



# **INTERACTION OF THE 2,4-DICHLOROPHENOXYACETIC ACID HERBICIDE WITH SOIL ORGANIC MATTER – A THEORETICAL STUDY**

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## BACKGROUND

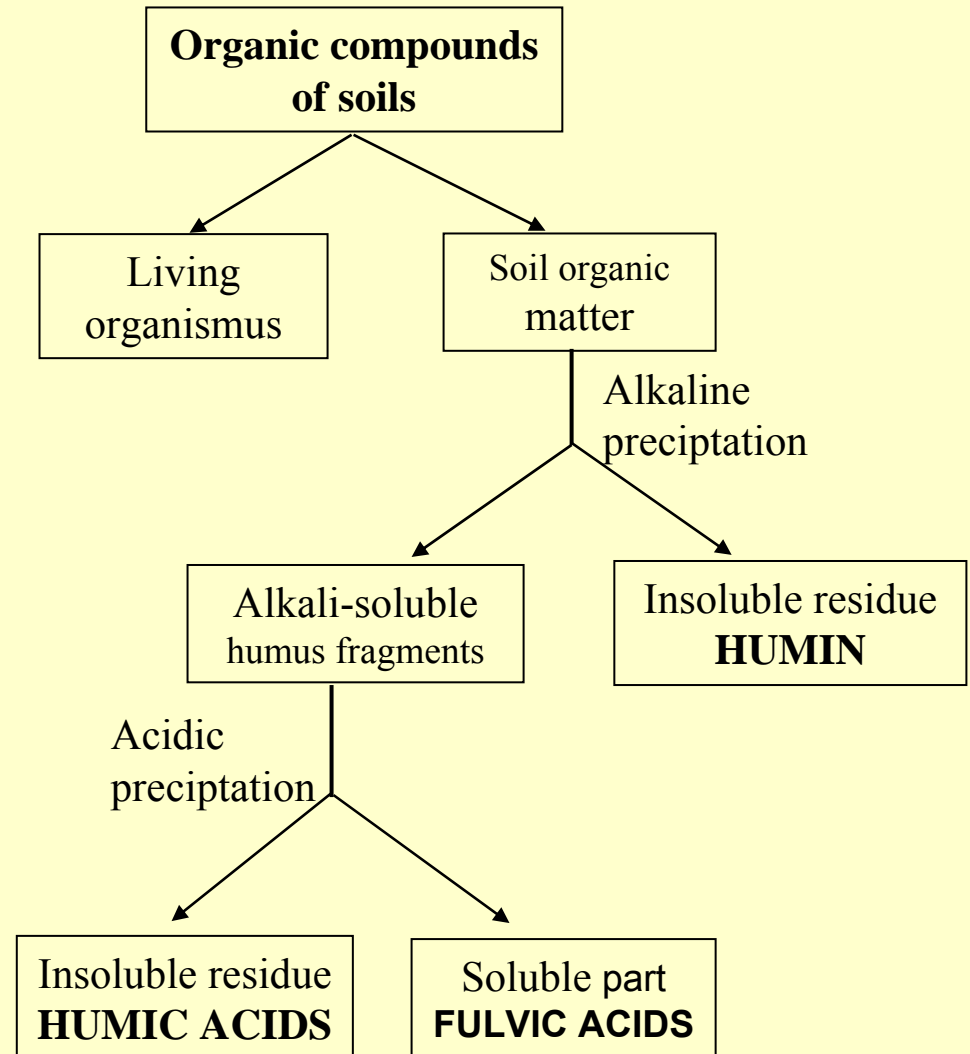
The term “**soil organic matter**” (SOM) is generally used to represent the organic constituents in the soil.

**Humic substances (HS)** are one of the major constituents of the terrestrial (SOM) and aquatic (dissolved SOM) carbon pool.

