

# 漓江地表水体有机碳来源

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**摘要:** 科学辨识河流有机碳来源是碳循环研究的关键. 本文选取典型岩溶流域漓江流域为研究对象, 通过同位素示踪法、相关分析法、端元混合模型, 利用碳稳定同位素、C/N 对其 2016 年 7~9 月有机碳来源进行研究. 结果表明: ① DIC 浓度空间分布特征为: 岩溶区 > 岩溶区与非岩溶区的混合区 > 非岩溶区; 干流区 DIC 浓度从上游到下游递增, 主要受控于流域碳酸盐岩的空间分布比例. ② DOC 是构成漓江水体 TOC 的主体, TOC 来源以内源有机碳为主, 内源碳浓度空间分布特征为: 岩溶区 > 混合区 > 非岩溶区, 可能与岩溶区水生植物丰茂、碳酸酐酶活性较强有关, TOC 中内源碳的浓度介于 1.02~5.14 mg·L<sup>-1</sup>, 平均为 2.54 mg·L<sup>-1</sup>; TOC 中内源碳的比例空间分布差异不大, 平均为 73.07%. ③ POC 浓度、POC 中内源碳的浓度及 POC 中内源碳的比例空间分布差异不大, POC 来源以外源碳为主, POC 中内源有机碳浓度介于 0.01~0.16 mg·L<sup>-1</sup>, 平均为 0.05 mg·L<sup>-1</sup>, 水生生物量对漓江流域 POC 贡献平均为 17.31%. ④ DOC 浓度及内源 DOC 浓度空间分布均为: 岩溶区 > 混合区 > 非岩溶区, DOC 主要来源于水生生物的初级生产力, DOC 中内源碳的浓度介于 0.97~5.10 mg·L<sup>-1</sup>, 平均为 2.48 mg·L<sup>-1</sup>; DOC 中内源碳的比例空间分布差异不大, 平均为 79.51%. 研究水生光合生物对流域有机碳的影响, 可以为岩溶碳汇稳定性科学问题的解答提供基础.

**关键词:** 漓江; 碳稳定同位素; C/N; 溶解有机碳; 颗粒有机碳; 来源

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## Sources of Organic Carbon in the Surface Water of Lijiang River

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**Abstract:** This study selected a larger typical karst basin, that of Lijiang River, as the research subject and studied the sources of organic carbon in the Lijiang basin in July, August, and September in 2016 by an isotope tracer method, a correlational analysis method, and endmember mixture model, using a stable isotope of carbon and the organic carbon to nitrogen ratio. The results showed the following. ① The spatial distribution characteristics of DIC concentration were as follows: karst area > karst and non-karst mixed area > non-karst area. The content of DIC downstream was higher than upstream. The spatial distribution of DIC concentration was mainly controlled by the distribution of carbonate rocks in the Lijiang basin. ② DOC was the main part of TOC in the Lijiang basin. TOC was mainly derived from the primary productivity of aquatic organisms. The spatial distribution characteristics of autochthonous organic carbon content were as follows: karst area > karst and non-karst mixed area > non-karst area, which may be related to more lush aquatic plants in the karst area than in the non-karst area and the carbonic anhydrase activity in the karst area being higher than in the non-karst area. The content of autochthonous organic carbon in the TOC ranged from 1.02 to 5.14 mg·L<sup>-1</sup>, with an average of 2.54 mg·L<sup>-1</sup>. There was no significant spatial difference of the proportion of autochthonous organic carbon in the TOC; it ranged from 51.68% to 85.99%, with an average of 73.07%. ③ The POC concentration, the content of autochthonous organic carbon in the POC, and the proportion of autochthonous organic carbon in the POC had no significant spatial differences. The main source of POC was allochthonous organic carbon, and the content of autochthonous organic carbon in the POC ranged from 0.01 to 0.16 mg·L<sup>-1</sup>, with an average of 0.05 mg·L<sup>-1</sup>. The proportion of autochthonous organic carbon in the POC ranged from 3.69% to 41.94%, with an average of 17.31%. ④ The spatial distribution of the content of DOC and autochthonous organic carbon in the DOC are as follows: karst area > karst and non-karst mixed area > non-karst area. DOC mainly came from the primary productivity of aquatic organisms. The content of autochthonous organic carbon of the DOC ranged from 0.97 to 5.10 mg·L<sup>-1</sup>, with an average of 2.48 mg·L<sup>-1</sup>. The spatial distribution of the proportion of autochthonous organic carbon in the DOC had no obvious difference and ranged from 54.43% to 94.69%, with an average of 79.51%. Studying the influence of aquatic photosynthetic organisms on organic carbon in rivers can provide basis for scientific problem solution of the stability of karst carbon sinks.

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**Key words:** Lijiang basin; stable isotope of carbon; C/N; dissolved organic carbon; particulate organic carbon; sources

河流作为连接陆地与海洋两大碳库的重要通道,研究其碳输送是全球碳循环研究的一个重要环节<sup>[1]</sup>. 根据组成形态,河流碳一般可分为溶解无机碳(dissolved inorganic carbon, DIC)、溶解有机碳、颗粒有机碳、颗粒无机碳(particulate inorganic carbon, PIC),4种形式的碳在水体内部相互转化:PIC可溶解成为DIC,DOC可降解为DIC,水生植物生长可利用DIC生成POC、DOC<sup>[2]</sup>. 每年由陆地生态系统通过河流向海洋排放的有机碳约0.4 Pg,其中约60%为溶解有机碳(dissolved organic carbon, DOC),40%是颗粒有机碳(particulate organic carbon, POC)<sup>[3]</sup>,通过河流陆地生态系统向海洋排放的有机碳大致相当于全球陆地生态系统净初级生产力的1%~2%<sup>[4]</sup>. 溶解有机碳根据生物可利用性分为三类:容易被降解的活性DOC(labile DOC, LDOC)、可被缓慢降解的半活性DOC(semi-labile DOC, SLDOC),以及难以被生物降解的惰性DOC(recalcitrant DOC, RDOC)<sup>[5]</sup>.

