Technical Note: Large overestimation of pCO_2 calculated from pH and alkalinity in acidic, organic-rich freshwaters

Gwenaël Abril[1,2], Steven Bouillon[3], François Darchambeau[4], Cristian R. Teodoru[3], Trent R. Marwick[3], Fredrick Tamooh[3], Fred Ochieng Omengo[3], Naomi Geeraert[3], Loris Deirmendjian[1], Pierre Polsenaere[1], and Alberto V. Borges[4]

[1] Laboratoire EPOC, Environnements et Paléoenvironnements Océaniques et Continentaux, CNRS, Université de Bordeaux, France.

[2] Programa de Geoquímica, Universidade Federal Fluminense, Niterói, Rio de Janeiro, Brazil

[3] Katholieke Universiteit Leuven, Department of Earth & Environmental Sciences, Leuven, Belgium

[4] Unité d'Océanographie Chimique, Université de Liège, Belgium

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). Currently, 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 14200 μmol L^{-1}), pH (3.94 to 9.17), measured pCO_2 (36 to 23000 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. No empirical relationship could be derived from our dataset in order to correct calculated pCO_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 pCO_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 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 1000 μmol 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, 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 (pCO_2) is relatively constant in the atmosphere compared to surface freshwaters pCO_2 that can vary by more than 4 orders of magnitude spatially and temporally (Sobek et al. 2005; Abril et al. 2014). Consequently, water pCO_2 controls the intensity of the air-water flux, together with the gas transfer velocity. Presently, 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 (*e.g.* Cole et al. 1994; Raymond et al. 2013). pCO_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 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 (Harned and Scholes 1941; Harned and Davis 1943; 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, stable and compact, and provide a large range of linear response well adapted to variability of pCO_2 found in freshwaters.

Only a limited number of studies have compared directly measured pCO_2 to computed pCO_2. Earlier examples provided a comparison between pCO_2 measured by headspace equilibration coupled to gas chromatography (GC), and pCO_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 pCO_2 values were linearly correlated but showed a variability 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 (2500-4800 µmol L^{-1}) and high pH (>7.4) system, they found a good agreement between both approaches, calculated pCO_2 being either overestimated or underestimated, but always by less than 7%. In 2003, concomitant measurements of pH, TA and pCO_2 were performed in acidic, humic-rich ("black" type) waters of the Sinnamary River in French Guiana (Abril et al. 2005; 2006). Calculation of pCO_2 from pH (~5) and TA (~200 µmol L^{-1}) gave unrealistically high values compared to those measured directly with a headspace technique (typically 30000 ppmv versus 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 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 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 the low number of samples in their study reflected the need for more research on this topic.

With the growing interest on pCO_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 pCO_2 in freshwaters has increased dramatically in the last decade. Some of these publications report extremely high and potentially biased pCO_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 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 (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), Tamooh 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 dataset. 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 pCO_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 minutes 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 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 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. 2). This highlights the consistency of the present data-set of direct pCO_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 GC 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 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: 0-20000 ppmv or 0-60000 ppmv. The linearity of a 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 check 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, pCO_2 was also measured with an INNOVA® 1312 optical filter IR photoacoustic gas analyser (range 0 – 25000 ppmv) connected to an equilibrator and with a Hewlett Packard® 5890 GC 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 ± 15% in the 0 – 13000 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 and 3 (Gran 1952). Precision based on replicate analyses was better than ±5 $\mu mol\ L^{-1}$. TA measurements should be done on filtered samples; otherwise some overestimation would occur in turbid samples, which may content significant amount 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 situ pH down to ~4.5, *i.e.* very close to the dissociation constant of HCO_3^-

/H_2CO_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 ~15min 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 µm and stored acidified with ultrapure 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 analyzer (Thermo HiperTOC, or IO Analytical Aurora 1030W) coupled to a Delta+XL or Delta V IRMS..

2.3 pCO_2 calculation from pH and TA

We calculated pCO_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 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 report 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 23000 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 µmol 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. When considering the whole dataset, measured pCO_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 the one hand, and basic, carbonate-buffered samples on the other hand.

3.2 Comparison between measured and calculated pCO_2

Calculated pCO_2 was more than 10% lower than measured pCO_2 in 16% of the samples; both methods were consistent at ±10% in 24% of the samples; calculated pCO_2 was more than 10% higher than measured pCO_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 toward overestimation, calculated *versus* measured pCO_2 data being well above the 1:1 line, and calculated minus measured pCO_2 values ranging between -6180 ppmv and +882022 ppmv (Fig. 4). The largest overestimation of calculated pCO_2 occurred in the most acidic samples, whereas underestimations of calculated pCO_2 occurred in neutral or slightly basic samples (Fig. 4b). Ranking the data according to the pH, TA and DOC 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. 5). 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 > 1000 µmol L^{-1}

and low to moderate DOC concentrations (< 400 µmol L^{-1}) (Fig. 5). In contrast, calculated pCO_2 was overestimated by >200% on average in the Congo, Leyre, Sinnamary and Amazon Rivers, which have acidic pH, TA <500 µmol 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. 5).

