CO₂ emissions from German drinking water reservoirs
estimated from routine monitoring data

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Abstract

Globally, reservoirs are a significant source of atmospheric CO₂. However, precise quantification of greenhouse gas emissions from drinking water reservoirs on the regional or national scale is still challenging. We calculated CO₂ fluxes for 39 German drinking water reservoirs during a period of 22 years (1991-2013) using routine monitoring data in order to quantify total emission of CO₂ from drinking water reservoirs in Germany.

All reservoirs were small net CO₂ sources with a median flux of 167 g C m⁻² y⁻¹, which makes gaseous emissions a relevant process for the reservoirs carbon budgets. In total, German drinking reservoirs emit 44000 t of CO₂ annually, which makes them a negligible CO₂ source in Germany. Fluxes varied seasonally with median fluxes of 30, 11, and 46 mmol m⁻² d⁻¹ in spring, summer, and autumn respectively. Differences between reservoirs appeared to be primarily caused by the concentration of CO₂ in the surface water rather than by the physical gas transfer coefficient. Consideration of short term fluctuations of the gas transfer coefficient due to variable wind had only a minor effect on the annual budgets. High CO₂ emission only occurred in reservoirs with pH < 7 and total alkalinity < 0.2 mEq l⁻¹. Annual CO₂ emission
correlated exponentially with pH, making pH a suitable proxy for CO$_2$ emission from German drinking water reservoirs.

1 Introduction

Reservoirs are a globally important source of the greenhouse gases (GHG) CO$_2$ and CH$_4$ (St Louis et al., 2000). Actually it is assumed that hydropower reservoirs globally emit 48 Tg C as CO$_2$ and 3 Tg C as CH$_4$ (Barros et al., 2011). Existing studies on GHG emissions from reservoirs focus on hydroelectric dams in boreal regions and the tropics and on dammed rivers. Drinking water reservoirs in the temperate zone typically have a low trophic state and GHG emissions are dominated by CO$_2$. Recent results indicate that they are a small source of CO$_2$ to the atmosphere and can rather be a CO$_2$ sink during summer (Knoll et al., 2013). However, existing CO$_2$ emission studies focus on few intensively studied reservoirs (Diem et al., 2012; Soumis et al., 2004; Tremblay et al., 2005). Global inventories probably give a realistic range of CO$_2$ emissions from surface waters (Raymond et al., 2013), but precise quantification of GHG from drinking water reservoirs on the regional or national scale is still challenging (McDonald et al., 2013; Seekell et al., 2014).

Upscaling is usually done by applying the thin boundary layer (TBL) approach (MacIntyre et al., 1995). CO$_2$ exchange across the water surface is driven by diffusion and thus, regulated by the concentration gradient between water and atmosphere and the physical gas transfer coefficient K. K depends on the turbulence of the surface water. Although there is more and more evidence that K is also influenced by convection (Read et al., 2012), in most studies it is still derived from measured wind speed, using empirical equations (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003).

The concentration of CO$_2$ in surface waters is usually not directly measured but calculated from two other measured parameters of the carbonate system, namely total inorganic carbon (TIC), pH, or total alkalinity (TA). Thus, minimum data requirements are two parameters of the carbonate system, water temperature, wind speed, and surface area. To obtain annual budgets of CO$_2$ emission, both differences among reservoirs and temporal changes within a system have to be considered. In practice, there is a trade-off between high monitoring frequency and spatial coverage of numerous reservoirs because not all systems can be monitored with high temporal resolution. Usually CO$_2$ concentration data are only available for a few days of the year. Calculation of annual budgets from such sporadic measurements...
may introduce systematic errors because high wind situations probably contribute significantly to annual emissions (Morales-Pineda et al., 2014). By combining routine monitoring data of CO$_2$ concentration from numerous German reservoirs with high temporal resolution wind speed data from public weather stations we check, whether the low temporal resolution of routine monitoring introduces a systematic bias in annual gas flux calculations.

