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湖泊沉积多指标记录的长寿湖 近 60 年来营养化过程

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摘 要:长寿湖位于重庆市长寿区境内,是重庆市最大的湖泊旅游风景区和淡水鱼养殖基地之一。 近年来,其营养化日趋严重。本文通过对有机质碳、氮含量、碳氮比值、有机质碳同位素等有机质 指标的分析,结合¹³⁷Cs放射性核素定年,探讨了长寿湖近60年来有机质转化及营养演化过程。结 果表明:长寿湖有机质主要来源于水生植物藻类,受陆源影响较小;湖泊环境演化分为两个截然不 同的阶段:1980年以前,有机质碳、氮含量较低,C/N比值较小,有机质碳同位素值较大,暗示湖 泊营养环境为贫营养化。1980年以后,有机质碳、氮含量较高,C/N比值较大,有机质碳同位素值 偏负,说明湖泊已经处于营养化阶段,人为活动的增强及养殖业的发展是导致湖泊生产力增大的主 要因素。长寿湖沉积物多指标忠实记录了湖泊环境的演化过程。 关键词:长寿湖;有机质碳同位素;营养化;人为活动

Trophication evolution recorded by multi-proxy evidences in Lake Changshou, Chongqing during the recent 60 years

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Abstract: *Background, aim, and scope* Lake Changshou, located in Changshou District, is one of the largest lake scenic spots and most important freshwater fish breeding bases in Chongqing. Recently, the eutrophication of this lake is increasing seriously. The aim of this study is to evaluate the process of eutrophication of Lake Changshou by using organic proxies, including carbon and nitrogen content of organic matter, C/N ratios, and carbon isotope composition of organic matter. *Materials and methods* Sediment core named CS1 and CS2 were retrieved from the central part of Lake Changshou in 2013 using a self-designed gravitational sediment sampler. Sediment samples were sectioned at 1 cm interval and put into plastic bags in the field. Sediment samples were dried using a vacuum freeze drier. Core CS1 samples were used for geochemical analysis, and CS2 samples were used for analyzing radionuclide

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¹³⁷Cs activities. Element analyses of total organic carbon (TOC) and nitrogen were measured by the element analyzer. Samples for organic carbon analysis were pretreated with HCl (1 mol \cdot L⁻¹), then placed in water bath for two hours at 60°C to remove carbonates, and rinsed repeatedly with distilled water for four times. After that, δ^{13} C values of organic matter were measured on the Finnigan Delta Plus isotope ratio mass spectrometer. A number of duplicate samples were also measured to monitor the measurement accuracy. The activity of ¹³⁷Cs was measured at 661.6 k eV by y-spectrometry using low-background germanium detector. **Results** Data of ¹³⁷Cs demonstrate that the average sedimentation rate of Lake Changshou is 0.85 cm \cdot a⁻¹. Total organic carbon contents vary between 0.85% and 4.3%, with the mean value of 1.75%. Before 1980 AD, the average TOC is 1.25%, and after 1980 AD, the average TOC is 2.43%. Nitrogen contents and C/N ratios show similar variations with TOC. However, carbon isotope composition of organic matter shows contrast variations. The results indicate that the source of organic matter in Lake Changshou is derived from aquatic plants and algae, rather than terrestrial plants, or little affected. The environmental evolution of Lake Changshou can be classified into two periods with the contrasting characteristics during the past 60 years. The change time of lake environment happened approximately in 1980 AD. Discussions C/N ratios can be used to identify the source of organic matter. In general, C/N ratios in algae are less than 10, while C/N ratios in terrestrial plants are high, varying between 20 and 200. In addition, δ^{13} C values are significantly different between aquatic and terrestrial plants. Therefore, C/N ratios and $\delta^{13}C_{org}$ are effective proxies to distinguish the source of organic matter from lake sediments. In Lake Changshou, data plot within the field of aquatic plants, rather than C_3/C_4 plants, implies that the source of organic matter is derived from aquatic plant. While TOC and TN are indicators of lake productivity and eutrophication. The increase of $\delta^{13}C_{org}$ value is interpreted as the increase of lake productivity. Based on the organic indicators, the environment evolution of Lake Changshou can be divided into two periods. Before 1980 AD, stable values of carbon isotope of organic matter, the low carbon and nitrogen content of organic matter, and low C/N ratios suggested that the lake environment was oligotrophication. After 1980 AD, notable increase of carbon and nitrogen content of organic matter, C/N ratios, and decrease of carbon isotope values of organic matter, demonstrated that the increase of lacustrine productivity and the eutrophication was the result of strong human activities and the development of fish breeding. Therefore, multiproxy has reliably recorded the environment evolution of Lake Changshou. It is obvious that there is a negative correlation between $\delta^{13}C_{org}$ and TOC, inconsistent with the previous views that such an increase in productivity would produce higher δ^{13} C values of organic matter. We believe that the degradation of aquatic algae during the process of eutrophication is the primary factor resulting in the decrease of δ^{13} C values of organic matter with the increase of productivity in Lake Changshou. Conclusions C/N ratios and carbon isotope composition of organic matter reveal that the origin of organic matter in Lake Changshou is aquatic plant, rather than terrestrial plant. The trophication state of Lake Changshou can be divided into two periods. Before 1980 AD, the lake was oligotrophication and was little affected by human activity. After 1980 AD, strong human activities and the development of fish breeding led to the serious trophication state. The eutrophication of Lake Changshou after 1980 AD produced the decrease of δ^{13} C values of organic matter. It is proposed that degradation of aquatic plant likely controls the carbon isotopic composition of organic matter. Recommendations and perspectives Thus, multi-proxy have reliably recorded the environmental evolution of Lake Changshou. The eutrophication of Lake Changshou should be paid much attention, especially on the controls of the human impacts. **Key words:** Lake Changshou; organic carbon isotope; eutrophication; human activity

