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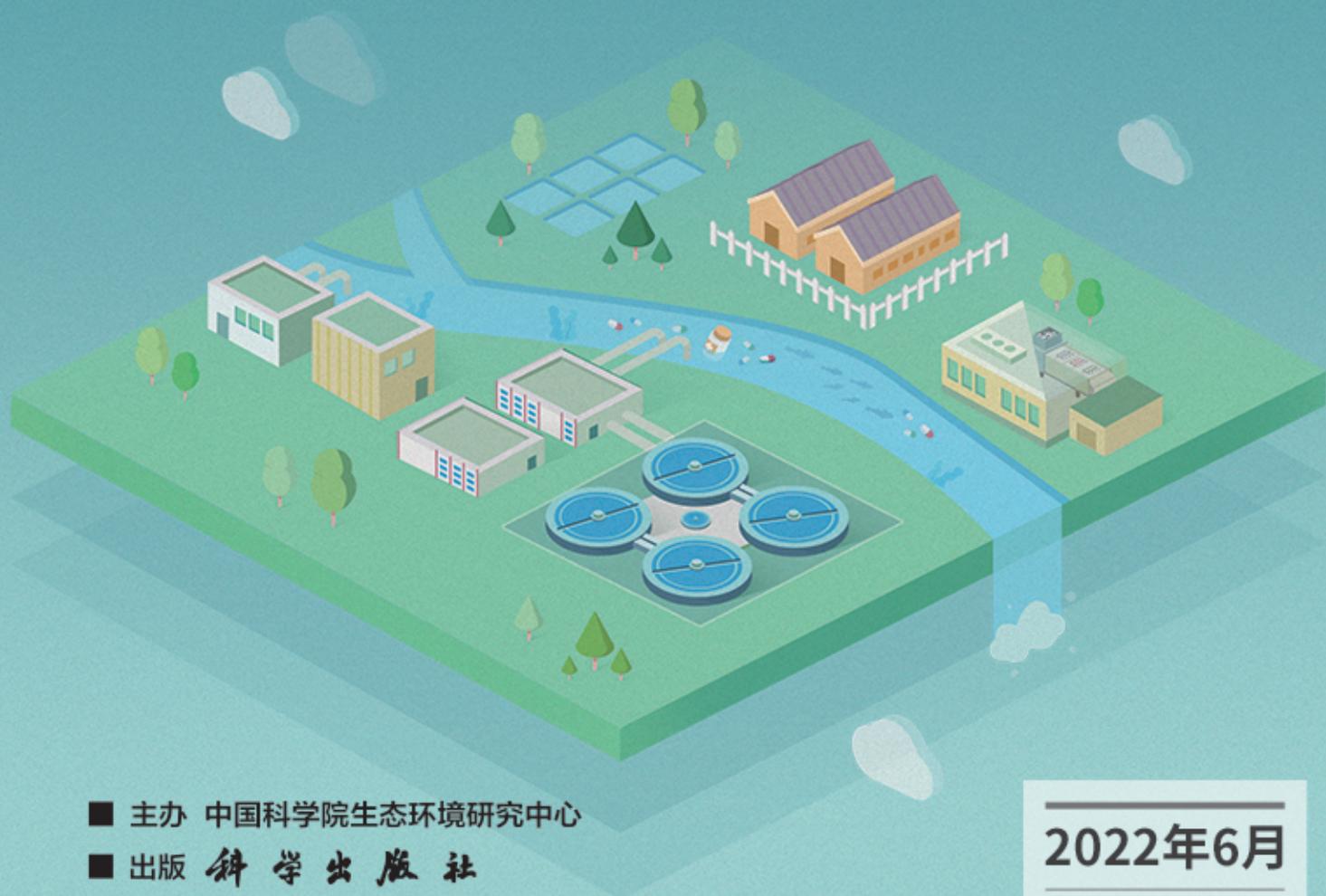
ENVIRONMENTAL SCIENCE

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HUANJING KEXUE

长江中游典型饮用水水源中药物的时空分布及风险评价

武俊梅, 魏琳, 彭晶倩, 何鹏, 施鸿媛, 汤冬梅, 吴振斌



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湖泊沉积物有机磷释放动力学特征及水质风险

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摘要: 为揭示湖泊沉积物有机磷释放特征及对水质影响, 选取我国云南高原及长江中下游 6 个湖泊沉积物, 研究了溶解态有机磷 (DOP) 和溶解态无机磷 (SRP) 释放动力学差异及有机磷形态与溶解性有机质 (DOM) 特征对沉积物磷释放影响, 并探讨了沉积物 DOP 释放的水质风险。结果表明: ①沉积物 DOP 和 SRP 释放动力学过程相似, 均遵循二级动力学模型, 首先是快速释放阶段, 随后慢速释放, 释放曲线逐渐平缓并达到最大释放量。②沉积物有机磷释放与有机磷形态和有机质有关。活性有机磷 (LOP) 和中活性有机磷 (MLOP) 是快速释放阶段主要向上覆水释放的 DOP 形态。释放后期 LOP 和 MLOP 占总有机磷 (DTP) 比例下降, 而非活性有机磷 (NLOP) 比例增加; 同时 DOM 腐殖化程度和芳香性随磷释放过程逐渐升高, DOM 活性不断降低, 导致 DOP 释放速率呈先快后慢趋势。③与 SRP 相比, DOP 释放量较大, 占 DTP 总释放量的 47%~77%, 释放风险较高; 湖泊营养水平较高, 沉积物 DOP 释放量较大, 水质下降风险也较高。因此, 湖泊沉积物磷释放不仅应关注无机磷释放, 也应关注有机磷释放, 否则会低估沉积物磷释放量及水质风险。

