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Sedimentary organic matter of channel type reservoirs: Input of lipid biomarker for source assessment

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Abstract: The cascade hydropower development has led to fragmentation of riparian habitats and increased sediment retention in reservoirs, while the impact of channel-type reservoirs on the distribution of organic matter (OM) sources is poorly studied and the mechanism is unclear. In this study, surface sediments from 11 sampling sites in the Pubugou Reservoir on the Dadu River were selected, and the sediment OM was extracted and analyzed by gas chromatography-mass spectrometry (GC-MS), and the OM was quantified and divided into natural, diagenesis, heat source and sewage markers. The results showed that OM was mainly derived from natural input (46.4%), mainly from riverine vegetation (i.e., higher plant sources) and microbial sources in aquatic environments. It is noteworthy that the head of the reservoir is close to the Hanyuan town area, where anthropogenic inputs are significantly higher (59.8%), and further studies on the proportion of effluent, rock-forming and thermal sources to anthropogenic inputs on this basis emphasise the contribution of effluent inputs, in addition to the average OM content of the head of the reservoir (10.7%) > the tail of the reservoir (7.3%) > the middle of the reservoir (6.7%), which may be related to the reservoir's role in trapping OM. Given the high overall primary productivity of reservoirs and the wide variation in the composition of OM sources in reservoirs, more attention should be paid to the discharge of anthropogenic pollution in reservoir areas in channel-type reservoir OM studies.

Key words: organic matter; reservoir; source apportionment; lipid biomarkers,

Introduction

The impoundment effect resulting from the construction of a riverine reservoir often directly affects the spatial and temporal distribution, burial and transport of sediment organic matter (OM) in the watershed. A comprehensive understanding of the dynamics of sediment OM remains challenging due to the morphological structure and throughput flow characteristics of reservoirs [1] as well as the complex structure and diversity of sources of sediment OM. The composition of OM in reservoir areas is closely related to its origin and is the joint result of multiple allochthonous and autochthonous primary producers, such as phytoplankton, benthic macroalgae, herbaceous plants, and anthropogenic OM [2-5]. However, a comprehensive origin and dynamics of reservoir sediment OM to further explore the transport transformation of OM in reservoirs is yet to be investigated.

A broad spectrum of characterization methods are available for OM, from basic measurements of dissolved organic carbon, ultra-violet (UV) absorption or molecular weight distribution [6] to advanced techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), homology and heterology correlation multidimensional nuclear magnetic resonance (NMR) and excitation-emission matrix spectroscopy combined with parallel factor analysis (EEM-PARAFAC) [7], and a variety of tools have been widely used to identify OM origins, including stable carbon isotopes, molecular biomarkers and spectral indices. Of these, the single technique of stable carbon isotopes has inherent limitations in revealing source assignment [8], spectral indices identify OM based on large molecules of humic acid and fulvic acid in a large number of water samples, while lipid biomarkers target a single group of molecules to track OM sources, which not only distinguish between exogenous, local sources and anthropogenic inputs, but also show the ability to identify subgroups of these three sources and, in some cases and

even identify the sources of specific species of organisms (e.g. bacteria, plants, plankton) [9-11], and thus are widely used in OM traceability efforts for their high resolution of mixed sources [12-14], while few studies have been reported to explore the distribution of organic matter sources in reservoir-type river sediments by this method [13-15].

The development of hydropower in the Dadu River terrace has led to increased fragmentation of riparian habitats and a significant increase in hydraulic retention time (HRT) [15], increasing sediment trapping [16], so it is important to study the impact of reservoir creation on the source distribution of OM. In this study, we used gas chromatography-mass spectrometry (GC-MS) to quantify molecular markers of OM in the sediments of the Dadu River (a mid-step control reservoir). The lipid markers were classified into natural markers (higher plants, bacteria and microalgae, algae), anthropogenic markers (including petrogenic ones, pyrogenic ones and fecal markers) and non-specific molecules according to their sources, so as to (1) compare anthropogenic and natural inputs; (2) explore the reservoir-type river OM distribution and sources to track the effects of industrialization and agriculture on this small hydrological system. The results of this study can enhance the understanding of OM retention during dam construction on typical rivers and provide a reference for river and dam management.