长寿湖是重庆市最大的湖泊旅游风景区和重 来,随旅游业、养殖业蓬勃发展,长寿湖已成为 要的淡水鱼养殖基地之一。自 20 世纪 80 年代以 集饮用、灌溉、旅游、养殖、发电为一体的多功

能水体。近年来,城市污水和工业废水排放量渐 增,大部分流入长寿湖区,严重影响其水质。湖 区"水华"现象引起社会各界广泛重视(杨钢等, 2003)。对长寿湖表层沉积物氮磷研究发现: 其 TN 平均含量为 2255.89 mg·kg⁻¹, TP 平均含 量为 622.03 mg·kg⁻¹,湖区氮磷污染严重。长寿 湖表层沉积物中有机氮是总氮的主要组成部分, 占总氮的 97.16 % (卢少勇等, 2012)。杨钢等 (2003) 对长寿湖水质的营养状况进行了综合评 价,结果表明长寿湖水质已呈中度富营养化状态, 有向富营养化发展的潜在趋势。胡鹏飞和何太蓉 (2012)对长寿湖表层沉积物中的氮赋存特征进 行了研究,认为长寿湖表层沉积物污染已较严重: 同时,他们还对长寿湖表层沉积物中磷的赋存状 态进行了研究,结果显示长寿湖表层沉积物具有 很强的释磷潜力,长寿湖沉积物呈中度污染,应 加强监测和治理。目前,人们对湖泊富营养化的 认识主要是通过水质和表层沉积物的调查(杨钢 等, 2003; 郭海涛等, 2011; 胡鹏飞和何太蓉, 2012; 卢少勇等, 2012), 这种方法无法追踪历 史时期湖泊的富营养化过程,特别是在缺乏长期 湖泊监测记录的情况下,对湖泊发生富营养化程 度的拐点、富营养化速率、发展趋势并不清楚。 对湖泊富营养化过程的了解有利于控制和采取措 施抑制湖泊的进一步营养化。湖泊沉积物,是湖 泊生态系统的重要组成部分,是入湖物质如有机 质、污染物等的主要储蓄所, 包含了丰富的生物 和理化方面的信息,通过湖泊沉积剖面的环境代 用指标的研究,可以了解湖泊及流域的污染状况, 重建湖泊环境变化的历史过程。

