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# Applications of stable water and carbon isotopes in watershed research: Weathering, carbon cycling, and water balances

Peter Schulte <sup>a,\*</sup>, Robert van Geldern <sup>a</sup>, Heiko Freitag <sup>b,c</sup>, Ajaz Karim <sup>b,d</sup>, Philippe Négrel <sup>e</sup>,  
Emmanuelle Petelet-Giraud <sup>e</sup>, Anne Probst <sup>f,g</sup>, Jean-Luc Probst <sup>f,g</sup>, Kevin Telmer <sup>h</sup>,  
Ján Veizer <sup>b</sup>, Johannes A.C. Barth <sup>a</sup>

<sup>a</sup> GeoZentrum Nordbayern, Universität Erlangen, Schlossgarten 5, D-91054 Erlangen, Germany

<sup>b</sup> Department of Earth Sciences and Ottawa-Carleton Geoscience Centre, University of Ottawa, Ottawa, Canada K1N 6N5

<sup>c</sup> Umwelt & Baugrund Consult, Alte Ziegelei 7, 51491 Overath, Germany

<sup>d</sup> Chinook Consulting Services, 742 Memorial Drive Northwest, Calgary, Canada T2N 3C7

<sup>e</sup> BRGM, 3 Avenue Claude Guillemin, BP 6009, 45060 Orléans Cedex 2, France

<sup>f</sup> Université de Toulouse, UPS, INPT, Laboratoire Ecologie fonctionnelle et Environnement (EcoLab), ENSAT, Avenue de l'Agrobiopôle, F-31326 Castanet-Tolosan, France

<sup>g</sup> CNRS; EcoLab; ENSAT, F-31326 Castanet-Tolosan, France

<sup>h</sup> School of Earth and Ocean Sciences, University of Victoria, Victoria, Canada V8W 3P6

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## ABSTRACT

Research on rivers has traditionally involved concentration and flux measurements to better understand weathering, transport and cycling of materials from land to ocean. As a relatively new tool, stable isotope measurements complement this type of research by providing an extra label to characterize origin of the transported material, its transfer mechanisms, and natural versus anthropogenic influences. These new stable isotope techniques are scalable across a wide range of geographic and temporal scales. This review focuses on three aspects of hydrological and geochemical river research that are of prime importance to the policy issues of climate change and include utilization of stable water and carbon isotopes: (i) silicate and carbonate weathering in river basins, (ii) the riverine carbon and oxygen cycles, and (iii) water balances at the catchment scale. Most studies at watershed scales currently focus on water and carbon balances but future applications hold promise to integrate sediment fluxes and turnover, ground and surface water interactions, as well as the understanding of contaminant sources and their effects in river systems.

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\* Corresponding author. Tel.: +49 9131 85 22514.

E-mail address: [schulte@geol.uni-erlangen.de](mailto:schulte@geol.uni-erlangen.de) (P. Schulte).

## 1. Introduction

Rivers are the veins of our continents and studies of river water and sediments help to understand and quantify biogeochemical dynamics in their basins as well as their ecological and environmental impacts. In this context, river watersheds are important because, more than ever, anthropogenic factors increasingly threaten the availability and quality of clean water supplies. Considering that more than one half of the accessible freshwater runoff globally is already appropriated for human use (e.g., Postel et al., 1996; Jackson et al., 2001), and that two-thirds of all Earth's rivers are impacted by regulations (e.g., Vitousek et al., 1997), such research is important in view of its geoscientific, ecological, and environmental context.

Initially, hydro-bio-geochemical work on rivers focused mostly on the concentrations of dissolved and particulate constituents and, when discharge rates were available, enabled calculations of fluxes and mass balances for entire catchments (e.g., Paces, 1985; Probst, 1986; Probst et al., 1992, 1995; Ramanathan et al., 1994; Jing, 1995; Guieu et al., 1998; Chiffolleau et al., 1999; Freyssinet and Farah, 2000; Vörösmarty et al., 2000; Anderson and Dietrich, 2001; Grosbois et al., 2001; Oliva et al., 2004; Lafrenière and Sharp, 2005; Zakharova et al., 2005).

Over the last few decades, the data on inorganic and organic constituents and ionic fluxes in river basins were complemented by isotope tracers, including stable water and carbon isotopes (Hitchon and Krouse, 1972; Négrel et al., 1993; Pawellek and Veizer, 1994; Flintrop et al., 1996; Gaillardet et al., 1997; Barth et al., 1998; Kendall and McDonnell, 1998; Amiotte-Suchet et al., 1999; Aucour et al., 1999; Barth and Veizer, 1999; Telmer and Veizer, 1999; Farah et al., 2000; Karim and Veizer, 2000; Telmer and Veizer, 2000; Kendall and Coplen, 2001; Hélie et al., 2002; Karim and Veizer, 2002; Barth et al., 2003; Darling et al., 2003; Lee and Veizer, 2003; Négrel et al., 2003; Barth and Veizer, 2004; Lambs, 2004; Brunet et al., 2005; Das et al., 2005; Diefendorf and Patterson, 2005; Lambs et al., 2005; Rodgers et al., 2005; Stephens and Rose, 2005; Barth et al., 2006; Amiotte-Suchet et al., 2007; Ferguson et al., 2007; Ferguson and Veizer, 2007; Doctor, 2008; Freitag et al., 2008; Stögbauer et al., 2008; Brunet et al., 2009; Lambs et al., 2009; Dubois et al., 2010; Ferguson et al., 2011; Karim et al., 2011). The main purpose of most of these studies was to constrain the sources and cycling of water and solutes in river systems.

In this review we will summarize three aspects of hydrological and geochemical research that are of prime importance to the policy issues of climate change and include utilization of stable isotopes:

- (i) Silicate and carbonate weathering
- (ii) Riverine carbon and oxygen cycles
- (iii) Water balances at the catchment scale.

Sediment transport and turnover impacted by agriculture and urbanization, investigation of the aquatic communities, and nutrient cycling are additional important applications of stable isotopes in riverine research. However, they are not discussed here to keep the review concise.

## 2. Silicate and carbonate weathering

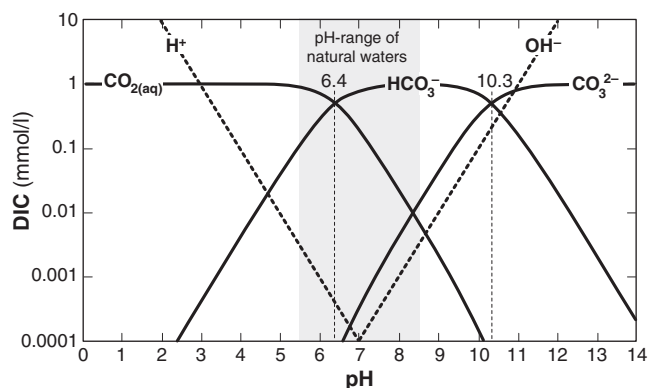
River water chemistry is to a large extent a product of chemical rock weathering, dissolution/hydrolysis, and precipitation of minerals. Chemical weathering processes involve interactions between hydrological and biogeochemical cycles that are among the major controls of terrestrial and seawater chemistry, factors that ultimately control the CO<sub>2</sub> sequestration in terrestrial and marine environments. This occurs at various timescales and happens at three major interfaces: (1) The atmosphere–lithosphere interface: Dissolution of carbonates in the terrestrial realm is usually considered to be balanced by carbonate precipitation in the oceans. Weathering of