关键词: 沉积物; 有机磷; 释放动力学; 磷形态; 水质风险

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Kinetic Release Characteristics of Organic Phosphorus of Sediment-water and Water Quality Risks

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Abstract: To reveal the characteristics of organic phosphorus release from lake sediments and its potential impact on water quality, six lake sediments from Yunnan Plateau and the middle and lower reaches of the Yangtze River in China were selected. We studied the differences in the kinetics of dissolved organic phosphorus (DOP) and dissolved inorganic phosphorus (SRP) release from sediments. The effects of organic phosphorus morphology and dissolved organic matter (DOM) characteristics on sediment phosphorus release were investigated, and the water quality risks of sediment DOP release were discussed. The results showed that: ① the release kinetics of sediment DOP and SRP were similar; both followed the second-order kinetic model, starting with a rapid release phase, followed by a slow release, and the release curve gradually leveled off and reached the maximum release. ② The release of organic phosphorus was related to organophosphorus morphology and organic matter. Active organic phosphorus (LOP) and medium active organic phosphorus (MLOP) were the DOP forms mainly released into the overlying water during the rapid release phase. The proportion of LOP and MLOP to total organic phosphorus (DTP) decreased in the late release stage, whereas the proportion of non-active organic phosphorus (NLOP) increased; further, the degree of humification and aromaticity of organic matter gradually increased with phosphorus release, and its activity decreased, resulting in a slower release rate at the later stage. ③ Compared with that of SRP, the risk of DOP release was higher, accounting for 47%-77% of the total amount of DTP. It was also found that the higher the nutrient level of the lake, the greater the release of DOP and the higher the water quality risk. Therefore, not only the release of inorganic phosphorus but also that of organic phosphorus should be of concern in the process of phosphorus release from lake sediments to prevent the underestimation of phosphorus release and water quality risk.

Key words: sediment; organic phosphorus; release kinetics; phosphorus forms; water quality risks

沉积物磷释放是影响湖泊水质的重要因素^[1-3], 磷释放特征是研究磷生物地球化学循环及湖泊水质风险关注的重点之一^[4]。近年来随沉积物外源磷负荷得到有效防控, 其沉积物内源磷释放正不断成为水体磷负荷的重要贡献来源^[5-7]。以往湖泊沉积物磷释放研究主要针对总磷和无机磷^[8-10], 而很少关注沉积物有机磷释放及其形态变化和对水质影响等问题。但有研究发现, 湖泊沉积物释放溶解性有机磷 (DOP) 占总磷比重较高, 可转化为溶解态无机磷 (SRP) 而被生物利用, 从而加重湖泊水污染

及富营养化^[11,12]。沉积物 DOP 是湖泊水体一种重要磷源, 其释放的水质风险较大^[12,13]。Ni 等^[14]在研究沉积物有机磷 (OP) 组成对湖泊营养状况响应时发现, 沉积物 OP 可能较总磷 (TP) 更能反映湖泊营养

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状况; Wang 等^[15]在不同营养水平湖泊沉积物磷释放动力学研究中也认为, 虽然 SRP 释放占比较高, 但 DOP 释放也不容忽视。因此, 综合考虑沉积物有机和无机磷释放特征及差异, 解析沉积物有机磷释放特征及对水质影响, 对深入揭示沉积物磷释放特征及湖泊富营养化机制具有重要意义。

湖泊沉积物有机磷释放主要受有机磷形态和有机磷矿化作用等影响^[16]。DOP 转化为活性有机磷释放进入水体, 或转化生成无机磷, 进而影响湖泊水质^[17,18]。根据以往研究, 并不是所有的磷组分都能从沉积物中释放到上覆水体^[19], 表明沉积物 DOP 释放和其形态之间存在一定的关联^[20]。DOP 是溶解性有机质 (DOM) 的重要组分, Long 等^[21]通过实验发现 DOM 和磷吸附解析过程密切相关, 是影响沉积物磷释放的重要机制。基于此, 本研究选择长江中下游及云南高原 6 个典型湖泊, 利用化学连续提取法, 结合沉积物磷释放动力学模型, 对比研究湖泊沉积物 DOP 和 SRP 释放动力学差异, 揭示沉积物有机磷释放特征, 以期阐明沉积物有机磷释放影响因素及机制, 并探讨其水质风险。

