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Evaluation of the diagenetic state of marine sediments from the Gulf of Cádiz (SW-Spain) by biomarker study of humic acids.

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Research on transport and storage of materials in areas of great sustainability and socioeconomic concern, such as coastal environments, has been recognized as critical for the understanding of the global C cycle. A crucial yet poorly understood component of organic matter (OM) preservation in oceans is the role of the composition of OM in various coastal margin settings, where roughly 80% of the global C burial occurs. There is a need to gain a better understanding of the basic processes that control the organic C cycle in river-dominated ocean margins to predict how climate change will impact its two main components —terrestrial and marine organic C. Organic compounds with high relative residence times and resistance to degradation, such as lignin (unambiguous marker of land-derived material inputs to aquatic systems), are of particular interest to monitor organic C cycle in oceans. Over the past 2-3 decades lignin oxidation products have been used extensively to trace the source and composition of terrigenous OM (TOM) inputs to aquatic systems. However, little effort has been devoted to estimate the relative contribution of humic matter-derived lignin to the bulk sediment (BS) sink or the influence, if any, of this humified material on the signature of the sedimentary TOM.

The objective of this work is to characterize the land-derived OM in both the BS and their corresponding humic acids (HA) in sediments from the inner continental shelf of Gulf of Cádiz, to evaluate the diagenetic state, source and fate of the SOM in the shelf. Relatively constant intensive lignin parameters (S:V = 1.0±0.1 and C:V = 0.22±0.04) indicate that non-woody angiosperm tissues constitute the predominant component of vascular plant materials reaching these sediments. The parallel analysis of the extracted HA provided an estimate of the proportion of lignin-derived terrigenous biomarkers that was comprised of HA-derived constituents (2%-67%). Substantial increases in diagenetic indicator parameters from BS ([Ad:Al]V: 0.41±0.10; [Ad:Al]S: 0.34±0.07; [3,5-Bd:V]: 0.14±0.05; P: [V+S]: 0.24±0.09) to HA ([Ad:Al]V: 0.85±0.20; [Ad:Al]S: 0.57±0.10; [3,5-Bd:V]: 0.27±0.10; P: [V+S]: 0.32±0.10) pointed to the enhanced degradation state of HA with respect to bulk sedimentary OM. The use of the 3,5-Bd:V ratio in conjunction with (Ad:Al)V supported the diagenetic continuum of sedimentary OM from BS to HA, ranging from fresh plant materials to highly altered soil humic constituents. Elemental and molecular analyses showed a decreased influence of TOM inputs across the land-to-sea gradient, accounting for larger terrestrial inputs (TOM: 53-81%) in sediments closer to one of main rivers mouth of the area (Guadiana), and predominantly autochthonous inputs (TOM: 22-31%) in basinward sediments. This study illustrates the benefits of perform molecular analyses on HA extracted from marine sediments: i) support of bulk analyses in the evaluation of the diagenetic state and origin of TOM reaching the continental margin, and ii) help to confirm the validity of specific biomarker ratios (3,5-dihydroxybenzoic acid over vanillyls; 3,5Bd:V) as a tracer of soil OC inputs to the ocean.