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The impacts of '05.6' extreme flood event on riverine carbon fluxes in Xijiang River

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An extreme flood event with a frequency of nearly 200 year occurred in June of 2005 in the Xijiang River, the main trunk stream of the Zhujiang River. Samples were systematically collected during the flood event, and water quality parameters, including total suspended sediment (TSS), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) were analyzed, and riverine carbon concentrations associated with its changing pattern through the flood process were discussed. These parameters reflect the changes in basin surface flow and subsurface flow during the flood. This flood event influenced annual flux estimations of POC, DOC, and DIC to great extents. Based on carbon flux estimations for the year 2005 and the flood event (June 21—28) in the Xijiang River, it was found that DIC, DOC, and POC fluxes during '05.6' flood event are 1.52×10^6 g.km^{-2}.a^{-1}, 0.24×10^6 g.km^{-2}.a^{-1}, and 0.54×10^6 g.km^{-2}.a^{-1}, and account for 14.87%, 24.75% and 44.89% of the annual fluxes in 2005, respectively. The results suggested that carbon exports during extreme flood events had great contributions to the total carbon fluxes and composition of various carbon components, being important for accurate estimates of annual carbon fluxes in rivers with frequent floods.

Xijiang River, flood, riverine carbon flux

Carbon cycling is an important component of studies of global change. In global carbon cycling system, the export processes by rivers represent a major linkage between terrestrial and ocean systems, the two important carbon reservoirs. Although riverine carbon flux from land to ocean accounts for a minor part of the global carbon cycling, it is significant and cannot be neglected[1−3]. Asian rivers play especially important roles in global riverine carbon exports[4]. Due to lack of data, however, many large Asian rivers, such as the Zhujiang River and the Mekong River, are not included in the global carbon cycling budget. Recently, some researchers have carried out the studies on the riverine biogeochemistry and carbon transport of the Zhujiang River[5−10], and provided a first estimation for its contribution. However, due to large seasonal change in hydrological aspects of the river and low sampling frequency, the results are rather indefinite. Similarly, there is a large discrepancy between different researchers[4,11−13] in estimation of the riverine carbon fluxes for the world's major rivers. One of important factors is the large seasonal variation of water discharge, sediment and water chemistry for most rivers. For example, in the Zhujiang River Basin, 90% of the total annual sediment is transported during the flood period from April to September, and in Garonne Basin, 50% of the total annual sediment is transported in the flood period around two weeks[14]. There are some extreme examples in the North America basins, where more than half of the total annual sediment is transported in several flood events or even a single flood event[15]. Hence, great attention should be paid to the hydrological processes and material transports during

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flood periods. Currently, there are little detailed studies on these aspects, especially on carbon transport fluxes during extreme flood events for many world major rivers[3,13,16−21] owing to great occasionalities of the occurrence. This paper presents the carbon transport fluxes of the Xijiang River during the extreme flood in June of 2005, the '05.6' flood, in the Zhujiang River Basin, including TSS, DIC, DOC, and POC. Based on annual monitoring work, the influence of this event on the annual carbon fluxes has been evaluated, which could provide new dataset for a more accurate estimation of the carbon flux budget in Zhujiang River, and could be of some help for estimating riverine carbon fluxes of other rivers with frequent floods.

1 The '05.6' flood event

The Zhujiang River is the second largest river in China after the Yangtze River in terms of annual water discharge, and is one of the major contributors of dissolved materials and sediment to South China Sea. The Xijiang River is the main of the Zhujiang River, accounting for 77.9% of the total drainage of the Zhujiang River catchment. It passes entirely through subtropical to tropical monsoon climate zones. Due to the large drainage area, intense rainfall, quick inflow from mountainous and hilly areas in the upper reaches, floods with high peak flow and large water discharge frequently occurred with continuous rainfall in the river catchment. Based on historical database, floods in the Xijiang River normally occur in June, July and August, with water discharge accounting for 50%—60% of the annual water discharge.

