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降雨对颗粒态和溶解态有机质陆海输送的影响

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题名页

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Impact of rain event on the land-ocean transfer of particulate and dissolved organic matter

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摘要

内 容 摘 要

河流向海洋输送有机质是全球碳循环中的重要过程，影响长时间尺度的气候变化。大部分有机碳快速的被降解氧化释放到大气中，一部分可以保存在海洋沉积物中，成为长时间尺度的碳埋藏；另一部分残留在水体中，特别是溶解态有机质，则会参与水环境的生物地球化学循环。物质从河流向海洋的输送受到极端降雨（例如台风）的影响，而在长时间尺度上，相对新鲜有机碳在海洋中的埋藏扮演了更重要的“碳汇”的作用。但是由于采样的困难，极端降雨对新鲜有机质输送的研究相对有限。

本研究通过对台湾高山河流流域内土壤样品中的木质素分析，发现大部分土壤中大部分木质素是分布在表层土壤，可以指征新鲜有机质。通过台风期间高密度的河流悬浮颗粒物样本中木质素的分析，我们发现台湾一条高山小河流（浊水溪），在 96 小时内的木质素输送通量可以达到密西西比河的年输送通量的 20%。台湾高山小河流的年木质素输送通量受登陆的台风的频率和强度的影响，因此年木质素输送通量具有较大的变异性，其年平均木质素输送效率是其他非高山河流的 10-100 倍。我们进一步估算出整个大洋小河流的新鲜有机碳的输送通量约为 37 ± 25 Tg yr^{-1}， 占到全球新鲜陆地有机碳输送的 20%，结合大洋高山小河流高的森林覆盖以及台风期间的异重流，高山小河流系统在全球新鲜生物碳生产、输出和埋藏中扮演了重要的角色。

通过对九龙江北溪输出溶解有机质的长时间观测，我们发现受降雨影响，溶解态黑碳和溶解木质素（都主要来自于土壤）的浓度和输送通量随流量增加都有上升的趋势，但当降雨达到一定程度后，其浓度和通量均呈现下降趋势，该结果表明降雨对流域溶解有机质的影响受限于降雨强度；超高分辨质谱结果的初步分析显示在降雨过程中，不同化合物的响应不同：相对较惰性的有机质其所占比例变化不显著，土壤有机质呈上升趋势，相对生物活性的有机质的比例则下降。降雨事件中输出的有机质的归宿及其对近海生物地球化学过程的影响需要进一步的研究。

关键词： 降雨；溶解有机质；颗粒有机碳；木质素；傅里叶变换离子回旋共振质谱

英文摘要

Abstract

The transfer of organic matter from land to ocean is an important process in the global carbon cycle, which affects the long-term climate change in geological time scales. The majority of the organic matter transferred to the coastal region is degraded and returned to atmosphere, while a fraction of this organic matter can be buried in the sediment, act as long-term carbon sink, another fraction of organic matter stays in the water column, especially dissolved organic matter, and enters the biogeochemical cycles. The land-ocean transfer is affected by extreme rain event (e.g., Typhoons), while in long-time scales, the preservation of recent organic carbon plays a more important role in carbon sequestration. However, due to the difficulties in sampling, studies regarding the effect of extreme rain events are limited.

In present study, lignin phenols were measured in surface and depth profiles soils collected from Jhuoshuei River basin. The results showed that approximately 80% of lignin is stored in surface soils (<30 cm), therefore, lignin can represent recent organic carbon. Lignin phenols were then further measured on riverine suspended particles exported by Taiwanese small mountainous rivers (SMRs) during typhoons. We found that the particulate lignin export in 96 hours by a single SMR amounting to ~20% of the annual export by Mississippi River. The yearly particulate lignin discharge from Taiwan Island (35,980 km^2) is governed by the frequency and magnitude of typhoon; thus, the historical lignin export ranged widely from 1.5 to 99.7 Gg yr^{-1}, which resulted in a 10-100 times higher areal yield relative to non-Oceanian rivers. The lignin-derived modern POC output from Oceania region is 37 ± 21 Tg C yr^{-1}, account for approximately 20% of the annual modern POC export from global rivers. Coupled with the hyperpycnal pathway, the forested watersheds of SMRs in Oceania may serve as a giant factory to rapidly produce and efficiently convey modern POC into deep sea for sequestration.