4 Discussion

4.1 Origin of overestimation of calculated pCO_2

Our dataset (Fig. 3; Table 1) probably covers the full range of conditions of carbon speciation that can be encountered in continental surface waters. A pCO_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 (CA). 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 assumed negligible and most of the NCA was 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 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 pCO_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 pCO_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 pCO_2 from the measured pH and the TA corrected from organic alkalinity. Calculated pCO_2 corrected with that method were, however, still very different from those measured in the field, being sometimes higher and sometimes lower than the measured pCO_2, without any meaningful pattern (indeed, corrected pCO_2 was negatively correlated ($p < 0.001$) with measured pCO_2). Consequently, we were unable to derive any empirical relationship to correct for the bias in pCO_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 strong control of organic acids on pH and DIC speciation across the 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 (Fig. 4b & 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 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 second 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. 6a), i.e. it is proportional to the H^+ concentration. 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 µmol L^{-1}). These calculations reveal an extreme sensitivity of calculated pCO_2 to TA at acidic pH (Figure 5b). For instance, increasing TA by 5 µmol 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 100 µmol 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 61560 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 100 µmol L^{-1} is sufficient to explain the overestimation of calculated pCO_2 of most samples at pH<6, whereas a NCA contribution higher than 500 µmol 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 µmol L^{-1}. A NCA value of 500 µmol 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. 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 pCO_2 compared to measured values. In general, it is not easy to judge how accurate are pH measurements, and even less when data come from environmental agencies. 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 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 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 100000 ppmv. These criteria would exclude only 8% of samples from our dataset. Indeed, from our analysis, it appears that overestimation of calculated pCO_2 occurs at pH much higher than 5.4 (Fig. 4,5&6; 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 1000 μmol 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 μmol L^{-1} appears as 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 a significant proportion of carbonate rocks, typically >30% of their surface area if the criteria of TA > 1000 µmol 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 µmol L^{-1} for world rivers and around 600 µmol L^{-1} for tropical rivers. Among the 25 largest rivers in the world, 15 have a TA > 1000 µmol 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 µmol L^{-1} and have large overestimation in calculated pCO_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 pCO_2 values in the literature come from tropical black water lakes and were also calculated rather than directly measured (Sobek et al. 2005). Calculated pCO_2 was 65250 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 70 µmol L^{-1}. It was 18950 ppmv in Kambanain Lake in Papua New Guinea corresponding to a pH value of 6.1 and a TA value of 350 µmol L^{-1} (Vyverman 1994). This suggests a widespread overestimation of calculated pCO_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 Conclusion

From our analysis, it appears that the validity of calculating pCO_2 from pH, TA, and temperature is most robust in freshwaters with circumneutral to basic pH and with TA exceeding 1000 µmol L^{-1}. At lower TA and pH, however, calculated pCO_2 (and hence, CO_2 degassing rates) are overestimated by 50 to 300% relative to direct, *in situ* pCO_2

measurements. Since a large majority of freshwater systems globally have characteristics outside of the range of applicability of pCO_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 pCO_2 data, are overestimated. We propose that while TA and pH measurements remain useful to describe the aquatic chemistry, data on pCO_2 should in the future rely on direct measurements of pCO_2. Even if some studies report relatively robust calculation of pCO_2 from pH and DIC measurements (Raymond et al. 1997; Kratz et al. 1997; Aberg and Wallin 2014), direct pCO_2 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 to carry out continuous measurements 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). The long-term instrument stability and accuracy based on newly developed Off-Axis Integrated Cavity Output Spectroscopy and Cavity Ring-Down Spectroscopy technologies seems to improve in comparison to traditional IR instruments, although the latter are more affordable, compact and with lower power requirements. Joint international efforts are necessary to define most appropriate protocols for the measurements of dissolved inorganic carbon parameters in freshwaters.

Acknowledgements

The dataset used in this study was collected in the framework of projects funded by the Cluster of Excellence COTE at the Université de Bordeaux (ANR-10-LABX-45, CNP-Leyre project), the European Research Council (ERC-StG 240002, AFRIVAL: African river basins: Catchment-scale carbon fluxes and transformations, http://ees.kuleuven.be/project/afrival/), the Fonds National de la Recherche Scientifique (FNRS, CAKI, 2.4.598.07, TransCongo, 14711103), the French national agency for research (ANR 08-BLAN-0221, CARBAMA project http://carbama.epoc.u-bordeaux1.fr/), the Research Foundation Flanders (FWO-Vlaanderen), the Belgian Federal Science Policy (BELSPO-SSD projects COBAFISH and EAGLES), the Research Council of the KU Leuven, and the Institut de Radioprotection et Sureté Nucléaire, France (FLORE project). We thank the Hydreco Laboratory in French Guiana, and Patrick Albéric (ISTO Orléans) who analysed some of the data reported here, Aurore Beulen (ULg) for collection of Meuse dataset, Marc-Vincent Commarieu (ULg) for analytical support, two anonymous reviewers and C.W. Hunt (reviewer) for constructive comments on the previous version of the paper. AVB is a senior research associate at the FNRS.

References

Åberg, J., and Wallin M. B.: Evaluating a fast headspace method for measuring DIC and subsequent calculation of pCO_2 in freshwater systems, Inland Wat., 4(2), 157-166, doi:10.5268/IW-4.2.694(2014), 2014.

Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Dos Santos, M.A. and Matvienko, B.: Carbon dioxide and methane emissions and the carbon budget of a 10-year old tropical reservoir (Petit-Saut. French Guiana), Global Biogeochem. Cy., 19, GB4007. doi:10.1029/2005GB002457. 2005.

Abril, G., Martinez, J.-M., Artigas, L.F., Moreira-Turcq, P., Benedetti, M.F., Vidal L., Meziane, T., Kim, J.-H., Bernardes, M.C., Savoye, N., Deborde, J., Albéric, P., Souza, M.F.L., Souza, E.L. and Roland, F.: Amazon River Carbon Dioxide Outgassing fuelled by Wetlands, Nature 505, 395–398, 2014.

Abril, G., Richard, S. and Guérin, F.: In-Situ measurements of dissolved gases (CO_2 and CH_4) in a wide range of concentrations in a tropical reservoir using an equilibrator, Sc. Total Envir., 354: 246-251, 2006.