The hydrological data in 2005 indicated that water discharge less than 4000 m^3/s was observed in the period of January to April with small variations. Since April, water discharge began to show an increasing trend. A number of small floods occurred in May and mid June. The extreme flood event '05.6' just occurred following a small flood. The daily water discharge in 2005 at the Gaoyao Hydrometric Station in the lower Xijiang River is shown in Figure 1, and a maximal discharge of 54900 m^3/s was monitored during this flood (the historical hydrological record is 52600 m^3/s in 1998) with an occurring frequency of near 200 years.

2 Sample collection and laboratory analysis

2.1 Sample collection

The samples used in this study were collected at the Gaoyao Hydrometric Station transect in the lower Xijiang River. Eleven flood samples were collected from 22 to 28 June, and monthly samples were collected from December of 2004 to December of 2005. All the samples were collected at 1m under water surface on the central line of the river.

On the sampling day, samples collected were filtered by vacuum filtration through two pieces of Whatman GF/F filter papers that were pre-weighed and preheated at 450℃ for 6 h. One filter paper was weighed to calcu-

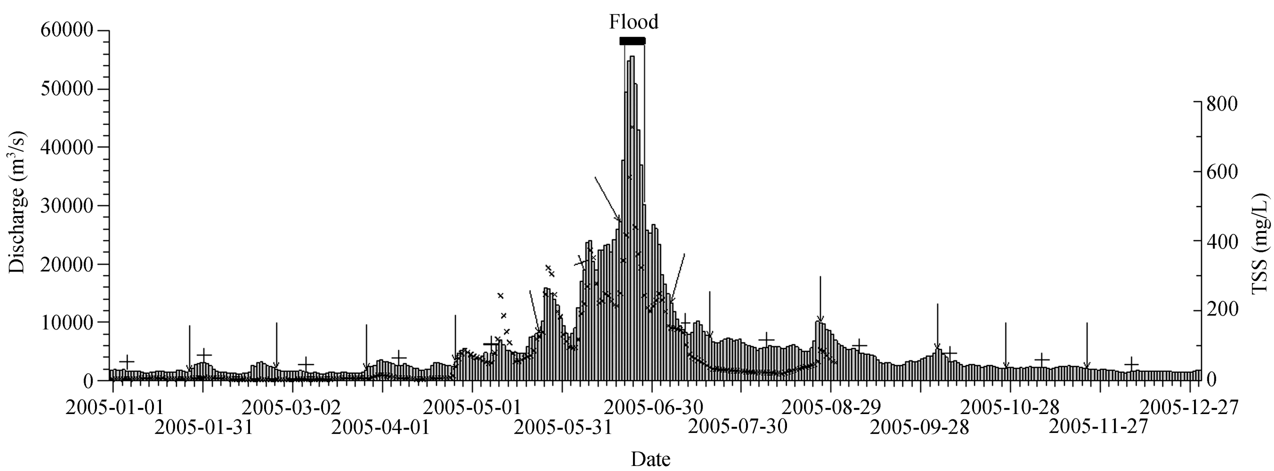

Figure 1 Daily water discharge in 2005 at the Gaoyao Hydrometric Station of the Xijiang River. + Marks sampling date; arrow indicates the box allocation range of the sample value; ×, daily mean TSS value in the corresponding date. "Flood" marks the period of the event from June 21—28, the bar underneath marks the sampling period on the flood.

late TSS after being dried at 103℃ for 24 h and the other was kept in plastic bag for further POC analysis after being dried at 50℃ for 24 h. Filtrates were acidified with concentrated HNO_3 until pH values became less than 2 and kept in 150 mL brown glass bottles in the refrigerator for further DOC analysis. Before filling, the glass bottles were immersed in acid solution for 24 h and rinsed with pure water for several times.

2.2 Sample analysis

HCO_3 was titrated with 0.01mmol HCl within 24 h after sampling. Each sample was repeated for 2 or 3 times and the analysis error was less than 5%.

