



# Reviews of Geophysics

## REVIEW ARTICLE

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### Key Points:

- In terms of carbon fluxes, high cumulative contributions of headwater streams are currently underrepresented in the global carbon cycle
- Representative quantification of carbon dioxide outgassing from headwater streams on a global scale is an important future challenge
- A global analysis of small catchment chemistry revealed substantial influences of trace carbonate weathering on stream carbon budgets

### Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3

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## A review of CO<sub>2</sub> and associated carbon dynamics in headwater streams: A global perspective

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**Abstract** Terrestrial carbon export via inland aquatic systems is a key process in the global carbon cycle. It includes loss of carbon to the atmosphere via outgassing from rivers, lakes, or reservoirs and carbon fixation in the water column as well as in sediments. This review focuses on headwater streams that are important because their stream biogeochemistry directly reflects carbon input from soils and groundwaters. Major drivers of carbon dioxide partial pressures ( $p\text{CO}_2$ ) in streams and mechanisms of terrestrial dissolved inorganic, organic and particulate organic carbon (DIC, DOC, and POC) influxes are summarized in this work. Our analysis indicates that the global river average  $p\text{CO}_2$  of 3100 ppmV is more often exceeded by contributions from small streams when compared to rivers with larger catchments ( $> 500 \text{ km}^2$ ). Because of their large proportion in global river networks ( $> 96\%$  of the total number of streams), headwaters contribute large—but still poorly quantified—amounts of CO<sub>2</sub> to the atmosphere. Conservative estimates imply that globally 36% (i.e.,  $0.93 \text{ Pg C yr}^{-1}$ ) of total CO<sub>2</sub> outgassing from rivers and streams originate from headwaters. We also discuss challenges in determination of CO<sub>2</sub> sources, concentrations, and fluxes. To overcome uncertainties of CO<sub>2</sub> sources and its outgassing from headwater streams on the global scale, new investigations are needed that should include groundwater data. Such studies would also benefit from applications of integral CO<sub>2</sub> outgassing isotope approaches and multiscale geophysical imaging techniques.

## 1. Introduction

Although water fluxes in river systems typically increase along river courses, much less carbon reaches the oceans than terrestrial aquatic ecosystems initially export to continental surface waters [Aufdenkampe et al., 2011; Cole et al., 2007; Kempe, 1982, 1984; Regnier et al., 2013; Wehrli, 2013]. This discrepancy results from carbon burial and aquatic carbon turnover, such as the mineralization of organic matter to CO<sub>2</sub> and its outgassing to the atmosphere. Excluding the amount of CO<sub>2</sub> outgassing from lakes and reservoirs as determined by Raymond et al. [2013] yields a recent estimate of 2.58 petagrams (Pg) CO<sub>2</sub> yr<sup>−1</sup> for rivers and streams alone [Sawakuchi et al., 2017]. This constitutes 45% of the global carbon transfer from terrestrial ecosystems to streams and rivers [Raymond et al., 2013], with potentially large amounts of carbon outgassing from headwater regions.

In order to outline uncertainties of such global CO<sub>2</sub> losses by rivers, it is worth to consider the Amazon as the biggest river system worldwide. A study on CO<sub>2</sub> outgassing only from Amazon first-order streams was determined with  $0.1 \text{ Pg C yr}^{-1}$  [Johnson et al., 2008]. This 9 year-old estimate incorporates uncertainties of spatial variations, and if investigated at more detail, this number is likely underestimated. Another study included the total surface area of the lower reaches of the Amazon River and estimated a CO<sub>2</sub> outgassing rate of  $1.39 \text{ Pg C yr}^{-1}$  [Sawakuchi et al., 2017]. They stated a 43% higher CO<sub>2</sub> outgassing from global inland waters (streams, rivers, lakes, and reservoirs) than estimated by Raymond et al. [2013]. The number by Sawakuchi et al. [2017] corresponds to a contribution of 54% to global river and stream CO<sub>2</sub> outgassing by the Amazon River alone. This is remarkable because its surface area is only 3% of the estimated global river surface area [Downing et al., 2012]. Such recent and ever upward revised global numbers are also confirmed by Ward et al. [2017] and outline why quantifications of CO<sub>2</sub> outgassing from rivers and streams is a major unknown factor in global carbon budgets for inland waters.

In terms of CO<sub>2</sub> outgassing intensities, the occurrence of disproportionately large contributions of CO<sub>2</sub> from streams in tropical areas was emphasized based on results by *Sawakuchi et al.* [2017]. However, the available tropical data are still limited to only a few areas [*Bouillon et al.*, 2007; *Sawakuchi et al.*, 2017; *Wit et al.*, 2015]. In addition to insufficient data on tropical areas, the global-scale quantification of CO<sub>2</sub> outgassing from small headwater streams is a future research challenge. This is in agreement with uncertainties and complexities of headwaters that were observed by other studies [*Halbedel and Koschorreck*, 2013; *Johnson et al.*, 2008; *Oquist et al.*, 2009; *Teodoru et al.*, 2009; *Wallin et al.*, 2013].

The atmosphere had a global average  $p\text{CO}_2$  of 400  $\mu\text{atm}$  in 2015 [*National Oceanic and Atmospheric Administration/Earth System Research Laboratory—Global Monitoring Division (ESRL/GMD)*, 2016]. For comparison, *Raymond et al.* [2013] showed that 95% of median river  $p\text{CO}_2$  values exceed this average atmospheric pressure, based on 6708 stream and river sampling locations worldwide. This trend was confirmed by *Regnier et al.* [2013], who reported that 82% of inland waters have CO<sub>2</sub> concentrations at least twice that of the atmosphere. In their study, *Raymond et al.* [2013] calculated a median  $p\text{CO}_2$  value of  $\sim 3100 \mu\text{atm}$  for streams and rivers with high uncertainties, particularly for lower-order streams. Similar studies by *Lauerwald et al.* [2015] excluded anthropogenically influenced stations and suggested a global average of  $\sim 2400 \mu\text{atm}$  for rivers and streams with Strahler stream orders above 2 (defined according to Strahler with 1 for smallest stream [*Strahler*, 1952]). Even though CO<sub>2</sub> concentrations in rivers and streams have been extensively investigated [*Aufdenkampe et al.*, 2011; *Cole et al.*, 2007; *Kempe*, 1982, 1984; *Lauerwald et al.*, 2015; *Raymond et al.*, 2013], sources and relative contributions by groundwaters and soil waters as well as within stream processing remain largely unknown.

Large error margins in global carbon losses can be explained by difficulties in defining river surface areas and by variable outgassing constants. Here we hypothesize that contributions from small streams with Strahler numbers below 3 and headwaters are another uncertainty to global carbon budgets. For instance, by excluding these streams, *Lauerwald et al.* [2015] estimated a global outgassing rate of 0.65 Pg C yr<sup>-1</sup> for the remainder of rivers worldwide and of 0.36 Pg C yr<sup>-1</sup> when excluding the Amazon River. Adding the latter value to the improved number for the lower part of the Amazon (1.29 Pg C yr<sup>-1</sup>) [*Sawakuchi et al.*, 2017] yields a global estimate of 1.65 Pg C yr<sup>-1</sup>. Subtracting this number for higher order streams from the 2.58 Pg C yr<sup>-1</sup> total contribution by all rivers and streams worldwide [*Sawakuchi et al.*, 2017] yields a CO<sub>2</sub> loss globally of 0.93 Pg C yr<sup>-1</sup> (i.e., about 36%) from headwater streams and 1.15 Pg C yr<sup>-1</sup> (i.e., about 64%) when using the estimate by *Raymond et al.* [2013]. These numbers are only rough estimates, but their range and considerable percentages show that smaller-order streams remain insufficiently represented in estimates of the global carbon cycle. This is although several individual studies have suggested that they are important emitters of CO<sub>2</sub> [*Aufdenkampe et al.*, 2011; *Cole et al.*, 2007; *Halbedel and Koschorreck*, 2013; *Lauerwald et al.*, 2015; *Raymond et al.*, 2013]. This lack of quantification is mostly attributed to limitations in global compilations of often remotely located streams with unknown spatiotemporal variations in terms of CO<sub>2</sub> outgassing.

This hypothesis is also strengthened by the fact that headwater streams and their catchments drain substantial proportions of the continental surface [*Barmuta et al.*, 2009]. For instance, headwater streams with a catchment size of less than 15 km<sup>2</sup> were found to comprise 90% of the total stream length in Sweden [*Bishop et al.*, 2008]. In another study, *Barmuta et al.* [2009] determined that small streams cover more than 75% of the entire drainage network in a river basin. Considering the large number of headwater catchments worldwide, they likely function as important elements in the global carbon balance.

With this work, we aim to summarize and discuss current knowledge gaps about carbon cycling, particularly in headwater streams. With data from the literature and from the Global River Chemistry database (GLORICH) by *Hartmann et al.* [2014], we compiled weathering dynamics and their classifications of headwater catchments and compared them to larger rivers and their current global averages. A so far open question is the role of carbonate- versus silicate-dominated catchments and their relative contributions toward carbon export. The weathering behavior of small headwater catchments may be different than those of entire river basins. Carbon fluxes from headwaters also vary in terms of climatic boundary conditions and soil types. For instance, a tropical carbonate catchment with thick soils is likely to have much more active carbon processing than a hard rock catchment in colder climates. While such differences are obvious, they are not systematically quantified. We therefore outline mechanisms of terrestrial organic and inorganic carbon fluxes with a focus on headwater streams.

In order to improve future attempts in quantifying the global carbon cycle, this work also reviews the most important mechanisms of headwater stream CO<sub>2</sub> dynamics. Understanding related measurement strategies is an important step to close knowledge gaps of carbon cycling in headwaters. This is also discussed together with isotope applications that can help to unravel carbon dynamics in streams. With this, the work presented here helps to establish a basis for future modeling approaches about carbon cycling in small catchments and for better evaluation of global carbon budgets.

