



## Preface: humic substances in the environment

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### 1 Background

The fate of natural organic matter, and especially humic substances (HSs), has attracted increasing interests of scientists representing various disciplines over recent decades. Among the various organic substances occurring naturally, HSs are the most widespread, being present in soil, water, lake sediments, peat, brown coal, and shales. HSs represent about 25% of the total organic carbon on the earth. These substances represent a class of naturally occurring complex molecular structures, formed by aggregation and assemblage processes through which biomolecules originating from plant and animal residues are progressively transformed via biotic and abiotic pathways. The research of HSs is complex because these organic compounds are bound by, or associated with, soil mineral fractions, and require physical and/or chemical separation from the inorganic components through an extraction procedure, prior to their physico-chemical analysis. The most efficient of these separation procedures implies an extraction with alkali which operatively identifies three HSs fractions, based on their water solubility; they are:

- (I) fulvic acid (FA)—soluble at all pH values;
- (II) humic acid (HA)—not soluble under acidic conditions (pH < 2) but soluble in solution of higher pH values;
- (III) humin—not soluble in water at any pH value.

Lately, a very controversial opinion has been proposed, that no HSs exist in soil, and “alkaline extracts should not be used as proxies for naturally occurring organic matter (OM) or a subset thereof” (Lehman and Kleber 2015). Admittedly, humic research concerns investigations of products obtained as a result of their extraction. Some research technologies applied to HSs require extracted and purified material, whereas others do not. Functions and reactions of HSs do not necessarily require extraction and also some studies applying C13–NMR spectra compared those of extracted material to spectra of the original soil material. Both sets of spectra were found to be the same, thereby indicating that the extraction does not change the structure of the HSs. Alkaline extraction of soil and natural waters produces OM fractions that have great ecological relevance and are involved in environmental processes. Thus, HSs research is the only way to explore and elaborate the important and complex role of these substances in the ecosystem. Nevertheless, the editors of this Special Issue believe that the concept of HSs and their functionalities will be advanced further and utilized to improve experimental approaches and theoretical framework in HSs research, as proposed by Gerke (2018).

Undoubtedly, a driving force for the growing interest in HSs is the increasing awareness in their immense role in terrestrial and aquatic systems, as well as their bio-stimulatory effects on plant growth. Soils contain more organic carbon than the atmosphere and vegetation combined; therefore, mineralization of soil SOM and release of carbon versus humification processes could greatly affect the global climate change. HSs are known to be a major component of soils, and they are crucial to human welfare due to their role in generating food, feed, and fiber. They closely relate to the biogeochemical cycling of nutrients and anthropogenic organics as well as some polluting elements. As a consequence, HSs are able to affect crops’ contaminant uptakes and/or leaching into groundwater. Studying the interactions of heavy metals or organic compounds with HSs provides insights into pollutant mobility, behavior, and fate, and allows better understanding of natural mitigation phenomena and potential impact on the environment.

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Due to the role of HSs in many complex chemical and biochemical reactions in soils, HSs largely determine soil quality, and they are vital to maintaining soil fertility. The ability of FA and HA to dissociate  $H^+$  ions from various functional groups (mostly carboxyl and phenolic) results in a wide array of different negative charges which markedly contribute to the soil cation exchange capacity. The sorption capacity of HSs, especially FA, exceeds by far (up to a factor of ten times) the sorption capacity of soil mineral components, and often dominates their sorption properties, especially in sandy to sandy loam soils. HSs also have a decisive impact on the pH buffering capacity of soils. Furthermore, they affect physical, chemical, and biological properties of soils to a much greater extent than other soil mass constituents. An increase in HSs content, especially that of HA in the presence of Ca, causes the formation of stable aggregates, which in turn, positively affects field water capacity, air capacity, porosity, and permeability of different soil types. Important losses of SOM, especially HA, contribute to an increase of soil compactness, mainly in sandy and sandy loam soils, a decrease of soil aeration, and a consequent occurrence of reductive chemical conditions. Among others, the dark color of HSs causes enhancement of sunlight absorption, and improvement of the thermal properties of soils, what is crucial especially at the beginning of the growing season. They are also the main source of energy for decomposition of OM. Finally, HSs are also formed during aerobic oxidation of different waste materials (composting), potentially recycled into soil amendments and beneficial for soil fertility and quality.

