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Technical Note: Large overestimation of pCO$_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters

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Overestimation of pCO$_2$ calculated from pH and alkalinity in acidic, organic-rich freshwaters

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Abstract

Inland waters have been recognized as a significant source of carbon dioxide (CO_2) to the atmosphere at the global scale. Fluxes of CO_2 between aquatic systems and the atmosphere are calculated from the gas transfer velocity and the water-air gradient of the partial pressure of CO_2 (pCO_2). Nowadays, direct measurements of water pCO_2 remain scarce in freshwaters and most published pCO_2 data are calculated from temperature, pH and total alkalinity (TA). Here, we compare calculated (pH and TA) and measured (Equilibrator and headspace) water pCO_2 in a large array of temperate and tropical freshwaters. The 761 data points cover a wide range of values for TA (0 to 14.2 mmol L^{-1}), pH (3.94 to 9.17), measured pCO_2 (36 to 23 000 ppmv), and dissolved organic carbon (DOC) (29 to 3970 µmol L^{-1}). Calculated pCO_2 were > 10 % higher than measured pCO_2 in 60 % of the samples (with a median overestimation of calculated pCO_2 compared to measured pCO_2 of 2560 ppmv) and were > 100 % higher in the 25 % most organic-rich and acidic samples (with a median overestimation of 9080 ppmv). We suggest these large overestimations of calculated pCO_2 with respect to measured pCO_2 are due to the combination of two cumulative effects: (1) a more significant contribution of organic acids anions to TA in waters with low carbonate alkalinity and high DOC concentrations; (2) a lower buffering capacity of the carbonate system at low pH, that increases the sensitivity of calculated pCO_2 to TA in acidic and organic-rich waters. We recommend that regional studies on pCO_2 should not be based on pH and TA data only, and that direct measurements of pCO_2 should become the primary method in inland waters in general, and in particular in acidic, poorly buffered, freshwaters.

1 Introduction

Inland waters (streams, rivers, lakes, reservoirs, wetlands) receive carbon from terrestrial landscapes, usually have a net heterotrophic metabolism, and emit signifi-

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cant amounts of CO$_2$ to the atmosphere (Kempe, 1984; Cole et al., 1994; Raymond et al., 2013). This terrestrial-aquatic-atmosphere link in the global carbon cycle is controlled by complex biogeographical drivers that generate strong spatial and temporal variations in the chemical composition of freshwaters and the intensity of CO$_2$ outgassing at the water-air interface (e.g. Tamooh et al., 2013; Dinsmore et al., 2013; Abril et al., 2014). Hence, large datasets are necessary in order to describe the environmental factors controlling these CO$_2$ emissions and to quantify global CO$_2$ fluxes from inland waters (Sobek et al., 2005; Barros et al., 2011; Raymond et al., 2013). Dissolved inorganic carbon (DIC) concentration and speciation in freshwaters greatly depend on the lithological nature of watersheds (Meybeck, 1987). For instance, rivers draining watersheds rich in carbonate rocks have a high DIC concentration, generally well above 1 mmol L^{-1}. Bicarbonate ions contribute to the majority of the total alkalinity (TA) in these waters, which have high conductivities and high pH. In these hard waters, dissolved CO$_2$ represents a minor fraction (5–15 %) of the DIC compared to bicarbonates. In rivers draining organic-rich soils and non-carbonate rocks, DIC concentrations are lower (typically a few hundred μmol L^{-1}) but dissolved organic carbon (DOC) concentrations are higher, sometimes exceeding the DIC concentration. Organic acid anions significantly contribute to TA of these soft waters (Driscoll et al., 1989; Hemond, 1990), which have low conductivities and low pH. Dissolved CO$_2$ represents a large, generally dominant, fraction of DIC in these acidic, organic-rich waters.

Fluxes of CO$_2$ between aquatic systems and the atmosphere can be computed from the water-air gradient of the concentration of CO$_2$ and the gas transfer velocity (Liss and Slater, 1974) at local (e.g. Raymond et al., 1997), regional (e.g. Teodoru et al., 2009), and global scales (e.g. Cole et al., 1994; Raymond et al., 2013). The partial pressure of CO$_2$ (pCO$_2$) is relatively constant in the atmosphere compared to surface freshwaters pCO$_2$ that can vary by more than 4 orders of magnitude (Sobek et al., 2005; Abril et al., 2014). Consequently, water pCO$_2$ controls spatially and temporally the intensity of the air-water flux, together with the gas transfer velocity. Nowadays, both measured and calculated water pCO$_2$ data are used to compute CO$_2$ fluxes from

freshwater systems, although calculated pCO_2 is overwhelmingly more abundant than directly measured pCO_2. pCO_2 can be calculated from the dissociation constants of carbon acid (function of temperature) and any of the following couples of measured variables: pH/TA, pH/DIC, DIC/TA (Park 1969). In a majority of cases, calculated pCO_2 is based on the measurements of pH/TA and water temperature. These three parameters are routinely measured by many environmental agencies, and constitute a very large database available for the scientific community. Calculation of pCO_2 from pH and TA has been initiated in World Rivers in the 1970's (Kempe, 1984) and relies on the dissociation constants of carbonic acid, and the solubility of CO_2, all of which are temperature-dependent (Millero, 1979; Stumm and Morgan, 1996). Measured pCO_2 is based on water-air phase equilibration either on discrete samples (headspace technique, e.g. Weiss, 1981) or continuously (equilibrator technique, e.g. Frankignoulle et al., 2001) using various systems and devices, followed by direct, generally infrared (IR), detection of CO_2 in the equilibrated gas. Commercial IR gas analysers are becoming cheaper and more accurate and provide a large range of linear response well adapted to water pCO_2 variability in freshwaters.

