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Sources and fluxes of particulate organic carbon in the Wujiang cascade reservoirs, southwest China

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ABSTRACT
Knowing the sources and behaviors of particulate organic carbon (POC) is essential for calculating the carbon pool of riverine systems, the natural properties of which have been strongly affected by damming. In this study, we investigated POC and related environmental factors in the Wujiang cascade reservoirs, southwest China, to understand sources and fluxes of POC under cascade-damming conditions. The results indicated that POC concentration and $\delta^{13}C_{POC}$ had obvious temporal and spatial variation, with average values of 0.39 mg L^{-1} and −28.98‰, respectively. Evidence from $\delta^{13}C_{POC}$ indicated that POC in the reservoirs was largely from phytoplankton-derived POC. POC flux was estimated as 2.17×10^9 g yr^{-1}, of which allochthonous POC flux was about 1.5×10^9 g yr^{-1} in the study area. The reservoir retained a large amount of POC, and the intercept rate of Wujiangdu Reservoir was up to 64.94%. These findings suggest that cascade damming significantly impacts the sources and fluxes of POC in the impounded Wujiang River, southwest China.

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cascade reservoir; flux; phytoplankton; POC; Wujiang River

Introduction

Rivers serve as a link between ocean and land and carry weathering products from land to ocean in the form of dissolved substances and particulate matter. The concentrations and fluxes of these materials are a function of environmental factors such as regional climate, bedrock, soil, agricultural activities, and anthropogenic emissions (Liu 2007). Rivers play a vital role in the global carbon cycle, and globally about 0.4 Gt of organic carbon is transported by rivers to the ocean annually, 37.5–42.5% of which is particulate organic carbon (POC; Schlesinger and Melack 1981, Ludwig et al. 1996, Hedges et al. 1997). Riverine export of POC to the ocean is not only a significant factor in balancing the carbon budget (Smith and Hollibaugh 1993) but also influences the atmospheric carbon inventory over a wide range of timescales (Galy et al. 2015).

Knowing the sources and behaviors of POC is essential for calculating the carbon pool of riverine systems (Blair et al. 2003, Galy et al. 2008, Hilton et al. 2010, Bouchez et al. 2014). Riverine POC consists partly of detrital compounds but can also be a product of *in situ* algal activity (Bouchez et al. 2014). The extent of *in situ* production of POC may influence the aqueous carbon cycle by consuming dissolved inorganic carbon (Atekawana and Krishnamurthy 1998), and stable carbon isotope analysis is a useful tool for understanding these processes in riverine systems (Cifuentes et al. 1988, Bernasconi et al. 1997, Moschen et al. 2009).

Damming interrupts the river continuum and is the most important anthropogenic perturbation of rivers. Human activities have significantly changed the carbon budget of inland waters (Regnier et al. 2013). Dam interception increases the retention time of river water and changes the geochemical cycle and flux of nutrients such as phosphorus and silicon (Maavara et al. 2014, 2015); however, its influence on POC has rarely been reported. In this study, we investigated POC and related environmental factors in the Wujiang cascade reservoirs, southwest China, to understand sources and fluxes of POC under cascade-damming conditions.

Methods

Study area

The Wujiang River is a tributary of the Changjiang (Yangtze) River, with a total length of 1037 km and a drainage area of 88 267 km^2 to the south of the Changjiang. The

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Wujiang River has a fall of 2124 m and is one of the main rivers in a west-to-east power transmission project. The study area is characteristic of the subtropical monsoon humid climate; its average annual temperature is 12.3 °C with extreme temperatures of 35.4 °C in summer and −10.1 °C in winter. The annual precipitation ranges from 1100 to 1300 mm, and precipitation from May to October accounts for about 75% of the annual total. The predominant lithological character of the Wujiang River catchment is pre-Jurassic strata, and carbonate rock is widespread. Eleven reservoirs have been built on the main stream of the Wujiang River, Guizhou Province, 3 of which were selected for study (Fig. 1).