SOM is a major source of organic carbon in aquatic systems, thus HSs are extensively investigated by the community of aquatic chemists. Aquatic carbon is not only important as a part of the global carbon cycle, but also for local biogeochemical processes in rivers, streams, and lakes. Water HSs directly and indirectly affect aquatic ecosystems, as well as living organisms. In the long term, dissolved HSs affect primarily the physical and chemical properties of waters, and can act as the most important purifying natural components in these environments, e.g., by stimulating biotransformation of xenobiotics. In the short term, they can act as a source of organic nutrients and also exhibit the capacity to regulate the bioconcentration and toxicity of xenobiotics and heavy metals. Dissolved HSs are a major factor affecting the optical properties of natural waters. They also have a direct impact on both the quantity and quality of light in waters. The strong specific UV absorption renders HSs like a natural biogeochemical filter against specific UV radiation. An important issue is the chemical removal of pollutants by HSs in water treatment and water purification technologies. On the other hand, HA are considered to act also as contaminants due to their reactions with disinfectants which can generate by-products that are toxic to humans.

## 2 Research areas of the HSE11 conference

The present Special Issue of the Journal of Soils and Sediments contains selected papers presented at the 11th international scientific conference “Humic Substances in the Environment” (HSE11). HSE are cyclic conferences organized every second year in Poland or Slovakia, devoted to exploring and discussing contemporary and emerging results relating to HSs and their environmental role. HSE11 was organized by the Polish Chapter of the International Humic Substances Society in Kudowa-Zdrój, Poland, and it took place on May 29–June 1, 2017.

The objective of the conference, and the resulting Special Issue, was to focus attention on the importance and the environmental implications of HSs occurrence in soil, water, sediments, and composts. The general aspects of HSs, as basis for life, are presented by Frimmel and Abbt-Braun (2018), while the majority of papers focus on more specific issues. Among them are three papers related to interactions with pesticides and PAHs (Bejger et al. 2018; Bielińska et al. 2018; Ćwieląg-Piasecka et al. 2018). Another two contributions deal with dissolved organic matter (DOM) in arable soils (Rosa and Debska 2018) as well as in an Antarctic soil core (Lepane et al. 2018). Several contributions provide information on the interactions of environmental processes involving HSs, including their effects of landslides (Błońska et al. 2018), as well as windstorms and wildfires (Barancikova et al. 2018). The transformations of forest litter and their effects on arsenic solubility are discussed by Karczewska et al. (2018), while nutrient dynamics under the influence of deadwood of different tree species at various stages of decomposition is presented in a paper by Lasota et al. (2018). Nicia et al. (2018) provide information on the impact of restoration processes on soil properties and OM transformation. HSs influence on the soil aggregate stability is shown by Kobierski et al. (2018) as well as by Pollakova et al. (2018). Problems with land use and the state of the SOM are discussed by Kwiatkowska-Malina (2018), Menšík et al. (2018), Oktaba et al. (2018), and Ukalska-Jaruga et al. (2018). Additional two papers deal with lake sediments, including the application possibilities of delayed luminescence method for the characterization of HSs (Mielnik and Asensio 2018), and using excitation-emission matrix fluorescence with PARAFAC model for optical characterization of HA (Mielnik and Kowalczyk 2018). Finally, three papers deal with humic products obtained from leonardite and/or lignite; Filcheva et al. (2018) provide information on their quantitative and qualitative properties, Huculak-Mączka et al. (2018) evaluate the possibilities of their utilization in the production of commercial fertilizers, while Olk et al. (2018) review their potential benefits and research challenges.

### 3 Conclusions

The 22 papers included in this issue provide information on different aspects of HSS role in the environment. Some of the research procedures employed in HSS research require extraction while other do not. Investigation of alkaline extracts of soils producing HSS is the most common approach to research focusing on HSS. Water HSS or DOM can be separated by dialysis without the employment of alkaline extractions. The major roles of SOM, DOM, and HSS in general in the environment and in agriculture are the focal points of this special issue of JSS.

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