1 材料与方法

1.1 样品采集

长江中下游和云南高原是我国湖泊水污染及富营养化严重区域^[22]。本研究选取长江中下游受流域经济和人类活动影响较大的湖泊: 太湖 (TH)、巢湖 (CH)、鄱阳湖 (PYH) 和云南高原受农业、藻类和外源污染影响的湖泊: 洱海 (EH)、滇池 (DC)、异龙湖 (YLH); 用彼得森采泥器采集表层 (0~5 cm) 沉积物样品, 装在密封袋中, 带回实验室真空冷冻干燥机冷干处理, 研磨混匀后过 100 目筛, 装入封口袋后冷藏密封保存备用。

1.2 沉积物磷释放动力学实验

准确称取 10 份 2.0 g 冷冻干燥的沉积物样品于离心管中, 加 50 mL 超纯水, 放入恒温振荡器振荡 (25℃, 200 r·min⁻¹), 分别于 5、15、30、60、90、120、180 和 300 min 取一份样品, 5 000 r·min⁻¹ 下离心 15 min 后用 0.45 μm 滤膜过滤, 上清液用于测定 DTP 与 SRP 浓度。将振荡 24 h 后的沉积物再次冷冻干燥、研磨过筛, 测定不同形态 OP 含量^[23]。

磷释放动力学模型可用于定量研究湖泊沉积物磷释放行为^[24,25]。根据初始浓度与平衡浓度之差, 计算沉积物磷释放量^[26], 选用二级动力学模型拟合沉积物磷释放动力学过程^[27]:

$$dq/dt = k(q_e - q_t)^2$$

式中, q_t 为 t 时刻湖泊沉积物磷释放量 (mg·kg⁻¹);

t 为释放时间 (min); k 为磷释放速率常数 [mg·(kg·min)⁻¹], 可指示沉积物磷释放强度^[28]; q_e 为平衡时沉积物磷释放量 (mg·kg⁻¹)。另外, 以 q_{max} 表示磷最大释放量 (mg·kg⁻¹), 二者均可表示本研究条件下沉积物磷释放能力^[11], 是表示沉积物磷释放动力学特征的重要参数。

1.3 测定方法

为掌握沉积物磷释放过程中不同活性有机磷形态变化特征, 采用基于 Ivanoff 等^[29]改进的顺序提取法。将沉积物有机磷分为活性有机磷 LOP, 即碳酸氢钠提取态有机磷 (NaHCO₃-P_o); 中活性有机磷 MLOP, 包括盐酸提取态有机磷 (HCl-P_o) 和富里酸提取态有机磷 (Ful-P_o); 以及非活性有机磷 NLOP, 包括胡敏酸提取态有机磷 (Hum-P_o) 和残渣态有机磷 (Res-P_o)。沉积物溶解性总磷 DTP 含量测定用过硫酸钾消解-钼锑抗分光光度法, SRP 用钼酸铵分光光度法, DOP 为二者之差。实验中所有样品测定重复 3 次并取其平均值, 实验误差控制在 5% 以内。

DOM 的紫外可见光谱是利用紫外分光光度计 (Hach DR-5000, 美国), 在 1 cm 石英比色皿及 190~700 nm 的扫描波长范围内测定的。紫外参数主要有 3 个: A_{253}/A_{203} 是 253 nm 与 203 nm 吸光度的比值; E_2/E_3 表示 250 nm 处与 365 nm 处吸光度的比值; $SUVA_{254}$ 为 254 nm 的吸光度乘以 100 除以该溶液的 TOC 值。

1.4 数据处理

本研究数据采用 Origin 2018 (Origin Lab, USA) 软件进行二级动力学方程拟合, 利用 SPSS 21 (IBM, Armonk, New York, USA) 和 R 语言软件进行图、表绘制与分析。

2 结果与分析

2.1 湖泊沉积物有机磷释放动力学特征及与无机磷差异

本研究湖泊沉积物 DOP 是释放磷的主要组成部分, 其释放量为 3.41~13.35 mg·kg⁻¹, 占 DTP 释放量的 47%~77% (图 1)。和 SRP 相比, 两者释放动力学过程基本一致, 均经历快速释放阶段和缓慢释放阶段, 并逐步达到释放平衡 (图 2), 这与前人研究结果相似^[17,21,30,31]。其中 DOP 的快速释放阶段主要在 60 min 内完成, 释放了约 90%, 释放量达到 3.04~10.99 mg·kg⁻¹; 相比而言, 与 SRP 释放存在一定差异, 其快速释放阶段发生在 0~90 min, 各沉积物样品 SRP 释放量较 DOP 低, 为 1.5~6.13 mg·kg⁻¹; 之后释放较为缓慢。在 180 min 沉积物 DOP 和 SRP

释放量达到最大值, DOP 为 3.26 ~ 13.33 $\text{mg}\cdot\text{kg}^{-1}$, SRP 为 1.61 ~ 6.71 $\text{mg}\cdot\text{kg}^{-1}$, 之后释放过程基本趋于平衡。

