1 **CO$_2$ emissions from German drinking water reservoirs**

2 **estimated from routine monitoring data**

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13 **Abstract**

14 Globally, reservoirs are a significant source of atmospheric CO$_2$. However, precise

15 quantification of greenhouse gas emissions from drinking water reservoirs on the regional or

16 national scale is still challenging. We calculated CO$_2$ fluxes for 39 German drinking water

17 reservoirs during a period of 22 years (1991-2013) using routine monitoring data in order to

18 quantify total emission of CO$_2$ from drinking water reservoirs in Germany.

19 All reservoirs were small net CO$_2$ sources with a median flux of 167 g C m^{-2} y^{-1}, which makes

20 gaseous emissions a relevant process for the reservoirs carbon budgets. In total, German

21 drinking reservoirs emit 44000 t of CO$_2$ annually, which makes them a negligible CO$_2$ source

22 in Germany. Fluxes varied seasonally with median fluxes of 30, 11, and 46 mmol m^{-2} d^{-1} in

23 spring, summer, and autumn respectively. Differences between reservoirs appeared to be

24 primarily caused by the concentration of CO$_2$ in the surface water rather than by the physical

25 gas transfer coefficient. Consideration of short term fluctuations of the gas transfer coefficient

26 due to variable wind had only a minor effect on the annual budgets. High CO$_2$ emission only

27 occurred in reservoirs with pH < 7 and total alkalinity < 0.2 mEq l^{-1}. Annual CO$_2$ emission

1   correlated exponentially with pH, making pH a suitable proxy for CO_2 emission from German

2   drinking water reservoirs.

3

1   Introduction

5   Reservoirs are a globally important source of the greenhouse gases (GHG) CO_2 and CH_4 (St

6   Louis et al., 2000). Actually it is assumed that hydropower reservoirs globally emit 48 Tg C

7   as CO_2 and 3 Tg C as CH_4 (Barros et al., 2011). Existing studies on GHG emissions from

8   reservoirs focus on hydroelectric dams in boreal regions and the tropics and on dammed

9   rivers. Drinking water reservoirs in the temperate zone typically have a low trophic state and

10 GHG emissions are dominated by CO_2. Recent results indicate that they are a small source of

11 CO_2 to the atmosphere and can rather be a CO_2 sink during summer (Knoll et al., 2013).

12 However, existing CO_2 emission studies focus on few intensively studied reservoirs (Diem et

13 al., 2012; Soumis et al., 2004; Tremblay et al., 2005). Global inventories probably give a

14 realistic range of CO_2 emissions from surface waters (Raymond et al., 2013), but precise

15 quantification of GHG from drinking water reservoirs on the regional or national scale is still

16 challenging (McDonald et al., 2013; Seekell et al., 2014).

17 Upscaling is usually done by applying the thin boundary layer (TBL) approach (MacIntyre et

18 al., 1995). CO_2 exchange across the water surface is driven by diffusion and thus, regulated

19 by the concentration gradient between water and atmosphere and the physical gas transfer

20 coefficient K. K depends on the turbulence of the surface water. Although there is more and

21 more evidence that K is also influenced by convection (Read et al., 2012), in most studies it is

22 still derived from measured wind speed, using empirical equations (Cole and Caraco, 1998;

23 Crusius and Wanninkhof, 2003).

24 The concentration of CO_2 in surface waters is usually not directly measured but calculated

25 from two other measured parameters of the carbonate system, namely total inorganic carbon

26 (TIC), pH, or total alkalinity (TA). Thus, minimum data requirements are two parameters of

27 the carbonate system, water temperature, wind speed, and surface area. To obtain annual

28 budgets of CO_2 emission, both differences among reservoirs and temporal changes within a

29 system have to be considered. In practice, there is a trade-off between high monitoring

30 frequency and spatial coverage of numerous reservoirs because not all systems can be

31 monitored with high temporal resolution. Usually CO_2 concentration data are only available

32 for a few days of the year. Calculation of annual budgets from such sporadic measurements

1   may introduce systematic errors because high wind situations probably contribute

2   significantly to annual emissions (Morales-Pineda et al., 2014). By combining routine

3   monitoring data of CO_2 concentration from numerous German reservoirs with high temporal

4   resolution wind speed data from public weather stations we check, whether the low temporal

5   resolution of routine monitoring introduces a systematic bias in annual gas flux calculations.