continental silicate rocks, on the other hand, consumes atmospheric CO<sub>2</sub>, and this negative feedback effect may thus control the long-term (>10<sup>4</sup> a) evolution of the global climate (e.g., Amiotte-Suchet and Probst, 1993a, 1993b; Probst et al., 1994; Amiotte-Suchet and Probst, 1995; Boeglin and Probst, 1998; Ludwig et al., 1998; Gaillardet et al., 1999; Galy and France-Lanord, 1999; Kump et al., 2000; Amiotte-Suchet et al., 2003; Dupré et al., 2003; Mortatti and Probst, 2003; Hartmann et al., 2009). Additional impacts on the weathering regime may arise from human activities that can lead, for example, to acid rain or to a modification of the atmospheric CO<sub>2</sub> budget (Paces, 1985; Thompson et al., 1986; Probst et al., 1992; Sverdrup et al., 1992; Amiotte-Suchet et al., 1995; Semhi et al., 2000a; Li et al., 2008; Perrin et al., 2008; Pierson-Wickmann et al., 2009; Raymond and Ho, 2009; Gandois et al., 2011). (2) The biosphere–lithosphere interface: The type and productivity of vegetation strongly influences the rate of weathering via decomposition of organic matter by micro- and macro-organisms. This usually decreases the pH and produces CO<sub>2</sub>, while the release of organic acids further enhances the dissolution and hydrolysis of minerals by (Ochs et al., 1993; Welch and Ullman, 1993; Hinsinger, 1998). This, in turn, releases cations, such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Fe<sup>3+</sup> that are essential for plant growth (Warfvinge et al., 1993; Quideau et al., 1996; Dambrine et al., 1998; Reynolds et al., 2000; Williams et al., 2003; Moncoulon et al., 2004; Karyotis et al., 2005). As a consequence, climate, chemical weathering rates, nutrient levels, and vegetation communities are strongly interdependent variables. It is this complex system that directly controls surface and groundwater chemistry and that also responds to climate changes and anthropogenic impacts, ranging from the human release of CO<sub>2</sub> into the atmosphere to dispersal of agricultural, domestic, and industrial pollutants. (3) The river–ocean interface: Rivers and near-shore aquifers deliver the products of continental weathering to estuarine and coastal zones and the open ocean, thus influencing the productivity of these ecosystems (e.g., Justic et al., 1997; Rabalais et al., 2009). This topic is of lesser interest here because our review focuses on riverine processes and on the ground and surface water interaction. This implies cycling of water and elements before they reach the ocean.

### 2.1. Weathering and stable isotopes of water and carbon

While weathering processes directly influence the geochemistry of groundwater (e.g., Drever, 1982; Dupré et al., 1996; Semhi et al., 2000a, 2000b; Barth et al., 2003; Zakharova et al., 2007), the attribution of major ion supply to distinct lithologies cannot be easily quantified for large catchments (Meybeck, 1979; Stallard and Edmond, 1987; Négrel et al., 1993; Probst et al., 1994; Gaillardet et al., 1999). This is due to the diversity of watershed lithologies coupled with difficulties in estimating their relative subsurface spatial distributions and weathering rates (Amiotte-Suchet et al., 2003). Such estimates are primarily based on a combination of river classification schemes complemented by most common mineral weathering reactions (Meybeck, 1987). However, this approach still ignores anthropogenic impacts on major ion chemistry and the potentially significant role of trace mineral dissolution (Anderson et al., 1997; Probst et al., 2000; Aubert et al., 2004; Oliva et al., 2004).

Stable isotopes may help to constrain the inputs from dissolution of various minerals and rock types. For example, carbonates dominate surface and groundwater chemistry due to their ubiquity and high solubility. When dealing with the aqueous carbonate system it is instructive to consider pH-dependency of the speciation of dissolved inorganic carbon (DIC) as shown in the Bjerrum plot (Fig. 1; Drever, 1982). The carbon isotopic composition of DIC is a function of relative abundance of the species CO<sub>2(aq)</sub>, H<sub>2</sub>CO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> and is defined by their corresponding temperature-dependent fractionation factors (e.g., Zhang et al., 1995). This means that for any pH the equilibrium isotopic composition of the DIC can be predicted if



**Fig. 1.** Concentrations of the dissolved inorganic carbon (DIC) species  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ , and  $\text{OH}^-$  as functions of pH (Bjerrum plot) for freshwater at a temperature of 25 °C; “aq” as subscript corresponds to the aqueous phase. Modified after Drever (1982).

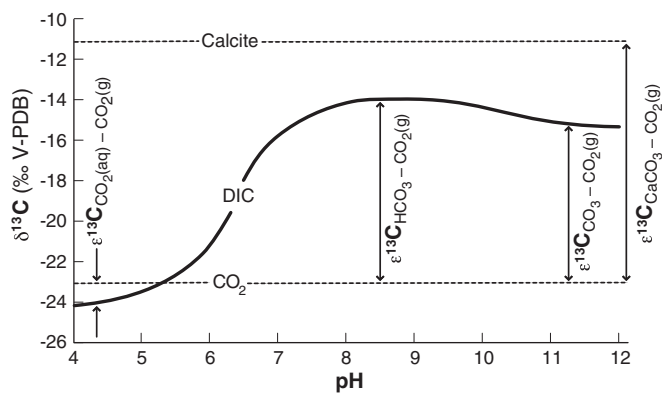
the isotope values of the soil  $\text{CO}_2$  and carbonates are known (Figs. 2 and 3).

The isotope values of these two end-members are usually known within narrow ranges. The  $\delta^{13}\text{C}$  values for most marine carbonates average at  $\sim 0\%$  (Clark and Fritz, 1997). Carbonates then react with carbonic acid derived mostly from higher  $\text{CO}_2$  levels in soils. The isotopic composition of this soil  $\text{CO}_2$  is inherited from decaying organic matter and depends on the photosynthetic pathway of the precursor vegetation with values of about  $-27\%$  for C3 plants and about  $-12.5\%$  for C4 plants (Vogel, 1993). Subsequently, the soil  $\text{CO}_2$  may become enriched, by about 4.4‰, due to diffusion processes (Cerling et al., 1991), thus yielding isotope values around  $-23\%$  for the globally dominant C3 ecosystems, or as high as  $-10\%$  for landscapes dominated by C4 plants, such as corn, salt marshes, or savannah ecosystems (e.g., Meyers, 1994; Sifeddine et al., 2004).

