universität wien

MASTERARBEIT

Titel der Masterarbeit

„Dynamics of dissolved organic matter in brown-water streams and potential impact on global carbon cycling“

verfasst von

Barbara Behounek BSc

angestrebter akademischer Grad

Master of Science (MSc)

Wien, 2013

Studienkennzahl lt. Studienblatt:	A 066 833
Studienrichtung lt. Studienblatt:	Masterstudium Ökologie
Betreut von:	Univ.-Prof. Doz. Mag. Dr. Tom Battin

Table of Contents

Abstract ... **3**
Introduction ... **4**
Inland waters and carbon cycling ... 4
DOM composition and microbial degradation ... 5
Aim of the Study ... 6
Material and methods ... **7**
Sampling sites ... 7
Sampling ... 7
Field parameters ... 9
Bioassays ... 9
DOM Bioavailability ... 10
Cell counts and carbon use efficiency (CUE) ... 10
CO_2 analyses ... 10
DOC analyses ... 11
DOM Optical analyses ... 11
Absorbance analyses ... 11
Fluorescence analyses & PARAFAC modeling ... 11
Analysis & Statistics ... 14
Results ... **16**
Field parameters ... 16
DOM Composition ... 18
Principal component analysis (PCA) of DOM quality ... 19
DOM Dynamics ... 20
Streamwater pCO_2 ... 26
Discussion ... **28**
DOM color and quality ... 28
DOM dynamics during bioassays ... 29
Microbial metabolism and control on carbon fluxes in streams ... 31
Conclusion ... 32
Zusammenfassung ... **33**
Acknowledgements ... **35**
References ... **36**
Curriculum Vitae ... **43**

Abstract

In most inland waters carbon cycling substantially depends on terrestrial dissolved organic matter (DOM). Several studies in the northern hemisphere revealed an increase in DOM export from terrigenous to freshwater systems, causing a "browning" of the receiving waters. Yet, the impact of changes in DOM quantity and quality on ecosystem functioning and global carbon cycling remains uncertain.

Here, I conducted biodegradation experiments in 20 first-order brown-water streams in the Bohemian Massif, Austria, where land use is dominated by coniferous forest and peatland. High-resolution absorbance and fluorescence measurements were used to investigate DOM properties and dynamics. Excitation-emission matrices (EEMs) were modeled by parallel factor analysis (PARAFAC).

The results highlight the dominance of humic-like terrigenous components in the investigated streams. During the assay microbial reworking of DOM caused a shift of DOM chemical properties from an initially terrestrial towards an increasing microbial imprint with freshly produced DOM. The intensity of changes in DOM quality increased along with an initial imprint of terrigenous DOM, emphasizing the role of imported DOM for in-stream metabolism. A higher degree of terrigenous material lowered microbial carbon use efficiency (CUE) and therefore contributed to potential CO_2 evasion in the study streams. These findings may contribute to a better understanding of mechanisms underlying carbon cycling in streams, especially considering observed increases in terrigenous organic carbon import into freshwater systems.

Introduction

Inland waters and carbon cycling

Ongoing climate change impacts freshwater ecosystems and thus makes it essential to understand how these systems function and react with regard to carbon cycling. These ecosystems not only provide humankind with services as e.g. drinking water, but are now also recognized as active components of the global carbon cycle (Battin *et al.*, 2009). About 70% of the earth's surface is covered by water, while inland waters account for only about 1%. This might have caused the initial disregard of the contribution of freshwater systems to global carbon dynamics. Inland waters conventionally have been considered to merely transport organic matter unaltered from the continents to the oceans. Yet, studies revealed the importance of inland waters for carbon transformation and storage processes which occur along the flowpath (Cole *et al.,* 2007; Battin *et al.*, 2008; Tranvik *et al.,* 2009). Annually organic carbon imports to inland waters were estimated to be 1.9 PgC yr^{-1} (Cole *et al.*, 2007), later even revised to 2.9 PgC yr^{-1} (Tranvik *et al.*, 2009). The export rate from inland waters to the ocean counts approximately 0.9 Pg (Cole *et al.*, 2007; Tranvik *et al.,* 2009). The residual of the imported carbon is either lost via burial in sediments (0.6 Pg) or via CO_2 gas evasion (1.4 Pg) (Tranvik *et al.*, 2009). The importance of inland waters for carbon cycling on a global scale becomes evident when compared to anthropogenic fossil fuel emissions of 5.3 Pg yr^{-1} (Chapin *et al.*, 2002) while changes in land use generate a flux of 1.7 Pg C yr^{-1} to the atmosphere (Chapin *et al.*, 2002).

Building evidence suggests elevated fluxes of terrigenous DOM to inland waters in North America and North and Central Europe (Evans *et al.*, 2005; Monteith *et al.*, 2007; Hansson *et al.*, 2012; Regnier *et al.*, 2013). Evans *et al.* (2005) report an increase in DOC concentration by 91% in UK upland waters over the past 15 years. Regnier *et al.* (2013) even estimate an increase as large as ~1.0Pg C yr^{-1} since pre-industrial times, primarily due to rising carbon exports from soils. This phenomenon impacts especially streams draining peatlands, which store over a third of the world's total soil carbon pool (Gorham, 1991) and are currently thought to act as a net sink in the global carbon cycle (Dinsmore *et al.*, 2010). Several hypothesis have been proposed for this increased export from terrestrial sources to freshwater systems, including changes in air temperature (Christ & David, 1996; Andersson *et al.*, 2000; Fenner *et al.*, 2007) augmented atmospheric CO_2 concentration (Freeman *et al.*, 2004), land use changes (Worrall, 2003;

Freeman *et al.*, 2001) and hydrological changes (Tranvik & Jansson, 2002; Berggren, 2009). Yet, the underlying mechanisms and the major contributors leading to the observed changes in carbon fluxes are not well understood.

Increased DOM export from the terrestrial environment leads to 'brownification' of inland waters, as most terrigenous DOM is optically active and absorbs light in the ultraviolet and in the visible range. Besides an increase in DOC concentration brownification may impact the transport of metals via complexation reactions or change the light regime, thereby affecting the distribution of primary producers in headwaters (Evans *et al.*, 2005). Additionally the chemical composition of bulk DOM may be shifted towards terrigenous and humic compounds typically considered recalcitrant to the microbial metabolism (Schmidt *et al.*, 2011).

DOM composition and microbial degradation

In order to gain better understanding of carbon cycling in fluvial ecosystems, it is imperative to understand how dissolved organic carbon (DOC) source and characteristics influence microbial metabolism. Heterotrophic microbial communities (including bacteria, archaea and protists) are present in streams on submerged surfaces (e.g. rocks, leaves), interstitial waters (i.e. benthic sediment) and the free water column. They have developed different live strategies e.g. attached to surfaces, as biofilms or as free floating cells in the water column to accomplish uptake and transformation processes of organic matter. Elongated residence time of DOM in storage and retention zones of streams and rivers increases the possibility of microbial processing (Battin *et al.*, 2008).

Microbial degradation of organic matter is strongly linked to its quality (del Giorgio, 1998). It is composed of a complex mixture of compounds and operationally defined by any organic compound <0.45µm. It contains low molecular weight (e.g. carbohydrates, amino acids) and high molecular weight substances (e.g. humic and fulvic acids) (Evans *et al.*, 2005). Humic substances mainly derive from allochthonous sources (i.e. terrestrial vegetation) (Allan & Castillo, 2007) and dominate the DOM pool in streams (Wallis & Ladd, 1983; Volk *et al.*, 1997; Battin *et al.*, 2008). Allochthonous DOM, containing humic and fulvic substances, is thought to be of recalcitrant nature (Tranvik, 1998) due to its long storage time in soils, with turnover times ranging from years to centuries (Trumbore, 1997) before its export to surrounding headwaters. Autochthonously

produced DOM, on the other hand, derives from microbial and algal biomass in aquatic systems, is of typically lower molecular weight and highly biodegradable. (Azam & Cho, 1987). However, Berggren *et al.* (2010) showed that also low molecular weight compounds of terrigenous origin were readily degraded in headwater streams. The remaining humic substances in the DOM pool may comprise to microbial processing to a low but constant degree, which is of particular importance at absence of other sources (Guillemette & del Giorgio, 2011).

The interaction of DOM quality and microbial degradation processes thus play a major role in fluvial ecosystems highlighting them as reactive systems in the global carbon cycle (Battin *et al.*, 2009). Hence, altered DOM quantity and quality may affect ecosystem processes and ultimately carbon dioxide emissions. Yet, possible consequences for ecosystem respiration and carbon cycling in fluvial ecosystems remain unclear.

Aim of the Study

On order to illuminate the effect of DOM quantity and quality on microbial degradation processes I conducted 20-day incubation experiments using water samples from 20 spatially independent catchments covered with coniferous forest and peatland in the Bohemian Massif, Austria. Streams have been chosen along a brown-water-gradient covering a range of dissolved organic carbon (DOC) concentrations. Absorbance and fluorescence measurements were used in order to gain information about DOM origin and composition. Using the optical information DOM quality and its temporal dynamics during the bioassay was monitored and related to DOM biodegradability and microbial metabolism.

The aim of this thesis was to (1) define the main contributors to color in the brown-water streams, (2) analyze DOM origin of streams differing in color, and (3) investigate how differences in DOM quantity and quality affect microbial degradation processes and in-stream metabolism.

Material and methods

Sampling sites

I studied DOC properties and bioavailability in 20 headwater streams in the Bohemian Massif (Austria) in October 2013. All streams were of first order and drained catchments covered with peatland and coniferous forest. Individual streams were selected along a gradient of color to evaluate the effect of browning on DOC composition and microbial metabolism. As crystalline rocks (gneiss and granite) form the bed-rock material of this region ionic concentrations are typically low, accompanied by low conductivity and low pH values (Table 3). Average precipitation among the study sites ranges from approx. 670 to 940 mm $year^{-1}$, mean annual temperature ranges from 5.4 to 6.9°C. The study sites were situated between 48°18' to 48°35' in latitude, from 14° 41' to 15°06' in longitude and approx. 670m to 980m altitude.

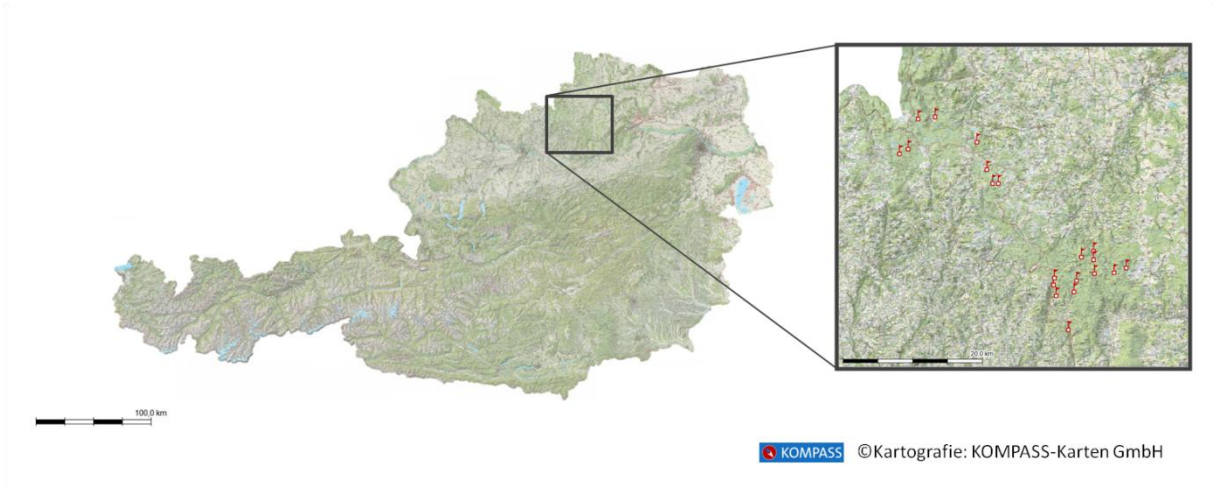


Figure 1 Map of sampling site locations in the Bohemian Massive, Austria.

