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# Linkage between the temporal and spatial variability of dissolved organic matter and whole stream metabolism

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## Abstract

Dissolved organic matter (DOM) is an important resource for microbes, thus affecting the whole stream metabolism. The factors influencing its chemical composition and thereby also its bio-availability are complex and not thoroughly understood. We hypothesized that the whole stream metabolism itself can affect the DOM composition and that the coupling of both is influenced by seasonality and different land use forms. We tested this hypothesis in a comparative study on two pristine forestry streams and on two non-forestry streams. The investigated streams were located in the Harz Mountains (Central Europe, Germany). The whole stream metabolism was measured with a classical two station oxygen change technique and the variability of DOM with fluorescence spectroscopy. We take also into account the geochemical and geophysical characteristic of each stream.

All streams were clearly net heterotrophic, whereby the non-forestry streams showed a higher primary production in general, which was correlated with irradiance and with the total phosphorus concentration. The whole stream metabolism but also the chromophoric DOM (CDOM) showed distinct seasonal patterns. We detected three CDOM component groups (C1, C2, C3) by the use of the parallel-factor-analysis (PARAFAC) and found temporarily variable, typical component fingerprints (C1 : C2, C1 : C3, C3 : C2) for CDOM originated from forestry streams and from non-forestry streams. Based on comparative literature studies and correlation analysis with different indices, we demonstrate that two of the components are clearly from terrigenous sources (C1, C3) and one is rather autochthonously (C2) derived. The whole CDOM matrix was dominated by humic like, high molecular-weight substances, followed by humic like, fulfic acids, low molecular-weight substances, and with minor amounts of amino-acids and proteins. We showed for the first time a correlation between the gross primary production (GPP) and the autochthonously derived, low molecular weight DOM. The amount of autochthonously produced DOM increased overall with increasing GPP, as indicated by a tight, positive correlation between the fluorescence index (FI,

$R^2 = 0.84$) or C2 ($R^2 = 0.48$) and the ratio of GPP and the daily community respiration (CR$_{24}$).

This study showed for the first time the linkage between whole stream metabolism and DOM composition, based on a new integrated approach. We demonstrated that
[5] this relationship is influenced by seasonality and different land use forms. These complex mechanisms lead to typical DOM fingerprints for streams pass through the different land use forms.

# 1 Introduction

Panta rhei, ouden menei = everything flows, nothing stands still. With this quotation
[10] the Greek philosopher Heraclitus (535–475 BC) described his finding, that every phenomenon underlies continual changes. This "law of nature" is also valid for the composition of dissolved organic matter (DOM) in aquatic ecosystems, which underlays seasonal and local variations, that are mainly determined by the different land use forms and changes in the aquatic and terrestrial biological activity (Jaffé et al., 2008;
[15] Stedmon and Markager, 2005b; Stedmon et al., 2006; Williams et al., 2010).

DOM is a complex mixture of soluble organic compounds that vary in their reactivity and ecological role (Jaffé et al., 2008; Wetzel, 1992). Depending on the chemical composition of DOM, it could supply main nutrients for the heterotrophic production in streams. It is one of the largest sources for biologically available organic carbon,
[20] nitrogen and phosphorus in aquatic ecosystems (Stedmon et al., 2006). The biogeochemical composition of DOM is mainly determined by its source (Ohno et al., 2007). Most streams in the northern hemisphere are net heterotrophic, i.e. they are net sinks of organic matter rather than sources (Marcarelli et al., 2011). This can only be sustainable if aquatic respiration is subsidized by organic inputs from allochthonous, i.e.
[25] terrigenous sources. Organic matter that avoids biological degradation in the terrestrial environment must at least partly become susceptible to the stream metabolism (Wetzel et al., 1995). Therefore, stream metabolism studies are important if carbon

turnover process studies are planned (cp. Cole and Caraco, 2001; Mulholland et al., 2001). But integrated investigations on the coupling of whole stream metabolism and DOM composition are rare.

The light availability often increases with an increasing distance from the stream source, and with this the phototrophic organic matter production becomes more important (Finlay et al., 2011; Minshall, 1978). Also the raising agricultural land use which leads to such changes in the light conditions and to an increase in the nutrient import from the terrestrial environment can affect the gross primary production (GPP) and community respiration ($CR_{24}$) (Bernot et al., 2010; Gücker et al., 2009; Williams et al., 2010; Young and Huryn, 1999). To our knowledge there exist no studies describing how land use changes can affect DOM composition and its ecological role driven by stream metabolism changes.

Different methods exist to characterize DOM in aquatic environments. Many studies focus on investigations on stoichiometry (C : N or C : P ratios), stable isotope composition ($\delta^{13}$C), and the detection of amino acids, carbohydrates, and lignin phenols (McDowell and Likens, 1988; Hood et al., 2005; Spencer et al., 2010). All these measures are helpful for describing the composition, origin and availability of DOM. However, the required analytical and financial efforts are high. This becomes disadvantages when high throughput-analyses are required, e.g. when comparing large-scale patterns in river networks. Alternative techniques are based on the finding that the biochemical characteristic of DOM can be related to its optical properties (Mueller et al., 2012; Herzsprung et al., 2012). The individual fluorescence and light absorption of the optical fraction (the chromophoric dissolved organic matter, CDOM) can therefore be used to trace the compositional changes of DOM (Jaffé et al., 2008; Fellman et al., 2010). Especially the fluorescence characterization of DOM, known as excitation emission matrices (EEM), provides solid proxies for the source, the redox state, and the biological availability of CDOM. In contrast to classical analytical techniques this is a helpful tool for sample-intensive investigations on the DOM dynamic in aquatic environments (Jaffé et al., 2008; Fellman et al., 2010). Parallel factor analysis (PARAFAC) is the

best method for analysing the CDOM composition on the basis of EEM's. It splits data matrixes of the EEM's into underlying fluorescence appearance and is therefore well-useable to distinguish between the different component groups (Stedmon et al., 2003; Stedmon and Bro, 2008; Williams et al., 2010). In combination with usual fluorescence indices, it is possible to distinguish between different humic like component groups and protein like substances, as well as between autochthonous or allochthonous CDOM sources (Fellman et al., 2010; Mueller et al., 2012; Stedmon and Bro, 2008). Fluorescence measurements are therefore a useful tool to analyze the dynamics and control of the DOM composition in streams (Huang and Chen, 2009; Williams et al., 2010; Wilson and Xenopoulos, 2009).

Increasing areas of cropland and decreasing areas of wetland in the catchment leads to an increase in the contribution of recently produced organic matter (Wilson and Xenopoulus, 2009). DOM released from autochthonous sources like living aquatic plants – i.e. vascular plants, mosses, phototrophic biofilms and phytoplankton – is generally of lower molecular weight and contains fewer aromatic rings than compounds leached from terrestrial soils and litter (Barrón et al., 2012; Lapierre and Frenette, 2009; Stepanauskas et al., 2000). The terrigenous organic matter can also consist of low molecular compounds; terrestrial plants and fungi produce easily available exudates that can enter the aquatic ecosystem and therefore influence the quality of DOM (McKnight, 2001; Jaffé et al., 2008). Detailed studies on how the DOM composition is linked to metabolism as a measure for stream respiration and assimilation are generally scarce.

The aim of the presented study was to detect linkages between whole stream metabolism and DOM composition in streams and to reveal how changes in the whole stream metabolism as well as the DOM composition are affected by seasonality and by the spatial variability of land use forms (forestry vs. non-forestry streams). In this purpose we combined the classical two station oxygen change technique for whole stream metabolism studies with fluorescence spectroscopy as an optical finger print technique for the detection of DOM component groups.

## 2 Material and methods

### 2.1 Study area

Our investigation area is located in the south-eastern part of the Harz Mountains, in Central Europe, Germany (Fig. 1). This area lies in the temperate zone in the Northern Hemisphere and has in general continental climate. Typically for this upland are rather wet summers and cold winters. The bedrock in the upper mountains consists of a Palaeozoic upland overlaid with brown earth and bleaching clay, based on loess layer and silt or silt-rubble. The geological basis of the middle and upper mountains consists of argillaceous shale and greywacke. Depending on the bedrock and the associated rubble layer alkaline brown earth, podsol-brown earth or podsols can be found there. Caused by the wet climate also gley and fens are located in this area (Karste et al., 2011).