## 2. Carbon Balances of Headwater Streams

On a global scale, one important feature of headwater catchments is that many of them are located in remote and pristine environments where anthropogenic influences from urban, industrial, and agricultural activities are low and often negligible. This positioning allows for a simplified carbon mass balance with negligible secondary anthropogenic influences [Cole *et al.*, 2007]:

$$I = G + S + E \quad (1)$$

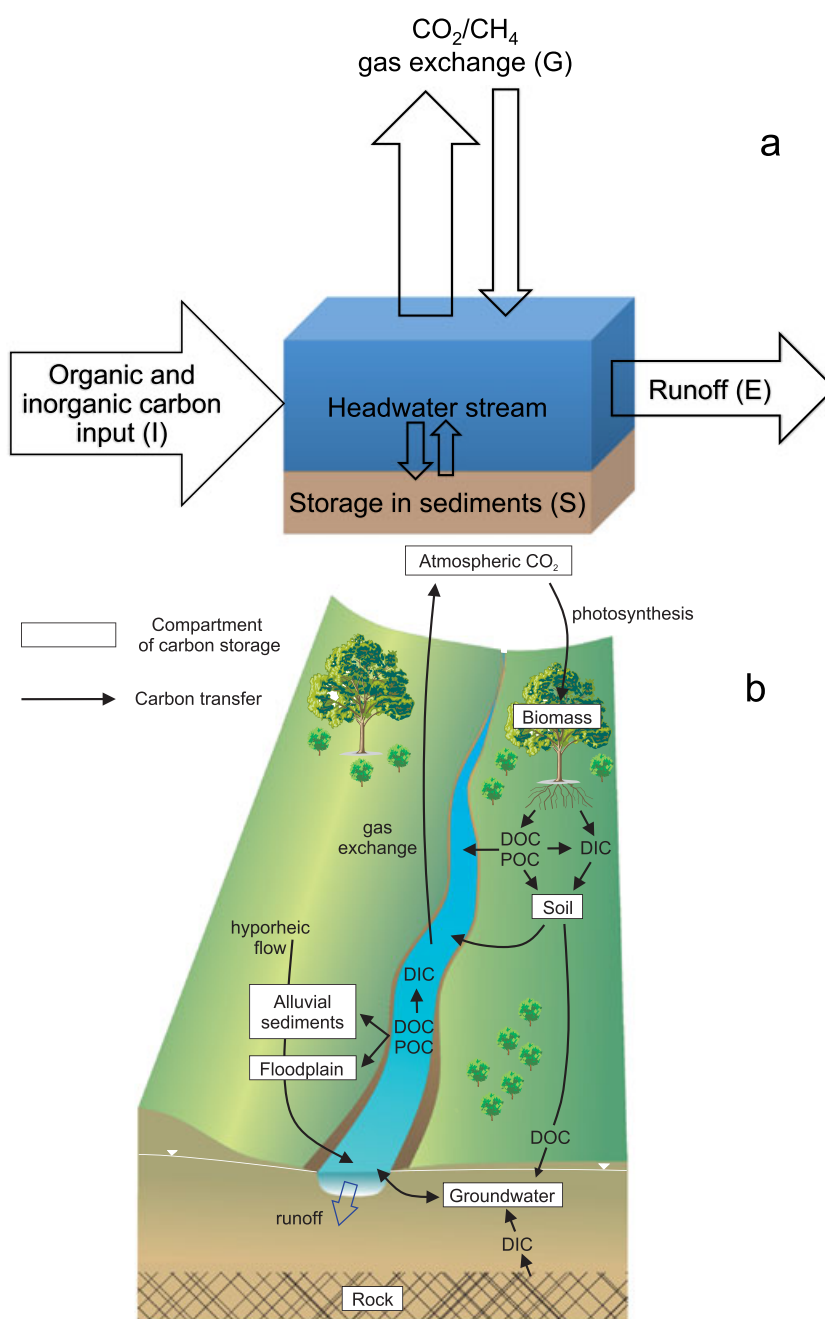
where  $I$  is the carbon imported from the catchment,  $G$  is the net carbon gas exchange of the headwater stream (mostly CO<sub>2</sub>) with the atmosphere,  $S$  is the carbon storage in sediments and wetland soils, and  $E$  is the long-term sum of all carbon phases exported via stream discharge. This scheme is displayed in Figure 1. Note that all variables have the same unit and are typically expressed in Pg C yr<sup>-1</sup>.

Such mass balances are essential to understand global carbon budgets. In this review, we particularly focus on  $G$  that is difficult to determine. The terrestrial input  $I$  to streams consists of both organic and inorganic carbon that are imported from land surfaces, soil waters, and aquifers. A conservative estimate by Cole *et al.* [2007] indicates that these inputs represent 50% to 70% of the total terrestrial net ecosystem production. The latter is defined as the portion of carbon gained via the photosynthetic assimilation of atmospheric CO<sub>2</sub> that is not mineralized in soils or in the geosphere. Note that the term  $I$  is so far not well known. This is because vegetation patterns, runoff generation, and associated carbon transport into the stream may vary considerably between headwater catchments. Nonetheless, many streams have smaller carbon exports via runoff ( $E$ ) than the amount of carbon that is imported from the catchment ( $I$ ). This argues for the fact that they actively process aquatic carbon. This processing often leads to CO<sub>2</sub> and CH<sub>4</sub> emissions to the atmosphere ( $G$ ), carbon burial in sediments ( $S$ ), as well as in-stream bioproduction, biodegradation, and photodegradation.

## 3. Carbon Contributions to Streams

### 3.1. Organic Carbon

Organic carbon in streams occurs in particulate or dissolved forms (POC or DOC, respectively). POC is defined as the fraction that is retained by a filter with a 0.45 μm pore size [Thurman, 1985]. Often 0.7 μm pore size filters are used, and thus, small amounts of the POC may become shifted into the DOC pool. This shift can be corrected if DOC and POC are considered together in complete carbon balances. POC includes detrital particles, aggregates, and living organisms, such as phytoplankton, yeasts, micro-zooplankton, and bacteria [Hope *et al.*, 1994; Wetzel, 2001]. In streams, the size of POC is reduced by mechanical abrasion and biological turnover. These processes contribute to the autochthonous input of DOC within streams, where biotic processing tends to substantially decrease the size of the POC pool [Meyer and Tate, 1983; Naiman, 1982]. The mobilization of POC from soils and sediments largely depends on precipitation and runoff intensities. For instance, POC concentrations are mostly low during base flow conditions. Typically, only a few larger storm events that exceed a catchment-specific threshold level of discharge can account for a significant fraction of the annual POC export [Bormann *et al.*, 1969; Hope *et al.*, 1994; Jeong *et al.*, 2012]. These exports are related to soil and surface erosion. POC mobilization can also be caused by extreme events, including landslides and gully erosion [Hilton *et al.*, 2008; West *et al.*, 2011]. It is to be expected that particularly small catchments with short transit times and overland pathways will experience strong increases in POC exports in the future if the frequency of storm events and flash floods increases. In their sum, these exports are probably a significant contribution to whole river POC exports. On the other hand, these exports might be reduced again by dams and reservoirs. On a global basis, this shift of POC is important because dams and reservoirs have established considerable anthropogenic storage basins within the last century. For instance, a generally accepted estimate is that they increased terrestrial water surfaces by 7.3% [Lehner *et al.*, 2011]. This shows that



**Figure 1.** Headwater streams' involvement in the carbon cycle. (a) A schematic overview and (b) a more detailed scheme including dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC).

upstream POC mobilization and its subsequent storage in reservoirs is so far poorly characterized and needs further research.

The complexity of POC release and storage is further underlined by the fact that literature reports a large variability in POC concentrations for headwater catchments. This holds particularly true in response to storms [Dhillon and Inamdar, 2014; Jeong et al., 2012; Jung et al., 2012] and in eroding systems [Evans and Warburton, 2005; Pawson et al., 2008]. For instance, Johnson et al. [2006] reported stormflow POC concentrations that exceeded 150 times their baseflow values. Moreover, although POC typically makes up less than 5% of the total fluvial organic carbon flux, it can represent over 80% in eroded peatland systems [Pawson et al., 2008].

Other studies confirmed this finding and identified peatland and wetland soils as major POC sources [Bouchard, 2007; Dawson et al., 2004; Laudon et al., 2004; Neal and Hill, 1994; Pastor et al., 2003; Pawson et al., 2008; Waddington and Roulet, 1997; Worrall et al., 2003].

When compared to DIC and DOC, POC is the phase that has been least frequently investigated in headwater streams. This is mostly because headwaters are typically low in suspended sediments and most POC exports occur in short events such as flash floods that are often difficult to capture. So far, few studies have reported high erosion-induced POC concentrations in small mountain catchments [Carey et al., 2005; Coynel et al., 2005; Lyons et al., 2002]. They revealed that catchments with steep slopes are more vulnerable to soil erosion and thus also export more POC. This is likely only one factor for POC release, and other mechanisms such as soil properties, closeness of wetlands to streams, and remobilization of sediments need to be investigated for event-driven carbon transport in headwater streams. In order to obtain reliable values for POC fluxes, individual catchment characteristics must be evaluated.

Another important organic carbon phase is DOC that is commonly defined as the fraction that can pass through a filter with a pore size of 0.45  $\mu\text{m}$  [Thurman, 1985]. Again, in several studies, filters with pore sizes of 0.8  $\mu\text{m}$  [Hossler and Bauer, 2013; Lofgren and Zetterberg, 2011], 0.7  $\mu\text{m}$  [Abril et al., 2000; Avagyan et al., 2014; Dinsmore et al., 2013a; Doctor et al., 2008; Polsenaere et al., 2013], or even 0.22  $\mu\text{m}$  [Brunet et al., 2011; Lambert et al., 2011] have been used. This inconsistency restricts comparisons of dissolved carbon fractions. However, general trends should remain similar. DOC consists of a heterogeneous mixture of complex molecules with a continuous spectrum of sizes [Herbert and Bertsch, 1995]. The main sources of stream DOC are soils [Billett et al., 2006; Evans et al., 2007]. Among the different soil types, riparian and organic-rich soils are the main contributors of carbon to headwater streams. Overall, DOC export via headwater streams should be considered as a two-stage process: First, DOC is produced in soils, and then it is transported to drainage networks [Evans et al., 2002]. One important step in this succession is that the DOC production rate is positively influenced by environmental conditions such as temperature, wet-dry cycles, water saturation, snowmelt, liming, and organic fertilization that promote microbial activity as well as fungal abundance [Kalbitz et al., 2000].

Increases in terrestrially derived DOC concentrations have been observed in many northern aquatic ecosystems during the last few decades. Potential drivers are changes in temperature, rainfall, land use, and nutrient inputs [Evans et al., 2005; Monteith et al., 2007; Worrall et al., 2004]. In addition, declines of atmospheric sulfur deposition likely have caused stream DOC increases in many regions. The argument behind this mechanism is that acid rain has been partially buffered by changes in organic acidity and the recovery from acidification causes increases in DOC transport [Monteith et al., 2007]. It remains a matter of debate if such increased DOC fluxes are a return to pre-acid rain conditions or if other anthropogenic factors such as changes in land use are the driving forces behind increased DOC fluxes [Graeber et al., 2012; Yallop and Clutterbuck, 2009].

Regarding DOC transport via soils to the stream network, better knowledge about the interactions between catchment hydrology and carbon reservoirs is crucial. For instance, stream water DOC concentrations and catchment soil C pools are related over a range of spatial scales [Aitkenhead et al., 1999]. One common feature is that close to stream carbon reservoirs may play a so far underestimated role. For instance, positive correlations were found between stream DOC fluxes and shallow peat coverage and the total percentage of wetland area of headwater regions [Andersson and Nyberg, 2008; Billett et al., 2006; Lauerwald et al., 2012]. However, such relationships are also sensible to flow regimes [Andersson and Nyberg, 2008; Lauerwald et al., 2012]. In addition to these natural inputs, land cover and slope gradients were identified as predictors of the DOC flux [Andersson and Nyberg, 2008; Lauerwald et al., 2012].

In addition, DOC concentrations are correlated with the episodic, seasonal, or interannual variability of stream discharge and are thus often indirectly related to precipitation [McDowell and Wood, 1984; Strohmeier et al., 2013; Worrall et al., 2002]. Soil carbon pools often only become mobilized when groundwater levels rise or soil waters exceed a critical moisture level. These phenomena enhance the hydrological connectivity for the transport of DOC within the catchment [McGlynn and McDonnell, 2003]. It is known that in headwater catchments governed by snowmelt, a significant portion of the DOC stored in organic layers is typically flushed during spring, leading to increased stream DOC concentrations soon after snowmelt [Boyer et al., 2000; Giesler et al., 2013; Jantze et al., 2015]. Higher runoff may dilute DOC contents and alter flow paths. In



addition, varying soil moisture levels or changing redox conditions may activate areas with higher DOC contents [Hagedorn et al., 2000; Lambert et al., 2013; Olivie-Lauquet et al., 2001]. These active areas can then function as spatiotemporal DOC sources.