1 Materials and methods

1.1 Study Area

Dadu River flows through central and western Sichuan Province, with a total length of about 1,062 km and a drainage area of about 77440 km². It is the largest tributary of Minjiang River, a tributary of the Yangtze River in China. Its main cascade development projects consist of three reservoirs and 22 levels. Among them, Pubugou Reservoir is the 17th hydropower station completed in 2009 and belongs to the control reservoir in the middle reaches of the cascade. In this study, Shufugou Reservoir is taken as the research area, with a reservoir capacity of up to 539 million m³, annual rainfall of 741.8 mm and average temperature of 22°C. Sampling points are selected in the middle, front and end of the reservoir, as shown in Fig 1.

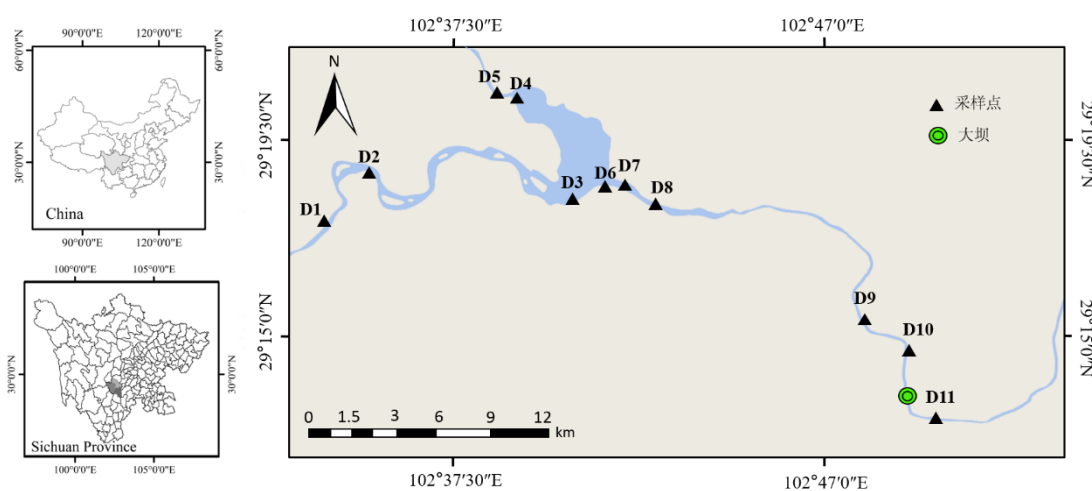


Fig.1 The map of sample sites

1.2 Sample collection

In this study, 11 representative sampling sites were selected in the watershed based on hydrogeological characteristics and the distribution of pollution sources, and the specific information of the sampling sites is shown in Table 1. sampling time was December 2019, and the sampling sites were spatially divided into three groups: (1)

D1-D5 represents the middle of the reservoir; (2) D6-D10 represents the reservoir; (3) D11 represents the end of the reservoir. Surface sediments were collected from 0-5 cm depth using Peterson samplers. To ensure sediment representativeness, triplicate samples were collected at each site, the three samples were mixed to obtain a single 500 g of sediment from each site, and after sampling, the samples were stored in sealed polyethylene plastic bags (stored at 4°C) for for the determination of the particle size and organic matter content. The lipid biomarkers preparation and analyses were performed at the Ladamo group of the CONDATE-eau analytical platform of Rennes University, France (<https://osur.univ-rennes1.fr/empreinte-moleculaire>).

1.3 Measurement and analysis

1.3.1 Determination of organic matter content and particle size

After drying and filtering the sediment samples, OM calcined each sediment sample in a muffle furnace for the amount of combustion loss (550 °C for 2 h). By the analysis of the LS 230 laser diffraction particle analyzer (Microtrac S3500), the sediment particle size is divided into three categories: (1) clay: < 4 µm; (2) silt: 4-63 µm; (3) coarse sand: > 63 µm.

1.3.2 Sample preparation for lipid biomarkers analysis

Samples were collected and frozen for two days and freeze-dried for three days. The freeze-dried samples were sieved and ground to 0-2 mm. freeze-dried samples were extracted with dichloromethane using an accelerated solvent extractor (Dionex™ ASE™ 200) according to the following conditions, modified from Derrien et al [18]: 33 mL cells, 5 min heating at 100°C and 60 bars, 10 min static phase, completed with 80% flush and 20-s purge with nitrogen. Elemental sulfur was removed from the total lipid fraction by reduction on metallic copper. The total lipid extract was then fractionated into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds on a silica column by successive elution with cyclohexane, cyclohexane/dichloromethane (2/1, v/v) and methanol/dichloromethane (1/1, v/v).

