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Technical Note: Large overestimation of $p\text{CO}_2$ 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 ($p\text{CO}_2$). Currently, direct measurements of water $p\text{CO}_2$ remain scarce in freshwaters, and most published $p\text{CO}_2$ data are calculated from temperature, pH and total alkalinity (TA). Here, we compare calculated (pH and TA) and measured (equilibrator and headspace) water $p\text{CO}_2$ in a large array of temperate and tropical freshwaters. The 761 data points cover a wide range of values for TA (0 to 14 200 $\mu\text{mol L}^{-1}$), pH (3.94 to 9.17), measured $p\text{CO}_2$ (36 to 23 000 ppmv), and dissolved organic carbon (DOC) (29 to 3970 $\mu\text{mol L}^{-1}$). Calculated $p\text{CO}_2$ were > 10 % higher than measured $p\text{CO}_2$ in 60 % of the samples (with a median overestimation of calculated $p\text{CO}_2$ compared to measured $p\text{CO}_2$ 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 $p\text{CO}_2$ with respect to measured $p\text{CO}_2$ 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, which increases the sensitivity of calculated $p\text{CO}_2$ to TA in acidic and organic-rich waters. No empirical relationship could be derived from our data set in order to correct calculated $p\text{CO}_2$ for this bias.

Owing to the widespread distribution of acidic, organic-rich freshwaters, we conclude that regional and global estimates of CO_2 outgassing from freshwaters based on pH and TA data only are most likely overestimated, although the magnitude of the overestimation needs further quantitative analysis. Direct measurements of $p\text{CO}_2$ are recommended 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 significant 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; Borges et al., 2014). Hence, large data sets 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 $1000\ \mu\text{mol L}^{-1}$. Bicarbonate ions contribute to most 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 $\mu\text{mol L}^{-1}$) but dissolved organic carbon (DOC) concentrations are higher, and commonly exceed the DIC concentrations. 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 ($p\text{CO}_2$) is relatively constant in the atmosphere compared to surface freshwaters $p\text{CO}_2$ that can vary by more than 4 orders of magnitude spatially and temporally (Sobek et al., 2005; Abril et al., 2014). Consequently, water $p\text{CO}_2$ controls the intensity of the air–water flux, together with the gas transfer velocity. At present, both measured and calculated water $p\text{CO}_2$ data are used to compute CO_2 fluxes from freshwater systems, although calculated $p\text{CO}_2$ is overwhelmingly more abundant than directly measured $p\text{CO}_2$ (e.g. Cole et al., 1994; Raymond et al., 2013). $p\text{CO}_2$ can be calculated from the dissociation constants of carbonic acid (which are a 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ from pH and TA was initiated in world rivers in the 1970s (Kempe, 1984) and relies on the dissociation constants of carbonic acid, and the solubility of CO_2 , all of which are temperature-dependent (Harned and Scholes, 1941; Harned and Davis, 1943; Millero, 1979; Stumm and Morgan, 1996). Measured $p\text{CO}_2$ 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, stable and compact, and provide a large range of linear response well adapted to variability of $p\text{CO}_2$ found in freshwaters.

A limited number of studies have compared directly measured $p\text{CO}_2$ to computed $p\text{CO}_2$. Earlier examples provided a comparison between $p\text{CO}_2$ measured by headspace equilibration coupled to gas chromatography (GC) and $p\text{CO}_2$ calculated from pH and DIC (Kratz et al., 1997; Raymond et al., 1997). Reports by these authors in Wisconsin lakes and the Hudson River show that the $p\text{CO}_2$ values were linearly correlated but showed a variability of ± 500 ppmv around the 1:1 line, over a range of measured $p\text{CO}_2$ from 300 to 4000 ppmv. Later, Frankignoulle and Borges (2001) reported the first comparison of $p\text{CO}_2$ calculated from pH and TA and $p\text{CO}_2$ measured by equilibration coupled to an IR analyser in an estuary in Belgium. In this high TA ($2500\text{--}4800\ \mu\text{mol L}^{-1}$) and high pH (> 7.4) system, they found a good agreement between the two approaches, calculated $p\text{CO}_2$ being either overestimated or underestimated, but always by less than 7 %. In 2003, concomitant measurements of pH, TA and $p\text{CO}_2$ were performed in acidic, humic-rich (“black” type) waters of the Sinnamary River in French Guiana (Abril et al., 2005, 2006). Calculation of $p\text{CO}_2$ from pH (~ 5) and TA ($\sim 200\ \mu\text{mol L}^{-1}$) gave unrealistically high values compared to those measured directly with a headspace technique (typically 30000 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 $p\text{CO}_2$ values calculated from pH and TA were overestimated compared to direct measurements in the Sinnamary River. More recently, Hunt et al. (2011) and Wang et al. (2013) provided evidence that organic acid anions in DOC may significantly contribute to TA in some rivers and generate an overestimation of calculated $p\text{CO}_2$. Butman and Raymond (2011) reported higher calculated than measured $p\text{CO}_2$ in some US streams and rivers, but no information was available on the potential role of organic acids in this overestimation. These authors concluded that the low number of samples in their study reflected the need for more research on this topic.

With the growing interest on $p\text{CO}_2$ determination in freshwaters globally, and given the apparent simplicity and low cost of pH and TA measurements, the number of publications that report calculated $p\text{CO}_2$ in freshwaters has increased dramatically in the past decade. Some of these publications report extremely high and potentially biased $p\text{CO}_2$ 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 data set of concomitant measurements of temperature, pH, TA, $p\text{CO}_2$, and DOC in freshwaters. This is the first comprehensive data set to investigate the magnitude of the bias between calculated and measured $p\text{CO}_2$, 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 $p\text{CO}_2$

Table 1. Summary of the presented data set. Average, minimum, and maximum values of temperature, DOC, pH (measured on the NBS scale), total alkalinity (TA), and measured partial pressure of CO_2 ($p\text{CO}_2$) in the different freshwater ecosystems.

