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Aromatic and conjugated structures dominate sulfurized organic matter in tidal salt marsh soils

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Tidal salt marshes are highly productive ecosystems that both sequester large quantities of organic carbon in their soils and export it to estuaries and the coastal ocean where it may contribute to heterotrophic processes or be exported to the open ocean. Because of the low oxygen, high sulfide, euxinic conditions in salt marsh soils, sulfurization reactions are hypothesized to play an outsized role in defining marsh organic matter composition, and by extension, its fate within soils and upon export. We conducted a suite of elemental and mass spectrometric biogeochemical measurements on salt marsh cores and porewaters to evaluate salt marsh organic matter (OM) characteristics. We hypothesized that sulfurized OM comprises a large portion of soil and porewater OM with its relative abundance increasing with depth in the soils and that it is comprised largely of highly unsaturated and aromatic OM compounds. Elemental analyses reveal C:S ratios that decline with core depth (from 10-30 in the root zone to 5-10 at >50 cm depth) consistent with the preferential preservation of sulfurized organics. High resolution mass spectrometric analyses of water extractable OM in soils show S-containing formulas to be very high (>50% of formula assignments) across all depths. S-containing formulas consistently show lower mean double bond equivalents (DBE = 9) than the rest of the formulas (DBE = 11.5) assigned to these extracts consistent with sulfurization reactions that add sulfide across a double bond reducing DBE. Liquid chromatography ICP-MS analyses conducted on solid phase extracted porewater DOM reveal that most organic S is hosted within isomerically complex organic compounds that form pi bonds with the chromatographic stationary phase. These results are consistent with non-specific S addition reactions involving degraded organic matter. Marsh organic S, thus, appears to be composed of compounds with conjugated double bond systems, including aromatic compounds. These structures may explain their relative chemical stability in marsh soils. Further work is needed to evaluate the fate of sulfurized OM upon export, but the aromatic compounds may be more susceptible to photodegradation and/or flocculation within estuaries as compared to microbial degradation.