Sampling

Samples for DOC and optical measurements were filtered on site (double layer of Whatman GF/F-filters, pre-combusted at 450°C for 4h) and stored in 30-ml glass vials (soaked with 0.1N HCl, rinsed with MilliQ water and combusted at 450°C for 4h) sealed with Teflon coated septa (soaked with 10% $Na_2S_2O_8$ solution at 60°C for 1h and rinsed thoroughly with MilliQ water).



Figure 2 Pictures from 5 selected 1st order streams. A range of different stream-water color-intensities has been chosen. Stream C (top left) represents the lightest, stream N (top right) the darkest one.

Triplicate water samples for the determination of streamwater CO_2 concentration were collected by submersing 50-ml serum vials (pre-treated with NaN_3, 0.02 % final concentration) into the streamwater, allowing them to overflow before closing them under water using a 1cm hick gas-tight rubber stopper. While closing the vials the stopper was transfixed by a needle to remove excess water. Finally the vials were crimped with aluminum-caps. Triplicate atmospheric air samples were collected with a gas-tight glass syringe, injected into pre-evacuated 7-ml headspace vials and sealed with silicon to prevent gas exchange.

Samples for bioassays were collected in polypropylene copolymer bottles (soaked with 0,1N HCl, rinsed with MilliQ-water (Millipore, Billerica, U.S.A.)) and filtered through a double layer of Whatman GF/F filters (precombusted, 450°C for 4h) within 12 hours. Samples for inocula (unfiltered streamwater) were collected in 1-L Schott© bottles (soaked with 0.1N HCl, rinsed with MilliQ water and combusted at 450°C for 4h).

All samples were kept cool and in the dark during transport until storage in the laboratory (4°C, in the dark).

Field parameters

Electrical conductivity, oxygen concentration and water temperature were measured using WTW probes (Cond340i, OxiCal-SL, Weilheim - Germany). PH was measured using a WTW pH320 probe, connected to a glass-electrode (Methrom) since its adequacy for measurements in waters with low ionic concentrations. All probes were calibrated regularly. Nutrient concentrations ($N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, $P\text{-}PO_4$), in the streamwater were determined using Continuous Flow Analysis (Alliance instruments). Detection limits for nutrient analyses were 4 µg L^{-1} for $N\text{-}NH_4$, 100 µg L^{-1} for $N\text{-}NO_3$ and 2 µg L^{-1} for $P\text{-}PO_4$. Additionally I measured ion concentrations ($Fe^{2+}/^{3+}$, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}) using ion chromatography (761 Compact IC, Methrom).

Bioassays

To investigate changes in DOM composition and microbial metabolism along the brownification gradient we conducted triplicate 20-day bioassays in 250-ml Schott© bottles (soaked with 0.1 N HCl, rinsed thoroughly with MilliQ water and combusted for 4h at 450°C) in the dark at 18°C. Briefly, 180ml sterile filtered streamwater was filled in bottles and inoculated with 10% of unfiltered streamwater from the same site, leaving 38% headspace. Bottles were transferred in to a water bath (18°C), capped loosely with aluminum foil for 6 hours to allow for equilibration, but avoid contamination and then closed gas-tight with Teflon coated septa (soaked with 10% $Na_2S_2O_8$ solution at 60°C for 1h and rinsed thoroughly with MilliQ water) and screw caps.

Samples for CO_2, DOC, optical measurements, nutrients and cell counts were obtained periodically (day 1, 3, 6, 10, 15 and 20) and stored in the dark at 4°C until further processing. Samples for respiration (i.e. 10ml headspace of each bottle) were collected using a gas-tight syringe equipped with a valve to avoid gas exchange during transfer into pre-evacuated 7-ml headspace vials (fitted with rubber stoppers and aluminum caps). Vials were immediately sealed with silicon to prevent gas exchange. Samples for DOC and optical measurements were filtered through a double layer of Whatman GF/F-filters, pre-combusted at 450°C for 4h and stored in 30-ml glass vials (soaked with 0.1N HCl, rinsed with MilliQ water and combusted at 450°C for 4h) and sealed with Teflon coated septa (soaked with 10% $Na_2S_2O_8$ solution at 60°C for 1h and rinsed thoroughly with MilliQ water). Samples for cell counting were collected into 1.5-ml Eppendorf©

tubes and preserved in formaldehyde (2.5% final concentration). Samples for nutrient analysis were filtered as described above and stored in 15-ml BD Falcon© tubes.

DOM Bioavailability

Bioavailable DOC (BDOC) was calculated as the decrease in DOC concentration during the bioassays over the incubation period.

$$\mathrm{BDOC} = \mathrm{DOC_{st}} - \mathrm{DOC_{end}}$$

where DOC_{st} and DOC_{end} are the DOC-concentrations at the start and the end of the bioassay, respectively.

Cell counts and carbon use efficiency (CUE)

Cell samples from bioassays were stained using the nucleic acid stain Sytox Green (Invitrogen) and filtered onto black polycarbonate filters (Millipore). 30 pictures per sample were taken using AxioVision (4.6.1.0). Cell width, length and abundance of at least 200 cells were measured by image analysis (ImageJ 1.410). Therefore a size threshold for cell identification was set via approximation to manually measured cell sizes. Exclusion of overlapping cells and particles with an area smaller than 0.1 μm^2 was conducted. Calculation of cell volumes was performed according to the formula $V = (w^2 * \pi/4) * (l - w) + (\pi * w^3/6)$ where V corresponds to the cell volume (μm^3), l is the cell length (µm), w the cell width (µm), respectively. The carbon content of cells (fg) was calculated with the allometric relationship $C = 120 * V^{0.72}$ (Norland, 1993). Microbial biomass is the product of average cell carbon content and cell numbers for each replicate.

The carbon use efficiency (CUE) was calculated as

$$\mathrm{CUE} = \frac{\mathrm{Prod}}{\mathrm{Prod} + \mathrm{Resp}}$$

where Prod is the increase in microbial biomass (mg C l^{-1}) just until the stationary phase (i.e. day 15) and Resp is the increase in CO_2 concentration (mg C l^{-1}) over the same period of time.

CO_2 analyses

Streamwater CO_2 samples and headspace samples from the bioassays were analyzed using an Agilent Technologies 7890A gas chromatograph with a headspace autosampler.

In liquid samples a headspace of known volume was created using N_2. Samples equilibrated by shaking for 45min and kept at constant temperatures during measurement.

The degree of CO_2 oversaturation (ΔCO_2) was calculated as the difference of the CO_2 concentration in the stream in mol l^{-1} to the concentration expected from the atmospheric equilibrium.

DOC analyses

DOC concentrations from streamwater and bioassay-samples were measured using a TOC analyzer (Sievers 5310C) operating with an inorganic carbon removal unit. The analyzer automatically acidifies the samples before injection.

DOM Optical analyses

DOM absorbance and fluorescence were measured simultaneously using an Aqualog© (Horriba Scientific). All measurements were performed using a 1cm quartz-cuvette. Scan speed was set to 12,000 nm min^{-1} with a response time of 0.01 s.

Absorbance analyses

CDOM absorbs visible and UV light with the strongest absorbance in the short wave region, decreasing exponentially (Twardowski *et al.*, 2004). It is mainly formed by humic substances, initially deriving from terrigenous vascular plants (Boyle *et al.*, 2009) and, regarding natural waters, represents one of the major light absorbing components. Absorbance measurements were used to analyze this colored fraction of DOM. Absorbance spectra were collected from 240 to 600nm with 5nm increments. Scans were corrected for the blank (MilliQ water). Absorption coefficients were calculated according to the equation

$$a_\lambda = 2.303 * \frac{A_\lambda}{r}$$

where A is the absorbance at wavelength λ and r is the cuvette path length (m) (Green and Blough, 1994).

Fluorescence analyses & PARAFAC modeling

Fluorescence describes the spontaneous emission of light by a certain material after excitation: an electron gets excited from the ground state to a higher level and eventually fluoresces by returning to the ground state. The emitted light is of lower energy, i.e. lower wavelength than the excitation wavelength, referred to as Stokes' shift.

Table 1 Absorbance Indices with calculation scheme and description.

Index name	Calculation	Description
a_{440}	a_{440} = abs. coeff. at 440nm	indicator of colored DOM (CDOM) (Cuthbert & del Giorgio, 1992)
SA_{440}	SA_{440} = abs. coeff. at 365nm	a DOC-standardized index for CDOM
Specific UV absorbance 254 ($SUVA_{254}$)	$SUVA_{254} = \frac{\text{abs. coeff. at 254nm}}{\text{DOC concentraiton [mg C L}^{-1}\text{]}}$	strong correlation with DOM aromaticity (Weishaar *et al.*,2003)
a_{255}/a_{365}	$a_{255}/a_{365} = \frac{\text{abs. coeff. at 254nm}}{\text{abs. coeff. at 365nm}}$	negatively correlated to average molecular weight of DOC (Dehaan, 1993; Dahlén *et al.*, 1996)
Slope ratio (S_R)	$S_R = \frac{S_{275-285}}{S_{350-400}}$ $S_{275\text{-}285}$, $S_{350\text{-}400}$: Slope of linearized abs. coeff. for 275-285nm and 350-400nm, respectively	negatively corrrelated to DOM molecular weight and photochemically induced shifts in molecular weight (Helms *et al.*, 2008)

Natural DOM comprises a complex mixture of substances, such as humic substances, carbohydrates, proteins and lipids. Some compounds contained in this DOM pool emit fluorescence when exited at specific wavelengths (Lakowicz, 1999). Thus, plotting the fluorescence of excitation wavelengths against emission wavelengths results in excitation-emission matrices (EEMs) that are indicative of the DOM composition (Stedmon *et al.*, 2003). For example, emission spectra shift towards longer wavelengths with increasing complexity of the molecule (Stedmon *et al.*, 2003). In contrast protein-like compounds are characterized by emission spectra in comparatively shorter wavelength regions (Coble, 1996).

Excitation emission matrices (EEMs) were recorded from 250 to 450nm excitation wavelength (5-nm increments) and 250 to 550nm emission wavelength (1.6-nm increments). All EEMs were corrected for the water Raman scatter, the Rayleigh-Tyndall effect and the inner filter effect (IFE).

The water Raman scatter is the visible effect of the vibration of the molecular O-H bonds of water caused by light and is visible as a line at excitation wavelengths between 260 and 350nm and emission wavelengths 280-400nm. The Rayleigh-Tyndall effect occurs as excitation energy is reflected off the cuvette walls. It is appears as a line at emission wavelength = emission wavelength and at emission wavelength = 2 x excitation wavelength in the visualization of the EEM. Both effects were largely removed by the

subtraction of fresh MilliQ (Millipore) from all EEMs. The remaining scatters were substituted by zeros and then interpolated using the statistical software R®.

High DOC concentrations increase absorbance, thereby causing a disproportional decrease in fluorescence known as IFE. This was corrected for using the corresponding absorbance measurements and applying the equation

$$F_{ideal} = F_{obs}^{10^{\frac{Abs_{Ex}+Abs_{Em}}{2}}}$$

to each excitation-emission wavelength coordinate of the EEM. F_{ideal} is ideal fluorescence-signal expected in the absence of the IFE, F_{obs} is the observed fluorescence signal and Abs_{Ex} and Abs_{Em} are the measured absorbance values at the respective excitation and emission wavelength-coordinates.

Fluorescent components were modeled from EEMs by parallel factor analysis (PARAFAC) using Matlab® (7.11.0) and the DOMFluor Toolbox (1.7) (Stedmon & Bro, 2008).

The parallel factor analysis (PARAFAC) modeling technique facilitates the separation of individual components in the fluorescence signature of the EEMs. The data are decomposed into trilinear terms and a residual array using the following equation:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{if} c_{kf} + \varepsilon_{ijk}$$

x_{ijk} represents the fluorescence intensity for the *i*th sample at emission wavelength *j* and excitation wavelength *k*. The a_{if} term is directly proportional to the concentration (in moles) of the *f*th analyte in the sample *i*. bif is a scaled estimate of the emission spectra at wavelengths *j* for the *f*th analyte and ckf is an estimate proportional to the excitation spectra at wavelengths k for the *f*th analyte. (Cory & Kaplan, 2012; Stedmon *et al.,* 2003, 2007) F is the number of components (factors) in the model and ε_{ijk} is the residual matrix thus representing residual signals that cannot be explained by the model.

