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辽河三角洲滨海湿地有机碳的时空演变、环境功能及其埋藏机制

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滨海湿地有机碳的时空分布规律, 是研究影响滨海湿地固碳能力及其对当今环境演化与全球气候变化的响应及反馈作用的关键。尽管土壤中总碳含量是评价固碳能力的重要指标, 但其中球囊霉素相关蛋白质(glomalin-related soil protein, GRSP)作为有机碳的一种重要组在部分, 可代表和行使有机碳在滨海湿地固碳能力中的相关作用。

GRSP 是丛枝菌根真菌(arbuscular mycorrhizal fungi, AMF)分泌的一类糖蛋白, 在菌根死亡/周转之后被释放进入土壤中。由于蛋白质的高稳定和难降解性, 其在土壤中的停留时间可达到数年至数十年, 在滨海厌氧环境中的储存时间可达千年以上。且 GRSP 为土壤碳组成中不可缺少的一部分, 有着重要的碳汇功能, GRSP 还有助于凝聚土壤颗粒以形成土壤团聚体来实现碳的长期储存。因此, 研究滨海湿地中 GRSP 的分布特征, 对于评价滨海湿地固碳和长期封存碳的能力具有十分重要的科学意义。

本研究以 GRSP 作为现代滨海湿地固碳作用的媒介物质, 探究其空间分布特征及与沉积物物理化学性质的关系, 分析现代滨海湿地环境中有利于 GRSP 累积和沉积物固碳的条件; 与之对应的沉积物固碳的时间分布特征, 则甄别钻孔沉积物所揭示的地质历史演化时期与相关元素的耦合关系, 进而探讨有机碳的埋藏机制。为评价有机碳在湿地过滤作用中所起到的环境功能, 本研究讨论了 GRSP 和有机碳的螯合作用对滨海湿地不同环境中重金属迁移分布的影响。

本研究提取了 150 个辽河三角洲不同植物类型中表层沉积物的 GRSP, 并采用考马斯亮蓝蛋白质显色方法(Bradford assay)测试其含量。结果显示 BR-GRSP(Bradford-reactive GRSP)的含量变化范围为 0.11~11.31 mg g^{-1}, 处在绝大多数温带土壤的范围(2~14 mg g^{-1})之内。不同植被类型之间 BR-GRSP 的含量具有显著性差异(p=0.001 8), 这是包括宿主植物类型、AMF 的定殖水平、土地利用类型和土壤物理地球化学性质等在内的多重因素共同作用的结果。BR-GRSP 含量最低的翅碱蓬主要影响因素是: 植物-AMF 的相互作用、盐度胁迫、海水入侵所引起的 SO_4^{2-} 浓度升高促进了硫酸盐还原菌的活性, 增强了 GRSP 的降解程度; 而 BR-GRSP 含量次低的玉米地主要和耕地的翻地活动、化肥农药的使用、单一植被等因素有关。

BR-GRSP 含量与表层沉积物总有机碳(Corg)之间有显著的正相关关系(r=0.511, p=0.000), 占有机碳库的比例变化范围为 6.213%~10.35%, 占沉积物总碳库的比例变化范围为 4.901%~8.35%, 占土壤总氮库的比例变化范围为 8.147%~13.219%, 表明 BR-GRSP 是辽河三角洲表层沉积物中总碳氮储存库的一个重要组成部分。BR-GRSP 含量与沉积物物理性质(原位密度、含水率和粘粒含量)之间显著的相关性表明沉积物粘粒对 AMF 和所分泌的 GRSP 具有物理保护作用, GRSP 和 AMF 反过来也对土壤结构具有改善作用, 两个作用共同促进了 GRSP 在滨海湿地中的累积。不同的沉积物化学性质, 包括营养元素(C、N、P), 化学计量比(TN/TP、TC/TP 和 TP/TK), 矿物质元素(Cu、Fe、Zn)等在内, 与 BR-GRSP 含量的关系表明本研究区中与 P 相关的养分比例平衡程度和沉积物中充足的养分有利于 GRSP 的累积。BR-GRSP 含量与多个重金属元素(As、Cd、Cr、Hg 和 Pb 等)均具有显著正相关性, 显示出对重金属元素的稳定作用, 但是鉴于 GRSP 结