Country	Watersheds	Temperature (°C)			DOC ($\mu\text{mol L}^{-1}$)			pH (NBS scale)			TA ($\mu\text{mol L}^{-1}$)			Measured $p\text{CO}_2$ (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	4.53	7.60	385	30	1092	4204	36	18400	155
Kenya	Athi-Galana-Sabaki	25.9	19.8	36.0	307	29	1133	7.69	6.49	8.57	2290	407	5042	2811	608	10 405	44
DRC	Congo	26.3	22.6	28.2	1002	149	3968	6.01	3.94	7.22	212	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	280	38	1082	4429	901	23 047	92
France	Loire	15.5	8.8	19.3	195	167	233	8.70	8.07	9.14	1768	1579	1886	284	65	717	18
Belgium	Meuse	18.1	13.3	25.9	229	102	404	7.89	6.95	8.59	2769	360	7141	2292	176	10 033	50
Madagascar	Rianila and Betsiboka	25.4	20.2	29.5	138	33	361	6.84	5.83	7.62	233	76	961	1701	508	3847	36
Kenya	Shimba Hills	25.1	21.9	31.8	214	36	548	7.37	6.22	8.93	1989	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	143	66	290	7770	1358	15 622	49
Kenya	Tana	26.6	25.0	27.9	321	193	651	7.65	7.32	8.02	1619	1338	2009	2700	845	6014	51
Zambia/Mozambique	Zambezi	26.9	18.8	31.8	252	103	492	7.59	5.06	9.08	1245	52	3134	2695	151	14 004	107
Entire data set		24.6	7.9	36.0	408	29	3968	7.00	3.94	9.17	1731	0	14 244	3707	36	23 047	761

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 $p\text{CO}_2$ calculation should be abandoned and the range where it still gives relatively accurate results.

2 Material and methods

2.1 Sample collection

Our data set consists of 761 concomitant measurements of temperature, pH, TA, water $p\text{CO}_2$, and DOC in 12 contrasting tropical and temperate systems in Europe, Amazonia, and Africa (Fig. 1; 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 the Congo (DRC), 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 (Fig. 1). Details on some of the sampling sites can be found in Abril et al. (2005, 2014), Borges et al. (2012, 2014), Marwick et al. (2014a, b), Polsenaere et al. (2013), Tamooch et al. (2013), Teodoru et al. (2014). 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, Zambezi), temperate pine forest growing on podzols (Leyre), mixed temperate forest, grassland, and cropland (Meuse), and cropland (Loire). 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

Although pH measurements might seem almost trivial, highly accurate and precise pH data are in fact not easy to obtain, especially in low-ionic strength waters, where electrode readings are generally less stable. Even though pH measurements in the laboratory might be more accurate, it is crucial to measure pH in situ or immediately after sampling, as pH determination several hours or days after sampling will be affected by CO_2 degassing and/or microbial respiration (Frankignoulle and Borges, 2001). In this work, water temperature and pH were measured in the field with different probes depending on the origin of the data set. However, all the pH data were obtained with glass electrodes and 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.

Several techniques were used to measure water $p\text{CO}_2$. Water–gas equilibration was performed with a marbles-type equilibrator (Frankignoulle et al., 2001) for the Amazon, Loire, Leyre, Sinnamary, and Congo rivers (December 2013) as well for Lake Kivu, or with a Liqui-Cel MiniModule membrane contactor equilibrator (see Teodoru et al., 2009, 2014) 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 ~ 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 the field 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

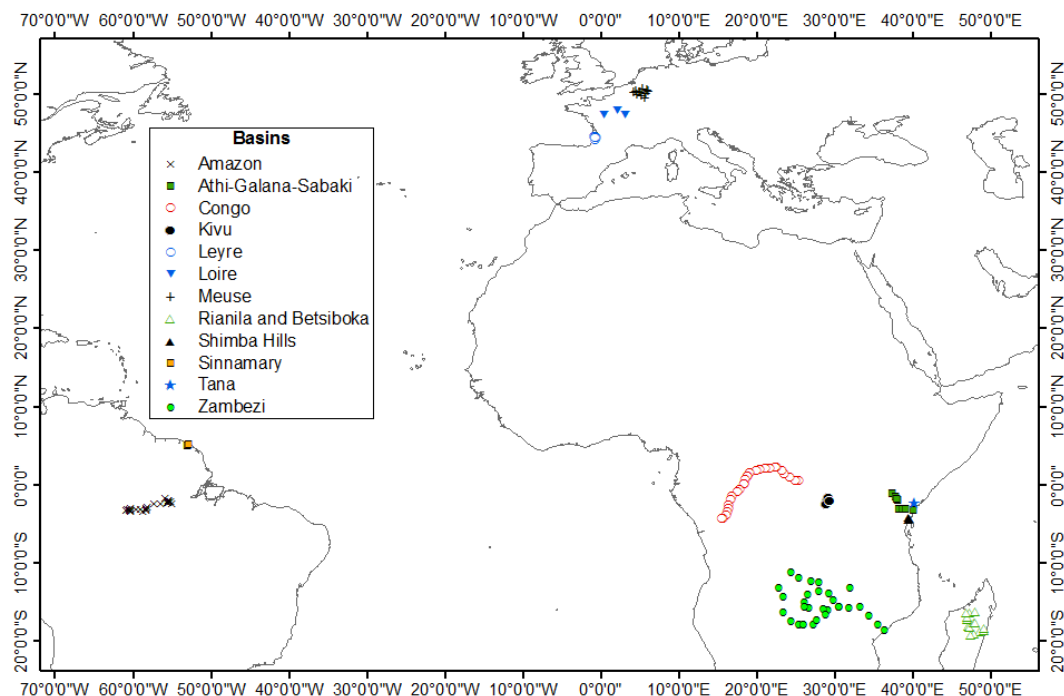


Figure 1. Location of the sampling sites in Africa, Amazonia, and Europe.

