



Review

Molecular modeling of soil organic matter: Squaring the circle?

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ABSTRACT

The structure of soil organic matter (SOM) and humic substances (HS) has been discussed from different viewpoints including molecular conformation, molecular aggregation, macromolecularity, supramolecular characteristics, domain mobility, and many others. Until now, the individual models appear partly contradictory, although each viewpoint provides important information on the structural and functional properties of SOM. This is most probably due to the huge heterogeneity of SOM. Therefore, the question: “How can molecular modeling help to further understand structure and functioning of soil organic matter?” needs to be addressed with care. This contribution reviews and discusses the potential of important molecular modeling approaches currently applied in soil organic matter science.

Computer models are useful in giving a visualization of the general structure and of the possible effects on soil chemistry and soil physics. Computational chemistry in this context aims to estimate a lowest energy conformation for a molecule or an assembly of molecules specified by the programmer. On the basis of the calculated conformation, physicochemical characteristics like surface area, polarity and other can be estimated and information on the stability of molecular assemblies can be derived. The significance of the obtained conformation and physicochemical information strongly depends on the initial hypothesis of the molecular structure of each involved molecule. Recent computer models have been developed on the base of computer assisted structure elucidation (CASE). In this procedure, all possible isomers or a statistically representative set of isomers consistent with the experimental input data are processed.

Further interesting fields of computational chemistry in soil research follow a different conception, where specific processes of interest are elucidated with the help of computational models which simplify the humic molecules with respect to the individual modeling problem. This way helps to understand the relevance of principal processes expected to occur in soil. In this context, complexes of Al with organic acids, clay mineral sorption sites, interactions of pesticides with organic functional groups or organic soil constituents as well as cross-linking of molecule segments by water molecules were modeled in targeted process-orientated models. The act of simplification is the crucial process in these kinds of models, and if the models are based on good conceptions, they allow to learn about potential SOM functioning. The transfer to more complex situations, however, needs special care and the predictive character of these models needs to be judged with care. Still, any computer model is only as good as its initial hypothesis.

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1. Introduction

Soil organic matter (SOM) determines the functioning of large parts of biogeochemical interfaces in the soil. Its unique heterogeneity in composition is the *sine qua non* for the huge versatility of SOM functioning, but, on the other hand, is extremely challenging for approaches attempting to link structure with function. Assessment of the structure of SOM and humic substances (HS) requires concepts accounting for its heterogeneous composition and polydispersity (Schaumann, 2006a). SOM is understood here as the total of organic compounds in soil excluding easily detachable plant and animal tissues and the soil biomass, and we subdivide humic substances (HS) on an operational basis, resulting in carbohydrates (CH), fulvic acids (FA), humic acids (HA) and humins (HU) (Swift, 1996). Reports on molecular sizes range from 100,000 Da and more (Haider, 1999; Stevenson, 1994 #2342) via 30,000–50,000 Da and 10,000 Da (Flaig and Beutelspacher, 1968) down to a few thousand Da for dissolved FA and HA (Piccolo, 2001). Main SOM constituents are aliphatic polymers, polysaccharides (e.g. cellulose), lignin and lignin degradation products, fats, proteins, pectines (Scheffer and Schachtschabel, 2010) and cutins (Wershaw, 1999) that are existent as a continuum from the primary biomolecules to highly transformed biogeochemical (pedogenic) products practically unaltered or transformed to various degrees. Polyphenolic structures from lignin as well as carbohydrate and aliphatic fragments may represent the backbone of molecules in SOM and humic substances (Schulten and Schnitzer, 1997). Micro-graphitic NOM represents another important constituent of SOM. It includes pyrolysed materials such as chars, soots and other highly carbonaceous material (black carbon) (Accardi-Dey and Gschwend, 2002; Cornelissen et al., 1997, 2004). These materials are composed of disordered polyaromatic sheets that may be functionalized along the edges (Pignatello, 2003). Hence, modern concepts of SOM regard them as supra-molecular assemblies of monomers to macromolecules, and as a continuum from biomolecules to highly transformed or carbonaceous compounds with polymer-like properties (Senesi et al., 2009).

