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Controls on the origin and cycling of riverine dissolved inorganic carbon in the Brazos River, Texas

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Abstract Rivers draining watersheds that include carbonate bedrock or organic matter (OM)-rich sedimentary rocks frequently have ^{14}C-depleted dissolved inorganic carbon (DIC) relative to rivers draining carbonate- and OM-free watersheds, due to dissolution of carbonate and/or decomposition of ancient OM. However, our results from a subtropical river, the Brazos River in Texas, USA, show that in this watershed human activities appear to dominate basin lithology in controlling the origin and metabolism of DIC. The middle Brazos flows through limestone and coal-bearing bedrock, but DIC isotope data suggest no limestone dissolution or respiration of ancient OM, and instead reflect efficient air–water CO_2 exchange, degradation of relatively young OM and photosynthesis in the river as a result of river damming and urban treated wastewater input. The lower Brazos drains only small areas of carbonate and coal-bearing bedrock, but DIC isotope data suggest the strong influence of carbonate dissolution, with a potentially minor contribution from decomposition of old soil organic matter (SOM). Oyster shells and crushed carbonate minerals used in road construction are likely sources of carbonate in the lower Brazos, in addition to natural marl and pedogenic carbonate. Additionally, the generally low pCO_2 and high DIC concentration in the Brazos River lead to a low CO_2 outgassing:DIC export ratio, distinguishing the Brazos River from other rivers.

Keywords Carbon cycle · Dissolved inorganic carbon · Lithology · pCO_2 · River system

Introduction

Conservative estimates show that globally, rivers receive at least 1 Gt C year^{-1} (in both organic and inorganic forms) from land (Cole et al. 2007; Meybeck 1993), equivalent to half of the net oceanic uptake of anthropogenic CO_2 (Sarmiento and Sundquist 1992). Of the terrestrial carbon transported by river systems, at least 0.35 Gt year^{-1} is released to the atmosphere as CO_2, and about 0.7 Gt year^{-1} is exported to the ocean (Cole et al. 2007).

One important control on the source and fate of terrestrial carbon in river systems is basin lithology, as reflected in the isotope values of riverine dissolved inorganic carbon (DIC = dissolved $CO_2 + HCO_3^- + CO_3^{2-}$). Black shales rich in organic matter (OM) in the northeast US provide rivers with very old organic carbon, and decomposition of this ancient terrestrial organic carbon may have contributed to the low Δ^{14}C values of the DIC (−69 to −6‰) and to evasion of CO_2

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from the northeast US rivers (Cole and Caraco 2001; Raymond et al. 2004). In watersheds composed of carbonate rocks (e.g., limestone and dolomite), dissolution of carbonate is generally an important source of riverine DIC (Chakrapani and Veizer 2005; Helie et al. 2002; Kanduc et al. 2007b; Karim and Veizer 2000; Lambs et al. 2009; Zhang et al. 2009). Even in the Tana River in Kenya, in which river particulate organic carbon (POC) is significantly decomposed during transit, the dissolution of carbonate and silicate in the watershed still dominates OM respiration as the major source of river DIC (Bouillon et al. 2009).

Human activities, such as river damming and urban development, are another control on river carbon cycling. Wachniew (2006) found that rapid decomposition of labile OM from effluents of two wastewater plants lowered δ^{13}C values of DIC in the Vistula River in Poland by about 1‰. Enrichment of ^{13}C in the DIC pool due to enhanced air–water CO_2 exchange in reservoirs also affects river carbon isotope values (Brunet et al. 2005; Wachniew 2006). Increased DIC export from urban watersheds as a result of increased chemical weathering, CO_2 production, and wastewater input has also been observed (Barnes and Raymond 2009).

Studies assessing the effects of lithology versus human activities on river carbon cycling are few, and these studies have generally found that the influence of lithology is more important than that of human activities. For example, although carbonates compose only $\sim$5% of the bedrock geology of the watershed in the densely populated Lagan River basin in Northern Ireland, they were a more important source of river DIC than wastewater discharged from industries and urban–rural areas (Barth et al. 2003). In the Vistula River in Poland, which receives high loads of pollutants from its watershed and drains a watershed mostly composed of carbonate bedrocks, δ^{13}C values of DIC suggest a predominant influence of carbonate rock dissolution (Wachniew 2006). Similarly, lithology showed a dominant control on carbon geochemistry in a mountainous tributary of the Zhujiang (Pearl River) in southeast China, although impacts of agricultural, urban, and river damming activities were also observed (Zhang et al. 2009).

Our first objective in this study was to determine the relative influence of basin lithology and human activities on carbon cycling in the Brazos River, a subtropical river in Texas. The Brazos River is the longest river (2060 km) in Texas. It runs through large areas of carbonate bedrock in its middle reach, which has minor outcrops of coal-bearing bedrock. Several cities are developing along this middle reach of the Brazos River, and the river main stem is dammed in two of these cities. These characteristics make the Brazos River an excellent field site to study the effects of basin lithology and human activities on the sources and carbon isotope values (δ^{13}C and Δ^{14}C) of riverine DIC.

The second objective of this study was to determine the fraction of the inorganic carbon in the Brazos River that is exported to the ocean. Cole et al. (2007) estimated that about 0.23 Pg year^{-1} of terrestrial carbon is lost from rivers to the atmosphere through CO_2 outgassing, and about the same amount of terrestrially derived inorganic carbon (0.26 Pg year^{-1}) is exported to the ocean, suggesting that the CO_2 outgassing:DIC export ratio of global rivers is about 1:1. However, tropical rivers tend to outgas substantially more CO_2 to the atmosphere relative to the inorganic carbon they deliver to the ocean. For example, in the Amazon River system, the amount of terrestrial carbon returned to the atmosphere each year is more than ten times the total carbon (organic and inorganic) the river exports to the ocean (CO_2 outgassing:DIC export >10:1) (Richey et al. 2002). Similarly, the Nyong River in Cameroon releases CO_2 to the atmosphere at a rate four times that of DIC export to the Gulf of Guinea (CO_2 outgassing:DIC export = 4:1) (Brunet et al. 2009). If river CO_2 evasion and DIC export are equal (0.23–0.26 Pg year^{-1}) on a global scale, then some rivers must export more inorganic carbon to the ocean than they release as CO_2 (i.e., CO_2 outgassing:DIC export <1:1). One example is the Ottawa River, of which CO_2 evasion is about 30% of DIC export by the river (CO_2 outgassing:DIC export = 0.3:1) (Telmer and Veizer 1999). Therefore, the second objective of this study was to quantify the CO_2 outgassing and DIC export fluxes, and the CO_2 outgassing:DIC export ratio of the Brazos River.

We measured concentration and carbon isotopes (δ^{13}C and Δ^{14}C) of DIC as well as pCO_2 to demonstrate that the Brazos River differs from previously studied rivers in that (1) human activities appear to have overprinted the natural isotope values of DIC in the Brazos River derived from basin lithology, and (2) the Brazos River degasses much less CO_2 to the atmosphere than it delivers DIC to the ocean.