1.3.3 Analytical Methods

Polar fractions were analyzed by capillary gas chromatograph-mass spectrometer (QP2010SE GC-MS, Shimadzu) after derivatization using a mixture of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMSC) (99/1, v/v), whereas the aliphatic and aromatic fractions were analyzed without further treatment. The injector used was in splitless mode and maintained at a temperature of 310°C. The chromatographic separation was performed on a SLB-5MS capillary column (length = 60m, diameter = 0.25mm, film thickness = 0.25 µm) under the following temperature conditions: 70°C (held for 1 min) to 130°C at 15°C/min, the 130°C to 300°C (held for 15 min) at 3°C/min. The helium flow was maintained at 1 ml/min. The chromatograph was coupled to the mass spectrometer by a transfer line heated at 280°C. The analyses were performed in full scan mode. The organic compounds were quantified by using an external calibration adding an internal standard in the solutions containing the aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds as per [30].

表 1 采样点经度、纬度和污染类型

Table 1 Longitude, latitude and pollution type of sampling sites

采样点	经纬度		Type of pollution
D1	102°26'32" E	29°15'58" N	Calcium carbonate plant, cement plant
D2	102°34'25" E	29°20'9" N	Relocation of lead and zinc mines
D3	102°39'40" E	29°18'27" N	Lead and zinc mine upstream inundation area
D4	102°38'8" E	29°23'20" N	Agricultural pollution
D5	102°37'34" E	29°24'30" N	Pig farm outfall
D6	102°41'28"E	29°19'4"N	Fishery aquaculture
D7	102°43'26" E	29°20'10" N	Industrial park outfalls

D8	102°43'18" E	29°19'34" N	Industrial sources of pollution
D9	102°48'25" E	29°15'4" N	Domestic sewage, black mackerel farming station
D10	102°49'43" E	29°14'14" N	Mine plant relocation
D11	102°50'37" E	29°12'15" N	No farmland nearby, no residents seen

2 Results and discussion

2.1 Sediment size and OM distribution

Grain size, as one of the basic properties of sediments, can reflect their material origin and the relationship between different grain size fractions and the source area of the sediment [20]. The surface sediments of the reservoir are dominated by chalk and coarse sand, of which the average contents of clay, chalk and coarse sand are $13.1 \pm 5.0\%$, $47.1 \pm 15.6\%$ and $39.7 \pm 18.9\%$, respectively (Table 2). The mean median grain size in the reservoir area is $42.8 \pm 25.6 \mu\text{m}$, with a decrease in coarse sand content and an increase in the proportion of clay; the median grain size downstream of the reservoir (dam) is $92.9 \mu\text{m}$. The mean grain size downstream of the reservoir dam is larger than that in the mid-stream river section before the dam, and similar phenomena have been found (e.g., downstream of the Black River channel (0.82 mm) > mid-stream (0.22 mm)) [21-23]. The mean OM content in the reservoir area ($10.7 \pm 4.8\%$) was significantly higher than in the downstream (7.3%) and upstream ($6.7 \pm 1.8\%$) reaches of the reservoir, indicating that OM was significantly trapped within the reservoir [24, 25].

The presence of the dam resulted in slower flow rates in the reservoir area, depositing large amounts of fine particles, which in turn adsorbed and preserved more OM, consistent with the findings of Rapin et al [26] and Xu et al [27]. In addition, the finer particle size of the sediments in the reservoir area creates favorable conditions for long-term physical or chemical accumulation and storage processes of OM [28]. In contrast, under fast flow conditions downstream of the dam, more fine-grained particles are washed away by the water flow and large agglomerates are less protective of OM, which may be a key factor for the lower OM content downstream [29].

OM consists mainly of polar compounds, an average of 51.6% (Figure 2). From upstream to downstream, the proportion of polar OM decreases from 53.7% to 44.4% and the proportion of aliphatic hydrocarbons increases from 33.7% to 42.4% . The proportion of aromatic hydrocarbons remained at around 13.9% .

