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Guest Editorial

The analytical challenge posed by fulvic and humic compounds

Humic and fulvic substances are a whole group of organic compounds formed in soil, water and sediment by the decay of dead organisms. Because of their very complex nature, they can still only be defined in a negative sense, i.e., as including all of the soil, water or sediment organic compounds except the proteins, polysaccharides and lipids. In fact they comprise the bulk (ca. 70%) of the organic constituents of each of the aforementioned environmental compartments. Because living organisms are made up of a very large number of different organic compounds, their degradation and the possible recombination of the resulting products may lead to an almost infinite number of different molecules. It is therefore not surprising that they exhibit a very broad range of properties, even if they behave as a whole, at the macroscopic environmental level. This whole group of compounds is operationally divided into the so-called fulvic and humic fractions, for the sake of simplicity. However, a close study of any particular property (e.g., molecular weight or content of functional groups) of the whole group often shows that it follows a wide frequency distribution, without a clear demarcation between fulvics and humics.

The non-specialized reader, unfamiliar with these substances, might wonder what their fundamental characteristics are. A few salient features outlined below will give a flavour, even though it is only a schematic representation.

Fulvic compounds represent the low-molecular-weight fraction of the fulvic + humic group. Their molecular weights are in the range of a few hundred to a few thousand, whereas those of humics range from thousands to millions.

Fulvics and humics originating from soil include a large proportion of aromatic compounds (in particular benzenecarboxylic and phenolic compounds), whereas the fulvics and humics from sediments and the aquagenic type (i.e., those formed in lakes, rivers and oceans) are much more aliphatic.

A common feature of all these compounds is that they are fairly resistant to degradation, i.e., refractory; their residence times are often in the range of centuries to millenia. For this reason and also because there is no clear distinction between fulvics and humics, some workers prefer to call this ensemble "refractory organic matter".

Their environmental importance is due to the multiplicity of their properties. They include both hydrophilic and hydrophobic moieties; they therefore may be adsorbed on surfaces of many particles, thus influencing processes such as dissolution, coagulation and crystal growth. They may complex metal ions and small organic molecules, therefore influencing the bioavailability of the latter or inducing their adsorption on and sedimentation with particles in water bodies. They have acid–base properties with a wide range of pK values, and consequently play an important role in the acid–base buffering of soils. These are only a few examples amongst the many roles they can play in environmental systems.

Fulvics and humics must be studied not only because they are the major organic constituents of soil, water and sediments, but more importantly because they are very representative of complex environmental chemical systems (such as complete soil and sediments), which pose an experimental and conceptual challenge to environmental chemists. Indeed, as discussed above, fulvics and humics should not be thought of as only a mixture of chemical compounds, but above all as a single chemical system; their important environmental roles are due not so much to the individual prop-

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erties of each of the particular constituent molecules, but to the resulting overall properties of the whole group. In addition, not only chemical, but also physical properties, such as aggregation, conformation changes and surface-active behaviour, are involved in this environmental role. Such a behaviour is typical of many other environmental systems (soil, sediments, etc.), where a particular property (e.g., pH, redox potential) is controlled by the collective actions of a large number of often complicated constituents. This contrasts with the situation encountered in synthetic solutions, under classical laboratory conditions, which are usually chosen to be as simple as possible and therefore include only a limited number of compounds.

New concepts and approaches must therefore be developed to study rigorously the complicated environmental systems. This is at present the most challenging task for environmental analytical chemists. Indeed, the ultimate goal of any analytical chemist is to characterize the sample (or system) of interest, in sufficient detail to be able to describe its reactivity and physico-chemical characteristics at the molecular level. On the other hand, to understand and model the environmental behaviour of the system of interest, the environmental chemist needs global, macroscopic parameters. The present challenge to environmental analytical chemistry is therefore not so much to develop new, more sensitive or selective, instrumental methods, but to find the intellectual tools necessary to fill the gap between the molecular and macroscopic levels. In the case of the fulvic and humic group, this leads to questions that are either basic or related to the interpretation of analytical signals, such as the following. Is it useful to try to separate and analyse individually each component of the group to understand its global environmental behaviour? Is this even feasible, as there may not be even two identical molecules in such a group of compounds? Is it possible to understand the global properties of these systems only by the summation of the individual properties of their multiple components? How is it possible to take into account the complexity of the studied system, while interpreting the signals of instrumental methods applied to fulvics and humics, despite the fact that so far theory has been developed only for relatively simple mixtures containing only a small number of components? In other words, how is it possible to deconvolute correctly a global signal in order to recover the fine structure due to each individual chemical compounds?

This issue of the journal tries to show the present state of the art in the development of new approaches to the study of the fulvic + humic environmental system. It includes a collection of papers on fulvic and humic compounds covering a broad range of characterization problems and methods. The first four papers deal with various approaches to differentiate the fulvics and humics of various origins (soil, sediment, water, etc.). The next six papers deal with various methods of spectroscopic and physical characterization. The five papers that follow treat various approaches to the study of the complexation of metals and small organic molecules by humics and fulvics. Finally, the last three papers discuss models allowing these complexation properties to be interpreted, by taking into account their full complexity, i.e., without oversimplification.

I would like to take this opportunity to pay special homage, on behalf of all scientists working on humic and fulvic substances, to Dr. M. Schnitzer, who has done fundamental pioneering work in the area of the characterization of humics and fulvics since the early 1950s, i.e., when instrumental analytical tools were very limited and the support of scientific community was lean. The present state of the art in the field of fulvics and humics is largely due to the solid foundation laid by M. Schnitzer.

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