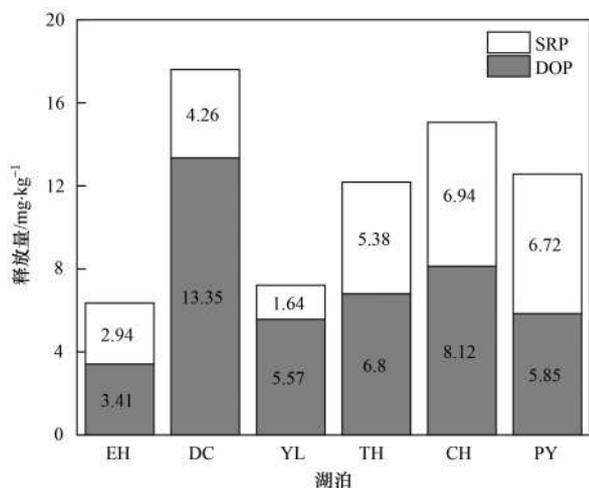


图 1 湖泊沉积物 DOP 和 SRP 释放量比较

Fig. 1 Comparison of DOP and SRP releases from lake sediments

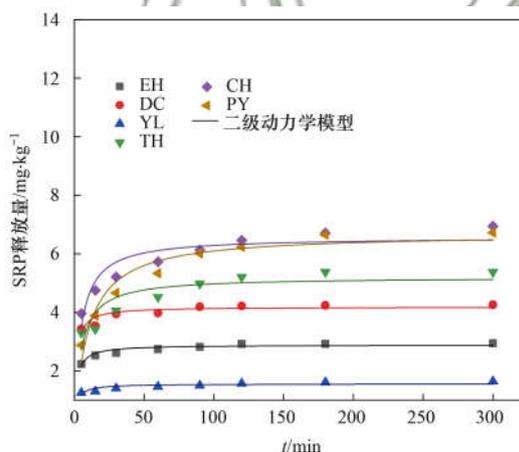
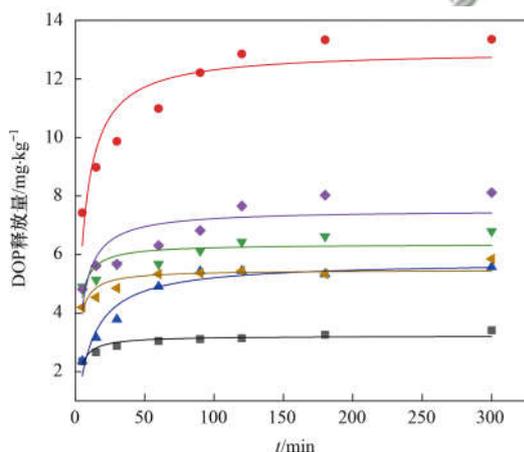


图 2 湖泊沉积物 DOP 和 SRP 释放动力学曲线

Fig. 2 Release kinetics curve of DTP and SRP in lake sediments

表 1 湖泊沉积物 DOP 和 SRP 释放准二级动力学模型参数

Table 1 Kinetic parameters of quasi-second-order kinetic model of DOP and SRP release from lake sediments

湖泊	DOP 二级动力学模型				SRP 二级动力学模型			
	q_{\max} / $\text{mg}\cdot\text{kg}^{-1}$	q_e / $\text{mg}\cdot\text{kg}^{-1}$	k / $\text{mg}\cdot(\text{kg}\cdot\text{min})^{-1}$	R^2	q_{\max} / $\text{mg}\cdot\text{kg}^{-1}$	q_e / $\text{mg}\cdot\text{kg}^{-1}$	k / $\text{mg}\cdot(\text{kg}\cdot\text{min})^{-1}$	R^2
洱海	3.41	3.22 ± 0.06	0.139 ± 0.030	0.87	2.94	2.88 ± 0.04	0.207 ± 0.037	0.90
滇池	13.35	12.96 ± 0.49	0.015 ± 0.004	0.85	4.26	4.18 ± 0.07	0.174 ± 0.045	0.79
异龙湖	5.57	5.75 ± 0.21	0.017 ± 0.004	0.94	1.64	1.56 ± 0.04	0.402 ± 0.130	0.71
太湖	6.8	6.36 ± 0.20	0.079 ± 0.028	0.69	5.38	5.20 ± 0.23	0.042 ± 0.015	0.77
巢湖	8.12	7.53 ± 0.38	0.032 ± 0.013	0.70	6.94	6.57 ± 0.22	0.034 ± 0.009	0.86
鄱阳湖	5.85	5.47 ± 0.12	0.097 ± 0.026	0.79	6.72	6.69 ± 0.24	0.015 ± 0.003	0.93

2.2 湖泊沉积物磷释放动力学过程中磷形态变化

为进一步了解沉积物有机磷释放,采用顺序提取法得到 5 种提取态有机磷^[30],发现沉积物 DOP 释放动力学过程与 DOP 形态关系密切^[32,33].而本研究各湖泊沉积物磷释放动力学过程中各形态 DOP