Sampling and analytical methods

The survey was conducted twice a month in the Wujiang River catchment between May 2011 and May 2012. Water samples were collected from the surface (upper 0.5 m). Water temperature, pH, and dissolved oxygen were measured *in situ* with an automated multiparameter profiler (model: YSI 6600; YSI Inc., Yellow Springs, OH, USA). Concentration of chlorophyll (μg L^{-1}) was measured with a Phyto-PAM (WALZ, Germany). Water samples were filtered through glass fiber filters (0.70 μm, Whatman GF/F) within 24 h at room temperature, freeze-dried, and fumed with hydrogen chloride before analysis to remove

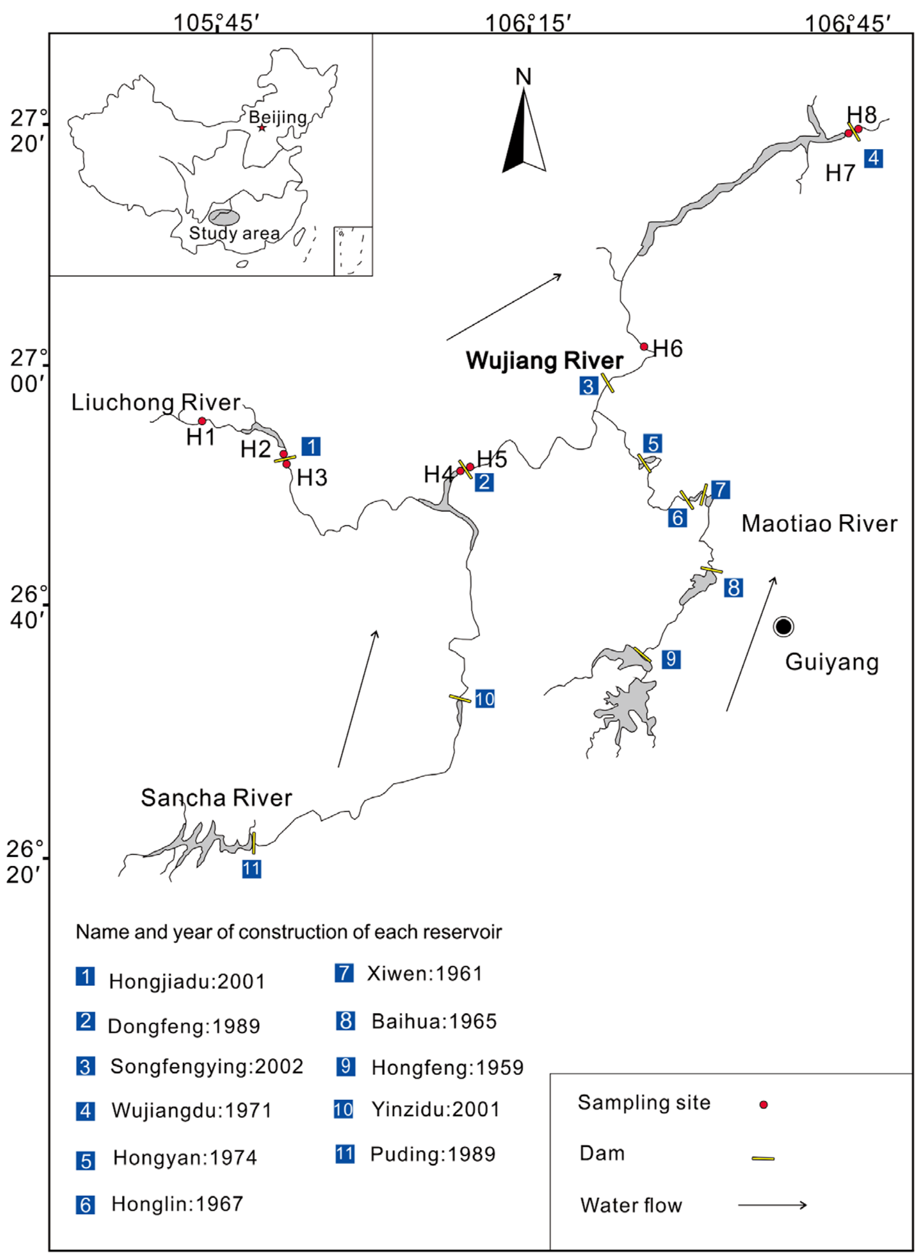

Figure 1. Location of sampling sites on the Wujiang River. H1 and H6 are rivers; H2, H4, and H7 are reservoirs; and H3, H5, and H8 are released waters.

