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# **Regulation of CO<sub>2</sub> emissions from temperate streams and reservoirs**

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Abstract. It has become more and more evident that  $CO_2$ emission  $(F_{CO_2})$  from freshwater systems is an important part of the global carbon cycle. To date, only a few studies have addressed the different mechanisms that regulate  $F_{CO_2}$ in lotic and lentic systems. In a comparative study we investigated how different biogeochemical and physical factors can affect  $F_{CO_2}$  values in streams and reservoirs. We examined the seasonal variability in CO<sub>2</sub> concentrations and emissions from four streams and two pre-dams of a large drinking water reservoir located in the same catchment, and compared them with environmental factors that were measured concurrently. All the streams were generally supersaturated with CO<sub>2</sub> throughout the year, while both reservoirs functioned to a small degree as CO2 sinks during summer stratification and CO<sub>2</sub> sources after circulation had set in.  $F_{\rm CO_2}$  from streams ranged from 23 to 355 mmol m<sup>-2</sup> d<sup>-1</sup> and exceeded the fluxes recorded for the reservoirs (-8.9 to)161.1 mmol  $m^{-2} d^{-1}$ ). Both the generally high piston velocity (k) and the CO<sub>2</sub> oversaturation contributed to the higher  $F_{\rm CO_2}$  from streams in comparison to lakes. In both streams and reservoirs  $F_{CO_2}$  was mainly governed by the CO<sub>2</sub> concentration (r = 0.92, p < 0.001 for dams; r = 0.90, p < 0.0010.001 for streams), which was in turn affected by metabolic processes and nutrients in both systems and also by lateral inflow in the streams. Besides CO<sub>2</sub> concentration, physical factors also influence  $F_{\text{CO}_2}$  in lakes and streams. During stratification,  $F_{CO_2}$  in both pre-dams was regulated by primary production in the epilimnion, which led to a decrease of  $F_{CO_2}$ . During circulation, when CO<sub>2</sub> from the hypolimnion was mixed with the epilimnion,  $F_{CO_2}$  increased on account of the  $CO_2$  input from the hypolimnion. The  $CO_2$  from the hypolimnion originates from the mineralisation of organic matter.  $F_{CO_2}$  from streams was mainly influenced by geomorphological and hydrological factors affecting k, which is less relevant in low-wind lakes. Under high-wind conditions, however, *k* regulates  $F_{CO_2}$  from lotic systems as well. We developed a theoretical framework describing the role of the different regulation mechanisms for  $F_{CO_2}$  from streams and lakes.

In summary, the dominant factor affecting  $F_{CO_2}$  is the concentration of CO<sub>2</sub> in the surface water. Lake stratification has a very important regulatory effect on  $F_{CO_2}$  from lakes on account of its influence on CO<sub>2</sub> concentrations and metabolic processes. Nevertheless,  $F_{CO_2}$  values in heterotrophic streams are generally higher. The higher *k* values are responsible for the comparatively high degree of  $F_{CO_2}$ . On a Central European scale, CO<sub>2</sub> emission from streams is probably of greater importance than the CO<sub>2</sub> flux from standing waters.

# 1 Introduction

Gaseous  $CO_2$  emission from inland waters is an important component of the global carbon cycle (Cole et al., 2007). The  $CO_2$  flux between waters and the atmosphere takes place through diffusion across the air–water interface, and this depends on the  $CO_2$  concentration difference between water and atmosphere and a transport coefficient (piston velocity, *k*). Typically, surface waters are oversaturated with respect to  $CO_2$ , making them a  $CO_2$  source. For European lakes, a mean  $CO_2$  emission of 24 mmol m<sup>-2</sup> d<sup>-1</sup> was estimated, indicating a total emission of 17 million t yr<sup>-1</sup> from all European lakes (Kastowski, 2011). A great deal of data is available for lakes and reservoirs (reviewed e.g. in Tremblay et al., 2005; Barros et al., 2011) or for rivers and streams (Owens et al., 1964; Billett and Harvey, 2013), but only a few studies include both lakes and river systems (Jonsson et al., 2007; Weyhenmeyer et al., 2012).

In freshwater systems, the total emission of  $CO_2$  and the associated concentrations are controlled by various environmental factors and by internal processes. It appears that the majority of the CO<sub>2</sub> in lakes and streams originates from terrestrial organic sources (Sobek et al., 2003; Humborg et al., 2010). The mineralisation of terrestrially derived dissolved organic carbon (DOC) is often considered to be the main cause of CO<sub>2</sub> oversaturation, which is encountered mainly in boreal lakes (Sobek et al., 2003). Although DOC would appear to be a predictor of  $pCO_2$  in many lakes, the exact nature of that relationship varies greatly from one region to another (Roehm et al., 2009). In a Finnish lake study, where pCO<sub>2</sub> was found to be elevated in agricultural catchments, it was strongly associated with total nitrogen (TN) and total phosphorus (TP) contents, but not with total organic carbon (TOC) (Rantakari and Kortelainen, 2008). In a long-term study in 37 large Finnish lakes,  $CO_2$  emission ( $F_{CO_2}$ ) was closely related to the annual precipitation pattern (Rantakari and Kortelainen, 2005), while only weak correlations to water chemistry, TOC or land use in the catchment were established.

CO<sub>2</sub> evasion may also depend on lake area. For very small and very large lakes, negative relationships between lake size and several characteristics (depth, land use characteristics, etc.) were found (Kelly et al., 2001). Especially in small, shallow lakes sediment respiration affects CO<sub>2</sub> concentration (Kortelainen et al., 2006). Metabolic processes in general can affect CO<sub>2</sub> concentration in lakes. Primary production consumes CO<sub>2</sub>, as is confirmed by several studies showing that a higher trophic state reduces CO<sub>2</sub> emission (Trolle et al., 2012). Nutrient-rich, eutrophic lakes may even be undersaturated with CO<sub>2</sub>, making them function as a CO<sub>2</sub> sink rather than a source (Balmer and Downing, 2011). However, the seasonal variability of CO2 concentrations is markedly synchronised with lake stratification. Accumulation of CO<sub>2</sub> in the hypolimnion during stratification leads to an increase in the CO2 concentration in the upper layers of water when mixing processes take place (Kortelainen et al., 2006; Tranvik et al., 2009).

Factors regulating  $CO_2$  emission from streams could be the same as those influencing the emission from lakes. Recent studies have shown that  $CO_2$  emission from lotic and lentic waters could be affected by pH, temperature, several nutrients, the  $CO_2$  concentration itself and general hydrological or geomorphological conditions (Alin et al., 2011; Wallin et al., 2011; Rantakari, 2010; Li et al., 2012).

In the Yangtze River,  $CO_2$  outgassing was determined by the pH level of the water (Li et al., 2012). The pH mainly regulates the speciation of dissolved inorganic carbon (DIC) and therefore also the  $CO_2$  concentration, and this may have direct effects on the  $CO_2$  emission (Neal et al., 1998). Genereux and Hemond (1992) reported that  $CO_2$  degassing is linked to water velocity and turbulence. Thus small, turbulent streams especially tend to emit large amounts of  $CO_2$ . Furthermore, groundwater DIC input regulates the  $CO_2$  concentration as well, especially in small streams, therefore affecting emissions (Battin et al., 2008). Varying adjacent soil or sediment types may give rise to differing water storage periods, which in turn have an effect on the DIC accumulation time (Rantakari, 2010).