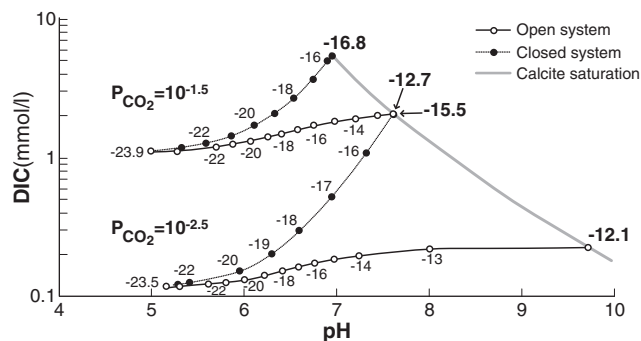
In any case, this combination of stable isotopes with pH and DIC provides a tool for quantification of the degree of carbonate dissolution versus silicate weathering. This technique is summarized in Fig. 3 and further applications are shown in Clark and Fritz (1997) and Cronin et al. (2005). A comprehensive case study on the use of stable water and carbon isotopes from the Lagan River in Northern Ireland (Barth et al., 2003) is outlined in the following inset.

### 2.2. Case study on the Lagan River (Northern Ireland)

This study investigated the chemistry and  $\delta^{13}\text{C}_{\text{DIC}}$  of the Lagan River that flows through Northern Ireland’s most densely populated



**Fig. 2.** pH-dependency of the  $^{13}\text{C}$  composition of the dissolved inorganic carbon (DIC) species in equilibrium with soil  $\text{CO}_2$  ( $\delta^{13}\text{C} = -23\%$  V-PDB) at 25 °C; “g” as subscript corresponds to the gas phase and “e” is the enrichment factor. Adapted from Clark and Fritz (1997).

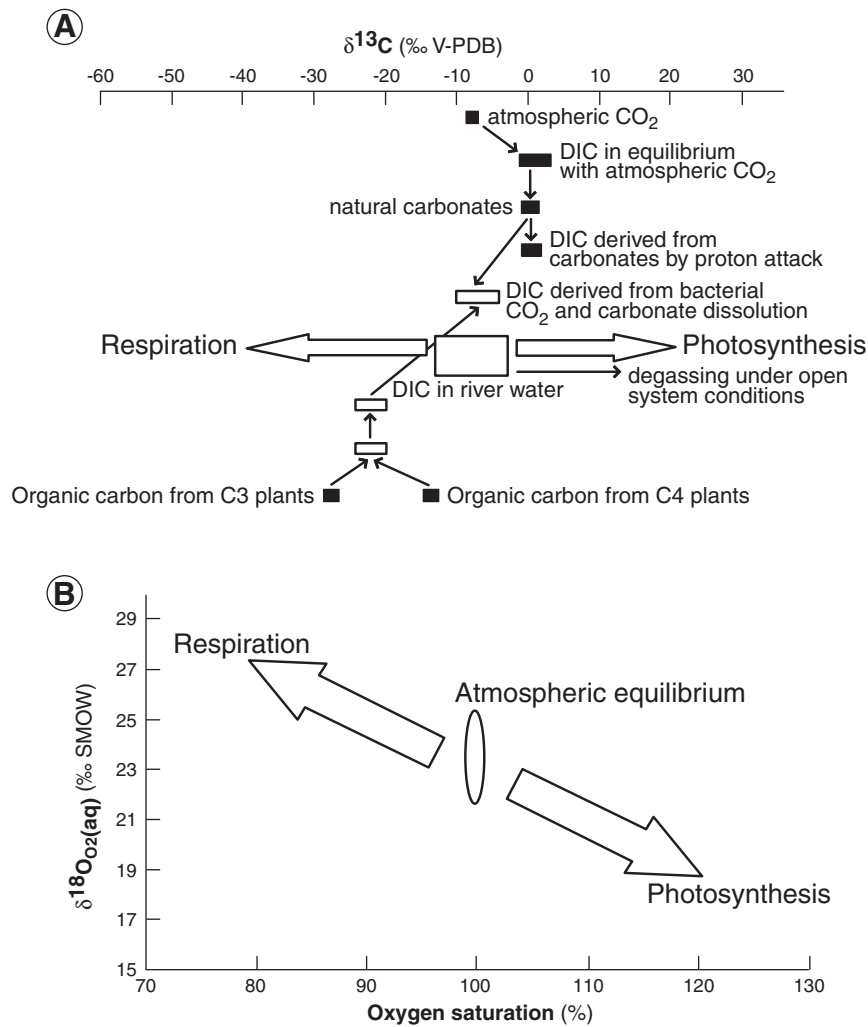


**Fig. 3.** Concentration of DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  as groundwater dissolves calcite ( $d^{13}\text{C} = 0\%$  V-PDB). Shown are conditions for open and closed systems at high ( $10^{-1.5}$ ) and low ( $10^{-2.5}$ ) partial pressures of soil  $\text{P}_{\text{CO}_2}$  from C3 vegetation ( $\delta^{13}\text{C}_{\text{CO}_2} = -23\%$ ). Final  $d^{13}\text{C}$  values at calcite saturation are shown in bold. Note that open system dissolution maintains a constant  $\text{pCO}_2$ . In contrast, under closed system conditions the  $\text{pCO}_2$  of groundwater decreases as calcite is dissolved. For open system conditions, the increase in  $d^{13}\text{C}$  results from the continuous exchange with the soil  $\text{CO}_2$  at increasing pH (see also Fig. 2) and replenishment of  $\text{CO}_2$  in open systems allows for considerably more calcite to be dissolved. The stronger increase in  $^{13}\text{C}$  enrichment for the closed systems results from dilution of the initial DIC with marine carbonate. Modified after Clark and Fritz (1997).

area and discharges to the Irish Sea at the city of Belfast. The Lagan catchment covers an area of 609  $\text{km}^2$ . Annual rainfall varies from 950 mm at Belfast to 1200 mm in the source region. Mafic igneous rocks in addition to sandstones, greywackes, and mudstones are the main rock types in the source region with only about 5% limestones. Yet, carbonates were shown to play the dominant role in the river carbon cycle (Barth et al., 2003). The pH values increased down-river, accompanied by  $\delta^{13}\text{C}_{\text{DIC}}$  approaching values expected for dissolution of sedimentary carbonates (Fig. 4A). The latter trend, however, was observed only in the river itself, but not in the groundwater samples across the catchment. The ground water point sources usually missed the minor carbonates and reflected mostly weathering of silicates. This observation shows that rivers are a better integration medium of dominant weathering processes than the localized groundwater sampling protocols. These observations also show a disproportionate impact of carbonate weathering processes on watershed scales. This should be even more pronounced for large rivers where carbonates frequently account for a larger proportion of the catchment lithology. A complementary control on the carbon cycle in the Lagan River was silicate weathering and the respiratory turnover of organic material that was mainly of anthropogenic origin. The latter resulted in a  $\sim 26\%$  increase of DIC concentration from the source to the river mouth. Stable isotope analyses of DIC confirmed this transition, from mainly natural controls of the carbon cycle near the river source to anthropogenic ones closer to its mouth. A recently installed weir near the river discharge to the sea, at Belfast Lough, added an additional complication. The resulting influx of stagnant seawater, accounting for 53 to 92% of the water mass up to next upstream weir near the city of Belfast, caused poor vertical mixing of water bodies and the loss of dissolved oxygen due to anaerobic activities that generated methane. The decline in  $\text{pCO}_2$  as well as the  $^{13}\text{C}$ -enriched DIC values at the sediment-water interface reflects this scenario. Installations of such weirs in estuaries of other rivers could result in similar anoxic effects and associated biogeochemistry.

