MATOUŠKOVÁ, M., FRAINDOVÁ, K., BEJČKOVÁ, M., KLIMENT, Z., VLACH, V., VLČEK, L., 2023. Dynamics of dissolved organic carbon in surface water during extreme rainfall-runoff events. In: TOLASZ, R., POLCAROVÁ, E. (Eds.), 2023. Sborník příspěvků z První konference projektu PERUN (TA ČR, SS02030040). Praha: ČHMÚ, 281-287, ISBN 978-80-7653-063-8.
https://doi.org/10.59984/978-80-7653-063-8.34

Dynamics of dissolved organic carbon in surface water during extreme rainfall-runoff events

(Dynamika rozpuštěného organického uhlíku v povrchových vodách během extrémních srážko-odtokových událostí)

https://doi.org/10.59984/978-80-7653-063-8.34

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Abstrakt: Uvolňování většího množství přírodní organické hmoty (NOM) v rámci klimatických změn je registrováno v mnoha povodích s rašeliništi. Cílem našeho výzkumu je studium dynamiky uvolňování rozpuštěného organického uhlíku (*DOC*) do povrchových vod v pramenných oblastech s rašeliništi. Koncentrace *DOC* jsou analyzovány ve vztahu k extrémním srážko-odtokovým událostem (R-R) a podle hydrologických předpokladů povodí. Tyto předpoklady jsou popsány pomocí vybraných hydroklimatických proměnných (14 dní před událostí R-R). Zdrojová data pocházejí ze stanic Přírodovědecké fakulty UK a Českého hydrometeorologického ústavu. Pro vyhodnocení vztahů a procesů byla použita analýza hlavních komponent (PCA), hysterezní smyčky nebo Pearsonův korelační koeficient. Byla studována doba zpoždění DOC_{max} za Q_{max}, závislost DOC_{max} a hladiny podzemní vody. Byl analyzován vliv rychlosti proudění na fáze poklesu a vzestupu koncentrací *DOC* pomocí hysterezních smyček a vliv počtu dílčích maxim průtoku na množství transportovaného *DOC* během události R-R. Vliv rychlosti proudění na fázi poklesu a vzestupu koncentrací *DOC* byl analyzován pomocí hysterezních smyček. Naše první výsledky ukazují, že velký vliv na dynamiku koncentrace *DOC* v povrchové vodě má změna hladiny podzemní vody v rašeliništi a množství odtoku během události R-R. Vliv na dynamiku koncentrace *DOC* v povrchové vodě má také změna hladiny podzemní vody v rašeliništi a množství odtoku. Významný vliv na uvolňování *DOC* mají také hydroklimatické předpoklady povodí. Ke změnám koncentrací během událostí R-R docházelo také u dalších sloučenin, které byly studovány dodatečně. Zvláště významný byl nárůst kovů (především Fe, Al, Mn) a bazických kationtů (K) a pokles dusičnanového dusíku.

Klíčová slova: organická hmota – organický uhlík

Abstract: The release of a greater amount of natural organic matter (NOM) within climate change is registered in many catchments with peatbog areas. The aim of our research is to study the dynamics of releasing dissolved organic carbon (*DOC*) into surface water in headwater areas with peatbogs. *DOC* concentrations are analysed in relation to extreme rainfall-runoff (R-R) events and according to the hydrological preconditions of the basin. These preconditions are described using selected hydroclimatic variables (14 days before the R-R event). The source data comes from stations of the Faculty of Science, Charles University, and the Czech Hydrometeorological Institute. For the evaluation of relations and processes, the Principal component analysis (PCA), hysteresis loops or Pearson correlation coefficient was used. The lag time of DOC_{max} for Q_{max}, the dependence of DOC_{max} and groundwater levels were studied. The influence of flow rate on the decline and ascent phases of *DOC* concentrations by hysteresis loops and the influence of the number of partial flow maximums on the amount of transported *DOC* during the R-R event was analysed. Our first results show that great influence on the dynamic of *DOC* concentration in surface water has the change in groundwater-levels in the peatbog and the outflow amount during the R-R event. The hydroclimatic preconditions of the basin have also a significant influence on the *DOC* release. Changes in concentrations during R-R events also occurred for other compounds that were studied additionally. Particularly significant was the increase in metals (mainly Fe, Al, Mn) and base cation (K) and decrease in nitrate nitrogen.

