

Molecular modeling of DDT's and it's major metabolites adsorption in the interlaminar space of montmorillonite

János ECKER^{1,*} and László FÜLÖP¹

¹Department of Chemistry and Biochemistry, Szent István University, Páter K.u.1., Gödöllő, H-2103 Hungary

*Corresponding Author; e-mail: Ecker.Janos.Mail@gmail.com

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Abbreviations:

DDT - 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane

DDD - 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene

DDE - 1,1-bis-(4-chlorophenyl)-2,2-dichloroethane

ABSTRACT

A simple adsorption mechanism of the organochloride insecticide DDT and it's most common metabolites DDD and DDE in the interlaminar layer of montmorillonite mineral is discussed in this paper, based on the results of molecular modeling. A model of a simple fragment of the montmorillonite crystal with the interlaminar layer was created and used. The interlaminar layer contained water as a solvent and the ionic forms of sodium or calcium as exchangeable cations along with the molecules of DDT/DDD/DDE. The molecular interactions were simulated by force fields and the results of the simulation could be explained by the physical characteristics of the models which were studied with bioinformatics tools as well. Based on the observed mechanisms, the adsorption of DDT and it's metabolites in the interlaminar layer of montmorillonite is possible and it is partly responsible for the persistent nature of these insecticides.

Introduction

DDT and the two metabolites (DDD, DDE) are still widely exist in soils and in other environmental elements with high concentrations [16, 21, 23] due to their persistence, long-distance transportation (mostly by atmospheric transport) and bioaccumulation [22]. The DDD and DDE metabolites come from the dehydrochlorination of DDT and their physical and chemical properties are similar [18]. The dehydrochlorination and other types of catalyzed reactions that result in a change of the chemical structure are possible by enzymes, expressed by resistant insects and

some species of bacteria and fungi [13, 19, 20], and a photooxidation mechanism of DDT and DDE has also been discovered [1, 11, 15].

Beside these chemical transformations, the decreasing tendency of DDT concentrations in soil is a result of volatilization, water runoff and the harvesting of plants that have absorbed the insecticide [7].

The persistence of DDT and it's metabolites is not only determined by the hydrophobic character, structure and the limited biodegradability of these molecules. In soils, adsorption characteristics of organic pollutants are especially affected by the

physicochemical properties and material compositions of the soil, for instance the decrease/increase in pH values [14] and contents of organic matters (mainly humic substances) [5]. Cheng [4] concluded that smaller soil particles has greater adsorption capacity to DDT and the adsorption is related to the composition and origin of organic matter and minerals.

The structure of montmorillonite (along with other minerals) was first proposed by Pauling (1930) by the X-ray diffraction method. The composition of montmorillonite is $[(\text{Na}, \text{Ca})(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}]$, so chemically it is a hydrated sodium calcium aluminium magnesium silicate hydroxide. The unit layer is composed of three tetrahedral-octahedral-tetrahedral sheets. The center of the tetrahedron is Si, it can be

substituted by Al. In the center of the octahedron there is Al and that can be substituted by Mg or Fe [3]. Due to its adsorptive character, montmorillonite is widely used as an adsorbent in a variety of fields for example the elimination of heavy metals from contaminated water [12].

The adsorption of various chemicals is possible on the surface of the layer and in the interlaminar layer as well. Simple cations can be adsorbed on the surface or in the interlaminar layer by the montmorillonite's cation exchange capacity [2] but beside these phenomena which are controlled by electrostatic interactions, the van der Waals forces and the hydrogen bonds are also responsible for the adsorption, as described by Hendricks [9] and in the molecular simulation studies of Karaborni [10].

Material and methods

Applications

Two applications were used during the study. The Avogadro software (v1.1.1) was a suitable tool to build the molecular structures atom by atom or from fragments and visualize their interactions. This application can render interactive, three-dimensional images and it is possible to optimize the structures geometrically and analyse the chemical and molecular data, as described by Hanwell [8]. Optimizing the structures of the "hand-drawn" molecules is an essential procedure to get the adequate bond lengths and angles. Two of Avogadro's force fields were used for

structure optimization but every force field has its limitations. The Merck Molecular Force Field (MMFF94) is ideal for visualize the molecular interactions but it cannot be used with every element of the periodic table. The Universal Force Field (UFF) can be used across the entire periodic table.

The Marvin Sketch application (v14.8.18, developed by ChemAxon Ltd., Hungary) has many features which can be used to analyze the various characteristics of the models (e.g., charges, protonation, solubility) previously built and optimized by Avogadro.

