

# RIVERINE INORGANIC CARBON DYNAMICS : OVERVIEW AND PERSPECTIVE

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**ABSTRACT:** Inorganic carbon, the great part of the riverine carbon exported to the ocean, plays an important role in the global carbon cycle and ultimately impacts the coupled carbon-climate system. An overview was made on both methods and results of the riverine inorganic carbon researches. In addition to routine in situ survey, measurement and calculation, the direct precipitation method and the gas evolution technique were commonly used to analyze dissolved inorganic carbon in natural water samples. Soil CO<sub>2</sub>, carbonate minerals and atmospheric CO<sub>2</sub> incorporated into riverine inorganic carbon pool via different means, with bicarbonate ion being the dominant component. The concentration of inorganic carbon, the composition of carbon isotopes ( <sup>13</sup>C and <sup>14</sup>C), and their temporal or spatial variations in the streams were controlled by carbon input, output and changes of carbon biogeochemistry within the riverine system. More accurate flux estimation, better understanding of different influential processes, and quantitative determination of various inputs or outputs need to be well researched in future.

**KEY WORDS:** riverine inorganic carbon; dissolved inorganic carbon; dynamics; flux

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## 1 INTRODUCTION

River systems are the major linkage between the land and the ocean, not only transporting carbon from terrestrial environment to the ocean, but also exchanging CO<sub>2</sub> with the atmosphere, actively involved in the global carbon biogeochemical cycle (RICHEY et al., 2002; COLE and CARACO, 2001). The inorganic carbon, mainly originating from soil CO<sub>2</sub>, carbonate minerals and atmospheric CO<sub>2</sub>, constituted the great part (about 60%) of the riverine carbon exported to the ocean (YANG et al., 1996; LUDWIG et al., 1996). Being a dynamic open-system, the riverine inorganic carbon pool was closely related with the characteristics of drainage basin, including lithology, climate and structure of river system. On the other hand, the riverine inorganic carbon pool was directly affected by vertically atmospheric CO<sub>2</sub> exchange at the air-water interface. In addition, the influx of riverine inorganic carbon to the ocean could adjust dissolved inorganic carbon content of the deep ocean and affect the CO<sub>2</sub> uptake capacity of the ocean, through subsequent

disturbance on the ocean "biotic pump" and "dissolved pump", thus ultimately affecting the climate system (BERNER, 1990).

In a word, the riverine inorganic carbon plays an important role in the global carbon cycle and should be considered in studies of the coupled carbon-climate system. An overview on dynamics of the riverine inorganic carbon pool was made in the paper, expecting a better knowledge of its role in the coupled carbon-climate system.

## 2 RIVERINE INORGANIC CARBON POOL

The riverine inorganic carbon pool consists of two components, the dissolved inorganic carbon (DIC) and the particulate inorganic carbon (PIC), generally with the DIC being the primary component in most rivers (with the exception of some arid temperate rivers, such as the Huanghe River and the Danube River where PIC is dominant). It was estimated that the global river systems transport annually about 0.51Gt ( ×10<sup>15</sup>g) inorganic car-

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bon from terrestrial environment to the ocean, about 60% of the total carbon flux carried by rivers, with 75% of which being DIC and 25% PIC (MEYBECK, 1982; 1987). The dominant role of the DIC in the riverine inorganic carbon pool was determined not only by its larger quantity, but also by its more actively biogeochemical activities involved in the global carbon biogeochemical cycle relative to the PIC.

## 2.1 Activities of Various Compositions

The riverine DIC pool was composed of aqueous carbon dioxide ( $\text{CO}_2(\text{aq})$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ions ( $\text{CO}_3^{2-}$ ), with bicarbonate being the dominant species (DREVER, 1988). These aqueous compounds can be in contact with gaseous carbon dioxide ( $\text{CO}_2(\text{g})$ ) and/or carbonate minerals such as calcite ( $\text{CaCO}_3$ ). The composition of the riverine DIC pool is then controlled by the chemical equilibrium among these five species. The concentration of each species in river water depends on its pH, temperature and total dissolved inorganic carbon ( $\text{CO}_2$ ) (AMIOTTE-SUCHET et al., 1999). In addition, the part of DIC can be transformed into PIC in rivers where the carbonate is supersaturated, through calcite precipi-

