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Sources of CO_2 evasion from two subtropical rivers in North America

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Abstract We directly measured the partial pressure of dissolved CO_2 (pCO_2) in two humid subtropical rivers in coastal Texas, one highly urbanized (Buffalo Bayou) and one relatively undeveloped (Spring Creek), and analyzed carbon isotopic signatures ($\Delta^{14}C$ and $\delta^{13}C$) of riverine dissolved inorganic carbon (DIC) to determine carbon sources sustaining river respiration. Both rivers were highly supersaturated with CO_2 at all study sites and on all dates sampled from June 2007 to February 2009. Mean riverine pCO_2 values are 3,052 ± 1,364 and 4,702 ± 1,980 μatm for Buffalo Bayou and Spring Creek, respectively. Calculated CO_2 emission fluxes per ha of water surface area from these rivers are intermediate between those in tropical and temperate rivers, indicating that globally, humid subtropical rivers may be a significant source of atmospheric CO_2. Carbon isotopic signatures revealed that CO_2 supersaturation is supported by different carbon sources for the two rivers. In the relatively undeveloped river (Spring Creek), young terrestrial organic matter (OM) is the predominant C source fueling river heterotrophic respiration. In the highly urbanized river (Buffalo Bayou), the high concentration of riverine CO_2 is additionally supported by dissolution of $CaCO_3$ likely from pedogenic carbonate, and crushed limestone/dolomite and oyster shells imbedded in old roads in the watershed. Because urban sources of acidity can include HNO_3 and H_2SO_4, whether the limestone/dolomite and shells used by humans act as a net sink or source of atmospheric CO_2 needs further study.

Keywords Carbonate · Carbon isotopes · Dissolved inorganic carbon (DIC) · Gulf coast · pCO_2 · River respiration

Introduction

Annually, a large amount of terrestrial carbon, including soil organic carbon, roots, and aboveground biomass, is transferred from land into river systems. A precise determination of the amount, source and fate of this carbon is critical for regional and global carbon budgets of terrestrial ecosystems (Houghton 2003; Richey et al. 2002).

Terrestrial carbon is exported to river systems through three pathways: (1) as litterfall in the form of particulate organic carbon (POC) carried to rivers by wind and storm water; (2) as soil dissolved organic carbon (DOC) and soil POC exported to rivers; and (3) as soil CO_2 from ecosystem respiration in the form of dissolved inorganic carbon (DIC) delivered to rivers by subsurface water flow. Determination of

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C losses through measurement of individual fluxes of each pathway is difficult because terrestrial carbon is not a point source, but an area source for river systems. A more practical approach is to track the fate of these C sources in river systems. After terrestrial carbon enters rivers, part of it (derived from soil CO_2 and from respiration of terrestrial organic carbon in the water column) is returned to the atmosphere as CO_2 during transit, part of it (some POC) is stored in floodplains and riparian corridors, and the rest is discharged to the oceans as DOC, POC and DIC. Mass balance calculations allow estimation of the rate of carbon losses from terra firma terrestrial environments to rivers by summing up these three fractions of terrestrial carbon (Cole et al. 2007).

CO_2 supersaturation is common in world river systems (Cai and Wang 1998; Cole and Caraco 2001; Mayorga et al. 2005; Raymond et al. 1997, 2000; Richey et al. 2002; Yao et al. 2007). The CO_2 outgassing rate from global rivers has been estimated to be on the order of 1 Gt C year^{-1}, comparable to annual river total carbon (organic and inorganic) export to the ocean (Cole and Caraco 2001; Cole et al. 2007; Rasera et al. 2008; Richey et al. 2002). However, there is significant uncertainty in the size of this flux. Conservative estimates from 45 major world rivers suggest that global rivers outgas 0.3 Gt C to the atmosphere annually (Cole and Caraco 2001), while a study in the Amazon suggested that CO_2 evasion flux from the global area covered by humid tropical forests alone is 0.9 Gt C year^{-1} (Richey et al. 2002).

There are three major reasons for the discrepancy in global river CO_2 flux estimates, all based on data sparsity. First, most (35 out of 45) of the large rivers compiled in Cole and Caraco (2001) are temperate rivers. To better estimate CO_2 evasion flux from global rivers, a more comprehensive survey of rivers in all climate regimes is necessary. To date, studies on CO_2 concentration of subtropical rivers are still very limited. Second, although small rivers are individually trivial CO_2 sources, they are likely to be more supersaturated in CO_2 than large rivers (Finlay 2003), and summed, their bulk CO_2 evasion flux may be significant (Rasera et al. 2008). Third, direct measurements of partial pressure of CO_2 (pCO_2) are very limited. In many previous studies, riverine pCO_2 was calculated from measured pH, alkalinity and temperature, which either overestimated or underestimated the true value of pCO_2 in different case studies (Herczeg et al. 1985; Raymond et al. 1997; Stauffer 1990).

Riverine CO_2 is primarily sustained by CO_2 export from soil by groundwater and in situ respiration of terrestrial organic matter (OM) (Cole and Caraco 2001; Finlay 2003; Mayorga et al. 2005). Richey et al. (2002) estimated that degradation of terrestrial OM (in soil or in the water column) contributes about 75% of the CO_2 evasion in the Amazon River basin. However, large spatial variability exists in the sources and turnover times of this terrestrial organic carbon. In the Hudson River in the northeastern US, respiration of ancient organic carbon (1,000–5,000 years old) in the watershed may be an important source of excess riverine CO_2 (Cole and Caraco 2001), while in Amazonian rivers, less than 5-year-old carbon fixed on land is the dominant labile OM fueling the river respiration (Mayorga et al. 2005). Also, not all riverine CO_2 is derived from decomposition of OM. Addition of bicarbonate (HCO_3^-) from carbonate dissolution is another possible source of riverine CO_2 as dissolved CO_2 is in chemical equilibrium with bicarbonate in the water.

The natural isotopic compositions ($\Delta^{14}C$ and $\delta^{13}C$) of riverine carbon species, including DOC, POC and DIC, are a powerful tool to identify sources and turnover times of riverine C (Mayorga et al. 2005; Raymond and Bauer 2001c; Raymond et al. 2004). Yet, coupled use of dual carbon isotopic signatures is rare, existing only for Amazonian rivers and some temperate rivers in northeast US (Mayorga et al. 2005; Raymond et al. 2004).

In this study, we directly measured pCO_2 and accompanying carbon isotopes (^{13}C and ^{14}C) to better understand the carbon cycling of small subtropical rivers.

Study area and methods

Study area

We conducted this study from June 2007 to February 2009 in Buffalo Bayou and Spring Creek in southeast Texas. Both rivers flow from west to east and drain into the Gulf of Mexico through Galveston Bay (Fig. 1).

