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VIEWPOINTS ON THE FUTURE OF HUMIC SUBSTANCES RESEARCH

Chemistry of Natural Organic Matter—The Next Step: Commentary on a Humic Substances Debate

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Abstract

Natural organic matter (NOM) is ubiquitous on the Earth surface and influences every biogeochemical reaction wherever it is present, and its impact on reactions varies with its abundance, structure, and chemistry. Because of decades of field and laboratory studies conducted on NOM in different environments, we are moving away from treating it as a black box to developing molecular structure–based approaches in investigations of soil, sediment, and aquatic systems and are beginning to make major advances in the detailed understanding of the molecular and structural characteristics of NOM, which in turn are helping in deciphering the biochemical processes involved in its evolution in the environment. Yet, many questions remain: How does NOM exist in different soil and aquatic environments? How should we obtain NOM from a sample, and does the isolated NOM represent the NOM in a sample? Do the geochemical reactions explored with extracted NOM represent the reality? How can we study NOM in situ? Here I present a synopsis of critical perspectives on the state of NOM research and a commentary on the reviews and debate presented in this special section on the NOM nomenclature, extraction procedures, and studies involving NOM in different environmental processes.

Natural organic matter (NOM) in soils, sediments, and aquatic systems is derived primarily from the physical, microbial, and chemical weathering of biological material. During this weathering process, the breakdown of larger biopolymers to smaller molecules, biochemical transformation of many of these molecules, and polymerization and formation of larger molecules may occur. However, the breakdown and biochemical alteration of NOM vary with the quality of the source material and the environmental conditions. Thus, NOM in any given environment coevolves with mineral weathering, changes in the microbial ecosystem, physical conditions (e.g., temperature, fire), and water abundance and chemistry, with each variable influencing the other (Fig. 1). These interactive processes ultimately lead to the accumulation of NOM in soil that is made up of mixtures of organic molecules, which exhibit a variety of bonds, including H-bonding, cation bridges, and covalent interactions. The makeup and chemistry of NOM pool thus vary as a function of the above-mentioned variables.

Studies conducted over several decades have shown that NOM plays an important role in many biogeochemical reactions wherever it is found, in both pristine and disturbed environments. Many of these studies used extracted NOM and then attempted to link the abundance, structure, and chemistry of NOM to its reactivity. There are big questions yet to be answered, however: Does the isolated NOM truly represent NOM in the natural environment? What is the composition and structure of NOM in situ? How do these vary and evolve with environmental conditions?

The two articles in this special section on the future of humic substances research (Kleber and Lehmann, 2019; Olk et al., 2019) comment on years of research into different aspects NOM and where this research is heading. Olk et al. (2019) review the literature on organic molecule extraction from soils (and the justification for using this method), macroscopic and molecular characterization of NOM using different techniques, and the role that extracted NOM plays in a variety of processes, including soil productivity, and the solubility and transport of organic and heavy metal contaminants. Kleber and Lehmann (2019) question the naming of NOM obtained by alkali extraction as humic substances/humic and fulvic acids/humus and object to the loose use and misuse of these words to represent

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Abbreviations: NOM, natural organic matter.

