The environmental role of organic matter in the fate and behaviour of trace metals and organic pollutants

N. Senesi

Istituto di Chimica Agraria - University of Bari, Bari 70126, Italy

Humic substances

The most ubiquitous and widespread natural non-living organic materials in all terrestrial and aquatic environments are humic substances. These substances represent a significant proportion of total organic carbon in the global carbon cycle, constituting the major pool of organic matter in soils (between 70 and 80%) (Stevenson, 1994), and the largest fraction of natural organic matter in stream, river, wetland, lake, sea and ground waters (40 to 60% of dissolved organic carbon) and sediments (Thurman, 1986).

Humic substances consist of a physically and chemically heterogeneous mixture of relatively high-molecular-weight, yellow-to-black-coloured organic compounds of mixed aliphatic and aromatic nature, formed by secondary synthesis reactions (humification) during the decay process and transformation of biomolecules that originate from dead or living organisms and microbial activity (Stevenson, 1994). These materials are exclusive of undecayed plant and animal tissues, their partial decomposition products, and the soil biomass.

On the basis of their solubility in water at various pHs, humic substances are divided in three main fractions: (a) humic acids, which are soluble in dilute alkaline solution and are precipitated upon acidification to pH 2; (b) fulvic acids, which are soluble at any pH value, even below 2; and (c) humins, which are insoluble at any pH.

Humic substances do not belong to any of the known, structurally and chemically recognizible classes of organic compounds, and cannot be described by unique, chemically defined molecular structures. These substances can be defined only operationally by a model structure constructed on the basis of available compositional, structural, functional, and behavioural data and containing the same basic structural units and the same types of reactive functional groups that can be, in principle, arranged in an infinite number of combinations but are common to all the single, indefinitely variable and unknown molecules. The macromolecular structure of humic substances consists of aromatic, phenolic, quinonic and heterocyclic 'building blocks' that are randomly condensed or linked by aliphatic, oxygen, nitrogen or sulphur bridges. The macromolecules bear aliphatic, glucidic, aminoacidic, and lipidic surface chains and chemically active functional groups such as carboxyls, phenolic and alchoolic hydroxyls, carbonyls, etc., which render the humic polymer acidic. Hydrophilic as well as hydrophobic sites are present. The structure and composition of humic acids are more complex than those of fulvic acids, which generally feature a lower aromatic character, more oxygen-containing functional groups and lower molecular weight. Humic substances are polydisperse and exhibit polyelectrolitic behaviour in aqueous media, assuming different size and conformation, more or less open, flexible, sponge-like, in different conditions.

Interactions between humic substances and organic pollutants

The typical physical and chemical structure and properties of humic substances and their ubiquity in terrestrial and aquatic environments qualify them as priviliged natural compounds in the interaction with organic pollutants that include a great variety of organic chemicals, such as pesticides and their degradation products, polynuclear aromatic hydrocarbons (PAH), phtalic acid diesters (PAE), organic solvents, surfactants and detergents, etc.

Humic substances may interact with and affect the behaviour and fate of organic pollutants in the environment in several ways, which include adsorption and partitioning, solubilization, and catalytic and photosensitization effects (Senesi and Miano, 1995). All these processes have important implications in the immobilization and accumulation, mobility and transport, biodegradation and detoxication, bioavailability and phytotoxicity, bioaccumulation, and residue persistence and monitoring of organic chemicals in environmental systems.

One of the purposes of this review presentation is to summarize and discuss molecular and mechanistic aspects of the most important modes of interaction between humic substances and some classes of organic pollutants, with emphasis on pesticides and their degradation products.

In particular, adsorption mechanisms of various classes of ionic and non-ionic, polar and non-polar pesticides on humic substances, and methodologies and techniques used for their elucidation will be illustrated with the aid of representative examples. Mechanisms discussed will include ionic, hydrogen, and covalent bonding, charge-transfer or electron-donor acceptor processes, dipole-dipole and van der Waals forces, ligand exchange, cation and water bridging, and non-specific, hydrophobic, or partitioning processes (Senesi and Miano, 1995).

Solubilization effects exerted by humic substances on several classes of organic pollutants will also be discussed providing adequate examples. As well, catalytic or inhibitory effects of humic substances in hydrolysis and other reactions to which organic pollutants are subjected in environment will be examined. Finally, the multiple role that humic substances can exert as photosensitizers and/or precursors of photoreactants, such as the solvated electron, singlet oxygen, superoxide anion, peroxy radicals, hydrogen peroxide and redox active species, involved in the photoreactions that organic pollutants can give on the soil and water surfaces will be discussed.

Interactions between humic substances and trace metals

The fate and behaviour of metals in terrestrial and aquatic environments and their impact on the global ecosystem is dependent not only on the total soluble and insoluble metal concentrations, but also on the relative distribution and chemical forms amd properties of the various metals in the solution and solid phases. Metal ion speciation is important in determining the general biological and physico-chemical behaviour of metal ions. This, in turn, influences bioavailability of metal nutrients to plants and soil microorganisms, toxicity hazard of potentially toxic metals, migration-accumulation phenomena of metals in the soil-water-sediment system, pedogenic processes, and geochemical transfer and mobility pathways (Stevenson, 1986; Buffle, 1988).

The distribution of metals ions in environmental systems is extremely complex and is governed by a variety of reactions that include complexation with organic and inorganic ligands, ion exchange, adsorption and desorption processes, precipitation and dissolution of solids, and acid-base equilibria. In particular, complexation reactions involving natural organic matter play a key role in establishing the behaviour of metal ions, particularly in trace concentrations.

One of the most striking characteristics of humic substances is their ability to interact with metal ions to form water-soluble, colloidal, and water-insoluble complexes of varying properties and widely differing chemical and biological stabilities (Stevenson, 1994). The evidence suggests that almost every aspect of the chemistry of trace metals in soils, waters, and sediments is related in some way to the formation complexes with humic substances.

In this review, attention will be focused on the molecular and mechanistic aspects of the complexation of metal ions by humic substances, that is, on the physico-chemical nature of sites involved and types of binding and formation mechanisms and stability of metal-humic susbtances complexes. The presentation will be based on the information generated by the application of several spectroscopic techniques, including infrared (IR), fluorescence, electron spin resonance (ESR), and Mössbauer, to environmental and laboratory-modeled metal-humic substance complexes, also providing representative examples (Senesi, 1992).

References

Buffle, J. (1988) *Complexation Reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood, Chichester.

Senesi, N. (1992) In: *Biogeochemistry of Trace Metals*, (D.C. Adriano ed.), pp. 16-496, Lewis Publishers, Boca Raton, Florida.

Senesi, N. and Miano, T.M. (1995) In: *Environmental Impact of Soil Component Interaction, Natural and Anthropogenic Organics*, (P.M. Huang *et al.*, eds.), pp. 311–335, CRC Lewis Publishers, Boca Raton, Florida.

Stevenson, F.J. (1986) *Cycles of Soil. Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients*, Wiley-Interscience, New-York.

Stevenson, F.J. (1994) *Humus Chemistry. Genesis, Composition, Reactions*, 2nd edition, Wiley-Interscience, New York.

Thurman, E.M. (1986) *Organic Geochemistry of Natural Waters*, Nijhoff, Dordrecht.