Barros, N., Cole, J. J., Tranvik L. J., Prairie Y. T., Bastviken D., Huszar V. L. M., del Giorgio P. and Roland F.: Carbon emission from hydroelectric reservoirs linked to reservoir age and latitude, Nature Geosciences, DOI: 10.1038/NGEO1211, 2011.

Borges, A. V., Bouillon, S., Abril, G., Delille, B., Poirier, D., Commarieu, M.-V., Lepoint, G., Morana, C., Servais, P., Descy, J.-P. and Darchambeau, F.: Variability of carbon dioxide and methane in the epilimnion of Lake Kivu: In J.-P. Descy et al. (eds.). Lake Kivu: Limnology and biogeochemistry of a tropical great lake, Aquatic Ecology Series 5, Springer DOI 10.1007/978-94-007-4243-7_4, 47-66, 2012.

Borges A.V., C. Morana, S. Bouillon, P. Servais, J.-P. Descy, F. Darchambeau, Carbon cycling of Lake Kivu (East Africa): net autotrophy in the epilimnion and emission of

CO_2 to the atmosphere sustained by geogenic inputs, PLoS ONE 9(10): e109500. doi:10.1371/journal.pone.0109500, 2014.

Butman, D. and Raymond, P.A.: Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geosci. 4, 839-842, 2011.

Cai, W.-J., Wang, Y., and Hodson, R. E.: Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA, Geochim. Cosmochim. Ac., 62, 473–483, 1998.

Cai, W.-J., Guo, X., Chen, C.T.A., Dai, M., Zhang, L., Zhai, W., Lohrenz, S.E., Yin, K., Harrison, P.J., Wang, Y.: A comparative overview of weathering intensity and HCO_3^- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. Continental Shelf Research 28(1-2), 1538-1549, 2008.

Cole, J. J., Caraco, N., Kling, G. W., and Kratz, T. K.: Carbon dioxide supersaturation in the surface waters of lakes, Science, 265, 1568–1570, 1994.

Cullison Gray, S. E., DeGranpre, M. E., Moore, T. S., Martz, T. R., Friedrich, G. E. and Johnson, K. S.: Applications of in situ pH measurements for inorganic carbon calculations, Mar. Chem., 125, 82-90, 2011.

Dinsmore, K. J., Wallin M. B., Johnson, M. S., Billett M. F., Bishop, K., Pumpanen, J. and Ojala, A.: Contrasting CO_2 concentration discharge dynamics in headwater streams: A multi-catchment comparison, J. Geophys. Res. Biogeosci., 118, 445–461., doi:10.1002/jgrg.20047, 2012.

Driscoll, C. T., Fuller, R., D. and Schecher, W. D.: The role of organic acids in the acidification of surface waters in the eastern U.S., Water Air and Soil Pollution 43, 21-40, 1989.

Frankignoulle, M., Borges, A. V., and Biondo, R.: A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. Water Res., 35, 1344–1347, 2001.

Frankignoulle, M. and Borges, A. V.: Direct and indirect pCO2 measurements in a wide range of pCO_2 and salinity values. Aquatic Geochemistry, 7, 267-273, 2001.

Gran, G.: Determination of the equivalence point in potentiometric titrations of seawater with hydrochloric acid, Oceanol. Acta, 5, 209-218, 1952.

Guérin, F., Abril, G., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A., and Varfalvy, L.: Gas transfer velocities of CO_2 and CH_4 in a tropical reservoir and its river downstream. J. Mar. Syst., 66, 161-172, 2007.

Harned, H.S., Scholes, S.R.: The ionization constant of HCO_3^- from 0 to 50°C. J. Am. Chem. Soc. 63, 1706–1709, 1941.

Harned H.S. and R.D. Davis: The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°C. J. Am. Chem. Soc. 65: 2030-2037, 1943.

Hemond, H. F.: Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids. Environ. Sci. Technol. 24, 1486–1489, 1990.

Humborg, C., C. M. Mörth, M. Sundbom, H. Borg, T. Blenckner, R. Giesler, and V. Ittekkot (2010), CO_2 supersaturation along the aquatic conduit in Swedish watersheds as constrained by terrestrial respiration, aquatic respiration and weathering, Glob. Change Biol., 16(7), 1966-1978, doi:10.1111/j.1365-2486.2009.02092.x

Hruska, J., S. Köhler, H. Laudon, and Bishop K.: Is a universal model of organic acidity possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones, Environ. Sci. Technol., 37(9), 1726-1730, doi:10.1021/es0201552, 2003.

Hope, D., Dawson, J. J. C., Cresser, M. S. and Billett, M. F.: A method for measuring free CO_2 in upland streamwater using headspace analysis. J. Hydrol., 166, 1–14, 1995.

Hunt, C. W., Salisbury, J. E. and Vandemark, D.: Contribution of non-carbonate anions to total alkalinity and overestimation of pCO_2 in New England and New Brunswick rivers. Biogeosciences, 8, 3069–3076, 2011.

Johnson M.J., Billett M.F., Dinsmore K.J., Wallin M., Dyson K.E. and Jassal R.S.: Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems-method and applications. Ecohydrol. 3, 68–78, 2010.

Kempe, S.: A computer program for hydrochemical problems in karstic water. Annales de Spéléologie 30, 699–702, 1975.

Kempe, S.: Sinks of the anthropogenically enhanced carbon cycle in surface freshwaters. J. Geophys. Res., 89, 4657-4676, 1984.

Kratz, T.K., Schindler, J., Hope, D., Riera, J. L., and Bowser, C. J.: Average annual carbon dioxide concentrations in eight neighboring lakes in northern Wisconsin, USA. Verh. Internat. Verein. Limnol., 26, 335-338, 1997.