Buffalo Bayou passes through downtown Houston in Harris County, TX. Its watershed, of which 80% is

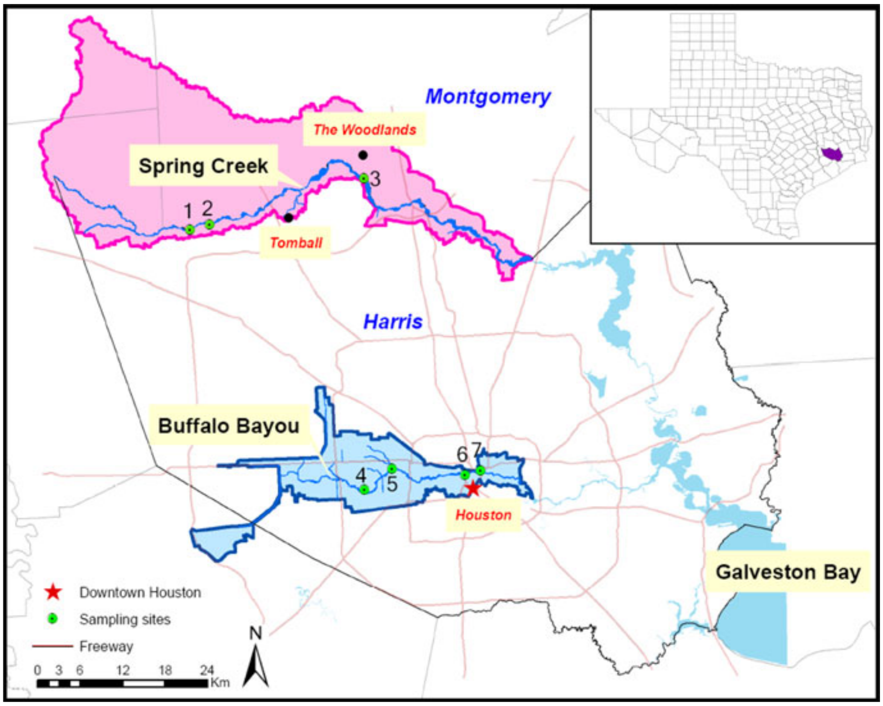


Fig. 1 Buffalo Bayou watershed and Spring Creek watershed. Both Buffalo Bayou and Spring Creek flow from west to east. The three sampling sites in Spring Creek are Roberts Cemetery (RC, 1), Mueschke (2), and Gosling (3), and the four sampling sites in Buffalo Bayou are South Piney Point (SPP, 4), Father Point (FP, 5), Sabine (6), and McKee (7). The *inset* shows the location of Harris County in Texas

urbanized, is almost entirely within the City of Houston. Spring Creek flows along the boundary of Texas' Harris and Montgomery Counties. Its watershed is mostly covered by forests, with some agricultural use upstream. The exceptions are the City of the Woodlands (61.8 km^2) and the City of Tomball (26.3 km^2), both of which are undergoing development.

The majority of the Buffalo Bayou watershed is underlain by the Beaumont Formation, with a minor contribution from the Lissie Formation in the north (Table 1, Fisher 1982). The watershed of Spring Creek is underlain mostly by the Willis Formation, and partially by the Lissie Formation and the Beaumont Formation (Table 1, Shelby et al. 1992). The Willis Formation covers the upper and middle reach of the Spring Creek, while the Lissie and Beaumont Formations cover the lower reach. All three formations were deposited during the Pleistocene (1.8 Ma–11,550 years BP) and are made of clay, silt and sand (Fisher 1982; Shelby et al. 1992).

Carbonate is commonly present in soils in the drainage basin of Buffalo Bayou, but only sparsely found in soils in the Spring Creek watershed (USDA 2009). Possible sources of carbonate are naturally occurring pedogenic carbonate (carbonate formed during soil development) in the Beaumont Formation (Nordt et al. 2006), and crushed limestone/dolomite and oyster shells. Crushed limestone/dolomite has been found in Gulf coast roads (Titi et al. 2003), and shell roads are distributed in a belt extending 80–110 km inland from the coastline of Texas (Doran 1965), just far enough to cover the Buffalo Bayou watershed, but only reaching the Spring Creek watershed near the Gosling site (see Fig. 1).

The two rivers are about 32 km apart and share a similar climate. The regional mean annual temperature is about 21°C, and the mean annual precipitation is 100–180 cm, with Spring Creek (122 cm at Tomball) having only a slightly lower annual average precipitation than Buffalo Bayou (Houston: 135 cm) (NOAA 2009).

We selected seven sampling sites in the study area, four in Buffalo Bayou [South Piney Point (SPP), Father Point (FP), Sabine and McKee] and three in Spring Creek [Roberts Cemetery (RC), Mueschke and Gosling] (Fig. 1). All sampling sites are bridges over the rivers. SPP and FP are located in residential areas; Sabine and McKee are in downtown Houston; while the three sites in Spring Creek are located next to private forests. SPP in Buffalo Bayou is additionally a US Geological Survey (USGS) monitoring

Table 1 Hydrological and lithologic characteristics of Buffalo Bayou and Spring Creek watersheds

River	Length of main stem (km)	Length of open streams[a] (km)	Watershed area (km^2)	Discharge[b] (m^3/year)	Lithology of watershed[c]
Buffalo Bayou	51	186	265	3.27×10^8	Beaumont Formation (80%): clay, silt and sand, concretions of calcium carbonate Lissie Formation (20%): clay, silt and sand, locally calcareous, concretions of calcium carbonate
Spring Creek	130	178	727	1.02×10^8	Willis Formation (87%): clay, silt and sand, noncalcareous Lissie Formation (10%) and Beaumont Formation (3%) with same lithology as above

[a] Includes main stem and tributaries; data for length and watershed area are from Harris County Flood Control District: www.hcfcd.org

[b] Discharge data for the South Piney Point station (08073700) in Buffalo Bayou and for the station near Tomball (08068275) in Spring Creek are for hydrological year 2008; data from USGS: www.usgs.gov

[c] Information from Fisher (1982) and Shelby et al. (1992). Numbers in parenthesis are percentages of the watershed

station (08073700), which allowed us to obtain river discharge data for this site.

Sample collection and analysis

We sampled pCO$_2$ monthly. To characterize daytime variation in riverine pCO$_2$, we conducted hourly pCO$_2$ sampling at the Sabine site in Buffalo Bayou on April 5, 2008 and the Mueschke site in Spring Creek on March 27, 2008 from before sunrise to after sunset (14 h). We also collected hourly pCO$_2$ samples at these two sites on two rainy days (on June 26, 2008 at Sabine, and on June 21, 2008 at Mueschke) to determine how riverine pCO$_2$ responds to rainfall events.

For each site we collected three ambient air pCO$_2$ and three water pCO$_2$ samples. We took ambient air pCO$_2$ samples on bridges (2–15 m above the river surface). Since in previous studies ambient air samples were collected closer to the river surface (Raymond et al. 1997; Yao et al. 2007), we also took air pCO$_2$ samples <2 m above the river surface where the river bank was accessible. We found no significant difference in CO$_2$ concentration between air over bridges and air near river surfaces (*t* test, $p = 0.76$ at 95% confidence level). We took water directly from the upper 30 cm of the river using a submersible pump and collected water pCO$_2$ samples by headspace equilibration as described in Raymond et al. (1997). All pCO$_2$ samples were transported to the laboratory and analyzed on an infrared CO$_2$ analyzer (Li-Cor 7000) in the same day of collection.

