

Identification of terrigenous and autochthonous organic carbon in sediment cores from cascade reservoirs in the upper stream of Pearl River and Wujiang River, southwest China: lignin phenol as a tracer

Li Gao¹ · Xin Lin¹ · Jun Fan² · Ming Yang¹ · Xueping Chen¹ · Fushun Wang¹ · Jing Ma¹ 

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Abstract Organic carbon (OC) source attribution for cascade reservoir sediments has been identified as a critical gap in understanding the effective carbon sink of inland waters. In this study, nine sediment cores were collected from cascade reservoirs in the Wujiang and Pearl Rivers. We analyzed lignin phenol ($\Lambda 8$), total organic carbon (TOC) content, and stable carbon isotopic composition ($\delta^{13}\text{C}$) of the sediments, focusing on the changes of terrigenous OC, and the variation of OC source in cascade reservoir sediments after damming. Our results showed that the $\Sigma 8$ and TOC contents decreased from upstream to downstream reservoirs, indicating the significant interception of terrigenous OC by cascade damming. Additionally, the $\Lambda 8$ content in the Pearl River reservoir sediments was much higher than that in the Wujiang River. From the three-end-member mixing model, we estimated that OC in reservoir sediments mainly comes from soil and plankton. After damming, the proportion of plankton OC in TOC slightly increased in seasonal and annual regulation reservoirs due to the limnetic evolution of the reservoir. These findings suggest that the cascade damming increases the interception capacity of the river to terrigenous OC and nutrients, and that slowing of water velocity caused by damming affected primary productivity and fluvial carbon cycling.

Keywords Cascade reservoirs · Terrigenous OC · Lignin · Autochthonous OC · Three-end-member mixing model

1 Introduction

Rivers act as an important channel connecting 87% of the Earth's land surface with the oceans and transport a large amount of terrestrial organic matter and nutrient elements (Gordon et al. 2003; Wang et al. 2019). Therefore, it is an active region of the carbon cycle. Sen et al. (2012) reported that rivers transport approximately 20 Pg/yr of sediment to the ocean (Sen et al. 2012). Terrigenous organic carbon (OC) in sediments is challenging to degrade and is a long-term stable carbon sink that primarily originates from soil organic matter and plant debris (Hedges et al. 1997; Sun et al. 2018). Conversely, a biological carbon pump can convert inorganic carbon (IC) into OC in water, and plankton primarily contributes to the labile autochthonous OC (Yi et al. 2021). Therefore, understanding the proportion and change processes of terrigenous and autochthonous OC is vital for understanding the migration and burial of terrigenous OC and the river carbon cycle.

More than 2.8 million dams have been built worldwide over the past several decades to solve the problems of agricultural irrigation, water use, and clean energy power supply (Grill et al. 2019; Lehner et al. 2011). Compared with a single dam, the interlocking regulation capability of cascade dams consisting of multiple dams allows for more efficient use of water resources. However, dam construction leads to changes in the physical and chemical conditions of the water, such as a decrease in flow velocity, an increase in water depth, and the formation of thermal stratification, which results in chemical and biological

✉ Jing Ma
jingma@shu.edu.cn

¹ School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

² Shimadzu (Shanghai), Global Laboratory Consumables Co., Ltd, Shanghai 200233, China

stratification (Yu et al. 2019). Similarly, it is reported that dam reservoirs store 25%–30% of the particulate matter (4.5 Gt/year), and OC for river transport to the ocean decreases by 26%, indicating the ability to intercept OC is enhanced (Rapin et al. 2020). Meanwhile, the static water effect formed by the weakening of hydrodynamic conditions in the reservoir area is conducive to the growth of algae and other plankton, implying that the proportion of terrigenous OC in the sediment will change. This causes the carbon cycle of the river to gradually change into a lake-like carbon cycle, increasing the autochthonous OC (Kondolf et al. 2014). This increase in autochthonous river OC significantly affects the global carbon cycle and is related to global warming and environmental problems, such as algal blooms.

Furthermore, the construction of large-scale cascade reservoirs causes the greenhouse gas (CO_2) flux in reservoirs to exhibit prominent spatiotemporal characteristics (Li 2018; Lehner et al. 2011; Shi et al. 2017). China currently has the highest number of dams in the world, but the utilization rate of water resources development is significantly lower than in developed countries. In the future, China will build new reservoirs and dismantle aging reservoirs to improve the utilization rate of water resources. However, a high density of cascade dam developments aggravates river fragmentation, hydrological changes, sediment deposition, and ecological impacts, potentially changing the river's capacity to transport and transform organic matter. Therefore, the quantitative identification of terrigenous and autochthonous OC in cascade reservoirs is essential to reveal all pathways of organic carbon input and its role in the organic carbon pool. At present, both the overall indicator and biomarker methods are commonly used to identify the OC source in sediments to avoid the limitations of a single method. For example, when using the C/N ratio to determine the source of OC, diagenesis and selective adsorption of NH_4^+ by sediments affect OC source discrimination (Hopmans et al. 2004). Furthermore, as a unique substance of terrestrial vascular plants, lignin has a single source and is difficult to degrade, it can be a good indicator of the input changes in terrigenous OC. This method has also been applied to discriminate between internal and external sources of sediments and particulate matter in estuaries and continental shelf areas (Ellis et al. 2012; Tareq et al. 2006).

This study used lignin as a tracer, combined with total organic carbon (TOC), C/N, and stable carbon isotopes ($\delta^{13}\text{C}$) to analyze the sediment cores in the reservoir area. We examined two large rivers: the Wujiang River and the upper reaches of the Pearl River in southwest China, on which characteristic cascade reservoir developments have taken place. The study aims to: (a) analyze the migration and burial of terrigenous OC after the construction of

cascade reservoirs in the basin; (b) quantitatively calculate the contribution rate of terrigenous and autochthonous OC through the three-end-member mixing model, and (c) analyze the changes in autochthonous OC before and after reservoir construction.