湖泊沉积物有机质代用指标如碳同位素、碳 氮含量在湖泊环境演化及富营养化过程示踪研究 方面的应用日益深入。有机质 C/N 比值和碳同位 素能有效判断湖泊沉积物有机质来源(Meyers, 1997),同时湖泊有机质碳同位素组成及有机质 碳氮含量是湖泊生产力变化的有效代用指标,从 而指示湖泊营养状况。基于对长寿湖区域环境演 变及营养化过程的了解为目的,本文通过对长寿 湖沉积物柱芯中有机质碳氮含量、C/N 比值、有机 质碳同位素等多指标的分析,结合精确的放射性 核素¹³⁷Cs 定年,探讨了长寿湖近 60 年湖泊沉积物 有机质转化及环境演化过程,以期为合理治理长 寿湖营养化提供依据。

1 湖区概况

长寿湖位于重庆市长寿区境内,地理坐标为 北纬 29°50′—30°04′,东经 107°15′—107°25′,是 狮子滩水电站拦河大坝建成以后形成的人工淡水 湖,是我国西南地区最大的人工淡水湖,也是重 庆市最大的湖泊旅游风景区和国家级生态旅游休 闲度假区。长寿湖水域面积约 65.5 km²,平均水深 15 m,最大水深 40 m,是重庆市重要的淡水养殖 基地。

2 样品采集和实验方法

使用重力采样器于 2013 年 10 月在长寿湖深 水区采得两根沉积物柱芯,编号为 CS1 和 CS2, 长度分别为 50 cm 和 49 cm,采样点远离湖岸,覆 水深 25 m。所采沉积物柱芯保存完好,悬浮层未 受扰动,界面水清晰。沉积物柱芯现场按 1 cm 间 隔分截样品装入塑料自封袋中密闭保存。CS1 和 CS2 柱芯样品运回实验室,经真空冷冻干燥器(型 号:FD-IA-50)干燥后,用玛瑙研钵研磨至 200 目以下备用。CS1 柱芯样品用于有机质指标测定, 包括有机碳、氮含量和有机质碳同位素,CS2 柱 芯样品用于放射性核素¹³⁷Cs 比活度测定。

2.1 放射性核素 ¹³⁷Cs 测定

¹³⁷Cs 的比活度采用 Caberra 公司生产的 S-100 多道能谱仪进行 γ-谱测定,根据样品量情况,分 别用 GC5019 同轴锗探测器(探测器效率 50%) 或 GCW 井型锗探测器(探测器效率 30%)。¹³⁷Cs 计数峰的位置为 661.6 k eV,测量误差 <5%。

2.2 元素含量分析方法

有机质碳、氮含量及 C/N 比值测定采用前处 理方法如下:称取样品 3g,加入 0.5 M 的 HCl 溶 液 25 mL,在水浴锅 60℃中反应 2h,去除碳酸 盐,后用氧水洗净,冷冻干燥后利用元素分析仪 (PE2400 II 型)测定有机质碳、氮含量及 C/N 比值, 分析误差小于 5%。

2.3 有机质碳同位素分析方法

将沉积物 0.5 g 放入 50 mL 离心管中,加入 0.5 M 的 HCl 溶液 25 mL,在水浴锅 60℃中反应 2 h,去 除碳酸盐,后用氧水洗净,冷冻干燥后以备有机质 碳同位素测定。有机质碳同位素测定采用连续流质 谱,仪器型号为 EA IsoPrime,以国际纤维素标样 IAEA-C3(δ^{13} C=-24.91‰)为参考标准校正分析结 果。测量误差小于 0.1‰,结果采用 PDB 标准。



图 1 长寿湖位置示意图及采样点位图 Fig.1 Location of Lake Changshou and sampling site

 δ^{13} C 计算公式为:

以上所有实验均在中国科学院地球化学研究 所环境地球化学国家重点实验室完成。

3 分析结果

3.1 沉积物柱芯年代的确定

由于长寿湖是人工湖泊,其形成年代较短,因此利用¹³⁷Cs测年是比较合理的方法。¹³⁷Cs是人类活动(核试验)释放后通过大气扩散而沉降

到地表的放射性核素,广泛用于湖泊现代沉积计年的研究(白占国和万国江,1998)。从长寿湖 沉积物¹³⁷Cs比活度图上可以看出,剖面上出现一 个明显峰值(图2),深度为36 cm,这个峰值被 认为是1963年全球性核试验高峰期(Wan et al, 1987)。全球核试验的初始时间是20世纪50年 代初期,而散落的高峰期是1963—1964年(Wan et al, 1987)。因此利用¹³⁷Cs散落峰的时间和沉 积深度可以获得沉积物堆积速率,平均堆积速率 为0.85 cm·a⁻¹,依据此速率从而建立起长寿湖沉积 底部年龄为1943 AD, 与长寿湖建于20世纪40年 代比较吻合。



图 2 长寿湖沉积物 CS2 柱芯¹³⁷Cs 比活度剖面变化图 Fig.2 Diagram of ¹³⁷Cs activities in Lake Changshou sediments

3.2 有机质碳、氮含量特征

长寿湖沉积物柱芯 TOC 含量在 0.85% - 4.30% 波动,平均值为1.79‰,最大变幅为3.45%(图 3):从有机碳含量曲线变化特征来看,1980年以 前 TOC 平均值为 1.25%, 1980 年以后 TOC 平均 值为 2.43%, 表现出显著增高的特征; TN 含量变 化范围为 0.13%-0.49%, 平均值为 0.23%, 最大 变幅为 0.36% (图 3),其变化特征与 TOC 含量 变化特征极为相似,以1980年为时间拐点,1980 年以后 TN 含量显著增高。此外, TOC 与 TN 呈 显著相关性变化(图4),相关系数接近1,一方 面表明这两者均与有机质有关,同时也说明长寿 湖沉积物中N的含量主要以有机氮为主,沉积物 有机质来源单一,与前人研究结果(卢少勇等, 2012)一致。卢少勇等(2012)的研究认为长寿 湖沉积物中有机氮是总氮的主要组成部分,占总 氮 97.16%。TOC/N 值变化范围为 6.61-11.62, 平均值为 8.92 (图 3), TOC/N 显示了与 TOC、 TN 相同的变化特征,在 1980 年以后 TOC/N 含量 显著增大。

3.3 有机质碳同位素变化特征

长寿湖沉积物柱芯有机质碳同位素值的变化 范围为-22.48‰—-28.23‰,平均值为-26.66%(图 3)。其变化特征显示了与 TOC、N、TOC/N 截然 相反的变化特征,在 1980 年以后有机质碳同位素 值显著偏负。



图 3 长寿湖沉积物 CS1 柱芯有机质碳、氮含量、C/N 比 值及有机质碳同位素值随年代变化特征 Fig.3 Evolution of organic carbon, nitrogen content, C/N

ratios and organic carbon isotope values in sediment core CS1 at Lake Changshou

4 讨论

4.1 长寿湖有机质来源

一般认为,湖泊水生植物含有较多的蛋白质, 其 C/N 值小于 10;陆生植物富含腐殖质,其 C/N 值较大,在 20—200 (Krishnamurthy et al, 1986; Lamb et al, 2004)。

湖泊沉积物有机质的陆源和内源具有完全不同的δ¹³C值。陆源植物按其光合作用途径分为 C₃、C₄和CAM三种类型。如果光合作用的最初 产物为四碳二羟酸,则相应植物称为C₄植物,C₄ 植物 δ^{13} C 值为 -9% — -21%, 平均为 -14%; 如 果光合作用的最初产物为三磷酸甘油酯,则相应 植物称为 C₃ 植物, C₃ 植物 δ^{13} C 值较低,一般为 -21% — -33%,平均为 -27%。CAM 植物类型较 少(例如仙人掌科),其典型生境为干旱环境, δ^{13} C 值变化范围较大。浮游植物由于其吸收水中 溶解 CO₂,与大气 CO₂ 处于同位素平衡,所以其 同位素组成与 C₃ 植物相似。



图 4 长寿沉积物柱芯有机质碳、氮含量的相关性图 Fig.4 The correlation between organic carbon and nitrogen content at Lake Changshou