岩溶地质作用的碳汇一度被质疑<sup>[6]</sup>,是源于传统的碳循环模型中把地质作用当作一种纯无机过程<sup>[7]</sup>,然而,近来的研究表明,岩溶作用并非纯无机地质过程,生物广泛参与岩溶作用,当水生系统的光合作用强度超过呼吸作用强度时,碳酸钙沉降过程将无机碳转化成有机碳<sup>[8~12]</sup>,进一步沉积和埋藏;同时海洋研究中发现, AAPB(aerobic anoxygenic phototrophic bacteria)作用下形成RDOC,使碳酸盐岩的风化也能形成长久的碳汇(千年尺度)<sup>[13, 14]</sup>,通过河流陆地生态系统向海洋排放的有机碳约0.1Pg的DOC循环周期可达到4~6千年<sup>[15]</sup>.

河流有机碳来源主要包括内源有机碳(水生植物光合作用产物)和外源有机碳(地表径流的侵蚀冲刷而进入河流的产物). 碳同位素示踪、水中有机质C/N及生物标记法是国内外常用的研究方法,能很好地解决河流有机碳的来源问题. Waterson等<sup>[16]</sup>利用C/N和 $\delta^{13}\text{C}_{\text{TOC}}$ 揭示了美国密西西比河水的总有机碳中50%是内源有机碳,唐文魁等<sup>[2]</sup>利用 $\delta^{13}\text{C}_{\text{POC}}$ 研究发现桂江流域水生光合产物对颗粒有机碳的贡献达25.1%,陶贞等<sup>[17]</sup>利用C/N研究发现增江流域河水悬移质中的有机碳以水生藻类(内源碳)的贡献为主(超过70%),Sun等<sup>[18]</sup>利用C/N和 $\delta^{13}\text{C}_{\text{DIC}}$ 、 $\delta^{13}\text{C}_{\text{POC}}$ 研究发现,我国西江流域雨季和旱季时河水中3%~21%和12%~22%的POC是河流

水生系统的光合作用利用碳酸盐盐风化产物DIC而形成的. 原雅琼<sup>[19]</sup>利用C/N、 $\delta^{13}\text{C}_{\text{POC}}$ 分析发现漓江水体在非洪水过程时,河流有机碳主要来源于水生植物,内源有机碳的比例可达92%,且在内源有机碳中来自植物光合利用 $\text{HCO}_3^-$ 生成的有机碳的比例达46%~77%. 原雅琼利用的C/N值与其他数据不是同一时间段,同时采样密度不够多,DOC与POC中内源有机碳的含量及比例也未做研究,因此,剖析水生光合生物对不同形式碳的作用和影响,有助于对漓江流域碳循环的认识.

本文以珠江支流桂江的上游河段漓江为研究对象,采用同位素示踪法及相关分析法,利用稳定同位素、C/N、端元混合模型来辨析漓江流域DOC、POC来源端元及贡献,分析水生光合生物对流域有机碳的影响,以期为岩溶碳汇稳定性科学问题的解答提供基础.

## 1 材料与方法

### 1.1 研究区概况

漓江流域位于广西壮族自治区的东北部,属珠江水系的桂江上游段. 发源于越城岭老山界南侧,由北向南经兴安、桂林、阳朔,桂林断面以上河段主要为花岗岩、碎屑岩非岩溶区,桂林到阳朔河段主要为覆盖型及裸露型岩溶区. 地理坐标为 $\text{E}109^{\circ}45' \sim 111^{\circ}02'$ , $\text{N}24^{\circ}16' \sim 26^{\circ}21'$ ,全长164 km,流域总面积12 680  $\text{km}^2$ ,整个漓江流域以漓江为轴线,呈南北向狭长带状分布(图1),属于中亚热带季风气候区,年平均气温为16.5~20.0 $^{\circ}\text{C}$ ,雨量充沛,年平均降雨量为1 367.5~1 932.9 mm,雨热同期. 漓江为雨源型河流,河道径流由流域降雨补给,汛期为每年的4~8月,其降雨量占全年降雨量的70%左右,枯季(11月至翌年2月)降雨稀少<sup>[20]</sup>. 漓江的地表径流来源于流域内的地表水和地下水,在雨季发洪水时地表水向地下渗透,低水期和枯水期地下水补给河槽<sup>[20]</sup>. 因流域内碳酸盐岩质纯层厚,加之雨热同期的季风气候条件,岩溶发育强烈,碳酸盐岩峰丛、峰林地貌广布,漓江贯穿于两者之间,形成流域区独特的自然景观.

### 1.2 样品的采集与前处理

在漓江兴安—阳朔段,上游(兴安段)、中游(桂林段)和下游(阳朔段)主要断面及支流汇入处布置了13个采样点(图1),分别为漓江上游华江

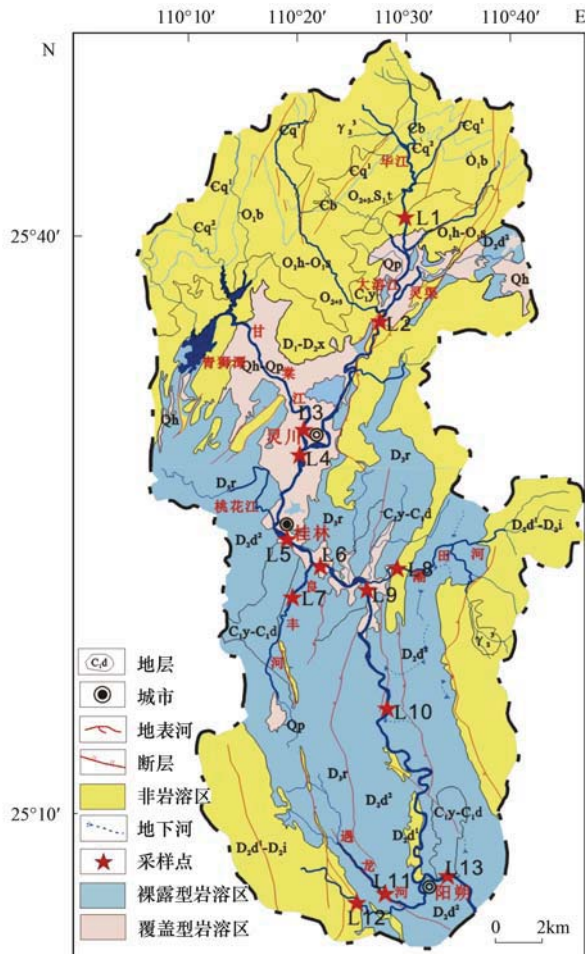


图1 研究区水文地质图与采样点位置<sup>[19]</sup>

Fig. 1 Hydrogeological map of the study area and the locations of the sampling sites