2 Materials and methods

2.1 Study area and sampling

The Pearl River is the second largest river in China, and the Wujiang River is the largest tributary of the upper reaches of the Yangtze River. In addition, the Pearl River upstream and the Wujiang River are located in southwestern China's karst areas. In this region, there is a characteristic cascade dam system, making these two rivers ideal for cascade reservoir studies. Taking the Pearl and Wujiang Rivers as the main study areas, we collected seventeen sediment cores from nine reservoir areas and selected nine sediment cores for analysis using the overall index and biomarker methods (Fig. 1). The lengths of sediment cores and location information etc. are given in Table 2. The basic information about all reservoirs is shown in Table 1. Sediment cores were collected using a custom-made columnar sediment sampler (maximum sampling depth is 80 cm). The sediment core information is shown in Table 2. A total of 199 samples were obtained by separating sediment cores into 1–2 cm thick layers. These samples were wrapped in sterilized aluminum foil, sealed in plastic bags, and stored in a refrigerator at $-20\text{ }^\circ\text{C}$ in the laboratory for further treatment.

2.2 Elemental analysis

To remove inorganic carbon, a dry sample weighing 0.25 g was treated with 6 mol/L of hydrochloric acid until the bubbling stopped. The sample was acidified overnight, washed with ultrapure water until a pH of 7 was reached, dried, and stored in a sample vial for further analysis. TOC and total nitrogen (TN) were measured using an elemental analyzer (FLASH 2000 HT, Thermo Fisher Scientific, MA, USA), while $\delta^{13}\text{C}$ was measured using a stable isotope analyzer (FLASH 2000 HT, Thermo Fisher Scientific, MA, USA).

2.3 Lignin phenol analysis

In this experiment, the copper oxide method proposed by Hedge (1982) was used to extract lignin phenol from sediments (Hedges et al. 1982, 1995). Freeze-dried the sample (0.25 g), CuO powder (0.05 g), and ferrous ammonium sulfate $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (0.025 g) were

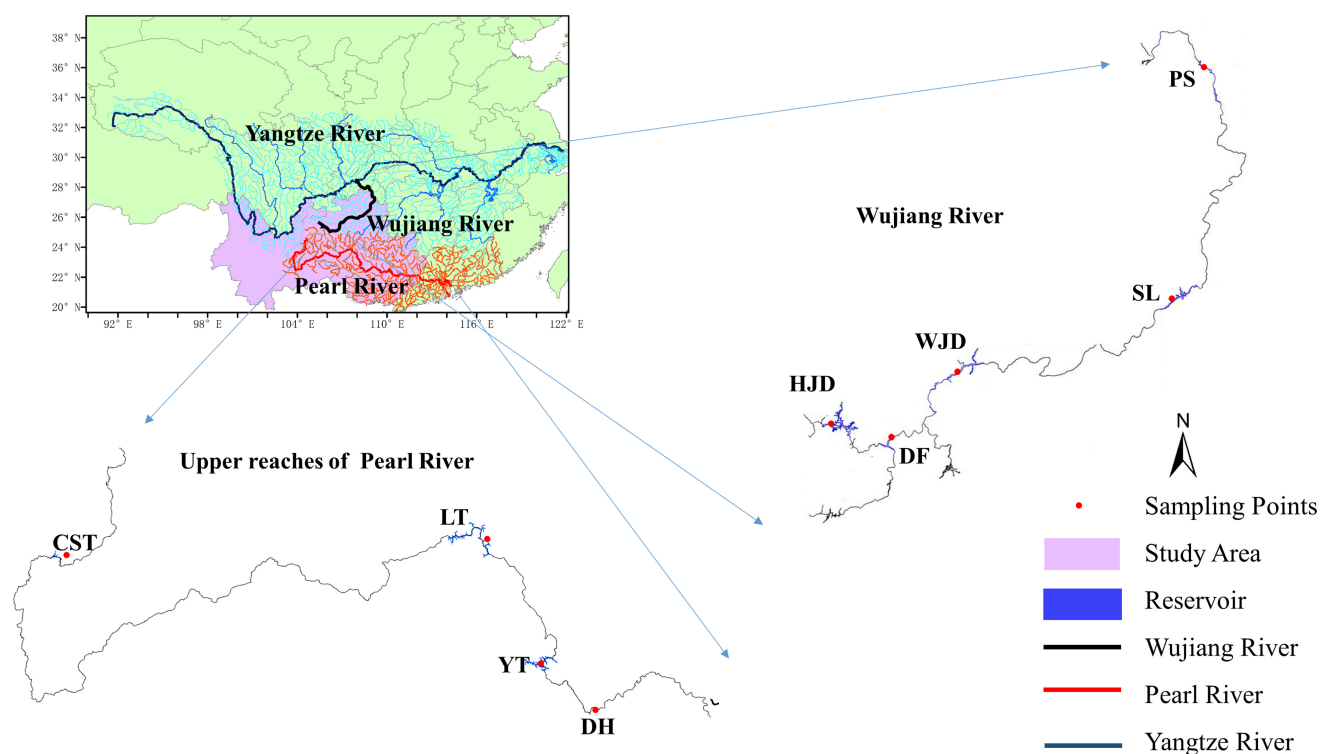


Fig. 1 Study area and sediment sampling locations

Table 1 Reservoir information

Reservoirs	Elapsed time (yr)	Average water depth (m)	Catchment area (km ²)	Annual runoff volume (10 ⁸ m ³)	Storage capacity (10 ⁸ m ³)	Hydraulic retention time (day)	Regulation mode
The Pearl River							
Chaishitan (CST)	21	1640.4	4556	48.4	4.37	103	Annual
Longtan (LT)	11	400	98,500	517	273	193	Annual
Yantan (YT)	28	223	106,580	555	26	21	Seasonal
Dahua (DH)	34	155	112,200	627	9.64	5	Daily
The Wujiang River							
Dongfeng (DF)	25	25	18,161	108.9	8.74	29	Seasonal
Hongjiadu (HJD)	19	60	9900	48.88	68.5	368	Annual
Wujiangdu (WJD)	40	33	27,790	158	50.24	49	Seasonal
Silin (SL)	12	22	48,558	266.16	34.02	17	Daily
Pengshui (PS)	12	NA	69,000	410	8.13	11	Daily

added to the polytetrafluoroethylene vessel, and 7 mL of NaOH solution (2 M) was added to the vessel under a nitrogen atmosphere for digestion in a microwave digestion system (WX-6000, PreeKem, Shanghai, China). After

oxidation, two types of internal standards (ethyl vanillin and trans-cinnamic acid) were added for recovery, and the pH value was adjusted to 1 with HCl (6 M). The samples were then loaded on a Cleanert PEP cartridge (150 mg/