By considering our research questions we were looking for streams with different light regimes and different organic matter loadings. Special attention was thereby given to the impact of seasonal changes and different land use forms (forestry versus non-forestry streams) on the coupling of these parameters. We selected two forestry first order streams (Zillierbach and Ochsenbach) and two non-forestry streams of higher ordering (Rappbode, third order stream and Hassel, second order stream). The forestry streams are rather pristine and running through dense alder forests in the upper Harz Mountains. The open-land streams are more influenced by cow ranching – with different intensity – which is a typical land use form in this region. They are located in the middle Harz Mountains. We selected for each stream a reach that was representative for the respective stream. An overview of the sampling periods and detailed stream reach characteristics are given in Table 1 and the correspondending air temperature and the precipitation data can be found in Fig. 2.

## 2.2 Sampling and sampling preparation

The whole stream metabolism and the DOM composition were measured at all four streams in different seasons. We investigated all streams only at base flow, where a nearly constant water level over the whole sampling period was guaranteed. The sampling period was 4 days per investigation. The chemical and physical parameters were sampled and measured in parallel to the metabolism studies in spring, summer and autumn 2011. In the winter 2012, only the chemical and selected physical parameters were measured (Tables 1, Fig. 3). In this season, all streams were found under a dense ice and snow cover, and the upper soil layers were frozen. This prevented accurate metabolism studies.

All water samples for further optical and chemical analysis were collected between eleven and thirteen o'clock (UTC), directly under the water surface, at the in- and out-flow of the stream reach that was selected for the metabolism studies. The samples were taken in parallel to the metabolism studies, in accordance with the water travel time ($t$) at the stations one and two, twice a day, behind one another. If necessary, all water samples were filtered and fixed directly in the field. For further DOC analysis and for optical analysis on CDOM components, the water samples were filtered through Whatmann glass fibre filters (0.7 μm, GF/F). The samples were acidified with $H_2SO_4$ (1 : 4) for total phosphorus (TP) analysis and samples for nitrogen analysis were fixed with $HgCl_2$. All water samples (filtered and non-filtered) were transferred into acid-rinsed and combusted brown glass bottles, and stored cool (6 °C) until further analyses. All fluid samples where measured not later than 2 days after sampling.

The parameter conductivity, pH and turbidity were measured in situ at the in- and out-flow station of the respective stream reach with multiparameter probes (YSI 6600-V2, and Hydrolab DS5X). The logging interval was set to 10 or 15 min.

## 2.3 Metabolism studies

The whole stream metabolism on all streams was estimated with the upstream-downstream diurnal dissolved oxygen change technique (Marzolf et al., 1994; Young and Huryn, 1998).

For each stream one representative stream reach was defined with lengths from 40 to 135 m (Table 1). Stream metabolism was measured using oxygen measurements at both ends of the reach at one-minute intervals, for over fifty hours. This allowed us to estimate two GPP and $CR_{24}$ values for each stream, in the respective season. Oxygen ($O_2$) and temperature ($T$) were measured with D-OptoLogger (ZEBRA-TECH LTD). Changes in dissolved oxygen between upstream and downstream ($\Delta DO$) were calculated after $t$, corrected for $T$, pressure, lateral inflow ($I$), depth ($z$) and reaeration and were then considered as the result of metabolic processes (GPP, $CR_{24}$).

The atmospheric pressure was measured two times per day with a barometer. The actual pressure was then interpolated. The travel time ($t$) and the reaeration coefficient ($k$) between both stations were measured by injecting a volatile (propane) and a conservative tracer (NaCl) into the stream. The conservative tracer was injected into the stream water by a slug. For the determination of $I$, discharge ($Q$), and $t$, the changes in conductivity where measured in a one-second interval with YSI probes at the stream reach in- and out-flow. After $t$ was determined, propane was bubbled into the stream by the use of special diffusors for minimum one $t$. In the following water samples were taken with an air headspace at the beginning and at the end of the reach. The data of these samples were than used for the classical reaeration calculation (Marzolf et al., 1994; Young and Huryn, 1998). For the control of a logical propane decrease between both stations we took additional samples at four stations in between. The samples were always taken in the middle of the main stream, with the wave, in triplicate, without turbulences in dense crimped vials and stored at 6 °C. The equilibrated headspace was analysed within one week after collection in the laboratory by flame ionization detection on a SRI 8610C gas chromatograph. We used hydrogen as carrier gas. The reaeration

of propane ($k_{\text{propane}}$) was calculated from the decline in dissolved propane content between both stations and corrected for $l$. The $k_{\text{propane}}$ was converted to $k_{\text{oxygen}}$ using the factor of 1.39 (Rathbun et al., 1978). Parallel to the oxygen measurements irradiance (photosynthetic active radiation, PAR) was monitored with a spherical quantum sensor (LI-COR) which was installed circa 1 m above the water surface. The actual irradiance was logged each minute.

The metabolism rate for one day was calculated based on two night measurements (PAR $< 1\,\mu\text{mol m}^{-2}\,\text{s}^{-1}$) and one daytime measurement (PAR $\geq 1\,\mu\text{mol m}^{-2}\,\text{s}^{-1}$). GPP and $CR_{24}$ were calculated referring to the description given in Marzolf et al. (1994) and Young and Huryn (1998). Thereby were the estimated $\Delta\text{DO}$ the basis for following calculation of the metabolism rates. The daily respiration rate was computed with the following equation:

$$CR_{24} = \frac{\sum_{t_0}^{t_1} \Delta\text{DO}}{\alpha 1 + \alpha 2} \cdot m, \tag{1}$$

whereby $t_0$ describes the sunset (first time with PAR $< 1\,\mu\text{mol m}^{-2}\,\text{s}^{-1}$) and $t_1$ represents sunrise (first time with PAR $\geq 1\,\mu\text{mol m}^{-2}\,\text{s}^{-1}$), $\alpha 1$ is the number of $\Delta\text{DO}$ values in the first night and $\alpha 2$ is the number of $\Delta\text{DO}$ values in the second night, $m$ is the number of measurements during one day pending on the logging interval (in this case $m = 1440$). GPP was than calculated as follow:

$$GPP = \frac{CR_{24}}{m} \cdot n - \sum_{t_1}^{t_0} \Delta\text{DO}, \tag{2}$$

with $n$ as the number of $\Delta\text{DO}$ between $t_1$ and $t_0$. All metabolism rates were converted to rates per unit area by dividing the area of stream bottom between the two stations.

For the ecologically characterisation of the investigated streams we calculated the indices $P/R$ and net ecosystem production (NEP). $P/R$ is the ratio of GPP and $CR_{24}$.

$P/R$ values $> 1$ indicate that the stream is rather phototrophic, and values $< 1$ indicate a rather heterotrophic stream ecosystem. NEP was calculated by subtracting $CR_{24}$ from GPP. This is an index for the ecological characterization of the metabolism in natural lotic systems. It excludes the possible bias coming from groundwater inflow changes that could lead to the overestimations of the oxygen consumption and therefor of $CR_{24}$. It is usually used to describe the source of energy for the whole stream metabolism. If NEP values are positive, the investigated stream has a positive energy budget, whilst negative values indicate a net energy loss from this ecosystem (Mulholland et al., 2001).

However, uncertainties in open channel estimates of the whole stream metabolism generally appears in the computation, the measurement techniques (instrument calibration, and the precision of measurements), as well as the detection of the environmental variables like $t$, $I$, $Q$, $k$, and $z$ (Reichert et al., 2009).

## 2.4 Chemical and optical analysis

The chemical and the optical analyses were done after standard protocols. We minimize uncertainties which could be occur directly in the sampling procedure or as analytical errors by parallel stock measurements, extremely short storage times (6 °C) and a clean field laboratory working place. Total phoshorus (TP) was measured with the ammonium molybdite spectrometric method. Nitrite ($NO_2^-$), nitrate ($NO_3^-$), and ammonium ($NH_4^+$) were photometrically determined with the segmented flow technique DIN EN ISO 13395. The measurements of DOC, spectral absorption and EEM analysis were carried out in parallel within 48 h after sampling. In more detail, the DOC concentrations were measured by high temperature combustion using a DIMATOC®2000. Fluorescence measurements were done using a Skalar fluorescence spectrophotometer. The excitation-emission matrix (EEM) was obtained by combining a series of emission scans made from 260 to 385 nm (5 nm steps) while excitation at wavelengths were ranging from 240 to 360 nm (5 nm steps). After we were not able to find a quenching

effect with a serial dilution test we decided that, because of the low DOM concentration in our samples, the EEM-spectra need no correction for the inner filter effect. Instrumental changes and biases were checked by the use of two quinine stocks with different concentrations. The EEMs were Raman calibrated with MilliQ water as blank
5 before their further computation.

