

Exploring molecular heterogeneity within bulk humic substances from terrestrial and aquatic sources using size-fractionation approach

I.V. Perminova

Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia

E-mail: iperm@org.chem.msu.ru

Understanding complex systems of many interacting objects is a key problem of modern environmental chemistry. Typical examples of such systems are humic substances (HS). The building blocks of HS are products of decomposition and stochastic synthesis of many different compounds which biomass is composed of. They produce an assembly of structurally close, but not identical molecules. Properties of such an assembly are consistent with steady – state dynamics of humification process and as such, should bear genetic information on HS formation (Cabaniss et al, 2005). This study hypothesized that it might be encoded by structure-molecular weight relationships.

To confirm this hypothesis, we analyzed data reported in the literature for off-line structural characterization of the size fractions of humic and NOM materials. Data analyses included humic materials isolated from major environmental sources: coal humic acids (HA), soil HA, peat HA, and freshwater NOM.

To prove this hypothesis, the literature data on size fractionated humics characterized by ^{13}C NMR spectroscopy were collected and treated to produce average molecular weight – aromaticity relationships. The sources of humics encompassed coal, peat, soil and water systems. It was established that for data sets for all terrestrial humic acid samples isolated from soil, peat, and coal, a decrease in molecular weight within fractions of bulk humic material was accompanied by an increase in the aromaticity of those fractions expressed either as content of aromatic carbon (Car, % determined from ^{13}C NMR spectrum as a partial integral of spectral density within 110-160 ppm region) or as specific ultraviolet absorption (SUVA, $\text{L}\cdot\text{mgC}^{-1}\cdot\text{m}^{-1}$ determined from UV absorbance spectrum as a ratio of optical density at 254 nm multiplied with a length of optical path to concentration of HS expressed on organic carbon basis mgC/L). In contrast, the opposite trend was observed for aquatic NOM dominated by fulvic acid fractions: aromaticity increased with an increase in molecular weight.

The trends obtained by treatment of literature data were tested in the lab by fractionating humic acid from peat and FA, HA and DOM from Suwannee River using size exclusion chromatography into five fractions and measuring SUVA of the obtained fractions. The SUVA versus molecular weight relationship for all samples studied was not linear reaching maximum values of SUVA within the range from 5000 to 7000 Da. For aquatic samples this relationship had a very steep slope in the range of $\text{MW} > 5000$, while for peat samples it had a very steep slope for MW values < 5000 Da.

These opposing trends for molecular weight versus aromaticity was explained assuming different vectors of evolution for humic and fulvic acid fractions: the humic acids evolve toward kerogen which represents a condensed form of carbon, while fulvic acid evolve into aliphatic structures with formation of small carbonic acids and CO_2 as end product.