6   The central aim of this study was to estimate the annual emission of CO_2 from Germany

7   drinking water reservoirs using data from routine water quality monitoring from a wide range

8   of reservoirs. By applying simple regression analysis we aimed to find out whether the CO_2

9   flux is primarily regulated by the gas transfer coefficient or by the CO_2 concentration. In

10   boreal surface waters, which are typically characterised by low alkalinity and high dissolved

11   organic carbon (DOC) concentration, the CO_2 concentration usually correlates well with the

12   DOC concentration (Jonsson et al., 2003; Whitfield et al., 2011), showing that aquatic

13   metabolism is a major driver of CO_2 oversaturation. In other regions, CO_2 in lakes seems to

14   be driven by DIC input from the catchment (McDonald et al., 2013). In high alkalinity lakes

15   in calcareous regions, CO_2 oversaturation is primarily caused by carbonate weathering (López

16   et al., 2011; Marcé et al., 2015). We used our dataset to get some information about the

17   principle drivers of the CO_2 flux from low DOC, low alkalinity waters, which are typical for

18   temperate drinking water reservoirs.

19   **2   Material and Methods**

20   **2.1   Data source**

21   We used a database containing routine water quality monitoring data from 39 German

22   drinking water reservoirs. Data were supplied by the reservoir operators and compiled in a

23   database in the framework of a research project about dissolved organic carbon in German

24   drinking water reservoirs (TALKO project). Available data span a period of 22 years (1991-

25   2013). Typical datasets for single reservoirs contained 10-20 years, the minimum period for a

26   single reservoir was 6 years with about monthly data. The data include both reservoirs and

27   pre-dams, which are characterised by a constant water level. A first quality control of these

28   data was performed using R statistic software. Typos, sign errors and rounding errors were

29   fixed using R functions. The dataset was checked for obviously wrong data by defining

30   minimum and maximum possible values.

31   Hourly wind speed data were provided by the German Meteorological Service (Deutscher

32   Wetterdienst) using the nearest weather station to each drinking water reservoir (Table S1).

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1   The median distance between reservoir and corresponding weather station was 15 km (1 km –

2   38 km).

2.2   Calculations

4   The TBL approach (MacIntyre et al., 1995; UNESCO/IHA, 2010) was adopted to estimate

5   CO_2 fluxes from the reservoirs surface. This method uses semi-empirical equations to

6   calculate emission from concentrations of CO_2 in the surface water and the CO_2 exchange

7   coefficient. The flux J [mmol CO_2 m^{-2} d^{-1}] of gas from water to air (diffusive emissions) was

8   calculated as the product of the gas exchange coefficient and the difference between gas

9   concentrations in surface water and air (Equation 1):

10    $J = K \times [CO_{2(water)} - CO_{2(air)}]$ (1)

11   Where

12   - $CO_{2(water)}$ is the concentration of CO_2 in surface water of the reservoir [µmol l^{-1}]

13   - $CO_{2(air)}$ is the concentration in air equilibrated water (calculated from the CO_2 partial

14   pressure in the air using Henry's law).

15   -   K [m d^{-1}] is the gas transfer velocity approximated from the wind speed and

16   normalised to a Schmidt number of 600 (Crusius and Wanninkhof, 2003).

17   All calculations were done assuming a water density of 1 kg l^{-1}.

2.2.1 Surface water concentration of CO_2

19   Because of the best data availability, we calculated CO_2 from pH and TA, using the "seacarb"

20   package of R (Lavigne et al., 2014). Input parameters were water temperature, salinity =0,

21   depth=0, TA [mmol l^{-1}], and pH. For comparison, data were also calculated with CO2SYS

22   (Lewis and Wallace, 1998). Both tools gave the same results.

2.2.2 Concentration in air equilibrated water

24   We calculated the partial pressure of the gas in the water if it were in equilibrium with the

25   atmosphere ($CO_{2(air)}$ [mmol l^{-1}]) from the CO_2 partial pressure (pCO_2) in the ambient air

26   samples using Henry's law:

27    $CO_{2(air)} = P \div K_H$ (2)

28   For pCO_2 in the atmosphere (P [µatm]) we used hourly data of the atmospheric mixing ratio

29   of CO_2 [ppm] from the public monitoring station at Schauinsland (WMO World Data: Center

1   for Greenhouse Gases http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html). This station is

2   located in the southern part of the Black Forest mountain range close to the top of mount

3   Schauinsland. It presents a reference site for the atmospheric background concentration in

4   Germany. The mixing ratios were converted to partial pressure by considering the altitude of

5   the particular reservoir:

6    $$P = mr \times P_{nn} \times e^{\frac{-alt}{scale\ height}} \times 10^{-6}$$ (3)

7   with mr being the CO_2 mixing ration [ppm], P_{nn} = standard barometric pressure at sea level =

8   1 atm, alt = altitude of reservoir [m], and the scale height being 8500m. K_H [atm l mol^{-1}] is

9   Henry's solubility coefficient for the actual water temperature.

10   **2.2.3 Gas transfer velocities**

11   There are several empirical expressions to derive the gas exchange coefficient (K) as a

12   function of wind speed and water temperature. We adopted the widely applied power function

13   presented in (Crusius and Wanninkhof, 2003):

