

Competitive adsorption of glyphosate and organic compounds at aluminum oxide

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Glyphosate is a commonly used herbicide that has received widespread attention due to its potential impact on the environment. After agricultural application, its fate is significantly determined by sorption to soil components, especially aluminum and iron (hydr-)oxides. However, various organic compounds present in natural systems can also affect sorption of glyphosate at minerals and thus its mobility in soils.

Glyphosate is a small organic compound carrying several functional groups, namely carboxyl ($-\text{COOH}$), amino ($-\text{NH}_2$) and phosphonate ($-\text{PO}_3\text{H}_2$) that give rise to charge but also can serve as ligands for complex formation. Nevertheless, it is generally accepted that glyphosate primarily adsorbs to soil by a similar mechanism as phosphate, i.e., through ligand exchange of its phosphonic acid moiety. As a result, glyphosate and phosphate potentially compete for same adsorption sites at minerals. Notably, it remains unknown whether the $-\text{COOH}$ of glyphosate also interacts with the mineral surface and how the adsorption of glyphosate would change in the presence of organic compounds.

In this study, we investigated the competitive effect of various organic compounds on glyphosate adsorption at aluminum oxide (Al_2O_3). To elucidate the effects of different structural features on adsorption and surface complexation, (aminomethyl)phosphonic acid (AMPA), aminotris(methylenephosphonic acid) (ATMP), phthalic acid (PA), glucose-6-phosphate (GP) and glycerophosphate disodium (GD) were selected as target competing compounds. We applied a combination of batch ad- and desorption experiments, liquid-phase analyses, speciation modeling and infrared spectroscopy to systematically evaluate the extent and mechanisms of competitive adsorption.

In general, we propose that both $-\text{COOH}$ and $-\text{PO}_3\text{H}_2$ interact with Al_2O_3 . Organic compounds with $-\text{COOH}$ as only functional group did not affect glyphosate adsorption. Consequently, the saturation of surface functional groups that interact with $-\text{PO}_3\text{H}_2$ did not prevent further adsorption via surface sites interacting with $-\text{COOH}$ moieties. The strength of competitive adsorption of organic phosphonates was related to their number of $-\text{PO}_3\text{H}_2$ functional groups. For a given number of P-containing functional groups, the adsorption of organophosphates, however, was stronger than that of organic phosphonates. Furthermore, desorption experiments revealed some hysteresis effects in that desorption from occupied surface sites was retarded or inhibited.