(L1)、峡背(L2:灵渠与大溶江汇合后)、灵川(L3:漓江支流甘棠江)、大面圩(L4:甘棠江水汇入漓江后)、漓江干流桂林水文站(L5)、父子岩(L6:干流良丰河水汇入漓江后)、漓江支流良丰河(L7)、潮田河水文站(L8:漓江支流潮田河)、省里(L9:干流潮田河水汇入漓江后)、下游干流杨堤(L10)、遇龙河(L11)、遇龙河支流(L12)、阳朔水文站(L13)。于2016年7月27日、8月27日、9月12日采集POC、DOC、 $\delta^{13}\text{C}_{\text{POC}}$ 、C/N水样,为避免采样过程中发生污染,采样前先用待采水样洗涤采样瓶3~5次。现场利用便携式水质分析仪(法国PONSEL)测定水样pH、水温( $T$ )和溶解氧(DO),见表1,其精度分别为0.01 pH单位,0.01 $^{\circ}\text{C}$ ,0.01  $\text{mg}\cdot\text{L}^{-1}$ ;用德国Merck公司生产的碱度计现场滴定 $\text{HCO}_3^-$ ,精度为0.1  $\text{mmol}\cdot\text{L}^{-1}$ 。

### 1.3 样品分析

DOC含量分析使用德国耶拿公司(Aanalytik Jena AG)生产的Multi C/N 3100测定,精度为

0.001  $\text{mg}\cdot\text{L}^{-1}$ 。POC和 $^{13}\text{C}_{\text{POC}}$ 的采样及测定:用于过滤水样的玻璃纤维膜预先在马弗炉450 $^{\circ}\text{C}$ 灼烧6 h以去除无机碳。用玻璃抽滤器加47 mm GF/F滤膜(孔径0.7  $\mu\text{m}$ )过滤,并送国家海洋局第三海洋研究所测试中心测试,分析精度为 $\pm 0.2\%$ ,测试流程如下:用不锈钢打孔器取固定面积酸熏后的玻璃纤维膜样,用5 $\times$ 9锡杯包样,用Thermo公司生产的元素分析仪-稳定同位素质谱仪联机(Flash EA 1112 HT-Delta V Advantages)测定膜样中POC、 $^{13}\text{C}_{\text{POC}}$ 值。载气He流速90  $\text{mL}\cdot\text{min}^{-1}$ ,反应管温度960 $^{\circ}\text{C}$ ,色谱柱温度50 $^{\circ}\text{C}$ 。

$\delta^{13}\text{C}_{\text{POC}}$ 值以PDB国际标准作为参考标准, $\delta^{13}\text{C}_{\text{POC}}$ 值按以下公式计算:

$$\delta^{13}\text{C}(\text{‰}) = \left[ \frac{R(^{13}\text{C}/^{12}\text{C}_{\text{sample}})}{R(^{13}\text{C}/^{12}\text{C}_{\text{VPDB}})} - 1 \right] \times 1000 \quad (1)$$

式中, $R(^{13}\text{C}/^{12}\text{C}_{\text{VPDB}})$ 为国际标准物VPDB(vienna peedee belemnite)的碳同位素丰度比值。

## 2 结果与讨论

### 2.1 溶解无机碳与有机碳浓度变化特征

本研究测得漓江流域DIC浓度介于24.4~183.0  $\text{mg}\cdot\text{L}^{-1}$ ,平均为91.66  $\text{mg}\cdot\text{L}^{-1}$ 。DOC浓度介于1.14~5.66  $\text{mg}\cdot\text{L}^{-1}$ ,平均为3.15  $\text{mg}\cdot\text{L}^{-1}$ ,低于全球DOC浓度平均值(5.29  $\text{mg}\cdot\text{L}^{-1}$ )<sup>[21]</sup>。POC浓度介于0.19~0.8  $\text{mg}\cdot\text{L}^{-1}$ ,平均为0.33  $\text{mg}\cdot\text{L}^{-1}$ 。

漓江流域DIC浓度空间分布特征为:岩溶区(L7、L11)>岩溶区与非岩溶区的混合区(L3、L4、L5、L6、L9、L8、L10、L13)>非岩溶区(L1、L2、L12),混合区干流DIC浓度从上游到下游递增,支流DIC浓度在干流DIC浓度的上下摆动(图2),主要受控于流域碳酸盐岩的空间分布比例,DIC质量浓度与碳酸盐岩的空间分布比例呈显著正相关关系( $R^2=0.80$ ),DIC质量浓度随着碳酸盐岩的分布比例增加而相应增大(图3)。POC含量上下游差异不大(图2)。漓江水体DOC浓度空间分布特征为:岩溶区(3.50  $\text{mg}\cdot\text{L}^{-1}$ )高于非岩溶区(1.80  $\text{mg}\cdot\text{L}^{-1}$ );上游(1.91  $\text{mg}\cdot\text{L}^{-1}$ )低于下游(3.58  $\text{mg}\cdot\text{L}^{-1}$ )(图2)。其原因可能为非岩溶区水进入岩溶区后,水生植物增加,水生植物利用 $\text{HCO}_3^-$ 进行光合作用,从而导致水体中DOC浓度岩溶区大于非岩溶区。DO也表现为岩溶区大于非岩溶区,主要是岩溶区水生植物光合作用的原因。一般情况下,小河流或大河的上游水流湍急,不利于水生植物的生长;在大河