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 (Li-Cor[®] models 820 or 840, or PP systems[®] model EGM-4); the first gas injection served as a purge for the air circuit and cell and the three other injections were used as triplicate $p\text{CO}_2$ determination (average repeatability of $\pm 1\%$). The $p\text{CO}_2$ in the river water was deduced from that measured in the headspace accounting for the initial $p\text{CO}_2$ 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. 2). This highlights the consistency of the present data set of direct $p\text{CO}_2$ measurements although different techniques were used. 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 poisoned with HgCl_2 and sealed excluding air bubbles. Back in the laboratory, a 40 mL 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 gas chromatograph calibrated with certified gas mixtures.

Immediately after water–gas phase equilibration, CO_2 was detected and quantified in most samples with non-dispersive 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 $p\text{CO}_2$ 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 manufacturer and model: 0–20 000 ppmv or 0–60 000 ppmv. The linearity of an Li-COR[®] Li-820 gas analyser was verified by connecting it to a closed circuit of gas equipped with a rubber septum to allow injection of pure CO_2 with a syringe. Linearity was checked by injecting increasing volumes of CO_2 in order to cover the whole range of measurement and was excellent between zero and ~ 20000 ppmv. In addition to the IR analysers generally used in this work, in the Sinnamary River, $p\text{CO}_2$ was also measured with an INNOVA[®] 1312 optical filter IR photoacoustic gas analyser (range 0–25 000 ppmv) connected to an equilibrator and with a Hewlett Packard[®] 5890 gas chromatograph equipped 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 $\pm 15\%$ in the 0–13 000 ppmv range (Abril et al., 2006). Sinnamary data reported here are from headspace and GC determination.

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

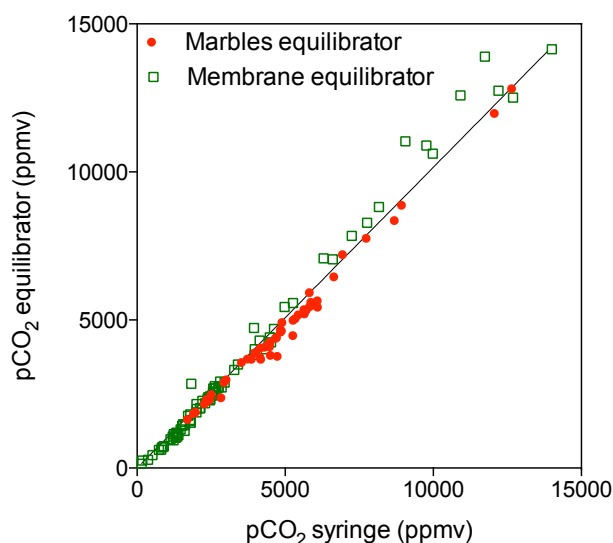


Figure 2. Comparison of results of different water–air equilibration designs for direct $p\text{CO}_2$ measurements; $p\text{CO}_2$ measured with a marbles equilibrator (Congo) and with a membrane equilibrator (Congo and Zambezi) are plotted against $p\text{CO}_2$ measured with a syringe headspace technique. Detection was made with an IR gas analyser.

and 3 (Gran, 1952). Precision based on replicate analyses was better than $\pm 5 \mu\text{mol L}^{-1}$. TA measurements should be done on filtered samples; otherwise some overestimation would occur in turbid samples, which may contain significant amounts of acid-neutralizing particles (e.g. calcium carbonate). In contrast to TA measurements based on titration to an endpoint of 5.6 (e.g. Wallin et al., 2014), the Gran titration method allows the determination of TA values in samples with in situ pH down to ~ 4.5 , i.e. very close to the dissociation constant of $\text{HCO}_3^- / \text{H}_2\text{CO}_3$. In most acidic samples with low TA, reproducibility was improved by slightly increasing the pH by up to 0.2 units by vigorously stirring during ~ 15 min in order to degas as much CO_2 as possible before starting the titration. DOC was measured on samples filtered through pre-combusted (490°C) glass fibre filter with a porosity of $0.7 \mu\text{m}$ and stored acidified with ultra-pure H_3PO_4 in borosilicate vials capped with polytetrafluoroethylene stoppers. Analysis was performed with a Shimadzu 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 analyser (Thermo HiperTOC, or IO Analytical Aurora 1030W) coupled to a Delta+XL or Delta V IRMS.

2.3 $p\text{CO}_2$ calculation from pH and TA

We calculated $p\text{CO}_2$ from TA, pH, and temperature measurements using carbonic acid dissociation constants of Millero (1979) (based on those of Harned and Scholes, 1941

and Harned and Davis, 1943) and the CO_2 solubility from Weiss (1974) as implemented in the CO2SYS program. Hunt et al. (2011) reported discrepancy lower than 2 % for $p\text{CO}_2$ 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 $p\text{CO}_2$ compared to measured $p\text{CO}_2$ we report in this paper.

3 Results

3.1 Data ranges and patterns in the entire data set

Measured $p\text{CO}_2$ 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). Minimum values of pH and TA occurred in the Congo River (pH = 3.94 and TA = 0) and maximum values in Lake Kivu (pH = 9.16 and TA = $14200 \mu\text{mol L}^{-1}$). Highest DOC concentrations ($> 3000 \mu\text{mol L}^{-1}$) were observed in small streams in the Congo basin and in first-order streams draining podzolized soils in the Leyre basin. Lowest DOC concentrations ($< 40 \mu\text{mol L}^{-1}$) occurred in some tributaries of the Athi-Galana-Sabaki, in the Rianila and Betsiboka rivers, and in the Shimba Hills streams. When considering the whole data set, measured $p\text{CO}_2$ and DOC were negatively correlated with pH, whereas TA was positively correlated with pH (Fig. 3, $p < 0.0001$ for the three variables). This illustrates the large contrast in acid–base properties between acidic, organic-rich, and poorly buffered samples on one hand, and basic, carbonate-buffered samples on the other.