Even if controlling factors often appear to be similar in both systems, several studies have shown higher CO<sub>2</sub> fluxes for streams than for lakes. Teodoru et al. (2009) estimated a daily CO<sub>2</sub> emission rate between 58 and 250 mmol C m<sup>-2</sup> for streams located in the north western boreal region in America. This could be as much as twice the emission rate from lakes in the same region. We assume that the impact of the different regulation mechanisms (for example metabolism, wind speed, temperature etc.) on the CO<sub>2</sub> emission are different for lakes and streams. This could be an important issue if CO<sub>2</sub> emission is studied on a catchment scale, because streams and lakes may be expected to react differently to changes in climate and/or land use.

Only a few studies exist in which the factors influencing CO<sub>2</sub> emission in lakes and streams are directly compared in a temperate ecosystem. The number of studies in which  $CO_2$ evasion from both streams and lakes located in a single catchment has been investigated is rather small, or data are only available from boreal catchments. In this study, we measured the CO<sub>2</sub> flux from four streams and two reservoirs within the same catchment located in central Europe. Our aim was to determine whether streams or lakes emit more CO<sub>2</sub> per unit area and what reasons may account for any differences. We assume that in the temperate zone both systems are affected by the same environmental factors, but to differing degrees. By analysing seasonal trends and correlations with various environmental parameters, we set out to identify and compare the mechanisms controlling the CO<sub>2</sub> flux from lotic and lentic waters.

## 2 Materials and methods

#### 2.1 Study sites

The study sites are located in the upper part of the Bode catchment in the Harz Mountains, Central Germany (Fig. 1). Two of the streams under investigation are rather pristine streams (Ochsenbach and Zillierbach) located near the Harz National Park, while the other two streams flow through areas under anthropogenic influence (Hassel and Rappbode). The following land-use types are encountered in the catchments: Rappbode – 6 % agriculture (cattle), 1 % urban, 93 % semi-natural areas and forest; and Hassel – 14 % agriculture (cattle), 3 % urban, 83 % semi-natural areas and forest. A detailed description of all the streams is given in Halbedel et al. (2013). They are parts of a stream network that drains into the Rappbode reservoir system (Rinke et al., 2013). The



Fig. 1. Map of the investigation area. D = pre-dam.

Hassel and the Rappbode drain directly into the pre-dams Hassel (DH) and Rappbode (DR), respectively, which were also investigated in this study. DR is a mesotrophic soft water reservoir, DH a eutrophic soft water reservoir. The reservoirs both have an elongated, winding shape without any major side basins. The maximum depths are 14 m (DH) and 17 m (DR). Since their water levels are not regulated and the excess water always flows over the containing dam, pre-dams represent suitable model systems for lakes. The general characteristics of the investigated sites are given in Table 1. Detailed information on the chemical characteristics of streams located in the Bode catchment and on the prevalent land-use forms are presented in Kamjunke et al. (2013).

## 2.2 Field work

# 2.2.1 Pre-dams

Both pre-dams were sampled between once and twice per month at a routine monitoring site at the deepest point close to the dam. The 14 samplings were conducted between 9 March 2011 and 19 December 2011, in the ice-free period. Samples for routine water analysis of the pre-dam water were taken using a Ruttner water sampler (Limnos, Finland). Samples were taken from depths of 0, 2, 5, 8, 10, 12 m and above ground. For CO<sub>2</sub> analysis, glass vials were half-filled and sealed with a rubber septum. To correct for ambient  $CO_2$  in the headspace, ambient air samples were taken in separate vials. From November 2011 onwards samples were taken using 60 mL syringes sealed by a three-way stopcock. Ambient air samples were also taken with the same type of syringes. The syringes were filled to halfway, stored cool and analysed within 24 h in the laboratory. Prior to analysis, a gas headspace of 30 mL N2 was added to the syringes and the syringes were shaken on a rotary shaker for 30 min. Vertical profiles of temperature (T), O<sub>2</sub> and pH were measured using a multi-parameter probe (Ocean-Seven, Idronaut, Italy).

# 2.2.2 Streams

The streams were sampled in the spring, summer and autumn of 2011. The  $CO_2$  measurements were performed at base flow and concurrently with whole stream metabolism studies. The latter have been described in Halbedel et al. (2013). The sampling campaigns were conducted in the Zillierbach between 16.-19.04.2011, 26.-28.07.2011 and 14.-18.10.2011, in the Ochsenbach between 07.-09.05.2011, 02.-04.08.2011 and 22.-25.10.2011, in the Rappbode between 28.-30.05.2011, 22.-25.08.2011, and 05.-08.11.2011 and in the Hassel between 06.-08.06.2011, 22.-25.08.2011 and 12.-15.11.2011. The CO<sub>2</sub> samples were taken twice a day, at noon and one hour before sunrise. We expected to record the highest primary production at noon and no primary production before sunrise. For CO<sub>2</sub> measurements, water samples were taken at regular intervals along stream reaches between 50 m and 135 m in length and in accordance with the water travel time (cf. Halbedel et al., 2013). The inflow and outflow of the respective reach and seven additional positions that were uniformly distributed over the stream reach under investigation were sampled in triplets during the daytime. The inflow and outflow of the respective reach and the midpoint of the reach were sampled in triplets at night. The water was collected using a 60 mL plastic syringe from a depth of approximately 10 cm below the stream surface in the thalweg and equilibrated with a headspace of ambient air by vigorous shaking for 1 min below the water surface (Kling et al., 1991; Hope et al., 2004). The equilibrated air was then injected into 12 mL evacuated crimp vials. Three additional samples of ambient air were taken at points of inflow and outflow and at the midpoint of the stream reach. All vials were stored at 4 °C until analysis, which was carried out within 48 h in the laboratory.

Detailed information about the collection of several environmental parameters such as the reaeration coefficient  $(k_{\text{propane}})$ , discharge (Q), lateral inflow (I), width (w) and depth (d) of the stream reach, velocity (v), reach length, water travel time (*t*), pH, conductivity (cond.), and oxygen (O<sub>2</sub>) can be found in Halbedel et al. (2013). This also contains detailed descriptions as to how samples for further chemical analysis were collected (ammonium  $(NH_4^+)$ , nitrate  $(NO_3^-)$ , total phosphorus (TP)). Water samples for chemical analysis were taken in the thalweg, at the points of inflow and outflow of the stream reach, and in accordance with the water travel time. For chlorophyll a (Chl a) analysis, water was filtered (GF/F) directly in the field and the filters were immediately frozen in liquid nitrogen and stored at -20 °C. For TIC, water samples were collected directly below the water surface without air bubbles. The local atmospheric pressure (p, mmHg) and the atmospheric temperature in close proximity to the stream  $(T_{air}, {}^{\circ}C)$  were measured using hand-held barometer or thermometer, respectively.