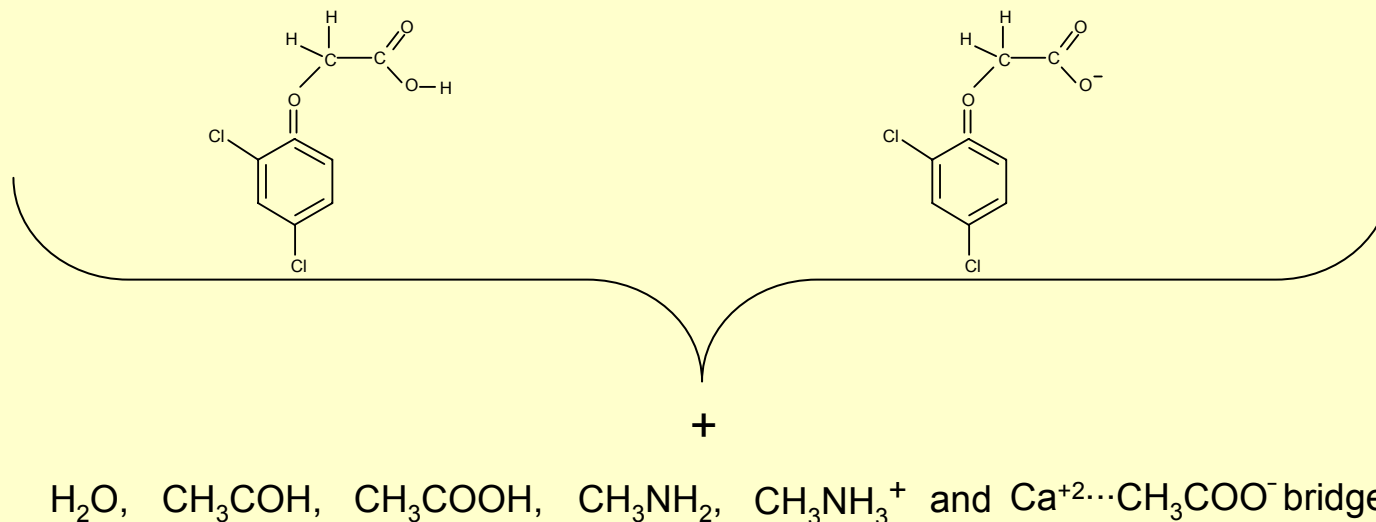
**Humic acids** - the fraction of HS that is not soluble in water under acidic conditions ( $\text{pH} < 2$ ) but is soluble at higher pH values.

**Fulvic acids** - the fraction of HS that is soluble in water under all pH conditions.

**Humin** - the fraction of HS that is not soluble in water at any pH value.



## STUDIED SYSTEMS



## GOAL

Humic acids contain several relevant functional groups, mainly carboxyl, carbonyl, alcoholic and phenolic units, which play a major role in binding of polar molecules from a polar solvent environment. The aim of this work was to study the interactions of molecular and anionic forms of 2,4-D herbicide with these functional groups.

## **COMPUTATIONAL DETAILS:**

All calculations were performed at **DFT** level of theory with the **TURBOMOLE** and **GAUSSIAN03** programs