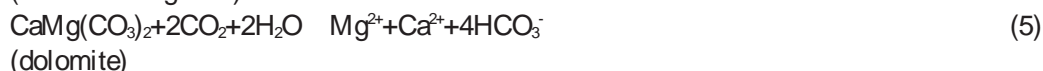
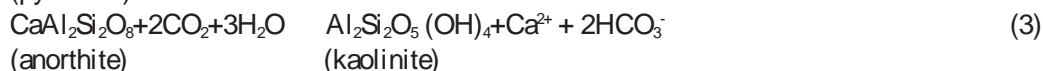
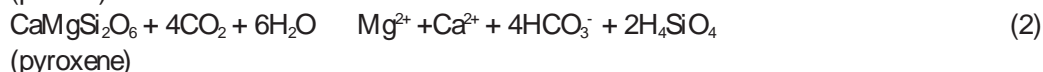
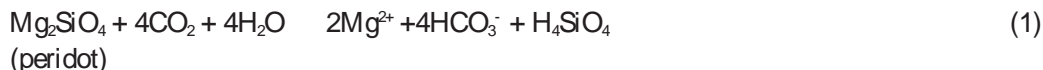
tation reaction (FENG and KEMPE, 1987), whereas the PIC also can be dissolved into DIC.

## 2.2 Sources of Riverine Inorganic Carbon Pool

The riverine PIC is mainly from mechanical erosion of carbonated rocks and of carbonaceous sedimentary rocks. In addition, in situ calcite precipitation in the streams, for example the lower reaches of Huanghe River where the carbonate is supersaturated, can supply portion of autochthonous PIC (FENG and KEMPE, 1987).

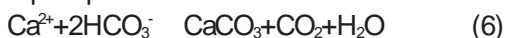
The riverine DIC pool has three main allochthonous sources: soil  $\text{CO}_2$ , bedrocks and soil minerals through carbonate dissolution and atmospheric  $\text{CO}_2$  exchange at the air-water interface (YANG et al., 1996).

Soil  $\text{CO}_2$  that originates from root respiration and decomposition of organic material, or from atmospheric  $\text{CO}_2$ , contributes to the riverine DIC pool via two means: direct inflow in the form of aqueous  $\text{CO}_2$  or/and other species through surface and groundwater flows, or indirect input totally in the form of  $\text{HCO}_3^-$  by silicate and carbonate minerals weathering, with the following representative reaction equations (BARTH et al., 2003):



In the case of silicate mineral weathering,  $\text{HCO}_3^-$  purely derives from soil  $\text{CO}_2$  (equations (1), (2), (3)), whereas for carbonate mineral weathering, soil  $\text{CO}_2$  and carbonate itself contribute  $\text{HCO}_3^-$  in a ratio of 1:1 as demonstrated by Equation (4) and Equation (5).

In the long term, silicates weathering plays a role as net sink of the increasing atmospheric  $\text{CO}_2$ , while half of  $\text{HCO}_3^-$  that originates from carbonates weathering will ultimately return to the atmosphere through subsequent calcite precipitation in the ocean:



However, on shorter time scales ( $10^3$ - $10^4$  years), the role of carbonates is particularly important because of their good solubility relative to silicates (YUAN, 1997; 1999). It has been proved that even if present in minor

amounts, carbonates still are the primary controlling factor of the riverine DIC pool (BARTH et al., 2003).

In addition to the  $\text{HCO}_3^-$  derived from the weathering of silicate or carbonate minerals by  $\text{CO}_2$ , carbonate dissolution by other naturally occurring acids including  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  (SHARP et al., 1995) and organic acids (SALOMONS and MOOK, 1986; BERNER, 1992) contributes another portion of  $\text{HCO}_3^-$  to the riverine DIC pool. In sum, rocks and soil minerals weathering contribute a significant portion of  $\text{HCO}_3^-$  to most rivers via ground water and surface flow inputs, and strongly influence the riverine carbon cycle.