The PARAFAC was conducted in Matlab (version 7.11.0, MathWorks) using the DOMFluor Toolbox (1.7), containing the N-Way toolbox v.3.1 and additional functions providing the PARAFAC procedure to work on fluorescence data (Andersen & Bro, 2003). On the basis of 420 EEMs fluorescent components were modeled following the procedures of Stedmon and Bro (2008). During this process the data are randomly separated into two parts, the SplitHalfValidation-function compares the loadings of

excitation and emission using Tucker Congruence Coefficients according to Lorenzo-Seva & ten Berge (2006). The half-validation was done for up to 10 components, finally validated for three (see Table 4, Figure 2).

To further characterize DOM composition we computed the fluorescence index (FI, McKnight 2001), the humificaiton index (HIX, Zsolnay *et al.*, 1999), the β/α-index (Wilson and Xenopoulos, 2009) from EEMs (Tab. 2). These are calculated by comparing the fluorescence maxima of different excitation and emission wavelength (-regions).

Table 2 Fluorescence Indices Em = emission wavelength (nm), ex = excitation wavelength (nm). All indices are calculated as ratios of fluorescence intensities of different emission wavelengths and at the same excitation wavelength.

Index name	Calculation	Description
Fluorescence index (FI)	$FI = \frac{em450}{em500}$ at ex of 370	The FI index indicates DOM source. A value of 1.9 indicates microbially derived, a value of 1.4 terrestrially derived compounds (McKnight, 2001).
Humification index (HIX)	$HIX = \frac{em435\ to\ 480}{em300\ to\ 445}$ at ex of 254	This index is representative of humic substance content or extent of humification. An increase in humification leads to a shift of the emission radiation towards longer wavelengths (caused by lower H:C-ratios) Higher values indicate an increasing degree of humification. (Zsolnay *et al.*, 1999; Ohno, 2002)
Beta over alpha (β/α)	$\frac{\beta}{\alpha} = \frac{em\ 380}{em_{max}\ between\ 420\ and\ 436}$ at ex of 310	ß and α indicate more freshly produced or more decomposed DOM, respectively. β/α increases with increasing autochthonous carbon production (Parlanti *et al.*, 2000; Wilson and Xenopoulos, 2009).

Analysis & Statistics

In order to test for significant changes of DOM fluorescence and absorbance indices and fluorescent components (C1, C2 and C3) over time (i.e. begin and end of the bioassay) a Wilcoxon-test for paired samples was performed.

A principal component analysis (PCA) was conducted based on fluorescence- and absorbance-measurements off all 20 streams. Indices either represent ratios or were normalized for DOC-concentration. The PCA was complemented by separate canonical correlation analyses (using the same dataset of optical measurements) in order to identify the linear set of optical measures (i.e. the first canonical axis) most strongly related to the constraints (i.e. a_{440}, %BDOC or CUE). Canonical loadings (i.e. correlations

between the one canonical variate and the respective variables) indicate the strength and the direction of the relationship of the individual DOM optical properties to the constraint. The significance of each canonical correlation was computed by permutation and the strength of the relationship between the canonical axis and the constraint was given as the canonical correlation coefficient.

All statistics were performed in RStudio® (Version 9.97.312 2009-2012 RStudio, Inc.). Graphs were created in RStudio® (Version 9.97.312 2009-2012 RStudio, Inc.) or SigmaPlot® (Version 10.0, Systat Software, 2006). The Austrian map displaying all sampling points was created using KOMASS Digital Map (Version 2.5.0.0, ©KOMPASS Karten GmbH (Innsbruck)).

Results

Field parameters

Water temperature, conductivity, pH, oxygen-, DOC-, and nutrient concentrations of the 20 sampled streams are shown in Table 3. Abiotic factors were comparable among study sites due to similar bedrock material and climate. Average precipitation among the study sites ranges from 670 to 940 mm year^{-1}, average temperature ranges from 5.4 to 6.9°C. Latitude ranged from 48°18' to 48°35' in, longitude from 14° 41' to 15°06' and altitude from approx. 670m to 980m. The DOC concentration of the 20 streams varied across the brownification gradient, ranging from 1.4 to 25.3 mg C L^{-1}. Color (a_{440}) increased significantly with DOC concentration (linear regression, p<0.001, n=20) (Fig. 1).

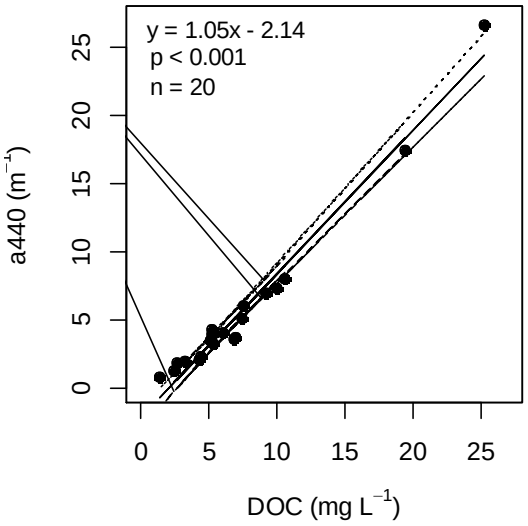


Figure 1 Relationship of DOC concentration and color (a440) of the 20 streams

Table 3 Abiotic parameters, DOC-concentration and nutrient concentrations of the 20 streams

Stream	Temperature (°C)	Conductivity (µS cm^{-1})	pH	Oxygen concentration (mg L^{-1})	DOC concentration (mg L^{-1})	NH_4^+ (mol L^{-1})	NO_2^- (mo l L^{-1})	NO_3^- (mol L^{-1})	PO_4^{3-} (mol L^{-1})
A	7.7	37.6	6.69	13.5	9.21	8.9	2.4	287.7	19.3
B	7.4	49.2	6.92	15.5	5.25	3.9	4.2	777.0	15.0
C	8.8	81.5	7.30	11.4	1.41	1.0	0.8	1417.4	14.1
D	8.4	44.7	6.81	13.9	7.63	9.4	2.6	448.2	17.5
E	8.7	71.4	7.00	15.2	2.66	1.0	0.1	675.5	6.5
F	7.8	56.1	7.02	15.4	5.31	3.0	2.4	538.0	6.7
G	6.3	59.6	6.83	12.9	5.16	4.7	1.5	511.0	17.2
H	7.9	43.0	6.36	11.3	19.49	1.9	1.6	165.3	11.7
I	7.4	51.3	6.84	10.7	6.85	1.0	0.9	712.3	8.9
J	6.3	72.4	7.14	13.4	10.04	13.6	9.1	42.1	65.5
K	6.8	67.5	6.77	11.1	3.28	9.2	2.9	694.2	15.6
L	6.9	59.4	6.90	14.2	10.60	6.6	3.8	591.1	23.4
M	5.6	53.0	6.88	11.1	6.07	3.1	3.4	531.7	11.8
N	6.1	55.4	6.53	8.9	25.31	251.8	17.7	274.3	93.8
O	6.7	76.3	7.14	13.7	7.48	9.0	1.4	372.6	31.5
P	7.1	122.5	7.16	16.0	4.33	6.0	0.8	643.9	10.5
Q	5.6	110.7	7.26	13.6	2.48	0.3	1.0	594.2	11.9
R	5.8	62.2	6.75	11.8	4.50	3.6	0.7	148.2	6.1
S	7.6	64.4	6.93	10.8	7.02	6.3	1.4	235.2	11.6
T	7.0	131.6	6.81	16.7	5.42	2.9	1.8	281.2	9.0

DOM Composition

Based on 420 EEMs the PARAFAC procedure (Stedmon & Bro, 2008) modeled and validated 3 components (Fig. 2 and Tab. 4). All of them were assigned as humic-like. Component 1 (C1) and Component 2 (C2) are likely of terrestrial origin while Component 3 (C3) indicates autochthonously produced material (Stedmon & Markager, 2005; Cory & Kaplan, 2012). Fluorescence peak values and their corresponding components described in other studies are listed in Table 4. C1 contributed 49.71 ± 3.26 % to total fluorescence, C2 and C3 22.84 ± 1.92 % and 27.46 ± 4.33 %, respectively.

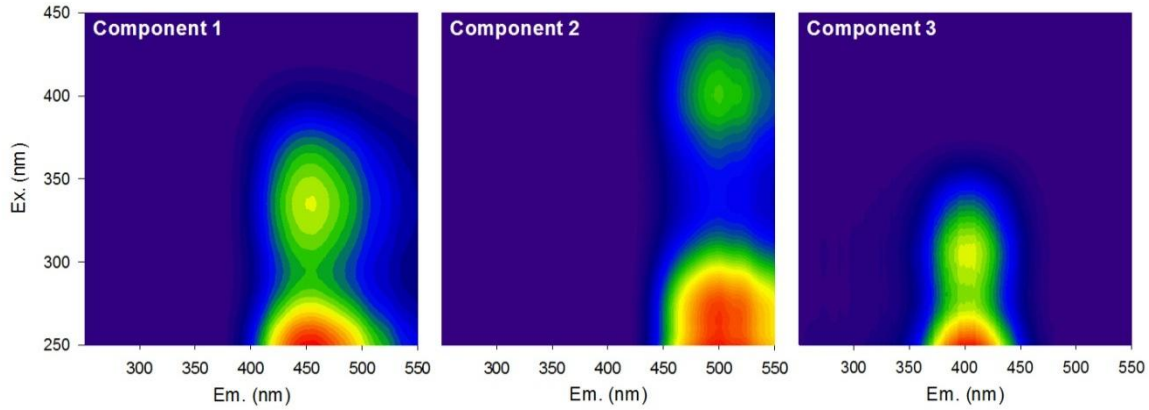


Figure 2 Excitation-emission matrices (EEMs) of the three validated components derived from the PARAFAC-procedure

Table 4 Fluorescence maxima of the three components modeled by PARAFAC. Secondary maxima are shown in brackets. Corresponding components and descriptions from previous studies are listed for comparison

Component	Excitation maxima (nm)	Emission maxima (nm)	Components identified from previous studies	Description
1	<250 (335)	455	Component C (Cory & Kaplan, 2012) Component 1 (Stedmon & Markager, 2005)	Humic-like, terrestrial
2	<250 (400)	500	Component A (Cory & Kaplan, 2012) Component 2 (Stedmon & Markager, 2005)	Humic-like, terrestrial
3	<250 (305)	408	Component M (Cory & Kaplan, 2012) Component 3 (Stedmon & Markager, 2005)	Humic-like, associated with new, biological production of humic substances from autochthonous sources

Principal component analysis (PCA) of DOM quality

The PCA showed a gradient of DOM quality across the streams ranging from mainly terrigenous to an autochthonously produced DOM (Fig. 3). The humic-like components C1 and C2, the extent of humification (HIX), color intensity (SA_{440}) and higher aromaticity ($SUVA_{254}$) suggest a terrigenous imprint of DOM. In contrast, the humic-like component C3 and the freshness index (β/α) indicate recently produced DOM and autochthonous production (FI). This DOM pool is further characterized by low apparent molecular weight (S_R) and low molecular weight of dissolved humic substances (a_{255}/a_{365}).

SA_{440} relates to $SUVA_{254}$, as indicated by the PCA. High FI-values are associated with a_{254}/a_{365}, where C3 correlates with β/α. S_R is positively related to a_{255}/a_{365} ($p=0.024$, $n=20$), β/α ($p=0.024$), and negatively related to HIX ($p=0.044$), $SUVA_{254}$ ($p=0.014$) and SA_{440} ($p=0.007$).