14   $$K = \left[0.168 + \left(0.228 \times U_{10}^{2.2}\right)\right] \times \left(\frac{SC_{CO2}}{600}\right)^{-\frac{2}{3}or-\frac{1}{2}}$$ (4)

15   where

16   - U_{10} is the wind speed at 10m height [m s^{-1}],

17   - SC is the Schmidt number for CO_2 (Wanninkhof, 1992):

18   $$SC_{CO2} = 1911.1 - 118.11 \times t + 3.4527 \times t^2 - 0.04132 \times t^3$$ (5)

19   Where t is the water surface temperature [°C].

20   **2.2.4 Calculation of seasonal budgets**

21   The temporal resolution of our data was heterogeneous. While gas transfer velocities could be

22   calculated with hourly resolution, CO_2 concentration data were typically available for 12 days

23   per year (4 to 293). To merge the data, we adopted 2 approaches:

24   a) "monthly" CO_2 fluxes were calculated by temporal upscaling of our measured data.

25   For each CO_2 concentration data point we determined the mean wind speed for the

26   same day and computed a daily mean flux for the day of sampling. For each month we

27   computed the mean of all available flux data within that particular month. If there

1   were no CO_2 data available for a particular month, we rejected that month from our

2   analysis.

3   b) For "hourly" CO_2 fluxes we assigned a CO_2 concentration for each wind speed data

4   point. We used the measured aquatic CO_2 concentration with the smallest time

5   difference to the particular wind data point.

6 Seasonal mean fluxes were calculated as: first, the means for each month were computed;

7 then the available monthly means were averaged within the following representative months:

8 spring (March-Mai), summer (June-August), and autumn (September-November). For annual

9 budgets the annual daily median flux was multiplied by 274 days, assuming that the CO_2

10 emissions are negligible during winter when reservoirs are ice covered. Summarised data for

11 each reservoir are provided in Table S2.

12 **2.3   Statistical Methods**

13 The statistical relationships between CO_2 evasion and different variables were calculated as

14 Spearman's linear correlations. Data were tested for log-normality by the Kolmogorov-

15 Smirnov test. To test for the significance of seasonal fluctuations we computed Tukey Honest

16 significant differences in conjunction with ANOVA. All statistical analyses were done using

17 R (R-Development-Core-Team, 2008).

18 **3   Results**

19 Surface CO_2 concentrations were between 0.002 and 11991 µmol l^{-1}. The annual median

20 concentrations in single reservoirs were mostly below 100 µmol l^{-1}, with a few reservoirs

21 having very high concentrations up to 2.4 mmol l^{-1} (Figure 1a). The reservoirs were mostly

22 oversaturated with respect to CO_2. Under-saturation was observed between May and October

23 in 25 reservoirs. The median CO_2 concentration of all reservoirs was 72 µmol l^{-1} (Table 1).

24 The reservoirs were typically exposed to low wind speeds, resulting in K values around 0.5 m

25 d^{-1} (Figure 1b). The reservoirs could be grouped into low wind reservoirs, having a K below 1

26 m d^{-1}, and high wind reservoirs with k around 2 m d^{-1}.

27 If we consider all the seasons, we observed significant seasonal differences in CO_2

28 concentration (ANOVA test: $F_{2,1426}=6.06$, p= 0.002), fluxes (ANOVA test: $F_{2,234}=3.72$,

29 p=0.02) and gas transfer coefficient (ANOVA test: $F_{2,1426}=8.48$, p=0.0002). CO_2

30 concentrations were significantly higher in spring than in summer (Figure 2a, Figure S1a).

31 The gas transfer coefficient (resp. wind speed) was significantly higher in fall compared to the

32 other seasons (median 0.71 compared to 0.63 m d^{-1}) (Figure 2b, Figure S1b). Consequently,

1   fluxes were significantly lower in summer than in spring (Figure 2c, Figure S1c). Median

2   fluxes were 30, 11, and 46 mmol m^{-2} d^{-1} in spring, summer, and autumn respectively. Also the

3   variability of the flux was higher in spring and autumn.

4   We calculated annual CO_2 fluxes for each reservoir with and without inclusion of hourly wind

5   data. Both approaches gave similar results, but inclusion of high resolution wind data often

6   resulted in higher fluxes (Figure 3). For 27 out of 39 reservoirs the median annual CO_2 flux

7   was higher, for 7 reservoirs it was unchanged (less than 10% difference) while in 5 cases

8   fluxes calculated with hourly wind data were lower. The median CO_2 flux, however, was

9   hardly different between the two approaches (Table 1). An example dataset (Figure 4) shows

10   the effect of short periods of high wind speed on the flux. In this case, the annual median flux

11   was 71 and 132 g C m^{-2} y^{-1} without and with consideration of hourly wind speed data. The

12   median under-estimation for all studied reservoirs when not using high resolution wind data

13   was 22%.

