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Atmospheric HULIS: How humic-like are they? A comprehensive and critical review

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Abstract. A class of organic molecules extracted from atmospheric aerosol particles and isolated from fog and cloud water has been termed HUMic-Like Substances (HULIS) due to a certain resemblance to terrestrial and aquatic humic and fulvic acids. In light of the interest that this class of atmospheric compounds currently attracts, we comprehensively review HULIS properties, as well as laboratory and field investigations concerning their formation and characterization in atmospheric samples. While sharing some important features such as polyacidic nature, accumulating evidence suggests that atmospheric HULIS differ substantially from terrestrial and aquatic humic substances. Major differences between HULIS and humic substances, including smaller average molecular weight, lower aromatic moiety content, greater surface activity, better droplet activation ability, as well as others, are highlighted. Several alternatives are proposed that may explain such differences: (1) the possibility that mono- and di-carboxylic acids and mineral acids abundant in the atmosphere prevent the formation of large humic "supramolecular associations"; (2) that large humic macromolecules are destroyed in the atmosphere by UV radiation, O₃, and OH⁻ radicals; (3) that "HULIS" actually consists of a complex, unresolved mixture of relatively small molecules rather than macromolecular entities; and (4) that HULIS formed via abiotic and short-lived oxidative reaction pathways differ substantially from humic substances formed over long time periods via biologically-mediated reactions. It should also be recalled that the vast majority of studies of HULIS relate to the water soluble fraction, which would include only the fulvic acid fraction of humic substances, and exclude the humic acid (base-soluble) and humin (insoluble) fractions of humic substances. A significant effort towards adopting standard extraction and characterization methods is required to develop a better and meaningful comparison between different HULIS samples.

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