TSS was calculated by weight difference before and after filtering. POC was analyzed by Perkin Elmer-2400 II (Elemental Analyzer CHNS/O) with analytical errors less than 0.3%. DOC was analyzed using TOC analyzer (Shimadzu TOC-Vwp) in the State Key Laboratory for Environmental Simulation and Pollution Control at Tsinghua University with an analytical error less than 2%.

3 Results and discussion

Riverine DIC is composed of HCO_3^-, CO_3^{2-}, and dissolved CO_2. Based on historical monitoring data at the Gaoyao Hydrometric Station (1987—1996), CO_3^{2-} cannot be detected in the Xijiang River, and the concentration of dissolved CO_2 is in the range of 0.19—2.17 mg/L with the mean of 1.40 mg/L, and the concentration of HCO_3^- is in the range of 43—158 mg/L with the mean of 114 mg/L. Hence, HCO_3^- is the major component of DIC in the Xijiang River. The Xijiang River water pH value during this flood event is within the range of 6.7—7.4[22], which is close to the multiyear range of 6.7—8.3. Therefore, HCO_3^- is the overwhelmingly dominant component for DIC in both normal circumstances and flood events in the Xijiang River. To make comparisons of the data with previous studies easier, HCO_3^- is used for an approximation of DIC. Table 1 shows the results of DIC (HCO_3^-), TSS, DOC, and POC of flood samples. In order to facilitate discussion further, monthly samples results and daily water discharge during the period of December, 2004 to December, 2005 are also presented in Table 1 and Figure 1.

3.1 Characteristics of TSS, DIC (HCO_3^-), DOC and POC during '05.6' flood event

TSS, DIC (HCO_3^-), DOC, and POC show drastic

Table 1 DIC (HCO_3^-), TSS, DOC and POC concentrations during '05.6' flood event and the period of December of 2004 to December of 2005

Sample	Date	Discharge (m^3/s)	TSS (mg/L)	HCO_3^- (mg/L)	DOC (mg/L)	POC (mg/L)
GY0412	2004-12-10	2111	–	111.47	1.84	–
GY0501	2005-01-06	1640	7.28	112.66	2.27	0.22
GY0502	2005-02-01	2520	12.69	113.21	1.67	0.29
GY0503	2005-03-07	1520	6.72	87.68	1.58	0.18
GY0504	2005-04-07	2972	9.50	89.32	1.70	0.27
GY0505	2005-05-08	7185	52.35	108.42	1.65	0.95
GY0506	2005-06-08	25933	205.37	82.35	1.88	3.44
F22.1	2005-06-22	49300	360.77	88.45	4.51	6.60
F22.2	2005-06-22	51800	802.02	86.62	3.24	13.31
F23.1	2005-06-23	54600	502.33	81.13	1.97	7.13
F23.2	2005-06-23	55000	380.55	76.86	2.12	5.29
F24.1	2005-06-24	51700	554.86	76.25	3.16	8.32
F24.2	2005-06-24	50500	581.14	86.01	2.66	8.54
F25.1	2005-06-25	47950	319.06	90.28	4.27	4.28
F25.2	2005-06-25	45400	307.47	92.11	3.10	4.37
F27.1	2005-06-27	33800	235.80	93.33	1.49	2.97
F28.1	2005-06-28	27900	195.64	96.38	1.59	3.09
F28.2	2005-06-28	27200	161.32	97.60	1.67	2.44
GY0507	2005-07-12	10746	116.47	114.22	2.07	1.70
GY0508	2005-08-08	6423	33.84	118.00	1.87	0.53
GY0509	2005-08-08	4760	114.66	17.82	1.17	0.298
GY0510	2005-08-08	3312	111.41	7.13	1.34	0.131
GY0511	2005-08-08	2340	129.64	36.40	0.93	0.361
GY0512	2005-08-08	1560	126.51	8.96	1.20	0.198

changes during the '05.6' flood event, which is very likely to reflect the inherent relationship between erosion and hydrological characteristics at different stages of the flood event. TSS increased rapidly in the beginning of the flood and the highest concentration of TSS occurred on June 22 (F22.1—F22.2 (Figure 2)), when the flood was going to get to the peak. Afterwards, TSS showed a rapid decreasing trend with the slow increase of water discharge. On June 23 (F23.2 (Figure 2)), TSS showed an increasing trend again. POC showed peak