The central aim of this study was to estimate the annual emission of CO$_2$ from Germany drinking water reservoirs using data from routine water quality monitoring from a wide range of reservoirs. By applying simple regression analysis we aimed to find out whether the CO$_2$ flux is primarily regulated by the gas transfer coefficient or by the CO$_2$ concentration. In boreal surface waters, which are typically characterised by low alkalinity and high dissolved organic carbon (DOC) concentration, the CO$_2$ concentration usually correlates well with the DOC concentration (Jonsson et al., 2003; Whitfield et al., 2011), showing that aquatic metabolism is a major driver of CO$_2$ oversaturation. In other regions, CO$_2$ in lakes seems to be driven by DIC input from the catchment (McDonald et al., 2013). In high alkalinity lakes in calcareous regions, CO$_2$ oversaturation is primarily caused by carbonate weathering (López et al., 2011; Marcé et al., 2015). We used our dataset to get some information about the principle drivers of the CO$_2$ flux from low DOC, low alkalinity waters, which are typical for temperate drinking water reservoirs.

2 Material and Methods

2.1 Data source

We used a database containing routine water quality monitoring data from 39 German drinking water reservoirs. Data were supplied by the reservoir operators and compiled in a database in the framework of a research project about dissolved organic carbon in German drinking water reservoirs (TALKO project). Available data span a period of 22 years (1991-2013). Typical datasets for single reservoirs contained 10-20 years, the minimum period for a single reservoir was 6 years with about monthly data. The data include both reservoirs and pre-dams, which are characterised by a constant water level. A first quality control of these data was performed using R statistic software. Typos, sign errors and rounding errors were fixed using R functions. The dataset was checked for obviously wrong data by defining minimum and maximum possible values.

Hourly wind speed data were provided by the German Meteorological Service (Deutscher Wetterdienst) using the nearest weather station to each drinking water reservoir (Table S1).
The median distance between reservoir and corresponding weather station was 15 km (1 km – 38 km).

2.2 Calculations

The TBL approach (MacIntyre et al., 1995; UNESCO/IHA, 2010) was adopted to estimate CO₂ fluxes from the reservoirs surface. This method uses semi-empirical equations to calculate emission from concentrations of CO₂ in the surface water and the CO₂ exchange coefficient. The flux $J$ [mmol CO₂ m⁻² d⁻¹] of gas from water to air (diffusive emissions) was calculated as the product of the gas exchange coefficient and the difference between gas concentrations in surface water and air (Equation 1):

$$J = K \times (C_{CO₂(water)} - C_{CO₂(air)})$$  

(1)

Where

- $C_{CO₂(water)}$ is the concentration of CO₂ in surface water of the reservoir [µmol l⁻¹]
- $C_{CO₂(air)}$ is the concentration in air equilibrated water (calculated from the CO₂ partial pressure in the air using Henry’s law).
- $K$ [m d⁻¹] is the gas transfer velocity approximated from the wind speed and normalised to a Schmidt number of 600 (Crusius and Wanninkhof, 2003).

All calculations were done assuming a water density of 1 kg l⁻¹.

2.2.1 Surface water concentration of CO₂

Because of the best data availability, we calculated CO₂ from pH and TA, using the “seacarb” package of R (Lavigne et al., 2014). Input parameters were water temperature, salinity =0, depth=0, TA [mmol l⁻¹], and pH. For comparison, data were also calculated with CO2SYS (Lewis and Wallace, 1998). Both tools gave the same results.

2.2.2 Concentration in air equilibrated water

We calculated the partial pressure of the gas in the water if it were in equilibrium with the atmosphere ($C_{CO₂(air)}$ [mmol l⁻¹]) from the CO₂ partial pressure (pCO₂) in the ambient air samples using Henry’s law:

$$C_{CO₂(air)} = P + K_H$$  

(2)

For pCO₂ in the atmosphere (P [µatm]) we used hourly data of the atmospheric mixing ratio of CO₂ [ppm] from the public monitoring station at Schauinsland (WMO World Data Center...
for Greenhouse Gases http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html). This station is located in the southern part of the Black Forest mountain range close to the top of mount Schauinsland. It presents a reference site for the atmospheric background concentration in Germany. The mixing ratios were converted to partial pressure by considering the altitude of the particular reservoir:

\[
P = \frac{m_r}{P_{\text{nn}}} \times e^{-\frac{\text{alt}}{\text{scale height}}} \times 10^{-6}
\]

with \( m_r \) being the CO\(_2\) mixing ratio [ppm], \( P_{\text{nn}} \) = standard barometric pressure at sea level = 1 atm, \( \text{alt} \) = altitude of reservoir [m], and the scale height being 8500m. \( K_H \) [atm l mol\(^{-1}\)] is Henry’s solubility coefficient for the actual water temperature.

