Composition of organic sulfur in riverine and marine sediments: Insights from sulfur stable isotopes and XANES spectroscopy

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Sulfur isotope and X-ray absorption near edge structure (XANES) spectroscopy were combined to characterize/compare three operational organic S (OS) pools, i.e. fulvic acid S (FA-S), humic acid S (HA-S) and non-Cr reducible OS (non-CROS) in marine [the East China Sea (ECS) and Jiaozhou Bay (JZB)] vs. riverine [Yangtze River (YR) and JZB tributaries] sediments. The isotopic composition of FA-S ($\delta^{34}S_{FA\text{-}S}$) and HA-S ($\delta^{34}S_{HA\text{-}S}$) indicated that a substantial fraction of sulfides had been incorporated into FA via sulfurization in the marine sediments, whereas terrigenous OS was almost the sole important source of HA-S. Compared with the ECS sediments, JZB sediments had more depleted $^{34}S_{FA\text{-}S}$ and a higher fraction of highly reduced FA-S due to eutrophication induced sulfurization. A similar average fraction of the highly reduced FA-S between the marine and riverine sediments (i.e. ECS vs. YR, JZB vs. JZB tributaries) indicated that the relative importance of the highly reduced FA-S in the marine sediments had not been enhanced despite substantial sulfurization of FAs. It follows that the terrestrial systems may be much more favorable for the formation/preservation of highly reduced biogenic FA-S than the marine environments. A similar fraction of the highly reduced HA-S in JZB and its tributary sediments, but much lower fraction in the ECS sediments than in the YR sediments, indicated that the highly reduced HA-S moieties in the YR sediments may have been subjected to extensive mineralization loss during transport in the large riverine/estuarine systems, in comparison with a relatively limited catchment area in the JZB tributaries. Distinct differences in isotopic and structural composition between humic-S (FA-S + HA-S) and non-CROS in the ECS sediments were observed, indicating that a combination of S isotope and S-XANES is needed for characterizing the two operational pools for a better understanding the nature of OS in the ocean.