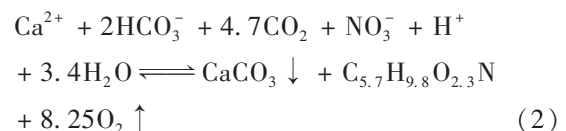
表 1 漓江地表水体部分测试数据  
Table 1 Part of the testing data of the Lijiang surface water

日期 (年-月)	采样点	pH	T /°C	DO /mg·L <sup>-1</sup>	DIC /mg·L <sup>-1</sup>	DOC /mg·L <sup>-1</sup>	POC /mg·L <sup>-1</sup>	C/N	δ <sup>13</sup> C <sub>POC</sub> /‰
2016-07	L1	7.41	27.55	7.2	30.5	1.14	0.24	9.34	-24.55
	L2	7.8	29	8.08	36.6	1.74	0.25	8.62	-25.22
	L3	8.5	33.61	10.22	79.3	2.60	0.21	9.53	-24.56
	L4	8.33	29.7	9.25	48.8	2.06	0.27	10.35	-24.90
	L5	8.7	33.9	6.07	67.1	2.68	0.39	8.83	-23.96
	L6	7.59	30.73	7.21	67.1	2.91	0.19	10.94	-25.05
	L7	7.54	32.11	14.07	183	3.82	0.39	9.05	-26.78
	L8	8.09	29.79	9.5	122	2.70	0.26	9.02	-24.40
	L9	9	32.76	12.47	67.1	2.80	0.37	8.80	-24.46
	L10	8.14	31.2	8.34	85.4	1.76	0.26	9.37	-25.24
	L11	7.88	31.54	10.41	164.7	3.23	0.22	8.57	-25.58
	L12	7.48	30.78	7.71	42.7	1.96	0.39	8.91	-25.68
	L13	7.83	30.93	12.14	134.2	3.71	0.80	9.96	-23.43
2016-08	L1	8.12	25.41	7.93	24.4	1.52	0.26	10.16	-24.14
	L2	7.8	27.54	7.68	42.7	1.85	0.40	11.18	-25.43
	L3	7.71	27.75	8.75	73.2	3.29	0.34	11.93	-23.62
	L4	7.81	28.25	8.73	54.9	3.01	0.26	10.46	-24.42
	L5	7.24	25.62	8.67	85.4	4.07	0.39	10.30	-23.83
	L6	7.33	26.37	6.06	79.3	3.84	0.57	10.82	-24.76
	L7	7.55	27.85	9.28	164.7	5.51	0.51	10.90	-23.63
	L8	8.19	24.21	8.79	128.1	2.18	0.29	12.33	-23.85
	L9	9	27.76	6.63	67.1	3.34	0.38	10.89	-23.33
	L10	8.79	28.09	8.82	85.4	3.27	0.27	10.38	-24.35
	L11	8.16	26.54	7.89	176.9	3.04	0.32	12.83	-24.62
	L12	7.86	26.31	8.59	36.6	2.43	0.28	11.56	-25.09
	L13	8.21	27.4	9	152.5	3.37	0.29	11.04	-24.50
2016-09	L1	8.36	24.24	8.93	30.5	1.45	0.37	12.78	-24.22
	L2	7.5	24.57	7.68	48.8	2.02	0.27	9.55	-25.83
	L3	7.62	24.79	8.75	79.3	3.36	0.32	10.20	-24.58
	L4	7.38	25.66	8.73	54.9	2.41	0.19	10.05	-24.57
	L5	8.53	26.32	12.5	54.9	5.66	0.48	8.88	-23.78
	L6	7.84	25.94	2.98	109.8	3.92	0.30	9.58	-24.12
	L7	8.76	25.8	14.18	164.7	5.63	0.67	10.93	-23.87
	L8	8.3	25.5	7.52	97.6	4.51	0.29	9.64	-24.21
	L9	8.43	25.4	7.21	103.7	2.97	0.23	13.41	-24.44
	L10	7.7	27	7.24	152.5	4.24	0.22	11.07	-24.99
	L11	8.36	27.05	7.97	164.7	3.78	0.20	12.77	-25.14
	L12	7.84	27.85	7.85	61	3.70	0.24	9.85	-24.90
	L13	8.28	27.28	12.74	152.5	5.21	0.31	10.63	-23.74
平均值		8.02	27.95	8.81	91.66	3.15	0.33	10.40	-24.56

的下游或河口区,水流较慢,营养物质丰富,有利于河流浮游生物的生长,因而下游较上游有较高的水生生物初级生产力<sup>[22]</sup>。

漓江流域 DOC 浓度与 DIC 质量浓度存在正相关关系(图 4),说明 DOC 来源除了外源,还存在 DIC 向 DOC 的转化; DOC 浓度与 DO 存在正相关关系(图 4),说明 DOC 和 DO 有共同的来源(水生生物光合作用)。综上,说明漓江岩溶地表水生系统中水生植物的光合作用可以利用 DIC 产生 DOC,其过

程表示如下:



漓江水体 POC 浓度与 DO 呈正相关关系(图 5),说明 POC 来源除了外源,还可能来源于水生生物的初级生产力; POC 浓度与 DOC 存在正相关关系(图 5),说明漓江岩溶地表水生系统可能存在 DOC 与 POC 之间的转化。