3.2 Comparison between measured and calculated $p\text{CO}_2$

Calculated $p\text{CO}_2$ was more than 10 % lower than measured $p\text{CO}_2$ in 16 % of the samples; the two methods were consistent at ± 10 % in 24 % of the samples; calculated $p\text{CO}_2$ was more than 10 % higher than measured $p\text{CO}_2$ in 60 % of the samples and more than 100 % higher in 26 % of the samples. Absolute values, as expressed in ppmv, were largely shifted towards overestimation, calculated vs. measured $p\text{CO}_2$ data being well above the 1 : 1 line, and calculated minus measured $p\text{CO}_2$ values ranging between -6180 and $+882\,022$ ppmv (Fig. 4). The largest overestimation of calculated $p\text{CO}_2$ occurred in the most acidic samples, whereas underestimations of calculated $p\text{CO}_2$ occurred in neutral or slightly basic samples (Fig. 4b). Ranking the data according to the pH, TA and DOC reveals that overestimation of calculated $p\text{CO}_2$ compared to measured $p\text{CO}_2$ increased in acidic, poorly buffered waters in parallel with an increase in the DOC concentration (Table 2). Discrepancies between calculated and measured $p\text{CO}_2$ were very different from one system to another, depending on the chemical status of the waters. On average at each sampled site, the

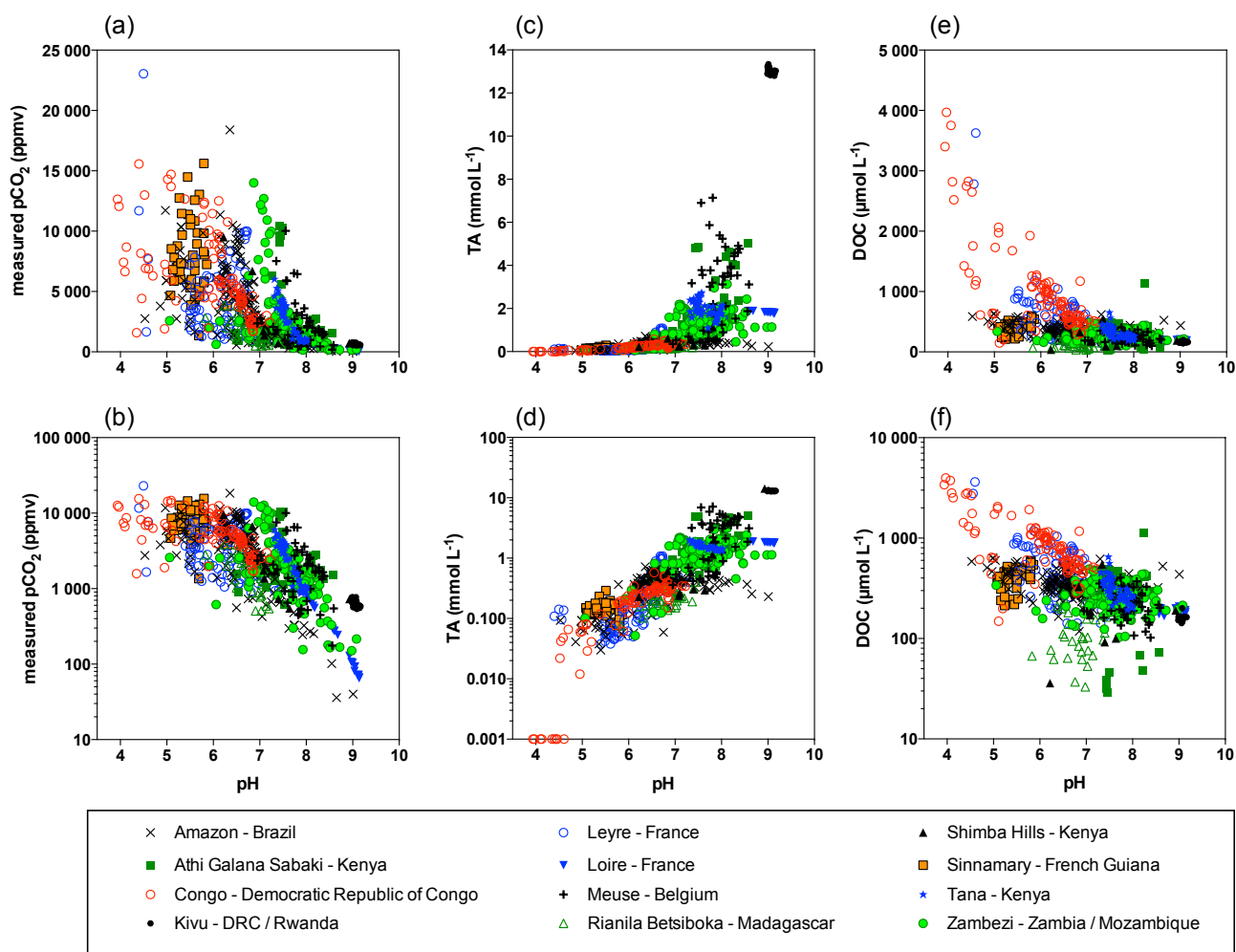


Figure 3. Plot of carbon variables vs. pH in the studied freshwater systems. Top panels are shown with a linear scale and bottom panels with a logarithmic scale; (a, b): measured $p\text{CO}_2$; (c, d) total alkalinity; (e, f) DOC. Zero TA values are plotted as 0.001 in order to be visible on the log $p\text{CO}_2$ scale. Rianila and Betsiboka are plotted together although they belong to different watersheds in Madagascar.

