

Schnitzer M. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. *Soil Sci. Soc. Amer. J.* 33:75-81, 1969.

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Fulvic acid is a water-soluble humic material that is found widely in soils and water. Because it is a naturally occurring metal-complexing agent, it affects the supply and availability of metals in terrestrial and aquatic environments. [The SCJ® indicates that this paper has been cited in over 125 publications.]

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This paper is a summary of 10 years of intensive research (1957 to 1967) in which I was assisted by two technicians and, from time to time, by colleagues. The work was performed in one of the soil science laboratories of Agriculture Canada in Ottawa.

My principal objective was to relate the chemical structure and properties of fulvic acid, an important humic material, to reactions with metal ions, oxides, hydroxides, and clay minerals. As relatively little was known in 1957 about the chemistry of fulvic acid, we focused our attention during the first few years on developing reliable analytical methods for its characterization. These included elemental analyses as well as determinations of oxygen-containing functional groups, molecular weight, spectroscopic properties, and chemical and thermal degradation. Especially important were data on functional groups and molecular weight. The latter enabled us to determine stability constants for a wide variety of metal-fulvic acid complexes at two different pH values and to demonstrate that stability

constants increased with increase in pH. From the chemical information obtained we could prepare in the laboratory a number of model metal-fulvic acid complexes. We characterized these by various different methods in order to uncover the mechanism(s) of metal-fulvic acid interactions. Two types of reactions of fulvic acid with di- and trivalent metals were observed: the major reaction involved  $\text{CO}_2\text{H}$  and phenolic OH groups simultaneously, while the minor one involved only  $\text{CO}_2\text{H}$  groups. The methods developed on model complexes were then used as diagnostic tools for the characterization of metal-organic complexes extracted from natural soils and occurring as distinct deposits in soil profiles. The model complexes were found to have much in common with the naturally occurring complexes.

During the course of our research we were able to show the formation of mixed ligand complexes in the form of fulvic acid-metal-phosphates. The addition of phosphate displaced increasing amounts of fulvic acid from the metal.

Interactions of fulvic acid with clays are important in soils. We demonstrated that fulvic acid could penetrate the interlamellar spaces of Na-montmorillonite at  $\text{pH} < 5$  and that the extent of interlayer adsorption also depended on the type of cation with which the clay was saturated and on the fulvic acid concentration. By contrast, the adsorption of fulvic acid on outer surfaces of Na-montmorillonite was independent of pH.

In recent years interest in fulvic acid, often the major organic component of aquatic systems, has increased significantly and so has the relevance of this paper. It has been frequently cited because it describes metal-organic interactions in soils and water in relatively simple and straightforward terms, unencumbered by complex mathematics. I have since published more recent reviews.<sup>1,2</sup>

1. Schnitzer M. Humic substances: chemistry and reactions. (Schnitzer M & Khan S U, eds.) *Soil organic matter*. Amsterdam: Elsevier, 1978. p. 1-64. (Cited 115 times.)

2. ———. Binding of humic substances by soil mineral colloids. (Huang P M & Schnitzer M, eds.) *Interactions of soil minerals with natural organics and microbes*. Madison, WI: Soil Science Society of America, 1986. p. 77-101.