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Continental Shelf Research 28 (2008) 1538–1549

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

A comparative overview of weathering intensity and HCO_3^- flux in the world's major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers

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ARTICLE INFO

Article history:
Received 18 December 2006
Received in revised form
7 June 2007
Accepted 1 October 2007
Available online 4 April 2008

Keywords:
River flux
Bicarbonate
Weathering

ABSTRACT

In this paper, general relationships of riverine bicarbonate concentrations and fluxes as a function of drainage basin mineral content and runoff are examined using a database of the 25 largest rivers in the world. Specific HCO_3^- flux normalized to unit basin area, which peaks in the mid latitudes, was found to be strongly correlated with the carbonate mineral content of river basins, while river HCO_3^- concentration was related to the balance of precipitation and evaporation. Within this global context, the weathering patterns of CO_2 in a few large rivers (Changjiang, Huanghe, Pearl, and Mississippi rivers) were examined in further detail. The Zhujiang (Pearl River), especially its largest branch (Xijiang), was characterized by the highest specific weathering rate among all the world's large rivers due to an exceptionally high carbonate mineral content (over 80%) in its drainage basin and its warm and wet environment. It has a moderate level of HCO_3^- concentration, however, due to dilution by relatively high precipitation in the watershed. In stark contrast, the Huanghe (Yellow River) has one of the lowest specific weathering rates because of low carbonate mineral content and a dry climate. However, it has a high HCO_3^- concentration due largely to the concentrating effects of high evaporative water loss, as a result of arid weather and the agricultural use of water through irrigation systems, as well as carbonate-containing surficial deposits (i.e., loess). The strong correlation between specific HCO_3^- fluxes and discharge in all four rivers with different discharge seasonality suggests that higher precipitation in drainage basins promotes higher weathering rates.

For the 25 large rivers studied here, rivers in low ($<30^\circ$), mid (30–60°) and high ($>60^\circ$) latitudes have an average HCO_3^- concentration of 0.584, 1.649, and 1.154 mM, respectively, and they account for 42.6%, 47.3% and 10.1%, respectively, of the total global dissolved inorganic carbon flux to the ocean. Thus the mid-latitude rivers carry a disproportionally high dissolved inorganic carbon flux with a relatively small (26%) amount of freshwater discharge. The discharge-averaged global river HCO_3^- concentration was estimated to be 1.1 mM.

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1. Introduction

Rivers, in particular, large rivers, play an essential role in the transport and transformation of carbon from the land and the atmosphere to the ocean (Sabine et al., 2003; Chen, 2004). Using an empirical model, Ludwig et al. (1998) estimated that a total of 60×10^{12} mol (or Tmol), or 0.72×10^{15} g of carbon (or Pg C) each year is exported from the continents to the ocean. Of this total continental erosion flux, about 8.0 Tmol C comes from the carbonate mineral dissolution and 52.1 Tmol from the atmosphere. Of the atmospheric portion, 17.1 Tmol is dissolved organic carbon (DOC), 15.6 Tmol particulate organic carbon (POC) and 19.4 Tmol HCO_3^-. The total organic carbon flux (32.7 Tmol yr^{-1} or 0.392 Pg C yr^{-1}) to the ocean estimated by Ludwig et al. (1998) is

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doi:10.1016/j.csr.2007.10.014

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similar to earlier estimates summarized in Smith and Hollibaugh (1993), although more recent literature has suggested higher fluxes between 0.43 and 0.50 Pg C yr^{-1} (Mackenzie et al., 2004). In a recent review, Richey (2004) argued that the POC flux alone can be as high as 0.5 Pg C yr^{-1} if higher sediment yield from tropical/subtropical mountainous rivers is included. The total riverine HCO_3^- flux of Ludwig et al. (1998) (i.e., 27.4 Tmol or 0.329 Pg C yr^{-1}) is somewhat lower than that reported by Mackenzie and co-workers (0.41 Pg C yr^{-1}, Mackenzie et al., 1998, 2004). In addition, another 15 Tmol yr^{-1} of particulate inorganic carbon (PIC), mostly refractory calcite, has been estimated to be transported from the land to the ocean as a result of continental (physical) erosion (Mackenzie et al., 2004).

Nearly all carbon in the form of DOC and POC in the rivers is directly or indirectly of atmospheric origin. Organic carbon flux (~1.5 Pg C or 125 Tmol per year) from land to the rivers carries the biomass produced by photosynthesis (~60 Pg C or 5000 Tmol per year) in excess of losses due to respiration and forest fires (Schlesinger, 1997). Enroute to the oceans, a large part of the organic carbon may be decomposed and released back to rivers and the atmosphere as CO_2 through microbial respiration (Richey et al., 2002). Most of the terrestrial DOC and POC (0.4–0.5 Pg or 33.3–41.7 Tmol of C per year) reaching the ocean is believed to be decomposed in the ocean margins with less than a total of 12.5 Tmol C yr^{-1} of POC being buried in marine sediments (Berner, 1982, 1989; Hedges and Keil, 1995; Mckee, 2003). Only about 4–8 Tmol of this buried POC is believed to be terrestrial (see a summary in McKee, 2003). DOC and POC exports from watersheds to ocean margins have been extensively reviewed in several recent syntheses involving spatially explicit models (Smith and Hollibaugh, 1993; Ludwig et al., 1996; Seitzinger et al., 2005). The current paper will thus focus on the dissolved inorganic carbon (DIC) flux and spatial distribution as DIC also represents an important terrestrial carbon source to the ocean.

Rock weathering involves both silicate and carbonate minerals as represented by the following simplified reactions:

$$\text{Carbonates}: \quad CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \tag{1}$$

$$\text{Silicates}: \quad CaSiO_3 + 2CO_2 + 3H_2O = 2HCO_3^- + Ca^{2+} + H_4SiO_4 \tag{2}$$

Thus all HCO_3^- generated from silicate weathering is derived from the atmospheric and soil CO_2 (i.e., from plant root respiration and bacterial degradation of organic matter, and these two parts will be lumped into one term in this paper as atmospheric CO_2 as soil CO_2 will eventually be released back to the atmosphere if not consumed). For carbonate weathering, half of the HCO_3^- comes from the atmospheric CO_2 and the other half is from the carbonate minerals. Traditionally, weathering rates are estimated from riverine Ca^{2+} and Mg^{2+} fluxes based on the charge balance principle and a few stoichiometric assumptions as to minerals being weathered (Berner et al., 1983; Lerman et al., 2007). A global carbonate weathering rate (as total HCO_3^- flux from calcite and dolomite) was estimated as 24.3 Tmol yr^{-1}, while the silicate weathering rate was estimated as 11.5 Tmol yr^{-1} (Berner et al., 1983). Thus, according to formulae (1) and (2), a global atmospheric CO_2 uptake rate via continental weathering was estimated as 23.3 Tmol yr^{-1} (= 24.3/2+11.5—dissolution due to sulfuric acid). A small amount of river HCO_3^- flux (0.28% of the total) is due to reactions with sulfuric acid produced during pyrite oxidation. Total riverine HCO_3^- flux resulting from Berner's approach would be 36.8 Tmol yr^{-1} or 0.44 Pg C yr^{-1}. A slightly lower value (32 Tmol yr^{-1} or 0.38 Pg C yr^{-1}) was estimated by Lerman et al. (2007).

Recently, Amiotte Suchet et al. (2003) and Ludwig et al. (1998) derived atmospheric CO_2 uptake based on model estimated fluxes of global inorganic carbon and dissolved silicate. Their continental weathering rates were determined using the Global Erosion Model for atmospheric CO_2 (GEM CO_2 model). The model was calibrated using small monolithologic watersheds in France (Meybeck, 1986, 1987) that have a short water residence time. On average, extrapolation to mid and high latitude large rivers with longer water residence time resulted in an underestimate of the overall river HCO_3^- flux by as much as 34% when compared to known river HCO_3^- fluxes compiled at the time by Ludwig et al. (1998). However, for many of the large rivers in the mid and high latitudes, the underestimation was more than 34%. In contrast, tropical and subtropical rivers were better represented as these rivers generally have relatively short water residence time (Ludwig et al., 1998).

While mineral weathering is known to be a major regulator of atmospheric carbon dioxide concentrations over geological time scales (Berner et al., 1983), recent studies of the Mississippi River suggest that weathering rates may change over much shorter time scales, e.g., over decades, and may respond to changes in land use (Cai, 2003; Raymond and Cole, 2003; Oh and Raymond, 2006). This additional information highlights the pressing need for a better understanding of DIC export associated with weathering processes and temporal and spatial variations.

In this paper, we first used an updated database to examine briefly the global distribution pattern of river HCO_3^- fluxes and their relationship to drainage basin mineralogy. In particular, the latitudinal distribution of river bicarbonate flux, an interesting feature that has been largely ignored in the past, is examined and linked to the mineral distribution in the drainage basin. A global HCO_3^- flux based on an up-to-date compilation of the 25 largest rivers is subsequently provided. In the context of the observed global pattern, we then examine the weathering processes of the three largest Chinese river basins and their corresponding HCO_3^- fluxes. As appropriate to this special issue, weathering intensity and HCO_3^- flux in the Mississippi River basin is also compared.