### 3. The riverine carbon cycle

Since rivers are potential sites for pollutant disposal, growing environmental concern led to investigations of their ecology and biogeochemistry (e.g., Barth et al., 2009). The understanding of the riverine carbon cycle is of particular interest because it reflects the state of aquatic life and its biodiversity, both within the rivers and in their catchments. Furthermore, the quantification of carbon transport



**Fig. 4.** (A) Carbon isotopic signature of various components of the carbon cycle in rivers. The effects of biogeochemical processes on  $\delta^{13}\text{C}$  are shown with arrows. White rectangles indicate  $\delta^{13}\text{C}_{\text{DIC}}$  measurements specific to the Mississippi. (B) General effects of production (photosynthesis), respiration and atmospheric exchange on the isotopic composition of dissolved  $\text{O}_2$  ( $\delta^{18}\text{O}_{\text{O}_2(\text{aq})}$ ) and the degree of oxygen saturation in aquatic ecosystems. Modified from Dubois et al. (2010).

by rivers, as particulate and dissolved organic and inorganic loads, is important for closure of the global carbon cycle budget. While concentration measurements alone are helpful in constraining the carbon fluxes (Degens et al., 1984), their combination with stable isotope measurements helps to delineate the sources, internal riverine cycling, and the interactions with the biosphere and the atmosphere (Pawellek and Veizer, 1994; Flintrop et al., 1996; Yang et al., 1996; Barth et al., 1998; Amiotte-Suchet et al., 1999; Aucour et al., 1999; Barth and Veizer, 1999; Telmer and Veizer, 1999; Pawellek et al., 2002; Barth et al., 2003; Das et al., 2005; Ferguson et al., 2007; Hori et al., 2008; Brunet et al., 2009; Dubois et al., 2010; Ferguson et al., 2011; Karim et al., 2011).

A prominent feature of most rivers is their significantly higher partial pressure of  $\text{CO}_2$  ("p $\text{CO}_2$ ", [bar]) in the water column compared to the atmosphere (Kempe, 1982; Telmer and Veizer, 1999). This excess  $\text{CO}_2$  may arise from enhanced dissolved organic carbon load from natural or anthropogenic sources and its respiratory turnover to  $\text{CO}_2$  and/or from groundwater input that usually has much higher  $\text{CO}_2$  concentrations due to its link to weathering and the soil zone. Regardless of the origin of this  $\text{CO}_2$  overpressure, most rivers degas the  $\text{CO}_2$  to the atmosphere, which leads to a positive shift in  $\delta^{13}\text{C}_{\text{DIC}}$  (e.g., Amiotte-Suchet et al., 1999). Because of this  $\text{CO}_2$  evasion, the most common pattern is a p $\text{CO}_2$  decline downriver, as seen for example for the Amazon (Richey et al., 2002) or the Nyong River in

Cameroon (Brunet et al., 2009). An exception to this pattern is rivers originating from or flowing through large lakes, these being largely degassed due to the prolonged residence time of their water bodies. Rivers discharging from such lakes have low  $\text{CO}_2$  levels, close to equilibrium with the atmosphere (Karim et al., 2011). This is the case, for example, for the St. Lawrence River that emerges from the Great Lakes (Yang et al., 1996; Barth and Veizer, 1999), the Upper Rhine below Lake Constance (Kempe, 1982; Buhl et al., 1991), the Rhone below Lake Lemman (Aucour et al., 1999), or the reservoir lakes of Patagonian rivers (Brunet et al., 2005). In this case, the riverine p $\text{CO}_2$  may even increase down-river, with the rate of increase proportional to the relative volume of water originating from the tributaries with their high p $\text{CO}_2$  levels. If the proportion of tributary water in the main stem river is small, such as the St. Lawrence River, the down-river p $\text{CO}_2$  rise is also subdued. On the other hand, such p $\text{CO}_2$  increases may be more pronounced if tributaries exert stronger influences on the main river such as for instance in the Rhine. Note that this observation for the Rhine was initially attributed to down-river increase in pollution and its respiratory turnover to  $\text{CO}_2$  (Kempe, 1982; Buhl et al., 1991) while more recent studies revealed that it is mostly a reflection of an increasing proportion of water from the poorly degassed tributaries (Flintrop et al., 1996). Another example of a down-river p $\text{CO}_2$  change may arise when the upstream watershed that is composed of silicate lithologies evolves into a

carbonate watershed downstream, such as for instance in the Ottawa River (Telmer and Veizer, 1999). Overall, terrestrial water bodies (rivers and lakes) likely serve as conduits for dissipation of CO<sub>2</sub> generated by biogenic activity in soils of the watershed (Amiotte-Suchet et al., 1999; Dubois et al., 2009; 2010) and the flux of CO<sub>2</sub> to the atmosphere may be comparable to that discharged annually to the oceans (Brunet et al., 2009; Dubois et al., 2010). It is therefore essential to understand the sources and sinks of carbon in aquatic systems (Kempe, 1979) in order to establish a closure of the terrestrial carbon budget.

In most cases, the dominant source of CO<sub>2</sub> in rivers is groundwater input, followed by processes within rivers, such as CO<sub>2</sub> increase by respiration or decline due to photosynthesis, and equilibration with or evasion to the atmosphere. The initial  $\delta^{13}\text{C}_{\text{DIC}}$  for groundwater from C4 plant ecosystems that dominate globally is about  $-23\%$  if no carbonate weathering is involved (Fig. 4). Photosynthesis in the water column preferentially selects the lighter carbon, thus enriching the remaining DIC in  $^{13}\text{C}$ . The third process, exchange with the atmosphere, involves equilibration between gaseous CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup><sub>(aq)</sub>, the dominant species of DIC at the pH range commonly found in rivers (Fig. 1). Although temperature-dependent, the isotopic fractionation for this equilibration is about  $+8\%$  (Mook et al., 1974; Zhang et al., 1986). With the  $\delta^{13}\text{C}$  of the atmosphere of  $-7.7\%$  (Ciais et al., 1995) this results in a value of  $-0\%$  for atmospherically equilibrated DIC.

In the upper St. Lawrence River, where most water originates from the isotopically equilibrated Great Lakes, with water residence time of more than 100 years (Yang et al., 1996; Barth and Veizer, 1999), the  $\delta^{13}\text{C}_{\text{DIC}}$  is about  $-1\%$  and decreases down-river to about  $-4\%$  due to the increasing proportion of soil CO<sub>2</sub> from the tributaries. In watersheds with ubiquitous carbonates, such as the lower Rhine, Rhone, or Danube, the  $\delta^{13}\text{C}_{\text{DIC}}$  is about  $-10 \pm 2\%$  reflecting the 1:1 mixture of carbon of bacterial and carbonate origin (Fig. 4A; Pawellek et al., 2002; Hartmann et al., 2007). Carbon from dissolution of carbonate rocks tends to dominate even in watersheds where carbonates are present only in trace amounts and sulfate loads are high (Das et al., 2011). Nevertheless, should weathering by sulfur-oxidation play a significant role, the proportion of carbonate carbon in the mixture can diminish (Calmels et al., 2007). Rivers draining silicate watersheds, such as the Amazon (Richey et al., 2002) or the upper Nyong in Cameroon (Brunet et al., 2009) that derive their carbon entirely from organic sources, have more negative  $\delta^{13}\text{C}_{\text{DIC}}$  values, down to  $-26\%$  (Fig. 4A), typical of ecosystems with a dominant C3 plant metabolism.