**Density functional:** B3LYP

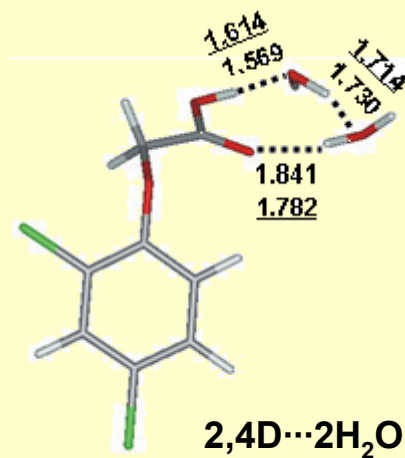
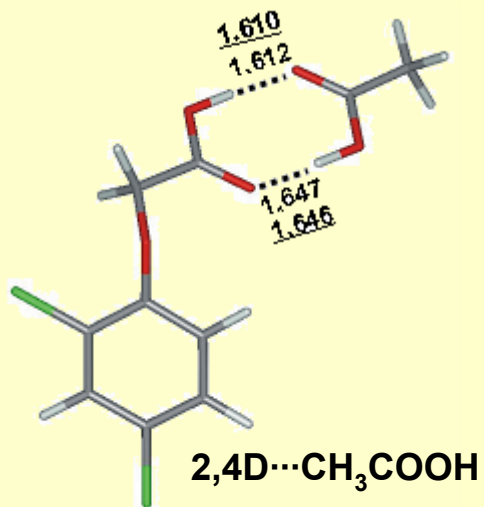
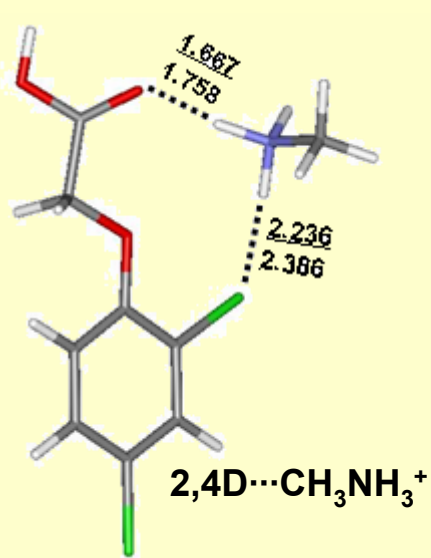
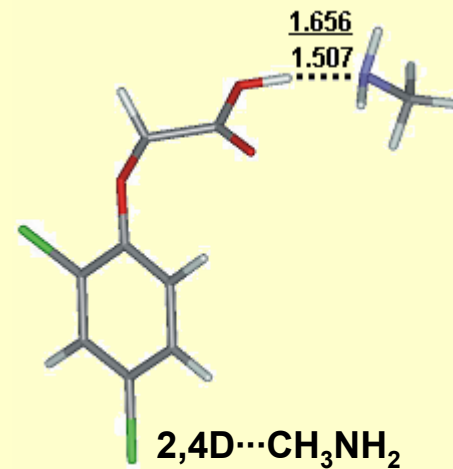
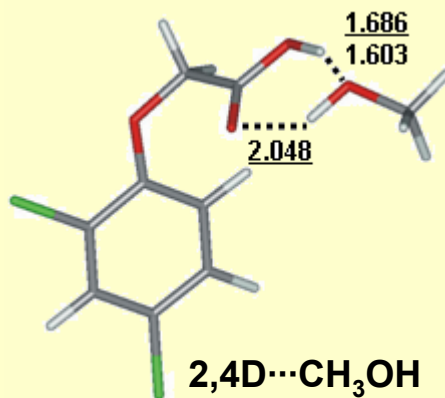
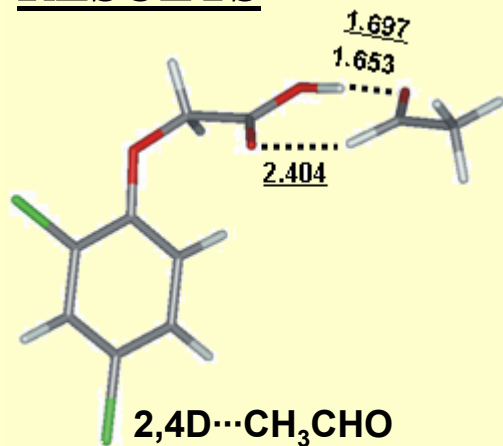
**Basis Set:** SVP, SVP+sp

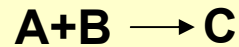
The polarizable continuum model, **PCM** and the conductor-like screening model, **COSMO** were used to computer the calculations in solution

Two models were used to perform the calculation in solution: the microsolvation (g) and the global solvation (gs) and the combination of them (gsm)