By investigating the dissolved organic matter exported by Jiulong River, we found that during rain events, the concentrations and fluxes of dissolved lignin and dissolved black carbon (both from the soil) showed an increase trend, however, when the discharge exceeds certain point, both concentrations and fluxes decreased, which suggested that the impact of rain events on the export of dissolved organic matter is limited by the strength of the rain. Applying the ultrahigh resolution mass spectrometry, we further found that different organic matter showed different responses to the rain event: the bio-refractory polyaromatics didn't show significant change, while soil derived polyphenols showed significant increase during the rain, and organic matter that may have a biological sources showed decrease trend. Future research regarding the fate and biogeochemical effect of dissolved organic matter in the coastal ocean are required.

Keywords: precipitation; dissolved organic matter, particulate organic matter; lignin; FT-ICR-MS

目录

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Chapter 1 主要研究工作和发现

陆地-海洋有机碳输送是全球碳循环的重要过程，影响长时间尺度的气候变化。河流向海洋输送的有机质，大部分快速的被降解氧化释放到大气中，一部分可以保存在海洋沉积物中，成为长时间尺度的碳埋藏，而另一部分残留在水体中。很多因素可以影响物质从陆地到海洋的输送，例如流域的地形地貌、流域土壤有机碳的储存以及流域的土地利用等。此外，受到气候变化和人类活动的影响，河流向海洋的物质输送也正在经历变化。

溶解态有机质（DOM）是水体环境的主要碳库，影响有机质的生物可利用性、水体的光学性质、金属的生物可利用性等[*Findlay and Sinsabaugh*, 2003]，了解其组成、分布和影响因素是碳循环研究的关键。但限制于分析技术，长时间以来多以分析总体溶解态有机碳浓度为主辅以利用稳定和放射性碳同位素表征其来源，对溶解态有机质组成的认识不足。

海洋溶解有机碳为什么那么“老”是长期以来的研究热点。近期的研究发现开阔大洋溶解黑碳的年龄可以达到万年以上，是迄今为止已知最老的碳库之一[*Ziolkowski and Druffel*, 2010; *Dittmar*, 2015]。进一步的研究发现溶解黑碳占河流输出有机质约 10.6% [Jaffe et al., 2013]，是河流输出有机质的主要组成之一。随着气候变化，极端降雨可能进一步增多，那么溶解态黑碳的响应如何呢？

傅里叶变换回旋共振质谱(FT-ICR-MS)在近年逐渐被应用在海洋 DOM 研究中，由于其超高的分辨率，可以更好的区分化合物组成。结合其他的分析软件和化学手段，FT-ICR-MS 可以解析复杂天然样品 DOM 中化合物的组成，为海洋中有机质的定性以及生物地球化学过程的研究提供了新的视角[*Koch and Dittmar*, 2006; *Dittmar and Paeng*, 2009].

本人在博士后期间延续博士的相关工作，将生物标志物（木质素）应用在台湾高山小河流，利用木质素表征陆源有机质在土壤中的分布以及对极端降雨的响应；并且在中国博士后科学基金和德国 Hanse -Wissenschaftskolleg 的支持下，与 Thorsten Dittmar 的实验室合作，定量分析了极端降雨对溶解黑碳输出的影响，同时应用 FT-ICR-MS 研究溶解有机质组成对极端降雨的响应。主要的研究发现包括以下方面：

1.1 降雨对颗粒有机质输出的影响

1.1.1 台湾高山河流流域内土壤木质素的受控因素 (Chapter 2)：

通过对台湾高山河流浊水溪流域内表层土壤和土壤剖面中木质素的分析，以及与气候因素的关联，我们发现

a) 木质素的植被参数主要受到降雨的季节分布影响，而木质素的降解则受到气温季节变化影响；

b) 台湾土壤中的木质素 80%以上分布在表层土壤（上层 30cm），并且其降解速率大于总体有机碳，表明木质素在土壤中具有相对较快的降解速率；

c) 侵蚀可以引起土壤中木质素以 200 年的速率周转，此速率远高于世界的平均速度。

1.1.2 极端降雨对陆源有机质向海洋输送通量的影响 (Chapter 3)：

通过对台湾高山小河流台风期间高频率水体悬浮颗粒物样本中木质素的分析，我们发现 a) 木质素的输送通量随着径流量的增加而呈指数关系增加;