The Montmorillonite Model

The montmorillonite layer used in the simulations was finalized by modifying the structure of the pyrophyllite. This mineral has only Si in the tetrahedral and Al in the octahedral positions without substitutions, so it was an ideal intermediate model for the further studies. In the montmorillonite, the tetrahedral and octahedral sheets are

repeating, so the size of the crystal is theoretically not limited. In the end it was duplicated and optimized with the UFF.

In the following step the covalent bonds between the aluminium and oxygen atoms were removed and the total amount of Al-s (48) in the two crystals were substituted by Mg and Fe atoms in random arrangement and

MMFF94 was used. Despite these metals are atoms in appearance, without the covalent bonds the program handles them as di- and trivalent cations (Mg^{2+} , Fe^{3+}). Substitutions in

the tetrahedral centers (Si to Al) were not performed, because the MMFF94 cannot be run with aluminium.

The Complete Model

The final model contained all of the components for which molecular interaction studies were planned. The interlaminar space of the montmorillonite was filled with water molecules (solvent), DDT/DDD/DDE molecules and $\text{Na}^+/\text{Ca}^{2+}$ (exchangeable

cations). The models of the pesticides were based on the chemical structures published in the work of Faroon & Harris [6] and they were inserted into the interlaminar space randomly. In the final step the optimization by the MMFF94 was performed.

Results and discussions

The optimized (UFF) fragment of the montmorillonite's starting model is shown in Fig. 1. Some substitutions in the tetrahedral (Al) and octahedral (Fe) positions have been

made for illustrative purposes. MMFF94 is not usable with this structure because of the presence of aluminium atoms.

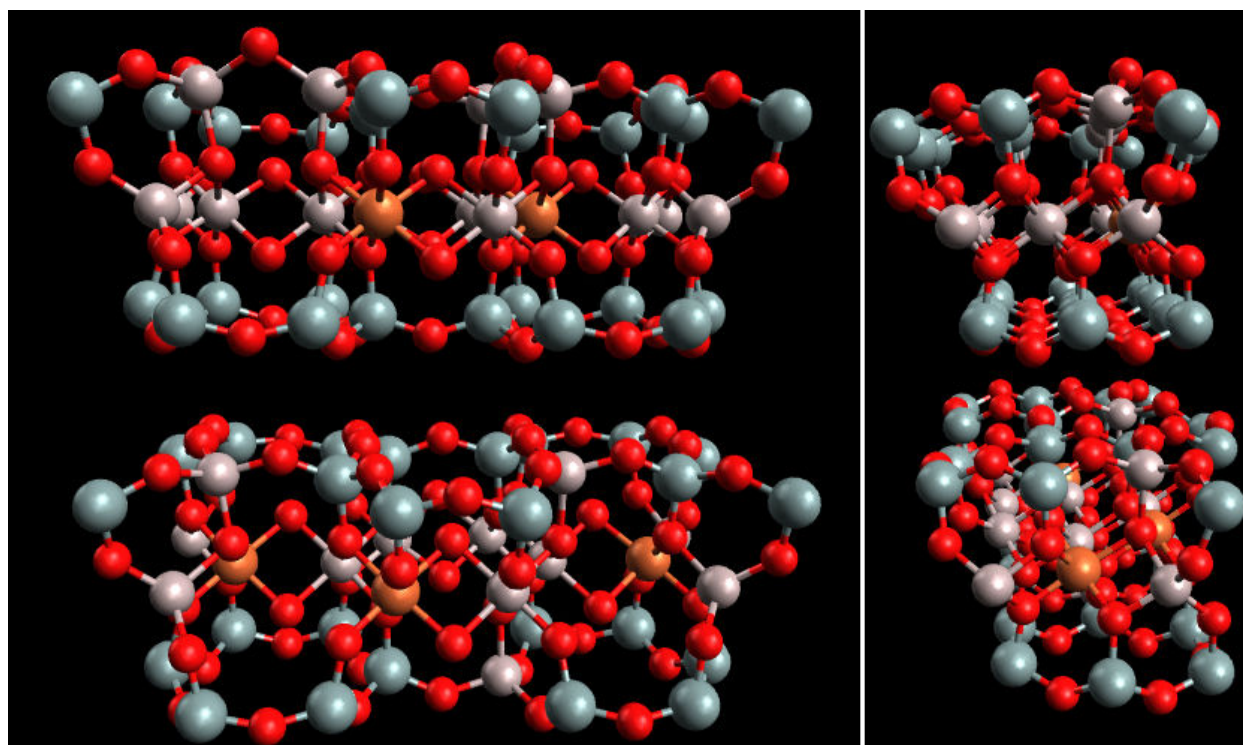


Fig. 1. Fragment of the montmorillonite starting model, based on the pyrophyllite with an empty interlaminar space, optimized by UFF (Avogadro 1.1.1). The pictures are rotated 90 degrees relative to each other. The colors indicate the following atoms: O (red), Si (blue), Al (grey), Fe (orange).

