**Biogeosciences
Discussions**

DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Limnological Research Station and Department of Hydrology, University of Bayreuth,
95440 Bayreuth, Germany

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**DOC exports
mediated by iron
reduction/oxidation
cycles?**

K.-H. Knorr

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Dissolved organic carbon (DOC) exports from many catchments in Europe and North-America are steadily increasing. Several studies have sought to explain this observation. As possible causes, a decrease in acid rain or sulfate deposition, concomitant reductions in ionic strength and increasing temperatures were identified. DOC often originates from riparian wetlands; but here, despite higher DOC concentrations, ionic strength in pore waters usually exceeds that in surface waters. In the catchment under study, DOC concentrations were synchronous with dissolved iron concentrations in pore and stream water. This study aims at testing the hypothesis that DOC exports are mediated by iron reduction/oxidation cycles. Following the observed hydrographs, $\delta^{18}O$ of water, and DOC fluorescence, the wetlands were identified as main source of DOC. Antecedent biogeochemical conditions, i.e. water table levels in the wetlands, influenced the discharge patterns of nitrate, iron, and DOC during an event. The correlation of DOC with pH was positive in pore waters but negative in surface waters; it was negative for DOC with sulfate in pore waters but only weak in surface waters. The positive correlation of DOC with iron was universal for pore and surface water, though. The decline of DOC and iron concentrations in transition from anoxic wetland pore water to oxic stream water suggests a flocculation of DOC with oxidizing iron, leading to a drop in pH in the stream during high DOC fluxes. The pore water did not per se differ in pH. There is thus a need to more thoroughly consider processes of DOC mobilization in wetlands when interpreting DOC exports from catchments. The coupling of DOC with iron fluxes suggested that increased DOC exports could at least in part be caused by increasing activities in iron reduction, possibly due to increases in temperature or wetness of riparian wetlands.

1   Introduction

Dissolved organic carbon (DOC) plays an important role in the acid-base chemistry of surface waters (Driscoll et al., 1994) and contributes significantly to carbon and nutrient cycling in many ecosystems (Billett et al., 2004; McDowell, 2003). Moreover, DOC influences mobility and thus fate of metals (Hiraide, 1992) and organic contaminants (Maxin and Kögel-Knabner, 1995), and negatively affects the use of waters as drinking water through formation of toxic disinfection by-products (Diehl et al., 2000). For many peatlands, DOC also represents a significant contribution to overall carbon fluxes (Limpens et al., 2008). Minding these facts, there has been increasing concern about the observation that DOC concentrations in the discharge of many temperate catchments are rising (Worrall and Burt, 2007; Roulet and Moore, 2006).

A number of studies have thus been carried out to investigate the causes for increased DOC mobilization and export. Explanations for the observed increase in DOC concentrations in streams and rivers have been proposed to be the observed decrease in acid rain and sulfate deposition, a decrease in ionic strength of surface waters, and increasing temperatures (Clark et al., 2010; Evans et al., 2006; Hruska et al., 2009). Also rewetting of fens during restoration measures has been shown to potentially increase DOC exports (Glatzel et al., 2003; Zak and Gelbrecht, 2007).

Regarding the source of DOC, wetlands within a catchment have been identified to play an important role (Laudon et al., 2011; Austnes et al., 2010). Here, high concentrations of DOC in the pore waters near the surface can be rapidly mobilized and discharge into the adjacent streams during rain events (Bishop et al., 2004; Frei et al., 2010). However, pore water chemistry of mostly anaerobic wetlands significantly differs from surface water in streams (e.g. compare data in Knorr et al., 2009; Hruska et al., 2009). For example, under reducing conditions high concentrations of DOC occur even in presence of dissolved ferrous iron in the millimolar range (Blodau et al., 2008). This is also supported by observations of Grybos et al. (2009), who report increasing DOC concentrations up to $8.94\,\mathrm{mmol\,l^{-1}}$ with increasing pH under reducing conditions and

in presence of 4.53 mmol l^{-1} Fe^{2+}. In contrast to observations in surface waters, ionic strength in such reduced waters exceeds by far ionic strength of surface waters.

On the process scale, absence of oxygen and thus reducing conditions in wetlands lead to reduction of ferric iron to ferrous iron and sulfate to sulfide; this process is re-
5 versible during drought phases, leading to precipitation of ferric iron and reoxidation of reduced sulfur compounds (Knorr et al., 2009). High ionic strength in reduced pore waters dominated by ferrous iron did not seem to have a negative impact on DOC solubility (Blodau et al., 2008; Grybos et al., 2009). On the other hand, in the transition to oxic conditions, oxidation of reduced iron and sulfur leads to a pH drop (Knorr
10 and Blodau, 2009; Clark et al., 2005) and may thus initiate flocculation of DOC (Grybos et al., 2009), probably also by ferric iron, which is besides aluminum long known as an effective flocculent for organic matter (Lefebvre and Legube, 1993; Libecki and Dziejowski, 2008). In summary, in pore waters one would expect an increase in DOC concentrations to be accompanied with increasing ferrous iron, decreasing sulfate con-
15 centrations, and increasing pH due to reducing conditions. In surface waters, increases in DOC concentrations would also be expected to be accompanied by increasing iron concentrations. However, oxidation of iron could lead to decreases in pH, and oxidation of reduced sulfur compounds could increase sulfate concentrations.

The aim of this study was to investigate the dynamics of DOC in the pore waters
20 of riparian wetlands, relate these dynamics to biogeochemical conditions and drivers thereof, and compare these observations to DOC dynamics in the discharge of the adjacent stream. We hypothesized that wet preconditions favor reductive dissolution of iron and release of bound DOC into the pore water, while under dry conditions DOC is flocculated and bound by iron(III) phases and thus immobilized. This mechanism
25 of DOC mobilization and immobilization should translate into a close and positive relationship of iron and DOC in the pore water and in the discharge. On a long term, increases in air temperature or increasing wetness due to climate change could favor iron reduction and thus lead to the observed increases in DOC. Moreover, we hypothesized that DOC mobilization is a priori not controlled by ionic strength or pH, as in

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

reduced, anaerobic pore waters of wetlands ionic strength and pH may well exceed values observed for aerobic surface water.

2 Materials and Methods

The study was conducted in the Lehstenbach catchment in Northeastern Bavaria (4.2 km^2, 695–877 m elevation, mean annual precipitation 1150 mm, mean annual temperature 5.3 °C) with about 30 % of the area covered by mostly shallow wetland soils (Gerstberger, 2001). The catchment is dominated by Norway spruce (*Picea abies*) with *Vaccinium myrtillus*, *Juncus effusus*, *Carex nigra*, *Carex rostrata*, *Carex canescens*, *Molinia caerulea*, *Eriophorum vaginatum*, and also *Sphagnum* mosses in the understory (Matzner, 2004). In the forested upland areas, groundwater tables are mostly > 10 m below surface, while groundwater tables are near the surface in the wetland areas (Lischeid et al., 2002). Details about the wetland and forest soil biogeochemistry have been reported elsewhere (e.g. Muhr et al., 2010; Knorr et al., 2009).