2. Global river bicarbonate or alkalinity fluxes

Aquatic inorganic carbon exists in three species, CO_{2aq} (including H_2CO_3), HCO_3^- and CO_3^{2-}. Total dissolved inorganic carbon (DIC) is defined as the sum of all three species. Total (or titration) alkalinity is defined as TAlk = $[HCO_3^-]+2[CO_3^{2-}]$ plus other weak bases that can be converted into acidic forms at the CO_2 equivalent point (< pH 4.5) through an HCl titration process (see Dickson, 1992 for details in seawater systems and Cai et al., 1998 for estuarine waters). $[HCO_3^-]$ can be calculated from a combination of any two of the following measured parameters DIC, TAlk, pH, or partial pressure of CO_2 (pCO_2), provided that the dissociation constants of the carbonic acid are known (as well as the total concentrations of other contributing acid-bases if TAlk is used). However, in most of the river chemistry literature, HCO_3^- flux was determined as alkalinity flux. This practice is acceptable as HCO_3^- is the dominant species contributing to alkalinity in most river waters. For example, in the Mississippi River water, the average HCO_3^- concentration is 99% of the average TAlk (Cai, 2003). On the other hand, uncertainties of many historical data are clearly higher than a few percent either due to analytical and sample handing errors or poor spatial and seasonal representation of samples. Therefore, in this paper, HCO_3^- flux, TAlk flux and, occasionally, DIC flux are not differentiated and whenever possible TAlk data are used.

We have compiled concentrations and fluxes of HCO_3^- in the 25 largest rivers in the world (Table 1). In most cases, data were

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Table 1
Basic information and flux data for the 25 world's largest rivers

No.	River name	Basin area (10^3 km^2)[a]	Discharge (km^3 yr^{-1})[a]	Runoff (mm yr^{-1})	Carbonate %[b]	Basin latitude	HCO_3^- (μM)	Specific DIC flux (10^3 mol km^{-2} yr^{-1})	DIC flux (10^9 mol yr^{-1})
1	Amazon	5854	6642	1135	3.9	2	369	419	2450
2	Congo	3699	1308	354	10.1	4	224	79	293
3	Orinoco	1039	1129	1087	1.3	7.5	423	460	477
4	Changjiang	1794	944	526	44.0	30	1780	937	1680
5	Brahmaputra	583	628	1077	33.8	25	1114	1200	700
6	Mississippi	3203	610	190	18.1	36	2074	395	1265
7	Yenisei	2582	599	232	6.9	60	905	210	542
8	Parana	2661	568	213	1.2	23	764	163	434
9	Lena	2418	531	220	11.2	63	870	191	462
10	Mekong	774	525	678	21.4	20	949	644	498
11	Ob	2570	412	160	2.7	60	1251	201	515
12	Ganges	956	404	423	33.8	26	1966	831	794
13	St Lawrence	1267	363	287	24.9	47	1339	384	486
14	Pearl River	477	343	719	–	23	1535	1104	527
15	Xijiang	409	270	660	82.4	23	1938	1279	523
16	Mackenzie	1713	290	169	20.6	64	1800	305	522
17	Columbia	724	252	348	–	42	1246	434	314
18	Ubangi	356	228	640	–	2.5	317	203	72
19	Yukon	852	212	249	0.0	64	1363	339	289
20	Danube	788	202	256	14.5	48	3115	798	629
21	Niger	2240	193	86	6.3	10	550	47	106
22	Kolyma	666	118	177	0.0	67	467	83	55
23	Indus	1143	104	91	26.0	29	1681	153	175
24	Godavari	312	97	311	0.0	21	2156	670	209
25	Huanghe	894	47	53	7.6	36	2591	136	122

As our interests were two-fold, using HCO_3^- content and flux as an overall measure of weathering intensity of an entire river basin as well as estimating HCO_3^- flux to the ocean, we placed a higher weight on data from the downstream sites. Data that were averaged over an annual cycle or multiple years were used preferentially.

1. Amazon—Gaillardet et al. (1997) reported a mid to downstream HCO_3^- value of 195–330 μM at high river stage in May 1989. Stallard and Edmond (1983) reported a downstream average HCO_3^- of 323 μM in Jun.–Jul. 1976 and May–Jun. 1977. Gibbs (1972) reported an average HCO_3^- of 369 μM for Apr. 1963–Apr. 1964 and Mar–Apr. 1967 at Macapa, a site representing >99.8% of the river's flow into the ocean based on monthly data. We adopted a value of 369 μM because it is an average based on an annual cycle at a downstream site.

2. Congo—Probst et al. (1992) reported an average HCO_3^- concentration of 224 μM from 1987–1989 based on monthly data at a site 40 km upstream of the estuary (Brazzaville).

3. Orinoco—Nemeth et al. (1982) reported monthly data from Feb. 1981 to Jan. 1982 and a discharge-weighted value of 423 μM at a downstream site. We adopted this value. Depetris and Paolini (1991) reported TAlk of 23–930 μM in the left bank rivers and 10–193 μM in the right bank rivers of the whole basin. $[HCO_3^-]$ in the left bank rivers is higher than the right bank. Edmond et al. (1996) determined that TAlk values ranged from 6 to 1719 μM in the left bank rivers from Mar. 1982 to Jun. 1986.

4. Changjiang (Yangtze)—Li and Zhang (2003b) reported monthly averaged HCO_3^- of Jan., Mar., May, Jul., Sep., and Nov. from 1996 to 2001 at Nantong (a downstream city) from which the discharge-weighted value is 1619 μM. Zhang et al. (1987) measured one datum of 2318 μM at Jiujiang in Aug. 1983. Chen et al. (2002) reported the arithmetic mean HCO_3^- value of 1887 μM from 1958 to 1990 at Datong (a major downstream hydrological station). Liu et al. (2002) also reported the averaged HCO_3^- concentration at Datong from 1963 to 1999 and their discharge-weighted value is 1785 μM. We adopted this long-term average value. Recently, Zhai et al. (2007) measured the discharge-weighted DIC as 1690 μM at the upper reach of the estuarine zone in Jul. 2005–Jun. 2006, after the first filling stage of Three-Gorges Dam began since after Jun. 2003.

5. Brahmaputra—Sarin and Krishnaswami (1984) reported an average mainstream $[HCO_3^-]$ of 957 μM before confluence with the Ganges. Sarin et al. (1989) reported a HCO_3^- concentration range of 884–1642 μM in Apr. and Dec. 1982 in mainstream, and an average of 1345 μM. As there are no wet season values in this paper, 1345 μM should be higher than the annually averaged value. Galy and France-Lanord (1999) reported $[HCO_3^-] = 1114$ μM at downstream in Aug. 1996 (a wet season). An average value should be slightly higher than the wet season value. Thus we adopted an average value of 1230 μM.

6. Mississippi—Cai (2003) reported the discharge-weighted multiple-year TAlk of 2074 μM at a downstream site from Sep 1997 to Apr. 2004 based on USGS data.

7. Yenisei—Gordeev et al. (1996) reported an average downstream HCO_3^- of 905 μM based on data from 1971 to1980. Stunzhas (1995) reported 1106 μM in Sep. 1993. Telang et al. (1991) cited a lower section HCO_3^- of 1213 μM. We used the downstream averaged value of 905 μM.

8. Parana—Depetris (1976) reported discharge-weighted HCO_3^- concentration from Apr. 1971 to Mar. 1972 to be 503 μM. Depetris and Lenardon (1983) reported TAlk from Mar. 1981 to Dec. 1982 to be between 112 and 2400 μM and the discharge-weighted value as 764 μM. Cascante et al. (1985) reported TAlk as 690 μM under unusual hydrological conditions. Thus, we used 764 μM as the average river TAlk.

9. Lena—Gordeev and Sidorov (1993) reported $[HCO_3^-] = 870$ μM at Kiusiur (a downstream site) based on monthly data from 1975 to 1990. Gordeev et al. (1996) reported average $[HCO_3^-] = 853$ μM from 1980 to1990. Huh et al. (1998) reported TAlk as 773–796 μM in Lena in Jul. 1991, Jan. 1992 and Jul. 1995. As these data were similar, we adopted a value of 870 μM.

10. Mekong—Meybeck and Carbonnel (1975) reported an average $[HCO_3^-] = 949$ μM at Phnom Penh from Jan 1961 to 1962. Recent DIC values reported by Borges et al. (2005) measured in Dec. 2003, Apr. 2004, Oct. 2004 are 1045, 1441 and 954 μM, and their discharge weighted value is 1014 μM. As they are similar, we used $[HCO_3^-] = 949$ μM.

