

Molecular modelling of humic substances, soil organic matter and soil particles: potential and limits

H.-R. Schulten

Institute for Soil Science, University of Rostock, Justus-von-Liebig-Weg 6, 18051 Rostock, Germany

The combination of pyrolysis-field ionization mass spectrometry (Py-FIMS) and Curie-point pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) together with a wide variety of analytical (chemical, thermal, spectroscopic) techniques has been utilized in an integrated approach to model molecular structures for humic acids (HA), fulvic acids (FA), total humic substance (THS), dissolved organic matter (DOM), soil organic matter (SOM) and soil particles. Personal computer-based molecular modelling of humic-xenobiotic complexes and computational chemistry (molecular-mechanics calculations; geometry optimization; determination of binding sites; transport-, energy-balances, quantitative structure-activity relationships) are reported. Examples for atrazine-, hydroxyatrazine-, DDT-, mecoprop-, metribuzin-, pentachlorophenol-, trinitrotoluene-, and dioctylphthalate-interactions with THS, DOM, SOM and soil particles are given and illustrate the processes of trapping and binding anthropogenic substances in soil and water (Schulten *et al.*, 1998).

Hypothetical structural models for humic substances such as HA monomer (Schulten *et al.*, 1991) Schulten and Schnitzer, 1993) and oligomeric humic acids (Schulten, 1996) were proposed in an integrated approach using a wide variety of analytical methods. The HA model is important because humic substances constitute 70-80% of soil organic matter (SOM) and all chemical reactions of the latter (large surface, voids, high adsorption capacity, good metal complexer, good medium for microorganisms, can store nutrients and especially water) can be explained on the basis of HAs. From the analytical aspect, main emphasis was put on pyrolysis-mass spectrometry and pyrolysis-gas chromatography/mass spectrometry. Modern personal computer-based techniques of molecular modelling (Hypercube[®], Inc., 1115 NW 4th Street, Gainesville, Florida, 32601-4256, U.S.A.) were employed to develop three-dimensional structures of humic acids (Schulten, 1995; Schulten and Schnitzer, 1993) and organomineral soil complexes (Schulten, 1996). In particular trapping and bonding of biological (peptides, carbohydrates)

and anthropogenic substances such as pesticides and plastizisers in the voids of the geometrically optimized structures were investigated. Basis of the presented work were improved structural concepts of SOM and soils (Schulten and Schnitzer, 1997) and the development to model humic xenobiotic complexes in water (Schulten *et al.*, 1998). In a recent survey on the role and structure of organic nitrogen in soils, the combination of analytical pyrolysis proved to be particularly powerful when the results of sophisticated analytical methods could be supported and by computer modelling (Schulten *et al.*, 1998). Despite an inspiring dispute on the value or nonsense of three-dimensional models of humic substances, in the meantime excellent textbooks on environmental soil chemistry cite and display these model structures.

Computational chemistry

For computational chemistry, model construction, three-dimensional (3D) illustration, chemical interaction studies, molecular mechanics and molecular dynamics calculations the HyperChem[®] software (release 5.0) for Microsoft Windows 95[®] was used. In the present text some main software commands are indicated in brackets (in *italics*). The original program output in Angstrom and kcal was given in nm and kJ, respectively. The employed IBM-compatible personal computer (PC) consisted of an Intel Pentium[®] Pro with 200 MHz in combination with 128 MB memory, 17" colour monitor, 2.1 GB disk, and peripheric hardware (e.g. Epson Stylus colour printer) plus utility programs.

As a first example for this relatively complex structure, in the attached figure the results of computational chemistry are illustrated in a preliminary form. For the organomineral complex the element composition of $C_{381}H_{807}O_{1607}N_{46}Si_{616}Fe_8Al_6S$, the elemental analysis: 9.21% C, 1.64% H, 51.75% O, 1.3% N, 34.82% Si, 0.9% Fe, 0.33% Al, 0.06% S, and the summed molecular weight of $49\,686.3277\text{ g mol}^{-1}$ were determined.

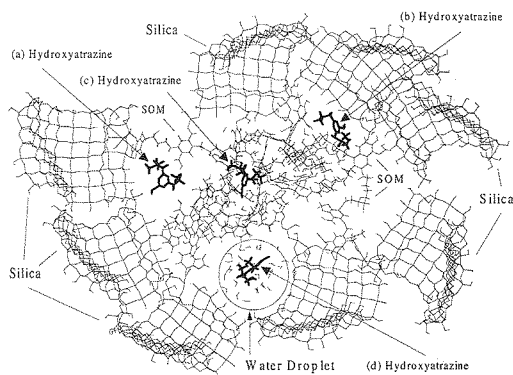


FIG. 1. Organomineral xenobiotic complex of hydroxyatrazine and SOM.