Only a limited number of studies have compared directly measured pCO_2 and computed pCO_2. First works consisted in comparison between pCO_2 measured by headspace equilibration coupled to gas chromatography (GC), and pCO_2 calculated from pH and DIC (Raymond et al., 1997; Kratz et al., 1997). Reports by these authors in the Hudson River and Wisconsin lakes show that the pCO_2 values were linearly correlated but showed of ±500 ppmv around the 1:1 line, over a range of measured pCO_2 from 300 to 4000 ppmv. Later, Frankignoulle and Borges (2001) reported the first comparison of pCO_2 calculated from pH and TA and pCO_2 measured by equilibration coupled to an IR analyzer in an estuary in Belgium. In this high TA system, they found an excellent agreement between both approaches, calculated pCO_2 being either overestimated or underestimated by, but always by less than 7 %. In 2003, we performed concurrent measurements of pH, TA and pCO_2 in acidic, humic-rich ("black" type) waters of the Sinnamary River in French Guiana (Abril et al., 2005; 2006), and we noted that

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pCO_2 calculation from pH and TA gave unrealistically high values compared to those measured directly with a headspace technique (typically 30 000 ppmv vs. 5000 ppmv). Direct measurements of CO_2 and CH_4 outgassing fluxes with floating chambers and the computation of the respective gas transfer velocities of these two gases (Guérin et al., 2007) confirmed that pCO_2 values calculated from pH and TA were overestimated compared to direct measurements. More recently, Hunt et al. (2011) and Wang et al. (2013) provided evidence that organic acids anions in dissolved organic carbon (DOC) may significantly contribute to TA in some rivers and generate an overestimation of calculated pCO_2. Butman and Raymond (2011) reported higher calculated than measured pCO_2 in some US streams and rivers, but no information was available on the potential role of organic acids on this overestimation. These authors concluded that their low number of samples reflected the need for more research on this topic.

With the growing interest on pCO_2 determination in freshwaters globally, and given the relative simplicity and low cost of pH and TA measurements, the number of publications that report calculated pCO_2 in freshwaters has increased exponentially in the last decade. Some of these publications report extremely high and potentially biased values in low-alkalinity and high DOC systems. It has thus become necessary to pay attention to this issue and investigate the occurrence of such potential bias and its magnitude in the different types of freshwaters. Here, we present a large dataset of concomitant measurements of temperature, pH, TA, pCO_2, and DOC in freshwaters. This is the first comprehensive dataset to investigate the magnitude of the bias between calculated and measured pCO_2, as it covers the entire range of variation of most parameters of the carbonate system in freshwaters. The objective of this paper is to alert the scientific community to the occurrence of a bias in pCO_2 calculation from pH and TA in acidic, poorly buffered and organic-rich freshwaters, to briefly discuss its origin in terms of water chemistry, and to provide the range of pH, TA and DOC values where pCO_2 calculation should be abandoned and the range where it still gives relatively accurate results.

2   Material and methods

2.1   Sample collection

Our dataset consists of 761 concomitant measurements of temperature, pH, TA, water pCO_2, and DOC in 12 contrasting tropical and temperate systems in Europe, Amazonia and Africa (Table 1). These samples were obtained in the Central Amazon River and floodplains system in Brazil, the Athi-Galana-Sabaki River in Kenya, the Tana River (Kenya), small rivers draining the Shimba Hills in southeastern Kenya, the Congo River and tributaries in the Democratic Republic of Congo, Lake Kivu in Rwanda and DRC, the Leyre River and tributaries in France, the Loire River in France, the Meuse River in Belgium, the Rianila and Betsiboka Rivers in Madagascar, the Sinnamary River downstream of the Petit Saut Reservoir in French Guiana, and the Zambezi River in Zambia and Mozambique. Details on some of the sampling sites can be found in Abril et al. (2005, 2014), Borges et al. (2012), Marwick et al. (2014a, b), Polsenaere et al. (2013), Tamooh et al. (2013). These watersheds span a range of climates and are occupied by different types of land cover, which include tropical rainforest (Amazon, Congo, Rianila), dry savannah (Tana, Athi-Galana-Sabaki, Betsiboka), temperate pine forest growing on podzols (Leyre), mixed temperate forest, grassland and cropland (Meuse) and cropland (Loire and Meuse). Lithology is also extremely contrasted as it includes for instance carbonate-rocks dominated watershed as for the Meuse, sandstone dominated silicates (Leyre), and precambrian crystalline magmatic and metamorphic rocks with a small proportion of carbonate and evaporite rocks for the Congo river.