14   On an annual scale, all reservoirs were a CO_2 source to the atmosphere (Figure 1c). By

15   multiplying the annual mean flux with the surface area we get the total annual flux from each

16   reservoir. The combined annual CO_2 flux from all reservoirs in our database was 13287 t y^{-1}

17   with a combined surface are of 35.56 km^2. If we assume a total surface area of all German

18   drinking water reservoirs of 118 km^2 (Köngeter et al., 2013), we can extrapolate a total CO_2

19   emission from all German drinking water reservoirs of 44091 t y^{-1}.

20   A simple regression analysis shows that the annual flux was regulated by the CO_2

21   concentration in the surface water rather than by the physical gas transfer (Figure 5). If we

22   analyse each reservoir separately, however, we observed significant correlations of the flux

23   both with CO_2 concentration and K. In 37 cases the flux was significantly correlated with CO_2

24   and in 32 cases with K. The fact that there were correlations between K and flux for single

25   reservoirs but not when all data are analysed together shows that the relation between K and

26   flux was reservoir specific.

27   Since the flux was correlated with the CO_2 concentration and the CO_2 concentration was

28   calculated from pH and Alkalinity, the CO_2 flux showed an exponential dependency on pH

29   (Figure 6a). High CO_2 fluxes only occurred in reservoirs with a median pH <6.5, which is the

30   dissociation constant of H_2CO_3 (Stumm and Morgan, 1981). The pH dependency can be

31   expressed by the following equation:

1    $$J = 3.8573 + 5769.11406 \times e^{-\frac{pH-4.94948}{0.63378}}$$ (6)

2   We also observed a correlation with alkalinity with high median fluxes only occurring in

3   reservoirs with alkalinity below 0.2 µEq l^{-1} (Figure 6b). On the other hand, there was no

4   relation between DOC and CO_2 flux (Figure 6c). There was a significant trend to smaller (by

5   area) reservoirs having higher CO_2 concentrations (Spearman rank correlation rho=-0.43, p=

6   0.006). For CO_2 fluxes there seemed to exist a similar relation, but the trend was statistically

7   not significant (rho=-0.23, p=0.1664).

8   ## 4   Discussion

9   ### 4.1 CO_2 emission from German drinking water reservoirs

10   German drinking water reservoirs are net emitters of CO_2 to the atmosphere. Our median CO_2

11   flux of 167 g C m^{-2} y^{-1} is high compared to the mean flux from hydroelectric reservoirs in the

12   temperate zone in the reviews of (St Louis et al., 2000) (150 g m^{-2} y^{-1}) and (Barros et al.,

13   2011) (120 g m^{-2} y^{-1}). A possible explanation is the high impact of stream water quality on the

14   drinking water reservoirs, caused by a typically low water residence time in the reservoirs.

15   Streams are known to be oversaturated with CO_2 (Raymond et al., 2013), with small streams

16   typically having higher pCO$_2$ (Hotchkiss et al., 2015). Because of better water quality,

17   drinking water reservoirs are preferably located in upstream areas with higher stream pCO$_2$.

18   This is supported by our observation of higher CO_2 concentrations occurring often in small

19   reservoirs, confirming earlier results (Raymond et al., 2013). It has been shown that the

20   gaseous CO_2 loss is linked to hydrology and shorter residence time increases surface carbon

21   loss (Striegl and Michmerhuizen, 1998).

22   Compared to typical CO_2 emission rates from temperate soils (745 ± 421 g C m^{-2} y^{-1}, (Bond-

23   Lamberty and Thomson, 2010)) or a typical German forest site (-550 ± 91 g C m^{-2} y^{-1}

24   (Grünwald and Bernhofer, 2007)), however, the area specific fluxes from drinking water

25   reservoirs are low. Considering further the small area of all German drinking water reservoirs

26   (0.03 % of German surface area), CO_2 emission from drinking water reservoirs is a negligible

27   CO_2 source in the national CO_2 inventory.

28   To investigate the significance of gaseous CO_2 exchange for the reservoirs carbon budget, we

29   estimated the total TIC content of reservoirs by multiplying the median TIC concentration

30   with the water volume of the particular reservoir for those eight reservoirs for which TIC data

31   were available. Total TIC inventories of reservoirs were between 1 t and 66 t resulting in

1   theoretical CO_2 residence times of 2 to 302 days. Thus, the annual CO_2 flux was of the same

2   order of magnitude as the TIC content of the particular reservoirs, showing that the gaseous

3   CO_2 flux was a significant process in the reservoirs carbon budget.

4   The observed seasonal pattern with low fluxes during summer is consistent with earlier

5   observations (Halbedel and Koschorreck, 2013; Knoll et al., 2013) and can be explained by

6   the seasonal stratification and depletion of CO_2 in the surface water due to primary

7   production, and increased surface concentration during autumnal mixing (Wendt-Potthoff et

8   al., 2014). Taken together, spring and fall contributed 87% to the annual CO_2 emissions. If the

9   focus is on the annual budget, we recommend to increase measuring efforts during the high

10   flux periods in spring and fall, on the cost of less intensive monitoring during summer.