Keywords: organic matter - organic carbon

1. Introduction

The release of a greater amount of natural organic matter (NOM) within climate change is registered in many catchments with peatbog areas. Increases in organic matter concentrations have been recorded in recent years in places such as Europe and North America (Lepistö et al. 2014; Ritson et al. 2014). Main reasons of increased levels of Dissolved organic carbon (*DOC*) in inland waters are connected to rising temperatures, changes of atmospheric depositions and the increased *pH* of surface water. Storms and snowmelt have great effect on releasing *DOC* into surface waters while more than 80% of the annual *DOC* flux could be exported during these events (Raymond and Saiers 2010). Nevertheless, there is still a lack of understanding of the process of releasing *DOC* into the surface water during rainfall-runoff events. The aim of our research is to study the dynamics of releasing dissolved organic carbon (*DOC*) into surface water in headwater areas with peatbogs. *DOC* concentrations are analysed in relation to extreme rainfall-runoff (R-R) events, with emphasis on the relationship between *DOC* concentration, discharge, ground water level and hydroclimate preconditions of the catchment. These preconditions are described using selected hydroclimatic variables within 14/5 days period before the R-R event.

2. Study area

This study was carried out in 7 small headwater catchments located in the upper Vydra Basin, the central Šumava Mts. (Bohemian Forest), the southwest part of the Czech Republic. All catchments – Ptačí brook (PTA), Javoří brook (JAV), Cikánský brook (CIK), Březnický brook (BRE), Rokytka Brook (ROK), Rokytka brook subcatchment ROK1 and its left tributary (ROK2) are in Šumava National Park with limited or completely negligible human activity. Our experimental catchment is the Rokytka Brook, the ROK1 site was selected for detailed analyses of *DOC* dynamics during different types of R-R events according to highest representation of peat bogs and wetlands. The altitude ranges between 1100 and 1260 m a.s.l. The soil cover consists mainly of podzols and organic soils, while more than 60% is covered by peat (Vlček et al. 2021).

3. Data sources and applied methods and data sources

Besides the field measurements, the study sites were equipped with automatic monitoring devices providing data in 10-minute steps. Tipping bucket gauges for precipitation, and air temperature probes (all Fiedler AMS comp.) were placed at the Rokytka catchment (ROK) and in the Modrava village. Groundwater levels at four peat bog sites (water-logged spruce stand - *Picea abies*; 2 pine stands - *Pinus mugo*; and open bog area with cotton grass - *Eriophorum*) at the Rokytka catchment and stream water levels monitoring (converted by rating curves to discharges) at all experimental catchments were measured by water level probes (also Fiedler AMS comp.). The ROK 1 site (Rokytka catchment - ROK) is also equipped with the automatic water sampler ISCO 6700 (TELEDYNE, Fig. 1). Further data source are data from meteorological stations of the CHMI Prague.

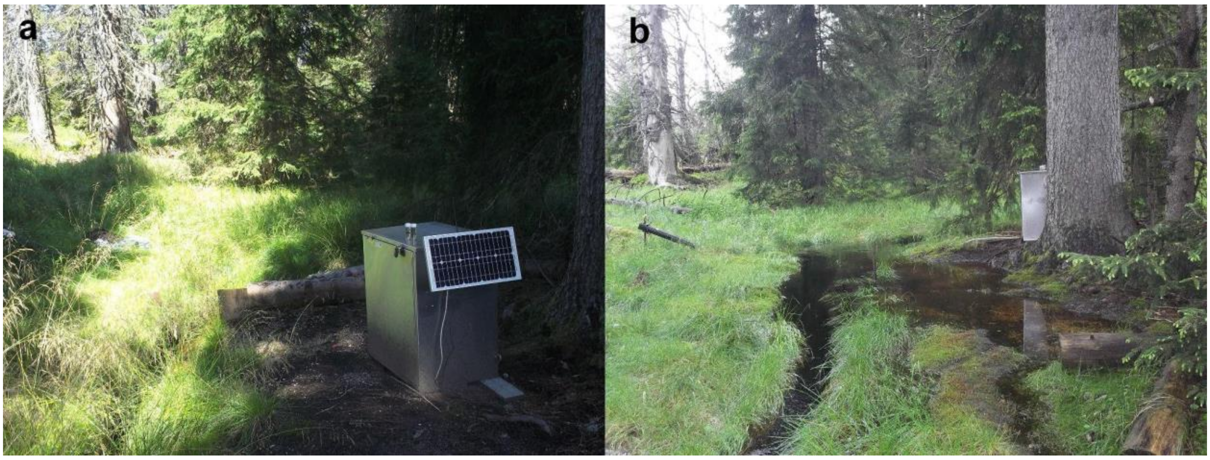

Fig. 1 Automatic water sampler ISCO 6700 Rokytka brook (R1 site). a) baseflow, b) R-R event.