The above discussion shows that variable mechanisms of runoff-induced hydrological connectivity act as the first-order control on DOC dynamics in streams at storm-event, diurnal, and seasonal scales [Laudon et al., 2011; Tunaley et al., 2016; Winterdahl et al., 2011]. In contrast, trends in long-term DOC fluxes require changes in its production, mobilization including sorption and desorption, and recovery from acidification or altered flow regimes. Often different water fluxes alone would not lead to long-term changes of DOC dynamics in streams without increases or declines in DOC supply from soils [Evans et al., 2002]. Note that some of the DOC can also enter streams from aquifers. While the ultimate sources of this DOC are also soils, this input mechanism—that often is connected via riparian and hyporheic zones—is so far poorly characterized and may represent an important DOC source with different characteristics and ages.

Mineralization of DOC to  $\text{CO}_2$  and DIC further controls the fate of carbon on its way from soils to stream networks [Bengtson and Bengtsson, 2007; Kalbitz et al., 2000; Palmer et al., 2001; Schiff et al., 1990]. Thus, stream  $\text{CO}_2$  and DIC concentrations are closely linked to DOC concentration patterns and compositions [D'amaro and Xenopoulos, 2015; Lapierre et al., 2013; Lennon, 2004].

### 3.2. Inorganic Carbon

In most streams and rivers, particulate inorganic carbon (PIC) is negligible, and the occurrence of PIC phases is even less probable in acidic waters [McConnaughey et al., 1994]. In cases where PIC was investigated, it was a result of rock weathering and can also be causally related to dissolved inorganic carbon (DIC). Indeed, PIC is known to precipitate in carbonate-oversaturated stream water where it reduces the DIC concentration [Huang et al., 2012; Michaelis et al., 1985].

In contrast to PIC, DIC typically is the most abundant carbon phase in rivers and streams. It is mostly added by groundwater, the input of which is often poorly quantified but can be assumed to play an important role, particularly in headwater streams. Better characterization of groundwater surface water exchanges in terms of DIC poses the challenge of establishing groundwater piezometers in remote headwater catchments.

DIC is defined as the sum of the  $\text{CO}_2^*$  (i.e., the sum of  $\text{CO}_{2(\text{aq})}$  and  $\text{H}_2\text{CO}_3$ ),  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . The relative proportion of inorganic carbon species in water depends on pH and, to a lesser extent, on temperature. The relative distribution of DIC species can be calculated for any known temperature and pH [Dickson et al., 2007]. Streams with silicate bedrock often have pH values below 6, and their DIC consists of  $\text{CO}_2^*$  and  $\text{HCO}_3^-$ . In streams with pH values below 4.4,  $\text{CO}_2^*$  makes up more than 99% of the DIC. These conditions favor  $\text{CO}_2$  outgassing and can often be found in catchments with little or no carbonates. Their global contribution to  $\text{CO}_2$  loss from rivers and streams is so far unknown but likely significant when considering that 26% of the continental surface is covered by hard rocks of metamorphic, plutonic, and volcanic origin. Note that this estimate excludes areas of ice and inland water bodies (10%) [Hartmann and Moosdorf, 2012]. Examples for such coverage include the Canadian and Fennoscandian Shields.

In headwater streams, most DIC originates from soil-respired  $\text{CO}_2$  that is produced by root (autotrophic) and microbial (heterotrophic) respiration. The latter includes decomposition of organic matter. This  $\text{CO}_2$  is then involved in mineral weathering, such as the dissolution of carbonates or silicates [Finlay, 2003; Lu et al., 2014; Polsenaere et al., 2013; Wallin et al., 2013]. However, currently, the relative contributions of DIC production processes remain generally unclear. The DIC concentrations of soil solutions typically range between 30 and  $280 \text{ mg C L}^{-1}$  [Fiedler et al., 2008; Marfia et al., 2004; Sigfusson et al., 2006].

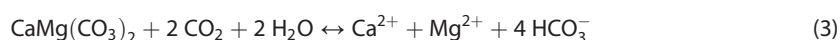
In addition to organic matter decomposition, DIC export from headwater streams is strongly related to lithology with weathering by  $\text{CO}_2$  of carbon-containing rocks. In such environments, the DIC phase in form of  $\text{HCO}_3^-$  is often much larger than the  $\text{CO}_2^*$  species because pH values are higher. This weathering process has been described as one of the main drivers of carbon fluxes in arctic, subarctic, and circumboreal streams, particularly during low-flow conditions [Jantze et al., 2015; Tank et al., 2012]. For headwater streams, this seems particularly important, because they usually have a larger ratio of streambed to catchment area. In such scenarios, weathering is also enhanced by contact to groundwaters and soil waters via springs and wetlands.

For the relationship between lithology and streams, major ions provide good proxies for the weathering of minerals present in the catchment's soils and geological formations. Some representative equations for weathering and DIC generation are as follows:

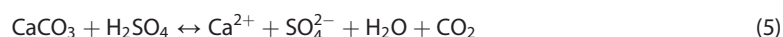
*weathering of calcite*



*weathering of dolomite*



These weathering reactions contribute DIC in the form of  $\text{HCO}_3^-$ . Other reactions, such as gypsum or anhydrite weathering can indirectly contribute DIC via the generation of sulfuric acid:



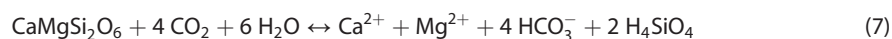
Note that the dissolution of carbonates by sulfuric acid (equation (5)) can also occur without the preceding natural dissolution of sulfate-containing minerals (equation (4)). This is for instance the case when acid rain inputs become important [Marx *et al.*, 2017]. In addition to sulfuric acid, nitric acid originating from either acid rain or N-fertilizers can become involved in carbonate dissolution [Perrin *et al.*, 2008; Suchet *et al.*, 1995].

Although silicate rocks weather much slower than their carbonate counterparts [Meybeck, 1987], their weathering reactions should also be considered as DIC sources. For instance, silicate bedrocks make up 45% of boreal catchments worldwide [FAO, 2001]. Some representative carbonic acid-induced weathering reactions of silicate minerals were compiled from the literature [Appelo and Postma, 2005; Berner and Berner, 2012; Klaminder *et al.*, 2011; Meybeck, 1987] and are listed here:

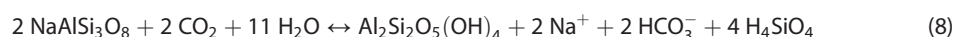
*weathering of enstatite (orthopyroxene)*



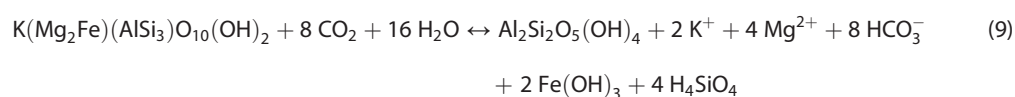
*weathering of diopside (clinopyroxene)*



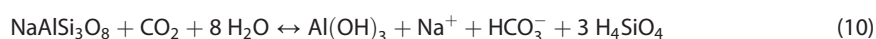
*weathering of albite (Na-feldspar) to kaolinite*



*weathering of biotite to kaolinite and iron(III)hydroxid*

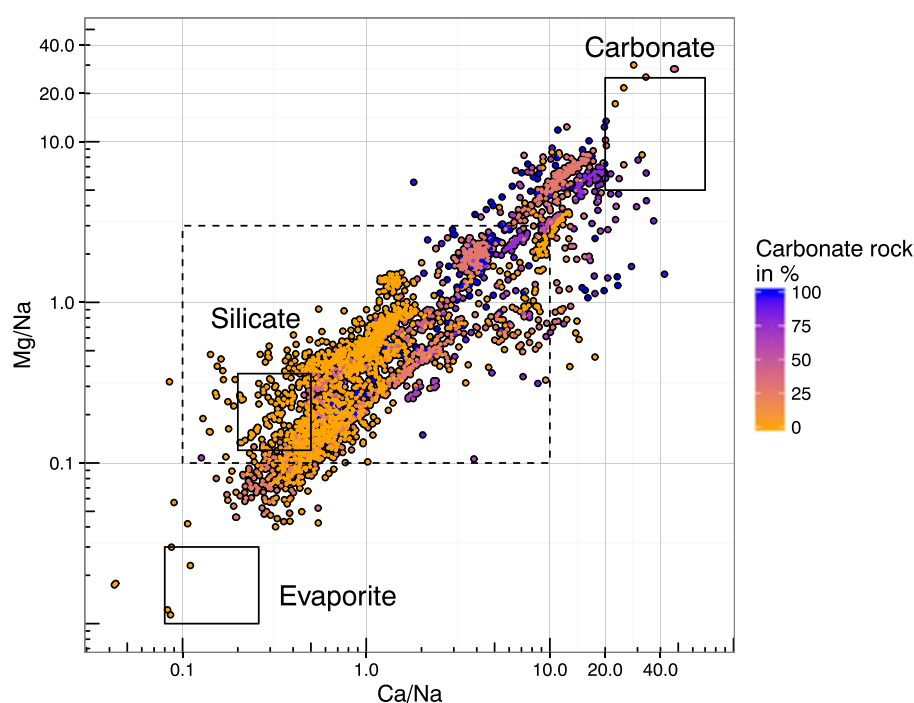


*weathering of albite (Na-feldspar) to gibbsite*



In these reactions,  $\text{H}_4\text{SiO}_4$  represents dissolved silica. This phase is also frequently referred to as  $\text{Si}(\text{OH})_4$  or  $\text{SiO}_2$  in the literature [Berner and Berner, 2012]. The above reactions were formulated with  $\text{CO}_2$ . However, sulfuric or nitric acid are other main drivers of weathering [Klaminder *et al.*, 2011].

The above reactions are important contributors of DIC, calcium, and magnesium in aqueous systems. They show that all DIC from silicate weathering originates from  $\text{CO}_2$ , which is typically derived from organic



**Figure 2.** Mixing diagrams based on  $\text{Na}^+$ -normalized molar ratios in the dissolved phase calculated from the GLORICH database for catchments with sizes smaller than  $30 \text{ km}^2$  [Hartmann *et al.*, 2014]. The color reflects the percentage of the carbonate rock contribution to the catchment lithology as extracted from the GLORICH database. Carbonate, silicate, and evaporite end-members were adopted from Gaillardet *et al.* [1999]. The dashed line indicates the range of the world's largest rivers, as summarized by Gaillardet *et al.* [1999].

matter decomposition and/or the fixation of atmospheric  $\text{CO}_2$  in headwater catchments. In contrast, during carbonate weathering,  $\text{CO}_2$  contributes only half of the carbon to the DIC pools. The other half is derived directly from the dissolution of carbonate rock (equations (2) and (3)). First indications show that streams in headwater catchments dominated by carbonates emit more  $\text{CO}_2$  than those dominated by silicate lithology [Doctor *et al.*, 2008; van Geldern *et al.*, 2015]. This may be related to  $\text{CO}_2$  release during carbonate precipitation in streams and a much higher abundance of carbon in form of carbonates. The exact conditions for such comparisons need further investigations.