relative overestimation of calculated $p\text{CO}_2$ decreased with pH and TA and increased with DOC (Fig. 5). Overestimation of calculated $p\text{CO}_2$ was on average $< 10\%$ in the Kivu Lake, and the Meuse, Loire, Shimba Hills and Tana rivers, which all have neutral or basic pH, $\text{TA} > 1000 \mu\text{mol L}^{-1}$ and low to moderate DOC concentrations ($< 400 \mu\text{mol L}^{-1}$) (Fig. 5). In contrast, calculated $p\text{CO}_2$ was overestimated by $> 200\%$ on average in the Congo, Leyre, Sinnamary and Amazon rivers, which have acidic pH, $\text{TA} < 500 \mu\text{mol L}^{-1}$ and highest DOC concentration, reaching $1000 \mu\text{mol L}^{-1}$ 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 $p\text{CO}_2$ of 50–90% (Fig. 5).

4 Discussion

4.1 Origin of overestimation of calculated $p\text{CO}_2$

Our data set (Fig. 3; Table 1) probably covers the full range of conditions of carbon speciation that can be encountered in continental surface waters. A $p\text{CO}_2$ overestimation negatively correlated with pH ($p = 0.001$) and TA ($p = 0.005$) and positively correlated with DOC ($p < 0.001$) (Fig. 5) is consistent with 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 England (USA) and New Brunswick (Canada). 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 greater part) of TA; in addition, the contribution of inorganic species other than carbonate was assumed negligible and most of the NCA was attributed to organic

Table 2. Median and average values of DOC, pH (measured on the NBS scale), total alkalinity (TA), and calculated minus measured $p\text{CO}_2$ in the data set.

	N	% of samples	cal – meas $p\text{CO}_2$ (ppmv)		cal – meas $p\text{CO}_2$ (% of meas $p\text{CO}_2$)		pH		TA ($\mu\text{mol L}^{-1}$)		DOC ($\mu\text{mol L}^{-1}$)	
			Med.	Av.	Med.	Av.	Med.	Av.	Med.	Av.	Med.	Av.
All samples	761	100 %	+611	+10692	+23%	+194%	6.94	7.00	467	1731	315	408
Ranked by calculated – measured $p\text{CO}_2$ as % of measured $p\text{CO}_2$												
< –10 %	122	16 %	–540	–890	–34 %	–36 %	7.89	7.85	1269	1766	259	275
± 10 %	174	23 %	+15	+50	+2%	+1%	7.67	7.78	1576	3735	228	273
> +10 %	465	61 %	+2430	+17710	+72%	+327%	6.52	6.49	308	972	360	497
> +50 %	280	37 %	+5490	+28660	+162%	+526%	6.18	6.14	192	460	375	567
> +100 %	199	26 %	+9080	+39120	+270%	+710%	5.89	5.96	166	364	389	602
Ranked by pH												
pH > 7	368	48 %	+1	+82	+1%	+15%	7.82	7.92	1572	3284	231	255
pH < 7	393	52 %	+3280	+20630	+71%	+362%	6.30	6.13	232	277	413	558
pH 6–7	256	34 %	+1580	+2710	+40%	+96%	6.58	6.55	334	370	350	427
pH < 6	136	18 %	+18410	+54486	+308%	+864%	5.50	5.35	93	101	487	828
pH < 5	25	3 %	+115580	+209910	+1645%	+3180%	4.53	4.53	41	45	1427	1,843
Ranked by TA												
TA > 2000 $\mu\text{mol L}^{-1}$	110	14 %	+20	+340	+2%	+12%	8.58	8.47	7023	8326	163	202
TA 1000–2000 $\mu\text{mol L}^{-1}$	157	21 %	–8	–163	–2 %	–9 %	7.81	7.83	1566	1534	271	295
TA 500–1000 $\mu\text{mol L}^{-1}$	99	13 %	+1307	+1900	+28%	+72%	6.97	7.11	651	697	304	318
TA < 500 $\mu\text{mol L}^{-1}$	395	52 %	+2070	+20090	+64%	+350%	6.30	6.24	222	232	400	538
TA < 100 $\mu\text{mol L}^{-1}$	82	11 %	+6840	+60560	+230%	+1040%	5.50	5.35	59	56	603	988
Ranked by DOC												
DOC < 200 $\mu\text{mol L}^{-1}$	179	24 %	+40	+776	+5%	+62%	7.89	7.92	1579	4807	163	149
DOC 200–300 $\mu\text{mol L}^{-1}$	167	22 %	+102	+2755	+5%	+69%	7.56	7.37	1132	1259	258	252
DOC 300–400 $\mu\text{mol L}^{-1}$	165	22 %	+887	+4473	+25%	+101%	6.90	6.93	499	866	341	344
DOC > 400 $\mu\text{mol L}^{-1}$	250	33 %	+3070	+27197	+59%	+434%	6.15	6.14	200	415	555	765
DOC > 800 $\mu\text{mol L}^{-1}$	79	10 %	+4995	+62784	+92%	+886%	5.80	5.62	94	180	1099	1438

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 the predominant role of organic acids in DIC speciation and pH in such acidic system. Because we did not directly measure DIC in this study, we could not calculate NCA with the same procedure as these studies. We attempted to calculate TA from our measured pH and $p\text{CO}_2$ with the CO2SYS program. However, TA values calculated this way were inconsistent with other measured variables (with sometimes negative values). Indeed, because pH and $p\text{CO}_2$ are too interdependent in the carbonate system, very small analytical errors on these variables lead to large uncertainties in the calculated TA (Cullison Gray et al., 2011). A second attempt to correct our TA data from NCA consisted in calculating organic alkalinity using pH and DOC as input parameters.