11. Ob—Gordeev et al. (1996) reported an average $[HCO_3^-] = 1251$ μM in 1971–1980. Stunzhas (1995) reported TAlk = 651 μM in Sep. 1993. We used 1251 μM because it is an averaged value, while 651 is a wet season value.

12. Ganges—Sarin and Krishnaswami (1984) reported an average $[HCO_3^-] = 1966$ μM at Patna. Sarin et al. (1989) reported $[HCO_3^-]$ at Patna in Mar. 1982, Sep. 1982, Dec. 1982 and Nov. 1983 as 3232, 1707, 3135 and 3132 μM respectively. We adopted the averaged value of 1966 μM. Galy and France-Lanord (1999) also reported a single $[HCO_3^-] = 1421$ μM at downstream (BGP 4) in Aug. 1996.

13. St. Lawrence—Helie et al. (2002) reported the TAlk at Quebec from Jan. 1998 to Apr. 1999 with a discharge-weighted value as 1339 μM. Barth and Veizer (1999) reported a $[HCO_3^-]$ in seven ecosystems of the St. Lawrence River near Cornwall ranging from 1500 to 4000 μM. Cossa and Tremblay (1983) reported a mean TAlk at Quebec as 1432 μM. Livingstone (1963) reported the $[HCO_3^-]$ data to be 100–3839 μM, and their arithmetical mean was 1459 μM. The above data are similar, and we adopted 1339 μM as this value is based on discharge-weight data and is most recent.

14. Pearl River—Guo et al. (2008) determined discharge weighted DIC as 1535 μM. Zhang et al. (1987) also reported $[HCO_3^-]$ in the West, North and East Rivers in Jul. and Aug. 1983 with a discharge-weighted average as 1860 μM. We adopted 1535 μM for the Pearl River as this value is seasonally averaged.

15. Xijiang—Long-term average $[HCO_3^-]$ reported by Chen and He (1999) is 1.8–2.0 mM. Cai et al. (2004) estimated from an estuarine mass balance calculation in the Pearl River estuary that the West River (Xijiang) has DIC = 2.0 mM. Unpublished data by Dai et al. show that the discharge-weighted DIC of one of the West River outlets is 1938 μM. This value is used here. Zhang et al. (1987) reported $[HCO_3^-] = 2182$ μM in the West River in August based on one sample.

16. Mackenzie—Reeder et al. (1972) reported $[HCO_3^-]$ in the whole basin from Jul. to Oct. 1969 as 44–4194 μM with a discharge-weighted value as 1760 μM. Millot et al. (2002) reported $[HCO_3^-]$ as 1674–1949 μM in a high flow season at the mainstream. Gordeev et al. (1996) reported average HCO_3^- concentration in downstream as 1582 μM.

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Telang et al. (1983) reported TAlk in February, March, April, May, October, November and December 1982 as 1920–2240 μM, with a discharge-weighted value as 2051 μM. Here we used 1800 μM as the average TAlk of the river.
17. Columbia—arithmetically averaged [HCO_3^-] in Livingstone (1963) is 1616 μM. Meybeck (1979) reported a value of 1246 μM. We adopted 1246 μM.
18. Ubangi—Probst et al. (1992) reported a mean [HCO_3^-] of 1988 and 1989 as 317 μM.
19. Yukon—Guo et al. (2004) reported DIC at Stevens Village from May to Sep. 2002 as between 1153–1550 μM. The discharge-weighted average value is 1363 μM.
20. Danube—Meybeck (1979) reported [HCO_3^-] for the Danube as 3115 μM.
21. Niger—Tardy et al. (2004) reported an average [HCO_3^-] in 1990–1992 as 299 μM in the upstream area of the Niger, while Boeglin and Probst (1998) gave a similar value based on the same dataset. Martins and Probst (1991) and Martins (1982) reported 562 and 546 μM respectively using the same dataset at Lokoja (downstream site) from May 1980 to May 1981. We adopted the latter (~550 μM) as it is the downstream value.
22. Kolyma—Gordeev et al. (1996) reported an average [HCO_3^-] at a downstream site between 1980 to 1990 as 467 μM. Huh et al. (1998) also reported 310–865 μM in Aug. 1992 and Jul. 1996 in the basin. We adopted 467 μM as the average concentration.
23. Indus—Karim and Veizer (2000) reported HCO_3^- data in summer and winter. Their data from the downstream sta. 20–25, can be averaged to 1658 and 2136 μM respectively. Assuming the river discharge of summer and winter is in the ratio of 8000 to 300 and that the wet season lasts for 5 months and the dry season for 7 months (Karim and Veizer, 2000), we derived a discharge-weighted [HCO_3^-] to be 1681 μM.
24. Gordavari—Subramanian (1979) reported the average [HCO_3^-] of Gordavari in summer of 1977 and winter of 1977 and 1978 as 2156 μM at Rajamundary (a downstream site).
25. Huanghe (Yellow River)—see text.
[a] Amiotte Suchet et al. (2003).
[b] Dai and Trenberth (2002).

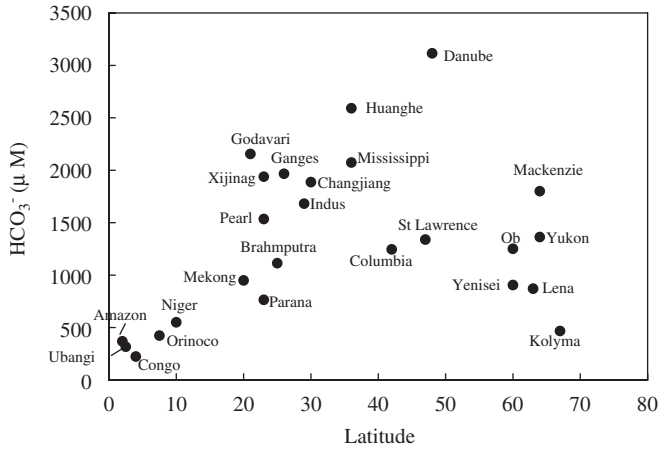

Fig. 1. Latitudinal distribution of river bicarbonate (HCO_3^-) concentrations. Note that an average latitude value for each drainage basin was assigned to a river.

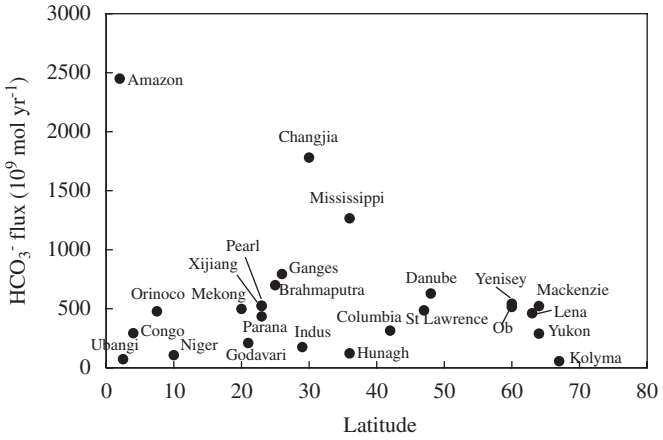

Fig. 3. Latitudinal distribution of total fluxes of riverine bicarbonate.

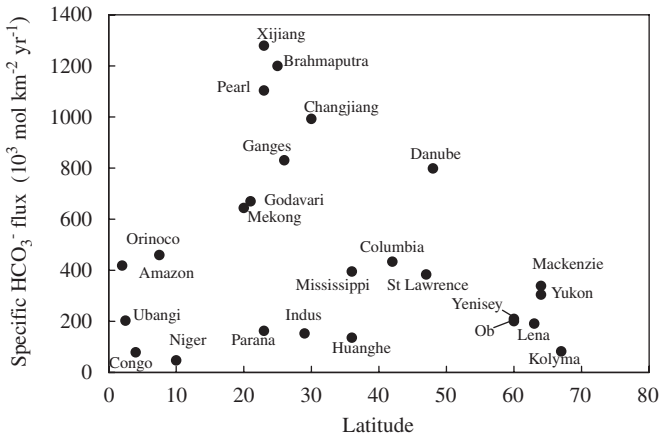

Fig. 2. Latitudinal distribution of specific fluxes of riverine bicarbonate.

collected in the lower reaches of rivers above the estuarine zone. Our database is generally similar to Ludwig et al. (1998) with several updates. Fluxes are calculated by multiplying concentrations (annually averaged if available; for details see Table 1 and a justification of data selection in the table footnotes) from various sources by annual discharges from Dai and Trenberth (2002).