2.2.3 Gas transfer velocities

There are several empirical expressions to derive the gas exchange coefficient (\( K \)) as a function of wind speed and water temperature. We adopted the widely applied power function presented in (Crusius and Wanninkhof, 2003):

\[
K = \left[0.168 + \left(0.228 \times U_{10}^{0.2}\right)\right] \times \left(\frac{SC_{CO2}}{600}\right)^{2/3} \times t^{1/3}
\]

where

- \( U_{10} \) is the wind speed at 10m height [m s\(^{-1}\)],
- \( SC \) is the Schmidt number for CO\(_2\) (Wanninkhof, 1992):

\[
SC_{CO2} = 1911.1 - 118.11 \times t + 3.4527 \times t^2 - 0.04132 \times t^3
\]

Where \( t \) is the water surface temperature [°C].

2.2.4 Calculation of seasonal budgets

The temporal resolution of our data was heterogeneous. While gas transfer velocities could be calculated with hourly resolution, CO\(_2\) concentration data were typically available for 12 days per year (4 to 293). To merge the data, we adopted 2 approaches:

a) “monthly” CO\(_2\) fluxes were calculated by temporal upscaling of our measured data. For each CO\(_2\) concentration data point we determined the mean wind speed for the same day and computed a daily mean flux for the day of sampling. For each month we computed the mean of all available flux data within that particular month. If there
were no CO\textsubscript{2} data available for a particular month, we rejected that month from our analysis. 

b) For “hourly” CO\textsubscript{2} fluxes we assigned a CO\textsubscript{2} concentration for each wind speed data point. We used the measured aquatic CO\textsubscript{2} concentration with the smallest time difference to the particular wind data point.

Seasonal mean fluxes were calculated as: first, the means for each month were computed; then the available monthly means were averaged within the following representative months: spring (March-May), summer (June-August), and autumn (September-November). For annual budgets the annual daily median flux was multiplied by 274 days, assuming that the CO\textsubscript{2} emissions are negligible during winter when reservoirs are ice covered. Summarised data for each reservoir are provided in Table S2.

2.3 Statistical Methods

The statistical relationships between CO\textsubscript{2} evasion and different variables were calculated as Spearman’s linear correlations. Data were tested for log-normality by the Kolmogorov-Smirnov test. To test for the significance of seasonal fluctuations we computed Tukey Honest significant differences in conjunction with ANOVA. All statistical analyses were done using R (R-Development-Core-Team, 2008).

3 Results

Surface CO\textsubscript{2} concentrations were between 0.002 and 11991 \mu mol l\textsuperscript{-1}. The annual median concentrations in single reservoirs were mostly below 100 \mu mol l\textsuperscript{-1}, with a few reservoirs having very high concentrations up to 2.4 mmol l\textsuperscript{-1} (Figure 1a). The reservoirs were mostly oversaturated with respect to CO\textsubscript{2}. Under-saturation was observed between May and October in 25 reservoirs. The median CO\textsubscript{2} concentration of all reservoirs was 72 \mu mol l\textsuperscript{-1} (Table 1).

The reservoirs were typically exposed to low wind speeds, resulting in $K$ values around 0.5 m\textsuperscript{-1}d\textsuperscript{-1} (Figure 1b). The reservoirs could be grouped into low wind reservoirs, having a $K$ below 1 m\textsuperscript{-1}d\textsuperscript{-1}, and high wind reservoirs with $K$ around 2 m\textsuperscript{-1}d\textsuperscript{-1}.