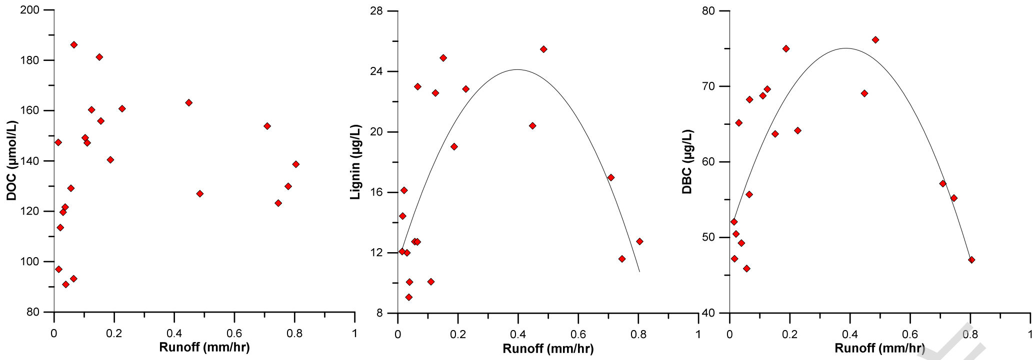
b) 通过建立浊水溪木质素流量和径流量的关系，我们估算出浊水溪在 96h 内木质素的输出通量相当于密西西比河（面积是浊水溪的 600 倍）年通量的 20%。

c) 虽然大洋高山小河流面积仅占陆地面积的 1.8%，但新鲜有机碳的输送通量可以占到全球新鲜陆地有机碳输送的 20%，表明高山小河流在全球新鲜生物碳的输出和埋藏中扮演了重要的角色。研究结果为预测大洋高山小河流在未来气候变化下的响应提供了依据 (Bao et al., 2015, Scientific Reports)。

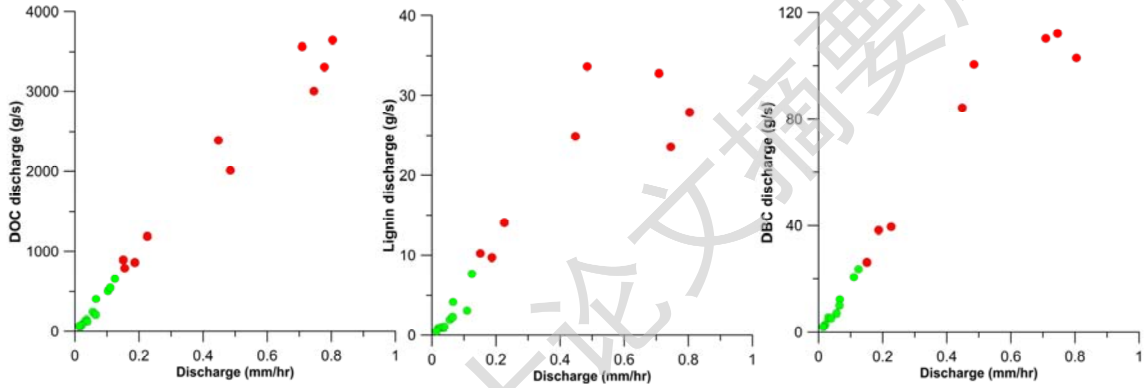
1.2. 降雨对溶解有机质输出以及组成的影响

1.2.1 极端降雨过程对不同溶解态有机质输出通量的影响:

不同的有机质结构的不同，其在水体环境中的归宿也不同。我们对九龙江北溪开展了为期一年的观测，首次同时分析了不同河流溶解态木质素和黑碳对降雨过程的响应。初步的研究结果显示**溶解态木质素和溶解态黑碳在降雨过程中浓度皆呈现上升的趋势，但当流量上升超过一定值时，木质素和黑碳的浓度均下降（图一），并且通量也呈现下降趋势（图二），表明降雨对流域溶解有机质的输送受限于降雨强度。**