The latitudinal distribution patterns of concentration (μM), annual flux (10^9 mol yr^{-1}) and specific flux normalized to drainage basin area (10^3 mol km^2 yr^{-1}) are presented respectively in Figs. 1–3. To our knowledge, such latitudinal distribution patterns have not been examined before for inorganic carbon. The following major features can be identified: (1) HCO_3^- concentrations are highest in the mid-latitude rivers and lowest in the tropical and subtropical rivers. For example, the Amazon has a low [HCO_3^-] of only 0.37 mM. This is in great contrast to the high average concentrations of 2.6, 1.9, 1.6–1.9 and 2.1 mM respectively in the Huanghe, Changjiang, Pearl and Mississippi rivers. (2) Similarly, bicarbonate specific fluxes are highest in the mid latitude although the maximum shifts somewhat towards the subtropical rivers. The three mid-latitude large rivers, the Changjiang, the Mississippi and the Columbia, have lower specific fluxes relative to the pattern of their concentrations, while the Huanghe has a very low specific HCO_3^- content. (3) As far as the total inorganic carbon flux is concerned, the three largest rivers that carry HCO_3^- to the oceans are the Amazon, the Changjiang and the Mississippi.

The above distribution patterns of HCO_3^- concentration and flux are consistent with the global distribution pattern of continental carbonate rocks. Amiotte Suchet et al. (2003) developed a $1^\circ \times 1^\circ$ resolution global distribution model of continental rock lithology. They simplified rock types into six groups: (1) carbonate rocks (all rocks with more than 50% of carbonate minerals such as limestone), (2) sand and sandstones, (3) shales (such as clays and evaporites), (4) shield rocks such as granites, (5) acid volcanic rocks, and (6) basalts. Their work built upon an earlier work by Meybeck (1986, 1987). In general, weathering rates are highest for carbonate rocks, moderate for basalts and shales, followed by sands and sandstones and acid volcanic rocks, and lowest for shield rocks (Amiotte Suchet et al., 2003).

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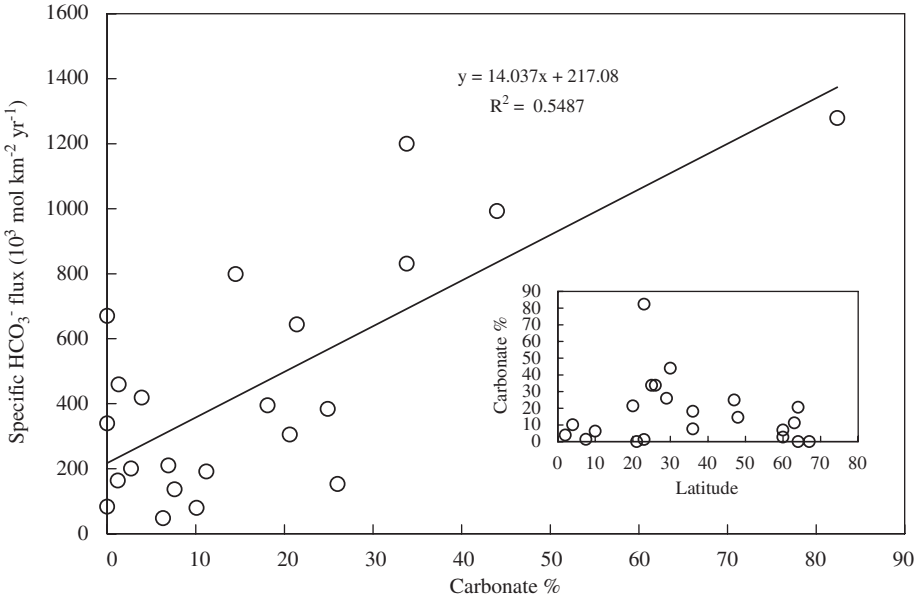

Fig. 4. Relationships between HCO_3^- flux and drainage basin lithology. Lithology data were from Amiotte Suchet et al. (2003).

The latitudinal distributions of land outcroppings of major rock types as presented by Amiotte Suchet et al. (2003) show that carbonate rocks are concentrated in temperate and subtropical areas between 20°N and 50°N (see insert in Fig. 4). Naturally, our river HCO_3^- specific fluxes are well correlated with the percentage of carbonate mineral distribution in their drainage basins as shown in Fig. 4. However, other factors are also important. When a multiple regression technique (LINEST in Excel®) is applied to specific HCO_3^- fluxes with regard to $CaCO_3$%, discharge, and basin area, the r^2 value increases slightly over 0.55 for $CaCO_3$% alone to 0.71 with all three parameters. Similarly, total HCO_3^- flux is significantly correlated with the three parameters ($r^2 = 0.71$, $N = 25$). The correlation equation and its statistics are given below.

River HCO_3^- Flux (10^9 mol yr^{-1}) = 9.864($\pm$3.91)*$CaCO_3$% +0.2870 ($\pm$0.0818)*Discharge (km^3 yr^{-1})+0.0769($\pm$0.0868)*Basin Area (10^3 km^2)+94.12($\pm$163.69) ($r^2 = 0.71$, $N = 25$).

River HCO_3^- concentrations are not significantly correlated with the percentage of carbonate mineral distribution (figure not shown). River HCO_3^- concentration however appears negatively correlated to river discharge (Fig. 5), suggesting that the concentration of a dissolved species is more strongly related to the precipitation and evaporation balance in the drainage basin (Table 1). Although on a global scale, the correlation in Fig. 5 is complex and not strong, the correlations are however very strong for individual rivers (see detailed discussion in Section 3.1 on the Mississippi and Section 3.2 on the Changjiang). For example, the Xijiang, a major branch of the Pearl River, has the highest percent carbonate minerals in its drainage basin and thus the highest specific river HCO_3^- flux. But it only has a moderate HCO_3^- concentration (1.5–1.9 mM) due to a high precipitation (i.e., high runoff in Table 1). In great contrast, the Huanghe basin has a very low percent carbonate content in its basement rocks and thus a low specific HCO_3^- flux. But it has a very high HCO_3^- concentration (2.6 mM or higher) due to the fact that it has a much higher evaporation water loss over precipitation rate in a large part of its river basins (i.e., low runoff in Table 1; also see Section 3.3). A comparison of the HCO_3^- concentration in the Huanghe with that of the Amazon is also interesting. The carbonate mineral content in the basement rocks in the Huanghe drainage basin is

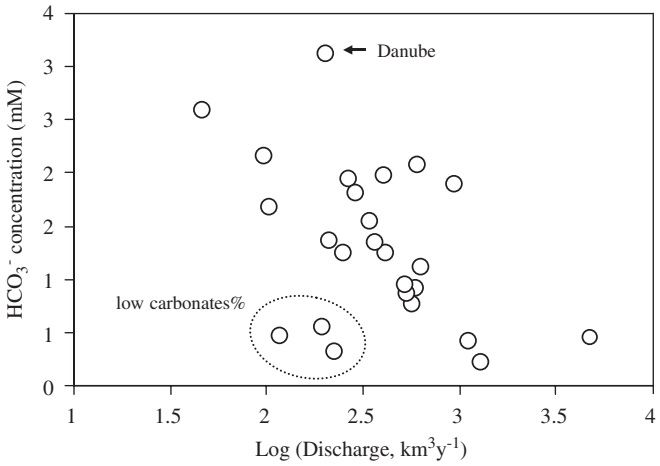

Fig. 5. Correlation between river HCO_3^- concentration and discharge. The high [HCO_3^-] in the Danube may be a result of excess carbonate dissolution in the watershed and river during anthropogenic input of acids.

only twice that of the Amazon, while the river water HCO_3^- content of the former is at least 8 times of the latter; further clear evidence of the dilution and concentration effect. More discussion and data will be presented later on how HCO_3^- concentration is correlated to river discharge for the rivers evaluated in this paper.

However, there are other complications that may contribute to the fact that riverwater bicarbonate concentration, on a global scale, is only weakly correlated to discharge and uncorrelated with the percentage of $CaCO_3$. The relatively simple classification in Amiotte Suchet et al. (2003) defines carbonate rocks as those that contain over 50% of carbonate minerals. A river basin may be classified as having zero or low $CaCO_3$% if none or few of its rocks contain over 50% of carbonate minerals. However, such a basin may indeed contain a significant amount of carbonates that can contribute to the dissolved load. For example, the Huanghe River flows through the Loess Plateau which contains an abundant amount of carbonate-rich glacial dusts and evaporite minerals which presumably contribute to the total effective $CaCO_3$% although the bedrock carbonate mineral content of the Huanghe

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is very low (see discussion in Section 3.3). Therefore, using the classification of Amiotte Suchet et al. (2003), the true carbonate mineral content in the basin rocks and sediments and thus their contribution to the dissolved load may be underestimated.

