



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 5437

To link to this article: DOI:10.1016/j.earscirev.2011.07.003
<http://dx.doi.org/10.1016/j.earscirev.2011.07.003>

To cite this version:

Schulte, Peter and Van Geldern, Robert and Freitag, Heiko and Karim, Ajaz and Négrel, Philippe and Petelet-Giraud, Emmanuelle and Probst, Anne and Probst, Jean-Luc and Telmer, Kevin and Veizer, Jan and Barth, Johannes A.C.
Applications of stable water and carbon isotopes in watershed research: Weathering, carbon cycling, and water balances. (2011) Earth-Science Reviews, vol. 109 (n° 1-2). pp. 20-31. ISSN 0012-8252

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

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

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

^a GeoZentrum Nordbayern, Universität Erlangen, Schlossgarten 5, D-91054 Erlangen, Germany

^b Department of Earth Sciences and Ottawa-Carleton Geoscience Centre, University of Ottawa, Ottawa, Canada K1N 6N5

^c Umwelt & Baugrund Consult, Alte Ziegelei 7, 51491 Overath, Germany

^d Chinook Consulting Services, 742 Memorial Drive Northwest, Calgary, Canada T2N 3C7

^e BRGM, 3 Avenue Claude Guillemin, BP 6009, 45060 Orléans Cedex 2, France

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

^g CNRS; EcoLab; ENSAT, F-31326 Castanet-Tolosan, France

^h School of Earth and Ocean Sciences, University of Victoria, Victoria, Canada V8W 3P6

ARTICLE INFO

Keywords:

Stable isotopes
Hydrology
Hydrogeology
Weathering
River basin

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.

Contents

1. Introduction
2. Silicate and carbonate weathering
 - 2.1. Weathering and stable isotopes of water and carbon
 - 2.2. Case study on the Lagan River (Northern Ireland)
3. The riverine carbon cycle
4. Water fluxes in river catchments
 - 4.1. Water transport and mixing
 - 4.2. Runoff and evapotranspiration
 - 4.3. Case study of stable isotope application in the Ebro Basin
 - 4.4. Evaluation of transpiration fluxes
 - 4.5. Case studies of water and carbon transpiration fluxes on watershed scales
5. Conclusions and challenges for future work

Acknowledgments

References

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

E-mail address: 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 CO₂ 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 CO₂, and this negative feedback effect may thus control the long-term (>10⁴ 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 CO₂ 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 CO₂, 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⁺, K⁺, Ca²⁺, Mg²⁺, and Fe³⁺ 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 CO₂ 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_{2(aq)}, H₂CO₃⁻, HCO₃⁻ and CO₃²⁻ 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

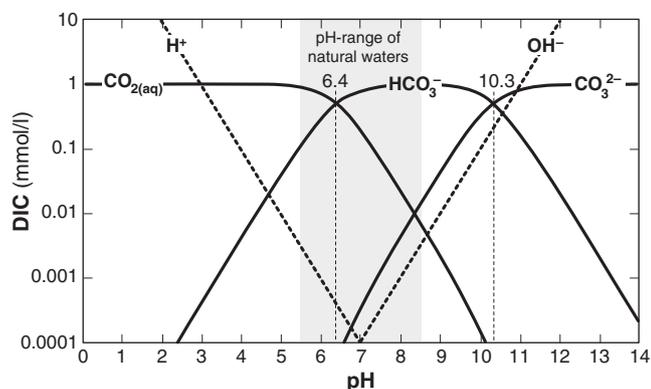


Fig. 1. Concentrations of the dissolved inorganic carbon (DIC) species CO_2 , HCO_3^- , CO_3^{2-} , H^+ , and OH^- as functions of pH (Bjerrum plot) for freshwater at a temperature of 25 °C; “aq” as subscript corresponds to the aqueous phase. Modified after Drever (1982).

the isotope values of the soil 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 CO_2 levels in soils. The isotopic composition of this soil 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 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

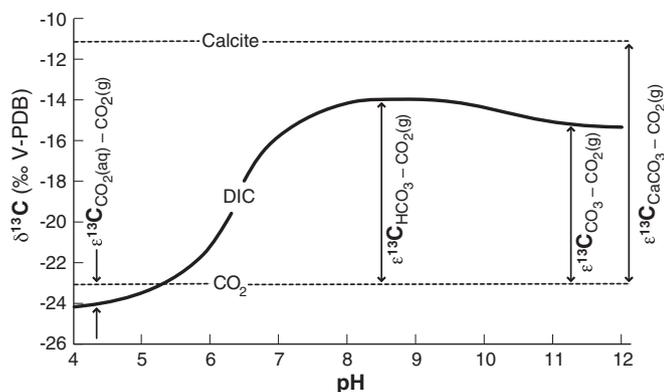


Fig. 2. pH-dependency of the ^{13}C composition of the dissolved inorganic carbon (DIC) species in equilibrium with soil CO_2 ($\delta^{13}\text{C} = -23\%$ V-PDB) at 25 °C; “g” as subscript corresponds to the gas phase and “e” is the enrichment factor. Adapted from Clark and Fritz (1997).

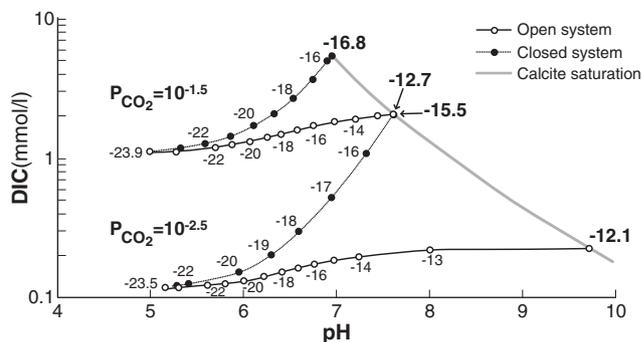


Fig. 3. Concentration of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ as groundwater dissolves calcite ($d^{13}\text{C} = 0\%$ V-PDB). Shown are conditions for open and closed systems at high ($10^{-1.5}$) and low ($10^{-2.5}$) partial pressures of soil P_{CO_2} from C3 vegetation ($\delta^{13}\text{C}_{\text{CO}_2} = -23\%$). Final $d^{13}\text{C}$ values at calcite saturation are shown in bold. Note that open system dissolution maintains a constant pCO_2 . In contrast, under closed system conditions the 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 CO_2 at increasing pH (see also Fig. 2) and replenishment of CO_2 in open systems allows for considerably more calcite to be dissolved. The stronger increase in ^{13}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 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 pCO_2 as well as the ^{13}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