因此,湖泊沉积物有机质 C/N 比结合其碳同 位素组成($\delta^{13}C_{org}$)是判断有机质来源的有效手段 (Meyers and Ishiwatari, 1993; Meyers, 1994, 1997)。长寿湖沉积物有机质 C/N 比和 $\delta^{13}C_{org}$ 值 显示其主要来源于水生植物和藻类(图 5),基本 不受或受陆源物质影响较小。

4.2 指标的环境指示意义

自从 Stuiver (1975) 首次使用湖泊沉积物 有机质碳同位素 ($\delta^{13}C_{org}$)恢复湖泊生产力变化 以来,有机质碳同位素被广泛应用于古气候和古 环 境 重 建(Stuiver, 1975; Mckenzie, 1985; Schelske and Hodell, 1991; Mayer and Schwark, 1999; Leng and Marshall, 2004; Xu et al, 2006; Henderson and Holmes, 2009; 赵 艳 等, 2013; Zhu et al, 2013)。湖泊沉积物有机质碳同位素 的变化可能受以下过程的影响: (1)不同来源 碳的相对含量变化(陆源植物和水生植物具有不 同的碳同位素组成); (2)内源为主的湖泊, 受湖水溶解无机碳(DIC)的碳同位素组成控制 (Hodell and Smith, 2001)。在内源有机质为主 的湖泊中,沉积物有机质碳同位素主要用来判断 历史时期湖泊生产力变化。众多研究者建立了湖 泊沉积物有机质 δ^{13} C 随湖泊初级生产力变化的响 应模式 (Schelske and Hodell, 1991; McKenzie and Hollander, 1993; Meyers, 1997; Teranes et al, 1999; Teranes and McKenzie, 1999; Teranes et al, 1999; Teranes and McKenzie, 1999; Teranes and Bernasconi, 2005),即随着湖泊初级生产力的逐 渐增大,使得水体中可利用 CO₂ 减少,水生植物倾 向于吸收湖水溶解无机碳 (DIC)中 HCO₃ 作为碳 源。由于 HCO₃ 的 δ^{13} C 值比可溶解 CO₂ 的 δ^{13} C 偏 正 (Meyers, 1997; Leng and Marshall, 2004; Xu et al, 2006),从而导致有机质 δ^{13} C 值偏正;反之, 随着湖泊初级生产力的逐渐减小,有机质 δ^{13} C 偏负。



图 5 长寿湖沉积物 C/N 比值和 $\delta^{13}C_{org}$ 示意图 不同来源有机质 C/N 比和 $\delta^{13}C_{org}$ 值引自 Mayers and Ishiwatari, 1993; Meyers, 1994, 1997。 Fig.5 C/N ratios and $\delta^{13}C_{org}$ values of sedimentary organic

matter from Lake Changshou General C/N ratios and $\delta^{13}C_{org}$ ranges for aquatic plants and C_3/C_4 land plants cited from Mayers and Ishiwatari, 1993; Meyers, 1994, 1997.

4.3 多指标记录的环境演化

根据长寿湖沉积物柱芯有机质 C、N 含量、 C/N 比值及有机质碳同位素综合来看(图3), 长寿湖近 60 年来的演化过程可以分为两个阶段, 以 1980 年为时间拐点: (1) 1980 年以前的湖泊 自然演化的贫营养特征。有机质碳、氮含量较低, C/N 比值较小,δ¹³Corg 值较大且变化稳定,说明 长寿湖从湖泊形成到 1980 年这段时间内属于自然 演化过程,各有机质指标均比较稳定,变化较小; (2) 1980 年以后的营养化阶段。有机质 C、N 含量、 C/N 比值及无机碳含量均呈现显著增大过程,C/N 比值增大说明长寿湖在 1980 年以后有少量陆源植 物的输入,δ¹³Corg 值的显著偏负暗示湖泊有机质 来源仍然以藻类为主。