For the purposes of estimating global average HCO_3^- concentration and flux, we separated the 25 large rivers examined here into three groups. The discharge-weighted average [HCO_3^-] of rivers at $<30^\circ$, 30–60°, and $>60^\circ$ are 0.584, 1.649, and 1.154 mM respectively. We then estimated HCO_3^- fluxes in the world's top 200 rivers in the three latitudinal zones by multiplying the average concentration to the total discharge in each latitudinal zone as 9.68, 10.8 and 2.30 Tmol yr^{-1}, respectively. This scaling to the top 200 rivers also leads to a discharge-averaged global river bicarbonate concentration of 1.1 mM. This is only slightly higher than the earlier estimate of 0.96 mM by Kempe et al. (1991) that was based on the early data of Livingstone (1963). The total HCO_3^- flux delivered by these 200 rivers is thus 22.7 Tmol yr^{-1}. While the freshwater discharge carried by the top 200 rivers in various latitudinal zones is 66%, 26%, and 7.9% respectively for each 30 degree zone from low to high latitude, the percentage of inorganic carbon flux that they carry is substantially different (42.6, 47.3 and 10.1%, respectively). In other words, we conclude that the mid-latitude rivers carry a disproportionately higher dissolved inorganic carbon flux. Finally, as the discharge of these top 200 rivers is only 67% of the global total freshwater discharge (37,288 $km^3\,yr^{-1}$; Table 4 of Dai and Trenberth, 2002), the global total inorganic carbon flux estimated by this approach would be 33.9 Tmol yr^{-1} or 0.407 Pg C yr^{-1} by scaling up with discharge. This estimate is somewhat higher than that (0.33 Pg C yr^{-1}) estimated by Ludwig et al. (1998), but very similar to that (0.38–0.41 Pg C yr^{-1}) cited in Mackenzie and co-workers (Mackenzie et al., 2004; Lerman et al., 2007) and that in Berner et al. (1983); all of which are essentially based on measured Ca^{2+} and Mg^{2+} fluxes.

3. Drainage basin mineralogy, weathering intensity and bicarbonate flux of the four rivers

3.1. The Mississippi River basin

The Mississippi-Atchafalaya River system has a total drainage basin area of 3.2×10^6 km^2; the third largest among the world major rivers (Meade, 1996; Milliman and Meade, 1983; also see Table 1). This river system also ranks sixth or seventh in annual average freshwater discharge (530×10^9 $m^3\,yr^{-1}$ or higher) and fifth in annual sediment discharge (210×10^{12} g yr^{-1}). The drainage basin has a low to moderate content (18%) of carbonate rocks, but is relatively high in silicate rocks (48% of shales and 34% of sands/sandstones and shield rocks) (Amiotte Suchet et al., 2003). This is somewhat surprising considering there is high dissolved HCO_3^- content in the river water. However, specific HCO_3^- flux (or weathering rate) of the Mississippi River is moderate and it agrees well with the global relationship of specific HCO_3^- flux and basin $CaCO_3$ mineral content (Fig. 4). Consequently, we infer that the high HCO_3^- concentration is at least partially a result of evaporative water loss. The fact that the Mississippi River has a relatively low runoff compared to its very large drainage basin area supports this view.

The Mississippi River discharge typically exhibits a seasonal pattern of high flow during winter and spring, decreasing flow in mid-year and lowest flow during late summer and fall. Nutrient concentrations exhibit a seasonal pattern similar to discharge (see Lohrenz et al., 2008). This pattern can be largely explained by a seasonal release of nutrients from the soil in the drainage basins subject to heavy agricultural activity over the last several decades (Goolsby et al., 1999). In contrast to nutrients, TAlk and DIC is negatively correlated with the river discharge, while their fluxes are positively correlated with discharge (Fig. 7 and Cai, 2003). This

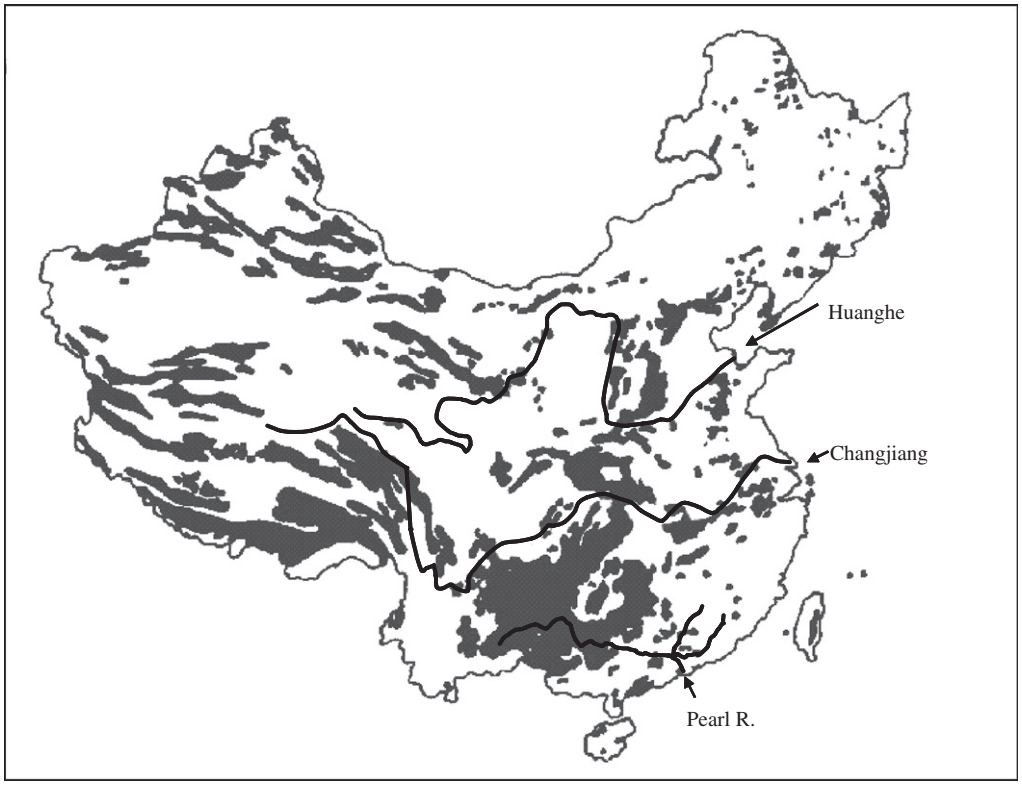

Fig. 6. A carbonate distribution map of the three Chinese river basins (modified from Zhang et al., 1990). Gray color shades indicate carbonate minerals. Dark lines indicate the rivers.

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result may be explained as the products of weathering are diluted in terms of river HCO_3^- concentration while at the same time the weathering rate is enhanced by precipitation in the Mississippi River drainage basin.

We recognize that a strong correlation of the flux against the discharge may represent an autocorrelation because the flux (F) is calculated as the product of the concentration (A) and the discharge (B) and as the variation of B is much greater than A (i.e., in Fig. 7, also see a similar situation for the Changjiang presented later in Fig. 8). However, we feel that there are good geochemical reasons as argued in this paper, that a positive correlation between HCO_3^- flux and river discharge is valid. The solute discharge flux is widely used in the literature as an indicator of chemical weathering rate (White and Blum, 1995; Gaillardet et al., 1999). We also wish to point out that while mathematically the flux is calculated with $A*B$, it is only a method of calculating the flux and it does not necessarily indicate that the flux is determined by the discharge. Quite the contrary, it is the concentration that is determined by both the flux and the discharge, as is demonstrated in this paper. In an extreme example, if one assumes a constant source material flux and a variable discharge, then, the concentration will show an exact anti-correlation with the discharge. In this case, the flux is constant and has no correlation with the discharge, even though the flux still equals $A*B$. Therefore, the conclusion derived in this paper based on an examination of flux and discharge relationship is meaningful, i.e., under a specific drainage basin mineralogy the wetness of a basin climate condition promotes the weathering rate. Thus while the concentration of HCO_3^- decreases with increasing discharge, the overall flux still increases.

Inorganic carbon flux in the Mississippi River and tributaries has increased over the past half century (Cai, 2003; Raymond and Cole, 2003). Between 1996 and 2000, average DIC flux was estimated to be 1.12 Tmol yr^{-1} (or 13.5 Tg C yr^{-1}) (Cai, 2003). This flux is 16% higher than the earlier estimates of 11.6 Tg C yr^{-1} (Kempe, 1982; Kempe et al., 1991) that were based on the data of Livingstone (1963). For the periods of 1964–2000, Cai (2003) found that TAlk flux exhibited an increasing trend with average fluxes of 0.828, 0.920, 0.996 and 1.09×10^{12} mol yr^{-1} respectively for each decade. The above calculations are for the Mississippi River discharge alone, and estimates are roughly 50% higher when the Atchafalaya River is included in the total flux (Raymond and Cole, 2003).

Two factors may contribute to the increase in inorganic carbon flux. The first is an increase in river discharge rate (Raymond and Cole, 2003). The second factor is a potential increase in the weathering rate. Land use activities may contribute to this effect. For example, use of N-fertilizer could increase the amount of proton delivery to the soil (i.e., via reaction $NH_4^+ + O_2 \rightarrow NO_3 + H^+$), which may promote carbonate dissolution. Such a land-use linkage was made by Raymond and Cole (2003). Recently, Oh and Raymond (2006) showed that the agriculture practice of liming (i.e., applying $CaCO_3$ to neutralize acid soil) in a Mississippi basin may be an important reason for HCO_3^- export.