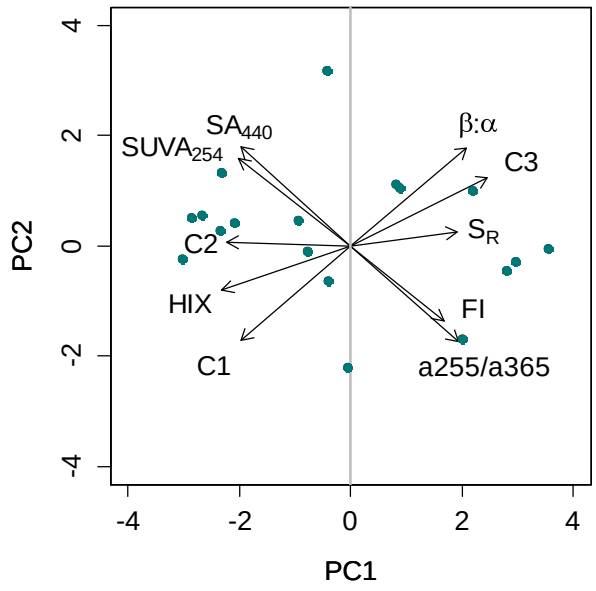


Figure 3 Principal component analysis based on indices resulting from absorbance- and fluorescence-measurements. C1, C2 and C3 are the respective fluorescent components. Absorption at 440nm ($a440$) indicates color, specifiv UV-absorcane at 440nm and 254nm (SA_{440}, $SUVA_{254}$) represent DOC-standardized indices for coloration and aromaticity, respectively. Apparent molecular weight is indicated by the slope ratio (S_R) and a_{255}/a_{365} (high values indicate low molecular weight), humification index (HIX) serves as a proxy for the degreee of humification, fluorescence index (FI) for DOM origin and freshness index (β/α) for recently produced DOM.

DOM Dynamics

DOM quality changed over the incubation period of the bioassays. The relative fluorescence of the components C1 and C2 decreased, while C3 increased (Wilcoxon-test, each $p<0.001$, n=20, Fig. 4). The percentage of C1 and C2 was higher in streams with rather terrigenous DOM compared to streams with a higher proportion of autochthonous DOM. Vice versa the percentage of C3 was higher in autochthonous than in terrigenous DOM.

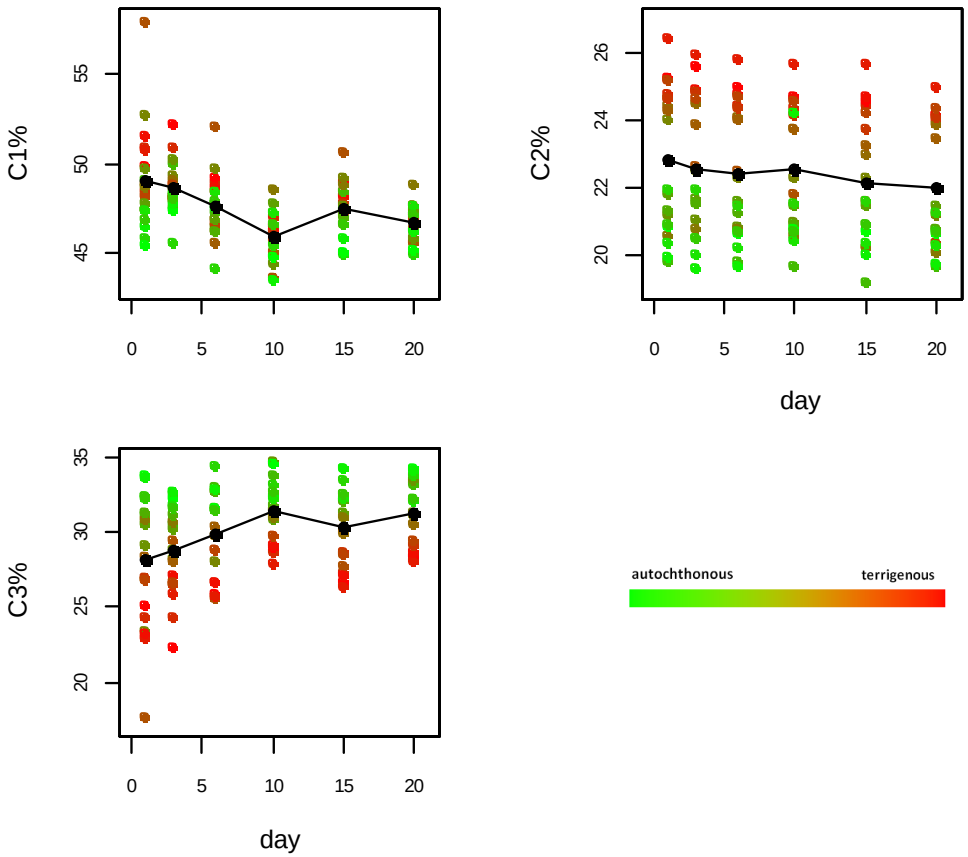


Figure 4 The 4 Temporal dynamic of the three humic-like components (C1, C2 and C3, in percent) over the 20 day incubation period of the bioassays. Color represents DOM quality as derived from the PCA. Green indicates autochthonous, red terrigenous derived DOM. Colored dots represent single streams, black dots the average of the 20 streams at each time point (n=3).

All components displayed a high variability in fluorescence over the incubation period. C1% decreased from day 1 to day 10 of the assay, increased again until day 15, to finally decrease until day 20, C3% showed an inverse pattern. However, C2% decreased continuously. Averaging the values of all streams, most of the optical indices do not follow a specific temporal pattern. Yet, HIX reveals a synchronal pattern with C1%, where the temporal behavior of β/α resembles C3%.

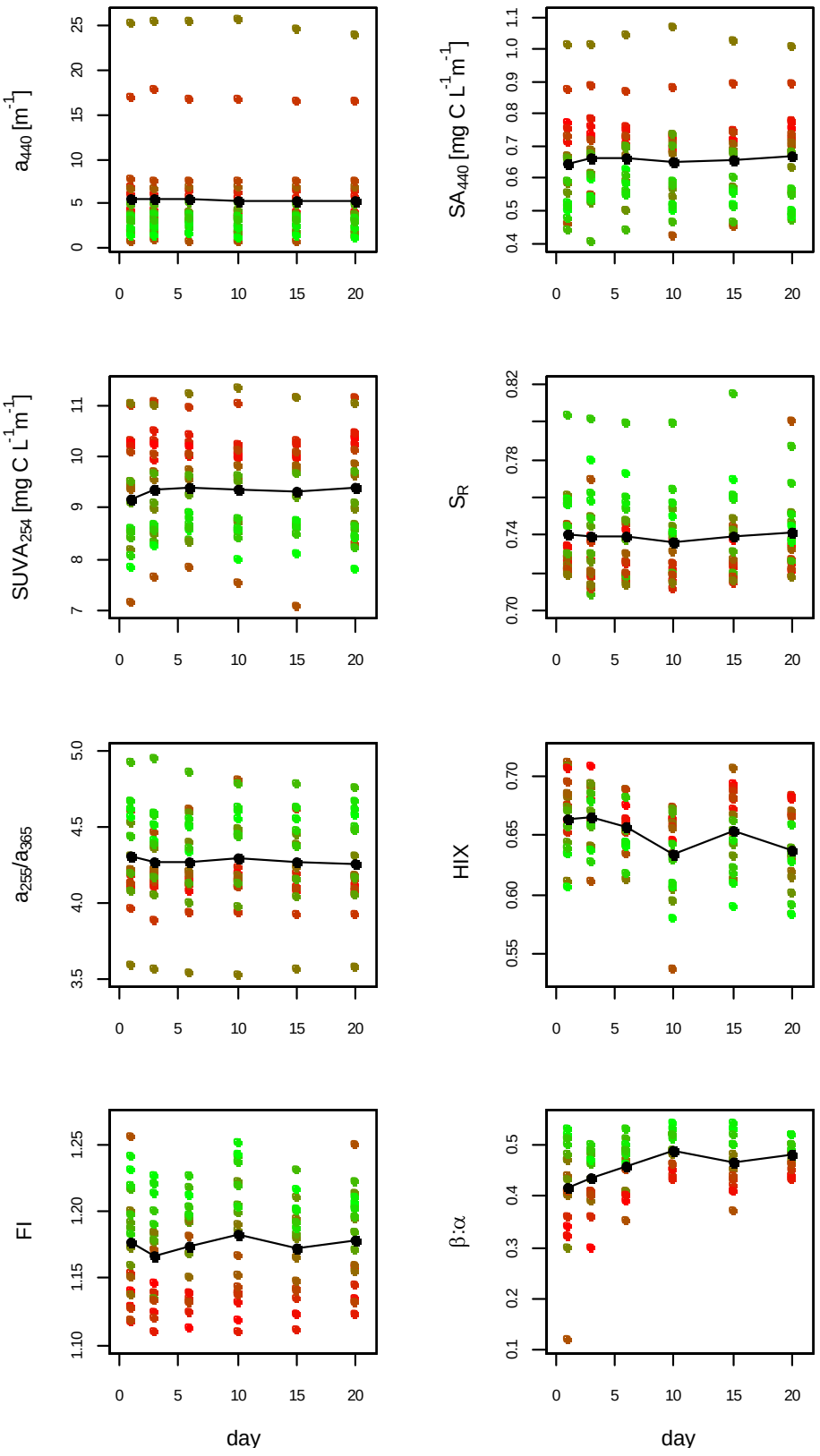


Figure 5: Temporal dynamic of absorbance and fluorescence-derived indices during the bioassays (n=3). The black line marks the mean of all streams per time point. Color indicates DOM quality as derived from the PCA (green=autochthonous, red=terrigenous). Absorbance at 440nm (***a*440)** indicates color, specific UV-absorbance at 440nm (**SA_{440})** and 254nm (**$SUVA_{254}$)** represent DOC-standardized inices for coloration and aromaticity, respectively. Slope ratio (**S_R)** and **a_{255}/a_{365}** indicate molecular weight (high values indicate low molecular weight), the humification index (**HIX)** the degreee humification, fluorescence index (**FI**) DOM origin and the freshness index (**β:α)** represents recently produced DOM.

Overall, the percentage of C1 and C2 fluorescence decreased significantly between the start and the end of the bioassay (both $p<0.001$, $n=20$) (Fig. 6). At the same time, the percentage of C3 significantly increased ($p<0.001$, $n=20$).

Color (a_{440}) significantly decreased ($p=0.048$, $n=20$) while SA_{440} did not change over time ($p=0.105$, $n=20$) (Fig. 6). Aromaticity ($SUVA_{254}$) and β/α increased ($p=0.015$ and $p<0.001$, respectively, $n=20$). Humification index (HIX) and a_{255}/a_{365} decreased ($p=0.015$, $p=0.003$, and $p=0.001$, $n=20$, respectively). No significant change over time was detected for S_R and FI values ($p=0.452$ and $p=0.701$, $n=20$, respectively).