Study area and methods

Study area

The Brazos River begins at the juncture of the Salt Fork and the Double Mountain Fork, which merge at 33°16′N, 100°0.5′W, about 110 km upstream of Seymour, TX. It then flows 1344 km across Texas in a southeasterly direction, and drains into the Gulf of Mexico at 28°52.5′N, 95°22.5′W, 3 km south of Freeport in Brazoria County, TX (Fig. 1a). Of the 116000 km^2 Brazos River basin, 107520 km^2 are in Texas. The relief of the Brazos River basin is generally low, with a channel gradient of no more than 0.67 m per kilometer (Stricklin 1961). Besides the Salt and Double Mountain forks, the Brazos has five other principal tributaries: the Clear Fork, the Bosques River, the Little River, Yegua Creek and the Navasota River (Fig. 1a).

The climate in the middle and lower Brazos varies from temperate to subtropical. During the entire study period (March 2007 to July 2009), the mean annual precipitation was 990 mm in Granbury, TX (middle Brazos, 32°26.5′N, 97°47.5′W) and 1050 mm in Freeport, and the mean annual temperature was 16°C in Granbury and 21°C in Freeport (NOAA 2009). Daily discharge variations were consistent along the Brazos River, with high river discharges in the spring and summer of 2007 and 2008, and spring and fall of 2009 (data from USGS).

The lithology of the Brazos River basin varies along the river (Fig. 1a). In the upper Brazos (upstream from Graham, TX), the bedrock is primarily composed of highly erodible Pennsylvanian (upper Carboniferous, 318–299 Ma BP) and Permian (299–251 Ma BP) red beds, with a large fraction of sand (Stricklin 1961). The middle Brazos (Graham to Waco, TX) is underlain by resistant Pennsylvanian and Cretaceous (145.5–65.5 Ma BP) limestone and red beds (Moore and Plummer 1922; Stricklin 1961). Bituminous coal is present in the Middle-Upper Pennsylvanian Strawn, Canyan, and Cisco groups (Hackley et al. 2009; Moore and Plummer 1922). In the lower Brazos (downstream from Waco), the predominant bedrock is Eocene (56–34 Ma BP), Miocene (23–5.3 Ma BP) and Pleistocene (2.6 Ma to 11.7 Ka BP) sand, silt and clay deposits (Cronin et al. 1963; Stricklin 1961). The channel floor and walls of the lower Brazos are alluvium (green color in Fig. 1a) formed in the Pleistocene and Holocene (11.7 Ka BP to present) (Phillips 2007; Stricklin 1961). This alluvium consists of aluminosilicate gravel, sand, clay and silt (Shah et al. 2007). The presence of old carbon in the drainage basin bedrock is very limited in the lower Brazos compared to the middle Brazos (Fig. 1a), but includes (1) carbonate existing as Cretaceous Taylor marl (99.6–65.5 Ma BP) about 40 km downstream Waco, TX in a belt 160 km long and 56 km wide parallel to the coast (Cronin et al. 1963); (2) lignite in the Tertiary Wilcox and Jackson groups (Ruppert et al. 2002); (3) pedogenic carbonate in the Beaumont Formation in the coastal region of Texas (Nordt et al. 2006); and (4) oyster shells and crushed carbonate minerals used in road construction in the US Gulf coast (Doran 1965; Titi et al. 2003). Although these small sources of old carbon are numerous, they are scattered and account for only a small portion of regional lithology.

The predominant land use in the entire Brazos watershed is agriculture (Phillips 2007) (Fig. 1b). Within the middle and lower Brazos watershed, forests and pasture dominate the northern region from 80 km upstream of Graham to Waco, while grassland and row-crop agriculture dominate downstream of Waco. Both sides of the land adjacent to the lower Brazos from Waco to College Station, TX are dominated by cropland, with little or no riparian borders. As the Brazos flows toward the Gulf of Mexico, it runs through or near several cities (Fig. 1b). The total population in the entire Brazos drainage basin is about 3.5 million (Phillips 2007). The Brazos is dammed in several places, and all three major dams are located north of Waco.

We collected samples at seven sites in the main stem of the middle and lower Brazos (Fig. 1a). The two sites (1 and 2) in the middle Brazos are located where the Brazos flows through urban areas, Granbury and Waco (Table 1). The main stem of the Brazos is dammed several kilometers downstream of these sites, forming Lake Granbury in Granbury and a town-lake in Waco. The river is wide and flows slowly at both sites 1 and 2 (Table 1). The five sites in the lower Brazos are located in rural areas. From north to south, they are at FM 60 about 10 km southwest of College Station (site 3), at US 290 (site 4), at FM 1458 (site 5), about 20 km upstream from the mouth (site 6), and the mouth (site 7) (Fig. 1a, b; Table 1). We sampled sites 1–5 on bridges over the Brazos River and sites 6 and 7 using a boat.