Unlike nutrients and organic matter, direct measurements of inorganic carbon species in the lower Mississippi River were not conducted until recently. The carbonate systems of the Mississippi and Atchafalaya Rivers are very similar and both have high pCO_2 on the order of 1000–2000 μatm (Cai, 2003; Dagg et al., 2005; Cai and Lohrenz, 2007).

3.2. The Changjiang River basin

The Changjiang originates in the Tibetan Plateau and is the longest and largest river in China (6380 km long, ranked third in the world; 960×10^9 m^3 yr^{-1} in discharge, ranked fourth in the world). Before entering the subtropical plains in central and eastern China, it drains the Yun-Gui Plateau, Sichuan Basin and the Three-Gorges region, where the basement rocks are composed of evaporites, continental deposits, and are abundant in marine carbonates (Chen et al., 2002). The river receives pollutants from megacities such as Shanghai before emptying into the East China Sea (ECS). The total area of the drainage basin is 1.81×10^6 km^2, or nearly 20% of the total area of China, and it alone sustains a population of 420 million. In the Changjiang basin, annual precipitation (1253 mm yr^{-1}) greatly exceeds the evaporation loss (801 mm yr^{-1}) (Kondoh et al., 2004).

Because of the weathering of the abundant carbonate rocks in the drainage basin, Ca^{2+} (~1.5 mM), Mg^{2+} (~0.6 mM) and HCO_3^- (~1.9 mM) concentrations are rather high in the river water, while pH is slightly basic (~7.9). These values are quite high compared to the global average concentration of Ca^{2+}, Mg^{2+} and HCO_3^- (respectively, of only 0.2, 0.1 and 0.5 mM; Meybeck and Helmer, 1989). In the Changjiang, the lowest concentrations of these ions occur in April–June, rather than during peak discharge (July) (see Fig. 8 for HCO_3^-). Also the lowest concentrations in flood seasons are within 50% of the highest concentrations in dry seasons (Fig. 8). This is noteworthy as the five- or six-fold increase in water discharge in summer would be expected to greatly dilute these major ion concentrations. Therefore, significant sources of these ions in the river basin would be needed in order to compensate for dilution during the peak flooding season. The most likely explanation for the mismatch of the lowest concentrations and the peak discharge, is that the flood season of the limestone-abundant upper region (in July–August) lags the flood season of the limestone-poor central and lower regions (in May–June) (Zhai et al., 2007). In addition to the probably enhanced weathering rate during flood seasons, *in situ* dissolution of calcite particles may have also buffered the HCO_3^- concentration in the river water as suspended detrital calcite in the river in the flooding season reaches 6–55 times that in the dry season (Gan, 1985; Shi et al., 1985; Chen et al., 2008). Furthermore, the dissolution of pedogenic calcite formed in soils during the dry season, which is later brought to the river during flood seasons, could be a possible cause of the less-than-expected reduction in Ca^{2+}, Mg^{2+} and HCO_3^- concentrations at the beginning of the flooding season (Chen et al., 2002).

pCO_2 of the river water is supersaturated year-round with the highest values observed in summer (Chen et al., 2008; Zhai et al., 2007), indicating decomposition of terrestrial organic matter in the river. Discharge of high pCO_2 groundwater may explain the secondary peak in the dry season. Both calcite and dolomite are undersaturated throughout the year, but not in July and August when water temperatures are the highest (Chen et al., 2008). Coal burning and acid deposition in recent years may have suppressed pH, causing carbonate ion concentrations to remain low. In other words, calcite and dolomite tend to dissolve. Acidification also makes pCO_2 higher because of the thermodynamics of the carbonate system.

The total dissolved solid (i.e., total ionic) concentration in the Changjiang (~200 mg L^{-1}; Chen et al., 2008) show slightly lower values in June and July, due to dilution by the larger water flux. Even so, the values are still higher than the global average by a factor of two (Meybeck and Helmer, 1989). On the other hand, the total suspended solid (TSS) concentration is the highest in summer, evidently due to a higher physical denudation rate and stronger currents in the warm, rainy season (see Fig. 5 of Chen et al., 2008). The fluxes of HCO_3^- and TSS seem to be higher in summer during the peak water flow (Chen et al., 2008).

Historical data for the Changjiang indicate that anthropogenic effects such as acid rain and fertilizer use have led to increased concentrations of sulfate and nitrate, while no significant trend

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for pH or HCO_3^- is evident (Chen et al., 2002, 2008). This differs from the situation in many North American and European rivers where elevated sulfate concentrations are often accompanied by decreases in pH and HCO_3^- (Stoddard et al., 1999). This may be a result of neutralization by carbonate rocks which are rich in many upstream and mid-stream regions in the Changjiang basin and accounts for the relatively high concentrations of Ca^{2+}, Mg^{2+} and HCO_3^-. The annual HCO_3^- flux amounts to almost 2.0 Tmol, which is among the largest in the world.

3.3. The Pearl River basin

The Pearl River is the largest river in southern China with a water discharge of $\sim 330 \times 10^9\,m^3\,yr^{-1}$ and a sediment delivery of $\sim 80 \times 10^6\,t\,yr^{-1}$ (Zhao, 1990; Tian, 1994; Zhang, 1999). It has a catchment area of $0.45 \times 10^6\,km^2$ and stretches for 2200 km. It is a subtropical river with its entire drainage basin located south of 27°N. The Pearl River system has three tributaries. Its largest tributary (contributes 70% of the total discharge) is located in its western basin and is known as the Xijiang (or Si Kiang in some literature, meaning the West River). The tributary located in its north basin is known as the Beijiang (North River), and the one in the east basin, the Dongjiang (East River). Annual precipitation ($1426\,mm\,yr^{-1}$) exceeds the evaporation loss ($1052\,mm\,yr^{-1}$) (Kondoh et al., 2004). It is estimated that about 80% of the freshwater discharge occurs in the wet season (April–September) (Zhao, 1990).

In the Xijiang drainage basin, carbonates are abundant with a "karst" landscape (Zhao, 1990; Zhang et al., 1999; Chen and He, 1999). The basin has an unusually high carbonate mineral content (80%). The Xijiang is listed here as a separate river in order to examine the relationship between HCO_3^- flux and basin carbonate mineral content. Another reason for distinguishing the Xijiang is that it only mixes with the other two rivers in the estuarine zone. Furthermore, the river basin area is warm and wet with high precipitation which causes a high weathering rate based on arguments presented here and elsewhere (Guo et al., 2008). Indeed, the Xijiang has the highest specific HCO_3 flux of all large rivers. Even with its high runoff rate, TAlk and major ions in the Xijiang are relatively high. The annual mean $[HCO_3^-]$ is 1.8–2.0 mM, and the total ion concentration is 111–123 $mg\,L^{-1}$ in the Xijiang (based on monitoring data between 1959 and 1984 from Chen and He, 1999).

In the eastern basin, granites are abundant. The East River thus has relatively low dissolved solids and TAlk ($[HCO_3^-] = 0.62$ mM, total ion content = 67.4 $mg\,L^{-1}$; Chen and He, 1999), while the North River is in the intermediate range ($[HCO_3^-] = 1.56$ mM, total ion content = 95.1 $mg\,L^{-1}$, Chen and He, 1999; Zhang et al., 1999). An increase in total ion content and a decrease in TAlk of the water were reported due to acidification in recent decades (Chen and He, 1999; Zhang and Chen, 2002).

Guo et al. (2008) determined a discharge-weighted DIC value of 1.535 mM and a flux of $527 \times 10^9\,mol\,yr^{-1}$. The freshwater discharge and the DIC flux have significant seasonal variation, i.e. discharge in the flood season is ~10 times of that in low flow season. Consequently, the DIC flux in flood seasons is 8 times higher than that in dry seasons, indicating again that the weathering rate is promoted by wet climate conditions.

3.4. The Huanghe basin

The Huanghe (Yellow River) ranks low in the world's large rivers in terms of its water discharge (average in 1919–1995 is $58 \times 10^9\,m^3\,yr^{-1}$; Chen et al., 2005, 2006), but it ranks among the top one or two world rivers in terms of suspended sediment load (average in 1950s–1970s is $1.6 \times 10^{15}\,g\,yr^{-1}$) with only a medium sized drainage basin area ($0.75 \times 10^6\,km^2$, Chen et al., 2005, 2006). The upper watershed, also from the Qinghai-Tibet Plateau, supplied 60% of the source water, but only 10% of the sediment (Zhang et al., 1995). In the Huanghe basin, the overall annual precipitation ($492\,mm\,yr^{-1}$) is less than the evaporation loss of water ($503\,mm\,yr^{-1}$) (Kondoh et al., 2004). However, in the majority of the basin, the evaporation ($700–1400\,mm\,yr^{-1}$) greatly exceeds the precipitation ($200–700\,mm\,yr^{-1}$) (Chen et al., 2006). Most of the voluminous suspended sediments come from the Loess Plateau (average thickness is 130–180 m) located in the mid reach of the river (which covers 40% of the entire drainage basin) (Zhang et al., 1995). The glacial loess deposits in northern China are some of the largest and thickest in the world and were formed by dust fall, following a major climate shift in the Early Pleistocene about 2.5 Ma ago and throughout the entire Quaternary (Chen et al., 2005). In addition to loess, outcrops of Archean to Tertiary granites and metamorphic rocks can be found in the Huanghe drainage basin (Zhang et al., 1995).