Table 1 Organic matter composition and particle size parameters of surface sediments

采样点	有机质 OM (%)	Clay (%)	sand (%)	Coarse sand (%)	Median size (μm)
D1	7.27	13.39	65.46	21.15	27.17
D2	8.92	14.55	55.63	29.83	41.35
D3	4.02	7.67	28.59	63.75	86.79
D4	6.95	11.77	41.46	46.77	57.21
D5	6.38	11.56	49.49	38.95	47.39
D6	4.03	6.88	29.92	63.2	84.23
D7	16.77	14.3	59.03	23.48	33.56
D8	8.80	20.86	67.15	11.99	20.74
D9	10.32	20.59	53.93	27.59	26.02
D10	13.55	15.94	41.11	42.95	49.3
D11	7.25	6.02	26.79	67.19	92.85

Table 2 Classification of organic compounds determined by GC-MS in organic matter

Class of biomarkers		Molecules
Natural	Higher plants	n-Alkanes nC25 to nC35 with CPIh1 > 5 except for nC24, nC25 and nC26 from terrestrial origin based on CPII and CPIh ; n-alcanoic acids from nC20 to nC30 ; w-hydroxyalcanoic acids ; a,w-alcanoic diacids n-Alkanols from nC20 to nC30 ; Campesterol ; Stigmasterol
	Bacteria and microalgae	n-Alkanes from nC15 to nC19 ; alcanoic acid iso and anteiso C15 and C17 ; Brassicasterol ; Cholesta-5,22(E)-dien-3b-ol
	Algae	n-Alkanes from nC20 to with CPII > 2 except for nC24, nC25, nC26 from algal origin based on CPII and CPIh; néophytadienes ; Fucosterol et Isofucosterol
	Fecal	Coprostanol ; Epicoprostanol ; 24-Ethylcoprostanol ; 24-Ethylepicoprostanol
Anthropogenic	Fecal contamination	
	Petroleum and petroleum product	n-Alkanes from nC12 to nC14 ; n-Alkanes from nC20 to nC24 with CPII = 1 ; n-Alkanes from nC25 to nC35 with CPIh = 1 ; Hopanes ; Triterpanes tricycliques, Pristane, Phytane, Bicyclohexane
	Pyrogenic (combustion)	Polycyclic aromatic hydrocarbones (PAH) from Naphthalene to Benzo(ghi)perylene including methyl-PAH
	Ubiquitous (non specific)	Cholesterol;Sitosterol;Cholestanol; Epicholestanol; Campestanol; Epicampestanol, 5b-campestanol, Sitostanol; Cholestan-3-one; alcanoic acid from nC10 to nC19 ; alcanoic acid with 12 to 15 carbon atom with a methyl group; alcanoic acid with 16, 18 and 22 carbon atoms; octadecadienoic acid (C18:2), n-Alkanols from nC11 to nC19