2.2   Field and laboratory measurements

Water temperature and pH were measured in the field with different probes depending on the origin of the dataset. However, all the pH data rely on daily calibration with two-point United States National Bureau of Standards (NBS) standards (4 and 7). Measurements were performed directly in the surface water, or in collected water immediately

after sampling. It is crucial to measure pH in situ or immediately after sampling, as pH determination in the laboratory several hours or days after sampling will be potentially affected by CO_2 degassing and/or microbial respiration (Frankignoulle and Borges, 2001). Several techniques were used to measure water pCO_2. Water-gas equilibration was performed with a marbles type equilibrator (Frankignoulle et al., 2001) for the Amazon, Loire, Leyre, Sinnamary and Congo (December 2013) Rivers as well for Lake Kivu, or with a Liqui-Cel MiniModule membrane contactor equilibrator (see Teodoru et al., 2009) for the Zambezi and some sites within the Congo basin (December 2012): water was pumped either continuously from a ship, or on an ad hoc basis from the bank of the rivers after waiting $\sim$ 15 min for complete equilibration; air was continuously pumped from the equilibrator to the gas analyser (see e.g. Abril et al., 2014 for a more detailed description of the system). A syringe-headspace technique (Kratz et al., 1997; Teodoru et al., 2009) was used in all African rivers and in the Meuse River: 30 mL volume of atmospheric air was equilibrated with 30 mL volume of river water by vigorously shaking during 5–10 min in four replicate gas-tight syringes. The four replicates 30 mL of equilibrated gas and a sample of atmospheric air were injected in an IR gas analyser in the field; the first gas injection served as a purge for the circuit and cell and the three other injections were used as triplicate pCO_2 determination (average repeatability of ± 1 %). The pCO_2 in the river water was deduced from that measured in the headspace accounting for the initial pCO_2 in the air used for equilibration, water temperature in the river and in the water at equilibrium in the syringe, and based on Henry's law. Comparison between syringe-headspace and marbles or membrane equilibrator was made during two cruises on the Congo River and three cruises in the Zambezi basin and gave very consistent results, deviation from the 1 : 1 line being always less than 15 % (see Fig. 1). A serum bottle-headspace technique (Hope et al., 1995) was also used on the Sinnamary River; surface water was sampled in 120 mL serum bottles that were sealed excluding air bubbles. Back in the laboratory, a headspace was created with pure N_2 (Abril et al., 2005). The CO_2 concentration of equilibrated gas in the headspace was

analysed by injecting small volumes (0.5 mL) of gas in a GC calibrated with certified gas mixtures.

Immediately after water-gas phase equilibration, CO_2 was detected and quantified in most samples with non-dispersive, infrared (IR), gas analysers (Frankignoulle et al., 2001; Abril et al., 2014). The gas analysers were calibrated before each field cruise, with air circulating through soda lime or pure N_2 for zero and with a certified gas standard for the span. Depending on the cruises and expected pCO_2 ranges, we used gas standard concentration of 1000–2000 ppmv, or a set of calibration gases at 400, 800, 4000 and 8000 ppmv. Stability of the instrument was checked after the cruise, and deviation of the signal was always less than 5 %. These instruments offer a large range of linear response, depending on manufacturers and model: 0–20 000 ppmv or 0–60 000 ppmv. We verified this linearity for a Li-Cor® Li-820 gas analyser, by connecting the analyser to a closed circuit of gas and equipped with a rubber septum, which allowed injection of pure CO_2 with a syringe. Linearity was check by injecting increasing volumes of CO_2 in order to cover the whole range of measurement and was excellent between zero and $\sim 20\,000$ ppmv; Apart from IR analysers used in general, in the Sinnamary River, pCO_2 was also measured with a photoacoustic infrared gas analyser (range 0–25 000 ppmv) connected to an equilibrator and by GC with a thermal conductivity detector (TCD); both analysers were calibrated with a gas mixture of 5000 ppmv of CO_2. Both methods gave results consistent at ±15 % in the 0–13 000 ppmv range (Abril et al., 2006). Sinnamary data reported here are from headspace and GC.

TA was analysed by automated electro-titration on 50 mL filtered samples with 0.1N HCl as titrant. Equivalence point was determined with a Gran method from pH between 4 and 3 (Gran 1952). Precision based on replicate analyses was better than ±5 µmol L^{-1}. In most acidic samples with low alkalinity, reproducibility was improved by slightly increasing the pH by up to 0.2 units by vigorously stirring in order to degass as much CO_2 as possible before starting the titration. DOC was measured on samples filtred through pre-combusted (490 °C) glass fibre filter with a porosity of 0.7 µm and stored acidified with ultrapure H_3PO_4 in borosilicate vials caped with Teflon stoppers.

Analysis was performed with a Shumadzu TOC5000 analyser based on high temperature catalytic oxidation, after removal of dissolved CO_2 for samples from Amazon, Loire, Leyre, and Sinnamary Rivers. DOC concentrations were measured with a customized wet oxidation TOC analyzer (Thermo HiperTOC, or IO Analytical Aurora 1030W) coupled to a Delta+XL or Delta V IRMS for the other rivers.

2.3 pCO_2 calculation from pH and TA

We calculated pCO_2 from TA, pH and temperature measurements using thermodynamic constants of Millero (1979) and the CO_2 solubility from Weiss (1974) as implemented in the CO2SYS program. Hunt et al. (2011) reported discrepancy lower than 2 % for pCO_2 computed this way with those obtained with the PHREEQC program (Parkhurst and Appelo, 1999). Differences in software or dissociation constants cannot account for the large bias in calculated pCO_2 compared to measured pCO_2 we are reporting in this paper.

3 Results

3.1 Data ranges and patterns in the entire dataset

Measured pCO_2 varied between 36 ppmv in a floodplain of the Amazon River and 23 000 ppmv in a first order stream of the Leyre River (Table 1). Maximum and minimum of pH and TA occurred concomitantly with lowest values in the Congo River (pH = 3.94 and TA = 0) and highest values in Lake Kivu (pH = 9.16 and TA = 14.2 mmol L^{-1}). Highest DOC concentrations (> 3000 µmol L^{-1}) were observed in small streams in the Congo basin and in first order streams draining podzolized soils in the Leyre basin. Lowest DOC concentrations (< 40 µmol L^{-1}) occurred in some tributaries of the Athi-Galana-Sabaki, in the Rianila and Betsiboka Rivers, and in the Shimba Hills streams. Some clear patterns were observed in the dataset, pCO_2 and DOC decreasing with pH and TA increasing with pH (Fig. 2). This illustrates the large contrast in acid-base

properties between acidic, organic-rich and poorly buffered samples on the one hand, and basic, carbonate-buffered samples on the other hand. Our dataset probably covers the full range of conditions of carbon speciation that can be encountered in continental surface waters.