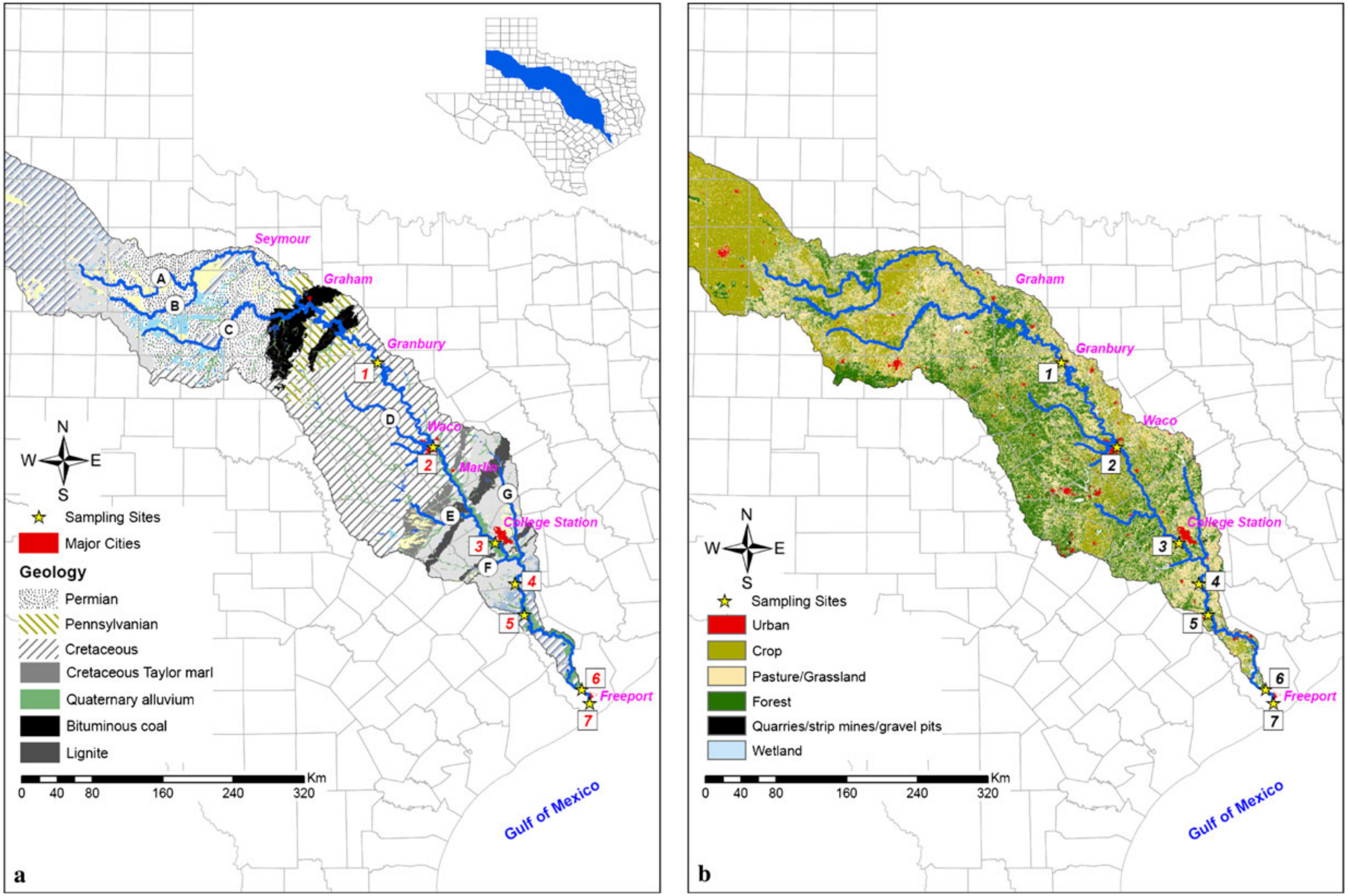

Fig. 1 **a** Surface geologic map of the Brazos drainage basin made according to digital maps by Stoeser et al. (2005) and Tewalt et al. (2008). Compositions of strata are: Permian age—red beds, with a large fraction of sand; Pennsylvanian age—red beds and limestone; Cretaceous age—limestone (Stricklin 1961). The seven tributaries of the Brazos (*letters in circles*) are Salt Fork (A), Double Mountain Fork (B), Clear Fork (C), Bosques River (D), Little River (E), Yegua Creek (F), and Navasota River (G). Cities are labeled in pink. There are seven sampling sites numbered in the boxes. Sites 1 and 2 are dammed several kilometers downstream. Dams cannot be seen because they are masked by sampling site symbols (*yellow stars*). **b** Land cover map of the Brazos drainage basin made according to the digital map by National Center for Earth Resources Observation and Science and U.S. Geological Survey (2005)

Table 1 Basin and hydrology information for the Brazos River basin

Site number	Site location	Distance from the site to the mouth (km)	Catchment area upstream of sites (km^2)	Elevation (m)	City adjacent	City area (km^2)	Population (in 2007)	Distance upstream of the nearest dam (km) (year dam completed)	Width of the river (m)		Annual mean discharge (m^3 s^{-1}) (period)
									Upstream of dam	Downstream of dam	
1	In Granbury (32°26.5′N, 97°46′W)	460	65,350	191.9	Granbury	15.9	8,029	12 (1969)	400	80	29.3 (1970–2008)
2	In Waco (31°33.7′N, 97°7.7′W)	344	75,671	106.5	Waco	247.4	122,222	4 (1970)	100	50	62.2 (1971–2008)
3	At FM 60* (30°33.5′N, 96°25.5′W)	230	99,965	57.7	–	–	–	–	70		149.9 (1994–2008)
4	At US 290* (30°7.7′N, 96°11.2′W)	160	112,333	32.9	–	–	–	–	100		198.7 (1939–2008)
5	At FM 1458* (29°48.5′N, 96°5.7′W)	125	113,903	20.7	–	–	–	–	140		206.2 (1939–2008)
6	Near the mouth (29°1.5′N, 95°27.7′W)	20	116,068	14.9	–	–	–	–	120		240.4 (1968–2008)
7	At the mouth (28°52.7′N, 95°22.8′W)	0		0.9	–	–	–	–	200		

Sites in the middle Brazos: sites 1 and 2, in Granbury and Waco, respectively. Sites in the lower Brazos: sites 3–7

Sites 1–5 were sampled on bridges crossing the Brazos River. Site 6 and 7 were sampled using a boat

Discharge, catchment and elevation data were obtained from US Geological Survey. For site 1: average of data from stations 08090800 and 08091000; for site 2: station 08096500; for site 3: station 08108700 (about 15 km upstream of site 3); for site 4: station 08111500; for site 5: average of data from stations 08111500 and 08114000; for sites 6 and 7: station 08116650 (about 30 km upstream of site 6)

* Numbers are the names of roads or highways

Methods

This study was conducted between March 2007 and July 2009. At each site, we measured surface water temperature and pH in situ using a YSI pH10 pH/Temperature meter. On July 23, 2009, we also measured dissolved oxygen content (DO) of surface water in situ at sites 1 and 2 using an HI 9828 multimeter from Hanna Instruments. All the water pCO_2 and DIC samples were taken directly from the middle part of river cross-sections at depths between 10 and 30 cm from bridges using a submersible pump (SHURflo 9325-043-101).

For each site we collected three ambient air pCO_2 and three water pCO_2 samples. We took ambient air CO_2 samples on bridges, and collected river 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 using an infrared CO_2 analyzer (Li-Cor 7000) on the same day they were collected, using a set of 349, 1500, 3000, and 10100 μatm CO_2 gas standards (Scott Specialty Gases).

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. To minimize CO_2 exchange between the sample and the air, we overflowed the bottle from the bottom 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. All DIC samples were sent to the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) for analysis of DIC concentration and isotopic composition ($\Delta^{14}C$ and $\delta^{13}C$). There, DIC samples were acidified using 85% H_3PO_4 and then sparged with high-purity N_2 gas (99.99%) (McNichol et al. 1994). The evolved CO_2 was collected cryogenically using liquid nitrogen traps (−190°C) on a vacuum line (McNichol et al. 1994). Small aliquots (10%) of the CO_2 gas were analyzed on an isotope ratio mass spectrometer VG PRISM or VG OPTIMA for $\delta^{13}C$. Larger aliquots (20%) of the CO_2 gas were reduced to a graphite target, which was finally analyzed by accelerator mass spectrometry (AMS) to determine $\Delta^{14}C$ (McNichol et al. 1994).

To explore the possible contribution of old organic carbon from coal weathering to the Brazos River's DIC pools, we analyzed the black carbon content of riverine particulate organic matter (POM) at site 3, which is downstream from most of the lignite deposits (Fig. 1a). We made this measurement using cross-polarization and magic angle spinning (CP/MAS) solid-state ^{13}C NMR (nuclear magnetic resonance) and a molecular mixing model. We collected about 120 L of river water, which was stored in a refrigerator overnight to let the particles settle. We then removed the top clear water and used a centrifuge to concentrate sediment from the bottom water. Finally we dried the sediment using a freeze dryer. We conducted NMR experiments on Rice University's 200 MHz Bruker Avance spectrometer, equipped with a 4 mm magic angle spinning (MAS) probe. We aquired CP spectra with a 1 ms contact time, at 5 kHz MAS frequency, and 2 s recycle delay. For each experiment, we collected 40,000 acquisitions (scans). We then processed and deconvoluted the NMR spectrum with the parameters and molecular mixing model described by Baldock et al. (2004). The molecular mixing model generates an estimate of black carbon content, among other properties.

We applied Student's *t*-test to examine if there is significant difference in river pCO_2, DIC concentration, $\delta^{13}C$ and $\Delta^{14}C$ of DIC between the middle and lower Brazos. p values equal to or less than 0.05 suggest that the difference is significant, and p values less than 0.01 suggest that the difference is very significant.