While the coverage of carbonate rocks as defined by Amiotte Suchet et al. (2003) (rocks containing more than 50% $CaCO_3$ minerals) is low (only 7.6%; also see Fig. 6), loess contains between 10% and 20% carbonates (Zhang et al., 1995). Assuming an average value of 15% carbonates in loess sediments and that loess covers 40% of the drainage basin, the average carbonates from this part alone is 6% of the total basin sediment which is comparable to the carbonate rocks, thus effectively increasing the total $CaCO_3$ content to 13%. In addition, newly deposited glaciated material such as loess, with its unconsolidated structure, must be more prone to weathering processes than well-weathered bedrocks, and this factor would also increase weathering flux. This example illustrates further the uncertainty of predicting HCO_3^- flux using the bedrock content of carbonates. It also emphasizes that besides lithology, surficial deposits and other influences (see below) can be very important and can, occasionally, be primary determining factors in controlling carbonate concentrations in river waters.

The Huanghe is distinct from the other three rivers discussed here and most of the other world's large rivers in which the dissolution of evaporite salts such as NaCl and gypsum substantially contributes to the total dissolved salt. The Huanghe is one of the few large rivers whose $[Na^+]$ (~2 mM) exceeds $[Ca^{2+}]$ (~1.3 mM) as the most abundant cation. Another important feature of the Huanghe River basin is that water evaporation exceeds precipitation in most of its drainage basin area (average precipitation is 476 mm and evaporation is 1100 mm, Chen et al., 2006). This concentration effect is a major reason for the greatly elevated Na^+, Ca^{2+}, K^+, SO_4^- and Cl^- concentrations to 10–20 times above the world average and HCO_3^- concentrations to among the highest in the world rivers.

Among the four rivers examined here, the Huanghe experiences the most intense anthropogenic pressure. It is evident that intensive agriculture/irrigation activities in the drainage basin, which cycle the leaching water back to the river many times over, have significantly increased the major ion concentrations (Chen et al., 2006). Such activities have continued for the past two millennia and have intensified in the past six decades. In addition, some 20 large dams and many smaller ones built in recent decades, have greatly reduced the delivery of sands to the coastal zone. Sediment discharge has been reduced from $1.6 \times 10^{15}\,g\,yr^{-1}$ (1950s–1970s) to as low as $0.8 \times 10^{15}\,g\,yr^{-1}$ in the 1980s (Chen et al., 2006). Water discharge was also reduced greatly resulting in a complete reduction in flow in the lower river for extended periods each year in the 1990s. In recent years, sand and water

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discharges are regulated by management plans. There is evidence to suggest that the alkalinity increase in the recent two decades in the lower river is related to this reduction in water discharge (L. Zhang, unpub. data).

Concentrations of HCO_3^- in the Huanghe have been determined over the years by several researchers. Li and Zhang (2003a) reported that the HCO_3^- concentration varied from 1.62 to 4.48 mM during Feb. 2000 to Aug. 2001, but only three of their samples were collected from a downstream site (Kenli). These three values were 1.95, 3.53 and 3.58 mM in Aug, Feb, and Mar, 2001, respectively. Based on the knowledge that discharge in the wet season (August) is about 3 times of that of the dry season (Feb) and that the duration of the wet season is about 4 months compared to about 8 months for the dry season (Chen et al., 2005), we calculated that the discharge-weighted [HCO_3^-] is 2.59 mM and its flux is 122×10^9 mol yr^{-1}. If we use the average downstream discharge in August, February and March (http://sqqx.hydroinfo.gov.cn/websq/river_cx) to estimate the discharge-weighted [HCO_3^-], we derive a value of 2.57 mM, which is very similar to the above estimation. Other data also support our estimates. Wu et al. (2005) reported the upstream TAlk as 0.891–3.82 mM in May 1999 and May 2000; Zhang et al. (1995) reported the HCO_3^- in Aug. 1986 of 3.22 mM at Lijin (also a downstream site). Cauwet and Mackenzie (1993) measured DIC values in the estuarine zone, and their DIC was linearly correlated with salinity, except for the low salinity zone where chemical removal occurred due to carbonate supersaturation in the early estuarine mixing zone. When extrapolating their high salinity DIC values to zero salinity, the result is ~2.55 mM in May 1985 (a relatively dry season).

4. Synthesis and comparison

For the 25 large rivers listed in Table 1, the Amazon basin has the lowest carbonate content (3.9%) and the Xijiang has the highest (82%). The median is 11.2% and the arithmetical mean is 16.9%. However, the drainage basin weighted mean value is only 12.6%, apparently as a result of the Amazon's predominant share. For the four rivers discussed in this paper, their basin mineral content is very different from each other. The Pearl River basin has the highest mineral carbonate content with its west branch watershed comprised of nearly exclusively carbonate karst. The Changjiang ranks second in its basin mineral carbonate content (44%) among the largest rivers. The Huanghe basin is at the opposite extreme with a very low fraction of carbonate rocks (<8%), but containing a readily available source of carbonates from surficial loess deposits. The Mississippi River basin is in the middle (18%). In this paper, it has been shown that specific carbonate fluxes in rivers, but not river HCO_3^- concentrations, are significantly correlated with the carbonate rock contents in the drainage basins. It also shows that other factors such as surficial deposits, net precipitation vs. evaporation, and agriculture activities can significantly affect and occasionally dominate river HCO_3^- flux.

The negative and nearly linear correlation between TAlk and discharge in the Mississippi River (Cai, 2003) and largely similar patterns in the three Chinese rivers (Chen et al., 2008; Guo et al., 2008; Cai et al., 2004) are in great contrast to the nutrient concentration patterns, which increase greatly with river runoff (Lohrenz et al., 1997, 2008). This suggests that the carbonate weathering rate in a drainage basin is relatively constant when

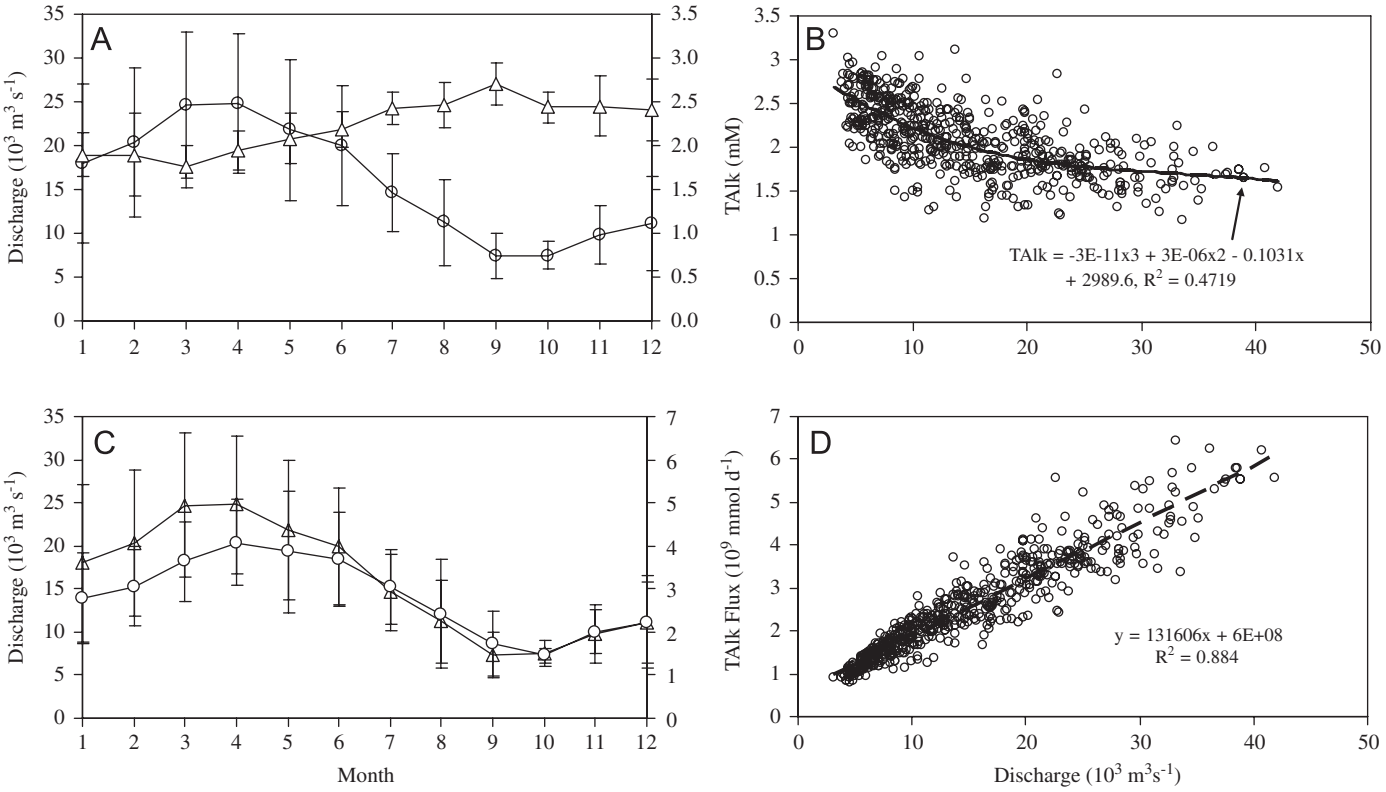

Fig. 7. Time series of the Mississippi River discharge and TAlk values (A) and TAlk flux (B) (data period: 1990s) as well as the correlation between TAlk and discharge (data period: 1964–2000) (C), and the correlation of TAlk flux with discharge (data period: 1964–2000) (D) at St. Francisville (USGS Station#: 07373420), LA. Data were from USGS web page, "Water-Quality Data for the Nation" (http://waterdata.usgs.gov/nwis/qw). In A and B, all data were averaged to monthly means with standard deviations. In Fig. 7C, TAlk unit is in mM in the graph but is in μM in the correlation equations. In plot C, a third-order polynomial equation provided a slightly better fit than a linear correlation (not shown).