Moreover, atmospheric  $\text{CO}_2$  invasion at the air-water interface, coupled with autochthonous  $\text{CO}_2$  production from respiration and decomposition of organic material

within the river water can result in a higher DIC concentration.

### 3 PROGRESS OF STUDY ON RIVERINE INORGANIC CARBON

#### 3.1 Focus on Riverine Inorganic Carbon Pool

The rivers can be regarded as complicated systems, containing several different components, such as main stream, tributary, groundwater, wetland, spring, estuary, etc. Previous studies of the riverine inorganic carbon mainly focused on fluxes and sources of the DIC pool in different sections of river systems (Table 1), and also investigated the temporal or spatial variations of the DIC pool as well as processes or mechanisms controlling those changes, using hydrological and water chemistry measurements including discharge, pH, temperature, alkalinity,  $\text{HCO}_3^-$  concentration, partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) and saturation index of calcite, and carbon stable isotope ( $^{13}\text{C}$ ) which have widely been used as an effective tool for distinguishing carbon originating from a variety of sources (YANG et al., 1996; TAYLOR and FOX, 1996; ATEKWANA and KRISHNAMURTHY, 1998; AUCOUR et al., 1999; AMIOTTE-SUCHET et al., 1999; BARTH and VEIZER, 1999; TELMER and VEIZER, 1999; WANG and VEIZER, 2000; HELIE et al., 2002; BARTH et al., 2003). Additionally, RAYMOND et al. (2004) studied the riverine DIC pool using  $^{13}\text{C}$  coupled with carbon radioactive isotope ( $^{14}\text{C}$ ) that can provide additional information about source and age of DIC.

#### 3.2 Method and Technique

In order to make clear the issues mentioned above, the earlier works selected different sections of the river systems located in various climate zones, and introduced a series of procedures including in situ survey and sampling, measurement and analysis in the laboratory as well as model simulation to study the dynamics of the riverine DIC pool.

##### 3.2.1 Sampling

For studies of riverine carbon cycle, whether the sampling scheme is reasonable or not will directly affect the reliability and accuracy of results. Different authors adopted different sampling schemes to carry out their studies based on the structure of river system or characteristics of drainage basin. For example, in order to investigate the spatial variations of the riverine DIC pool in a large river system that contains several tributaries being of different properties, or to illuminate respective contributions of tributaries to these variations, multiple sampling sites should be selected along the entire river, including headwater, outlet, points in the mouth of major tributaries where hundreds of meters away from confluences of main stream and tributaries (no influences from main stream), and points in main stream where tributary influxes mixed completely with the main stream, and the water samples should be taken at the same sampling period (TELMER and VEIZER, 1999; AUCOUR et al., 1999). However, sampling in different seasons at the same sampling site can reflect the temporal variations. In addition, the interval time of samplings is another notable aspect because it affects

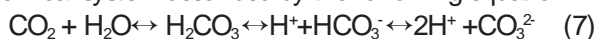
Table 1 Different sections of river system investigated in previous studies on riverine DIC

Section	Drainage/ Catchment	Continent	Reference
Main stream	Rhine Fraser	Europe North America	BUHL et al., 1991 CAMERON et al., 1999
River-tributary system	Kalamazoo Danube Rhône Ottawa	North America Europe Europe North America	ATEKWANA and KRISHNAMURTHY, 1998 PAWELLEK and VEIZER, 1994 AUCOUR et al., 1999 TELMER and VEIZER, 1999
River-lake-tributary system	St. Lawrence	North America	YANG et al., 1996; HÉLIE et al., 2002
River-tributary- groundwater system	Amazon Wainakari	South America Europe	LONGINELLI and EDMOND, 1983 WANG and VEIZER, 2000
Soil-spring-stream system	Strengbach	Europe	AMIOTTE-SUCHET et al., 1999
Groundwater-surface runoff-anthropogenic inputs	Lagan	Europe	BARTH et al., 2003
River-wetland system	Amazon	South America	RICHEY et al., 2002
River-lake-creek system	Ottawa	North America	TAYLOR and FOX, 1996
Near-shore system	St. Lawrence	North America	BARTH and VEIZER, 1999
Estuary	Scheldt Zhujiang River	Europe Asia	MOOK, 1970 ZHAI et al., 2005

the accuracy of flux estimation. Generally, the shorter the sampling interval time, the closer the estimation to the truth (HÉLIE et al., 2002).