Results

Longitudinal variation in pCO_2, concentration and isotope values of DIC

Measured concentration of atmospheric CO_2 at all study sites averaged 424 ± 43 μatm (Table 2). Riverine pCO_2 values in the Brazos were generally low. Average pCO_2 was 760 ± 243 μatm in the middle Brazos and was 1174 ± 418 μatm in the lower Brazos (Table 2; Fig. 2a), showing no significant difference ($p = 0.0564$) between the middle and lower Brazos. Riverine pCO_2 values at sites 6 and 7 were about three times the atmospheric pCO_2, slightly lower than those at sites 4 and 5 (4–5 times the atmospheric pCO_2) probably due to mixing of high-pCO_2 river water with low-pCO_2 ocean water in

Table 2 Measured parameters for all sampling sites in the Brazos River

Site number	Date sampled	pH	T (°C)	DO (mg L^{-1})	$\mathrm{pCO}_{2,\mathrm{a}}$ (μatm)	$\mathrm{pCO}_{2,\mathrm{w}}$[a] (μatm)	DIC[b] (mM)	Δ^{14}C-DIC[c*] (‰)	δ^{13}C-DIC[d*] (‰)
The middle Brazos									
1	3/5/2009	8.08	15.6	–	361	439	3.0	+10	−4.2
	7/23/2009	8.55	27.3	3.36	415	966	2.3	−10	−3.5
	Mean ± SD	8.32 ± 0.33	21.5 ± 8.3	–	388 ± 38	703 ± 373	2.6 ± 0.5	0 ± 14	−3.9 ± 0.5
2	1/6/2008	8.65	12.6	–	443	858	3.5	+73	−7.5
	7/3/2008	7.92	27.5	–	447	805	2.8	+162	−5.9
	10/30/2008	7.70	18.7	–	389	483	2.8	+96	−5.7
	7/23/2009	8.69	28.9	5.47	389	1007	2.6	+179	−4.6
	Mean ± SD	8.24 ± 0.50	21.9 ± 7.7	–	417 ± 32	788 ± 221	2.9 ± 0.4	+128 ± 51	−5.9 ± 1.2
1–2	Mean ± SD	8.27 ± 0.42	21.8 ± 7.0	–	407 ± 34	760 ± 243	2.8 ± 0.4	+85 ± 77	−5.2 ± 1.4
The lower Brazos									
3	3/5/2009	8.01	21.1	–	363	435	4.2	−84	−6.8
4	3/25/2007	8.22	22.8	–	456	1351	2.4	−135	−9.4
	6/13/2007	–	–	–	480	1770	4.1	−220	−6.6
	Mean ± SD	8.22	22.8	–	468 ± 17	1561 ± 296	3.3 ± 1.2	−177 ± 60	−8.0 ± 1.9
5	3/25/2007	8.24	22.7	–	468	1451	2.5	−141	−9.2
6	11/28/2007	8.32	16.6	–	451	1120	2.3	−194	−9.9
	11/19/2008	7.83	17.4	–	379	1029	2.0	−192	−10.6
	Mean ± SD	8.08 ± 0.35	17.0 ± 0.60	–	415 ± 51	1075 ± 64	2.2 ± 0.3	−193 ± 1.5	−10.3 ± 0.6
7	11/28/2007	7.94	15.8	–	466	1060	2.2	−94	−9.9
3–7	Mean ± SD	8.09 ± 0.19	19.4 ± 3.2	–	438 ± 47	1174 ± 418	2.8 ± 0.9	−151 ± 52	−8.9 ± 1.6

Sites 3, 5, and 7 were measured only once during the study period. We applied Student's *t*-test to examine if there is significant difference between the middle Brazos (sites 1 and 2) and the lower Brazos (sites 3–7) in the parameters

* Means that the difference is significant

[a] $p = 0.0564$, [b] $p = 0.9732$, [c] $p < 0.0001$, [d] $p = 0.0011$

the Gulf of Mexico (Green et al. 2006; Lohrenz and Cai 2006).

The concentration of DIC was consistent along the Brazos ($p = 0.9732$), averaging 2.8 ± 0.4 mM in the middle Brazos and 2.8 ± 0.9 mM in the lower Brazos (Table 2; Fig. 2b). However, the Δ^{14}C ($p < 0.0001$) and δ^{13}C ($p = 0.0011$) values of DIC differed significantly between the middle and lower Brazos (Table 2; Fig. 2c–d). Average Δ^{14}C values of DIC in the middle and lower Brazos were +85 ± 77‰ and −151 ± 52‰, respectively, and average δ^{13}C values of DIC in the middle and lower Brazos were −5.2 ± 1.4‰ and −8.9 ± 1.6‰, respectively (Table 2). Temporal variations in these parameters were minor relative to longitudinal variations (Table 2). The statistically significant differences in carbon isotope values between the middle and lower Brazos suggest distinctive, regional sources and metabolism patterns of DIC.

Black carbon content of riverine POM at site 3 in the lower Brazos

Black carbon is detected within the NMR peak occurring between 110 and 145 ppm. This peak is small relative to other peaks in the spectrum of riverine POM at site 3 (Fig. 3). Because aromatic carbon within lignin is also detected between 110 and 145 ppm, it is necessary to use a molecular mixing model to determine the black carbon concentration. Using the molecular mixing model of Baldock et al. (2004), we calculated black carbon to be 3.8% of the riverine POM. Since NMR-measured black carbon identifies both coal-derived black carbon and soil-derived charcoal black carbon as one pool, our final measurement of 3.8% is an upper estimate for coal input to river POM, allowing us to conclude that coal contributed to no more than 3.8% of POM in the Brazos.