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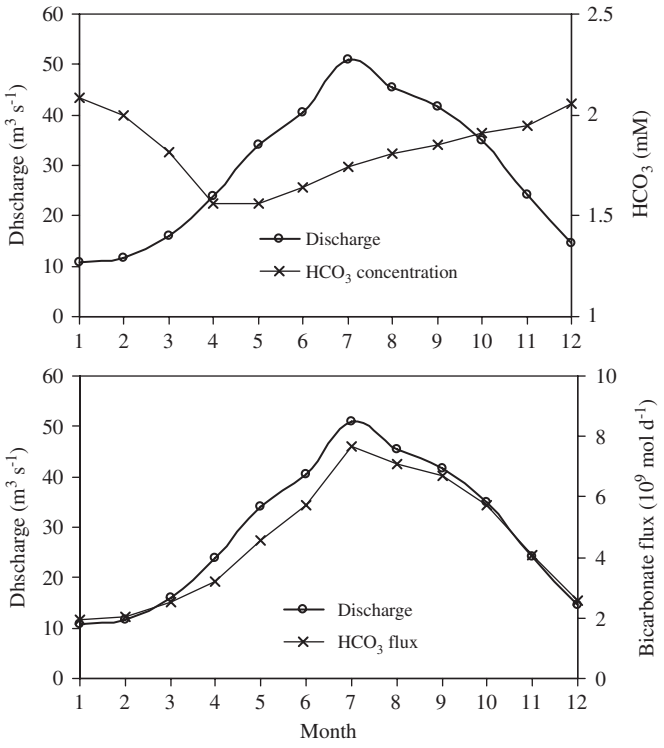

Fig. 8. Time series of discharge and HCO_3^- concentration in the Changjiang at Datong station (a major downstream hydrological station). The data were from Liu et al. (2002).

compared with mobilization of nutrients. Variations in the river HCO_3^- concentration or TAlk appear to reflect a dilution of the weathering-derived sources of HCO_3^- in the drainage basin. In all four rivers, HCO_3^- concentration and TAlk are lowest during or around peak river discharge seasons and highest during low flow seasons (Cai, 2003; Chen et al., 2008; Guo et al., 2008). However, in all four rivers, total river fluxes and specific fluxes are positively correlated with the river discharge. Figs. 7 and 8 illustrate this for the Mississippi and Changjiang, respectively. Also, in the Pearl River basin, weathering rate in the peak discharge season is 8 times more than that in the lowest flow season (Guo et al., 2008). Thus, in conclusion, higher discharge in river drainage basins in wet seasons most likely promotes chemical weathering rate. In addition, it is interesting to note that the timing of the wet seasons differs for each river basin and has a south-to-north delay in China. The wet season occurs generally between April and October in the Pearl River basin. The peak discharge season for the Changjiang is between June and August. The peak discharge season lags until August and September for the Huanghe. The peak discharge season for the Mississippi generally occurs in late winter or spring, while it has its lowest flow in summer or fall. The strong correlation between specific HCO_3^- flux and discharge in all four rivers with different discharge seasonality thus provides further support that precipitation in the drainage basin enhances weathering rate.

The very high HCO_3^- concentrations in the Huanghe and Mississippi River basins should not be interpreted mainly as an indication of high weathering rates of carbonate rocks in these basins as they do not contain high carbonate-containing source rocks, nor should they be construed as evidence of strong silicate weathering. The GEM CO_2 model (Amiotte Suchet and Probst, 1995; Amiotte Suchet et al., 2003) shows that the weathering rate of silicate rocks can be 15 times lower than that of carbonates. GEM CO_2 model was developed based on small monolithogenic basins. The very high HCO_3^- concentrations in the Huanghe and Mississippi basins, despite low carbonate-containing source rocks, could be misinterpreted as evidence that in these large mid-latitude basins, the difference in weathering rates of carbonate vs. silicates is small and weathering supplies of HCO_3^- are mainly from the silicates. It could be argued that the large content of shale (43%) in the Mississippi River basin is at least partially responsible for the high HCO_3^- content as shales can contain variable amounts of carbonates (Amiotte Suchet et al., 2003). Alternatively, intense weathering of carbonate-containing loess could explain the extremely high HCO_3^- in the Huanghe. However, specific HCO_3^- fluxes are relatively low in these two river basins. Thus for both river basins, and particularly for the Huanghe, excessive water loss due to evaporation appears to be the most important reason for the relatively high alkalinity. In contrast, while the specific HCO_3^- fluxes in the Xijiang basin are extremely high, the HCO_3^- concentration of the Xijiang is only moderately high due to high precipitation and runoff in the area.

High pCO_2 levels have been observed in the four rivers as well as in other rivers, and have been attributed to upstream microbial activities and/or inputs from groundwater (Kempe et al., 1991; Cai, 2003; Zhai et al., 2005, 2007; Dai et al., 2006). pCO_2 in all four rivers examined here are relatively high ($>1000\,\mu$atm), but much less than the Amazon River which has a high pCO_2 of up to 10,000 μatm (Richey et al., 2002). High pCO_2 of some small coastal rivers, for example the Satilla River in Georgia, USA, have been attributed to low pH due to high humic acid concentrations (Cai and Wang, 1998). A major difference between the four rivers in this study and the Amazon River is the large difference in carbonate buffer capacity. The four rivers discussed here have high buffering capacity due to high alkalinity (thus high pH and intermediate pCO_2) while the Amazon River has a low buffering capacity due to low alkalinity (thus relatively low pH but extremely high pCO_2). Therefore, carbonate buffering capacity is an important influencing factor on riverine/estuarine CO_2 outgassing, although the major CO_2 flux supporting mechanism in Amazon River (anaerobically methanogenesis, Richey et al., 1988) is different from aerobic biogeochemical processes in the Pearl River Estuary and the Changjiang Estuary (Zhai et al., 2005, 2007; Dai et al., 2006). CO_2 degassing in the Amazon River may became the most important mechanism to reduce its DIC level to a mere 0.37 mM in its lower section, while degassing of CO_2 must be only a small to moderate process in the four rivers examined here, except for some highly polluted sections of the rivers such as upstream in the Pearl River Estuary (Zhai et al., 2005; Dai et al., 2006).

The drainage basin areas of all the four rivers discussed here are well-cultivated with economical crops. As a result of fertilizer usage, nitrate concentrations are high in all these rivers, and phosphate can be a limiting nutrient in the estuaries (Zhang, 1999; Edmond et al., 1985; Cai et al., 2004). The Pearl River is a large subtropical river with its low river sections located in a highly populated and recently industrialized area. It therefore differs from the large temperate rivers, the Changjiang and the Mississippi River, which are located in heavily populated temperate areas, and tropical rivers such as the Amazon and the Zaire that are less influenced by nutrients introduced by anthropogenic development. Further comparative studies of these rivers will provide insights as to how various rivers behave naturally with different characteristics and how they have responded to human-induced environmental changes and will respond to future anthropogenic influences.

Acknowledgment

The paper was initiated when WJC was a visiting professor at Xiamen University during the summer of 2006 and 2007. WJC

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and SEL would like to acknowledge the support of NASA (NNG05GD22G and NNS04AB84H) and NSF (OCE-0752110 and OCE-0752254) for our research on the influence of larger river systems on coastal ocean carbon cycling. CTAC acknowledges financial support from the National Science Council of Taiwan (NSC 95-2621-Z-110-005). PJH and KDY acknowledge the support from the University Grants Council of Hong Kong for the Area of Excellence project AoE/P-04/04. KDY acknowledges the support from NSFC 40676074. This work was also supported by the CAS/SAFEA International Partnership Program for Creative Research Teams.

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