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合重金属的能力低于腐殖质，因此农田中 BR-GRSP/Corg 比例的增大会降低农田有机质对重金属的螯合作用。

为验证农田中有机质螯合作用降低对重金属迁移的影响，明确辽河三角洲重金属的空间分布特征，识别影响重金属迁移的主要环境动力，辨别重金属的污染来源和评价湿地过滤功能在辽河三角洲的作用，在辽河三角洲的不同环境中，包括上三角洲平原(upper delta plain wetlands, UDPW)、相邻的辽东湾浅海湿地(shallow sea wetland, SSW)和流经辽河三角洲的河道，共采集了 373 个表层沉积物样品，分析了沉积物的粒径分布、Corg 浓度和颗粒态重金属(particulate heavy metals , PHMs)浓度，所测重金属元素包括 As, Cd, Cr, Cu, Hg, Pb, Zn, Al, Fe 和 Mn，和 67 个表层水样，以分析水样盐度。结果显示 UDPW 中 PHMs 的浓度比 SSW 中的同名参数高约 10%~22%，说明 PHMs 在 UDPW 有显著累积现象，也说明了 UDPW 可以有效地以不同的物理化学方式来储存和保留人为来源的 PHMs，进而阻止 PHMs 流向海洋环境。然而，UDPW 在历史上有大量的天然植被被开垦为耕地，耕地中的污水灌溉所引起的强烈 Cd 污染导致了约有 86 km^2 面积的浅海湿地范围内 Cd 浓度较高。最应当注意的是 PHMs 在 SSW 中的分布还受多个因素的影响，其中包括盐度引发的解析-再吸附机制，河流淡水注入和 SSW 中的洋流(主要是 NE-SW 向潮流和 NE-E 向沿岸流)所控制的三维复杂水动力和沉积过程，均使得在 SSW 中的 PHMs 污染大面积扩散。对 UDPW 和 SSW 样品数据集进行主成分分析，发现二者的结果具有高度相似性，这反映了 SSW 的 PHMs 污染来源特征实际上继承于 UDPW。但从相关系数判断，SSW 中重金属、有机质和粘粒的关系更加密切，且 SSW 中相关系数的值域范围为 0.406~0.919，而 UDPW 的范围为 0.042~0.654。分析不同土地利用类型中 Corg 与 PHMs 的相关性发现，农田中有机质的螯合作用比湿地生态系统的确有所降低，且加速了向河流和邻近海洋的迁移，换言之，湿地生态系统对 PHMs 的移除作用是显著的。

土壤侵蚀和淋滤作用使 GRSP 进入河流，进而被搬运到湿地生态环境中并沉积下来，对降解作用的抵抗性可使其作为滨海湿地沉积物中陆源土壤成分沉积模式的指示物质。因此，在海洋-陆地交界的滨海湿地环境中，GRSP 的来源有两种：一是与湿地植被形成共生关系的丛枝菌根真菌所分泌的 GRSP，即原位自生来源；二是通过河流、风和地下水搬运而来的外来陆源 GRSP。本研究中采用上游 C3 植物和本地 C4 植物所产生的 GRSP $\delta^{13}C$ 差别来进行两种来源 GRSP 的区分，计算得到辽河三角洲玉米地中自生来源的 GRSP 为主要来源，所占比例变化范围为 45.87%到 97.79%，均值为(70.47±0.84)%。沉积物(SED)和 BR-GRSP 总的同位素之差可以排除陆源和湿地植物影响，直接反映来自海洋环境的物质输入，$\delta^{15}N_{SED}-\delta^{15}N_{BR\text{-}GRSP}$ 和 $\delta^{13}C_{SED}-\delta^{13}C_{BR\text{-}GRSP}$ 指标的空间分布可以反映河口混合机制及海岸线侵蚀作用的强弱，可为海洋-陆地交界处的沉积模式提供直接证据。