Following indices were calculated based on the corrected EEM-spectra: (i) the two dimensional fluorescence index (FI), which provides information about the source of DOM (McKnight, 2001); (ii) the freshness index ($\beta : \alpha$), which indicates if DOM is rather recently produced or decomposed (Parlanti et al., 2000) and where it origi-
10 nally comes from (Huguet et al., 2009); and (iii) the humification index (HIX) which is an indicator of the extent of humification and biologically degradation (Ohno, 2002). Based on instrumental limitations, FI was calculated as the ratio of emission intensity at wavelength of 450 nm to that of 500 nm, obtained with an excitation at 360 nm. In the original work done by McKnight et al. (2001), the aforementioned ratio was calcu-
15 lated for an excitation at 370 nm. $\beta : \alpha$ was used as an additional indicator for the DOM source to avoid biases based on this adjustment. This index was computed as the ratio of the emission intensity at 380 nm divided by the highest detected emission intensity between 420 and 435 nm, all obtained for an excitation at 310 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009; Fellman et al., 2010). $\beta : \alpha$ values > 1 indicate an
20 rather autochthonous origin and values < 0.6 indicate primarily allochthonous sources (Huguet et al., 2009; Williams et al., 2010). The HIX index was calculated by dividing the peak area under the emission spectra between 435–480 nm with the peak area under the emission spectra between 300–445 nm, both at 254 nm excitation (Zsolnay et al., 1999).

25 The whole EEM data set was examined by the use of PARAFAC. The PARAFAC analysis was carried out in MATLAB (version R2011a) using the "N-way toolbox for MATLAB" (Anderson and Bro, 2000) and following the tutorial of Stedmon and Bro (2008). The whole dataset were thereby outlier corrected in accordance with this tutorial. The components that were valid – i.e. their excitation and emission maxima – were

compared with the components described in the actual literature. This procedure was for example recently used by Mueller et al. (2012) but also by many other authors (see Cory and McKnight, 2005; Murphy et al., 2006; Stedmon and Markager, 2005a; Williams et al., 2010). An overview of the most common components can be found in the review published by Fellman et al. (2010).

The absorption by CDOM was measured from 200 to 800 nm using a Hach Lange DR 5000 spectrophotometer and a 1 cm quarz cuvette. Deionised water was used as blank. An additional background correction was applied by subtracting the average absorbance value per nm from 700 to 800 nm from the rest of the spectrum. We calculated the absorption coefficients by multiplying the optical density by 2.303/cuvette path length. From these data the absorption was computed at 375 nm ($a_{375}$), which is an indicator of the DOM concentration (Stedmon et al., 2006).

## 2.5 Statistical analysis

Linear regression models were used to test and to describe relationships between regarded parameters, like the CDOM compounds, indices, and metabolism parameters. Spearman's rank correlation coefficients and Pearson correlation were used to test the significance of correlations. A residual analysis was performed for the linear models describing relationship between the CDOM components to check the assumption of normal distribution of the residuals. A linear model is only valid if the residuals are normal distributed (Draper and Smith, 1998). The parameters of the regression (slope and y-intersect) were calculated by the least square estimation. An F-Test for significance of regressions was conducted with null hypothesis $H_0: \beta_1 = 0$ against the alternative $H_0: \beta_1 \neq 0$. All statistical analyses were performed with MATLAB, Sigma Plot 12.0, and Microsoft Exel 2010.

## 3 Results

### 3.1 Geochemical and geophysical stream characteristics

Table 1 and Fig. 3 give an overview of the geochemical and physical stream characteristics. Whilst the streams Zillierbach, Ochsenbach and Hassel had discharges around $3\,L\,s^{-1}$, the average discharge measured for the Rappbode exceeded those measured in the other streams for over nine times. The Hassel had the highest nutrient concentrations, i.e. on average $0.66\,mg\,L^{-1}\,NH_4^+$, $0.10\,mg\,L^{-1}\,NO_2$, $2.07\,mg\,L^{-1}\,NO_3$, $4.78\,mg\,L^{-1}$ DOC, and $0.14\,mg\,L^{-1}$ TP . In addition, the DOC concentration ($8.86\,mg\,L^{-1}$, mean) and the total phosphorus concentration ($0.40\,mg\,L^{-1}$, mean) were especially highest in summer. Based on these comparable high nutrient concentrations of the Hassel we summarize the other three streams in the following as nutrient poor streams. However, in summer also the Rappbode revealed with average $5.06\,mg\,L^{-1}$ high DOC concentrations. The mean DOC concentrations in the Hassel ($3.42\,mg\,L^{-1}$) were in spring, fall and winter in the range of those measured in the Zillierbach ($3.61\,mg\,L^{-1}$). In contrast to these streams, the Ochsenbach revealed the lowest DOC concentration with a mean of $1.58\,mg\,L^{-1}$. The lowest nitrate concentrations were observed in the Rappbode, where the mean values were $0.22\,mg\,L^{-1}$. Both non-forestry streams – Hassel and Rappbode – had generally higher phosphorus concentrations. Their respective mean phosphorus values ranged from 0.022 to $0.396\,mg\,L^{-1}$ for the Hassel and from 0.011 to $0.054\,mg\,L^{-1}$ for the Rappbode. As shown in Table 1, all streams are neutral with respect to the pH. The measured average pH values range from 7.3 to 7.9 with the Ochsenbach having the lowest pH values (7.4, average over all seasons). The Ochsenbach has also the lowest conductivity ($151\,\mu S\,cm^{-1}$, mean). With mean values from $183\,\mu S\,cm^{-1}$ in winter and $429\,\mu S\,cm^{-1}$ in autumn, the Hassel has the highest conductivity nearly over the whole year. Only the winter values were in the range of the conductivity measured for the other streams. The water temperature and $Q$ followed the typical seasonal variability in most of the streams (Table 1). Only

the Hassel had the highest discharge and slightly decreased temperatures in summer. This is the result of the previous raining period (Fig. 2).

## 3.2 Whole stream metabolism

The results of the metabolism studies are summarized in Fig. 4. $P/R$ values for all streams were below 1, indicating the heterotrophic character of all streams. With mean ratios ranging from 0.01 to 0.11 the forestry streams were more heterotrophic than the non-forestry streams, which had mean $P/R$ ratios of 0.3. Especially the Rappbode showed highest $P/R$ ratios from average 0.28 to 0.51. The $P/R$ is influenced by changes in GPP and $CR_{24}$. All streams showed the highest GPP and $CR_{24}$ values in spring. In this season the average estimated GPP in the forestry streams was 0.77 g $O_2$ m$^{-2}$ d$^{-1}$ and in the non-forestry streams 3.19 g $O_2$ m$^{-2}$ d$^{-1}$. With mean rates above 9 g $O_2$ m$^{-2}$ d$^{-1}$ the Zillierbach and the Hassel had the highest $CR_{24}$. In comparison to the spring data, the metabolic activity was clearly decreased in all streams during summer, as indicated by the lower GPP and $CR_{24}$ values. In fall $CR_{24}$ increased again in the pristine forestry streams and in the Hassel, with different magnitudes (Fig. 4). This increasing $CR_{24}$ leads to very low average $P/R$ values ranging from 0.01 to 0.07. The mean GPP increased in this season only in the Hassel (from 0.10 to 0.54 g $O_2$ m$^{-2}$ d$^{-1}$) and less pronounced in the Zillierbach (from 0.11 to 0.15 g $O_2$ m$^{-2}$ d$^{-1}$). With these changes also the trophic status that is indicated by the $P/R$ values changes during the seasons.

We found a tight correlation ($R^2 = 0.695$, $p < 0.001$) between GPP and daily irradiance (Fig. 5). When considering only the nutrient poor streams Zillierbach, the Ochsenbach, and the Rappbode, this correlation even becomes distinctly stronger ($R^2 = 0.830$, $p < 0.001$). Besides the pronounced light effect and if excluding the summer values from the Hassel, 82 % of the GPP variability can be explained by changes in TP ($R^2 = 0.822$, $p < 0.001$). We found no indications (i.e. no significant correlations) that the different metabolism parameters (GPP or $CR_{24}$) are coupled to other nutrients.