Note: CPI is the carbon preference index; CPII = nC20 to nC25; CPIh=nC25 to nC35

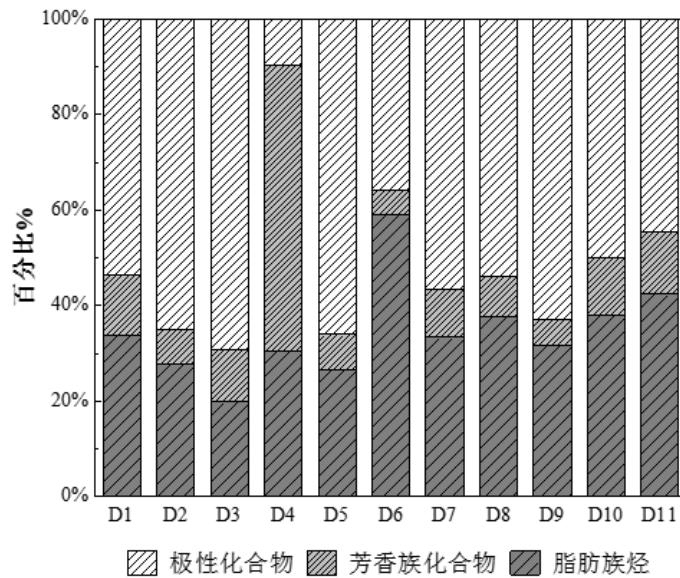


Fig.2 Composition of the extractable organic matter

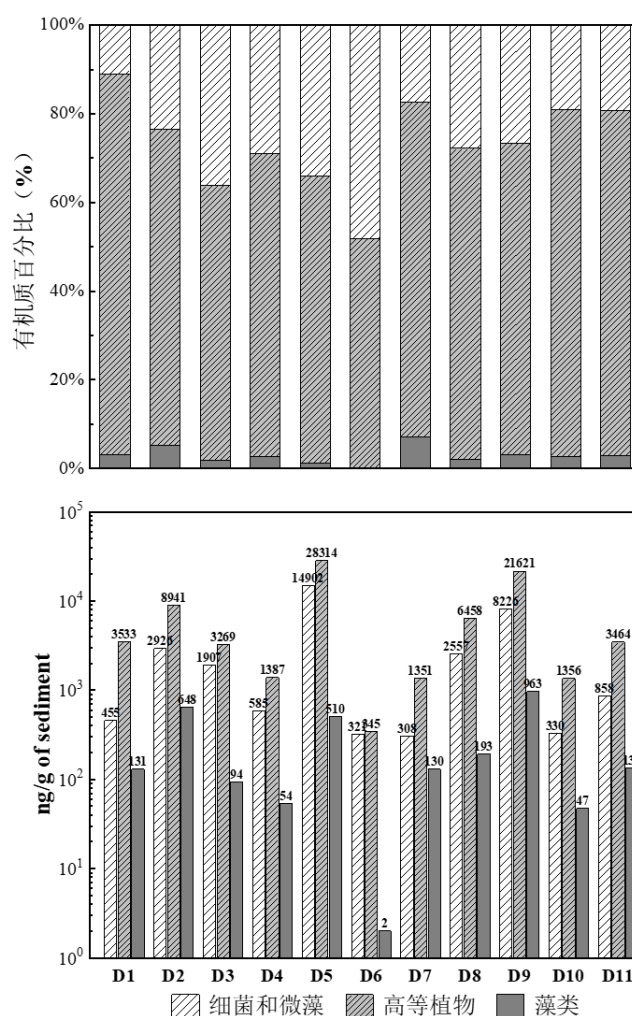
2.2 Sources of natural markers

Sediment OM natural source markers can be divided into bacteria and microalgae, higher plants and algae (Figure 3). Among them, the input sources of higher plants were the most prominent, with an average of $70.5 \pm 9.1\%$ (ranging from 51.7%-85.3%); bacterial and microbial inputs were approximately $26.5 \pm 10.3\%$ (ranging from 11.0% to 48.1%); OM also contained trace algal inputs of $2.9 \pm 1.9\%$ (ranging from 0.1% to 7.2%). This may indicate that higher plant inputs dominate the natural sources of organic matter in the sediment.

Natural molecular markers present in the sediments (Table 2) are mainly terrestrial plants of neophytadiene [34] from chlorophyll a and nC24-nC34 n-alkanes (odd carbon more than even carbon predominates), indicating that OM is mainly derived from riparian vegetation. The carbon preference index (CPI) numerically represents the degree of preservation of the length of the original biological chain [35]. When CPI (from nC21 to nC25) > 5 , it means that high molecular weight n-alkanes ($> nC20$) are dominant [36], and there are odd and even carbon advantages, which are the characteristics of input from higher plants [37]. When CPI values are close to 1.0, there is no preference for odd or even carbon, indicating a source of petroleum hydrocarbons [38, 39]. In the sediments of the study area, CPI ranges from 1.7 to 2.7 (Table 4), emphasizing the mixed input of natural and anthropogenic sources [40, 41]. The main land use and cover types in this area are mainly woodland and cultivated land, which may be related to local villagers' annual pruning of fruit tree branches and discarding abandoned branches and vegetable leaves on the shore during crop harvest.

Natural input sources are also characterised by the occurrence of n-alkanols, which have an even over odd carbon number predominance, and these compounds are resistant to degradation after plant decay, so they can be used as biomarkers for the transport of terrestrial higher plants into the water column [31]. The contribution of phytosterols is also evidenced by their presence, such as campesterol and stigmasterol, they are the main sterols in higher plants and they are present in large quantities in the loquat, grape and orange crops that are most grown in the region [32], so agricultural activities may be their main source. Brassicasterol may also be markers of aquatic primary production, as this molecule is the main sterol in the early algae family as well as several diatoms (Bacillariophyceae) and methanogens (Methanogaster) [33]. The high primary productivity resulting from the

enrichment of planktonic nutrients required by agricultural and urban activities suggests a high source of primary OM in the Dadu River.