All results are BSSE corrected

# RESULTS



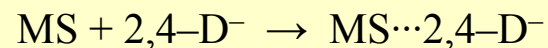
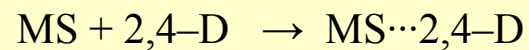


Complex formation <sup>a</sup>	$\Delta E_g$	$\Delta H_g$	$\Delta G_g$	$\Delta E_{gs}$	$\Delta H_{gs}$	$\Delta G_{gs}$
Me-CHO + 2,4-D $\rightarrow$ Me-CHO $\cdots$ 2,4-D	-11.4	-8.6	<u>1.2</u>	-2.6	0.2	10.0
Me-OH + 2,4-D $\rightarrow$ Me-OH $\cdots$ 2,4-D	-12.5	-9.4	<u>0.2</u>	-4.2	-1.1	4.1
Me-NH <sub>2</sub> + 2,4-D $\rightarrow$ Me-NH <sub>2</sub> $\cdots$ 2,4-D	-13.9	-11.1	-2.0	-7.3	-4.5	4.6
Me-COOH + 2,4-D $\rightarrow$ Me-COOH $\cdots$ 2,4-D	-18.0	-15.1	-4.0	-1.6	1.3	12.4
(H <sub>2</sub> O) <sub>2</sub> + 2,4-D $\rightarrow$ 2H <sub>2</sub> O $\cdots$ 2,4-D	-18.8	-15.2	-2.5	-4.0	-0.4	12.3
Me-NH <sub>3</sub> <sup>+</sup> + 2,4-D $\rightarrow$ Me-NH <sub>3</sub> <sup>+</sup> $\cdots$ 2,4-D	-33.2	-29.6	-18.9	-4.9	-1.3	9.4

<sup>a</sup> – Me= -CH<sub>3</sub>

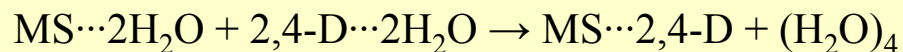
$$\Delta H_{gs} = \Delta H_g - \Delta E_g + \Delta E_{gs}$$

