# Long Term Development and Short Term Dynamics of DOC in Runoff from a Forested Watershed

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**Abstract:** Dissolved organic carbon (DOC) is transported in considerable amounts from terrestrial to aquatic systems and plays an important role in the global carbon cycle. The objective of this study was to analyze the long term trend and the short term dynamics of DOC in a forested catchment, characterized by a large proportion of Histosols.

The long term data set on discharge and runoff chemistry from the Lehstenbach catchment, Germany, from 1987 to 2009 is based on biweekly sampling and daily average discharge. In addition, DOC in runoff was measured during several discharge events in 2010 and 2011 in high temporal resolution (15 min) by a spectrometric device. Simultaneously, the groundwater table was monitored by pressure sensors in a fen site close to the watershed outlet.

The long term data revealed that DOC concentrations in runoff increased from about 5 mg DOC  $L^{-1}$  in 1987 to 9 mg DOC  $L^{-1}$  in 2009. DOC concentrations were highly variable at biweekly time scales. Runoff did not change significantly in the given period of time, while sulfate concentrations decreased significantly.

Following rain events the discharge increases within a few hours. Measurements with high temporal resolution showed that DOC increased with discharge and maximum concentrations were observed shortly after maximum discharge. The relation of discharge and DOC is characterized by a hysteresis with higher concentrations at falling discharge as compared to rising discharge. Furthermore, the relation is temperature dependent with largest response during the summer period. High concentrations of DOC in runoff coincide with near surface groundwater table, indicating that the peaty riparian zones are the major source of DOC in runoff.

In the Lehstenbach catchment, the long term trend in DOC seems to be due to decreased sulphate deposition. The short term temporal variation of DOC in runoff is hydrologically driven and overlapped by temperature. Changes in the climatic regime, e.g. by changing precipitation pattern and changing temperature will influence DOC export from the watershed.

Keywords: DOC, runoff, forested watershed, hydrologic control, temperature

## 1. Introduction

Dissolved organic carbon (DOC) is transported in considerable amounts from inland watersheds to oceans which makes DOC an important compound in the balancing and understanding of the global carbon cycle (Meybeck, 1993; Druffel et al., 1992). According to Hope et al. (1994) approx. 0.4 Pg yr<sup>-1</sup> of organic carbon is transported as DOC from terrestrial inland waters to oceans. DOC plays a crucial role in terrestrial systems as it influences nutrient cycling, pollutant transport and genesis of soils (Gueguen et al., 2004; Gjessing et al., 1999). It is also of importance in freshwater systems as it affects freshwater biota by influencing light penetration and eutrophication.

DOC concentrations steadily increased over the past two decades in many surface waters of Europe and North

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America (Skjelkvale et al. 2005). Possible drivers, that might explain the upward trend of DOC concentrations, are climate change (a change in temperature or precipitation), land use change and a change in atmospheric deposition (Freeman et al., 2001; Tranvik and Jansson, 2002). Recent publications (Clark et al., 2011; Hruska et al., 2009) focus on decreased atmospheric sulphur deposition as the unifying factor behind the increased solubility of DOC. The mechanism of increasing DOC release from soils to surface water is seen in the increasing pH and decreasing ionic strength of precipitation, both triggering the solubility of soil organic matter.

Several studies have shown that DOC concentrations in runoff from forested watershed are highly variable (Hruska et. al., 2009) The reasons for the variability are a matter of debate. Discharge and the proportion of near surface flow seem to be important drivers. Using high temporal resolution of DOC measurements (Koehler et al., 2009) showed that DOC concentrations were higher in summer than in winter and that air temperature might account more for this variability than discharge.

The goals of the present study were 1) to assess the long term trends of DOC concentrations in the Lehstenbach catchment runoff with regard to potential drivers of the trend and 2) to explain the huge temporal variation of the DOC concentrations. To achieve the second goal we used high temporal resolution measurements at several discharge events in 2010 and 2011.

## 2. Material & Methods

#### 2.1 Study Site

The Lehstenbach catchment is located in the Fichtelgebirge region  $(50^{\circ} 8'35" \text{ N}, 11^{\circ} 52' 8" \text{ E})$  in south eastern Germany. The catchment area is 4.2 km<sup>2</sup>. Its elevation ranges between 695 and 877 m above sea level. Mean annual precipitation is 1150 mm (1971–2000). Annual temperature averages at 5.3 °C (1971–2000). Most abundant soil types are Dystric Cambisols, Haplic Podsols and Histosols. About one third of the catchment area is covered by Histosols close to the stream banks (Lischeid and Bittersohl, 2008; Matzner, 2004).