11   Another information gap is winter. In winter, German drinking water reservoirs are usually

12   frozen, but the exact duration and timing of ice coverage is highly variable. CO_2 emissions

13   from non frozen reservoirs during winter would further contribute to annual emissions. To

14   improve the accuracy of annual budgets, the exact duration of ice cover have to be known for

15   each reservoir and year. Accumulation of CO_2 under ice is probably of minor relevance,

16   because water residence time in the reservoirs is low during high flow conditions in winter

17   and especially during snowmelt. Furthermore, our data give no hint on high CO_2

18   concentrations during early spring.

19   Our median K of 0.70 m d^{-1} is virtually identical to the global average for lakes and reservoirs

20   estimated from global wind data (0.74 m d^{-1} (Raymond et al., 2013)). It is well known that the

21   determination of K from wind speed is prone to some error, especially at low wind speed

22   (Crusius and Wanninkhof, 2003). The location of the weather station represents another

23   source of error. All the weather stations used for the reservoirs with high k-values are located

24   in more wind exposed crests. Four of the "high K reservoirs" were caused by the weather

25   station Zinnwald-Georgenfeld which is located at 877 m a.s.l. in the Ore Mountains. Since the

26   reservoirs are located in valleys, CO_2 fluxes in the "high K reservoirs" are probably over

27   estimated. A way to circumvent this problem would be the determination of reservoir specific

28   correction factors for the wind speed. Considering the uncertainty related to the

29   representativeness of the wind data from public weather stations for the reservoirs, the use of

30   a constant K might introduce only a minor error. Applying a constant K of 0.7 m d^{-1} results in

31   a median CO_2 emission from all reservoirs of 107 g m^{-2} y^{-1}, which is 28% lower than the

32   median flux calculated using monthly wind data. We interpret this as an estimate of the error

33   caused by the non-representative location of weather stations. However, considering the

1 observed low dependency of the flux on K, uncertainty in the determination of K is probably

2 not a serious problem for our upscaling approach.

4.2 Effect of short term wind fluctuations

4 We found a significant under-estimation of the total annual CO_2 flux by 22% when only

5 considering wind data from the day of which we also had CO_2 concentration data. This was

6 because we missed some high wind periods, especially in fall, which contributed significantly

7 to the annual flux. Even if the local wind at the reservoir was not perfectly represented by the

8 weather stations, this conclusion is justified, since the probability for storm events was

9 probably comparable at the reservoir and corresponding weather station.

10 Our mean error of 22% is most probably a conservative estimate because recently it has been

11 shown that wind does not only directly influence K but due to enhanced surface mixing also

12 affects the surface concentration of CO_2 (Morales-Pineda et al., 2014). Storm events can also

13 affect pCO_2 by flushing CO_2 from the catchment into the lake (Vachon and del Giorgio,

14 2014). In our case the error was highly case specific. Some reservoirs even showed an

15 opposite effect, most probably because low wind periods were more frequent. Thus, an

16 analysis of typical wind patterns at a particular reservoir should allow to predict whether the

17 inclusion of high frequency wind data have the potential to significantly improve the CO_2 flux

18 estimate for a particular site.

19 Besides periodic changes in wind speeds and storms, there exists a typical diurnal wind

20 pattern at the reservoirs in our study. Wind is increasing during the day and then calms down

21 around sunset and during the night. This diurnal pattern is included in our simple approach,

22 since we used the daily mean wind speed for the low resolution flux calculation. The use of

23 wind data obtained during water sampling by hand-held wind meters, a common practice in

24 many studies, most probably overestimates the daily CO_2 flux, because low wind periods

25 during the night are not considered. However, wind is not the only factor causing diurnal

26 pattern. Recent research indicates that night-time cooling causes convective mixing near the

27 surface and thus, may enhance gas fluxes during the night (Eugster et al., 2003; Read et al.,

28 2012). Neglecting this effect is probably the main reason for the commonly poor

29 parametrisation of K at low wind-speed (Cole and Caraco, 1998) and would result in an

30 under-estimation of the real flux. Our study does not consider the effect of convection on K

31 and thus, our annual budgets are probably conservative estimates. The role of convection and

32 a better parametrisation of K for upscaling deserve further research.