	Depth m	Area km <sup>2</sup>	Volume Mio m <sup>3</sup>	$\begin{array}{c} Q \\ L s^{-1} \end{array}$	$\frac{v}{m s^{-1}}$	рН	$k \cosh h^{-1}$	I %
PD Rappbode	5.73	0.243	1.66	n.d.	n.d.	7.76 (SD 0.4)	2.9 (SD 2.1)	n.d.
PD Hassel	5.03	0.260	1.64	n.d.	n.d.	8.31 (SD 0.8)	2.8 (SD 2.1)	n.d.
Rappbode	0.26 (SD 0.02)	0.047	n.d.	30.38 (SD 7.0)	0.06 (SD 0.0)	7.80 (SD 0.1)	12.08 (SD 2.4)	-0.60 (SD 5.0)
Hassel	0.10 (SD 0.02)	0.043	n.d.	3.23 (SD 1.8)	0.03 (SD 0.0)	7.66 (SD 0.1)	10.13 (SD 2.8)	23.83 (SD 6.2)
Zillierbach	0.10 (SD 0.02)	0.011	n.d.	2.38 (SD 1.1)	0.02 (SD 0.0)	7.66 (SD 0.0)	9.05 (SD 2.0)	-4.76 (SD 9.3)
Ochsenbach	0.09 (SD 0.02)	0.002	n.d.	3.45 (SD 1.1)	0.03 (SD 0.0)	7.31 (SD 0.0)	10.28 (SD 2.6)	1.13 (SD 7.9)

Table 1. Characterisation of the streams and reservoirs under investigation.\*

\* The data shown are mean values. Q = discharge, v = velocity,  $k = CO_2$  gas transfer velocity, I = lateral inflow (negative values indicate outflow), SD = standard deviation, n.d. = not determined.

# 2.3 Analytics

Equilibrated air from the stream and lake samples and all the environmental air samples were analysed using a SRI 8610C gas chromatograph equipped with a flame ionisation detector. The concentrations of  $CO_2$  in the water (mmol L<sup>-1</sup>) were calculated by applying Henry's law (Kling et al., 1991) to the gas concentrations in equilibrated headspace samples, together with the pressure and temperature recordings.

 $NO_3^-$  and  $NH_4^+$  were determined photometrically by applying the segmented flow technique (Halbedel et al., 2013). Total phosphorus (TP) was measured using the ammonium molybdate spectrometric method (Halbedel et al., 2013). Total inorganic carbon (TIC) and dissolved organic carbon (DOC) were analysed using a method based on high temperature oxidation with NDIR-detection (Kamjunke et al., 2013). Chlorophyll *a* (Chl *a*) was measured by HPLC (DIONEX Corporation, Germany) using the ethanol extraction method (Koschorreck and Wendt-Potthoff, 2012).

# 2.4 Calculations

#### 2.4.1 Flux calculations

The CO<sub>2</sub> flux between the water surface and the atmosphere  $(F_{CO_2})$  was determined from the difference between the actual CO<sub>2</sub> concentration in the surface water (CO<sub>2 water</sub>) and the concentration in air equilibrated water (CO<sub>2 air</sub>) multiplied by the gas transfer velocity (*k*):

$$F_{\rm CO_2} = (\rm CO_{2 water} - \rm CO_{2 air}) \times k.$$
<sup>(1)</sup>

 $CO_{2 air}$  was calculated from the  $CO_2$  partial pressure in the ambient air samples using Henry's law.

The value of k was determined using different methods for reservoirs and for streams. For reservoirs, k (in this case  $k_{600}$ ) was calculated from the wind speed and normalised to a Schmidt number of 600 (Crusius and Wanninkhof, 2003):

$$k_{600} = \left[1.68 + \left(0.228 \times U_{10}^{2.2}\right)\right] \times \left(\frac{SC_{\rm CO_2}}{600}\right)^{-0.5}.$$
 (2)

 $U_{10}$  is the wind speed at 10 m above the surface (m s<sup>-1</sup>) and was taken from a nearby weather station (Harzgerode,

distance to pre-dams 22 km). We used the daily mean wind speed for the specific flux calculations.

The average annual wind speed at the weather station was  $3.7 \pm 1.9 \text{ m s}^{-1}$ . This is very similar to our episodic measurements taken at the reservoirs ( $U_{10} = 3.66 \pm 1.7 \text{ m s}^{-1}$ ). The episodic measurements were done using a hand-held anemometer at 1 m over the water surface and converted to  $U_{10}$  by means of the following equation:

$$U_{10} = U \times 1.22. \tag{3}$$

The Schmidt number  $SC_{CO_2}$  was calculated from the surface water temperature *T* (°C):

$$SC_{\rm CO_2} = 1911.1 + (118.11 \times T) + (3.4527 \times T^2)$$
(4)  
- (0.04132 \times T^3).

The *k* value for streams was calculated from gas transfer coefficients for propane ( $k_{\text{propane}}$ ) obtained from metabolism studies that were conducted at the same time (Halbedel et al., 2013). These coefficients were converted to the reaeration coefficient  $k_{\text{CO}_2}$  (Genereux and Hemond, 1992) thus:

$$k_{\rm CO_2} = k_{\rm propane} \times \left(\frac{d_{\rm CO_2}}{d_{\rm propane}}\right)^n.$$
 (5)

The exponent n can vary from -0.66 to -0.5. We used the value -0.5 that was given in Hope et al. (2001).  $d_{CO_2}$  and  $d_{propane}$  were calculated for the current stream temperature (in °C) using the following equations (Hope et al., 2001):

$$d_{\rm CO_2} = 1.005 \times \exp^{(0.00231 \times T)}$$
 and (6)  
 $d_{\rm propane} = 1.092 \times \exp^{(0.0235 \times T)}$ .

k was than calculated using Eq. (7):

$$k = k_{\rm CO_2} \times t \times \frac{Q}{A},\tag{7}$$

where t = travel time (min), Q = discharge (L s<sup>-1</sup>), A = stream reach surface area (m<sup>2</sup>), which was calculated from the mean width and reach lengths (data from Halbedel et al., 2013).

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# 2.4.2 Upscaling and error estimation

We estimated the annual CO<sub>2</sub> flux for the streams Hassel, Rappbode, Ochsenbach and Zillierbach by multiplying the mean surface area of each stream by mean values for the experimentally determined  $CO_2$  flux per m<sup>2</sup>. The mean area was calculated on the basis of a detailed data set (width, length) gathered from different organisations (Ute Enders: Unterhaltungsverband Holtemme, Detlef Cöster: Talsperrenbetrieb Sachsen-Anhalt and Otfried Wüster: Nationalparkverwaltung Harz). This upscaling procedure excludes data from various events that can affect the wetted width, k and the CO<sub>2</sub> concentration (discharge events, storm, etc.). We used the minimum and maximum variability of the width of each stream for the error estimation. Varying the stream width brought about flux values that differed by less than one order of magnitude. We also tested errors based on a possible k variability of 50%. This also changed the resulting flux data by less than one order of magnitude. The minimum and maximum CO2 concentrations measured in each stream were also used for the error propagation. The variability of the resulting flux data was higher than one order of magnitude. Thus the greatest error for this estimation arises from the possible variability of the CO<sub>2</sub> concentration. Since several short-term events are known to increase the CO2 concentration as well as k and the stream surface area we conclude that our upscaling causes underestimation of the real CO<sub>2</sub> flux from these streams.