We compared the model of Driscoll et al. (1989), which assumes a single pK value for all organic acids, and the triprotic model of Hruska et al. (2003), which assumes three apparent pK values for organic acids. These two models applied to our pH and DOC gave very similar organic alkalinity values, which could be subtracted from the measured TA. In the most acidic samples (e.g. some sites from the Congo basin), modelled organic alkalinities were larger than measured TA and the difference was thus negative. Nevertheless, we then recalculated $p\text{CO}_2$ from the measured pH and the TA corrected from organic alkalinity. Calculated $p\text{CO}_2$ values corrected with that method were, however, still very different from those measured in the field, being sometimes higher and sometimes lower than the measured $p\text{CO}_2$, without any meaningful pattern (indeed, corrected $p\text{CO}_2$ was negatively correlated ($p < 0.001$) with measured $p\text{CO}_2$). Consequently, we were unable to derive any empirical relationship to correct for the bias in $p\text{CO}_2$ calculation from pH and TA. Nevertheless, the negative correlation between pH and DOC and positive correlation between pH and TA (Fig. 3) confirm a

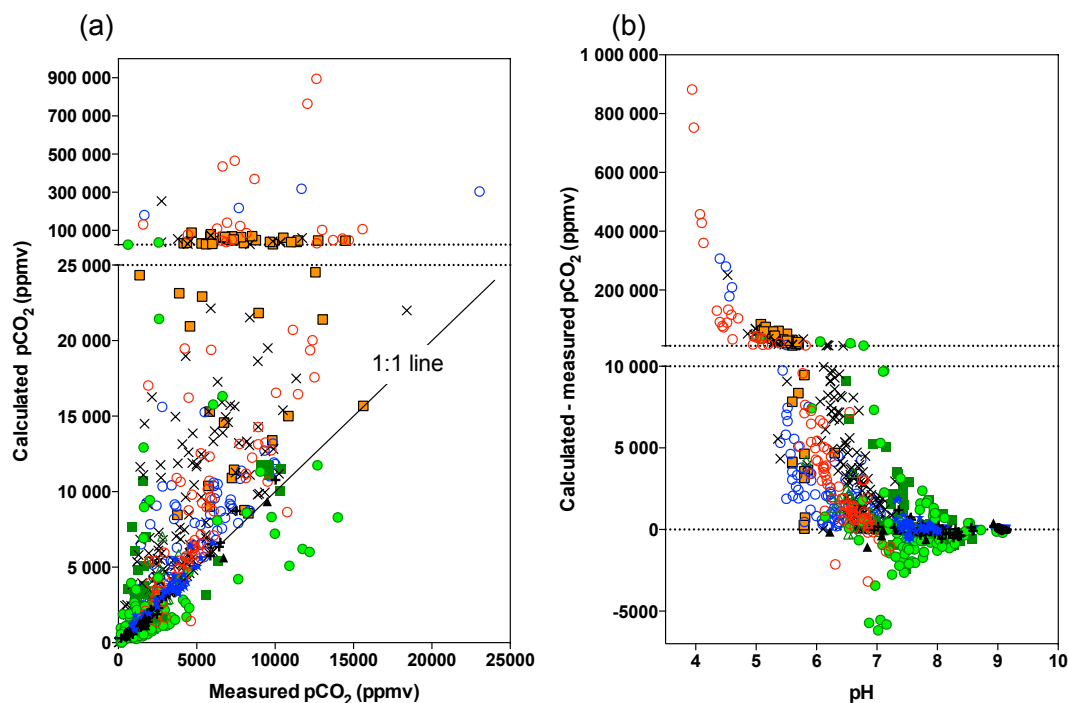


Figure 4. Comparison between measured and calculated $p\text{CO}_2$ for the whole data set: (a) calculated vs. measured $p\text{CO}_2$, the line shows when measured $p\text{CO}_2$ equals calculated $p\text{CO}_2$; (b) the difference between calculated and measured $p\text{CO}_2$ as a function of pH; same symbols as in Fig. 3.