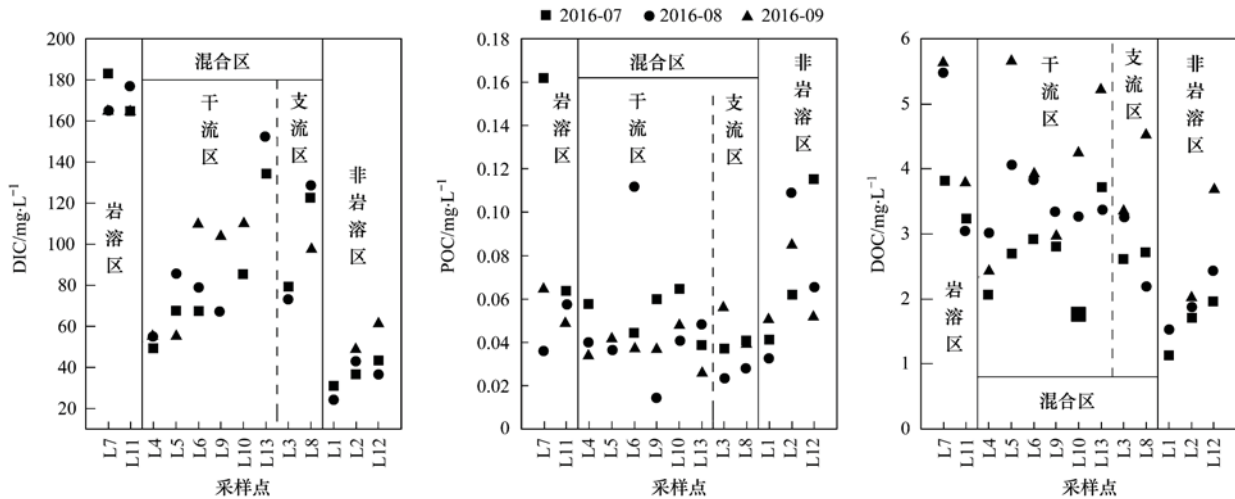
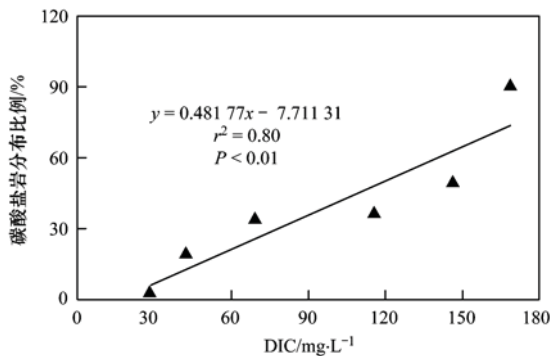


图2 漓江流域 DIC、DOC、POC 浓度变化特征

Fig. 2 Variations in content of DIC, DOC, and POC in the Lijiang basin



碳酸盐岩分布比例数据来源于文献[19]

图3 DIC 与碳酸盐岩分布比例相关关系

Fig. 3 Correlation between DIC and distribution proportion of carbonate rocks

### 2.2 模型 1: <sup>13</sup>C<sub>POC</sub> 计算 POC 来源

漓江流域<sup>13</sup>C<sub>POC</sub>值介于-26.78‰~-23.33‰,平均为-24.56‰,上下游差异不明显. 河流输送的颗粒有机碳可以看作水生生物的生物量(内源碳)

与外源土壤颗粒有机碳的端元混合. 考虑内源、外源端元组分的<sup>13</sup>C<sub>POC</sub>,可以定量估算河水 POC 中内源碳与外源碳的比例,其同位素质量平衡方程如下:

$$\delta^{13}C_{POC} = f_{au/POC} \cdot \delta_{au} + f_{al/POC} \cdot \delta_{al} \quad (3)$$

$$f_{au/POC} + f_{al/POC} = 1 \quad (4)$$

式中,<sup>13</sup>C<sub>POC</sub>为样品的碳同位素值; δ<sub>au</sub>、δ<sub>al</sub>分别为内源碳与外源碳端元组分的碳同位素值; f<sub>au/POC</sub>、f<sub>al/POC</sub>分别表示 POC 中内源碳与外源碳所占的比例.

两个端元的确定如下:其中 δ<sub>al</sub>可以参照 Sun 等<sup>[18]</sup>关于西江 2005 年<sup>13</sup>C<sub>POC</sub>的数据,6 月西江发生罕见洪水,期间<sup>13</sup>C<sub>POC</sub>介于-23.8‰~-22.2‰,平均为-23.0‰,河流初级生产对 POC 的贡献可以忽略不计,POC 几乎全部来自于陆源侵蚀,此时的<sup>13</sup>C<sub>POC</sub>可以作为 δ<sub>al</sub>的典型值,为-23.0‰; δ<sub>au</sub>则选择 Sun 在西江下游水生生物量的<sup>13</sup>C取值,为-32‰.