In order to indicate the main source of energy for the whole stream metabolism we also calculated NEP, which indicates the net oxygen production of a stream and therefore the status of the metabolic balance. NEP shows negative values in all streams, indicating that they rely on additional external, terrestrially derived energy for covering their metabolic demands. With average values of $-5.4\,\mathrm{g\,O_2\,m^{-2}\,d^{-1}}$ the Zillierbach and the Hassel had the lowest NEP. In contrast to this, the NEP values for the Ochsenbach and especially for the Rappbode were clearly above the average NEP of the other streams. With mean values ranging from $-0.42$ to $-3.79\,\mathrm{g\,O_2\,m^{-2}\,d^{-1}}$ the Rappbode has the highest NEP in comparison to all other streams (Fig. 4).

## 3.3 CDOM composition

A significant linear relationship between $a_{375}$, which is an optical indicator for the DOM concentration, and DOC, which has the main fraction in DOM, was found ($R^2 = 0.637$, $p < 0.0001$). Most of the detected DOM components are reproducible by comparison of their excitation and emission maxima with the recent literature (see Cory and McKnight, 2005; Fellman et al., 2010; Murphy et al., 2006; Stedmon and Markager, 2005a; Williams et al., 2010). Figure 6 shows the three components that were detected with PARAFAC-analysis using the EEM's from all four streams ($n = 100$, after outlier selection $n = 98$). These components are termed C1, C2 and C3 in the following. A detailed description of them as well as their origin is presented in Table 2. The main component in all samples was C1. It consists mainly of UVC humic-like, aromatic substances with higher molecular weights and is descripted as terrestrially derived and highest in wetlands and forests. The minor part in C1 consists of UVA humic-like fulvic acid. Both C1 fractions are generally widespread. The component C2 is a UVA low-molecular weight humic-like substance, which is rather associated with autochthonous but also terrigenous biological activity and was hitherto mostly found in wastewaters, wetlands and agricultural environments. C3 is again a mixed component. In this mixture an additional UVC high-molecular-weight humic-like component is present as well as amino

acids and proteins. Likewise to C2 it is described as derived from allochthonous and autochthonous sources (Table 2).

## 3.4  Correlation analyses: DOM components, DOM indices and $P/R$

To get a more detailed picture about the origin of the components we considered the correlations between the components where we exactly know the origin from the literature (C1) and the other components (C2, C3). All single component groups (C1, C2, C3) correlate with each other significantly (Fig. 7). Figure 7 shows the linear models that were computed for testing the normal distribution of the respective residuals. Under considering the residual distribution it becomes clear, that C2 : C3 as well as C1 : C2 does not fit with the assumption of a linear relationship. Only C1 : C3 followed the linear model significantly, indicating that both are components from the same source. In detail, the component C3 must be terrigenous derived because C1 has a terrigenouse origin (Table 2). In contrast, C2 has DOM components originated from different sources.

For a further proof of our findings and for testing the degree of biologically degradation (humification) of each component we tested also the relationships between the ratios of all components and the calculated DOM-indexes: $\beta : \alpha$, FI, and HIX (Fig. 8). The modelled components and the DOM indexes were computed based on the same 98 EEM samples. The C3 : C2 ratios correlated positively with $\beta : \alpha$ ($R^2 = 0.569$, $p < 0.001$) , which is an indicator for the amount of recently produced DOM and for its source. Thereby all calculated $\beta : \alpha$ values were below 1 and many of them are next to or below 0.6. More than 50 % of the $\beta : \alpha$ values were below 0.75. In contrast to this finding, an increase of the ratio C1/C2 lead rather to a decrease of $\beta : \alpha$ ($R^2 = 0.626$, $p < 0.001$), indicated that especially C1 is more degraded than C2. Both relationships indicating that allochthonous, relatively older DOM has the main amount in the whole DOM matrix. And they show that C2 as well as C3 is rather recently produced in comparison to C1. There was also a decrease of FI, the freshness index, with an increase of C3 in comparison to C2 ($R^2 = 0.525$, $p < 0.001$), indicating further that C2 is rather

autochthonous derived than C3. It is additionally shown in Fig. 8 that increases of HIX could be explained to 70 % with C1 : C3 variations ($R^2 = 0.698$, $p < 0.001$). This indicates that with an increase of C1 the humification of the whole DOM increases. C1 seems to be more degraded than C3.

5    The relationship between the trophic status of a stream ($P/R$) and the source of DOM (FI) as well as C2 can be seen in Fig. 9. Because the summer metabolism in the Hassel was clearly affected by high nutrient concentrations (Fig. 3) and precipitation (Fig. 2, Table 1), the presented correlations exclude the summer data of this stream. Both correlations are significant. FI ($R^2 = 0.825$, $p < 0.001$) as well as C2 ($R^2 = 0.482$,
10  $p = 0.026$) increase with an increase of the phototrophic status of the streams, indicated by increasing $P/R$ values.

## 3.5  Temporal and spatial variability of the CDOM composition

Figure 10 shows boxplots describing the temporal changes of the different component ratios (C1 : C2, C1 : C3, C3 : C2) sorted after the different land use forms, i.e. forestry
15  streams and non-forestry streams. C1 was the dominant component in all streams, over the whole year. This is shown especially for the forestry streams, where the means of C1 : C2 as well as of C1 : C3 were above 2 (median), but these ratios were generally above 1.4 also in the non-forestry streams. However, the CDOM composition in the forestry streams differed clearly from that found in the non-forestry streams (Fig. 10).
20  In the non-forestry streams the values for C1 : C2 – ranging from 1.42 to 2.35 – were significantly below the C1 : C2 medians found for the forestry streams (2.5) over the whole year. In winter the C1 : C2 ratios increased in the open-land streams up to 2.3, but did not reach the level of the higher C1 : C2 ratios of the forestry streams. In the forestry streams the C1 : C2 ratios spread highest in summer, with values ranging from
25  1.5 to 3.5. Thereby the lowest 25 % of the values are comparable with the ratios found for the open-land streams, whilst 25 % of the higher values are located above 2.5. These higher values were also found in the forestry streams in spring, summer and

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autumn. In contrast to the non-forestry streams in winter the C1 : C2 ratios are lower in the forestry streams.

However, with values ranging from 0.6 to 1, the C3 : C2 ratios in the non-forestry streams were significantly below the ratios found in the forestry streams (1.1, median value over all seasons). There the highest C3 : C2 values were found in spring (1.3). In the winter the C3 : C2 ratio in the forestry stream dropped to a median of 1. Therefore, C2 was in general highest in the non-forestry streams, indicated by median C3 : C2 values of 0.8, whilst C2 plays a minor role in the CDOM mixture of the forestry streams. In the forestry streams C3 seems to be more important (median C3 : C2 > 1).

## 4 Discussion

### 4.1 The linkage between land-use forms and whole stream metabolism

In the Northern Hemisphere small streams are generally heterotrophic in different magnitudes. They have to cover their metabolic requirements especially by allochthonous nutrient supply (Marcarelli et al., 2011). All streams considered here were also of heterotrophic character, as indicated by $P/R$ values below 1. However, clear differences between the streams were shown, which can largely be explained by differences in land-use and present weather conditions. With $P/R$ values > 0.4 in spring and fall, particularly the Rappbode was more phototrophic than the forestry streams. But also the Hassel showed higher $P/R$ values, in spring. In both non-forestry streams the whole stream metabolism was diminished in summer, which results in a decrease of $P/R$. The humid weather in the summer period leads to a multitude of high discharge events that affected the community negatively and thereby also the metabolic processes in the non-forestry streams, especially in the Hassel (Figs. 2 and 4). In addition, also the extensive ranching along the non-forestry streams should have affected the metabolic processes of the open land streams in summer. The Hassel for instance was directly investigated after a herd of cows was grazing on the grassland there. The

high ammonium concentrations in summer (Fig. 3) can be explained with the fact that the cows were allowed to go directly into the Hassel for drinking and to urinate. It is well known that eutrophication can support the primary production and respiration in streams (Gücker et al., 2009). But in this case we found a substantial decrease of both metabolism values. It appears to be possible that the extremely nutrient increase after cow grazing (Fig. 3) could have had toxic effects on the whole stream biota. Mulholland et al. (2005) described that disturbances can generally affect the whole stream metabolism. Therefore, our presented data show that the extensive ranging on the adjacent cow pasturage in combination with the period of rain has in this case negatively affected GPP and $CR_{24}$.

In the forestry streams, $P/R$ values decreased from spring to summer. This can be explained by the diminished PAR at the water surface with increasing forest canopy in the dense alder forests. GPP was clearly influenced by the irradiance in the investigated streams. 69.5 % of the variability in GPP can be explained by changes in irradiance as a result of the different land use forms. Moreover, this relationship is much stronger in the nutrient poor streams (Rappbode, Zillierbach, Spielbach). This finding can explain the lower GPP values in the forestry streams. The generally tight coupling between irradiance and primary production was shown earlier and suggests light instead of nutrient limitation. For example Matheson et al. (2012) showed recently the positive correlation between light intensity and stream periphyton productivity.