Gaillardet *et al.* [1997, 1999] compiled global river  $\text{HCO}_3^-$  concentrations and the ratios of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to  $\text{Na}^+$  and compared them to the silicate, carbonate, and evaporite end-members of weathering. In Figure 2, we repeated this analysis exclusively for small streams with catchment sizes smaller than  $30 \text{ km}^2$  with data from the GLORICH database [Hartmann *et al.*, 2014]. This analysis revealed a much stronger variability among the end-members of silicate-, carbonate- and evaporite-dominated catchments when compared to the study by Gaillardet *et al.* [1999]. In addition, Figure 2 reveals that more data points plot close to the carbonate end-member. Because these data belong to catchment areas smaller than  $30 \text{ km}^2$ , the probability of a pure catchment lithology increases as the catchment size decreases. This may be further enhanced because shorter residence times of water in small headwater catchments favor weathering of carbonates due to better dilution kinetics when compared to silicates. This is further supported by the observation that catchments with silicate-dominated lithology and only small amounts of carbonates also approach the carbonate weathering end-member (Figure 2). Other studies also observed that even small or trace amounts of carbonates in a catchment can account for noticeable effects of carbonate weathering and subsequent DIC input to rivers and streams [Barth *et al.*, 2003]. This also bears an important implication for the global contribution of  $\text{CO}_2$  outgassing by small streams that remain underestimated if they are biased toward the carbonate end-member with typically larger  $\text{CO}_2$  emissions than silicate catchments. This is particularly important because approximately 8–13% of the total continental surface area is covered by carbonates [Hartmann and Moosdorf, 2012].



## 4. CO<sub>2</sub> Contents in Streams

### 4.1. Aqueous Partial Pressures of CO<sub>2</sub> in Streams and Their Detection

Most literature sources report the CO<sub>2</sub> contents of natural waters as partial volumetric pressures as  $p\text{CO}_2$  in  $\mu\text{atm}$  or  $\text{ppmV}$ . However, the partial volumetric pressure is a measure of ideal gases and does not account for the nonideal nature of CO<sub>2</sub>. The correct term is the effective pressure or activity of the gas that is known as fugacity ( $f\text{CO}_2$ ) [Atkins and De Paula, 2006]. Nonetheless, small deviations of less than 1% between  $f\text{CO}_2$  and  $p\text{CO}_2$  at ambient conditions justify the use of  $p\text{CO}_2$  for surface waters [Dickson et al., 2007].

One common method to determine CO<sub>2</sub> in stream waters is the use of gas-phase detectors. These devices operate via equilibration or diffusion through a gas-permeable membrane [Almeida et al., 2001; Gonzalez-Valencia et al., 2014; Hope et al., 1995; Johnson et al., 2010; Kling et al., 1992]. For instance, Gonzalez-Valencia et al. [2014] used an off-axis integrated cavity output spectrometer combined with an ultraportable greenhouse gas analyzer, and Johnson et al. [2010] applied submerged infrared gas analysis for direct and continuous in situ monitoring of  $p\text{CO}_2$ . Both methods are based on CO<sub>2</sub> diffusion through a hydrophobic membrane and facilitate achieving high temporal resolution. Alternatively,  $p\text{CO}_2$  can be analyzed from head-space samples that have been equilibrated with water. Gas-phase measurements are then performed with either infrared spectrometry or gas chromatography [Cole et al., 1994; Hope et al., 1995; Kling et al., 1992]. Direct measurements of  $p\text{CO}_2$  with nondispersive infrared sensors inside floating chambers are another method for collecting field measurements of aqueous CO<sub>2</sub> pressure [Bastviken et al., 2004; Billet, 2006; Duc et al., 2013; Galfalk et al., 2013]. This method is based on water-gas equilibration and provides time-weighted average values.

Note that most published  $p\text{CO}_2$  data for aqueous systems were not determined by these direct measurements that demand more costs and logistics. Due to low cost and effort, the majority of published  $p\text{CO}_2$  data in the literature was calculated from total alkalinity (TA) by assuming that TA is equal to carbonate alkalinity (CA). In this case,  $p\text{CO}_2$  is derived from  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and pH at a given temperature, pressure, and salinity [Dickson et al., 2007]. According to Plummer and Busenberg [1982],  $p\text{CO}_2$  (in atm) can be calculated using the following equation:

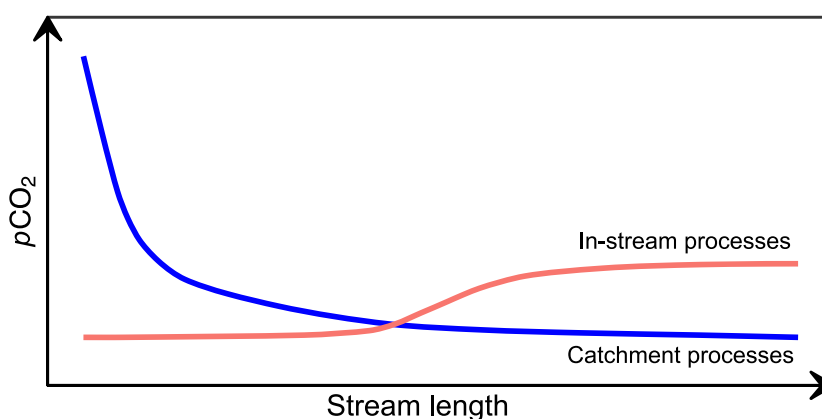
$$p\text{CO}_2 = \frac{\text{HCO}_3^- \times \text{H}^+}{K_H \times K_1} \quad (11)$$

where  $\text{HCO}_3^-$  is the activity of bicarbonate,  $\text{H}^+$  is  $10^{-\text{pH}}$ ,  $K_1$  is the temperature-dependent first dissociation constant for the dissociation of  $\text{H}_2\text{CO}_3$  (all variables in  $\text{mol L}^{-1}$ ), and  $K_H$  is the Henry's law constant in  $\text{mol L}^{-1} \text{atm}^{-1}$ .

The accuracy of this calculation strongly depends on the quality of the pH measurements. For instance, because of measurement uncertainties of  $\pm 0.05$  pH units,  $p\text{CO}_2$  values calculated using equation (11) have an error of approximately  $\pm 11\%$ . Typically, field measurements have accuracies in the range of  $\pm 0.1$  pH units. This error may be even higher in waters with low ionic strengths and low pH values that are characteristic for upstream catchments in noncarbonate environments. In such cases, the calculated  $p\text{CO}_2$  values can have uncertainties of up to  $\pm 21\%$ . Moreover, especially in water samples where organic acids and DOC make up significant contributions to TA,  $p\text{CO}_2$  calculations from TA are often insufficiently robust [Hunt et al., 2011]. Large differences in  $p\text{CO}_2$  values calculated based on pH, TA, and temperature have been reported when compared to direct measurements. For instance, Abril et al. [2015] found  $p\text{CO}_2$  values that were between 50% and 300% of the values obtained by direct in situ measurements in temperate and tropical freshwaters with pH lower than  $\sim 7$  and alkalinity values lower than  $1000 \mu\text{mol L}^{-1}$ . However, other studies that calculated  $p\text{CO}_2$  based on DIC measurements instead of alkalinity obtained robust results [Aberg and Wallin, 2014; Raymond et al., 1997]. Thus, for  $p\text{CO}_2$  estimations generated by these calculations, higher uncertainties must be accounted for and therefore direct measurements of  $p\text{CO}_2$  in the field are preferable.

### 4.2. Driving Processes of $p\text{CO}_2$ in Streams

The interplay of biological, chemical, and physical processes that influence CO<sub>2</sub> in headwater streams is complex and often causes high spatiotemporal variability [Dawson et al., 1995; Hope et al., 2001; Peter et al., 2014;



**Figure 3.** Theoretical curves of stream  $p\text{CO}_2$  for soil water and groundwater inputs of  $\text{CO}_2$  originating from catchment processes (i.e., soil respiration and weathering) and for  $\text{CO}_2$  originating from in-stream processes (biodegradation and photodegradation of organic carbon). Arbitrary units were applied here because the actual proportions of source contributions to  $p\text{CO}_2$  loss from headwaters need to be quantified. For this purpose, representative functional relationships based on catchment properties are needed to further quantify  $p\text{CO}_2$  loss from headwaters by their relative sources.

Wallin *et al.*, 2011]. First models highlight the variability and outline that DOC transport and turnover often start in soils [Dusek *et al.*, 2017].

Within streams, the two major in situ processes that drive stream  $p\text{CO}_2$  dynamics are aquatic biodegradation and photodegradation. These processes are mostly controlled by solar radiation and temperature [Demars *et al.*, 2011; Moran and Zepp, 1997; Porcal *et al.*, 2015]. In addition, sunlight, particularly ultraviolet radiation, can oxidize DOC to  $\text{CO}_2$  and CO [Vähätalo, 2010]. The organic carbon decay rate was found to decrease across the continuum of inland waters from headwaters downstream and to be more pronounced at higher initial DOC concentrations [Catalan *et al.*, 2016; Moody and Worrall, 2016]. This, together with disproportionately large amounts of organic carbon processing, indicates that freshwaters are potentially important areas of organic carbon degradation and thus also of in-stream  $\text{CO}_2$  production [Catalan *et al.*, 2016]. Results by Catalan *et al.* [2016] also show that the organic carbon decay rates are negatively related to water residence times. They determined a mean decay rate of  $2.37 \pm 4.4 \text{ yr}^{-1}$ . Thus, high flow rates and short water residence times often leave insufficient time for substantial degradation of DOC in the water column of lower-order streams.

Initial modeling on the basis of the so called pulse-shunt concept suggests that most of the dissolved organic matter becomes passively transported in upper reaches of catchments during infrequent yet major high-discharge events [Raymond *et al.*, 2016]. However, to date the relative amounts of  $\text{CO}_2$  that originate from in-stream (i.e., biodegradation and photodegradation) and catchment processes (i.e., soil respiration and weathering) remain poorly constrained. Figure 3 shows theoretical curves of stream  $p\text{CO}_2$  for these two sources. A large amount of  $\text{CO}_2$  rapidly outgasses during the first few meters of openly flowing waters. This is because  $p\text{CO}_2$  values in groundwater are typically more than four times higher than in the stream [Crawford *et al.*, 2014]. In comparison to this,  $\text{CO}_2$  contribution from in-stream organic carbon processing would lead to increases of stream  $p\text{CO}_2$  values further downstream.