Liss, P. S., and Slater P. G,: Flux of gases across the air-sea interface. Nature, 233:327-9, 1974.

Marwick, T.R., Tamooh, F., Ogwoka, B., Teodoru, C., Borges, A. V., Darchambeau, F., and Bouillon S.: Dynamic seasonal nitrogen cycling in response to anthropogenic N loading in a tropical catchment, Athi–Galana–Sabaki River, Kenya, Biogeosciences, 11, 1–18, doi:10.5194/bg-11-1-2014, 2014a

Marwick, T. R., Borges A. V., Van Acker K., Darchambeau F. and Bouillon S.: Disproportionate contribution of riparian inputs to organic carbon pools in freshwater systems, Ecosystems, 17(6), 974-989, doi: 10.1007/s10021-014-9772-6, 2014b.

Meybeck, M.: Global chemical weathering of surficial rocks estimated from river dissolved loads, American J. Science, 287, 401-428, 1987.

Millero, F. J.: The thermodynamics of the carbonic acid system in seawater. Geochim Cosmochim Acta 43:1651-1661, 1979.

Neal, C., House, W.A., Down, K.: An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements, Sc. Total Envir., 210–211, 173–185, 1998.

Park, P. K.: Oceanic CO_2 system: An evaluation of ten methods of investigation, Limnol. Oceanogr. 14, 179-186, 1969.

Parkhurst, D. L. and Appelo, C. A. J.: User's guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US. Geological Survey Water-Resources Investigations Report 99-4259, 312 pp., 1999.

Polsenaere, P., Savoye, N., Etcheber, H., Canton, M., Poirier, D., Bouillon, S. and Abril ,G.: Export and degassing of terrestrial carbon through watercourses draining a temperate podsolised catchment, Aquatic Sciences, 75, 299–319, 2013.

Raymond, P. A., Caraco, N. F. and Cole J. J.: Carbon dioxide concentration and atmospheric flux in the Hudson River, Estuaries 20(2), 381-390, 1997.

Raymond, P. A., Hartmann, J., Lauerwald R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503, 355-359, 2013.

Sobek, S., Tranvik L. J., and Cole, J. J.: Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochem. Cy., 19. GB2003. doi:10.1029/2004GB002264, 2005.

Stumm, W. and Morgan, J. J.: Aquatic Chemistry, Wiley- Interscience, New York, 1996.

Tamooh, F., Borges, A. V., Meysman, F. J. R., Van Den Meersche, K., Dehairs F., Merckx R., and Bouillon S.: Dynamics of dissolved inorganic carbon and aquatic metabolism in the Tana River basin, Kenya, Biogeosciences, 10, 6911-6928, 2013

Teodoru, C. R., del Giorgio P. A., Prairie Y. T., and Camire M., Patterns in pCO_2 in boreal streams and rivers of northern Quebec, Canada, Global Biogeochem. Cycles, 23, GB2012, doi:10.1029/2008GB003404, 2009.

Teodoru C. R., F. C. Nyoni, A. V. Borges, F. Darchambeau, I. Nyambe, and Bouillon S.: Spatial variability and temporal dynamics of greenhouse gas (CO_2, CH_4, N_2O) concentrations and fluxes along the Zambezi River mainstem and major tributaries, Biogeosciences Discussions, 2014.

Vyverman, W.: Limnological Features of Lakes on the Sepik-Ramu Floodplain, Papua New Guinea Aust. J. Mar. Freshwater Res., 45, 1209-1224, 1994.

Wallin, M. B., Löfgren, S., Erlandsson, M. and Bishop, K.: Representative regional sampling of carbon dioxide and methane concentrations in hemiboreal headwater streams reveal underestimates in less systematic approaches. Glob. Biogeochem. Cy. 28, 465-479, 2014.

Wang, Z. A., Bienvenu, D. J., Mann, P. J., Hoering, K. A., Poulsen, J. R., Spencer, R. G. M. and Holmes, R. M. Inorganic carbon speciation and fluxes in the Congo River. Geophys. Res. Lett., 40(3), 511-516, doi:10.1002/grl.50160, 2013.

Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem. 2, 203–215, 1974.

Weiss, R. F.: Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. J Chromatogr Sci 19: 611-616, 1981.

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 (μmol 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	4.53	7.60	385	30	1092	4204	36	18400	155
Kenya	Athi-Galana-Sabaki	25.9	19.8	36.0	307	29	1,133	7.69	6.49	8.57	2290	407	5042	2811	608	10405	44
DRC	Congo	26.3	22.6	28.2	1002	149	3968	6.01	3.94	7.22	212	0	576	6093	1582	15571	97
DRC / Rwanda	Lake Kivu	24.0	23.0	24.7	162	142	201	9.05	8.99	9.17	13037	12802	13338	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	23047	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	10033	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	14244	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	15622	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	14004	107
Entire dataset		24.6	7.9	36.0	408	29	3968	7.00	3.94	9.17	1731	0	14244	3707	36	23047	761

Table 2. Median and average values of dissolved organic carbon (DOC), pH (measured on the NBS scale), total alkalinity (TA), and calculated *minus* measured partial pressure of CO_2 (pCO_2) in the dataset.

