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„Linking dissolved organic matter composition to stream ecosystem metabolism across a land-use gradient“

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1 Abstract

Stream ecosystem metabolism integrates production and respiration of organic matter at ecosystem scale. Dissolved organic matter (DOM) in aquatic environments is a complex, diverse mixture of various chemical species differing in origin; its composition likely controls respiration but may also carry an imprint of recent autotroph assimilation and microbial processing.

I investigated effects of land use on DOM composition and nutrient and carbon quantities and explored linkages to whole-stream metabolism, i.e. ecosystem respiration (ER) and gross primary production (GPP). The 33 investigated streams are located in a region with diverse land use in Northern Austria, representative for a contemporary Central European landscape. The various catchments constitute a gradient of land-use distributions from semi-natural, forested areas to agriculturally used and urban areas. DOM composition was investigated by excitation-emission matrices (EEMs) from fluorescence measurements used for modeling by parallel factor analysis (PARAFAC). Metabolism was measured based on dissolved oxygen dynamics by one- and two-station open-channel methods. GPP and ER were estimated by using the empirical oxygen record to fit a model containing a photosynthesis-irradiance curve and correction for reaeration. DOM composition, nutrient concentrations and ecosystem functions were finally linked by structural equation modeling, which indicated land use to strongly affect DOM composition and nutrient and carbon quantities. Especially DOM composition and phosphorus had further influence on ER. GPP, however, left no clear imprint on DOM composition, and seemed to be more affected by daily light conditions than by other factors.

Our results highlight the major influence of land use on ER via shifting DOM composition and nutrient quantities in streams. This is relevant in the light of land use rated as the most pervasive human influence on natural ecosystems and in the context of inland waters actively contributing to the global carbon cycle.

2 Introduction

2.1 Metabolism and its controls

Metabolism in stream ecosystems is the result of gross primary production (GPP), which is the rate of converting solar energy into organic matter by photosynthesis of autotrophs, and the decay of organic matter into inorganic compounds by ecosystem respiration (ER) of all autotroph and heterotroph biota in the stream ecosystem. Since autotrophs require light as energy source and nutrients for growth, GPP is often controlled by light (Steinman 1992; Hill, Ryon, and Schilling 1995; Hunt et al. 2012) and nutrient availability (Elwood et al. 1981; Mulholland et al. 2001). Further, grazing pressure can be an additional factor controlling GPP (Hill, Boston, and Steinman 1992; Rosemond 1993). Temperature was found to influence both GPP and ER (Demars et al. 2011). Since heterotrophic microbes require nutrients for growth and organic carbon as external energy source, ER is often controlled by nutrient availability (Elwood et al. 1981; Tank and Webster 1998; Mulholland et al. 2001) and quantity and composition of organic matter (Fisher and Likens 1973; Webster and Meyer 1997). In addition ER can be linked to the size of transient storage zones (Mulholland et al. 2001), which reflects the positive effect of increased residence time of water and the fact that total surface area available for microbial colonization by heterotrophs includes subsurface, interstitial surfaces in addition to the light-exposed streambed.

2.2 Importance of aquatic metabolism

While at ecosystem-scale streams were recognized to be metabolically active since the early work of Odum (1956), at a larger landscape and global scale the conventional conception of streams and rivers as passively piping organic carbon from land to the oceans prevailed until recently. During the last decade, however, the important role of inland waters in the global carbon cycle, namely as locations of intensive metabolic processing and CO_2-evasion as well as efficient carbon sequestration (Cole et al. 2007; Battin et al. 2009; Battin et al. 2008; Tranvik et al. 2009) has been recognized. The continuous supply of organic carbon from land and the diversity of geomorphologically defined opportunities for microbial processing result in fluvial ecosystems to be mostly net heterotrophic, i.e., they are net sinks of organic matter (Duarte and Prairie 2005; Battin et al. 2008). Hydrological storage and retention zones extend the transit time of organic carbon in fluvial networks from days

to months and therefore increase the possibility of microbial processing along the flowpath (Battin et al. 2008). Of the globally about 2.7 Pg C yr^{-1} entering inland waters only approximately 0.9 Pg C yr^{-1} actually reach the oceans, about 0.6 Pg C yr^{-1} are accumulated in inland waters, and aquatic metabolism is responsible for the outgassing of approximately 1.2 Pg C yr^{-1} in the form of climatically active CO_2 from inland waters into the atmosphere (Battin et al. 2009; Tranvik et al. 2009). The fact that these carbon fluxes are in the range of anthropogenic CO_2-emissions of approximately 9.1 Pg C yr^{-1} emphasizes the importance of inland waters in the global movement of carbon and the role they could play in CO_2 management and climate change mitigation (Battin et al. 2009). While these impressive upscaled estimates reflect the ever improving knowledge about the role of inland waters in the global carbon cycle, research into the underlying mechanisms acting across scales from microbes to whole biomes remain underdeveloped and largely conceptual. Importantly, anthropogenic perturbation on underlying functions controlling CO_2-evasion, such as in-stream metabolism, remain elusive as well (Regnier et al. 2013).

2.3 Dissolved organic matter, its sources, properties and linkages to metabolism

Dissolved organic matter (DOM) represents the largest fraction of organic carbon transported along the fluvial continuum (Wetzel 2001). Moreover, DOM represents the most bioavailable pool of organic carbon, because in contrast to particulate organic matter (POM), microbial cells are capable of immediate uptake of DOM without previous enzymatic hydrolysis (Battin et al. 2008). DOM in lotic ecosystems originates from autochthonous sources, i.e., releases from autotrophic biofilms, phytoplankton and submerged macrophytes (Bertilsson and Jones 2003), and from allochthonous sources, i.e., terrestrial ecosystems (Webster and Meyer 1997). This multitude of sources and manifold in-stream processing pathways including microbial, geochemical and photochemical reactions result in a complex and diverse mixture of DOM compounds (Seitzinger et al. 2005; Hertkorn et al. 2008). Autochthonous DOM typically contains lower molecular weight substances with fewer aromatic rings, e.g., amino acids and carbohydrates, than allochthonous DOM, and is therefore considered to be highly biodegradable (Azam and Cho 1987; Barrón, Apostolaki, and Duarte 2012). In contrast, allochthonous DOM is thought to be of a more recalcitrant nature due to its composition of mostly highly complex molecules, e.g., humic and fulvic substances (Tranvik 1998; Graeber et al. 2012). This view is challenged, however, by recent findings of relatively biolabile

terrigenous material, reflected for instance in high biodegradability of DOC and high partial pressure of CO_2 in humic-rich, "brown" streams (Fasching et al. 2014) or considerable concentrations of terrestrially sourced monomeric carbohydrates fueling microbial respiration (Berggren et al. 2010). Clearly, fluvial DOM is tightly linked to aquatic metabolism: Shifts in DOM composition affect its susceptibility to microbial metabolism (Williams et al. 2010) and, vice versa, metabolism can induce shifts in DOM composition by primary production of DOM (Halbedel, Büttner, and Weitere 2013).

2.4 Land use as a fundamental ecosystem and process control of anthropogenic origin

To enhance our understanding of the linkage between DOM and metabolism, experimental studies across land-use gradients seem promising. Due to the tight connection of fluvial networks with the surrounding terrestrial ecosystems, land use affects all major controls on GPP (Bernot et al. 2010) as well as the composition of terrestrially derived DOM supporting the bulk of ER in most streams (Wallis and Ladd 1983; Volk, Volk, and Kaplan 1997). Changes in land use often involve shifts in riparian vegetation, with less riparian canopy cover in agricultural and urban streams, which allows higher light transmission to the stream surface while it simultaneously decreases the input of leaf litter (Gücker, Boëchat, and Giani 2009; Bernot et al. 2010). Further, nutrient loading is a well-documented consequence of sewage and fertilizer runoff from urban and agricultural sources (Young and Huryn 1999; Bernot et al. 2006; Mulholland et al. 2008). Enhanced light availability and nutrient concentrations in agricultural streams often stimulate in-stream metabolism and as a consequence autochthonous DOM production becomes more important relative to allochthonous DOM (Minshall 1978; Finlay et al. 2011). In addition, agricultural land use may reduce the structural complexity of DOM as source diversity diminishes compared to species-rich native vegetation (Stedmon et al. 2006; Stanley et al. 2012; Kominoski and Rosemond 2012), albeit findings remain contradictory with some studies indicating increased DOM diversity in agricultural streams due to changed contributions from various soil sources (Graeber et al. 2012). Overall, agricultural and urban land use seem to increase DOM susceptibility to microbial in-stream metabolism (Wilson and Xenopoulos 2009; Williams et al. 2010). To date, roughly 43% of the global land surface has been transformed by human action (Daily 1995) and land-use change is rated the most pervasive human influence on natural ecosystems (Vitousek 1997). To better constrain the anthropogenic influence

on the role of inland waters in the global carbon cycle, we have to study DOM dynamics as both a control and indicator of metabolism within a land-use context.

2.5 Methods to estimate metabolism

Various methods have been developed to estimate metabolism in aquatic ecosystems but most of them rely on the measurement of oxygen production and consumption. Especially metabolism measurements in streams present unique challenges (Mulholland et al. 2001). The use of enclosed microcosms (chambers) for metabolism measurements lead to altered flow conditions and makes it difficult to incorporate habitat heterogeneity (Bott 1996) and hyporheic zone respiration, which accounts for a large fraction of ecosystem respiration (Mulholland et al. 1997; Naegeli and Uehlinger 1997; Fellows, Valett, and Dahm 2001; Uzarski et al. 2004). The one-station (Odum 1956) and the two-station open stream channel methods (Marzolf, Mulholland, and Steinman 1998; Young and Huryn 1998) reduce the above mentioned problems, but require reliable estimates of reaeration, which is the oxygen exchange flux at the water-atmosphere interface. The two-station method may be more suitable for heterogeneous streams (Bott 1996), because the change in oxygen signal can be assigned to a defined reach between the upstream and downstream stations. In contrast, the upstream distance integrated by the one-station method remains unclear. Although refinements to the two-station method were developed (Marzolf, Mulholland, and Steinman 1998; Young and Huryn 1998), its use remains problematic in unproductive streams when oxygen changes between upstream and downstream stations are close to the detection limit (Grace and Imberger 2006). Estimating reaeration is seen as the most critical step in open stream channel methods (Thyssen et al. 1987; Mulholland et al. 2001); it is best achieved by an experimental tracer gas injection (Rathbun et al. 1978; Wanninkhof, Mulholland, and Elwood 1990), an accurate (Marzolf, Mulholland, and Steinman 1998) but expensive and time-consuming method. Alternatively, reaeration can be calculated by one of countless hydraulics-based empirical equations (Tsivoglou and Neal 1976; Bennett and Rathbun 1972) or with the night-time regression method (Hornberger and Kelly 1975). The latter is based on recorded oxygen dynamics during the night and only works provided changes in the oxygen concentration are large enough (Thyssen et al. 1987), which is not the case in turbulent or unproductive streams (Young and Huryn 1996; Uehlinger, König, and Reichert 2000). Recently, inverse modeling approaches have been increasingly used to estimate metabolism as well as

reaeration terms in variously formulated ecosystem-scale models (Venkiteswaran, Wassenaar, and Schiff 2007; Holtgrieve et al. 2010; Hotchkiss and Hall 2014). Given reasonable starting parameter estimates and using modern, reliable fitting algorithms this approach is capable of delivering reasonable estimates for GPP and ER, potentially including confidence or credibility intervals besides the point estimates.

2.6 Methods to characterize DOM composition

The DOM pool in aquatic ecosystems is increasingly characterized using relatively inexpensive spectroscopic techniques (e.g., absorbance and fluorescence), which rely on the assumption that optical properties can be related to functional groups and molecular structures (Coble et al. 1990; Wetzel 1992; Fellman, Hood, and Spencer 2010). Indicators derived from spectroscopic measurements provide information about various relevant characteristics such as aromaticity (Weishaar et al. 2003), molecular weight (De Haan 1993; Helms et al. 2008), extent of humification (Zsolnay et al. 1999), origin (McKnight et al. 2001; Wilson and Xenopoulos 2008) and humic-like or protein-like fractions (Ohno 2002; Fellman, Hood, and Spencer 2010). While these techniques are analytically practicable, they cannot describe the enormous molecular diversity of DOM, which has been started to be revealed only recently using modern high-resolution analytical techniques such as FT-ICR-MS (Kim et al. 2003; Seitzinger et al. 2005; Hertkorn et al. 2008; Singer et al. 2012).

2.7 This study

In this study I analyzed DOM composition using absorbance and fluorescence measurements of 33 streams across a land-use gradient in a contemporary Central European landscape. In the same streams I measured in-stream metabolism using the one- and two-station open stream channel methods, light availability, nutrient and carbon quantities. Our aim was to investigate effects of the physical template (land use and light) on the biogeochemical structure (DOM composition and nutrient and carbon quantities) and explore linkages to ecosystem functions (in-stream metabolism) (Figure 1). Following the conceptual approach of a path analysis (Figure 1) I predicted that (i) land use would directly affect DOM composition and nutrient and carbon quantities; (ii) land use-controlled light availability and nutrient quantity would control GPP; (iii) ER would depend on DOM

composition, nutrient and carbon quantities besides being linked to GPP; and (iv) GPP would leave an additional imprint on DOM composition.

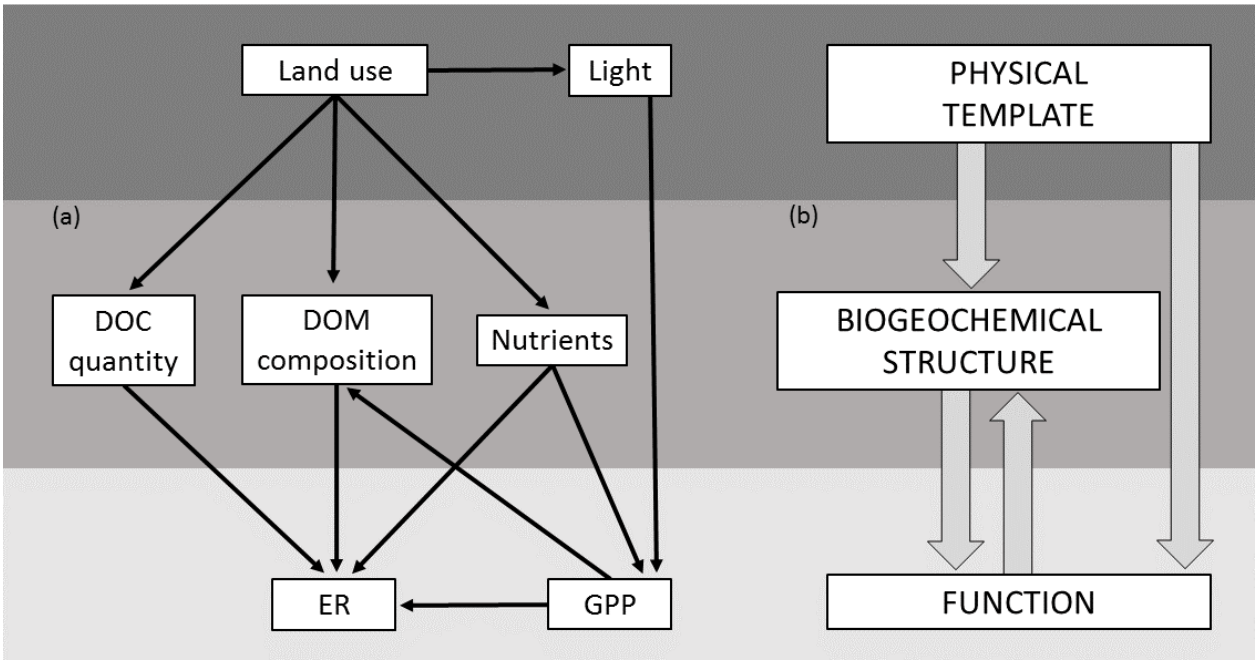

Figure 1 (a) Arrows illustrate hypothesized effects of land use on dissolved organic matter composition (DOM) and the concentrations of nutrients and dissolved organic carbon (DOC), and their linkage to ecosystem respiration (ER) and gross primary production (GPP). **(b)** Conceptual diagram of **(a)** where the physical template summarizes the most important long-term (land use) and short-term (light) physical controls, the biogeochemical structure consists of concentrations describing resource pools (DOC, DOM and nutrients) and the functions are represented by ER and GPP.

3 Material and Methods

3.1 Study area

Research was based on measuring metabolism and field sampling in 33 streams located predominantly in Mühl- and Waldviertel, north-eastern Austria (Figure 2), a region representative for a contemporary Central European landscape. The study was conducted from 3rd to 24th of October 2013. The chosen study period is a seasonal time period of high allochthonous input due to leaf-fall, moderate to high autochthonous production due to lower canopy cover and increased irradiance, and comparatively low water levels.

The study was conducted in conjunction with another project, where mixing of stream water at confluences was investigated, hence sampling sites were the most downstream located sites of neighbouring tributary catchments, i.e. sites were located immediately upstream of a stream junction in a pairwise fashion. Individual streams were chosen according to the following criteria: (i) The stream catchments constitute a gradient of land cover distributions from semi-natural, forested areas to agriculturally used and urban areas. (ii) The study reaches for measuring metabolism at the lowermost site in the catchment should not contain considerable inflows, outflows and water cascades, which can perturb the oxygen signal. (iii) Streams should be of intermediate size, approximately 3rd (2nd-4th) order according to Strahler and with an expected discharge below 1 $m^3 s^{-1}$. In a former study of the river Ybbs in lower Austria (G. Singer, unpubl. data), this stream size was identified as having maximally differentiated DOM, presumably due to a measurable allochthonous legacy from upstream sources and already increased potential for in-stream production. Smaller streams may have DOM with a clearer terrigenous signature stronger linked to land use, but allow only moderate in-stream production effects on DOM. Larger streams tend to be more similar due to a downstream averaging effect of multiple DOM sources and increased ratio of autochthonous:allochthonous DOM.

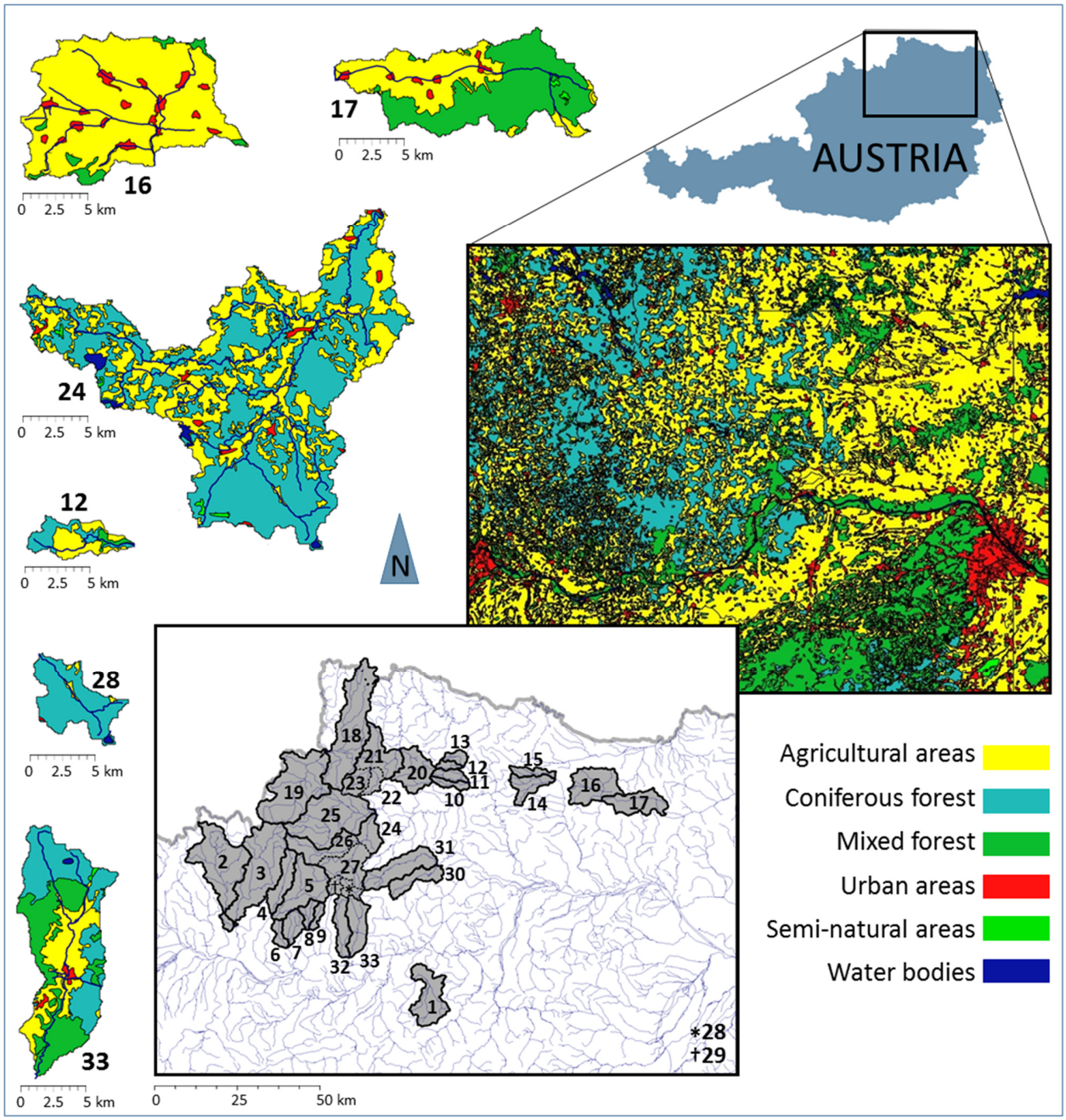

Figure 2 Maps of the study area with indicated land-use categories and catchment areas of investigated streams. Numbers 1 to 33 are indicating the site codes (Table 3, *Appendix*). Sites 12, 16, 17, 24, 28, 33 are examples of catchment areas with their land-use categories.