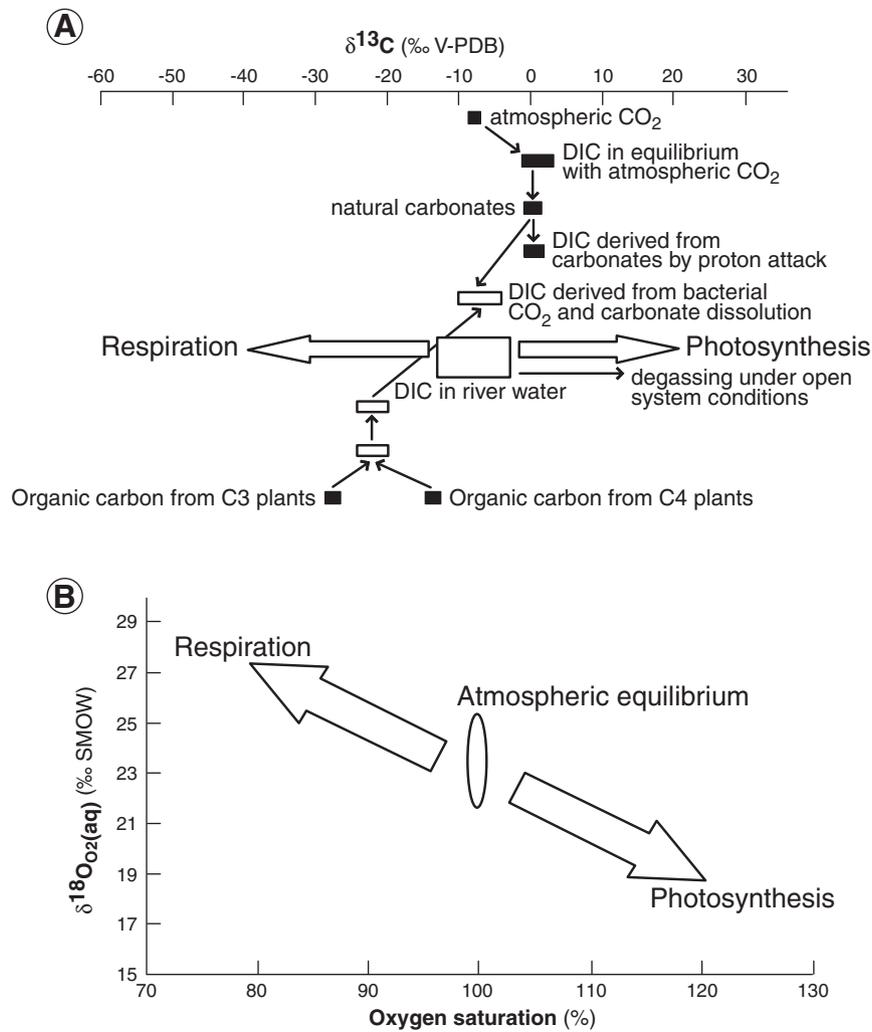


Fig. 4. (A) Carbon isotopic signature of various components of the carbon cycle in rivers. The effects of biogeochemical processes on $\delta^{13}\text{C}$ are shown with arrows. White rectangles indicate $\delta^{13}\text{C}_{\text{DIC}}$ measurements specific to the Mississippi. (B) General effects of production (photosynthesis), respiration and atmospheric exchange on the isotopic composition of dissolved 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 CO_2 ("p CO_2 ", [bar]) in the water column compared to the atmosphere (Kempe, 1982; Telmer and Veizer, 1999). This excess CO_2 may arise from enhanced dissolved organic carbon load from natural or anthropogenic sources and its respiratory turnover to CO_2 and/or from groundwater input that usually has much higher CO_2 concentrations due to its link to weathering and the soil zone. Regardless of the origin of this CO_2 overpressure, most rivers degas the 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 CO_2 evasion, the most common pattern is a p 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 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 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 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 CO_2 rise is also subdued. On the other hand, such p 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 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 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 CO₂ generated by biogenic activity in soils of the watershed (Amiotte-Suchet et al., 1999; Dubois et al., 2009; 2010) and the flux of CO₂ 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 CO₂ in rivers is groundwater input, followed by processes within rivers, such as CO₂ increase by respiration or decline due to photosynthesis, and equilibration with or evasion to the atmosphere. The initial δ¹³C_{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 ¹³C. The third process, exchange with the atmosphere, involves equilibration between gaseous CO₂ and HCO₃⁻_(aq), 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 δ¹³C 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 δ¹³C_{DIC} is about -1‰ and decreases down-river to about -4‰ due to the increasing proportion of soil CO₂ from the tributaries. In watersheds with ubiquitous carbonates, such as the lower Rhine, Rhone, or Danube, the δ¹³C_{DIC} is about -10 ± 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 δ¹³C_{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 CO₂ or uptake during phytoplankton blooms), carbonate dissolution, or photosynthesis is responsible for positive δ¹³C_{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 (δ¹⁸O_{O₂(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 CO₂ 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 M₁ and M₂ 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 ΔS 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 ΔS 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 %)

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

δI = average isotope composition of incoming precipitation

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

α = 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 δD 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 δD 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 $\delta^{18}O$ - δD 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

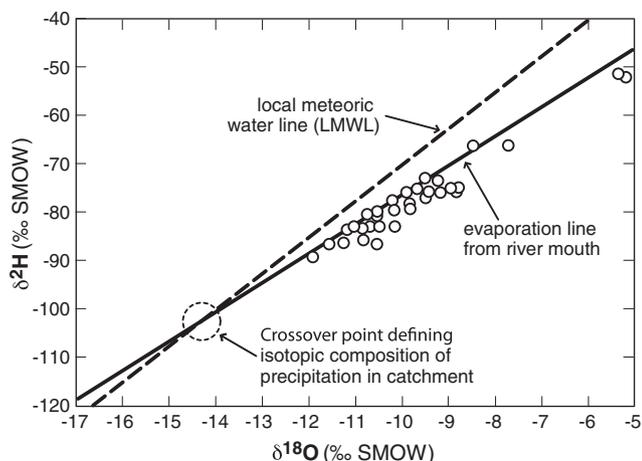


Fig. 5. The $\delta^2\text{H}$ versus the $\delta^{18}\text{O}$ for the Ottawa River and its tributaries. Note that the intersection of the Local Meteoric Water Lines (LMWL) with the evaporation line from the Ottawa River gives the average isotope composition of the precipitation input within the river 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 CO_2

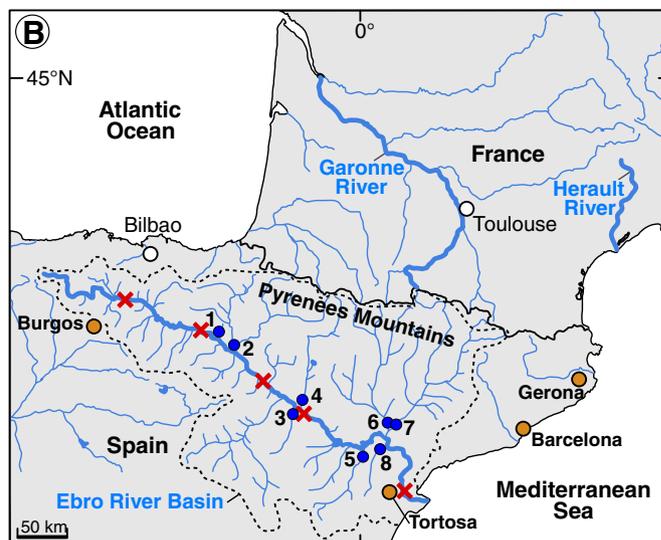
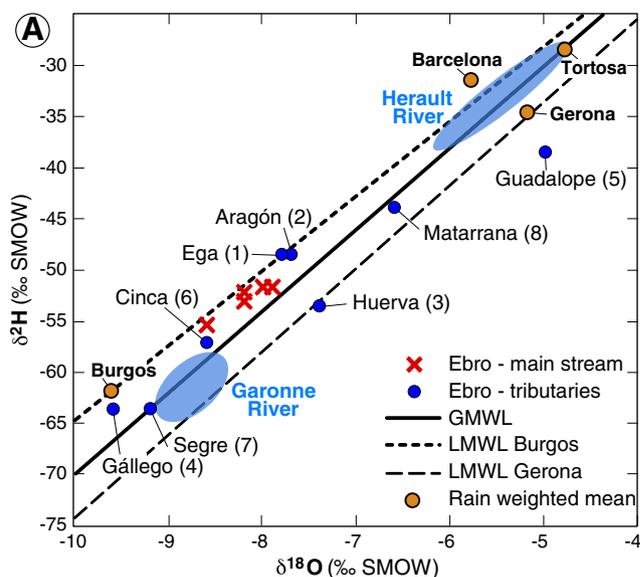


Fig. 6. (A) Compilation of stable water isotope ratios of the surface waters along the course of the Ebro River and its tributaries (locations given in part B) and comparison with the Garonne River ([Lambs, 2004; Lambs et al., 2009](#)), the Herault River ([Petelet, 1998](#)), and the local rainwater 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 O_2 and H_2O 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 H_2O that are transpired to enable the uptake of one mole of 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 mol CO_2 to $925 \pm 506 \text{ mol H}_2\text{O}$ ([Jones, 1992](#)) and for C4 plants 1 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 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 CO₂. 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 CO₂ 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 CO₂ sequestration (in g C m⁻² a⁻¹) to the amount of transpired water (in 10³ g H₂O m⁻² a⁻¹) 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 CO₂. The generated additional O₂ 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](#)