### 3.2.2 Measurement, calculation and analysis

Generally, the water chemistry parameters are easily obtained through measurement and calculation. The saturation indexes of calcite and dolomite in rivers can be calculated using the WATEQ Computer Program (TRUEDELL and JONES, 1974) or following STUMM and MORGAN's method (1996). Alkalinity can be obtained by sulfuric acid titration.  $\text{HCO}_3^-$  concentration is commonly used to represent the DIC concentration due to its dominance in aquatic systems, and can be obtained by in situ hydrochloric acid titration. In addition, concentration of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , aqueous  $\text{CO}_2$  and  $\text{pCO}_2$  can be calculated by using a classical carbonate chemical system described by the following equation:



DIC-flux can be estimated from DIC concentration and discharge, using either interpolated values or one equation proposed by MEYBECK et al. (1992) and HÉLIE et al. (2002) (Equation (8)),

$$F = 365 \bar{Q} \left[ \frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \right] \quad (8)$$

where  $F$  is the annual flux,  $\bar{Q}$  is the mean annual discharge,  $C_i$  is the instantaneous DIC concentration in sampling site  $i$  (measured in situ) and  $Q_i$  is the instantaneous discharge in sampling site  $i$ .

For  $^{13}\text{C}$  analysis, two methods are commonly used in natural water samples: the direct precipitation (GLEASON et al., 1969; FRIEDMAN, 1970; DEINES et al., 1974; BARNES et al., 1978; PEARSON et al., 1978; HASSAN, 1982; HEATHCOTE, 1985; BISHOP, 1990; TAYLOR and FOX, 1996; AUCOUR et al., 1999) and the gas evolution technique (MOOK, 1968; TAN et al., 1973; GAMES and HAYES, 1976; REARDON et al., 1979; HASSAN, 1982; GRABER and AHARON, 1991; HOLT et al., 1995; ATEKWANA and KRISHNAMURTHY, 1998; HÉLIE et al., 2002). The carbon stable isotopic compositions of samples are analyzed by using a VG-Prism mass spectrometer, and reported against V-PDB in the notation:

$$^{13}\text{C} = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 10^3 \quad (9)$$

where  $R$  is for  $^{13}\text{C}/^{12}\text{C}$ . BISHOP (1990) modified previous works and presented a standard method of precipitation, which has been tested and proved to enable to yield satisfactory and accurate  $^{13}\text{C}$ -values for natural water. However, this method is inadequate for high sul-

fate-bearing waters because incomplete precipitation and isotope fractionation may occur where large sulfate concentration is encountered. The gas evolution technique, especially the modified version by ATEKWANA and KRISHNAMURTHY (1998), allows for simultaneously accurate determination of both  $^{13}\text{C}$ -values and the true DIC concentration (all species, not just  $\text{HCO}_3^-$ ) using smaller amount of water sample. While the DIC concentration cannot be obtained from the same sample used for isotope determination using the direct precipitation method.

Riverine  $^{14}\text{C}_{\text{DIC}}$  can be analyzed by using the same method for  $^{13}\text{C}$  analysis, with accelerator mass spectrometry (AMS) replacing VG-Prism mass spectrometer, and reported in the notation:

$$^{14}\text{C} = ((A_s/A_{\text{abs}}) - 1) \times 10^3 \quad (10)$$

where  $A$  is for  $^{14}\text{C}/^{12}\text{C}$ ,  $A_s$  represents the specific  $^{14}\text{C}$  activity of a sample,  $A_{\text{abs}}$  represents the absolute  $^{14}\text{C}$  activity in the international isotopic standard (DONAHUE et al., 1990).