Catchment delineation and catchment area calculation were done using the European Catchments and Rivers Network System (ECRINS v1.1, June 2012; http://www.eea.europa.eu/data-and-maps/data/european-catchments-and-rivers-network). Land use data was sourced from the CORINE Land Cover 2006 inventory (CLC06; http://land.copernicus.eu/pan-european/corine-land-cover).
I reduced and reclassified the original set of CLC06 land use categories to six regionally important land use categories: agricultural areas, coniferous forest, mixed forest, urban areas, semi natural areas and water bodies (Table 2, *Appendix*). Areas and percentages of land use categories in entire catchments were calculated (Table 3, *Appendix*). All computations and analysis were conducted in the geographical information system QuantumGIS (version Valmiera 2.2.0).

3.2 Fieldwork

Dissolved oxygen (DO) and water temperature data were collected using MiniDOT loggers with optodes as DO sensors (PME, Vista, California, USA). Loggers were placed in calmly flowing stream water, one at an upstream station and one at a downstream station. The two monitoring loggers were separated between 200.5 to 602 m and the water travel time from upstream to downstream station ranged from 9 to 67 min. Photosynthetically active radiation (PAR; 400-700 nm) was recorded with HOBO Pendant Temperature/Light Data Loggers 64K - UA-002-64 (Onset, Bourne, Massachusetts, USA). I placed the light meters at identical locations with the oxygen loggers and slightly above the water level. When this was not possible, the light meter was placed at a location where representative light conditions for the respective study reach could be expected. DO, temperature and light were logged every minute for at least one entire day including the full preceding and following night. For modeling I defined a "metabolism day" as 32 hours duration from 22:00 h, after sunset, on the first day of measurement, to 6:00 h, before sunrise, on the third day. I measured barometric pressure at the time the loggers were deployed and recovered. For computation of saturated oxygen concentrations the mean of the two barometric measurements was used.

To describe hydromorphological conditions, I took at least 40 measurements of stream width along the length of each reach with a Leica DISTO^{TM} D8 laser distance meter (Leica Geosystems AG,

Heerbrugg, Switzerland). Stream depth was measured every few steps with a scale while walking along a zigzag-transect through the entire reach; the step interval for measuring was scaled to reach length to achieve a minimum of 80 measurements. Average width and depth were computed as the arithmetic mean of all collected measurements per stream. In addition, thalweg slope and water surface slope were measured with a level instrument. To avoid disturbing effects on the DO record, width, depth and slope measurements were conducted on the day of logger recovery. Travel time and study reach average velocity between both stations were determined by injecting a conservative solute (NaCl) into the stream. NaCl-injection was done upstream of the first station to allow estimation of discharge at both stations and thereby determine potential inflow of ground water. The distances between the salt injection point and the upstream station was chosen long enough to guarantee full mixing of stream water with salt before arrival at the upstream station. NaCl (mass ranging from 913 g to 15,199 g depending on stream size) was dissolved in stream water in a bucket before injecting it by a slug (Bales and Nardi 2007). Conductivity served as a simple proxy for salt concentration and was measured at one-second intervals with a WTW Multi 340i conductivity meter (WTW GmbH, Weilheim, Germany) at upstream and downstream stations. Travel time, i.e., the time a water parcel requires to move from the upstream station to the downstream station, was calculated by subtracting the time when salt concentration peaked at the upstream station from time when salt concentration peaked at the downstream station. I calculated the reach average velocity by dividing the travel time by reach length. Discharge was computed from the total added mass of salt and the integrated area under the salt breakthrough curve at both stations. In addition, discharge was calculated as the product of average width, average depth and average velocity. NaCl slug injections were carried out either on the day of logger deployment or recovery.

At each study stream, water was sampled at upstream and downstream stations for water chemistry analysis, either on the day of logger deployment or recovery. Duplicate samples per station for DOC and optical measurements were field-filtered through a double-layer of pre-combusted (450°C, 4 h) Whatman GF/F filters (nominal pore size 0.7 µm) and collected into 40 ml acid-washed (soaked with 0.1M HCl, rinsed with MilliQ water) and pre-combusted (450°C, 4 h) glass vials with teflon-coated silicon septa caps (soaked with 0.1M NaOH for at least 8 h and rinsed several times with MilliQ water). Sample water for nutrient analysis and determination of major anion and cation

concentrations was field-filtered at upstream and downstream stations through sterile 0.2 µm Acrodisc® GHP filters (GE, Boulder, Colorado, USA) into 15 ml glass vials (prepared identically as for DOC samples). After returning to the laboratory on the same day, the samples were stored at 4°C in the dark pending analysis within days. Samples were brought to room temperature just before chemical analysis.

3.3 Chemical and optical analysis

Phosphorous (PO_4-P), nitrite (NO_2^-) and ammonium (NH_4^+) concentrations were photometrically determined (DIN EN ISO 6878, DIN 38406-5, DIN EN 26777) using a Hach-Lange DR 2800 spectral photometer (Hach Lange GmbH, Düsseldorf, Germany). Additionally I chromatographically determined nitrate (NO_3^-) with the Metrohm Compact 761 ion chromatograph (Metrohm, Herisau, Switzerland). DOC concentration was measured using a Sievers 5310C (GE, Boulder, Colorado, USA) total organic carbon analyzer fitted with an inorganic carbon removal unit.

DOM absorbance spectra and fluorescence excitation-emission matrices (EEMs) were measured simultaneously on an Aqualog (Horiba Ltd, Kyoto, Japan) using a 1 cm quartz cuvette and a scan speed of 12,000 nm min^{-1} with a response time of 0.01 s. MilliQ-Water was used as a blank.

Natural DOM contains visible and UV light absorbing molecules or functional groups. This chromophores-containing part of DOM is termed chromophoric DOM (CDOM). Absorption spectra of CDOM were measured from 250 to 600 nm with 5 nm increments. Naperian absorption coefficients were computed by multiplying the decadal absorbance at each wavelength by 2.303/cuvette path length in meters (Green and Blough 1994). The absorption coefficient at 440 nm (a_{440}) is used as a general indicator of the total amount of CDOM (Cuthbert & del Giorgio, 1992). The DOC-standardized version of a_{440}, SA_{440}, and the specific UV absorption at 254 nm ($SUVA_{254}$), which commonly serves as a predictor of aromaticity (Weishaar et al. 2003), were computed by dividing decadal absorbance at wavelengths 440 nm and 255 nm, respectively, by the cuvette path length (in m) multiplied by the DOC concentration (mg C L^{-1}). The ratio of the absorption coefficients a_{255} and a_{365} (a_{255}/a_{365}) is negatively correlated with molecular weight (De Haan 1993; Dahlén, Bertilsson, and Pettersson 1996). Furthermore I computed a commonly used slope ratio (S_R), which is the ratio

of the slopes of the linearized absorption coefficients at wavelength 275 to 295 nm and 350 to 400 nm; S_R is negatively correlated to molecular weight of DOM and has been identified as an indicator of photodegradation-induced shifts in molecular weight (Helms et al. 2008).

Certain DOM-fractions have fluorescent properties (FDOM). Fluorescence is the emission of light by a substance following excitation by light of higher energy, i.e. shorter wavelength. It occurs, when an electron, which got excited due to absorbed light, returns to its initial state. The Stokes' shift is the difference in wavelength between excitation light and emitted light. Emitted light principally has a longer wavelength than the excitation light due to lower energy. Analyzing EEMs is an approach to characterize DOM mixtures, since excitation and emission wavelength are specific to molecules or at least functional groups of molecules known as fluorophores (Lakowicz 1999; Stedmon and Markager 2005). EEMs were obtained by scanning fluorescence over an excitation wavelength from 250 to 600 nm (5 nm increments) and an emission range of 250 to 550 nm (1.77 nm increments). I corrected EEMs for: (i) the water Raman scatter, the light induced, visible effect of vibrating molecular O-H bonds of water; (ii) the Rayleigh-Tyndall effect, the reflection of excitation energy off the cuvette walls; and (iii) the inner filter effect, which is the disproportional decrease in fluorescence with increasing absorbance, hence higher DOC concentration (McKnight et al. 2001; Parlanti et al. 2000).

Based on EEM spectra, I calculated the fluorescence index (FI), the humification index (HIX) and the freshness index (β/α). The FI provides information about the source of DOM, which is either terrestrially derived (FI~1.2) or microbially derived (FI~1.9*).* I calculated the FI as the ratio of emission intensity at a wavelength 450 to that at 500 nm for an excitation of 370 nm (McKnight et al. 2001). The HIX was computed as the peak area under the emission spectra from 435 to 480 nm divided by the peak area under the emission spectra from 300 to 445 nm at an excitation wavelength of 254 nm (Zsolnay et al. 1999). The HIX indicates the extent of humification or the humic substance content and is based on the assumption that decreasing H:C ratios, due to humification of DOM, cause a shift in emission spectra towards longer wavelengths. A high HIX value indicates an increased degree of humification (Zsolnay et al. 1999; Ohno 2002). I also calculated the β/α index by dividing the emission intensity at 380 nm to the maximum emission intensity observed between 420 and 435

nm, all obtained for an excitation wavelength of 310 nm (Wilson and Xenopoulos 2009). β indicates more recently produced, respectively more autochthonous DOM, and α indicates more decomposed, respectively more allochthonous DOM (Parlanti et al. 2000; Wilson and Xenopoulos 2009); the ratio β/α is thus used as an indicator for freshness.

EEMs obtained from this study and additional EEMs obtained from the confluences of the investigated streams were subjected to parallel factor analysis (PARAFAC). PARAFAC is a multivariate modeling technique that extracts a structure of redundant, wavelength- independent excitation and emission maxima from all analyzed EEMs. I modeled five fluorescent components on the basis of 386 EEMs and estimated their contribution to the additively formed total signal (Bro 1997; Stedmon and Bro 2008). PARAFAC was conducted using Matlab (version 7.11.0, MathWorks) and the DOMFluor Toolbox (1.7) following the manual of Stedmon & Bro (2008). For identifying the fluorescent components, I compared our excitation/emission maxima with fluorophores reported in the literature (Table 1).

3.4 Metabolism modeling

I calculated whole-stream metabolism using the one- and two-station open stream channel method based on diel dissolved oxygen (DO) concentrations in the water (Odum 1956; Marzolf, Mulholland, and Steinman 1998). Both methods rely on the assumption that temporal changes in DO concentration (*dDO/dt*) are the result of gross primary production (*GPP*), ecosystem respiration (*ER*) and reaeration (*RF*, Eqn 1.):

$$dDO/dt = GPP - ER + RF \quad (1)$$

where *GPP* is the rate of converting solar energy to chemical energy by photosynthesis, hence adding DO to the water; *ER* is the rate of respiration of all autotroph and heterotroph biota, therefore consuming DO; and *RF* is the gas exchange at the water-air interface and is either responsible for DO loss or gain in the stream water. All three terms are expressed as area-specific fluxes (g O_2 m^{-2} min^{-1}) and need to be scaled by depth to be expressed as changes in volumetric DO concentration. DO-based open stream channel methods rely on an observed record of discrete DO measurements,

which is either used to compute the various fluxes by manual integration across time intervals (Marzolf, Mulholland, and Steinman 1998) or for fitting an adequate numerically solvable differential equation model (e.g., Van de Bogert et al. 2007; Hotchkiss & Hall 2014).

3.4.1 **Modelling metabolism for one-station DO data**

For the one-station approach, *dDO/dt* is approximated by *ΔDO/Δt*, i.e. the observable change of DO concentration from one measurement to the next measurement in time at one station.

To account for light-saturated photosynthesis, I expressed *GPP* (g O_2 m^{-2} min^{-1}) with a photosynthesis-irradiance (P-I) curve (Ratkowsky 1986; Uehlinger, König, and Reichert 2000);

$$GPP = \frac{PAR}{P1+P2\times PAR} \quad (2)$$

where *PAR* (W m^{-2}) is the time-specific photosynthetically active radiation. P_1 (W min g^{-1} O_2) is the inverse of the slope of the P-I curve at low light intensity and P_2 (m^2 min g^{-1} O_2) is the inverse maximum photosynthesis rate. Setting P_2 = 0 turns the light-saturated curve to a linear model with no light saturation. For an entire day, i.e. a time period [t_0, t_{end}] covering 24 hours, *GPP24* (g O_2 m^{-2} day^{-1}) can be calculated in a next step from P_1, P_2, the light record and the time step Δt between light measurements:

$$GPP24 = \sum_{t=t0}^{tend} \frac{PAR_t}{P1+P2\times PAR_t} \times \Delta t \quad (3)$$

ER (g O_2 m^{-2} min^{-1}) is a strongly temperature-dependent process with increasing rate at increasing temperature (Kirschbaum 1995). I therefore modified *ER* with the van't Hoff–Arrhenius equation (Parkhill and Gulliver 1999):

$$ER = \frac{ER24_{20}}{(24\times60)} \times 1.045^{(T-20)} \quad (4)$$

where $ER24_{20}$ (g O_2 m^{-2} d^{-1}) is the daily rate of ecosystem respiration standardized to 20°C and *T* (°C) is the time-specific observed water temperature. In order to investigate ER at in-situ temperature ($ER24_{insitu}$; g O_2 m^{-2} d^{-1}) I converted estimated $ER24_{20}$ with the van't Hoff–Arrhenius equation (Parkhill and Gulliver 1999) using recorded in-situ temperature measurements *T* (°C) for every time interval Δt.

$$ER24_{insitu} = \sum_{t=t0}^{tend} \frac{ER24_{20}}{(24\times60)} \times 1.045^{(T_t-20)} \times \Delta t \quad (5)$$

The reaeration flux *RF* (units: g O_2 m^{-2} min^{-1}) was computed as

$$RF = k \times DO_{deficit} \quad (6)$$

where *k* is the temperature-dependent vertical gas exchange velocity (m min^{-1}), and $DO_{deficit}$ (g m^{-3}) is the difference of the observed DO concentration (*DO*) to DO at 100% saturation (DO_{Sat}):

$$DO_{deficit} = DO_{Sat} - DO \quad (7)$$

DO_{Sat} (g m^{-3}) is the time-specific theoretical concentration of DO at saturation (stream water in equilibrium with the atmosphere, hence no exchange of oxygen across the air-water interface) calculated from water temperature and atmospheric pressure (Benson and Krause 1984). I used time-specific observed water temperature, but constant atmospheric pressure averaged from two readings taken before and after DO sonde deployment. A positive $DO_{deficit}$ (g m^{-3}) indicates oxygen undersaturation in the stream water, resulting in a positive *RF* and net oxygen transfer from the atmosphere into the stream water. A negative $DO_{deficit}$ indicates oxygen oversaturation in the stream water, resulting in a negative *RF* and net O_2 transfer from the stream water to the atmosphere.

The vertical gas exchange velocity *k* (m min^{-1}) can be computed from the reaeration coefficient *K* (min^{-1}) by multiplication with depth (m); it describes how well the water body can exchange gas with the atmosphere and is purely physically controlled by turbulence features of the water body and

characteristics of the surface layer (Marzolf, Mulholland, and Steinman 1998; Raymond et al. 2012). Temperature-dependence of gas exchange is described by Elmore and West (1961) and Bott (2007) as:

$$K_T = K_{20} \times 1.024^{T-20} \quad (8)$$

where K_T is the reaeration coefficient at an arbitrary target temperature and K_{20} is a reference value for K at 20°C. Vertical gas exchange efficiency and reaeration fluxes are critical for metabolism estimations and I followed 3 different strategies to reliably constrain k:

First, I analyzed the night-time drop in DO concentration according to Hornberger and Kelly (1975). This method is based on equation (1) at nighttime, when GPP equals 0:

$$dDO/dt = -ER + RF \quad (9)$$

Expressing RF as in equation (5) and following equation (8) to standardize K to 20°C (K_{20}, min^{-1}) equation (9) results in:

$$dDO/dt = -ER + K_{20} \times 1.024^{T-20} \times DO_{deficit} \quad (10)$$

which is a linear equation $Y=b_0+b_1X$ *with* $Y=dDO/dt$, $b_0=-ER$, $X=1.024^{T-20}DO_{deficit}$ and $b_1=K_{20}$. A regression line was fitted to the plotted decrease in dissolved oxygen concentration per minute ($\Delta DO/\Delta t$) after sunset (according to the measured PAR) versus $DO_{deficit}$ multiplied by the temperature correction. The regression equation (10) described the regression line, where the slope is the estimate of K_{20} (min^{-1}) and the intercept is an estimate of ER (g O_2 m^{-2} min^{-1}).

Secondly, three empirically derived equations were used for K_{20} estimations:

$$K_{20} = K' \times 10^3 \times (\Delta H/\Delta X) \times v \quad (11)$$

$$K_{20} = 2.422 \times v^{0.607}/z^{1.689} \quad (12)$$

$$K_{20} = 14.12 \times v^{0.607} \times s^{0.273}/z^{1.408} \quad (13)$$

The energy dissipation model (Eqn 11; Tsivoglou & Neal 1976) computes K_{20} (d^{-1}) from the average velocity v (m s^{-1}), the water surface slope $\Delta H/\Delta X$ (m m^{-1}), and the discharge Q-dependent constant K' (s m^{-1} d^{-1}). The Q-dependent constant K' is 31.1 for small streams with Q < 0.3 m^3 s^{-1}, 21.3 for a Q of 0.3 to 0.56 m^3 s^{-1} and 15.3 for larger streams with Q > 0.56 m^3 s^{-1}. Equations (12) and (13) are provided by Bennett & Rathbun (1972) and compute K_{20} (d^{-1}) from the streambed slope s (m m^{-1}) and the average depth z (m). Equations (11) to (13) estimate K_{20} in units d^{-1} and were converted to min^{-1}.

Thirdly, I directly estimated K_{20} as part of the model fitting process (see below) with starting values estimated by the first two methods.

For a final model of whole-stream metabolism based on the one-station approach, equations (1-5) and (6-8) are combined to predict a discretized time series of DO using observed time-specific temperature and light conditions, barometric pressure and an arbitrarily chosen parameter set P_1, P_2, $ER24_{20}$ and K_{20} (Van de Bogert et al. 2007; Hotchkiss and Hall 2014):

$$DO_{t+1} = DO_t + (GPP_t - ER_t + RF_t) \times \Delta t \times \frac{1}{z} \quad (14)$$

Here, DO_{t+1}, the DO concentration at the next point in time t+1 (g O_2 m^{-3}) is computed from DO_t, the DO concentration at the previous time point t, and the terms *GPP*, *ER* and *RF* computed from temperature and light conditions at the previous time point t. Δt is the time interval between t and t+1, it is needed to scale up the minute-specific rates accordingly and is appropriately chosen identical to the observed time series. The average depth z (m) converts areal fluxes into volumetric units of concentration. For the one-station approach I took the average PAR from both upstream and downstream stations. Barometric pressure was assumed constant. Equation (13) is essentially a numerical solution of the differential equation given by equation (1) by forward differencing or Eulerian integration (Soetaert and Herman 2009). A first observed DO measurement is used as a boundary condition (DO_{t0}), from which all subsequent DO_t values are computed.