$$\Delta G_{gs} = \Delta G_g - \Delta E_g + \Delta E_{gs}$$

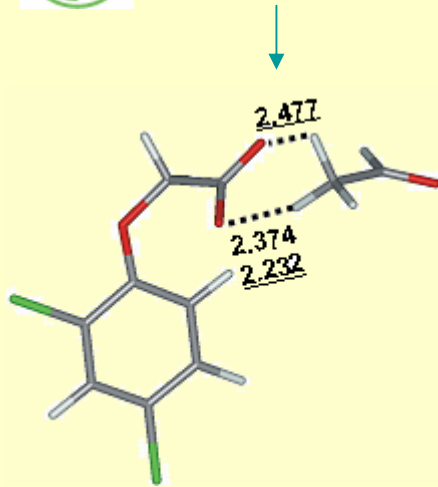


Model reaction <sup>a</sup>	microsolvation			global solvation + microsolvation		
	$\Delta E_g$	$\Delta H_g$	$\Delta G_g$	$\Delta E_{gsm}$	$\Delta H_{gsm}$	$\Delta G_{gsm}$
Me-CHO $\cdots$ 2H <sub>2</sub> O + 2,4-D $\cdots$ 2H <sub>2</sub> O $\rightarrow$ Me-CHO $\cdots$ 2,4-D + (H <sub>2</sub> O) <sub>4</sub>	-2.2	-1.8	-1.5	-4.1	-3.7	-3.4
Me-OH $\cdots$ 2H <sub>2</sub> O + 2,4-D $\cdots$ 2H <sub>2</sub> O $\rightarrow$ Me-OH $\cdots$ 2,4-D + (H <sub>2</sub> O) <sub>4</sub>	-3.9	-3.6	<u>-4.3</u>	-8.9	-8.6	-9.3
Me-NH <sub>2</sub> $\cdots$ 2H <sub>2</sub> O + 2,4-D $\cdots$ 2H <sub>2</sub> O $\rightarrow$ Me-NH <sub>2</sub> $\cdots$ 2,4-D + (H <sub>2</sub> O) <sub>4</sub>	-3.1	-3.1	-3.8	-4.7	-4.7	-5.4
Me-NH <sub>3</sub> <sup>+</sup> $\cdots$ 2H <sub>2</sub> O + 2,4-D $\cdots$ 2H <sub>2</sub> O $\rightarrow$ Me-NH <sub>3</sub> <sup>+</sup> $\cdots$ 2,4-D + (H <sub>2</sub> O) <sub>4</sub>	-2.8	-2.2	0.9	-0.6	-0.1	3.0
Me-COOH $\cdots$ 2H <sub>2</sub> O + 2,4-D $\cdots$ 2H <sub>2</sub> O $\rightarrow$ Me-COOH $\cdots$ 2,4-D + (H <sub>2</sub> O) <sub>4</sub>	-0.8	-0.8	<u>-1.5</u>	-0.2	-0.2	<u>-0.9</u>

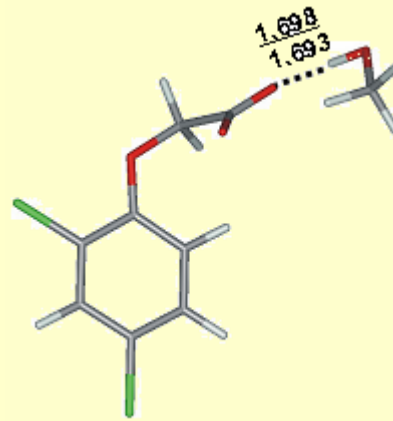
<sup>a</sup> – Me = -CH<sub>3</sub>



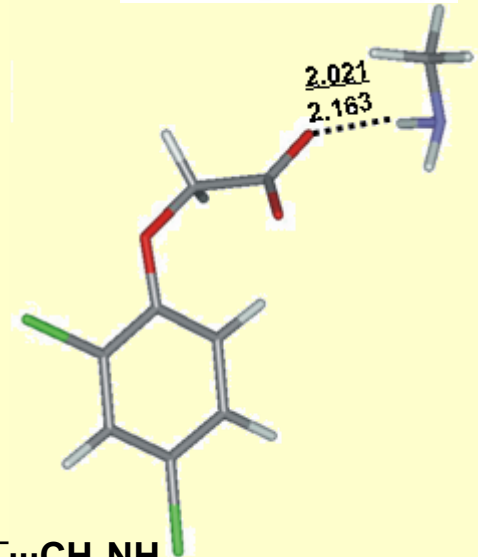
**T $\Delta$ S= -11.1 kcal/mol**  
**-0.7 kcal/mol**



