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

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Abstract

Inland waters have been recognized as a significant source of carbon dioxide (CO$_2$) to the atmosphere at the global scale. Fluxes of CO$_2$ between aquatic systems and the atmosphere are calculated from the gas transfer velocity and the water-air gradient of the partial pressure of CO$_2$ (pCO$_2$). 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.
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. Frankignouille 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 pCO₂ values were linearly correlated but showed a variability of ±500 ppmv around the 1:1 line, over a range of measured pCO₂ from 300 to 4000 ppmv. Later, Frankignoulle and Borges (2001) reported the first comparison of pCO₂ calculated from pH and TA and pCO₂ 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 pCO₂ being either overestimated or underestimated, but always by less than 7%. In 2003, concomitant measurements of pH, TA and pCO₂ were performed in acidic, humic-rich (“black” type) waters of the Sinnamary River in French Guiana (Abril et al. 2005; 2006). Calculation of pCO₂ 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 CO₂ and CH₄ outgassing fluxes with floating chambers and the computation of the respective gas transfer velocities of these two gases (Guérin et al. 2007) confirmed that pCO₂ 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 pCO₂. Butman and Raymond (2011) reported higher calculated than measured pCO₂ 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 pCO₂ determination in freshwaters globally, and given the apparent simplicity and low cost of pH and TA measurements, the number of publications that report calculated pCO₂ in freshwaters has increased dramatically in the last decade. Some
of these publications report extremely high and potentially biased pCO₂ 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, pCO₂, and DOC in freshwaters. This is the first comprehensive dataset to investigate
the magnitude of the bias between calculated and measured pCO₂, 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 pCO₂ 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 pCO₂
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 pCO₂,
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 Loire River
and tributaries 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 CO₂ 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 pCO₂. 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 µmol 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$_3^{-}$.
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 CO₂ 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 H₃PO₄ 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 CO₂ 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 pCO₂ calculation from pH and TA

We calculated pCO₂ 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 CO₂ solubility from Weiss (1974) as implemented in the CO2SYS program. Hunt et al. (2011) reported discrepancy lower than 2% for pCO₂ 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 pCO₂ compared to measured pCO₂ we report in this paper.

3 Results

3.1 Data ranges and patterns in the entire dataset

Measured pCO₂ 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 pCO₂ 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 pCO₂

Calculated pCO₂ was more than 10% lower than measured pCO₂ in 16% of the samples; both methods were consistent at ±10% in 24% of the samples; calculated pCO₂ was more than 10% higher than measured pCO₂ 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 pCO₂ data being well above the 1:1 line, and calculated minus measured pCO₂ values ranging between -6180 ppmv and +882022 ppmv (Fig. 4). The largest overestimation of calculated pCO₂ occurred in the most acidic samples, whereas underestimations of calculated pCO₂ occurred in neutral or slightly basic samples (Fig. 4b). Ranking the data according to the pH, TA and DOC reveal that overestimation of calculated pCO₂ compared to measured pCO₂ increased in acidic, poorly buffered waters in parallel with an increase in the DOC concentration (Table 2). Discrepancies between calculated and measured pCO₂ 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 pCO₂ decreased with pH and TA and increased with DOC (Fig. 5). Overestimation of calculated pCO₂ 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
pCO₂ 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 pCO₂ of 50-90% (Fig. 5).

4 Discussion

4.1 Origin of overestimation of calculated pCO₂

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 pCO₂ 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 $\text{dpCO}_2/\text{dTA}$ (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 pCO₂ 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 pCO₂ measurements with very stable gas analysers.

4.2 Impact on estimates of CO₂ emissions from freshwaters

According to our analysis, overestimation of calculated pCO₂ is largest in acidic, poorly buffered and organic-rich waters. Consequently, the overestimation of regional and global CO₂ emissions computed from calculated pCO₂ depends on the relative contribution of these types of waters worldwide. In their analysis, Raymond et al. (2013) have discarded all calculated pCO₂ values with a pH value of less than 5.4, as well as all pCO₂ 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 pCO₂ 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 pCO₂ affected by bias from those consistent with measured pCO₂ (Table 2). In fact, pCO₂ 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 $\mu$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 $\mu$mol L$^{-1}$ for world rivers and around 600 $\mu$mol L$^{-1}$ for tropical rivers. Among the 25 largest rivers in the world, 15 have a TA > 1000 $\mu$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 $\mu$mol 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 $\mu$mol 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 $\mu$mol 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 $\mu$mol 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

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the Fonds National de la Recherche Scientifique (FNRS, CAKI, 2.4.598.07, TransCongo, 1471103), 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.
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Table 1. Summary of the presented dataset. Average, minimum and maximum values of temperature, dissolved organic carbon (DOC), pH (measured on the NBS scale), total alkalinity (TA) and measured partial pressure of CO$_2$ (pCO$_2$) in the different freshwater ecosystems.

