

Steric hindrance for glyphosate adsorption to metal (hydr)oxides: a novel modeling approach for organic matter-mineral interactions

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The environmental fate of the herbicide glyphosate (PMG) is determined by its favorable binding to metal (hydr)oxides.[1, 2] A major competitor for binding on metal (hydr)oxide is natural organic matter (NOM).[3] This study investigated the competitive binding between humic acids (HA) and PMG on goethite with varying pH, ionic strength, and HA surface loading in batch adsorption experiments. The PMG solution concentration increased up to 3 orders of magnitude in the presence of HA, underlining the importance of understanding the competition.

In our interpretation of the competitive adsorption, we made use of the natural organic matter charge distribution (NOM-CD) model,[4] which describes the effect of site- and electrostatic competition of NOM to oxyanions. As we found this to be insufficient to model the competitive adsorption of the larger-sized PMG, we introduced the concept of space limitation at the interface. We expanded the NOM-CD model to additionally include steric hindrance, yielding the S-NOM-CD model. By relating the space limitation to the Stern layer occupation,[5] we mechanistically substantiated the model and could predict the NOM conformation-dependent steric effect, and consequently PMG adsorption in competitive systems, using only a single adjustable parameter. Our model reveals that steric hindrance is most significant in acidic conditions, where NOM maximizes its interaction with the surface, while at high pH, NOM tends to move outwards and competition is mainly electrostatically controlled. Our study provides a new framework to include space-limitation in competitive NOM-mineral interactions, and furthermore show that NOM plays a key role in assessing the availability, mobility, and risk of PMG in the environment.

References

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