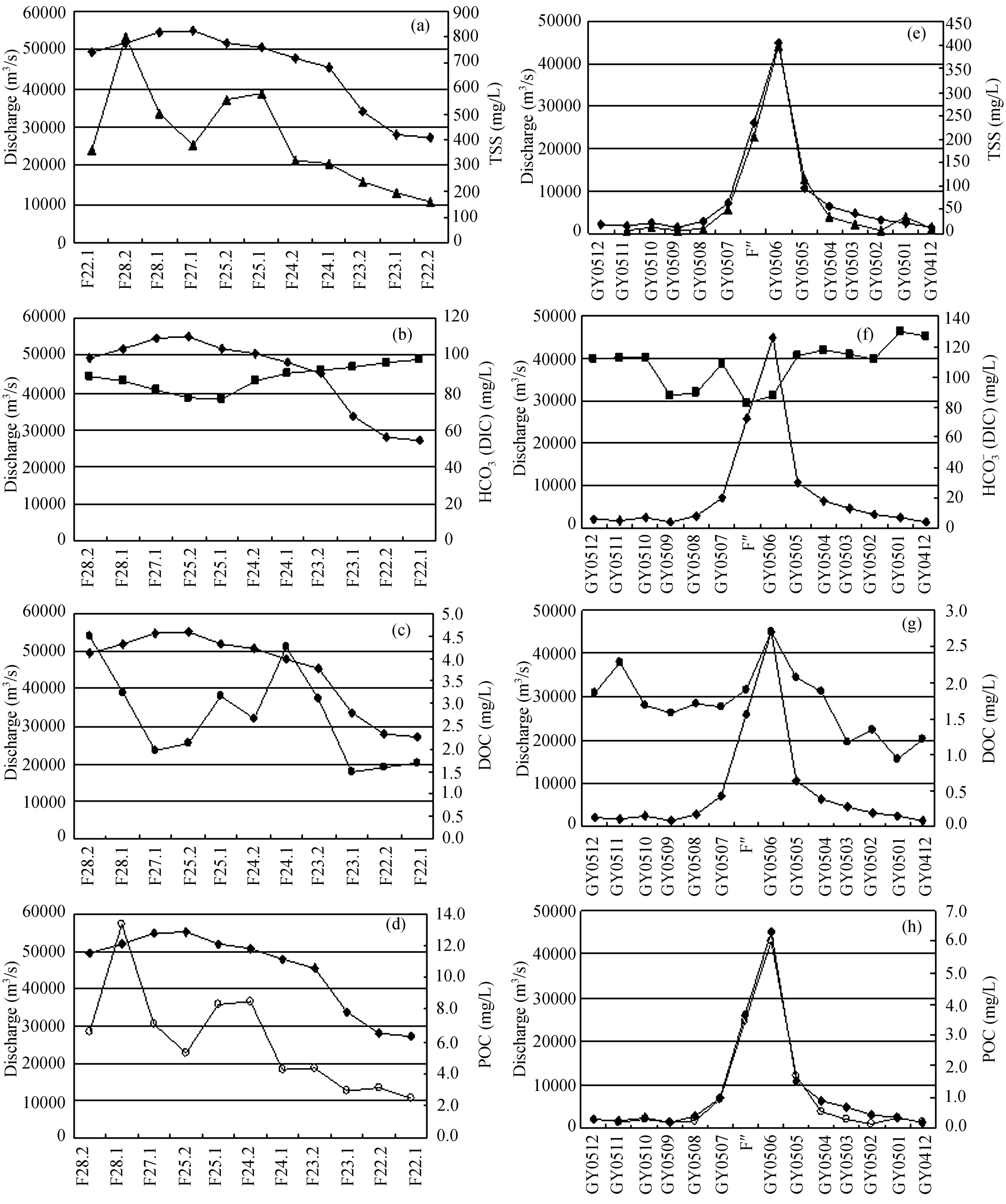

Figure 2 Relation between TSS, DIC, DOC, POC and discharge. (a)—(d) '05.6' flood period; (e)—(h) monthly data; F″ in (e)—(h) mean value of the flood period. Symbol diamond represents water discharge rate.

