Supplementary Information:

Unravelling the nature of glyphosate binding to goethite surfaces by ab initio molecular dynamics simulations

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Figures



Figure S1. Potential energy of the GLP-goethite-water system along the MD trajectory of the monodentate binding motif at the 010 goethite surface plane.



Figure S2. Temperature of the GLP-goethite-water system along the MD trajectory of the monodentate binding motif at the 010 goethite surface plane.



Figure S3. Root mean square deviation (RMSD) of the change in the spatial configurations of GLP (black), goethite (red), water (blue), and the GLP-goethite-water-system (green) along the MD trajectory of the monodentate binding motif at the 010 goethite surface plane. RMSD was calculated here with respect to the initial configuration of each subsystem as well as the whole system.



Figure S4. Intermolecular distance between the GLP phosphonate O atoms and surface Fe contributed to the monodentate binding motif (a), water O atoms and different surface Fe atoms (b), and water H atoms and different surface O atoms (c) along the MD trajectory of the monodentate binding motif at the 010 goethite surface plane.



Figure S5. Intermolecular proton transfer from GLP to goethite surface (a), and water (b,c) along the MD trajectory of the monodentate binding motif at the 010 goethite surface plane.



Figure S6. Interaction energy in kcal/mol along the production trajectory between GLP and the different goethite surface planes. Red, green, black, blue, brown, cyan, violet colours are corresponding to the monodentate at 010–, bidentate at 010–, monodentate at 001–, bidentate at 001–, monodentate at 100–, bidentate at 100–, and outer surface complex at 100–goethite surface plane, respectively.



Figure S7. Spatial configuration of the starting bidentate binding motif for GLP at the 001 goethite surface plane. Here we only showed GLP with small part of the modelled surface. Labels of the GLP phosphonate O atoms and goethite Fe atoms will be used in the following figures to characterize the bidentate \rightarrow monodentate transformation.



Figure S8. Intermolecular distance between all GLP phosphonate O atoms and the interacted surface Fe atoms showing the bidentate \rightarrow monodentate transformation at the 001 goethite surface plane along the MD trajectory.



Figure S9. Focus on intermolecular distance between the GLP phosphonate O atoms (O1 & O2) and surface Fe atoms (Fe1 and Fe2) contributed to the bidentate \rightarrow monodentate transformation at the 001 goethite surface plane around the transformation process' period.



Figure S10. Intermolecular distance between the GLP phosphonate P atom and the interacted surface Fe atoms (Fe1 and Fe2) at the 001 goethite surface plane along the MD trajectory for the bidentate \rightarrow monodentate transformation case.



Figure S11. Spatial configuration of the starting monodentate binding motif for GLP at the 001 goethite surface plane. Here we only showed GLP with small part of the modelled surface. Labels of the GLP phosphonate O atoms and goethite Fe atoms will be used in the following figures to characterize the monodentate \rightarrow bidentate transformation.



Figure S12. Intermolecular distance between all GLP phosphonate O atoms and the interacted surface Fe atoms (Fe1 and Fe2) showing the monodentate \rightarrow bidentate transformation at the 001 goethite surface plane along the MD trajectory.



Figure S13. Focus on intermolecular distance between the GLP phosphonate O atom (O1) and surface Fe atoms (Fe1 and Fe2) contributed to the monodentate \rightarrow bidentate transformation at the 001 goethite surface plane along the first 4 ps of the MD trajectory.



Figure S14. Intermolecular distance between the GLP phosphonate P atom and the interacted surface Fe (Fe1 and Fe2) at the 001 goethite surface plane along the MD trajectory for the monodentate \rightarrow bidentate transformation case.

Table

surface plane	binding motif	distance [Å]			
		C–N	C-P	Fegoethite-OGLP	Fe–P
010	monodentate	1.45	1.82	1.96	3.00
	bidentate (2O+1Fe)	1.49	1.83	2.02 & 2.05	2.52
001	bidentate (1O+2Fe)	1.45	1.84	1.89 & 1.99	2.99 & 3.47
	bidentate (2O+2Fe)	1.47	1.84	1.90 & 1.91	2.76 & 2.87
100	monodentate	1.45	1.83	2.08	3.51
	bidentate (20+2Fe)	1.49	1.84	2.02 & 2.03	3.20 & 3.20

Table S1. Selected bond lengths in Å for the geometry optimized binding motifs at the 010, 001, and 100 goethite surface planes.

Notes

1. Regarding Eq. 1 in the main article

In general, the effect of water on the GLP-goethite-interaction has been taken into account during the MD simulations due to the water-GLP-goethite-interactions based on the electronic and Van der Waals interactions. However, this effect has not been considered explicitly for computing the interaction energy in Eq. 1 at each snapshot. In practice, at every snapshot the molecular system is composed of three sub-systems (fragments) involving GLP (fragment1), goethite (fragment2), and water (fragment3). Within CP2K it is possible to calculate the pair interaction energy between two fragments. According to Eq. 1 ($E_{int} = E_{GLP-goethite-complex} - (E_{GLP} + E_{goethite surface})$), we have defined GLP as the first fragment and goethite as the second fragment. The water enters only insofar as it determines the actual geometry of the interacting fragments. The interaction energy is calculated within the BSSE counterpoise correction philosophy, i.e. by performing five energy calculations as follows: total electronic energy of GLP including only the GLP basis functions (E_{GLP}^{GLP}), goethite including only the goethite basis functions $(E_{goethite}^{goethite})$, GLP including the basis functions of GLP and goethite $(E_{GLP}^{GLP+goethite})$, goethite including the basis functions of GLP and goethite ($E_{goethite}^{GLP+goethite}$), and finally GLP-goethite complex including the basis functions of GLP and goethite ($E_{GLP-goethite-complex}^{GLP+goethite}$). From these numbers one gets the interaction energy between GLP and goethite as $E_{int} = E_{GLP-goethite-complex}^{GLP+goethite} - (E_{GLP}^{GLP+goethite} + E_{goethite}^{GLP+goethite})$. Similarly, the interaction energies between GLP and water $(E_{int} = E_{GLP-water-complex}^{GLP+water} - (E_{GLP}^{GLP+water} + E_{GLP-water-complex}^{GLP+water})$ $E_{water}^{GLP+water}$)) and between goethite and water ($E_{int} = E_{goethite-water-complex}^{goethite+water} - (E_{goethite}^{goethite+water} + E_{goethite}^{goethite+water})$ $E_{water}^{goethite+water}$)) have been calculated.

For a specific GLP-goethite-water-complex model, the same box dimensions for the complete model have been used for all energy calculations' processes whether for the individual fragments (GLP and goethite) or for the GLP-goethite-complex.

2. Regarding the average interaction energy between GLP and goethite

In the previous note, we showed how to calculate the interaction energy between GLP and goethite for one snapshot. For 25 ps MD simulation, snapshots are taken every 50 fs and the corresponding interaction energy for every snapshot has been calculated. The interaction energy values along the equilibrated production trajectory (last 15 ps, see Figure S6) are averaged giving rise to only one value. This average interaction energy value represents the binding strength between GLP and goethite for a certain GLP-goethite-model along the equilibrated MD trajectory. For our GLP-goethite-models with different binding motifs and different goethite surface planes, the corresponding average interaction energy of -110 kcal/mol corresponds to the average interaction energy between GLP and goethite for M motif at the 010 goethite surface plane (see Figure 3a in the main article).