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Introduction

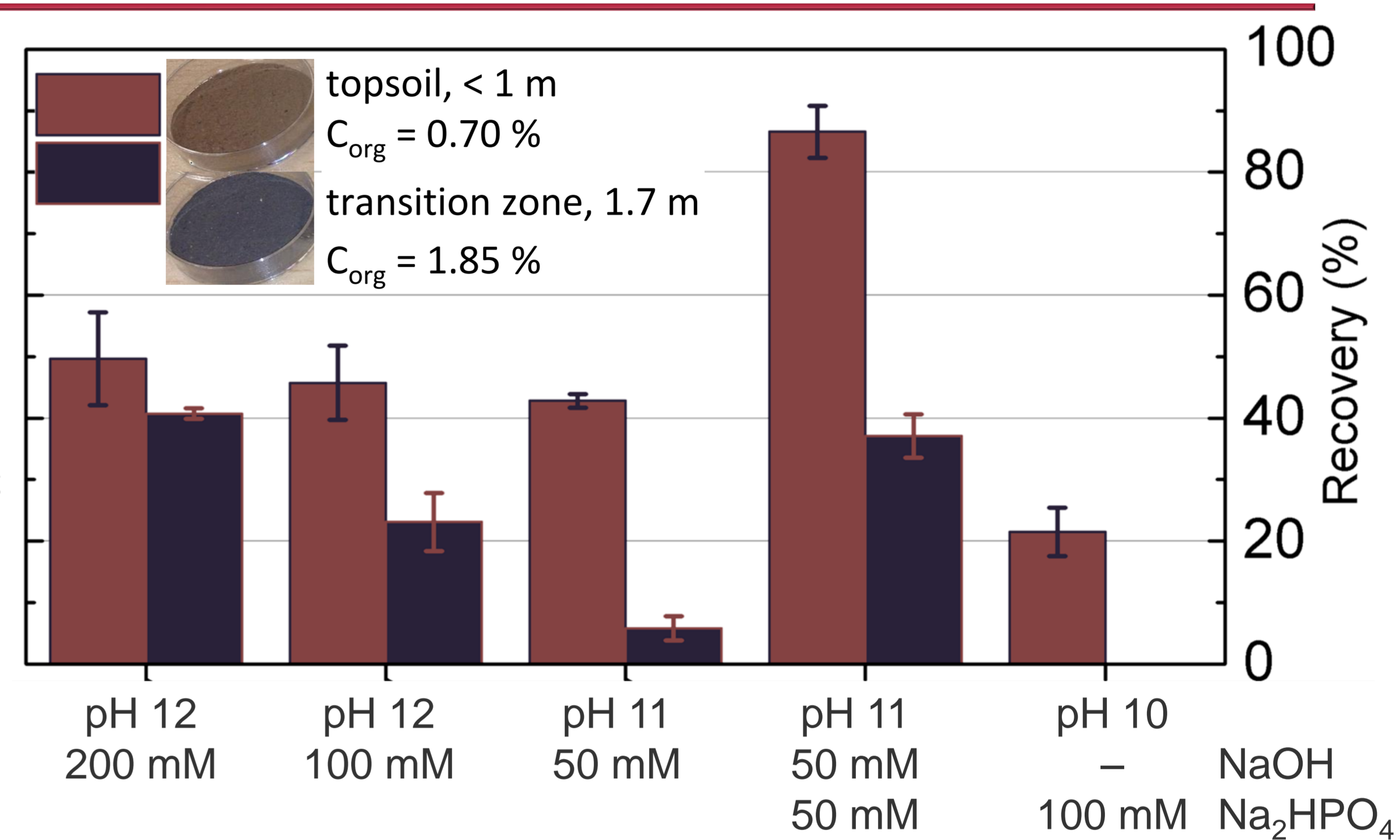
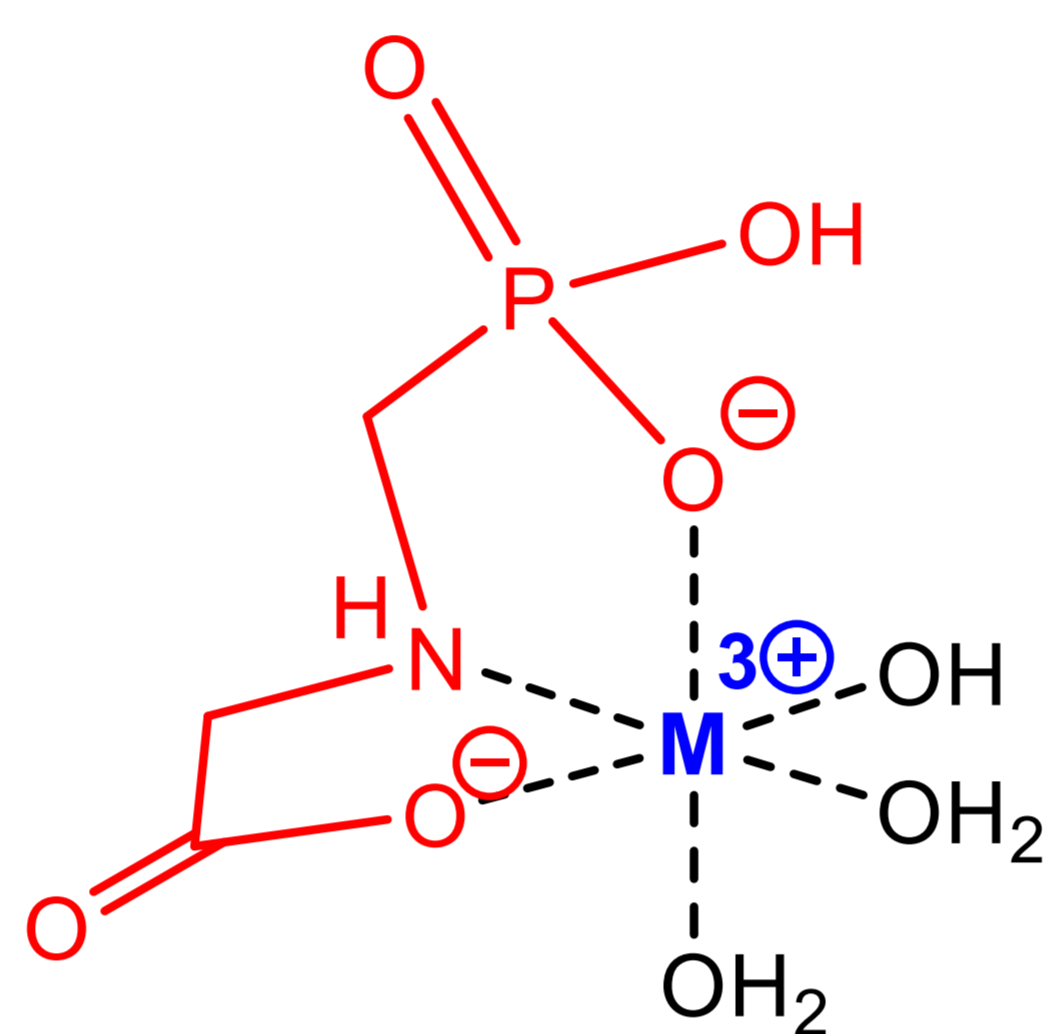
Glyphosate is the most frequently used herbicide worldwide, due to its low toxicity to mammals, strong sorption to soil, low leakage to ground water, and fair biodegradability. It is doubly negatively charged at environmentally relevant pH, forms chelate complexes, and readily sorbs to soil minerals, predominantly mineral oxides via its phosphonic acid moiety. To better understand glyphosate degradation, interdependencies of speciation (complexed and sorbed), bioavailability, and microbial communities must be investigated. Especially a linkage between mobility, bioavailability and microbial transformation is missing. Therefore, sequential and quantitative extractions are applied to soils and minerals, and linked to degradation studies using different microcosms in soils.