inorganic carbon. For δ^{13}C of POC (δ$^{13}C_{POC}$) measurements, organic carbon on the filters was converted to carbon dioxide (CO_2) at 850 °C for 5 h in sealed quartz tubes containing copper oxide as an oxidant (Buchanan and Corcoran 1959, Tao et al. 2009), and the $^{13}C/^{12}C$ ratio of CO_2 was then determined on an MAT252 mass spectrometer. The δ$^{13}C_{POC}$ measurements were normalized to a Pee Dee Belemnite standard (PDB) with an analytical precision of ±0.1‰. POC content was measured using an elemental analyzer (Vario macro cube, Germany). The biomass of algae was estimated using the conversion factor of 40 mg carbon per mg chlorophyll (Giorgio and Gasol 1995). The proportion of algal (autochthonous) POC (P_{Auto}) to the total POC was calculated as: P_{Auto} = Biomas/POC. The proportion of nonalgal (allochthonous) organic carbon (P_{Allo}) was calculated as: $P_{Allo} = 1 - P_{Auto}$. Pearson's correlation coefficient analysis was calculated using the Statistical Package for Social Science (SPSS) software 18.0 (SPSS Inc.).

Results

Physical, chemical, and biological parameters

The average water temperature and pH were 17.28 °C and 7.90, respectively (Table 1). Average concentrations of dissolved oxygen and chlorophyll (Chl) were 8.30 mg L^{-1} and 3.57 μg L^{-1}, respectively. Usually, temperature and pH were higher in reservoirs than in the released waters (Table 1).

Temporal and spatial variation of POC

The POC concentration ranged from 0.03 to 1.84 mg L^{-1} with an average of 0.39 mg L^{-1}. The temporal changes of POC concentration differed among the sampling sites: site H7 had the largest amplitude (Fig. 2). In general, the POC concentration during May to October was higher than that during November to April. The maximum value (1.84 mg L^{-1}) occurred in August and the minimum (0.03 mg L^{-1}) in April. Comparing the different types of samples, the average POC concentrations were 0.33, 0.53, and 0.30 mg L^{-1} in rivers, reservoirs, and released waters, respectively.

Temporal and spatial variation of δ$^{13}C_{POC}$

The average value of δ$^{13}C_{POC}$ was −28.98‰ and ranged from −35.30‰ to −25.03‰. Overall, the pattern of δ$^{13}C_{POC}$ in the Wujiang River changed seasonally but differed at each sampling site with time (Fig. 2). In rivers, δ$^{13}C_{POC}$ varied from −30.78‰ to −25.03‰, with a mean value of −26.95‰. In reservoirs, δ$^{13}C_{POC}$ varied within a wide range from −33.89‰ to −26.09‰, with a mean value

Table 1. Annual means and variation of hydrogeochemical parameters at 7 sites on the Wujiang River, southwest China. T = water temperature; DO = dissolved oxygen; Chl = chlorophyll.

Site	Site type		T (°C)	pH	DO (mg L^{-1})	Chl (μg L^{-1})
H1	River	Min	8.11	7.99	7.42	1.05
		Max	23.75	8.61	11.08	2.78
		Aver	17.16	8.23[a]	9.17	1.6
		SD	4.94	0.13	1.06	0.44
H2	Reservoir	Min	9.11	7.76	6.41	1.41
		Max	25.82	8.49	9.74	3.42
		Aver	18.55	8.11[a]	7.94	2.38
		SD	5.6	0.21	0.75	0.63
H3	Released water	Min	9.21	7.38	4.64	1.21
		Max	21	8.1	9.76	3.26
		Aver	14.77	7.73[a]	7.63	2.02
		SD	3.54	0.18	1.38	0.51
H4	Reservoir	Min	9.59	7.73	7.65	1.61
		Max	26.09	8.42	10.55	10.33
		Aver	18.44	8.14[a]	9.22	4.73
		SD	5.4	0.17	0.84	2.54
H5	Released water	Min	9.67	7.55	7.18	1.4
		Max	23.62	8.11	11.81	4
		Aver	16.34	7.85[a]	8.64	2.31
		SD	4.29	0.15	1.26	0.72
H6	River	Min	9.7	7.69	7.8	0.92
		Max	24.37	8.15	10.68	7.6
		Aver	16.81	7.91[a]	9.14	2.23
		SD	4.14	0.11	0.72	1.28
H7	Reservoir	Min	9.7	7.53	3.76	1.35
		Max	29.66	8.54	12.38	40.64
		Aver	19.75	7.86[a]	7.38	11.31
		SD	5.97	0.3	2.56	10.11
H8	Released water	Min	9.84	7.36	3.15	1.11
		Max	24.62	8.01	10.19	4.94
		Aver	16.4	7.66[a]	7.27	2.01
		SD	4.76	0.18	2.09	0.9