The annual CO<sub>2</sub> flux from the reservoirs was estimated on the basis of the mean CO<sub>2</sub> flux per unit area that was multiplied by the mean wetted width of the reservoirs. These estimates are probably subject to errors on account of excluding the different wind extremes from our sampling campaigns. Therefore the variability of k in reservoirs could represent a pronounced source of error. To estimate this error we computed hourly flux data by interpolating the measured CO<sub>2</sub> concentrations and combining them with hourly atmospheric CO<sub>2</sub> and wind data from the weather station. This procedure neglects short-term changes in the  $CO_2$  concentrations in the water but does take account of short-term wind fluctuations. The mean annual flux values computed in this way were 15 (SD 55.4) mmol  $m^{-2} d^{-1}$  and 18.9 (SD 32.4) mmol  $m^{-2} d^{-1}$  for DH and DR, respectively. These flux figures are practically the same as those calculated on the basis of our 14 sampling days. Clearly, the opposing effects of extremely high and low winds cancelled each other out and our estimate of an annual flux from the reservoir was probably not affected a great deal by the exclusion of extreme values. The analytical error for CO<sub>2</sub> determination in reservoirs was about 5 %.

## 2.4.3 Statistics

The significance of correlations was tested using the Spearman rank order correlation. The Kruskal–Wallis test and the Tukey test were used to test the significance of differences between groups. The significance interval (p) was set to be 0.05. All statistical analyses were conducted in SigmaPlot 12.0.

# **3** Results

## **3.1** CO<sub>2</sub> concentrations and evasion

All the streams that were investigated were supersaturated with CO<sub>2</sub>. With values ranging from 28 to 200 µmol L<sup>-1</sup>, the CO<sub>2</sub> concentrations in the streams were generally higher than in the reservoirs, which had values ranging from 0 to 131 µmol L<sup>-1</sup> (Fig. 2). The Hassel stream, which had the highest CO<sub>2</sub> concentrations in general (mean: 123 (SD 43) µmol L<sup>-1</sup>, p < 0.001) yielded data that were widely scattered. The data for CO<sub>2</sub> showed a relatively small degree of scatter for the other three streams. The CO<sub>2</sub> concentrations for the pre-dams were similar but widely scattered.

Values for  $k_{CO_2}$  in the streams ranged from 0.01 to  $0.05 \text{ min}^{-1}$ . The gas transfer coefficients were higher in all the streams than in the reservoirs (Table 1). Both reservoirs had similar k values and  $CO_2$  fluxes (Fig. 3). The  $CO_2$  emission from streams lay between 23 and 355 mmol  $m^{-2} d^{-1}$ . These fluxes are higher than the evasion calculated for the pre-dams (from -24 to 97 mmol m<sup>-2</sup> d<sup>-1</sup>). Whilst the CO<sub>2</sub> evasion from both reservoirs was in the same range, more variable emission values were obtained for the streams. With a mean of 251.9 (SD 52.7) mmol  $m^{-2} d^{-1}$ , the Hassel yielded by far the highest CO<sub>2</sub> emission rate, while the other streams yielded lower area-specific emission rates (but these were still higher than those obtained for the reservoirs) (Fig. 3). We estimated the yearly CO<sub>2</sub> emission from the different bodies of water based on mean values and surface area:  $4.06 \times 10^3$  kmol yr<sup>-1</sup> for the Hassel,  $1.73 \times 10^3$  kmol yr<sup>-1</sup> for the Rappbode,  $5.61 \times 10^1$  kmol yr<sup>-1</sup> for the Ochsenbach, and  $2.11 \times 10^2$  kmol yr<sup>-1</sup> for the Zillierbach. For the reservoirs the equivalent values were  $1.2 \times 10^3$  kmol yr<sup>-1</sup> for DH and  $1.3 \times 10^3$  kmol yr<sup>-1</sup> for DR. We assume thereby that the  $CO_2$  flux is negligible during the winter months when both bodies of water are frozen over (cp. Striegl et al., 2001; Karlsson et al., 2013).

# 3.2 Seasonality

The seasonal changes in the  $CO_2$  data give a more detailed picture of the emissions (Fig. 4a). We determined the following mean  $CO_2$  values for the streams: Zillierbach – 44.1 (SD 9.6) µmol L<sup>-1</sup> (spring), 51.1 (SD 8.8) µmol L<sup>-1</sup> (summer), 47.2 (SD 4.7) µmol L<sup>-1</sup> (autumn); Ochsenbach



**Fig. 2.** Boxplots describing the yearly CO<sub>2</sub> concentration ( $\mu$ mol L<sup>-1</sup>) in the investigated streams (Rappbode (R, n = 52), Hassel (H, n = 53), Zillierbach (Z, n = 59), Ochsenbach (O, n = 47)) and the pre-dams (Rappbode (DR, n = 14), Hassel (DH, n = 14)). The following parameters are displayed: medians, quartiles, whiskers and outliers. The letters a, b, c, d and e indicate the significance of differences between groups (p < 0.05).



**Fig. 3.** Boxplots describing the CO<sub>2</sub> evasion  $(\text{mmol}^{-2} \text{d}^{-1})$  from the streams Rappbode (R, n = 52), Hassel (H, n = 53), Zillierbach (Z, n = 59) and Ochsenbach (O, n = 47) and the pre-dams Rappbode (DR, n = 14) and Hassel (DH, n = 14). The letters a, b, c and d indicate the significance of differences between groups (p < 0.05).

- 54.0 (SD 10.0) μmol L<sup>-1</sup> (spring), 46.9 (SD 6.8) μmol L<sup>-1</sup> (summer), 42.1 (SD 5.3) μmol L<sup>-1</sup> (autumn); Rappbode – 56.8 (SD 5.0) μmol L<sup>-1</sup> (spring), 59.3 (SD 6.1) μmol L<sup>-1</sup> (summer), 64.9 (SD 19.3) μmol L<sup>-1</sup> (autumn); and Hassel – 100.9 (SD 22.1) μmol L<sup>-1</sup> (spring), 84.6 (SD 13.3) μmol L<sup>-1</sup> (summer), 175.2 (SD 17.4) μmol L<sup>-1</sup> (autumn). Although we detected certain seasonality in the CO<sub>2</sub> concentrations for all the streams, especially in the Rappbode and the Zillierbach, they remained fairly constant throughout the year. Nevertheless, all streams displayed significantly



**Fig. 4.** Boxplots describing the annual fluctuation of  $CO_2$  concentrations (**a**) and evasion (**b**) from streams Rappbode (R), Hassel (H), Zillierbach (Z) and Ochsenbach (O) and the pre-dams Rappbode (DR) and Hassel (DH). Seasons are abbreviated as follows: Sp is spring, S is summer and F is fall. Significant differences between groups are indicated by letters a and b.

different CO<sub>2</sub> fluxes from one season to another (p < 0.05, Fig. 4b). We detected the highest mean values for the Rappbode in spring (132.9 (SD 15.6) mmol m<sup>-2</sup> d<sup>-1</sup>) and lower values in summer (92.2 (SD 13.0) mmol m<sup>-2</sup> d<sup>-1</sup>) and in the autumn (81.6 (SD 44.0) mmol m<sup>-2</sup> d<sup>-1</sup>). The streams Zillierbach and Ochsenbach also returned the highest values in spring (69.3 (SD 23.7) mmol m<sup>-2</sup> d<sup>-1</sup>, 90.9 (SD 30.8) mmol m<sup>-2</sup> d<sup>-1</sup>, respectively) and the lowest values in summer (55.8 (SD 14.4) mmol m<sup>-2</sup> d<sup>-1</sup>, 68.3 (SD 19.6) mmol m<sup>-2</sup> d<sup>-1</sup>) and the autumn (35.8 (SD 6.6) mmol m<sup>-2</sup> d<sup>-1</sup>, 46.1 (SD 13.1) mmol m<sup>-2</sup> d<sup>-1</sup>), whereas the Hassel returned the lowest mean values in spring with 226.3 (SD 56.3) mmol m<sup>-2</sup> d<sup>-1</sup> and the highest values in summer and autumn with 279.0 (SD 52.6) mmol m<sup>-2</sup> d<sup>-1</sup> and 269.5 (SD 29.1) mmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 4b).