长寿湖近 60 来的环境演化过程的转换期为 1980 年。1980 年以前长寿湖为自然演化过程,湖 泊生产力水平低下,湖泊处于稳定状态。1980 年 以后所有指标均呈现出显著变化特征,说明湖泊 已经处于营养化状态。事实上,自 20 世纪 80 年 代以来,随旅游业、养殖业蓬勃发展,长寿湖已 成为集饮用、灌溉、旅游、养殖、发电为一体的 多功能水体。伴随着旅游业和养殖业的快速发展, 严重影响了长寿湖的区域环境,内源物质的逐渐 积累,导致湖泊生产力的增大;湖区偶尔爆发的"水 华"现象说明了其湖泊生态环境已遭到破坏(杨 钢等,2003)。近 60 年来长寿湖沉积物有机质多 指标反映的环境演化特征与人类活动显示了一致 的变化过程,忠实记录了长寿湖从自然演化环境 逐步过渡到富营养化的过程。

从图 3a、3c、3d 可以看出,长寿湖沉积物有 机质碳同位素值随着有机质碳、氮含量的增加而 减小; 而传统的研究认为湖泊初级生产力的逐渐 增大,导致有机质 δ^{13} C 值增大。随着湖泊生产力 的提高,导致有机质碳同位素值偏负的原因可能 有: (1)同位素的非平衡沉淀。有研究结果认 为湖泊营养化过程的同位素非平衡沉淀导致有机 质 δ^{13} C 值偏负 (Fronval et al, 1995; Teranes and McKenzie, 1999; 吴敬禄等, 2002; Wu et al, 2004; Teranes and Bernasconi, 2005); (2) 藻 类吸收的 CO,来源会受到湖泊环境制约而改变。 营养化初级阶段湖泊生产力得到提高,藻类吸收 的 CO, 部分来源于大气 CO, 随着营养化加剧, 藻类发育,水中溶解的 CO,与大气 CO,的交换平 衡被打破,水体中溶解的 CO,已经不能满足藻类 生长的需要,有机质降解作用产生的 CO,逐渐被 藻类吸收,导致有机质碳同位素组成偏负(周志 华等, 2007; Zhu et al, 2011)。一般认为同位素 的非平衡沉淀发生在特别富营养化的湖泊中(Wu et al, 2004), 而长寿湖显然没有达到超级富营养 化阶段。因此,可以认为长寿湖沉积物有机质碳 同位素值随着湖泊生产力的增大而偏负的原因主 要是藻类吸收偏负的同位素所致。周志华等(2007) 在研究巢湖时也发现随着巢湖富营养化过程的进 一步加剧,其有机质碳同位素逐渐偏负。Zhu et al (2011)研究了不同水生植物类型湖泊,沉积物 有机质 δ^{13} C 值与湖泊初级生产力变化的响应过程,

认为大型水草为主的湖泊(如草海),其沉积物 有机质δ¹³C值随湖泊生产力的增大呈现增加的变 化趋势;藻类为主的湖泊(巢湖、程海、长寿湖 等),其沉积物有机质δ¹³C随湖泊生产力的增大 呈现减小的变化趋势,藻类易降解是导致δ¹³C值 随湖泊生产力的增大呈现减小变化趋势的主要原 因(周志华等,2007)。因此,长寿湖富营养化 过程中藻类发育及藻类易降解是导致其沉积物有 机质δ¹³C值随湖泊生产力的增大呈现减小趋势的 主要原因。

5 结论

 (1)长寿湖沉积物有机质 C/N 比和 δ¹³C_{org} 值 表明长寿湖沉积物有机质主要源于水生植物和藻
 类,基本不受或受陆源物质的影响较小。

(2)近60年来长寿湖沉积物有机质多指标 反映的环境演化特征与人类活动影响一致,忠实 记录了长寿湖从自然演化环境逐步过渡到富营养 化的过程。1980年以前长寿湖为自然演化过程, 湖泊生产力水平低下,湖泊处于稳定状态;1980 年以后所有指标均呈现了显著的变化特征,说明 湖泊已经处于营养化状态。长寿湖沉积物有机质 碳同位素值随着有机质碳、氮含量的增加而减小 与传统的研究认为湖泊初级生产力的逐渐增大导 致有机质δ¹³C值增大不一致,湖泊营养化过程中 藻类发育及藻类易降解是导致长寿湖有机质δ¹³C 值随湖泊生产力增大呈现减小趋势的主要原因。 长寿湖营养化过程的逐渐加剧提醒人们需要对其 进行监管和采取有效防治措施。

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