Roles of Natural Humic Substances in Biogeochemical Transformation of Mercury in the Environment

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Mercury (Hg) is a pervasive and highly toxic global pollutant that, in the methylated form (as CH_3Hg^+), bioaccumulates in the food web, endangering humans and other organisms. Despite decades of research, the biogeochemical mechanisms controlling CH_3Hg^+ production in the environment remain unclear. Natural humic substances or organic matter (NOM), consisting of redox reactive but chemically heterogeneous organic substances, are one of the controlling factors responsible for Hg transformation and cycling. NOM exists ubiquitously in aquatic and terrestrial environments and can directly or indirectly participate in both Hg complexation and electron transfer reactions. NOM forms exceptionally strong complexes with Hg through thiolate functional groups although this complexation is found to be kinetically limited thereby affecting bioavailable Hg species for methylation. Furthermore, depending on its redox state and NOM/Hg ratio, NOM can reduce or oxidize Hg. Even under strict anoxic environments, NOM is shown to oxidize the elemental Hg(0) to Hg(II) species through a novel mechanism of thiol-ligand induced oxidative complexation. These multiple roles of NOM may thus strongly influence the availability of reactive Hg with important implications for microbial uptake and methylation in natural water and sediments.