If we consider all the seasons, we observed significant seasonal differences in CO\textsubscript{2} concentration (ANOVA test: $F_{2,1426}=6.06$, $p=0.002$), fluxes (ANOVA test: $F_{2,234}=3.72$, $p=0.02$) and gas transfer coefficient (ANOVA test: $F_{2,1426}=8.48$, $p=0.0002$). CO\textsubscript{2} concentrations were significantly higher in spring than in summer (Figure 2a, Figure S1a). The gas transfer coefficient (resp. wind speed) was significantly higher in fall compared to the other seasons (median 0.71 compared to 0.63 m d\textsuperscript{-1}) (Figure 2b, Figure S1b). Consequently,
fluxes were significantly lower in summer than in spring (Figure 2c, Figure S1c). Median fluxes were 30, 11, and 46 mmol m$^{-2}$ d$^{-1}$ in spring, summer, and autumn respectively. Also the variability of the flux was higher in spring and autumn.

We calculated annual CO$_2$ fluxes for each reservoir with and without inclusion of hourly wind data. Both approaches gave similar results, but inclusion of high resolution wind data often resulted in higher fluxes (Figure 3). For 27 out of 39 reservoirs the median annual CO$_2$ flux was higher, for 7 reservoirs it was unchanged (less than 10% difference) while in 5 cases fluxes calculated with hourly wind data were lower. The median CO$_2$ flux, however, was hardly different between the two approaches (Table 1). An example dataset (Figure 4) shows the effect of short periods of high wind speed on the flux. In this case, the annual median flux was 71 and 132 g C m$^{-2}$ y$^{-1}$ without and with consideration of hourly wind speed data. The median under-estimation for all studied reservoirs when not using high resolution wind data was 22%.

On an annual scale, all reservoirs were a CO$_2$ source to the atmosphere (Figure 1c). By multiplying the annual mean flux with the surface area we get the total annual flux from each reservoir. The combined annual CO$_2$ flux from all reservoirs in our database was 13287 t y$^{-1}$ with a combined surface area of 35.56 km$^2$. If we assume a total surface area of all German drinking water reservoirs of 118 km$^2$ (Köngeter et al., 2013), we can extrapolate a total CO$_2$ emission from all German drinking water reservoirs of 44091 t y$^{-1}$.

A simple regression analysis shows that the annual flux was regulated by the CO$_2$ concentration in the surface water rather than by the physical gas transfer (Figure 5). If we analyse each reservoir separately, however, we observed significant correlations of the flux both with CO$_2$ concentration and K. In 37 cases the flux was significantly correlated with CO$_2$ and in 32 cases with K. The fact that there were correlations between K and flux for single reservoirs but not when all data are analysed together shows that the relation between K and flux was reservoir specific.

Since the flux was correlated with the CO$_2$ concentration and the CO$_2$ concentration was calculated from pH and Alkalinity, the CO$_2$ flux showed an exponential dependency on pH (Figure 6a). High CO$_2$ fluxes only occurred in reservoirs with a median pH <6.5, which is the dissociation constant of H$_2$CO$_3$ (Stumm and Morgan, 1981). The pH dependency can be expressed by the following equation:
We also observed a correlation with alkalinity with high median fluxes only occurring in reservoirs with alkalinity below 0.2 µEq l⁻¹ (Figure 6b). On the other hand, there was no relation between DOC and CO₂ flux (Figure 6c). There was a significant trend to smaller (by area) reservoirs having higher CO₂ concentrations (Spearman rank correlation rho=-0.43, p=0.006). For CO₂ fluxes there seemed to exist a similar relation, but the trend was statistically not significant (rho=-0.23, p=0.1664).