To estimate whole stream metabolism, i.e., cumulative diurnal gross primary production (GPP24) and $ER24_{20}$, from an observed DO time series covering 24 hours, I used equation (14) in an inverse

modeling approach that repeatedly models a DO time series with updated parameter values and checks the quality of fit to the observed DO time series. The parameters P_1, P_2, $ER24_{20}$ and – optionally in a second step – K_{20} were fitted using the normal negative log likelihood (Hilborn and Mangel 1997) of squared deviations between measured DO concentration and predicted DO concentration as the objective function for minimization.

3.4.2 **Two-station method**

In the two-station approach, *dDO/dt* is again approximated by $\Delta DO/\Delta t$, which, however, here is the observed change of DO concentration in a water parcel travelling from the upstream site to the downstream site over travel time τ (min).

Similar to equation (13) the DO at the downstream site one travel time later is predicted from DO measured at the upstream site by:

$$\mathrm{DO}_{dw,t+\tau} = \mathrm{DO}_{up,t} + (\mathrm{GPP} - \mathrm{ER} + \mathrm{RF}) \times \tau \times \frac{1}{z} \quad (15)$$

where *GPP*, *ER* and *RF* are average fluxes computed from the (average) light and temperature conditions during the interval [t,t+τ]. The travel time τ (min) upscales the minute-specific rates accordingly. The average depth *z* (m) converts areal fluxes into volumetric units of concentration. For equation (14) an average *GPP* is computed by:

$$GPP = (\sum_{i=1}^{n} \frac{\overline{PAR}_i}{P1+P2\times\overline{PAR}_i})/n \quad (16)$$

where $\overline{PAR}$ is the average PAR across upstream and downstream station at *n* points in time in the interval [t,t+τ]. ER was expressed as shown in equation (4) and using the average water temperature measured at the upstream and at the downstream site one travel time later. Similarly, average *RF* was expressed based on gas exchange and DO saturation computed from water temperature measured at the upstream and at the downstream site one travel time later:

$$RF = \left[k_{up,t} \times (DO_{Sat,up,t} - DO_{up,t}) + k_{dw,t+\tau} \times (DO_{Sat,dw,t+\tau} - DO_{dw,t+\tau})\right] \times 0.5 \quad (17)$$

Here, k (m min^{-1}) computation followed equations (8-13), or was fitted during the inverse modeling step. $DO_{Sat,up,t}$ (g m^{-3}) is the upstream site-concentration of DO at saturation and $DO_{Sat,dw,t+\tau}$ is the downstream site-concentration of DO at saturation one τ later, both calculated from measured water temperature at the corresponding site and atmospheric pressure (Benson and Krause 1984). Plugging in equation (17) into equation (15) and solving for $DO_{dw,t+tau}$ gives:

$$DO_{dw,t+\tau} = [DO_{up,t} + GPP \times \frac{1}{z} \times \tau - ER \times \frac{1}{z} \times \tau + \left(k_{up,t} \times (DO_{Sat,up,t} - DO_{up,t}) + k_{dw,t+\tau} \times DO_{Sat,dw,t+\tau}\right) \times 0.5 \times \frac{1}{z} \times \tau] \times \frac{1}{1+k_{dw,t+\tau} \times 0.5 \times \frac{1}{z} \times \tau} \quad (18)$$

which predicts a discretized time series of downstream DO from observed time series of upstream DO, temperature and light conditions, barometric pressure and an arbitrarily chosen parameter set P_1, P_2, $ER24_{20}$ and k_{20} (Hotchkiss and Hall 2014). Again, equation (18) can be used in an inverse modeling approach that repeatedly models the downstream DO time series with updated parameter values and checks the quality of fit to the observed downstream DO time series using the normal negative log likelihood (Hilborn and Mangel 1997) of squared deviations between measured DO concentration and predicted DO concentration as the objective function for minimization.

3.5 Statistical methods and data analysis

In order to compare reaeration coefficients and estimates for GPP and ER derived by the various above explained methods, I employed Pearson's product moment analyses. To assess consistency among one-station and two-station methods, I conducted a paired t-test on square root transformed GPP and ER values.

A principal component analysis (PCA) based on percentages of land-use categories in the stream catchment reduced the multivariate dataset of land-use categories to two conspicuous principal components (PC). I further employed PCA to describe "DOM quality" by two linear combinations of absorption-derived indices (S_R, SA_{440}, $SUVA_{254}$, a_{255}/a_{365}), fluorescence indices (FI, β/α, HIX) and PARAFAC-components (C1 to C5) of all 33 sites. For this analysis, all used variables either represent

ratios of optical measurements or were standardized for DOC concentration to strictly explore DOM composition independent of concentration.

Further, I used structural equation modelling (SEM) for testing our a priori formulated hypotheses. GPP is thought to be driven by light rather than by temperature. Also, water temperature was fairly similar among studied streams (9.3°C ± 12%) while the variation in daily global radiation at the reference site 24 (910 J cm^{-2} ± 44%) during study duration was substantial. Thus I considered only light as a short-term physical control on GPP (Figure 1). Prior to SEM a Shapiro-Wilk test was used to test all variables for normal distribution. SEM was conducted on PC 1 and PC 2 derived by the PCA of the land-use categories, PC 1 and PC 2 derived by the PCA of the optical DOM parameters, log-transformed light, DOC, DIN and SRP data and square root transformed GPP and ER (standardized to 20°C) data. Starting with the full model with all hypothesized paths, I identified the most parsimonious model by stepwise backward elimination of weak paths as assessed by their p-values and comparing the resulting Akaike Information Criterion (AIC) with the previous model.

All statistical analyses were performed with R version 3.0.3. (R Core Team 2014), using packages *vegan* (Oksanen et al. 2013), *sem* (Fox 2006), *shape* (Soetaert 2014) and *chron* (James, Horni, and Grothendieck 2014).

4 Results

4.1 Characteristics of the investigated catchment areas and streams

The catchment areas of the 33 investigated sites ranged between 15.85 km^2 at site 12 and 316.44 at site 24 (Table 3, *Appendix*). Agricultural areas dominated land use in the catchment areas with an average relative cover of 52%; across individual catchments the fraction of agricultural areas ranged from 4% at site 28 to 90% at site 16 (Table 3, *Appendix*). Coniferous forest contributed on average 36% to all catchments, ranging from no coniferous forest at sites 16 and 17 to 94% at site 28. Even though mixed forest accounted for only 8% in average, it was the dominant land-use type at sites 32 and 17 with 59% at the latter. Urban areas with a mean of 2%, semi-natural areas and water bodies with a mean below 1% contributed little to the catchment land-use composition. The PCA based on percentages of land-use categories in stream catchments produced two conspicuous gradients (Figure 3). PC 1 accounted for 45.7% of the variance and was a gradient ranging from agricultural land use-dominated catchments combined with smaller contributions of urban areas to catchments dominated by coniferous forest. PC 2 additionally explained 22.5% of the variance and ordered streams along a gradient specifically identifying mixed forest contribution relative to the other land-use categories.

The slope of the streambed ranged from 0.01 to 2.59 cm m^{-1}, mean depth ranged from 0.11 to 0.63 m, mean width ranged from 1.48 m 16.54 m and the mean velocity between upstream and downstream station ranged from 0.06 to 0.42 m s^{-1}. Discharge values estimated at the downstream station ranged from 0.030 to 1.155 m^3 s^{-1}. The variations across the individual depth and width measurements can serve as a proxy for habitat heterogeneity; the standard deviation of the depth ranged from 0.07 to 0.35 m and of the width from 0.30 to 3.23 m (Table 4, *Appendix*).

Dissolved inorganic nitrogen (DIN) was calculated as the sum of NH_4-N and NO_3-N and varied by a factor 10, from 3.1 to 31.4 mg N L^{-1}. NH_4-N never contributed more than 1.6% to DIN at any stream. Soluble reactive phosphorous (SRP) ranged from 9.2 to 157.3 µg P L^{-1} (Table 4, *Appendix*). The N:P ratio based on above mentioned concentrations, ranged from 80 to 1198.

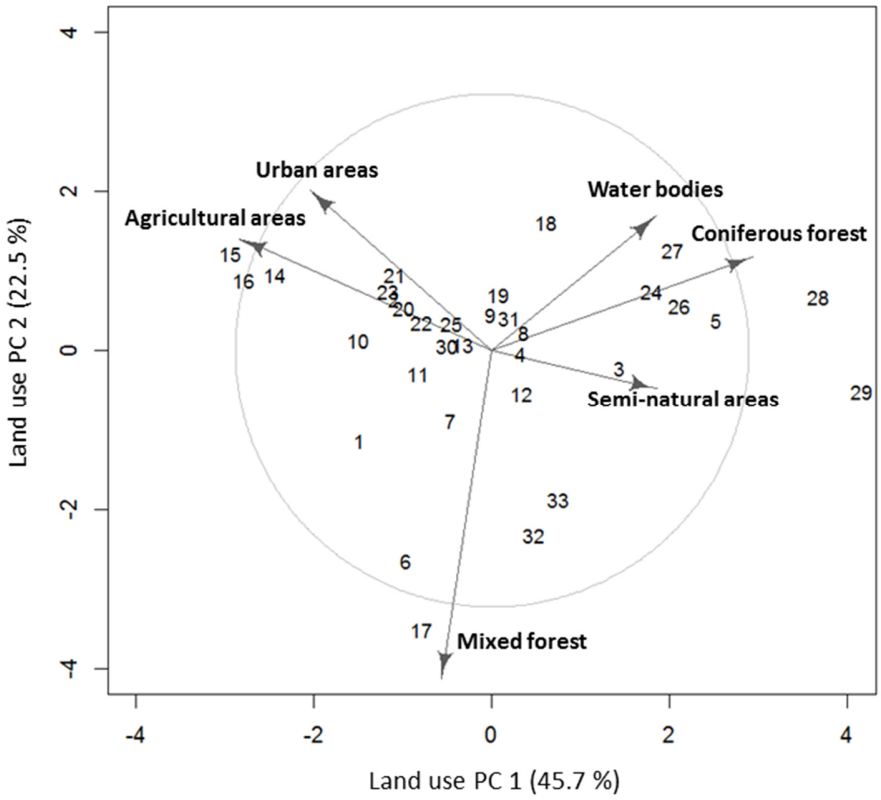

Figure 3 Principal component analysis (PCA) based on land-use distribution in the entire catchments of all 33 investigated streams. Arrows are based on PCA structure coefficients; those reaching beyond the circle contribute more than on average.

4.2 DOM composition

PARAFAC identified 5 components from the excitation-emission matrices (Figure 4, Table 1). Components 1 to 3 were all identified as clearly humic-like and likely of terrestrial origin, but differed in their degree of processing. Component 4 and 5 originated from allochthonous and autochthonous sources, in which the first was identified as humic-like and the latter as protein-like.

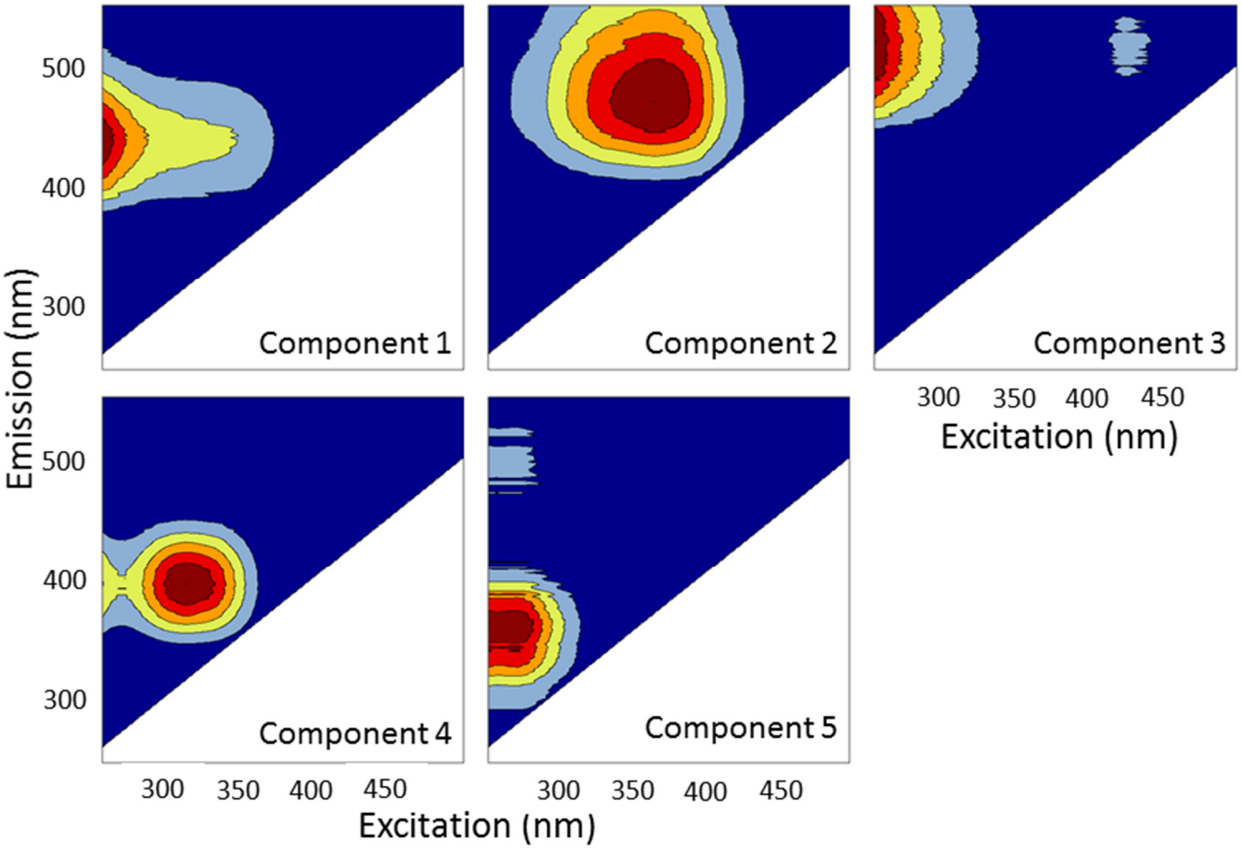

Figure 4 Excitation and emission matrices (EEMs) of the five components modelled with the PARAFAC analysis.

Table 1 The excitation and emission peaks of the five PARAFAC components (Figure 4) with corresponding peaks and descriptions from previous studies.

PARAFAC component	Excitation peak (nm)	Emission peak (nm)	classical peak (Coble, 1996)	Description*
C1	260	442	Peak A	humic-like , highly processed, of terrestrial origin
C2	370	470	Peak C	humic-like, less processed, of terrestrial origin
C3	260	520	shoulder of Peak A	humic-like, highly processed, of terrestrial origin
C4	315	394	Peak M/N	humic-like, microbially processed of terrestrial origin and from autochthony
C5	260	362	Peak T	protein-like, freshly added, of terrestrial origin and from autochthony

*The following literature was used: Coble (1996), Parlanti et al. (2000), Baker (2001) , Stedmon et al. (2003), Stubbins et al. (2014)

The PCA based on the optical properties of all 33 investigated streams produced two conspicuous gradients (Figure 5). PC 1, which explained 57.0% of the variance, was mainly formed by the positively loading optical parameters FI, β/α and a_{255}/a_{365} and the PARAFAC component 5, which were all negatively correlated with $SUVA_{254,}$ HIX and SA_{440}. This main gradient of DOM composition identified by PC 1 largely agreed with the main land-use gradient identified by the respective PCA on land-use data (Pearson´s correlation coefficient: $r = 0.86$, $n = 33$, $P < 0.001$). PC 2 accounted for further 23.3% of the variance and was primarily defined by the PARAFAC components 2 and 3, which both were negatively correlated with the S_R. PARAFAC components 1 and 4 could not be related to PC 1 or PC 2.

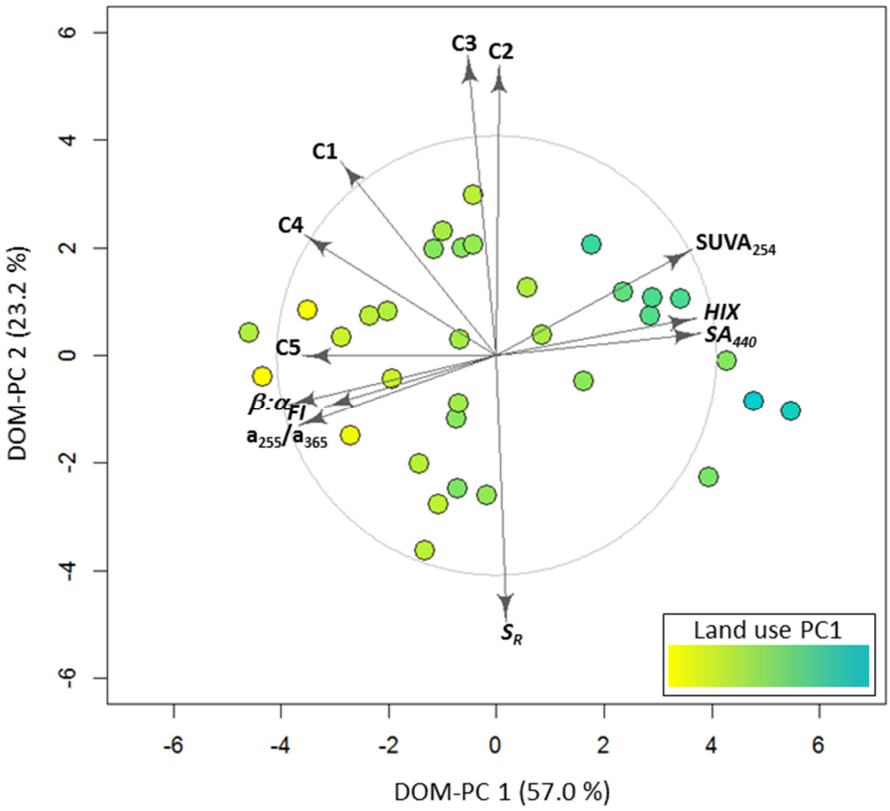

Figure 5 Principal component analysis (PCA) based on absorbance coefficients, fluorescence indices and the DOC-normalized PARAFAC-components for all of the 33 streams. DOC-standardized specific absorption at 440 nm (SA_{440}) and 254 nm ($SUVA_{254}$) represent the relative amount of CDOM and aromaticity, respectively. The slope ratio (S_R) and a_{255}/a_{365} are inversely correlated with molecular weight. The humification index (HIX) serves as a proxy for the extent of humification or the humic substance content. The fluorescence index (FI) and the freshness index (β/α) are positively correlated to more recently produced, thus, more autochthonous DOM. C1 to C5 are the DOC-standardized fluorescent components identified by PARAFAC (Table 1). Arrows are based on PCA structure coefficients and contribute more than on average when reaching out of the circle. The sites are color-labeled by the principal component 1 derived from the land-use PCA (Figure 3).

4.3 Assessment of reaeration

Knowledge about reaeration is crucial for metabolism estimation (Thyssen et al. 1987; Mulholland et al. 2001), but due to time constraints I could not directly measure reaeration by gas tracer injection in the field. I therefore assessed multiple approaches to estimate reaeration: reaeration coefficients (K_{20}) were derived either by the night-time regression method, empirically derived equations or directly modeled in concert with metabolism.

Since the night-time method of Hornberger and Kelly (1975) is based on recorded DO data and is recommended by Young et al. (2004), it was our method of choice for estimating K_{20}. A potential disadvantage of this method is its low reliability in cases of low GPP or very efficient gas-exchange, which both cause DO to stay close to saturation; then this method results in poor linear fits and hence poor estimates of K_{20} (Young and Huryn 1996, Uehlinger 2000). I decided to use K_{20} estimations derived from night-time regressions with good fits assessed by an arbitrarily chosen r^2 threshold of 0.25. The resulting 11 sites with a reliable K_{20} estimation by the night-time method (Table 5) were compared with the K_{20} estimates from empirically derived equations (11) to (13) and modeled K_{20} values derived by the one-station model (Eqn. 14) as well as by the two station model (Eqn. 15) (Figure 6). Pearson's product moment analyses showed the highest correlation between K_{20} values estimated by the night-time method and the K_{20} values estimated by the one-station ($r = 0.99$, $n = 11$, $P < 0.001$) and the two-station model ($r = 0.99$, $n = 11$, $P < 0.001$). Both methods have their asset in estimating K_{20} based on recorded DO concentrations but as in the night-time method the reliability of the modeled K_{20} declines in unproductive or turbulent streams.