3.2 Comparison between measured and calculated pCO_2

Calculated pCO_2 was $> 10\%$ lower than measured pCO_2 in 16 % of the samples; both methods were consistent at $\pm 10\%$ in 24 % of the samples; calculated pCO_2 was $> 10\%$ higher than measured pCO_2 in 60 % of the samples and $> 100\%$ higher in 26 % of the samples. Absolute values, as expressed in ppmv, were largely shifted toward overestimation, calculated vs. measured pCO_2 data being well above the 1 : 1 line, and calculated minus measured pCO_2 values ranging between -6180 ppmv and $+882\,022$ ppmv (Fig. 3). Largest overestimation of calculated pCO_2 occurred in most acidic samples, whereas underestimations occurred in neutral or slightly basic samples (Fig. 2b). Ranking the data according to the pH and TA reveal that overestimation of calculated pCO_2 compared to measured pCO_2 increased in acidic, poorly buffered waters in parallel with an increase in the DOC concentration (Table 2). Discrepancies between calculated and measured pCO_2 were very different from one system to another, depending on the chemical status of the waters. On average at each sampled site, the relative overestimation of calculated pCO_2 decreased with pH and TA and increased with DOC (Fig. 4). Overestimation of calculated pCO_2 was on average $< 10\%$ in the Kivu Lake, and the Meuse, Loire, Shimba Hills and Tana Rivers, which all have neutral or basic pH, TA > 1 mmol L^{-1} and low to moderate DOC concentrations (< 400 µmol L^{-1}) (Fig. 4). In contrast, calculated pCO_2 was overestimated by $> 200\%$ on average in the Congo, Leyre, Sinnamary and Amazon Rivers, which have acidic pH, TA < 0.5 mmol L^{-1} and highest DOC concentration, reaching 1000 µmol L^{-1} on average in the Congo. The cases of Athi-Galana-Sabaki, Rianila, Betsiboka, and Zambezi Rivers were intermediate in pH, TA and DOC, and with average overestimations of calculated pCO_2 of 50–90 % (Fig. 4).

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4   Discussion

4.1   Origin of overestimation of calculated pCO_2

The fact that calculated pCO_2 overestimation is negatively correlated with pH and TA and positively correlated with DOC (Table 2, Fig. 4) is consistent with some of the observations of Cai et al. (1998) in the freshwater end-members of some estuaries in Georgia, USA, and of Hunt et al. (2011) in rivers in New Hampshire, USA. These authors performed NaOH back-titration in order to measure non-carbonate alkalinity (NCA). They found that NCA accounted for a large fraction (in some cases the majority) of TA; in addition, the contribution of inorganic species other than carbonate was negligible and most of the NCA could be attributed to organic acid anions. Hunt et al. (2011) also showed that in the absence of direct titration of NCA, which is labour-intensive and whose precision may be poor, this parameter could be calculated as the difference between the measured TA and the alkalinity calculated from measurements of pH and DIC and the dissociation constants of carbonic acid. Using the latter approach, Wang et al. (2013) obtained a positive correlation between NCA and DOC concentrations in the Congo River, evidencing a predominant role of organic acids on the water pH and DIC speciation in such acidic system. Because we did not measure directly DIC in this study, we could not calculate NCA with the same procedure as these studies. An attempt to calculate TA from our measured pH and pCO_2 with the CO2SYS program failed. Indeed, TA values calculated this way were inconsistent with other measured variables (with sometimes negative values), probably because pH and pCO_2 are too interdependent in the carbonate system, very small analytical errors on these variables lead to large uncertainties in the calculated TA. Nevertheless, the negative correlation between pH and DOC and positive correlation between pH and TA (Fig. 2) confirm a strong control of organic acids on pH and DIC speciation across our entire dataset.

As discussed by Hunt et al. (2011), a significant contribution of organic acids to TA leads to an overestimation of calculated pCO_2 with the CO2SYS program, or with any program that accounts only for the inorganic species that contribute to TA. It is

thus obvious that the observed increase in pCO_2 overestimation when pH decreases (Figs. 3b and 4; Table 2) is due to an increasing contribution of organic acid anions to TA. However, this effect is far from being the only driver of the observed overestimation of pCO_2, which is also due to a decrease in the buffering capacity of the carbonate system at acidic pH. To investigate the magnitude of this effect, we calculated the factor $dpCO_2/dTA$ (in ppmv mol^{-1}), which describes the change in calculated pCO_2 induced by a change in TA. This factor, which is the opposite of a buffer factor as it reflects the sensitivity of pCO_2 calculation to the TA, increases exponentially when pH decreases (Fig. 5a). To go further in this theoretical analysis, we computed the difference between the pCO_2 calculated at a given TA value and the one calculated at a slightly higher TA value (TA + X mmol L^{-1}). These calculations reveal an extreme sensitivity of calculated pCO_2 to TA at acidic pH (Fig. 5b). For instance, increasing TA by 0.005 mmol L^{-1} (a value close to the precision of TA titrations) increases the calculated pCO_2 by 31 ppmv at pH 7, by 307 ppmv at pH 6 and by 3070 at pH 5. Increasing TA by 0.100 mmol L^{-1} (a typical value of NCA found in freshwaters, Driscoll et al., 1994; Cai et al., 1998; Hunt et al., 2011), increases the calculated pCO_2 by 615 ppmv at pH 7, by 6156 ppmv at pH 6 and by 61 560 ppmv at pH 5. Note that this increase in calculated pCO_2 is independent of the chosen initial TA value. The difference between calculated and measured pCO_2 from our data-set, shows that a NCA contribution around 0.100 mmol L^{-1} is sufficient to explain the overestimation of calculated pCO_2 of most samples at pH < 6, whereas a NCA contribution higher than 0.500 mmol L^{-1} would be necessary for several samples at circumneutral and slightly basic pH (Fig. 4b). Samples above this high NCA contribution are from the Athi-Galana-Sabaki and Zambezi watersheds, and correspond to TA values well above 1 mmol L^{-1}. A NCA value of 0.500 mmol L^{-1} in these samples is thus plausible.