<table>
<thead>
<tr>
<th>Country</th>
<th>Watersheds</th>
<th>Temperature (°C)</th>
<th>DOC (µmol L$^{-1}$)</th>
<th>pH (NBS scale)</th>
<th>TA (µmol L$^{-1}$)</th>
<th>Measured pCO$_2$ (ppmv)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>Amazon</td>
<td>Av. 30.3 Min. 27.4 Max. 34.3</td>
<td>Av. 352 Min. 118 Max. 633</td>
<td>Av. 6.60 Min. 4.53 Max. 7.60</td>
<td>Av. 385 Min. 30 Max. 1092</td>
<td>Av. 4204 Min. 36 Max. 18400</td>
<td>155</td>
</tr>
<tr>
<td>Kenya</td>
<td>Athi-Galana-Sabaki</td>
<td>25.9 19.8 36.0</td>
<td>307 29 1.13 3</td>
<td>7.69 6.49 8.57</td>
<td>2290 407 5042</td>
<td>2811 608 10405</td>
<td>44</td>
</tr>
<tr>
<td>DRC</td>
<td>Congo</td>
<td>26.3 22.6 28.2</td>
<td>1002 149 3968</td>
<td>6.01 3.94 7.22</td>
<td>212 0 576</td>
<td>6093 1582 15571</td>
<td>97</td>
</tr>
<tr>
<td>DRC / Rwanda</td>
<td>Lake Kivu</td>
<td>24.0 23.0 24.7</td>
<td>162 142 201</td>
<td>9.05 8.99 9.17</td>
<td>13037 12802 13338</td>
<td>660 537 772</td>
<td>53</td>
</tr>
<tr>
<td>France</td>
<td>Leyre</td>
<td>12.5 7.9 19.2</td>
<td>588 142 3625</td>
<td>6.20 4.40 7.41</td>
<td>280 38 1082</td>
<td>4429 901 23047</td>
<td>92</td>
</tr>
<tr>
<td>France</td>
<td>Loire</td>
<td>15.5 8.8 19.3</td>
<td>195 167 233</td>
<td>8.70 8.07 9.14</td>
<td>1768 1579 1886</td>
<td>284 65 717</td>
<td>18</td>
</tr>
<tr>
<td>Belgium</td>
<td>Meuse</td>
<td>18.1 13.3 25.9</td>
<td>229 102 404</td>
<td>7.89 6.95 8.59</td>
<td>2769 360 7141</td>
<td>2292 176 10033</td>
<td>50</td>
</tr>
<tr>
<td>Madagascar</td>
<td>Rianila and Betsiboka Shimbila Hills</td>
<td>25.4 20.2 29.5</td>
<td>138 33 361</td>
<td>6.84 5.83 7.62</td>
<td>233 76 961</td>
<td>1701 508 3847</td>
<td>36</td>
</tr>
<tr>
<td>Kenya</td>
<td>Tana</td>
<td>26.6 25.0 27.9</td>
<td>321 193 651</td>
<td>7.65 7.32 8.02</td>
<td>1619 1338 2009</td>
<td>2700 845 6014</td>
<td>51</td>
</tr>
<tr>
<td>Zambia / Mozambique</td>
<td>Zambezi</td>
<td>26.9 18.8 31.8</td>
<td>252 103 492</td>
<td>7.59 5.06 9.08</td>
<td>1245 52 3134</td>
<td>2695 151 14004</td>
<td>107</td>
</tr>
<tr>
<td>Entire dataset</td>
<td></td>
<td>24.6 7.9 36.0</td>
<td>408 29 3968</td>
<td>7.00 3.94 9.17</td>
<td>1731 0 14244</td>
<td>3707 36 23047</td>
<td>761</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>N % of samples</th>
<th>cal – meas pCO$_2$ (ppmv)</th>
<th>cal – meas pCO$_2$ (% of meas pCO$_2$)</th>
<th>pH</th>
<th>TA (µmol L$^{-1}$)</th>
<th>DOC (µmol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All samples</td>
<td>761</td>
<td>100%</td>
<td>Med.</td>
<td>+611</td>
<td>Av. +10692</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+23%</td>
<td>+194%</td>
<td>6.94</td>
</tr>
</tbody>
</table>
| Rank by calculated-measured pCO$_2$ as % of measured pCO$_2$
| < -10%         | 122                       | 16%                                    | -34% | -36%               | 7.89                | 1269              | 259               |
|                |                           |                                        | 7.85 | 1269               | 1766               | 259               |
| ± 10%          | 174                       | 23%                                    | +2%  | +1%                | 7.67                | 1576              | 228               |
| > +10%         | 465                       | 61%                                    | +72% | +327%              | 6.52                | 308               | 360               |
| > +50%         | 280                       | 37%                                    | +162%| +526%              | 6.18                | 192               | 375               |
| > +100%        | 199                       | 26%                                    | +270%| +710%              | 5.89                | 166               | 389               |
| Rank by pH
| pH > 7         | 368                       | 48%                                    | +1%  | +15%               | 7.82                | 1572              | 231               |
| pH < 7         | 393                       | 52%                                    | +71% | +362%              | 6.30                | 232               | 413               |
| pH 6-7         | 256                       | 34%                                    | +40% | +96%               | 6.58                | 334               | 350               |
| pH < 6         | 136                       | 18%                                    | +308%| +864%              | 5.50                | 93                | 487               |
| pH < 5         | 25                        | 3%                                     | +115580| +209910          | +1645%              | +3180%            | 4.53              | 41                | 1427 | 1,843 |
| Rank by TA
| TA > 2000 µmol L$^{-1}$ | 110                       | 14%                                    | +2%  | +12%               | 8.58                | 7023              | 163               |
| TA 1000-2000 µmol L$^{-1}$ | 157 | 21% | -8  | -163               | -2%  | -9%               | 7.81              | 1566              | 271               |
| TA 500-1000 µmol L$^{-1}$ | 99  | 13% | +1307 | +1900              | +28% | +72%               | 6.97              | 651               | 304               |
| TA < 500 µmol L$^{-1}$ | 395 | 52% | +2070 | +20090              | +64% | +350%              | 6.30              | 222               | 400               |
| TA < 100 µmol L$^{-1}$ | 82  | 11% | +6840 | +60560              | +230%| +1040%             | 5.50              | 59                | 603               |
| Rank by DOC
| DOC < 200 µmol L$^{-1}$ | 179 | 24% | +440 | +776               | +5%  | +62%               | 7.89              | 1579              | 163               |
| DOC 200-300 µmol L$^{-1}$ | 167 | 22% | +102 | +2755              | +5%  | +69%               | 7.56              | 1132              | 258               |
| DOC 300-400 µmol L$^{-1}$ | 165 | 22% | +887 | +4473              | +25% | +101%              | 6.90              | 499               | 341               |
| DOC > 400 µmol L$^{-1}$ | 250 | 33% | +3070 | +27197              | +59% | +434%              | 6.15              | 200               | 555               |
| DOC > 800 µmol L$^{-1}$ | 79  | 10% | +4995 | +62784              | +92% | +886%              | 5.80              | 94                | 1099              |
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 pCO₂ measurements; pCO₂ measured with a marbles equilibrator (Congo) and with a membrane equilibrator (Congo and Zambezi) are plotted against pCO₂ 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 pCO₂; (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 pCO₂ scale. Rianila and Bestiboka are plotted together although they belong to different watersheds in Madagascar.