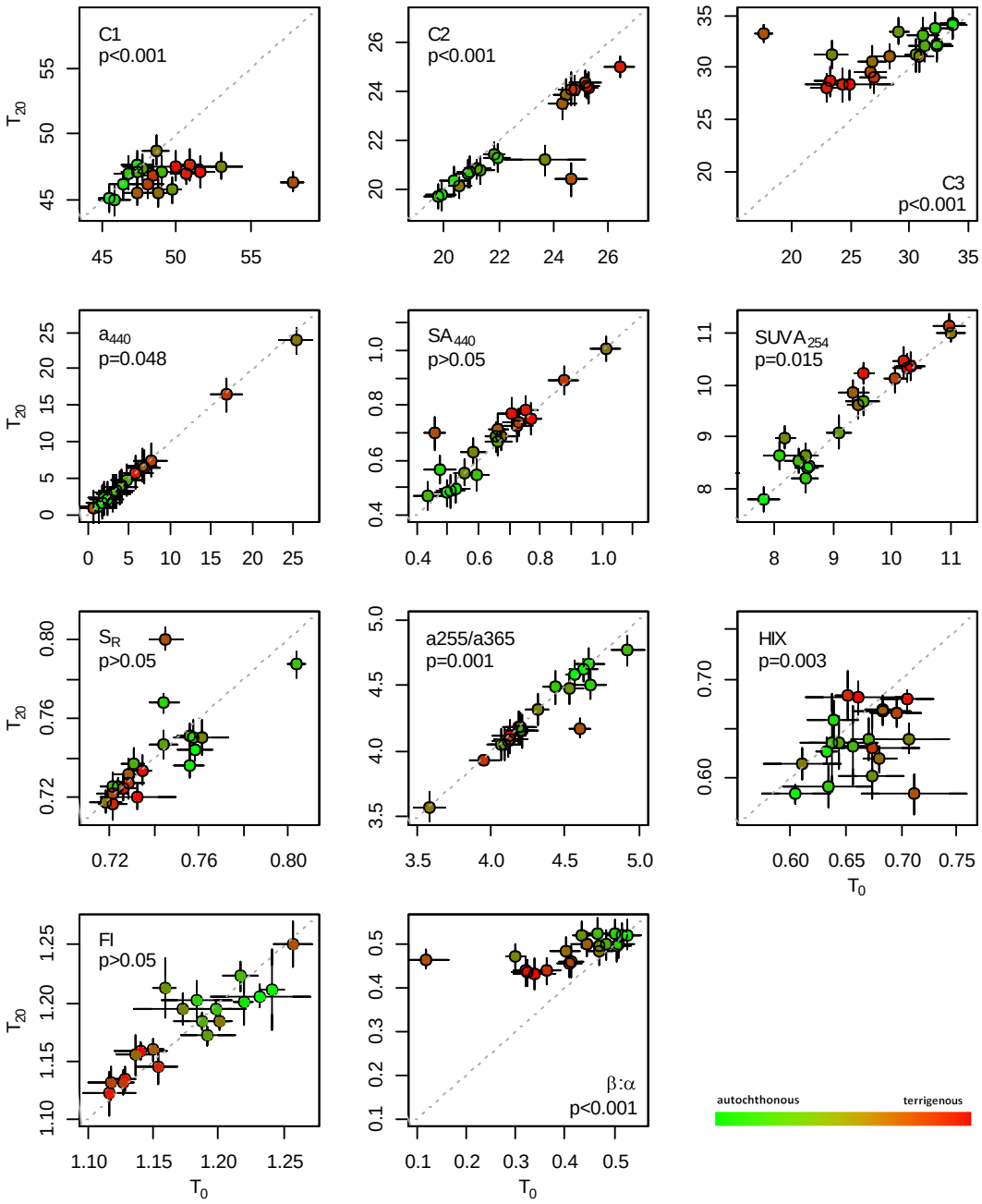


Figure 6 EEM-Components and optical indices at the beginning (T0) and the end (T20) of the bioassays. Mean values and standard deviation (n=3) are given. Indices were tested using a Wilcoxon-test for paired samples. The dotted line marks a 1:1 relationship (i.e., values above this line increased, values below decreased during the assay). Color indicates DOM quality as derived from the PCA. **C1**, **C2** and **C3** are the percentage of each fluorescent component on total fluorescence. Absorbance at 440nm (***a*$_{440}$**) indicates color, specific UV-absorbance at 440nm (**SA$_{440}$**) and 254nm (**SUVA$_{254}$**) represent DOC-standardized inices for coloration and aromaticity, respectively. Slope ratio (**S$_R$**) and **a$_{255}$/a$_{365}$** indicate molecular weight (high values indicate low molecular weight), the humification index (**HIX**) the degreee humification, fluorescence index (**FI**) DOM origin and the freshness index (**β:α**) represents recently produced DOM. Note different scales for the three fluorescent components.

DOM quality dynamics during the bioassay are shown in Figure 7. Initially terrigenous DOM (left side) shifted to DOM with a relatively autochthonous imprint (right side) upon microbial degradation. Autochthonous DOM was less reworked by microorganisms which resulted in only slight changes of DOM signature. Furthermore, the CUE was lower for terrigenous than for autochthonous DOM.

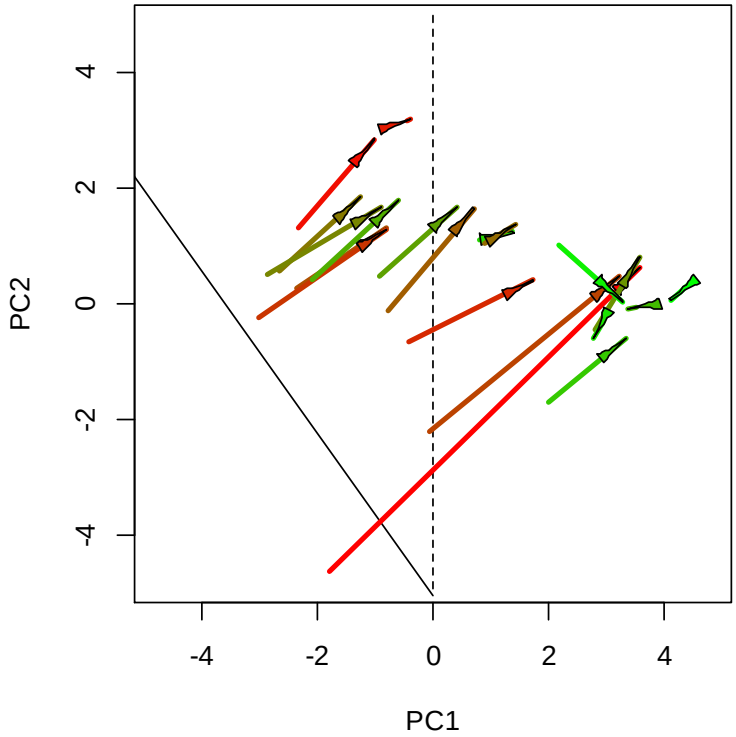


Figure 7 Impact of microbial degradation on DOM composition. The starting coordinates derive from scores of the PCA (Figure 3). Scores were computed with the PCA eigenvectors and optical indices at day 20 represent the end coordinates. Each arrow indicates the shift in DOM quality during the 20 day incubation period, the length represents the intensity of change, color denotes CUE (green=high, red=low).

The terrigenous DOM imprint increased with brownification (Fig. 8a) as indicated by high aromaticity ($SUVA_{254}$) and high molecular weight (a_{255}/a_{365}). Thereby brownification may not only increase DOC-concentration but cause a shift in DOM composition as well. This relationship can be observed even when excluding SA_{440} and $SUVA_{254}$.

To define whether differences in DOM composition affect microbial metabolism, optical measures were related to the percentage of bioavailable fraction of DOC (%BDOC) and the carbon use efficiency (CUE). No significant ($p=0.24$) effects of DOM quality on BDOC (%) could be found (Fig. 8b). CUE increased with low molecular weight (indicated by S_R and a_{255}/a_{365}) and freshly produced DOM (β/α) with microbial imprint (FI). Increasing imprint

of terrigenous DOM caused a decrease in CUE (indicated by color, aromaticity, degree of humification and fluorescent components 1 and 2) (Fig. 8c).

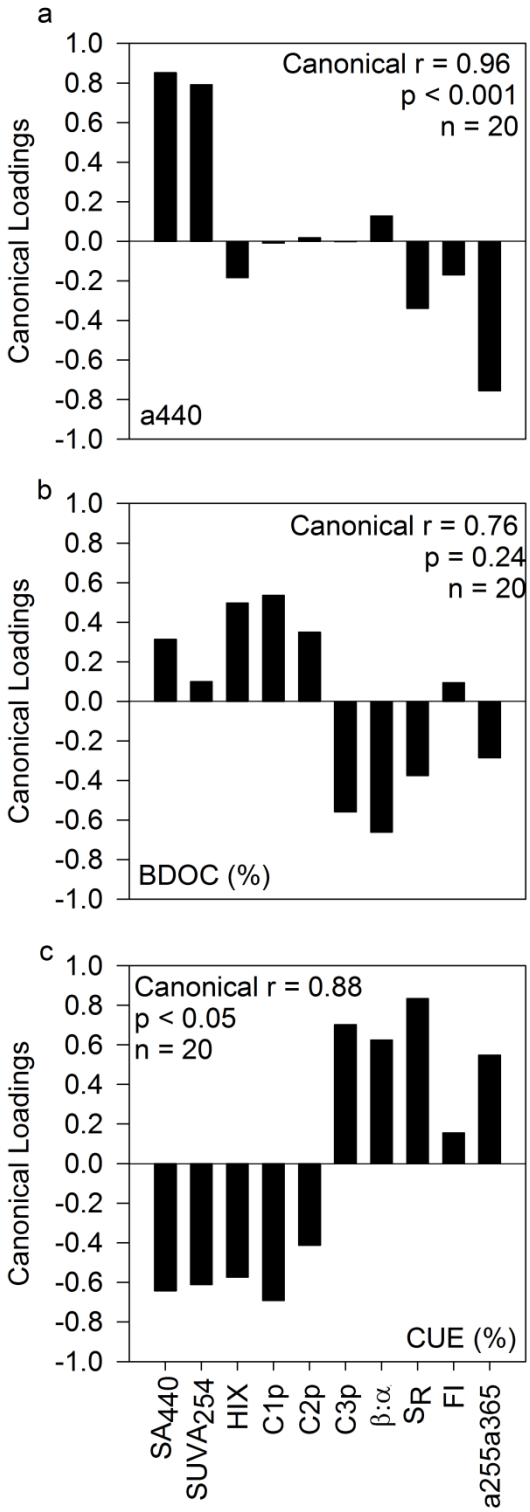


Figure 8: Canonical correlation analyses based on optical measurements of the 20 streams illustrate optical properties of DOM most strongly related to (**a**) color (a_{440}), (**b**) bioavailable DOC (BDOC) and (**c**) carbon use efficiency (CUE). Canonical loadings represent the correlations between respective variables and the one canonical variate of our analysis and show the relationship (strength and direction) between the respective constraint and optical measures. Color (SA_{440}), aromaticity ($SVUA_{254}$), degree of humification (HIX) and fluorescent component 1 and 2 (C1p and C2p, respectively) indicate DOM of likely terrigenous origin. Fluorescent component 3 (C3p), apparent freshness (β:α), molecular weight (SR and a_{255}/a_{365}) indicate rather autochthonous DOM.

Streamwater pCO_2

Streamwater pCO_2 averaged 1.61 ± 1.05 µatm. The difference of the streamwater CO_2 concentration minus the concentration expected at equilibrium with the atmosphere is expressed as ΔCO_2. All streams were CO_2 supersaturated as indicated by the positive ΔCO_2 values. A mechanistic linear model was constructed based on the idea that ΔCO_2, as a proxy for in-stream metabolism, depends on the amount of DOC, its bioavailability (%BDOC) and the carbon use efficiency (CUE):

$$\log \Delta CO_2 = b_0 * \log DOC + b_1 * \log \%BDOC + b_2 * \log\ (1 - CUE)$$

The regression analysis reveals DOC concentration and CUE as major controls on in-stream metabolism as they explained 51% ($p<0.01$) of the variance in ΔCO_2 values while %BDOC was not a significant term in the model ($p=0.43$) (Fig. 9 and Tab. 5). However, the sums of squares reveal DOC concentration as the major control on ΔCO_2.

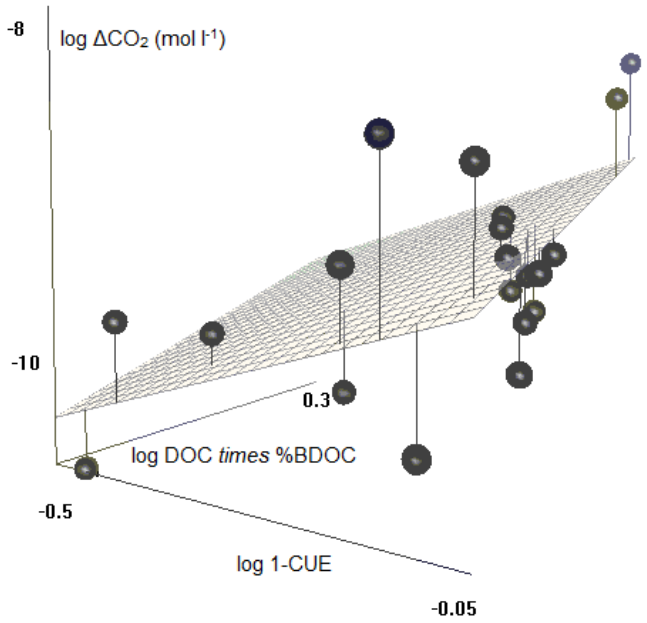


Figure 9 Model of streamwater CO_2 partial pressure dependent on bioavailable dissolved organic carbon (%BDOC) and carbon use efficiency (CUE). The lines (residuals) connect the measured values (points) to the modeled surface.