We have no definitive explanation for lower calculated than measured pCO_2, which is observed mainly at neutral to slightly basic pH, e.g., in the Zambezi River (Fig. 3). In most of these samples, owing to the relatively high TA value, an overestimation of pH of less than 0.2 units is sufficient to account for the low calculated pCO_2 compared

to measured values. Thus, one factor of variability throughout the dataset as well as in literature data is the accuracy of pH measurements – despite the care taken (e.g, calibrations with NBS buffers for each day of measurements), we cannot rule out that drift or malfunction of pH electrodes contribute to the observed variability, constituting
5 an additional disadvantage compared to direct pCO_2 measurements with very stable gas analysers.

4.2 Impact on estimates of CO$_2$ emissions from freshwaters

According to our analysis, overestimation of calculated pCO_2 is largest in acidic, poorly buffered and organic-rich waters. Consequently, the overestimation of regional and
10 global CO$_2$ emissions computed from calculated pCO_2 depends on the relative contribution of these types of waters worldwide. In their analysis, Raymond et al. (2013) have discarded all calculated pCO_2 values with a pH value of less than 5.4, as well as all pCO_2 values above 100 000 ppmv. These criteria would exclude only 8 % of samples from our dataset. Indeed, from our analysis, it appears that overestimation of calculated
15 pCO_2 occurs at pH much higher than 5.4 (Figs. 3–5; Table 2). Both techniques were consistent at ±10 % on average in only five of the twelve studied systems, which combine a circumneutral to basic pH with a TA concentration well above 1 mmol L^{-1} (Fig. 4). Although it would not be sufficient for the cases of the Zambezi and Athi-Galana-Sabaki Rivers where overestimation is still significant, a TA value above 1 mmol L^{-1} appears as
20 a more robust criteria, rather than a pH threshold, to separate calculated pCO_2 affected by bias from those consistent with measured pCO_2 (Table 2). In fact, pCO_2 calculation from pH and TA in freshwaters historically relies on theoretical background and validation data in high alkalinity waters (Neal et al., 1998), including karstic waters (Kempe, 1975). At the global scale, high TA typically occurs in rivers draining watersheds with
25 a significant proportion of carbonate rocks, typically > 30 % of their surface area if the criteria of TA > 1 mmol L^{-1} is chosen and the normalized weathering rates of Meybeck (1987) are applied. According to Meybeck (1987), the average and discharge-weighted TA is around 0.9 mmol L^{-1} for world rivers and around 0.6 mmol L^{-1} for tropical rivers;

the two largest rivers in the World in terms of discharge, the Amazon and the Congo, are also well below this limit of $1\,\mathrm{mmol\,L^{-1}}$ and have large overestimation in calculated $p\mathrm{CO_2}$ (on average 200 % and 360 %, respectively). Very low TA values have also been reported in boreal streams (Dinsmore et al., 2012; Wallin et al., 2014).

5   In lakes, the highest $p\mathrm{CO_2}$ values in the literature are also calculated rather than directly measured ones (Sobek et al., 2005) and come from tropical black water lakes: 65 250 ppmv in Lago Tupé in the Brazilian Amazon, a Ria Lake connected to the Rio Negro, where, according to our own dataset, pH is below 5 and TA is around $0.070\,\mathrm{mmol\,L^{-1}}$; and 18 950 ppmv in Kambanain Lake in Papua New Guinea corre-

10 sponding to a pH value of 6.1 and a TA value of $0.350\,\mathrm{mmol\,L^{-1}}$ (Vyverman, 1994). This suggests a widespread overestimation of calculated $p\mathrm{CO_2}$ that significantly impacts the estimation of global $\mathrm{CO_2}$ emissions from inland waters. However, a precise analysis based on exact quantitative information on the relative contribution of acidic and high and low alkalinity waters to the total surface area of inland waters is necessary

15 in order to evaluate the exact magnitude of the overestimation.