Table 2 Sediment cores information

Reservoirs	Construction Time (yr)	Sediment core length (cm)	Reservoir construction nodes (cm)	Longitude and Latitude
The Pearl River				
Chaishitan (CST)	2000	37	– 18	N25°4'1", E103°38'5"
Longtan (LT)	2010	24	– 10	N25°7'43", E106°59'21.8"
Yantan (YT)	1993	34	– 29	N24°6'55", E107°29'16"
Dahua (DH)	1987	8	NA	N23°43'17", E107°58'20"
The Wujiang River				
Dongfeng (DF)	1995	25	– 11	N26°47'39", E106°8'25"
Hongjiadu (HJD)	2001	14	– 8	N26°55'27", E105°47'41"
Wujiangdu (WJD)	1982	20	– 17	N27°8'33", E106°21'34"
Silin (SL)	2008	29	– 4	N27°47'51", E108°11'45"
Pengshui (PS)	2007	26	– 5	N29°11'40", E108°12'13"

6 mL; Bonna-Agela Technologies, CA, USA) and eluted using ethyl acetate. The eluents were concentrated to near dryness under a gentle nitrogen stream and reconstituted with 800 μ L of acetonitrile and 200 μ L of triisopropylbenzene. The 25 μ L acetonitrile resolution sample and 75 μ L 99 % bis-trimethylsilyl trifluoroacetamide (BSTFA) + 1 % trimethylchlorosilane (TMCS) were placed in the liner at 70 °C for pre-column derivatization for 10 min. The analytical instrument was a gas chromatograph coupled with a mass spectrometer (GCMS-QP2020, Shimadzu, Kyoto, Japan), and a DB-1 quartz capillary column (DB-1, 30.00 m $\times$ 0.32 mm $\times$ 0.25 μ m; Agilent, CA, USA) was used for separation. The initial temperature of 70 °C was maintained for 1 min, and then increased to 300 °C at a rate of 4 °C/min and maintained for 10 min. The ion source temperature was set to 230 °C, and the samples were scanned using ion monitoring (SIM) mode. The recoveries of trans-cinnamic acid and ethyl vanillin were 70–110 %.

Four categories of monomer phenols produced after the oxidative decomposition of lignin include P-hydroxy series (P), vanillin (V) series, syringyl (S), and cinnamyl (C). A total of 11 monomers were produced: vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, *p*-coumaric, ferulic acids, *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, and *p*-hydroxybenzoic acid (Hedges, 1995). Lignin-phenolic parameters have specific indicative abilities because different sources and geochemical processes lead to different lignin-phenolic monomer ratios.

2.4 Three-end-member mixing model

A three-end-member mixing model with soil, terrestrial vascular plants, and phytoplankton as sources of OC was applied to the quantitative analysis of OC sources

(Akerjord et al. 1996). The equations, marked by $\delta^{13}\text{C}$ and $\Lambda 8$ (mg/100 mg OC) are as follows:

$$\Lambda 8_{\text{sample}} = \Lambda 8_{\text{soil}} \times f_{\text{soil}} + \Lambda 8_{\text{phyt}} \times f_{\text{phyt}} + \Lambda 8_{\text{plant}} \times f_{\text{plant}} \quad (1)$$

$$\delta^{13}\text{C}_{\text{sample}} = \delta^{13}\text{C}_{\text{soil}} \times f_{\text{soil}} + \delta^{13}\text{C}_{\text{phyt}} \times f_{\text{phyt}} + \delta^{13}\text{C}_{\text{plant}} \times f_{\text{plant}} \quad (2)$$

$$1 = f_{\text{soil}} + f_{\text{phyt}} + f_{\text{plant}} \quad (3)$$

where, f_{soil} , f_{phyt} , and f_{plant} represent the relative proportions of OC from the soil, freshwater plankton, and terrestrial vascular plants to TOC, respectively. Regarding the selection of background parameters, we used soil, plant, and plankton data from the Pearl and Wujiang River Basins, which are representative of previous studies, as background parameters. The following assumptions were used: $\Lambda 8_{\text{soil}} = 0.58$ mg/100 mg OC (Zhang et al. 2014), $\Lambda 8_{\text{plant}} = 15 \pm 5$ mg/100 mg OC (Goñi et al. 2003), and it is generally believed that freshwater phytoplankton do not contain lignin (Rezende et al. 2010); $\delta^{13}\text{C}_{\text{soil}} = -24.1 \pm 1\text{‰}$ (Yu et al. 2010), $\delta^{13}\text{C}_{\text{phyt}} = -30 \pm 2.6\text{‰}$ and $\delta^{13}\text{C}_{\text{plant}} = -27 \pm 2\text{‰}$ (Chen et al. 2009; Wei et al. 2020). MATLAB software was used to calculate the relative contribution value of each end-member of the OC in the sediments.