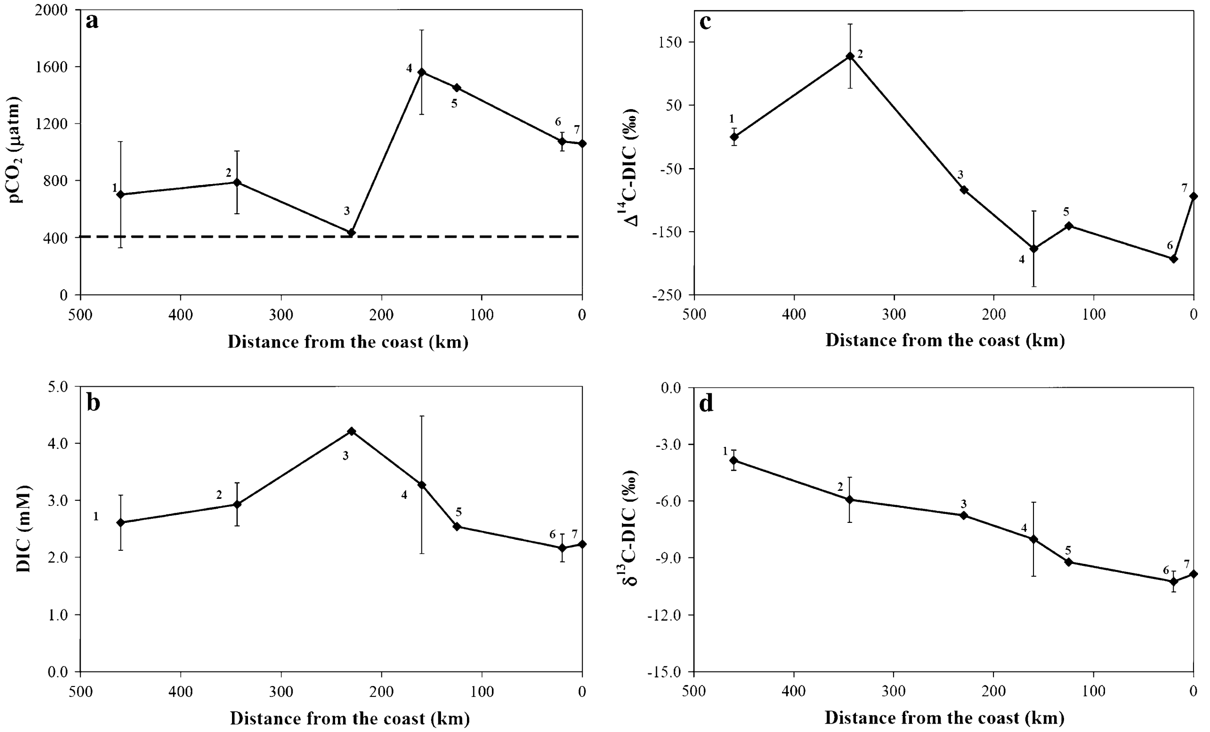

Fig. 2 Longitudinal variations in river water pCO_2 (**a**), DIC concentration (**b**), $\Delta^{14}C$ of DIC (**c**), and $\delta^{13}C$ of DIC (**d**) in the middle and lower Brazos. The dashed line in **a** is the measured mean pCO_2 value of the atmosphere (428 µatm) at the study sites. Numbers on the figures are study site numbers (Table 1). Vertical bars represent the standard deviation of all the data for the site

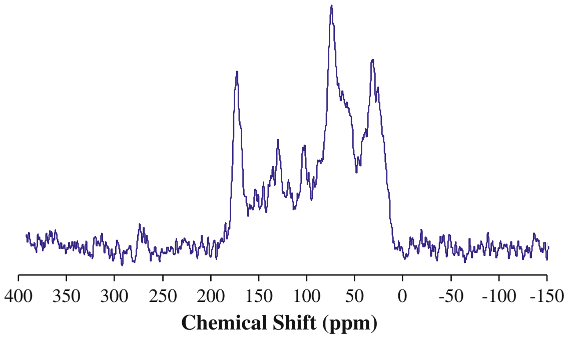

Fig. 3 CP/MAS ^{13}C NMR spectrum of riverine POM at site 3 in the lower Brazos

Discussion

Isotope values of potential DIC sources in the Brazos River basin

We investigated the origins of riverine DIC using a plot of $\delta^{13}C$ versus $\Delta^{14}C$ for our samples and potential DIC sources (Raymond et al. 2004; Zeng and Masiello 2010) which include atmospheric CO_2 invasion, OM respiration (young and old), and dissolution of carbonate (Fig. 4). There are three potential sources of carbonate in the Brazos watershed: (1) natural carbonate rocks (Pennsylvanian and Cretaceous limestone in the middle Brazos and Cretaceous Taylor marl in the lower Brazos), (2) natural pedogenic carbonate in the lower Brazos, and (3) anthropogenic carbonate minerals (oyster shells and crushed limestone used in road construction) in the lower Brazos. Each potential DIC source has a characteristic range of carbon isotope ratios (Fig. 4), which we outline below.

Atmospheric CO_2 invasion is one potential source of DIC. The $\Delta^{14}C$ values of atmospheric CO_2 were +55 to +66‰ in 2004 (Hsueh et al. 2007), and have been dropping at a rate of 6‰ per year (Trumbore et al. 2006), implying that for 2007–2008 DIC from atmospheric CO_2 invasion had $\Delta^{14}C$ values of +31 to +48‰ and $\delta^{13}C$ values of −5 to −3‰ (Raymond et al. 2004).

A second potential source of DIC is CO_2 derived from respiration of terrestrial OM. $\delta^{13}C$ values of

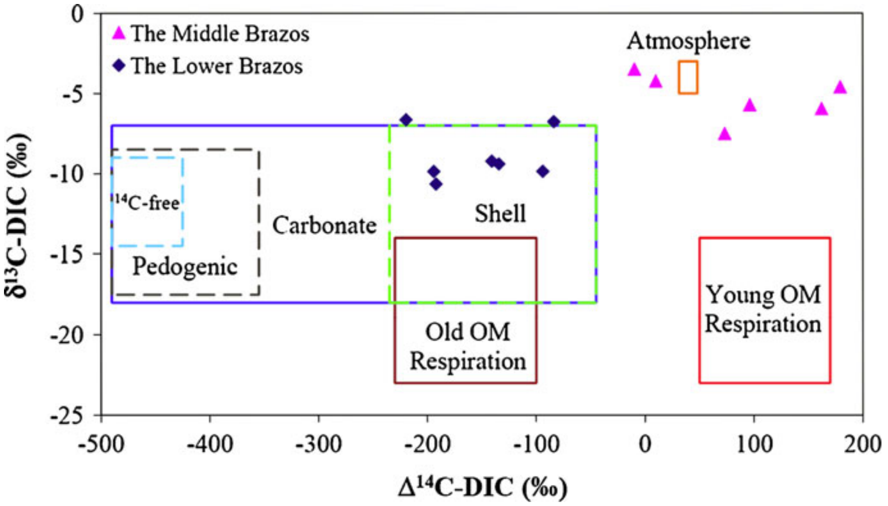

Fig. 4 δ^{13}C versus Δ^{14}C of riverine DIC in the middle (*pink triangles*) and lower (*blue diamonds*) Brazos. Also plotted are δ^{13}C versus Δ^{14}C of potential DIC sources (*in solid boxes*): atmospheric CO_2 (*orange*), young OM respiration (*red*), old OM respiration (*brown*), and carbonate dissolution (*blue*). There are four possible sources of carbonate in the study watershed (*in dashed boxes*): natural sedimentary carbonate minerals and crushed carbonate minerals (*blue*), natural pedogenic carbonate (*black*), and oyster shells (*green*). Carbon isotope values of each source are discussed in detail in the text

DIC from terrestrial OM respiration are typically in the range −23 to −14‰, after correction for fractionation (Barth et al. 2003; Mook et al. 1974; Raymond et al. 2004; Zhang et al. 1995), and Δ^{14}C values of DIC from OM respiration are +50 to +170‰ for young OM and −230 to −100‰ for old OM (Raymond et al. 2004). A recent study (Griffith et al. 2009) found that OM in municipal wastewater treatment plant effluent had a mean radiocarbon age of about 1600 ± 500 years (Δ^{14}C = −180 ± 50‰). Thus, DIC from the respiration of municipal waste falls within old OM respiration in Fig. 4.