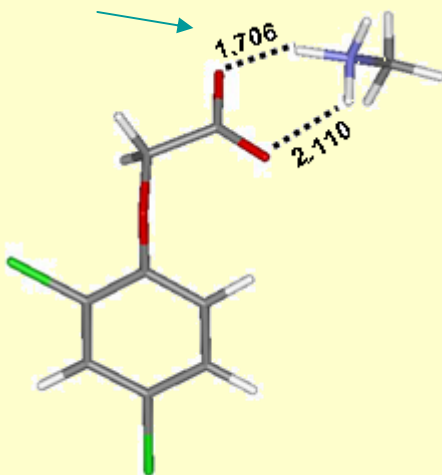
2,4D<sup>-</sup>...CH<sub>3</sub>CHO



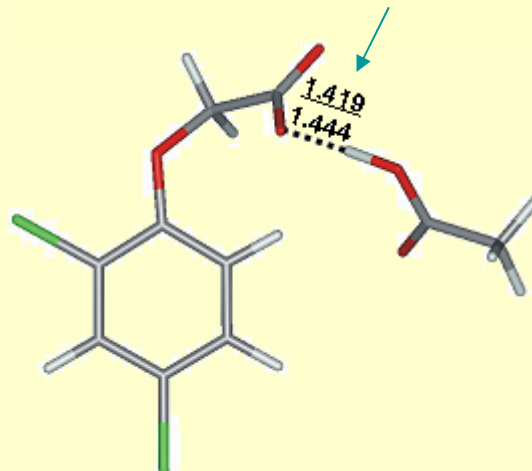
2,4D<sup>-</sup>...CH<sub>3</sub>OH



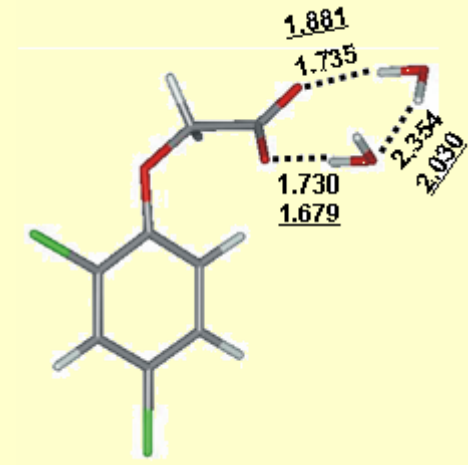
2,4D<sup>-</sup>...CH<sub>3</sub>NH<sub>2</sub>