3 Results

3.1 Contents of lignin phenols, organic carbon, and isotopes in sediments

The values of $\Sigma 8$ and $\Lambda 8$ represent the lignin content in the sediment and organic carbon, respectively. Figure 2 shows the $\Sigma 8$ and $\Lambda 8$ values of the reservoir sediment cores from

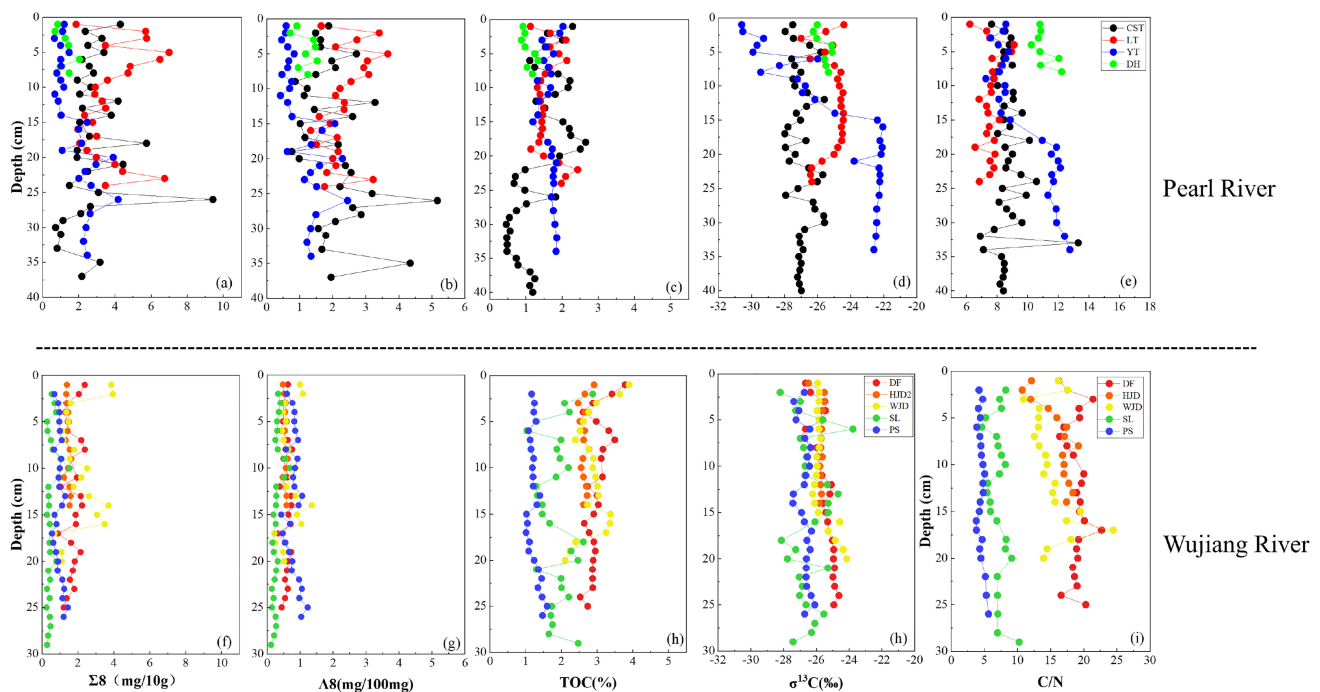


Fig. 2 Change in lignin content parameters $\Sigma 8$, $\Lambda 8$, TOC, and $\delta^{13}\text{C}$ with the depth of sediment cores

the Pearl River and Wujiang River. The $\Sigma 8$ value of the Chaishitan (CST) reservoir fluctuated more with an increase in depth and reached its maximum value at -26 cm. The variation range for both $\Sigma 8$ and $\Lambda 8$ was small in the shallow layer (-5 – 0 cm), and no considerable upward or downward trend was observed. The $\Sigma 8$ value showed the same trend as $\Lambda 8$ in the Longtan (LT) reservoir and increased lignin content in the shallow layer (-1 – 9 cm). In the Yantan (YT) reservoir, the $\Sigma 8$ and $\Lambda 8$ values had large fluctuations in the middle layer (-15 – 29 cm). The average lignin content ($\Sigma 8$) of the Dahua (DH) reservoir was the lowest. In the Wujiang River, the maximum value obtained was at -2 cm of the Wujiangdu (WJD) reservoir, and the maximum $\Lambda 8$ value was obtained at -14 cm of the WJD. Compared with the Pearl River sediment cores, there was a minor variation in the $\Sigma 8$ values.

The TOC contents of the reservoir sediment cores from the Pearl and Wujiang Rivers are shown in Fig. 2. The TOC curve of the CST1 was wave-shaped. The TOC content of LT remained stable in the middle layer (-19 – -7 cm) but increased in the shallow (-6 – -1 cm) and lower layers (-24 – -19 cm). The TOC content of the YT did not vary significantly but slightly increased at the surface (-2 – -1 cm). In the Wujiang River, TOC content was visibly higher than that in the Pearl River. Additionally, the TOC content in the SL reservoir fluctuated greatly.

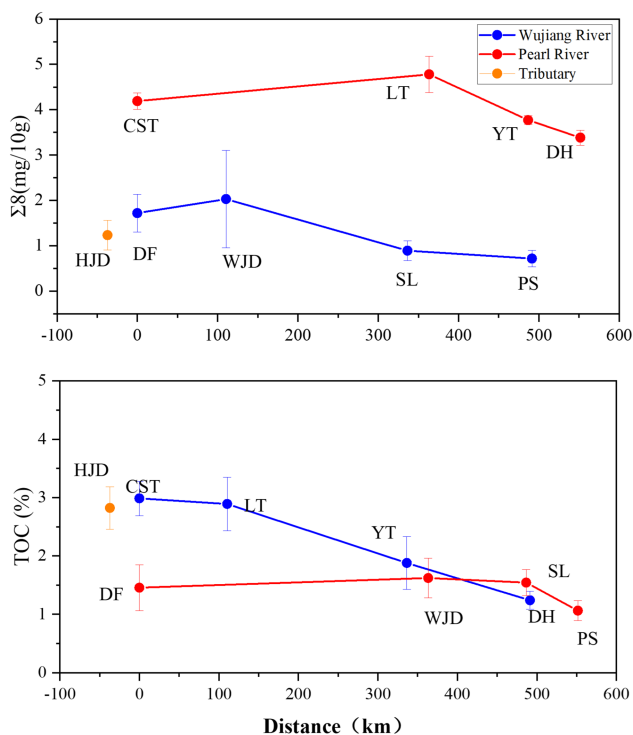
The mean value of sediment C/N in the Pearl River reservoir was 9.15, with insignificant changes. In contrast,