values twice similarly and was consistent with TSS in the occurrence time with the second peak in the afternoon of June 24 (F24.2 (Figure 2)). The consistence between POC and TSS variations can be easily understood, because POC is one of TSS components (Figure 2(a)).

The double peak phenomenon of TSS concentration in the flood event reflects different depth erosions associated with hydrological processes of the flood. In the beginning of the flood, surface flow and surface erosion increased with the increasing water discharge, forming the first peak of TSS and POC. When the surface materials were washed out during strong surface flow, TSS and POC rapidly decreased. With continuous raining, soils became over-saturated and subsurface flow increased correspondingly, resulting in deep erosion and the second peak of TSS. From Figure 2, it can be found that the second peak showed a slower rate of change compared with the first peak, suggesting that the deep erosion was less rapid but lasted longer than surface erosion.

DOC concentration decreased rapidly down to the lowest point at the flood event with increasing water discharge in the early stage of the flood (Figure 2(c)), which suggests that runoff caused intense dilution to the DOC concentration. Since June 23 (F23.2), DOC showed a continuous increase and reached the highest peak in the morning on June 25 (F25.1), which has a time lag of half day behind the highest peak of TSS and POC. It indicates the significant contribution of soil subsurface flow at this stage, and on the other hand, the time lag would suggest that the release of DOC requires longer time than that of POC, the mechanical erosion. After the peak, DOC concentration rapidly decreased and declined to 1.49 mg/L, a level even lower than the concentration in normal, indicating that there were little dissolved organic materials available for transport. With the subsidising of the flood, DOC turned to increase again toward the normal level of the season (Figure 2 (c), (g)).

During the flood event, DIC showed an obvious decrease in the waxing phase, and then increased to the normal level with the waning of the flood, displaying a negative correlation between DIC concentration and water discharge (Figure 2(b)), suggesting that rapid flooding runoff with lower DIC concentration caused by intense raining diluted the DIC of the river water, and also, outgassing of CO_2 in the first stage might have some impact. Compared with the change in water discharge, DIC concentration changed with smaller amplitude, which indicates that the extensive outcrop of carbonate rocks in the Xijiang River Basin (173500 km^2, accounting for 39% of the total basin area) provided large amount of HCO_3^- during flood process. Besides, DIC concentration showed a rapid increase with enhanced subsurface flow (Figure 2(b)), sample F24.2, F25.1 to F25.2), suggesting that DIC concentration in the deeper soil water was higher than that the surface runoff probably due to longer time of contact between subsurface flow and rocks, and higher solubility of the carbonates caused by higher CO_2 concentration in soils.

3.2 Comparison of TSS, DIC, DOC and POC during ‘05.6’ flood event and non-flood periods

TSS shows a significant increase with the increasing water discharge during the flood event compared with that during the non-flood periods (Figure 2(e)). The highest concentration of TSS rises up to 802.02 mg/L with a mean concentration of 400 mg/L during the flood event, while 0—40 mg/L is observed for non-flood periods with little variation. DIC during the flood event shows a similar concentration to that in March, April and June, but lower than other months with small difference. The ratio of the maximum to minimum value is less than 1.7. The mean concentration of DOC during the flood event is 2.71 mg/L, and 1—2 times the mean concentration in non-flood periods. The maximum value of DOC during the flood is 4.51 mg/L, being 4.8 times the minimum value (0.93 mg/L) in the other months (Figure 2(g)). The linear correlation between DOC and water discharge is rather weak (R^2 = 0.28), which is probably complicated by DOC absorption and release of suspended materials, and biogeochemical processes such as biodegradation and regeneration[23−25].