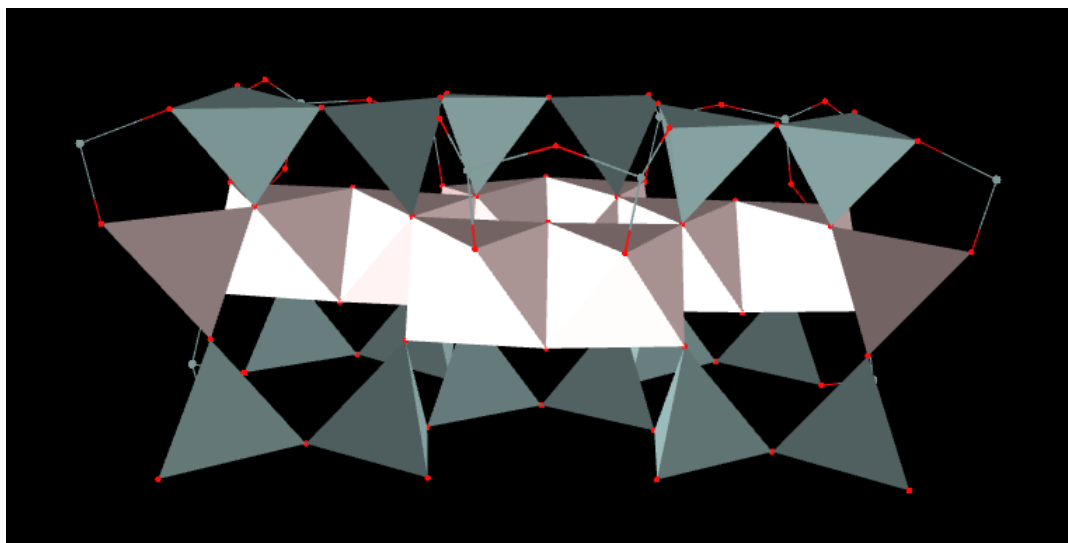


Fig. 2. Tetrahedral and octahedral sheets in the montmorillonite fragment (Avogadro 1.1.1).

In Fig. 2. the tetrahedral and octahedral sheets are visualized, the geometry of the layer is clearly visible. The final layer which is compatible with MMFF94 is an extended and

modified version of the model shown in Fig. 1. The final structure used in the simulations is shown in Fig. 3.

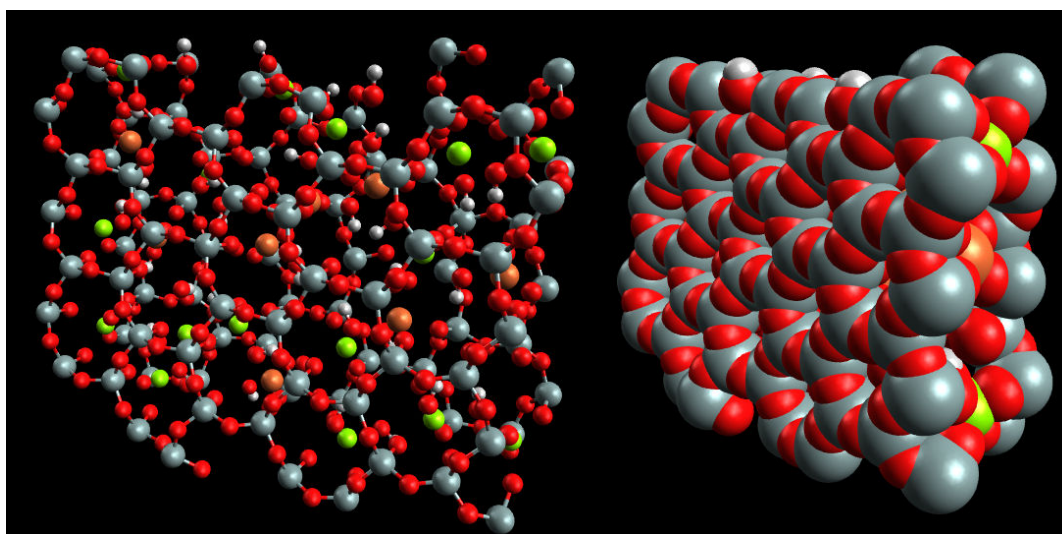


Fig. 3. Structure of the model (Avogadro 1.1.1) used in the simulations, optimized by MMFF94, visualized by ball-and-stick model (left) and van der Waals spheres (right). The colors indicate the following atoms/ions: O (red), Si (blue), Fe^{3+} (orange), Mg^{2+} (green), H (white)