5   Conclusions

From our analysis, it appears that the validity of calculating $p\mathrm{CO_2}$ from pH, TA, and temperature is most robust in freshwaters with circumneutral to basic pH and with TA exceeding $1\,\mathrm{mmol\,L^{-1}}$. At lower TA and pH, however, calculated $p\mathrm{CO_2}$ (and hence,

20 $\mathrm{CO_2}$ degassing rates) are overestimated by 50 to 300 % relative to direct, in situ $p\mathrm{CO_2}$ measurements. Since a large majority of freshwater systems globally have characteristics outside of the range of applicability of $p\mathrm{CO_2}$ calculation, it appears reasonable to assume that recent estimates of global $\mathrm{CO_2}$ emission from lakes and rivers, which are based exclusively on calculated $p\mathrm{CO_2}$ data, are overestimated. We propose that while

25 TA and pH measurements remain useful to describe the aquatic chemistry as such, data on $p\mathrm{CO_2}$ should in the future rely on direct measurements of $p\mathrm{CO_2}$. Calculation of $p\mathrm{CO_2}$ from pH and DIC should also be quantitatively tested as an alternative to di-

rect pCO_2 measurements (Raymond et al., 1997; Kratz et al., 1997; Wallin et al., 2014). Joint international efforts are necessary to define most appropriate protocols for pCO_2, DIC and pH measurements in freshwaters.

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Table 1. Summary of the presented dataset. Average, minimum and maximum values of temperature, dissolved organic carbon (DOC), pH (measured on the NBS scale), total alkalinity (TA) and measured partial pressure of CO_2 (pCO_2) in the different freshwater ecosystems.

Country	Watersheds	Temperature (°C)			DOC (µmol L^{-1})			pH (NBS scale)			TA (mmol L^{-1})			Measured pCO_2 (ppmv)			N
		Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	
Brazil	Amazon	30.3	27.4	34.3	352	118	633	6.60	0.53	7.60	0.385	0.030	1.092	4204	36	18 400	155
Kenya	Athi-Galana-Sabaki	25.9	19.8	36.0	307	29	1133	7.69	6.49	8.57	2.290	0.407	5.042	2811	608	10 405	44
DRC	Congo	26.3	22.6	28.2	1002	149	3968	6.01	3.94	7.22	0.212	0.000	0.576	6093	1582	15 571	97
DRC/Rwanda	Lake Kivu	24.0	23.0	24.7	162	142	201	9.05	8.99	9.17	13.037	12.802	13.338	660	537	772	53
France	Leyre	12.5	7.9	19.2	588	142	3625	6.20	4.40	7.41	0.280	0.038	1.082	4429	901	23 047	92
France	Loire	15.5	8.8	19.3	195	167	233	8.70	8.07	9.14	1.768	1.579	1.886	284	65	717	18
Belgium	Meuse	18.1	13.3	25.9	229	102	404	7.89	6.95	8.59	2.769	0.360	7.141	2292	176	10 033	50
Madagascar	Rianila and Betsiboka	25.4	20.2	29.5	138	33	361	6.84	5.83	7.62	0.233	0.076	0.961	1701	508	3847	36
Kenya	Shimba Hills	25.1	21.9	31.8	214	36	548	7.37	6.22	8.93	1.989	0.227	14.244	2751	546	9497	9
French Guiana	Sinnamary	27.1	24.1	28.7	419	213	596	5.50	5.08	6.30	0.143	0.066	0.290	7770	1358	15 622	49
Kenya	Tana	26.6	25.0	27.9	321	193	651	7.65	7.32	8.02	1.619	1.338	2.009	2700	845	6014	51
Zambia/Mozambique	Zambezi	26.9	18.8	31.8	252	103	492	7.59	5.06	9.08	1.245	0.052	3.134	2695	151	14 004	107
Entire dataset		24.6	7.9	36.0	408	29	3968	7.00	3.94	9.17	1.731	0.000	14.244	3707	36	23 047	761

Table 2. Median and average values of calculated *minus* measured pCO_2 in the dataset.