During rain storm events, peak runoff usually occurs 3-5 h after precipitation peaks. Groundwater at > 3m depth in the upslope regions usually has a long residence time and contributes mainly to the Lehstenbach runoff under base flow conditions (Lischeid et al., 2004).

#### 2.2 Runoff Chemistry and Discharge

The long term data set on runoff chemistry (1987–2009) was provided by the Bavarian Environment Agency. Samples were taken at the watershed outlet biweekly and analyzed for DOC, major cations and anions, pH and temperature. Discharge was measured by a weir at the watershed outlet. Rates of discharge and precipitation were available as daily mean values and daily sums, respectively.

High frequency measurements of DOC in runoff at the watershed outlet were taken in 2010 and 2011 at several discharge events. DOC was measured every 15 minutes using a  $UV/UV_{vis}$  spectrometric device (spectro::lyser, Scan Messtechnik GmbH, Vienna).

The groundwater table was monitored continuously in 2010 by pressure sensors in a fen site close to the watershed outlet.

### **3. Results**

#### **3.1 Long Term Development**

DOC concentrations increased with an annual rate of approx. 0.3 mg DOC  $L^{-1}$  yr<sup>-1</sup> from 4.7 mg DOC  $L^{-1}$  in 1987 to 9.0 mg DOC  $L^{-1}$  in 2009 (Figure 1 a). The increase was most pronounced from the year 2000 on.

The discharge (Figure 1 b) averaged at 61.6 L s<sup>-1</sup> from 1987 to 2009 and did not show any trend. The pH values (not shown) only changed slightly over the 1987–2009 period. PH values were around 4.63 in the year 1987 and slightly decreased to 4.69 in the year 2009. Sulfate concentrations averaged at 15.58 mg L<sup>-1</sup> in the year 1987 and steadily decreased to average values of 11.24 mg L<sup>-1</sup> in the year 2009 (Figure 1c). The peak values of more than 30 mg L<sup>-1</sup> only occurred before 1995. Water temperature (not shown) in the Lehstenbach runoff increased from 5.74 °C in the year 1987 to 6.29 °C in the year 2009. This corresponds to an increase of approx. 0.50 Kelvin in 20 years. Ionic strength (IS = 0.5  $\Sigma$  ci zi<sup>2</sup>) of the Lehstenbach stream runoff (not shown) was calculated using the major cations and anions (Ca2+, Mg2+, Na+, K+, NH4+, Al3+, H+, SO4 2-, NO3-, Cl-). Ionic strength

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decreased slightly from 1.0 mmol  $L^{-1}$  in the year 1987 to 0.9 mmol  $L^{-1}$  in the year 2009. It has to be noted that peak points got less pronounced in the late 1990's.

The temporal variation of the DOC concentration was huge, ranging from about 3 to 35 mg C L<sup>-1</sup>. Based on the fortnightly sampling and the daily averages of discharge, the relation of DOC concentrations to discharge was generally weak, but significantly positive and linear in the range up to 250 L s<sup>-1</sup> daily discharge (Figure 2). The increase of DOC during discharge events was about twice as high in summer as compared to winter.



Figure 1. DOC concentrations a), discharge b) and sulphate concentrations c) of the Lehstenbach runoff. The continuous lines show a trend as a linear regression, the dashed lines correspond to a locally-weighted trend regression.

#### **3.2 Short Term DOC Dynamics**

The rainfall event on the 12th of August 2010 provided 27 mm and triggered the groundwater table to the surface level, a sharp peak in discharge up to about 500 L s<sup>-1</sup>, coinciding with a peak in DOC concentrations reaching 35 mg L<sup>-1</sup> (Figure 3). The second rainfall event of 15 mm on the 14th of August 2010 also triggered the groundwater table to the surface level, and resulted in a maximum discharge of 350 L s<sup>-1</sup> and a DOC peak of 32 mg L<sup>-1</sup>. A small rainfall event on the 15th of August 2010 (4 mm) only triggered a small peak of the groundwater table which did not reach surface level. As a consequence, no peak in discharge and DOC occurred. The subsequent rainfall event on the 17th of August 2010 (25 mm) again triggered the groundwater table to near surface level, caused a discharge maximum of 400 L s<sup>-1</sup> and DOC concentrations of up to 35 mg DOC L<sup>-1</sup>.