Discharge and surface water chemistry were studied at the catchment outlet, using a pressure sensor (Solinst Canada Ltd. Georgetown, ON, Canada) immersed at a discharge flume and weir and an automatic bottle sampler (Teledyne ISCO, Lincoln, NE, USA). Within this study, we obtained discharge chemistry data during several sampling campaigns from August 2010 until September 2011 in 1–4 h sampling intervals analyzed as outlined below. Along with the discharge data, we monitored the groundwater table in 2 m distance from the stream near the catchment outlet as a reference to relate discharge dynamics and chemistry to hydrological preconditions (pressure transducer as for discharge). Long term DOC monitoring data was provided for the catchment outlet from 1987 until 2009 by courtesy from the Bavarian Federal Environmental Authority (LFU, Hof, Germany). Detailed pore water chemistry data (from suction samplers; Rhizon®, Eijkelkamp, Giesbeck, The Netherlands) was available on a weekly basis for six plots and 6 depths (5–50 cm) from a former field experiment with natural and manipulatively enforced drying and wetting in 2007 (Knorr et al., 2009) and unpublished

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

DOC data analyzed as indicated below. Moreover, pore water and corresponding discharge chemistry data was available on a biweekly basis from April to June 2010 (Knorr 2010, unpublished). In 2011, 28 shallow wetland groundwater samples (40–100 cm depth from piezometers) and 12 deeper groundwater samples (300–1500 cm depth from monitoring wells) were obtained. In total, more than 260 discharge samples and approx. 1000 pore water samples were included in this study. Air temperature data from 1994–2012 was kindly provided by the Department of Micrometeorology (T. Foken) at the University of Bayreuth. Long term data series (DOC, sulfate, and air temperature) were evaluated using LOWESS regression (LOcally WEighted Scatterplot Smoothing) as implemented in MATLAB Version 2011 (MathWorks, Natick, MA, USA).

DOC concentrations were measured by thermo-catalytic oxidation on a TOC-VCPN Analyzer (Shimadzu, Kyoto, Japan), major anions were analyzed with anion chromatography (Metrohm modular IC system IC 752 with chemical suppression, A-Supp 4 column; Metrohm, Herisau, Switzerland). Dissolved iron (after reduction with ascorbic acid) was measured as ferric iron and total iron (after reduction with ascorbic acid) with the phenanthroline assay (Tamura et al., 1974) in pore water samples, and using atomic absorption spectroscopy (PE AAS 4100 XL, Perkin Elmer LAS, Waltham, MA, USA) for total iron in surface water samples. Values of pH were measured potentiometrically with a glass electrode (Inlab 412, WTW, Weilheim, Germany). Stable isotope analysis of ^{18}O and ^{2}H in discharge and rainwater was done by thermo-conversion isotope ratio mass spectrometry (TC-IRMS; HTO pyrolysis unit, HEKATech, Wegberg, Germany, coupled to a delta V advantage IRMS via ConFlo IV, Thermo Fisher, Bremen, Germany).

For DOC quality investigations, fluorescence excitation-emission matrices (EEMs) were measured on 0.45 µm filtered samples, diluted to absorption at 254 nm < 0.3 if necessary to minimize inner-filter effects. UV-VIS spectra were recorded on a Varian Cary 1E spectrophotometer (range 200–800 nm, 0.5 nm resolution; Varian Inc./Agilent Tech., Canta Clara, CA, USA); Fluorescence spectra were recorded on a LS 55 fluorescence spectrometer (excitation range 240–450 nm in steps of 5 nm, emission range 300–600 nm in steps of 0.5 nm; Perkin Elmer, Waltham, MA, USA). Inner filter

correction and EEM pretreatment (blank subtraction, Raman normalization) were performed using the toolbox from Cory and McKnight (2005) and MATLAB Version 2011 (MathWorks, Natick, MA, USA). Samples were reshaped and subjected to a parallel factor analysis (PARAFAC) using toolboxes of Murphy et al. (2010) and of Stedmon and Bro (2008). Following the toolbox of Stedmon and Bro (2008), a 5 component model could be split-half validated and was subsequently used for data interpretation. In total, 160 discharge samples and 40 shallow (wetland) and deep groundwater samples were included in the PARAFAC model.

3 Results

3.1 Long term discharge series

Regarding the long term data series of the catchment outlet, mean DOC concentrations in the discharge as estimated by LOWESS regression increased from about $4.7\,\mathrm{mg\,l^{-1}}$ to $8.6\,\mathrm{mg\,l^{-1}}$ from 1987 until 2009 (Fig. 1). Also mean annual temperatures increased from $5.6\,^\circ\mathrm{C}$ in 1994 to about $6.7\,^\circ\mathrm{C}$ in 2011 (LOWESS regression, site specific records available from 1994 onwards). On the other hand, mean sulfate concentrations in the discharge declined from about $16\,\mathrm{mg\,l^{-1}}$ (1987) to about $11\,\mathrm{mg\,l^{-1}}$ (2009), nitrate declined from 4.1 (1987) to $2.8\,\mathrm{mg\,l^{-1}}$ (2009), but values of pH from the long term record did not show a consistent trend according to the LOWESS regression (4.72 to 4.77, data not shown). Unfortunately, the time series of iron ends in 2001. From 1987 to 2001, iron concentrations in the discharge increased from 0.15 to $0.22\,\mathrm{mg\,l^{-1}}$. As an estimate for current iron, sulfate and DOC exports, we included the median of the 2010–2011 dataset from this study as a red X in Fig. 1. This rough estimate would suggest a stabilization of sulfate and DOC exports in the last years and an increase of iron exports from 2001 until today, parallel to DOC.