结合 POC 浓度值,可计算出漓江流域颗粒有机

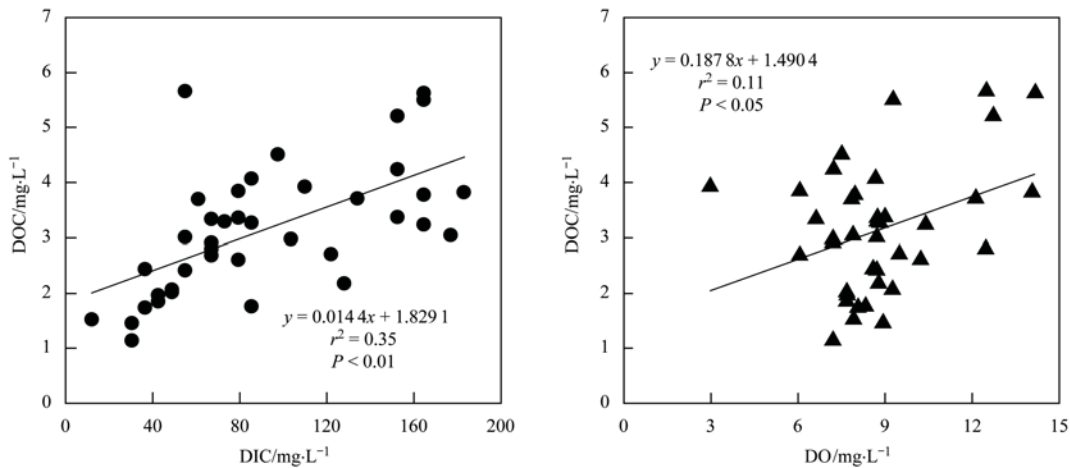


图4 DOC 与 DIC 及 DOC 与 DO 的相关关系

Fig. 4 Correlation between DOC and DIC, DOC, and DO

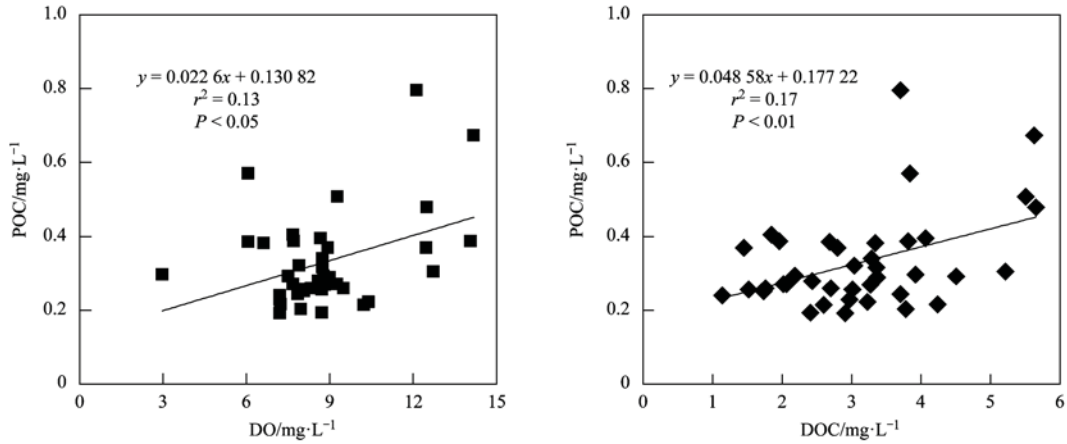


图 5 POC 与 DO、POC 与 DOC 的相关关系

Fig. 5 Correlation between POC and DO, POC, and DOC

碳中内源有机碳浓度,方程如下:

$$POC_{au} = POC \cdot f_{au/POC} \quad (5)$$

式中,POC 为样品的 POC 浓度值;  $f_{au/POC}$  为 POC 中内源碳所占比例;  $POC_{au}$  为 POC 中内源有机碳的浓度。

计算结果表明水生生物量对漓江流域 POC 贡献率范围为 3.69% ~ 41.94%, 平均为 17.31%, 低于桂江水体水生生物量对 POC 的贡献 7 月平均值 (25.1%)<sup>[2]</sup>; POC 中内源有机碳浓度 ( $POC_{au}$ ) 介于 0.01 ~ 0.16  $mg \cdot L^{-1}$ , 平均为 0.05  $mg \cdot L^{-1}$  (图 6、图 7)。总体而言,漓江流域 POC 以外源有机碳为主, 上下游差异不大。即漓江水体中 83% 的 POC 来源于陆生生物, 由水生生物转化过来的 POC 占的比例为 17%。

### 2.3 模型 2: C/N 计算 TOC 来源

本研究测得漓江流域 C/N 值介于 8.57 ~ 13.41

之间,平均为 10.40。已有研究表明外源有机碳 C/N 值大于 15<sup>[23]</sup>; 根据典型藻类光合作用形成产物为  $C_{5.7}H_{9.8}O_{2.3}N$ , 其 C/N 应为 6 左右, 真菌 ( $C_{10}H_{17}O_6N$ ) 的 C/N 为 10, 细菌 ( $C_5H_7O_2N$ ) 的 C/N 为 5, 因此,内源有机质的 C/N 介于 5 ~ 10 之间。以 C/N 值 6.6 为内源端元<sup>[24, 25]</sup>, 20.69 为外源端元<sup>[26]</sup>, 可以利用端元混合模型计算内源有机碳占总有机碳的比例, 方程如下:

$$C/N = f_{au} \cdot f_B + f_{al} \cdot (1 - f_B) \quad (6)$$

式中 C/N 为样品的 C/N 值;  $f_{au}$  为 C/N 值的内源端元, 取 6.6;  $f_{al}$  为 C/N 值的外源端元, 取 20.69;  $f_B$  为内源有机碳在总有机碳中的比例。

结合漓江流域 TOC (POC + DOC) 浓度值, 可计算出总有机碳中内源碳的浓度 ( $TOC_{au}$ ), 方程如下:

$$TOC_{au} = TOC \cdot f_B \quad (7)$$

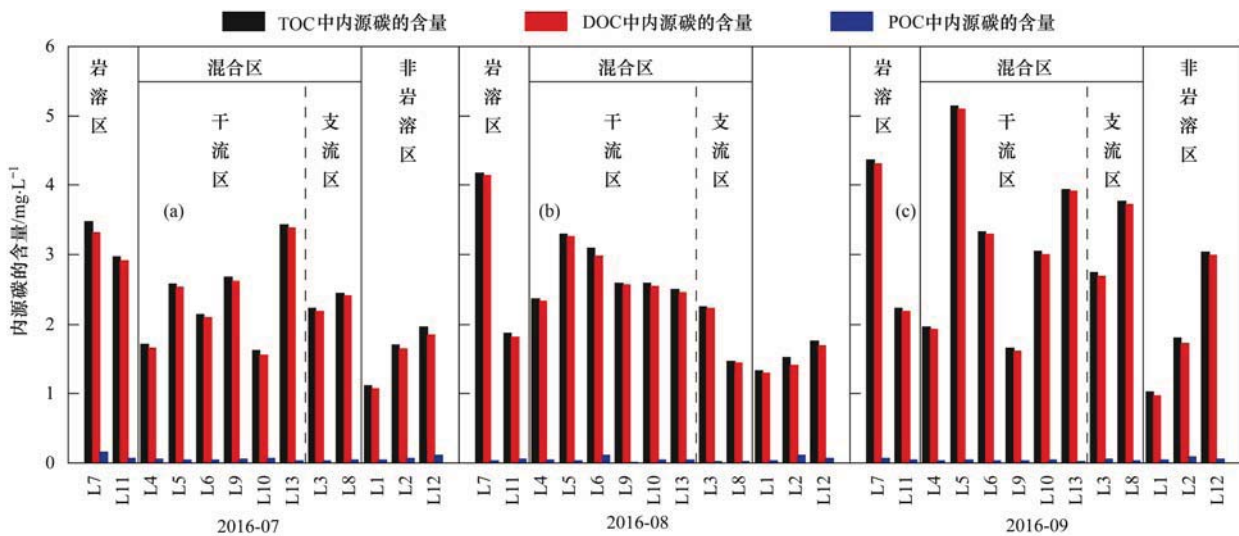


图 6 漓江流域 TOC、DOC、POC 中内源碳的含量

Fig. 6 Content of autochthonous organic carbon in the TOC, DOC, and POC of the Lijiang basin