Table 5. Liner model results. Whereas heterotrophic metabolism is expressed as ΔCO_2, and related to dissolved organic carbon (DOC), and its susceptibility to metabolism by microorganisms (expressed via %BDOC and CUE).

Variable	Mean ± SD	Range (min – max)	ß	t- statistic and P-value	Sum of squares
Dissolved organic carbon (DOC)	7.47 ± 5.73 mg L^{-1}	1.41 - 24.31 mg L^{-1}	0.45	2.4 P<0.05	3.91
Fraction of bioavailable DOC (%BDOC)	4.55 ± 2.14 %	1.63 - 9.30 %	-0.17	-0.81 P=0.43	0.2
Carbon use efficiency (CUE)	12.73 ± 9.58 %	4.57 - 37.10 %	0.53	2.58 P<0.05	1.68
CO_2 oversaturation (ΔCO_2)	0.88 ± 0.77 mg L^{-1}	0.16 - 3.38 mg L^{-1}			

Discussion

Recent studies have shown an increased export of DOC to freshwater systems over the last decades (Evans *et al.*, 2005; Monteith, 2007), causing a browning of the receiving streams. Yet, the effects of such an increase are still hard to predict. Here I conducted bioassays using brown-water stream samples differing in DOC-concentration in order to predict whether changes in DOC quantity and quality can alter metabolism and ultimately affect carbon cycling.

Stream color increases with DOC-concentration and contribution of terrigenous material to the DOM pool. In general, humic-like terrigenous substances dominated, though degradation experiments revealed high dynamics in DOM composition leading to a general shift towards an autochthonous DOM imprint. Terrigenous DOM was liable to microbial metabolism, yet at high cost, resulting in low carbon use efficiencies. Both, increased DOC concentration and larger contribution of terrigenous DOM, resulted in higher stream water CO_2-pressure and possibly increases CO_2-evasion to the atmosphere.

DOM color and quality

The positive correlation of color and DOC-concentration (Fig. 1) has already been described (Rasmussen *et al.*,1989; Cuthbert & del Giorgio, 1992; Roulet & Moore, 2006) and supports the assumption that increasing DOC-concentration contributes to color-intensity in streams. The brownish color of DOM can be addressed to the intrinsic light absorbing ability of CDOM, mainly dominated by humic substances (Boyle *et al.*, 2009). Terrestrial vegetation releases notable amounts of DOM rich in humic substances into headwater streams (Chapin *et al.*, 2002). Therefore the influence of DOM quality on color has to be taken into account as well. Analysis of DOM quality, based on the PCA, resulted in a separation of the DOM pool into terrigenously and autochthonously derived substances (Fig. 3).

The terrigenous fraction is dominated by high values of $a440$, highlighting the influence of terrigenous organic matter to DOM-color (Fig. 8). Aromatic substances are known to constitute a certain fraction of humic substances. A strong correlation of color (SA_{440}) and aromaticity ($SUVA_{254}$) has already been recognized by Weishaar *et al.* (2003), underlining the contribution of humic substances to color. However, the missing relationship of $SUVA_{254}$ and HIX, indicating the degree of humification, may be due to high diversity in chemical structure of the humic substances. These indices, one deriving from absorbance-,

the other from fluorescence measurements, may cover different fractions of these substances hence leading to inconsistent results. In general, all three fluorescent components are of humic-like nature (Tab. 4). C1 and C2 match the terrigenously derived organic matter, S_R and a_{255}/a_{365} are indicative for high molecular weight of this terrigenous DOM.

The autochthonous partition of DOM, however, is associated with the humic-like fluorescent component C3, an indicator for in-situ produced material (Cory & Kaplan, 2012). The correlation of C3 with β/α further underscores the freshness of this component. The positive relationship of FI and a_{255}/a_{365} addresses low molecular weight to autochthonous and high molecular weight to terrigenous DOM, consistent with the general knowledge that terrigenous DOM mainly derives from terrestrial vegetation hence consisting of complex molecules high in molecular weight (Hauer & Lamberti, 1996). The slope ratio, as calculated by Helms *et al.* (2008), covers a quite narrow range of wavelengths. The use of such narrow spectra has been suggested in order to detect even subtle compositional changes of DOM (Sarpal *et al.*, 1995). However, Helms *et al.* (2008) note that lacking standardization of S_R (e.g. the use of different wavelength ranges or mathematical operations) made a comparison of these indices among different studies difficult and even lead to contrary conclusions. Therefore the usage and interpretation of these indices should probably be carried out with caution. In general, all streams exhibit a rather terrigenous DOM composition, with varying contributions of autochthonous DOM.

DOM dynamics during bioassays

During the biodegradation assays the DOM pool underwent intense modification. Humic substances were removed, as suggested by a decrease of C1% and C2%, while C3%, associated with microbial production, increased (Fig. 4). Terrigenous humic substances initially were thought to be of recalcitrant nature (Schmidt *et al.*, 2011) and transported through streams rather unaltered. However, McCallister & del Giorgio (2012) and Ward *et al.* (2013) have shown the microbial degradability of terrigenous DOM. As C1 decreased relatively more with increasing terrigenous imprint of DOM, microorganisms may preferentially use the terrigenous, humic-like C1 if the availability of easier biodegradable DOM is limited, resulting in an increased production of C3. The suggested consumption of humic substances is supported by a decrease in the humification index HIX. A decrease in this index is caused by an increase in H/C-ratios, which has been attributed to lower

aromaticities (Fuchsman, 1986). Therefore a concomitant decrease in the aromaticity-index $SUVA_{254}$ along with HIX could be anticipated. However, $SUVA_{254}$ even increased during the assays, but as the index is standardized for DOC-concentration the increase may be addressed to a decrease in DOC concentration. In fact, a_{254} (absorbance at 254nm, not standardized for DOC-concentration) decreases during the assay, indicating microbial rework and reduction of humic substances. So a_{254} and DOC-concentration both decreased, but the letter one to a greater extent, causing the higher $SUVA_{254}$-values. The stronger decrease of DOC than a_{254} may be due to the contribution of other degraded substances not detectable by absorbance measurements. However, the proposed contribution of possibly new microbially produced substances absorbing at long wavelength regions should be taken into account as well (Helms *et al.*, 2008). It remains unsure whether such new microbially produced substances are even absent or merely superposed by a net decrease in a_{254}. Similar patterns can be observed with the color-index SA_{440}. The supposed decrease in humic substance content and concomitant decrease in aromatic substances should lead to a decrease in color. Yet, SA_{440} did not decrease during the assays, again due to the DOC-standardization, while $a440$ (not DOC-standardized) decreased significantly.

Microbial production of fluorescent DOM has been shown by Guillemette & del Giorgio (2012). The fluorescent component C4 described in their study was defined as humic-like and microbially produced and resembles C3 of this study. Thereby the production of *in-situ* novel compounds is suggested by an increase in C3% and supported by an increase in apparent freshness (β/α) (Wilson & Xenopoulos, 2009). Generally, autochthonous defined DOM exhibits higher values for FI and S_R than terrigenous DOM, supporting its higher imprint of autochthonous substances of low molecular weight. However, neither the FI nor the S_R-values shifted significantly during the assays. FI-values between 1.1 and 1.4 and S_R-values between 0.71 and 0.82 are indicative for rather terrigenous organic matter (McKnight *et al.*, 2001; Helms *et al.*, 2008), underlining the still dominant terrigenous DOM-imprint at the end of the assay. Yet, the S_R has also been related to photochemically induced shifts in molecular weight (Helms *et al.*, 2008). Since the samples have been kept in the dark, a shift caused by exposure to light can be excluded, justifying a stable S_R-value. The decrease in a_{255}/a_{365} (Dahlén *et al.*, 1996; Berggren *et al.*, 2007), on the other hand, indicates a significant increase in molecular weight of dissolved humic substances. This contradicts the assumption that microbial rework lowers DOM molecular weight, as supposed by de Haan (1993). Young *et al.* (2004) measured DOM average molecular weight

using high-pressure size exclusion chromatography and observed an increase in DOM molecular weight after 12 hours of incubation. They addressed it to microbial consumption of low and intermediate molecular weight fractions of the DOM pool and concluded microbial rework of humic and fulvic acids, coinciding with the findings of this study.

Microbial metabolism and control on carbon fluxes in streams

Brownification was revealed not to be only dependent on DOM quantity but also quality. The strong correlation of DOC-concentration and color (Fig. 1) emphasizes the contribution of terrigenous "brown" DOM to the total DOC pool in streams, as reported by Evans *et al.* (2005). However, qualitative aspects of DOM also exercise control on color (Fig. 8a), possibly influencing microbial metabolism.

The overall %BDOC was low (Tab. 5), yet can be compared to %BODC-values of other peat-dominated systems in Sweden (Guillemette & del Giorgio, 2012) and the UK (Stutter *et al.*, 2013). %BDOC was not dependent on DOM quality (Fig. 8b). On average, the values for CUE were quite low compared to other studies (del Giorgio & Cole, 1998) but revealed a significant relation to the quality of DOM (Fig. 8c). An increased imprint in autochthonous DOM (i.e. increase in freshly produced substances of low molecular weight) lead to an increase in CUE, where an increased terrigenous portion (with a high degree of humification and aromatic substance content) lowered the CUE. During the bioassay, DOM of most streams shifted towards a more autochthonous imprint (Fig. 7). Terrigenous DOM exhibits a more intense modification than DOM with higher imprints of autochthonously produced material. Microorganisms may spend more energy to assimilate substrates with higher contributions of terrigenous matter, leading to smaller fractions of DOC incorporated into biomass and larger fractions used to maintain metabolism.

The mechanistic model (Fig. 9) served to investigate the effects of DOM properties and microbial metabolism on in-stream metabolism, expressed as ΔCO_2. The average ΔCO_2-values were positive (Tab. 5), indicating CO_2 supersaturation of the investigated streams. The mechanism of supersaturation has been observed in both lakes (Cole *et al.*, 1994; Lapierre & del Giorgio, 2012) and streams (Jonsson *et al.*, 2007; Teodoru *et al.*, 2009) and was mainly addressed to the mineralization of terrigenous DOC. In this study DOC concentration is shown to exhibit the strongest control on ΔCO_2 (Fig. 9). This finding is in coherence with other studies predicting pCO_2-values and in-situ mineralization on the basis of DOC-concentrations. (Sobek *et al.*, 2003; Teodoru, 2009; Lapierre & del Giorgio,

2012). DOC corresponds to the potential energy basis for microbial degradation, where BDOC represents the actual available amount of DOC for microbial metabolism. However, the fact that %BDOC was not a significant contributor points to a quite constant BDOC fraction of the total carbon pool, explaining the missing link with DOM quality. Yet, CUE emphasizes the significance of DOM quality as contributor to CO_2 production in streams. Especially colored DOM was metabolized with low efficiency, potentially leading to an increase in CO_2 oversaturation and ultimately evasion to the atmosphere.

Conclusion

This study was based on the idea of a space-for-time substitution, where streams have been chosen to cover a range of DOC-concentrations to investigate whether increased DOC export from surrounding soils affects in-stream microbial metabolism and carbon cycling.

Stream water color was determined by both DOC quantity and quality. Indices derived from absorbance and fluorescence measurements revealed a generally terrigenous, humic-like DOM-pool, though imprints of autochthonously produced substances were also present. The PCA allowed to separate DOM quality into terrigenously and autochthonously derived fractions. Bioassays were conducted to observe DOM dynamics over time, revealing that microbial degradation of colored DOM resulted in a shift of DOM quality towards higher imprints of autochthonous DOM. In general, CUE-values were comparatively low, indicating low DOM susceptibility to microbial metabolism in those brown water systems and little trophic transfer to the microbial foodweb, especially with increasing terrigenous imprint. The linear model suggests that high DOC concentration and low CUE increase potential CO_2 evasion. It can be assumed that DOM quantity increases the carbon pool available for microbial metabolism while its metabolic fate is controlled by quality.