3.2 Concentration levels and correlations in surface, ground-, and pore water

Based on the observed concentrations, highest DOC concentrations occurred in the pore water of the upper 50 cm of the wetland soils (about 6–150 mg l^{-1}), while concentrations in the deeper groundwater were mostly below 2–3 mg l^{-1}. Nitrate was mostly absent in wetland pore waters, except of few and short-lived occasions during dry weather conditions (see also Goldberg et al., 2010), while concentrations in the deeper groundwater were between 3 and 8 mg l^{-1}. Sulfate concentrations in the wetland pore waters were variable, depending on weather conditions and groundwater table, ranging from < 0.05 mg l^{-1} to 20 mg l^{-1}. In the deeper groundwater, sulfate ranged from 10–21 mg l^{-1}. An overview of ranges in concentrations of DOC, nitrate, sulfate, and total iron and ranges in pH is given in Table 1. Aluminum concentrations in pore and surface water (not given in the Table) ranged from 7–14 mg l^{-1} and 0.4–1.0 mg l^{-1}, respectively. Using two different observations of solute concentrations of either high or low ionic strength, considering also other dissolved metals, chloride, and bicarbonate (data not shown), we obtained two upper and lower ionic strength estimates for pore and surface water. For the wetland pore water, ionic strength spanned from about 2.90 to 6.80 mmol l^{-1} at an pH of 3.5 to 6, and dominated by Fe^{2+}, Al^{3+}, and negative charge from dissociated organic acids as estimated from charge balance considerations. In the surface water (discharge samples), ionic strength was notably lower and ranged from 0.53 to 1.04 mmol l^{-1} at a comparable pH range of 3.8 to 6, but dominated by Ca^{2+}, Al^{3+}, SO_4^{2-}, and negative charge from dissociated organic acids.

Within the surface water samples from this study, we found a positive correlation of DOC and iron concentrations with discharge. For nitrate and pH there was in general a negative correlation with discharge. At comparably high discharge events and during snow melt high nitrate concentrations coincided with high discharges (not shown), yielding a lower correlation coefficient reported in Table 2. Sulfate was not significantly correlated to discharge, as concentrations depended strongly on preconditions (dry, wet). No correlations with discharge were calculated for the long term data, as the time

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►◄

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

CC BY

point of sampling could only be correlated with an average discharge for the sampling day, which obscures the hourly dynamics of discharge chemistry (Table 3). Regarding the correlations among solutes in the surface water samples, i.e. of DOC with nitrate, sulfate, iron, and pH, DOC was most strongly and positively correlated with dissolved iron, while being negatively correlated with pH and nitrate, albeit weaker (Table 2). While most correlations of the long term data (Table 3) agree with the data obtained in this study, some pairs yielded opposite dependencies. While pH correlated positively with nitrate and sulfate in this study, pH was negatively correlated to nitrate and sulfate in the long term dataset. Also the correlation of iron with sulfate inverted.

In the pore water samples, DOC was again most strongly and again positively correlated with dissolved iron, but in contrast to the surface water samples also positively correlated with values of pH. Nitrate was similarly, albeit weaker correlated with DOC in a negative manner; for sulfate also a slight negative correlation with DOC was observed, contrarily to surface water samples from 2010–2011 of this study (Table 4).

3.3 Discharge dynamics of DOC and nitrate and event water contribution

For the identification of flow components, their possible respective source areas, and antecedent biogeochemical conditions, two discharge events of similar magnitude (peak discharge 0.11 to 0.12 $m^3 s^{-1}$), but different preconditions in terms of groundwater table were chosen (Fig. 2). Under wet preconditions (20 July 2011, 23 mm of rainfall, groundwater table 19 cm below surface at the reference monitoring well), DOC concentrations increased with discharge as usually observed, although the maximum of DOC concentrations was about 240 min delayed compared to the maximum in discharge. Under dry preconditions (31 May 2011, 41 mm of rainfall, groundwater table 62 cm below surface at the reference monitoring well), DOC concentrations similarly increased with discharge with a delay of the DOC maximum about 150 min compared to discharge. According to a translation of the discharge-time relationship into a discharge-concentration plot (as e.g. proposed in Evans and Davies, 1998), DOC followed under both conditions a counter-clockwise hysteresis loop, indicating a fast flow component

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

poorer in DOC at the begin of the discharge event, until high DOC concentrations appeared by an intermediate flow component. Finally, DOC concentrations declined, lagging behind the decline in discharge, indicative of a slow flow component rich in DOC, until base flow poor in DOC was reached again. For nitrate, the two different preconditions translated into two different discharge-concentration patterns. Under wet preconditions, nitrate concentrations in the stream are diluted by a fast flow component and subsequent intermediate flow component, until recovering to pre-event values when approaching base flow conditions. Under dry preconditions, nitrate concentrations first increased ("nitrate flush"), following a clockwise hysteresis and indicative of a fast flow component rich in nitrate. Thereafter, nitrate concentrations were slowly declining back to pre-event values when approaching base flow. Summarized, DOC seemed to be mainly released from an intermediate flow component in terms of time scales, irrespective of preconditions, while the fast flow component at the begin of the discharge event contained somehow less DOC and was either free of nitrate (wet preconditions), or had higher concentrations of nitrate compared to the other flow components (dry preconditions).

Regarding the contribution of rain event water to discharge, the maximum of event water contribution was under both wet and dry preconditions shortly before the maximum of the discharge (1–2 h, Fig. 2). In case of the dry preconditions, this maximum apparently coincided with the initial flush of nitrate rich water. Irrespective of the preconditions, the decline of the event water coincided with the retarded decline in DOC concentrations (Fig. 2). In summary, the isotope data of the discharging waters also suggested some surface near fast flow component induced by rain event water, as derived from solute data. The slow decline of event water contribution towards the end of the discharge event suggested a shallow and intermediate flow component susceptible for dilution with rainwater. Nevertheless, also a modeled base flow for both events declined in a way paralleling the decline in DOC (not shown).

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

3.4 Discharge dynamics of DOC and nitrate and event water contribution

Using a set of 200 DOC samples from deep groundwater, shallow wetland groundwater, and discharge, a 5 fluorescence component model could be obtained and split-half validated following the toolbox and suggestions of Stedmon and Bro (2008). Of these hypothetical fluorophores, fluorescent components number 1, 2 and 3 had higher contributions in samples obtained from wetlands (shallow wetland groundwater) (Fig. 3). Fluorescent component 5 contributed more to total fluorescence in deep groundwater samples, while component 4 did not differ between the sampled DOC sources. DOC samples from discharge were either quite similar to the wetland samples (components 2, 3, 5) or lined up between deep groundwater and wetland groundwater quality indices (component 1). From these observations, components 1, 2, and 3 may be termed to be indicative of wetland-borne DOC, component 5 indicative of deep groundwater-borne DOC. Using a plot of component 2 (wetland-borne) versus component 5 (deep groundwater-borne), the similarity of DOC in discharge to the quality of DOC from wetlands was obvious (Fig. 3). Only few DOC samples in discharge that have been sampled close to an area with exfiltrating deep groundwater with little influence of soils or during base-flow conditions lined up along a mixing line of components 2 and 5. As depicted exemplarily in Fig. 3, the fluorescence component assigned to deep groundwater declined during discharge events and recovered to the pre-event level when approaching base-flow conditions again, while the component assigned to wetland DOC increases and remains high.