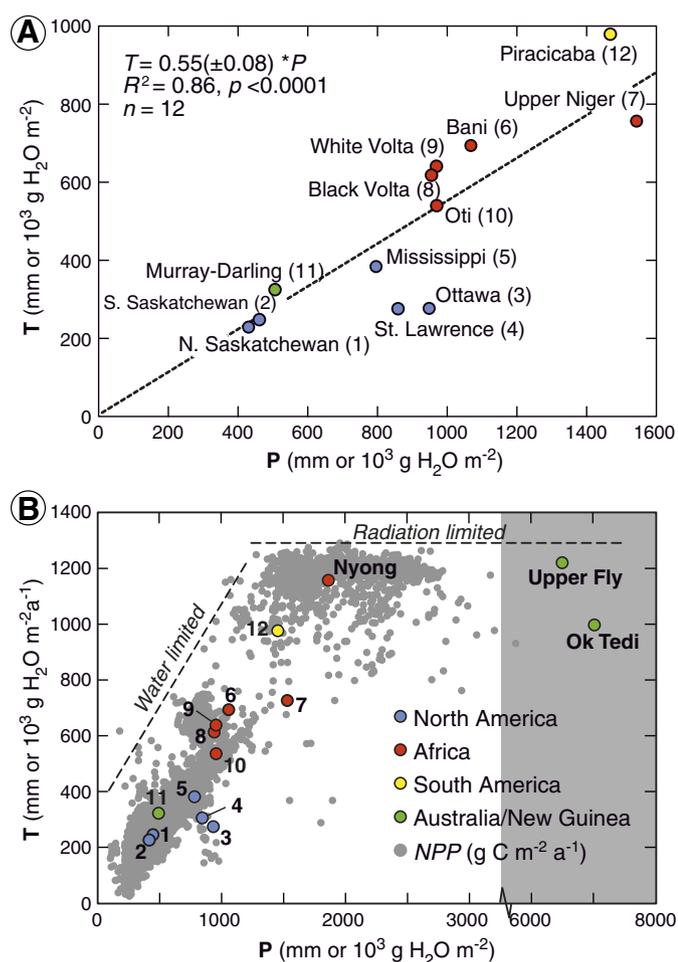


Fig. 7. (A) The relationship between mean annual precipitation (P) and plant transpiration (T) for watersheds that receive less than 1500 mm of precipitation. (B) The relationship between P and T for watersheds in North America, South America, Africa, Australia, and New Guinea (shaded region represents 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 \(2007\)](#).

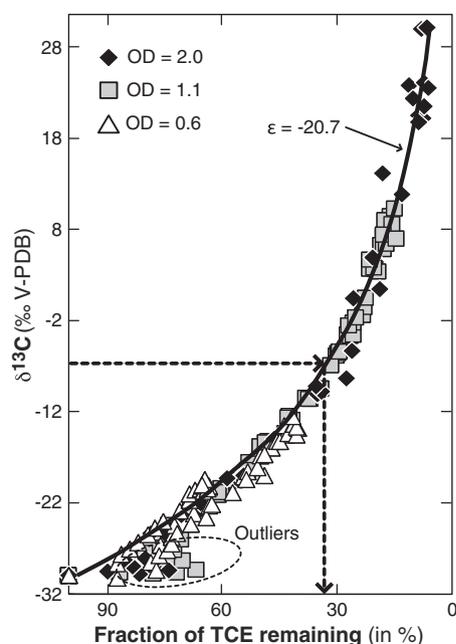


Fig. 8. Rayleigh enrichment of the remaining Trichloroethylene (TCE) during aerobic degradation. OD expresses the different cell densities, ϵ is the calculated enrichment factor and the arrows indicate that it is possible to determine the amount of contaminant degraded if the initial and any other isotope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

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada, the Canadian Institute for Advanced Research, the Deutsche Forschungsgemeinschaft (DFG), the German Academic Exchange Service (DAAD), as well as the Sonderfonds of the University of Erlangen for support. In addition, we greatly acknowledge Patricia Wickham for assistance and two anonymous reviewers for valuable suggestions.

References

Aggarwal, P.K., Dillon, M.A., 1998. Stable isotope composition of molecular oxygen in soil gas and groundwater: a potentially robust tracer for diffusion and oxygen consumption processes. *Geochimica et Cosmochimica Acta* 62, 577–584. doi:10.1016/S0016-7037(97)00377-3.

Ahad, J.M.E., Barth, J.A.C., Ganeshram, R.S., Spencer, R.G.M., Uher, G., 2008. Controls on carbon cycling in two contrasting temperate zone estuaries: the Tyne and Tweed, UK. *Estuarine, Coastal and Shelf Science* 78, 685–693. doi:10.1016/j.ecss.2008.02.006.

Amiotte-Suchet, P., Probst, J.L., 1993a. Modelling of atmospheric CO₂ consumption by chemical weathering of rocks: application to the Garonne, Congo and Amazon basins. *Chemical Geology* 107, 205–210. doi:10.1016/0009-2541(93)90174-H.

Amiotte-Suchet, P., Probst, J.L., 1993b. CO₂ consumed by chemical weathering of continents: influences of drainage and lithology. *Comptes Rendus de l'Académie des Sciences, Serie II: Sciences de la Terre et des Planètes* 317 (série II), 615–622.

Amiotte-Suchet, P., Probst, J.L., 1995. A global model for present day atmospheric CO₂ consumption by chemical erosion of continental rocks (GEM CO₂). *Tellus* 47B, 273–280. doi:10.1034/j.1600-0889.47.issue1.23.x.

Amiotte-Suchet, P., Probst, A., Probst, J.L., 1995. Influence of acid rain on the CO₂ weathering consumption: local and global scale. *Water, Air and Soil Pollution* 85, 1563–1568. doi:10.1007/BF00477203.

Amiotte-Suchet, P., Aubert, D., Probst, J.L., Gauthier-Lafaye, F., Probst, A., Viville, D., Andreux, F., 1999. $\delta^{13}\text{C}$ pattern of dissolved inorganic carbon in a small granitic

catchment: the Strengbach case study (Vosges mountains, France). *Chemical Geology* 159, 129–145. doi:10.1016/S0009-2541(99)00037-6.

Amiotte-Suchet, P., Probst, J.L., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochemical Cycles* 17, 1038. doi:10.1029/2002GB001891.

Amiotte-Suchet, P., Linglois, N., Leveque, J., Andreux, F., 2007. ^{13}C composition of dissolved organic carbon in upland forested catchments of the Morvan Mountains (France): influence of coniferous and deciduous vegetation. *Journal of Hydrology* 335, 354–363. doi:10.1016/j.jhydrol.2006.12.002.

Anderson, S.P., Dietrich, W.E., 2001. Chemical weathering and runoff chemistry in a steep headwater catchment. *Hydrological Processes* 15, 1791–1815. doi:10.1002/hyp.240.

Anderson, S.P., Drever, J.L., Humphrey, N.F., 1997. Chemical weathering in glacial environments. *Geology* 25, 399–402. doi:10.1130/0091-7613(1997)025<0399: CWIGE>2.3.CO;2.

Aregbe, Y., Valkiers, S., Gonfiantini, R., Nørgaard, J., Taylor, P.D.P., 2002. A method to induce and assess isotopic equilibrium of oxygen. *International Journal of Mass Spectrometry* 214, 233–246. doi:10.1016/S1387-3806(01)00560-7.

Aubert, D., Probst, A., Stille, P., 2004. Distribution and origin of major and trace elements into labile and residual phase in an acid soil profile (Vosges mountains, France). *Applied Geochemistry* 19, 899–916. doi:10.1016/j.apgeochem.2003.11.005.

Aucour, A.-M., Sheppard, S.M.F., Guyomar, O., Wattlelet, J., 1999. Use of ^{13}C to trace origin and cycling of inorganic carbon in the Rhône river system. *Chemical Geology* 159, 87–105. doi:10.1016/S0009-2541(99)00035-2.

Barth, J.A.C., Veizer, J., 1999. Carbon cycle in St. Lawrence aquatic ecosystems at Cornwall (Ontario), Canada: seasonal and spatial variations. *Chemical Geology* 159, 107–128. doi:10.1016/S0009-2541(99)00036-4.

Barth, J.A.C., Veizer, J., 2004. Water mixing in a St. Lawrence river embayment to outline potential sources of pollution. *Applied Geochemistry* 19, 1637–1641. doi:10.1016/j.apgeochem.2004.02.005.

Barth, J.A.C., Veizer, J., Mayer, B., 1998. Origin of particulate organic carbon in the upper St. Lawrence: isotopic constraints. *Earth and Planetary Science Letters* 162, 111–121. doi:10.1016/S0012-821X(98)00160-5.

Barth, J.A.C., Slater, G., Schüth, C., Bill, M., Downey, A., Larkin, M., Kalin, R.M., 2002. Carbon isotope fractionation during aerobic biodegradation of Trichloroethene by *Burkholderia cepacia* G4: a tool to map degradation mechanisms. *Applied and Environmental Microbiology* 68, 1728–1734. doi:10.1128/AEM.68.4.1728-1734.2002.

Barth, J.A.C., Cronin, A.A., Dunlop, J., Kalin, R.M., 2003. Influence of carbonates on the riverine carbon cycle in an anthropogenically dominated catchment basin: evidence from major elements and stable carbon isotopes in the Lagan River (N. Ireland). *Chemical Geology* 200, 203–216. doi:10.1016/S0009-2541(03)00193-1.