(Bacteria and microalgae, higher plants, algae)

Fig.3 Source of natural markers

2.3 Sources of anthropogenic markers

With the speeding up of urbanization process, many industrial park rise in rural areas. From upstream to reservoir areas, industrial and agricultural areas have increased significantly, and the input of different organic compounds from industrial and domestic sewage, leaching from urban and industrial surfaces, atmospheric deposition and accidental leakage will all lead to the importation of different organic matter from anthropogenic sources. These inputs induce the occurrence of anthropogenic activities signature molecules such as polycyclic aromatic hydrocarbons (PAH) and hopanes (Table 3) [40].

Among the anthropogenic source markers, petrogenic markers contributed the most, with an average proportion of $80.8 \pm 13.6\%$ (maximum reached 6262.1 ng/g) (Figure 4). These molecules come from non-heat source uses of fossil organics, such as lubricating oils, greases, and road asphalt. Hopanes is the main diagenetic molecular marker in the sediments of the Dadu River. Diagenetic markers in reservoir sediments, with the predominance of hopanes, tricyclic triterpanes, pristane, phytane and n-alkane distributions with a slight predominance of odd-numbered compounds, indicate the presence of OM from petroleum crude oil (crude unprocessed petroleum) or petroleum by-

products (e.g. fuels, oils, lubricants or bitumen). Municipal and industrial wastewater, atmospheric fallout, leaching in urbanized areas and accidental oil spills are the causes of their accumulation in river sediments, such as by-products from industrial activities (industrial wastewater, atmospheric fallout, etc.); oil, asphalt washed down from roads in rain; Exhaust gases from automobiles are hydrocarbons that settle through atmospheric dry and wet settlement.

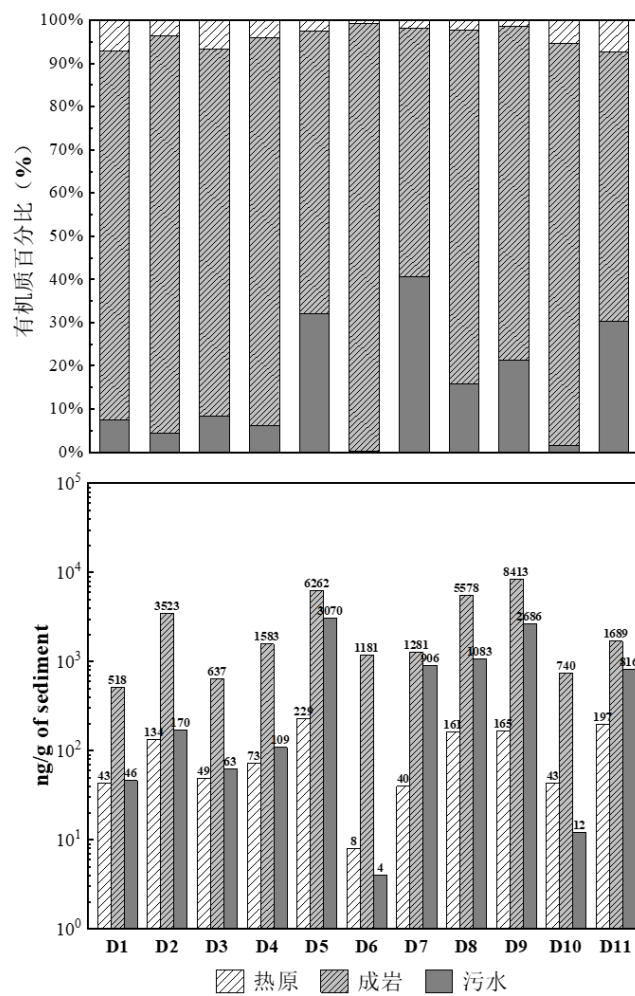
The sewage marker was greater at $16.0 \pm 16.6\%$ in the reservoir than at $11.7 \pm 11.5\%$ in the upper reservoir (Figure 4). The main sewage marker compounds present in the samples is coprostanol, which is derived from the degradation of cholesterol by the digestive systems of sheep, cattle, pigs, cats and humans [41]. The ratio of fecal prostatic coprostanol/cholesterol to fecal coprostanol depends on the animal that produces it, and values above 0.06 are characteristic of human feces [42]. In the Dadu River sediment, the ratio ranged from 0.1 to 0.7, suggesting that fecal coprostanol was deriving from human origin and domestic sewage. According to the actual site pollution source survey, the coverage of domestic sewage treatment facilities in the area is very low and the vast majority of domestic sewage is discharged on site [43].