4.3 Regulation of the CO_2 flux

4.3.1 pCO_2 versus K

The difference in the CO_2 flux between reservoirs was primarily caused by the concentration of CO_2 in the surface water rather than by the physical exchange coefficient K. This was caused by the higher between reservoir variability of pCO_2 compared to K. Thus, to quantify the annual flux in an unknown reservoir, high frequency monitoring of the CO_2 concentration is more important than increasing the quality of the wind data. Since the surface CO_2 concentration in the reservoirs is probably predominantly determined by inflow water quality rather than reservoir internal processes, CO_2 emissions are probably largely regulated by catchment processes (Stets et al., 2009). This confirms studies showing that the CO_2 emission from lakes may be controlled by catchment productivity (Maberly et al., 2013) or carbonate weathering (Marcé et al., 2015). Catchment processes and inflow water quality are obviously more important than hydrodynamics in regulating the annual CO_2 emission from German drinking water reservoirs. The major effect of reservoir internal processes seems to be the reduction of the CO_2 flux during summer, caused by stratification and primary production (Halbedel and Koschorreck, 2013). However, the effect of this flux reduction in summer is at least partly compensated by enhanced fluxes in fall because then CO_2 from the hypolimnion is mixed to the surface. Because of the highly dynamic nature of these mixing processes, high frequency monitoring of CO_2 would increase the precision of the flux quantification especially in fall.

Besides these seasonal fluctuations, the CO_2 concentration can also fluctuate diurnally, driven by photosynthesis during the day. Thus, the daytime of sampling should have an influence on the quality of the CO_2 data. We consider this effect less relevant in our case, since routine water samples are taken during normal working hours, when CO_2 concentrations are probably intermediate.

4.3.2 No correlation with DOC

Our results confirm earlier studies that the aquatic pCO_2 in temperate lakes and reservoirs does not depend on the DOC concentration (McDonald et al., 2013). This is in contrast to observations in boreal lakes and tropical waters (Borges et al., 2015), where often a correlation between DOC and pCO_2 has been observed. One reason could be that our DOC concentrations (Table 1) are low compared to a global average of lakes (7.6 ± 0.2 mg l^{-1}). Boreal lakes typically contain even higher DOC concentrations (Sobek et al., 2007). More

1 probable, however, is that any effect of DOC is masked by the influence of TIC import from

2 the catchment and pH effects (López et al., 2011). There is no simple link between lake

3 metabolism and annual CO_2 flux. The net annual CO_2 flux cannot be used to judge whether a

4 reservoir is net heterotrophic or not, since the flux is both influenced by TIC transport and

5 metabolism (Stets et al., 2009).

6 ## 4.4   pH as a proxy for the CO_2 flux

7 The CO_2 concentration in the reservoirs clearly correlated with pH, confirming results from

8 Knoll et al., who found that the pH was the best predictor of pCO_2 in the Midwestern

9 reservoirs they studied (Knoll et al., 2013). A similar correlation between diffusive CO_2 flux

10 and pH has been observed in 151 Danish lakes (Trolle et al., 2012), 948 Florida lakes

11 (Lazzarino et al., 2009), and several reservoirs (Alshboul and Lorke, 2015; Halbedel and

12 Koschorreck, 2013; Quiñones-Rivera et al., 2015; Soumis et al., 2004). Thus, pH dependency

13 of the CO_2 flux seems to be a general observation in temperate surface waters. These results

14 also highlight the importance of precise pH measurements for accurate surface water GHG

15 budgets (Herczeg and Hesslein, 1984). Because of its logarithmic nature, pH is especially

16 prone to analytical error. This is critical when using routine monitoring data for CO_2

17 calculations.

18 The pH is a result of alkalinity (mainly influenced by catchment geochemistry) and TIC

19 (influenced both by catchment processes and aquatic metabolism) (Marcé et al., 2015; Müller

20 et al., 2015). Especially between pH 5 and 7 even small changes in CO_2 significantly alter the

21 pH. This effect is less relevant in DOC rich boreal lakes, which are often acidic, and in

22 eutrophic lakes, were primary production shifts the pH to high values. In acidic waters the

23 situation is complicated by the fact that organic acids contribute to alkalinity (Abril et al.,

24 2015). This could be relevant in our high-emission reservoirs, which are all low in alkalinity

25 (Figure 6b). Regardless the underlying mechanisms, the strong correlation with pH suggests

26 the use of pH as a proxy for the CO_2 flux for modeling or upscaling. We calculated the CO_2

27 flux from each reservoir from its mean pH (J_{pH}) using equation 6 (Fig. S2). The resulting

28 median CO_2 flux of was virtually identical to the flux obtained from our monthly data (Table

29 1). As a rule of thumb, relevant CO_2 emissions do only occur in reservoirs with pH<7 and

30 alkalinity below 0.2 µEq l^{-1}.

31 The surprisingly good fit to pH can be partly explained by the rather uniform and low

32 alkalinity values. Larger differences in alkalinity would result in more variable pCO_2 at

33 similar pH values. Thus, the use of pH as a proxy for CO_2 emissions might be applicable only

1 under low DOC, low alkalinity conditions as they are typical for German drinking water

2 reservoirs.