This structure is the result of the energy minimization, generated by the MMFF94 force field. The structure of the model does not contradict the previously published figures and it has the known physical properties. By comparison with the starting model, the geometry of this final structure is obviously different, the sheets of the crystal

are both horizontally and vertically displaced. Considering the fact that montmorillonite is a mild and easily mouldable mineral, we can safely assume that this model represents the actual geometry better. It has an inner surface large enough to reproduce the molecular interactions in the interlaminar layer authentically.

It is an important observation that the electrostatic interactions between the $\text{Mg}^{2+}/\text{Fe}^{3+}/\text{OH}^-$ ions and oxygens are primarily responsible for forming and stabilizing the structure and they have little

influence on the mechanisms that take place in the interlaminar space. This can be explained by the surface charge conditions of the montmorillonite, visualized by Marvin Sketch (Fig. 4.).

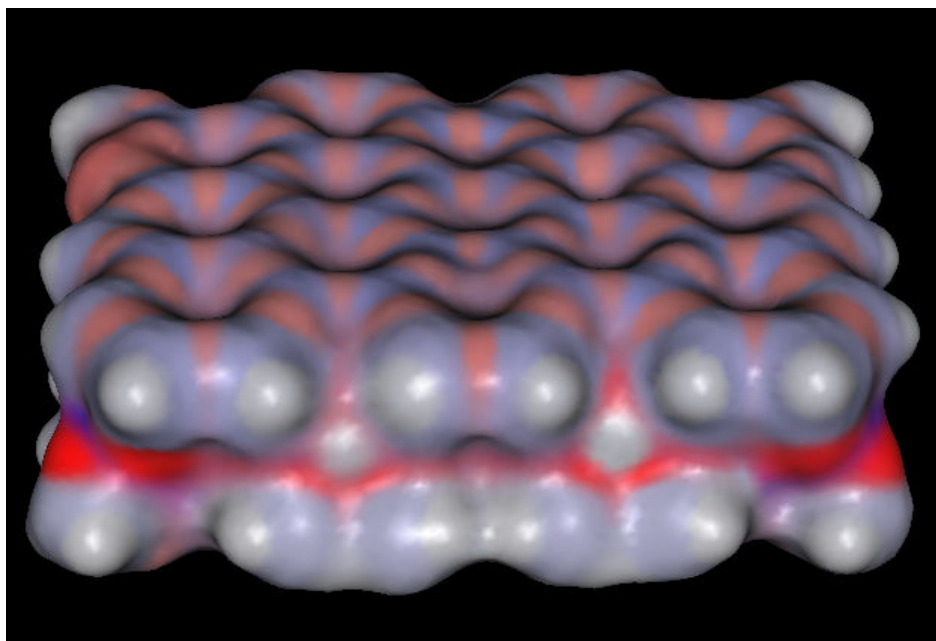


Fig. 4. Surface charge conditions of the montmorillonite layer optimized by MMFF94 (Marvin Sketch 14.8.18). Positive charges are blue, negative charges are red.

The positive (blue) and the negative (red) charges on the surface present a smooth, not intensely colored texture. The electrostatic fields of the ions within the octahedrons are shielded by the atoms of the tetrahedral sheets, therefore outside non electrostatic forces are more relevant, while in the interlaminar layer, electrostatic interactions dominate. The further studies (see below) have confirmed the hypothesis that the mechanisms that take place in the interlaminar layer are mostly affected by the charges of the tetrahedral sheets, if we consider only the montmorillonite's role in the adsorption of the DDT.

In the complete model (montmorillonite with pesticide molecules, water and $\text{Na}^+/\text{Ca}^{2+}$ in the interlaminar space) the water molecules were connected to each other and to some of the oxygens of the Si atoms by hydrogen bonds, so the model has the capability to chemically bind water. In order to create the

hydrogen bond, the distance between the hydrogen and the oxygen of the Si-tetrahedral must be within 2 angstroms (Å), based on Avogadro's calculations. This bonds proved to be unstable, some of them existed during the optimization only for a short time, so we can assume that they can detach due to temperature change. The possible explanation to this phenomenon is that the oxygens in the tetrahedrons are connected with two Si-atoms that are larger in van der Waals radius, so the force field of the oxygen is partially shielded. Beside this, the electronegativity of the oxygen has a significantly higher value (3.5) than the Si (1.8), so there is a partially positive charge on Si and on the hydrogens of the water as well, therefore the proper orientation required for hydrogen bonds is energetically unfavorable.