3.5 DOC dynamics in the pore waters of the riparian wetlands

DOC concentrations in the pore water were closely related to the release of ferrous iron into the pore water, thus mirroring the dynamics of iron reduction and oxidation. This is exemplarily shown for 4 experimental plots in the Schlöppnerbrunnen wetland of catchment under study (Fig. 4) that has been described previously (Knorr et al., 2009). During phases of high water tables, iron reduction was favored and led to concomitant

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

DOC release, during phases of lower water tables DOC concentrations declined again. This translated into the described high correlation of dissolved iron and DOC in the porewater in Table 4. Regarding the dynamics of sulfate, the observed concentration pattern was inverse compared to DOC, as during reducing conditions not only iron was

5 reduced and released into the porewater, but also sulfate reduction initiated and led to depletion of sulfate. Generally and as expected, values of pH increased during phases of reducing conditions, while decreasing during phases of oxidation (not shown). Especially in the mid of the growing season (about days 160–220) reducing conditions and associated DOC release were also observed very close to the soil surface above

10 the water table. Although differing in the absolute concentrations and partly also in response times upon wetting and drying, the parallel dynamics of dissolved iron and DOC and the opposite dynamics of sulfate and DOC was obvious for all plots under study.

3.6 Indicators in the surface water for redox induced DOC mobilization

15 While nitrate was negatively correlated with DOC in pore and surface water (Tables 2–4), high nitrate concentrations in the discharge also only occurred at low groundwater tables, i.e. under oxidized preconditions, or during initial nitrate flushing events after drought phases (Fig. 3). For iron, the opposite trend was observed, with high iron concentrations – along with high DOC concentrations – at high groundwater tables, i.e.

20 reducing preconditions. For sulfate there was an obvious difference between seasons. While the correlation with DOC was in general weakly negative (see above), lower sulfate concentrations at high DOC concentrations were mainly observed for summer months at high water tables (reducing conditions). In winter, a positive correlation with DOC may be postulated with higher sulfate concentrations at higher DOC concentra-

25 tions, despite high groundwater table levels.

4   Discussion

The aim of this study was to find support for the hypothesis that the long term in-
crease in DOC exports from the catchment is not only due to a decline in sulfate or
acid rain deposition or due to a decrease in ionic strength (Clark et al., 2010; Hruska
5   et al., 2009), but also by changes in biogeochemical processes and DOC mobilization
processes in the source areas, i.e. the riparian wetlands. Many studies have so far in-
vestigated DOC exports from catchments and the controls thereof (Clark et al., 2010),
but fewer studies are available investigating the DOC source areas and the DOC in
runoff in a complementary approach (Worrall et al., 2008; Clark et al., 2008). If data
10   from wetlands as DOC source areas are available, often no redox sensitive probing
of predominant pore water species had been achieved, especially in monitoring pro-
grams (Clark et al., 2005; Worrall and Burt, 2007). In this study, we added DOC data
to a one growing season, redox sensitive pore water dataset that has been previously
presented (Knorr et al., 2009). These data were compared to a long term record of dis-
15   charge chemistry (1987–2009) and several short term investigations of high temporal
resolution. This approach yields several new insights in DOC production and mobiliza-
tion in pore waters, the response of DOC in pore water to drought effects, the transition
of DOC from the source areas into the stream, and the impact of differing hydrological
preconditions (dry – wet) on the respective DOC and solute outputs.
20   It was beyond the scope of the study to elaborate statistical models to predict DOC
in stream waters and to elucidate controls of DOC release based on advanced sta-
tistical tools. The focus of this study was more on finding a link between processes
in the riparian peatlands and the observed stream water chemistry, and to relate this
process based understanding to an alternative hypothesis to explain increased DOC
25   concentrations in the discharge of catchments with a significant proportion of peat soils.
Therefore, correlations of solutes, discharge, groundwater levels, and pH were calcu-
lated for linear relationships only, which may be seen as a limitation of this study but
should not affect the overall argumentation.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

As presented in Fig. 1, the observed long term increase of DOC concentrations at the catchment outlet was paralleled by an increase in temperature, a decline in sulfate and nitrate, no clear change in pH, but a remarkable increase of dissolved iron. It was also reported that increases in DOC concentrations have mostly been observed for catchments with a relatively high proportion of peat soil coverage (Worrall and Burt, 2007; Billett et al., 2006) which is also the case in the catchment under study here (about 30 %). These observations are therefore quite similar to what has been reported from other catchments with increasing DOC concentrations and the respective deposition histories (Evans et al., 2006; Monteith et al., 2007), although little information is available for iron in the discharge. Nevertheless, also increased temperatures, as observed here, have already been identified to contribute to increased DOC exports (Evans et al., 2006; Worrall et al., 2004).

4.1 Source identification for DOC to assign relevant processes

Regarding the pore water data compared to the stream water chemistry, highest DOC concentrations occurred in the wetland pore and ground water, lowest concentrations in the deep groundwater, and intermediate concentrations in the discharge. Thus, based on the observed concentration ranges, the source of DOC must have been the wetlands, a finding which was supported by our DOC quality investigations (Fig. 5) and could be expected based on previous studies (Austnes et al., 2010; Laudon et al., 2011; Morel et al., 2009). An increase of DOC concentrations was always paralleled by an increase of DOC quality parameters assigned to the wetlands as source areas, while quality indices indicative of groundwater-borne DOC declined. This suitability of PARAFAC modeling of fluorescence components of DOC has already been demonstrated by Fellman et al. (2009). The wetlands represented not only sources of DOC, and iron, though, but also of acidity, as pH decreased with increasing DOC concentrations originating from the wetlands. Sulfate stemmed mostly from deep groundwater, as deep groundwater has longer residence times and therefore still contains high sulfate loads from the past high deposition (Lischeid, 2001). For nitrate, the predominant

source was probably also deeper groundwater, however, after longer drought phases followed by strong rain events, nitrate was initially flushed out from a fast flow component, which could also be attributed to the shallow surface layers of wetlands. Although there is little data available about nitrate in wetlands, this is reasonable, regarding the earlier study of Goldberg et al. (2010), who reported the occurrence of peaks of nitrate in surface near pore waters in the wetland Schlöppnerbrunnen (situated in the same catchment as under study here) under dry conditions.