The mean concentration of POC during the flood event is 6.03 mg/L, which is 2—46 times that in other months. A strong linear correlation between POC content and TSS concentration (R^2 = 0.98, Figure 3(a)) suggests that sediment in the river is the major source for POC. However, the mass percentage of TSS decreases with increasing TSS (Figure 3(b)). The range of POC content is 1.26%—1.83% with a mean value 1.50%, less than that in other months. A plausible explanation is that deep soil erosion will be intensified

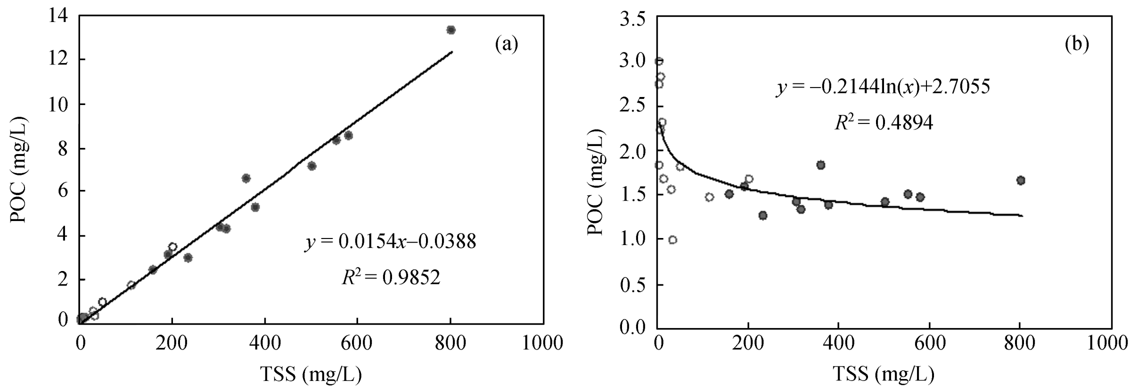

Figure 3 Diagrams showing the correlations TSS with POC content and POC-TSS ratios (percentage). (a) POC content versus TSS; (b) POC-TSS ratios versus TSS.

with increasing water discharge, while organic carbon content decreases in a logarithmic fashion through soil profile[21].

3.3 Estimation of DIC, DOC and POC fluxes

Fluxes of DIC, DOC, and POC can be estimated using water discharge flux and concentrations of various components of riveine carbon. Daily water discharge data were used to construct Box model[26,27], in which each box stands for one day. The water discharge and carbon concentration in each box are assumed to be constant. Sample results measured are assigned to their corresponding boxes/days. During the flood event, an average value from two samples of the day is used (Figure 1) for the corresponding box.

It was detected that DIC, DOC, and POC fluxes during '05.6' flood event were 1.52×10^6 $g.km^{-2}.a^{-1}$, 0.24×10^6 $g.km^{-2}.a^{-1}$, and 0.54×10^6 $g.km^{-2}.a^{-1}$ respectively, accounting for 14.87%, 24.75% and 44.89% in the annual DIC, DOC and POC fluxes in 2005, respectively (Table 2). The total carbon (TC) fluxes during '05.6' flood event accounts for 18.57% of the annual TC in 2005 (Table 2).

Table 2 Carbon fluxes during '05.6' flood event and the year 2005 in the Xijiang River (10^6 $g\cdot km^{-2}\cdot a^{-1}$)a)

	DIC	DOC	POC	TC
'05.6' Flood	1.52	0.24	0.54	2.3
Year 2005	10.20	0.96	1.21	12.37
Flood%	14.87	24.75	44.89	18.57

a) Water discharge of the Xijiang River in 2005 is $1.82\times10^{11}m^3$ and the drainage area is 353000 km^2.