### 3.2.3 GEM- $\text{CO}_2$ model simulation

The consumption of atmospheric  $\text{CO}_2$  by continental weathering is primarily influenced by drainage, temperature and lithology (AMIOTTE-SUCHET and PROBST, 1993; PROBST et al., 1992). For a homogeneous basin, the flux of atmospheric  $\text{CO}_2$  consumed by rock weathering can be estimated from the flux of  $\text{HCO}_3^-$  transported by river waters at the outlet of the basin. AMIOTTE-SUCHEET and PROBST (1993) have developed a simple model GEM- $\text{CO}_2$ , which based on a set of empirical relationships between the flux of atmospheric  $\text{CO}_2$  consumed by rock weathering ( $F_{\text{CO}_2}$ ) and the discharge ( $Q$ ), to calculate the flux of atmospheric  $\text{CO}_2$  consumed by rock weathering. This model later has been successfully applied to several different large river basins such as the Garonne (France), the Congo and the Amazon, and also to China (QIU et al., 2004) and global continent (PROBST et al., 1992). The results were in agreement with other studies (Table 2), indicating that GEM- $\text{CO}_2$  model is reliable and can be used globally.

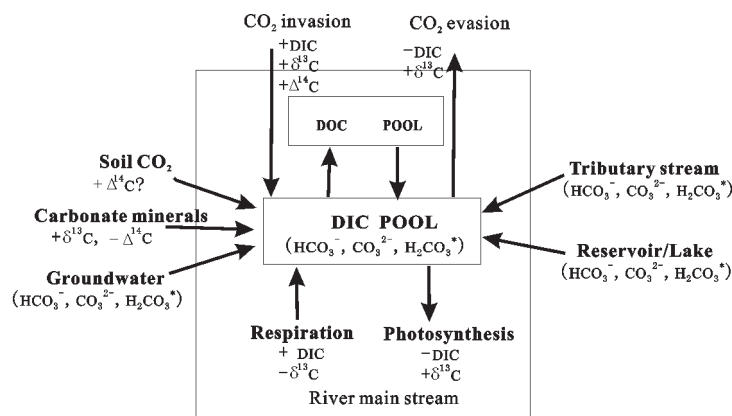
## 3.3 Major Process Controlling Riverine Inorganic Carbon Pool

For any given rivers, the DIC pool can be influenced by contributions from different water sources, biogenic uptake and release, and  $\text{CO}_2$  exchange between atmosphere and surface water (Fig. 1). Changes in the DIC concentrations result from carbon input or output from the DIC pool by series of processes, while changes in the carbon isotopic ratios (both  $^{13}\text{C}_{\text{DIC}}$  and  $^{14}\text{C}_{\text{DIC}}$ ) re-



Table 2 Atmospheric CO<sub>2</sub> consumption flux by rock weathering

	GEM-CO <sub>2</sub> Model	Others		
		Method 1	Method 2	Method 3
Global flux (GtC/a)	0.26	0.288	0.29	0.28
Reference	AMLOTTE-SUCHET and PROBST, 1995	GAILLARDET et al., 1999	MEYBECK, 1987	BERNER et al., 1983
Flux of China (GtC/a)	0.047	0.066	0.018	-
Reference	QIU et al., 2004	LIU, 2000	XU and JIANG, 1997	



Note:  $\text{H}_2\text{CO}_3^*$  is the analytical sum of  $\text{CO}_2(\text{aq})$  and of the true carbonic acid ( $\text{H}_2\text{CO}_3$ )

Fig. 1 Schema of change in  $^{13}\text{C}_{\text{DIC}}$ ,  $^{14}\text{C}_{\text{DIC}}$  and DIC content in relation to process of controlling riverine DIC

sult from fractionation accompanying transformation of carbon, or from mixing of carbon from different sources. In addition, the dilution effect of flood events can result in decreases of DIC concentration, but no influence on the  $^{13}\text{C}_{\text{DIC}}$  and  $^{14}\text{C}_{\text{DIC}}$  (ATEKWANA and KRISHNAMURTHY, 1998).

