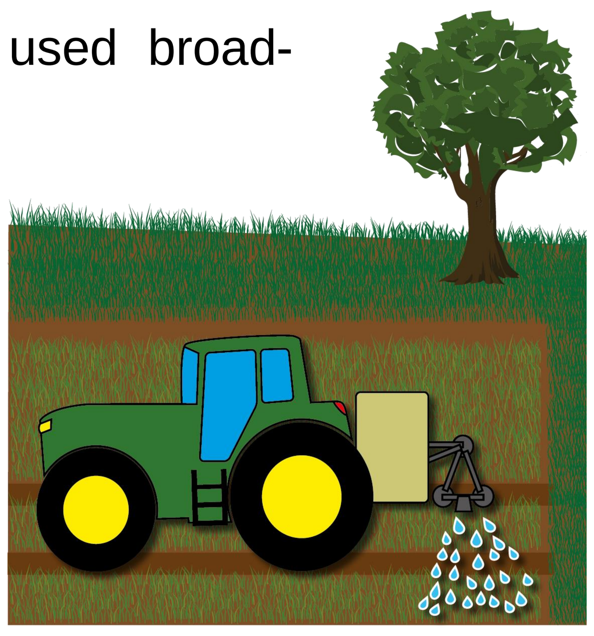
Environmental fate of glyphosate analyzed by capillary electrophoresis – mass spectrometry

Benedikt Wimmer, J. Schlögl, M. Schwientek, A. Langarica-Fuentes, J. Wirsching, E. Kandeler, S. Kleindienst, S. Haderlein, C. Huhn

Introduction

Glyphosate (GLP): most frequently used broad-band herbicide world wide

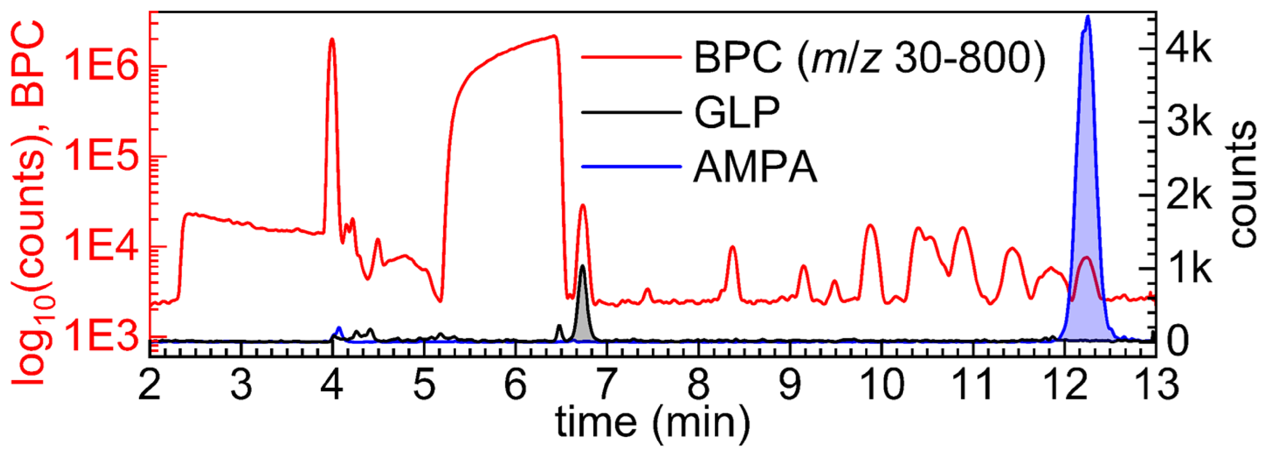
- applied on plant foliage
- strong sorption onto oxidic soil minerals → **immobilization**
- low bioavailability for microbial degradation
- main degradation product: AMPA (aminomethylphosphonic acid)