C/N values varied widely in the sediment cores of the Wujiang River reservoir; C/N values in the downstream reservoir were small, with a mean value of 6.32, while in the upstream reservoir they were large and decreased slightly after the construction of the reservoir (Table 2 for the construction node). As shown in Table 3, the $\delta^{13}\text{C}$ values of substances from different sources were different. This can be used to identify the source of the OC (Kendall et al. 2001). For the Pearl River reservoir, the $\delta^{13}\text{C}$ values of the sediment cores ranged from -30.60 ‰ to -22.05 ‰. In the upper sediments, the $\delta^{13}\text{C}$ values gradually increased with depth, whereas values remained stable in the deeper deposits. The $\delta^{13}\text{C}$ values of the sediment cores from the Wujiang River reservoirs ranged from -28.209 ‰ to -23.768 ‰. Except for the SL, where the $\delta^{13}\text{C}$ values varied dramatically, the $\delta^{13}\text{C}$ values of the other sediment cores were relatively stable.

The (Ad/Al)_v, (Ad/Al)_s, and P/(V + S) values of the reservoir sediment cores from the Pearl and Wujiang Rivers are shown in Fig. 3. The degree of sediment degradation in the upper reaches of the Pearl River was more significant than that in the Wujiang River. Moreover, the (Ad/Al)_s and (Ad/Al)_v had similar variation trends ($R^2 = 0.78$, $p < 0.01$). The maximum value was obtained at -21 cm in the CST. Compared with the upper and lower layers, the degree of degradation of the middle part of the CST (-21 to -7 cm), LT (-19 to -9 cm), and YT (-22 to -13 cm) sediment cores changed more significantly. The (Ad/Al) values of the Dongfeng (DF) reservoir

Table 3 Degradation parameters in different river basins

River Basin	TOC	TN	(Ad/Al) _v	(Ad/Al) _s	References
Amazon	0.58	NA	0.81	0.71	Sun et al. (2017)
Cyprus	0.2	0.04	0.23	NA	Thomas et al. (1999)
Baltic	2.59	NA	0.37	NA	Anja and Kay (2000)
Churchill Falls Hydroelectric (Canada)	1.29	0.078	0.69	0.34	Teisserenc et al. (2013)
Gulf of Mexico	1.323	0.157	0.474	NA	Sampere et al. (2011)
Qiantang River	0.762	0.091	1.063	0.339	(Yuan et al. 2017)
Pearl River (downstream)	1.38	0.12	0.3	0.24	Li et al. (2017)
Shuang River	1.01	0.17	0.402	0.579	Loh et al. (2020)
Jiao River	0.64	0.1	0.545	0.324	Loh et al. (2020)
Ximen River	0.61	0.11	0.379	0.937	Loh et al. (2020)
Feiyue River	0.67	0.09	0.331	0.482	Loh et al. (2020)
Ao River	0.85	0.13	0.262	0.242	Loh et al. (2020)
Yellow River	0.1183	0.094	0.525	0.226	Sun et al. (2011)
Bo Hai	0.177	0.014	0.645	0.228	Sun et al. (2011)
Sanxia	0.93	0.115	0.425	0.358	Ding et al. (2017)

**Fig. 3** Variation of TOC and $\Sigma 8$ content in the Pearl River and Wujiang River basin

sediment cores were higher in the middle layers (−12 to −8 cm). The (Ad/Al) values of the WJD decreased in the surface layer (−2 to −1 cm). The (Ad/Al) value of the central part (−14 to −3 cm) of the WJD was approximately 0.4, which is similar to that of the HJD, Silin (SL), and Pengshui (PS) reservoir (Ad/Al) values. The $P/(V + S)$ values of the upper layers (−17–0 cm) of the CST and LT were significantly greater than 0.4 and varied greatly, while

the $P/(V + S)$ values of the other sediment cores were all less than 0.4.

3.2 Three-end-member mixing model analysis

The three-end-member model calculation results indicated that, in the Pearl River reservoir, the contribution of soil to the sedimentary OC is 30.9–87.1%. In most sediment cores, (except SL, PS, and DH), the contribution of the soil OC in the shallow sediments was lower. The contribution rate of the soil at all sites increased with increasing depth. The contribution rate of vascular plants was 2.30–23.8%, lower than that of soil and phytoplankton, but its variation was relatively stable, with an average of 10.4%. The contribution rate of phytoplankton was 3.47–58.3%, in contrast to the soil contribution rate, the phytoplankton contribution rate decreased with increasing depth. In the Wujiang River sediment, the soil OC contribution rate was 17.8–95.1%, and the soil contribution rate was the highest in the upstream DF reservoir. The contribution rate of vascular plants ranged from 0.03–35.6%, with the maximum value appearing in the SL reservoir. The contribution rate of plankton was 2.82–79.7%, and the minimum value was obtained in WJD. Overall, the vascular plants contributed the least, and soil was the primary source of OC, similar to the sediment of the Pearl River reservoir.