|	N	% of samples	cal – meas pCO_2 (ppmv) Med.	Av.	cal – meas pCO_2 (% of meas pCO_2) Med.	Av.	pH Med.	Av.	TA (mmol L^{-1}) Med.	Av.	DOC µmol L^{-1} Med.	Av.
All samples	761	100 %	+611	+10 692	+23 %	+194 %	6.94	7.00	0.467	1.731	315	408
Ranked by calculated-measured pCO_2 as % of measured pCO_2												
< −10 %	122	16 %	−540	−890	−34 %	−36 %	7.89	7.85	1.269	1.766	259	275
±10 %	174	23 %	+15	+50	+2 %	+1 %	7.67	7.78	1.576	3.735	228	273
> +10 %	465	61 %	+2430	+17 710	+72 %	+327 %	6.52	6.49	0.308	0.972	360	497
> +50 %	280	37 %	+5490	+28 660	+162 %	+526 %	6.18	6.14	0.192	0.460	375	567
> +100 %	199	26 %	+ 9080	+39 120	+270 %	+710 %	5.89	5.96	0.166	0.364	389	602
Ranked by pH												
pH > 7	368	48 %	+1	+82	+1 %	+15 %	7.82	7.92	1.572	3.284	231	255
pH < 7	393	52 %	+3280	+20 630	+71 %	+362 %	6.30	6.13	0.232	0.277	413	558
pH 6–7	256	34 %	+1580	+2710	+40 %	+96 %	6.58	6.55	0.334	0.370	350	427
pH < 6	136	18 %	+18 410	+ 54 486	+308 %	+864 %	5.50	5.35	0.093	0.101	487	828
pH < 5	25	3 %	+115 580	+209 910	+1645 %	+3180 %	4.53	4.53	0.041	0.045	1427	1843
Ranked by TA												
TA > 2 mmol L^{-1}	110	14 %	+20	+340	+2 %	+12 %	8.58	8.47	7.023	8.326	163	202
TA 1–2 mmol L^{-1}	157	21 %	−8	−163	−2 %	−9 %	7.81	7.83	1.566	1.534	271	295
TA 0.5–1 mmol L^{-1}	99	13 %	+1307	+1900	+28 %	+72 %	6.97	7.11	0.651	0.697	304	318
TA < 0.5 mmol L^{-1}	395	52 %	+2070	+20 090	+64 %	+350 %	6.30	6.24	0.222	0.232	400	538
TA < 0.1 mmol L^{-1}	82	11 %	+6840	+60 560	+230 %	+1040 %	5.50	5.35	0.059	0.056	603	988
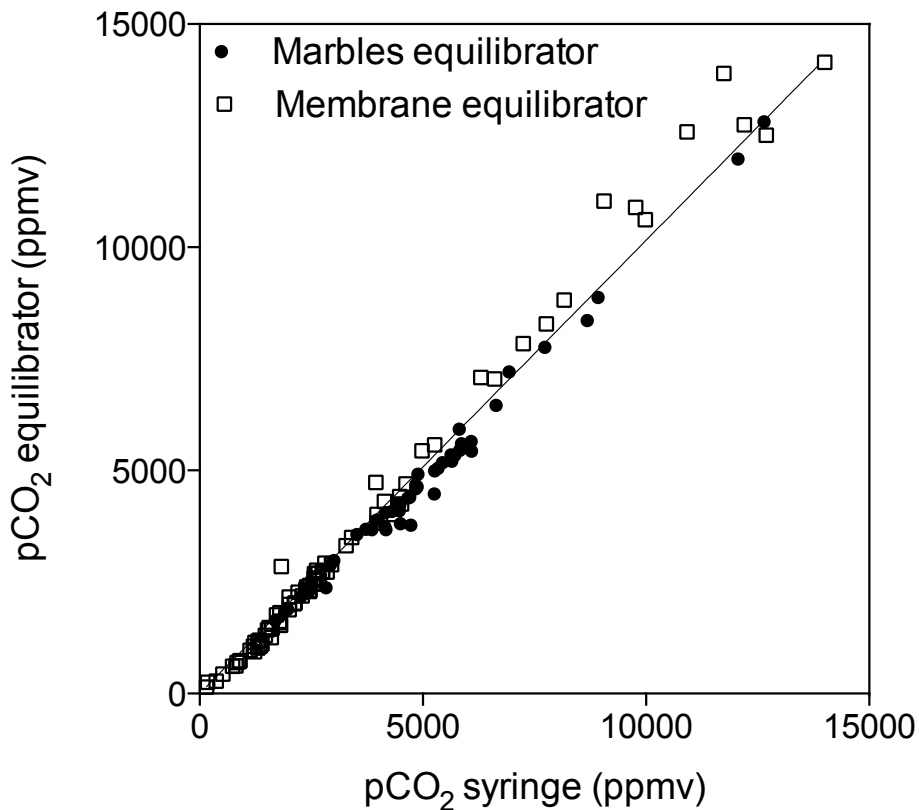
Figure 1. Comparison of results of different water-air equilibration designs for direct pCO_2 measurements; pCO_2 measured with a marbles equilibrator (Congo) and with a membrane equilibrator (Congo and Zambezi) are plotted against pCO_2 measured with a syringe headspace technique. Detection was made with an IR gas analyser.
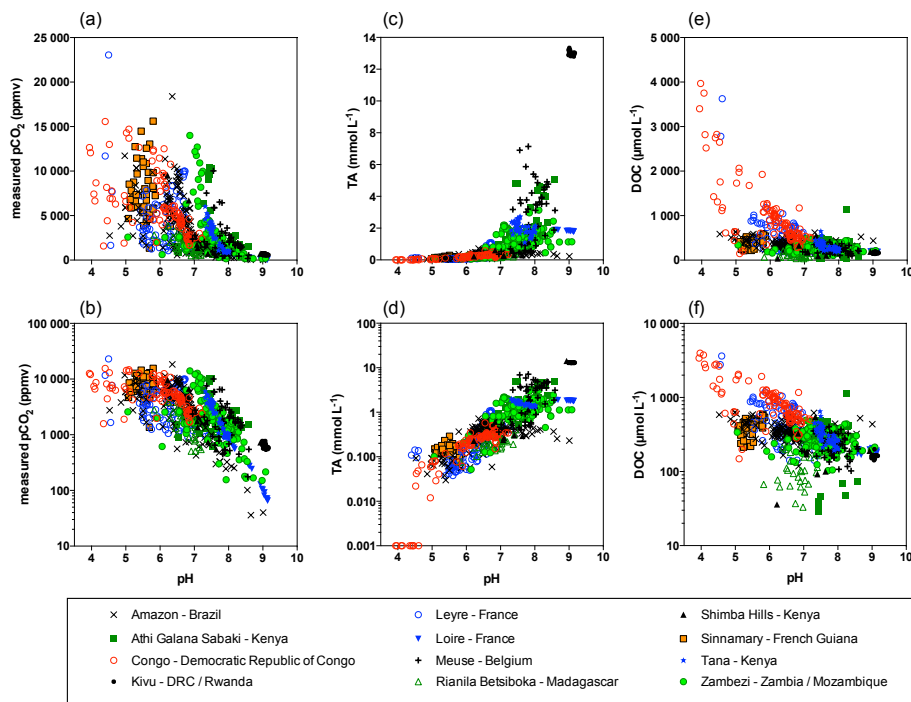
Figure 2. Plot of carbon variables vs. pH in the studied freshwater systems. Top panels are shown with a linear scale and bottom panels with a logarithmic scale; **(a, b)**: measured pCO_2; **(c, d)** total alkalinity; **(e, f)** dissolved organic carbon. Zero TA values are plotted as 0.001 in order to be visible on the log pCO_2 scale. Rianila and Bestiboka are plotted together although they belong to different watersheds in Madagascar.
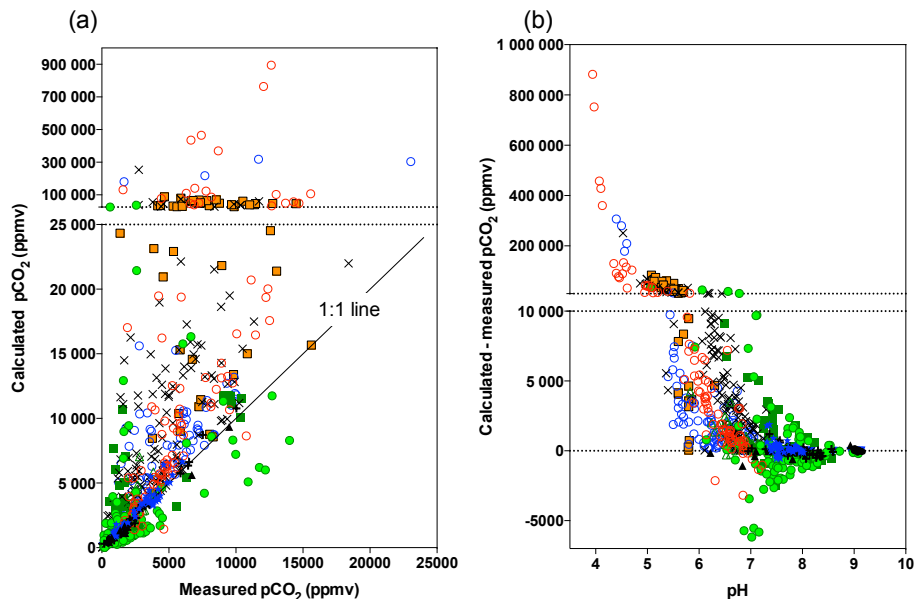
Figure 3. Comparison between measured and calculated pCO$_2$ for the whole dataset; **(a)** calculated vs. measured pCO$_2$, the line shows when measured pCO$_2$ equals calculated pCO$_2$; **(b)** the difference between calculated and measured pCO$_2$ as a function of pH; same symbols as in Fig. 2.