An ion-induced dipole interaction occurred between the $\text{Na}^+/\text{Ca}^{2+}$ ions and the water molecules, as it was expected (see Fig. 5.).

The DDT and the metabolites could not mix with the water due to the size and the hydrophobic character of the pesticide molecules. The water molecules and the cations showed a significant shift within the interlaminar space during the optimization time (some water molecules and ions got out of the interlaminar layer) but the pesticide molecules showed no appreciable movement. The explanation is that these hydrophobic molecules could not interact with the other components of the interlaminar layer, they

have only a low partial charge on the chlorine atoms. The van der Waals forces of the two montmorillonite layers are also responsible for keeping the molecules in the interlaminar space. No difference was observed in the behavior of the DDD and DDE metabolites compared to DDT and the three-dimensional structures of the pesticide molecules were not changed during the optimization. One final state of the model after the optimization is shown in Fig. 5. The distance between the two layers is approximately 28.5 Å.

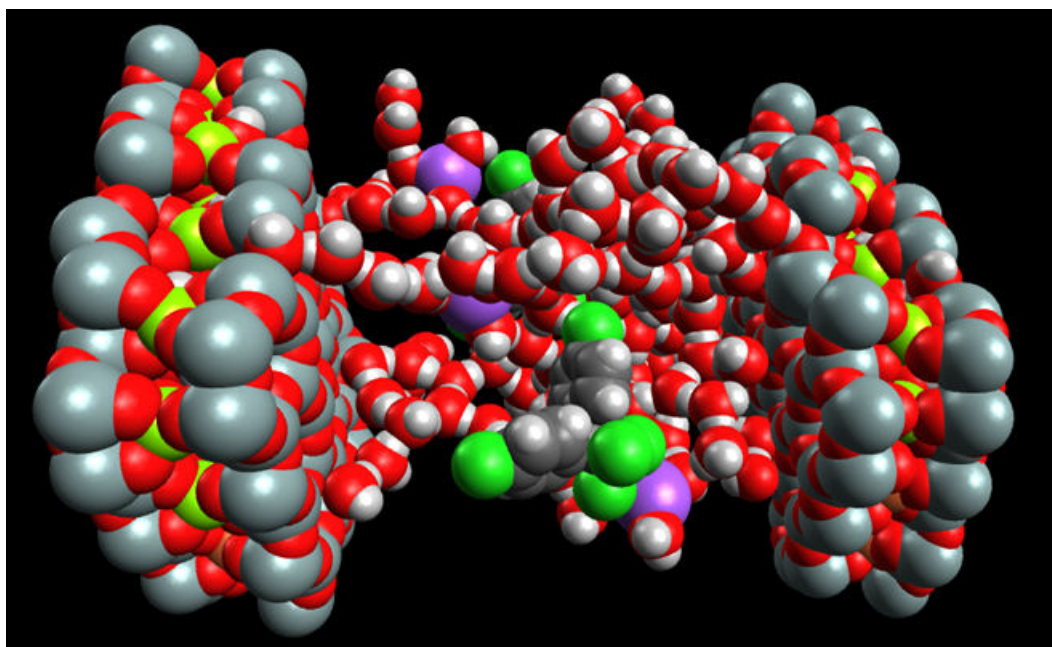


Fig. 5. The final state of the model after the MMFF94 optimization (Avogadro 1.1.1). Water molecules are connected by H-bonds, Na^+ -s (purple) are hydrated but the DDT (with green chlorine atoms) is not dissolved in water and its structure is unchanged.

Conclusions

The results of this short report reveal that the adsorption of the DDT and its metabolites in the interlaminar space of the montmorillonite clay mineral is possible, primarily due to their hydrophobicity and the presence of van der Waals forces. This could only partly be responsible for the persistence of these insecticides. The complete model was a simplified structure that did not include many of the components that are present in real

environmental conditions, e.g. humic substances which are the major organic constituents of soils and the examination of the surface adsorption of the pesticides was not part of this work.

With the use of a more complex model and other applications, it would be possible to understand the mechanism and dynamics of DDT's adsorption in more detail.

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