图一：溶解有机碳，溶解态木质素以及溶解态黑碳浓度随径流变化关系。



图二：溶解有机碳、溶解黑碳以及溶解木质素通量随径流变化，红色点表示降雨事件采集的样品。

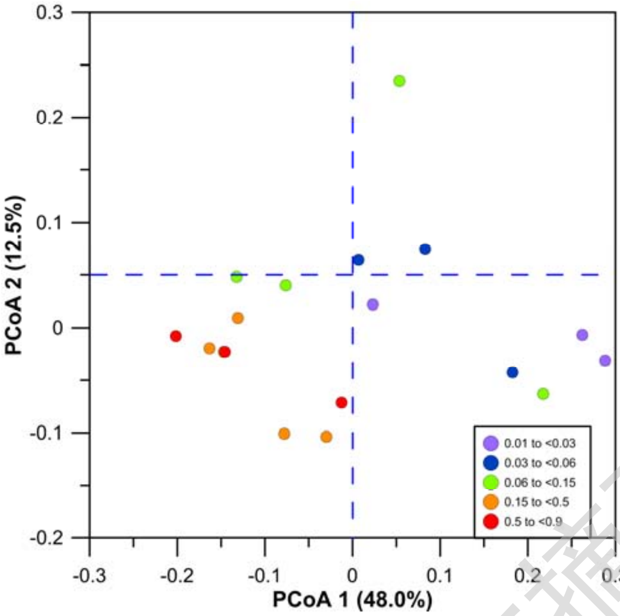
1.2.2 极端降雨过程中有机质组成的变化

通过对九龙江有机质组成的 FT-ICR-MS 的分析，我们发现：

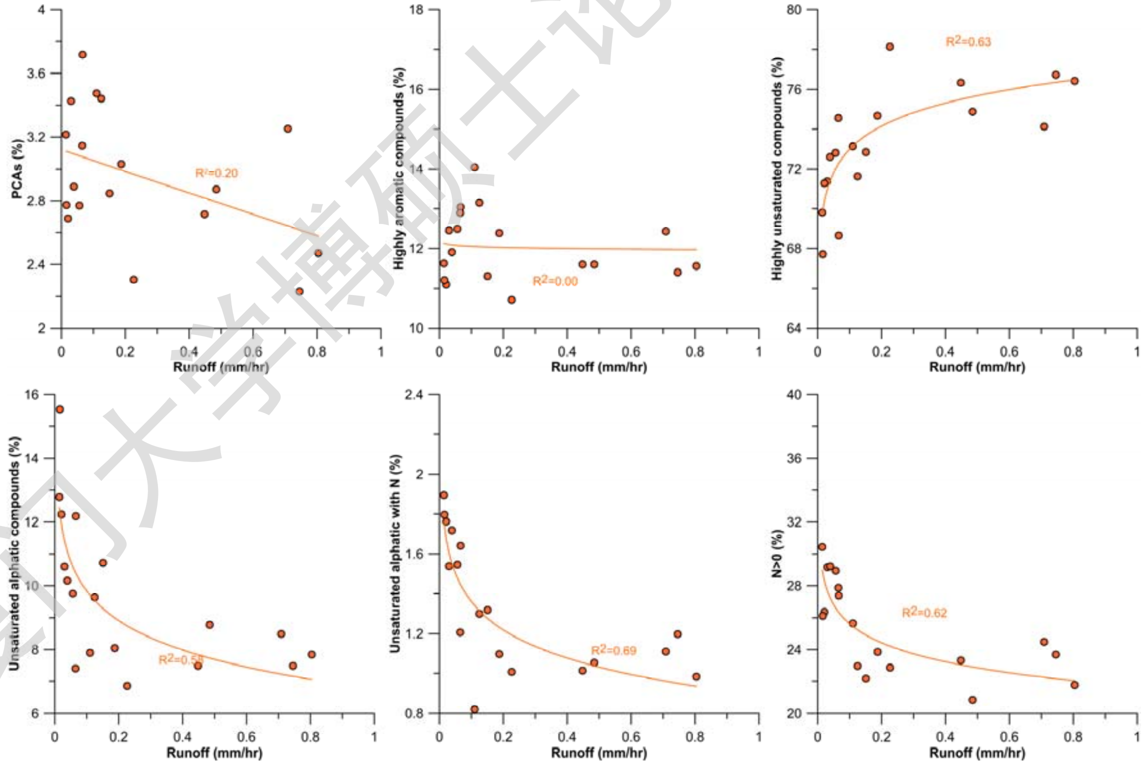
a) 河流有机碳中含有大量不同的化合物，九龙江北溪中发现超过 10,000 种化合物；

b) 高流量和低流量时期有机质的组成存在明显差异（图三）；

c) 不同组分随着降雨的变化其响应不同：高度芳香性化合物，例如燃烧产物等，随着径流的增加，其在河流 DOM 中的比例没有显著变化，而土壤有机质的比例则随着径流的增加呈现对数增加的关系；一些来自生物的活性有机质的比例则下降（图四）。



图三：基于 FT-ICR-MS 分子组成的主因子分析，图中点的不同颜色代表流量的变化，单位：mm/hr.