Both reservoirs exhibited a degree of seasonality in the  $CO_2$  concentrations of the surface water and  $CO_2$ fluxes, with low values during spring (mean values: 24.7 (SD 25.5)  $\mu$ mol L<sup>-1</sup>, 8.8 (SD 24.2) mmol m<sup>-2</sup> d<sup>-1</sup> for DR and HR, respectively) and summer (mean values:  $17.4 (SD 8.5) \mu mol L^{-1}$ ,  $1.4 (SD 7.8) mmol m^{-2} d^{-1}$ ), and high values during the autumn  $(74.0 (SD 47.5) \mu mol L^{-1})$ , 50.3 (SD 57.9) mmol m<sup>-2</sup> d<sup>-1</sup>) when the data also varied more (Fig. 4). Because of the high data spread in the autumn and spring, these differences were generally not significant. The reservoirs were stratified from March until November. During the stratification period the surface water contained low concentrations of CO<sub>2</sub>, while CO<sub>2</sub> accumulated in the bottom water to maximum concentrations of  $400 \,\mu mol \, L^{-1}$ (Fig. 5). This value exceeds the stream concentrations. Sometimes, the reservoirs were even undersaturated in the surface water during summer. In the fall, the bottom water was mixed into the epilimnion, leading to high surface concentrations and evasion rates.



Fig. 5. Vertical profiles of temperature (lines) and  $CO_2$  concentrations (dots) in both pre-dams in spring (a), summer (b) and autumn (c).

### 3.3 The role of environmental factors

Table 2 gives an overview of the correlations between different environmental parameters and CO2 flux. Since CO2 evasion was calculated from concentration data, we expect some correlation between both. Not surprisingly, the CO<sub>2</sub> emissions correlated positively with the CO<sub>2</sub> values measured directly in the streams (r = 0.90, p < 0.001) and pre-dams (r = 0.92, p < 0.001). The CO<sub>2</sub> flux from these streams to the atmosphere can be predicted from the following regression:  $CO_2$  flux =  $-13.217 + (1.920 \times CO_2)$ , with p < 0.001, and CO<sub>2</sub> emission from the reservoirs can be predicted from  $CO_2$  flux =  $-10.476 + (0.791 \times CO_2)$ , with p < 0.001. Because k is also a part of the flux equation (Eq. 1), some correlations can be expected. Nevertheless, we found no significant correlation between these parameters (r = 0.35, p >(0.05) for the reservoirs, even though we obtained the highest flux data when k was highest ( $R^2 = 0.78$ , p < 0.001). However,  $CO_2$  flux and k correlated significantly for the streams (r = 0.66, p < 0.05). Furthermore, we found a significant correlation between CO<sub>2</sub> flux and flow velocity (r = 0.75, p < 0.05) as well as discharge (r = 0.72, p < 0.05) when we only entered data from the Rappbode, the Ochsenbach and the Zillierbach and excluded the Hassel values. We excluded the Hassel because it had significantly higher CO<sub>2</sub> values in comparison to the other streams and these relationships are very site specific. CO2 evasion was also negatively correlated with temperature and pH in both dams.

In the reservoirs, CO<sub>2</sub> emission was also negatively correlated to Chl *a* (r = -0.51, p = 0.008) and there was a negative correlation between Chl *a* and CO<sub>2</sub> concentration (r = -0.56, p = 0.003). The Chl *a* concentration in the reservoirs followed a typically seasonal trend, with increasing mean concentrations from spring (DR: 5.9 (SD 4.0) mg L<sup>-1</sup>, DH 6.3 (SD 3.7) mg L<sup>-1</sup>) to summer (DR: 15.5 (SD 9.0) mg L<sup>-1</sup>, DH: 39.4 (SD 37.4) mg L<sup>-1</sup>) and a decrease in the autumn (DR: 3.5 (SD 2.1) mg L<sup>-1</sup>, DH: 7.8 (SD 5.6) mg L<sup>-1</sup>). The seasonal concentrations of parameters (Chl *a*, DOC, TIC, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, TP) that are associated with primary produc-

**Table 2.** Correlation of  $CO_2$  evasion with different parameters, sorted for dams and streams.<sup>\*</sup>

	parameter	r	р	п
dams	CO <sub>2</sub>	0.92	< 0.001	28
	k	0.34	0.074	28
	Temperature	-0.66	< 0.001	28
	O <sub>2</sub>	-0.32	0.105	27
	pН	-0.88	< 0.001	28
	Chl a	-0.51	0.008	26
	DOC	0.04	0.836	28
	TIC	0.12	0.546	28
	$NH_4^+$	0.41	0.035	27
	$NO_3^{-}$	0.06	0.759	25
	TP	-0.25	0.203	28
	cond.	0.07	0.704	28
	$CO_2$	0.90	< 0.001	209
	$     CO_2     k $	0.90 0.66	< 0.001 0.017	209 12
	CO <sub>2</sub> k Temperature	<b>0.90</b> <b>0.66</b> 0.41	< 0.001 0.017 0.173	<b>209</b> <b>12</b> 12
	$CO_2$ k Temperature O_2	<b>0.90</b> <b>0.66</b> 0.41 -0.25	< 0.001 0.017 0.173 0.429	<b>209</b> <b>12</b> 12 12
	CO <sub>2</sub> k Temperature O <sub>2</sub> pH	<b>0.90</b> <b>0.66</b> 0.41 -0.25 0.21	< 0.001 0.017 0.173 0.429 0.498	<b>209</b> <b>12</b> 12 12 12 12
	CO <sub>2</sub> k Temperature O <sub>2</sub> pH Chl a	<b>0.90</b> <b>0.66</b> 0.41 -0.25 0.21 0.50	< 0.001 0.017 0.173 0.429 0.498 0.089	<b>209</b> <b>12</b> 12 12 12 12 12
ms	$CO_2$ k Temperature $O_2$ pH Chl a DOC	<b>0.90</b> <b>0.66</b> 0.41 -0.25 0.21 0.50 0.34	< <b>0.001</b> <b>0.017</b> 0.173 0.429 0.498 0.089 0.263	<b>209</b> <b>12</b> 12 12 12 12 12 12
treams	CO <sub>2</sub> k Temperature O <sub>2</sub> pH Chl a DOC TIC	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80	< 0.001 0.017 0.173 0.429 0.498 0.089 0.263 0.001	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 11</pre>
streams	$CO_2$ k Temperature $O_2$ pH Chl a DOC TIC NH <sup>+</sup> _4	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80 0.87	<0.001 0.017 0.173 0.429 0.498 0.498 0.263 0.001 < 0.001	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 12</pre>
streams	$CO_2$ k Temperature $O_2$ pH Chl a DOC TIC NH_4 NO_3	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80 0.87 -0.11	<0.001 0.017 0.173 0.429 0.498 0.263 0.001 <0.001 0.733	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 12</pre>
streams	$CO_2$ k Temperature $O_2$ pH Chl a DOC TIC NH <sup>+</sup> NO <sup>-</sup> <sub>3</sub> TP	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80 0.87 -0.11 0.84	<0.001 0.017 0.173 0.429 0.498 0.263 0.089 0.263 0.001 <0.001 0.733 <0.001	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 12</pre>
streams	$CO_2$ k Temperature $O_2$ pH Chl a DOC TIC NH <sup>+</sup> NO <sub>3</sub> TP Q	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80 0.87 -0.11 0.84 0.34	<0.001 0.017 0.173 0.429 0.498 0.263 0.009 0.263 0.001 0.733 <0.001 0.263	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 12</pre>
streams	$CO_2$ k Temperature $O_2$ pH Chl a DOC TIC NH <sup>+</sup> NO <sub>3</sub> TP Q v	0.90 0.66 0.41 -0.25 0.21 0.50 0.34 0.80 0.87 -0.11 0.84 0.34 0.27	<0.001 0.017 0.173 0.429 0.498 0.089 0.263 0.001 0.733 <0.001 0.263 0.389	<pre>209 12 12 12 12 12 12 12 12 12 12 12 12 12</pre>