Barth, J.A.C., Tait, A., Bolshaw, M., 2004. Automated analyses of $^{18}\text{O}/^{16}\text{O}$ ratios in dissolved oxygen from 12-ml water samples. *Limnology and Oceanography: Methods* 2, 35–41.

Barth, J.A.C., Stichler, W., Bergemann, M., Reincke, H., 2006. Can conductivity and stable isotope tracers determine water sources during flooding? An example from the Elbe River in 2002. *International Journal of River Basin Management* 4, 77–83.

Barth, J.A.C., Grathwohl, P., Fowler, H.J., Bellin, A., Gerzabek, M.H., Lair, G.J., Barceló, D., Petrovic, M., Navarro, A., Négrel, P., Petelet-Giraud, E., Darmendrail, D., Rijnaarts, H., Langenhoff, A., de Weert, J., Slob, A., van der Zaan, B.M., Gerritse, J., Frank, E., Gutierrez, A., Kretzschmar, R., Gocht, T., Steidle, D., Garrido, F., Jones, K.C., Meijer, S., Moeckel, C., Marsman, A., Klaver, G., Vogel, T., Bürger, C., Kolditz, O., Broers, H.P., Baran, N., Joziassé, J., Von Tümpling, W., Van Gaans, P., Merly, C., Chapman, A., Brouyère, S., Battle Aguilar, J., Orban, P., Tas, N., Smidt, H., 2009. Mobility, turnover and storage of pollutants in soils, sediments and waters: achievements and results of the EU project AquaTerra. A review. *Agronomy for Sustainable Development* 29, 161–173. doi:10.1051/agro:2007060.

Benson, B.B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen dissolved in fresh-water and seawater in equilibrium with the atmosphere. *Limnology and Oceanography* 29, 620–632.

Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air, and Geochemical Cycles*. Prentice Hall, Upper Saddle River. 376 pp.

Boeglin, J.L., Probst, J.L., 1998. Physical and chemical weathering rates and CO₂ consumption in a tropical lateritic environment: the upper Niger basin. *Chemical Geology* 148, 137–156. doi:10.1016/S0009-2541(98)00025-4.

Braud, I., Dantas-Antonino, A.C., Vauclin, M., Thony, J.L., Ruelle, P., 1995. A simple soil-plant-atmosphere transfer model (SISPAT) development and field verification. *Journal of Hydrology* 166, 213–250. doi:10.1016/0022-1694(94)05085-C.

Brunet, F., Probst, J.L., Gaiero, D.M., Depetris, P.J., Gauthier-Lafaye, F., Stille, P., 2005. $\delta^{13}\text{C}$ tracing of dissolved inorganic carbon sources in southern rivers. *Hydrological Processes* 19, 3321–3344. doi:10.1002/hyp.5973.

Brunet, F., Dubois, K., Veizer, J., Ndong, G.R.N., Ngoupayou, J.R.N., Boeglin, J.L., Probst, J.L., 2009. Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology* 265, 563–572. doi:10.1016/j.chemgeo.2009.05.020.

Buhl, D., Neuser, R.D., Richter, D.K., Riedel, D., Roberts, B., Strauss, H., Veizer, J., 1991. Nature and nurture: environmental isotope story of the river Rhine. *Naturwissenschaften* 78, 337–346. doi:10.1007/BF01131605.

Calmels, D., Gaillardet, J., Brenot, A., France-Lanord, C., 2007. Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: climatic perspectives. *Geology* 35, 1003–1006. doi:10.1130/G24132A.1.

Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta* 55, 3403–3405. doi:10.1016/0016-7037(91)90498-T.

Chiffolleau, J.F., Auger, D., Chartier, E., 1999. Fluxes of selected trace metals from the Seine estuary to the eastern English Channel during the period August 1994 to July 1995. *Continental Shelf Research* 19, 2063–2082. doi:10.1016/S0278-4343(99)00053-9.