为探究湖泊沉积物磷释放特征,选用二级动力学模型拟合磷释放动力学过程,发现拟合效果较好 (R_{DOP}^2 为 0.69 ~ 0.94, R_{SRP}^2 为 0.71 ~ 0.93), 均达到了显著相关水平 ($P < 0.05$). 本研究湖泊沉积物 DOP 与 SRP 释放动力学参数值存在差异,其中 DOP 释放动力学参数值较大,结果见表 1. 本研究各湖泊沉积物 SRP 释放速率常数 k [$(0.015 \pm 0.003) \sim (0.402 \pm 0.130) \text{mg}\cdot(\text{kg}\cdot\text{min})^{-1}$] 大多高于 DOP [$(0.015 \pm 0.004) \sim (0.139 \pm 0.030) \text{mg}\cdot(\text{kg}\cdot\text{min})^{-1}$], 是 DOP 释放速率常数 k 的 1.49 ~ 24.20 倍,说明 DOP 释放强度略低于 SRP; 而 DOP 释放量则均高于 SRP,在 DTP 中占比较高,且较快达到最大释放量, DOP 模型参数 q_e 和 q_{\max} 均高于 SRP,分别为 SRP 释放模型参数 q_e 和 q_{\max} 的 1.12 ~ 3.70 倍和 1.07 ~ 3.40 倍. 因此,与 SRP 相比,本研究湖泊沉积物 DOP 释放动力学参数值均较高,即再悬浮过程中湖泊沉积物 DOP 释放可更快达平衡,且释放量较大.

含量也发生一定变化(图 3),其中快速释放阶段(0 ~ 60 min) HCl-P_o 与 Ful-P_o 含量呈增加趋势, NaHCO₃-P_o 和 Hum-P_o 含量递减, Res-P_o 含量有增加趋势;而慢速释放阶段(60 ~ 180 min) NaHCO₃-P_o、HCl-P_o 和 Ful-P_o 总体呈降低趋势, Hum-P_o 和

