Oceanological and Hydrobiological Studies
International Journal of Oceanography and Hydrobiology
Vol. XXXIX, No. 2

Institute of Oceanography (97-103) University of Gdańsk
ISSN 1730-413X 2010 eISSN 1897-3191

DOI 10.2478/v10009-010-0021-9
**Original research paper**

*Received:* *July 03, 2008*
*Accepted:* *March 07, 2009*

# Dissolved organic matter transformation in the hyporheic zone of a small lowland river

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**Key words:** dissolved organic carbon, SUVA, hyporheic zone, lowland river

## Abstract

The objective of this study was to examine dissolved organic carbon (DOC) concentration and specific ultraviolet absorbance (SUVA) changes in porewaters that occur over a small scale (cm) in the hyporheic zone (HZ) of a lowland stream in the Knyszynska Forest in northeast Poland. Hyporheic zone porewaters were sampled at different depths of 10, 30, 50, 70 cm at two study sites with different sediment material. The results showed significant differences in DOC concentrations between the upper and lower stream HZ. The current results indicate that small lowland sediments provide both a source and a sink of DOC for stream water, depending on the river course. The higher DOC level observed in the hyporheic zone suggests that porewater can be an autonomic site of biogeochemical changes of dissolved organic matter, which is very clear in the SUVA fluctuations.

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## INTRODUCTION

Stream ecologists have recently recognized that sediments beneath streams play an important role in lotic ecosystems (Jones and Holmes 1996). Active exchanges of water and dissolved material, between the stream and groundwater in many porous sand- and gravel-bed rivers, create a dynamic ecotone called the hyporheic zone (Hancock 2002). Most water enters rivers via exfiltrating groundwater, which passes the river sediments (Fischer et al. 2002) especially in first order streams. Interactions between groundwater and surface water are of primary importance for the organic matter budgets of streams. Streams receive and export terrestrially fixed particulate and dissolved carbon by overland and subsurface flows (Schindler and Krabbenhoft 1998). It is currently widely accepted that the hyporheic zone is an important lotic ecosystem component, and may significantly affect oxygen, carbon, and nutrient dynamics in streams (Findlay et al. 1993). The amount and distribution of organic matter depends on the input rate, abiotic as well as biotic processing, hydraulic transport capacity, retentive structures, and channel morphology (Brunke 1998).

The aim of this study was to describe exchanges between shallow groundwater, hyporheic water, and surface water in a small lowland stream. The objectives were to examine the importance of the hyporheic zone in supporting the stream water DOC pool, and the changing structure of dissolved organic matter (by SUVA parameter).

## MATERIALS AND METHODS

The Krzemianka River is a first order forested stream draining 34.1 $km^2$ of northeastern Poland's postglacial area. The total river length is 7.7 km, and the percentage of forests in the catchment is 82.2%. The average discharge during the period of this study (2002-2003 hydrological years) was 0.127 $m^3 s^{-1}$, and ranged from 0.087 $m^3 s^{-1}$ to 0.156 $m^3 s^{-1}$.

Two sites were sampled: the upper Krzemianka (UK) site located in the headwater part of the stream, and the lower Krzemianka (LK) site located 1 km from the river mouth. Selected sampling sites have present groundwater upwelling into the stream, but at the upper site (UK) the upwelling was more rapid than at the lower site (LK). Sediment material was dominated by sand at both sites, with 28% gravel at the UK and only 8% at the LK sites. All sampling was done once a month during the study period. At both investigated sites, porewater samples were taken from different depths: 10, 30, 50, 70 cm - using piezometers (PVC pipes of 5 cm diameter) located in the mid-stream channel. Two PVC wells were located on both banks at both investigated sites of the

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stream. They were placed in the soil at a 100 cm depth, and at a 2-3 m distance from the river, for sampling representative local groundwater.