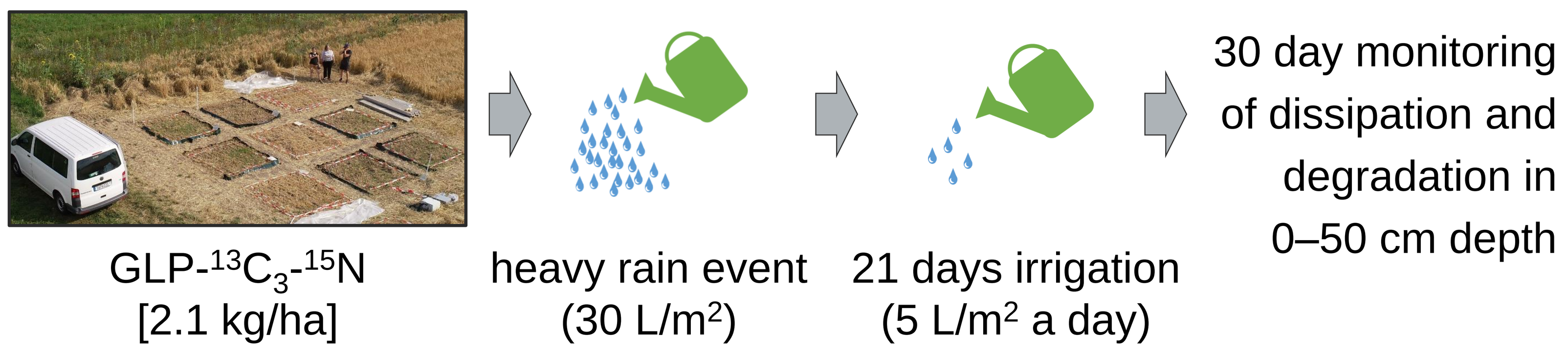
CE-MS method

Extreme physicochemical properties → incompatible with commonly used multiresidue methods

- derivatization-free method
- BGE buffer at pH 2.8
- separation voltage: –30 kV
- high matrix tolerance
- Q-ToF MS quantification
- LOD: 10 and 30 µg/kg for GLP and AMPA