We collected DIC samples using 250 ml pre-cleaned (soapy water, deionized water and Milli-Q water) and pre-combusted (500°C for 2 h) bottles. We collected DIC samples prior to collection of water pCO$_2$ samples to avoid any contamination. To minimize CO$_2$ exchange between the sample and the air, we overflowed the bottle three times. DIC samples were stored at 0°C from time of collection to poisoning with saturated HgCl$_2$ solution and sealing with Apiezon-N grease in the lab. Samples were always poisoned within 8 h of collection.

All DIC samples were sent to the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) for Δ^{14}C and δ^{13}C analyses, where samples were processed according to McNichol et al. (1994). δ^{13}C values were reported, while ^{14}C/^{12}C ratios were expressed as Fraction Modern (FM). We calculated Δ^{14}C values from FM values according to Stuiver and Polach (1977).

Results and discussion

Daytime riverine pCO$_2$ variation

A previous study (Raymond et al. 1997) indicated low diurnal pCO$_2$ variability in river waters. Our data are consistent with this study (except on days of rainfall events, see below). We saw little change in riverine pCO$_2$ values at Sabine (April 5, 2008) in Buffalo Bayou and Mueschke (March 27, 2008) in

Spring Creek from predawn (7 a.m.; sunrise 7:30 a.m.) through after sunset (8 p.m.; sunset 7:30 p.m.) (Fig. 2). Mean riverine pCO_2 was 3,839 ± 291 µatm at Sabine, and was 4,146 ± 126 µatm at Mueschke. Daytime variations were much smaller than seasonal variations for both sites (3,157 ± 1,454 µatm for Sabine and 3,660 ± 706 µatm for Mueschke) (Table 2). We interpreted the low daytime pCO_2 variability to indicate that pCO_2 samples collected at a specific time of day are generally representative of the average riverine pCO_2 of the day sampled.

Effect of rainfall events on riverine pCO_2

Rainfall events control riverine pCO_2 primarily via two concurrent and competitive mechanisms: (1) rainfall events enhance the export of soil CO_2 and soil organic carbon to rivers, which increases riverine pCO_2 (Yao et al. 2007); and (2) rainfall events generally increase river discharge and gas transfer velocity (Ho et al. 1997), both of which lower riverine pCO_2. We saw evidence of both mechanisms, with the dominant mechanism depending on rainfall intensity and watershed impermeability.

On rainy days, daytime variations in riverine pCO_2 were larger, with mean riverine pCO_2 of 2,964 ± 1,020 µatm for Sabine (June 26, 2008) and 3,205 ± 357 µatm for Mueschke (June 21, 2008) (Fig. 3). Enhanced river photosynthesis/respiration processes due to abundant phytoplankton and high water temperatures in summer (Cole et al. 1992) alone can not explain why the pCO_2 fluctuation was higher at Sabine than at Mueschke.

The pronounced changes in riverine pCO_2 at Sabine on June 26, 2008 were likely caused by the intensive rainfall event, which produced about 15 mm (the Spatial Sciences Laboratory at Texas A&M University) of water within 6 h in the Buffalo Bayou watershed (Fig. 3a) and significantly raised the water level (river discharge was 1.7 m^3/s in the morning and 23.9 m^3/s in the late afternoon) (Data from USGS). Similar to others' results (Paquay et al. 2007), we found a negative relationship between riverine pCO_2 and precipitation at Sabine, but with a time lag of about 3 h (Fig. 3a). We hypothesize that the 3-h lag was caused by an initial flushing of soil CO_2 by subsurface flow of storm water, which compensated for the dilution effect of nearly CO_2-free storm water which flowed over urban impervious surfaces (e.g. concrete). As the rain continued, soil CO_2 was flushed out, and hence the storm water dilution effect dominated.

Although there was also a rainfall event at Mueschke on June 21, 2008, we observed a different pattern in riverine pCO_2 (Fig. 3b), probably due to much lower precipitation (about 1.72 mm in total, lasted for only 2 h: 5–6 p.m., the Spatial Sciences Laboratory at Texas A&M University) and higher soil permeability in the Spring Creek watershed. There was a continuous decrease in riverine pCO_2 from 11 a.m. to 4 p.m. (Fig. 3b). A dilution effect of storm water from upstream can be ruled out because upstream Mueschke rainfall also started at 5 p.m.,

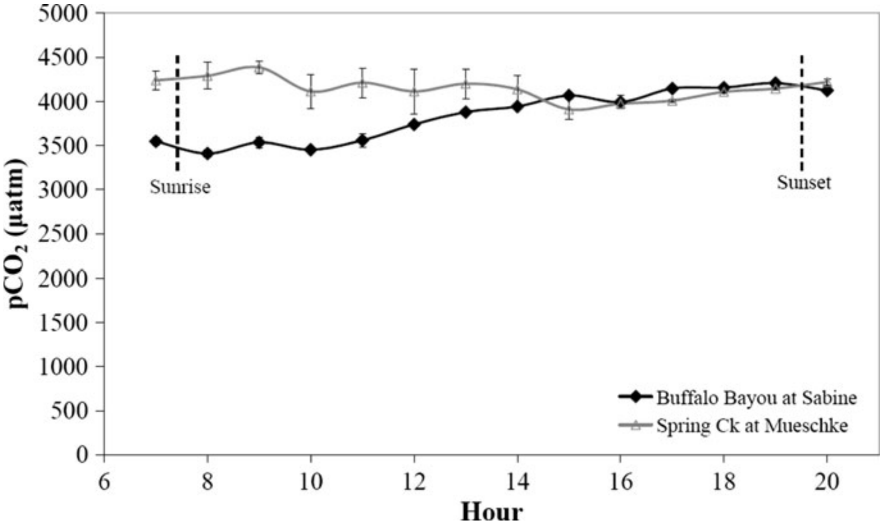


Fig. 2 Daytime variation in riverine pCO_2 in Buffalo Bayou (Sabine) and Spring Creek (Mueschke) in late March and early April (Sabine 4-5-2008; Mueschke 3-27-2008; Sunrise 7:30 a.m.; Sunset: 7:30 p.m.). *Error bar* is 1σ on the replicates

Table 2 Measured mean pCO_2 and calculated mean CO_2 emission flux for each study site in Buffalo Bayou and Spring Creek

Site	Study period (number of samples)	Width (m)	Depth (m)	$pCO_{2,w}$ (μatm)	$pCO_{2,a}$ (μatm)	CO_2 emission flux (Mg C ha^{-1} $year^{-1}$)
Buffalo Bayou						
SPP	08/07–02/09 (19)	10 ± 2	1.0–2.0	3,158 ± 1,044	414 ± 69	3.37 ± 1.26
FP	06/07–02/09 (20)	10 ± 2	0.5–1.5	3,087 ± 1,610	415 ± 80	3.29 ± 1.94
Sabine	06/07–02/09 (20)	20 ± 4	0.8–2.5	3,157 ± 1,454	408 ± 79	3.38 ± 1.77
McKee	06/07–02/09 (20)	25 ± 5	1.5–3.0	2,813 ± 1,347	405 ± 78	2.97 ± 1.63
Average				3,052 ± 1,364	411 ± 75	3.25 ± 1.65
Spring Creek						
RC	09/07–02/09 (19)	1.5 ± 0.3	0.2–0.6	6,277 ± 2,357	408 ± 64	7.24 ± 2.85
Mueschke	09/07–02/09 (19)	3 ± 0.6	0.8–1.2	3,660 ± 706	403 ± 69	4.02 ± 0.82
Gosling	10/07–02/09 (16)	10 ± 2	0.5–1.5	4,070 ± 1,285	389 ± 57	4.56 ± 1.57
Average				4,702 ± 1,980	401 ± 63	5.31 ± 2.40