The final DIC source is carbonate dissolution. Isotope values of DIC produced by carbonate dissolution vary depending both on the source of carbonate and on the dissolving acid. Soil CO_2 is generally the dominant source of acidity that dissolves carbonate in river systems (Garrels and Mackenzie 1971; Karim and Veizer 2000). Dissolution of different types of carbonate by soil CO_2 produces DIC with isotope values intermediate between the carbonate and soil CO_2, which for soil CO_2 are Δ^{14}C = +20 to +150‰ and δ^{13}C = −29 to −18‰ (Raymond et al. 2004; Trumbore 2000; Trumbore et al. 2006). The dissolution of carbonate rocks and crushed limestone (Δ^{14}C = −1000‰, δ^{13}C = ~0‰) by soil CO_2 produces DIC with Δ^{14}C values of −490 to −425‰ and δ^{13}C values of −14.5 to −9‰. Pedogenic carbonate in Texas has Δ^{14}C values of −1000 to −860‰, and δ^{13}C values of −6 to +1‰ (Nordt et al. 1998; Rightmire 1967; Valastro et al. 1968). Therefore, the DIC sourced from pedogenic carbonate and soil CO_2 has Δ^{14}C values of −490 to −355‰ and δ^{13}C values of −17.5 to −8.5‰. The Δ^{14}C and δ^{13}C values of shell carbonates have been measured in many studies (Douglas and Staines-Urias 2007; Gentry et al. 2008; Keller et al. 2002; McConnaughey and Gillikin 2008; Wisshak et al. 2009). Combining data from all these studies, we estimate shell carbonate Δ^{14}C = −489 to −240‰ and δ^{13}C = −7 to +4‰. The dissolution of shell carbonate by soil CO_2 generates DIC with Δ^{14}C values of −235 to −45‰ and δ^{13}C values of −18 to −7‰.

The broad ranges of isotopic values for every potential DIC source precluded identifying the amount of DIC derived from each source. For example, carbonate Δ^{14}C values could range from −490‰ to −45‰; respirable OM Δ^{14}C values could range from −230‰ to +170‰, and atmospheric CO_2 Δ^{14}C values could range from +31 to +48‰. There are also large ranges of values for the δ^{13}C of each source. The range of Δ^{14}C values for carbonates alone, holding all other potential contributors' Δ^{14}C and δ^{13}C values constant, is enough to cause the potential carbonate contribution to vary between 32 and 94% of DIC in the lower Brazos. Isotopic data do allow us to say conclusively what the major sources of DIC are likely to be, but we cannot assign specific fractions to each source.

Assuming that basin lithology is the dominant control on the source and cycling of riverine DIC in the Brazos River as in other river systems (Helie et al. 2002; Kanduc et al. 2007b; Raymond et al. 2004), we expected to see a clear longitudinal trend in carbon isotope values of riverine DIC. In the middle Brazos, DIC should be highly depleted in ^{14}C relative to the atmosphere resulting from dissolution of large areas of carbonate bedrock and perhaps respiration of ancient OM from bituminous coal erosion. In the lower Brazos, due to the limited sources of old carbon, we expected DIC with a higher Δ^{14}C value compared to DIC in the middle Brazos. Our observation that DIC in the middle Brazos was generally enriched in ^{14}C relative to the lower Brazos was opposite to predictions based upon lithology. This suggests a dominant influence of human activities on carbon cycling in the Brazos River.

Major controls on riverine DIC in the middle Brazos: damming and urbanization

The Δ^{14}C values of DIC in the middle Brazos (+85 ± 77‰) suggest that the Pennsylvanian and Cretaceous limestone and bituminous coal contribute little or no carbon to riverine DIC (Fig. 4), although they outcrop in large areas in the middle Brazos. The relatively low Δ^{14}C-DIC values at site 1 (+10‰ and −10‰) could be due to a very minor input of these ancient carbonate rocks. They could also be due to decomposition of old OM from treated urban wastewater. However, either case suggests that carbonate dissolution is not the predominant source of DIC at site 1. The average Δ^{14}C-DIC value of +128 ± 51‰ at site 2 rules out a carbonate input, and instead likely reflects an 8- to 50-year residence time of carbon in drainage basin ecosystems (Burchuladze et al. 1989; Hsueh et al. 2007; Trumbore et al. 2006).

The concurrently high Δ^{14}C-DIC and δ^{13}C-DIC values and low pCO_2 values in the middle Brazos are likely due to damming and urbanization of the Brazos River in Granbury and Waco. The low pCO_2 values that we observed in the middle Brazos were consistent with observations in dammed, urbanized Chinese rivers. In China, river damming activities and increasing eutrophy driven by urban growth have reduced dissolved CO_2 concentrations in the Changjiang River, the largest river in China (Wang et al. 2007). Iwata et al. (2007) also observed that streams draining more urbanized watersheds were less heterotrophic (meaning with lower dissolved CO_2 concentrations) than streams in intensively farmed watersheds. Damming and urbanization control the geochemistry of river water by: (1) enhancing exchange between riverine DIC and atmospheric CO_2, (2) leading to respiration of relatively young OM in river sediments above the dams; and (3) stimulating surface algal production. The influence of each mechanism is discussed below.

Enhanced air–water CO_2 exchange

Damming of rivers creates reservoirs that have large surface areas and relatively long hydraulic residence times, both of which enhance the exchange of gas between river water and the atmosphere. At sites 1 and 2 the river is 2–5 times its original width (Table 1). Extensive air–water exchange reduces the concentration gradient of dissolved gases between river water and the atmosphere, and draws riverine pCO_2 values closer to that of the atmospheric CO_2 (for sites 1 and 2, average water $pCO_2 = 760 \pm 243$ μatm, average ambient air $pCO_2 = 407 \pm 34$ μatm).

Extensive air–water exchange also resulted in relatively high Δ^{14}C and δ^{13}C values of riverine DIC. Atmospheric CO_2 has Δ^{14}C values of +31 to +48‰ in 2007–2008 (Hsueh et al. 2007; Trumbore et al. 2006) and a δ^{13}C value of −8‰ (Levin et al. 1987). The invasion of atmospheric CO_2, therefore, shifted both Δ^{14}C and δ^{13}C values of riverine DIC to heavier values. Since dissolved CO_2 is more ^{13}C-depleted relative to other DIC components (i.e., HCO_3^- and CO_3^{2-}) (Alin et al. 2008; Mook et al. 1974), removal of dissolved CO_2 through outgassing could increase δ^{13}C values of DIC in the water. Our pCO_2 and DIC isotope data in the middle Brazos are consistent with the results of previous studies (Brunet et al. 2005; Finlay 2003; Zhang et al. 2009), in which high δ^{13}C values of DIC (up to −1.8‰) and lower concentrations of dissolved CO_2 were attributed to efficient air–water exchange in large rivers and impoundment due to dam construction.

Respiration of young OM

The Δ^{14}C-DIC values of +73 to +179‰ at site 2 can only be explained by decomposition of relatively young OM, because neither atmospheric CO_2 invasion nor carbonate dissolution could produce DIC with values this high (Fig. 4). Northern hemisphere atmospheric ^{14}C values spiked at ~900‰ between 1962 and 1963, at the peak of atmospheric nuclear weapons testing (Burchuladze et al. 1989). Since the late 1960s, the bomb spike has mixed into the oceans and terrestrial biosphere, leading to a drop in the atmosphere's ^{14}C value (Burchuladze et al. 1989). Because of the spiked shape of the atmosphere's ^{14}C value since 1950, environmental ^{14}C values >0‰ do not correspond to unique carbon residence times. Instead, each ^{14}C value corresponds to two possible carbon residence times, one on each side of the bomb spike. The Δ^{14}C-DIC values (approx. +170‰) in July 2008 and July 2009 suggest that the OM decomposed was either ~20 or ~50 years old (Burchuladze et al. 1989), while the Δ^{14}C-DIC values (approx. +85‰) in January and October of 2008 correspond to OM 8–10 or ~50 years old (Hsueh et al. 2007; Trumbore et al. 2006). The longer ^{14}C-derived residence times in this ecosystem are unlikely, given the region's high temperature and precipitation. The Amazon, draining a similarly warm and wet climate, has a carbon residence time of ~5 years (Mayorga et al. 2005), making the 8–10 and 20 year residence time interpretations of our ^{14}C data most likely.