Among the empirically derived K_{20} values, estimates by the energy dissipation model (Eqn 11; Tsivoglou & Neal 1976) showed the highest accordance with K_{20} values estimated by the night-time method ($r = 0.91$, $n = 11$, $P < 0.001$). This result is in accordance with a study by Aristegi et al. (2009) comparing several methods to calculate reaeration coefficients. Further, the energy dissipation model has been recommended by APHA (1992) for use in open-stream channel methods and Mulholland et al. (2001) assume acceptable K_{20} estimations derived by this model in streams with a water depth > 6 cm. The shallowest stream in our study had an average depth of 11 cm. Thus, I used

the energy dissipation model for K_{20} estimations at those sites, where unreliable K_{20} values were estimated by the night-time method.

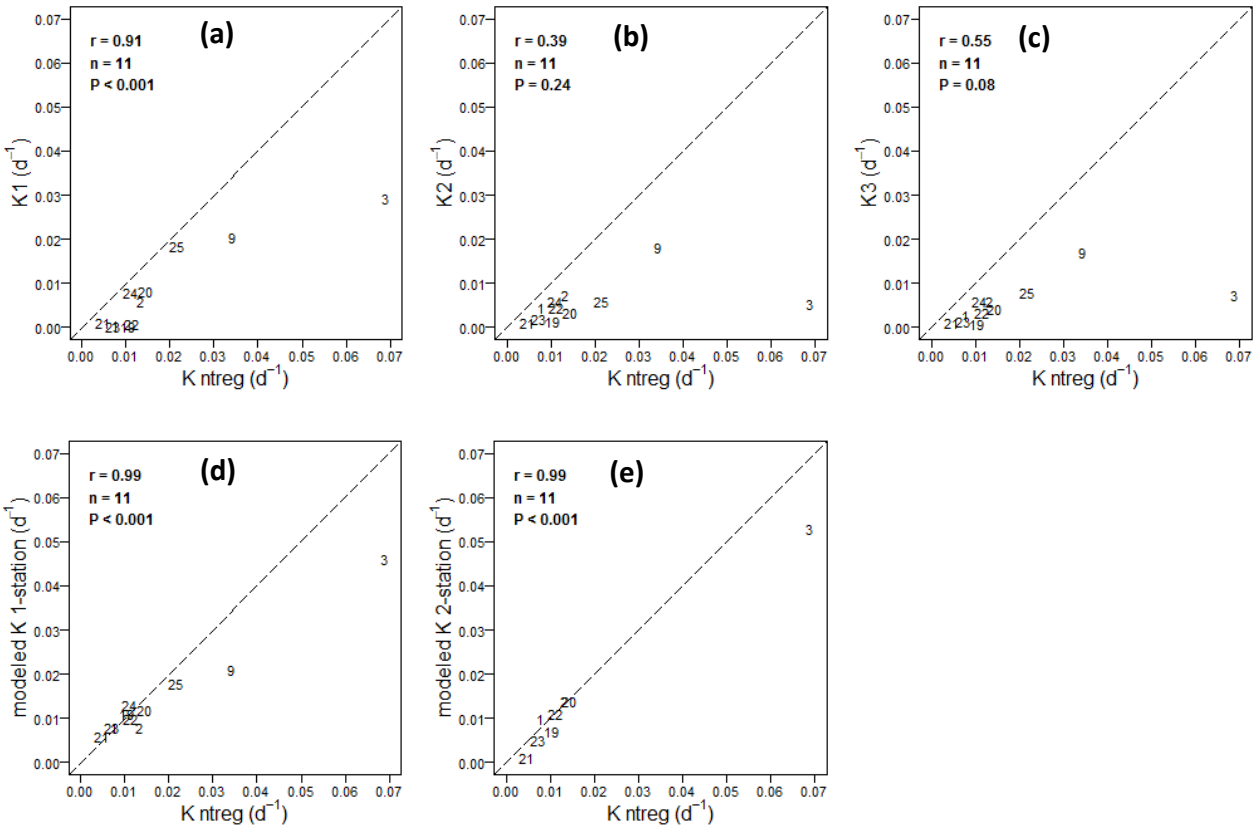

Figure 6 Correlations between reaeration coefficients derived by night-time regression (K ntreg) and reaeration coefficients derived by empirical equations (11) to (13) **(a-c)** and modeled reaeration coefficients by one-station **(d)** and two-station **(e)** approach. Dashed lines indicate 1:1 relationships. Site code is given in Table 3

4.4 Metabolism

I estimated whole-stream metabolism, i.e. ecosystem respiration (ER) and gross primary production (GPP) using the one- and two-station open stream channel method.

In a first trial metabolism was modeled using a more parsimonious model under the assumption of a linear PI-curve. Comparisons with model results using a 2 parameter PI-curve revealed clearly superior fitting quality for the latter and I therefore modeled metabolism at all sites using the 2 parameter PI-curve (Figure 7).

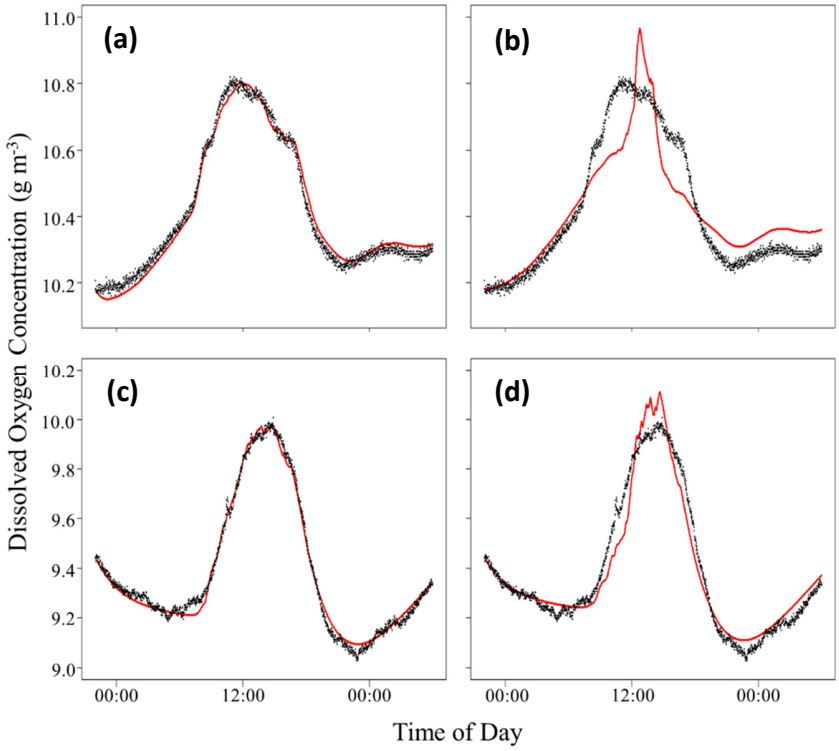

Figure 7 Black points indicate measured DO concentrations and the red line indicates predicted DO concentrations by the one-station model for site 2 **(a,b)** and site 15 **(c,d)** with saturating photosynthesis-irradiance curve **(a,c)** and with linear photosynthesis-irradiance relationship **(b,d)**.

Across all sites, GPP ranged from 0.001 to 6.025 g O_2 m^{-2} d^{-1} and ER_{20} ranged from 1.774 to 45.504 g O_2 m^{-2} d^{-1} (ER_{insitu}: 1.121 to 30.035 g O_2 m^{-2} d^{-1}) derived by the one-station approach modeled with fixed K_{20} estimates. GPP estimates modeled by the two-station approach with fixed K_{20} estimates ranged from 0.001 to 5.698 g O_2 m^{-2} d^{-1} and ER_{20} ranged from 0.996 to 45.639 g O_2 m^{-2} d^{-1} (Table 6, *Appendix*). To evaluate consistency of the two approaches, paired t-tests with square root transformed GPP and ER values were conducted. Estimates of GPP and ER using the one-station approach were not different than those made with the two-station approach (paired t-test; GPP: T-value = -1.35, P = 0.19, df = 25; Figure 8 (a); ER: T-value = 0.33, P = 0.74, df = 25; Figure 8 (d)). The variation of GPP and ER estimates was lower at comparisons among one- and two-station approaches (Figure 8 (a), (d)) compared to comparisons among same approaches with different methods of estimating K_{20} (Figure 8 (b), (c), (e), (f)). Hence, different estimating methods of K_{20} had higher influence on estimates of GPP and ER than the choice between one- and two-station

approaches. Estimates for ER were more variable across methods; all comparisons among the different approaches for estimating ER (Figure 8 (d-f)) resulted in lower correlation coefficients compared to the correlations among the estimates of GPP (Figure 8 (a-c)). Oxygen logger malfunction or a hardly measurable signal of DO changes in concentration between upstream and downstream station precluded the use of seven GPP and ER estimates derived by the two-station approach. Thus, all further analysis performed used GPP and ER measurements derived from the one-station model.

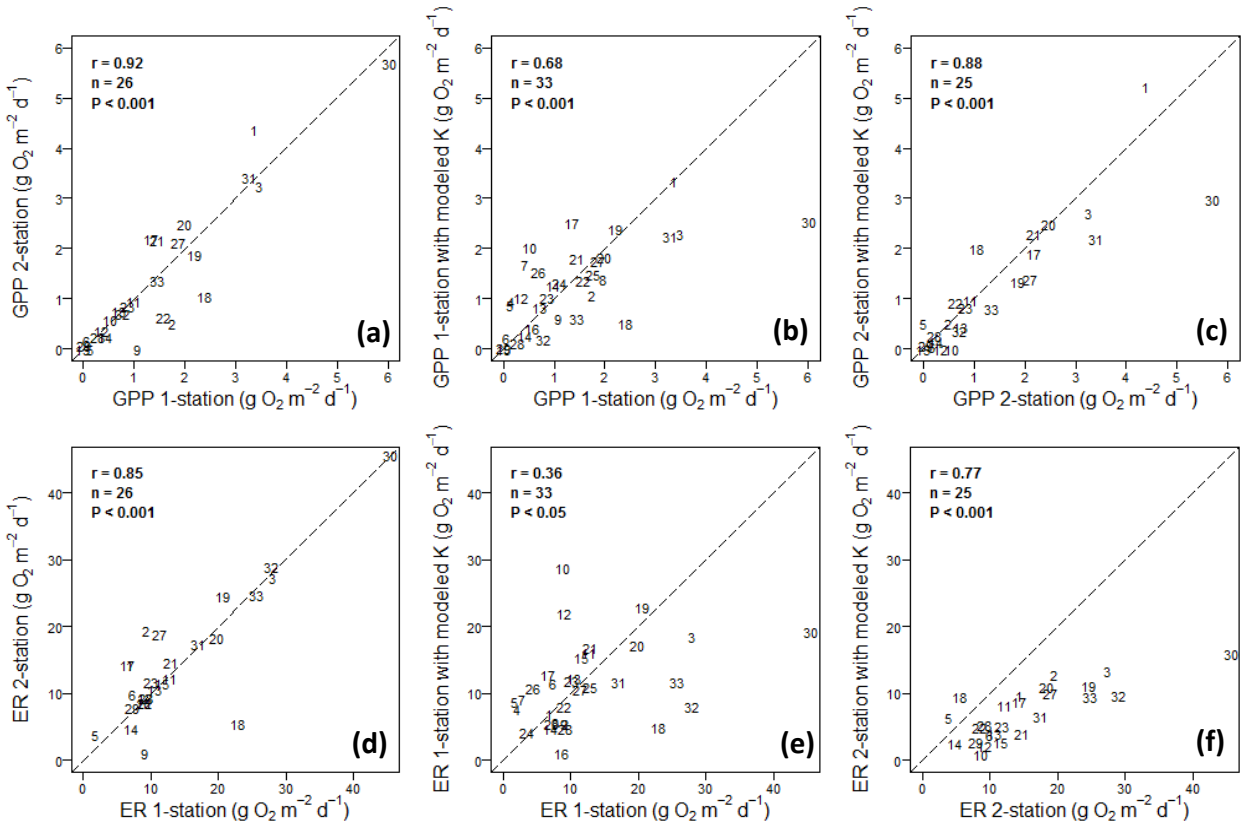

Figure 8 Correlations between estimates of gross primary production (GPP) **(a-c)** and ecosystem respiration **(d-f)** derived by four different approaches: (i) one-station and (ii) two-station approach with reaeration coefficients (K) derived by the night-time method and empirically derived equation (Tsivoglou and Neal 1976) and (iii) one-station and (iv) two-station approach with modeled K values. Dashed lines indicate 1:1 relationships. Site code is given in Table 3.

ER at in-situ temperature was significantly associated with GPP (r^2 = 0.51, $F_{1, 31}$ = 32.87, P < 0.001; Figure 9) and exceeded GPP at all sites. Higher ER rates compared to GPP resulted in a negative net ecosystem productivity (NEP), which is the difference between GPP and ER. NEP ranged from -0.762 g O_2 m^{-2} d^{-1} at site 1 to -23.873 g O_2 m^{-2} d^{-1} at site 30.

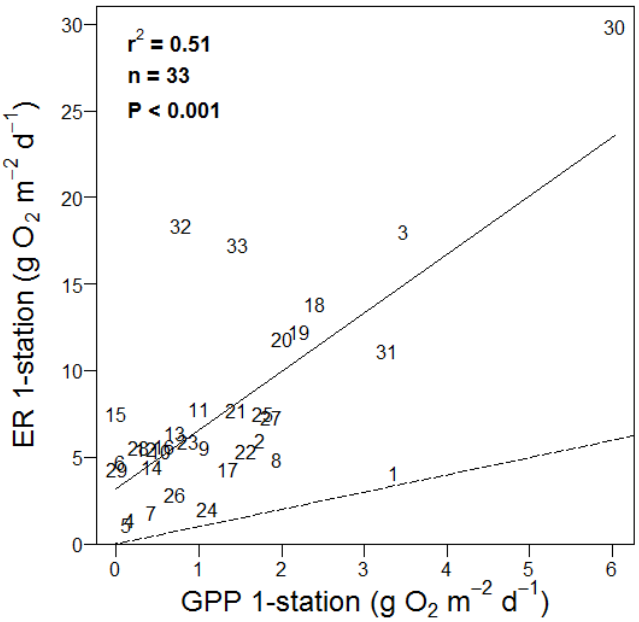

Figure 9 Relationship between daily ecosystem respiration at in-situ temperature (ER) and daily gross primary production (GPP) estimated by the one-station approach. Solid line is the statistically significant (P < 0.001) linear regression ($\boldsymbol{ER} = \mathbf{3.2}\ (\pm\mathbf{1.1}) + \mathbf{3.4}\ (\pm\mathbf{0.6}) \times \boldsymbol{GPP}$). Dashed line indicates 1:1 relationship. Site code is given in Table 3.

4.5 Results of SEM

Structural equation modeling identified significant effects of the physical template (land use and light) on the biogeochemical structure in the streams (DOM composition and DIN, SRP and DOC quantities) and on the stream-function (GPP). Furthermore our model revealed effects of the biogeochemical structure (DOM composition and SRP) on the stream-function (ER) (Figure 10). In detail, significant pathways included positive land-use PC 1 effects on DOM composition PC 1 and

negative effects on DIN and SRP; positive land-use PC 2 effects on DOC quantity and negative effects on DIN; positive light effects on GPP; positive DOM composition PC 1, SRP and GPP and negative DOM composition PC 2 effects on ER at 20°C. The effect of GPP on ER at in situ temperature is shown in Figure 9. Land use did not affect light conditions and GPP showed no significant imprint on DOM composition. Further, the concentration of DIN and SRP had no significant influence on GPP and DOC quantity had no significant effect on ER. The final model was no significant fit to the covariance matrix (χ^2 = 65.2, df = 34, P < 0.01).

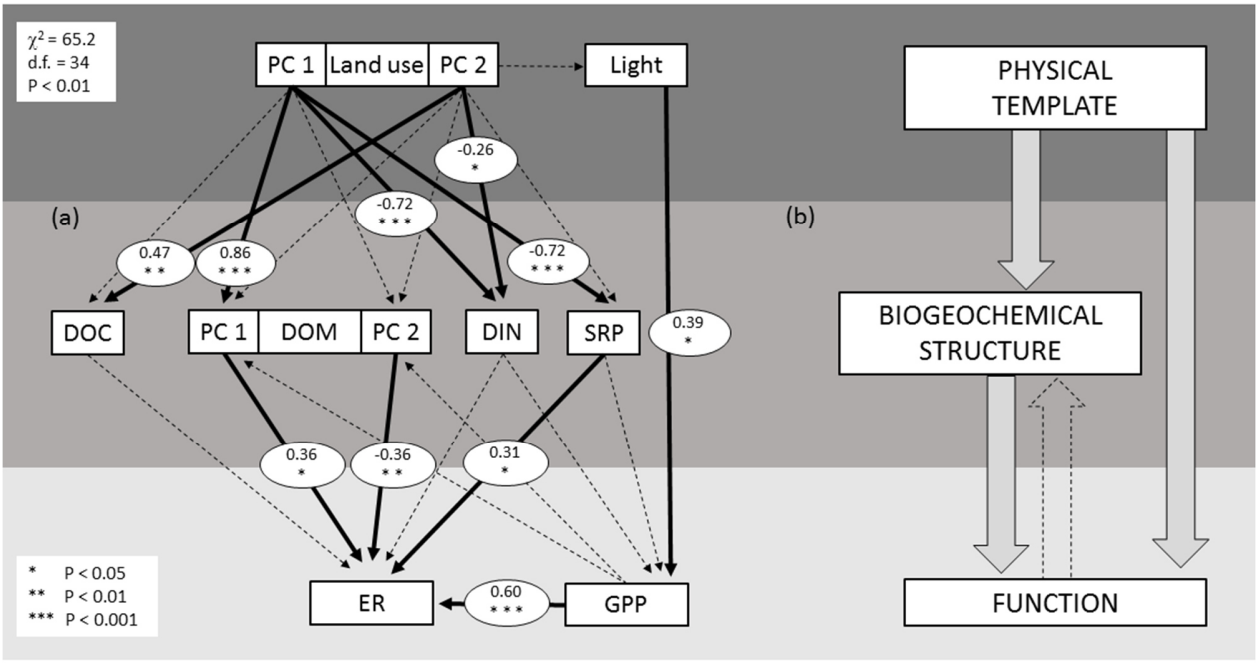

Figure 10 (a) Structural equation model to describe effects of land use on dissolved organic matter composition (DOM) and the concentrations of dissolved inorganic nitrogen (DIN), soluble reactive phosphor (SRP) and dissolved organic carbon (DOC), and their linkage to ecosystem respiration at 20°C (ER) and gross primary production (GPP). Boxes are variables in the model, where DOC, DIN, SRP and light variables were log-transformed, ER and GPP were square root-transformed. Numbers and asterisks in ellipses are path coefficients and their significance levels (legend given at lower left), respectively. Dashed arrows indicate a priori hypothesized pathways that were not significant in previous model runs and removed prior to producing the final fit shown here. Model fit statistics are given at upper left. **(b)** Conceptual diagram of **(a)** where the physical template summarizes the most important long-term (land use) and short-term (light) physical controls, the biogeochemical structure consists of concentrations describing resource pools (DOC, DOM, DIN and SRP) and the functions are represented by ER and GPP.

5 Discussion

5.1 Land-use controls on quantity and composition of DOM and on nutrient concentrations

Due to the tight linkage between fluvial networks and their surrounding terrestrial ecosystems, I hypothesized that land use affects the composition of aquatic DOM (Figure 1). The PCA based on the optical properties of all 33 investigated streams suggested a strong effect of land use on the DOM composition (Figure 5). This finding was supported by SEM, which revealed a highly significant influence of land use on DOM composition (Figure 10, path coefficient (PaC) = 0.86, $P < 0.001$).