Width is the average width of the river at the site sampled with 20% uncertainty

Depth is the range of water depth at the site sampled

$pCO_{2,w}$ riverine pCO_2, $pCO_{2,a}$ pCO_2 of air on bridges

CO_2 emission flux is for per area of water surfaces, not for per area of the basins

SPP South Piney Point, *FP* Father Point, *RC* Roberts Cemetery

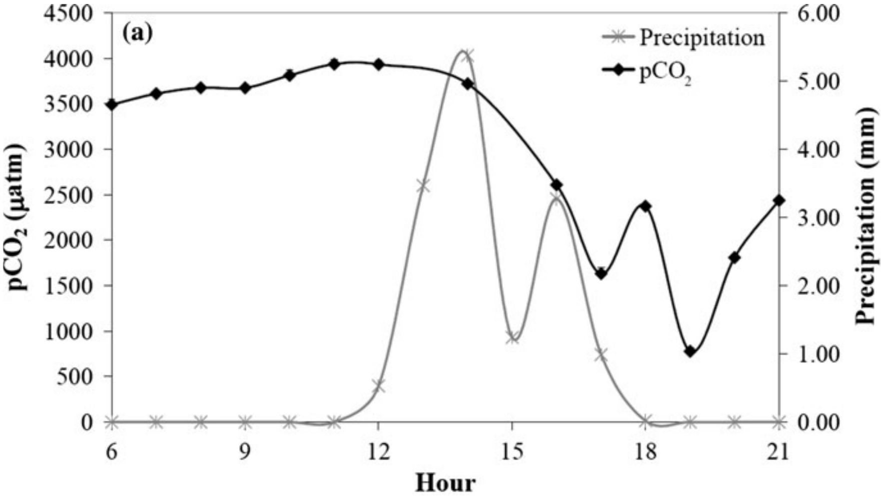
after the pCO_2 drop (the Spatial Sciences Laboratory at Texas A&M University). Instead, biological uptake of CO_2 through photosynthesis has likely caused the drop in riverine pCO_2. A rise in riverine pCO_2 occurred from the onset of the rainfall event (Fig. 3b). This was likely caused by the export of soil CO_2 by rain water. Weaker CO_2 uptake through photosynthesis due to lower sun angle might be an additional reason, but it alone could not explain the rapid pCO_2 increase from 5:30 p.m. to 6:30 p.m., as indicated by the small daytime variation in riverine pCO_2 observed in late March (Fig. 2).

Seasonal variation in riverine pCO_2

During the study period, riverine pCO_2 was 2–20 times supersaturated in CO_2 with respect to the atmosphere throughout the year in both rivers (Fig. 4). Riverine pCO_2 averaged 3,052 ± 1,364 μatm for Buffalo Bayou and 4,702 ± 1,980 μatm for Spring Creek (Table 2). The generally lower riverine pCO_2 values in Buffalo Bayou relative to Spring Creek were likely because of (1) the smaller watershed and larger river discharge (Table 1); (2) the buffering effect of carbonate; and (3) less biomass in the urban environment, reducing primary production and respiration associated carbon fluxes in the Buffalo Bayou watershed.

The seasonal patterns in riverine pCO_2 were highly consistent across sites within rivers (Fig. 4). This was also observed in Xijiang River in south China by Yao et al. (2007). Consistent with previous studies (Raymond et al. 1997, 2000; Richey et al. 2002; Yao et al. 2007), riverine pCO_2 was generally higher in summer and fall than in winter and spring. Temporal variation in riverine pCO_2 was also much higher in summer and fall than in winter and spring, probably due to more precipitation in summer and fall (Table 3, the Spatial Sciences Laboratory at Texas A&M University).

There are two major pCO_2 peaks in our record, one in early August 2007 and a second in late September 2008. The peak in early August 2007 (Fig. 4) may be associated with the abundant (253 mm in a month) and evenly distributed precipitation in July 2007 (NOAA 2009), which allowed the rain water to infiltrate and flush out soil CO_2 to the river while limiting the dilution effect of rainfall. On September 13–14, 2008, Hurricane Ike, the 3rd most destructive hurricane to ever make landfall in the United States, hit Houston and brought 98 mm of rain (the Spatial Sciences Laboratory at Texas A&M University). The storm water flushed out a large amount of waste water into Buffalo Bayou, making river water dark and fetid. Decomposition of OM from waste water



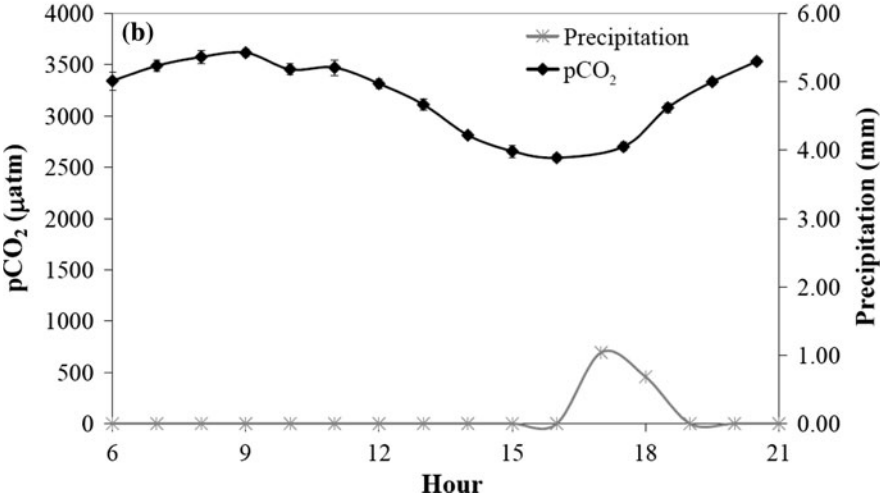


Fig. 3 Effect of rainfall events on riverine pCO$_2$ at **a** Sabine in Buffalo Bayou and at **b** Mueschke in Spring Creek (Sabine 6-26-2008; Mueschke 6-21-2008; Sunrise 6:30 a.m.; Sunset: 8:30 p.m.). Hourly precipitation data were obtained from the Spatial Sciences Laboratory at Texas A&M University. *Error bar* is 1σ on the replicates