4 Discussion

4.1 CO₂ emission from German drinking water reservoirs

German drinking water reservoirs are net emitters of CO₂ to the atmosphere. Our median CO₂ flux of 167 g C m⁻² y⁻¹ is high compared to the mean flux from hydroelectric reservoirs in the temperate zone in the reviews of (St Louis et al., 2000) (150 g m⁻² y⁻¹) and (Barros et al., 2011) (120 g m⁻² y⁻¹). A possible explanation is the high impact of stream water quality on the drinking water reservoirs, caused by a typically low water residence time in the reservoirs. Streams are known to be oversaturated with CO₂ (Raymond et al., 2013), with small streams typically having higher pCO₂ (Hotchkiss et al., 2015). Because of better water quality, drinking water reservoirs are preferably located in upstream areas with higher stream pCO₂. This is supported by our observation of higher CO₂ concentrations occurring often in small reservoirs, confirming earlier results (Raymond et al., 2013). It has been shown that the gaseous CO₂ loss is linked to hydrology and shorter residence time increases surface carbon loss (Striegl and Michmerhuizen, 1998).

Compared to typical CO₂ emission rates from temperate soils (745 ± 421 g C m⁻² y⁻¹, (Bond-Lamberty and Thomson, 2010)) or a typical German forest site (~550 ± 91 g C m⁻² y⁻¹ (Grönwald and Bernhofer, 2007)), however, the area specific fluxes from drinking water reservoirs are low. Considering further the small area of all German drinking water reservoirs (0.03 % of German surface area), CO₂ emission from drinking water reservoirs is a negligible CO₂ source in the national CO₂ inventory.

To investigate the significance of gaseous CO₂ exchange for the reservoirs carbon budget, we estimated the total TIC content of reservoirs by multiplying the median TIC concentration with the water volume of the particular reservoir for those eight reservoirs for which TIC data were available. Total TIC inventories of reservoirs were between 1 t and 66 t resulting in
theoretical CO$_2$ residence times of 2 to 302 days. Thus, the annual CO$_2$ flux was of the same order of magnitude as the TIC content of the particular reservoirs, showing that the gaseous CO$_2$ flux was a significant process in the reservoirs carbon budget.

The observed seasonal pattern with low fluxes during summer is consistent with earlier observations (Halbedel and Koschorreck, 2013; Knoll et al., 2013) and can be explained by the seasonal stratification and depletion of CO$_2$ in the surface water due to primary production, and increased surface concentration during autumnal mixing (Wendt-Potthoff et al., 2014). Taken together, spring and fall contributed 87% to the annual CO$_2$ emissions. If the focus is on the annual budget, we recommend to increase measuring efforts during the high flux periods in spring and fall, on the cost of less intensive monitoring during summer.

Another information gap is winter. In winter, German drinking water reservoirs are usually frozen, but the exact duration and timing of ice coverage is highly variable. CO$_2$ emissions from non frozen reservoirs during winter would further contribute to annual emissions. To improve the accuracy of annual budgets, the exact duration of ice cover have to be known for each reservoir and year. Accumulation of CO$_2$ under ice is probably of minor relevance, because water residence time in the reservoirs is low during high flow conditions in winter and especially during snowmelt. Furthermore, our data give no hint on high CO$_2$ concentrations during early spring.

Our median K of 0.70 m d$^{-1}$ is virtually identical to the global average for lakes and reservoirs estimated from global wind data (0.74 m d$^{-1}$ (Raymond et al., 2013)). It is well known that the determination of K from wind speed is prone to some error, especially at low wind speed (Crusius and Wanninkhof, 2003). The location of the weather station represents another source of error. All the weather stations used for the reservoirs with high k-values are located in more wind exposed crests. Four of the “high K reservoirs” were caused by the weather station Zinnwald-Georgenfeld which is located at 877 m a.s.l. in the Ore Mountains. Since the reservoirs are located in valleys, CO$_2$ fluxes in the “high K reservoirs” are probably overestimated. A way to circumvent this problem would be the determination of reservoir specific correction factors for the wind speed. Considering the uncertainty related to the representativeness of the wind data from public weather stations for the reservoirs, the use of a constant K might introduce only a minor error. Applying a constant K of 0.7 m d$^{-1}$ results in a median CO$_2$ emission from all reservoirs of 107 g m$^{-2}$ y$^{-1}$, which is 28% lower than the median flux calculated using monthly wind data. We interpret this as an estimate of the error caused by the non-representative location of weather stations. However, considering the
observed low dependency of the flux on K, uncertainty in the determination of K is probably not a serious problem for our upscaling approach.