Fig. 4A also demonstrates the complexity of processes that influence the isotopic composition of DIC. For instance, it is difficult to decide whether equilibration with the atmosphere (e.g., degassing of CO<sub>2</sub> or uptake during phytoplankton blooms), carbonate dissolution, or photosynthesis is responsible for positive  $\delta^{13}\text{C}_{\text{DIC}}$  shifts frequently observed down-river (Doctor et al., 2008; Brunet et al., 2009). To further constrain sources, sinks, and turnover of carbon, the stable isotopic compositions of complementary species may therefore be useful. One application is the combination of the isotopic composition of the DIC with that of the particulate organic carbon (POC) and the dissolved organic carbon (DOC) in order to better understand the *in situ* production of algae (Barth et al., 1998; Hellings et al., 1999; Kao and Liu, 2000; Raymond and Bauer, 2001; Savoye et al., 2003; Wang et al., 2004). This may help in quantification of relative inputs from allochthonous and autochthonous carbon production, enabling us to outline the ecologically most fragile sections of rivers.

Another complementary tool to constrain the riverine carbon cycle is the isotopic composition of the dissolved oxygen ( $\delta^{18}\text{O}_{\text{O}_2(\text{aq})}$ ). This innovative technique (Wassenaar, in press) adds additional information to concentration measurements of dissolved oxygen, the latter being one of the most commonly measured parameters in marine and

freshwater studies. The present dearth of such data is due to difficult analytical techniques that require molecular oxygen to be turned into CO<sub>2</sub> on graphite in the presence of a platinum catalyst with water requirement in excess of 1 l (Quay et al., 1993). The few studies that have investigated the isotopic composition of dissolved oxygen already provided insights into the dissolution of atmospheric gases, respiration, and photosynthesis in aqueous systems. These studies also brought to light new information for our understanding of oxygen turnover and the operation of the carbon cycle in the deep-sea (Kroopnick and Craig, 1976), surface ocean (Quay et al., 1993; Luz and Barkan, 2000), groundwater (Aggarwal and Dillon, 1998), fresh surface waters (Quay et al., 1995; Aggarwal and Dillon, 1998; Wassenaar and Koehler, 1999; Wang and Veizer, 2000; Venkiteswaran et al., 2007; Dubois et al., 2009), and estuaries (Ahad et al., 2008). Other studies have focused on oxygen isotope effects and their associated physical aspects, such as equilibrium dissolution (Benson and Krause, 1984; Aregbe et al., 2002). An overview and recent improvements of this technique for bulk measurements on small sample volumes is provided by Barth et al. (2004). The oxygen isotope method nicely complements carbon isotope studies because photosynthesis and respiration cause isotope effects opposite to those of DIC. Respiration, photosynthesis, and atmospheric exchange can thus be better quantified (Fig. 4B).

## 4. Water fluxes in river catchments

### 4.1. Water transport and mixing

Water has two elements, oxygen and hydrogen, the stable isotope systems isotope ratios of which can be readily measured without much concern for storage and preservation, providing evaporation after sampling is avoided and samples are stored in suitable sample containers (preferably made from glass or high-density polyethylene; cf. Clark and Fritz, 1997; Mook, 2000; Spangenberg and Vennemann, 2008). Specifically, stable water isotopes can serve as a conservative tracer as long as their ratios have not been influenced by evaporation in water bodies or by water rock interaction at elevated temperatures (e.g., Gat, 1996). For instance, stable water isotopes can help to determine mixing of water masses with distinct isotopic compositions. In the case of two component mixing, the formula of weighted averages is:

$$C = (A \cdot M_1 + B \cdot M_2) / (M_1 + M_2)$$

where  $M_1$  and  $M_2$  are the proportions of the water masses involved and A, B, and C are the isotope compositions of the so called end-members and the mixture, respectively. When all isotope compositions are known this equation can easily be solved to quantify the proportions of the water masses originating from different tributaries or from different flow components (Ladouche et al., 2001; Winston and Criss, 2003).

While such techniques are frequently applied to groundwater flowpath and provenance analysis (e.g., Vennemann and Angloher-Reichert, 2005), they can also be useful also for mass balances in rivers if the end members are known. However, when more than two end members are involved, other conservative tracers, such as dissolved chloride, have to be included in the system of equations (Barth and Veizer, 2004). Indeed, the composition of the "end-members" can vary during hydrological events depending on various contributions. A combination of multiple tracers, such as stable water isotopes and major and trace elements, is recommended to constrain the processes and the types of water involved (Ladouche et al., 2001). Such mixing calculations are useful for understanding ground and surface water interactions as well as for associated transport of water and its dissolved and particulate constituents.

## 4.2. Runoff and evapotranspiration

Water isotopes have been also utilized for investigation of global runoff patterns and climate (e.g., Kayser et al., 1990; Tardy et al., 1995; Berner and Berner, 1996; Lambs et al., 2005). However, in this context relatively little is known about the processes that govern the evapotranspirative loss from continents. In most cases, less water leaves watersheds via river discharge than provided by precipitation, the difference being accounted for by evapotranspiration (ET). ET describes the sum of the evaporative and plant transpiration fluxes from the Earth's land surface to the atmosphere. Evaporation accounts for the movement of water to the air from sources such as the soil, canopy interception, and water bodies. Transpiration accounts for the movement of water within a plant and the subsequent loss of water as vapor through stomata in its leaves. Thus, evaporation and transpiration have to be quantified if a detailed water balance for a large area needs to be investigated. Such knowledge may be required for example for water husbandry related to application of selected vegetation schemes.

Traditional separations of evaporation and transpiration rely on empirical estimates, such as the Penman, Thornthwaite, or Haude methods, or on lysimeter measurements (for a review see Domenico and Schwartz, 1998, and references therein). These methods, appropriate for small catchments, either require an estimate of a large number of parameters, such as wind speed, sunshine intensity, and duration (Viville et al., 1993), or have to be scaled up from point measurements to larger geographic areas, resulting in considerable uncertainties when dealing with large and variable catchments. In contrast, the stable isotope method presented below has the advantage of yielding integrated information that is valid for entire river basins (Lee and Veizer, 2003; Barth et al., 2006; Ferguson and Veizer, 2007; Freitag et al., 2008; Karim et al., 2008). This method relies on the fact that among interception, transpiration, and evaporation, only evaporation causes isotope fractionation of water molecules (e.g., Pate, 2001). By sampling the tributaries, the sub-catchments of river basins can also be characterized with this technique.

The general hydrologic balance of a watershed (Braud et al., 1995; Leopoldo et al., 1995) can be expressed as follows:

$$ET = P - (Q_{DS} + Q_{BF}) \pm \Delta S = P - Q_t \pm \Delta S$$

where ET is water lost to evapotranspiration, P represents precipitation,  $Q_{DS}$  is direct surface runoff,  $Q_{BF}$  is the base flow,  $Q_t$  corresponds to the total runoff, and  $\Delta S$  is the change in groundwater storage.