DIC flux accounts for 66.09% of the total carbon fluxes during '05.6' flood event and 82.48% in the whole year 2005, suggesting that inorganic chemical weathering is the dominant factor for carbon export in the Xijiang River. The ratio of annual DOC to POC is 0.79, indicating that POC flux is larger than DOC flux and severe mechanical erosion by intense rainfall[28]. If '05.6' flood event were not considered, the ratio of DOC/POC would be larger than 1. Therefore, the impact of extreme flood events not only affects the annual carbon flux budget but also changes the type of the river with regard to riverine carbon transport.

TSS, POC, and DOC of '05.6' flood event reached the annual peak values, demonstrating an extreme flushing effect of the intense rainfall. During this event, TSS and POC increased with the largest amplitude, followed by DOC. By contrast, DIC showed only small variations through the event (Figure 2).

Gao[8,29] and Wei[30] have estimated the carbon fluxes of the Xijiang River for the hydrological years of 1997—1998 and 2000—2001, respectively. The DIC, DOC, and POC fluxes are 13.24×10^6 $g.km^{-2}.a^{-1}$, 1.88×10^6 $g.km^{-2}.a^{-1}$, and 8.30×10^6 $g.km^{-2}.a^{-1}$ respectively for 1997 — 1998 and 12.10×10^6 $g.km^{-2}.a^{-1}$, 1.02×10^6 $g.km^{-2}.a^{-1}$, and 0.46×10^6 $g.km^{-2}.a^{-1}$ respectively for 2000—2001. In their estimations, averaged annual water discharge of $2.3\times10^{11}m^3$ was used. The sampling schemes in their studies were similar, that is, four times a year to cover various typical seasons of the river discharge. However, the results of DOC and POC they obtained sharply differed. In particular, the difference in POC is as large as 17 times. The huge difference between the two estimations comes possibly from low sampling frequency that cannot adequately reflect the seasonal variations of various carbon components in the Xijiang River. The former overestimated POC fluxes when using one flood sample to represent the entire flood period, while the latter underestimated POC fluxes by neglecting flood events.

For major rivers of the world, various components in the water show different responses to water discharge. For example, in the Yangtze River, Yellow River[31,32], and the Zhujiang River as well as other rivers draining from carbonate regions[33], the ionic species show slight decrease with increasing water discharge, as the water is saturated or over-saturated with calcite/dolomite. While in Amazon[34] and Lena[35] rivers, ionic species show marked decrease with increasing water discharge, and thus the estimation of DIC fluxes should consider the dilution effects of flood.

The Xijiang River is located in the southeast Asian monsoon region with the most intensive mechanical erosions in the world[36]. Figure 1 shows a strong linear relationship between TSS and water discharge in the Xijiang River in 2005 ($R^2 = 0.87$), implying intense erosion by the flood. However, for other rivers in this monsoon region, such as the Yangtze River and Yellow River rivers, TSS shows an exponential increase with increasing water discharge[37,38], which indicates that the mechanical erosions for these rivers are much severer and the impacts of flood events should be more significant on TSS, POC and DOC fluxes estimation. For rivers in other regions, floods normally impose dilution effects on TSS, albeit the amplitude may vary in different basins. Hence, accurate estimations of carbon fluxes in a river can be made only after detailed study of all the hydrologic processes involved, particularly flood processes.

4 Conclusions

The '05.6' extreme flood event in the Xijiang River represented a strong physical and chemical erosion process. During the flood, concentrations of TSS, POC, and DOC all reached the highest values of the year 2005. DIC concentration shows a less decrease due to large exposure of carbonate rocks in the drainage basin. This flood event remarkably influenced the annual flux estimations of POC, DOC, and DIC to different but great extents, with an order from larger to smaller. By comparing annual carbon fluxes with the carbon fluxes of the flood, it can be found that carbon exports during this extreme flood event had great contributions to riverine carbon fluxes. DIC, DOC and POC fluxes during this flood event account for 15.27%, 24.03% and 44.47% of the annual DIC, DOC and POC fluxes respectively. This study suggests that the carbon fluxes during flood events cannot be neglected or oversimplified for accurate estimation of annual carbon fluxes and understanding of their variations in the rivers with frequent flood.

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