Stream water, sediment porewater from the stream bed, and groundwaters were sampled to determine the basic physicochemical parameters of the waters, according to the method outlined by Hermanowicz et al. (1999). Water samples were filtered through 0.45 μm filters for dissolved organic carbon (DOC) analyses. DOC samples were analyzed using a high-temperature catalytic oxidation Shimadzu TOC analyzer. Specific Ultraviolet Absorbance (SUVA) was used to determine the relative amount of aromatic and aliphatic compounds of the total DOC in the water samples. SUVA was measured on samples at 260 nm using a 1 cm analysis cell on a Beckman DU-650 spectrophotometer, and was calculated using the relation:

$$SUVA = \frac{Abs_{260} \times 1000}{DOC}\left[Abs_{260} gC^{-1}\right]$$

## RESULTS

The dissolved organic carbon in the studied time period ranged from 0.45 mg $dm^{-3}$ in upstream water to 50.7 mg $dm^{-3}$ in the soil porewater at the UK river bank. Porewater samples from the hyporheic zone (HZ), taken from the mid stream channel at the UK and LK sites, had a DOC average value of 7.1 mg $dm^{-3}$ and 4.5 mg $dm^{-3}$, respectively. Porewater DOC concentrations were statistically significantly higher at the UK than in the stream water (Table 1).

**Table 1**

The hydrochemical characteristic of different types of investigated waters; UK - Upper Krzemianka, LK - Lower Krzemianka, (mean values ±SD from 2002-2003); SRP - soluble reactive phosphorus.

| Parameters | Groundwater | | Interstitial water | | Surface water | |
|---|---|---|---|---|---|---|
| | UK | LK | UK | LK | UK | LK |
| **Conductivity** (μ $cm^{-1}$ S) | 475 ±85 | 369 ±50 | 526 ±169 | 365 ±68 | 438 ±45 | 412 ±31 |
| **Oxygen saturation** (%) | 50 ±22 | 56 ±23 | 56 ±22 | 52 ±23 | 96 ±15 | 85 ±17 |
| **Water color** (mg $dm^{-3}$ Pt) | 97 ±79 | 39 ±33 | 33 ±21 | 35 ±26 | 23 ±27 | 49 ±37 |
| **DOC** (mg $dm^{-3}$) | 16.3 ±14.3 | 4.3 ±4.2 | 7.1 ±6.6 | 4.5 ±3.8 | 2.0 ±1.2 | 9.5 ±7.1 |
| **SUVA** ($Abs_{260}$ $g^{-1}$ C) | 39 ±36 | 73 ±101 | 36 ±31 | 59 ±45 | 36 ±30 | 43 ±34 |
| **N-$NH_4$** (μg $dm^{-3}$) | 220 ±120 | 359 ±365 | 441 ±470 | 300 ±261 | 166 ±68 | 180 ±78 |
| **N-$NO_3$** (μg $dm^{-3}$) | 149 ±141 | 413 ±239 | 147 ±86 | 292 ±291 | 294 ±156 | 891 ±560 |
| **SRP** (μg $dm^{-3}$) | 52 ±28 | 58 ±39 | 57 ±43 | 108 ±207 | 53 ±18 | 64 ±20 |
| **TP** (μg $dm^{-3}$) | 164 ±104 | 237 ±154 | 255 ±320 | 304 ±256 | 179 ±128 | 241 ±143 |

The groundwater DOC concentrations in the Krzemianka watershed were generally higher (at the UK) or similar (at the LK) to those noted in HZ waters (Table 1). The quality of dissolved organic matter (SUVA) was significantly different from study site to study site in all the investigated water. The different types of LK waters represented more aromatic fractions of DOC than did UK waters (Table 1). Most of the hydrochemical parameters in the HZ were statistically significant (ANOVA, $p<0.0001$), different, and higher than in the stream water (Table 1).

Vertical DOC concentrations at the UK site were similar (about 6 mg $dm^{-3}$), except for shallow porewater (10 cm), where average DOC concentration was higher and the coefficient of variation (CV) was the highest at the site (CV=122%). DOC in the HZ ranged widely, from CV=67% to CV=122%. Stream water concentration in the UK, during the investigated period was 3-4 times lower than in the HZ (Fig. 1). The rapid decrease of DOC concentration in