2,4D<sup>-</sup>...CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>



2,4D<sup>-</sup>...CH<sub>3</sub>COOH



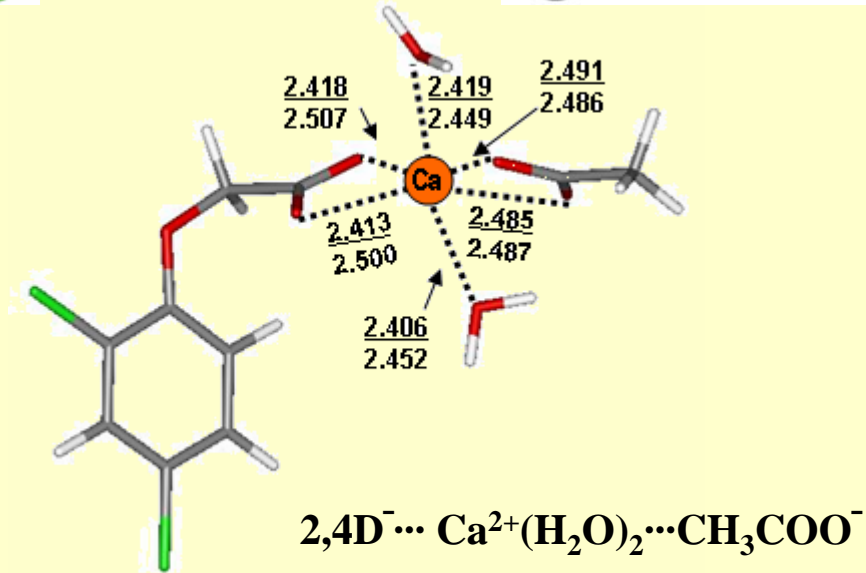
2,4D<sup>-</sup>...2H<sub>2</sub>O

Complex formation <sup>b</sup>	$\Delta E_g$	$\Delta H_g$	$\Delta G_g$	$\Delta E_{gs}$	$\Delta H_{gs}$	$\Delta G_{gs}$
$\text{Me-CHO} + 2,4\text{-D}^- \rightarrow \text{Me-CHO}\cdots 2,4\text{-D}^-$	-11.5	-9.4	-1.3	1.4	3.5	11.6
$\text{Me-OH} + 2,4\text{-D}^- \rightarrow \text{Me-OH}\cdots 2,4\text{-D}^-$	-15.3	-13.0	-4.4	-1.6	0.7	9.3
$\text{Me-NH}_2 + 2,4\text{-D}^- \rightarrow \text{Me-NH}_2\cdots 2,4\text{-D}^-$	-8.2	-6.1	1.6	2.1	4.2	11.9
$\text{Me-COOH} + 2,4\text{-D}^- \rightarrow \text{Me-COOH}\cdots 2,4\text{-D}^-$	-21.2	-19.6	-8.6	-2.4	-0.8	10.2
$2\text{H}_2\text{O} + 2,4\text{-D}^- \rightarrow 2\text{H}_2\text{O}\cdots 2,4\text{-D}^-$	-26.7	-24.0	-12.4	-3.8	-1.1	10.5
$\text{Me-NH}_3^+ + 2,4\text{-D}^- \rightarrow \text{Me-NH}_3^+\cdots 2,4\text{-D}^-$	-116.0	-115.8	-106.6	-0.6	-0.5	8.8

<sup>b</sup> – Me = -CH<sub>3</sub>

Model reaction <sup>a</sup>	microsolvation			global solvation + microsolvation		
	$\Delta E_g$	$\Delta H_g$	$\Delta G_g$	$\Delta E_{gsm}$	$\Delta H_{gsm}$	$\Delta G_{gsm}$
$\text{Me-CHO} \cdots 2\text{H}_2\text{O} + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $\text{Me-CHO} \cdots 2,4\text{-D}^- + (\text{H}_2\text{O})_4$	5.7	5.3	5.1	-1.1	-1.5	-1.7
$\text{Me-OH} \cdots 2\text{H}_2\text{O} + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $\text{Me-OH} \cdots 2,4\text{-D}^- + (\text{H}_2\text{O})_4$	1.2	0.8	0.1	-7.4	-7.8	-8.5
$\text{Me-NH}_2 \cdots 2\text{H}_2\text{O} + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $\text{Me-NH}_2 \cdots 2,4\text{-D}^- + (\text{H}_2\text{O})_4$	10.5	10.2	9.2	4.1	3.8	2.8
$\text{Me-NH}_3^+ \cdots 2\text{H}_2\text{O} + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $\text{Me-NH}_3^+ \cdots 2,4\text{-D}^- + (\text{H}_2\text{O})_4$	-88.3	-89.2	-86.5	3.1	2.2	4.9
$\text{Me-COOH} \cdots 2\text{H}_2\text{O} + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $\text{Me-COOH} \cdots 2,4\text{-D}^- + (\text{H}_2\text{O})_4$	3.9	2.5	2.8	-2.3	-3.7	-3.4
$\text{Ca}^{2+}(\text{H}_2\text{O})_6 + 2,4\text{-D}^- \cdots 2\text{H}_2\text{O} + \text{Ac}^- \cdots 2\text{H}_2\text{O} \rightarrow$ $2,4\text{-D}^- \cdots \text{Ca}^{2+}(\text{H}_2\text{O})_2 \cdots \text{Ac}^- + 2(\text{H}_2\text{O})_4$	-220.9	-221.0	-216.3	-11.5	-11.6	-6.6

a – Me= -CH<sub>3</sub>;



## CONCLUSIONS:

It has been shown that the consideration of this combined solvation model is crucial for the evaluation of chemical reaction energies;

The application of the exchange reaction showed that the neutral 2,4-D molecule is able to form stable complexes in a polar solvent environment with a large variety of functional groups;

On the other hand, the anionic form of 2,4-D is found to form stable complexes in a polar solvent like the soil solution only with hydroxyl and carboxyl functional groups;

In general, the interactions of solvated ionic species are very stable in the gas phase and in the microsolvation model;

Continuum solvation has a destabilizing effect due to a preferred solvation of the individual charged reactants as compared to the neutral or charged complexes;

The cation bridge, which is by far the most important interaction mechanism in soil, has been found to be very stable with a final  $\Delta G$  value of  $-6.6$  kcal/mol taking  $\text{Ca}^{2+}$  as example.