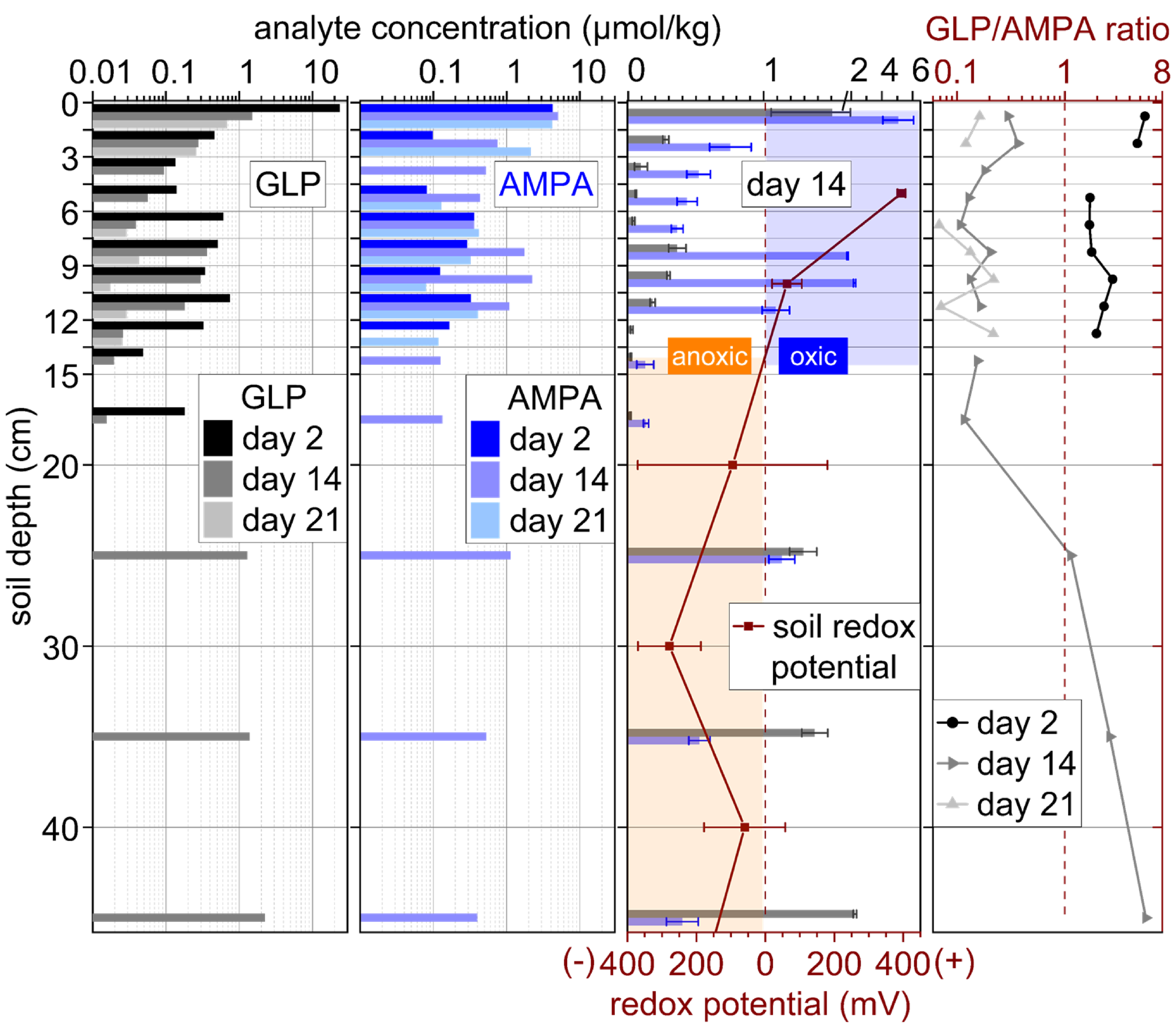


GLP mobility in soils

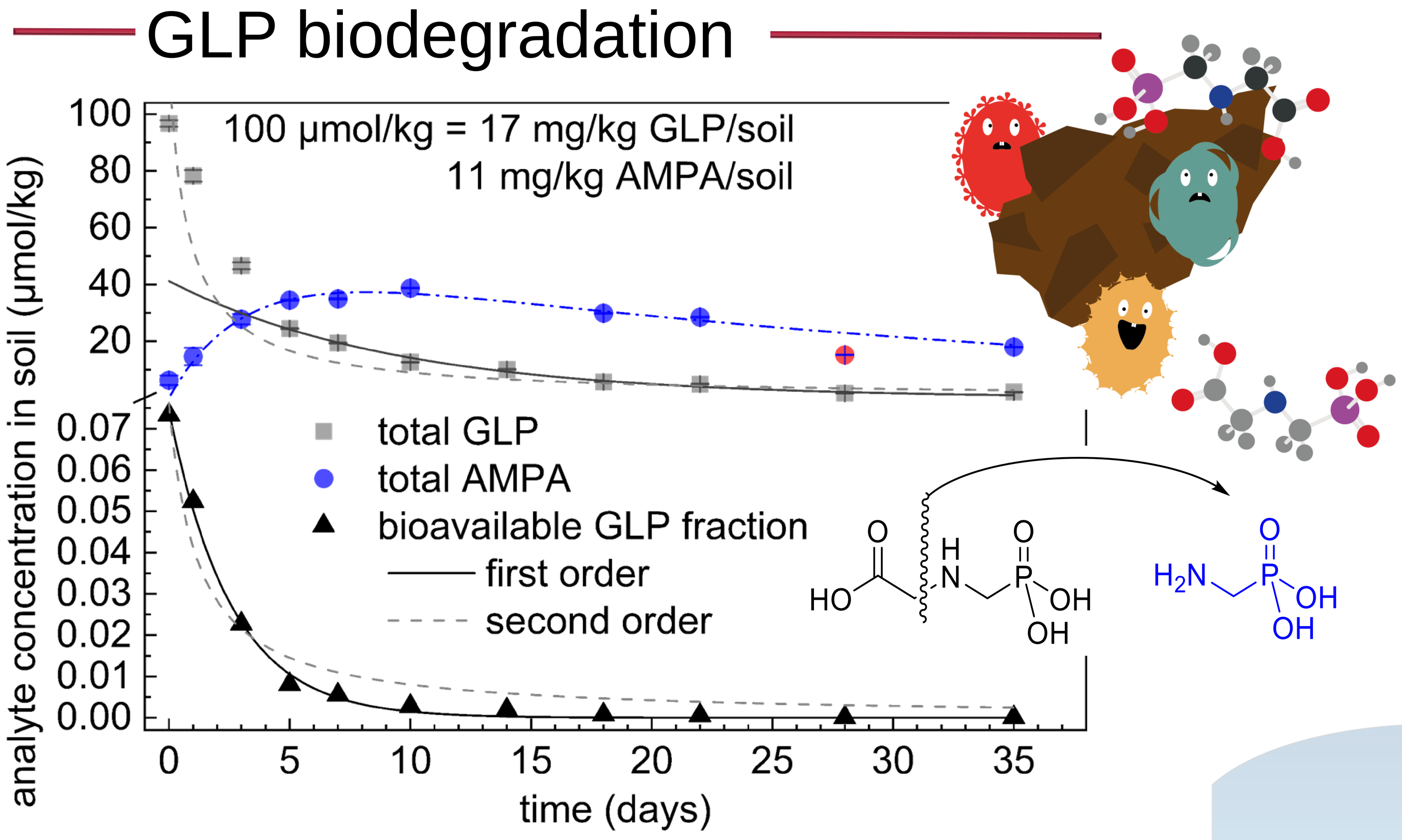


- minor dissipation into deeper soil zones by **particle-facilitated transport**:
  - root canals (15 cm depth)
  - shrinkage cracks (>50 cm depth)
- shrinkage cracks (day 14) cause increasing GLP concentrations in greater depths (GLP/AMPA-ratio similar to day 2)