This study highlights the potential effects of increased DOM exports into streamwater systems on carbon cycling, coinciding recent studies in boreal (Berggren *et al.* 2010; McCallister & del Giorgio, 2012) and tropical (Ward *et al.*, 2013) systems. It contradicts the assumption that “brown” DOM is of recalcitrant nature and transported through streams unmodified. These findings could be particularly important with respect to supposed increases in DOM export from terrigenous sources into inland waters (Monteith *et al.*, 2007), especially concerning major carbon stores like permafrost soils and peatlands.

Zusammenfassung

Fließgewässer wurden lange Zeit primär als „pipelines“von Material und Energie vom Land in die Ozeane betrachtet. Inzwischen wird jedoch der metabolischen Aktivität dieser Systeme zunehmend Beachtung geschenkt und ihr Beitrag zu Stoffkreisläufen auf globaler Ebene mit einbezogen. Fließgewässer gelten generell als Quellen für atmosphärisches CO_2, ein Treibhausgas, das insbesondere im Zuge von Diskussionen um globale Erwärmung auch in der Öffentlichkeit zunehmend an Interesse gewonnen hat. Insbesondere in Quellbächen und Flussoberläufen werden die Energie- und Stoffflüsse stark von den Eigenschaften des Einzugsgebiets reguliert, was ihre Sensibilität gegenüber Veränderungen im Umland erhöht. Diverse Studien wiesen einen erhöhten Eintrag von gelöstem organischen Material (dissolved organic matter, DOM) in Bäche aus umgebenden Böden nach. Obgleich Fließgewässer einen relativ geringen Anteil der Erdoberfläche einnehmen, tragen sie in bedeutendem Ausmaß zur globalen Kohlenstoffbilanz bei. Es ist daher von Interesse die Auswirkungen veränderter DOM-Konzentrationen und Qualitäten in Gewässern zu untersuchen und zu verstehen.

Diese Arbeit befasst sich mit den regulatorischen Wirkungen unterschiedlicher DOM-Konzentrationen und Eigenschaften auf den mikrobiellen Metabolismus und ihre potentielle Auswirkung auf ökosystemarer Ebene. Hierfür wurden Degradationsexperimente an Bachwasser aus der Region des Böhmischen Massivs durchgeführt, das durch seinen hohen Gehalt an Huminstoffen eine bräunliche Färbung aufweist. Die Bäche wurden so gewählt, dass sie ein breites Spektrum an unterschiedlichen Konzentrationen gelösten organischen Kohlenstoffs (dissolved organic carbon, DOC) umfassen. Diese sollten stellvertretend für eine Zeitreihenanalyse Aussagen über die potentiellen Auswirkungen steigender DOC-Konzentrationen ermöglichen. Optische Analysen (Absorption und Fluoreszenz) wurden zur Beschreibung von Qualität und Dynamik des Bachwasser-DOMs herangezogen. Mittels paralleler Faktorenanalyse (PARAFAC) konnten ferner einzelne DOM-Komponenten identifiziert werden. Das organische Material der Bäche war generell stark von terrestrischen Merkmalen geprägt. Es zeigte sich, dass der mikrobielle Abbau von Material mit besonders hohem terrestrischen Imprint mit geringerer Effizienz erfolgte, was in einer niedrigeren Kohlenstoff-Nutzungseffizienz (carbon use efficieny, CUE) resultierte. Dies weist darauf hin, dass die Mikroorganismen einen relativ geringen Anteil des aufgenommenen Kohlenstoffs in den Aufbau von Biomasse investieren und einen relativ größeren Anteil in

Form von CO_2 in das Bachwasser abgeben. Dadurch erhöht sich der CO_2-Partialdruck im Wasser und somit die potentielle Menge an CO_2 die an die Atmosphäre abgegeben werden kann.

Diese Arbeit gewährt somit einen Einblick in die Dynamik und Mechanismen biologischer Aktivität kleiner Fließgewässer und zeigt ihre potentielle Bedeutung für den globalen Kohlenstoffkreislauf auf.

Acknowledgements

I would like to thank my advisor Prof. Tom Battin for giving me the opportunity to write my thesis at the Department of Limnology at the University of Vienna and his friendly and encouraging support.

Further I would like to thank Christina Fasching. Working with her was always motivating and her patience and willingness to share her knowledge with me considerably helped me to improve my thesis.

My sincere thanks go to all people at the Department of Limnology who supported me throughout my thesis. Especially I would like to thank Linda Wilhelm for her advice and Gabriel Singer for discussion. Hubert Kraill, Thomas Fuss and Markus Dengg considerably assisted me in the lab.

Of course, I would like to thank my family for their patience and financial support during my whole study.

Last but not least thanks also to all of my other friends for their help and encouragement.

References

Allan, J. D.; Castillo, M. M. (2007). *Stream Ecology: Structure and Function of Running Waters.* 2nd ed. Springer, Netherlands. 436pp.

Andersen, C. M.; Bro, R. (2003) Practical aspects of PARAFAC modeling of fluorescence excitation-emission data JOURNAL OF CHEMOMETRICS **17** (4) 200-215 DOI: 10.1002/cem.790

Andersson, S.; Nilsson, S. I.; Saetre, P. (2000) Leaching of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in mor humus as affected by temperature and pH *SOIL BIOLOGY & BIOCHEMISTRY* **32**(1), 1-10 DOI: 10.1016/S0038-0717(99)00103-0

Azam, F.; Cho, B., (1987) Bacterial utilization of organic matter in the sea. In: Fletcher, M., Gray, T.R.G., Jones, J.G. (Eds.), *Ecology of Microbial Communities*. Cambridge University Press, Cambridge, UK 261–281.

Battin, T. J.; Kaplan, L. A.; Findlay, S.; Hopkinson, C. S.; Marti, E.; Packman, A. I.; Newbold, J. D.; Sabater, F. (2008). Biophysical controls on organic carbon fluxes in fluvial networks *NATURE GEOSCIENCE* **1**(2), 95 DOI: 10.1038/ngeo602

Battin, T. J.; Luyssaert, S.; Kaplan, L. A.; Aufdenkampe, A. K.; Richter, A.; Tranvik, L. J. (2009). The boundless carbon cycle *NATURE GEOSCIENCE* **2**(9), 598-600 DOI: 10.1038/ngeo618

Berggren, M.; Laudon, H.; Jansson, M. (2007) Landscape regulation of bacterial growth efficiency in boreal freshwaters *GLOBAL BIOGEOCHEMICAL CYCLES* **21** (4) Article Number: GB4002 DOI: 10.1029/2006GB002844

Berggren, M.; Laudon, H.; Jansson, M. (2009) Hydrological Control of Organic Carbon Support for Bacterial Growth in Boreal Headwater Streams *MICROBIAL ECOLOGY* **57** (1) 170-178 DOI: 10.1007/s00248-008-9423-6

Berggren, M.; Laudon, H.; Haei, M.; Strom, L.; Jansson, M. (2010) Efficient aquatic bacterial metabolism of dissolved low-molecular-weight compounds from terrestrial sources *ISME JOURNAL* **4**(3), 408-416 DOI: 10.1038/ismej.2009.120

Boyle, E. S.; Guerriero, N.; Thiallet, A.; Del Vecchio, R.; Blough, N. V. (2009) Optical Properties of Humic Substances and CDOM: Relation to Structure *ENVIRONMENTAL SCIENCE & TECHNOLOGY* **43**(12), 4612-4612 DOI: 10.1021/es901255m

Chapin F. S. III; Matson, P. A.; Mooney, H. A. (2002) *Principles of Terrestrial Ecosystem Ecology* Springer-Verlag New York, Inc

Christ, M. J.; David, M. B. (1996) Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol *SOIL BIOLOGY & BIOCHEMISTRY* **28**(9), 1191-1199 DOI: 10.1016/0038-0717(96)00120-4

Coble, P.G. (1996) Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy *MARINE CHEMISTRY* **51**(4), 325-346 DOI: 10.1016/0304-4203(95)00062-3

Cole, J. J.; Caraco, N. F.; Kling, G. W.; Kratz, T. K. (1994) Carbon-dioxide supersaturation in the surface waters of lakes *SCIENCE* **265**(5178) 1568-1570 DOI: 10.1126/science.265.5178.1568

Cole, J. J.; Prairie, Y. T.; Caraco, N. F.; McDowell, W. H.; Tranvik, L. J.; Striegl, R. G.; Duarte, C. M.; Kortelainen, P.; Downing, J. A.; Middelburg, J. J.; Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget *ECOSYSTEMS* **10** (1), 171-184 DOI: 10.1007/s10021-006-9013-8

Cory, R. M.; Kaplan, L. A. (2012) Biological lability of streamwater fluorescent dissolved organic matter *LIMNOLOGY AND OCEANOGRAPHY* **57**(5), 1347-1360 DOI: 10.4319/lo.2012.57.5.1347

Cuthbert, I. D.; del Giorgio, P. (1992) Toward a standard method of measuring color in freshwater *LIMNOLOGY AND OCEANOGRAPHY* **37**(6), 1319-1326

Dahlén, J.; Bertilsson, S.; Pettersson, C. (1996) Effects of UV-A irradiation on dissolved organic matter in humic surface waters *ENVIRONMENT INTERNATIONAL* **22**(5), 501-506 DOI: 10.1016/0160-4120(96)00038-4

de Haan, H. (1993) Solar UV-light penetration and photodegradation of humic substances in peaty lake water *LIMNOLOGY AND OCEANOGRAPHY* **38** (5), 1072-1076

del Giorgio, P. A.; Cole, J. J. (1998) Bacterial growth efficiency in natural aquatic systems *ANNUAL REVIEW OF ECOLOGY AND SYSTEMATICS* **29,** 503-541 DOI: 10.1146/annurev.ecolsys.29.1.503

Dinsmore, K. J.; Billett, M. F.; Skiba, U. M.; Rees, R. M.; Drewer, J.; Helfter, C. (2010) Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment *GLOBAL CHANGE BIOLOGY* **16**(10), 2750-2762 DOI: 10.1111/j.1365-2486.2009.02119.x

Evans, C. D.; Monteith, D. T.; Cooper, D. M. (2005) Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts *ENVIRONMENTAL POLLUTION* **137**(1), 55-71 DOI: 10.1016/j.envpol.2004.12.031

Fenner, N.; Freeman, C.; Lock, M. A.; Harmens, H.; Reynolds, B.; Sparks, T. (2007) Interactions between elevated CO2 and warming could amplify DOC exports from peatland catchments *ENVIRONMENTAL SCIENCE & TECHNOLOGY* **41**(9), 3146-3152 DOI: 10.1021/es061765v

Freeman, C.; Ostle, N.; Kang, H. (2001) An enzymic 'latch' on a global carbon store - A shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. *NATURE* **409**(6817), 149-149 DOI: 10.1038/35051650

Freeman, C.; Fenner, N.; Ostle, N. J.; Kang, H.; Dowrick, D. J.; Reynolds, B.; Lock, M. A.; Sleep, D.; Hughes, S.; Hudson, J. (2004) Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels *NATURE* **430**(6996) 195-198 DOI: 10.1038/nature02707

Fuchsman, C. H. (1986) Peat and water: Aspects of Water Retention and Dewatering in Peat *Elsevier Applied Science Publishers LTD,* New York, USA

Gorham, E. (1991) Northern Peatlands – Role in the Carbon-Cycle and probable Responses to Climatic Warming *ECOLOGOCAL APPLICATIONS* Volume: 1 Issue: 2 Pages: 182-195 DOI: 10.2307/1941811

Green, S. A.; Blough, N. V. (1994) Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters *LIMNOLOGY AND OCEANOGRAPHY* **39**(8), 1903-1916

Guillemette, F.; del Giorgio, P. A. (2011) Reconstructing the various facets of dissolved organic carbon bioavailability in freshwater ecosystems *LIMNOLOGY AND OCEANOGRAPHY* **56**(2), 734-748 DOI: 10.4319/lo

Guillemette, F.; del Giorgio, P. A. (2012) Simultaneous consumption and production of fluorescent dissolved organic matter by lake bacterioplankton *ENVIRONMENTAL MICROBIOLOGY* **14**(6), 1432-1443 DOI: 10.1111/j.1462-2920.2012.02728.x

Hansson, L. A.; Nicolle, A.; Graneli, W.; Hallgren, P.; Kritzberg, E.; Persson, A.; Bjork, J.; Nilsson, P. A.; Bronmark, C. (2013) Food-chain length alters community responses to global change in aquatic systems *NATURE CLIMATE CHANGE* **3**(3), 228-233 DOI: 10.1038/NCLIMATE1689

Hauer, F. R.; Lamberti, G. A. (1996) Methods in Stream Ecology, *ACADEMIC PRESS*, San Diego, California

Helms, J. R.; Stubbins, A.; Ritchie, J. D.; Minor, E. C.; Kieber, D. J.; Mopper, K. (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter *LIMNOLOGY AND OCEANOGRAPHY* **53**(3), 955-969 DOI: 10.4319/lo.2008.53.3.0955

Jonsson, A.; Algesten, G.; Bergstrom, A. K.; Bishop, K.; Sobek, S.; Tranvik, L. J.; Jansson, M. (2007) Integrating aquatic carbon fluxes in a boreal catchment carbon budget JOURNAL OF HYDROLOGY **334**(1-2), 141-150 DOI: 10.1016/j.jhydrol.2006.10.003

Lakowicz, J. R. (1999) Principle of Fluorescence Spectroscopy 2nd Edition. *Kluwer Academic/Plenum* Publishers: New York.