Besides the light effect, the GPP in the tested streams was also correlated with TP, which clearly indicates a phosphorus limitation of the primary production. Interestingly, Mulholland et al. (2001) described in their paper a multiple regression model that included log PAR and soluble reactive phosphorus. Based on this model they explained 90 % of the log GPP variations of their streams. It is feasible, that according to Liebig's law of minimum, GPP in streams is coupled to the most limited resource, which seems to be TP especially in the low nutrient streams beside PAR.

## 4.2 The linkage between the whole stream metabolism and the DOM composition

The whole stream metabolism, especially GPP can influence the DOM composition. The strong and tight relationship between the fluorescence index FI and $P/R$ indicated a general impact of GPP on the amount of autochthonously derived organic matter in the investigated streams (Fig. 8). Beside FI, also C2 was positively related to $P/R$. We concluded that also C2 is at least partly phototrophically produced in the streams. In this context it has to be pointed out, that also $\beta : \alpha$ increases with an decreasing C3/C2 ratio and C1/C2 ratio (Fig. 8), which indicates an relatively increase of C2 and therefore again the autotrophic source for C2. Especially the open-land streams which have the highest GPP values reveal the highest amount of C2 during the vegetation period and the lowest in winter. Changes in the DOM matrix driven by GPP should affect the microbial stream communities which prefer low molecular-weight DOM (like C2) from autochthonous sources (Minor et al., 2006; Barrón et al., 2012).

The DOM variability driven by different environmental factors can influence the metabolic processes in waters vice versa (Finlay et al., 2011; Minor et al., 2006; Stedmon and Markager, 2001; Williams et al., 2010). In particular, an increase of low molecular-weight DOM in streams that was found especially in the DOM fractions C2 and C3 can support the heterotrophic activity and therefore also the further degradation of the organic matter (Finlay et al., 2011; Matheson et al., 2012; Ogawa et al., 2001). Autochthonously produced (Barrón et al., 2012) or allochthonously derived low molecular weight substances can support the heterotrophic turnover in streams (Berggren et al., 2010). In contrast, high molecular-weight DOM fractions (like C1) are known to be rather recalcitrant and under suspicion to inhibit the heterotrophic stream community (Freeman et al., 1990; Freeman and Lock, 1992). But on the other hand, beside DOM fine and coarse particular organic matter like seston, litter or wood could also fuel the heterotrophic activity in streams (Rugenski et al., 2012; Vannote et al., 1980). These complex relationships make the direct proof of the linkage between the DOM

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composition and whole stream metabolism difficult. This is seen as the reason why $CR_{24}$ values estimated in the presented streams were not correlated to FI or C2 as we originally expected. In contrast, with a NEP of $-8.67\,\mathrm{g\,O_2\,m^{-2}\,d^{-1}}$, the highest energy demand was found in spring for the Zillierbach, which is a non-forestry stream with lower GPP and where the mean $P/R$ values were ranging from 0.02 to 0.11. We concluded that the respiration in the streams was mainly supported by an energy supply from terrestrial sources. One kind of such a terrestrial source is the increasing $CR_{24}$ found in the forestry streams in fall, as a result of the temporary litter fall (Fig. 4). Unfortunately, the autumnally leaf entry was not quantified in this study, but the increase of $CR_{24}$ from summer to fall in the forestry streams clearly exceeds the increase of $CR_{24}$ in the Rappbode, a non-forestry stream with similar low nutrient loadings (Fig. 3). An additional increase of $CR_{24}$ in autumn was detected in the Hassel. The degradation of plant material in the neighbouring wetland which drains into this stream thus probably had the same effect on $CR_{24}$ like leave fall has for the forestry streams. However, it was very surprising to find such high $CR_{24}$ values especially in the Hassel, because in fall the air temperature was so low that the upper water layer and the top soil layer gets frozen during the night (cp. Table 1). However, it becomes clear that beside the amount of labile DOM derived from allochthonous or autochthonous sources also particular organic matter like leaf litter could promotes the heterotrophic turnover in the aquatic environment.

## 4.3 The impact of land use forms on the temporal and spatial variability of the DOM composition

The different CDOM pattern (C1 : C2, C1 : C3, C3 : C2) allows to distinguish between DOM from forestry streams and from non-forestry streams. For example, the values for C1 : C2 in the non-forestry streams were below the means of the forestry streams over the whole year. In winter the C1 : C2 ratio increased in the open-land streams, but did not reach the level of the higher C1 : C2 ratio of the forestry streams. That is seen as an effect of the winter-related decreased biological activity in these streams.

Such a seasonal effect was already shown for examples by Minor et al. (2006) who observed higher autochthonous DOM signals in summer during a phytoplankton bloom. In contrast, the C1 : C2 ratios in the forestry streams are diminished in winter, indicating a reduced entry of the terrigenous C1 into the stream. Based on the low air temperature the soil was frozen and this reduced the flux of terrestrially derived DOM to a minimum. However, also Williams et al. (2010) have recently shown that DOM from agricultural streams is more labile than DOM from wetland streams, which indicates a clear impact of the different land use forms on the DOM matrix.

We also found an effect of the different land use forms on the C3 : C2 ratio, which give us information about the role of terrestrially derived, biologically produced organic substances in comparison to autochthonous organic material. The C3 : C2 ratios of the non-forestry streams (all < 1) were distinctly below the ratios found in the forestry streams (all > 1). This finding highlights the role of the low molecular-weight DOM compound C2 for the open-land streams. On the other hand C3 peaked in the forestry streams. In this environment the highest ratios were found in spring, where the biological activity in the neighbouring soil is especially high. Leachates from plant material, also from the last autumn and exudates from different biological sources could enter the stream during a fast link between soil water and stream water. Indeed the beginning of the year there is higher discharge and soil moisture, around summer the discharges and also the groundwater decrease rapidly and the soils become dryer. The extremely low discharges measured especially in the forestry streams in summer also indicate the depleted soil moisture in this season (Table 1). This of course diminished also the soil water – stream water DOM flux, which should have an impact on the DOM composition in the streams. In winter, when soils were frozen, the flux between soil water and stream is totally depleted. Accordingly, the C3 : C2 ratio in the forestry stream moves down to values close to 1.

The different land-use forms lead also to different values for the C1 : C3 ratios, which should not be directly influenced by the in-stream metabolic processes. Especially in spring and summer the median of C1 : C3 in the forestry streams was clearly below

2.2, which indicates comparable higher C3 values. These values can also be explained with the high allochthonous biological activity in this season, based on the organic matter from the previous autumn, which is available for the biological degradation. Also the dense vegetation that produces exudates and leachates should contribute to the terrigenous DOM. With decreasing biological activity and further decreased soil water – stream water coupling, the C1 : C3 ratio of the forestry streams reached values comparable to the non-forestry streams in autumn. In contrast to these observations, the open-land streams showed hardly changes in their C1 : C3 ratio. Only in spring the means of the C1 : C3 ratios were close to 2.2. That indicates a comparable higher C3 content in this season, based on a higher terrestrial biological production and a stronger coupling to the soil. The coupling between DOM quantity and quality and the hydrological input was recently demonstrated by Spencer et al. (2008, 2010). They showed on the one hand a decrease of the DOM concentration and a diminished labile DOM fraction with decreasing wetness for different streams. On the other hand they found the highest DOM concentration in the Yukon River in Canada during the spring flush, where the wetness is generally higher (Spencer et al., 2008). Taken together, the impact of the different land use forms on the DOM composition is very complex. We showed that this mechanism is driven by the allochthonous and autochthonous biological activity as well as by the linkage between the stream water and the allochthonous environment. Both variables are varying in space and time.

## 5  Conclusion remarks

We were able to distinguish between the different, temporally varying CDOM patterns of forestry streams and non-forestry streams. This was possible by the use of DOM component ratios. Furthermore, the used combination of DOM component ratios, fluorescence indices, and whole stream metabolism studies is a new integrated approach allowing us to characterise the stream ecosystem function as a whole.