If the +170‰ Δ^{14}C value reflects about a 20 year residence time, and the +85‰ Δ^{14}C value reflects an 8–10 year residence time at our site 2 (Waco), then the Brazos respires older OM in the summer and younger OM in the winter. Respiration of older OM in summer may be a result of more intensive heterotrophic microbial activity or a shift in microbial community stimulated by warmer water (Table 2) (Boer et al. 2009). Alternatively, crops are typically harvested and replanted in May and June in this part of the US. Increased soil mobility after crop harvest in summer could have led to loss of old soil organic matter (SOM) to the river.

The respiration of OM at site 2 may involve methanogenesis, which can highly enrich ^{13}C in the DIC pool. It has been reported that OM in bottom sediments of lakes can be respired by anaerobic bacteria via methanogenesis, producing highly ^{13}C-depleted methane (CH_4) and ^{13}C-enriched CO_2 relative to the OM source (Gu et al. 2004; Stiller and Magaritz 1974; Stiller et al. 1985; Wachniew and Rozanski 1997). Lake Apopka in central Florida (Gu et al. 2004) has δ^{13}C-DIC values as high as +6 to +8‰ due to methanogenesis of sedimentary OM. Compared to the DO content of Lake Apopka (about 7.5 mg L^{-1}), measured DO contents in the surface water at sites 1 and 2 (averaging 4.4 ± 1.5 mg L^{-1}, Table 2) were lower, suggesting that methanogenesis of OM may have occurred and provided ^{13}C-heavy CO_2 to the water column. However, without CH_4 measurements in the water column, this hypothesis cannot be confirmed.

Algal growth

CO_2 uptake by algae can also lead to ^{13}C enrichment of DIC. In algal photosynthesis, dissolved CO_2 is preferentially used because of lower energetic costs of dissolved CO_2 acquisition relative to HCO_3^- (Burkhardt et al. 2001; Rotatore et al. 1995). Like removal of dissolved CO_2 through outgassing, CO_2 uptake by algal photosynthesis causes a reduction of dissolved CO_2 concentrations, and increases δ^{13}C-DIC values. For example, in a study conducted in the Dead Sea (Oren et al. 1995), δ^{13}C-DIC values as high as +5.1‰ were driven by a *Dunaliella* bloom, while δ^{13}C-DIC values were 8.5‰ lighter before the bloom.

Chlorophyll *a* concentration in Lake Granbury (site 1) can reach 90 µg L^{-1} in March (Roelke et al. 2007), comparable to levels published for a eutrophic lake in central Florida (96 µg L^{-1}) (Gu et al. 2004), suggesting intensive algal photosynthetic activity in Lake Granbury. The growth of algae is favored by nutrient enrichment. Total phosphorus was about 50 µg L^{-1} in Lake Granbury (BRA 2009), within the range of mesotrophic conditions (moderately nutrient enriched, total phosphorus ranging from 25 to 75 µg L^{-1}) (EPA 2001). Most of the lake nutrients are from wastewater treatment plants and on-site sewage facilities near the Granbury site (Riebschleager and Karthikeyan 2008).

The river water passing through Waco is partially from Lake Waco, a reservoir constructed in the Bosque River (Fig. 1) about ten river kilometers before the Bosque River merges with the Brazos

River at a point only three river kilometers upstream of our sampling site in Waco. Lake Waco has been classified to be mesotrophic or eutrophic in different time periods primarily due to the input of nutrients from dairy waste and forage fields in the Lake Waco-Bosque River watershed (McFarland et al. 2001; McFarland and Hauck 2001). Enhanced algal growth in Lake Waco is confirmed by increased chlorophyll *a* concentration (Jones 2009; McFarland et al. 2001).

Natural and anthropogenic carbonate input to the lower Brazos

DIC in the lower Brazos was strongly influenced by old carbon (Fig. 4), although ancient carbon sources, carbonate and lignite outcrops, are very limited in the lower Brazos. The black carbon content from NMR analysis was 3.8% of the riverine POM at site 3, of which a fraction is from the Mollisol soils drained in this region. These soils have been shown to be rich in charcoal (Skjemstad et al. 2002), leading us to conclude that lignite is much less than 3.8% of the riverine POM. Longworth et al. (2007) observed young dissolved organic matter (DOM) in watersheds draining OM-rich shale, suggesting little or no contribution of shale organic carbon to riverine DOM. Assuming that contributions of lignite black carbon to the DOM pool are also negligible in the lower Brazos River, we conclude that lignite decomposition has a trivial impact on ^{14}C content of riverine DIC. Soil erosion due to agricultural practices in the lower Brazos could have caused loss of old SOM to the river as described in other studies (Krusche et al. 2002; Longworth et al. 2007; Raymond et al. 2004) and decomposition of this old OM may be a source of old riverine DIC. However, this process is less important compared to carbonate dissolution in driving the carbon isotope values of DIC, as indicated by the relatively high δ^{13}C values of DIC (Fig. 4).

Possible carbonate sources in the lower Brazos include naturally occurring Cretaceous Taylor marl and pedogenic carbonate, and oyster shells and crushed carbonate minerals used in road construction (Doran 1965; Titi et al. 2003; Zeng and Masiello 2010). Taylor marl consists of highly calcareous clay or clay marl, which is a loose mixture of clay (65–35%) and calcium carbonate (35–65%) (Matson and Hopkins 1917). This soft bedrock material is susceptible to erosion and could have added to the riverine DIC pool.

Pedogenic carbonate present in the Vertisols of the Beaumont Formation in coastal Texas is another source of carbonate (Nordt et al. 2006). Pedogenic carbonate is generally formed in arid and semi-arid areas. However, Vertisols in the Beaumont Formation of the east Texas Gulf coast preserve pedogenic carbonate despite the high rainfall (>1000 mm per year), due to their high clay content and shrink-swell properties (Nordt et al. 2006).

Oyster shells and crushed carbonate minerals are a significant regional anthropogenic source of soil carbonate. Oyster shells were widely used in the US Gulf coast as aggregate for the construction of roads and parking lots through the mid-twentieth century (Doran 1965). In the 1960s, shell roads could be found in a belt about 100 km wide along the Texas coast (Doran 1965), and their remnants are ubiquitous in coastal Texas urban environments. Crushed limestone has also been used in Gulf coast roads (Titi et al. 2003). In Buffalo Bayou, one of the rivers draining Houston about 50 km east of the lower Brazos, dissolution of shell and crushed limestone/dolomite imbedded in old city roads has contributed to the river's old DIC ($\Delta^{14}C = -117 \pm 45‰$) (Zeng and Masiello 2010). Our isotope data show that shells and crushed carbonate minerals are also likely an important source of DIC in the lower Brazos, as illustrated by Fig. 4.

Comparison of Brazos pCO$_2$ and DIC with other rivers

Riverine pCO$_2$

Measured pCO$_2$ values in the middle and lower Brazos ranged from 435 to 1770 µatm, with an average (±SD) of 983 ± 397 µatm during the study period (March 2007 to July 2009). Compared to other subtropical rivers, pCO$_2$ values in the Brazos were much lower than those of the Xijiang River in southeast China (about 2600 µatm, Yao et al. 2007), the Satilla and Altamaha rivers in the coastal region of Georgia (4000–8500 µatm, Cai and Wang 1998), and Buffalo Bayou and Spring Creek in Harris County, TX (3000–4200 µatm, Zeng and Masiello 2010).