4.2 Effect of short term wind fluctuations

We found a significant under-estimation of the total annual CO$_2$ flux by 22% when only considering wind data from the day of which we also had CO$_2$ concentration data. This was because we missed some high wind periods, especially in fall, which contributed significantly to the annual flux. Even if the local wind at the reservoir was not perfectly represented by the weather stations, this conclusion is justified, since the probability for storm events was probably comparable at the reservoir and corresponding weather station.

Our mean error of 22% is most probably a conservative estimate because recently it has been shown that wind does not only directly influence K but due to enhanced surface mixing also affects the surface concentration of CO$_2$ (Morales-Pineda et al., 2014). Storm events can also affect pCO$_2$ by flushing CO$_2$ from the catchment into the lake (Vachon and del Giorgio, 2014). In our case the error was highly case specific. Some reservoirs even showed an opposite effect, most probably because low wind periods were more frequent. Thus, an analysis of typical wind patterns at a particular reservoir should allow to predict whether the inclusion of high frequency wind data have the potential to significantly improve the CO$_2$ flux estimate for a particular site.

Besides periodic changes in wind speeds and storms, there exists a typical diurnal wind pattern at the reservoirs in our study. Wind is increasing during the day and then calms down around sunset and during the night. This diurnal pattern is included in our simple approach, since we used the daily mean wind speed for the low resolution flux calculation. The use of wind data obtained during water sampling by hand-held wind meters, a common practice in many studies, most probably overestimates the daily CO$_2$ flux, because low wind periods during the night are not considered. However, wind is not the only factor causing diurnal pattern. Recent research indicates that night-time cooling causes convective mixing near the surface and thus, may enhance gas fluxes during the night (Eugster et al., 2003; Read et al., 2012). Neglecting this effect is probably the main reason for the commonly poor parametrisation of K at low wind-speed (Cole and Caraco, 1998) and would result in an under-estimation of the real flux. Our study does not consider the effect of convection on K and thus, our annual budgets are probably conservative estimates. The role of convection and a better parametrisation of K for upscaling deserve further research.
4.3 Regulation of the CO\textsubscript{2} flux

4.3.1 pCO\textsubscript{2} versus K

The difference in the CO\textsubscript{2} flux between reservoirs was primarily caused by the concentration of CO\textsubscript{2} in the surface water rather than by the physical exchange coefficient K. This was caused by the higher between reservoir variability of pCO\textsubscript{2} compared to K. Thus, to quantify the annual flux in an unknown reservoir, high frequency monitoring of the CO\textsubscript{2} concentration is more important than increasing the quality of the wind data. Since the surface CO\textsubscript{2} concentration in the reservoirs is probably predominantly determined by inflow water quality rather than reservoir internal processes, CO\textsubscript{2} emissions are probably largely regulated by catchment processes (Stets et al., 2009). This confirms studies showing that the CO\textsubscript{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\textsubscript{2} emission from German drinking water reservoirs. The major effect of reservoir internal processes seems to be the reduction of the CO\textsubscript{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\textsubscript{2} from the hypolimnion is mixed to the surface. Because of the highly dynamic nature of these mixing processes, high frequency monitoring of CO\textsubscript{2} would increase the precision of the flux quantification especially in fall.

Besides these seasonal fluctuations, the CO\textsubscript{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\textsubscript{2} data. We consider this effect less relevant in our case, since routine water samples are taken during normal working hours, when CO\textsubscript{2} concentrations are probably intermediate.

4.3.2 No correlation with DOC

Our results confirm earlier studies that the aquatic pCO\textsubscript{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\textsubscript{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\textsuperscript{-1}). Boreal lakes typically contain even higher DOC concentrations (Sobek et al., 2007). More
probable, however, is that any effect of DOC is masked by the influence of TIC import from
the catchment and pH effects (López et al., 2011). There is no simple link between lake
metabolism and annual CO$_2$ flux. The net annual CO$_2$ flux cannot be used to judge whether a
reservoir is net heterotrophic or not, since the flux is both influenced by TIC transport and
metabolism (Stets et al., 2009).