基于辽河三角洲沉积物中 BR-GRSP 含量与 Corg、多种沉积物的物理化学性质之间具有的显著相关性，说明现代滨海湿地中，以 BR-GRSP 为媒介，沉积物的固碳作用和多个物理化学指标均具相关性，即现代碳循环与其他元素的循环过程具有相互耦合的性质。而在地质历史变化时期，由于海平面的变化使得现代滨海湿地历经了不同的海相和陆相沉积环境演替过程，沉积物的固碳作用会显示出不同的变化特征。本研究探讨了 Si 和 Fe 元素在辽河三角洲的地质演化历史时期对沉积物固碳的影响，结果表明沉积物的固碳作用与 Si 和 Fe 元素之间的耦合关系更为突出。为此，本研究 2012 年 5 月在下辽河平原西南缘获得到了钻孔 LHDC12-2，通过对其沉积物有孔虫鉴定、物理化学参数以及 AMS^{14}C 和 OSL 测年分析，将本区 33 000 cal yr BP 年以来的沉积环境划分为河道沉积(U1)、湖相沉积(U2)、海洋主导的沉积(U3)、上三角洲平原相沉积(U4)等 4 个沉积单元，特别地对 U3 进一步又划分为 5 个亚相。研究发现，不同沉积环境 BSi 和 Corg 的埋藏速率差别较大：在沉积期为更新世的 U1 和 U2 阶段的 BSi 埋藏速率的均值分别为(11.34±0.22) g m^{-2} yr^{-1} 和 (16.69±0.91) g m^{-2} yr^{-1}，均小于全新世沉积的 U3((23.59±2.89)~(41.74±6.37) g m^{-2} yr^{-1}) 和 U4((37.25±9.96) g m^{-2} yr^{-1})，且沉积物 BSi 埋藏速率对全球冷气候事件及北半球夏季光照强度的响应比 Corg 埋藏速率更敏感。此外，Fe_2O_3 含量与 BSi/Corg 呈负相关关系揭示了对于相对富铁的河口环境，铁元素的供给变化对硅藻生长过程影响同样明显迅速，从而导致即使是在很短的时间尺度上，铁元素的不足也会增强硅酸的较强利用效率，从而制约 Corg 的埋藏效率。特别是，本文指出随着未来海平面的进一步上升，淹没具较高 Corg 埋藏效率((17.87±1.71) g m^{-2} yr^{-1})的上三角洲平原地区，会降低河口地区有机碳的埋藏效率。

关键词：球囊霉素；辽河三角洲；稳定同位素；重金属；生物硅
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Organic Carbon Distribution, Function and Its Burial Processes in the Coastal Wetlands of the Liaohe Delta, Northeast of China

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The distribution characteristics of organic carbon (Corg) in coastal wetlands were significant for researching carbon sequestration and responding to environmental evolution and global climate changes. While total soil carbon is an important indicator of carbon sequestration capacity, the form this carbon takes is perhaps more important. Glomalin-related soil protein (GRSP), one existence form of Corg, could represent and perform the relevant influences of Corg to carbon sequestration in coastal wetlands.

GRSP, the recently described glycoprotein formed by arbuscular mycorrhizal fungi (AMF), was released to soil after hyphal death/turnover. The residence time of GRSP were estimated to be from 6 to 42 years, even thousands of years under the anaerobic environment in an coastal area. With about 30%~50% of carbon in GRSP, up to 30%~60% of soil carbon may be contributed by GRSP under certain conditions in upland agricultural soils, whereas more typical values may be around 5%, These observations demonstrate that GRSP has the potential to accumulate and comprise a substantial proportion of soil carbon. In addition to being refractory, GRSP also helps bind soil particles to form soil aggregates. Such soil aggregation may further contribute to long-term carbon storage by protecting soil organic matter from oxygen and microbial decomposers. GRSP is therefore considered the key link between AMF and soil carbon storage, having scientific significance for coastal wetland carbon sequestration and subsequent long-term storage.