Conclusion

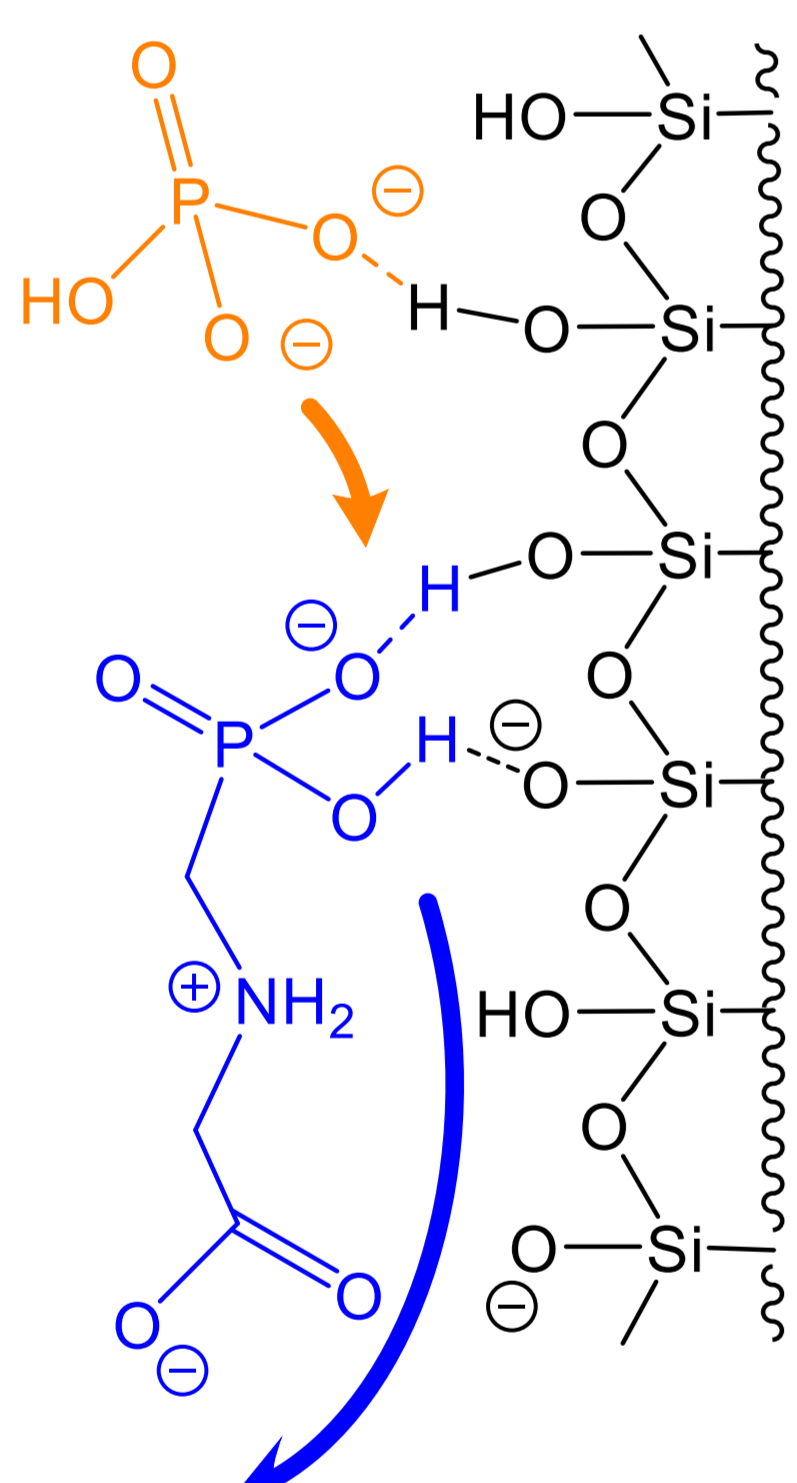
- A direct, derivatization-free and highly matrix tolerant CE-MS method for glyphosate analysis was developed and validated for direct analysis of soil sample extracts despite high contents of organic carbon.
- Some minerals already released bound glyphosate at pH 7 (NaCl).
- Specific phosphonate binding sites in minerals can be assumed by phosphate competition.
- Extraction of glyphosate from soil required strong base and phosphate.
- Degradation of glyphosate to AMPA was observed, but indicates different kinetics, possibly dependent on bioavailability.
- Half-lives of glyphosate between 7 and 20 days for different time segments were determined.