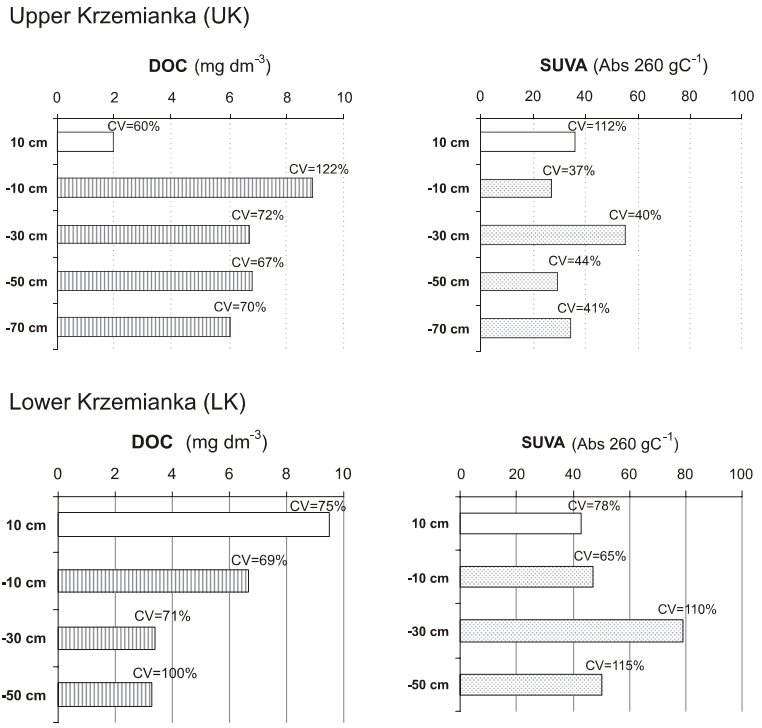



**Fig. 1.** Average DOC concentrations and SUVA parameter in stream water (10 cm) and the hyporheic zone (at different depths) at the Upper Krzemianka (UK) and Lower Krzemianka (LK) sites; CV – coefficient of variation.

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the HZ (from 6.59 mg $dm^{-3}$ to 3.27 mg $dm^{-3}$) was evident at the lower LK site between 10 cm and 50 cm (Fig. 1), but stream water DOC concentration was always higher (Fig. 1). The SUVA parameter determined was lower at the UK than at the LK, comparing different depths of the HZ (Fig. 1).

A high seasonal variability in DOC concentration was observed in the HZ at the UK site. The average DOC was often higher than 10 mg $dm^{-3}$ at each depth in spring, and at the 10 cm depth in fall (Fig. 2). DOC concentration in the upper stream HZ was two times higher during spring and fall than in summer. Despite the lower variability in DOC concentrations in the HZ at the LK, there were marked seasonal changes in DOC. Decreasing DOC concentration from the upper to the deeper layer of the HZ has been observed in seasons at the LK. At the lower stream site, DOC was low and more stable than at the UK site (Fig. 2). In the lower stream HZ, changes in DOC concentrations were not very different, with the highest DOC at the 10 cm depth of sediments. Seasonal changes of organic carbon quality were more stable at the UK site than at the LK site, where DOC is dominated by aromatic structures (Fig. 2).