To our knowledge, only two large-scale studies about such relative contributions have been performed. The study by Butman and Raymond [2011] estimated that 4% of the total  $\text{CO}_2$  outgassing originated from in-stream respiration involving DOC and that approximately 21–32% came from soil water  $\text{CO}_2$ . Hotchkiss *et al.* [2015] assessed  $\text{CO}_2$  production from aquatic metabolism by measuring net ecosystem production. They found that aquatic metabolism contributed with a median of 14% (range: 0–19%) of  $\text{CO}_2$  outgassing from streams of systems with discharge smaller than  $0.01 \text{ m}^3 \text{ s}^{-1}$ . This percentage increased to 39% (range: 25–54%) in larger rivers with discharge exceeding  $100 \text{ m}^3 \text{ s}^{-1}$ . Similar studies on smaller rivers have so far hardly been conducted but show a huge variance of  $\text{CO}_2$  processing. Direct connections to groundwater often enable steep geochemical gradients [Hope *et al.*, 2004]. This is because springs and their following run-off are direct and nearly undiluted forms of groundwater that reaches the surface. For the southern Amazon

basin, *Johnson et al.* [2008] measured strongly differing dissolved  $\text{CO}_2$  concentrations of 1.76 and 0.21 mol  $\text{L}^{-1}$  in groundwater-fed springs and in first to second order streams. This corresponds to a range of 88%. When applying the assumption of 14% DOC contribution to  $\text{CO}_2$  production by *Hotchkiss et al.* [2015], the internal  $\text{CO}_2$  gain in these streams only amounted to 0.03 mol  $\text{L}^{-1}$ . In another example of Indonesian rivers with their catchments draining tropical peatlands [*Wit et al.*, 2015], the assumed 14% of DOC contribution only amounted to less than 0.14 mol  $\text{L}^{-1}$   $\text{CO}_2$  gain. This highlights the dominance of groundwater contributions for  $\text{CO}_2$  outgassing in headwater streams, even when high amounts of DOC are present.

The above considerations highlight that influxes of terrestrially derived  $\text{CO}_2$  via groundwater must be important to obtain large  $p\text{CO}_2$  concentrations in streams. This input must be particularly pronounced in shallow headwater streams with water residence times of minutes to hours during which in-stream processes do not have enough time to develop large  $p\text{CO}_2$  levels. In addition, because of different chemical compositions of stream water, groundwater, and water in the riparian zones, the accumulated organic matter in sediments and microbial metabolism are enhanced. This often leads to increased  $\text{CO}_2$  production in riparian zones and the close to stream groundwater section that is known as the hyporheic zone [*Boano et al.*, 2014; *Jones and Mulholland*, 2000; *McKnight et al.*, 2004; *Schindler and Krabbenhoft*, 1998]. For instance, *Peter et al.* [2014] found  $p\text{CO}_2$  values in hyporheic zones to be much higher than in stream water concentrations. However, for an alpine catchment, they assumed that terrestrial  $\text{CO}_2$  from soil and root respiration as well as weathering largely exceeds hyporheic respiration. Modeling advances in the hyporheic zone such as reviewed by *Boano et al.* [2014] offer the opportunity to evaluate their influence on stream  $p\text{CO}_2$  dynamics across different climate zones. One common finding is that spatially rapid changes in downstream  $p\text{CO}_2$  often characterize hot spots linked to zones of groundwater influx or to more turbulent areas of the stream network [*Dawson et al.*, 1995; *Doctor et al.*, 2008; *van Geldern et al.*, 2015].

Additional inputs of soil waters with  $\text{CO}_2$  levels of 50,000  $\mu\text{atm}$  and more can complicate the allocation of stream-external  $\text{CO}_2$  sources [*Crawford et al.*, 2014; *Davidson and Trumbore*, 1995; *Johnson et al.*, 2008]. Due to their dependence on temperature and moisture, soil  $\text{CO}_2$  levels in tropical areas are generally higher than those in temperate, alpine, and arctic regions [*Brook et al.*, 1983]. Either soil waters enter the stream directly or they feed groundwater. While floodplains and influences of soils may be important elements for carbon processing in lowland rivers, they are mostly negligible in headwaters. Their lack of occurrence in headwaters may be a further reason why riparian and hyporheic zones assume a prominent role as carbon reactors in headwater streams. This  $\text{CO}_2$ -enriched groundwater can then enter the stream along its course and mix with its surface waters. Thus, relative contributions of groundwater and soil water inputs strongly affect  $p\text{CO}_2$  in headwater streams [*Finlay*, 2003; *Giesler et al.*, 2013; *Oquist et al.*, 2009].

Moreover, many headwater streams exhibit a particularly complex and spatially variable morphology with riffles, pools, and even a *step stair* continuum of small waterfalls [*Billett and Harvey*, 2013]. Such morphological variations strongly influence the generation of surface water turbulence, which affects the aquatic boundary layer and, thus, enhances gas exchange at the water-air interface. For the same flowing water mass, shallow and wide stream sections typically generate more surface turbulence than narrow and deep sections [*MacIntyre et al.*, 1995]. In headwater streams, streambed roughness, channel flow constriction, twisting and winding flow paths, and variable stream gradients are common and also control spatial turbulence formation [*Wallin et al.*, 2011]. For instance, *Oquist et al.* [2009] found that within 200 m of the water entering the stream, about 65% of the DIC in groundwater was lost to the atmosphere. Additionally, in a carbonate headwater catchment, *van Geldern et al.* [2015] observed a  $p\text{CO}_2$  decline of 84% within the first 7 km downstream after the spring. Based on these results, both carbonate and noncarbonate headwater catchments exhibit this pattern of rapid downstream  $p\text{CO}_2$  decrease due to outgassing to the atmosphere (Figure 3). As  $p\text{CO}_2$  values decline, stream pH values increase and the pH-dependent distribution of inorganic carbon species shifts toward predominance of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . As a result, the buffering of  $p\text{CO}_2$  to lower values occurs at waters with high pH values and typically from the source to locations further downstream.

Stream  $p\text{CO}_2$  also responds to discharge, which tends to increase the  $\text{CO}_2$  gas transfer velocity ( $k_{\text{CO}_2}$ ) via surface turbulence [*Demars and Manson*, 2013; *Long et al.*, 2015; *Raymond et al.*, 2012; *Wallin et al.*, 2011]. In addition to flow velocity, turbulence depends on stream hydraulics such as stream depth, width, and slope. This highlights that catchment hydrology is another factor that strongly influences stream  $p\text{CO}_2$  dynamics in

terms of hydrological exchanges of  $\text{CO}_2$  from terrestrial ecosystems [Crawford *et al.*, 2013, 2014; Humborg *et al.*, 2010; Sobek *et al.*, 2003; Striegl and Michmerhuizen, 1998; Teodoru *et al.*, 2009; Wallin *et al.*, 2010].

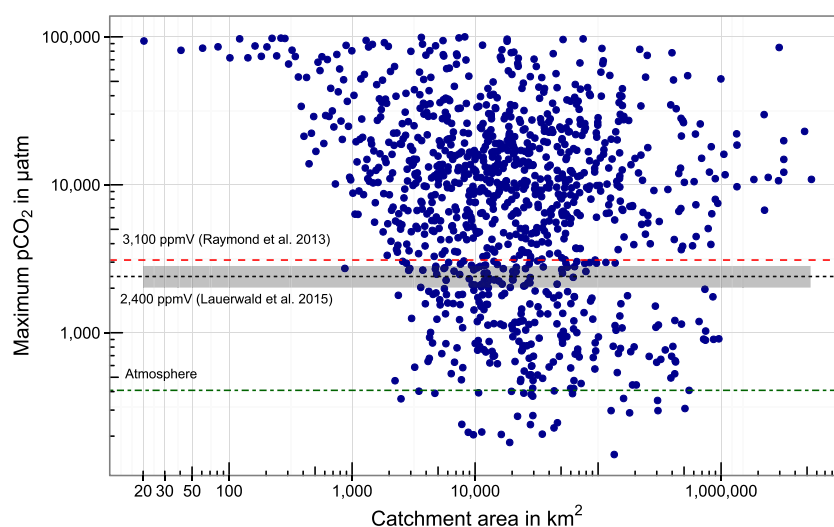
Moreover, stream  $p\text{CO}_2$  also varies on temporal (i.e., diurnal and seasonal) bases [Beaulieu *et al.*, 2013; Elayouty *et al.*, 2016; Hotchkiss *et al.*, 2015; Peter *et al.*, 2014; Weyhenmeyer *et al.*, 2012]. Hydrological alterations of stream  $p\text{CO}_2$  dynamics often mask the physical and biological processes that are dominant drivers of temporal  $\text{CO}_2$  variations during base flow conditions [Peter *et al.*, 2014]. These conditions often prevail during warm seasons and drought and are associated with groundwater as a primary contributing source of  $\text{CO}_2$  to stream water [Call *et al.*, 2015; Looman *et al.*, 2016]. The most important seasonal drivers are mostly temperature and  $\text{CO}_2$  outgassing fluxes [Dinsmore *et al.*, 2013a; Peter *et al.*, 2014]. In warm seasons, high temperatures together with availability of organic material promote stream respiration, and more pronounced hyporheic exchanges occur relative to discharge [Peter *et al.*, 2014]. On the other hand, seasonally controlled low discharge is typically associated with less turbulent flow and thus smaller  $\text{CO}_2$  outgassing fluxes. Resulting lower flow velocities may also enhance in-stream biological activity. Overall, on the diurnal scale, water temperature, photosynthetically active radiation (PAR), and  $k_{\text{CO}_2}$  have the strongest influence on stream water  $p\text{CO}_2$  dynamics [Crawford *et al.*, 2013; Peter *et al.*, 2014; Weyhenmeyer *et al.*, 2012]. PAR is related to primary production [Peter *et al.*, 2014], while  $k_{\text{CO}_2}$  primarily depends on turbulence, which includes hydrological parameters such as flow velocity, stream depth, width, and slope. Additionally, water temperature is an obvious driver of  $\text{CO}_2$  transfer velocities [Demars and Manson, 2013]. For instance, elevated water temperatures enhance  $\text{CO}_2$  outgassing and reduce its accumulation in stream waters.

Overall, low-order streams show high  $p\text{CO}_2$  levels. While the interplay of the influences discussed above is complex, terrestrial  $\text{CO}_2$  inputs via soil water and groundwater are likely the strongest control. However, in headwater streams, the location, timing, and spatial extent of surface water/groundwater exchange remains largely unknown. As a new approach, geophysical imaging techniques have the potential to complement studies of the subsurface and can add to results from piezometers and in-stream measurements. For instance, Mwakanyamale *et al.* [2013] were able to reliably quantify exchange versus non-exchange zones from a portion of the Columbia River with fiber-optic distributed temperature sensing data. Such geophysical methods provide useful tools to improve our understanding of  $p\text{CO}_2$  origins in headwater streams by quantifying changing  $\text{CO}_2$  influxes over time at much higher spatial resolution than direct measurements [Parsekian *et al.*, 2015].

#### 4.3. Global Analyses of $p\text{CO}_2$ Concentrations in Rivers and Streams

We performed a global analysis of  $p\text{CO}_2$  values for rivers and streams from the GLORICH database [Hartmann *et al.*, 2014]. Most of these  $p\text{CO}_2$  values were based on pH, temperature, and alkalinity data (supporting information Table S2). Additional data for streams with catchment areas smaller than  $20 \text{ km}^2$  were included in this analysis (supporting information Table S3). Figure 4 shows the calculated maximum  $p\text{CO}_2$  values for rivers grouped in intervals of  $20 \text{ km}^2$  catchment area.  $p\text{CO}_2$  values above  $100,000 \mu\text{atm}$  (114 values from a total of 120,050) were neglected in this analysis. The reason for this sorting out of data was that although these large values might occur in low pH waters, they most likely result from errors in pH and  $\text{HCO}_3^-$  measurements. Figure 4 shows that maximum  $p\text{CO}_2$  values of rivers and streams mostly exceed the global atmospheric average. Our analysis shows that all groups up to a catchment size of  $500 \text{ km}^2$  show consistently high maximum  $p\text{CO}_2$  values that exceed global river averages. In contrast, rivers with catchment areas exceeding  $\sim 2000 \text{ km}^2$  often have more variable maximum  $p\text{CO}_2$  values that sometimes also fall below the global average.

