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厦门大学

硕 士 学 位 论 文

九龙江口有色颗粒有机物的光谱特性及其河口行为

Optical Properties and Estuarine Behavior of Chromophoric Particulate Organic Matter in the Jiulong Estuary

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摘要

河口是连接陆地和海洋两大有机碳储库的重要纽带。颗粒有机物（POM）在河口环境的生物地球化学循环和生态学过程中扮演着重要角色。与有色溶解有机物（CDOM）一样，有色颗粒有机物（CPOM）也是河口有机碳储库的重要组分，对河口碳循环、河口光化学和光生物学等过程同样具有显著影响。目前对河口CDOM 已有大量研究报道，但以 CPOM 的光谱特征来示踪河口 POM 的组成、来源、迁移和转化等过程的研究却并不常见。本论文以亚热带中小河口的代表–九龙江口为研究对象，以吸收光谱和荧光光谱作为表征手段，首先比较了不同提取方法（水溶法、碱溶法）对 CPOM 光谱特征的影响，进而探讨了碱溶性 CPOM 在九龙江口的时空变化、河口行为及其影响因素，并结合 Chl-a 和 $\delta^{13}C$ 数据，阐述了利用 CPOM 的光谱特征示踪河口 POM 来源和组成的可行性。此外，还探讨了九龙江口最大浑浊带定点站 CPOM 含量和组成随潮汐的动态变化及其控制因素，并比较了底层沉降颗粒物与悬浮颗粒物中 CPOM 性质及组成上的差异。主要研究结果如下：

（1）九龙江口水溶性与碱溶性 CPOM 之间、CPOM 与 CDOM 之间在分子结构和化学组成上存在明显的差异。水溶性和碱溶性 CPOM 的吸收光谱在 250~280 nm 波长区间均存在一个 CDOM 所没有的肩峰；河口下游的水溶性 CPOM 在 300~320 nm 区间还存在一个次级肩峰，可能与藻类释放的生源有机小分子有关；水溶性 CPOM 以及河口中、下游的碱溶性 CPOM，其三维荧光谱图始终呈现不连续的孤立荧光峰结构，只有河端的碱溶性 CPOM 具有与水体 CDOM 类似的连续带状谱图。此外，碱溶性 CPOM 的荧光组分以长波类腐殖质组分、类色氨酸和类酪氨酸组分为主，而 CDOM 则以短波类腐殖质组分占主导。

（2）水溶性和碱溶性 CPOM 在九龙江口具有不同的来源与地球化学特征，其中，水溶性 CPOM 主要以吸附在颗粒物表面的可交换态有机质为主，而碱溶性 CPOM 则更多表征了 POM 整体的化学组成。水溶性和碱溶性 CPOM 整体均呈现河端高、海端低的分布趋势。在河口上游，碱溶性 CPOM 的丰度高于水溶性 CPOM，随盐度增加，两者之间的差距变小；到河口中、下游，水溶性 CPOM 的丰度反而超过了碱溶性 CPOM。水溶性 CPOM 的光谱斜率（$S_{275\text{-}295}$p）变化较

小，表明沿河口梯度其平均分子量变化不大。碱溶性 CPOM 的 $S_{275\text{-}295}$p、类蛋白质组分所占百分比（protein-like%）以及新鲜度指数（BIX）均表现出海端>河端>最大浑浊带的分布趋势，而腐殖化指数（HIX）则正好相反，表明从河端向海端，陆源 CPOM 所占比例降低、而自生源 CPOM 比例增加，最大浑浊带则相对富集高腐殖化程度、高分子量的 POM。

（3）九龙江口碱溶性 CPOM 的吸收系数（a_{350}p）与 6 个荧光组分均大致随盐度升高而降低，但存在较大的空间与季节性变化。在河流–河口界面，CPOM 表现出显著的先添加后去除现象，而水体 CDOM 的行为却正好相反，表明 POM 的非保守行为可能与 DOM 的絮凝–溶解、颗粒物的吸附–解吸等过程有关。在河口中、下游，碱溶性 CPOM 主要受控于咸淡水之间的混合。在常态下，淡水端元 a_{350}p 季节变化明显，表现为春季的“富集”–夏季的“稀释”–冬季的再“富集”，这可能与流域内 POM 向河流的运移、输出路径的季节性变化有关；但在夏季台风影响下，淡水端元 a_{350}p 显著增加，反而超过了枯水期，表明河口 CPOM 动力学对极端天气事件的响应迅速。