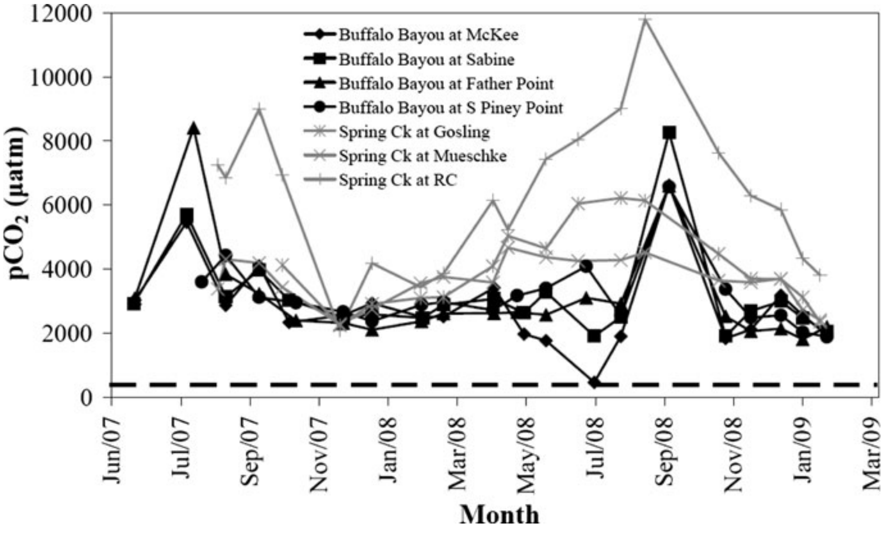


Fig. 4 Seasonal variation in riverine pCO$_2$ in Buffalo Bayou and Spring Creek from June 2007 to February 2009. Direct measurement of riverine pCO$_2$ was made monthly at each study site. Dash line is the measured mean pCO$_2$ value of the atmosphere (about 410 μatm) at our study sites from June 2007 to February 2009

Table 3 Precipitation data (in mm) for the study period for the Buffalo Bayou and Spring Creek watersheds

Watershed	Summer 07	Fall 07	Winter 07	Spring 08	Summer 08	Fall 08	Winter 08
Buffalo Bayou	311	220	193	121	278	214	74
Spring Creek	200	157	178	161	200	230	55

Spring March–May, *Summer* June–August, *Fall* September–November, *Winter* December–February

Data obtained from the Spatial Sciences Laboratory at Texas A&M University

likely led to the pCO$_2$ peak on September 27, 2008. The lowest riverine pCO$_2$ value, 476 μatm, was observed at the McKee site in Buffalo Bayou on July 24, 2008 due to Hurricane Dolly, which produced 63 mm of rain in 2 days (July 23–24, 2008) (the Spatial Sciences Laboratory at Texas A&M University).

Riverine pCO$_2$ at Roberts Cemetery in Spring Creek was highly variable. This is likely because river discharge at this site is so low (i.e. shallow water and narrow channel, Table 2) that slight changes in river discharge caused large changes in river CO$_2$ concentration. The much higher riverine pCO$_2$ values at Roberts Cemetery also likely resulted from the shallow water and narrow channel at this site because: (1) narrow aquatic systems are likely to receive a heavier loading of terrestrial OM per unit discharge from litterfall due to more canopy cover for small streams (Finlay 2003); (2) sediment processing of OM is strong in shallow aquatic systems (Torgersen and Branco 2008).

CO$_2$ emission rates of Buffalo Bayou and Spring Creek

Riverine CO$_2$ evasion rates depend on the CO$_2$ concentration gradient between the surface water and the overlying air, and the gas exchange coefficient (also known as gas transfer velocity) (Raymond et al. 1997; Wanninkhof 1992):

$$\text{Flux} = k_{\text{CO}_2} \times (\text{pCO}_{2,w} \times K_\text{h} - \text{pCO}_{2,a} \times K_h) \qquad (1)$$

where K_h is Henry's law constant at a given temperature and salinity; pCO$_{2,w}$ × K_h and pCO$_{2,a}$ × K_h are the actual concentration of CO$_2$ in the surface water and the concentration of CO$_2$ the water would have if it were in equilibrium with the overlying air, respectively; and k_{CO_2} is the gas exchange coefficient for CO$_2$ at a given temperature for a given type of river. All the CO$_2$ evasion rates presented in this study are reported per area of water surface, not per area of the basins.

We used two methods to estimate k_{CO_2} for our systems. First, we derived k_{CO_2} from empirical models (Melching and Flores 1999). Second, we estimated k_{CO_2} from the wind speed relationship (Raymond and Cole 2001).

In the first method we calculated the reaeration-rate coefficient (K_2) from the hydraulic characteristics of our river systems using the empirical models in Melching and Flores (1999), and then converted the reaeration-rate coefficient to the gas exchange coefficient for O$_2$ (k_{O_2}, Hemond and Fechner-Levy 2000), from which we derived k_{CO_2} (Wanninkhof 1992). However, k_{CO_2} values calculated in this way are in a range of 13–26 cm h^{-1}, much higher than those applied to other river systems (Cai and Wang 1998; Raymond et al. 1997, 2000; Richey et al. 2002; Yao et al. 2007).

To be conservative, we chose to use the k_{CO_2} estimated from the second method, in which k_{CO_2} values were calculated from k_{600} values using the following power function (Jahne et al. 1987):

$$k_{600}/k_{\text{CO}_2} = (600/Sc_{\text{CO}_2})^n \qquad (2)$$

k_{600} is the gas exchange coefficient for CO$_2$ at 20°C in freshwater (CO$_2$ has a Schmidt number of 600 in this condition). k_{600} and n estimated for estuaries in 39 coastal cities in the United States with a mean daily wind speed of 4.6 ± 0.28 m s^{-1} (ranging from 3 to 7.7 m s^{-1}) are 3–7 cm h^{-1} and −0.5, respectively (Raymond and Cole 2001). The average wind speed in Houston for the study period, obtained from the same wind speed data resource (NOAA 2009) as in Raymond and Cole (2001), was 3.4 m s^{-1} (ranging from 0.5 to 9.7 m s^{-1}), so conservatively we applied a k_{600} value of 3 cm h^{-1} and the same n value (−0.5) in the calculation. The Schmidt number for freshwater CO_2 (Sc_{CO_2}) is a function of temperature (t) in °C (Wanninkhof 1992):

$$Sc_{CO_2} = 1911.1 - 118.11 \times t + 3.4527 \times t^2 - 0.04132 \times t^3 \quad (3)$$

Our most conservative calculations (based on k_{CO_2} values estimated from the wind speed relationship) show that average CO_2 emission rates are consistent across sites within rivers, again with the exception of Roberts Cemetery, which has a much higher CO_2 outgassing rate than the other two sites in Spring Creek (Table 2). Due to its generally higher riverine pCO_2 values, Spring Creek released CO_2 to the atmosphere at a rate of 5.31 ± 2.4 Mg C ha^{-1} $year^{-1}$, about 1.5 times that in Buffalo Bayou, 3.25 ± 1.65 Mg C ha^{-1} $year^{-1}$.

Compared to other rivers in which pCO_2 values or CO_2 evasion fluxes were directly measured, the CO_2 emission rates of Buffalo Bayou and Spring Creek are intermediate between those of temperate rivers in northeast US and those of Amazonian rivers (Table 4). However, it should be emphasized that the k_{CO_2} values we used to estimate CO_2 emission rates are very conservative. If the k_{CO_2} values derived from empirical models and hydraulic characteristics were used, our river systems would have CO_2 emission rates (24.98 ± 10.76 Mg C ha^{-1} $year^{-1}$ for Buffalo Bayou and 22.85 ± 8.85 Mg C ha^{-1} $year^{-1}$ for Spring Creek) higher than those in Amazonian rivers (Table 4), as in the case of two other subtropical rivers (Cai and Wang 1998; Yao et al. 2007). Even with the most conservative estimates of k_{CO_2}, results of this study suggest that humid subtropical rivers are releasing CO_2 to the atmosphere at a rate comparable to large humid tropical rivers, and globally they may be a large source of atmospheric CO_2.