- Ciais, P., Tans, P.P., Trolier, M., White, J.W.C., Francey, R.J., 1995. A large northern hemisphere terrestrial CO₂ sink indicated by the ¹³C/¹²C ratio of atmospheric CO₂. *Science* 269, 1098–1102. doi:10.1126/science.269.5227.1098.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis, Boca Raton, Florida. 328 pp.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703. doi:10.1126/science.133.3465.1702.
- Cronin, A.A., Barth, J.A.C., Elliot, T., Kalin, R.M., 2005. Recharge velocity and geochemical evolution for the Permo-Triassic Sherwood Sandstone, Northern Ireland. *Journal of Hydrology* 315, 308–324. doi:10.1016/j.jhydrol.2005.04.016.
- Dambrine, E., Pollier, B., Poszwa, A., Ranger, J., Probst, A., Viville, D., Biron, P., Granier, A., 1998. Evidence of current soil acidification in spruce (Strengbach catchment, Vosges mountains, North-Eastern France). *Water, Air and Soil Pollution* 105, 43–52. doi:10.1023/A:1005030331423.
- Darling, W.G., Talbot, J.C., Bath, A.H., 2003. The O and H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrology and Earth System Sciences* 7, 183–195. doi:10.5194/hess-7-183-2003.
- Das, A., Krishnaswami, S., Bhattacharya, S.K., 2005. Carbon isotope ratio of dissolved inorganic carbon (DIC) in rivers draining the Deccan Traps: sources of DIC and their magnitudes. *Earth and Planetary Science Letters* 236, 419–429. doi:10.1016/j.epsl.2005.05.009.
- Das, A., Pawar, N.J., Veizer, J., 2011. Sources of sulfur in Decan Trap rivers: a reconnaissance isotope study. *Applied Geochemistry* 26, 301–307. doi:10.1016/j.apgeochem.2010.12.003.
- DeFries, R.S., Hansen, M.C., Townshend, J.R.G., Janetos, A.C., Loveland, T.R., 2000. A new global 1-km dataset of percentage tree cover derived from remote sensing. *Global Change Biology* 6, 247–254. doi:10.1046/j.1365-2486.2000.00296.x.
- Degens, E., Kempe, S., Ittekkot, V., 1984. Monitoring carbon in world rivers. *Environment* 26, 29–33.
- Diefendorf, A.F., Patterson, W.P., 2005. Survey of stable isotope values in Irish surface waters. *Journal of Paleolimnology* 34, 257–269. doi:10.1007/s10933-005-3571-1.
- Doctor, D.H., 2008. Hydrologic connections and dynamics of water movement in the Classical Karst (Kras) aquifer: evidence from frequent chemical and stable isotope sampling. *Acta Carsologica* 37, 101–123.
- Doctor, D.H., Kendall, C., Sebestyen, S.D., Shanley, J.B., Ohte, N., Boyer, E.W., 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. *Hydrological Processes* 22, 2410–2423. doi:10.1002/hyp.6833.
- Domenico, P.A., Schwartz, F.W., 1998. *Physical and Chemical Hydrogeology*. Wiley, New York. 506 pp.
- Drever, J.I., 1982. *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, New Jersey. 388 pp.
- Dubois, K., Carignan, R., Veizer, J., 2009. Can pelagic net heterotrophy account for carbon fluxes from eastern Canadian lakes? *Applied Geochemistry* 24, 988–998. doi:10.1016/j.apgeochem.2009.03.001.
- Dubois, K.D., Lee, D., Veizer, J., 2010. Isotopic constraints on alkalinity, dissolved organic carbon and atmospheric carbon dioxide fluxes in the Mississippi River. *Journal of Geophysical Research – Biogeosciences* 115, G02018. doi:10.1029/2009JG001102.
- Dupré, B., Gaillardet, J., Allègre, C.J., Rousseau, D., 1996. Major and trace elements of river-borne material: the Congo Basin. *Geochimica et Cosmochimica Acta* 60, 1301–1321. doi:10.1016/0016-7037(96)00043-9.
- Dupré, B., Dessert, C., Oliva, P., Goddés, Y., Viers, J., François, L., Millot, R., Gaillardet, J., 2003. Rivers, chemical weathering and Earth's climate. *Compte Rendus Geoscience* 335, 1141–1160. doi:10.1016/j.crte.2003.09.015.
- Ellis, A.S., Johnson, T.M., Bullen, T.D., 2002. Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* 295, 2060–2062. doi:10.1126/science.1068368.
- Farah, E.A., Mustafa, E.M.A., Kumai, H., 2000. Sources of groundwater recharge at the confluence of the Nile, Sudan. *Environmental Geology* 39, 667–672. doi:10.1007/s002540050479.
- Ferguson, P.R., Veizer, J., 2007. Coupling of water and carbon fluxes via the terrestrial biosphere and its significance to the Earth's climate system. *Journal of Geophysical Research – Atmospheres* 112, D24S06. doi:10.1029/2007JD008431.
- Ferguson, P.R., Weinrauch, N., Wassenaar, L.L., Mayer, B., Veizer, J., 2007. Partitioning regional evaporation and transpiration water vapor fluxes in the northern Great Plains of North America. *Global Biogeochemical Cycles* 21, GB2023. doi:10.1029/2006GB002702.
- Ferguson, P.R., Dubois, K.D., Veizer, J., 2011. Fluvial carbon fluxes under extreme rainfall conditions: inferences from the Fly River, Papua New Guinea. *Chemical Geology* 281, 283–292. doi:10.1016/j.chemgeo.2010.12.015.
- Fietzke, J., Liebetrau, V., Eisenhauer, A., Dullo, C., 2005. Determination of uranium isotope ratios by multi-static IMIC-ICP-MS: method and implementation for precise U- and Th-series isotope measurements. *Journal of Analytical Atomic Spectrometry* 20, 395–401. doi:10.1039/b415958f.
- Flintrop, C., Hohlmann, B., Jasper, T., Korte, C., Podlaha, O.G., Scheele, S., Veizer, J., 1996. Anatomy of pollution: rivers of North Rhine-Westphalia, Germany. *American Journal of Science* 296, 58–98.
- Freitag, H., Ferguson, P.R., Dubois, K., Hayford, E.K., von Vordzobge, V., Veizer, J., 2008. Water and carbon fluxes from savanna ecosystems of the Volta River watershed, West Africa. *Global and Planetary Change* 61, 3–14. doi:10.1016/j.gloplacha.2007.08.003.
- Freysinet, P., Farah, A.S., 2000. Geochemical mass balance and weathering rates of ultramafic schists in Amazonia. *Chemical Geology* 170, 133–151. doi:10.1016/S0009-2541(99)00245-4.
- Gaillardet, J., Dupré, B., Allègre, C.J., Négrel, P., 1997. Chemical and physical denudation in the Amazon River Basin. *Chemical Geology* 142, 141–173. doi:10.1016/S0009-2541(97)00074-0.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chemical Geology* 159, 3–30. doi:10.1016/S0009-2541(99)00031-5.
- Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget. *Chemical Geology* 159, 31–60. doi:10.1016/S0009-2541(99)00033-9.
- Gandois, L., Perrin, A.-S., Probst, A., 2011. Impact of nitrogenous fertiliser-induced proton release on cultivated soils with contrasting carbonate contents: a column experiment. *Geochimica et Cosmochimica Acta* 75, 1185–1198. doi:10.1016/j.gca.2010.11.025.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrological cycle. *Annual Review of Earth and Planetary Sciences* 24, 225–262. doi:10.1146/annurev.earth.24.1.225.
- Gibson, J.J., Edwards, T.W.D., 2002. Regional water balance trends and evaporation-transpiration partitioning from a stable isotope survey of lakes in northern Canada. *Global Biogeochemical Cycles* 16, 1026. doi:10.1029/2001GB001839.
- Gibson, J.J., Edwards, T.W.D., Birks, S.J., St. Amour, N.A., Buhay, W.M., McEachern, P., Wolfe, B.B., Peters, D.L., 2005. Progress in isotope tracer hydrology in Canada. *Hydrological Processes* 19, 303–327. doi:10.1002/hyp.5766.
- Giger, W., Albrecht, P., Richling, E., Heckel, F., Schreier, P., Budzinski, H., Mazéas, L., Le Menach, K., Zwank, L., Berg, M., Schwarzenbach, R.P., Schmidt, T.C., Haderlein, S.B., 2003. B. Isotope gas chromatography – mass spectrometry. *Chimia* 57, 39–44.
- Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.C. (Eds.), *Handbook of Environmental Isotope Geochemistry*. Elsevier Scientific Publishing Company, New York, pp. 113–168.
- Gordon, L.J., Steffen, W., Jonsson, B.F., Folke, C., Falkenmark, M., Johannessen, A., 2005. Human modification of global water vapor flows from the land surface. *Proceedings of the National Academy of Sciences of the United States of America* 102, 7612–7617. doi:10.1073/pnas.0500208102.
- Grosbois, C., Négrel, P., Grimaud, D., Fouillac, C., 2001. An overview of dissolved and suspended matter fluxes in the Loire River basin: natural and anthropogenic inputs. *Aquatic Geochemistry* 7, 81–105. doi:10.1023/A:1017518831860.
- Guieu, C., Martin, J.M., Mousty, F., Trincherini, P., Tanké, S.P.C., Bazot, M., Dai, M.H., 1998. On trace metal geochemistry in the Danube River and western Black Sea. *Estuarine, Coastal and Shelf Science* 47, 471–485. doi:10.1006/ecss.1998.0377.
- Gupta, P., Noone, D., Galewsky, J., Sweeney, C., Vaughn, B.H., 2009. Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology. *Rapid Communications in Mass Spectrometry* 23, 2534–2542. doi:10.1002/rcm.4100.
- Hartmann, J., Jansen, N., Kempe, S., Dürr, H., 2007. Geochemistry of the river Rhine and the upper Danube: recent trends and lithological influence on baselines. *Journal of Environmental Science for Sustainable Society* 1, 39–46. doi:10.3107/jess.1.39.
- Hartmann, J., Jansen, N., Dörr, H.H., Kempe, S., Köhler, P., 2009. Global CO₂-consumption by chemical weathering: what is the contribution of highly active weathering regions? *Global and Planetary Change* 69, 185–194. doi:10.1016/j.gloplacha.2009.07.007.
- Hélie, J.F., Hillaire-Marcel, C., Rondeau, B., 2002. Seasonal changes in the sources and fluxes of dissolved organic carbon through the St. Lawrence River – isotopic and chemical constraints. *Chemical Geology* 186, 117–138. doi:10.1016/S0009-2541(01)00417-X.
- Hellings, L., Dehairs, F., Baeyens, W., Tackx, M., Keppens, E., 1999. Origin and fate of organic carbon in the freshwater part of the Scheldt Estuary as traced by stable carbon isotope composition. *Biogeochemistry* 47, 167–186. doi:10.1007/BF00994921.
- Henderson, G.M., 2002. New oceanic proxies for paleoclimate. *Earth and Planetary Science Letters* 203, 1–13. doi:10.1016/S0012-821X(02)00809-9.
- Hinsinger, P., 1998. How do plant roots acquire mineral nutrients? *Chemical Processes Involved in the Rhizosphere*. *Advances in Agronomy*, 64 Book Series. 225 pp.
- Hitchon, B., Krouse, H.R., 1972. Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada. III. Stable isotopes of oxygen, carbon and sulphur. *Geochimica et Cosmochimica Acta* 36, 1337–1357. doi:10.1016/0016-7037(72)90066-X.
- Hori, M., Hoshino, K., Okumura, K., Kano, A., 2008. Seasonal patterns of carbon chemistry and isotopes in tufa depositing groundwaters of southwestern Japan. *Geochimica et Cosmochimica Acta* 72, 480–492. doi:10.1016/j.gca.2007.10.025.
- IAEA/WMO, 2001. Global network of isotopes in precipitation. The GNIP database. Available on the web: <http://isohis.iaea.org>.
- Jackson, R.B., Carpenter, S.R., Dahm, C.N., McKnight, D.M., Naiman, R.J., Postel, S.L., Running, S.W., 2001. Water in a changing world. *Ecological Applications* 11, 1027–1045. doi:10.1890/1051-0761(2001)011[1027:WIACW]2.0.CO;2.
- Jing, Z., 1995. Geochemistry of trace metals from Chinese river/estuary systems: an overview. *Estuarine, Coastal and Shelf Science* 41, 631–658. doi:10.1006/ecss.1995.0082.
- Jones, H.G., 1992. *Plants and Microclimate: A Quantitative Approach to Environmental Plant Physiology*, 2nd ed. Cambridge University Press, Cambridge. 428 pp.
- Justic, D., Rabalais, N.N., Turner, R.E., 1997. Impacts of climate change on net productivity of coastal waters: implications for carbon budgets and hypoxia. *Climate Research* 8, 225–237. doi:10.3354/cr008225.
- Kao, S.J., Liu, K.K., 2000. Stable carbon and nitrogen isotope systematics in a human-disturbed watershed (Lanyang-Hsi) in Taiwan and the estimation of biogenic particulate organic carbon and nitrogen fluxes. *Global Biogeochemical Cycles* 14, 189–198. doi:10.1029/1999GB900079.
- Karim, A., Veizer, J., 2000. Weathering processes in the Indus River Basin: implications from riverine carbon, sulfur, oxygen, and strontium isotopes. *Chemical Geology* 170, 153–177. doi:10.1016/S0009-2541(99)00246-6.
- Karim, A., Veizer, J., 2002. Water balance of the Indus River Basin and moisture source in the Karakoram and western Himalayas: implications from hydrogen and oxygen