The source attribution of DOC was further supported by a more detailed analysis of the hydrographs. DOC concentrations in a concentration-over-discharge plot (C-Q plot) always followed a counter clockwise hysteresis loop, irrespective of the preconditions (Fig. 2). This suggested a surface near fast flow component, as in the upper layers of the riparian wetland soils (Bishop et al., 2004) and in between the hummock/hollow structures (Frei et al., 2010) hydraulic conductivities increase and allow for a fast response towards rain events. Thus, also the contribution of rain event water based on δ^{18}O data peaked during this initial rise in discharge (Fig. 2), while the increase of DOC concentration lagged behind due to lower DOC concentrations in the oxic upper wetland layers and a slower response of less shallow pore waters rich in DOC (Figs. 2, 4). If there was dry preconditions, an initial nitrate flush at the begin of a discharge event occurred, as could be explained by the occasionally occurring elevated nitrate concentrations in the aerated surface layers of the wetlands. Under wet preconditions, no nitrate was observed in also in the surface near wetland pore water (Goldberg et al., 2010), thus no initial nitrate flush occurred. This was also obvious from the observation that high nitrate concentrations in the discharge always coincided with low groundwater table levels (Fig. 5), except if there was an initial nitrate flushing effect, when groundwater tables quickly rose after drought phases and nitrate concentrations were still high. As the high DOC concentrations originated also from pore waters below 5–10 cm (Fig. 4) and these depths are probably less affected by surficial rainfall, the DOC dynamics during discharge remained similar irrespective of the preconditions and during peaks of DOC, the contribution of event water already declined.

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◀◀   ▶▶

◀   ▶

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

This particular discharge pattern may not be universal, as e.g. McGlynn and McDonnel (2003) observed a clockwise hysteresis for DOC, i.e. DOC concentrations rising faster than discharge, but the authors also claimed the importance of connecting observed hydrological dynamics in the discharge to the biogeochemical conditions and hydro-
logical dynamics of the particular source areas. The observed pattern in DOC, nitrate, and iron concentrations in the discharge therefore further support the importance of hydrological, and thus biogeochemical redox preconditions in the wetlands for solute exports.

4.2 Processes at the wetland-stream interface

An important point is that there was a strong decline in concentration levels of DOC during the transition from pore waters to surface water. Taking the medians as robust estimates for average concentrations, about 68 % and 81 %, respectively of DOC and iron, was eliminated during the transition from pore to surface water. Thus, compared to the pore water, one should expect a formation of a relatively iron enriched flocculation or precipitation product. Such enrichment of iron at the transition from anoxic to oxic conditions was also observed for the capillary fringe of wetlands (Küsel et al., 2008; Knorr et al., 2009; Biester et al., 2012). As iron(III) salts are known as a strong floccu-
lant for DOC (Lefebvre and Legube, 1993), this flocculation and precipitation may be explained by an oxidation of ferrous to ferric iron and subsequent flocculation of DOC. Compared to aluminum, iron(III) salts also proved to be more effective for humic acid removal especially at pH values below 4 (Libecki and Dziejowski, 2008), which is why we believe that the flocculation is mainly initiated by iron. Moreover, the oxidation of fer-
rous to ferric iron leads to the formation of ferric hydroxides and dissolved complexes with hydroxyl ligands with a subsequent drop in pH, i.e. ferric iron is a strong cationic acid (Stumm and Morgan, 1996). Therefore, this oxidation and subsequent floccula-
tion may also explain the observed drop in pH during phases of high discharge and high DOC, as the anaerobic pore waters in the wetlands did not show much lower pH than the surface waters (Table 1). Aluminum, on the other hand, does not change in

redox state during transition from anaerobic to aerobic waters, has thus no effect on pH. Moreover, concentrations in the pore water were also much higher than in the surface water and did obviously not affect DOC mobilization. A contribution of aluminum to DOC flocculation cannot be excluded, though.

Along with the observed differences in concentrations of solutes in the compartments wetland pore water, groundwater and surface water, it was obvious that ionic strengths in the wetland pore waters may exceed ionic strength in the surface waters by far. Thus, while for surface waters ionic strength was found to negatively affect solubility of DOC (Hruska et al., 2009), this relation is more or less reversed in pore waters, where DOC concentrations were found to increase almost infinitely along with ferrous iron concentrations not only in this study (Table 3, Fig. 4) (Grybos et al., 2009; Zak and Gelbrecht, 2007).

4.3 Pore water biogeochemistry and associated DOC dynamics

Many studies found support that the decline in sulfate deposition can explain increases in the release of DOC into streams (e.g. Clark et al., 2006). Nevertheless, this relation was not universal, also in catchments with peat soils (Clark et al., 2010; Worrall and Burt, 2007). Therefore, the effects of sulfate addition into wetlands will be briefly outlined in the following. While sulfate is the anion of a strong acid and thus does not affect pH in the transition from pore or ground water into surface water, it can be used as an electron acceptor for anaerobic respiration in wetlands (Keller and Bridgham, 2007; Limpens et al., 2008; Pester et al., 2012) and sulfate reduction will increase pH here by consumption of acidity (Stumm and Morgan, 1996). Thus, addition of sulfate to wetlands could be expected to increase anaerobic respiration by increasing sulfate reduction, as e.g. observed after droughts (e.g. Knorr et al., 2009) and for sulfate deposition experiments (e.g. Gauci and Chapman, 2006). From these considerations one may even postulate an increase of DOC production under elevated sulfate deposition onto wetlands due to increased availability of electron acceptors for respiratory

breakdown of solid organic matter and subsequent increases in pH, which further supports microbial activity.

Due to this outlined process pattern, could be expected that there was a negative correlation of sulfate and DOC in the wetland pore water. This could be explained on a mechanistic level as DOC was released under iron and sulfate reducing conditions and higher pH, probably due to reductive dissolution of iron oxides and release of associated DOC (Zak and Gelbrecht, 2007). Also in the surface water a negative correlation of sulfate and DOC was observed, at least for summer months (Fig. 5), when reducing processes are more intense than in winter (see also Fig. 4 for seasonal dynamics of reducing conditions from spring to summer). Therefore, in this case the analysis of the hydrograph, the separation of sources based on event water contributions, and sulfate elimination in the wetlands due to reduction demonstrated that this was due to the fact that sulfate and DOC have different hydrological sources, at least in summer. High DOC concentrations were released from the wetland waters (wetland pore water, shallow wetland groundwater) during discharge events, while during these events the contribution of deeper groundwater – as the main source of sulfate – decreased. On the other hand there was a strong positive correlation of DOC and iron in pore water, groundwater, and surface water. The detailed pore water investigations of this and former studies (Knorr et al., 2009; Blodau et al., 2008) support the hypothesis, that DOC was predominantly released during phases of iron reducing activity (e.g. Fig. 4). Although iron and DOC are eliminated to a large extent during the transition from pore to surface water, this strong correlation remained with higher iron concentrations at higher DOC concentrations in the discharge, especially at shallow groundwater table levels favoring reducing conditions (Fig. 5).