Lapierre, J. F.; del Giorgio, P. A. (2012) Geographical and environmental drivers of regional differences in the lake pCO_2 versus DOC relationship across northern landscapes *JOURNAL OF GEOPHYSICAL RESEARCH-BIOGEOSCIENCES* **117**, Article Number: G03015 DOI: 10.1029/2012JG001945

Lorenzo-Seva, U.; ten Berge, M. F. (2006) Tucker's Congruence Coefficient as a Meaningful Index of Factor Similarity *Methodology* **2**(2), 57–64 DOI 10.1027/1614-2241.2.2.57

McCallister, S. L.; del Giorgio, P. A. (2012) Evidence for the respiration of ancient terrestrial organic C in northern temperate lakes and streams *PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA* **109**(42), 16963-16968 DOI: 10.1073/pnas.1207305109

McKnight, D. M.; Boyer, E. W.; Westerhoff, P. K.; Doran, P. T.; Kulbe, T.; Andersen, D. T. (2001) Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity *LIMNOLOGY AND OCEANOGRAPHY* **46**(1), 38-48

Monteith, D. T.; Stoddard, J. L.; Evans, C. D.; de Wit, H. A.; Forsius, M.; Hogasen, T.; Wilander, A.; Skjelkvale, B. L.; Jeffries, D. S.; Vuorenmaa, J.; Keller, B.; Kopacek, J.; Vesely, J. (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry *NATURE* **450**(7169), 537-U9 DOI: 10.1038/nature06316

Norland, S. (1993) The relationship between biomass and volume of bacteria. In: Kemp, P.F., Sherr, B., Cole, J.J. (eds) Handbook of methods of aquatic microbial ecology. Lewis, Boca Raton, Pages: 303–308.

Ohno, T. (2002) Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter *ENVIRONMENTAL SCIENCE & TECHNOLOGY* **36**(4), 742-746 DOI: 10.1021/es0155276

Parlanti, E.; Worz, K.; Geoffroy, L.; Lamotte, M. (2000) Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs *ORGANIC GEOCHEMISTRY* **31**(12), 1765-1781 DOI: 10.1016/S0146-6380(00)00124-8

Rasmussen, J. B.; Godbout, L.; Schallenberg, M. (1989) The humic content of lake water and its relationship to watershed and lake morphometry *LIMNOLOGY AND OCEANOGRAPHY* **34**(7), 1336-1343

Regnier, P.; Friedlingstein, P.; Ciais, P.; Mackenzie, F. T.; Gruber, N.; Janssens, I. A.;... & Thullner, M. (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean *NATURE GEOSCIENCE* **6**(8), 597-607 DOI: 10.1038/NGEO1830

Roulet, N.; Moore, T. R. (2006) Environmental chemistry - Browning the waters *NATURE* **444**(7117), 283-284 DOI: 10.1038/444283a

Sarpal, R. S.; Mopper, K.; Kieber, D. J. (1995) Absorbance properties of dissolved organic matter in Antarctic sea water *Antarctic Journal of the United States*, **30**(5), 139-140

Schmidt, M. W. I.; Torn, M. S.; Abiven, S.; Dittmar, T.; Guggenberger, G.; Janssens, I. A.; Kleber, M.; Kogel-Knabner, I.; Lehmann, J.; Manning, D. A. C.; Nannipieri, P.; Rasse, D. P.; Weiner, S.; Trumbore, S. E. (2011) Persistence of soil organic matter as an ecosystem property *NATURE* **478**(7367), 49-56 DOI: 10.1038/nature10386

Sobek, S.; Algesten, G.; Bergstrom, A. K.; Jansson, M.; Tranvik, L. J. (2003) The catchment and climate regulation of pCO(2) in boreal lakes *GLOBAL CHANGE BIOLOGY* **9**(4), 630-641 DOI: 10.1046/j.1365-2486.2003.00619.x

Stedmon, C. A.; Markager, S.; Bro, R. (2003) Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy MARINE CHEMISTRY **82**(3-4), 239-254 DOI: 10.1016/S0304-4203(03)00072-0

Stedmon, C. A.; Markager, S. (2005) Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis *LIMNOLOGY AND OCEANOGRAPHY* **50**(2), 686-697

Stedmon, C. A.; Thomas, D. N.; Granskog, M.; Kaartokallio, H.; Papadimitriou, S.; Kuosa, H. (2007) Characteristics of dissolved organic matter in Baltic coastal sea ice: Allochthonous or autochthonous origins? *ENVIRONMENTAL SCIENCE & TECHNOLOGY* **41**(21), 7273-7279 DOI: 10.1021/es071210f

Stedmon, C. A.; Bro, R. (2008) Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial *LIMNOLOGY AND OCEANOGRAPHY-METHODS* **6**, 572-579

Stutter, M. I.; Richards, S.; Dawson, J. J. C. (2012) Biodegradability of natural dissolved organic matter collected from a UK moorland stream *WATER RESEARCH* **47**(3), 1169-1180 DOI: 10.1016/j.watres.2012.11.035

Teodoru, C. R.; Del Giorgio, P. A.; Prairie, Y. T.; Camire, M. (2009) Patterns in pCO_2 in boreal streams and rivers of northern Quebec, Canada *GLOBAL BIOGEOCHEMICAL CYCLES* **23,** Article Number: GB2012 DOI: 10.1029/2008GB003404

Tranvik, L. J. (1998) Degradation of Dissolved Organic Matter in Humic Waters by Bacteria *ECOLOGICAL STUDIES; AQUATIC HUMIC SUBSTANCES: ECOLOGY AND BIOGEOCHEMISTRY* **133,** 259-283

Tranvik, L. J.; Jansson, M. (2002) Climate change - Terrestrial export of organic carbon *NATURE* **415**(6874), 861-862 DOI: 10.1038/415861b

Tranvik, L. J.; Downing, J. A.; Cotner, J. B.; Loiselle, S. A.; Striegl, R. G.; Ballatore, T. J.; … & Weyhenmeyer, G. A. (2009) Lakes and reservoirs as regulators of carbon cycling and climate *LIMNOLOGY AND OCEANOGRAPHY* **54**(6), 2298-2314 DOI: 10.4319/lo.2009.54.6_part_2.2298

Trumbore, S. E. (1997) Potential responses of soil organic carbon to global environmental change *PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA* **94**(16), 8284-8291 DOI: 10.1073/pnas.94.16.8284

Twardowski, M. S.; Boss, E.; Sullivan, J. M.; Donaghay, P. L. (2004) Modeling the spectral shape of absorption by chromophoric dissolved organic matter *MARINE CHEMISTRY* **89**(1-4), 69-88 DOI: 10.1016/j.marchem.2004.02.008

Volk, C. J.; Volk, C. B.; Kaplan, L. A. (1997) Chemical composition of biodegradable dissolved organic matter in streamwater *LIMNOLOGY AND OCEANOGRAPHY* **42**(1), 39-44

Wallis, P. M.; T. I., Ladd (1983) Organic biogeochemistry of groundwater at a mountain coal mine. *GEOMICROBIOLOGY JOURNAL* **3**(1), 49-78

Ward, N. D.; Keil, R. G.; Medeiros, P. M.; Brito, D. C.; Cunha, A. C.; Dittmar, T.; Yager, P. L.; Krusche, A. V.; Richey, J. E. (2013) Degradation of terrestrially derived macromolecules in the Amazon River *NATURE GEOSCIENCE* **6**(7), 530-533 DOI: 10.1038/NGEO1817

Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon ENVIRONMENTAL SCIENCE & TECHNOLOGY **37**(20), 4702-4708 DOI: 10.1021/es030360x

Wilson, H. F.; Xenopoulos, M. A. (2009) Effects of agricultural land use on the composition of fluvial dissolved organic matter *NATURE GEOSCIENCE* **2**(1), 37-41 DOI: 10.1038/NGEO391

Worrall, F.; Burt, T.; Shedden, R. (2003) Long term records of riverine dissolved organic matter *BIOGEOCHEMISTRY* **64**(2), 165-178 DOI: 10.1023/A:1024924216148

Young, K. C.; Maurice, P. A.; Docherty, K. M.; Bridgham, S. D. (2004) Bacterial degradation of dissolved organic matter from two northern Michigan streams *GEOMICROBIOLOGY JOURNAL* **21**(8), 521-528 DOI: 10.1080/01490450490888208

Zsolnay, A.; Baigar, E.; Jimenez, M.; Steinweg, B.; Saccomandi, F. (1999) Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying *CHEMOSPHERE* **38**(1), 45-50 DOI: 10.1016/S0045-6535(98)00166-0

Curriculum Vitae

BARBARA BEHOUNEK

Education

University of Vienna, Austria *Expected in December 2013*

- Master's degree in Ecology/Biology
- Master thesis title (so far): "Dynamics of dissolved organic matter in brown-water streams"

University of Vienna, Austria *October 2007 – April 2011*

- Bachelor's degree in Biology

Grammar School *September 1999 – June 2007*

- University-entrance qualification

Teaching Experience

Tutor at the Department of Limnology, University of Vienna, Austria

- Practical course "Biogeochemistry of streams and lakes" (field methods & lab work; metabolism, nutrient dynamics) *June 2013*

- Practical course "Ecosystem Stream" (field methods & lab work; hydrology, dynamics of macrozoobenthos and algae communities) *September 2012*

Further Skills

Languages: German & English fluently, knowledge of Latin, basic knowledge of Spanish

Computer skills: European Computer Driving Licence (ECDL), R, SigmaPlot, Matlab, Statgraphics, SPSS

Poster Presentation

Fresh Blood for Fresh Water Meeting, Wassercluster Lunz and SIL-Austria, Lunz am See, Austria — *February 2013*

Selected Courses

- Practical Course "Aquatic Microbial Ecology" — *May 2013*
- Course "Experimental Design and Statistical Methods in Limnology" — *February 2013*
- Lecture "Ecosystem Ecology and Biogeochemistry" — *Winter 2012*
- Practical Course Costa Rica "Metabolic Cycles of Terrestrial Ecosystems" — *Spring 2012*
- Lecture and Field Course "Hydrology and Stream Ecology" — *Winter 2011*
- Practical Course "Stable Isotopes in Ecology" — *Winter 2011*
- Practical Course "Chemical Methods in Ecology" — *Winter 2011*
- Practical Course "Aquatic Biocoenosis " — *August 2011*
- Practical Course „Design and Analysis of Multifactorial Experiments" — *Summer 2011*
- Practical Course "Biogeochemistry of Streams and Lakes" — *Spring 2011*

Work Experience

- Contract for Services: Lab work, Department of Terrestrial Ecology (formerly Department of Chemical Ecology), University of Vienna, Austria — *Winter 2011*
- Contract for Services: Practical Work & Public Presentation, Research Institute of Wildlife Ecology, University of Veterinary Medicine Vienna, Austria — *Autumn 2011*
- Contract for Services: Guiding School Excursions, Vienna Ombuds Office for Environmental Protection — *Spring 2011*
- Project Collaborator: Project ARCARNET (The architecture of carbon fluxes in fluvial networks), Department of Limnology, University of Vienna, Austria — *September 2010*