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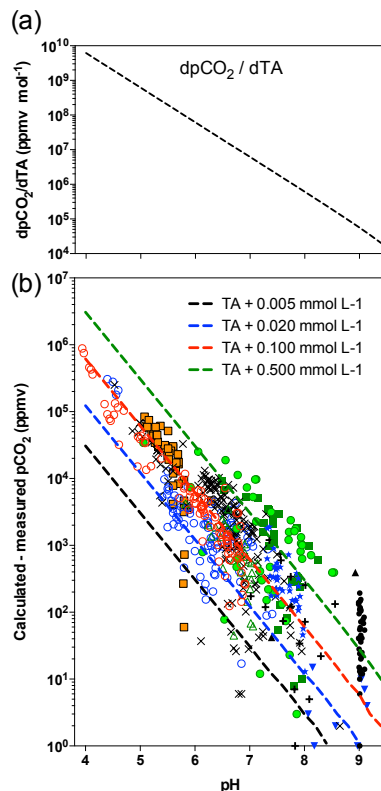
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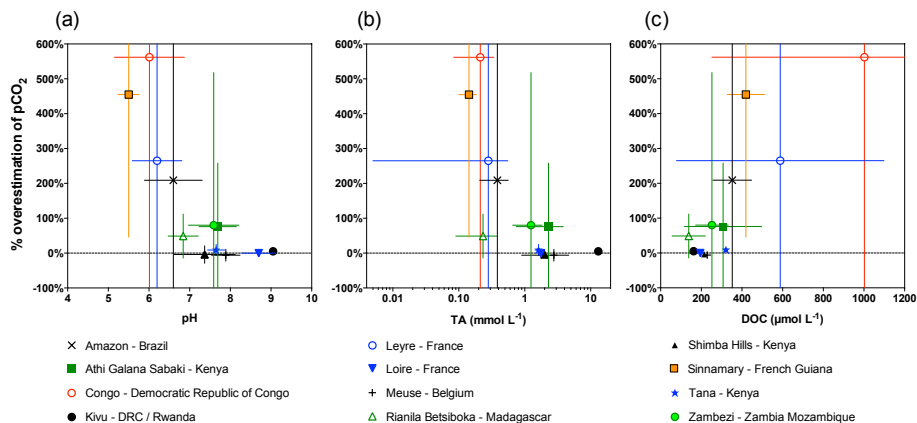
Figure 4. Average percentages of pCO_2 overestimation (calculated as $100 \times$ (calculated pCO_2 – measured pCO_2) / measured pCO_2), as a function of **(a)** pH, **(b)** TA and **(c)** DOC, for the 12 studied sites. Error bars indicate the standard deviation from the mean for each freshwater systems.

Figure 5. Sensitivity of pCO_2 overestimation to pH; **(a)** theoretical factor dpCO_2/dTA, which describes the sensitivity of calculated pCO_2 to the TA value; **(b)** the solid lines show the increase in calculated pCO_2 induced by various increases in TA, as functions of pH; these lines mimic the overestimation of calculated pCO_2 generated by increasing contributions of organic alkalinity to the TA; field data (as calculated – measured pCO_2) have been plotted for comparison; same symbols as in Fig. 2. Note that negative values do not appear in the logarithmic scale.