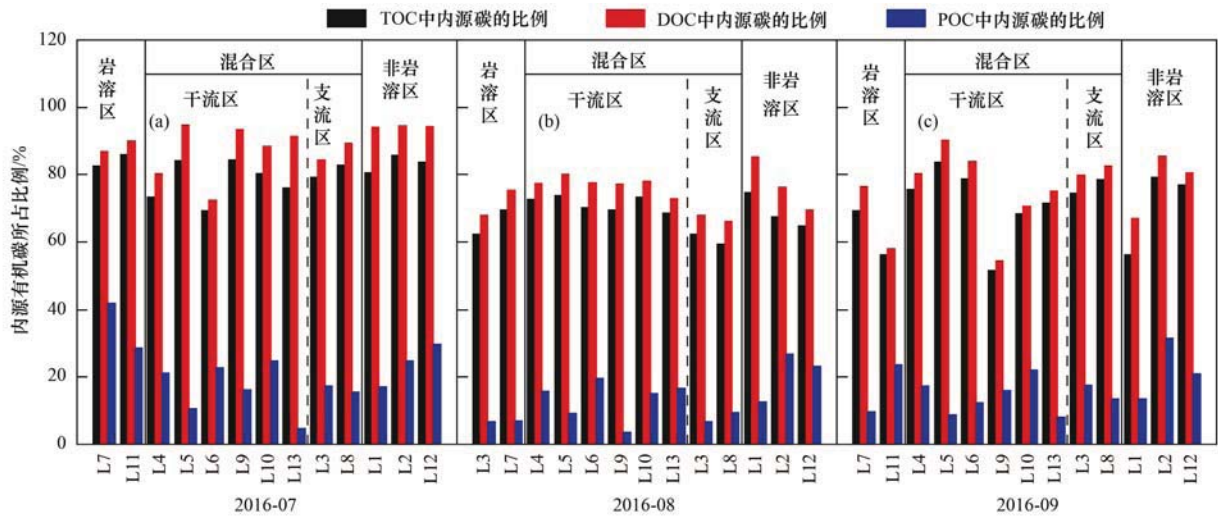


图 7 漓江流域 TOC、DOC、POC 中内源碳的比例

Fig. 7 Proportion of allochthonous organic carbon in the TOC, DOC, and POC of the Lijiang basin

式中,TOC 为样品的总有机碳含量值;  $f_B$  为内源有机碳在总有机碳中的比例;  $TOC_{au}$  为总有机碳中内源碳的浓度。

计算表明内源有机碳占总有机碳的比例( $f_B$ )介于 51.68% ~ 85.99%, 平均为 73.07%; 总有机碳中内源碳的含量介于  $0.97 \sim 5.10 \text{ mg}\cdot\text{L}^{-1}$ , 平均为  $2.48 \text{ mg}\cdot\text{L}^{-1}$  (图 6、图 7)。即漓江水体中 27% 的 TOC 来源于陆源, 73% 的 TOC 来源于水生植物光合作用产物。

2.4 DOC、TOC、POC 内外源比例及含量分析

结合总有机碳中内源碳的浓度、颗粒有机碳中内源碳的浓度、溶解有机碳浓度, 可以计算出 DOC 中内源碳的浓度 ( $DOC_{au}$ ) 及 DOC 中内源碳所占比例 ( $f_{au/DOC}$ )。计算公式如下:

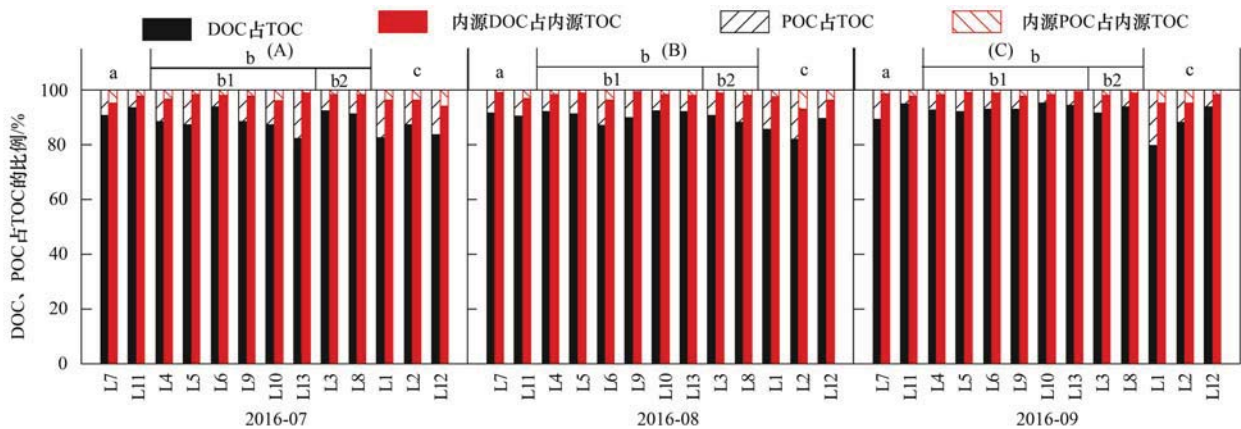
$$DOC_{au} = TOC_{au} - POC_{au} \quad (8)$$

$$f_{au/DOC} = DOC_{au}/DOC \quad (9)$$

式中,  $DOC_{au}$  为 DOC 中内源碳的浓度;  $TOC_{au}$  为总有机碳中内源碳的浓度;  $POC_{au}$  为 POC 中内源碳的浓度; DOC 为样品的溶解有机碳浓度;  $f_{au/DOC}$  为 DOC 中内源碳所占比例。