In order to set these higher  $p\text{CO}_2$  values in smaller rivers into a global context, we present an analysis of their cumulative area. Downing *et al.* [2012] analyzed the global abundance and size distribution of streams and rivers. This analysis did not provide catchment areas, and as a substitute, we used average surface areas of streams. They were calculated by dividing the total cumulative stream surface area by the number of rivers and streams in each category of Strahler stream order. This analysis yielded Figure 5 that plots the average surface areas of rivers and streams versus the number of rivers in each category. The labeled values indicate Strahler stream orders [Strahler, 1952]. This compilation demonstrates a strong bias toward streams with small average surface areas. For instance, an estimated 36,074,000 streams worldwide have average areas of  $0.275 \text{ km}^2$  and less, corresponding to Strahler stream orders of 1 to 4. In contrast, globally only 654 streams have average surface areas of  $144,272 \text{ km}^2$  or above, which corresponds to Strahler stream orders of 8 to 12.

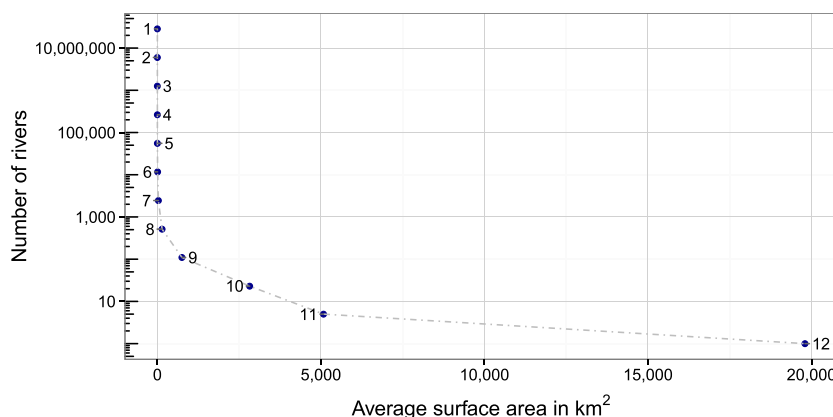


**Figure 4.** Log-log diagram of calculated maximum  $p\text{CO}_2$  values ( $\mu\text{atm}$ ) in  $20 \text{ km}^2$  catchment area intervals using river and stream data from the GLORICH database [Hartmann *et al.*, 2014] with additional data for the calculation of the interval from 0 to  $20 \text{ km}^2$  (supporting information Tables S2 and S3). The horizontal lines indicate the global average atmospheric  $p\text{CO}_2$  of  $400 \mu\text{atm}$  in 2015 [ESRL/GMD, 2016] and the estimated stream and river global average values of  $3100 \mu\text{atm}$  [Raymond *et al.*, 2013]. Another global average of  $2400 \mu\text{atm}$  was estimated by excluding anthropogenically influenced stations and is displayed with the uncertainty range [Lauerwald *et al.*, 2015].

This distribution highlights the enormous contribution of headwater streams to global river networks. Together with the consistently high maximum  $p\text{CO}_2$  values observed in smaller catchments, this result indicates that representative inclusion of these streams in future data analyses is necessary for better global carbon budgets.

Figure 5 shows that headwater streams with Strahler stream orders between 1 and 3 make up the largest portion with 96% of all rivers and streams. Even though they only have a cumulative area of 17.4% of total streams and rivers on the global continental surface, they cover the largest fractional stream network area [Butman and Raymond, 2011].

In a conservative estimate, we assumed that these small streams have at least three times the  $p\text{CO}_2$  values than the global average and calculated an increase from  $3100 \text{ ppmV}$  to  $4180 \text{ ppmV}$ . This would correspond to an increase of 34.8%. With the current data, such calculations remain speculative; however, they show the large potential of  $\text{CO}_2$  outgassing to the atmosphere by headwater streams. This estimate conforms with an analysis on the continental-scale that revealed a continuous decline of  $\text{CO}_2$  outgassing from rivers and



**Figure 5.** Diagram of global river and stream numbers and their corresponding average surface area in  $\text{km}^2$  derived from Downing *et al.* [2012]. Labels indicate the associated Strahler stream orders [Strahler, 1952].



streams with increasing size and discharge [Hotchkiss et al., 2015]. The importance of these CO<sub>2</sub> fluxes to global carbon budgets is comparable to that of the global oceanic CO<sub>2</sub> sink [Butman and Raymond, 2011; Giesler et al., 2013; Humborg et al., 2010; Lauerwald et al., 2015; Raymond et al., 2013; Zappa et al., 2007].

Despite their obvious importance, biogeochemical data on headwater streams are spatially and temporally sparse and more difficult to generalize. Strongly variable surface areas, rapid changes between turbulent and laminar flow, and variable gas exchange velocities complicate the determination of CO<sub>2</sub> outgassing fluxes and their upscaling with associated carbon transport and processing. Thus, reliable methods are required to better constrain headwater stream CO<sub>2</sub> emissions to improve our understanding of mechanisms that drive carbon turnover and CO<sub>2</sub> fluxes in headwater streams. New investigations in this research area are important because they can contribute to improve models on the global carbon cycle. They can also help to constrain future predictions of CO<sub>2</sub> emissions. Therefore, we outline here the most important aspects of determination of CO<sub>2</sub> loss from surface waters with a particular focus on small streams.

#### 4.4. Quantification of CO<sub>2</sub> Fluxes From Streams

High-quality direct CO<sub>2</sub> flux measurements for headwater streams are often difficult to realize. The application of gas tracers is generally considered as the most robust and reliable method to determine CO<sub>2</sub> outgassing rates on the scale of 100 m to a few kilometers. However, this method is not suitable for frequent or continuous monitoring or to show dynamics at small spatial scales of less than 10 m. Basically, an inert, volatile tracer gas that does not naturally occur in the water system (e.g., sulfur hexafluoride, chloromethane, or propane) is injected upstream [Dinsmore et al., 2013a; Halbedel and Koschorreck, 2013; Raymond et al., 2012; Wallin et al., 2011] and altered dissolved gas concentrations are measured downstream. The loss of the tracer gas along a stream reach or over time together with the known relationship between the tracer gas and CO<sub>2</sub> can be used to calculate the gas transfer velocity of CO<sub>2</sub>. These tracer gases do not disturb the water-air interface and provide an integrated measure of the gas exchange ability over a specific stream reach at a point in time [Hope et al., 2001; MacIntyre et al., 1995; Raymond and Cole, 2001; Wallin et al., 2011].

Floating chambers are another methodological approach and have been used in numerous studies [Billett and Moore, 2008; Campeau et al., 2014; Kremer et al., 2003; Matthews et al., 2003; Vachon et al., 2010]. The chambers are closed to the surrounding atmosphere but open to the CO<sub>2</sub> source at the bottom. A sensor, such as an infrared gas analyzer, continuously monitors CO<sub>2</sub> in the chamber headspace [Lorke et al., 2015]. When the chamber is placed on the water surface, the monitored CO<sub>2</sub> concentration typically shows an exponential increase in the chamber headspace. A linear regression can then be used to determine the CO<sub>2</sub> outgassing fluxes [Bastviken et al., 2015]. Potential benefits of the method include its low costs, the small spatial scale of the measurements, and its easy replication [Bastviken et al., 2015]. Note that the floating chamber methods have been criticized because of their inherent effects that include extra turbulence at the water-air boundary layer and deviating air temperature and pressure conditions inside the chamber [Billett and Moore, 2008; Campeau et al., 2014; Matthews et al., 2003]. As a result, some studies with floating chambers have reported potentially overestimated gas fluxes [Kremer et al., 2003; Matthews et al., 2003; Vachon et al., 2010]. The magnitude of inherent chamber effects varies depending on the chamber design and its application. A first guideline based on the comparison of anchored to freely drifting chambers describes how to apply floating chambers on running waters [Lorke et al., 2015]. Results show that freely drifting chambers have a very small impact on the water turbulence under the chamber when compared to anchored chambers. However, for a large number of headwater streams, the application of freely drifting chambers is restricted by obstacles in the streambed and also by turbulence presumably during increased runoff. In this case, anchored chambers modified with a flexible plastic foil collar to seal the chambers to the water surface could provide an alternative for moderate flow conditions [Lorke et al., 2015].

A widely applied alternative to direct measurements consists of flux calculations from pCO<sub>2</sub> [Lauerwald et al., 2015; Raymond et al., 2012; Teodoru et al., 2009; van Geldern et al., 2015]. The underlying principle is diffusion that controls CO<sub>2</sub> exchange between stream water and the atmosphere. This diffusive flux depends on two factors:

1. The concentration gradient of CO<sub>2</sub> at the water-air interface and
2. The turbulent energy exchange across this interface, expressed by a constant known as the gas transfer velocity,  $k$ .

With these two inputs, the diffusive gas flux ( $F$ ) can be calculated and is typically expressed in  $\text{mol m}^{-2} \text{yr}^{-1}$  [Cole and Caraco, 2001; Wanninkhof and Knox, 1996]:

$$F = k \times \alpha \times K_H \times (p\text{CO}_{2\text{aq}} - p\text{CO}_{2\text{air}}) \quad (12)$$

where  $k$  is the gas transfer velocity in  $\text{m yr}^{-1}$ ,  $K_H$  is the Henry's law constant in  $\text{mol m}^{-3} \text{atm}^{-1}$ ,  $p\text{CO}_{2\text{aq}}$  is the partial pressure of  $\text{CO}_2$  in the stream water, and  $p\text{CO}_{2\text{air}}$  is the partial pressure of  $\text{CO}_2$  above the stream water (both in atm), and  $\alpha$  is a dimensionless coefficient for chemical enhancement for  $\text{CO}_2$ . The latter factor only becomes relevant at pH values above 10, at which  $\text{CO}_2$  reacts more quickly with aqueous carbonate, and this process begins to compete with the diffusive losses of  $\text{CO}_2$  [Wanninkhof et al., 2009].

The gas transfer velocity is known as a generalized value and is often expressed by a term known as the piston velocity ( $k_{\text{TV}}$  or  $k_L$ ). This factor is defined as the height of the water column that equilibrates with the atmosphere per time unit and is generally expressed in  $\text{cm h}^{-1}$  [Frankignoulle et al., 1998; Raymond and Cole, 2001]. Because of high uncertainties in the definition of the channel depth for rivers and streams, the gas transfer coefficient ( $k_{\text{TC}}$ ) is often used instead. This coefficient can be determined via the gas tracer method and is defined as the portion of the tracer gas that is lost over a specific reach per unit time [Wallin et al., 2011]. The gas transfer coefficient ( $k_{\text{TC}}$ ) is converted to gas transfer velocity ( $k$  or  $k_{\text{TV}}$ ) by the following equation [Genereux and Hemond, 1992; MacIntyre et al., 1995]:

$$k_{\text{TC}} = \frac{k_{\text{TV}}}{z} \quad (13)$$

where  $z$  is the average stream channel depth.