Pyrogenic markers can be obtained from several combustion processes, such as vehicle emissions, wood combustion, coal combustion, and coal tar. Using the ratios calculated from isomers of the same molecular mass to distinguish different heat sources (Figure 5), the ratio of fluorene to fluoranthene and pyrene (Fl/Fl+Py) was used to distinguish between oil combustion and other types of combustion. Fl/Fl+Py is between 0.52 and 0.61, indicating that the heat source is mainly the combustion of grass, wood and coal. In addition, the allocation of combustion sources should also be confirmed by the ratio of other molecules, such as IP/IP+Bghi, BaA/228 ratios between 0.38 and 0.48 and 0.28 and 0.44, all of which further emphasize the combined contribution of grass, wood coal combustion and liquefied petroleum fuels, indicating that nearby rural residents still maintain a more traditional agricultural production lifestyle.

表 4 正构烷烃、芳香分子和类固醇的比率
Table 3 Ratio of n-alkanes, aromatic molecules and steroids

		D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11
正构烷烃	CPI	2.6	2.4	1.9	1.7	1.9	1.9	1.7	2.2	2.7	1.8	1.8
芳香分子	Fl/Fl+Py	0.6	0.5	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.6	0.6
	IP/IP+Bghi	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.4	0.5	0.5	0.5
	BaA/228	0.4	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.3	0.4
类固醇	Coprostanoll to cholesterol+coprostanol	0.3	0.1	0.1	0.2	0.4	0.11	0.7	0.7	0.4	0.1	0.7

注: $CPI = 0.5 * ((n-C21 - 25) / (n-C20 - 24) + (n-C21 - 25) / (n-C22 - 26))$.



(pyrogenic, petrogenic, sewage markers)

Fig.4 Source of human activity markers

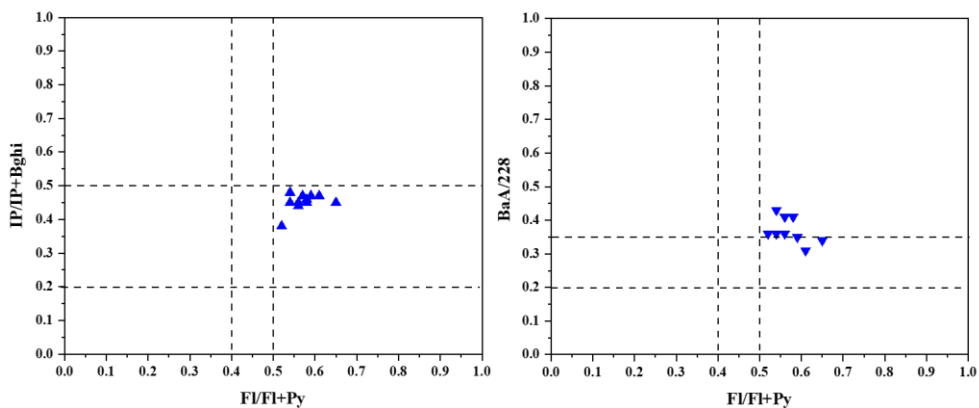


Fig.5 Sources of Polycyclic Aromatic Hydrocarbons

2.4 Comparison of natural and anthropogenic inputs

Although irregular discharges from towns as well as industrial agriculture were present in the vicinity of the Dadu River at the time of the actual site contamination survey, the presence of molecular markers in the sediment clearly indicates that OM is predominantly a natural input (Fig. 6), with these molecules accounting for $46.4 \pm 13.4\%$ (21.5%-67.3%) of the quantitative molecules. The organic matter in the sediment was mainly derived from terrestrial plants and bacterial microalgae, indicating high reservoir productivity, and similar results have been obtained in previous studies [14, 46, 47]. Rainfall is one of the main routes of terrestrial input, and the splashing, scouring and transport of surface soils around river dams by rainfall results in runoff carrying large amounts of terrestrial organic matter. With an average annual rainfall of 741.8 mm in the area, the Cascade Gorge Reservoir considers the flood control needs of the Sichuan and Chongqing sections of the river while intercepting and reducing flooding in the basin [48].