Potential sources of riverine CO_2 and their carbon isotopic signatures

Potential sources of riverine DIC include atmospheric CO_2, soil CO_2 and in situ respiration of terrestrial OM, and dissolution of carbonate. Each of these sources has distinct $\Delta^{14}C$ and $\delta^{13}C$ signatures, allowing individual sources to be visualized separately on a plot of $\delta^{13}C$ vs. $\Delta^{14}C$ (Fig. 5). In the next few paragraphs, we will discuss the range of possible $\Delta^{14}C$ and $\delta^{13}C$ signatures of DIC from each potential source.

As river water is in contact with the atmosphere, atmospheric CO_2 exchanges with CO_2 in river water and thus may potentially make up a fraction of riverine DIC. CO_2 in surface air across North America had $\Delta^{14}C$ values of 55–66‰ in 2004 (Hsueh et al. 2007). If we assume that $\Delta^{14}C$ of atmospheric

Table 4 Riverine pCO_2 values and CO_2 emission fluxes for some world rivers

River	Mean pCO_2 (μatm)	k (cm h^{-1})	CO_2 emission flux (Mg C ha^{-1} $year^{-1}$)	References
Tropical				
Amazon	4,350 ± 1,900 (mainstem)	9.58 ± 3.75 (mainstem)	8.3 ± 2.4	Richey et al. (2002)
	5,000 ± 3,300 (major tributaries)	5 ± 2.08 (major tributaries)		
Ji-Parana	–	–	2.27–47.80	Rasera et al. (2008)
Subtropical				
Xijiang River	2,600	8–15	8.3–15.6	Yao et al. (2007)
Satilla River Estuary	–	12.5	18 to >30.6	Cai and Wang (1998)
Buffalo Bayou	3,014 ± 603	2.59–4.18	3.25 ± 1.65	This study
Spring Creek	4,214 ± 843	2.31–3.78	5.31 ± 2.40	This study
Temperate				
Hudson	1,125 ± 403	1.54–4.1	0.7–1.62	Raymond et al. (1997)
York River Estuary	1,070 ± 867	4.7	0.53–0.75	Raymond et al. (2000)

All the riverine pCO_2 values were directly measured except for the Xijiang River. CO_2 emission fluxes were computed from directly measured riverine pCO_2, or were directly measured where riverine pCO_2 values were not available

CO_2 emission flux is for per area of water surfaces, not for per area of the basins

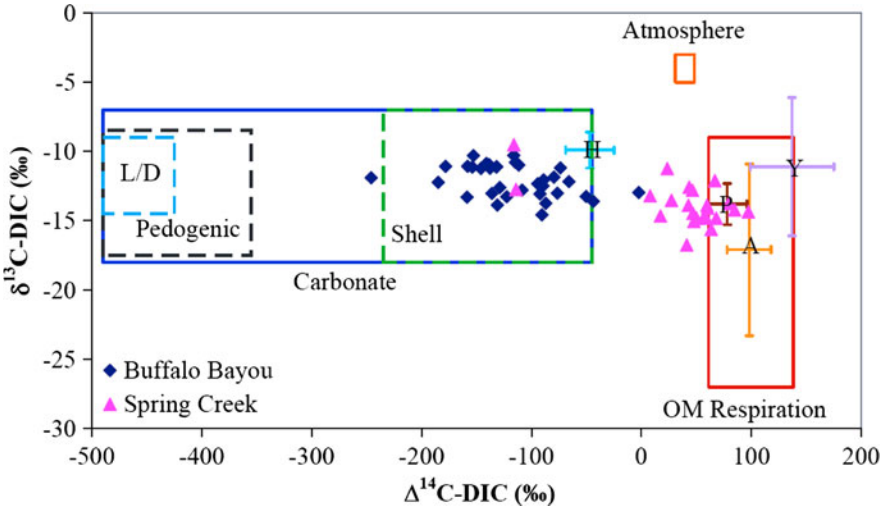


Fig. 5 δ^{13}C versus Δ^{14}C of riverine DIC in Buffalo Bayou (*diamonds*) and Spring Creek (*triangles*) in comparison with those in Amazonian rivers (A, carbonate free), the Hudson River (H), the Parker River (P), and the York River (Y) (Mayorga et al. 2005; Raymond and Bauer 2001a; Raymond et al. 2004). Also plotted are δ^{13}C versus Δ^{14}C of DIC from potential sources (in *solid boxes*): atmospheric CO_2 (*Atmosphere*), OM respiration, and carbonate dissolution (*Carbonate*). There are three sources of carbonate in the study watersheds (in *dashed boxes*): natural pedogenic carbonate (*Pedogenic*), and anthropogenic use of crushed limestone/dolomite (*L/D*) and shells (*Shell*)

CO_2 has been dropping at a rate of about 6‰ per year (Trumbore et al. 2006), Δ^{14}C of atmospheric CO_2 in 2007 and 2008 should be in the range of 31–48‰. Since by definition Δ^{14}C is fractionation corrected, atmosphere-derived DIC should have the same Δ^{14}C values as atmospheric CO_2. For the δ^{13}C of DIC from atmospheric CO_2 invasion, we chose the range of −5 to −3‰ from an earlier study (Raymond et al. 2004).

We grouped soil CO_2 and decay of terrestrial OM together as one source, OM respiration (Fig. 5). To estimate the age of subtropical soil-respired terrestrial OM, we assumed it was intermediate between that of temperate and tropical soils. Since the mean age of soil respired C in temperate forests is three times of that in tropical forests (Trumbore 2000), we assumed that turnover time of OM in temperate rivers is 15 years, three times of that in Amazonian rivers (<5 years) (Mayorga et al. 2005), unless there is ancient OM respired in rivers as in the Hudson (Cole and Caraco 2001; Raymond et al. 2004). There is no OM-rich shale in the basins of Buffalo Bayou and Spring Creek. Residence time of OM was, therefore, assumed to be in a range of 5–15 years. Based on the average Δ^{14}C values of 31–48‰ for atmospheric CO_2 in 2007 and 2008 and the annual decreasing rate of about 6‰, DIC from OM respiration has Δ^{14}C values in a range of 61–138‰. The δ^{13}C values of DIC derived from soil CO_2 and in situ OM respiration is determined by the δ^{13}C signatures of the OM remineralized, which fall in the range from −34 to −20‰ for other rivers (Masiello and Druffel 2001; Mayorga et al. 2005; Raymond and Bauer 2001b; Raymond et al. 2004; Trumbore et al. 2006). Since there is a 7–11‰ isotopic fractionation (Mook et al. 1974; Zhang et al. 1995) when CO_2 from soil and in situ OM respiration is dissolved and converted to DIC, riverine DIC from these sources would have δ^{13}C values ranging from −27 to −9‰.