To further simplify comparisons of  $k$  values for different gases and water temperatures, the gas transfer velocity is standardized to the dimensionless Schmidt number ( $Sc$ ). It is defined as the ratio between the kinematic viscosity of water and the diffusion coefficient of the gas and is calculated with the following equation [Wanninkhof, 1992]:

$$Sc = A + B \times T + C \times T^2 + D \times T^3 \quad (14)$$

where  $T$  is the temperature in  $^{\circ}\text{C}$  and  $A$ ,  $B$ ,  $C$ , and  $D$  are dimensionless constants:  $A = 1742$  (1911),  $B = -91.24$  ( $-118.11$ ),  $C = 2.208$  (3.453), and  $D = -0.0219$  ( $-0.0413$ ). These constants are valid for  $\text{CO}_2$  and temperatures from 4 to  $35^{\circ}\text{C}$ . Note that the numbers in parenthesis are relevant from  $10^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  [Raymond et al., 2012; Wanninkhof, 1992].

For freshwater investigations, the gas transfer velocity is typically normalized to a Schmidt number of 600 (for  $\text{CO}_2$  at  $20^{\circ}\text{C}$ ). The conversion from  $k$  to the normalized  $k_{600}$  is achieved according to the following equation [Jähne et al., 1987]:

$$k_{600} = k \times \left( \frac{600}{Sc_{\text{CO}_2}} \right)^{-n} \quad (15)$$

where  $Sc_{\text{CO}_2}$  is the  $\text{CO}_2$  Schmidt number for a given temperature (equation (14)) [Vachon et al., 2010; Wanninkhof, 1992] and  $n$  is the Schmidt number exponent that depends on the surface state of the water [Jähne et al., 1987]. For wind speeds exceeding  $3.7 \text{ m s}^{-1}$ ,  $n$  is approximated with 0.5. This value increases to 0.75 when wind speeds are below  $3.7 \text{ m s}^{-1}$  [Guerin et al., 2007].

Identification of a suitable gas transfer velocity value ( $k$ ) in the calculation of  $\text{CO}_2$  outgassing fluxes is a critical step in evaluating  $\text{CO}_2$  emissions. Particularly in headwater streams, strong variations in  $k$  are the main determinant of  $\text{CO}_2$  outgassing, when compared to  $p\text{CO}_2$  [Wallin et al., 2011]. Various measurement options and empirical equations have been proposed for the determination of  $k$  [Galfalk et al., 2013; Raymond et al., 2012]. Most approaches agree that turbulence in the stream water is the main driver of outgassing because they increase diffusive gas exchange. These occur when small eddies constantly renew the surface mass content. Turbulence, in turn, is enhanced by variations in discharge and variable streambed morphology [Hope et al., 2001; Wanninkhof et al., 1990]. A comprehensive study by Raymond et al. [2012] revealed that gas transfer velocities for low-order streams may be predicted over a large range of spatial scales. This is achieved by weighting the relative importance of gas exchange in bulk biogeochemical budgets via regression equations that also account for stream-slope and velocity parameters ( $r^2 = 0.76$ ). These models were tested mostly on small systems with a median depth of 0.28 m and during low flow with a median discharge of  $0.54 \text{ m}^3 \text{s}^{-1}$ .

**Table 1.** Gas Transfer Velocities and Gas Transfer Coefficients ( $k_{600}$ ) of Streams and Rivers at a Stream Temperature of 20°C Grouped by Strahler Stream Order [Strahler, 1952]<sup>a</sup>

| Region                                                         | Stream Order | $k_{600}$          | Method                                | Reference                 |
|----------------------------------------------------------------|--------------|--------------------|---------------------------------------|---------------------------|
| <i>Gas transfer coefficient (<math>\text{min}^{-1}</math>)</i> |              |                    |                                       |                           |
| Northern Sweden<br>(Boreal streams)                            | 1            | 0.028 <sup>b</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Wallin et al. [2011]      |
|                                                                | 2            | 0.022 <sup>b</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Wallin et al. [2011]      |
|                                                                | 3            | 0.020 <sup>b</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Wallin et al. [2011]      |
|                                                                | 4            | 0.017 <sup>b</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Wallin et al. [2011]      |
| United Kingdom (peatland streams)                              | <3           | 0.087 <sup>b</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Billett and Harvey [2013] |
| United Kingdom (peatland stream)                               | —            | 0.073 <sup>c</sup> | Gas tracer ( $\text{C}_3\text{H}_8$ ) | Hope et al. [2001]        |
| <i>Gas transfer velocity (<math>\text{cm h}^{-1}</math>)</i>   |              |                    |                                       |                           |
| United States                                                  | <4           | 18.75 <sup>b</sup> | Regression equation                   | Butman and Raymond [2011] |
| Québec, Canada                                                 | 1            | 2.3 <sup>c</sup>   | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
|                                                                | 2            | 2.4 <sup>c</sup>   | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
|                                                                | 3            | 2.04 <sup>c</sup>  | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
|                                                                | 4            | 5.75 <sup>c</sup>  | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
|                                                                | 5            | 9.5 <sup>c</sup>   | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
|                                                                | 6            | 5.16 <sup>c</sup>  | Headspace method <sup>d</sup>         | Campeau et al. [2014]     |
| Alaska, United States                                          | ≤4           | 26.96 <sup>c</sup> | CO <sub>2</sub> chamber               | Crawford et al. [2013]    |
| Germany                                                        | —            | 26.25 <sup>c</sup> | Regression equation                   | van Geldern et al. [2015] |
| Boreal and arctic streams (50°–90°)                            | —            | 13.1 <sup>b</sup>  | Data synthesis                        | Aufdenkampe et al. [2011] |
| Temperate streams (25°–50°)                                    | —            | 20.2 <sup>b</sup>  | Data synthesis                        | Aufdenkampe et al. [2011] |
| Tropical streams (0°–25°)                                      | —            | 17.2 <sup>b</sup>  | Data synthesis                        | Aufdenkampe et al. [2011] |

<sup>a</sup>Running waters in Aufdenkampe et al. [2011] have <60–100 m width. Regression equations are summarized in Raymond et al. [2012].

<sup>b</sup>Median values.

<sup>c</sup>Mean values.

<sup>d</sup>pCO<sub>2</sub> measurement via the headspace method and calculation of  $k$  with the diffusive gas flux equation (equation (12)).

However, especially for high flow velocities and steep slopes, which characterize many headwater streams, gas transfer velocities could so far not be well predicted by their associated slopes and velocities. Only a few attempts have been made to improve these models that predict  $k$  based on stream hydraulics. For instance, Bicudo and Giorgetti [1991] included a proxy for bottom roughness that approximates streambed friction. Melching and Flores [1999] used a different approach and separated pool and riffle systems from channel controls (stream with uniform prismatic morphology) to improve the predictive capability of their model. The  $k_{600}$  values determined in these ways can serve as input to equation (15) to calculate  $k$ , which is necessary to determine the CO<sub>2</sub> flux from equation (12). The determination of a correct  $k$  value is critical for accurate gas exchange calculations. For instance, Wallin et al. [2011] observed that the variability in the CO<sub>2</sub> outgassing flux was larger than 80% and attributed this mostly to the variability of  $k$ .

The above considerations show that variabilities of  $k$  on spatial and temporal scales can be large. While slopes mostly explain spatial  $k$  variability, the flow velocity explains temporal  $k$  variations to some extent. Nonetheless, the coefficients of variation remain high with 66% and 60%, respectively [Wallin et al., 2011]. Thus, even if catchments superficially look alike, with similar slopes and flow velocities, they may reveal largely different in situ  $k$  measurements. To illustrate this, Table 1 compiles  $k$  values from the literature. Generally, higher flow velocities and the associated enhanced turbulent flow also decrease the gas transfer with increasing stream order [Butman and Raymond, 2011; Genereux and Hemond, 1992; Wallin et al., 2011]. Contrary to this, in low morphology landscapes,  $k$  may remain stable with stream order (Table 1, Campeau et al. [2014]). The above implies that direct measurements of  $k$  values are more reliable when determined at higher spatial and temporal frequency in the field.

In addition, large-scale carbon flux estimates are biased toward lower summer values in the Northern Hemisphere north of 40°N and are mostly restricted to daytime data [Cole et al., 2007; Tranvik et al., 2009]. Despite the coverage of seasonal variations, the lack of data on diurnal variations can lead to significant underestimations of CO<sub>2</sub> fluxes from streams to the atmosphere. This may thus compromise scaling efforts. We therefore suggest better coverage of studies that also include observations of diurnal cycles. These may be differently pronounced in cold and warm seasons and would have to be researched in typical periods of a hydrologic year and under different typical runoff and climate scenarios, including summer, winter, storm

events, or droughts. The next sections will also outline new integral methods with stable isotopes, which are promising to reveal CO<sub>2</sub> fluxes in complex systems.

## 5. Carbon Isotope Applications

Natural abundance of stable carbon isotopes can be used either qualitatively [Ahad *et al.*, 2008; Amiotte-Suchet *et al.*, 1999; Barth *et al.*, 2003; Cartwright, 2010; Doctor *et al.*, 2008; Kanduč *et al.*, 2007; Stögbauer *et al.*, 2008; Telmer and Veizer, 1999] or quantitatively, such as via a linear mixing model based on isotopic mass balances [Aucour *et al.*, 1999; Cole and Caraco, 2001; Hagedorn and Cartwright, 2010; Kanduč *et al.*, 2012; van Geldern *et al.*, 2015; Waldron *et al.*, 2007]. Systematics of stable isotopes is available in Clark and Fritz [1997] and Coplen [2011]. The underlying concept of mixing models is that input end-members with distinct and clearly defined isotope values can be used for mass balance calculations. One restriction of linear mixing approaches is that temporal variations typically have to be assumed to be negligible for the period of interest. In consequence, temporal variations of stream carbon isotope distributions that depend on changes in relative source contributions increase uncertainties of such mixing models. Drivers such as hydrology, temperature, and length of photoactive periods may modify contributions from potential sources. For instance, proportions of terrestrial to in-stream inputs, of C3 to C4 plants or of different calcite sources such as limestones or pedogenic carbonates, may shift isotope ratios. These source-related uncertainties also apply to <sup>14</sup>C approaches [Cole and Caraco, 2001; Hossler and Bauer, 2012]. First higher-resolution mixing models were based on approaches incorporating such temporal variations to approximate source isotopic signatures [Hossler and Bauer, 2012; Layman *et al.*, 2012].

As a promising approach, stable carbon isotope-based methods have also revealed details about the outgassing processes of aqueous CO<sub>2</sub> [Cartwright, 2010; Doctor *et al.*, 2008; Gray *et al.*, 2011; Kanduč *et al.*, 2007; Michaelis *et al.*, 1985; Palmer *et al.*, 2001; van Geldern *et al.*, 2015]. They enable quantifications of groundwater fluxes, weathering, and biological inputs into streams. New approaches combined with modeling proposed by Polsenaere and Abril [2012] and Venkiteswaran *et al.* [2014] are based on the fact that stream  $\delta^{13}\text{C}_{\text{DIC}}$  values are controlled by isotope signatures of their sources but also by the intensities of CO<sub>2</sub> outgassing. An important observation is that the diffusional loss of CO<sub>2</sub> leads to an enrichment of <sup>13</sup>C in the residual  $\delta^{13}\text{C}_{\text{DIC}}$ . These methods rely on equilibrium isotopic fractionation among aqueous CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> during CO<sub>2</sub> exchange with the atmosphere. Calculations of the entire amount of CO<sub>2</sub> lost upstream of the sampling point then provide good integral CO<sub>2</sub> fluxes from streams to the atmosphere over stream segments. One of the most important aspects in this concept is that they also avoid uncertainties in the determination of *k* values. A further advantage of these new approaches is that only few parameters ( $\delta^{13}\text{C}_{\text{DIC}}$ , DIC concentration, pH, and temperature) are required. So far, these models have mostly been applied to carbonate-free catchments and are ready to become expanded to buffered streams that also receive waters containing dissolved carbonates.