8 **Author contribution**

9 H. Saidi analysed the data and wrote the manuscript. M. Koschorreck designed the study and

10 wrote the manuscript.

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3

4

1 **Tables**

2 **Table 1.** Descriptive statistics of annual median data from all reservoirs K=gas transfer

3 coefficient, J_{hourly}=CO_2 flux calculated using high resolution wind data, $J_{monthly}$=CO_2 flux

4 calculated using mean wind, J_{pH}=CO_2 flux calculated from mean pH of each reservoir (n=39,

5 for DOC and pH annual means).

|	min	max	median	mean	SD
CO_2 [μmol l^{-1}]	15	2365	72	283	523
K [m d^{-1}]	0.5	2.17	0.7	0.9	0.5
J_{hourly} [g C m^{-2} y^{-1}]	14	7386	167	765	1545
$J_{monthly}$ [g C m^{-2} y^{-1}]	-3	6710	148	689	1518
J_{pH} [g C m^{-2} y^{-1}]	20	6271	146	769	1442
DOC [mg l^{-1}] (n=19)	0.92	6.15	3	3.18	1.44
pH	4.9	8.7	7.3	7.05	0.98

6

7

1 **Figures**
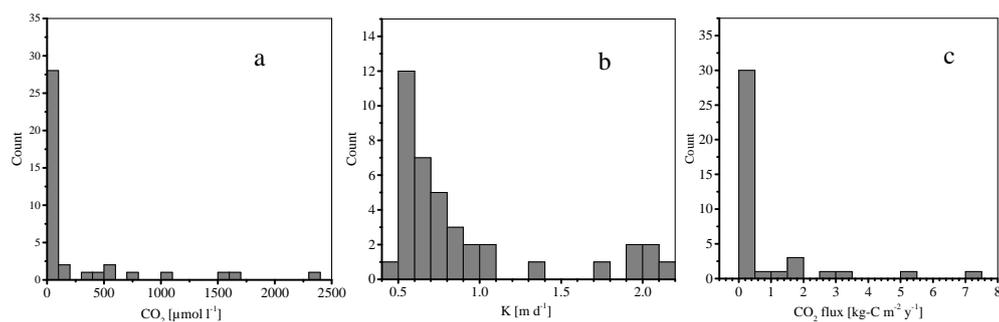
2

3 Figure 1: Histograms of median annual data of the different reservoirs: a) CO_2 concentration,

4 b) K, c) CO_2 flux. A Kolmogorov-Smirnov test showed that the data were not log-normal

5 distributed.

6
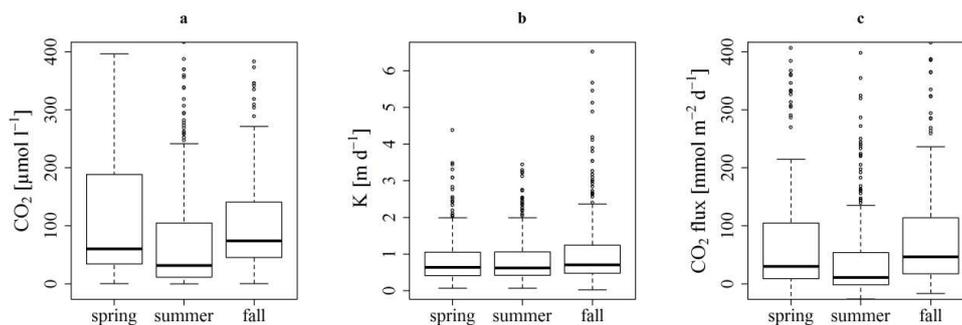
Figure 2: Boxplots describing the seasonal fluctuation of CO_2 concentration (a), K (b), and CO_2 flux (c). Data points are the mean seasonal data for each reservoir (n=39). Extreme values (higher than 400 μmol l^{-1} and 400 mmol m^{-2}d^{-1}) are outside the plots.
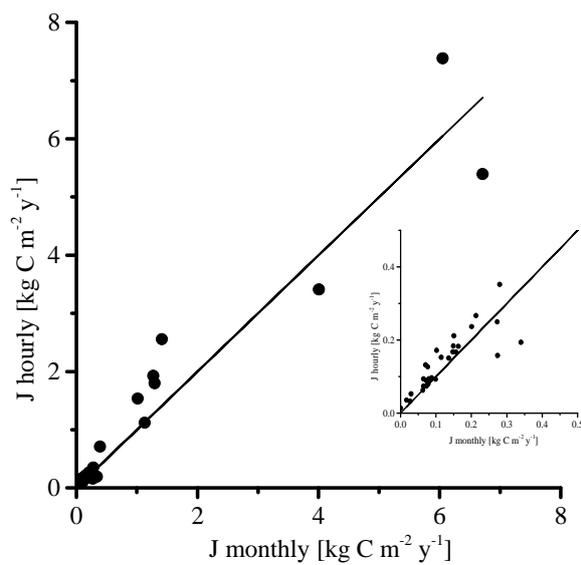
1

2   Figure 3: Median annual CO_2 flux for different reservoirs calculated on an hourly or monthly

3   basis. The insert shows a magnification of the left part of the graph.