All investigated streams were heterotrophic, with a general net energy loss in their metabolic balance. Nevertheless, the trophic state showed pronounced differences with respect to land use forms and seasons. Especially GPP was directly linked to irradiance and phosphorus availability. We demonstrated that seasonal and local changes in the trophic state ($P/R$) could also affect the DOM composition, and postulated a cross-correlation between GPP and the composition of the DOM matrix. In detail, the availability of low molecular-weight, autochthonously produced DOM could affect the whole stream metabolism and vice versa. This includes also that GPP and the amount of autotrophically derived DOM are linked to different land use forms. It becomes clear that further environmental changes, such as the increasing reduction of forestry areas, will not only change the trophic status of the streams, it could also change the whole DOM composition and therefore the availability of DOM for the whole stream metabolic processes.

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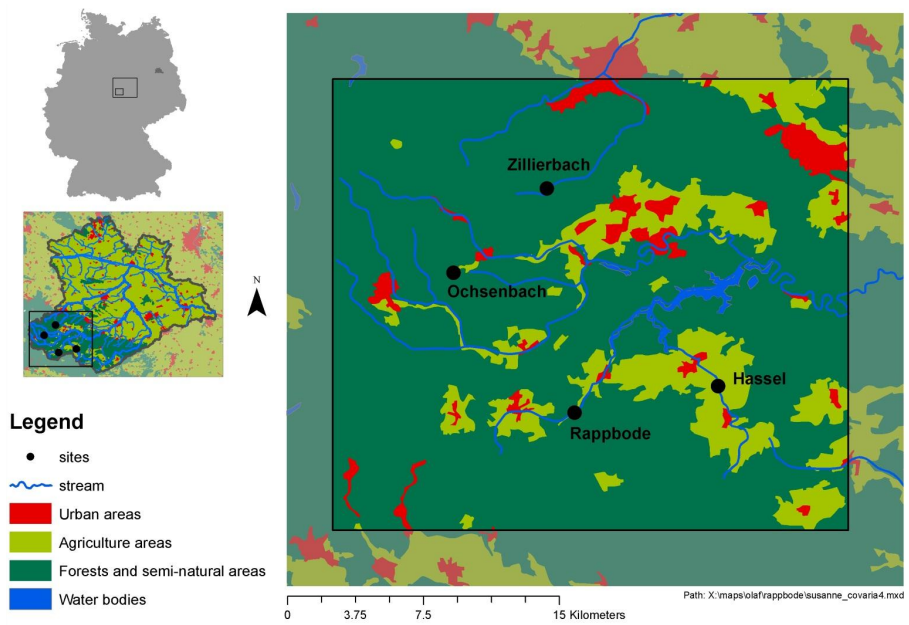
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**Table 1.** The general stream characteristic of the investigated streams*.

| | | sample period | reach m | depth cm | width m | surface $m^2$ | $Q$ $L\,s^{-1}$ | $T$ °C | Cond. µS cm$^{-1}$ | pH |
|---|---|---|---|---|---|---|---|---|---|---|
| forestry | Zillierbach | spring | 16.04.2011–19.04.2011 | 126 | 11.5 | 1.1 | 140 | 4 | 6.9 (SD 2.3) | 183 (SD 2) | 7.6 (SD 0.04) |
| | | summer | 26.07.2011–28.07.2011 | 50 | 7.7 | 1.0 | 52 | 1 | 12.5 (SD 1.2) | 209 (SD 7) | 7.7 (SD 0.07) |
| | | fall | 14.10.2011–18.10.2011 | 50 | 11.4 | 1.1 | 55 | 2 | 6.6 (SD 0.7) | 220 (SD 4) | 7.7 (SD 0.02) |
| | | winter | 14.02.2012 | 50 | n.d. | n.d. | n.d. | n.d. | 0.0 (SD 0.0) | 185 (SD 1) | 7.3 (SD 0.04) |
| | Ochsenbach | spring | 07.05.2011–09.05.2011 | 86 | 10.0 | 1.1 | 98 | 4 | 9.4 (SD 2.7) | 145 (SD 6) | 7.3 (SD 0.31) |
| | | summer | 02.08.2011–04.08.2011 | 86 | 7.2 | 1.1 | 90 | 2 | 13.4 (SD 1.6) | 154 (SD 4) | 7.3 (SD 0.05) |
| | | fall | 22.10.2011–25.10.2011 | 86 | 9.8 | 1.1 | 97 | 4 | 4.8 (SD 1.3) | 153 (SD 5) | 7.4 (SD 0.02) |
| | | winter | 14.02.2012 | 86 | n.d. | n.d. | n.d. | n.d. | 2.0 (SD 0.0) | 150 (SD 0) | 7.4 (SD 0.01) |
| non-forestry | Rappbode | spring | 28.05.2011–30.05.2011 | 135 | 25.3 | 1.9 | 259 | 30 | 14.1 (SD 2.0) | 198 (SD 2) | 7.7 (SD 0.09) |
| | | summer | 22.08.2011–25.08.2011 | 88 | 25.7 | 2.1 | 181 | 23 | 15.9 (SD 1.0) | 238 (SD 4) | 7.8 (SD 0.15) |
| | | fall | 05.11.2011–08.11.2011 | 88 | 28.4 | 1.9 | 166 | 37 | 5.8 (SD 0.6) | 208 (SD 0) | 7.9 (SD 0.13) |
| | | winter | 16.02.2012 | 88 | n.d. | n.d. | n.d. | n.d. | 0.5 (SD 0.0) | 167 (SD 0) | 7.6 (SD 0.03) |
| | Hassel | spring | 06.06.2011–08.06.2011 | 40 | 7.2 | 0.9 | 37 | 1 | 17.5 (SD 2.7) | 359 (SD 7) | 7.6 (SD 0.08) |
| | | summer | 22.08.2011–25.08.2011 | 40 | 11.9 | 1.1 | 46 | 5 | 15.6 (SD 1.1) | 299 (SD 1) | 7.6 (SD 1.07) |
| | | fall | 12.11.2011–15.11.2011 | 50 | 10.5 | 1.1 | 54 | 3 | 0.8 (SD 0.6) | 429 (SD 8) | 7.8 (SD 0.02) |
| | | winter | 16.02.2012 | 50 | n.d. | n.d. | n.d. | n.d. | 0.6 (SD 0.1) | 183 (SD 0) | 7.4 (SD 0.03) |

* The presented data are mean values of the physical, chemical and geomorphological data measured during each field campaign. The following abbreviations were used: $Q$ = discharge, $T$ = temperature, Cond. = conductivity, n.d. = not determined. Standard deviations (SD) are showing in parenthesis.

**Table 2.** The ecological definitions for the different fluorescence components (Fig. 6)*.

|  | C1 | C2 | C3 |
|---|---|---|---|
| Ex/Em | 355 (260)/ 435 | 315/370 (390, 510) | 290/450 (335) |
| Interpretation* | UVC humic-like substances, high-molecular-weight and aromatic humic, widespread, highest in wetlands and forested environments; UVA humic-like, fulvic acid, widespread | UVA humic-like substances, low molecular weight, associated with biological activity, common in marine environment, found in wastewater, wetland, and agricultural environments; 315/510 unknown | Mixed component: Amino acids and proteins, microbial; UVC humic-like, high molecular weight and aromatic humic, widespread, found in wetlands and in forests |
| Source* | Terrestrial plant material or soil organic matter | Rather autochthonous production and from microbial processing; but also terrestrially sources (plant material and soils) | Terrestrially derived, autochthonous produced and from microbial processes |

*Abbreviations are EM = emission and EX = excitation. The ecological role of the modelled components was reproduced by comparing their Ex/Em-maxima with the literature (Fellmann et al., 2010; Williams et al., 2010; Murphy et al., 2006; Stedmon and Markager, 2005; Coble et al., 1990, 1998; Coble, 1996; Cory and McKnight, 2005).