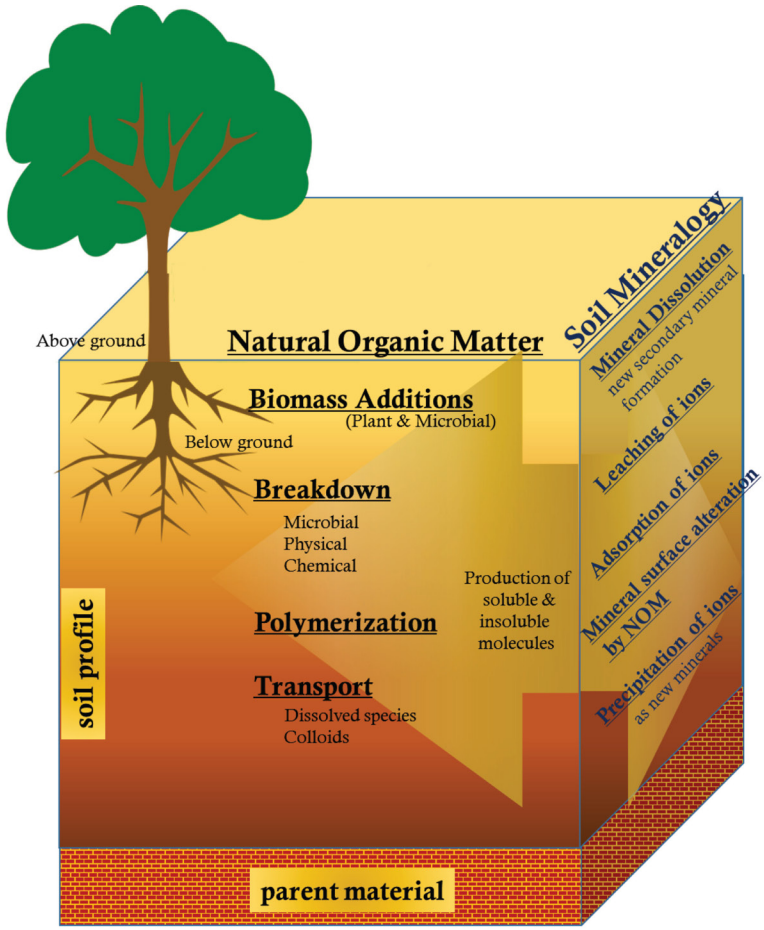

Fig. 1. A summary of the processes controlling the evolution of natural organic matter (NOM) (front) and soil minerals (right) in a soil profile. Strong chemical, biological, and mineralogical gradients exist from the uppermost portions of the soil to the parent material. Although different processes are listed in the soil profile vertically for NOM, they occur in all parts of the soil profile, except for the biomass additions, which are the highest in the uppermost part of the soil and in the rhiozosphere. Soil mineralogy typically evolves with dissolution reactions dominating in the uppermost parts of soil profile, promoted by acidic carbonic acid containing rain water and soluble NOM, and precipitation reactions toward the lower parts. Strong redox gradients might reverse this trend for mineral dissolution and precipitation in soils. Both soil NOM and mineralogy coevolve (as shown by arrows) in weathering environments, with each biogeochemical process, such as breakdown and polymerization of organic molecules, solubility, adsorption, and transport of organic molecules, strongly tied to mineral evolution. Similarly, dissolution and precipitation reactions of minerals and their rates, leaching of inorganic species, and mineral surface characteristics are strongly controlled by the quality and concentration of NOM. Hence, NOM is unique in each part of this soil column, and its characteristics vary with the hydrobiogeochemical conditions, time of sampling, and sampling location in this soil profile.

NOM. Because of how these terms originated and how they can potentially affect ongoing research, Kleber and Lehmann argue that these words should be abandoned and recommend NOM be defined in a new way that reflects the characteristics and processes by which NOM is formed.

Here are some observations from years of research:

> NOM characterization by a majority of researchers typically used to start with an extraction, usually alkali, from the solid phase. Extractions of various types do not yield identical results for both the quantity extracted and the forms of organic molecules extracted. An extraction method well suited to certain types of molecules is not ideal for other types of molecules. Furthermore, no method can extract the entire NOM pool present in a solid phase and preserve its integrity, and thus these methods may not represent NOM in its native state. For this reason, results obtained from studies based on extracted NOM may not truly represent the full role of NOM in different processes (the two articles concur on this point) and can lead to misrepresentation of the role of NOM.
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> Does one extraction method represent NOM better than another?
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> Because extractions do not tell us about all the characteristics of NOM in its pristine state, how can we study NOM in the pristine state directly, i.e., avoiding extraction? What techniques are available to do this—nuclear magnetic resonance, X-ray, infrared, or other? Beyond measuring NOM abundance and generating information on a few characteristic functional groups, each technique is limited when it comes to studying natural samples directly. For example, the most promising technique for evaluating molecular structure, nuclear magnetic resonance, is well suited for more pristine systems but is almost unusable for many soils and sediments with high Fe abundance and low NOM fractions. Similarly, high-resolution mass spectrometry, such as Fourier-transform ion cyclotron resonance mass spectrometry, well known for obtaining molecular formulas, cannot be used without initial extraction (and purification) for many types of samples and is not suitable for small and non-ionizable molecules. The X-ray and infrared methods are excellent tools for directly probing molecular structures in soils and sediments but are limited in the information they provide for different functional groups and their structures.

When a direct-probing method for determining detailed NOM structural characteristics is lacking, how do we obtain these details and link them to the impacts of NOM in different environmental processes? What is the next step in studying the chemistry of NOM?

If the goal is to evaluate the role of NOM on different biogeochemical processes, separation of NOM from the solid matrix using gentle extraction can help us make some progress; findings from past decades provide a wealth of information on the role of NOM (Olk et al., 2019). For example, results obtained from studies conducted on the complexation of NOM with nutrients

and metals, and sorption of hydrophobic organic contaminants, have helped in understanding the magnitude of effects of NOM presence on some of geochemical processes. However, proposing a three-dimensional structure of NOM based on the spectral characteristics of organic molecules extracted from a solid phase is an example of an extreme case where the validity is highly questionable. According to Kleber and Lehmann (2019), we must understand that results obtained using extracted NOM can have serious limitations.

There are many similarities between NOM research and studies with soil–sediment inorganic phases. Many studies focusing on nutrient and contaminant reactions involving minerals in soils and sediments focus on clean and structurally simple mineral systems, often involving laboratory synthetic minerals. The mineral phases in nature are rarely pure and often contain many impurities and structural deformations, which lead to major changes in mineral reactivity. However, studies on pure mineral systems offer important clues and are the first step to understanding complex natural systems.

Nomenclature for NOM and words like *humus*, *humic substances*, *humic acids*, and *fulvic acids* are often used differently, leading to confusion in the literature. As suggested by Kleber and Lehmann (2019), defining (or redefining) terms, and following these new terms strictly, will be useful for the scientific community. In my opinion, nomenclature may be less of a problem than the belief that extracted NOM is unique and identical to soil or sedimentary NOM.

In summary, NOM is not a unique molecule; it is made up of mixtures of many different types of molecules, its chemical and structural characteristics evolve with environmental conditions, and its impact on biogeochemical process in the environment varies with the geochemical conditions of the site from where it is collected and the time (or a season) at which it is collected. Extracted NOM provides important clues about the behavior of NOM. However, the extraction method has limitations, and the results obtained represent only one time point in NOM evolution. Going forward, researchers studying NOM should be aware of the problems related to the existing nomenclature, as well as questions regarding the validity of using extracted NOM to represent the original NOM. Moreover, researchers should consider using multiple molecular probes to obtain comprehensive information on the chemistry of NOM and enhance our understanding of the relationship between NOM structure and reactivity.

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