	N	% of samples	cal – meas pCO_2 (ppmv)		cal – meas pCO_2 (% of meas pCO_2)		pH		TA (μmol L^{-1})		DOC (μmol 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 pCO_2 as % of measured pCO_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 μmol L^{-1}	110	14%	+20	+340	+2%	+12%	8.58	8.47	7023	8326	163	202
TA 1000-2000 μmol L^{-1}	157	21%	-8	-163	-2%	-9%	7.81	7.83	1566	1534	271	295
TA 500-1000 μmol L^{-1}	99	13%	+1307	+1900	+28%	+72%	6.97	7.11	651	697	304	318
TA < 500 μmol L^{-1}	395	52%	+2070	+20090	+64%	+350%	6.30	6.24	222	232	400	538
TA < 100 μmol L^{-1}	82	11%	+6840	+60560	+230%	+1040%	5.50	5.35	59	56	603	988
Ranked by DOC												
DOC < 200 μmol L^{-1}	179	24%	+40	+776	+5%	+62%	7.89	7.92	1579	4807	163	149
DOC 200-300 μmol L^{-1}	167	22%	+102	+2755	+5%	+69%	7.56	7.37	1132	1259	258	252
DOC 300-400 μmol L^{-1}	165	22%	+887	+4473	+25%	+101%	6.90	6.93	499	866	341	344
DOC > 400 μmol L^{-1}	250	33%	+3070	+27197	+59%	+434%	6.15	6.14	200	415	555	765
DOC > 800 μmol L^{-1}	79	10%	+4995	+62784	+92%	+886%	5.80	5.62	94	180	1099	1438

Figure captions

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

Figure 2. – 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 3. - Plot of carbon variables *versus* 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 4. - Comparison between measured and calculated pCO_2 for the whole dataset; (a) calculated *versus* 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 Figure 3.

Figure 5. - Average percentages of pCO_2 overestimation (calculated as 100 x (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 6. - 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 Figure 3. Note that negative values do not appear in the logarithmic scale.

Figure 1. –

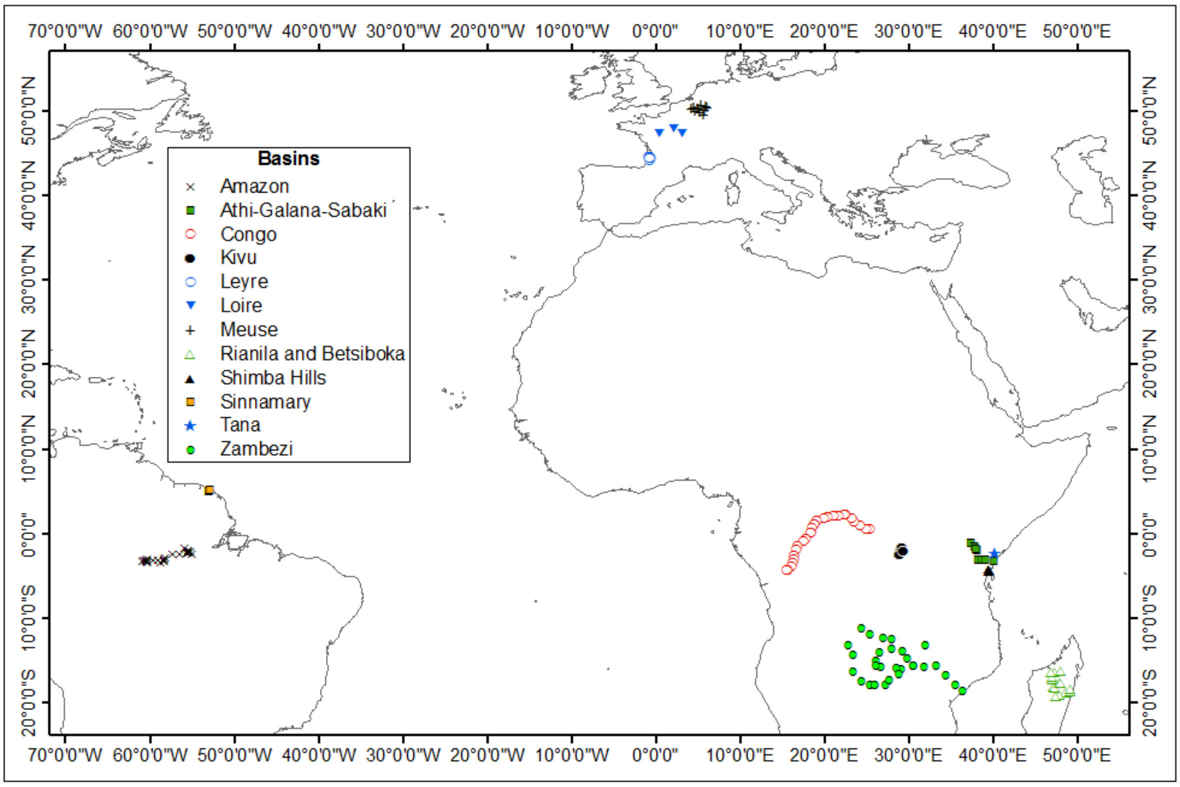

70°0'0"W
60°0'0"W
50°0'0"W
40°0'0"W
30°0'0"W
20°0'0"W
10°0'0"W
0°0'0"
10°0'0"E
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
50°0'0"N
40°0'0"N
30°0'0"N
20°0'0"N
10°0'0"N
0°0'0"
10°0'0"S
20°0'0"S
Basins
× Amazon
■ Athi-Galana-Sabaki
○ Congo
● Kivu
○ Leyre
▼ Loire
+ Meuse
△ Rianila and Betsiboka
▲ Shimba Hills
■ Sinnamary
★ Tana
● Zambezi