- isotopes in river water. *Journal of Geophysical Research – Atmospheres* 107, 4362. doi:10.1029/2000JD000253.
- Karim, A., Veizer, J., Barth, J., 2008. Net ecosystem production in the Great Lakes basin and its implications for the North American missing carbon sink: a hydrologic and stable isotope approach. *Global and Planetary Change* 61, 15–27. doi:10.1016/j.gloplacha.2007.08.004.
- Karim, A., Dubois, K., Veizer, J., 2011. Carbon and oxygen in the Laurentian Great Lakes: implications for CO₂ flux from terrestrial aquatic systems to the atmosphere. *Chemical Geology* 281, 133–141. doi:10.1016/j.chemgeo.2010.12.006.
- Karyotis, T., Charoulis, A., Mitsimponas, T., Vavoulidou, E., 2005. Nutrients and trace elements of arable soils rich in organic matter. *Communications in Soil Science and Plant Analysis* 36, 403–414. doi:10.1081/CSS-200043113.
- Kaysers, N., Probst, J.L., Cadet, D., Tardy, Y., 1990. Global world propagation of dryness and wetness waves. *Comptes Rendus - Académie des Sciences, Serie II* 310, 757–763.
- Kempe, S., 1979. Carbon in the freshwater cycle. *SCOPE* 13. The Global Carbon Cycle. 317 pp.
- Kempe, S., 1982. Long-term records of CO₂ pressure fluctuations in fresh water. In: Degens, E.T. (Ed.), *Transport of Carbon and Minerals in Major World Rivers*. Mitteilungen aus dem Geologischen-Paläontologischen Institut der Universität Hamburg 52, Hamburg, Germany, pp. 91–332.
- Kendall, C., Coplen, T.B., 2001. Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes* 15, 1363–1393. doi:10.1002/hyp.217.
- Kendall, C., McDonnell, J.J., 1998. *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam, The Netherlands. 839 pp.
- Kroopnick, P., Craig, H., 1976. Oxygen isotope fractionation in dissolved-oxygen in the deep-sea. *Earth and Planetary Science Letters* 32, 375–388. doi:10.1016/0012-821X(76)90078-9.
- Kump, L.R., Brantley, S.L., Arthur, M.A., 2000. Chemical weathering, atmospheric CO₂, and climate. *Annual Review of Earth and Planetary Sciences* 28, 611–667. doi:10.1146/annurev.earth.28.1.611.
- Ladouche, B., Probst, A., Viville, D., Idir, S., Baque, D., Loubet, M., Probst, J.L., Bariac, T., 2001. Hydrograph separation of stormflow components using isotopic, chemical and hydrological approaches (Strengbach, France). *Journal of Hydrology* 242, 255–274. doi:10.1016/S0022-1694(00)00391-7.
- Lafrenière, M.J., Sharp, M.J., 2005. A comparison of solute fluxes and sources from glacial and non-glacial catchments over contrasting melt seasons. *Hydrological Processes* 19, 2991–3012. doi:10.1002/hyp.5812.
- Lamb, L., 2004. Interactions between groundwater and surface water at river banks and the confluence of rivers. *Journal of Hydrology* 288, 312–326. doi:10.1016/j.jhydrol.2003.10.013.
- Lamb, L., Balakrishna, K., Brunet, F., Probst, J.L., 2005. Oxygen and hydrogen isotopic composition of major Indian rivers: a first global assessment. *Hydrological Processes* 19, 3345–3355. doi:10.1002/hyp.5974.
- Lamb, L., Brunet, F., Probst, J.L., 2009. Isotopic characteristics of the Garonne River and its tributaries. *Rapid Communications in Mass Spectrometry* 23, 2543–2550. doi:10.1002/rcm.4102.
- Lee, D., Veizer, J., 2003. Water and carbon cycles in the Mississippi River basin: potential implications for the Northern Hemisphere residual terrestrial sink. *Global Biogeochemical Cycles* 17, 1037. doi:10.1029/2002GB001984.
- Leopoldo, P.R., Franken, W.K., Villa Nova, N.A., 1995. Real evapotranspiration and transpiration through a tropical rain forest in central Amazonia as estimated by the water balance method. *Forest Ecology and Management* 73, 185–195. doi:10.1016/0378-1127(94)03487-H.
- Li, S.L., Liu, Q., Lang, Y.C., Tao, F., Zhao, Z., Zhou, Z., 2008. Stable carbon isotope biogeochemistry and anthropogenic impacts on karst ground water, Zunyi, Southwest China. *Aquatic Geochemistry* 14, 211–221. doi:10.1007/s10498-008-9033-4.
- Lis, G., Wassenaar, L.L., Hendry, M.J., 2008. High-precision laser spectroscopy D/H and ¹⁸O/¹⁶O measurements of microliter natural water samples. *Analytical Chemistry* 80, 287–293. doi:10.1021/ac701716q.
- Ludwig, W., Amiotte-Suchet, P., Munhoven, G., Probst, J.L., 1998. Atmospheric CO₂ consumption by continental erosion: present-day controls and implications for the last glacial maximum. *Global and Planetary Change* 16, 107–120. doi:10.1016/S0921-8181(98)00016-2.
- Luz, B., Barkan, E., 2000. Assessment of oceanic productivity with the triple-isotope composition of dissolved oxygen. *Science* 288, 2028–2031. doi:10.1126/science.288.5473.2028.
- Martin, C.E., Peucker-Ehrenbrink, B., Brunskill, G., Szymczak, R., 2001. Osmium isotope geochemistry of a tropical estuary. *Geochimica et Cosmochimica Acta* 65, 3193–3200. doi:10.1016/S0016-7037(01)00654-8.
- Meybeck, M., 1979. Major elements contents of river waters and dissolved inputs to the oceans. *Revue de Géologie Dynamique et de Géographie Physique* 21, 191–246.
- Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. *American Journal of Science* 287, 401–428.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic-matter. *Chemical Geology* 114, 289–302. doi:10.1016/0009-2541(94)90059-0.
- Millot, R., Vigier, N., Gaillardet, J., 2010. Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada. *Geochimica et Cosmochimica Acta* 74, 3897–3912. doi:10.1016/j.gca.2010.04.025.
- Molles, M., 2002. *Ecology: Concepts and Applications*. McGraw-Hill, New York. 586 pp.
- Moncoulon, D., Probst, A., Party, J.-P., 2004. Weathering, atmospheric deposition and vegetation uptake: role for ecosystem sensitivity to acid deposition and critical load. *Comptes Rendus Geosciences* 336, 1417–1426. doi:10.1016/j.crte.2004.09.008.
- Mook, W.G., 2000. Volume I, Introduction: Theory Methods Review. In: Mook, W.G. (Ed.), *Environmental Isotopes in the Hydrological Cycle – Principles and Applications*, International Hydrological Programme (IHP-V), Technical Documents in Hydrology (IAEA/UNESCO) No 39, Vol. I, Paris. 280 pp.