4 Discussion

4.1 Lignin phenol

Lignin content in the surface sediments and TOC content showed a decreasing trend in both basins from the

upstream to downstream regions, reflecting the interception effect of dams on particulate matter (Fig. 3). Similar results were obtained in a study of surface sediments in the Wujiang River (Lin et al. 2021). Some studies have shown that the construction of reservoirs leads to interception, and larger particles can be easily intercepted upstream (Wang et al. 2019). Although the Pearl and Wujiang River Basins belong to the karst region of southwestern China and have similar climate types (subtropical monsoon climate) and major vegetation types of evergreen broadleaf forests, there was a significant difference in the lignin content in the sediments of their reservoirs. The lignin content in the sediments of the Pearl River Basin was much higher than that of the Wujiang River Basin. The maximum lignin content in the Pearl and Wujiang River sediments was obtained from the LT and WJD reservoirs, respectively. Important tributaries flow into both reservoirs, indicating that interval recharge of the tributaries is an essential supplement to terrestrial OC content in the sediments. (Figs. 4, 5)

The vegetation and soil around the reservoir were submerged at the initial stage of reservoir impaction, resulting in plant decomposition in the fluctuation zone and the

release of soil OC. With an increase in reservoir operation time, the input OC of the fluctuation zone tends to be stable (Routh et al. 2004). We estimated the depth of the sediment cores corresponding to the time node of the dam construction based on special events before and after the construction of the reservoir (data from our group) and the data are shown in Table 2. We observed that in the depth nodes of most sediment cores lignin content fluctuations were more consistent with the presumed reservoir construction time. In particular, WJD sediment cores were the most evident in the Wujiang River, and lignin content increased approximately 2.7 times after WJD water storage. Based on the grain size data and sediment color observations, we found that the grain size and color of sediment at -17 cm changed significantly, so we presumed that the year corresponding to -17 cm was 1982, the time of WJD reservoir construction. Studies have shown that the lignin content in sediments increases by 50–300 % after water storage (Houel et al. 2006).

Unlike lignin, the TOC content in sediment cores from the Wujiang River Basin was higher than those from the Pearl River Basin. First, there is low forest cover in the Wujiang River basin and thus low lignin content in the soil

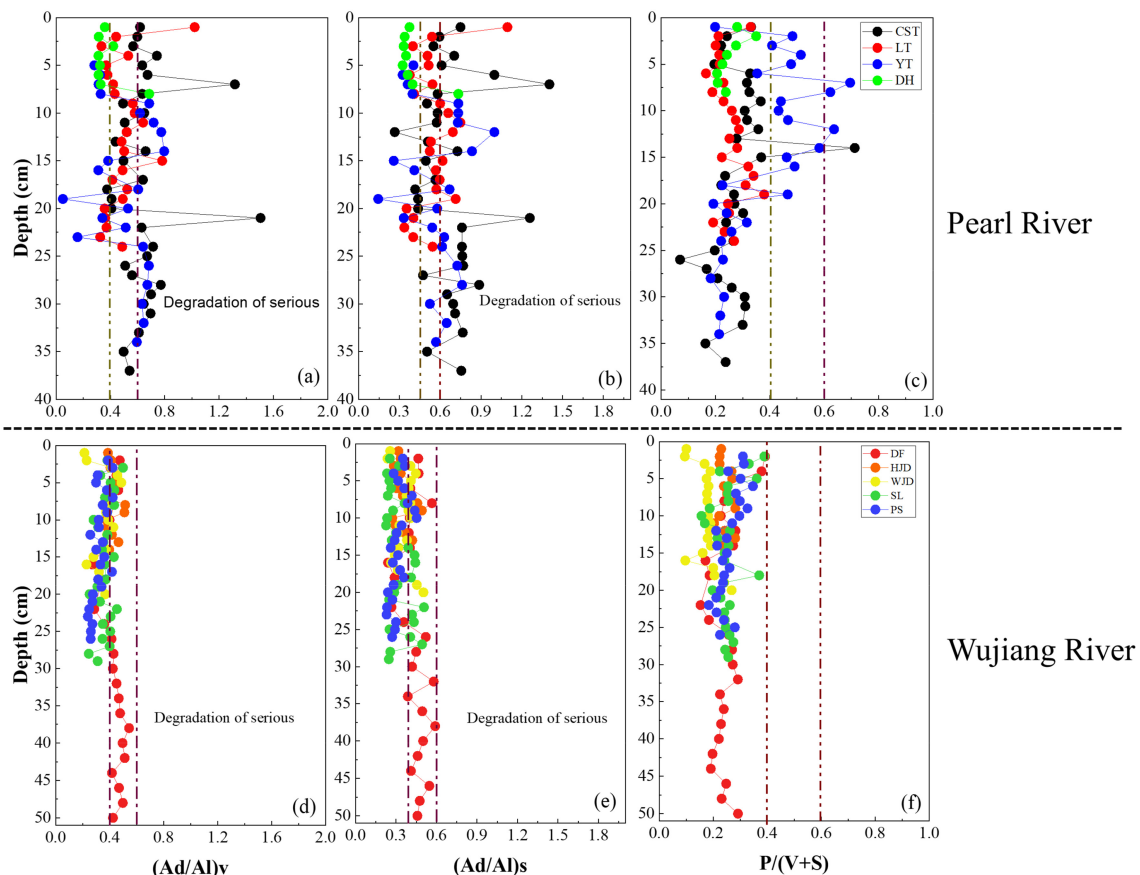


Fig. 4 Relationship between the information of degradation parameters with depth in different locations When Ad/Al ratio or $P/(V+S)$ exceed 0.4, it indicates degradation, and when they are greater than 0.6, it indicates extreme degradation