Over time intervals of at least one hydrological year or longer, it can be assumed that the groundwater storage is homogeneous and thus  $\Delta S$  becomes negligible. Then the equation simplifies to:

$$ET = P - Q_t$$

P and  $Q_t$  are directly measurable, and such data are often freely available from public databases. The evapotranspiration term (ET) can then be separated into its components evaporation (E) and transpiration (T) (Gibson and Edwards, 2002; Gibson et al., 2005; Ferguson and Veizer, 2007). As a first step, (E) can be calculated with an isotope balance equation developed by Gonfiantini (1986):

$$X = (\delta S - \delta I)(1 - h + \delta \epsilon) / (\delta S + 1)(\delta \epsilon + \epsilon / \alpha) + h * (\delta a - \delta S)$$

with

X = proportion of precipitation that is lost to evaporation (usually expressed in %)

$\delta S$  = mean value of  $\delta^{18}O$  (or  $\delta D$ ) of the river water at the outflow

$\delta I$  = average isotope composition of incoming precipitation

$\delta a$  = mean  $\delta^{18}O$  (or  $\delta D$ ) value of the water vapor

$\alpha$  = equilibrium fractionation factor for oxygen or hydrogen isotopes

$$\epsilon = \alpha - 1$$

$\delta \epsilon$  = kinetic enrichment factor for oxygen

h = average relative humidity that can be calculated by average  $\delta D$  and  $\delta^{18}O$  values ( $0.015 * (\delta D_p - (8 * \delta^{18}O_p)) + 1$ ) with the subscripts "p" meaning the average values for precipitation (Clark and Fritz, 1997).

Note that the isotope ratios in the above equation have to be converted from per mille (‰) values.

In the above equation, one difficulty arises from the average isotope composition of the incoming precipitation, because watersheds often contain only few sampling stations that also provide the isotope values for precipitation. For a small river basin, it can be assumed that the isotopic composition of precipitation over the entire basin equals that of this single station. In this case, the average isotope composition can be obtained from the measured isotope values of the individual events that have to be weighted by their intensity. For example in the Vosges mountains (northeastern France), the  $\delta^{18}O$  deviation with elevation during two rain events was found to be 0.13 and 0.17‰ per 100 m. This is negligible compared to the variation during the rainfall events (between 7 and 1.5‰, respectively; Ladouche et al., 2001). Alternatively, the average isotopic composition of precipitation can be obtained with the help of the meteoric water line. This is a cross-plot of the measured  $\delta^{18}O$  versus  $\delta D$  values of precipitation events that is very systematic. Following Craig (1961) and Rozanski et al. (1993), the linear relationship on a global scale is about:

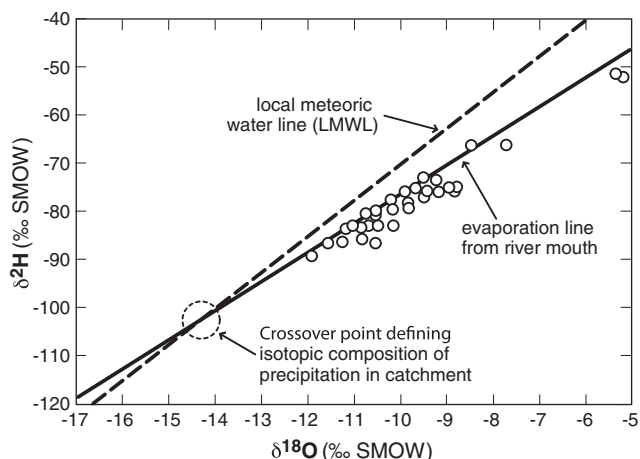
$$\delta D = 8 * \delta^{18}O + 10$$

The linear regression of the data points of this equation is known as the Global Meteoric Water Line (GMWL). Note, however, that precipitation series in individual catchments often exhibit different slopes and intercepts, reflecting the local hydroclimatic factors, such as origin of vapor mass, secondary evaporation during rainfall, temperature, humidity and seasonality of precipitation. These are termed the Local Meteoric Water Lines (LMWL). As a result of evaporation, the residual water in surficial water bodies that was subject to evaporation will also plot along a linear relationship in the  $\delta^{18}O$ - $\delta D$  crossplot, but with a lower slope; a consequence of preferential non-equilibrium enrichment due to molecular diffusion during evaporation. This enrichment is larger for the lighter  $H_2^{16}O$  than for the heavier  $2D^{16}O$  and  $H_2^{18}O$ , causing a lower slope than that of the LMWL (for a review see Clark and Fritz, 1997). When plotting the LMWL and the evaporation line of the remaining water, the crossover point of both lines establishes the average isotopic composition of the incoming water (Fig. 5). When the evaporation line is constructed for the mouth of a river, it represents an integrated evaporative signal for the entire basin (Telmer and Veizer, 2000). An application of this stable isotope method for river systems draining the Pyrenees mountains in northern Spain and southern France in comparison to coastal lowlands of the Mediterranean Sea is outlined in the following section.

## 4.3. Case study of stable isotope application in the Ebro Basin

Variations in the stable-isotope composition in a catchment water balance are mainly caused by natural variations in the isotopic composition of rainfall, by mixing with pre-existing waters, and by evaporation. Taking into account the temperatures generally encountered in catchment studies, the stable isotopes of water can be considered as conservative with no impact from exchanges with soil or rock.

Stable isotopes in the surface waters along the course of the Ebro River and its main tributaries are illustrated in Fig. 6 together with other rivers draining the French side of the Pyrenees (the Garonne River: Lambs, 2004; Lambs et al., 2009) or along the Mediterranean



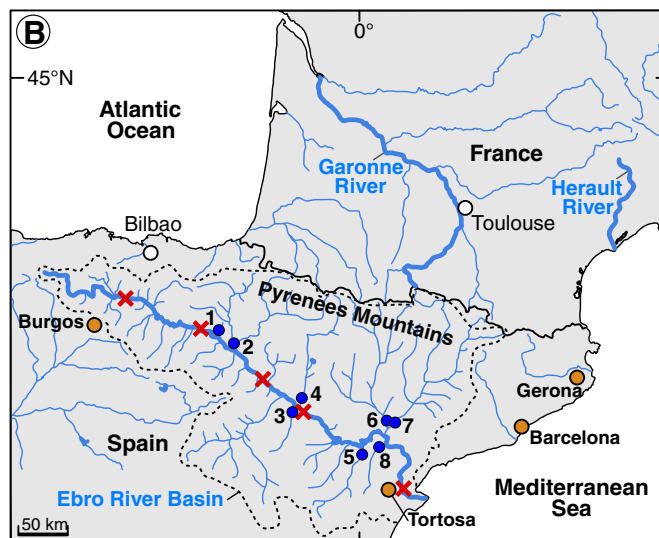
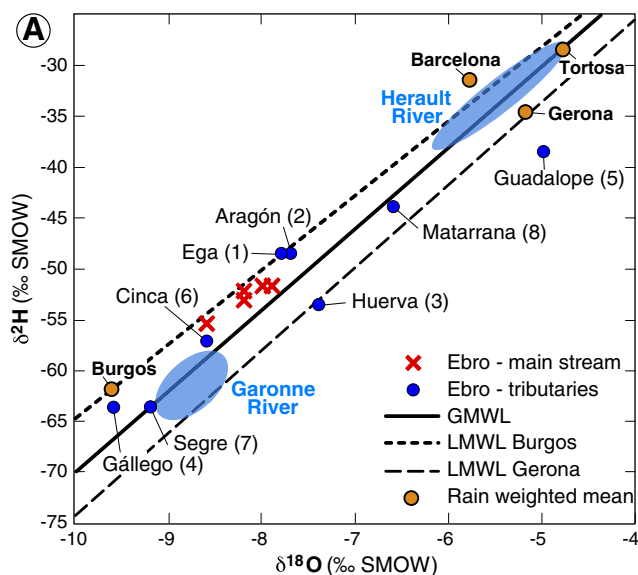
**Fig. 5.** The  $\delta^2\text{H}$  versus the  $\delta^{18}\text{O}$  for the Ottawa River and its tributaries. Note that the intersection of the Local Meteoric Water Lines (LMWL) with the evaporation line from the Ottawa River gives the average isotope composition of the precipitation input within the river basin. Modified from [Telmer and Veizer \(2000\)](#).

