Determination of glyphosate in soils - analytical considerations

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Glyphosate is the most commonly used herbicide worldwide with almost one million tons applied in 2014. At environmental pH it is anionic, forms chelate complexes with bi- and trivalent metal cations and readily sorbs to oxidic (soil) minerals via its phosphonic acid moiety. The impact of these parameters on sorption and thus mobility and bioavailability are not yet well understood. This lack of knowledge about its environmental fate and relevance is in sharp contrast to its extensive use.

Due to its high polarity and charge, glyphosate is not well suited for conventional chromatographic techniques and thus commonly derivatized prior to analysis. In contrast, our new method based on capillary electrophoresis-mass spectrometry is able to directly quantify glyphosate and reaches high selectivity and matrix tolerance with a separation at pH 2.8. Contrary to most carboxylic acids, glyphosate is still negatively charged under these conditions. We show that glyphosate can be directly analyzed in acidified soil extracts with high precision and limits of detection in the low µg/L-range without any purification or preconcentration.

With this method we studied the impact of critical parameters in soil known to affect sorption: mineralogical composition, grain size distribution and organic content. For this, soil from the Ammer Valley near Tübingen, pure clay minerals and mineral oxides present therein were spiked with glyphosate. Different extraction sequences with varying pH and phosphate concentration were applied and compared to total glyphosate sorption to better understand glyphosate's sorption specificities. We show that glyphosate extraction requires strongly basic conditions and competing phosphate (both $c > 0.05$ mol/L) to achieve highest recovery and reduce the influence of glyphosate chelation events. Recoveries up to 90 % for soil samples with initial glyphosate concentrations of 100 µg/kg were achieved. Our new method is currently used to understand glyphosate's biodegradation potential in microcosm studies with the same soils.