Carbon isotopic signatures of DIC from the three types of carbonate in the Buffalo Bayou watershed (pedogenic carbonate, crushed limestone/dolomite and shells), both individually and as a group, are distinctive from those of DIC from atmospheric CO_2 and OM respiration (Fig. 5). Pedogenic carbonate in Texas has δ^{13}C values of −6 to +1‰, and Δ^{14}C values of −1000 to −860‰ (Nordt et al. 1998; Rightmire 1967; Valastro et al. 1968). Crushed limestone/dolomite is radiocarbon dead ($\Delta^{14}C = -1000$‰) and has δ^{13}C values of ~0‰. The conventional radiocarbon ages of shells in Galveston Bay range from 2,200 to 5,400 years (Kibler 1999), corresponding to Δ^{14}C values of −489 to −240‰, and δ^{13}C values of shells span a range of −7 to +4‰ (Douglas and Staines-Urias 2007; Gentry et al. 2008;

Keller et al. 2002; McConnaughey and Gillikin 2008; Wisshak et al. 2009). When carbonate is dissolved by soil CO_2, DIC produced has $\Delta^{14}C$ and $\delta^{13}C$ signatures intermediate between those of carbonate and soil CO_2. Using a $\Delta^{14}C$ range of +20 to +150‰ (Trumbore 2000; Trumbore et al. 2006) and a $\delta^{13}C$ range of −29 to −18‰ as in Raymond et al. (2004) for soil CO_2, we estimated isotopic signatures of DIC from dissolution of each type of carbonate, as showed in Fig. 5.

Temporal and spatial variation in sources of riverine CO_2

Large variations in river discharge (Fig. 6a) caused the concentration of riverine DIC in Buffalo Bayou to vary significantly throughout the entire study period (Fig. 6b). We found a negative relationship between DIC concentration and river discharge in Buffalo Bayou: DIC concentration was lower when the river had a higher discharge (Fig. 7a). A similar observation was reported for a river in Hawaii by Paquay et al. (2007). However, at times when river discharge was high, DIC mass flow rates (DIC concentration × discharge) were higher (Fig. 7b). This implies that DIC was added to rivers during rainfall events although the overall concentration of riverine DIC was diluted. There was no obvious seasonal variation in DIC concentration in Spring Creek, probably due to relatively constant river discharge on all dates sampled (Fig. 6a). Concentration of DIC was generally higher in Buffalo Bayou (0.78–3.87 mM, averaging 2.35 ± 1.03 mM) than in Spring Creek (0.74–1.89 mM, averaging 1.14 ± 0.30 mM) (Fig. 6b), likely associated with carbonate dissolution in the Buffalo Bayou watershed.

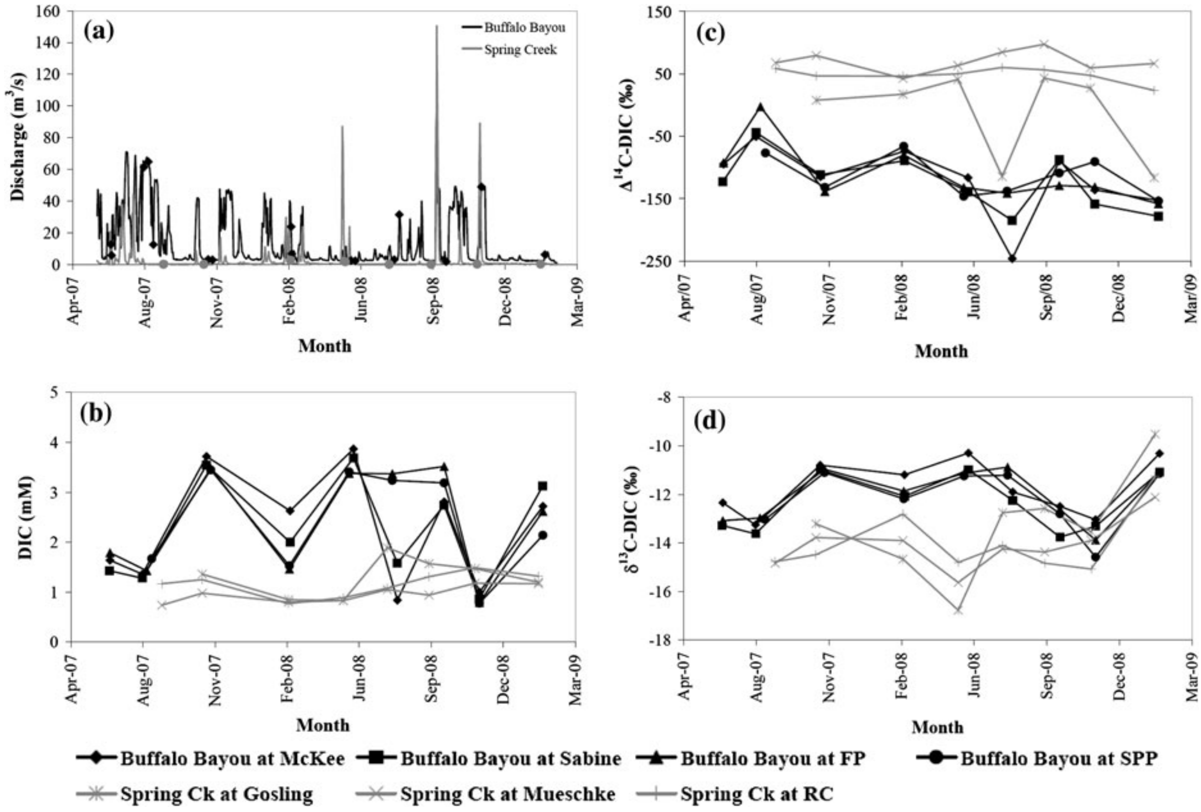


Fig. 6 Seasonal variation in **a** river discharge, **b** concentration of DIC, **c** $\Delta^{14}C$ of DIC, and **d** $\delta^{13}C$ of DIC for Buffalo Bayou and Spring Creek from June 2007 to February 2009. River discharge data were obtained from the USGS for the station at SPP (08073700) in Buffalo Bayou and a station near Tomball (08068275) in Spring Creek. *Diamonds* and *solid circles* are daily discharge for Buffalo Bayou and Spring Creek, respectively, on the days sampled. *Error bars* on mM DIC, $\Delta^{14}C$-DIC and $\delta^{13}C$-DIC are smaller than symbols

Like riverine pCO_2 for both Buffalo Bayou and Spring Creek, $\Delta^{14}C$ and $\delta^{13}C$ values of DIC were generally consistent among sites within the same river (Fig. 6c, d), suggesting that sources of DIC were generally similar for different segments of the same river. There was no clear seasonal pattern in $\Delta^{14}C$-DIC and $\delta^{13}C$-DIC (Fig. 6c, d).

DIC in Buffalo Bayou was more depleted in $\Delta^{14}C$ than in Spring Creek at all times, and was more enriched in $\delta^{13}C$ than in Spring Creek most of the time (Fig. 6c, d). Averaging all sites in each river yields mean $\Delta^{14}C$-DIC values of $-117.3 \pm 45.3‰$ for Buffalo Bayou and $37.3 \pm 52.5‰$ for Spring Creek. Overall average $\delta^{13}C$-DIC for Buffalo Bayou was $-12.1 \pm 1.1‰$ and for Spring Creek was $-13.8 \pm 1.5‰$.