coast (the Herault River: [Petelet, 1998](#)). The Global Meteoric Water Line (GMW) is shown together with the Local Meteoric Water Lines (LMWLs) for the stations Gerona and Burgos that surround the Ebro catchment, as well as the mean weighted rain values of Barcelona and Tortosa ([IAEA/WMO, 2001](#)). All river samples on this  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  diagram clearly plot close to the global and local meteoric-water lines, indicating only minor impact of evaporation in the studied watersheds. Among the tributaries of the Ebro River with large variations in their  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures, only the sample from the Guadalope tributary shows a clear evaporative signal. The most depleted  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values are observed for the tributaries draining the southern Pyrenees (Cinca, Gállego, and Segre) and are similar to the Garonne River that drains the northern side of the Pyrenees. Note, however, that all Ebro tributaries have more depleted values than the mean rainwater signal for the Ebro catchment as given by the rain-survey stations. If the Burgos precipitation sampling is considered as representation of long-range continental transport, the depleted values in the tributaries of the Ebro River originate from depleted rainwater from the Pyrenees. In contrast, low altitude rains from the Mediterranean coastal area result in enriched  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values as observed for the Barcelona, Gerona and Tortosa rain sampling stations, and are in full agreement with values analyzed for Mediterranean coastal river as illustrated by the Herault River in southern France ([Fig. 6](#)).

#### 4.4. Evaluation of transpiration fluxes

Subtracting the evaporative loss (E) from the precipitation input (P) yields the biological water flux composed of transpiration (T) and interception (I). As an example, globally the annual evapotranspiration is reduced by about 4% ( $\sim 3000 \text{ km}^3$ ) due to deforestation, a decrease that is quantitatively as large as the increased vapor flow resulting from irrigation ( $\sim 2600 \text{ km}^3$ ; [Gordon et al., 2005](#)). Most of these changes in the regional ET patterns are related to changes in (T) and (I), and thus their quantification is of considerable importance in the management of vegetation schemes in agriculture and forestry. The interception term can be isolated by taking the leaf area index for different vegetation types and estimating their proportions in a given watershed using a geographic information system (GIS) ([Lee and Veizer, 2003](#)). Such data are for instance available from the global map of vegetation cover ([DeFries et al., 2000](#)).

With quantification of (E) and (I), the transpiration term (T) is the residual difference. The transpiration process involves also  $\text{CO}_2$



**Fig. 6.** (A) Compilation of stable water isotope ratios of the surface waters along the course of the Ebro River and its tributaries (locations given in part B) and comparison with the Garonne River ([Lambs, 2004; Lambs et al., 2009](#)), the Herault River ([Petelet, 1998](#)), and the local rainwater signal ([IAEA/WMO, 2001](#)). (B) Map of northern Spain and southern France with the location of the river and rainwater sampling stations along the Ebro River as well as the Garonne River and the Herault River.

diffusion into the plant and  $\text{O}_2$  and  $\text{H}_2\text{O}$  release via leaf stomata. Biological water and carbon cycles are inherently coupled at a specific  $\text{H}_2\text{O}/\text{CO}_2$  ratio, known as the Water Use Efficiency (WUE) simply defined as the net carbon uptake per unit of water transpired. This term quantifies the number of moles of  $\text{H}_2\text{O}$  that are transpired to enable the uptake of one mole of  $\text{CO}_2$ . Different plant species show large differences in WUE that are mainly related to their photosynthetic pathways. Average long term WUE for C3 plants is  $1 \text{ mol CO}_2$  to  $925 \pm 506 \text{ mol H}_2\text{O}$  ([Jones, 1992](#)) and for C4 plants  $1 \text{ mol CO}_2$  per  $425 \pm 96 \text{ mol H}_2\text{O}$  ([Molles, 2002](#)). The value of the WUE is important because it enables a first order calculation of the Net Primary Productivity (NPP) for a given catchment:

$$\text{NPP} = T/\text{WUE}$$

With NPP representing the Net Primary Productivity in moles  $\text{C a}^{-1}$ , T is transpiration given in moles  $\text{H}_2\text{O a}^{-1}$ , and WUE is given in moles  $\text{H}_2\text{O}/\text{moles CO}_2$ .



The knowledge of (T) obtained via the above isotope and GIS methods, enables us not only to estimate the water balance for a given catchment but also provides a first order evaluation of the large scale biological uptake of CO<sub>2</sub>. Further details of this type of basin wide water and carbon balance studies can be found in [Telmer and Veizer \(2000\)](#), [Lee and Veizer \(2003\)](#), [Ferguson et al. \(2007\)](#), [Freitag et al. \(2008\)](#), [Karim et al. \(2008\)](#), and [Brunet et al. \(2009\)](#). As an example, a detailed case study by [Ferguson and Veizer \(2007\)](#) is outlined in the following.

#### 4.5. Case studies of water and carbon transpiration fluxes on watershed scales

The above methodology was applied to 15 large watersheds in the Americas, Africa, Australia and New Guinea ([Ferguson and Veizer, 2007](#)) and the calculated transpiration fluxes of water and CO<sub>2</sub> were compared to a global dataset of precipitation and biological estimates of Net Primary Productivity (NPP), the latter reproduced from the Global Primary Production Data Initiative (GPPDI) grid cells NPP data set ([Zheng et al., 2001](#)). This NPP database is a collection of worldwide multibiome productivities, mostly established by biological methods. The shaded pattern in [Fig. 7](#) is that of the biologically estimated pattern of NPP versus precipitation. The tropical biomes

(see Nyong) show a rather flat pattern, independent of the amount of precipitation, due to the fact that the biological system operates at about 6 to 8% capacity with respect to the input of solar energy. At higher latitudes, on the other hand, the NPP appears to be limited by the available moisture. An interesting observation is that the flux of transpiration water established by the above described isotope approach for the 15 watersheds shows exactly the same pattern. Moreover, the ratio of CO<sub>2</sub> sequestration (in g C m<sup>-2</sup> a<sup>-1</sup>) to the amount of transpired water (in 10<sup>3</sup> g H<sub>2</sub>O m<sup>-2</sup> a<sup>-1</sup>) is close to 1000 to 1, the WUE value within the range of C3 vegetation ecosystems ([Jones, 1992](#)) as outlined above.

