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Investigation into Humic-like Substance Production via Aqueous Photo-oxidation of Polycyclic Aromatic Hydrocarbons

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Polycyclic aromatic hydrocarbons (PAH) are produced by the inefficient burning of organic fuels and display extended lifetimes in the atmosphere. These aromatics are toxic to human health and many structures are considered highly carcinogenic. Although PAH have many atmospheric reaction pathways, one unexplored endpoint is the formation of humic-like substances (HULIS). Aerosolized HULIS are consistently correlated with reactive oxygen species and soluble metals, and as such, they are implicated with respiratory problems, oxidative stress, and Earth's energy balance. This study evaluates the mechanistic pathways of HULIS production by oxidation of aqueous suspensions of PAH with only exposure to sunlight. HULIS material is a class of light absorbing compounds and is presented as a collective of organic species, each containing significant aromatic and carboxylic acid character. They are found to be a major component of brown carbon and are implicated with radiative forcing in the atmosphere. PAH and HULIS are commonly observed in particles sourced from pyrogenic processes, e.g. biomass burning and vehicle exhaust. The long range transport of PAH lend themselves to extended exposures to sunlight and oxidants, potentially producing other branched and oxidized PAH (oxPAH) products such as anthraquinone and naphthol, which may then act as intermediates for larger structures, e.g. HULIS. Environmental PAH and HULIS are correlated with reactive oxygen species in cloud water and aerosolized particles. Particle surfaces containing aromatics may use ultraviolet radiation as a catalyst in an electron transfer interaction with elemental oxygen or water molecules to produce radicals, such as superoxide or hydroxyl radicals. These radicals are highly reactive oxidation agents and may initiate several oxidizing pathways, resulting in the further production of HULIS via oxPAH.
Reaction parameters use varying PAH reagent and matrix composition, oxidizing agents, and time duration. Analytical techniques for detecting organic products include UV-vis, SPE, HPLC, GCMS, and FTIR - used to define the spectroscopic properties, retention activities, and elucidate the number and structure of these products. Initial oxPAH data include the evolution of discolored samples demonstrating an exponential featureless decay within the UV-vis analysis and the growth of many new HPLC peaks during and following light exposure periods, which indicate the production of several new species. This chromatographic spectrum and array of products are emblematic of HULIS materials. The growth of peaks at specific retention times throughout the reaction demonstrates the evolution of explicit reaction pathways toward predictable products. Evaluating the formation of products from dissolved and suspended PAH solutions with photo-reactions conducted within purified water, formate buffer, and suspended soil allows for the determination of specific reaction mechanisms. A higher understanding of the creation of HULIS in atmospheric conditions will greatly aid in predictive models for air quality and human health downwind of pollution sources.