4.4 pH as a proxy for the CO$_2$ flux

The CO$_2$ concentration in the reservoirs clearly correlated with pH, confirming results from
Knoll et al., who found that the pH was the best predictor of pCO$_2$ in the Midwestern
reservoirs they studied (Knoll et al., 2013). A similar correlation between diffusive CO$_2$
and pH has been observed in 151 Danish lakes (Tolle et al., 2012), 948 Florida lakes
(Lazzarino et al., 2009), and several reservoirs (Alshboul and Lorke, 2015; Halbedel and
Koschorreck, 2013; Quinnones-Rivera et al., 2015; Soumis et al., 2004). Thus, pH dependency
of the CO$_2$ flux seems to be a general observation in temperate surface waters. These results
also highlight the importance of precise pH measurements for accurate surface water GHG
budgets (Herczeg and Hesslein, 1984). Because of its logarithmic nature, pH is especially
prone to analytical error. This is critical when using routine monitoring data for CO$_2$
calculations.

The pH is a result of alkalinity (mainly influenced by catchment geochemistry) and TIC
(influenced both by catchment processes and aquatic metabolism) (Marcé et al., 2015; Müller
et al., 2015). Especially between pH 5 and 7 even small changes in CO$_2$ significantly alter the
pH. This effect is less relevant in DOC rich boreal lakes, which are often acidic, and in
eutrophic lakes, were primary production shifts the pH to high values. In acidic waters the
situation is complicated by the fact that organic acids contribute to alkalinity (Abril et al.,
2015). This could be relevant in our high-emission reservoirs, which are all low in alkalinity
(Figure 6b). Regardless the underlying mechanisms, the strong correlation with pH suggests
the use of pH as a proxy for the CO$_2$ flux for modeling or upscaling. We calculated the CO$_2$
flux from each reservoir from its mean pH ($J_{ph}$) using equation 6 (Fig. S2). The resulting
median CO$_2$ flux of was virtually identical to the flux obtained from our monthly data (Table
1). As a rule of thumb, relevant CO$_2$ emissions do only occur in reservoirs with pH<7 and
alkalinity below 0.2 µEq l$^{-1}$.

The surprisingly good fit to pH can be partly explained by the rather uniform and low
alkalinity values. Larger differences in alkalinity would result in more variable pCO$_2$ at
similar pH values. Thus, the use of pH as a proxy for CO$_2$ emissions might be applicable only
under low DOC, low alkalinity conditions as they are typical for German drinking water reservoirs.

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Author contribution

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

**Table 1.** Descriptive statistics of annual median data from all reservoirs K=gas transfer coefficient, \( J_{\text{hourly}} \)=CO₂ flux calculated using high resolution wind data, \( J_{\text{monthly}} \)=CO₂ flux calculated using mean wind, \( J_{\text{pH}} \)=CO₂ flux calculated from mean pH of each reservoir (n=39, for DOC and pH annual means).

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<th></th>
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<th>max</th>
<th>median</th>
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</table>
Figures

Figure 1: Histograms of median annual data of the different reservoirs: a) CO$_2$ concentration, b) K, c) CO$_2$ flux. A Kolmogorov-Smirnov test showed that the data were not log-normal distributed.
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.
Figure 3: Median annual CO$_2$ flux for different reservoirs calculated on an hourly or monthly basis. The insert shows a magnification of the left part of the graph.
Figure 4: CO$_2$ flux from Rappbode pre dam calculated with (line) and without (circles) using high frequency wind data.
Figure 5: Dependence of the annual median CO$_2$ flux on the annual median CO$_2$ concentration (a) and K (b).

\[ y = \frac{x \times 2.74 - 9.48529}{1000} \]

\[ R^2 = 0.86 \]
Figure 6: Dependence of the median CO₂ flux on a) mean pH, b) alkalinity, and c) mean DOC concentration in the different reservoirs. Lines in a) show an exponential fit with 95% confidence interval ($R^2 = 0.85$).