图四：九龙江北溪溶解有机质中不同组分随径流的变化。

Chapter 2 Microclimatic and erosional influence on lignin storage in a subtropical small mountainous river basin

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Abstract

The cycling of soil organic carbon (OC) is controlled by various environmental factors, including physical erosion, which may be significant in Oceanian small mountainous rivers (SMRs) due to the extraordinary high erosion rate. Moreover, due to the steep slope, the change of microclimate are quick in SMRs and further influence the storage of soil OC. Bulk OC% and lignin were determined on the surface soils and soil profiles collected from a Taiwanese mountainous watershed along a large altitude gradient (3-2970 m, a reflection of microclimate change) The objective was to study the influence of microclimate and physical erosion on the storage of soil OC and lignin. Soil OC% showed positive relation with elevation, suggesting a higher preservation of bulk soil OC in the cold region. We further found that lignin vegetation and degradation in surface soils were more affected by the seasonality of precipitation and temperature, rather than mean annual precipitation and temperature, respectively. Soil lignin were mainly (>70-90%) stored in surface soils (<30 cm) and the proportion of lignin stored in surface soils were higher than bulk OC. Preferential retention of lignin in surface soils and/or preferential degradation of lignin could both led to this phenomenon, which could further facilitate the erosional loss of lignin. The physical erosion induced annual loss of lignin for Taiwan is 10 times higher than the global mean of the erosional loss of soil OC, which suggests that physical erosion acted as an additional factor for destabilize the storage of soil lignin.

Keywords: small mountainous rivers, soil, lignin phenols, organic carbon

2.1 **Introduction**

Soil organic carbon (OC) is an important component in the global carbon cycle. The stocks of soil OC amount to approximately 1600 Pg, which represents 80% of the total terrestrial active carbon pool [*Hedges et al.*, 1997; *Schlesinger and Andrews*, 2000] and more than twice the atmospheric or oceanic refractory OC pool [*Hedges et al.*, 1997]. Therefore, changes in soil OC storage and internal cycling may potentially affect the atmospheric CO_2 content and thus the global climate. On the other hand, the transfer of soil OC from land via rivers to the ocean is a one-way process that connects the terrestrial and marine carbon stocks. Such a unidirectional process exerts an important control on the carbon cycle on a geological time scale [*Berner*, 1990] and synergistically determines the cycling and storage of OC at the catchment system scale.

Oceanian small mountainous rivers (SMRs) are hotspots in the global sediment and carbon export map [*Lyons et al.*, 2002; *Dadson et al.*, 2003]. These rivers only cover 1.8% of the global land area but transfer ~40% of the global sediment and OC to the ocean. The distribution of organic matter in the soils would be particular important in such a high erosion region, which could determine what kind of organic matter will be exported to the ocean. Despite their importance, little information is available regarding the storage and distribution of soil organic matter in those small mountainous regions [*Cheng and Hseu*, 1997; *Alin et al.*, 2008; *Goñi et al.*, 2014].

Lignin phenols, contributing up to 30% of vascular plant biomass, are an unique marker of terrigenous OM [*Hedges and Mann*, 1979]. Lignin is a class of macromolecules, upon CuO oxidation, it can release different monomers. Ratios of those monomers can indicate the vegetation sources and degradation degree of organic matter [*Hedges and Mann*, 1979]. Therefore, lignin phenols have been widely applied to trace the sources and cycling of terrigenous OM in a wide spectrum of environmental samples, e.g., soils, sediments, and riverine or estuarine suspended particles [*Hedges et al.*, 1986; *Goñi et al.*, 1997; *Feng et al.*, 2008; *Duboc et al.*, 2014]. Soil lignin processes (degradation, leaching and sorption) are important for organic matter that can be exported to the ocean and buried on long-term time scales [*Hedges and Oades*, 1997; *Goñi et al.*, 2014].

Most of the studies regarding soil lignin have shown that the degradation of lignin phenols are sensitive to the climate [*Otto and Simpson*, 2006b; *Feng et al.*, 2008], and were affected by mean annual temperature (MAT) and mean annual precipitation (MAP) [*Thevenot et al.*, 2010]. However, most of the studies were carried out in temperate region, the transferring of the knowledge from temperate region to a warmer region might not be suitable. One of the example is the recent study in tropical mountainous Amazon River system that observed a reversed lignin degradation indicator distribution pattern down the soil profile, which might be related to the special microclimate, e.g., tropical montane cloud forest [*Feng et al.*, 2016]. One of the most unique feature of SMRs is their steep river basins. The altitudes of these river basins vary from near sea level to > 3000 m within 100 km, which creates steep gradients [*Kao and Milliman*, 2008], potentially greater than 10 times of that of some major rivers, such as Changjiang. Accompanied with