Figure 2. –

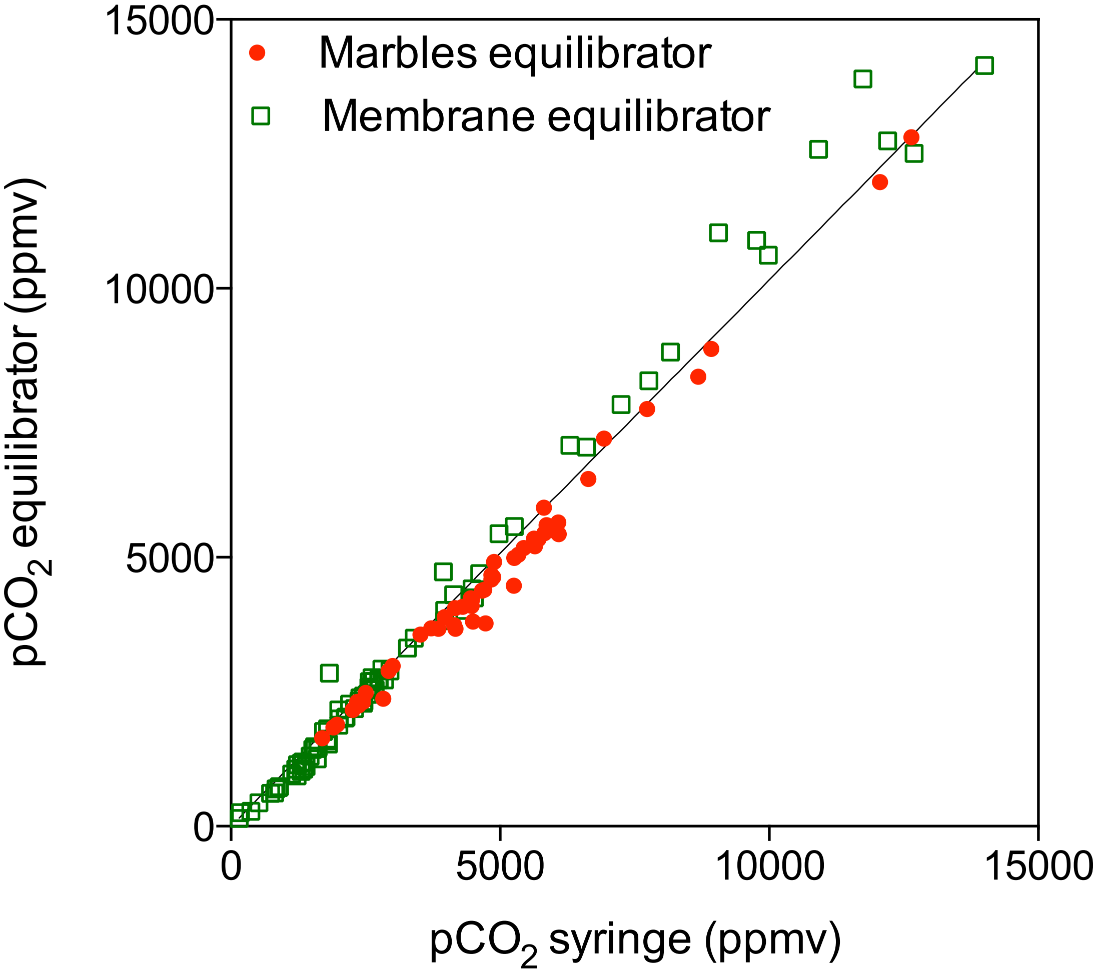

15000
10000
5000
0
0
5000
10000
15000
Marbles equilibrator
Membrane equilibrator
pCO2 equilibrator (ppmv)
pCO2 syringe (ppmv)