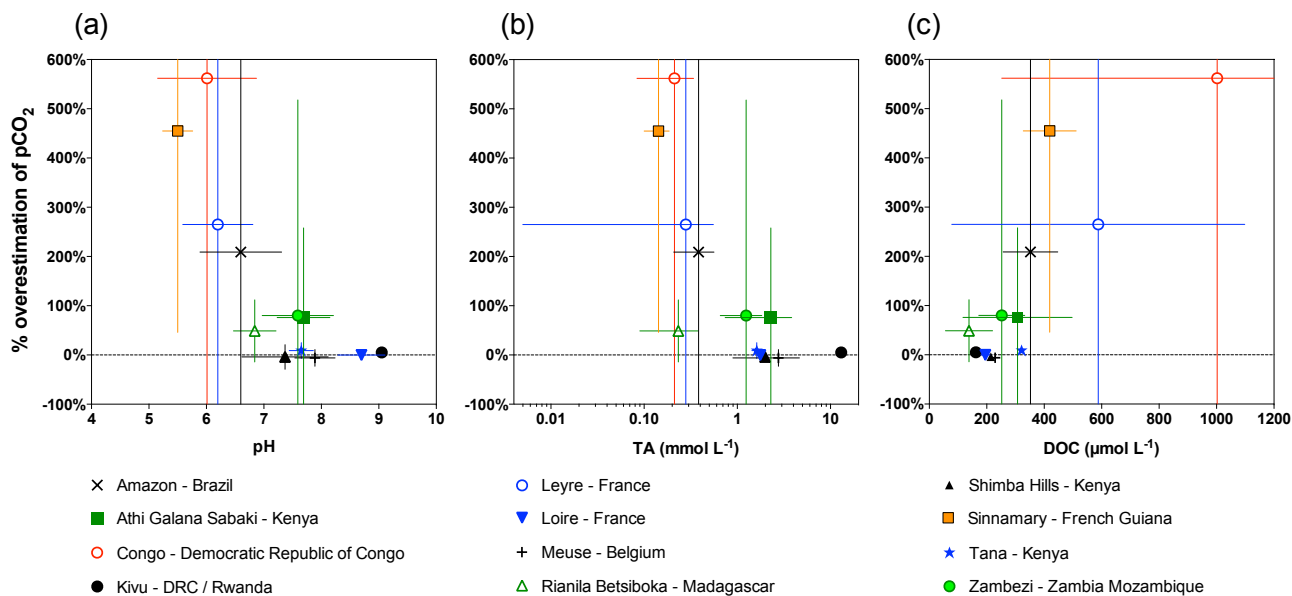


Figure 5. Average percentages of $p\text{CO}_2$ overestimation, calculated as $100 \times (\text{calculated } p\text{CO}_2 - \text{measured } p\text{CO}_2) / \text{measured } p\text{CO}_2$, as a function of (a) pH, (b) TA, and (c) DOC, for the 12 studied sites. Error bars indicate the standard deviation from the mean for each freshwater system.

strong control of organic acids on pH and DIC speciation across the entire data set.

As discussed by Hunt et al. (2011), a significant contribution of organic acids to TA leads to an overestimation of cal-

culated $p\text{CO}_2$ 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 $p\text{CO}_2$ overestimation when pH decreases (Figs. 4b and

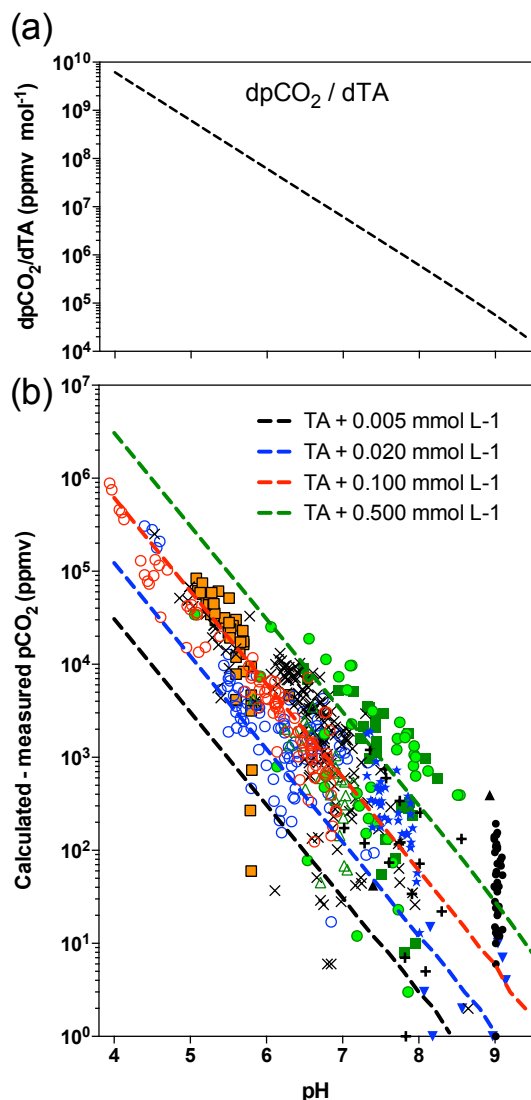


Figure 6. Sensitivity of $p\text{CO}_2$ overestimation to pH: (a) theoretical factor $dp\text{CO}_2/d\text{TA}$, which describes the sensitivity of calculated $p\text{CO}_2$ to the TA value; (b) the solid lines show the increase in calculated $p\text{CO}_2$ induced by various increases in TA, as functions of pH; these lines mimic the overestimation of calculated $p\text{CO}_2$ generated by increasing contributions of organic alkalinity to the TA; field data (as calculated – measured $p\text{CO}_2$) have been plotted for comparison; same symbols as in Fig. 3. Note that negative values do not appear in the logarithmic scale.

5; Table 2) is due to an increasing contribution of organic acid anions to TA. However, this effect is not the only driver of the observed overestimation of $p\text{CO}_2$, which is also due to a decrease in the buffering capacity of the carbonate system at acidic pH. To investigate the magnitude of this second effect, we calculated the factor $dp\text{CO}_2/d\text{TA}$ (in ppmv mol^{-1}), which describes the change in calculated $p\text{CO}_2$ induced by a change in TA. This factor, which is the opposite of a buffer factor as it reflects the sensitivity of $p\text{CO}_2$

calculation to the TA, increases exponentially when pH decreases (Fig. 6a), i.e. it is proportional to the H^+ concentration. To go further in this theoretical analysis, we computed the difference between the $p\text{CO}_2$ calculated at a given TA value and the one calculated at a slightly higher TA value ($\text{TA} + X \mu\text{mol L}^{-1}$). These calculations reveal an extreme sensitivity of calculated $p\text{CO}_2$ to TA at acidic pH (Fig. 6b). For instance, increasing TA by $5 \mu\text{mol L}^{-1}$ (a value close to the precision of TA titrations) increases the calculated $p\text{CO}_2$ by 31 ppmv at pH 7, by 307 ppmv at pH 6 and by 3070 at pH 5. Increasing TA by $100 \mu\text{mol L}^{-1}$ (a typical value of NCA found in freshwaters; Driscoll et al., 1994; Cai et al., 1998; Hunt et al., 2011), increases the calculated $p\text{CO}_2$ by 615 ppmv at pH 7, by 6156 ppmv at pH 6 and by 61560 ppmv at pH 5. Note that this increase in calculated $p\text{CO}_2$ is independent of the chosen initial TA value. The difference between calculated and measured $p\text{CO}_2$ from our data set shows that an NCA contribution around $100 \mu\text{mol L}^{-1}$ is sufficient to explain the overestimation of calculated $p\text{CO}_2$ of most samples at $\text{pH} < 6$, whereas an NCA contribution higher than $500 \mu\text{mol L}^{-1}$ would be necessary for several samples at circumneutral and slightly basic pH (Fig. 5b). Samples requiring this high NCA contribution are from the Athi-Galana-Sabaki and Zambezi watersheds, and correspond to TA values well above $1000 \mu\text{mol L}^{-1}$. An NCA value of $500 \mu\text{mol L}^{-1}$ in these samples is thus plausible.