There is thus a good understanding of DOC mobilization in the pore water and export paths via different flow paths and sources for the catchment under study and these processes probably apply to a number of other sites as well (Morel et al., 2009; McGlynn and McDonnell, 2003). While the effect of acid and/or sulfate deposition on catchment DOC export has been demonstrated for many sites and may be responsible

for a large part of the observed long term trends (e.g. reviewed in Clark et al., 2010), the process based understanding from this study adds another potential factor to cause increased DOC exports from catchments. Due to the tight coupling of DOC and iron dynamics and due to the high release of DOC under reducing conditions in wetlands ⁵ (Zak and Gelbrecht, 2007; Grybos et al., 2009), an increase in iron reducing activity or an increase in reducing conditions and associated increases in pH causing higher DOC mobility and higher microbial activity in general would also explain rising DOC concentrations in catchment exports in a long term perspective. Higher microbial activity and higher iron reduction could e.g. be caused by increased temperatures due ¹⁰ to climate change, as depicted for the site under study here in Fig. 1, or due to increased wetness as a result of changed precipitation patterns. Furthermore, reduced inputs of sulfate and nitrate could shift anaerobic respiration towards iron reduction and thereby increase the release of iron oxide-bound organic matter. Moreover, more frequent drought and rewetting events could have stimulated anaerobic mineralization by ¹⁵ regeneration of electron acceptors, as has been demonstrated for laboratory and field experiments (Knorr et al., 2009, 2008; Deppe et al., 2010; Blodau and Moore, 2003).

5   Conclusions

In summary, this study demonstrated that for an understanding of increasing DOC exports from catchments, besides the accepted effects of acid rain deposition, processes ²⁰ within the source areas (i.e. the wetlands), processes during the transition from the source to the receiving stream (during which a large fraction of DOC is captured), and the impact of different hydrological and biogeochemical preconditions have to be considered. DOC concentrations in pore and surface waters were strongly and linearly correlated with iron, supporting the hypothesis that iron redox dynamics exerts a major ²⁵ control on DOC mobilization. Also increases in pH under reducing conditions may have exerted a positive feedback mechanism on DOC solubilization. On the other hand, ionic strength in the pore waters exceeded ionic strength in surface waters by far and did thus

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄ ►|

◄ ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

not limit DOC solubility. The importance of redox conditions in the wetlands was further demonstrated by the observed patterns of nitrate and sulfate concentration versus groundwater table levels. Opposing relationships of DOC with pH or pH with sulfate in pore water of wetlands and adjacent streams pointed out the importance of consider-
ing biogeochemical processes and hydrological flow paths leading to these observed signals. Although such a statement cannot be verified yet, an alternative hypothesis for increased DOC exports from catchments in the long term could be an increase of DOC release from wetland source areas by increased reductive processes, associated release of DOC from reductively dissolved iron oxides, and generally increased min-
eralization and DOC production by increased pH. This could potentially be driven by increasing temperatures due to global warming or by changes in precipitation patterns stimulating DOC production.

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

K.-H. Knorr

Table 1. Ranges in concentrations of DOC, nitrate, sulfate, and total iron, and ranges in pH in the different analyzed compartments "wetland pore water", "wetland groundwater", "deep groundwater", and "surface water". Values represent observed minima/medians/means/observed maxima from the available dataset.

Compartment	DOC (mg l⁻¹)	NO₃ (mg l⁻¹)	SO₄²⁻ (mg l⁻¹)	Fe^tot (mg l⁻¹)	pH (−)
Wetland pore water	6.4/25.3/31.9/150.3 (N = 919)[1]	0.0/0.1/1.1/22.0 (N = 943)[1,2]	0.0/0.9/2.3/22.1 (N = 945)[3]	0.1/1.6/2.2/20.4 (N = 858)[3,4]	2.6/4.8/4.6/6.1 (N = 893)[3]
Wetland groundwater	3.9/16.9/17.7/61.2 (N = 28)[5]	0.0/0.2/0.5/4.1 (N = 28)[5]	0.8/4.0/6.6/36.1 (N = 28)[5]	0.2/0.7/1.5/5.9 (N = 28)[5]	4.3–6.4[6]
Deep groundwater	0.8/1.5/1.8/3.4 (N = 12)[5]	0.7/3.5/4.0/7.8 (N = 12)[5]	8.9/17.1/18.0/21.4 (N = 12)[5]	< LOQ (0.05), max. 0.24 (N = 12)[5]	4.8–5.8[6]
Surface water	2.8/8.1/10.9/33.7 (N = 547)[5]	1.1/3.1/2.9/5.4 (N = 534)[5]	0.4/11.3/11.2/41.0 (N = 536)[5]	0.0/0.3/0.4/1.5 (N = 474)[5]	3.9/4.5/4.6/5.9 (N = 155)[7]
	1.3/5.7/7.3/34.0 (N = 536)[8]	0.5/3.7/3.8/9.3 (N = 544)[8]	6.9/13.0/14.1/34.5 (N = 544)[8]		

[1] K.-H. Knorr 2007 (unpublished).
[2] Goldberg et al. (2010).
[3] Knorr et al. (2009).
[4] Fe^{2+} only.
[5] This study.
[6] Range from G. Lischeid 2005 (unpublished).
[7] K.-H. Knorr 2010 (unpublished).
[8] Long term record 1987–2009, Bavarian Federal Environmental Authority 2010 (unpublished).

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Table 2. Correlations (Pearson) in surface water between discharge, solutes, and groundwater level (GW, in m below surface). Data for Q, DOC, nitrate, sulfate, and iron: this study; data for pH from K.-H. Knorr 2010 (unpublished).

	Q (m^3 s^{-1})	DOC (mg l^{-1})	NO_3 (mg l^{-1})	SO_4^{2-} (mg l^{-1})	Fe^{tot} (mg l^{-1})	pH (−)	GW level (m)
Q (m^3 s^{-1})	–	0.756[2]	−0.297[2]	−0.052	0.450[2]	No data	−0.452[2]
DOC (mg l^{-1})	$N = 547$	–	−0.673[2]	−0.230[2]	0.954[2]	−0.498[2]	−0.514[2]
NO_3 (mg l^{-1})	$N = 534$	$N = 534$	–	0.344[2]	−0.586[2]	0.448[2]	0.157[2]
SO_4^{2-} (mg l^{-1})	$N = 536$	$N = 536$	$N = 534$	–	−0.310[2]	0.444[2]	0.025
Fe^{tot} (mg l^{-1})	$N = 474$	$N = 474$	$N = 466$	$N = 468$	–	−0.481[2]	−0.459[2]
pH (−)	No data	$N = 157$	$N = 157$	$N = 157$	$N = 140$	–	No data
GW level (m)	$N = 547$	$N = 547$	$N = 534$	$N = 536$	$N = 474$	No data	–