The PCA separated sites with seemingly more autochthonous from sites with mainly terrigenous DOM on the PC 1 (Figure 5). One end of this gradient was characterized by DOM with a higher extent of humification, a higher relative amount of humic substances (HIX), higher fractional content of CDOM (SA_{440}) and enhanced aromaticity ($SUVA_{254}$). These features point towards a predominantly terrestrial origin of DOM at sites with higher percentages of coniferous forest. The other end of the compositional gradient depicted by the first PC was characterized by lower molecular weight (a_{255}/a_{365}), high values of the freshness index (β/α) and the fluorescence index (FI) and increased fluorescence of the protein-like component C5. These optical characteristics suggest DOM with a more autochthonous and thus more recently produced origin. However, there is evidence that these optical characteristics may also apply to DOM originating from human activities such as fertilization and sewage runoff (Baker 2001; Hudson, Baker, and Reynolds 2007; Naden et al. 2010). Overall, the streams with relatively more DOM of autochthonous nature where those with higher percentages of agricultural and urban areas in their catchment and streams where terrigenous DOM was dominant had higher percentages of coniferous forest in their catchment. These findings suggest that putatively autochthonous DOM plays a larger role in agricultural and urban streams, hence highly anthropogenically impacted streams, and allochthonous DOM is more relevant in streams with high percentages of coniferous forest in their catchments (Figure 5). In contrast to the obvious alignment of DOM composition with land use along PC1, no such alignment of DOM composition with land use could be obtained along other DOM compositional main axes.

In contrast to the strong diverging effects of the land-use types agriculture/urban and coniferous forest on DOM composition, DOM showed no shift in its composition along the land-use gradient

mixed (coniferous/deciduous) forest to all other land-use categories suggested by the PC 2 (Figure 3). I attribute this to the high variation of the other land-use categories from anthropogenically impacted to semi-natural land cover, which all co-occurred with the category mixed forest in the various catchments. Another gradient of DOM composition not linked to land use was identified by the PC 2. This axis separated smaller DOM substances (high S_R) to larger, humic-like DOM (C2 and C3) without any obvious effect of land use (Figure 5).

The PARAFAC component C4 tended to correlate with C5, which confirms the similar mixed origin description, whereas the humic-like C1 showed closer relation to the other humic-like components, C2 and C3, which indicated terrigenous derived DOM.

Previous studies do not provide a consistent picture on how land use is related to in-stream DOM composition. For instance, our findings confirm earlier studies (Wilson and Xenopoulos 2009; Williams et al. 2010; Halbedel, Büttner, and Weitere 2013), which found an increase of structurally less complex, autochthonously DOM in agricultural streams, whereas Graeber et al. (2012) stated a higher amount of structurally complex, humic DOM in streams with increased agricultural areas in their catchments. To reconcile those contrasting findings, it might be useful to consider the agricultural management and soil types (Graeber et al. 2012) together with the stream size. DOM mobilization from various soil types due to tillage, plowing and drainage (Ogle, Breidt, and Paustian 2005) may play an important role in shifting DOM composition towards higher structural complexity, especially in smaller streams (catchment area: 0.01–43 km^2; Graeber et al. 2012). In contrast, with increasing stream size (catchment area: 10-963 km^2; Wilson & Xenopoulos 2009), structural complexity of DOM may decrease because of relatively less impact of the various agricultural practices on the streams but higher rates of GPP as suggested by our results ($r^2 = 0.23$, $F_{1, 31} = 9.22$, $P < 0.01$; Figure 11 (c)). Higher rates of GPP in larger streams may increase the imprint on DOM composition, albeit our study does not provide evidence of an effect of GPP on DOM composition (see section below). I did not plan to include stream size as a potentially important control in our study, but rather aimed to sample streams with similar stream order, catchment size (16-316 km^2) and thus discharge (Q). Still, the limited range of discharges here proved enough to identify stream size as a significant control on GPP, light availability and DIN concentration (Figure 11). The gradient

of stream size covered all land uses, so that no confounding of land use and stream size was evident (land-use PC 1 and Q: r = 0.34, n = 33, P = 0.055; land-use PC 2 and Q: r = 0.17, n = 33, P = 0.345).

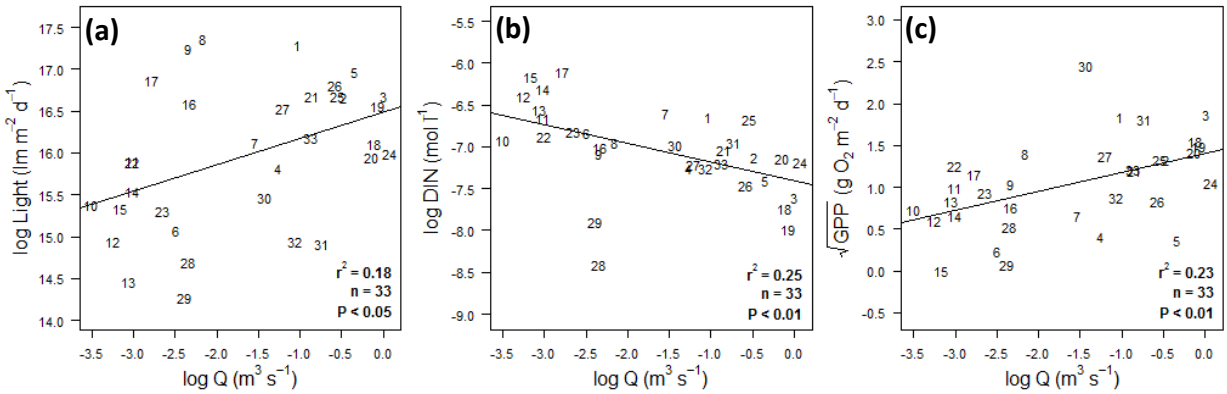

Figure 11 Discharge (Q) affects **(a)** light, **(b)** dissolved inorganic nitrogen (DIN) and **(c)** gross primary production (GPP). Solid lines are the statistically significant linear regressions Site code is given in Table 3.

Diverging effects of land use on stream water DOC concentration were found in previous studies, ranging from no effect of agricultural land in stream catchments (Wilson and Xenopoulos 2008) to enhanced DOC concentration with increasing agricultural land in stream catchments (Graeber et al. 2012). Here, agricultural and urban streams could not be distinguished from coniferous streams in terms of in-stream DOC concentration. However, streams draining mainly agricultural areas and coniferous forest exhibited higher amounts of DOC than streams draining catchment areas dominated by mixed forest (Figure 10; PaC = 0.47, P < 0.01). This may indicate that DOC is mobilized from agricultural soils by tillage and plowing (Ogle, Breidt, and Paustian 2005) and retention time of DOC is diminished due to the common practice of linking agricultural soils and streams by tile drains (Blann et al. 2009; Graeber et al. 2012). Additionally, increased soil and stream bank erosion in agriculturally dominated catchments (Stallard 1998; Quinton et al. 2010) and consistent leaf litter input of coniferous forest may have caused a greater amount of DOC concentration than seasonal leaf fall in catchments dominated by mixed forest during the period of measurement.

Land use strongly affected the in-stream nutrient concentration. Augmented concentration of DIN (Figure 10; PaC = -0.72, P < 0.001) and SRP (Figure 10; PaC = -0.72, P < 0.001) in agricultural and urban streams compared to coniferous forested streams was most likely a consequence of

anthropogenic activities, such as fertilization and sewage runoff (Bernot et al. 2006; Mulholland et al. 2008). Additionally, I found a slight increase in DIN concentration towards streams with larger areas of mixed forest (Figure 10; PaC = -0.26, $P < 0.05$). This result could be attributed to the higher percentages of agricultural and urban land use in catchments with high mixed forest percentages (Figure 3), with their above-mentioned implications.

Next to land use, DIN concentration was positively affected by stream size, approximated by discharge ($r^2 = 0.25$, $F_{1,31} = 10.28$, $P < 0.01$; Figure 11 (b)). Stream size influences physical and biological characteristics of a stream (Vannote et al. 1980), consequently, nutrient transport and processing is affected (Wollheim et al. 2001). Smaller streams with higher surface to volume ratios compared to larger streams take up and process nutrients more efficiently (Alexander, Smith, and Schwarz 2000) and may therefore prevent downstream transport of dissolved nutrients.

5.2 Controls on GPP in the land-use gradient and linkage to DOM composition

I assumed increased light availability in agricultural and urban streams because of expectedly sparser riparian vegetation. Increased light was then hypothesized to support increased GPP in these streams (Figure 1). Surprisingly, while GPP depended on light in our study (Figure 10; PaC = 0.39, $P < 0.05$), I could not identify a link between land use and light conditions. In contrast, discharge, acting as a proxy for stream size, was identified as a significant control on light availability ($r^2 = 0.18$, $F_{1, 31} = 6.73$, $P < 0.05$; Figure 11 (a)), likely because of reduced shading by riparian vegetation in wider streams. This relationship also translated into a positive relationship of GPP with stream size ($r^2 = 0.23$, $F_{1, 31} = 9.22$, $P < 0.01$; Figure 11 (c)), which could indicate a prolonged effect of increased light availability as streams widen and shading decreases (Figure 11 (a)) and/or an increasing amount of autotrophic biomass, which Bernot et al. (2010) found as a predictive variable for GPP.

I also hypothesized that next to light availability GPP is controlled by nutrient concentration (Figure 1). According to our results, however, GPP was not controlled by in-stream nutrient concentration (Figure 10). Previous studies showed that the effect of SRP on GPP is not straightforward: Positive (Mulholland et al. 2001) and negative (Roberts, Mulholland, and Hill 2007; Beaulieu et al. 2013) correlations between SRP and GPP were reported, while several investigators found no relationship (Izagirre et al. 2008; Bernot et al. 2010). Streams investigated in this study exhibited higher SRP (9-157 µg L^{-1}) concentration compared to streams investigated in a previous study (3-14 µg L^{-1} in

Mulholland et al. 2001), where SRP concentration was found as a significant control on GPP. I would expect a more pronounced effect of nutrient loading on GPP in low-nutrient streams, and GPP was probably not limited by SRP in our study streams. On the other hand, the autotrophic SRP uptake rate also was not high enough to result in a negative correlation of SRP and GPP (Roberts, Mulholland, and Hill 2007). Moreover, no DIN effects on GPP were found, agreeing with several metabolism studies (Mulholland et al. 2001; Izagirre et al. 2008; Beaulieu et al. 2013) identifying GPP as independent from nitrogen supply. According to Bernot et al. (2010), snap-shot nutrient concentration measurements may not be a proper way to characterize in-stream nutrient availability because of its potentially strong temporal variability. Our results suggest that light, as the ultimate energy source for autotrophs, rather than nutrients, was the main control on GPP which is in accordance with other multiple stream comparison studies (Young and Huryn 1999; Mulholland et al. 2001; Bernot et al. 2010)

Evidence suggests that an increase in GPP leads to a shift in DOM composition towards more autochthonous low molecular weight substances (Halbedel, Büttner, and Weitere 2013). In our study, GPP left no clear imprint on DOM composition (Figure 10). This is surprising when considering the strong linkage of land use to DOM composition with seemingly larger amounts of autochthonous material in agricultural streams (Figure 5, Figure 10.). The latter points to increased GPP, which, however, I obviously failed to identify with the direct O_2-based measurement. From this apparent uncoupling of O_2-based GPP to land use via light or nutrients, which so strongly contrasts the strong control of land use on DOM composition, I can draw two mutually exclusive conclusions:

A) GPP is indeed not controlled by land use and the optical indicators show altered allochthonous DOM input rather than autochthonous production. Indeed, the various optical descriptors are expressed on a relative basis (e.g. β/α) and the demonstrated strong effect of land use on DOM composition may just mirror altered input rather than GPP changes. The DOM putatively described as autochthonous may in fact origin from human activities, which are recognized as source for labile DOM entering the aquatic network through diffuse leaching and point sources (Hudson, Baker, and Reynolds 2007). Anthropogenic impact is apparently higher in streams draining agricultural and urban areas. Fluorescence peak T (Coble 1996), which I related to the protein-like component C5, was found as general tracer and residue for anthropogenic material in aquatic networks (Baker 2002). Furthermore, Naden et al. (2010) characterized DOM derived by organic fertilizers as low in

its humification state (low HIX) and with enhanced ratios of protein-like to humic-like components. This result highlights the importance of land use-related allochthonous input vectors as the primary control on DOM composition.

B) GPP is indeed controlled by land use and shapes the DOM compositional gradient by contributing autochthonous material in productive streams. However, while DOM composition effectively integrates land-use controls in the whole upstream catchment, the direct O_2-based GPP measurements fail to catch a GPP-signal with catchment-wide validity. This may have multiple reasons, such as: (i) Strong day-to-day and weather-connected variability in cloud cover controls light rather than land use (daily global radiation at the reference site 24 during measurement days was 910 J cm^{-2} and varied by ±44%). (ii) Local streambed and valley morphology controls light independent of land use. For example, some deeply incised streambeds were observed in the field in some but not all agriculturally dominated catchments, hence occurrence of intense side slope shading may have been very variable across study streams. (iii) Upstream distances integrated by the oxygen loggers (Grace and Imberger 2006) may have inadequate length at some sites and thus be not representative for land uses of whole catchments.

5.3 Controls on ER

I predicted ER to be controlled by DOM composition, DOC and nutrient concentrations and GPP. The latter was found as the main control on ER (Figure 7). The stimulation of ER by GPP may be based on enhanced exudation of bioavailable substrates from autotrophs and enhanced autotrophic respiration by the primary producers themselves with increasing GPP. The fact that no evidence of GPP effects on DOM composition were found, leads to the assumption that exudates played a minor role in the tight coupling of GPP and ER, whereas autotrophic respiration contributed a lot to ER. Beaulieu et al. (2013) also reported GPP as the best predictor for ER and found autotrophic respiration relative to heterotrophic respiration as the more important component of ER, especially at high ER and GPP rates. On the other hand, ER also exceeded GPP in all streams, hence NEP values for all streams were negative, indicating the general heterotrophy of all streams. Thus, ER must have been substantially subsidized by organic input from terrestrial sources fueling heterotrophic respiration. Also, ER was significantly affected by SRP (Figure 10; PaC = 0.31, $P < 0.05$), while autotrophs were neither nitrogen nor phosphorus limited. This finding suggests that SRP was a

limiting factor for ER and confirms the results from Mulholland et al. (2001). Further, studies documented an increase in heterotrophic microbial processes such as leaf decomposition with increasing phosphorus supply (Elwood et al. 1981).

ER was also under strong control from DOM composition, yet rather independent from DOC concentration. DOC concentration was no significant control on ER, whereas both conspicuous principal components derived by the PCA, which characterized DOM composition, influenced ER (Figure 5, Figure 10; PC 1: PaC = 0.36, $P < 0.05$; PC 2: PaC = -0.36, $P < 0.01$). The PC 1, which indicated a gradient from putatively autochthonous to allochthonous DOM, well aligned with agricultural areas and coniferous forest, positively affected ER. This suggests a higher ER at higher amounts of allochthonous DOM characterized by higher molecular weight and elevated amount of aromaticity and humic-like substances (Figure 5). I attribute this outcome to the reported dependency of bacterial growth efficiency (BGE) on DOM composition and inorganic nutrient availability (del Giorgio and Cole 1998; Asmala et al. 2013). BGE describes the proportion of organic C incorporated into new bacterial biomass of total assimilated organic C substrate (del Giorgio and Cole 1998). For instance, Asmala et al. (2013) reported lower BGE in an estuary with pristine, peatland and forest-dominated catchment compared to estuaries with higher percentages of urban and agricultural areas because of prevailing DOM characterized as aromatic and humic-like with large molecular size, which consequently resulted in higher bacterial CO_2 emissions in this particular estuary. Further, Fasching et al. (2014) found allochthonous DOM to be metabolized by heterotrophs readily but at high metabolic costs, i.e. at low BGE. These studies provide evidence for lower BGE on more allochthonous DOM, additionally attenuated by lower nutrient concentrations at streams draining mostly coniferous forest. Assumed low BGE implies overproportional respiration of allochthonous DOM by heterotrophs rather than incorporation into microbial biomass. This is in line with our results, suggesting increased ER towards more allochthonous DOM which I could assign to increased coniferous forest in stream catchments. Although POM, which was not examined in this study because it is thought to be of minor metabolic relevance compared to DOM (Battin et al. 2008), could additionally fuel ER, especially in coniferous streams, where I assume higher leaf litter and wood inputs (Golladay 1997; Rugenski, Múrria, and Whiles 2012).

SEM further detected a significant effect of the PC 2 resulting from the PCA describing DOM composition on ER, suggesting a decrease of ER along a gradient from small molecular-sized (high

S_R) to larger, humic-like DOM (high C2 and C3). Marine biology studies showed the alteration of labile DOM via bacterial processing towards structurally diverse, refractory DOM of small size (Ogawa et al. 2001; Lechtenfeld et al. 2015). Therefore the PC 2 may be translated to a gradient of diagenetic state from old, i.e. refractory highly processed microbial end-products, to freshly added larger humic-like substances. As a consequence, I would assume lower susceptibility to microbial incorporation of the smaller, refractory microbial end-products, which is in line with the size-reactivity continuum model (Amon and Benner 1996). This low susceptibility could have resulted in overproportional ER of this type of substrate. However, the size-reactivity continuum model is controversial and other studies identified low-molecular weight DOM as more susceptible for heterotrophic degradation (Williams et al. 2010; Asmala et al. 2013) and because the PC 2 could neither be linked to land use nor to GPP, assumptions on origins and processes controlling the PC 2 and its further impact on ER are rather hypothetical.

5.4 Conclusions

This study identified pronounced effects of long-term (land use) and short-term (light) physical controls on stream ecosystem functioning in a contemporary Central European landscape, partly via the biogeochemical "structure" of these ecosystems, i.e., the concentrations describing the various resource pools (DOC, DOM and nutrients). Both, physical template and biogeochemical structure, influence in-stream metabolism, one of the most integrative ecosystem functions.

The remarkable shift from large, aromatic and humic-like DOM (allochthonous) in streams draining mainly coniferous forest towards smaller, fresher, more protein-like DOM (autochthonous-like) in agricultural and urban streams was rather attributed to altered allochtonous DOM due to anthropogenic activities, such as fertilization and sewage runoff in agricultural and urban streams than autochthonous imprint of GPP. GPP, which was basically influenced by daily-light conditions, was the primary control on ER. I assigned this outcome to high rates of autotrophic respiration, even though all streams were heterotrophic implying substantial supply of allochthonous DOM fueling ER. These results emphasize the importance of land use-related allochthonous input vectors as the primary control on DOM composition. The shift in DOM composition along a land-use gradient stimulated a shift in ER. Lower ER at sites with higher amount of autochthonous-like material was probably due to increased susceptibility of this type of substrate to heterotrophs and therefore

shifted the balance between respiration and biomass production towards the latter. Elevated nutrient concentrations in agricultural and urban streams enhanced this effect, especially SRP, which was identified as a limiting nutrient for ER.

I expressly underlined the key role of anthropogenic land use, which is considered as the most pervasive human influence on natural ecosystems, in controlling C-cycling in inland waters. To better constrain the role of inland waters in contemporary landscapes, we have to study DOM dynamics as both a control and indicator of metabolism within a land-use context.

6 Appendix

6.1 Tables

Table 2 Reclassification of the original set of land use categories sourced from the CORINE Land Cover 2006 inventory (CLC06) with their descriptions.