[a]Geometric average.

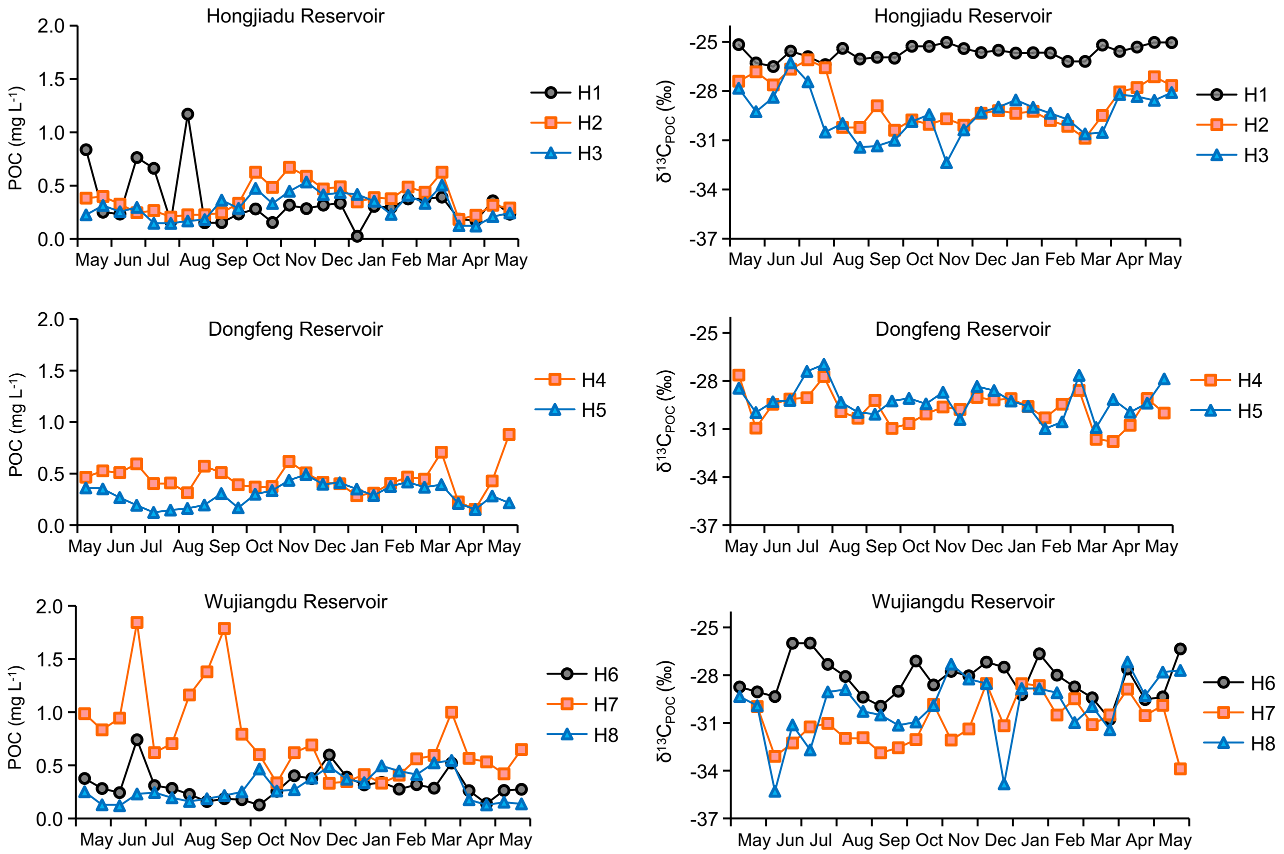

Figure 2. Temporal and spatial variation of POC concentration and $\delta^{13}C_{POC}$ in the study reservoirs and their related rivers. Black circles represent river; orange squares represent reservoirs; and blue triangles represent released water.

of −29.81‰. In released waters, the $\delta^{13}C_{POC}$ varied from −35.30‰ to −26.28‰, with a mean value of −29.53‰. The released water showed a similar temporal variation to that in the reservoirs, and $\delta^{13}C_{POC}$ was more negative than that in the rivers.