### 3.3.1 Influx of different water sources

The influences from different water sources such as groundwater, surface flow, lake/reservoir and tributary streams depend on their respective total inorganic carbon input relative to that of the main stream and their isotopic compositions. For example, in the St. Lawrence River that is mainly fed by the Great Lakes, the second largest terrestrial freshwater reservoir in the world, the relative contributions of the Great Lakes and tributaries to its total DIC flux are 82% and 18%, respectively (HÉLIE et al., 2002). And its carbon isotopic compositions present characteristics of both water sources: isotopically heavy DIC signatures were observed upstream due to the long residence time of DIC in the lakes, then  $^{13}\text{C}_{\text{DIC}}$  values decreased downstream because of the influx of  $^{13}\text{C}$ -depleted DIC from tributaries (YANG et al., 1995).

### 3.3.2 Contribution of soil CO<sub>2</sub>

Soil CO<sub>2</sub> is produced by decomposition of soil organic matter (SOM) and by root respiration (CERLING, 1984; SALOMONS and MOOK, 1986; CERLING et

al., 1991). Its role as an important source of the riverine inorganic carbon pool has been discussed in above section. The isotopic composition of soil CO<sub>2</sub> inherits from SOM in the drainage basin area, while the  $^{13}\text{C}$  value of SOM is directly related to the type of vegetation cover with an estimated average of -26‰ (-22‰ to -30‰) for C<sub>3</sub> plants and -12‰ (-6‰ to -19‰) for C<sub>4</sub> plants (DEINES, 1980; MARIOTTI, 1991). However, the mineralization and decomposition of SOM can cause carbon fractionation (DÖRR and MÜNNICH, 1980; SALOMONS and MOOK, 1986; CERLING et al., 1991), making the  $^{13}\text{C}$  of the residual soil CO<sub>2</sub> enrich about 4.4‰. This is due to the molecular diffusion of the gas through the soil pores (DÖRR and MÜNNICH, 1980; CERLING et al., 1991). The  $^{13}\text{C}$  values of soil CO<sub>2</sub> thus depend on the source material being decomposed (i.e., C<sub>3</sub> or C<sub>4</sub> plant remains) and on the rate of SOM mineralization/decomposition.

CH<sub>4</sub> produced by the degradation of SOM under anaerobic conditions could isotopically contaminate the soil CO<sub>2</sub>. WADA and UEDA (1996) studied a rice paddy field and reported that aerobic bacterial decomposition of SOM produces very depleted CH<sub>4</sub> ( $^{13}\text{C}$  around -50‰) but relatively enriched CO<sub>2</sub> ( $^{13}\text{C}$  from -9‰ to -12‰), resulting in a decrease in the  $^{13}\text{C}$  of the accumulated SOM (-29.2‰) relative to the fresh organic matter (-26.8‰).

$^{14}\text{C}$  of soil  $\text{CO}_2$  theoretically should change with the decomposed SOM of varying ages, however, studies on the  $^{14}\text{C}$  content of soil  $\text{CO}_2$  indicated that the majority of soil  $\text{CO}_2$  derives from SOM that have a  $^{14}\text{C}$  greater than 0 (RAYMOND et al., 2004). If this perspective is reliable, the contribution of soil  $\text{CO}_2$  to the river would make the riverine DIC enrich  $^{14}\text{C}$ .

### 3.3.3 Weathering of land surface

The isotopic composition ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) and concentration of DIC resulting from carbonate/silicate minerals weathering by  $\text{CO}_2$  should depend on the degree to which the water-mineral system is "open" to the  $\text{CO}_2$  gas reservoir during weathering, the  $\text{pCO}_2$  in the water-mineral system (DEINES et al., 1974) and the contribution of the biogenic  $\text{CO}_2$ . For carbonate mineral weathering, both carbonate mineral ( $^{14}\text{C}$ -dead,  $^{13}\text{C}=0$ ) and soil  $\text{CO}_2$  (variable  $^{14}\text{C}$ ,  $^{13}\text{C}$  of  $-8\text{‰}$  to  $-22\text{‰}$ ) contribute to riverine DIC approximately in a ratio of 11. While in the case of silicate mineral weathering, the isotopic composition of DIC should just reflect that of soil  $\text{CO}_2$ . In addition, the other portion of DIC originating from the dissolution of carbonate minerals by other naturally occurring acids, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and organic acids, should have an isotopic composition close to that of the initial carbonate, because this kind of reaction consumes neither atmospheric nor biogenic  $\text{CO}_2$ .