The anthropogenic input (31.4%) OM was greater in the reservoir area (D6-D10) than upstream of the reservoir (D1-D5) (15.9%). Significant anthropogenic input (59.8%) was observed at points D6 and D7, probably because D6 and D7 are located in Hanyuan County town, at the end of Hanyuan Lake, where the river channel narrows and is densely populated with multiple sources of discharge such as aquaculture and sewage; at the same time, the flow velocity in the reservoir area slow, coupled with the retention effect of the dam, the OM retention capacity of the reservoir area is enhanced, limiting biodegradation under the conditions of low water velocity [49]. In a study by Zeng Hongping and others [50] on the same reservoir-type river, the Yangtze River, it was also found that most of the organic matter was retained in the reservoir area under the influence of the dam. The proportion of rock-forming molecules remained constant throughout the sampling area, with petroleum crude oil and petroleum by-products (e.g. fuels, lubricants and bitumen) being the main source of rock-forming material in the Dadu River.

The low proportion of anthropogenic input to the Dadu River in reservoir-type rivers compared to natural input may be due to the fact that the waterfall ditch reservoir has both a water supply function and a high demand for water quality, so the anthropogenic input of organic matter to the Dadu River in reservoir-type rivers is better controlled.

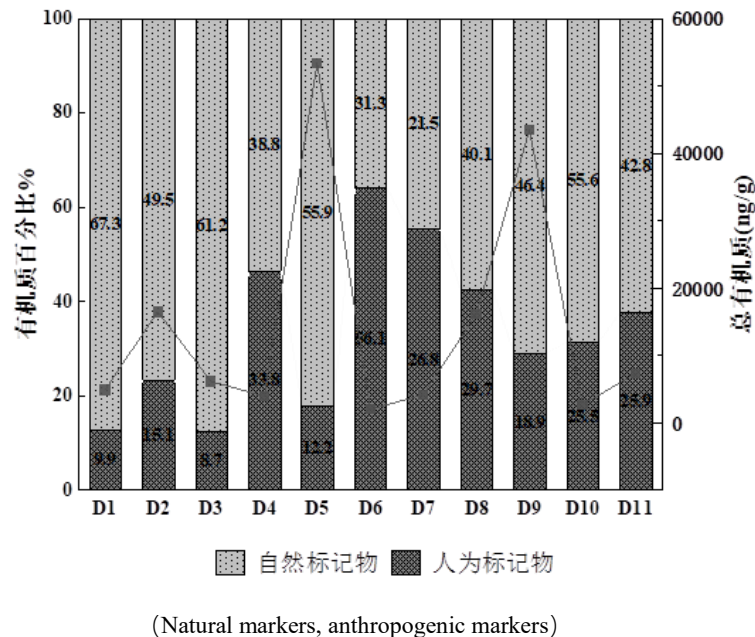


Fig.6 Comparison of human and anthropogenic markers

3 Conclusion

(1) The average content of OM in this river-type reservoir was $(10.7 \pm 4.8\%) > (7.3\%) > (6.7 \pm 1.8\%)$. OM was obviously retained in the head of the reservoir, which was related to the deposition of a large number of fine particles in the head of the reservoir.

(2) Natural input was the main contributor of OM content ($46.4\% \pm 13.4\%$), mainly from riverine vegetation (33.1%) and from aquatic microorganisms (12.0%). The main organic compounds were nC24-nC34 n-alkanes.

(3) The source of OM at the head of the reservoir (near Hanyuan town) was dominated by anthropogenic input (31.4%). Compared with the source of OM in the reservoir (15.9%), the anthropogenic input significantly increased, and the contribution rate of sewage input was larger, which was considered to be related to the low coverage rate of domestic sewage treatment facilities in the residential area, and its core mechanism was related to the coupling effect of reservoir retention effect. Therefore, when studying the distribution characteristics of OM sources in channel reservoirs, more attention should be paid to the anthropogenic pollution emission at the head of the reservoir and the influence of cascade dam construction on OM sources.

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