\* Spearman correlation was used for detecting the significance (*p*) of correlations (*r*). Bold numbers show significant correlations indicated by p < 0.05. *n* represents the number of compared values. The values shown are means. Further abbreviations used:  $CO_2 = carbon dioxide, k = gas transfer velocity, <math>O_2 = oxygen$ , Chl *a* = chlorophyll *a*, DOC = dissolved organic carbon, TIC = total inorganic carbon,  $NH_4^+ = ammonium, NO_3^- = nitrate, TP = total phosphorus, <math>Q = discharge; v = velocity; cond. = conductivity.$ 

tion or respiration are given in Figs. 6 and 7. In comparison to both pre-dams, all investigated streams were less productive. This is indicated by low Chl a concentrations (mean: 2.9 (SD 1.5) mg  $L^{-1}$ , Fig. 6c) and generally low gross primary production (GPP, data from Halbedel et al., 2013). A positive correlation between  $F_{CO_2}$  and total phosphorus (TP) was detected for the streams (r = 0.84, p < 0.001), but not for the reservoirs (r = -0.25, p = 0.203). TP was highest in the Hassel (mean: 0.2 (SD 0.2) mg L<sup>-1</sup>, Fig. 7), and lowest in the two forest streams (mean:  $0.01 (SD 0.01) \text{ mg } \text{L}^{-1}$ ), but also in the DR (mean:  $0.02 (SD 0.01) \text{ mg L}^{-1}$ ). Slightly higher but still low concentrations were measured in the Rappbode (mean: 0.04 (SD 0.01) mg L<sup>-1</sup>) and in DH (mean:  $0.03 (SD 0.01) \text{ mg L}^{-1}$ ). CO<sub>2</sub> emission from both systems correlated with ammonium concentration (dams: r = 0.41, p = 0.035, streams: r = 0.87, p < 0.001). Both the pristine streams and the Rappbode returned low ammonium



**Fig. 6.** Seasonal concentrations of DOC, TIC, and Chl *a* in the streams Rappbode (R), Hassel (H), Zillierbach (Z) and Ochsenbach (O) and the pre-dams Rappbode (DH) and Hassel (DH). Seasons are abbreviated as follows: Sp indicates spring, S indicates summer, and F indicates fall. The following numbers of samples were pooled in the box plots for DOC and TIC: in spring n = 6 for DR and DH, n = 7 for R, n = 8 for H and O, and n = 4 for Z; in summer n = 4 for DR, DH, R and H, and n = 8 for Z and O; in fall n = 4 for DR and DH, n = 8 for R, H, Z and O. For Chl *a* the following numbers were pooled: in spring n = 5 for DR and DH, n = 3 for R, H, Z and O. Significant differences between groups are indicated by letters a, b and c.

concentrations (mean: 0.02 (SD 0.01) mg L<sup>-1</sup>, Fig. 7a). The highest ammonium concentrations were measured with 0.66 (SD 0.10) mg L<sup>-1</sup> in the Hassel, in summer, after extensive cattle grazing had taken place in the neighbouring areas. In this stream, ammonium was also slightly elevated in spring  $(0.06 (SD 0.00) \text{ mg } \text{L}^{-1})$  and fall  $(0.04 (SD 0.01) \text{ mg } \text{L}^{-1})$ . Both reservoirs had comparatively high ammonium concentrations in autumn (mean:  $0.07 (SD 0.05) \text{ mg L}^{-1}$ ). During other periods, the mean ammonium concentrations in the pre-dams were within the range of the stream values  $(0.03 (SD 0.02) \text{ mg L}^{-1})$ . The CO<sub>2</sub> flux from streams also correlated positively with TIC (r = 0.80, p = 0.001). Here, the highest TIC concentrations were measured for the Hassel (mean:  $18.6(\text{SD}1.9) \text{ mg } \text{L}^{-1}$ ). The lowest values were measured there in summer  $(16.6 (SD 0.2) \text{ mg L}^{-1})$ , and with 20.0 (SD 0.9) mg  $L^{-1}$  and 20.2 (SD 0.4) mg  $L^{-1}$  the highest values were found in spring and fall (Fig. 6b). Also, high TIC concentrations were detected for the Rappbode (13.6 (SD 1.4)), where the highest values were found in summer  $(14.8 (SD 0.5) \text{ mg L}^{-1})$  and the lowest values were found in the fall  $(12.1 (SD 0.3) \text{ mg L}^{-1})$ . The Zillierbach showed the highest TIC concentrations in summer (10.9 (0.3) mg  $L^{-1}$ ), and the lowest in spring  $(7.7 (SD 0.0) \text{ mg } \text{L}^{-1})$ . The lowest TIC altogether was measured for the Ochsenbach (mean:  $4.8 (\text{SD} 0.2) \text{ mg L}^{-1}$ ). The TIC increased in both pre-dams continuously from spring (mean:  $6.3 (SD 0.3) \text{ mg L}^{-1}$ ) to the autumn (mean:  $11.0 (SD 2.3) \text{ mg L}^{-1}$ ). We found no other significant cor-



**Fig. 7.** Seasonal concentrations of  $NH_4^+$ ,  $NO_3^-$  and TP in the streams Rappbode (R), Hassel (H), Zillierbach (Z) and Ochsenbach (O) and the pre-dams Rappbode (DH) and Hassel (DH). Seasons are abbreviated as follows: Sp indicates spring, S indicates summer, and F indicates fall. The following numbers of samples were pooled in the box plots: in spring n = 6 for DR and DH, n = 7 for R, n = 8 for H and O and n = 4 for Z; in summer n = 4 for DR, DH, R and H, and n = 8 for Z and O; in fall n = 4 for DR and DH, n = 8 for R, H, Z and O. Significant differences between groups are indicated by letters a, b and c.

relations between  $CO_2$  evasion and environmental factors. Specifically, no correlation was found with DOC or  $NO_3^-$ .