### 3.3.4 $\text{CO}_2$ exchange of air-water interface

Air-water  $\text{CO}_2$  exchange, i.e.,  $\text{CO}_2$  invasion from the atmosphere and  $\text{CO}_2$  evasion to the atmosphere (degassing of  $\text{CO}_2$ ), will modify the riverine DIC pool.  $\text{CO}_2$  invasion from the atmosphere that had a  $^{13}\text{C}$  of  $-7\text{‰}$  (ZHANG et al., 1994) and a modern  $^{14}\text{C}$  value (MOOK et al., 1974) resulted in an increase of DIC concentration, more positive  $^{13}\text{C}_{\text{DIC}}$  values and  $^{14}\text{C}$  values approaching modern ages, while  $\text{CO}_2$  evasion to the atmosphere caused a decrease both in DIC concentration and in the  $^{13}\text{C}_{\text{DIC}}$ . Previous studies showed that the  $\text{CO}_2$  degassing flux was higher in humid tropical and subtropical river systems where the partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ) was supersaturated with respect to the atmosphere (RICHEY et al., 2002; ZHAI et al., 2005). The isotopic exchange with atmosphere might be enhanced in the slow-velocity reaches or during low flow periods because of a longer residence time of the water in the stream, whereas a shorter residence time in the fast-velocity reached or during high flow period would lead to minimizing air-water isotopic exchange (AMIOTTE-SUCHET et al., 1999).

Moreover, AMIOTTE-SUCHET et al. (1999) pointed out that the isotopic exchange between aqueous  $\text{CO}_2$

and atmospheric  $\text{CO}_2$  was easier and/or faster than that between bicarbonate ions and atmospheric  $\text{CO}_2$ , i.e., it was the aqueous  $\text{CO}_2$  (not all DIC) that equilibrates with atmospheric  $\text{CO}_2$ .

### 3.3.5 Biogenic $\text{CO}_2$ uptake and release

Biogenic  $\text{CO}_2$  uptake and release, i.e., photosynthesis uptake and respiration and decay/decomposition of organic matter in the river itself also impact the riverine DIC pool. In general, in situ photosynthesis decreases DIC concentration and enriches the remaining DIC pool in  $^{13}\text{C}$ , because algae preferentially uptakes lighter carbon ( $^{12}\text{C}$ ) from the DIC pool, while respiration and decomposition of organic matter which release isotopically more negative  $\text{CO}_2$  would result in an increase in DIC concentration and a decrease in the  $^{13}\text{C}_{\text{DIC}}$  (BUHL et al., 1991; PAWELLEK and VEIZER, 1994; TAYLOR and FOX, 1996; YANG et al., 1996; FLINTROP et al., 1996). If biological activity were significant, biogenic  $\text{CO}_2$  uptake and release would cause relative great shifts in the riverine inorganic carbon pool.

### 3.3.6 Coupling with riverine organic carbon pool

Decomposition of the dissolved organic carbon (DOC) produces  $\text{CO}_2$  with a fairly negative isotopic composition. The isotopically depleted  $\text{CO}_2$  is then incorporated into the DIC pool, thus yielding more negative  $^{13}\text{C}$  values. In general, the labial DOC is readily decomposed into  $\text{CO}_2$  by either photodecomposition or respiration, causing more negative  $^{13}\text{C}_{\text{DIC}}$  values. While the  $^{13}\text{C}_{\text{DIC}}$  compositions were more positive when the DOC consists of fractions that are much more difficult to decompose (SCHIFF et al., 1997; BARTH and VEIZER, 1999). Inversely, DIC could be transformed into organic material through biogenic  $\text{CO}_2$  uptake. This inter-transformation is more active in near-shore ecosystems or streams with longer residence time (BARTH and VEIZER, 1999). To sum up, the riverine DIC pool is closely coupled with riverine organic carbon pool, indicating that river systems do not only transport carbon but also actively recycle it.