Levels of significance: [1] $p < 0.1$, [2] $p < 0.05$, no asterisk: not significant.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

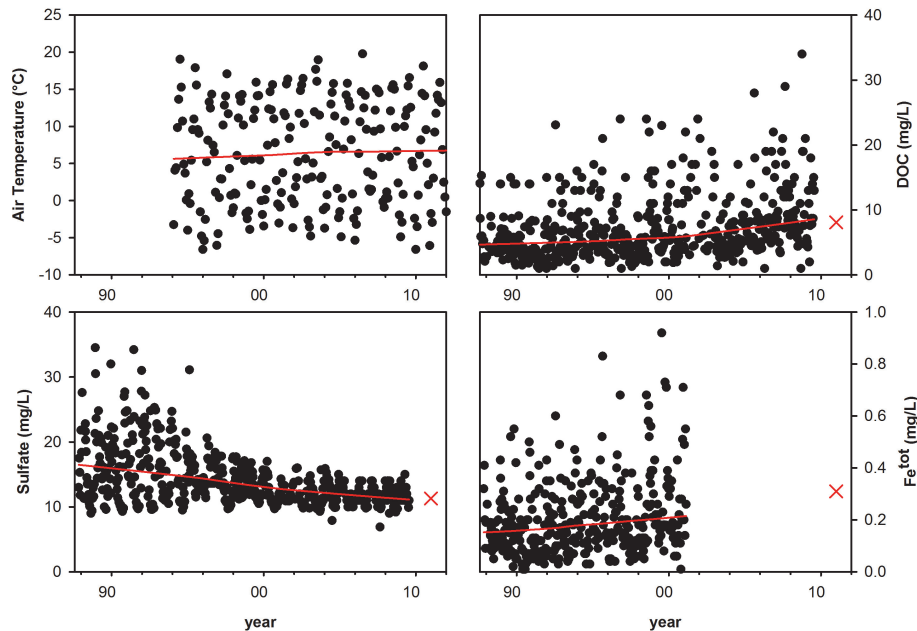Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 3. Correlations (Pearson) among solutes in long term data 1987–2009 (Bavarian Federal Environmental Authority, 2010, unpublished).

	DOC ($mg\,l^{-1}$)	NO_3 ($mg\,l^{-1}$)	SO_4^{2-} ($mg\,l^{-1}$)	Fe^{tot} ($mg\,l^{-1}$)	pH (–)
DOC ($mg\,l^{-1}$)	–	-0.376^*	0.120^*	0.762^*	-0.583^*
NO_3 ($mg\,l^{-1}$)	$N = 521$	–	0.467^*	-0.273^*	-0.219^*
SO_4^{2-} ($mg\,l^{-1}$)	$N = 521$	$N = 533$	–	0.281^*	-0.646^*
Fe^{tot} ($mg\,l^{-1}$)	$N = 330$	$N = 337$	$N = 337$	–	-0.525^*
pH (–)	$N = 526$	$N = 533$	$N = 533$	$N = 341$	–

Levels of significance: $^* p < 0.05$.
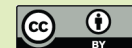
Table 4. Correlations (Pearson) between solutes in pore water. Data for nitrate, sulfate, iron and pH from Knorr et al. (2009), DOC data from K.-H. Knorr 2007 (unpublished).

	DOC $(mg\,l^{-1})$	NO_3 $(mg\,l^{-1})$	SO_4^{2-} $(mg\,l^{-1})$	Fe^{2+} $(mg\,l^{-1})$	pH $(-)$
DOC $(mg\,l^{-1})$	–	-0.110^2	-0.441^2	0.776^2	0.405^2
NO_3 $(mg\,l^{-1})$	$N = 650$	–	0.174^2	-0.095^1	-0.134^2
SO_4^{2-} $(mg\,l^{-1})$	$N = 651$	$N = 679$	–	-0.395^2	-0.538^2
Fe^{2+} $(mg\,l^{-1})$	$N = 615$	$N = 638$	$N = 640$	–	0.303^2
pH $(-)$	$N = 654$	$N = 679$	$N = 680$	$N = 642$	–

Levels of significance: $^1 p < 0.1$, $^2 p < 0.05$, no asterisk: not significant.

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Fig. 1. Air temperature at the study site, and DOC, sulfate, and total iron (Fe^{tot}) concentrations at the catchment outlet. Temperature data was provided by the Department of Micrometeorology (Foken, University of Bayreuth). Solute chemistry (filled dots) is from the long term record of the Bavarian Federal Environmental Authority (unpublished). The red line trend was derived by LOWESS regression; the thin X marks the median of the one year measurement campaign results of this study as a rough estimate for current trend values. Note that the time scale is similar in all graphs (1 August 1987–1 January 2011) to facilitate comparison, although not all data was available for the displayed period. Increase of Temperature from LOWESS: 5.63 °C (1994) to 6.75 °C (2012), DOC (LOWESS): 4.68 (1987) to 8.57 mg l^{-1} (2009), Iron: 0.15 (1987, LOWESS) to 0.30 mg l^{-1} (Median 2010–2011, see Table 1), Sulfate decrease (LOWESS): 16.48 (1987) to 11.14 mg l^{-1} (2009).
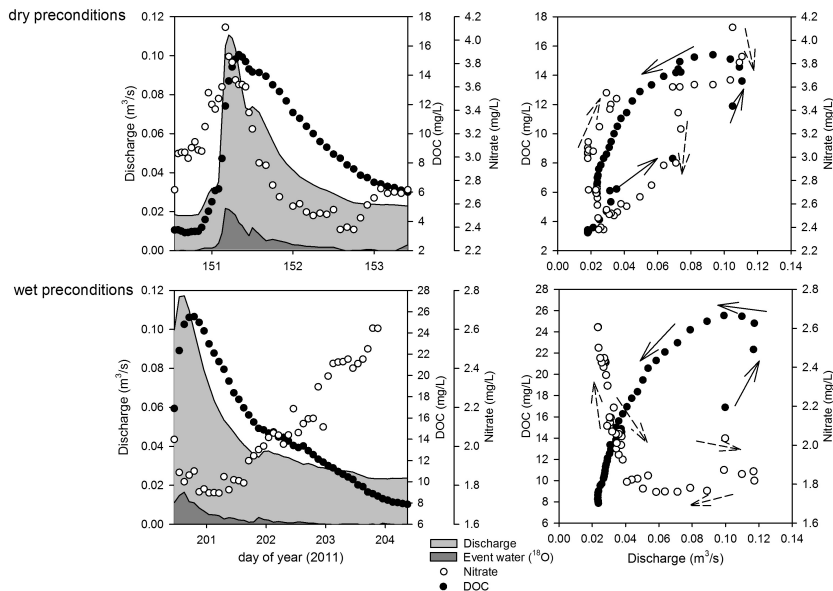
Fig. 2. Hydrographs (light gray) and concentrations of DOC and nitrate for the two selected discharge events under dry antecedent conditions (groundwater table 62 cm below surface at reference well, 31 May 2011, 41 mm of rainfall) and wet preconditions (groundwater table 19 cm below surface at reference well, 20 July 2011, 23 mm of rainfall). Contributions of event water as estimated from a two component mixing model of δ^{18}O from rainwater and pre-event base flow are depicted in dark gray. Note that the initial nitrate peak under dry preconditions coincided with the maximum in event water distribution, while under wet preconditions there was no nitrate flushing and the concentration minimum coincided with the DOC maximum. Furthermore, under dry preconditions concentrations of DOC remained lower, despite a comparable contribution of event water. Corresponding graphs on the right represent the same events as concentration vs. discharge plots (C-Q-plots) to identify the discharge patterns of the respective source terms (Evans and Davies, 1998). Dashed arrows mark the C-Q hysteresis of nitrate (open circles), solid arrows indicate the pattern for DOC (solid dots).