Figure 3. –

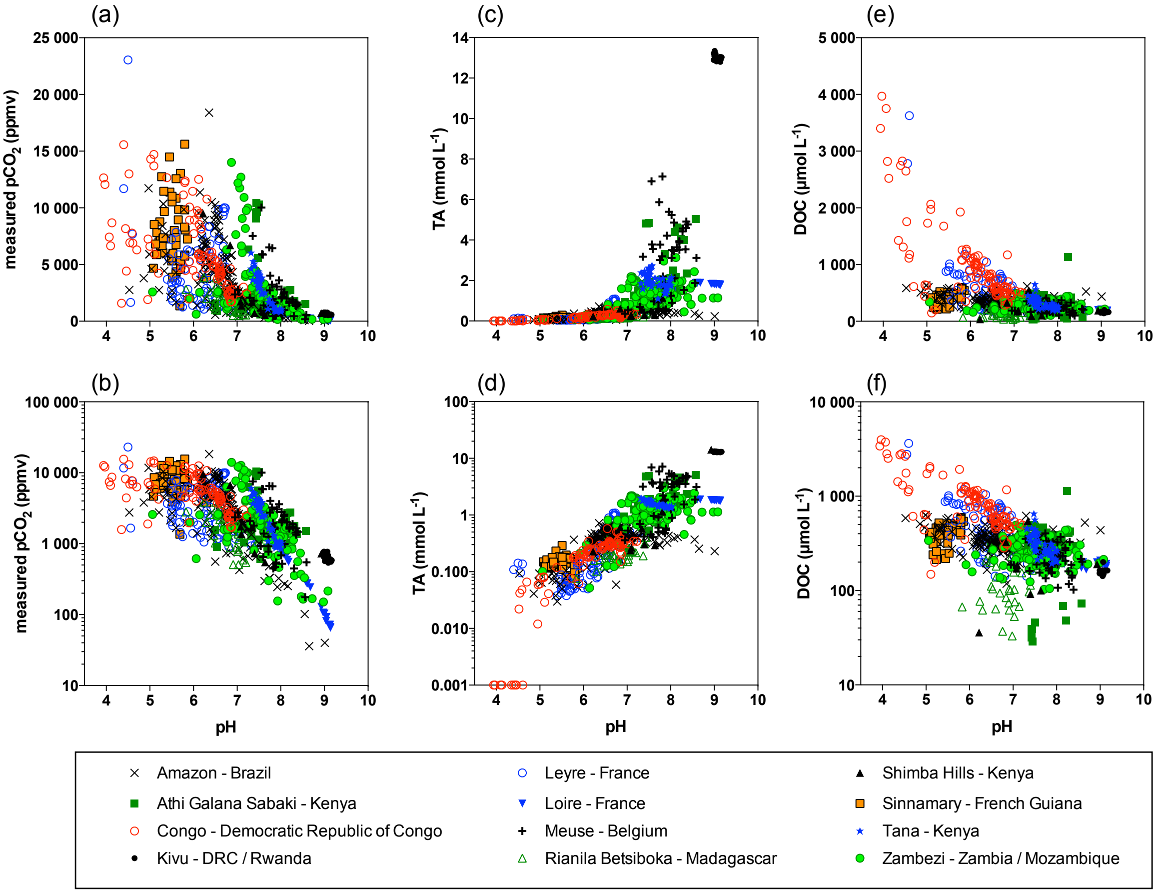

(a)
measured pCO$_2$ (ppmv)
25 000
20 000
15 000
10 000
5 000
0
4
5
6
7
8
9
10
(b)
measured pCO$_2$ (ppmv)
100 000
10 000
1 000
100
10
pH
(c)
TA (mmol L^{-1})
14
12
10
8
6
4
2
0
(d)
TA (mmol L^{-1})
100
10
1
0.100
0.010
0.001
pH
(e)
DOC (µmol L^{-1})
5 000
4 000
3 000
2 000
1 000
0
(f)
DOC (µmol L^{-1})
10 000
1 000
100
10
pH
Amazon - Brazil
Athi Galana Sabaki - Kenya
Congo - Democratic Republic of Congo
Kivu - DRC / Rwanda
Leyre - France
Loire - France
Meuse - Belgium
Rianila Betsiboka - Madagascar
Shimba Hills - Kenya
Sinnamary - French Guiana
Tana - Kenya
Zambezi - Zambia / Mozambique