Water samples were collected from 7 sites of selected catchments (PTA, JAV, CIK, BRE, ROK, ROK1, ROK2) seasonally from May 2018 to August 2021 (101 samples). Samples from R-R events were collected using an automatic sampler ISCO. This device sampled stream water during R-R after every 1500 m^3 of water left the outlet – that means a sample of water between 1.5 and 6 hours. Water sampling took place between August 2019 and October 2021, when 231 samples were taken from 18 events. These events were divided into two main groups according to previous conditions: 1 – events with no increase of rainfall and runoff 5 days before these events, so called unaffected events, 2 – events, which were influenced by rainfall and increase of runoff 5 days before these events, labelled affected events.

The basic evaluated variables are discharge (Q), maximum discharge during event (Q_{max}), maximum concentration of dissolved organic carbon during event (DOC_{max}), mean concentration of dissolved organic carbon during event (DOC_{mean}), water temperature (Tw), air temperature (Ta), groundwater level Picea abies ($GWLpa$).

The *DOC* water samples were analysed using the differential method on the Shimadzu TOC analyser (TOC-L CSH) at the Institute of Hydrodynamics of the CAS. Other chemical parameters were analysed in the Geochemical laboratory, Geological Institute, Faculty of Science, Charles University.

For the evaluation of relations and processes, the Principal Component Analysis (PCA), hysteresis loops, Pearson and Spearman correlation coefficients were used. The lag time of DOC_{max} for Q_{max}, the dependence of DOC_{max} and groundwater levels were studied. The influence of flow rate on the decline and ascent phases of *DOC* concentrations by hysteresis loops and the influence of the number of partial flow maximums on the amount of transported *DOC* during the R-R event was analysed.

4. Results

From a total of 18 events evaluated, 11 of them were unaffected and 7 were affected by a previous event 5 days before (examples are given in Fig. 2). If the focus is on the relationship between *DOC*, *Q* and *GWL Picea abies* during these events, it is possible to observe positive correlation between these variables. Higher positive correlation is present between *DOC* and *GWL Picea abies* (both event types *p-value* < 0.0001) than between *DOC* and *Q*, where there is a different lag time of the *DOC* maxima after the peak flow and therefore direct correlation is not so obvious. The difference between affected events is evident, because the groundwater levels are not as low as in unaffected events (mean value of *GWL* in unaffected *events* = −0.087 m and in affected *events* = −0.018 m). Although the affected events had higher discharges (Q_{mean} in unaffected *events* = 92 $l \cdot s^{-1}$and in affected *events* = 193 $l \cdot s^{-1}$) in some cases than the unaffected ones, *DOC* concentrations were still higher in the unaffected events (DOC_{mean} = 38 $mg \cdot l^{-1}$; DOC_{max} = 55 $mg \cdot l^{-1}$; vs affected events DOC_{mean} = 36 $mg \cdot l^{-1}$ DOC_{max} = 50 $mg \cdot l^{-1}$), representation was especially for values higher than 40 $mg \cdot l^{-1}$, while in the affected events lower than 40 $mg \cdot l^{-1}$ (Fig. 2).

Focusing on the *DOC* seasonality across all sites (Fig. 3), some changes can be observed. However, these changes are significantly influenced by the different discharges at the time of sampling. It is obvious that discharges were lowest in the July–September period, which affected *DOC* concentrations, which are also the lowest *(*< 10 $mg \cdot l^{-1}$, except for CIK and ROK2 sites). However, during the months of October-December it is possible to observe the influence of catchment preconditions. As this is a period of relatively lower discharges, the *DOC* concentrations are significantly higher at most sites *(*> 20 $mg \cdot l^{-1}$, except for BRE site). This *DOC* concentration behaviour is likely due to the *DOC* accumulation in the summer and subsequent flushing into the water. Especially in 2018 and 2019 the summer months were very dry; groundwater level was low and significant decomposition and accumulation of organic matter occurred. Subsequently even a lower increase in discharge causes a large increase in *DOC* concentration in the stream. Even during different parts of the year, it is possible to observe increased *DOC* values for the CIK and ROK2 sites compared to the other sites.