Distinctive isotopic compositions of riverine DIC indicate that Buffalo Bayou and Spring Creek have different primary DIC sources. DIC isotopic signatures for Buffalo Bayou are close to those for the Hudson River (Fig. 5) in which old DIC was sourced from ancient shale OM and carbonate (Raymond et al. 2004). Since there is no shale OM in our study watersheds, the old DIC in Buffalo Bayou was likely from carbonate dissolution. The much older DIC at Sabine and McKee on July 24, 2008 implies higher input of carbonate to Buffalo Bayou due to Hurricane Dolly.

The carbon isotopic signatures of DIC in Spring Creek resemble those observed in Amazonian rivers, the Parker River, and the York River (Fig. 5), in which respiration of young terrestrial OM support river CO_2 supersaturation (Mayorga et al. 2005; Raymond and Bauer 2001a; Raymond et al. 2000). The riparian zone (100–1,000 m from the creek on both sides) along most of the course of Spring Creek is covered by trees. Litterfall production could be very high in such small watersheds (Selva et al. 2007). Direct export of this litterfall, and DOC leached out from this litterfall and eventually delivered to the creek is likely a large source of the relatively young OM sustaining river respiration in Spring Creek. There are two exceptions, both occurred at the Gosling site in Spring Creek, on July 10, 2008 and on February 5, 2009. On these two sampling dates the Gosling site had much older (lower $\Delta^{14}C$) and significantly more ^{13}C-enriched DIC than the other two sites in Spring Creek, indicating a carbonate input. Without these two data points, average $\Delta^{14}C$ value of DIC in Spring Creek is +52‰. This is consistent with carbon fixed in 2005 (Hsueh et al. 2007) or in 1956–1957 (Broecker and Walton 1959; Burchuladze et al. 1989), giving a carbon residence time of four or 53 years.

Potential role of anthropogenic carbonate as a source of atmospheric CO_2

Carbonate dissolution is generally regarded as a sink of atmospheric CO_2, because when carbonate is dissolved by soil CO_2, CO_2 is sequestrated as bicarbonate ($CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$). However, carbonate can also be dissolved by stronger environmental acids, like HNO_3 or H_2SO_4 from urban air pollution or fertilizer use, or by soil organic acids from OM decomposition. In the case of these acids, the reaction is $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$, and this induces a net flux of CO_2 into the atmosphere. The net effect of carbonate dissolution on atmospheric CO_2 concentration, therefore, depends on the sources of acidity driving the dissolution process.

Although results from this study suggest that crushed limestone/dolomite and shells contribute to river CO_2, we can not determine whether this carbonate is a net source or sink of atmospheric CO_2 because the sources of acidity in our watersheds are not well-constrained. Evaluation of the size and direction of anthropogenic carbonate-driven CO_2 fluxes also requires a much finer-scale knowledge of forms of carbonate used, locations of application, amounts applied, and timescales of both human application and dissolution processes.

Despite the difficulties, estimating the role of anthropogenic carbonate as a potential source of atmospheric CO_2 is important for regional and global carbon budgets for two reasons. First, every year crushed limestone/dolomite (shell use is negligible compared to use of crushed limestone/dolomite) is used in large amounts nation-wide. In 2006–2007, about 1.2 Gt of crushed limestone/dolomite was consumed per year in the US (USGS 2007, 2009). Second, strong acids in the environment are capable of dissolving these carbonate minerals and contributing to atmospheric CO_2. One example is the presence of HNO_3 in agricultural soils due to nitrogen fertilizer use, which caused a net 4.4–6.6 Tg CO_2 emission from the use of 20–30 Tg of crushed limestone/dolomite in agricultural land in the US in

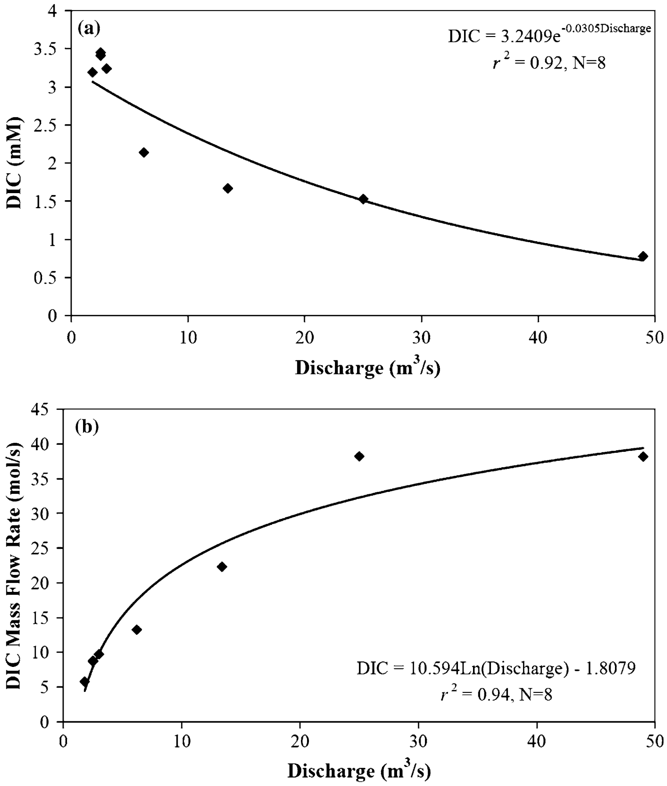


Fig. 7 Relationship between **a** DIC concentration and discharge, **b** DIC mass flow rate (DIC concentration × discharge) and discharge, for the SPP site in Buffalo Bayou. Daily discharge data were from the USGS (2009)

2001 (West and McBride 2005). Acid rain is another common environmental source of acidity (Aulenbach et al. 1996; Bricker and Rice 1993; Gatz 1991). To date, attention has been paid only to the 2% of crushed limestone/dolomite used in agriculture, while the fate of the rest 98% used for other purposes remains unknown (USGS 2007; West and McBride 2005) and needs further study.

Conclusions

pCO_2 measurements indicate that both subtropical rivers we studied are supersaturated with CO_2 relative to the atmosphere throughout the year. Mean riverine pCO_2 values of the two rivers are 7–10 times the CO_2 concentration of the atmosphere, consistent with a recent study conducted in a subtropical river in southern China (Yao et al. 2007). Estimated CO_2 evasion fluxes per unit area of these two rivers are intermediate between those of temperate rivers and Amazonian rivers (Mayorga et al. 2005; Raymond et al. 1997, 2000), implying that humid subtropical rivers may be a large CO_2 source to the atmosphere.

Precipitation is an important control on daytime and seasonal variations in riverine pCO_2 at our sites, probably driving changes in the production and transport of soil CO_2 to rivers. The effect of rainfall events on river CO_2 concentration depends on the intensity of rainfall and watershed impermeability.

Isotopic signatures of riverine DIC suggest that the two subtropical rivers have different carbon sources supporting river CO_2 supersaturation. In Spring Creek, which is relatively undeveloped, river heterotrophic respiration is fueled by relatively young OM (years to decades old), while in Buffalo Bayou, which is 80% urbanized, we observed a significant input of old and relatively ^{13}C-enriched DIC. Potential sources of the old DIC are pedogenic carbonate, and anthropogenically added carbonate (crushed limestone/dolomite and shells) used as aggregate in road construction in the drainage basin. Further study is needed to evaluate the role of the carbonate used by humans in the global carbon cycle.

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