4
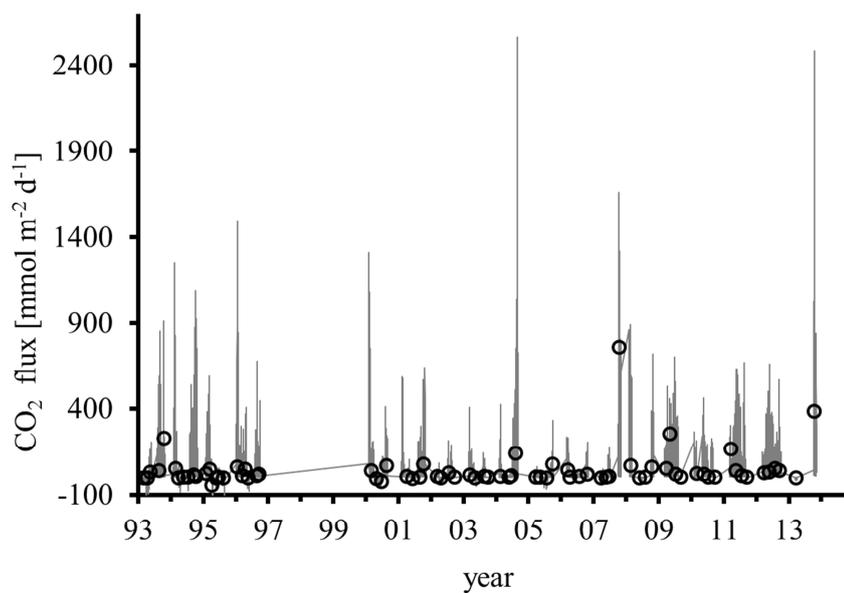
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2   Figure 4: CO_2 flux from Rappbode pre dam calculated with (line) and without (circles) using

3   high frequency wind data.

4
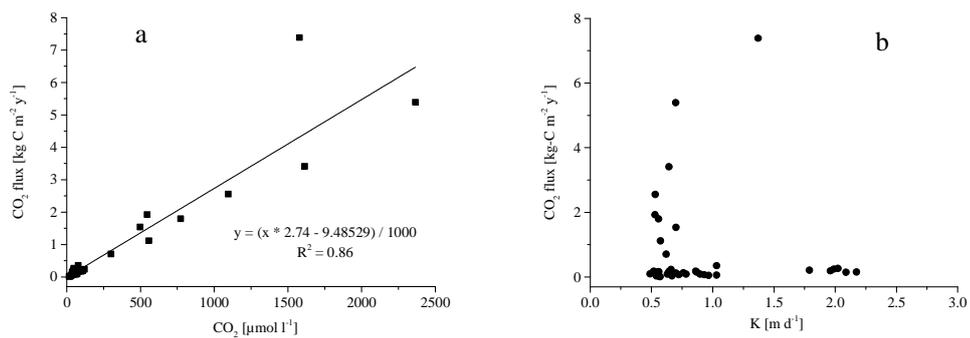
Figure 5: Dependence of the annual median CO_2 flux on the annual median CO_2 concentration (a) and K (b).
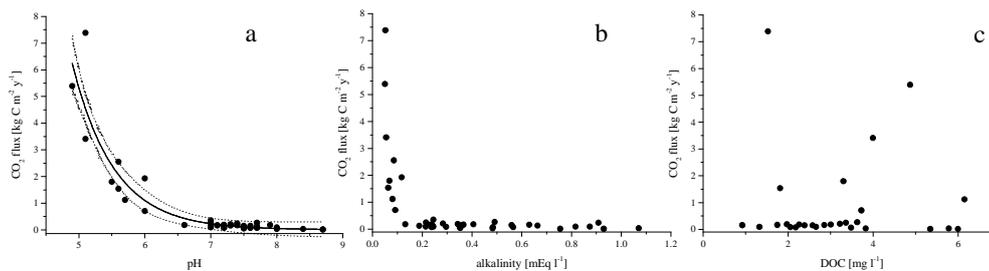
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2 Figure 6: Dependence of the median CO_2 flux on a) mean pH, b) alkalinity, and c) mean DOC

3 concentration in the different reservoirs. Lines in a) show an exponential fit with 95%

4 confidence interval ($R^2 = 0.85$).