The relation of DOC in runoff to discharge based on high frequency measurements during selected events in 2010 and 2011 was strongly positive, but characterized by a hysteresis (Figure 4). The maximum DOC concentrations occurred after maximum discharge, with a short temporal delay of about 2-3 h. The direction of the hysteresis loops was always counterclockwise: The DOC concentrations were higher at falling discharge as compared to rising discharge. The dependence of DOC on discharge was much more pronounced during the summer season as compared to winter. The autumnal event did not reach high discharge rates but has a similar response function than the summer event. The general level of DOC in dependence of discharge was similar when comparing the long term data set and the high frequency measurements.

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Figure 2. Dependency of DOC concentration on average daily discharge for the summer (solid circles) and winter (triangle) months



Figure 3. Precipitation (upper panel), DOC concentrations and discharge (middle panel), and groundwater table distance to surface (lower panel) from  $12^{th}$  to  $22^{nd}$  of August 2010



Figure 4. DOC concentrations in relation to discharge during three discharge events

### 4. Discussion

Different drivers such as climate change, land use change and change in atmospheric deposition are discussed in the literature to explain upward trends in DOC concentrations in northern hemispheric surface waters (Freeman et al., 2001). In our study the climate change influence might be neglected as both discharge and precipitation (not shown) do not change significantly over the 1987–2009 period. Water and air temperature slightly increased by approx. 0.5 Kelvin per 20 years. With regard to Q10-values it is very unlikely that long term trends in temperature have an effect on the upward trends of DOC. A small temperature increase and a doubling in DOC concentrations over 20 years would result in unusually high Q10 -values of DOC production.

PH values in runoff vary only very slightly between 4.63 units in 1987 and peak values at 4.73 units in 2002. Thus, a change in pH is unlikely to explain the upward trend in DOC concentrations.

Similar to the conclusion of Clark et al. (2011), we see the most likely cause for the increase of DOC in the reduction in sulphate deposition and the resulting decrease of ionic strength and increase of pH in precipitation. Both changes are supposed to increase the solubility of soil organic matter and thereby causing the long term trend in runoff DOC. A general increase of DOC in forest floor percolates in German forests has also been observed and was attributed also to decreasing sulphate deposition (Borken et al., 2011).

Both, long term data and high frequency measurements show the strong positive dependence of DOC in runoff from discharge. The relationship between groundwater table, discharge (Frei et al. 2010) and DOC reveals that near surface and riparian zones are the main sources for DOC in runoff. Thus, the short term variations of DOC can largely be explained by the hydrological drivers.

The larger DOC response to discharge in summer points to the temperature dependency of DOC release from the source pools. Seasonal dynamics of DOC in forest floor percolates have often been reported with maximum concentrations in summer (Michalzik and Matzner, 1999; Guggenberger and Zech, 1993). In our fen site the DOC concentrations in the upper 10 cm also had the same seasonal pattern (Chen et al. unpublished).

Koehler et al. (2009) stated by means of high frequency measurements of DOC in runoff from a bog that the temperature was more important for DOC than discharge. The relevance of different drivers seems to vary with watershed properties and precipitation regime. Our data for the Lehstenbach catchment document the dominating role of discharge and groundwater table while temperature has a less important, but still significant role.

Within the TERRECO framework we will compare the DOC dynamics in runoff of the Lehstenbach catchment with those of the forested catchment in the Haean basin, South Korea. The latter is not influenced by Histosols,

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has steeper slopes and is characterized by a monsoon-like precipitation regime.

Overall, our data suggest that changes in the climatic regime, e.g. by changing precipitation pattern and changing temperature will influence DOC export from forested watersheds.

#### Acknowledgements

This study was carried out as part of the International Research Training Group TERRECO (GRK 1565/1) funded by the Deutsche Forschungsgemeinschaft (DFG) at the University of Bayreuth, Germany and the Korean Research Foundation (KRF) at Kangwon National University, Chuncheon, S. Korea.

Furthermore we like to thank the Bavarian Environment Agency (LfU) for financial support of this study and for providing the long term monitoring data of the Lehstenbach catchment.

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