The low pCO_2 values in the Brazos River are probably due to the combined effects of lower precipitation, an important control on river pCO_2 (Yao et al. 2007; Zeng and Masiello 2010), larger river size, and damming and urbanization as discussed above. The mean annual temperature in the middle and lower Brazos was 16.5–21.3°C for the study period, similar to that in the Xijiang River (14–22°C) (Yao et al. 2007) and that in the Satilla and Altamaha river basins in 1995 (about 21°C, NOAA). However, the mean annual precipitation in the study area for the study period, 898–1050 mm, is much lower than that in the Xijiang River basin (1451 mm, China Meteorological Data Sharing Service System), the Satilla and Altamaha river basins (1580 mm in 1995, NOAA), and the Buffalo Bayou and Spring Creek watersheds (1220–1350 mm, NOAA). Also, large rivers in general are less supersaturated in CO_2 compared to smaller streams under similar climate conditions (Finlay 2003).

Riverine DIC concentration

The DIC concentration in the Brazos River, 2.8 ± 0.7 mM, far exceeded the average value of world rivers (0.9 mM) (Livingstone 1963). It is an order of magnitude higher than some northeast US rivers (Raymond et al. 2004), and higher than those in some rivers in the Coast Range of northern California (Finlay 2003).

High DIC concentrations have also been observed in the St. Lawrence River (0.5–5 mM) (Helie et al. 2002), the Sava River (2.9 ± 1.0 mM) (Kanduc et al. 2007a), three major US rivers (Ohio, upper Mississippi, and Missouri, 1–5 mM) (Raymond and Oh 2007), and Buffalo Bayou (2.4 ± 1.0 mM) (Zeng and Masiello 2010). Most of these high DIC concentrations are associated with carbonate input to the river systems, and sources of carbonate include bedrock, oyster shells and crushed limestone used in road construction and as agricultural soil amendments. Dissolution of limestone and dolomite accounts for up to 26% of DIC in the Sava River (Kanduc et al. 2007a), and agricultural liming contributed 17% of DIC in the Ohio River (Oh and Raymond 2006). Similarly, $\Delta^{14}C$ and $\delta^{13}C$ values of DIC in the lower Brazos suggest that although lithologic sources of carbonate are minor, anthropogenic and possibly pedogenic carbonates are a significant source of DIC.

For the middle Brazos, the high DIC concentration was not due to dissolution of carbonate bedrock, but instead due to urbanization. It has been observed that wastewater treatment plant effluent contributes up to 22% of the total DIC in the Hockanum River, Connecticut (Barnes and Raymond 2009). Weathering of bedrock material exposed to the surface due to urban soil disturbance, and dissolution of urban concrete are two other mechanisms for the high DIC concentration in urbanized watersheds (Baker et al. 2008).

CO_2 outgassing and DIC export from the Brazos

We used pCO_2, DIC concentration and river discharge data (obtained from the USGS) to calculate the fluxes of CO_2 outgassing and DIC export from the Brazos in a preliminary attempt to estimate the Brazos River basin as a C source to the atmosphere and the ocean.

CO_2 outgassing is calculated using the following equation (modified from Raymond et al. 1997):

$$\text{Outgas} = k_{CO_2} \times \left(pCO_{2,w} \times K_h - pCO_{2,a} \times K_h\right) \times A$$

where K_h is Henry's law constant at a given temperature and salinity; $pCO_{2,w}$ and $pCO_{2,a}$ are the partial pressure of CO_2 in surface water and the overlying air, respectively; k_{CO_2} is the gas exchange coefficient for CO_2 at a given temperature for a given type of river; and A is the area of water surface.

Measured mean $pCO_{2,w}$ and $pCO_{2,a}$ values for the Brazos were 983 and 424 μatm, respectively. The average temperature was 20.6°C, so K_h was 0.0383 mol l^{-1} atm^{-1} (Stumm and Morgan 1996). We chose a commonly used range of k_{CO_2} values, 2.5–5 cm h^{-1} (Raymond et al. 1997; Richey et al. 2002; Zeng and Masiello 2010), in our calculation. Using a water surface area (A) of 565.79 km^2 for the Brazos River (including the river itself and the three main reservoirs along the main stem river channel) (BRA 2010), we calculated CO_2 outgassing rate from the Brazos River to be 0.03–0.06 Tg C $year^{-1}$.

DIC export from the Brazos River to the Gulf of Mexico is the product of average DIC concentration and average river discharge at the river mouth. Average DIC concentration at the Brazos mouth was 2.8 ± 0.7 mM. River discharge data were obtained from a US Geological Survey station (08116650) located about

50 km upstream of the river mouth. Annual mean river discharge for 2007–2008 at this station was 349 $m^3\ s^{-1}$. Our estimated rate of river DIC export to the Gulf of Mexico is 0.37 ± 0.09 Tg C $year^{-1}$. Since the discharge at the river mouth should be higher than at the 50 km upstream USGS station, the estimated DIC export here is a conservative value.

The CO_2 outgassing : DIC export ratio of the Brazos River is, therefore, about 0.1:1. This value is not only lower than those of tropical rivers, but also lower than those of northern rivers such as the Ottawa River (Brunet et al. 2009; Richey et al. 2002; Telmer and Veizer 1999). The low CO_2 outgassing:DIC export ratio implies that of the total DIC in the Brazos River, about 90% is exported to Gulf of Mexico, while only about 10% is released to the atmosphere. It is possible that this very low CO_2 outgassing:DIC export ratio is also a result of human activities, with pCO_2 driven down by damming and urban treated wastewater input and DIC driven up by carbonate dissolution.

Conclusions

Our results show that human activities (i.e., damming and urbanization) dominate geology as a control on the origin and cycling of DIC in the Brazos River. Although limestone bedrock underlies a large area of the middle Brazos River watershed, this limestone does not influence riverine DIC, as shown by the radiocarbon values (+85 ± 77‰) of riverine DIC in the middle Brazos. Neither does the coal-bearing bedrock present in the watershed. $\Delta^{14}C$ (+85 ± 77‰) and $\delta^{13}C$ (−5.2 ± 1.4‰) values of DIC in the middle Brazos are likely due to extensive air–water CO_2 exchange, respiration of decades old OM in river sediments, and algal growth, all of which are driven by a combination of damming and wastewater input from urban areas. In contrast, $\Delta^{14}C$ (−151 ± 52‰) and $\delta^{13}C$ (−8.9 ± 1.6‰) values of DIC in the lower Brazos suggest input of carbonate-sourced DIC to the lower Brazos, despite the absence of carbonate bedrock in the lower Brazos watershed. Oyster shells and crushed limestone used as aggregate in road construction in the Gulf coast areas are two likely sources of carbonate, in addition to naturally occurring marl and pedogenic carbonate in the lower Brazos.

The pCO_2 values in the Brazos River are generally lower than other subtropical rivers, while the DIC concentration in the Brazos River is relatively high compared to many other rivers. As a result, the amount of DIC the Brazos River releases to the atmosphere as CO_2 gas is much smaller than the amount of DIC it delivers to the ocean.

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