We have no definitive explanation for lower calculated than measured $p\text{CO}_2$, which is observed mainly at neutral to slightly basic pH, for example in the Zambezi River (Fig. 4). 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 $p\text{CO}_2$ compared to measured values. In general, it is not easy to judge the accuracy of pH measurements, especially when data come from environmental agencies. Thus, one factor of variability throughout the data set 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 contributes to the observed variability, constituting an additional disadvantage compared to direct $p\text{CO}_2$ measurements with very stable gas analysers.

4.2 Impact on estimates of CO_2 emissions from freshwaters

According to our analysis, overestimation of calculated $p\text{CO}_2$ is largest in acidic, poorly buffered and organic-rich waters. Consequently, the overestimation of regional and global CO_2 emissions computed from calculated $p\text{CO}_2$ depends on the relative contribution of these types of waters worldwide. In their analysis, Raymond et al. (2013) have discarded all calculated $p\text{CO}_2$ values with a pH value of less than 5.4, as well as all $p\text{CO}_2$ values above 100 000 ppmv . These criteria would exclude only 8 % of samples from our

data set. Indeed, from our analysis, it appears that overestimation of calculated $p\text{CO}_2$ occurs at pH much higher than 5.4 (Figs. 4, 5 and 6; Table 2). The two techniques were consistent at $\pm 10\%$ on average in only 5 of the 12 studied systems, which combine a circumneutral to basic pH with a TA concentration well above $1000\ \mu\text{mol L}^{-1}$ (Fig. 5). 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 $1000\ \mu\text{mol L}^{-1}$ appears as a more robust criterion than a pH threshold to separate calculated $p\text{CO}_2$ values affected by bias from those consistent with measured $p\text{CO}_2$ (Table 2). In fact, $p\text{CO}_2$ 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 a significant proportion of carbonate rocks, typically $> 30\%$ of their surface area if the criterion of $\text{TA} > 1000\ \mu\text{mol L}^{-1}$ is chosen and the normalized weathering rates of Meybeck (1987) are applied. According to Meybeck (1987), the average and discharge-weighted TA is around $900\ \mu\text{mol L}^{-1}$ for world rivers and around $600\ \mu\text{mol L}^{-1}$ for tropical rivers. Among the 25 largest rivers in the world, 15 have a $\text{TA} > 1000\ \mu\text{mol L}^{-1}$ according to Cai et al. (2008). The two largest rivers in the world in terms of discharge, the Amazon and the Congo, are also well below this limit of $1000\ \mu\text{mol L}^{-1}$ and have large overestimation in calculated $p\text{CO}_2$ (on average 200 and 360 %, respectively). Very low TA and pH and high DOC values have also been reported in boreal streams and rivers (Humborg et al., 2010; Dinsmore et al., 2012; Wallin et al., 2014).

In lakes, the highest $p\text{CO}_2$ values in the literature come from tropical black water lakes and were also calculated rather than directly measured (Sobek et al., 2005). Calculated $p\text{CO}_2$ was 65 250 ppmv in Lago Tupé in the Brazilian Amazon, a Ria lake connected to the Rio Negro, where, according to our own data set, pH is below 5 and TA is around $70\ \mu\text{mol L}^{-1}$. It was 18 950 ppmv in Kambanain Lake in Papua New Guinea, corresponding to a pH value of 6.1 and a TA value of $350\ \mu\text{mol L}^{-1}$ (Vyverman, 1994). This suggests a widespread overestimation of calculated $p\text{CO}_2$ that significantly impacts the estimation of global 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 in order to evaluate the exact magnitude of the overestimation.

5 Conclusions

From our analysis, it appears that the validity of calculating $p\text{CO}_2$ from pH, TA and temperature is most robust in freshwaters with circumneutral to basic pH and with TA exceeding $1000\ \mu\text{mol L}^{-1}$. At lower TA and pH, however, cal-

culated $p\text{CO}_2$ (and hence, CO_2 degassing rates) are overestimated by 50 to 300 % relative to direct, in situ $p\text{CO}_2$ measurements. Since a large majority of freshwater systems globally have characteristics outside the range of applicability of $p\text{CO}_2$ calculation, it appears reasonable to assume that recent estimates of global CO_2 emission from lakes and rivers, which are based exclusively on calculated $p\text{CO}_2$ data, are too high. We propose that while TA and pH measurements remain useful to describe the aquatic chemistry, data on $p\text{CO}_2$ should in the future rely on direct measurements of $p\text{CO}_2$. Even if some studies report relatively robust calculation of $p\text{CO}_2$ from pH and DIC measurements (Raymond et al., 1997; Kratz et al., 1997; Aberg and Wallin, 2014), direct $p\text{CO}_2$ values in the field are stable, precise and straightforward and do not depend on the quality of pH measurements, which are often uncertain. Further, high-quality DIC measurements are very time-consuming, fairly complicated to set up and do not allow continuous measurements to be carried out in a simple and straightforward fashion. Although there are some practical limitations to their use in the field, submerged IR sensors, which allow high temporal resolution, are also promising (Johnson et al., 2010). Long-term instrument stability and accuracy based on newly developed off-axis integrated cavity output spectroscopy and cavity ring-down spectroscopy technologies seem to improve in comparison to traditional IR instruments, although the latter are more affordable, more compact and have lower power requirements. Joint international efforts are necessary to define the most appropriate protocols for the measurement of DIC parameters in freshwaters.

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