- Mook, W.G., Bommerson, J.C., Staverman, W.H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth and Planetary Science Letters* 22, 169–176. doi:10.1016/0012-821X(74)90078-8.
- Mortatti, J., Probst, J.L., 2003. Silicate rock weathering and atmospheric/soil CO₂ uptake in the Amazon basin estimated from river water geochemistry: seasonal and spatial variations. *Chemical Geology* 197, 177–196. doi:10.1016/S0009-2541(02)00349-2.
- Négrel, P., Allègre, C.J., Dupré, B., Lewin, E., 1993. Erosion sources determined from inversion of major, trace element ratios, and strontium isotopic ratio in river water: the Congo Basin case. *Earth and Planetary Science Letters* 120, 59–76. doi:10.1016/0012-821X(93)90023-3.
- Négrel, P., Petelet-Giraud, E., Barbier, J., Gautier, E., 2003. Surface water-groundwater interactions in an alluvial plain: chemical and isotopic systematics. *Journal of Hydrology* 277, 248–267. doi:10.1016/S0022-1694(03)00125-2.
- Nielsen, S.G., Rehkämper, M., Halliday, A.N., Porcelli, D., Andersson, P., Swarzenski, P.W., Latkoczy, C., Günther, D., 2005. Thallium isotope composition of the upper continental crust and rivers – an investigation of the continental sources of dissolved marine thallium. *Geochimica et Cosmochimica Acta* 69, 2007–2019. doi:10.1016/j.gca.2004.10.025.
- Ochs, M., Brunner, I., Stumm, W., Cosovic, B., 1993. Effects of root exudates and humic substances on weathering kinetics. *Water Air and Soil Pollution* 68, 213–229. doi:10.1007/BF00479404.
- Oliva, P., Dupré, B., Martin, F., Viers, J., 2004. The role of trace minerals in chemical weathering in a high-elevation granitic watershed (Estibère, France): chemical and mineralogical evidence. *Geochimica et Cosmochimica Acta* 68, 2223–2243. doi:10.1016/j.gca.2003.10.043.
- Paces, T., 1985. Sources of acidification in Central Europe estimated from elemental budgets in small catchments. *Nature* 315, 31–36. doi:10.1038/315031a0.
- Pate, J.S., 2001. Carbon isotope discrimination and plant water-use efficiency. Case scenarios for C3 plants. In: Unkovich, M., Pate, J.S., McNeill, A., Gibbs, D.J. (Eds.), *Carbon Isotope Discrimination and Plant Wateruse Efficiency. Case Scenarios for C3 Plants*. Stable Isotope Techniques in the Study of Biological Processes and Functioning of Ecosystems. Kluwer Academic Publishing, Dordrecht, The Netherlands, pp. 19–37.
- Pawellek, F., Veizer, J., 1994. Carbon cycle in the upper Danube and its tributaries: δ¹³C_{DIC} constraints. *Israel Journal of Earth Sciences* 43, 187–194.
- Pawellek, F., Frauenstein, F., Veizer, J., 2002. Hydrochemistry and isotope geochemistry of the upper Danube River. *Geochimica et Cosmochimica Acta* 66, 3839–3853. doi:10.1016/S0016-7037(01)00880-8.
- Perrin, A.S., Probst, A., Probst, J.L., 2008. Impact of nitrogenous fertilizers on the dissolution of carbonate bedrock in small agricultural catchments: implications for regional and global atmospheric CO₂ source/sink. *Geochimica Cosmochimica Acta* 72, 3105–3123. doi:10.1016/j.gca.2008.04.011.
- Petelet, E., 1998. Application de la géochimie à l'étude des mouvements d'eaux à moyenne et petite échelle: Les bassins versants de l'Hérault et de la Peyne (S. France). Utilisation des éléments majeurs, traces et des isotopes du Sr et du Pb. Université Montpellier II, Montpellier, France. 512 pp.
- Pierson-Wickmann, A.C., Aquilina, L., Weyer, C., Molénat, J., Lischeid, G., 2009. Acidification processes and soil leaching influenced by agricultural practices revealed by strontium isotopic ratios. *Geochimica et Cosmochimica Acta* 73, 4688–4704. doi:10.1016/j.gca.2009.05.051.
- Postel, S.L., Daily, G.C., Ehrlich, P.R., 1996. Human appropriation of renewable fresh water. *Science* 271, 785–788. doi:10.1126/science.271.5250.785.
- Probst, J.L., 1986. Dissolved and suspended matter transported by the Girou river (France): mechanical and chemical erosion rates in a calcareous molasse basin. *Hydrological Sciences* 31, 61–79. doi:10.1080/02626668609491028.
- Probst, A., Viville, D., Fritz, B., Ambroise, B., Dambrine, E., 1992. Hydrochemical budgets of a small granitic catchment: the Strengbach catchment case study (Vosges Massif, France). *Water, Air and Soil Pollution* 62, 337–347. doi:10.1007/BF00480265.
- Probst, J.L., Mortatti, J., Tardy, Y., 1994. Carbon river fluxes and global weathering CO₂ consumption in the Congo and Amazon river basins. *Applied Geochemistry* 9, 1–13. doi:10.1016/0883-2927(94)90047-7.
- Probst, A., Lelong, F., Viville, D., Durand, P., Ambroise, B., Fritz, B., 1995. Comparative hydrochemical behaviour and element budgets of the Aubure (Vosges Massif) and Mont-Lozère (Massif Central) spruce forested catchments. *Forest Decline and Atmospheric Deposition Effects in the French Mountains*. Springer, Berlin, Germany, pp. 203–225.
- Probst, A., El Gh'mari, A., Aubert, D., Fritz, B., Mc Nutt, R.H., 2000. Strontium as tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs, Strengbach, France. *Chemical Geology* 170, 203–219. doi:10.1016/S0009-2541(99)00248-X.
- Quay, P.D., Emerson, S., Wilbur, D.O., Stump, C., Knox, M., 1993. The δ¹⁸O of dissolved O₂ in the surface waters of the sub-arctic Pacific: a tracer of biological productivity. *Journal of Geophysical Research – Oceans* 98, 8447–8458. doi:10.1029/92JC03017.
- Quay, P.D., Wilbur, D.O., Richey, J.E., Devol, A.H., Benner, R., Forsberg, B.R., 1995. The ¹⁸O/¹⁶O of dissolved-oxygen in rivers and lakes in the Amazon Basin – determining the ratio of respiration to photosynthesis rates in fresh-waters. *Limnology and Oceanography* 40, 718–729.
- Quideau, S.A., Chadwick, O.A., Graham, R.C., Wood, H.B., 1996. Base cation biogeochemistry and weathering under oak and pine: a controlled long-term experiment. *Biogeochemistry* 35, 377–398. doi:10.1007/BF02179961.
- Rabalais, N.N., Turner, R.E., Diaz, R.J., Justic, D., 2009. Global change and eutrophication of coastal waters. *ICES Journal of Marine Science* 66, 1528–1537. doi:10.1093/icesjms/isp047.