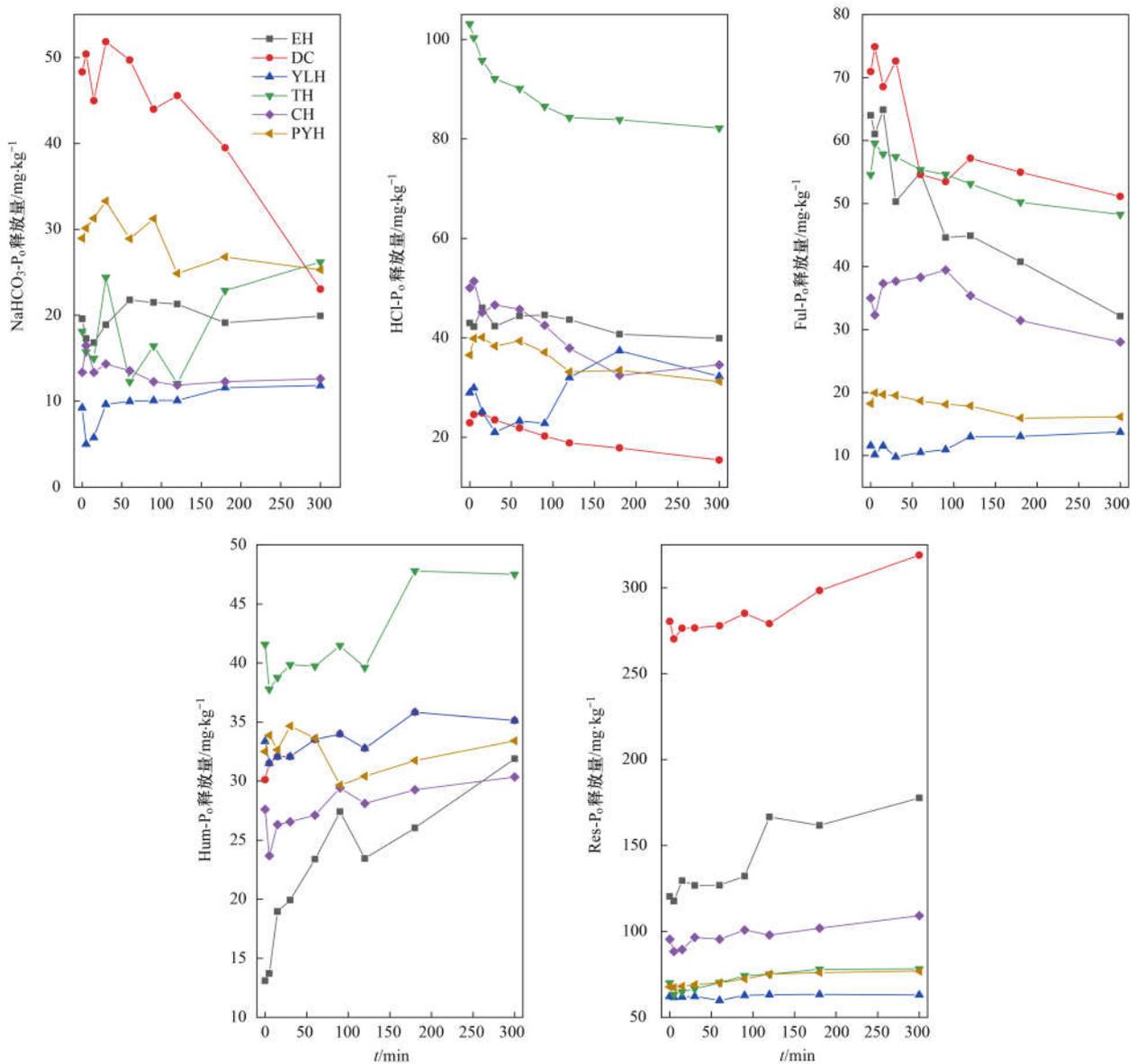


图3 湖泊沉积物磷释放动力学过程中各有机磷形态含量变化

Fig. 3 Change in organic phosphorus forms in the process of release dynamics

Res-P_o 则与之相反. 具体来看, NaHCO₃-P_o 最先被释放^[23], 其含量在释放初期(0 min) 占总有机磷的 6.3%~15.7%, 在 0~15 min 和 15~60 min 时间段内先降后升, 60 min 后下降到 6.0%~15.2%, 整个释放过程呈明显下降趋势. HCl-P_o 和 Ful-P_o 稳定性较差^[34], 其含量先升后降, 释放初期(0 min) HCl-P_o 占总有机磷的 5.1%~35.9%, 释放 5 min 后其含量上升至 5.4%~36.3%, 之后的 5~300 min 其含量整体呈下降趋势. Ful-P_o 含量也从释放初期的 9.9%~24.6% 上升再下降至平衡时的 8.8%~14.1%. Hum-P_o 释放过程中含量整体呈上升趋势, 从 5.0%~17.7% 上升到 10.6%~18.2%. Res-P_o 在释放有机磷中占有最大比例(35.2%~72%), 相较其他活性磷稳定, 释放过程中浓度变化不大.

本研究湖泊沉积物各 DOP 形态含量差异较大,

磷释放过程中大部分湖泊沉积物 LOP 含量减少, NLOP 含量波动性增加, MLOP 含量波动性减少, 但含量大小顺序相同, 均呈现 NLOP > MLOP > LOP 的趋势, 这与已有的研究结果一致^[14,22,32]. 同时, 相关性分析也表明湖泊沉积物各 DOP 形态含量与其磷释放显著正相关(图 4).

3 讨论

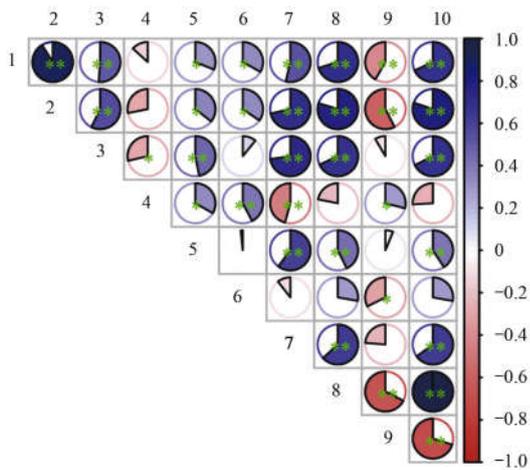
3.1 湖泊沉积物有机磷释放影响因素

湖泊沉积物磷释放过程受沉积物 pH、有机质含量、黏土颗粒大小和有机磷形态等多种因素影响^[11,35]. 其中, DOP 形态和 DOM 对研究磷释放动力学特征及其机制具有重要意义, 本研究沉积物各形态 DOP 释放量与释放参数 k 和 q_e 显著相关, 其形态是影响各阶段释放速率和释放量差异的重要原

因^[33]; 除此之外, 沉积物 DOM 苯环上羟基、羧基和羰基等官能团结构的变化也会影响沉积物磷的释放^[36].

3.1.1 磷形态对湖泊沉积物有机磷释放影响

已有研究发现湖泊沉积物磷释放很大程度取决于有机磷形态特征变化^[23,33,37], 本文在磷释放动力学特征研究中也得到了类似结果. 湖泊沉积物磷释放呈现先快后慢趋势, 且释放过程中 DOP 形态组成均发生了一定变化, 其原因可能是各形态有机磷释放及转化所致^[38]. 水体扰动可促进活性和中活性有机磷释放, 影响沉积物 DOP 形态分布, 最终影响湖泊沉积物磷释放动力学过程^[4,39,40]. 因此本文分析了 DOP 形态与其释放特征参数间的相关性(图 4).



1. DTP, 2. DOP, 3. $\text{NaHCO}_3\text{-P}_o$, 4. HCl-P_o , 5. Ful-P_o , 6. Hum-P_o , 7. Res-P_o , 8. q_{\max} , 9. k , 10. q_e ; 圆面积占比和颜色深浅对应相关性的数值; 不同星号表示相关性显著, * 表示 $P < 0.05$, ** 表示 $P < 0.01$

图 4 湖泊沉积物磷形态和有机磷释放特征参数指标皮尔森相关性分析

Fig. 4 Pearson's correlation analysis between phosphorus forms and characteristic parameters of organic phosphorus release

沉积物 $\text{NaHCO}_3\text{-P}_o$ 与 DOP 及释放参数 q_e 显著相关 ($R = 0.572, P < 0.01$; $R = 0.677, P < 0.01$), 且作为一种活性物质, $\text{NaHCO}_3\text{-P}_o$ 被松散地吸附在沉积物颗粒表面或者吸收进沉积物间隙水中, 易矿化释放进入水体^[38, 41], 转化为生物有效磷, 被微生物、植物等吸收利用^[38]. 快速释放阶段 (0 ~ 60 min) 湖泊沉积物-水界面的相互作用较为强烈^[22], 即使活性 $\text{NaHCO}_3\text{-P}_o$ 含量较低, 其释放依旧会影响沉积物 DOP 的释放速率 k ^[27], 在湖泊沉积物磷释放过程中起重要的释放作用.