（4）探讨了利用 CPOM 的光谱参数示踪河口区 POM 来源的可行性。结果发现，类蛋白质组分（C4 与 C6）的荧光强度之和（以 P 表示）与类腐殖质组分（C1~C3、C5）的荧光强度之和（以 H 表示）的比值（P/H）与 δ^{13}C-POC 以及定量估算的藻类来源 POC（algal-POC%）之间具有显著的正相关关系，并且光谱斜率 $S_{275\text{-}295}$p 也随盐度的升高而增加，反映出河口区 POM 随盐度梯度从以陆源高分子量组分为主向以海源低分子量组分占优势的转化趋势，表明河口区 CPOM 的光谱特征具有较好的物源示踪意义。至于文献中提出的“浮游生物源”特征荧光组分（本文为 C2，Ex/Em 为 255, 360/452 nm），其荧光强度在九龙江口颗粒态与溶解态之间的比值与δ^{13}C-POC 的变化趋势相反，这与弱潮河口（例如 Neuse 河口）两者之间的同步变化趋势截然不同，表明在与九龙江口类似的强潮河口，该组分并不适于作为自生源 POM 的示踪信号。

（5）九龙江口最大浑浊带定点站 CPOM 的含量与化学组成受径流、潮流的相互作用具有明显的潮周期变化和季节变化特征。a_{350}p 和总荧光强度在高、低平潮期间含量较低，但在高潮后和低潮后的 1~3h 内出现高值区，并且 $S_{275\text{-}295}$p 和 protein-like%均随潮汐的涨落发生同步变化，表明在最大浑浊带，CPOM 含量与

组成主要受控于潮汐和再悬浮引起的 POM 来源的变化。底层水体的 $S_{275\text{-}295}$p 数值普遍低于表层，表明再悬浮过程主要向底层水体输送了比较惰性的高分子量 POM。CPOM 含量的季节变化具有“枯兴洪衰”的特征，主要受最大浑浊带发育状况及流域输沙性质的季节性差异的影响。冬季 POM 的平均分子量最高、protein-like%最低，夏季正好相反，说明最大浑浊带 CPOM 的化学组成也有明显的季节性变化。

（6）与悬浮 CPOM 相比，沉积物捕获器收集的沉降 CPOM 具有较低的 $S_{275\text{-}295}$p、P/H 比值、BIX 以及较高的 HIX 值和较高的长波类腐殖质组分（C3 与 C5）占总荧光的百分比，显示出沉降颗粒物比悬浮颗粒物更加富含高芳香度、高腐殖化程度的惰性高分子量 POM，表明九龙江口沉降颗粒物中 POM 主要来源于沉积物的再悬浮作用。

关键词：有色颗粒有机物；悬浮颗粒物；沉降颗粒物；分离提取；河口；最大浑浊带

Abstract

Estuaries are the major link between land and ocean organic carbon pool. Particulate organic matter (POM) plays important roles in the biogeochemical cycles and ecological processes in estuarine environments. Similar to Chromophoric dissolved organic matter (CDOM), chromophoric POM (CPOM) is a vital component of estuarine organic carbon pool and has significant influences on the fields of carbon cycle, aquatic photochemistry and photobiology in the estuary. There were considerable studies focused on the estuarine CDOM, however, the researches using CPOM optical properties to trace estuarine POM are scarce. Here, we carried out studies that focused on a medium-sized subtropical estuary-Jiulong Estuary, using UV-Vis absorption spectroscopy and excitation-emission matrix fluorescence spectroscopy. Our objectives were 1) to compare the effects of different extraction methods (Milli-Q vs. NaOH) on the optical properties of CPOM; 2) to understand the temporal and spatial variations, estuarine behaviours and controlling factors of base soluble CPOM in the Jiulong Estuary; 3) to investigate the potential of CPOM optical signatures as an indicator to trace different sources of estuarine POM, combined with Chl-a and $\delta^{13}C$ data; 4) to discuss the dynamic variation of CPOM with tidal cycles at the fixed station of estuarine turbidity maximum (ETM) zone in the Jiulong Estuary, and to compare the qualitative and quantitative differences of CPOM between suspended and sinking particles collected by sediment trap. Main findings were:

(1) There were obvious differences in the molecular structure and composition between the water soluble and base soluble CPOM, and between CPOM and CDOM in the Jiulong Estuary. Both the absorption spectra of water and base soluble CPOM showed a shoulder peak around 250~280 nm which CDOM did not. A secondary shoulder around 300~320 nm was found in the absorption spectra of water soluble CPOM in the lower reach of the estuary. These shoulders were related to the autochthonous organic molecules produced by phytoplankton. Similar to water soluble CPOM, EEM spectra of base soluble CPOM from the middle and lower reach of the estuary showed discrete peaks. These peaks were linked each other for the upper reach CPOM samples which resembled CDOM fluorescence spectra. Besides, base soluble CPOM was dominated by visible humic-like, tryptophan-like and tyrosine-like

components, while microbial humic-like component dominated CDOM fluorescence.

