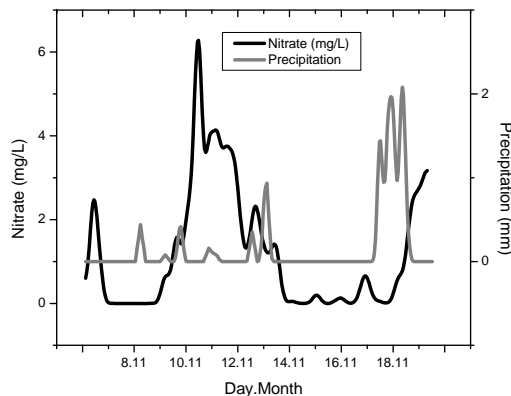


Fig. 2. Daily distribution and quantity of precipitation and nitrate.

High values for nitrate had been registered during the first precipitation period (short daily rains up to 1 mm). As this period followed a long dry period, nitrate compounds must have accumulated into the soil and in the storm sewers. Therefore, the first rain event, on November 8, generated the highest quantities of nitrate, but decreased gradually with every rain event that followed until November 14. The second precipitation event (heavy rain) determined high quantities of nitrate to leach into the river, but it did not have the same impact even though larger quantities of precipitation were registered. Provided that there is no anthropogenic influence to the river system, the nitrate behavior under the precipitation action can be determined by taking into account two important factors: the length of the dry period before the precipitation event and the quantity of precipitation. This experiment proved that a longer dry period determines higher quantities of nitrates. However, more research is needed to determine if there is a linear relationship between the length of the dry period, the accumulation of nitrate in the external environment and the nitrate quantity in a river system after a rain event.

Similar to nitrates, the phosphate compounds were discharged, in large quantities, into the river during precipitation events. This behavior can be observed in Fig. 3. Values obtained in the dry periods did not exceed 0.18 mg/L, but in the precipitation days values up to 0.65 mg/L were recorded.

In comparison with nitrates, phosphates exhibited a different behavior regarding the quantities between events. The first rain (on November 8) did not

generate the highest value, this being obtained after repeated rains events. Significant quantities had been registered during the last precipitation period. This shows that the quantity of phosphate released into the river is proportional to the quantity of precipitation.

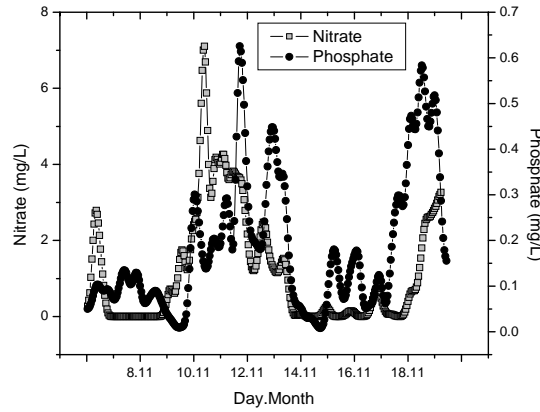


Fig. 3. Daily distribution and quantity of phosphate in comparison with nitrate.

Organic matter tends to have the same behavior as nitrate. The organic matter fluorescence intensities, protein-like and humic-like, are presented in Figs. 4 a and b. The fluorescence intensity of the protein-like fraction followed the same trend as nitrate. That is, the highest value was registered after the dry period and low ones when higher precipitation quantities were recorded during the second precipitations. On the humic-like component, the second precipitation event, with rain and snow, had a larger impact, releasing as much humic substances as the first rain, do to the soil input to the river system.

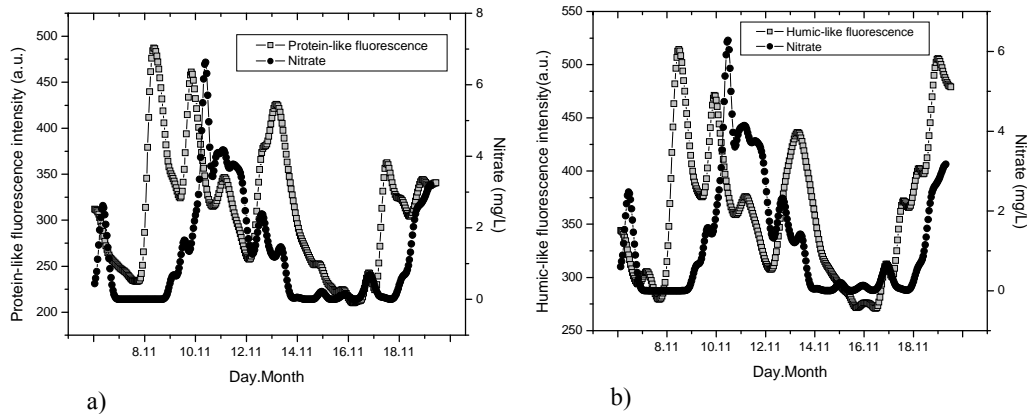


Fig. 4. Daily monitoring of the protein-like (a) and humic-like (b) fractions fluorescence intensities.

It has been noticed a more rapid response at organic matter compared to nitrate and phosphate. The quantity of organic matter started to increase immediately and showed a peak 2 hours after the beginning of the first rain event. Nitrates were detected 20 hours after the release of organic matter. The second rain event generated a more rapid response from nitrate, 2 hours after, and a similar response from organic matter.

6. Conclusions

The influence of rain events on the quantity of organic matter, nitrate and phosphate discharged in the river water was analysed. Nitrate had been shown to be dependent on the quantity of precipitation, the length of the precipitation period and the interval between precipitation periods, as was obtained also for protein-like fluorescence. The last factor allowed nitrates to concentrate into the external environment and to be discharged in higher quantities into the river water after the rain. Shortly after rain a high contribution from allochthonous organic matter was detected.

By taking into account all quick available information (weather and hydrology data, intensity of protein-like fluorescence) the approximated quantity of the released nitrate and the time of discharge can be easily predicted.

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