Ful-P_o 在磷释放过程具有中等占比, 与 $\text{NaHCO}_3\text{-P}_o$ 相比其与磷释放参数 q_e 相关性较为显著 ($R = 0.408, P < 0.01$), 表明其对 DOP 的释放也发挥着重要作用(图 4). Ful-P_o 在整个释放阶段的

含量先增后降, 总体含量降低, 显著影响了上覆水体的磷含量^[41]. 这种趋势可能与 MLOP 与其他 OP 形态释放转化有关^[22], MLOP 易水解或矿化, 溶解并易通过孔隙水扩散^[42], 释放后期含量逐渐下降. 这也解释了前期释放速率 k 快, 释放量 q 较大的原因.

即使 Res-P_o 与 DOP 及释放特征参数 q_e 相关性显著 ($R = 0.714, P < 0.01$; $R = 0.649, P < 0.01$), NLOP 对沉积物有机磷释放影响依旧很小. 一个原因是 NLOP 总量占 DOP 含量比例最高 (39% ~ 69%), 且在释放过程中含量变化不大; 另一个原因是 Res-P_o 和 Hum-P_o 主要为大分子有机磷或其他难溶性磷, 难以被生物利用, 不能轻易转化或释放^[43].

综上, 磷释放前期沉积物各形态 DOP 均有贡献, 各形态磷释放量占比为 $\text{LOP} (35\%) > \text{MLOP} (25.5\%) > \text{NLOP} (21\%)$, 即 LOP 和 MLOP 是主要影响沉积物有机磷释放速率和释放量的 OP 形态; 释放后期 LOP 和 MLOP 占 DOP 比例下降, 而 NLOP 占比增加, 导致后期释放速率减慢^[23].

3.1.2 沉积物 DOM 特征对其有机磷释放影响

DOM 可在活性基团作用下促进沉积物磷释放^[5,14], 是影响沉积物磷释放关键因素之一^[44], 也是 DOP 在快速释放阶段较慢速释放阶段更易释放、释放速率 k 更大的另一原因. 本研究发现, 沉积物疏水性 DOM 苯环上羟基、羧基和羰基等官能团结构的变化会影响沉积物磷的释放^[33], 沉积物 DOM 的特征参数 SUVA_{254} 、 A_{253}/A_{203} 和 E_2/E_3 值均发生一定变化, 导致磷释放过程中释放速率和释放量产生差异.

SUVA_{254} 值已被证实是估算 DOM 中芳香族化合物比例的有效指标, SUVA_{254} 值越高, DOM 的腐殖化和芳香性越大, 分子量越小^[45]. A_{253}/A_{203} 的值可以反映 DOM 取代基的浓度, 比值越大, 说明芳香环取代基的浓度越高^[44]. 沉积物磷释放动力学过程中, SUVA_{254} 和 A_{253}/A_{203} 值呈稳定上升趋势, 且 SUVA_{254} 值 < 3 (表 2), 说明 DOP 快速释放阶段 DOM 腐殖化程度、取代基及芳香性均低于慢速释放阶段, 利于前期 DOP 释放, 解释了其释放速率 k 及释放量 q 较慢速释放阶段大的原因. 表征 DOM 的另一紫外特征参数 E_2/E_3 与 DOM 腐殖化水平和分子量有关, 比值越低, 其分子量越高^[45,46]. 本实验 E_2/E_3 值从释放开始到平衡后数值变小(表 2), 表明沉积物 DOM 分子量随释放增大, DOM 结构更为复杂. 这也解释了释放前期大分子 Hum-P_o 所占比例较小, 以小分子量的 Ful-P_o 为主^[42], 同时, 由于小分子物质稳定性低, 且前期 DOM 腐殖化程度和疏水性 (矿化程度) 较低, 活性更强; 更易于沉积物磷释放,

表 2 湖泊表层沉积物 DOP 释放过程紫外可见光光谱特征参数

Table 2 Characteristic parameters of UV-vis spectra of DOP release process in surface sediments of each lake

紫外可见光光谱指数	时间/min	采样点					
		洱海	滇池	异龙湖	太湖	巢湖	鄱阳湖
A_{253}/A_{203}	5	0.22	0.16	0.04	0.32	0.26	0.28
	60	0.24	0.18	0.04	0.48	0.29	0.31
	180	0.24	0.21	0.05	0.42	0.36	0.31
	300	0.24	0.22	0.05	0.47	0.37	0.35
E_2/E_3	5	5.44	5.06	8.57	3.75	5.09	5.81
	60	5.36	4.73	8.33	3.67	4.71	5.83
	180	5.24	4.95	8.23	3.55	4.69	4.4
	300	5.22	4.88	8.13	3.33	4.66	4.11
SUVA ₂₅₄	5	0.28	0.37	0.13	0.02	0.05	0.08
	60	0.31	0.39	0.14	0.05	0.05	0.09
	180	0.34	0.43	0.15	0.07	0.08	0.11
	300	0.33	0.45	0.15	0.08	0.09	0.12

