The Herbicide MCPA is Enhancing Mobility of Copper in Soil

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Crops designed and genetically modified to be tolerant to smart herbicides have led to a boost in soil agrochemicals application. Carboxylic acid herbicides such as 4-chloro-2-methylphenoxyacetic acid (MCPA) are worldwide the 2nd most widely applied herbicide class after glyphosate because of claimed favorable toxicological properties. In MCPA, one methyl group of the phenoxy moeity is replaced by a chlorine atom, increasing its polarity and hence solubility in pure water. Therefore, pure MCPA is relatively weakly retarded by soil at ambient pH values [1]. However, a fact yet neglected is that the residual carboxylate group of MCPA has strong chelating capacity with Cu and other trace metals to form dissolved bidentate complexes. This is of major concern, since the application of Cu-containing fertilizers and of Cu-bearing fungicides in the past have steadily increased soil Cu content. Copper is less mobile in soil at ambient pH values, but its mobility could be enhanced drastically if applied together or in sequence with the herbicide. On the other hand, Cu-MCPA interactions may also facilitate immobilization via co-adsorption processes by ternary surface complex formation as has been shown already for the case of glyphosate. Our batch equilibrium experiments and CD-MUSIC adsorption modeling, however, have shown that the latter is not retarding Cu-MCPA. An overall good match with experimental data on Cu adsorption in presence of MCPA was found when the Cu adsorption model is combined with the dissolved Cu-$MCPA_2$ complex formation constant. The Cu-$MCPA_2$ complex becomes highly insoluble (rather than adsorbed) and hence immobile at pH values above 6. In the pH range 4 – 6, i.e. in acidic soils, there is a mobility window where Cu may become mobilized in presence of the herbicide. We used this mobility window for soil column tests at pH values of 5-6, where the high mobility of Cu in presence of the herbicide could be visualized by radioisotope labeling with ^{64}Cu and positron emission tomography. Movies will be shown of the rapid Cu migration in the soil column as output of the sophisticated PET molecular imaging experiments.

[1] Kersten et al. (2014) *Environ. Sci. Technol.* **48**, 11803.