Optimized soil extraction

- High organic carbon content requires high pH
- Phosphate addition increased glyphosate extraction significantly
- Chelate complexes of divalent cations do not influence quantification
- Phosphate precipitated trivalent cations, facilitating separation and quantification
- Highest recovery (90 %) for topsoils using 50 mM NaOH and Na₂HPO₄
- Acidified extracts were injected directly and analyzed with CE-MS
- Recovery for glyphosate: 78–84 % (0.1–10 mg/kg on soil, LOD of 0.03 mg/kg)
- Recovery for AMPA: 93–112 % (0.26–2.6 mg/kg on soil, LOD of 0.1 mg/kg)

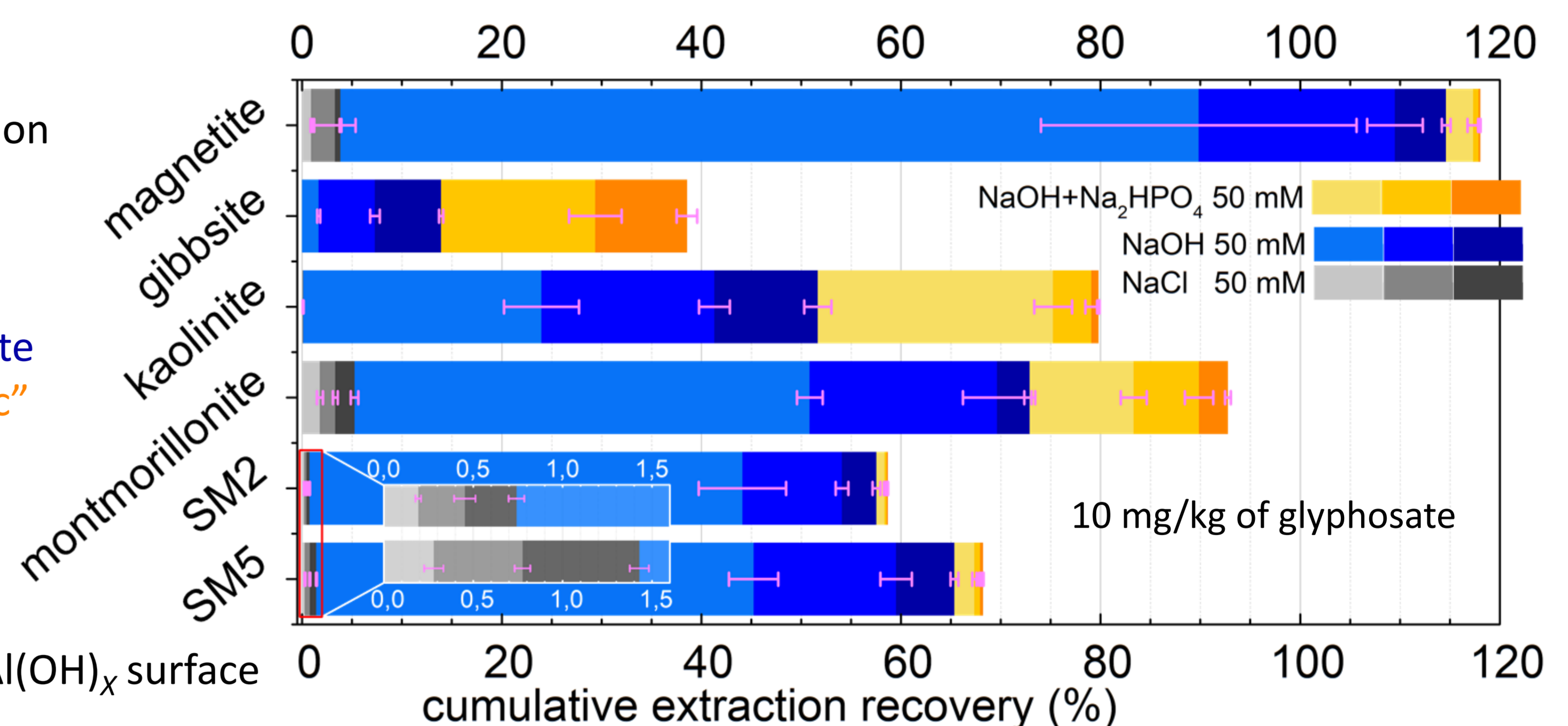


Different glyphosate pools

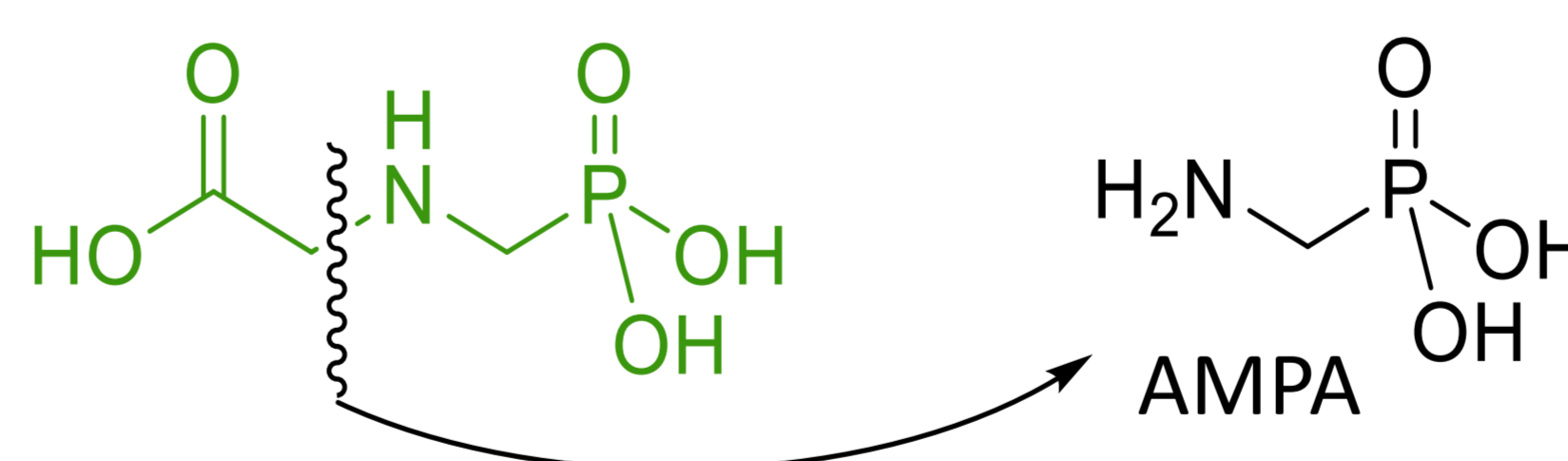
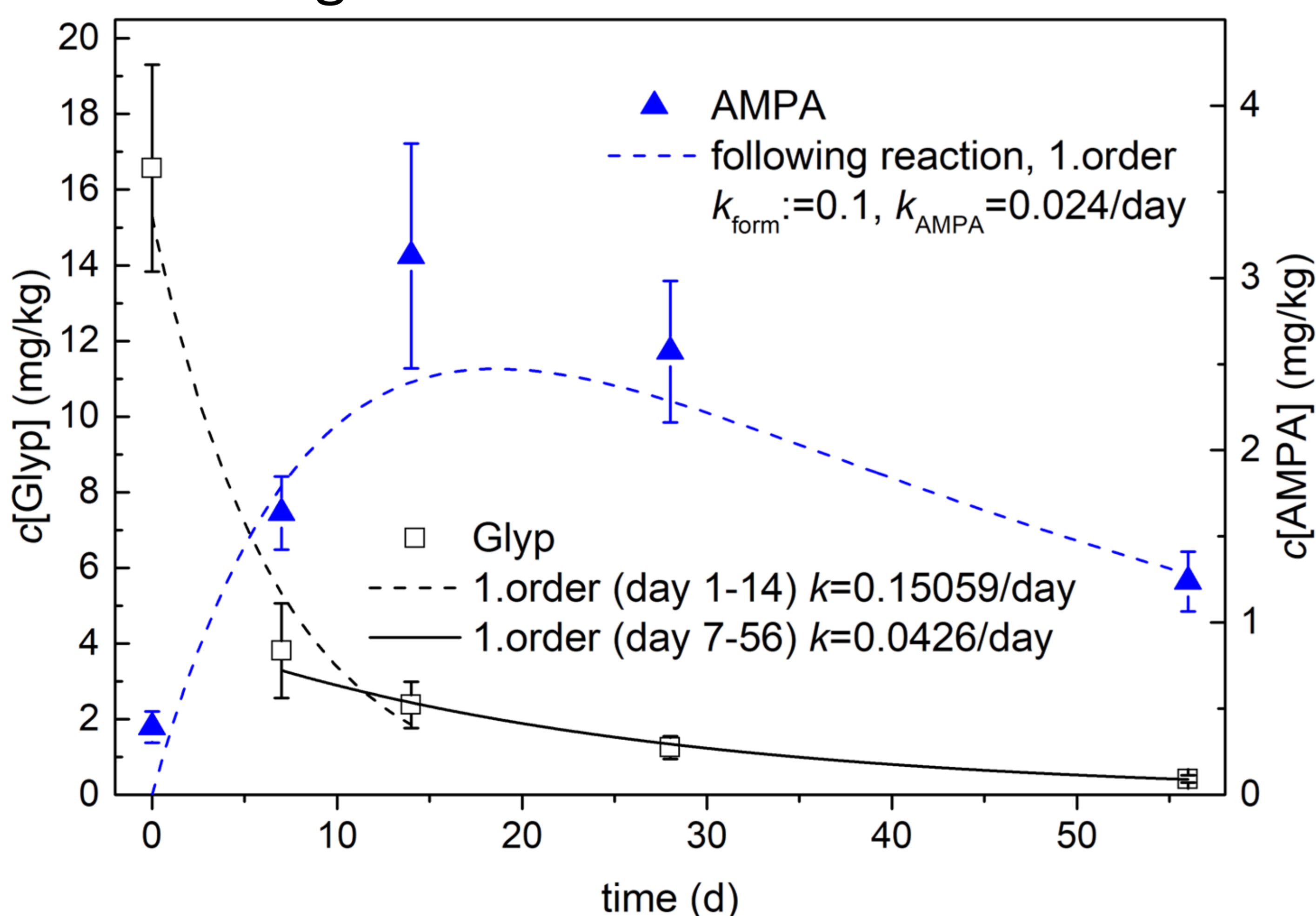