**Fig. 1.** Map of the investigation area with indicated sampling stations.

Legend

- sites
- stream
- Urban areas
- Agriculture areas
- Forests and semi-natural areas
- Water bodies

Zillierbach

Ochsenbach

Hassel

Rappbode

Path: X:\maps\olaf\rappbode\susanne_covaria4.mxd

0    3.75    7.5    15 Kilometers
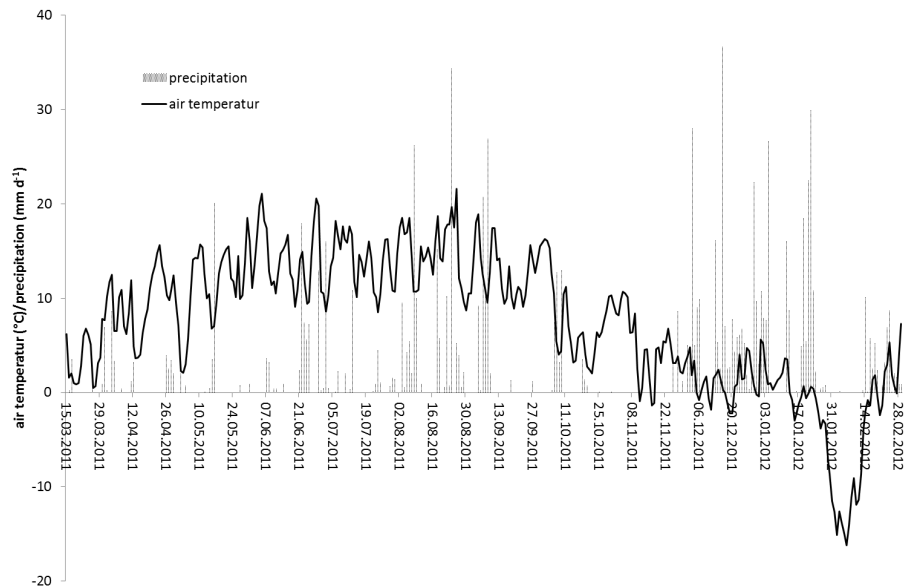
**Fig. 2.** Overview of the air temperature (black line) and the precipitation (bars) over the whole sampling period. The weather data were representative data from the weather station in Braunlage, Harz Mountains, Germany.
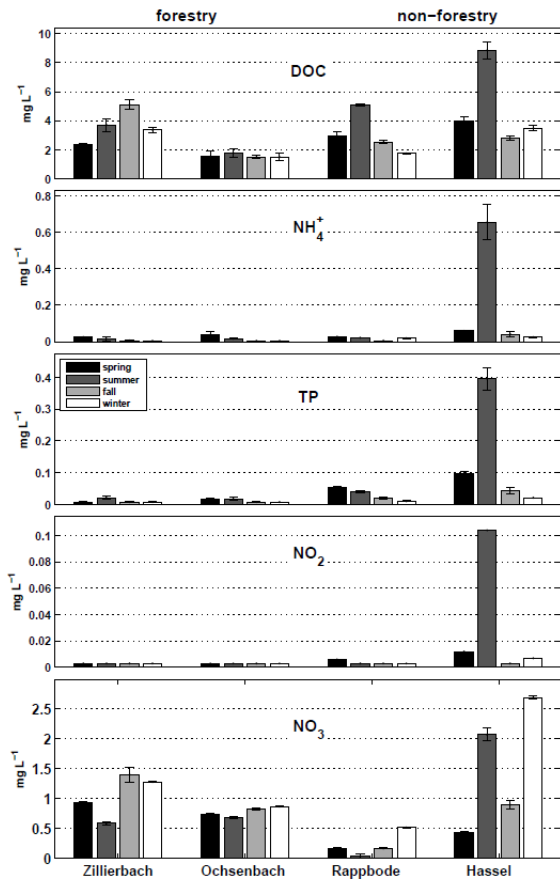
**Fig. 3.** Overview of the chemical characteristic of the investigated streams. The presented values are mean values of the chemical data measured during each field campaign. Following parameters are showing: DOC = dissolved organic carbon, $NH_4^+$ = ammonium, TP = total phosphorus, $NO_2$ = nitrite and $NO_3$ = nitrate (all in $mg\,L^{-1}$). Standard deviations are also given.

**Linkage between dissolved organic matter variability and metabolism**

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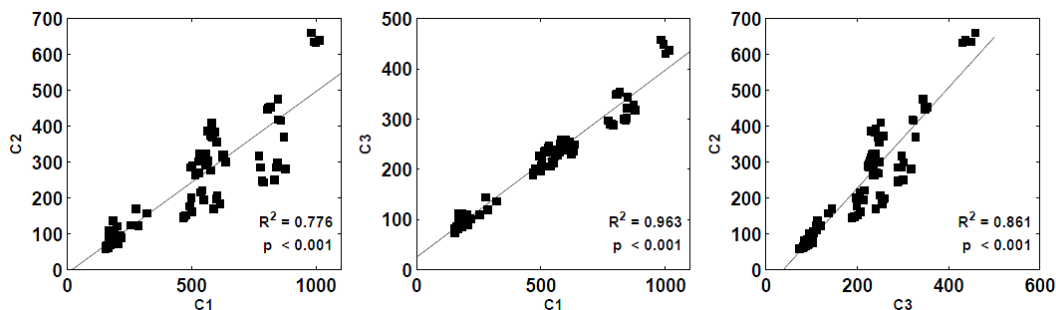◄ | ►►

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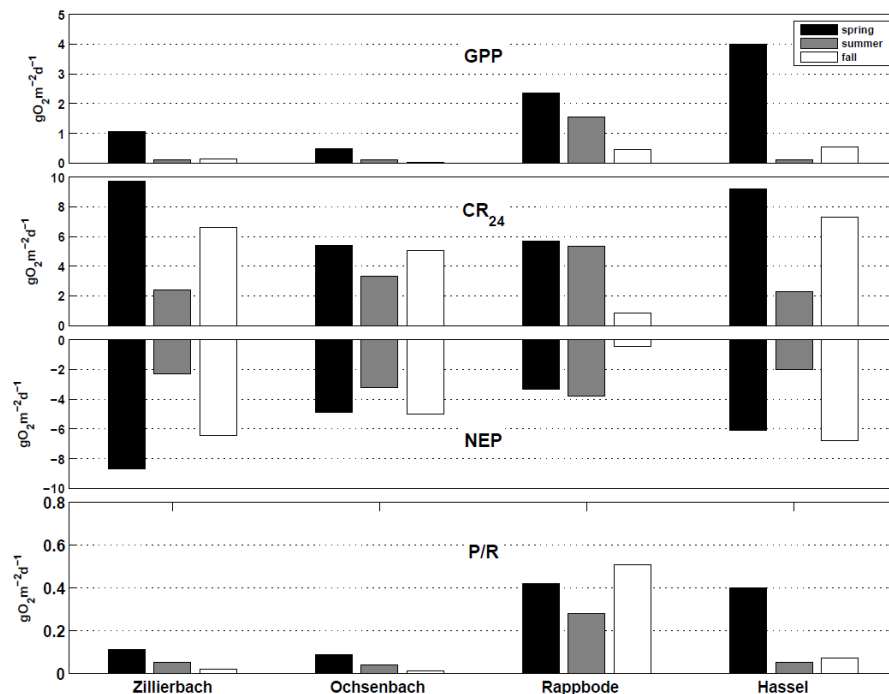
**Fig. 4.** Summary of the estimated metabolism data. The showing data are means ($n = 2$). Abbreviations are GPP = gross primary production, $CR_{24}$ = daily community respiration, NEP = net ecosystem production (positive NEP = net energy production, negative NEP = net energy loss), $P/R$ = ratio of GPP and $CR_{24}$ ($P/R > 1$ = phototrophic, $P/R < 1$ = heterotrophic).

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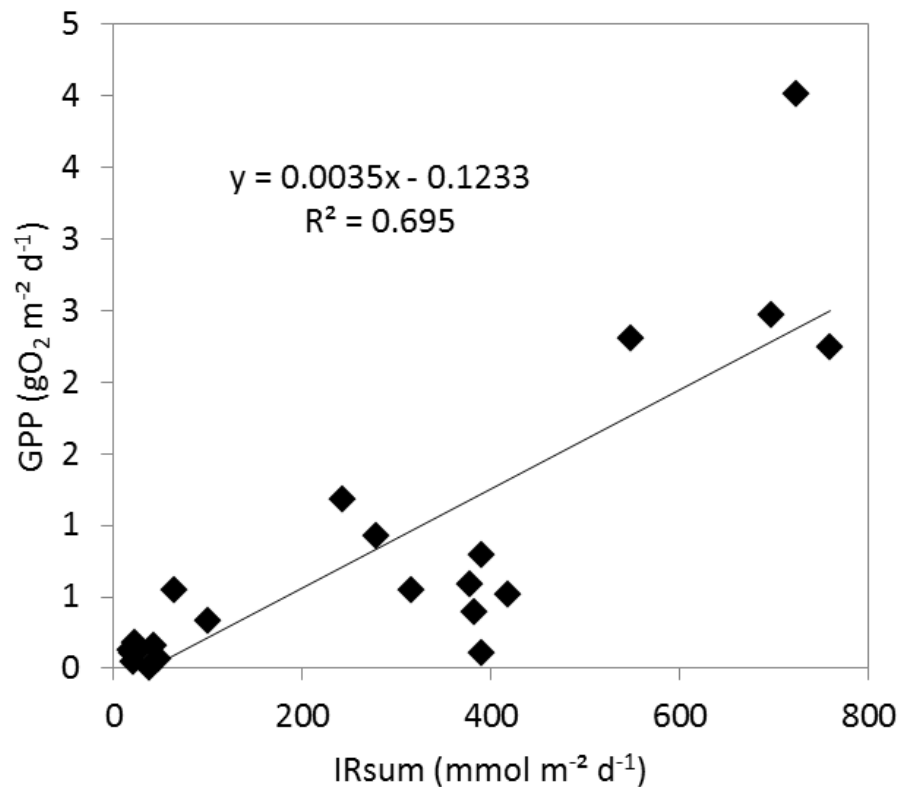
**Fig. 5.** Relationship between the sum of irradiance per day ($Ir_{sum}$ in mmol m$^{-2}$ d$^{-1}$) and the gross primary production (GPP in g O$_2$ m$^{-2}$ d$^{-1}$) in the whole stream over all streams and samples.