→ **low GLP degradation due to anoxic redox potential**



GLP biodegradation

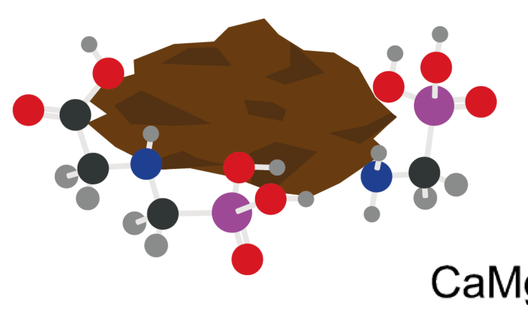


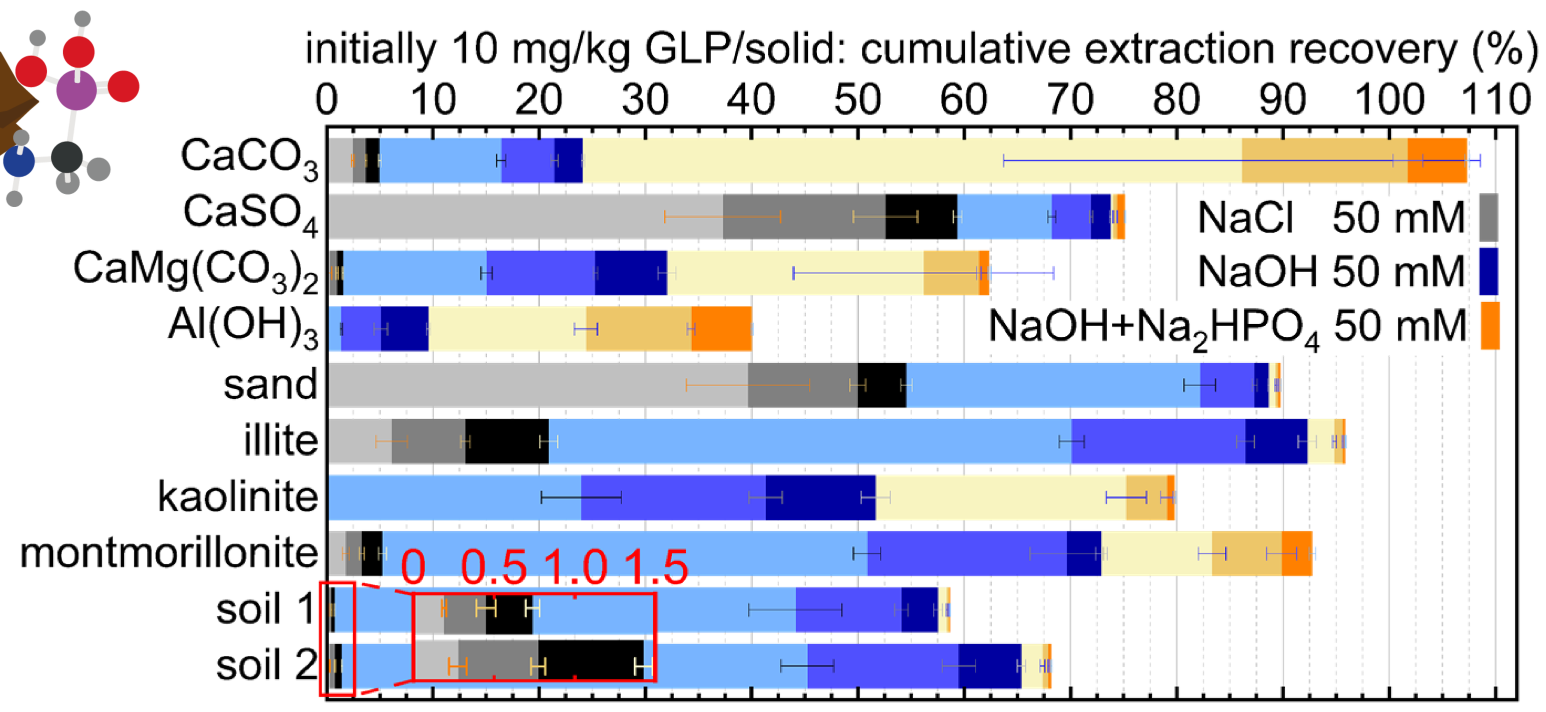
Complex degradation kinetics:

- >3 mg/kg: fast ($t_{1/2}$<5 days)
- <3 mg/kg: slower ($t_{1/2}$>10 days)
- isotherm data unveil strong sorption (>99.9 %)
- considering only bioavailable GLP fraction:

→ **single fit over a large concentration range possible ($t_{1/2}$<2 days)**

GLP sorption on different minerals





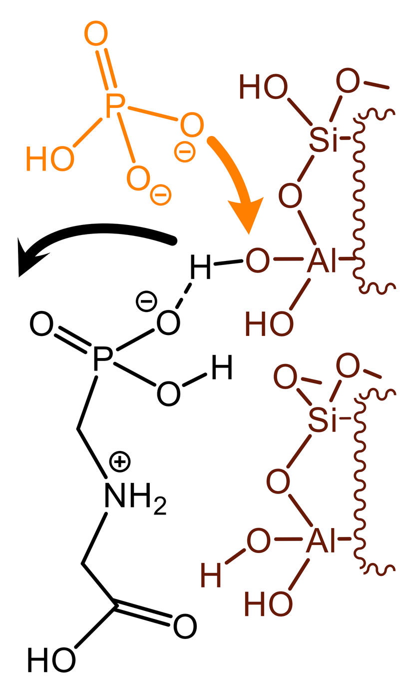
Sequential extraction revealed different GLP pools:

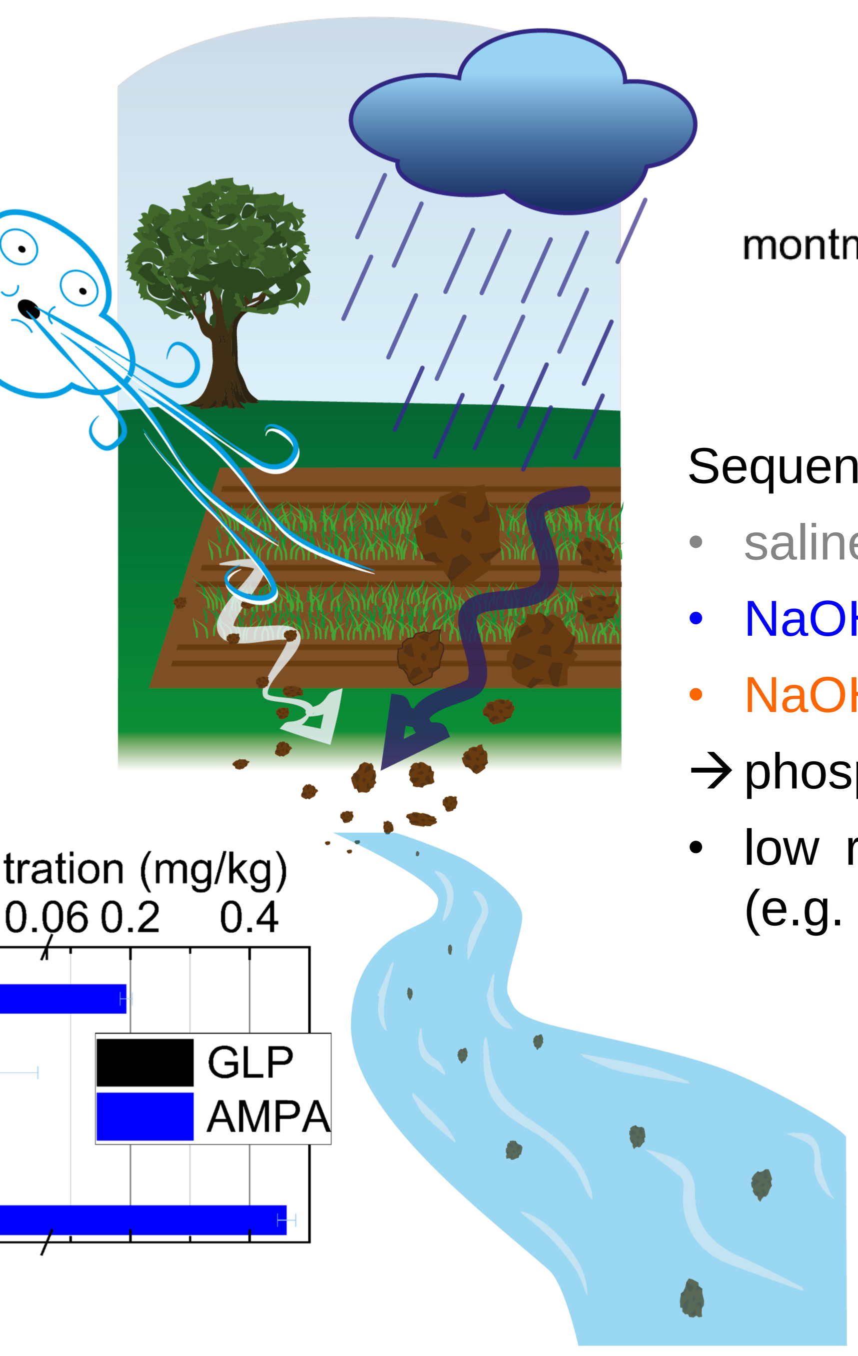
- saline extraction: readily desorbable GLP
- NaOH extracts: semi-strong sorption
- NaOH and phosphate: most of residual GLP