- Ramanathan, A.L., Vaithiyathan, P., Subramanian, V., Das, B.K., 1994. Nature and transport of solute load in the Cauvery River Basin, India. *Water Research* 28, 1585–1593. doi:10.1016/0043-1354(94)90225-9.
- Rauch, S., Hemond, H.F., Peucker-Ehrenbrink, B., 2004. Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. *Environmental Science and Technology* 38, 396–402. doi:10.1021/es0347686.
- Raymond, P.A., Bauer, J.E., 2001. Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. *Organic Geochemistry* 32, 469–485. doi:10.1016/S0146-6380(00)00190-X.
- Raymond, P.A., Ho, N.H., 2009. Long term changes of chemical weathering products in rivers heavily impacted from acid mine drainage: insights on the impact of coal mining on regional and global carbon and sulfur budgets. *Earth and Planetary Science Letters* 284, 50–56. doi:10.1016/j.epsl.2009.04.006.
- Reynolds, B., Wood, M.J., Truscott, A.M., Brittain, S.A., Williams, D.L., 2000. Cycling of nutrient base cations in a twelve year old Sitka spruce plantation in upland mid-Wales. *Hydrology and Earth System Sciences* 4, 311–321.
- Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., Hess, L.L., 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2 . *Nature* 416, 617–620. doi:10.1038/416617a.
- Rodgers, P., Soulsby, C., Tetzlaff, D., Waldron, S., 2005. Using stable isotope tracers to assess hydrological flow paths, residence times and landscape influences in a nested mesoscale catchment. *Hydrology and Earth System Sciences* 9, 139–155.
- Rozanski, K., Arguas-Arguas, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. *Continental Isotope Indicators of Climate*. American Geophysical Union Monograph 78, American Geophysical Union. 36 pp.
- Savoie, N., Aminot, A., Treguer, P., Fontugne, M., Naulet, N., Kerouel, R., 2003. Dynamics of particulate organic matter $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France). *Marine Ecology-Progress Series* 255, 27–41. doi:10.3354/meps255027.
- Schmidt, T.C., Zwanck, L., Elsner, M., Berg, M., Meckenstock, R.U., Haderlein, S.B., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and Bioanalytical Chemistry* 378, 283–300. doi:10.1007/s00216-003-2350-y.
- Schoenberg, R., von Blanckenburg, F., 2005. An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS. *International Journal of Mass Spectrometry* 242, 257–272. doi:10.1016/j.ijms.2004.11.025.
- Scrivner, A.E., Vance, D., Rohling, E.J., 2004. New neodymium isotope data quantify Nile involvement in Mediterranean anoxic episodes. *Geology* 32, 565–568. doi:10.1130/G20419.1.
- Semhi, K., Amiotte-Suchet, P., Clauer, N., Probst, J.L., 2000a. Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin. *Applied Geochemistry* 15, 865–878. doi:10.1016/S0883-2927(99)00076-1.
- Semhi, K., Clauer, N., Probst, J.L., 2000b. Strontium isotope compositions of river waters as records of lithology-dependent mass transfers: the Garonne river and its tributaries (SW France). *Chemical Geology* 168, 173–193. doi:10.1016/S0009-2541(00)00226-6.
- Sifeddine, A., Wirmann, D., Albuquerque, A.L.S., Turcq, B., Cordeiro, R.C., Gurgel, M.H.C., Abrao, J.J., 2004. Bulk composition of sedimentary organic matter used in palaeoenvironmental reconstructions: examples from the tropical belt of South America and Africa. *Palaeogeography, Palaeoclimatology, Palaeoecology* 214, 41–53. doi:10.1016/S0031-0182(04)00322-0.
- Spangenberg, J.E., Vennemann, T.W., 2008. The stable hydrogen and oxygen isotope variation of water stored in polyethylene terephthalate (PET) bottles. *Rapid Communications in Mass Spectrometry* 22, 672–676. doi:10.1002/rcm.3415.
- Stallard, R.F., Edmond, J.M., 1987. Geochemistry of the Amazon. 3. Weathering chemistry and limits to dissolved inputs. *Journal of Geophysical Research* 92, 8293–8302. doi:10.1029/JC092iC08p08293.
- Stephens, M., Rose, J., 2005. Modern stable isotopic ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$) variation in terrestrial, fluvial, estuarine and marine waters from north-central Sarawak, Malaysian Borneo. *Earth Surface Processes and Landforms* 30, 901–912. doi:10.1002/esp.1218.
- Stögbauer, A., Strauss, H., Arndt, J., Marek, V., Einsiedl, F., van Geldern, R., 2008. Rivers of North-Rhine Westphalia revisited: tracing changes in river chemistry. *Applied Geochemistry* 23, 3290–3304. doi:10.1016/j.apgeochem.2008.06.030.
- Sverdrup, H., Warfvinge, P., Rabenhorst, M., Janicki, A., Morgan, R., Bowman, M., 1992. Critical loads and steady-state chemistry for streams in the state of Maryland. *Environmental Pollution* 77, 195–203. doi:10.1016/0269-7491(92)90077-N.
- Tardy, Y., Furlan, J., Mortatti, J., Probst, J.L., 1995. Global distribution of climate oscillations over the past century and fifty large river discharge fluctuations. *Comptes Rendus – Académie des Sciences, Serie II: Sciences de la Terre et des Planètes* 320, 945–952.
- Telmer, K., Veizer, J., 1999. Carbon fluxes, pCO_2 and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives. *Chemical Geology* 159, 61–86. doi:10.1016/S0009-2541(99)00034-0.
- Telmer, K., Veizer, J., 2000. Isotopic constraints on the transpiration, evaporation, energy, and gross primary production budgets of a large boreal watershed: Ottawa River Basin, Canada. *Global Biogeochemical Cycles* 14, 149–165. doi:10.1029/1999GB900078.
- Thompson, M.E., Fraser, A.S., Thode, H.G., 1986. Sulfate yields and isotopic ratios of sulfate sulfur in rivers of the Northwest Territories, Canada. *Applied Geochemistry* 1, 311–314. doi:10.1016/0883-2927(86)90016-8.
- Venkiteswaran, J., Wassenaar, L., Schiff, S., 2007. Dynamics of dissolved oxygen isotopic ratios: a transient model to quantify primary production, community respiration, and air-water exchange in aquatic ecosystems. *Oecologia* 153, 385–398. doi:10.1007/s00442-007-0744-9.
- Vennemann, T.W., Anglhofer-Reichelt, S., 2005. Anatomy of contaminated aquifers of an industrial site: insights from the stable isotope compositions of waters and dissolved inorganic carbon. *Geological Quarterly* 49, 113–126.
- Vigier, N., Gislason, S.R., Burton, K.W., Millot, R., Mokadem, F., 2009. The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland. *Earth and Planetary Science Letters* 287, 434–441.
- Vitousek, P.M., Mooney, H.A., Lubchenco, J., Melillo, J.M., 1997. Human domination of Earth's ecosystems. *Science* 277, 494–499. doi:10.1126/science.277.5325.494.
- Viville, D., Biron, P., Granier, A., Dambrine, E., Probst, A., 1993. Interception in a mountainous declining spruce stand in the Strengbach catchment (Vosges, France). *Journal of Hydrology* 144, 273–282. doi:10.1016/0022-1694(93)90175-9.
- Vogel, J.C., 1993. Variability of carbon isotope fractionation during photosynthesis. *Stable Isotopes and Plant Carbon-Water Relations*. Academic Press, San Diego, California. pp. 29–38.
- Vörösmarty, C.J., Fekete, B.M., Meybeck, M., Lammers, R.B., 2000. Global system of rivers: its role in organizing continental land mass and defining land-to-ocean linkages. *Global Biogeochemical Cycles* 14, 599–621. doi:10.1029/1999GB900092.
- Wang, X., Veizer, J., 2000. Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochimica et Cosmochimica Acta* 64, 3775–3786. doi:10.1016/S0016-7037(00)00477-4.
- Wang, X.C., Chen, R.F., Gardner, G.B., 2004. Sources and transport of dissolved and particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the northern Gulf of Mexico. *Marine Chemistry* 89, 241–256. doi:10.1016/j.marchem.2004.02.014.
- Warfvinge, P., Falkengrengrer, U., Sverdrup, H., Andersen, B., 1993. Modeling long-term cation supply in acidified forest stands. *Environmental Pollution* 80, 209–221. doi:10.1016/0269-7491(93)90041-L.
- Wassenaar, L.L., in press. Dissolved oxygen status of Lake Winnipeg: spatio-temporal and isotopic ($\text{d}^{18}\text{O}-\text{O}_2$) patterns. *Journal of Great Lakes Research*. doi: 10.1016/j.jglr.2010.12.011.
- Wassenaar, L.L., Koehler, G., 1999. An on-line technique for the determination of the d^{18}O and d^{17}O of gaseous and dissolved oxygen. *Analytical Chemistry* 71, 4965–4968. doi:10.1021/ac9903961.
- Welch, S.A., Ullman, W.J., 1993. The effect of organic-acids on plagioclase dissolution rates and stoichiometry. *Geochimica et Cosmochimica Acta* 57, 2725–2736. doi:10.1016/0016-7037(93)90386-B.
- Williams, E.L., Walter, L.M., Ku, T.C.W., Kling, G.W., Zak, D.R., 2003. Effects of CO_2 and nutrient availability on mineral weathering in controlled tree growth experiments. *Global Biogeochemical Cycles* 17, 1041. doi:10.1029/2002GB001925.
- Winston, W., Criss, R., 2003. Oxygen isotope and geochemical variations in the Missouri River. *Environmental Geology* 43, 546–556. doi:10.1007/s00254-002-0679-8.
- Yang, C., Telmer, K., Veizer, J., 1996. Chemical dynamics of the “St. Lawrence” riverine system: $\delta^2\text{H}_2\text{O}$, $\delta^{18}\text{O}_2$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, and dissolved $^{87}\text{Sr}/^{86}\text{Sr}$. *Geochimica et Cosmochimica Acta* 60, 851–866. doi:10.1016/0016-7037(95)00445-9.
- Zakharova, E.A., Pokrovsky, O.S., Dupré, B., Zaslavskaya, M.B., 2005. Chemical weathering of silicate rocks in Aldan Shield and Baikal Uplift: insights from long-term seasonal measurements of solute fluxes in rivers. *Chemical Geology* 214, 223–248. doi:10.1016/j.chemgeo.2004.10.003.
- Zakharova, E.A., Pokrovsky, O.S., Dupré, B., Gaillardet, J., Efimova, L.E., 2007. Chemical weathering of silicate rocks in Karelia region and Kola peninsula, NW Russia: assessing the effect of rock composition, wetlands and vegetation. *Chemical Geology* 242, 255–277. doi:10.1016/j.chemgeo.2007.03.018.
- Zhang, Q., Lin, F., Li, X., Hu, M., 1986. Major ion chemistry and oceanic flux of rivers in southern coastal China. *Acta Oceanologica Sinica* 5, 57–62.
- Zhang, J., Quay, P.D., Wilbour, D.O., 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO_2 . *Geochimica et Cosmochimica Acta* 59, 107–114. doi:10.1016/0016-7037(95)91550-D.
- Zheng, D.L., Prince, S.D., Wright, R., 2001. NPP Multi-Biome: Gridded Estimates for Selected Regions Worldwide, 1989–2001. Oak Ridge National Laboratory Distribution Active Archive Central, Oak Ridge, Tennessee. Available online at <http://www.daac.ornl.gov/>.