Therefore, this study analyzed the spatial distribution pattern of GRSP in modern coastal wetland, and explored its relationship with the physical and geochemical properties of surface sediments, to identify the conditions that result in a maximum production and preservation of GRSP, also the carbon sequence. Correspondingly, the temporal distribution of carbon sequence was analyzed based on core sediment, which revealed the coupling association between carbon burial and other elements in geological evolution historical periods. To access the function of Corg in wetlands filtration, this study also investigated the influence of GRSP and Corg chelation to heavy metal migration.

Bradford-reactive GRSP (BR-GRSP) were analyzed for 150 surface sediment samples in Liaohe Delta (LHD), showing a range of 0.11~11.31 mg g^{-1}, which was among the scope of most temperate soil (2~14 mg g^{-1}). Significant differences were found for different vegetation types (p=0.0018), and this was the synthetic influence of plant type, the colonization level of AMF, land-use type and the physical and geochemical properties of sediments. For the lowest BR-GRSP content in seablite, the plant-AMF interaction, salt stress, and the accelerated microbial organic matter mineralization and increased sulfate reduction following salt-water intrusion could be responsible. However, the second lower BR-GRSP content in maize field, the main reasons were increased tilling, crop monoculture and use of certain fungicides.

The significant positive relation was recognized between BR-GRSP and Corg (r =0.511, p=0.000), and 6.213%~10.35% of sediment total Corg, 4.901%~8.35% of sediment total carbon, and 8.147%~13.219% of sediment total nitrogen could be bound directly to BR-GRSP, which indicated that BR-GRSP was an important constituent in sediment carbon/nitrogen sink of LHD. Moreover, significant relationships between BR-GRSP and sediment physical properties (bulk density, water content and clay content) suggested that clay particles could offer physical protection for AMF and GRSP, in return, AMF and GRSP could also improve the sediment/soil structure, both facilitating the accumulation of GRSP in coastal wetland. Various chemical properties, including nutrition elements (C, N, P), stoichiometric ratio (TN/TP, TC/TP and TP/TK), and mineral element (Cu, Fe, Zn), had relation with BR-GRSP content, implying the stoichiometric ratio related P and sufficient nutrient in sediment could favour GRSP accumulation. Multi-heavy metal elements (As, Cd, Cr, Hg, and Pb) showed significant positive relation with BR-GRSP content, indicated the heavy metal fixed effect of GRSP. Nevertheless, the ability of GRSP to absorb heavy metal was weaker than humic substance, the increased BR-GRSP/Corg in farmland could reduce the Corg-heavy metal chelation degree.

To proof the influence of decreased farmland Corg-heavy metal chelation to heavy metal migration, also to evaluate the spatial distribution, transportation environmental dynamics of metals, the provenance of metal pollution, and assess the filtration functions of wetlands in LHD, grain size, concentrations of Corg