Figure 1. Black/white 3D-structure of a xenobiotic soil particle following geometry optimization. Four hydroxyatrazine molecules (highlighted by thick lines and indicated by arrows) are adsorbed and bound in the four different bonding situations (a, b, c, d).

The soil particle is constructed from 8 silica sheets which have been described in detail (Schulten, 1995). In the fairly planar circle of these silica sheets a novel, improved model of SOM (Schulten *et al.*, 1998) was inserted and is fixed by iron and aluminum bonds. Following geometry optimization *in vacuo*, stable voids of widely different sizes are observed and are characteristic for humic substances and SOM. The trapping and binding of biological substances such as sugars and peptides in the voids has been reported. Thus, in this case a trisaccharide and a hexapeptide were immobilized by hydrogen bonds in the SOM voids. Furthermore, simulating approx. 10% water content 10 water molecules were randomly introduced into the organic portion of the complex. At this stage the SOM model consisting in total of 3257 atoms was again optimized using molecular mechanics calculations.

Four hydroxyatrazine molecules were now introduced into four different positions: a) inserted in a wide, spacious void and formed 2 hydrogen bridges during molecular mechanics calculation; b) inserted in a narrow void and was first trapped by strong van der Waals forces, but later on also developed hydrogen bonds; c) this molecule was squeezed into the dense SOM center, created its own void during the calculations; and d) most interestingly, the hydroxyatrazine was firstly optimized in a water box containing 200 water molecules, secondly a spherical droplet comprising 33 water molecules and the dissolved hydroxyatrazine, was cut out of this water box and inserted in a void between SOM and the silica

ring (see arrow in Fig. 1). Thus the total xenobiotic soil particle contained 3 472 atoms in total.

Following geometry optimization a total energy of 16523.20 kJ mol⁻¹ was determined at a (*rms*) gradient of 16.36 kJ mol⁻¹ nm⁻¹. Running a *log file* the energy distribution of the complex can be evaluated as bond- (2380.58 kJ mol⁻¹); angle- (20021.83); dihedral- (1639.68); van der Waals- (-1694.14) stretch-bend- (-2586.47) and electrostatic-energy contributions (-3 228.11).

Structure-activity relationships

Quantitative structure-activity relationship (QSAR) properties are easily obtained, for instance for solvent accessible surface area: (Grid) = 3743.324 nm⁺²; surface-bounded molecular volume = 375.6207 nm⁺³ and van der Waals surface area: (Grid) = 1041.983 nm⁺²; surface-bounded molecular volume = 57.96165 nm⁺³; and the hydration energy of the trapped hexapeptide (1Asp2Gly3Arg4Glu5Ala 6Lys) = 1030.15 kJ mol⁻¹.

Computational chemistry offers relatively economical, powerful tools to observe binding of humic substances to biological molecules, mineral surfaces, metal ions, and anthropogenic compounds at nanometer level using exact bond distances, bond angles, torsion angles, non-bonded distances, van der Waals forces, hydrogen bonds and ionic charges. Therefore, the proposed methodology for the environmental and soil sciences should be well suited for fundamental and applied investigations of physical and biological properties, adsorption and desorption processes, chemical reactivity and molecular dynamics of humic substances.

References

- Schulten, H.-R., Plage, B. and Schnitzer, M. (1991) *Naturwissenschaften*, **78**, 311–2.
- Schulten, H.-R. and Schnitzer, M. (1993) *Naturwissenschaften*, **80**, 29–30.
- Schulten, H.-R. (1995) *Fresenius J. Anal. Chem.*, **351**, 62–73.
- Schulten, H.-R. (1996) In: Gaffney, J.S., Marley, N.A., Clark, S.B., Eds., *Humic and Fulvic Acids - Isolation, Structure and Environmental Role*, ACS, Series No. 651, Washington, DC, pp. 42–56.
- Schulten, H.-R. and Schnitzer, M. (1997) *Soil Sci.*, **162**, 115–30.
- Schulten, H.-R., Leinweber, P. and Schnitzer, M. (1998) In: Huang, P.M., Senesi, N. and Buffle, J., Eds. *Structure and Surface Reactions of Soil Particles*, John Wiley, Chichester, England, pp. 281–324.