(2) Water and base soluble CPOM exhibited diverse sources and geochemical characteristics in the Jiulong Estuary that water soluble CPOM was mainly expressed as the exchangeable organic matter adsorbed into the surface of particles and base soluble CPOM mostly presented the composition of bulk POM. Water and base soluble CPOM both showed significant decreases along the estuary. In the upper reach, the abundance of base soluble CPOM was higher than water soluble CPOM which was the opposite in the lower reach. Spectral slope ($S_{275\text{-}295}$p) of water soluble CPOM was less variable, suggesting a reltively consistent molecular weright (MW) of POM along the estuary. All $S_{275\text{-}295}$p, protein-like fraction and BIX of base soluble CPOM exhibited obviously spatial distributions, with an order of marine end-member>freshwater end-member>ETM. The HIX index showed the opposite tendency. These changes indicated that autochthonous CPOM fraction generally increased with increasing salinity, while more humified and higher MW POM was relatively riched in the ETM zone.

(3) Absorption coefficient (a_{350}p) and all fluorescence components of base soluble CPOM generally decreased with the increasing salinity, but showing considerably spatial and seasonal changes. In the river-estuary interface, base soluble CPOM was sequently subjected to addition and removal which was the opposite to CDOM, indicating that the non-conservative behavior of POM may be influenced by the processes of DOM flocculation and dissolution, adsorption and desorption of particles. In the middle and lower reach, base soluble CPOM was dominated by the mixing of freshwater and seawater. Normally, a_{350}p in the freshwater end-member exhibited significantly seasonal changes with the enrichment in spring followed by dilution in summer and re-enrichment in winter, likely due to seasonal changes of DOM transport pathway into the river. Howver, a_{350}p could increased dramatically in summer due to the typhoon event and were even much higher than those in winter, indicating the rapid response of estuarine CPOM dynamics to extreme climate events.

(4) The tracer potential of spectral parameters of CPOM to estuarine POM were examined. The results showed that the ratio of protein-like and humic-like components intensity (P/H), δ^{13}C-POC and the quantitatively estimated algal-POC% had significantly positive relationships, and $S_{275\text{-}295}$p generally increased with the increasing salinity, suggesting the additions from autochthonous sources of POM with the increasing salinity. Thus, it can be proved that the optical properties of CPOM had good

tracing implication of POM in the estuary. As for the planktonic fluorescence components mentioned in previous papers, the ratio of C2 (Ex/Em: 255, 360/452 nm) in particulate and dissolved form showed inverse spatial distribution with δ^{13}C-POC in the macrotidal Jiulong Estuary, which was the opposite to the microtidal estuary (e.g. Neuse River Estuary), indicating that this typical component was not suitable for tracing autochthonous POM in the macrotidal estuary.

(5) The concentration and composition of CPOM at the fixed station of ETM in the Jiulong Estuary showed obviously tidal and seasonal changes during the tidal cycles. a_{350}p and total fluorescence intensity showed lower values in the high and low tide slack, but existing high value ranges in the next 1~3 h after tide slack. $S_{275\text{-}295}$p and protein-like fraction also showed synchronous changes with tidal cycles, all these suggested that CPOM concentration and composition in the ETM zone was also controlled by the process of sediment resuspension other than the mixing of freshwater and seawater caused by tidal cycle. $S_{275\text{-}295}$p values in the bottom layer was commonly lower than those in the surface water, demonstrating that more refractory and higher MW POM was input to the bottom layer due to the resuspension process. The concentration of CPOM showed seasonal changes with high values in winter and low values in summer and mainly affected by seasonal variations of developing condition of ETM and sediment transport from the watershed. POM exhibited high MW and low protein-like fraction in winter which was just the opposite in summer, suggesting that there were also seasonal variations in the compostion of CPOM in the ETM.

(6) Compared with suspended CPOM, the lower values of $S_{275\text{-}295}$p, P/H ratio, BIX, higher HIX and higher visible humic-like fraction (the sum of C3 and C5) to the total fluorescence intensity in the sinking CPOM collected from sediment trap indicated that more aromatic, humified and refractory POM with high MW was enriched in sinking particles than suspended POM. This may result from the sediment resuspension which drives a greater amount of POM upwards into bottom waters.

Key words: Chromophoric particulate organic matter; suspended particles; sinking particles; separation and extraction; estuary; estuarine turbidity maximum