Sequential glyphosate extraction

- Extraction ratio soil:solution 1:3, 30 min agitation
- Different extraction efficiencies indicate:
 1. NaCl, pH 7: readily desorbed glyphosate, mobile fraction at environmental pH
 2. NaOH, pH 11: alkaline extractable glyphosate
 3. NaOH + Na₂HPO₄, pH 11: "phosphateophilic" sorption sites
 4. "Glyphosateophilic" sorption sites
- Significant mobile fraction at environmental conditions only on magnetite and 2:1 silicates
- Poor recovery from gibbsite, probably due to Al(OH)_x surface



Biodegradation



Initial glyphosate concentration of 15 mg/kg, 60 % water filled pores, 20 °C and sampled five times within 56 days.

- Degradation rate of glyphosate seems to be strongly time dependent, it cannot be described by 1st or 2nd order.
- Formation and degradation of AMPA was observed with maximum concentration at 3.6 mg/kg.
- Fast glyphosate degradation at days 0–14 with half-life of 7 days, slow degradation at days 7–56 with half-life of 23 days.
- Different kinetics indicate:
 1. Shifts of microbial communities
 2. Adaption of gene expression to glyphosate availability and
 3. Several pools of glyphosate with different bioavailability
- Sequential extraction indicates readily bioavailable glyphosate pool
- Degradation velocities and results from sequential extraction corroborate hypothesis of limited bioavailable fractions