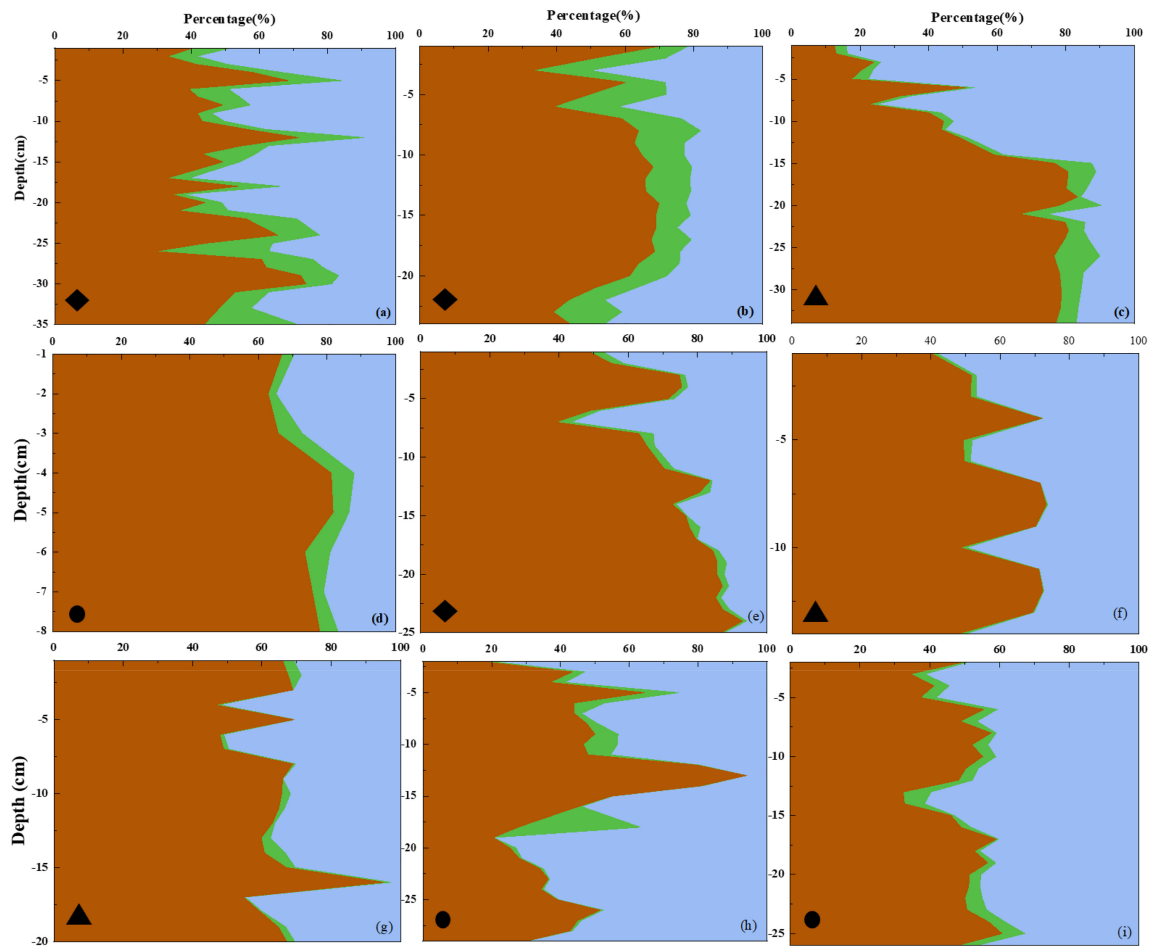


Fig. 5 Relationship between the analysis results of the source carbon of sediment cores and the depth **a** CST, **b** LT, YT, DH, DF, HJD, WJD, SL, PS; ♦ Annual regulation, ▲ Seasonal regulation, ● Daily regulation; blue: plankton; green: vascular plants; brown: soil

(Tao et al. 2009), resulting in the terrigenous OC input being less than that in the Pearl River Basin. Second, the Wujiang River water bodies had higher nutrient levels and autochthonous OC content, and several anthropogenic activities in the Wujiang River Basin have significantly influenced the exogenous OC input (Sekar et al. 2021). Different $\delta^{13}\text{C}$ values can be used to distinguish the source of organic matter (details can be seen in Table 3). For example, both $\delta^{13}\text{C}$ and C/N values decreased to different degrees after damming, indicating that the autochthonous OC content increased. Since most tissues of higher terrestrial plants do not contain nitrogen, the C/N value is normally higher than 20, whereas the C/N value of algae is generally around 7 (Robert et al. 1989). The variation of C/N and $\delta^{13}\text{C}$ in the sediment cores of the Pearl and Wujiang Rivers indicates that sediment OC is mainly a mixed input of terrigenous and endogenous OC. At the same time, the sediments in the upper reservoir of the Wujiang River were influenced by diagenesis resulting in a large C/N. (Table 4)

4.2 Degradation of OC in sediments within the catchment

Due to the difficulty of lignin degradation, only two basidiomycete fungi can degrade plant litter (Bugg et al. 2011). White-rot fungi oxidize lignin side chains through peroxidase or laccase (Daly et al. 2021). Normally, Ad/Al ratio increases with increasing degradation degree; when values exceed 0.4, it indicates degradation, and when they are greater than 0.6, it indicates extreme degradation. The demethylation of the methoxy, vanillyl, and syringyl components of lignin by brown rot fungi through a non-enzymatic Fenton reaction can significantly increase the P/(V + S) ratio (Lundell et al. 2010). The higher Ad/Al ratios indicate that the degradation in the Pearl River and Wujiang River reservoir sediments are the primary side-chain degradations caused by white-rot fungus oxidation. Compared with the Pearl River sediment, the degradation degree of the Wujiang River sediment was lower (moderate to low degradation). This indicates that although the climatic conditions and major vegetation types of the upper

Table 4 Range of $\delta^{13}\text{C}$ values from different OC sources

Sources	Range (‰)	Average (‰)	References
C3 Plant	– 33 ~ – 22	– 27	Yu et al. (2010)
C4 Plant	– 16 ~ – 9	– 13	Yu et al. (2010)
Marine phytoplankton	– 22 ~ – 20	NA	Zhang et al. (2008)
Freshwater phytoplankton	– 42 ~ 24	– 30	Cloern (2002)
Riverine soil	NA	– 24.1	Yu et al. (2010)

Pearl and the Wujiang Rivers are similar, there are large differences in lignin characteristics (degree of degradation and lignin content) between the two basin soils. The effect of brown rot bacteria on sediment degradation was low, except for YT. Considering the YT sampling site was close to the riverbank and the fact that the source of P-series phenols is not unique (Delwiche et al. 1989), the P/(V + S) of YT may be affected by human activities. Some studies on refractory OC in soil have found that adding easily decomposed OC (biogenic factors) has a positive excitation effect on the degradation of the refractory OC (Nottingham et al. 2009; Fontaine et al. 2007). Therefore, we investigated the relationship between TOC and TN content in sediment and the degradation parameters (Ad/Al)_v and (Ad/Al)_s. Unfortunately, there was no apparent linear correlation between them (Supporting Information).