Temporal and spatial variation of P_{Auto}

The average value of P_{Auto} was 0.33, ranging from 0.06 to 0.95. The temporal changes of P_{Auto} differed among the sampling sites; site H7 showed the largest amplitude (Fig. 3). In general, P_{Auto} was higher during May to October than during November to April. The maximum value (0.95) occurred in July and the minimum (0.06) in December. P_{Auto} ranged from 0.06 to 0.58 with an average of 0.26 in the rivers, from 0.13 to 0.95 with an average of 0.39 in the reservoirs, from 0.13 to 0.65 with an average of 0.32 in the released waters.

Discussion

Sources of POC

The POC included autochthonous POC derived from algal photosynthesis and allochthonous POC derived from soil and plant litter (Bianchi 2011). The $\delta^{13}C$ value is an effective tool to trace these carbon sources. The allochthonous POC in the studied area has a $\delta^{13}C$ of about −23‰ (Peng 2013) while the autochthonous algae have an average $\delta^{13}C$ of −30.8‰ (Wang et al. 2013). Soil organic matter often originates from decomposition of C_3 plant debris with a $\delta^{13}C$ value of about −27‰, and riverine algal fractions are often more ^{13}C-depleted than the detrital fractions in POC (e.g., Hamilton and Lewis 1992). In natural river waters (site H1), the $\delta^{13}C_{POC}$ (average about −26‰) is close to allochthonous POC, suggesting that riverine POC is mainly derived from soil and plant litter in the catchment. The range of riverine $\delta^{13}C_{POC}$ here was consistent with that in the River Scheldt (average about −29.44‰; Hellings et al. 1999). The low Chl concentration and contribution of algae to POC in H1 also support this finding (Figs. 4 and 5). Downstream of several dams, however, $\delta^{13}C_{POC}$ at river site H6 was more depleted than at H1 (Fig. 4), suggesting that the intervening dams affected the source of POC, whereas for the reservoirs and the released waters, phytoplankton contributed a major part of POC.

The POC concentration showed clear seasonal variation, with high values during May to October (rainy season) and low values during November to April (dry

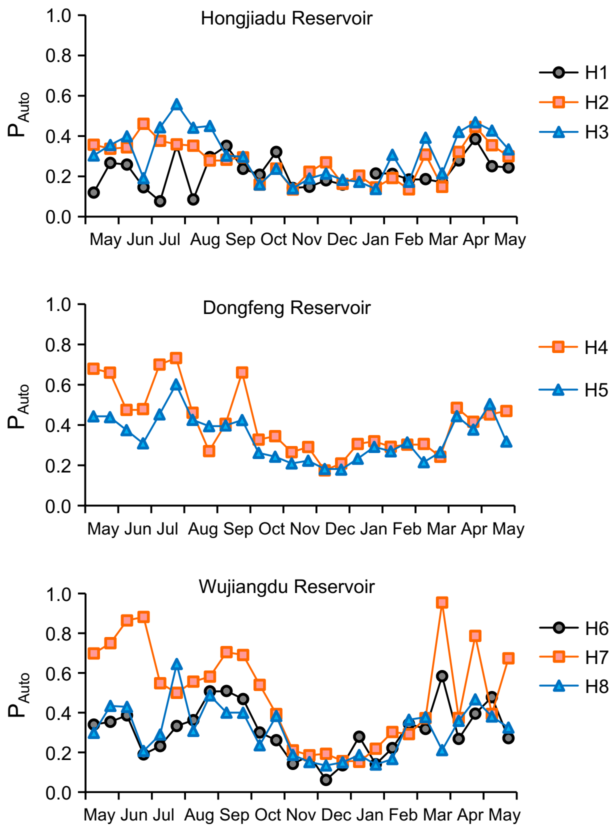

Figure 3. Temporal and spatial variation of the estimated proportion of algae (P_{Auto}, autochthonous carbon) to total POC in the study reservoirs and their related rivers. Black circles represent rivers; orange squares represent reservoirs; and blue triangles represent released water.