Figure 4. - Comparison between measured and calculated pCO₂ for the whole dataset; (a) calculated versus measured pCO₂, the line shows when measured pCO₂ equals calculated pCO₂; (b) the difference between calculated and measured pCO₂ as a function of pH; same symbols as in Figure 3.

Figure 5. - Average percentages of pCO₂ overestimation (calculated as 100 x (calculated pCO₂-measured pCO₂)/measured pCO₂, 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 pCO₂ overestimation to pH; (a) theoretical factor dpCO₂ / dTA, which describes the sensitivity of calculated pCO₂ to the TA value; (b) the solid lines show the increase in calculated pCO₂ induced by various increases in TA, as functions of pH; these lines mimic the overestimation of calculated pCO₂ generated by increasing contributions of organic alkalinity to the TA; field data (as calculated – measured pCO₂) have been plotted for
comparison; same symbols as in Figure 3. Note that negative values do not appear in the logarithmic scale.
Figure 2.

- $p_{CO_2}$ equilibrator (ppmv) vs. $p_{CO_2}$ syringe (ppmv)

- Marbles equilibrator
- Membrane equilibrator
Figure 3.
Figure 4. –

(a) Calculated vs. measured pCO$_2$ (ppmv)

(b) Calculated - measured pCO$_2$ (ppmv) vs. pH
Figure 5.

(a) Amazon - Brazil
- Afri Galana Sabaki - Kenya
- Congo - Democratic Republic of Congo
- Kib - DRC / Rwanda

(b) Leyre - France
- Loire - France
- Mouse - Belgium
- Rania Betsiboka - Madagascar

(c) Shinba Hills - Kenya
- Sinnamary - French Guiana
- Tana - Kenya
- Zambezi - Zambia Mozambique
Figure 6. –

(a) $\frac{dpCO_2}{dT}\text{A}$

(b) Calculated - measured $pCO_2$ (ppmv)