计算结果表明漓江水体 DOC 中内源碳所占比例 ( $f_{au/DOC}$ ) 介于 54.43% ~ 94.69%, 平均为 79.51%; DOC 中内源碳的浓度介于  $0.97 \sim 5.10 \text{ mg}\cdot\text{L}^{-1}$ , 平均为  $2.48 \text{ mg}\cdot\text{L}^{-1}$ 。即漓江水体中 20% 的 DOC 是地表径流的侵蚀冲刷而进入河流的产物, 80% 的 DOC 来源于水生生物的初级生产力。

漓江水体内源 DOC 占内源 TOC 的比例介于 92.83% ~ 99.46%, 平均为 97.58%, 空间分布无明显差异; DOC 占 TOC 的比例平均为 89.83% (DOC 是构成有机碳的主体), 空间分布表现为岩溶区、混



(A)2016-07, (B) 2016-08, (C)2016-09

a 表示岩溶区, b 表示岩溶区与非岩溶区的混合区 (b1 表示干流区, b2 表示支流区), c 表示非岩溶区

图 8 DOC、POC 占 TOC 比例

Fig. 8 Proportion of DOC and POC in the TOC

合区 > 非岩溶区 (图 8)。DOC 浓度空间分布特征为: 岩溶区 > 混合区 > 非岩溶区, POC 浓度空间分布差异不大 (图 2)。内源 TOC、DOC 浓度空间分布特征为: 岩溶区 > 混合区 > 非岩溶区, 内源 POC 浓度空间分布差异不大 (图 6), 可能与岩溶区水生植物丰茂、碳酸酐酶 (carbonic anhydrase, CA) 活性较强有关 (CA 活性与  $\text{HCO}_3^-$  浓度呈正相关)<sup>[27]</sup>; 漓江水体 TOC、DOC、POC 中内源碳的比例空间分布差异不大 (图 7); TOC 来源以内源碳为主 (内源碳的比例为 73%), 而 POC 主要来源于陆生生物 (内源碳的比例为 17%), DOC 主要来源于水生生物的初级生产力 (内源碳的比例为 80%)。

综上所述漓江流域 TOC、DOC 以内源碳为主, POC 中水生生物量也占一定比例。

内源有机碳中有多少比例是水生生物利用  $\text{HCO}_3^-$  生成的、内源有机碳的稳定性及 DOC 与 POC 之间的转化本文都未做研究, 以后可以展开这方面的研究。

### 3 结论

(1) 漓江流域 DIC 浓度空间分布特征为: 岩溶区 (良丰河、遇龙河) > 岩溶区与非岩溶区的混合区 (灵川、大面圩、桂林水文站、父子岩、潮田河水文站、省里、杨堤、阳朔水文站) > 非岩溶区 (华江、峡背、遇龙河支流); 混合区干流 DIC 含量从上游到下游递增。主要受控于流域碳酸盐岩的空间分布比例, DIC 质量浓度与碳酸盐岩的空间分布比例呈显著正相关关系 ( $R^2 = 0.80, P < 0.01$ )。

(2) 漓江水体 DOC 浓度与 DIC 质量浓度、DOC 浓度与 DO 均存在正相关关系, 说明岩溶地表水生系统中水生植物的光合作用可以利用 DIC 而形成 DOC; POC 浓度与 DO 呈正相关关系, 说明 POC 来源除了外源, 还可能来源于水生生物的初级生产力; POC 浓度与 DOC 存在正相关关系, 岩溶地表水生系统存在 DOC 与 POC 转化。

(3) POC 浓度、POC 中内源碳的浓度及 POC 中内源碳的比例空间分布差异不大, POC 来源以外源碳为主, POC 中内源有机碳浓度介于  $0.01 \sim 0.16 \text{ mg} \cdot \text{L}^{-1}$ , 平均为  $0.05 \text{ mg} \cdot \text{L}^{-1}$ , 水生生物量对漓江流域 POC 贡献介于  $3.69\% \sim 41.94\%$ , 平均为  $17.31\%$ , 即 83% 的 POC 来源于陆生生物, 由水生生物转化过来的 POC 占的比例为 17%。

(4) DOC 是构成漓江水体 TOC 的主体, TOC 来源以内源有机碳为主, 内源碳的浓度空间分布特征

为: 岩溶区 > 混合区 > 非岩溶区, 可能与岩溶区水生植物丰茂、碳酸酐酶活性较强有关, TOC 中内源碳的浓度介于  $1.02 \sim 5.14 \text{ mg} \cdot \text{L}^{-1}$ , 平均为  $2.54 \text{ mg} \cdot \text{L}^{-1}$ ; TOC 中内源碳的比例空间分布差异不大, 介于  $51.68\% \sim 85.99\%$ , 平均为  $73.07\%$ , 即 27% 的 TOC 来源于陆源, 73% 的 TOC 来源于水生植物光合作用产物。

(5) DOC 浓度、内源 DOC 浓度空间分布均为岩溶区 > 混合区 > 非岩溶区, DOC 主要来源于水生生物的初级生产力, DOC 中内源碳的浓度介于  $0.97 \sim 5.10 \text{ mg} \cdot \text{L}^{-1}$ , 平均为  $2.48 \text{ mg} \cdot \text{L}^{-1}$ ; DOC 中内源碳的比例空间分布差异不大, DOC 中内源碳所占比例介于  $54.43\% \sim 94.69\%$ , 平均为  $79.51\%$ , 20% 的 DOC 是地表径流的侵蚀冲刷而进入河流的产物, 80% 的 DOC 来源于水生生物的初级生产力。

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