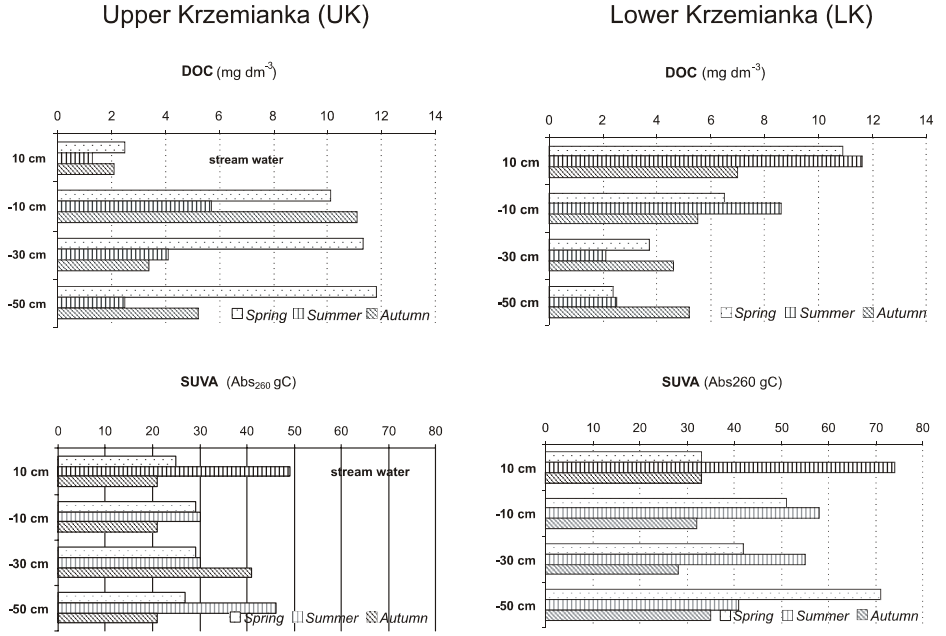



**Fig. 2.** Seasonal changes of DOC concentration and SUVA parameter in stream water (10 cm) and the hyporheic zone (depths from 10 to 70 cm) at the Upper Krzemianka (UK) and Lower Krzemianka (LK) sites.

## DISCUSSION

The dissolved organic carbon geochemistry of groundwater flowing through the hyporheic zone and discharging into the stream exhibited substantial changes at two investigated sites on the Krzemianka River (Fig. 1). The current results showed a significant decrease of organic carbon from upstream (UK) to downstream (LK) in the hyporheic zone, even though temporal fluctuations of water level were great (Fig. 1). The HZ is important for filtration processes that occur continuously. This is clearly seen in the higher values of most chemical parameters (Table 1). The hydrology of the lower site is spatially more complicated due to its location in the catchment basin, and due to the hyporheic zone substrate size. In the finer sediments of the LK stream site, the dynamic for DOC quality (SUVA parameter) is lower than at the UK (Fig. 1). Fine-grained stream sediments contain larger amounts of stored detritus than streams with coarse sediments (Brunke 1998). The size of the HZ and its activity varies from stream to stream, and it is highly dependent upon basin ecology (Uzarski et al. 2004). Basin particulate organic matter (POM) is trapped by the physical filter, where it may be degraded biologically (Bencala 2000, Hancock 2002). This detritus builds up a standing stock within the sediments and, in part, DOC may be leached from this POM. DOC retention in sediments is the result of abiotic and biotic processes (Fischer et al. 2002). Approximately 50% of streamwater dissolved organic carbon (DOC) disappeared from interstitial water moving along a hyporheic flowpath below a gravel bar (Findlay et al. 1993).

A clear temporal trend was observed in the HZ at both investigated profiles (Fig. 2). The highest average DOC concentration was observed in spring in deeper sediment porewaters of the UK (about 12 mg $dm^{-3}$), which was connected with snowmelt leaching DOC from forest soils. The smallest DOC concentration (2.12 mg $dm^{-3}$) was always in the middle HZ of the LK in summer time (Fig. 2). The current results indicate that a summer with small discharge can lead to a deficit of organic matter for deeper layers of the HZ at the LK. There are higher DOC concentrations in fall. Leaf fall during October did not bring any significant change to the river water. At the upper site (UK), groundwater discharges as springs can modify water quality significantly in the hyporheic zone. Sometimes, in fall, an important increase in DOC concentrations have been noted in the HZ (Fig. 2), which can be connected with the decomposition of macrophyte roots in the shallow sediment layer. Differences between DOC concentrations at the UK and LK sites indicated that the hyporheic zone can differ along the stream. The current results suggest that observed differences between DOC in the stream and the HZ at the UK might be due to the leaching of DOM stored in stream sediments during base flow conditions (Buttorini and Sabater 2000). However, the current study shows that

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the hyporheic zone can be a source and a sink of DOC for a single stream. In the Krzemianka River, the upper stream HZ is more a source of DOC, while the lower stream HZ is more a sink for dissolved organic compounds. Most previous studies describe the HZ as a sink for DOC (Schindler and Krabbenhoft 1998). The current results indicate that the HZ is an unstable environment in a small stream, where the quality and quantity of DOC changes seamlessly.

## ACKNOWLEDGEMENTS

This research was supported by the State Committee of Scientific Research, grant no. 3 P04S 017 23.

We would like to thank H. Samsonowicz for her assistance in the field and the laboratory.

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