New description	CLC06 CODE	Description 1	Description 2	Description 3
Urban areas	111	Artificial surfaces	Urban fabric	Continuous urban fabric
Urban areas	112	Artificial surfaces	Urban fabric	Discontinuous urban fabric
Urban areas	121	Artificial surfaces	Industrial, commercial and transport units	Industrial or commercial units
Urban areas	122	Artificial surfaces	Industrial, commercial and transport units	Road and rail networks and associated land
Urban areas	123	Artificial surfaces	Industrial, commercial and transport units	Port areas
Urban areas	124	Artificial surfaces	Industrial, commercial and transport units	Airports
Urban areas	131	Artificial surfaces	Mine, dump and construction sites	Mineral extraction sites
Urban areas	132	Artificial surfaces	Mine, dump and construction sites	Dump sites
Urban areas	133	Artificial surfaces	Mine, dump and construction sites	Construction sites
Urban areas	141	Artificial surfaces	Artificial, non-agricultural vegetated areas	Green urban areas
Urban areas	142	Artificial surfaces	Artificial, non-agricultural vegetated areas	Sport and leisure facilities
Agricultural areas	211	Agricultural areas	Arable land	Non-irrigated arable land
Agricultural areas	221	Agricultural areas	Permanent crops	Vineyards
Agricultural areas	222	Agricultural areas	Permanent crops	Fruit trees and berry plantations
Agricultural areas	231	Agricultural areas	Pastures	Pastures
Agricultural areas	241	Agricultural areas	Heterogeneous agricultural areas	Annual crops associated with permanent crops
Agricultural areas	242	Agricultural areas	Heterogeneous agricultural areas	Complex cultivation patterns
Agricultural areas	243	Agricultural areas	Heterogeneous agricultural areas	Land principally occupied by agriculture, with areas of natural vegetation
Agricultural areas	244	Agricultural areas	Heterogeneous agricultural areas	Agro-forestry areas
Mixed forest	311	Forest and semi natural areas	Forests	Broad-leaved forest
Coniferous forest	312	Forest and semi natural areas	Forests	Coniferous forest
Mixed forest	313	Forest and semi natural areas	Forests	Mixed forest
Semi-natural areas	321	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Natural grasslands
Semi-natural areas	322	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Moors and heathland
Semi-natural areas	323	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Sclerophyllous vegetation
Semi-natural areas	324	Forest and semi natural areas	Scrub and/or herbaceous vegetation associations	Transitional woodland-shrub
Water bodies	411	Wetlands	Inland wetlands	Inland marshes
Water bodies	412	Wetlands	Inland wetlands	Peat bogs
Water bodies	511	Water bodies	Inland waters	Water courses

Table 3 Percentages of the six land use categories (agricultural areas, coniferous forest, mixed forest, urban areas, semi natural areas and water bodies) on the entire catchment area of all 33 investigated sites.

Stream	Code	Drainage area (km^2)	Agricultural areas (%)	Coniferous Forest (%)	Mixed Forest (%)	Urban areas (%)	Semi Natural Areas (%)	Water bodies (%)
Mank	1	128.58	0.71	0.05	0.23	0.02	0.00	0.00
Feldaist	2	261.14	0.59	0.31	0.04	0.05	0.00	0.00
Waldaist	3	282.13	0.34	0.61	0.03	0.01	0.01	0.00
Kleine Naarn	4	77.96	0.47	0.48	0.04	0.01	0.00	0.00
Große Naarn	5	160.29	0.35	0.62	0.01	0.00	0.01	0.01
Klambach	6	24.87	0.50	0.05	0.44	0.01	0.00	0.00
Klausbach	7	48.04	0.53	0.27	0.18	0.02	0.00	0.00
Giessenbach	8	27.80	0.49	0.50	0.00	0.01	0.00	0.00
Blümelbach	9	18.93	0.51	0.46	0.00	0.03	0.00	0.00
Taffabach	10	23.48	0.80	0.13	0.05	0.02	0.00	0.00
Kleine Taffa	11	30.18	0.68	0.22	0.09	0.01	0.00	0.00
Farnbach	12	15.85	0.50	0.42	0.08	0.00	0.00	0.00
Große Taffa	13	22.48	0.53	0.38	0.06	0.03	0.00	0.00
Schmida	14	60.39	0.80	0.05	0.06	0.08	0.01	0.00
Maignerbach	15	29.03	0.84	0.04	0.04	0.08	0.00	0.00
Gmoosbach	16	130.80	0.90	0.00	0.04	0.06	0.00	0.00
Göllersbach	17	98.39	0.38	0.00	0.59	0.02	0.01	0.00
Braunaubach	18	298.91	0.49	0.44	0.01	0.05	0.00	0.01
Lainsitz	19	289.61	0.43	0.51	0.01	0.04	0.00	0.00
Thauabach	20	106.93	0.66	0.29	0.02	0.03	0.00	0.00
Thaya1	21	197.76	0.71	0.25	0.00	0.04	0.00	0.00
Rotbach	22	29.05	0.71	0.28	0.00	0.02	0.00	0.00
Thaya2	23	51.61	0.68	0.28	0.00	0.04	0.00	0.00
Kamp	24	316.44	0.39	0.59	0.00	0.01	0.00	0.01
Zwettl	25	269.30	0.64	0.35	0.00	0.02	0.00	0.00
Kleiner Kamp1	26	155.63	0.30	0.68	0.00	0.01	0.00	0.01
Großer Kamp	27	106.41	0.47	0.50	0.00	0.01	0.00	0.02
Prinzbach	28	25.18	0.04	0.94	0.00	0.00	0.00	0.01
Kleiner Kamp2	29	20.18	0.10	0.85	0.00	0.01	0.04	0.00
Kleine Krems	30	68.90	0.72	0.28	0.00	0.00	0.00	0.00
Große Krems	31	128.97	0.48	0.50	0.00	0.02	0.00	0.00
Kleine Ysper	32	68.34	0.27	0.36	0.37	0.01	0.00	0.00
Große Ysper	33	88.27	0.26	0.37	0.35	0.01	0.00	0.00

Table 4 Hydromorphological and hydraulic parameters, dissolved organic carbon (DOC) concentrations and nutrient concentrations of the 33 investigated streams.

	Hydromorphology and hydraulics					Water chemistry			
	Slope streambed	Mean depth ± SD	Mean width ± SD	Mean velocity	Q downstream station	DOC	PO_4-P	NH_4-N	NO_3-N
Code	cm m^{-1}	m	m	m s^{-1}	m^3 s^{-1}	mg C L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}
1	0.03	0.28 ± 0.18	8.22 ± 1.89	0.15	0.358	1.74	34.6	1.7	18.2
2	0.13	0.30 ± 0.17	6.20 ± 0.98	0.42	0.623	3.30	42.3	18.2	11.3
3	0.76	0.36 ± 0.18	9.57 ± 1.87	0.36	1.006	3.10	18.2	3.2	6.9
4	0.19	0.29 ± 0.16	4.47 ± 0.76	0.27	0.283	2.05	39.9	3.4	9.9
5	0.06	0.38 ± 0.20	6.36 ± 1.11	0.41	0.707	2.35	13.3	1.7	8.5
6	0.45	0.18 ± 0.12	2.78 ± 0.79	0.16	0.083	2.30	24.3	13.2	14.9
7	0.27	0.23 ± 0.14	3.97 ± 0.85	0.33	0.214	1.79	31.8	1.4	19.1
8	0.51	0.17 ± 0.09	2.37 ± 0.46	0.39	0.115	1.68	21.4	2.4	13.3
9	0.34	0.15 ± 0.11	2.39 ± 0.51	0.28	0.096	1.89	49.5	1.9	11.8
10	1.25	0.16 ± 0.12	2.20 ± 0.72	0.09	0.030	3.78	27.3	2.7	13.8
11	1.47	0.18 ± 0.11	2.84 ± 0.72	0.10	0.049	4.59	28.9	3.4	18.0
12	1.23	0.15 ± 0.13	2.62 ± 0.71	0.11	0.039	2.70	9.9	2.4	23.4
13	2.17	0.11 ± 0.07	2.92 ± 0.71	0.14	0.047	4.53	32.9	2.4	19.8
14	0.34	0.15 ± 0.09	1.80 ± 0.34	0.16	0.049	4.25	112.4	6.4	25.7
15	0.47	0.20 ± 0.09	1.48 ± 0.30	0.14	0.042	3.67	116.1	4.7	29.5
16	0.27	0.30 ± 0.11	2.58 ± 0.41	0.08	0.097	6.34	157.3	6.2	12.6
17	0.23	0.21 ± 0.08	2.05 ± 0.40	0.18	0.062	2.80	39.6	21.2	31.4
18	1.94	0.40 ± 0.23	6.92 ± 2.46	0.26	0.892	8.34	9.2	97.6	6.0
19	0.01	0.61 ± 0.25	7.30 ± 1.19	0.17	0.932	5.78	28.8	7.2	4.8
20	0.30	0.33 ± 0.17	5.80 ± 1.29	0.13	0.233	6.14	110.2	15.7	11.0
21	0.05	0.63 ± 0.35	4.95 ± 1.11	0.15	0.427	7.85	39.2	13.2	12.3
22	0.04	0.24 ± 0.17	2.93 ± 0.71	0.09	0.049	4.80	24.3	6.7	14.5
23	0.02	0.35 ± 0.18	3.42 ± 0.64	0.06	0.071	6.49	12.9	40.0	15.4
24	0.22	0.32 ± 0.19	16.54 ± 3.22	0.33	1.155	3.46	19.2	4.9	10.6
25	0.59	0.31 ± 0.17	9.94 ± 2.13	0.29	0.580	3.94	61.1	60.0	17.6
26	0.20	0.40 ± 0.24	6.61 ± 1.46	0.28	0.562	3.55	14.8	7.2	8.0
27	0.48	0.25 ± 0.15	5.95 ± 1.17	0.26	0.299	4.25	16.5	5.2	10.3
28	0.85	0.19 ± 0.12	3.51 ± 1.09	0.18	0.096	4.49	11.0	3.7	3.1
29	0.68	0.17 ± 0.10	3.38 ± 0.81	0.19	0.092	3.68	11.5	13.7	5.2
30	2.59	0.21 ± 0.12	6.21 ± 1.74	0.25	0.239	3.11	56.3	5.2	13.0
31	1.69	0.26 ± 0.19	7.83 ± 2.18	0.26	0.480	3.32	20.7	3.2	13.5
32	1.94	0.21 ± 0.10	5.47 ± 1.44	0.36	0.345	3.82	28.6	3.9	9.9
33	1.68	0.25 ± 0.15	6.79 ± 1.52	0.33	0.420	3.02	53.0	3.4	10.5

SD, standard deviation; mean depth, n ≥ 80; mean width, n ≥ 40; Q, discharge.

Table 5 Estimated reaeration coefficients by various approaches.

	fixed K_{20}				modeled K_{20}	
	K ntreg	K1	K2	K3	One-station	Two-station
Code	min^{-1}	min^{-1}	min^{-1}	min^{-1}	min^{-1}	min^{-1}
1	0.008	0.001	0.005	0.003	0.008	0.010
2	0.013	0.006	0.007	0.006	0.008	0.014
3	0.069	0.029	0.005	0.007	0.046	0.053
4	NA	0.007	0.006	0.006	0.024	0.014
5	NA	0.002	0.005	0.003	0.011	0.011
6	NA	0.016	0.010	0.012	0.025	0.007
7	NA	0.020	0.011	0.010	0.059	0.045
8	NA	0.043	0.020	0.020	0.031	NA
9	0.034	0.020	0.018	0.017	0.021	NA
10	NA	0.024	0.009	0.015	0.075	0.006
11	NA	0.033	0.008	0.014	0.042	0.036
12	NA	0.031	0.011	0.017	0.073	0.012
13	NA	0.065	0.020	0.032	0.075	0.040
14	NA	0.012	0.014	0.014	0.008	0.011
15	NA	0.014	0.008	0.010	0.019	0.006
16	NA	0.005	0.003	0.004	0.001	NA
17	NA	0.009	0.008	0.008	0.017	0.008
18	NA	0.053	0.003	0.007	0.011	0.065
19	0.010	0.000	0.001	0.001	0.011	0.007
20	0.014	0.008	0.003	0.004	0.012	0.014
21	0.005	0.001	0.001	0.001	0.006	0.001
22	0.011	0.001	0.004	0.003	0.010	0.011
23	0.007	0.000	0.002	0.001	0.008	0.005
24	0.011	0.008	0.006	0.006	0.013	NA
25	0.022	0.019	0.006	0.008	0.018	NA
26	NA	0.006	0.004	0.004	0.015	NA
27	NA	0.027	0.008	0.009	0.025	0.017
28	NA	0.033	0.010	0.014	0.017	0.032
29	NA	0.028	0.012	0.015	0.020	0.014
30	NA	0.140	0.011	0.019	0.059	0.074
31	NA	0.065	0.007	0.012	0.045	0.036
32	NA	0.103	0.012	0.020	0.029	0.043
33	NA	0.083	0.009	0.015	0.038	0.051

NA, data not available due to poor linear fits (K ntreg) or upstream logger malfunction or too small DO change along reach (modeled K_{20}); K_{20}, reaeration coefficient at 20°C derived by the night-time method (K ntreg), empirical equations (11-13) (K1, K2, K3) and modeled reaeration coefficients by one-station and two-station approach.

Table 6 Gross primary production and ecosystem respiration estimates derived by one-station and two station method with either fixed or modeled reaeration coefficients.

	One-station method with fixed K_{20}		Two-station method with fixed K_{20}		fixed K_{20} one- & two-station		One-station method with modeled K_{20}			Two-station method with modeled K_{20}		
	GPP24	$ER24_{20}$	GPP24	$ER24_{20}$	K_{20}	approach	GPP24	$ER24_{20}$	modeled K_{20}	GPP24	$ER24_{20}$	modeled K_{20}
Code	g O2 m^{-2} d^{-1}	g O2 m^{-2} d^{-1}	g O2 m^{-2} d^{-1}	g O2 m^{-2} d^{-1}	min^{-1}		g O2 m^{-2} d^{-1}	g O2 m^{-2} d^{-1}	min^{-1}	g O2 m^{-2} d^{-1}	g O2 m^{-2} d^{-1}	min^{-1}
1	3.363	6.877	4.375	14.328	0.008	K ntreg	3.354	6.858	0.008	5.215	9.644	0.010
2	1.748	9.239	0.494	19.380	0.013	K ntreg	1.059	5.457	0.008	0.507	12.747	0.014
3	3.473	27.934	3.247	27.276	0.069	K ntreg	2.290	18.448	0.046	2.698	13.300	0.053
4	0.167	2.169	NA	NA	0.007	K1	0.942	7.716	0.024	0.546	0.624	0.014
5	0.131	1.774	0.000	3.805	0.002	K1	0.881	8.703	0.011	0.494	6.430	0.011
6	0.056	7.341	0.169	9.899	0.016	K1	0.202	11.501	0.025	0.044	3.738	0.007
7	0.429	2.817	NA	NA	0.020	K1	1.676	9.090	0.059	0.678	1.016	0.045
8	1.954	7.792	NA	NA	0.043	K1	1.374	5.592	0.031	NA	NA	NA
9	1.074	9.059	0.000	0.996	0.034	K ntreg	0.609	5.427	0.021	NA	NA	NA
10	0.533	8.887	0.573	8.639	0.024	K1	2.022	28.648	0.075	0.000	0.795	0.006
11	0.997	12.799	0.941	12.150	0.033	K1	1.275	16.117	0.042	0.966	8.183	0.036
12	0.362	9.096	0.347	9.225	0.031	K1	1.022	21.951	0.073	0.000	2.170	0.012
13	0.706	10.538	0.744	10.628	0.065	K1	0.831	12.279	0.075	0.443	3.996	0.040
14	0.433	7.040	0.234	4.700	0.012	K1	0.255	4.741	0.008	0.133	2.443	0.011
15	0.000	11.634	0.000	11.502	0.014	K1	0.001	15.348	0.019	0.000	2.765	0.006
16	0.576	8.642	NA	NA	0.005	K1	0.412	1.019	0.001	NA	NA	NA
17	1.349	6.623	2.184	14.259	0.009	K1	2.521	12.734	0.017	1.904	8.789	0.008
18	2.400	22.960	1.047	5.442	0.053	K1	0.503	4.836	0.011	1.992	9.408	0.065
19	2.205	20.693	1.863	24.535	0.010	K ntreg	2.397	22.806	0.011	1.329	11.161	0.007
20	2.001	19.793	2.480	18.337	0.014	K ntreg	1.818	17.254	0.012	2.487	10.904	0.014
21	1.448	12.972	2.172	14.604	0.005	K ntreg	1.805	16.870	0.006	2.288	3.992	0.001
22	1.574	9.047	0.639	8.529	0.011	K ntreg	1.371	7.958	0.010	0.926	4.978	0.011
23	0.870	10.125	0.843	11.660	0.007	K ntreg	1.008	11.886	0.008	0.819	5.109	0.005
24	1.099	3.506	NA	NA	0.011	K ntreg	1.308	4.208	0.013	NA	NA	NA
25	1.767	12.902	NA	NA	0.022	K ntreg	1.481	10.896	0.018	NA	NA	NA
26	0.704	4.504	NA	NA	0.006	K1	1.533	10.671	0.015	NA	NA	NA
27	1.879	11.351	2.111	18.863	0.027	K1	1.741	10.546	0.025	1.391	10.040	0.017
28	0.277	9.287	0.229	9.228	0.033	K1	0.123	4.676	0.017	0.260	5.262	0.032
29	0.005	7.228	0.061	7.819	0.028	K1	0.011	5.381	0.020	0.054	2.617	0.014
30	6.025	45.504	5.698	45.639	0.140	K1	2.531	19.159	0.059	2.971	15.809	0.074
31	3.278	17.061	3.412	17.365	0.065	K1	2.247	11.691	0.045	2.193	6.521	0.036
32	0.781	27.880	0.709	29.005	0.103	K1	0.182	7.986	0.029	0.368	9.703	0.043
33	1.462	25.687	1.349	24.781	0.083	K1	0.607	11.631	0.038	0.810	9.500	0.051

NA, data not available due to upstream logger malfunction or too small DO change along reach; GPP, gross primary production; ER, ecosystem respiration;
K ntreg, reaeration coefficient at 20°C derived by the night-time method; K1, reaeration coefficient at 20°C derived by the energy dissipation model.

Table 7 Absorption coefficients and fluorescence indices

	Absorption coefficients					Fluorescence indices		
	a_{440}	SA_{440}	$SUVA_{254}$	a_{255}/a_{365}	S_R	FI	HIX	β/α
Code	m^{-1}	L mg^{-1} m^{-1}	L mg^{-1} m^{-1}	dim. less	dim. less	dim. less	dim. less	dim. less
1	0.37	0.09	1.99	5.88	0.78	2.15	0.68	1.16
2	0.87	0.12	2.07	5.40	0.88	2.08	0.68	1.16
3	1.24	0.17	2.56	4.67	0.86	1.81	0.76	1.04
4	0.54	0.12	2.25	5.34	0.78	1.98	0.69	1.05
5	0.83	0.16	2.38	4.43	0.74	1.84	0.69	1.01
6	0.64	0.12	2.27	5.19	0.76	1.87	0.71	1.14
7	0.42	0.10	2.06	5.37	0.70	1.86	0.67	1.13
8	0.34	0.09	1.94	5.26	0.70	1.94	0.66	1.19
9	0.46	0.11	2.02	4.97	0.73	1.98	0.70	1.11
10	0.85	0.10	1.78	5.27	0.86	2.01	0.67	1.21
11	0.90	0.09	1.88	5.65	0.79	2.03	0.69	1.17
12	0.72	0.12	1.92	5.27	0.82	2.11	0.68	1.15
13	1.19	0.11	1.99	5.31	0.85	2.05	0.69	1.15
14	0.93	0.10	1.76	5.66	0.88	2.04	0.63	1.19
15	0.77	0.09	1.66	5.50	0.82	2.25	0.62	1.23
16	1.17	0.08	1.79	5.92	0.85	2.12	0.67	1.18
17	0.43	0.07	1.65	6.41	0.70	2.23	0.64	1.23
18	1.75	0.09	1.89	5.68	0.91	2.00	0.69	1.15
19	1.50	0.11	2.05	5.37	0.95	1.94	0.68	1.15
20	1.23	0.09	1.98	6.24	0.95	1.95	0.69	1.16
21	1.45	0.08	1.63	5.99	0.98	1.93	0.68	1.18
22	1.66	0.15	2.51	4.82	0.81	1.96	0.73	1.11
23	1.34	0.09	1.86	5.98	0.95	1.95	0.69	1.17
24	1.44	0.18	2.59	4.61	0.84	1.87	0.77	1.01
25	1.12	0.12	2.13	5.30	0.86	1.98	0.71	1.14
26	1.54	0.19	2.64	4.44	0.81	1.83	0.77	1.01
27	1.81	0.19	2.68	4.55	0.82	1.88	0.77	1.04
28	2.08	0.20	2.56	4.17	0.83	1.78	0.77	0.96
29	1.69	0.20	2.43	3.95	0.82	1.84	0.75	0.99
30	1.20	0.17	2.18	4.54	0.92	1.99	0.73	1.07
31	1.36	0.18	2.33	4.47	0.88	1.98	0.72	1.07
32	2.04	0.23	2.72	4.10	0.83	1.95	0.77	0.99
33	1.58	0.23	2.48	4.01	0.85	1.99	0.74	0.98

a_{440}, absorption coefficient at 440 nm; SA_{440}, DOC-standardized version of a_{440}; $SUVA_{254}$, specific UV absorption at 254 nm; a_{255}/a_{365}, ratio of the absorption coefficients a_{255} and a_{365}; S_R, slope ratio; FI, fluorescence index; HIX, humification index; β/α, freshness index

6.2 Zusammenfassung

Metabolismus in Fließgewässern integriert die Produktion und die Respiration von organischem Material auf der Ebene eines Ökosystems. Gelöstes organisches Material (dissolved organic matter, DOM) in aquatischen Lebensräumen ist ein komplexer, extrem diverser Mix aus in-situ produzierten leichteren, proteinähnlicheren, frisch zugeführten- (autochthon) und von terrestrischen Ökosystemen stammenden schwereren, aromatischen und huminstoffreichen chemischen Substanzen (allochthon).