Other than <sup>13</sup>C/<sup>12</sup>C ratios of DIC, stable isotope compositions of DOC have been used to differentiate between water from wetland and upland soils by using selected DOC size fractions [Lambert *et al.*, 2011]. These authors observed vertical and lateral variations of 3‰ to 5‰ in the DOC fraction, which enabled source determinations. However, expected associated links between potential DOC sources in soils and stream DOC require catchment-scale spatial variations of  $\delta^{13}\text{C}_{\text{DOC}}$ . Moreover, biodegradation is associated with the removal of <sup>12</sup>C and causes an increase of the residual  $\delta^{13}\text{C}_{\text{DOC}}$  [Opsahl and Zepp, 2001]. Alteration of the <sup>13</sup>C/<sup>12</sup>C ratio of DOC may occur in cases where DOC is transported mostly laterally through microbial active soil horizons [Lambert *et al.*, 2011]. This can be prevented if the bedrock is permeable and large amounts of carbon are transported vertically. Even though in-stream  $\delta^{13}\text{C}_{\text{DOC}}$  alterations as a result of photodegradation and biodegradation have been observed during laboratory investigations [Opsahl and Zepp, 2001; Spencer *et al.*, 2009], these findings could not be applied in other headwater-scale carbon budget studies.

Apart from natural abundance studies, artificial labeling with stable isotopes can be used to study carbon cycling [Kaplan *et al.*, 2008; Kuzyakov and Domanski, 2000; Studer *et al.*, 2015]. So far, their applications are mostly restricted to laboratory experiments, food web investigations, or studies in lakes and to whole-stream application of labeled <sup>13</sup>C<sub>DOC</sub> tracers [Kaplan *et al.*, 2008]. Novel multi-isotope labeling techniques,

such as simultaneous application and tracking of the three major soil organic matter characteristics (C, O, and H), exist [Studer *et al.*, 2015]. Nevertheless, to date they were neither used to track decomposition pathways nor to highlight changes in organic matter characteristics in the field and thus have a promising potential for future applications of headwater catchments. Note that field studies with aqueous carbon labeling in streams are challenging because even on scales of a few hundred meters influences by natural abundance material can easily mask the artificially introduced labels. Therefore, open system studies of this sort in headwaters need to be carefully planned with beforehand evaluation of realistic amounts of labeled material.

In addition to stable carbon isotopes,  $^{14}\text{C}$  measurements are routinely applied in aqueous carbon research to obtain dates of carbon inputs from the biosphere into soils and/or exchanges with the atmosphere in surface water and groundwater [Bourke *et al.*, 2014; Broecker and Walton, 1959; Chasar *et al.*, 2000; Clark, 2015; Clark and Fritz, 1997; Mook, 2000; Tittel *et al.*, 2013; Trumbore, 2009; Wakeham and Canuel, 2016]. Recent review papers addressed  $^{14}\text{C}$  analyses in groundwater and were published by Geyh [2000] and Han and Plummer [2013, 2016]. Associated radiocarbon units, conventions, and calculations are best compiled in Stuiver and Polach [1977], Mook and van der Plicht [1999], and Stenström *et al.* [2011]. Trends of elevated DOC concentrations and identifications of  $\text{CO}_2$  outgassing as dominant components of carbon export in headwater streams have attracted particular interest in associated carbon ages [Evans *et al.*, 2005; Guo *et al.*, 2007; Hruska *et al.*, 2009; Mayorga *et al.*, 2005; Monteith *et al.*, 2007; Wallin *et al.*, 2013]. Larger amounts of older carbon in streams raise concerns that long-term soil carbon stocks may have become unstable [Gustafsson *et al.*, 2011; Tittel *et al.*, 2013]. Moreover, increased anthropogenic disturbances were found to promote the release of older DOC fractions [Evans *et al.*, 2007; Schiff *et al.*, 1997; Sickman *et al.*, 2010]. For instance, DOC with radiocarbon ages from modern to 202 years B.P. (before A.D. 1950, Geyh [2000]) and outgassing  $\text{CO}_2$  with ages up to 1449 years B.P. were observed in streams draining temperate and subarctic peatlands [Billett *et al.*, 2007, 2012a; Garnett *et al.*, 2013; Leith *et al.*, 2014]. These findings have been challenged by other studies on headwater streams that showed the dominance of DOC sources from recently fixed carbon [Benner *et al.*, 2004; Billett *et al.*, 2012b; Evans *et al.*, 2007; Longworth *et al.*, 2007; Lu *et al.*, 2014; Neff *et al.*, 2006; Palmer *et al.*, 2001; Tipping *et al.*, 2010]. These examples show that carbon ages in streams may be variable and that further correlations with export rates and determinations of source and sink terms are necessary.

## 6. Conclusions and Perspectives

Terrestrial carbon transfer to water and corresponding  $\text{CO}_2$  outgassing are particularly important for headwater catchments that cover a significant portion of the global continental area and thus need to be included with their cumulative area and dynamic processes in global carbon budgets.

In terms of carbon turnover and transport, the cumulative influences of headwaters remain largely unknown, even though our understanding of mechanisms in individual catchments continuously improves. For instance, the mobilization of POC in headwaters largely depends on soil coverage and precipitation rates. Resulting discharge-activated flow pathways drive the temporal and spatial variability of stream POC. For headwater streams, the literature reports a wide range and high POC concentrations in response to storms, in eroding systems and in peatland catchments. Predictions of this dynamic carbon phase remain challenging, and specific catchment characteristics together with individual rainfall-runoff events should be characterized at higher spatial and temporal resolution.

Similarly, DOC transport is often governed by complex hydrological regimes. Temporal DOC dynamics in small streams are primarily controlled by runoff-induced hydrological connectivity of source areas such as soils. Here changes in DOC production and its mobilization often establish the basis for long-term changes in DOC fluxes. For such mass balances, the differentiation of various DOC fractions and determination of their isotope values is a promising approach that allows for improved source allocation [Lambert *et al.*, 2014]. Moreover, sink and source allocations and correlations with export rates in cases of variable  $^{14}\text{C}$  ages in streams are essential techniques to better understand their carbon dynamics.

While organic carbon phases in headwater streams are dominated by soils and the biosphere, DIC is mostly related to lithology and remains largely a product of soil/bedrock weathering. These processes are in turn enhanced by root respiration and the turnover of organic matter in the soil and its soil pore water. We



outlined that relative inputs of DIC by biological turnover and weathering and their combination often remain unclear. Moreover, headwater streams with large DOC concentrations, little canopy shading and long water transit times of more than 2 days can also receive further contributions to the DIC pool from biodegradation and photodegradation of organic carbon. Even small proportions of carbonate rocks in catchments are able to dominate their hydrochemistry and with that of their DIC fluxes.

We summarized that CO<sub>2</sub> outgassing from headwater streams to the atmosphere may be larger than lateral downstream aqueous carbon exports [Venkiteswaran *et al.*, 2014; Wallin *et al.*, 2013]. Known mechanisms are hydrological flow paths that connect CO<sub>2</sub>-rich groundwaters and soil solutions with streams. These hydrological inputs, combined with associated turbulence and related gas transfer velocity values, drive stream CO<sub>2</sub> concentrations and outgassing in headwater streams. Our global analysis of *p*CO<sub>2</sub> for catchment size intervals of 20 km<sup>2</sup> indicated that rivers and streams with catchment areas smaller than 500 km<sup>2</sup> exhibit consistently high maximum *p*CO<sub>2</sub> values. However, it is also evident that large variances remain between individual catchments. By taking into account the cumulative area of headwater streams with Strahler stream orders 1 to 3 [Downing *et al.*, 2012] and by assuming the *p*CO<sub>2</sub> values to be at least three times the global average, we were able to estimate a 35% increase of *p*CO<sub>2</sub> values from the global average. Despite its uncertainty, this value stresses the important and so far hardly studied potential of CO<sub>2</sub> outgassing to the atmosphere by headwater streams.

We also showed that radio- and stable isotope investigations facilitate mass balance calculations, source attributions, and evaluations of the turnover rates of organic matter within soil water, groundwater, and surface water compartments. They also enable subsequent estimates of carbon residence times in headwater catchments. New methods that are based on changes in <sup>13</sup>C/<sup>12</sup>C ratios of DIC during outgassing from rivers and streams are promising tools for adding more accurate numbers to global estimates [Doctor *et al.*, 2008; Polsenaere and Abril, 2012; Raymond and Bauer, 2001; van Geldern *et al.*, 2015; Venkiteswaran *et al.*, 2014]. Such inversed modeling enables determination of integral CO<sub>2</sub> losses upstream from the measurement point [Polsenaere and Abril, 2012; Venkiteswaran *et al.*, 2014]. The benefits of these approaches are that only few parameters are required. Another advantage is that they are independent of the largely variable gas transfer velocity (*k*). Thus, these approaches have a huge potential to be applied in future evaluations of CO<sub>2</sub> losses in headwater catchments.

Moreover, the role of groundwater inputs to streams and their influence on headwaters need to be better characterized. So far, most headwater studies either completely leave out groundwater components or approximate them via springs. Better instrumentation of headwater catchments thus needs to include additional piezometers, the application of multiscale geophysical imaging approaches, and of integral CO<sub>2</sub> outgassing isotope approaches. Such approaches will also help to fill knowledge gaps with respect to high-resolution temporal (i.e., diurnal) and spatial variations of carbon fluxes. Also, optical isotope techniques and new field-deployable laser isotope techniques are promising to allow for monitoring carbon dynamics based on real-time data [Griffis, 2013; van Geldern *et al.*, 2014].

This study complements research on higher-order streams and the downstream parts of larger catchments [Gaillardet *et al.*, 1999; Oni *et al.*, 2011; Schulte *et al.*, 2011; Temnerud and Bishop, 2005; Yang *et al.*, 1996]. Overall, studies on headwaters and their carbon cycles are currently not systematic enough, and we suggest a global network that is similar to other international approaches such as the International Continental Scientific Drilling Program or the International Ocean Discovery Program [Prevedel, 2007]. Such international efforts have successfully unified scientists from various fields and from different continents to systematically work on one big scheme. Such concerted efforts can also be transposed to representative headwater catchments from different climate zones and with representative lithologies, soils, and land use types. For this effort, typical headwater catchments will have to be selected to allow realistic upscaling of determined carbon fluxes and should include a range from peatland to sandy soil types as well as clastic, carbonate, and hard rock lithologies in tropical, midlatitude, and cold climates. Such a network would provide better data sets and establish the basis for models on carbon turnover in headwaters and global data analyses. Expansion of existing networks such as the one of biogeochemical monitoring (BIOGEMON) [Novak *et al.*, 2008], of CO<sub>2</sub> flux assessment in European running waters (EuroRun) [Attermeyer and Bodmer, 2017] and the Critical Zone Observatories (CZO) [Anderson *et al.*, 2008] are a good basis for expansion toward studies on headwater streams.

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