**Fig. 6.** Contour plots describing the fluorescence characteristic of three components, modelled based on 98 samples with the PARAFAC analysis. The detailed description of component 1, 2 and 3 (C1, C2, and C3) can be found in Table 2.

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**Fig. 7.** Linear relationship between C1, C2 and C3 (Table 2). C1 and C2: $R^2 = 0.775$ (left), C1 and C3: $R^2 = 0.963$ (middle), C3 and C2: $R^2 = 0.860$ (right). All correlations are highly significant ($p < 0.001$). But only the high correlative relationship C1 : C3 followed significantly a linear model, indicating the same allochthonous source (see method chapter).
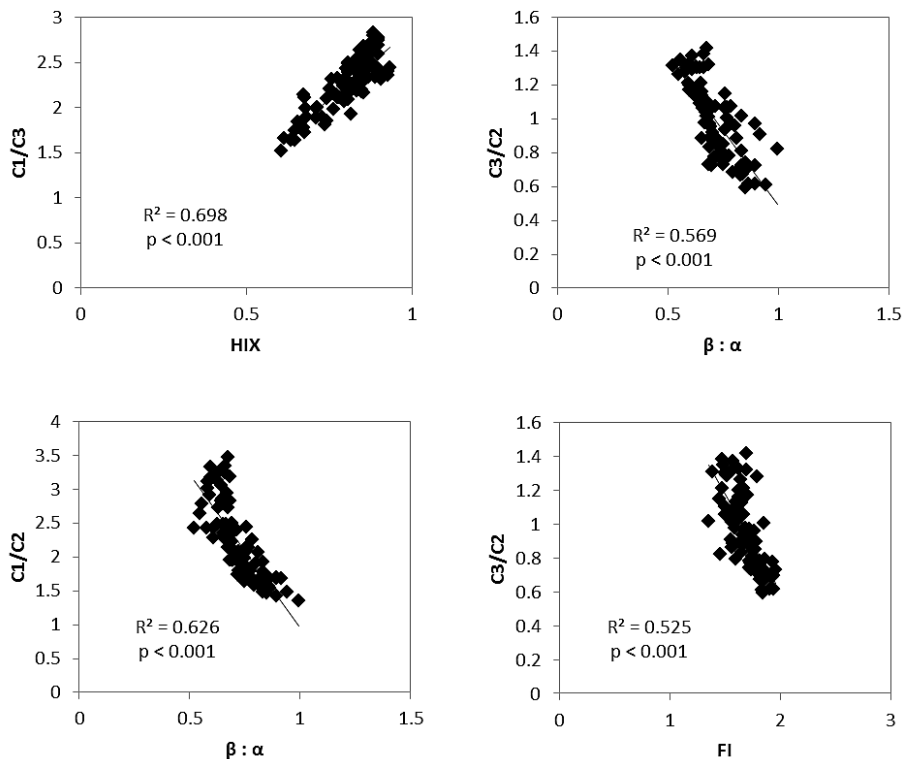
**Fig. 8.** The relationship between CDOM composition and fluorescence indices. Changes in the CDOM matrix are expressed as ratios of the computed DOM components: C1 : C3, C3 : C2, and C1 : C2. Following indices are showing: HIX = humification index; $\beta : \alpha$ = freshness index; FI = fluorescence index. The respective linear regression models and correlation coefficients are presented in the panels.

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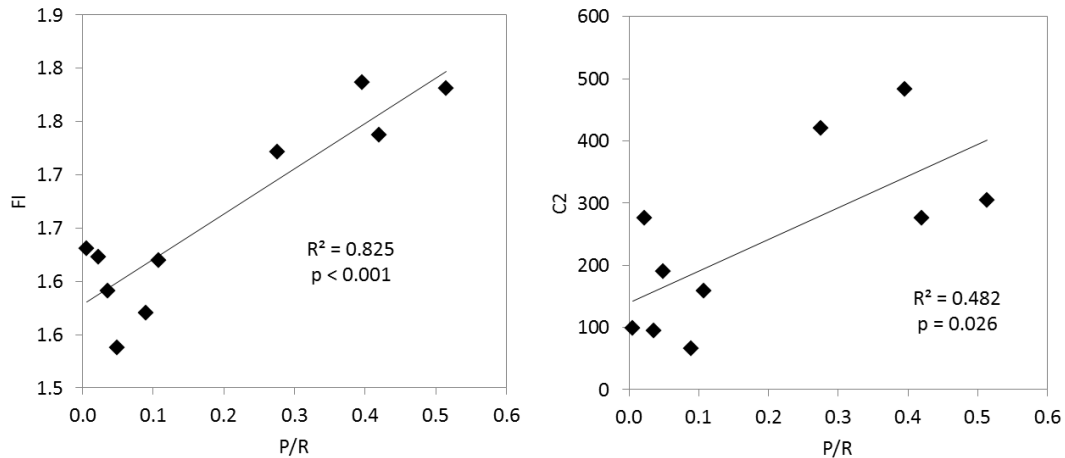
**Fig. 9.** The relationship between GPP and $CR_{24}$ ($P/R$) as a measure for the trophic status of the streams and FI, respectively C2. With an increasing phototrophic character also the amount of autochthonously derived DOM increased (as indicated by increases in FI and C2).
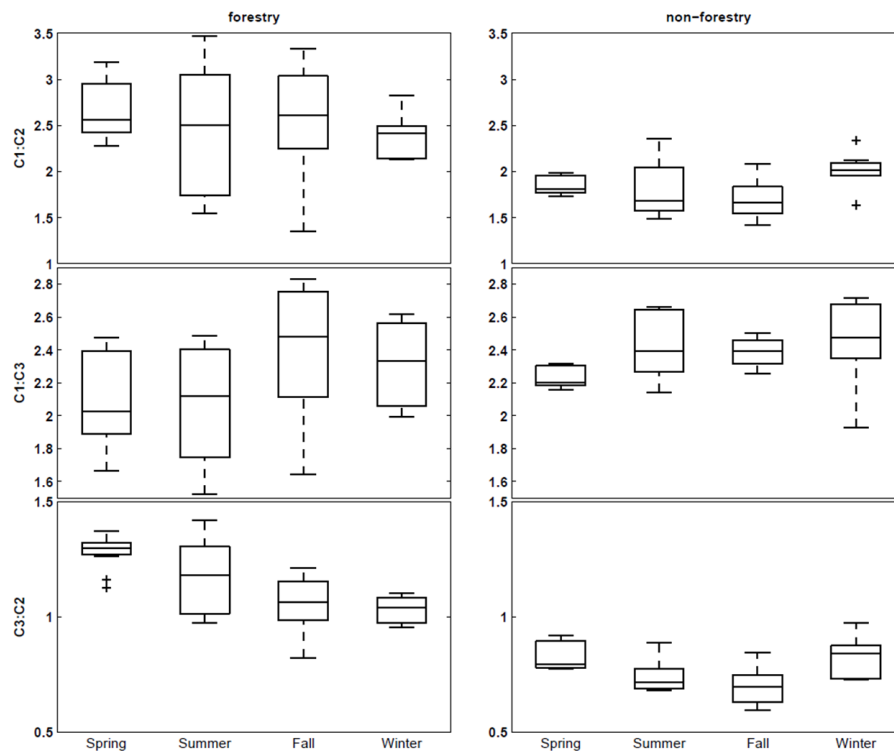
**Fig. 10.** Boxplots of seasonal changes of the DOM composition expressed as changes in the component ratios and sorted for the different land use forms (forestry versus non-forestry streams).