Figure 4. –

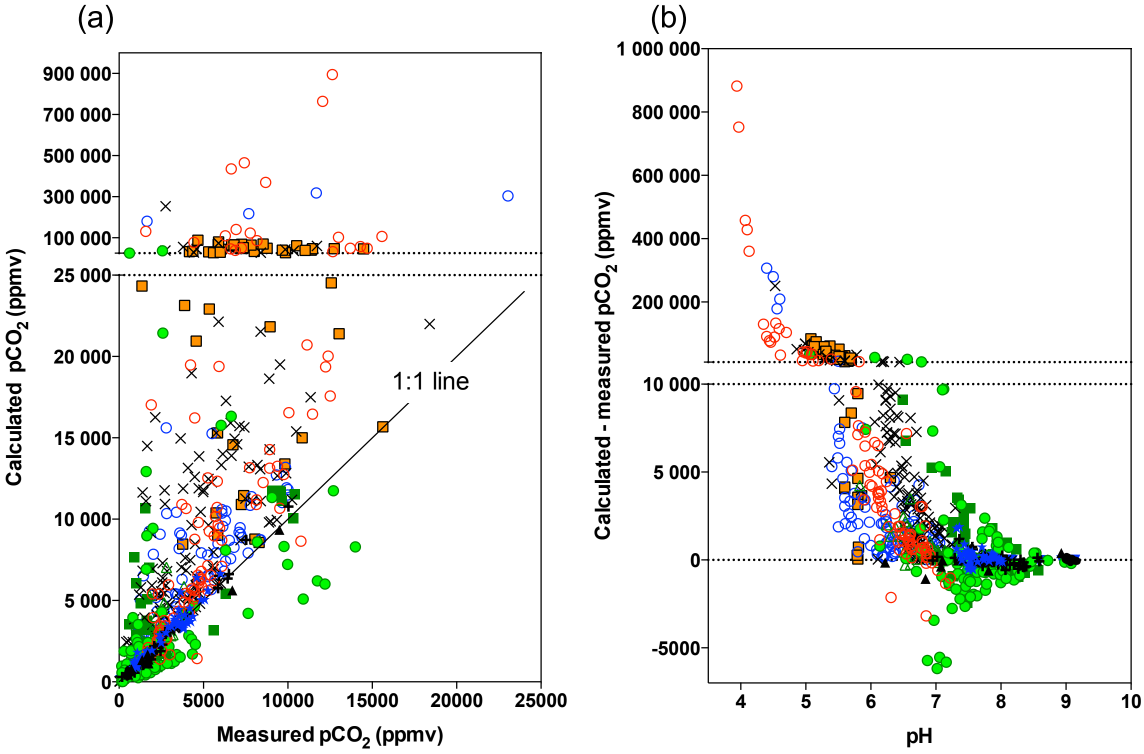
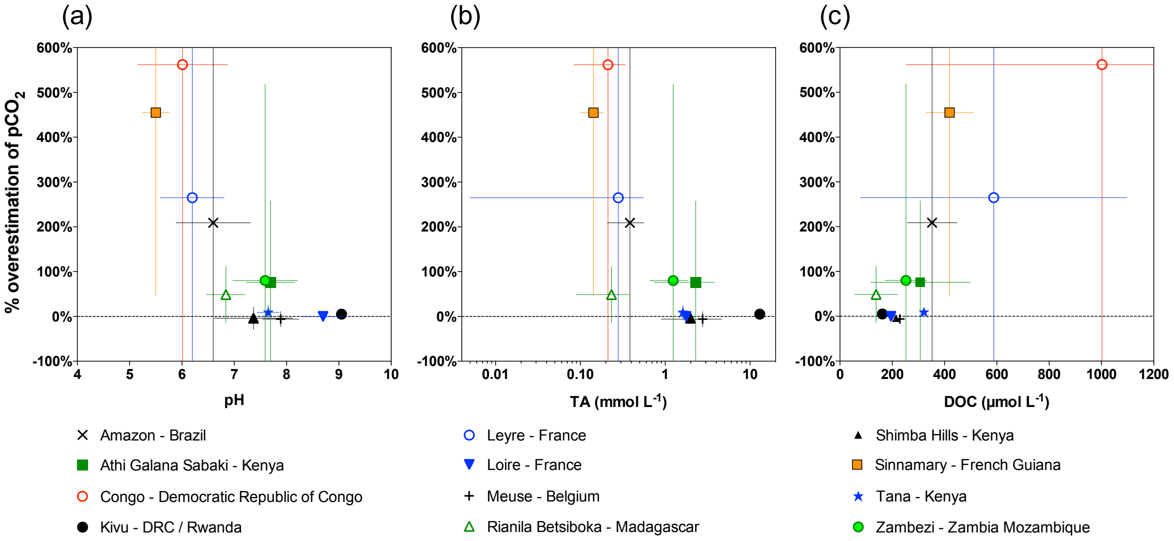
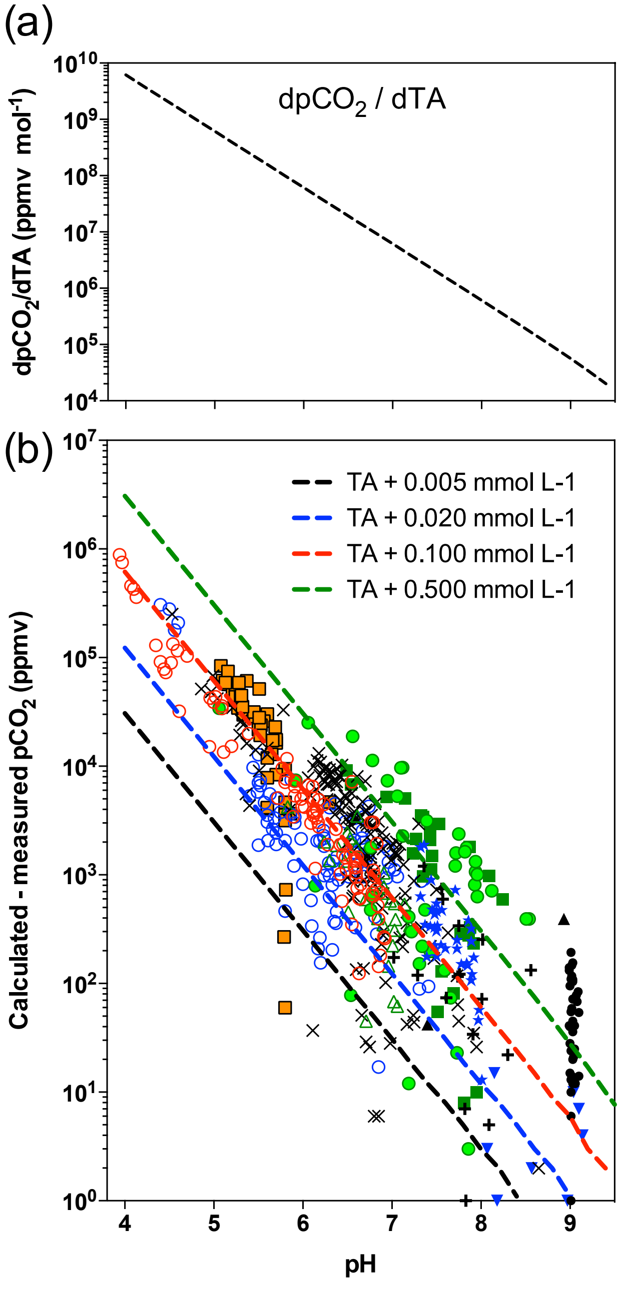

(a)
900 000
700 000
500 000
300 000
100 000
25 000
20 000
15 000
10 000
5 000
0
Calculated pCO$_2$ (ppmv)
1:1 line
0
5000
10000
15000
20000
25000
Measured pCO$_2$ (ppmv)
(b)
1 000 000
800 000
600 000
400 000
200 000
10 000
5 000
0
-5000
Calculated - measured pCO$_2$ (ppmv)
4
5
6
7
8
9
10
pH

Figure 5. –



(a)
(b)
(c)
% overestimation of pCO$_2$
600%
500%
400%
300%
200%
100%
0%
-100%
4
5
6
7
8
9
10
pH
0.01
0.10
1
10
TA (mmol L^{-1})
0
200
400
600
800
1000
1200
DOC (µmol L^{-1})
× Amazon - Brazil
■ Athi Galana Sabaki - Kenya
○ Congo - Democratic Republic of Congo
● Kivu - DRC / Rwanda
○ Leyre - France
▼ Loire - France
+ Meuse - Belgium
△ Rianila Betsiboka - Madagascar
▲ Shimba Hills - Kenya
■ Sinnamary - French Guiana
★ Tana - Kenya
● Zambezi - Zambia Mozambique

Figure 6. –


(a)
dpCO$_2$ / dTA
dpCO$_2$/dTA (ppmv mol^{-1})
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
(b)
TA + 0.005 mmol L-1
TA + 0.020 mmol L-1
TA + 0.100 mmol L-1
TA + 0.500 mmol L-1
Calculated - measured pCO$_2$ (ppmv)
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
4
5
6
7
8
9
pH