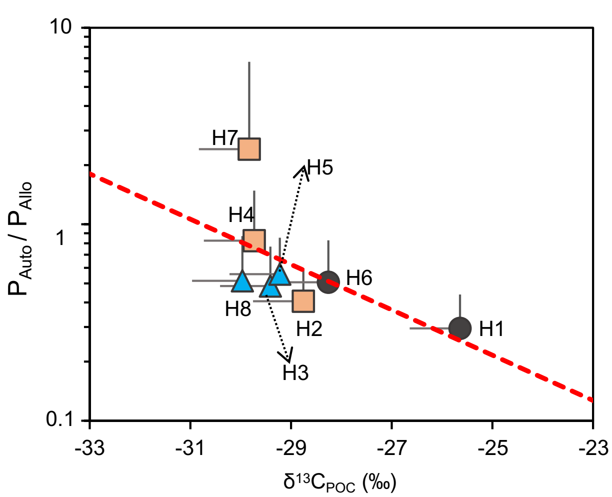

Figure 4. Relationship between the quotient of authochthonous to allochthonous POC (P_{Auto}/P_{Allo}) and $\delta^{13}C_{POC}$. Values are the annual average and standard deviation (SD) at each site (see Fig. 1). Black circles represent rivers; orange squares represent reservoirs; blue triangles represent released water. The red dashed line represents the regression line of (P_{Auto}/P_{Allo}) and $\delta^{13}C_{POC}$: $y = 0.0003e^{-0.266x}$ ($R^2 = 0.355$, $P < 0.05$).

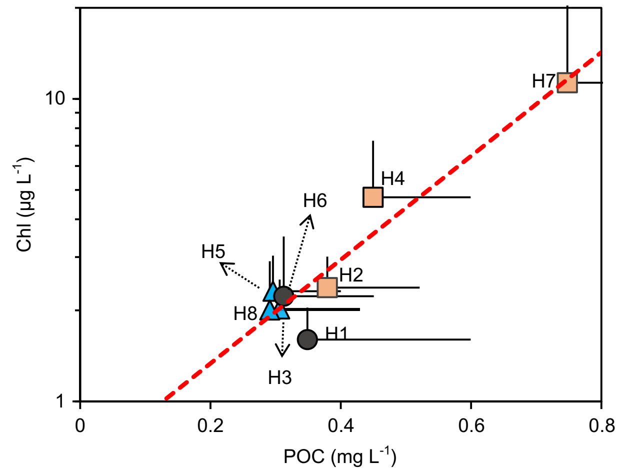

Figure 5. Relationship between concentration of particulate organic carbon (POC) and chlorophyll (Chl). Values are the annual average and standard deviation (SD) at each site (see Fig. 1). Black circles represent rivers; orange squares represent reservoirs; and blue triangles represent released water. The red dashed line represents the regression line of concentration of POC and Chl, and its equation is $y = 0.6063e^{3.947x}$ ($R^2 = 0.896$, $P < 0.05$).

Table 2. Results of Pearson's correlation coefficient analysis. T = water temperature; DO = dissolved oxygen; Chl = chlorophyll; POC = particulate organic carbon.

	T	pH	DO	Chl	POC
pH	0.150*				
DO	−0.0382**	0.579**			
Chl	0.339**	0.192**	0.031		
POC	0.232**	0.205**	−0.030	0.805**	
$\delta^{13}C_{POC}$	−0.023	0.352**	0.328**	−0.138*	−0.106

*Significant correlations at 0.05 level (2-tailed); ** significant correlation at 0.01 level (2-tailed).

season), in part because high temperatures in the rainy season can simulate algal growth. Accordingly, a significant relationship was found among the POC, Chl, and temperature (Table 2). Another reason for the seasonal POC concentrations is that during the rainy season, erosion within the catchment will bring more soil and plant litter into the river.