# 4 Discussion

The CO<sub>2</sub> evasion per m<sup>2</sup> from streams exceeded the CO<sub>2</sub> emission from the reservoirs by more than one order of magnitude (Fig. 3). As was recently shown by Knoll et al. (2013), older reservoirs in particular could even function temporarily as CO<sub>2</sub> sinks in a temperate landscape. However, streams are generally known to be CO<sub>2</sub> sources rather than sinks (Teodoru et al., 2009; Wallin et al., 2013). Why do CO<sub>2</sub> emissions from streams and rivers exceed the CO<sub>2</sub> flux from lakes per unit area? As shown in Eq. (1), CO<sub>2</sub> emissions from streams and lakes depend both on the surface concentration of CO<sub>2</sub>, which is probably primarily regulated by biogeochemical processes, and the physical transfer coefficient *k*. The question presents itself as to whether both factors are equally important in the two types of aquatic systems.

The mean emission from the reservoirs was  $74.9 \text{ g C m}^{-2} \text{ yr}^{-1}$  for DH and  $87.6 \text{ g C m}^{-2} \text{ yr}^{-1}$  for DR. On an annual basis, both reservoirs were CO<sub>2</sub> sources. The mean emission from both bodies of water was higher than emissions presented by Knoll et al. (2013) for two reservoirs located in the temperate zone in the USA (11.5–33.6 g C m<sup>-2</sup> yr<sup>-1</sup>). Those reservoirs, however, were seasonally undersaturated and therefore also temporary CO<sub>2</sub> sinks. In contrast, all the streams investigated in the present study were supersaturated with CO<sub>2</sub> throughout the year. Another study conducted in the same catchment revealed that all the streams and rivers investigated in this landscape

were also supersaturated (Kamjunke et al., 2013). Most streams draining temperate or boreal regions, arctic tundra, peatlands and tropical ecosystems are supersaturated with  $CO_2$  (Richey et al., 2002; Hope et al., 2001; Rantakari, 2010; Butman and Raymond, 2011; Hope et al., 2004; Wallin et al., 2010). Thus, the differential occurrence of temporary undersaturation seems to be a principle difference between lentic and lotic systems.

A comparison of gas transfer velocities in lentic and lotic waters is rendered difficult on account of the different methods used in river and lake research. Traditionally, in lake research the transfer velocity is expressed as k (or  $k_{600}$ ), with k having the unit of a velocity  $[m s^{-1}]$ . The analogous parameter in river research is called the "reaeration coefficient"  $(k_{\rm CO_2})$ , with the unit m<sup>-1</sup>. Both parameters are related by Eq. (7). Thus in order to be able to convert  $k_{CO_2}$  to k data on travel time, discharge and stream area are required. The precise measurement of a stream's surface area, in particular, is not trivial and this introduces an additional source of error into the determination of k in streams. We also tested the approach of Alin et al. (2011), which is based on depth values and yields a significant increase in all values. This is indicative of the degree to which the results are influenced by the hydromorphological data. However, the comparison of literature values is difficult, especially if no travel time, stream area, depth or discharge data are provided.

In standing waters, *k* depends on surface turbulence, which in turn depends on the weather conditions (wind, precipitation). *k* is assumed to be proportional to wind speed, and this was borne out in the reservoirs under investigation, where the mean annual wind speed was low at 3.7 (SD 1.9) m s<sup>-1</sup>. Typically, *k* values fluctuate in a narrow range between 1 and  $6 \text{ cm h}^{-1}$  at wind speeds below  $5 \text{ m s}^{-1}$  (Crusius and Wanninkhof, 2003). Only short periods of higher wind intensities (Crusius and Wanninkhof, 2003) or precipitation (Cole and Caraco, 1998) lead to episodically higher *k* values. In the study area this was the case during spring and autumn. Only during these short periods of high wind was  $F_{CO_2}$  regulated by elevated *k* values.

In the streams, k was twofold higher than in the reservoirs on average. The k values were in the upper range of those published in Alin et al. (2011) for small rivers and streams. The latter are based on different  $k_{CO_2}$  values from the literature, as well as their own data. The  $k_{CO_2}$  values detected for the Harz Mountain streams are within the range of those published for boreal headwater streams (0.001–0.207 m<sup>-1</sup>, Wallin et al., 2011) and temperate peatland streams (0.015– 0.344 m<sup>-1</sup>, Hope et al., 2001). Thus, since both the mean CO<sub>2</sub> concentration and k were twofold higher in streams than in reservoirs, we conclude that both factors are similarly responsible for the higher areal CO<sub>2</sub> emission from streams.

Knowing the reasons for the higher  $CO_2$  emission fluxes from streams (in absolute terms), the question arises as to how the  $CO_2$  flux is regulated in the two systems. We analysed the seasonal dynamics as well as the correlation with different environmental parameters. The fact that the CO<sub>2</sub> flux correlated more distinctly with surface concentration than with k showed that the CO<sub>2</sub> concentration was the dominant factor in both systems. The CO<sub>2</sub> concentration showed a high variability in both reservoirs (31.6 (SD 39.7) and  $41.8 (SD 35.5) \mu mol L^{-1}$  in the Hassel and Rappbode reservoir, respectively), resulting in a high degree of variability in  $F_{CO_2}$  and indicative of the impact of different environmental factors. The CO<sub>2</sub> concentration in the surface water is a result of the balance between CO2-consuming primary production, the respiratory mineralisation of organic matter and the physical gas transport. At least during summer, the surface CO<sub>2</sub> concentration and therefore also its flux from the reservoirs was controlled by primary production. This is supported by the correlation of the CO<sub>2</sub> flux with pH and Chl a. Many authors have suggested that natural lentic systems with high primary production levels are sinks for  $CO_2$  (Cole et al., 2007; Downing et al., 2008; Tranvik et al., 2009). In contrast, Knoll et al. (2013) showed recently that productive reservoirs could also function as minor CO2 sources on a landscapewide scale. They found that reservoirs could be sinks only during dry summers and deduced a weather-related summer difference in their net-autotrophic lakes which is in accordance with previous findings (Cole and Caraco, 1998; Rantakari and Kortelainen, 2005). In the streams, there was no correlation between Chl *a* or GPP and  $F_{CO_2}$ , indicating that respiration was more relevant for  $F_{CO_2}$  from streams than primary production. Dawson et al. (2004) showed that the role of primary production increases with increasing distance from the source. The streams investigated in the current study are in the upper part of the Bode catchment. We expect that the role of primary production increases downstream of the Bode catchment. The impact of respiration on  $CO_2$  emission is shown by the correlation of  $F_{CO_2}$  with ammonium, which is a product of the mineralisation of organic matter (cp. Tranvik and Kokalj, 1998). It has already been demonstrated that the different chemical nitrogen forms as well as phosphorus correlate with CO<sub>2</sub> evasion or CO<sub>2</sub> concentrations in streams (Teodoru et al., 2009; Neal et al., 1998) and lakes (Kortelainen et al., 2000). In addition, we recently showed that all these streams were of a net-heterotrophic nature (Halbedel et al., 2013). Thus, metabolism is generally a controlling factor for CO2 concentration and flux in both water systems.

