Humic substances – what is behind this term?

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Humic substances (HS) are considered as a special category of natural compounds ubiquitous in soils, sediments and waters. They have long time been described as a series of polydisperse dark-colored macromolecules that are resistant to biodegradation and have no analogues in living organisms. According to hypotheses, HS are formed during degradation of organic debris and by secondary synthesis reactions (a process called humification). On the basis of solubility characteristics HS are divided into humic acids (HA, soluble, precipitated at pH <2), fulvic acids (FA, soluble at all pH values) and humin (insoluble residue). It was estimated that HS comprise about 85-90% of soil humus and about 50% of dissolved organic matter in natural waters. However, there is still much confusion around the term "HS" and around all humic paradigm. Recent experimental evidence, based on non-destructive spectroscopic methods led a number of scientists to a conclusion, that alkali-extractable HS are plant and microbial components on the different stages of decomposition. It has been suggested to abandon all humic terminology as well as a concept of secondary synthesis. Such criticism is not new and dates back to the beginning of XX century. We are going to discuss the problems of humic terminology and nomenclature, the paradigm of secondary synthesis, the concept of stability of alkali-extractable HS and their macromolecular organization. The old definition of HS is ambiguous and uncertain: specific chemically unique and newly synthesized compounds from the one hand and a sum of operational fractions of humus (humic matter) from the other hand. The first definition turns the term HS into hypothetical abstraction, making almost impossible their identification in already formed humus. Operational definition is inconsistent with humic nomenclature, which divides humus into identifiable molecules (non-HS) and substances with poorly defined structure (HS). It is obvious that the alkali extracts and the residue (humin) contain both types of compounds. It is under the debate whether to include humin into the group of HS or not. The definition of HS requires revision. Identifiable molecules and compounds with uncertain structure form the dynamic system which determines the functioning of natural organic matter in the environment and separation of these compounds is unreasonable from the functional and practical points of view. One of the solutions might be re-definition of HS as compounds comprising humified organic matter as a whole (substances of humus or humic matter). Another solution is exclusively operational definition of HS as alkali-extractable components of humus because in this sense the term is used in most studies. The terms HA, FA, humin should be retained as the names of preparations obtained in a certain way. Alkaline extraction is effective method for the isolation of hydrophilic polar substances, acid precipitation allows their concentration for further study. Description of HS as macromolecular products of secondary synthesis or recalcitrant compounds should be avoided. We will show that macromolecular fractions of soil HA are unstable once separated from the mineral matrix. We will also show that under the environmentally relevant concentrations and dynamic conditions no macromolecular compounds are formed from monomeric precursors in the presence of the biocatalyst and the mineral phase. However, free-radical reactions favor stabilization of certain phenolic compounds on the mineral phase and determine the composition of organo-mineral complexes. Contribution of free-radical reactions to the formation of humic matter need further investigations.

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