与 SUVA₂₅₄ 和 A_{253}/A_{203} 得出的结论一致。

3.2 沉积物有机磷释放的水质风险

沉积物磷释放是影响上覆水磷浓度的重要因素^[47],也是导致富营养化湖泊持续富营养化的重要原因^[3]. 过量磷输入会导致水体富营养化; 湖泊营养化程度较重情况下,即使减少或控制外部污染负荷,湖泊水质也较难恢复^[48,49]. 有研究发现湖泊营养水平较高,其沉积物 SRP 释放水平也较大^[15], Guo 等^[50]的研究也发现湖泊营养的水平增加会导致 DOP 积累,造成更多的 SRP 释放. 同时也有研究表明不同营养水平湖泊沉积物 DOP 释放能力可能存在较大差异^[15,22,38,47],本研究也得到相似结果,长江中下游与云南高原 6 个不同营养水平湖泊沉积物 DOP 均以 NLOP 为主,但两湖区营养水平较高的湖泊 LOP 和 MLOP 占比相对较低营养湖泊高. 同时,营养水平高的湖泊沉积物 DOP 释放量要高于低营养湖泊. 如表 3,处于富营养水平的太湖、巢湖和中营养水平的鄱阳湖分别释放了 55.79%、53.93% 和 46.52% 的 DOP,云南高原湖区的异龙湖为重度营养水平,其沉积物释放了 77.31% 的 DOP,高于中营养和富营养水平的滇池(75.81%)和洱海

(53.69%). 由此可见,湖泊富营养化程度越高,其沉积物有机磷释放的水质风险越大.

湖泊沉积物释放 DOP 占 DTP 比例较高,其水质风险较 SRP 高; 其中 DOP 最大释放量较 SRP 更大,本研究 DTP 总释放量为 6.35 ~ 17.61 mg·kg⁻¹,沉积物释放 3.41 ~ 13.35 mg·kg⁻¹ DOP 进入水体,磷释放占比较初始阶段明显上升(62% ~ 70%),其中有 90% 会水解为无机磷释放出来,并最终被生物利用^[11]. 同时 DOP 与 DTP 含量间的关系达到极显著水平,相关系数最高, $R = 0.912 (P < 0.01)$,表明扰动条件下 DOP 的释放在湖泊沉积物磷的释放过程中发挥着重要作用,同时也表明沉积物磷释放过程中 DOP 不容忽视^[15]. 综上所述, DOP 作为湖泊沉积物 DTP 释放的主要部分,在湖泊沉积物磷释放过程中占主导作用,对湖泊沉积物内源磷负荷作用及贡献不容忽视. 随着外源磷负荷逐步得到控制,环境条件变化及微生物等作用,可能会进一步提高湖泊沉积物 DOP 的释放风险. 因此,在湖泊沉积物磷释放过程中不仅要关注无机磷的释放,有机磷释放特征的研究也是很有必要的,否则会低估沉积物磷释放的水质影响及风险.

表 3 长江中下游湖泊和云南高原湖泊沉积物有机磷释放特征比较

Table 3 Comparison of organic phosphorus release characteristics from sediments of lakes in the middle and lower reaches of Yangtze River and Yunnan Plateau

项目	长江中下游湖泊			云南高原湖泊		
	太湖	巢湖	鄱阳湖	洱海	滇池	异龙湖
营养水平	富营养	富营养	中营养	中营养	富营养	重度营养
DOP 释放量/mg·kg ⁻¹	6.80	8.12	5.85	3.41	13.35	5.57
MLOP/DOP/%	46.20	29.14	25.88	23.89	15.00	29.49
DOP/DTP/%	55.79	53.93	46.52	53.69	75.81	77.31

4 结论

(1) 沉积物 DOP 与 SRP 释放动力学过程相似,

遵循二级动力学模型,释放速率均呈现先快后慢的变化趋势; DOP 快速反应阶段主要发生在前 60 min, SRP 则主要在 0 ~ 90 min, DOP 最大释放量和

总释放量较 SRP 更大。

(2) 沉积物 DOP 形态及 DOM 是影响磷释放动力学过程的重要因素。LOP 释放量最大(16%~54%), 其次为 MLOP(18%~33%), NLOP 最小, 增加了约 5%~37%, 表明 LOP 和 MLOP 是主要向上覆水体释放的 DOP 形态。DOM 腐殖化程度和芳香性随磷释放过程逐渐升高, DOM 活性不断降低, 且有机质活性较低, 导致 DOP 释放速率先快后慢。

(3) 湖泊沉积物 DOP 较 SRP 释放风险高, 其释放量占 DTP 总释放量的 47%~77%; 且通过对比长江中下游和云南高原 6 个不同营养水平湖泊表明, 湖泊营养水平较高, 其沉积物 DOP 释放量也较大, 表现出较大的水质风险。

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