## 3.4 Spatial and Temporal Variations of Riverine Inorganic Carbon

Within a given drainage basin, the riverine inorganic carbon dynamics generally underwent strong seasonal changes that were mainly directly controlled by riverine biogeochemistry and by water levels that caused different proportions of the influencing water masses (ATEKWANA and KRISHNAMURTHY, 1998; AMIOTTE-SUCHET et al., 1999; BARTH and VEIZER, 1999; TELMER and VEIZER, 1999; WANG and VEIZER, 2000; HÉLIE et al., 2002). For example,

HÉLIE et al. (2002) observed very strong seasonal variations in a survey on DIC pool of the St. Lawrence River between the summer low water levels when water supplies from the Great Lakes into the riverine system may represent up to 80% of the total outflow of the St. Lawrence River, and the spring snowmelt period when tributaries may provide up to 80% of this outflow.

On the other hand, spatial variations of riverine inorganic carbon extensively existed. Small rivers in homogeneous basins generally showed downstream trends (AMIOTTE-SUCHET et al., 1999), whereas condition became complicated in larger river-tributary systems flowing heterogeneous basins, where spatial variation of riverine inorganic carbon was controlled by influxes of different tributaries (AUCOUR et al., 1999; TELMER and VEIZER, 1999; BARTH et al., 2003). In addition, inflows of other water masses such as groundwater, anthropogenic effluent, reservoir or lake also resulted in spatial variation (HÉLIE et al., 2002; BARTH et al., 2003).

#### 4 PROBLEM FOR FURTHER STUDY

##### 4.1 Flux Estimation of Global Riverine Inorganic Carbon

Previous flux estimations of global riverine inorganic carbon were nearly all obtained using extrapolating method based on surveys during one specific hydrological year in world major rivers, moreover, different surveys were almost conducted in different years (MEY-BECK, 1982; DEGENS et al., 1991), thus weakening the accuracy of the estimations because of data absence from amount of small rivers, and of the extreme climatic and hydrological events occurring in the surveying years which can not represent the general condition of rivers. For dynamic open systems like rivers, at least ten years continuous survey on most of global rivers needs to be conducted to get a better result.

##### 4.2 Different Sources of Riverine DIC

Many studies have attempted to distinguish various sources of riverine inorganic carbon through measuring its  $^{13}\text{C}_{\text{DIC}}$  values. Yet, despite the fact that carbon isotopic signatures of major inorganic carbon sources are distinctive, the variations of carbon isotopic composition of riverine DIC remain quite difficult to be interpreted, because additional processes, such as biogenic activities occurring within the river system and isotopic equilibration with atmospheric  $\text{CO}_2$  further make it more complex.

##### 4.3 Riverine Carbon Sinks and Sources

The global flux of  $\text{CO}_2$  evasion from rivers approximated  $10^{13}$ - $10^{14}\text{g/a}$  (DEGENS et al., 1991; TELMER and VEIZER, 1999; COLE and CARACO, 2001; RICHEY et al., 2002). RICHEY et al. (2002) computed that the flux of  $\text{CO}_2$  evasion from the Amazon alone was about  $0.5\text{GtC/a}$ , which was an order of magnitude greater than the riverine export of organic carbon and DIC from the Amazon to the ocean. Such a large source would demand additional sinks, bringing us challenges to reconsider the global carbon budget and to find new sinks to compensate the identified but obviously insufficient sinks. On the other hand, influx of atmospheric or soil  $\text{CO}_2$  to global rivers via mineral weathering estimated about  $10^{14}\text{g/a}$ , making global rivers system itself a sink of atmospheric  $\text{CO}_2$ . Therefore, to determine further the role of global rivers system as a sink or a source of atmospheric  $\text{CO}_2$  is necessary in later studies.

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