Ich versuchte mögliche Auswirkungen der Landnutzung auf die DOM-Zusammensetzung und Nährstoff- und Kohlenstoffkonzentrationen im Fließgewässer zu detektieren und diese in Bezug zum Metabolismus des gesamten Fließgewässers, d.h. Bruttoprimärproduktion (BPP) und Gesamtrespiration des Ökosystems, zu stellen. Dafür untersuchte ich 33 Fließgewässer im Norden Österreichs, deren Einzugsgebiete einen Landnutzungsgradienten von landwirtschaftlich und urban geprägten zu bewaldeten und naturnahen Flächen umspannten. Zur Charakterisierung der DOM-Zusammensetzung wurden Absorptions- und Fluoreszenzindizes, sowie DOM-Komponenten identifiziert durch parallele Faktorenanalyse (PARAFAC), verwendet. Zur Metabolismusberechnung wurde sowohl der 1-Station- als auch 2-Stationen-Ansatz verfolgt, welche beide auf den täglichen Sauerstoffdynamiken im Fließgewässer basieren. Raten der BPP und der Respiration wurden durch Anpassung eines mathematischen Modells an die empirischen Sauerstoffdaten berechnet. Das Modell korrigierte für eine eventuell aufgetretene Lichtsättigung der Photosynthese sowie für physikalisch-bedingten Sauerstoffaustausch an der Wasser-Atmosphären-Grenzschicht.

In dieser Studie konnte ich ausgeprägte Effekte von langfristigen (Landnutzung) und kurzfristigen (Lichtverfügbarkeit) physikalischen Gegebenheiten auf die biogeochemische Struktur in Bächen, welche DOM-Zusammensetzung und DOC- und Nährstoffkonzentrationen zusammenfasst, nachweisen. Sowohl die physikalischen Gegebenheiten als auch die biogeochemische Struktur der Fließgewässer beeinflussten deren Metabolismus.

Ich konnte eine beachtliche Veränderung der DOM-Zusammensetzung entlang des Landnutzungsgradienten beobachten: Von mehrheitlich allochthonen Substanzen in Fließgewässern mit großen Nadelwaldgebieten im Einzugsgebiet zu autochthon-ähnlichen Substanzen in landwirtschaftlich- und stadtgeprägten Bächen. Diese Veränderung der DOM-Zusammensetzung wurde eher einem veränderten allochthonen DOM Eintrag durch erhöhte

anthropogene Aktivität, z.B. Abfluss von Abwasser und Düngung, als der zu Beginn erwarteten größeren Bedeutung von BPP und deswegen autochthonem DOM in landwirtschaftlich und urban geprägten Bächen, zugeschrieben. Der BPP konnte nämlich kein Einfluss auf die DOM-Zusammensetzung nachgewiesen werden. Die BPP, welche hauptsächlich von Lichtverfügbarkeit kontrolliert war, hatte den größten positiven Einfluss auf die ökosystemare Respiration. Hohe Raten an autotropher Respiration dürften hierfür verantwortlich gewesen sein. Die Respiration überstieg die BPP in allen Fließgewässern, das bedeutet, dass die Respiration erheblich durch allochthonen Eintrag unterstützt wurde und alle Fließgewässer CO_2 in die Atmosphäre emittierten. Diese Resultate unterstreichen die Wichtigkeit des stark von der Landnutzung beeinflussten allochthonen Eintrages als Primärkontrolle auf die DOM-Zusammensetzung. Die Veränderung dieser Zusammensetzung entlang des Landnutzungsgradienten verursachte auch eine Veränderung in der Respirationsrate des Ökosystems. Niedrigere Raten wurden dort festgestellt, wo mehr Anteil von autochthon-ähnlichem Material als DOM im Fließgewässer vorhanden war. Ich führte dies auf eine höhere Verfügbarkeit dieses Materials für Mikroorganismen zurück, welche das Gleichgewicht zwischen Respiration und dem Einbau dieser Substanzen in die Zellbiomasse in Richtung des letzteren verschiebt. Erhöhte Nährstoffkonzentrationen in landwirtschaftlich und urban geprägten Bächen, vor allem Phosphor, welcher als limitierender Nährstoff für die Respiration detektiert wurde, verstärkten diesen Effekt.

Ich konnte deutlich zeigen, welche Schlüsselrolle anthropogene Landnutzung in der Kontrolle des Kohlenstoff-Kreislaufes der Binnengewässer einnimmt. Landnutzung wird als die tiefgreifendste vom Menschen verursachte Auswirkung auf die natürlichen Ökosysteme dieser Erde angesehen und Binnengewässer geraten zunehmend als bedeutende Umsatzorte für das klimatisch wirksame Treibhausgas CO_2 in den Fokus wissenschaftlicher Betrachtung. In Anbetracht dieser Tatsachen ist es wichtig DOM-Dynamiken sowohl als Kontrollen als auch als Indikatoren von Metabolismus mit Bedacht auf die Landnutzung zu untersuchen, um die Rolle der Binnengewässer in gegenwärtigen Landschaften genauer einordnen zu können.

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6.4 References

Alexander, R. B., R. A. Smith, and G. E. Schwarz. 2000. “Effect of Stream Channel Size on the Delivery of Nitrogen to the Gulf of Mexico.” *Nature* 403 (February): 758–62. doi:10.1038/35001562.

Amon, R., and R. Benner. 1996. “Bacterial Utilization of Different Size Classes of Dissolved Organic Matter.” *Limnology and Oceanography*. http://www.riversystems.washington.edu/lc/RIVERS/77_amon_rmw_41-41-51.pdf.

APHA. 1992. *Standard Methods for the Examination of Water and Wastewater*. *American Public Health Association*. 18th ed. Washington, DC, USA.

Aristegi, L., O. Izagirre, and A. Elosegi. 2009. “Comparison of Several Methods to Calculate Reaeration in Streams, and Their Effects on Estimation of Metabolism.” *Hydrobiologia* 635 (1): 113–24. doi:10.1007/s10750-009-9904-8.

Asmala, E., R. Autio, H. Kaartokallio, L. Pitkänen, C. A. Stedmon, and D. N. Thomas. 2013. “Bioavailability of Riverine Dissolved Organic Matter in Three Baltic Sea Estuaries and the Effect of Catchment Land Use.” *Biogeosciences* 10 (11): 6969–86. doi:10.5194/bg-10-6969-2013.

Azam, F., and B. C. Cho. 1987. “Bacterial Utilization of Organic Matter in the Sea.” *Symposia of the Society for General Microbiology*.

Baker, A. 2001. “Fluorescence Excitation - Emission Matrix Characterization of Some Sewage-Impacted Rivers.” *Environmental Science and Technology* 35 (5): 948–53. doi:10.1021/es000177t.

———. 2002. “Fluorescence Properties of Some Farm Wastes: Implications for Water Quality Monitoring.” *Water Research* 36 (1): 189–95. doi:10.1016/S0043-1354(01)00210-X.

Bales, J. D., and M. R. Nardi. 2007. “Automated Routines for Calculating Whole-Stream Metabolism: Theoretical Background and User’s Guide.” *US Geological Survey Techniques and Methods*, 33.

Barrón, C., E. T. Apostolaki, and C. M. Duarte. 2012. “Dissolved Organic Carbon Release by Marine Macrophytes.” *Biogeosciences Discussions* 9 (2): 1529–55. doi:10.5194/bgd-9-1529-2012.

Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater. 2008. “Biophysical Controls on Organic Carbon Fluxes in Fluvial Networks.” *Nature Geoscience* 1: 95–100. doi:10.1038/ngeo602.

Battin, T. J., S. Luyssaert, L. A. Kaplan, A. K. Aufdenkampe, A. Richter, and L. J. Tranvik. 2009. “The Boundless Carbon Cycle.” *Nature Geoscience* 2 (9). Nature Publishing Group: 598–600. doi:10.1038/ngeo618.

Beaulieu, J. J., C. P. Arango, D. A. Balz, and W. D. Shuster. 2013. “Continuous Monitoring Reveals Multiple Controls on Ecosystem Metabolism in a Suburban Stream.” *Freshwater Biology* 58 (5): 918–37. doi:10.1111/fwb.12097.

Bennett, J. B., and R. E. Rathbun. 1972. “Reaeration in Open-Channel Flow.” *U.S. Geological Survey Professional Paper*, 737.

Benson, B. B., and D. Krause. 1984. “The Concentration and Isotopic Fractionation of Oxygen Dissolved in Freshwater and Seawater in Equilibrium with the Atmosphere.” *Limnology and Oceanography* 29 (3): 620–32. doi:10.4319/lo.1984.29.3.0620.

Berggren, M., H. Laudon, M. Haei, L. Ström, and M. Jansson. 2010. “Efficient Aquatic Bacterial Metabolism of Dissolved Low-Molecular-Weight Compounds from Terrestrial Sources.” *The ISME Journal* 4 (3): 408–16. doi:10.1038/ismej.2009.120.

Bernot, M. J., D. J. Sobota, R. O. Hall, P. J. Mulholland, W. K. Dodds, J. R. Webster, J. L. Tank, et al. 2010. “Inter-Regional Comparison of Land-Use Effects on Stream Metabolism.” *Freshwater Biology* 55 (9): 1874–90. doi:10.1111/j.1365-2427.2010.02422.x.

Bernot, M. J., J. L. Tank, T. V. Royer, and M. B. David. 2006. “Nutrient Uptake in Streams Draining Agricultural Catchments of the Midwestern United States.” *Freshwater Biology* 51 (3): 499–509. doi:10.1111/j.1365-2427.2006.01508.x.

Bertilsson, S., and J. B. Jones. 2003. “Supply of Dissolved Organic Matter to Aquatic Ecosystems: Autochthonous Sources.” In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, 512. doi:10.1016/B978-012256371-3/50002-0.

Blann, K. L., J. L. Anderson, G. R. Sands, and B. Vondracek. 2009. “Effects of Agricultural Drainage on Aquatic Ecosystems: A Review.” *Critical Reviews in Environmental Science and Technology*. doi:10.1080/10643380801977966.

Bott, T. L. 1996. “Primary Productivity and Community Response.” In *F. R. Hauer and G. A. Lamberti [eds.], Methods in Stream Ecology*, 533–56.

———. 2007. “Primary Productivity and Community Respiration.” In *Methods in Stream Ecology*, 663–90.

Bro, Rasmus. 1997. “PARAFAC. Tutorial and Applications.” In *Chemometrics and Intelligent Laboratory Systems*, 38:149–71. doi:10.1016/S0169-7439(97)00032-4.

Coble, P. G. 1996. “Characterization of Marine and Terrestrial DOM in Seawater Using Excitation-Emission Matrix Spectroscopy.” *Marine Chemistry* 51 (4): 325–46. doi:10.1016/0304-4203(95)00062-3.

Coble, P. G., S. A. Green, N. V. Blough, and R. B. Gagosian. 1990. “Characterization of Dissolved Organic Matter in the Black Sea by Fluorescence Spectroscopy.” *Nature*. doi:10.1038/348432a0.

Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl, C. M. Duarte, et al. 2007. “Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget.” *Ecosystems* 10 (1): 171–84. doi:10.1007/s10021-006-9013-8.

Dahlén, J., S. Bertilsson, and C. Pettersson. 1996. “Effects of UV-A Irradiation on Dissolved Organic Matter in Humic Surface Waters.” *Environment International* 22 (5): 501–6. doi:10.1016/0160-4120(96)00038-4.

Daily, G. C. 1995. “Restoring Value to the World’s Degraded Lands.” *Science* 269 (5222): 350–54. doi:10.1126/science.269.5222.350.

De Haan, H. 1993. “Solar UV-Light Penetration and Photodegradation of Humic Substances in Peaty Lake Water.” *Limnology and Oceanography* 38 (5): 1072–76. doi:10.4319/lo.1993.38.5.1072.

Del Giorgio, P. A., and J. J. Cole. 1998. “Bacterial Growth Efficiency In Natural Aquatic Systems.” *Annual Review of Ecology and Systematics*. doi:10.1146/annurev.ecolsys.29.1.503.

Demars, B. O. L., J. R. Manson, J. S. Ólafsson, G. M. Gíslason, and N. Friberg. 2011. "Stream Hydraulics and Temperature Determine the Metabolism of Geothermal Icelandic Streams." *Knowledge and Management of Aquatic Ecosystems*. doi:10.1051/kmae/2011046.

Duarte, C. M., and Y. T. Prairie. 2005. "Prevalence of Heterotrophy and Atmospheric CO2 Emissions from Aquatic Ecosystems." *Ecosystems* 8 (7): 862–70. doi:10.1007/s10021-005-0177-4.

Elmore, H. L., and W. F. West. 1961. "Effect of Water Temperature on Stream Reaeration." *Journal of the Sanitary Engineering Division* 87: 59–71.

Elwood, Jerry W., J. Denis Newbold, Ann F. Trimble, and Robert W. Stark. 1981. "The Limiting Role of Phosphorus in a Woodland Stream Ecosystem: Effects of P Enrichment on Leaf Decomposition and Primary Producers." *Ecology* 62 (1): 146–58. doi:10.2307/1936678.

Fasching, C., B. Behounek, G. A. Singer, and T. J. Battin. 2014. "Microbial Degradation of Terrigenous Dissolved Organic Matter and Potential Consequences for Carbon Cycling in Brown-Water Streams." *Scientific Reports* 4: 4981. doi:10.1038/srep04981.

Fellman, J. B., E. Hood, and R. G. M. Spencer. 2010. "Fluorescence Spectroscopy Opens New Windows into Dissolved Organic Matter Dynamics in Freshwater Ecosystems: A Review." *Limnology and Oceanography* 55 (6): 2452–62. doi:10.4319/lo.2010.55.6.2452.

Fellows, C. S., H. M. Valett, and C. N. Dahm. 2001. "Whole-Stream Metabolism in Two Montane Streams: Contribution of the Hyporheic Zone." *Limnology and Oceanography*. doi:10.4319/lo.2001.46.3.0523.

Finlay, J. C., J. M. Hood, M. P. Limm, M. E. Power, J. D. Schade, and J. R. Welter. 2011. "Light-Mediated Thresholds in Stream-Water Nutrient Composition in a River Network." *Ecology* 92 (1): 140–50. doi:10.1890/09-2243.1.

Fisher, S. G., and G. E. Likens. 1973. "Energy Flow in Bear Brook, New Hampshire: An Integrative Approach to Stream Ecosystem Metabolism." *Ecological Monographs* 43 (4): pp. 421–39. doi:10.2307/1942301.

Fox, J. 2006. "Structural Equation Modeling With the Sem Package in R." *Structural Equation Modeling* 13 (3): 465–86. doi:10.1207/s15328007sem1303_7.

Golladay, S. W. 1997. "Suspended Particulate Organic Matter Concentration and Export in Streams." *Journal of the North American Benthological Society* 16 (1): 122–30.

Grace, M., and S. Imberger. 2006. "Stream Metabolism : Performing & Interpreting Measurements." *Water Studies Centre Monash University, Murray Darling Basin Commission and New South Wales Department of Environment and Climate Change* 31 (September): 204. doi:10.4296/cwrj3101041.

Graeber, D., J. Gelbrecht, M. T. Pusch, C. Anlanger, and D. von Schiller. 2012. "Agriculture Has Changed the Amount and Composition of Dissolved Organic Matter in Central European Headwater Streams." *Science of the Total Environment* 438. Elsevier B.V.: 435–46. doi:10.1016/j.scitotenv.2012.08.087.

Green, S. A., and N. V. Blough. 1994. "Optical Absorption and Fluorescence Properties of Chromophoric Dissolved Organic Matter in Natural Waters." *Limonology And Oceanography* 39 (8): 1903–16. doi:10.4319/lo.1994.39.8.1903.

Gücker, B., I. G. Boëchat, and A. Giani. 2009. “Impacts of Agricultural Land Use on Ecosystem Structure and Whole-Stream Metabolism of Tropical Cerrado Streams.” *Freshwater Biology* 54 (10): 2069–85. doi:10.1111/j.1365-2427.2008.02069.x.

Halbedel, S., O. Büttner, and M. Weitere. 2013. “Linkage between the Temporal and Spatial Variability of Dissolved Organic Matter and Whole-Stream Metabolism.” *Biogeosciences* 10 (8): 5555–69. doi:10.5194/bg-10-5555-2013.

Helms, J. R., A. Stubbins, J. D. Ritchie, E. C. Minor, D. J. Kieber, and K. Mopper. 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): 955–69. doi:10.4319/lo.2008.53.3.0955.

Hertkorn, N., M. Frommberger, M. Witt, B. P. Koch, Ph. Schmitt-Kopplin, and E. M. Perdue. 2008. “Natural Organic Matter and the Event Horizon of Mass Spectrometry Natural Organic Matter and the Event Horizon of.” *German Research* 80 (October): 8908–19.

Hilborn, R., and M. Mangel. 1997. *The Ecological Detective: Confronting Models with Data*. *Monographs in Population Biology*. Vol. 28. doi:10.1046/j.1365-2664.1999.04462.x.

Hill, W. R., H. L. Boston, and A. D. Steinman. 1992. “Grazers and Nutrients Simultaneously Limit Lotic Primary Productivity.” *Canadian Journal of Fisheries and Aquatic Sciences*. doi:10.1139/f92-059.

Hill, W. R., M. G. Ryon, and E. M. Schilling. 1995. “Light Limitation in a Stream Ecosystem: Responses by Primary Producers and Consumers.” *Ecology* 76 (4): 1297–1309. doi:10.2307/1940936.

Holtgrieve, G. W., D. E. Schindler, T. A. Branch, and Z. T. A’mar. 2010. “Simultaneous Quantification of Aquatic Ecosystem Metabolism and Reaeration Using a Bayesian Statistical Model of Oxygen Dynamics.” *Limnology and Oceanography* 55 (3): 1047–62. doi:10.4319/lo.2010.55.3.1047.

Hornberger, G. M., and M. G. Kelly. 1975. “Atmospheric Reaeration in a River Using Productivity Analysis.” *Journal of the Environmental Engineering Division* 101 (5). ASCE: 729–39. http://cedb.asce.org/cgi/WWWdisplay.cgi?6260.

Hotchkiss, E. R., and R. O. Jr. Hall. 2014. “High Rates of Daytime Respiration in Three Streams: Use of δ18OO2 and O2 to Model Diel Ecosystem Metabolism.” *Limnology and Oceanography* 59 (3): 798–810. doi:10.4319/lo.2014.59.3.0798.

Hudson, N., A. Baker, and D. Reynolds. 2007. “Fluorescence Analysis of Dissolved Organic Matter in Natural, Waste and Polluted Waters - A Review.” *River Research and Applications*. doi:10.1002/rra.1005.

Hunt, R. J., T. D. Jardine, S. K. Hamilton, and S. E. Bunn. 2012. “Temporal and Spatial Variation in Ecosystem Metabolism and Food Web Carbon Transfer in a Wet-Dry Tropical River.” *Freshwater Biology* 57 (3): 435–50. doi:10.1111/j.1365-2427.2011.02708.x.

Izagirre, O., U. Agirre, M. Bermejo, J. Pozo, and A. Elosegi. 2008. “Environmental Controls of Whole-Stream Metabolism Identified from Continuous Monitoring of Basque Streams.” *Journal of the North American Benthological Society*. doi:10.1899/07-022.1.