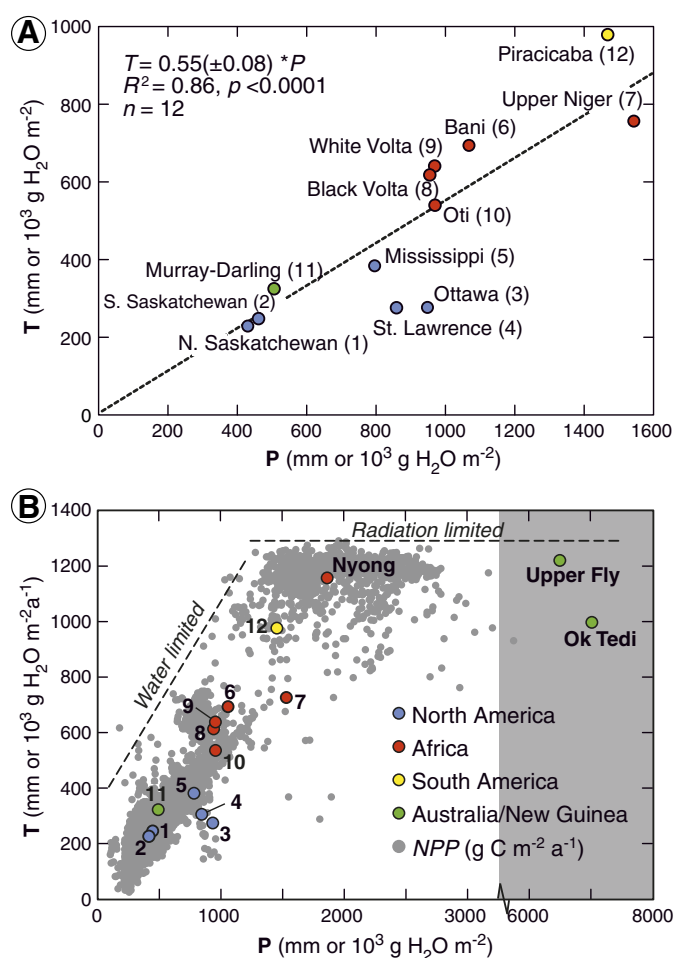
#### 5. Conclusions and challenges for future work

Our outline of selected applications of stable isotopes in river research shows the usefulness and growing importance of this technique. In this context it is particularly worthwhile to combine isotope applications with other modern biogeochemical methods of quantification, such as element concentrations, runoff, precipitation, and flux measurements. It will become increasingly important to couple water balances with other modern biogeochemical methods including ecological indicators microbial and plant activities, sediment transport, and sediment water interactions, if we are to develop an integrated understanding of material cycling with the biogeochemistry of rivers and their basins. Recently, new transportable laser-based water isotope mass spectrometers became available (e.g., [Lis et al., 2008](#); [Gupta et al., 2009](#)). These instruments will decrease analytical costs and make onsite isotope analysis available to explore trends in river systems at higher spatial and temporal resolution.

Most stable isotope applications within river research so far have focused on the water molecule itself and/or on its inorganic constituents such as the dissolved inorganic carbon. In the future it will likely become increasingly important to target also other dissolved and particulate loads with these isotope methods with emphasis on organic materials. These can be separated into natural (e.g., humic and fulvic acid compounds or natural lipids) and man-made organic compounds such as various pollutants. Isotope considerations for the latter can become particularly important for studies of groundwater-surface water interactions.

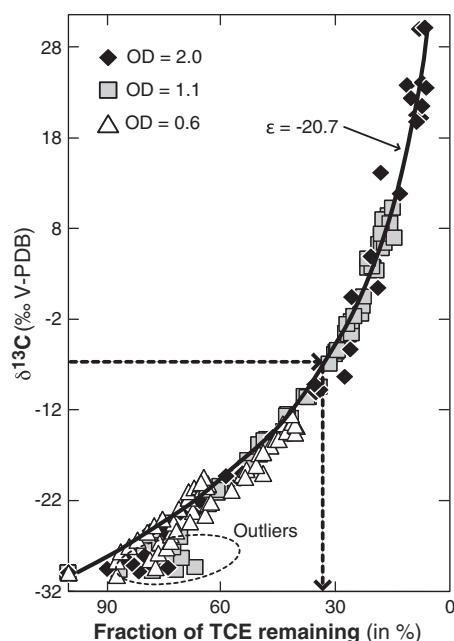
New stable isotope investigations in river systems will likely face the challenge of compound specific stable isotope analysis (CSIA) (for a review see [Giger et al., 2003](#); [Schmidt et al., 2004](#)). For surface water systems the organic isotope techniques probably hold additional complications, compared to groundwater studies, because solar radiation and resulting photosynthesis will further enhance degradation processes, either directly through substrate competition or indirectly via reduction of CO<sub>2</sub>. The generated additional O<sub>2</sub> may turn the system to be more aerobic which in turn may accelerate degradation of pollutants (see [Fig. 8](#) as an example). Further difficulties may arise from the fact that concentrations of organic compounds in river systems are usually very low. This increases the challenge for compound specific isotope work because most compound specific stable isotope ratio mass spectrometers work under high vacuum and need extra splitting units in order to dilute the carrier gas stream.

Finally, a new development in the field is the advent of multiple collector stable isotope inductively coupled plasma mass spectrometry (MC-ICP-MS). This instrumentation is applied for instance for the uranium and thorium series ([Fietzke et al., 2005](#)) and for iron ([Schoenberg and von Blanckenburg, 2005](#)), silicon ([Henderson, 2002](#)), and chromium isotopes ([Ellis et al., 2002](#)), to name only a few. In most of these studies, these isotope systems serve as proxies for temperature, pH, and nutrient reconstructions in terrestrial and marine environments or as tracers of redox changes. Unfortunately, to date only a very few of these applications have focused on terrestrial water systems (e.g., [Martin et al., 2001](#); [Rauch et al., 2004](#); [Scrivner](#)



**Fig. 7.** (A) The relationship between mean annual precipitation (P) and plant transpiration (T) for watersheds that receive less than 1500 mm of precipitation. (B) The relationship between P and T for watersheds in North America, South America, Africa, Australia, and New Guinea (shaded region represents  $P > 5500$  mm). The NPP data from the Global Primary Production Data Initiative (GPPDI) is shown as gray background data points.

Modified from [Ferguson and Veizer \(2007\)](#).



**Fig. 8.** Rayleigh enrichment of the remaining Trichloroethylene (TCE) during aerobic degradation. OD expresses the different cell densities,  $\epsilon$  is the calculated enrichment factor and the arrows indicate that it is possible to determine the amount of contaminant degraded if the initial and any other isotope value along the degradation is known.

Modified after Barth et al. (2002).

et al., 2004; Nielsen et al., 2005). Clearly, these novel techniques – together with stable isotope measurements of the lighter elements and concentration and flux estimates – hold huge promise for river research, for better understanding of elemental transport and for cycling by natural as well as anthropogenic processes (Vigier et al., 2009; Millot et al., 2010).

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