Flux of POC

Globally, riverine carbon flux (0.45×10^9 t yr^{-1}) has a similar estimated magnitude to that from burning fossil fuels (5.20×10^9 t yr^{-1}) and a net carbon flux between the atmosphere and ocean (1.70×10^9 to 2.80×10^9 t yr^{-1}; Milliman and Meade 1983, Detwiler and Hall 1988, Sarmiento and Sundquist 1992, Siegenthaler and Sarmiento 1993). Carbon flux can be used to understand the changes in the natural environment, especially the riverine POC flux, which reflects the extent of soil erosion. In this study, POC flux (F, g yr^{-1}) was estimated by F = C × D (Tao et al. 2009), where C and D refer to POC concentration and water discharge, respectively. The POC flux calculated by Tao et al. (2009) in the Wujiang River catchment was 3.12×10^{10} g yr^{-1}, markedly lower than the value (11×10^{10} g yr^{-1}) from the Forestry Department of Guizhou Province (FDGP 2003), which suggests possible interception due to cascade damming in this karstic area. The total flux of POC was 2.17×10^{9} g yr^{-1} in the studied area. The cascade reservoirs retained a large amount of POC, and the interception ratios varied between 43.2% and 64.9% (Table 3).

In the study reservoirs, the POC flux and the corresponding interception rate increased downstream (Table 4), possibly caused by different trophic levels. The nutritional status of Hongjiadu, Dongfeng, and Wujiangdu reservoirs, respectively, is mesotrophic, eutrophic, and hypereutrophic (Wang et al. 2008). POC flux of Wujiangdu Reservoir (6.19×10^{9} g yr^{-1}) was almost 5 times as much as Hongjiadu Reservoir (1.11×10^{9} g yr^{-1}), indicating that the eutrophic reservoir has the larger flux of POC.

Land cover is another factor influencing POC flux. Transformation in agricultural management could improve organic carbon cycling in some soils and alter the proportion of organic matter–mineral associations (Donigian et al. 1994). In this study area, the upstream catchments have few forests, and the land is largely unused with thin soils and frequently exposed bedrock, whereas arable and forest are the main land types in the downstream catchments. Forest land is considered to contain a greater proportion of erosive area than unused land (Wu et al. 2005); however, the extent of influence of land cover in this area is still lacking.

Table 3. Average interception ratios of POC in reservoirs on the Wujiang River. Interception ratio = 100(F-F′)/F, where F is POC flux in a given reservoir, F′ is POC flux in the corresponding released water.

Interception ratio	Hongjiadu Reservoir	Dongfeng Reservoir	Wujiangdu Reservoir
POC (%)	43.24	43.87	64.94

Table 4. Calculation of POC flux at 7 sites on the Wujiang River, southwest China.

Site	Site type	Discharge, D (10^4 m^3 yr^{-1})[a]	POC concentration, C (mg L^{-1})	POC flux, F (10^9 g yr^{-1})
H1	River	229 950	0.35	0.80
H2	Reservoir	290 939	0.38	1.11
H3	Released water	202 497	0.31	0.63
H4	Reservoir	689 677	0.45	3.10
H5	Released water	578 920	0.30	1.74
H6	River	702 063	0.31	2.17
H7	Reservoir	825 618	0.75	6.19
H8	Released water	751 170	0.29	2.17

[a]Data from Yu (2008).

Conclusions

POC concentration and $\delta^{13}C_{POC}$ showed marked temporal and spatial variation in the Wujiang cascade reservoirs, with average values of 0.39 mg L^{-1} and −28.98‰, respectively. Evidence from $\delta^{13}C_{POC}$ indicated that POC in rivers is mainly derived from allochthonous soil and plant litter while POC in reservoirs is mainly derived from the autochthonous phytoplankton, especially in the rainy season. Our estimate of annual POC flux in the Wujiang River suggests that 2.17×10^{9} g is transported, of which about 1.5×10^{9} g (nearly 70%) is allochthonous. At the same time, the reservoirs have a high interception rate for POC, and the intercept rate of Wujiangdu Reservoir is up to 64.94%. Our study indicates that cascade damming has a significant impact on the sources and fluxes of POC in the impounded Wujiang River.

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