5. Discussion

The results showed that the presence and area of wetlands and peatbogs significantly influences DOC concentrations. Catchments with > 20% wetlands have higher mean *DOC* concentrations (> 20 $mg \cdot l^{-1}$) corresponding to e.g. Ducharme et al. (2021) or Fraindová et al. (2022). Higher *DOC* concentrations were observed in these catchments even during periods of low flows compared to other catchments. However, comparison of *DOC* variability between sites during the whole year showed the highest variability in catchments with the lowest cover of wetlands and peatbogs.

Changes of *DOC* concentrations were mainly influenced by hydroclimatic preconditions of the catchment, with groundwater level and discharge being the main drivers. The significant effect of discharge and groundwater level on the amount of *DOC* concentrations is also confirmed by e.g. Rosset et al. (2020).

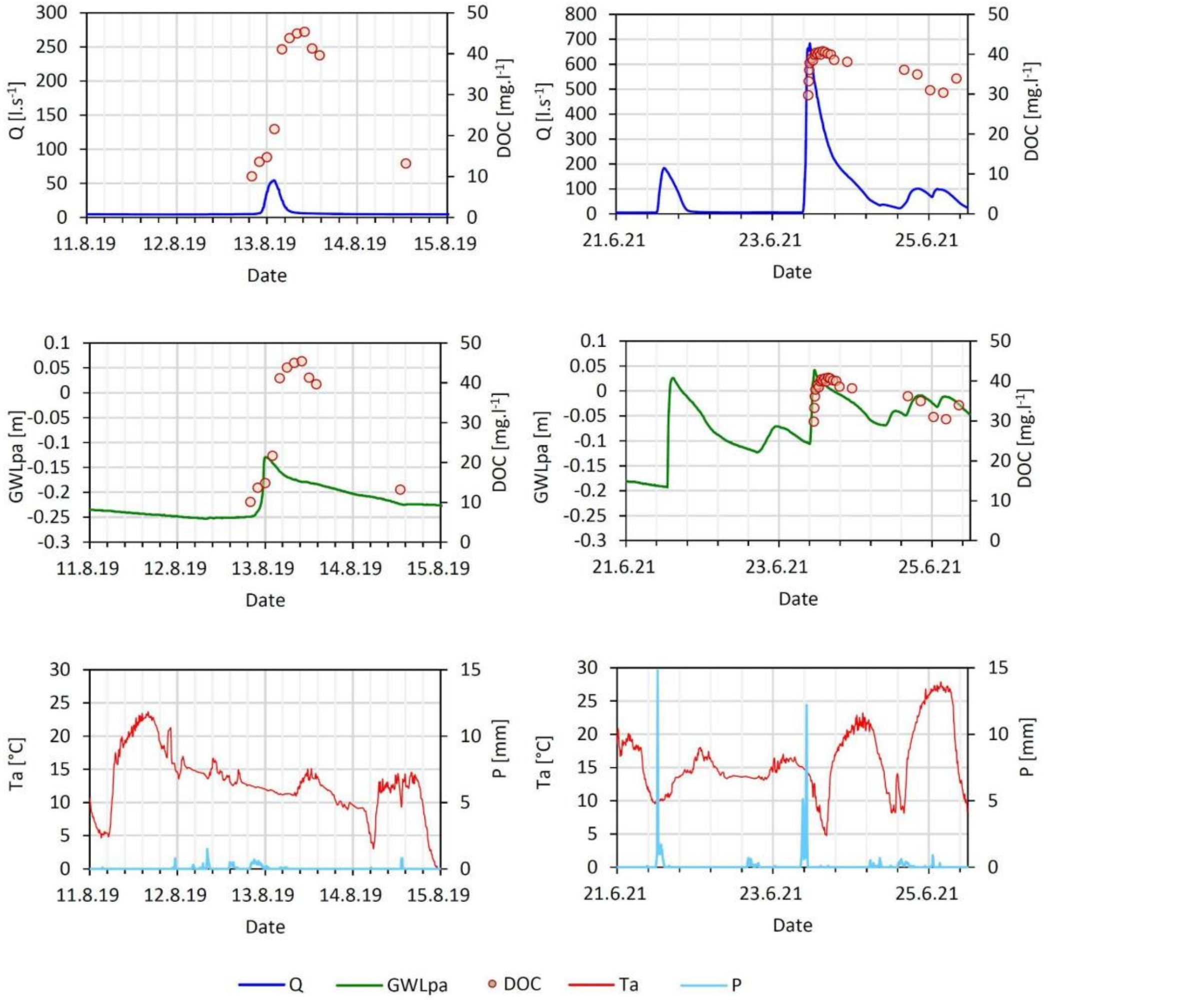

Fig. 2 Example of rainfall-runoff events. Left – unaffected event, Right – affected event. Q = discharge [l·s⁻¹], GWLpa = groundwater level Picea abies [m], DOC = dissolved organic carbon [mg·l⁻¹], Ta = mean air temperature [°C], P = precipitation amount [mm]; all variables are in 10-minute step.