Although up to now not completely experimentally assessed, each of these structures as well as the interplay between them provides important characteristics for the functioning of SOM as biogeochemical interface. SOM can store water (Jaeger et al., 2006, 2010), but can also be or become water repellent and can change its wettability (Bayer and Schaumann, 2007; Diehl and Schaumann, 2007; Doerr et al., 2000; Ellerbrock et al., 2005; Graber et al., 2007). SOM is subjected to physicochemical aging (Schaumann, 2006b; Schaumann and Bertmer, 2008) and controls soil-contaminant interactions (Sander et al., 2006; Sun et al., 2008; Sutton and Sposito, 2005; Yang and Xing, 2009; Zhang et al., 2008), as well as biogeochemical transformations and habitat quality for microorganisms (Coleman et al., 2004; Totsche et al., 2009). Large parts of the underlying mechanisms are still unknown. Not only the molecular structure, but also the supramolecular arrangement of the various molecules in SOM will control these functions (Schaumann, 2006a,b). Even more, many of these functions are rather interactions and the influenced entities will feed back on the composition, structure, properties, and turnover of SOM.

Hence, it seems an unrealistic goal to search for the ideal and universal molecular model of HS.

Numerous approaches have been undergone to use defined synthetic chemicals as models for humic compounds explaining (i) NOM–metal interactions, (ii) the polymeric nature of humic substances and (iii) chemical reactivity of humic compounds and their ability to form bound residues:

NOM–metal interactions and NOM acid–base properties were mostly studied using polycarboxylates and more general polyelectrolytes including polyacrylates, polymethacrylates, polyacrylate-co-maleates (Crea et al., 2006, 2009), or proton-metal exchange of humic acids (Benegas et al., 2003; Montavon and Grambow, 2003). Slaveykova et al.

(2004) monitored bioavailability of Pb using tiron and nitrilotriacetic, iminodiacetic, malonic, citric, polyacrylic acid as model substances, and dihydroxyphenylalanine was used as model humic compound to study sorption of humic acids to alumina and silica minerals (Zimmerman et al., 2004). Hess and Chin (1996) showed certain suitability of polymaleic acid as a model compound FA.

The polymer analogy of natural organic matter (NOM) was studied using synthetic polymers like polyacrylic acids with respect to sorption irregularities of organic chemicals to NOM (e.g., LeBoeuf and Weber, 1997, 2000; Weber et al., 1999, 2001). Ji et al. (2000) and Kappler et al. (2000) showed that peroxidase-initiated radical polymerization of a mixture of phenolic compounds, peptides, amino acids, and carbohydrates resulted in reaction products resembling natural humic substances in their elemental content, infrared spectra, and molecular weight distribution. Polymeric substances, and melanoidins were used as model compounds for biorecalcitrant polymers and synthetic humic acids (Dehorter and Blondeau, 1993), and synthetic surfactants were applied to investigate micellar structure (Wu et al., 2011).

Polyphenol and polyphenol derivatives were used to mimic humic acid reactivity, e.g., for enzyme-catalyzed cross-coupling reaction with sulfonamides in order to study mechanisms of bound residue formation (Bialk et al., 2005, 2007; Schwarz et al., 2010). Photodegradation of HA was studied with model substances like tannic acid and/or p-hydroxybenzoic acid (Cowen and Al-Abadleh, 2009). Barriquello et al. (2011) synthesized a polymer with characteristics analogous to those of humic acids isolated from soils, through oxidative polymerization in an alkaline medium using para-benzoquinone as precursor.

Synthetic humic compound models thus can be used to describe certain properties of NOM. Despite some similarities between the mentioned synthetic models, the choice of the synthetic model depends on the property to be studied. To our best knowledge, up to now, no synthetic humic compound model has been found which can mimic all chemical and physical NOM properties.

Even more, using molecular models for computational chemistry application could be a highly versatile tool helping to understand processes, and the involved mechanisms, sites and interactions on molecular scales within a 3D structural network. Molecular models are images of a simplified reality based on targeted hypotheses and represent pictures from the chosen point of view. In this context, molecular models may themselves be regarded as hypotheses. A good model should match available experimental data, but at the same time correctly predict up to now unknown properties. Computational chemistry in this context aims to estimate a lowest energy conformation for a molecule or an assembly of molecules specified by the programmer. On the basis of the calculated conformation, physicochemical characteristics like surface area, polarity and other can be estimated and information on the probability of formation and the stability of molecular assemblies can be derived. Experimental verification is required to reject or verify and further optimize the model assumptions.

This contribution discusses the potential of some of the most important molecular modeling approaches currently applied in SOM science. Current SOM structural models are based on various working hypotheses, which can be grouped as follows:

1. SOM function can be described on the basis of representative large SOM-molecules,
2. SOM can be described as a mixture of defined structural sub-units (molecules, building blocks or functional groups),
3. SOM function can be described on the basis of intermolecular interactions overbalancing the effect of exact primary structure.

This contribution reports on the potential of computational approaches based on these hypotheses. Models are discussed with regard to the simplification hypotheses and their significance for

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