DOC exports mediated by iron reduction/oxidation cycles?

K.-H. Knorr

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

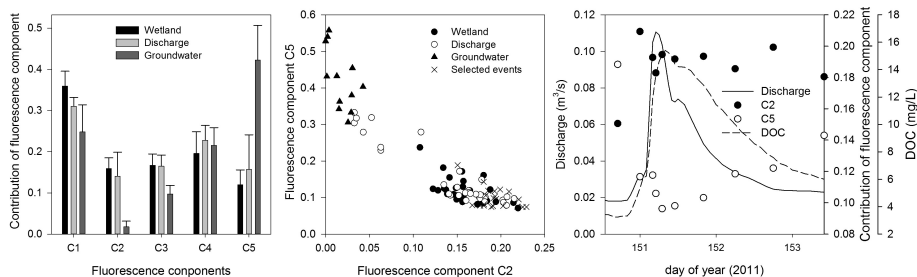Printer-friendly Version

Interactive Discussion

Fig. 3. Left: contributions of the 5 identified fluorescence components (PARAFAC Model after Stedmon and Bro, 2008) to the samples from the compartments "shallow wetland groundwater" (Wetlands) and "deep groundwater" (Groundwater), and in the stream water (Discharge). Middle: separation of the DOC sources by use of the two fluorescence components C2 (characterizing wetland DOC quality) and C5 (characterizing groundwater DOC quality). Those of the discharge samples (open circles) resembling groundwater samples (solid triangles) were all sampled upstream close to a groundwater seepage area with little impact by wetland soils. Samples from the two selected discharge events (see results section) are depicted as X. Right: contribution of fluorescence components C2 and C5 to total DOC fluorescence during the discharge event from 31 May 2011 (dry preconditions), discharge hydrograph, and DOC concentrations over time.
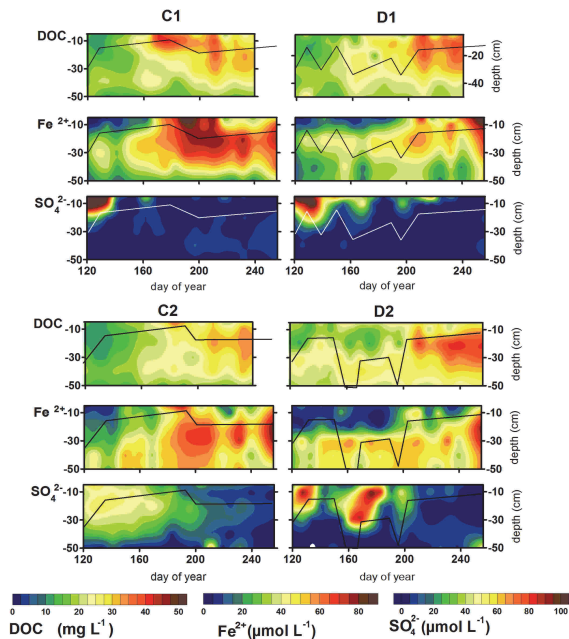
Fig. 4. Porewater DOC, Fe^{2+}, and SO_4^{2-} concentration dynamics (color scale) during water table fluctuations in 4 experimental plots in the Schlöppnerbrunnen Fen in the Lehstenbach catchment over depth (y-axis) and time (x-axis). Experimental details of the in-situ water table manipulation experiments carried out at this site and details about the biogeochemical processes in the plots have been reported elsewhere (Knorr et al., 2009). The color scale of the solutes applies to all 4 plots C1, C2, D1, and D2; the thin solid line represents the approximate water table level in the respective experimental plots. Due to measurement problems, the DOC time series ended earlier compared to the Fe^{2+} and SO_4^{2-} time series in plots C1, D1, and C2; therefore, the size of the graphs has been adjusted to a similar x-axis scaling. Graphs were interpolated from weekly samplings (7 days) over 6 depths (5, 10, 20, 30, 40, and 50 cm) with an inverse distance weight approach, as implemented in Surfer Version 8 (Golden Software, Golden CO, USA).
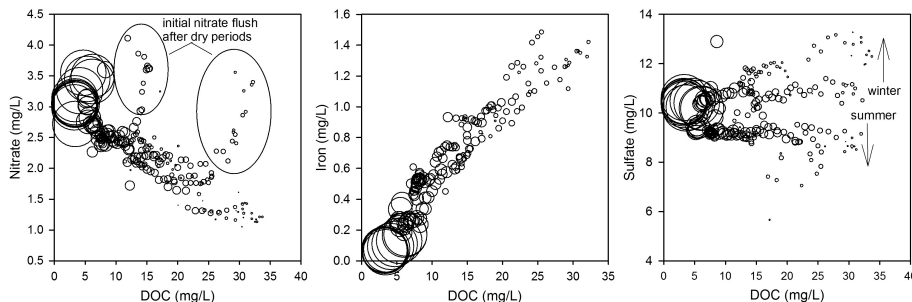
Fig. 5. Plots of DOC concentrations versus nitrate, iron, and sulfate from the one year dataset of this study. The size of the open circles represents the depth of the groundwater table at the specific point of time, with largest circles meaning a groundwater table depth of 62 cm below surface and smallest dots a groundwater table depths of 2 cm below surface at the reference well. Note that deviations from the linear relationship of DOC with nitrate occurred at high rainfall after dry conditions, causing an initial nitrate flush (see Fig. 2, upper graphs). For sulfate, the correlation tended to be negative in summer, while positive in winter.