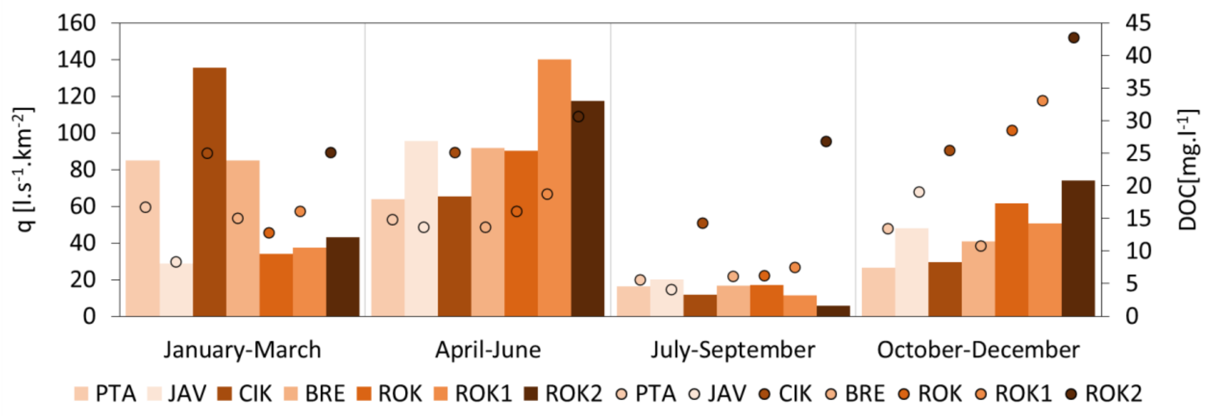

Fig. 3 Mean DOC changes over the year (dots), with mean actual specific discharges shown (columns). Ptačí Brook (PTA), Javoří Brook (JAV), Cikánský Brook (CIK), Březnický Brook (BRE), Rokytka Brook (ROK), ROK1 and Rokytka Brook left tributary (ROK2). 2018–2021. A darker brown colour indicates a higher proportion of wetlands (according to © AOPK ČR).

6. Conclusions

It is clear from several studies dealing with the issue of changes in *DOC* concentrations that in recent decades there have been increases in concentrations of these substances in some natural/near natural river basins. It is therefore important to look at the dynamics of *DOC* changes in relation to hydrological extremes. Increased concentrations of organic substances in watercourses then negatively affect the environment and subsequently water treatment processes when being treated for drinking water.

This study investigates the dissolved organic carbon (*DOC*) changes in variability and concentration amount with respect to hydro-climatic variables. The variables were examined in terms of antecedent conditions and preconditions before the individual event. Air temperature, precipitation, discharge, and groundwater level were considered as hydro-climatic variables. Changes in groundwater level and discharge had the greatest influence on the change and variability of *DOC* concentrations in streams, whereby the response of *DOC* concentration was related to the nature and magnitude of hydrological changes. Greater lag times of DOC_{max} behind Q_{max} and higher mean *DOC* concentrations were registered during the unaffected events. The *DOC* amount and lag time of maximum *DOC* concentrations are also significantly influenced by the dilution process (increased precipitation) and by the leaching of organic matter from individual peat layers by increased groundwater level.

DOC concentrations and *DOC* variability during rainfall-runoff events are influenced by the proportion of wetlands in the catchment. Relationship between *DOC* and discharge is less significant with higher proportion of wetlands. Longer periods of hydrological drought in headwater areas with peat bogs, followed by extreme R-R events, cause increased leaching of DOC concentrations.

Acknowledgements

The research was funded by the GAČR Project No. 22-12837S "Hydrological and hydrochemical response of montane peat bogs to climate change", by the TAČR project PERUN No. SS02030040 and by the Charles University Project GAUK 1168820: "Hydrological extremes and their influence on surface water quality in headwaters of Czechia".

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