However, even if the  $CO_2$  concentration in Hassel followed the net ecosystem production (compared to data from Halbedel et al., 2013), the detected seasonal changes in the  $CO_2$  concentrations were quite low in most of the streams. Dinsmore et al. (2013) suggested that  $CO_2$  does not follow a temperature-related seasonal pattern if it is derived mainly from groundwater sources. Especially in streams, lateral fluxes (such as groundwater) might be a significant source of  $CO_2$  (Humborg et al., 2010; Battin et al., 2008). In a parallel study (Halbedel et al., 2013), we measured the lateral inflow using chloride as a conservative tracer. The highest lateral inflow was detected for the stream Hassel (Table 1). Thus terrestrial metabolism might also contribute to the stream-related results in this case. However, we also found that besides the Hassel, all the other streams have only very low lateral inflow or even flow out into the adjacent soil or sediment. No data exist on the CO<sub>2</sub> concentration of the lateral inflow. Thus, lateral inflow could also be relevant for these streams and the groundwater, in its capacity as a mediator to terrestrial metabolism, would appear to be a general regulator of the CO<sub>2</sub> concentration in our streams. That the annual CO<sub>2</sub> variability can be correlated with the catchment metabolism has been confirmed by Dinsmore et al. (2013) as well as Jones and Mulholland (1998), for instance. Even though we have not investigated the groundwater inflow into the reservoirs, we think that in view of the underlying geological conditions (bedrock) and volume the former is not directly affecting the CO<sub>2</sub> evasion.

There were no correlations between  $CO_2$  evasion and DOC, neither in streams nor in lakes. This deviates from the results of several studies on boreal lakes and streams, where especially the turnover of organic carbon with terrestrial origin is considered to be the main source for the  $CO_2$  oversaturation (Sobek et al., 2003; Prairie et al., 2002; Jonsson et al., 2003; Dawson et al., 2009; and many more). However, particulate organic matter (POM) like seston, soil, sediment, litter and wood could also fuel heterotrophic activity in waters (Rugenski et al., 2012; Vannote et al., 1980). Although POM variability was not subjected to investigation in this study, we assume that the heterotrophic turnover in particular is affected by POM in both water systems.

However, in addition to metabolic processes, physical processes could also have a significant impact on the CO<sub>2</sub> concentration. In stratified lakes, the zone of CO<sub>2</sub> consumption (epilimnion) is physically separated from the zone of CO<sub>2</sub> production (hypolimnion) (Boehrer and Schultze, 2008). Weyhenmeyer et al. (2012) showed recently that temperature and thermal stratification are major drivers for CO2 stratification in boreal lakes. The physical stratification results in a depletion of  $CO_2$  at the surface and an accumulation of  $CO_2$ in deeper regions. In the streams, these two zones do not exist and the pelagial and benthal regions are closely connected throughout the year. Thus the standing waters can function as temporary CO<sub>2</sub> sinks despite being net heterotrophic, while in streams net heterotrophy is always indicated by CO2 oversaturation. As a result, lakes typically show highest CO<sub>2</sub> emissions during the circulation process when CO2-rich bottom water comes to the surface (Kortelainen et al., 2000). In other words, the seasonal patterns of  $F_{CO_2}$  in reservoirs are governed by physical processes rather than the rates of biogeochemical reactions. In contrast to this, the seasonal patterns in streams are driven to a greater extent by biogeochemical factors.

When k is fairly constant or subject to meteorological influences (wind, precipitation) in lentic waters, then it is governed by hydrodynamic factors in streams and rivers (Alin et al., 2011). We found no correlation between discharge and  $k_{\rm CO_2}$ . The literature contains conflicting findings regarding the linkage between  $k_{CO_2}$  and Q. Billett and Harvey (2013) found  $k_{CO_2}$  positively to be related to Q, whilst Wallin et al. (2011) found no clear evidence for a connection between  $k_{\text{CO}_2}$  and Q. They concluded that the impact on the variability of  $k_{CO_2}$  is highly site specific. The discharge is generally considered to be the main factor influencing the CO<sub>2</sub> flux from stream water to the atmosphere (Hope et al., 2001; Roberts et al., 2007). We found a positive correlation between O and  $CO_2$  flux if the values from the Rappbode, the Zillierbach and the Ochsenbach are summed. There is no correlation between Q and  $F_{CO_2}$  if all four streams are included in the calculation. This finding highlights once again that the effect of hydrological factors on  $F_{CO_2}$  is very site specific. Although slopes were not measured in our study site, it has to be assumed that slope variations could have a general effect on the gas transfer. Wallin et al. (2011) indicated that the slope has an overall impact on  $k_{CO_2}$  for boreal streams, and this is supported by the results of earlier studies (Bennett and Rathbun, 1972; Gualtieri et al., 2002). Studies also exist showing that the geometrical factors width and depth could correlate with  $k_{CO_2}$  (Wanninkhof et al., 1990; Genereux and Hemond, 1992). Therefore k in streams appears to be dominated by hydrodynamic factors, which can be very site specific.

It is clear that the interplay of  $F_{CO_2}$  regulation factors is very complex. We developed a framework to include all relevant mechanisms (concentration, metabolism, lake stratification, k) and explain their effects on  $F_{CO_2}$  (Fig. 8). However, our results also highlight the role of CO2 emissions from streams on a landscape-wide scale. The CO<sub>2</sub> emission per unit area was very high in streams in comparison to reservoirs. Furthermore, the error estimations indicate that our upscaling procedure leads to a clear underestimation of the annual flux from streams. As CO2 measurements were only conducted at base flow, we excluded short-term events that are known to increase the CO<sub>2</sub> emission. The high emission values estimated for the streams themselves clearly show the importance of lotic systems on a catchment scale as well as for the CO<sub>2</sub> emission on a central European landscape level. This is in accordance to findings from other climate zones. For example, Lundin et al. (2013) showed recently that streams emit significant amounts of CO<sub>2</sub> from sub-arctic catchments.



Fig. 8. Schematic presentation of the effect of different regulation mechanisms on  $CO_2$  emissions (per unit area) from streams and low-wind lakes.

## 5 Conclusions

The variability of CO<sub>2</sub> emissions from streams and reservoirs is mainly governed by the CO<sub>2</sub> concentration, which varies according to time and is affected by various environmental factors. Metabolic processes, which are known to be affected by nutrient availability and weather conditions, appear to play a major role affecting the CO<sub>2</sub> concentrations and flux to the atmosphere in reservoirs and streams. In streams, the CO<sub>2</sub> concentration is often also linked to lateral inflows (including groundwater) which act as mediators between the terrestrial and aquatic metabolic scenarios. During periods in which standing waters are stratified, primary production and organic matter mineralisation take place independently of each other, which means that the influence of primary production on the CO<sub>2</sub> flux from the water surface to the atmosphere is particularly pronounced. During circulation, CO<sub>2</sub> accumulating from heterotrophic turnover represents the main factor governing the CO<sub>2</sub> concentration and increasing  $F_{CO_2}$ . Heterotrophic streams are influenced by lateral inflow as well as respiratory processes throughout the year, with the result that CO<sub>2</sub> concentrations are higher. Even if CO<sub>2</sub> concentrations in streams and lentic waters are in the same range during circulation,  $F_{CO_2}$  is generally higher in streams. The higher k values are responsible for the comparatively high CO<sub>2</sub> emissions. Thus, the annual CO<sub>2</sub> emission from temperate streams exceeds the evasion from temperate lentic waters. Although the total stream surface area may appear to be relatively small, CO<sub>2</sub> emissions from stream can affect the regional C balance on a landscape-wide level.

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