James, D., K. Horni, and G. Grothendieck. 2014. “Chron: Chronological Objects Which Can Handle Dates and Times.”

Kim, S., A. J. Simpson, E. B. Kujawinski, M. A. Freitas, and P. G. Hatcher. 2003. “High Resolution Electrospray Ionization Mass Spectrometry and 2D Solution NMR for the Analysis of DOM Extracted by C18 Solid Phase Disk.” *Organic Geochemistry* 34 (9): 1325–35. doi:10.1016/S0146-6380(03)00101-3.

Kirschbaum, M. U. F. 1995. “The Temperature Dependence of Soil Organic Matter Decomposition, and the Effect of Global Warming on Soil Organic C Storage.” *Soil Biology and Biochemistry* 27 (6): 753–60. doi:papers2://publication/doi/10.1016/0038-0717(94)00242-S.

Kominoski, J. S., and A. D. Rosemond. 2012. “Conservation from the Bottom up: Forecasting Effects of Global Change on Dynamics of Organic Matter and Management Needs for River Networks.” *Freshwater Science*. doi:10.1899/10-160.1.

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

Lechtenfeld, O. J., N. Hertkorn, Y. Shen, M. Witt, and R. Benner. 2015. “Marine Sequestration of Carbon in Bacterial Metabolites.” *Nature Communications* 6. Nature Publishing Group: 6711. doi:10.1038/ncomms7711.

Marzolf, E. R., P. J. Mulholland, and A. D. Steinman. 1998. “Comment: Improvements to the Diurnal Upstream-Downstream Dissolved Oxygen Change Technique for Determining Whole-Stream Metabolism in Small Streams.” *Canadian Journal of Fisheries and Aquatic Sciences*. doi:10.1139/f98-052.

McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen. 2001. “Spectrofluorometric Characterization of Dissolved Organic Matter for Indication of Precursor Organic Material and Aromaticity.” *Limnology and Oceanography* 46 (1): 38–48. doi:10.4319/lo.2001.46.1.0038.

Minshall, G. W. 1978. “Autotrophy in Stream Ecosystems.” *BioScience* 28 (12): 767–71. doi:10.2307/1307250.

Mulholland, P. J., C. S. Fellows, J. L. Tank, N. B. Grimm, J. R. Webster, S. K. Hamilton, E. Martí, et al. 2001. “Inter-Biome Comparison of Factors Controlling Stream Metabolism.” *Freshwater Biology* 46 (11): 1503–17. doi:10.1046/j.1365-2427.2001.00773.x.

Mulholland, P. J., A. M. Helton, G. C. Poole, R. O. Hall, S. K. Hamilton, B. J. Peterson, J. L. Tank, et al. 2008. “Stream Denitrification across Biomes and Its Response to Anthropogenic Nitrate Loading.” *Nature* 452 (7184): 202–5. doi:10.1038/nature06686.

Mulholland, P. J., E. R. Marzolf, J. R. Webster, and D. R. Hart. 1997. “Evidence That Hyporheic Zones Increase Heterotrophic Metabolism and Phosphorus Uptake in Forest Streams.” *Limnology and Oceanography*.

Naden, P. S., G. H. Old, C. Eliot-Laize, S. J. Granger, J. M. B. Hawkins, R. Bol, and P. Haygarth. 2010. “Assessment of Natural Fluorescence as a Tracer of Diffuse Agricultural Pollution from Slurry Spreading on Intensely-Farmed Grasslands.” *Water Research* 44 (6): 1701–12. doi:10.1016/j.watres.2009.11.038.

Naegeli, M. W., and U. Uehlinger. 1997. “Contribution of the Hyporheic Zone to Ecosystem Metabolism in a Prealpine Gravel-Bed River.” *Journal of the North American Benthological Society* 16 (4): 794–804. doi:10.2307/1468172.

Odum, H. T. 1956. “Primary Production in Flowing Waters.” *Limnology and Oceanography* 1 (1): 102–17.

Ogawa, H., Y. Amagai, I. Koike, K. Kaiser, and R. Benner. 2001. “Production of Refractory Dissolved Organic Matter by Bacteria.” *Science (New York, N.Y.)* 292 (5518): 917–20. doi:10.1126/science.1057627.

Ogle, S. M., F. J. Breidt, and K. Paustian. 2005. “Agricultural Management Impacts on Soil Organic Carbon Storage under Moist and Dry Climatic Conditions of Temperate and Tropical Regions.” *Biogeochemistry* 72 (1): 87–121. doi:10.1007/s10533-004-0360-2.

Ohno, T. 2002. “Fluorescence Inner-FIltering Correction for Determining the Humification Index of Dissolved Organic Matte.” *Environmental Science & Technology* 36 (4): 742–46.

Oksanen, J., F. G. Blanchet, R. Kindt, P. Legendre, P. R. Minchin, R. B. O’Hara, G. L. Simpson, P. Solymos, M. H. H. Stevens, and H. Wagner. 2013. “R Package ‘vegan.’” *Vegan: Community Ecology Package*. http://cran.r-project.org/package=vegan.

Parkhill, K. L., and J. S. Gulliver. 1999. “Modeling the Effect of Light on Whole-Stream Respiration.” *Ecological Modelling* 117 (2-3): 333–42. doi:10.1016/S0304-3800(99)00017-4.

Parlanti, E., K. Wörz, L. Geoffroy, and M. Lamotte. 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): 1765–81. doi:10.1016/S0146-6380(00)00124-8.

Quinton, J. N., G. Govers, K. Van Oost, and R. D. Bardgett. 2010. “The Impact of Agricultural Soil Erosion on Biogeochemical Cycling.” *Nature Publishing Group* 3 (5). Nature Publishing Group: 311–14. doi:10.1038/ngeo838.

Rathbun, R. E., D. Y. Tai, D. J. Shultz, and D. W. Stephens. 1978. “Laboratory Studies of Gas Tracers for Reaeration.” *Journal of the Environmental Engineering Division* 104 (2): 3. http://cedb.asce.org/cgi/WWWdisplay.cgi?5013679.

Ratkowsky, D. A. 1986. “A Suitable Parameterization of the Michaelis-Menten Enzyme Reaction.” *The Biochemical Journal* 240 (2): 357–60.

Raymond, P. A., C. J. Zappa, D. Butman, T. L. Bott, J. Potter, P. Mulholland, A. E. Laursen, W. H. McDowell, and D. Newbold. 2012. “Scaling the Gas Transfer Velocity and Hydraulic Geometry in Streams and Small Rivers.” *Limnology & Oceanography: Fluids & Environments* 2 (0): 41–53. doi:10.1215/21573689-1597669.

R-Core-Team. 2014. “R: A Language and Environment for Statistical Computing.” R Foundation for Statistical Computing: Vienna, Austria. http://www.r-project.org/.

Regnier, P., P. Friedlingstein, P. Ciais, F. T. Mackenzie, N. Gruber, I. A. Janssens, G. G. Laruelle, et al. 2013. “Anthropogenic Perturbation of the Carbon Fluxes from Land to Ocean.” *Nature Geoscience* 6 (8): 597–607. doi:10.1038/ngeo1830.

Roberts, B. J., P. J. Mulholland, and W. R. Hill. 2007. “Multiple Scales of Temporal Variability in Ecosystem Metabolism Rates: Results from 2 Years of Continuous Monitoring in a Forested Headwater Stream.” *Ecosystems*. http://link.springer.com/article/10.1007/s10021-007-9059-2.

Rosemond, A. D. 1993. “Interactions among Irradiance, Nutrients, and Herbivores Constrain a Stream Algal Community.” *Oecologia* 94 (4): 585–94. doi:10.1007/BF00566976.

Rugenski, A. T., C. Múrria, and M. R. Whiles. 2012. “Tadpoles Enhance Microbial Activity and Leaf Decomposition in a Neotropical Headwater Stream.” *Freshwater Biology* 57 (9): 1904–13. doi:10.1111/j.1365-2427.2012.02853.x.

Seitzinger, S. P., H. Hartnett, R. Lauck, M. Mazurek, T. Minegishi, G. Spyres, and R. Styles. 2005. “Molecular-Level Chemical Characterization and Bioavailability of Dissolved Organic Matter in Stream Water Using Electrospray-Ionization Mass Spectrometry.” *Limnology and Oceanography*. doi:10.4319/lo.2005.50.1.0001.

Singer, G. A., C. Fasching, L. Wilhelm, J. Niggemann, P. Steier, T. Dittmar, and T. J. Battin. 2012. “Biogeochemically Diverse Organic Matter in Alpine Glaciers and Its Downstream Fate.” *Nature Geoscience*. doi:10.1038/ngeo1581.

Singer, G. A., F. O. Omengo, M. E. McClain, and T. J. Battin. n.d. *Land Use Impacts Dissolved Organic Matter with Implications for Carbon Cycling in the Headwaters of the Mara River Catchment, Kenya*. *Global Change Biology*.

Soetaert, K. 2014. “Shape: Functions for Plotting Graphical Shapes, Colors.” http://cran.r-project.org/package=shape.

Soetaert, K., and P. M. J. Herman. 2009. *A Practical Guide to Ecological Modelling: Using R as a Simulation Platform*. *Media*. Springer. http://books.google.com/books?hl=en&lr=&id=aVjDtSmJqhAC&oi=fnd&pg=PA1&dq=A+practical+guide+to+ecological+modelling:+using+R+as+a+simulation+platform&ots=AJvxfEks26&sig=SjlKXYb6q0s20bguvB7Kd9i4gpM.

Stallard, R. F. 1998. “Terrestrial Sedimentation and the Carbon Cycle: Coupling Weathering and Erosion to Carbon Burial.” *Global Biogeochemical Cycles* 12 (2): 231. doi:10.1029/98GB00741.

Stanley, E. H., S. M. Powers, N. R. Lottig, I. Buffam, and J. T. Crawford. 2012. “Contemporary Changes in Dissolved Organic Carbon (DOC) in Human-Dominated Rivers: Is There a Role for DOC Management?” *Freshwater Biology* 57 (SUPPL. 1): 26–42. doi:10.1111/j.1365-2427.2011.02613.x.

Stedmon, C. A, S. Markager, and R. Bro. 2003. “Tracing Dissolved Organic Matter in Aquatic Environments Using a New Approach to Fluorescence Spectroscopy.” *Marine Chemistry* 82 (3-4): 239–54. doi:10.1016/S0304-4203(03)00072-0.

Stedmon, C. A., and R. Bro. 2008. “Characterizing Dissolved Organic Matter Fluorescence with Parallel Factor Analysis: A Tutorial.” *Limnology and Oceanography: Methods* 6: 572–79. doi:10.4319/lom.2008.6.572.

Stedmon, C. A., and S. Markager. 2005. “Resolving the Variability of Dissolved Organic Matter Fluorescence in a Temperate Estuary and Its Catchment Using PARAFAC Analysis.” *Limnology and Oceanography* 50 (2): 686–97. doi:10.4319/lo.2005.50.2.0686.

Stedmon, C. A., S. Markager, M. Sondergaard, T. Vang, A. Laubel, N. H. Borch, and A. Windelin. 2006. “Dissolved Organic Matter (DOM) Export to a Temperate Estuary: Seasonal Variations and Implications of Land Use.” *Estuaries and Coasts* 29 (3): 388–400. <Go to ISI>://000239912400005\nhttp://link.springer.com/content/pdf/10.1007/BF02784988.pdf.

Steinman, A. D. 1992. “Does an Increase in Irradiance Influence Periphyton in a Heavily-Grazed Woodland Stream?” *Oecologia* 91 (2): 163–70. doi:10.1007/BF00317779.

Stubbins, A., J.-F. Lapierre, M. Berggren, Y. T. Prairie, T. Dittmar, and P. A. del Giorgio. 2014. “What’s in an EEM? Molecular Signatures Associated with Dissolved Organic Fluorescence in Boreal Canada.” *Environmental Science & Technology* 48: 10598–606.

Tank, J. L., and J. R. Webster. 1998. “Interaction of Substrate and Nutrient Availability on Wood Biofilm Processes in Streams.” *Ecology* 79 (6): 2168–79. doi:10.1890/0012-9658(1998)079[2168:IOSANA]2.0.CO;2.

Thyssen, N., M. Erlandsen, E. Jeppesen, and C. Ursin. 1987. “Reaeration of Oxygen in Shallow, Macrophyte Rich Streams: I - Determination of the Reaeration Rate Coefficient.” *Internationale Revue Der Gesamten Hydrobiologie Und Hydrographie* 72 (4): 405–29. doi:10.1002/iroh.19870720403.

Tranvik, L. J. 1998. “Degradation of Dissolved Organic Matter in Humic Waters by Bacteria.” *Ecological Studies; Aquatic Humic Substances: Ecology and Biogeochemistry* 133: 259–83.

Tranvik, L. J., J. A. Downing, J. B. Cotner, S. A. Loiselle, R. G. Striegl, T. J. Ballatore, P. Dillon, K. Finlay, K. Fortino, and L. B. Knoll. 2009. “Lakes and Reservoirs as Regulators of Carbon Cycling and Climate.” *Limnology and Oceanography*. doi:10.4319/lo.2009.54.6_part_2.2298.

Tsivoglou, E. C., and L. A. Neal. 1976. “Tracer Measurement of Reaeration: III. Predicting the Reaeration Capacity of Inland Streams.” *Journal (Water Pollution Control Federation)* 489: 2669–89.

Uehlinger, U., C. König, and P. Reichert. 2000. “Variability of Photosynthesis-Irradiance Curves and Ecosystem Respiration in a Small River.” *Freshwater Biology* 44 (3): 493–507. doi:10.1046/j.1365-2427.2000.00602.x.

Uzarski, D. G., C. A. Stricker, T. M. Burton, D. K. King, and A. D. Steinman. 2004. “The Importance of Hyporheic Sediment Respiration in Several Mid-Order Michigan Rivers: Comparison between Methods in Estimates of Lotic Metabolism.” *Hydrobiologia* 518 (1-3): 47–57. doi:10.1023/B:HYDR.0000025056.18736.d6.

Van de Bogert, M: C., S. R. Carpenter, J. J. Cole, and M. L. Pace. 2007. “Assessing Pelagic and Benthic Metabolism Using Free Water Measurements.” *Limnology and Oceanography: Methods* 5: 145–55. doi:10.4319/lom.2007.5.145.

Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing. 1980. “The River Continuum Concept.” *Canadian Journal of Fisheries and Aquatic Sciences*. doi:10.1139/f80-017.

Venkiteswaran, J. J., L. I. Wassenaar, and S. L. Schiff. 2007. “Dynamics of Dissolved Oxygen Isotopic Ratios: A Transient Model to Quantify Primary Production, Community Respiration, and Air-Water Exchange in Aquatic Ecosystems.” *Oecologia* 153 (2): 385–98. doi:10.1007/s00442-007-0744-9.

Vitousek, P. M. 1997. “Human Domination of Earth’s Ecosystems.” *Science* 277 (5325): 494–99. doi:10.1126/science.277.5325.494.

Volk, C. J., C. B. Volk, and L. A. Kaplan. 1997. “Chemical Composition of Biodegradable Dissolved Organic Matter in Streamwater.” *Limnology and Oceanography*. doi:10.4319/lo.1997.42.1.0039.

Wallis, P. M., and T. I. Ladd. 1983. “Organic Biogeochemistry of Groundwater at a Mountain Coal Mine.” *Geomicrobiology Journal* 3 (1). Taylor & Francis Group: 49–78. doi:10.1080/01490458309377783.

Wanninkhof, R., P. J. Mulholland, and J. W. Elwood. 1990. “Gas Exchange Rates for a First-Order Stream Determined with Deliberate and Natural Tracers.” *Water Resources Research*. doi:10.1029/90WR00140.

Webster, J. R., and J. L. Meyer. 1997. “Organic Matter Budgets for Streams: A Synthesis.” *Journal of the North American Benthological Society* 16 (1): 141–61. doi:10.2307/1468247.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. “Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon.” *Environmental Science and Technology* 37 (20): 4702–8. doi:10.1021/es030360x.

Wetzel, R. G. 1992. “Gradient-Dominated Ecosystems: Sources and Regulatory Functions of Dissolved Organic Matter in Freshwater Ecosystems.” *Hydrobiologia* 229 (1): 181–98. doi:10.1007/BF00007000.

———. 2001. *Limnology: Lake and River Ecosystems*. *Journal of Phycology*. Vol. 37. doi:10.1046/j.1529-8817.2001.37602.x.

Williams, C. J., Y. Yamashita, H. F. Wilson, R. Jaffé, and M. A. Xenopoulos. 2010. “Unraveling the Role of Land Use and Microbial Activity in Shaping Dissolved Organic Matter Characteristics in Stream Ecosystems.” *Limnology and Oceanography* 55 (3): 1159–71. doi:10.4319/lo.2010.55.3.1159.

Wilson, H. F., and M. A. Xenopoulos. 2008. “Ecosystem and Seasonal Control of Stream Dissolved Organic Carbon along a Gradient of Land Use.” *Ecosystems* 11 (4): 555–68. doi:10.1007/s10021-008-9142-3.

———. 2009. “Effects of Agricultural Land Use on the Composition of Fluvial Dissolved Organic Matter.” *Nature Geoscience* 2 (1). Nature Publishing Group: 37–41. doi:10.1038/ngeo391.

Wollheim, W. M., B. J. Peterson, L. A. Deegan, J. E. Hobbie, B. Hooker, W. B. Bowden, K. J. Edwardson, D. B. Arscott, A. E. Hershey, and J. Finlay. 2001. “Influence of Stream Size on Ammonium and Suspended Particulate Nitrogen Processing.” *Limnology and Oceanography*. doi:10.4319/lo.2001.46.1.0001.

Young, R. G., and A. D. Huryn. 1996. “Interannual Variation in Discharge Controls Ecosystem Metabolism along a Grassland River Continuum.” *Canadian Journal of Fisheries and Aquatic Sciences*. doi:10.1139/f96-186.

———. 1998. “Comment: Improvements to the Diurnal Upstream-Downstream Dissolved Oxygen Change Technique for Determining Whole-Stream Metabolism in Small Streams.” *Canadian Journal of Fisheries and Aquatic Sciences* 55 (7): 1784–85. doi:10.1139/f98-052.

———. 1999. “Effects of Land Use on Stream Metabolism and Organic Matter Turnover.” *Ecological Applications* 9 (4): 1359–76. doi:10.1890/1051-0761(1999)009[1359:EOLUOS]2.0.CO;2.

Young, R. G., C. R. Townsend, and C. D. Matthaei. 2004. “Functional Indicators of River Ecosystem Health - an Interim Guide for Use in New Zealand.” *Report No. 870. Cawthron, Dunedin, New Zealand*, 57.

Zsolnay, A., E. Baigar, M. Jimenez, B. Steinweg, and F. Saccomandi. 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.

6.5 Curriculum Vitae

Personal Data

Name:	Thomas Fuß
Date of birth:	10th of March 1988
Place of birth:	Vienna (Austria)

Education

September 1994 – June 1998:	Primary School, Vienna, Austria
September 1998 – June 2006:	Grammar School, Vienna, Austria
October 2007 – May 2009:	studies of Architecture at the Vienna University of Technology, Austria
October 2009 – July 2012:	Bachelor degree in Biology at the University of Vienna, Austria Title of Bachelor thesis: "Nitrogen decomposition in two different woodlands and the finding of a bottleneck"
Since October 2012:	Studies of Ecology at the University of Vienna, Austria Title of Master thesis: "Linking dissolved organic matter composition to stream ecosystem metabolism across a land-use gradient"

Teaching Experience

December 2013 & February 2015:	Tutor at the University of Vienna, Austria Practical course in statistics: "Multivariate statistische Methoden in der Ökologie"

Work Experience in Science

September to December 2012:	Contract for services: Lab work Department of Limnology, University of Vienna, Austria
July 2013:	Contract for services: Field and Lab work, Department of Limnology & Bio-Oceanography, University of Vienna, Austria
Since January 2015:	Student assistant position at Leibnitz-Institut für Gewässerökologie und Binnenfischerei (IGB), Berlin, Germany

Further Skills

Languages:	German & English fluently, basic knowledge of Spanish
Computer literacy:	MS Word, MS Excel, MS PowerPoint, R, GrassGis, SPSS
February 2015:	Poster Presentation at ASLO meeting, Granada, Spain