4.3 Identification of terrigenous and autochthonous buried OC in sediment cores

As an essential link in the global carbon cycle, the change in a river's ability to bury OC reflects the impact of reservoir construction on the river carbon cycle. Therefore, identifying the source of OC in sediments can help us better understand the role of rivers in the global carbon cycle. We analyzed sediment cores in the reservoir areas to analyze the terrigenous and autochthonous sources of sedimentary OC using the three-end-member mixing model. Compared with the sediment cores in other reservoir locations, the planktonic OC contribution of the WJD sediment core did not show an increase due to the construction of the reservoir, presumably related to the location of the sampling site. The WJD sampling site was located in the inlet area, and the hydraulic conditions in this location are similar to the delta locations at the river inlets. Delta locations have shown to be favorable to the deposition of particulate matter and unfavorable to the growth of plankton (Sobrinho et al. 2021). Therefore, this explains the difference in the variation of planktonic OC sources between the WJD sediment core and other reservoir locations.

In the upper reaches of the Pearl and Wujiang Rivers, soil and plankton were the primary sources of OC in the sediments, and the proportion of OC from plants was small,

consistent with the C/N and $\delta^{13}\text{C}$ results. The plankton contribution in the sediment of the Wujiang Reservoir was higher than that of the Pearl River (Wujiang: $39.09 \pm 10.81\%$; Pearl River: $31.80 \pm 8.17\%$), and the contribution rate of plants was lower than that of the Pearl River (Wujiang: $2.54 \pm 1.26\%$; Pearl River: $8.79 \pm 4.34\%$). This trend is consistent with the previous hypothesis that the lignin content in the sediments of the Wujiang River Basin is low, but TOC content is high. OC in the sediments of the Wujiang River Basin mainly originates from autochthonous OC. The PS reservoir, located in the Chongqing Province, had the highest contribution rate from plankton. After the construction of the reservoir, the contribution rates of sediment cores from different sources fluctuated remarkably, indicating that the construction of the reservoir affected the input of terrigenous OC. Overall, the contribution of soil decreased, whereas that of plankton increased.

The reservoirs in the Pearl and Wujiang Rivers belong to sub-deep-water (water depth: 10–50 m) and deep-water (water depth > 50 m) reservoirs with seasonal thermal stratification, among which DH, WJD, and SL are sub-deep-water reservoirs. After dam construction, the river velocity slows down and produces a static water effect prone to seasonal thermal stratification and limnetic evolution of the reservoir. The occurrence of limnetic evolution of the reservoir is beneficial to nutrient deposition and algal growth, which leads to an increase in the effective carbon sink in the river and thus affects the river carbon cycle (Williamson et al. 2009). According to the hydraulic retention time, the nine reservoirs can be divided into annual, seasonal, and daily regulation reservoirs. According to the results of the three-end-member mixing model, the plankton contribution rate in the annually and seasonally regulated reservoirs increased after dam construction.

Overall, the phytoplankton contribution rate in the annual regulation reservoir of the Pearl River increased by $6.90 \pm 1.48\%$, whereas the seasonal regulation reservoir of the YT increased by 29.09%. The annual and seasonal regulating reservoirs in the Wujiang River increased by 5.48% and 17.61%, respectively. However, the daily regulated DH, SL, and PS reservoirs did not show a noticeable increase in plankton contribution rate (DH sediment core was too short to analyze the change of phytoplankton OC

after reservoir construction). This may be because: (a) these reservoirs are downstream of the cascade reservoirs and are blocked by dams, resulting in a low nutrient load that is not conducive to plankton production; and (b) the daily hydraulic residence time of the regulating reservoir is short, and limnetic evolution of reservoir is not apparent. Therefore, the reservoir regulation type is an essential factor affecting autochthonous OC accumulation.

5 Conclusion

This study aimed to analyze the effect of cascade reservoir construction on the input of OC in river sediments and the change in autochthonous OC of the effective carbon sink. Lignin was used as a biomarker to trace terrigenous OC in sediment cores collected from the cascade reservoirs of the Wujiang and Pearl Rivers. Moreover, the contribution rate of autochthonous OC was calculated using a three-end-member mixing model. The results showed that dam construction had a blocking effect on terrigenous OC, and lignin content in the two rivers showed a decreasing trend from the upper to the lower reaches due to cascade interception. The lignin content in sediments from the Pearl River was much higher than in the Wujiang River. The reservoir sediments in Southwest China are mainly degraded by side-chain oxidation caused by white-rot bacteria under aerobic conditions, except for sediment cores near the shore, which show a high degree of methoxyl degradation caused by brown-rot bacteria. The three-end member mixing model results show that OC in the sediments of the Pearl and Wujiang Rivers mainly originated from soil and plankton. Due to the change in hydraulic conditions in the reservoir area, the contribution rate of plankton to the annual and seasonal regulation reservoirs increased. In contrast, the plankton contribution rate in the daily regulation reservoirs did not increase or decrease.

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Author's contributions All authors contributed to the study conception and design. Li Gao: experimental analysis; data curation; formal analysis; writing—original draft; writing—review and editing. Xin Lin: sample collection; data curation; experimental analysis. Jun Fan: sample testing. Ming Yang: supervision. Xueping Chen: supervision. Fushun Wang: investigation. Jing Ma: validation; supervision.

Availability of data and material All data generated and analyzed during this study are included in this published article and its supplementary information files.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Consent for publication Not applicable.

Consent to participate Not applicable.

Ethical approval Not applicable.

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