and particulate heavy metals (PHMs) As, Cd, Cr, Cu, Hg, Pb, Zn, Al, Fe, Mn of 373 surface sediment samples, salinities in 67 surface water samples, were analyzed in various environments, including the upper delta plain wetlands (UDPW), its adjacent shallow sea wetland (SSW) in the Liaodong Bay, and river channels that are running through the LHD. The concentrations of PHMs for UDPW were generally higher by a factor of ~10%~22% compared with its analogues in SSW, suggesting the accumulation of PHMs within the UDPW, indicate that the UDPW systems are efficiently physical and chemical traps for PHMs of anthropogenic sources by retaining and storing pollutants flowing into the sea. However, there was sever sewage-irrigation-induced-Cd-pollution in an area of ~86 km^2 of the adjacent shallow sea wetland, where large amount wetlands were historical moved for agriculture in the UDPW. Remarkably, the distributions of PHMs were controlled by salinity induced desorption and re-adsorption mechanisms, and significantly dispersed the contamination coverage by the three-dimensional hydrodynamic and sedimentation processes that dominated by inputs of freshwater and ocean dynamics including NE-SW tidal currents and NE-E longshore drifts in the SSW of the Liaodong Bay. A high agreement between the UDPW and the SSW datasets in Principle Component Analysis essentially reflects that the characteristics of PHM sources in the SSW were actually inherited from that in the UDPW, with a much closer relationship among heavy metals, organic matter and fine particulates in SSW than that of UDPW, which was judged by their correlation coefficient range of 0.406~0.919 in SSW against the those of 0.042~0.654 in UDPW. By analyzing the correlationship between Corg and PHMs in different land-use types, the degree of farmland Corg-heavy metal chelation was indeed declined, accelerating heavy metal migration to rivers and SSW.

In the case of coastal wetlands, glomalin is expected to have both autochthonous and allochthonous sources. The difference between GRSP $\delta^{13}C$ of upland C3 plant and wetland C4 wetland may help distinguish between allochthonous and autochthonous glomalin in the wetland. By calculation, the autochthonous glomalin were major component with range of 45.87%~97.79% and mean value of (70.47±0.84)%. The differences between isotope values of BR-GRSP and SED could rule out the influence terrestrial and wetland plants, directly reflecting the material input of marine environments. Spatial distribution of $\delta^{15}N_{SED} - \delta^{15}N_{BR\text{-}GRSP}$ and $\delta^{13}C_{SED} - \delta^{13}C_{BR\text{-}GRSP}$ could mirror the degree of mixing mechanism in estuary and coastal erosion, providing evidences for ocean-land interaction.

Based on the significant correlation between BR-GRSP, Corg and multiple physical and geochemical properties of sediments, the associations between carbon sequestration and several physical and chemical index with the mediation of BR-GRSP in modern coastal wetlands were identified, which is the coupling nature of carbon cycle and other elements cycle. However, in geological evolution historical periods, the modern coastal wetlands have experienced different marine and terrestrial depositional environments because of sea-level changes, the carbon sequestration in sediments could revealed distinct characteristics. This paper studied the impact of Si and Fe to carbon burial in sedimentary environment evolution history, and highlight the more significant coupled relationship between carbon and Si and Fe. To explore these relationships, we present foraminifera data, physical and chemical parameters, and ages determined by accelerator mass spectrometry ^{14}C and optically stimulated luminescence from a core drilled at the southwestern edge of the Lower Liaohe Plain in May 2012. We divide the sedimentary environments since 33 000 cal yr BP into four depositional units, namely, a fluvial deposit (U1), lacustrine deposit (U2), marine-related deposit (U3) and upper delta plain deposit (U4). Environmentally mediated differences in apparent mass accumulation rates (AMARs) of BSi and organic carbon (C_{org}) were significant. The BSi-AMAR in the later parts of U1 and U2 occurred mainly in the Pleistocene and averaged (11.34±0.22) g m^{-2} yr^{-1} and (16.69±0.91) g m^{-2} yr^{-1}, which is lower than the analogues for U3 ((23.59±2.89) g m^{-2} yr^{-1}~(41.74±6.37) g m^{-2} yr^{-1}) and U4 ((37.25 ± 9.96) g m^{-2} yr^{-1}) that occurred during the Holocene. The BSi record responded more coherently and was more sensitive than C_{org} to Northern Hemisphere paleoclimatic variations on a long timescale and to abrupt/periodic winter monsoon winds or warming forcings on a short timescale. There was a negative correlation between the concentration of bio-available Fe_2O_3 and the ratio of BSi/C_{org}, the implication being that Fe availability may have modulated silicic acid uptake on a very short timescale and in turn impacted the dynamics of carbon burial.

Key words: Glomalin; Liaohe Delta; stable isotope; heavy metal; biogenic silica

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