→ phosphate competes with GLP to binding sites

- low recoveries from Al-OH containing minerals (e.g. kaolinite)

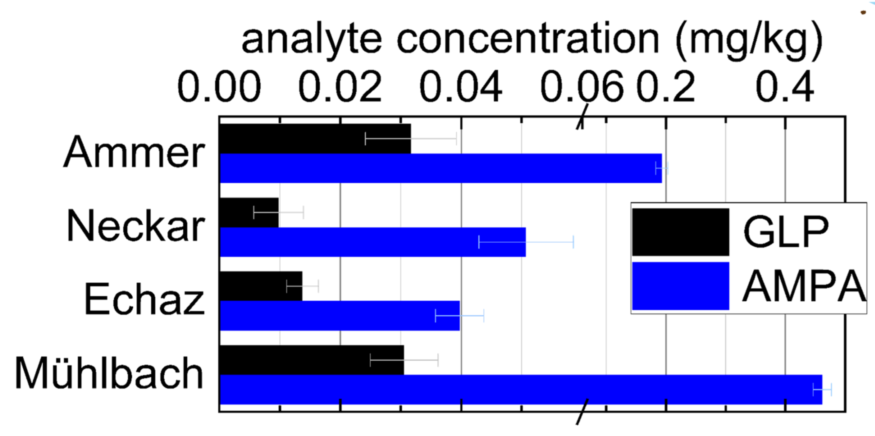
→ **results aid understanding GLP mobilization in the environment upon**
- **P-fertilization**
- **particle-facilitated transport**

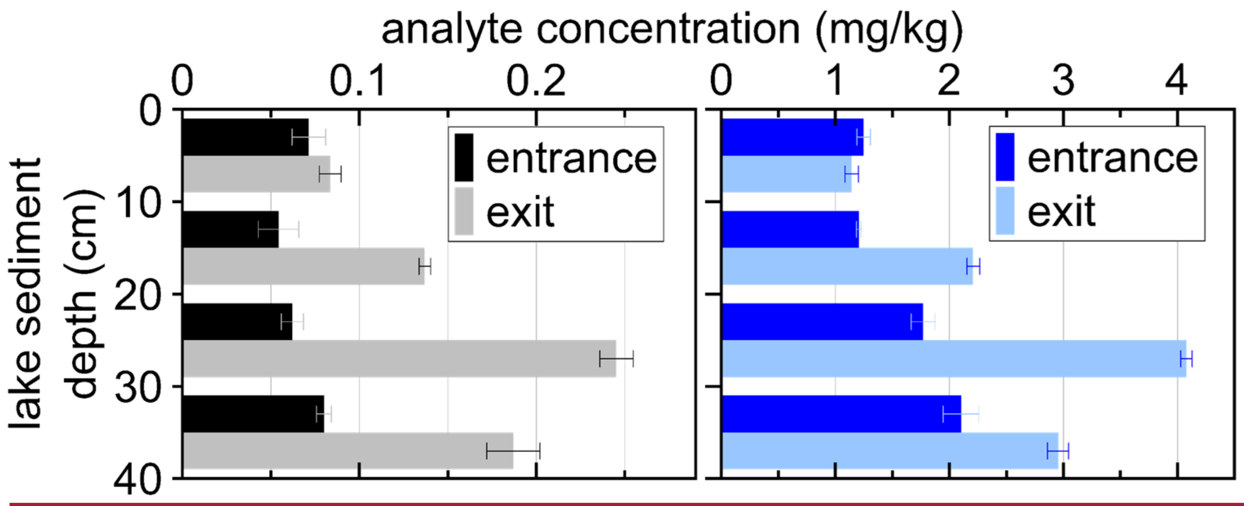




GLP in aquatic sediments

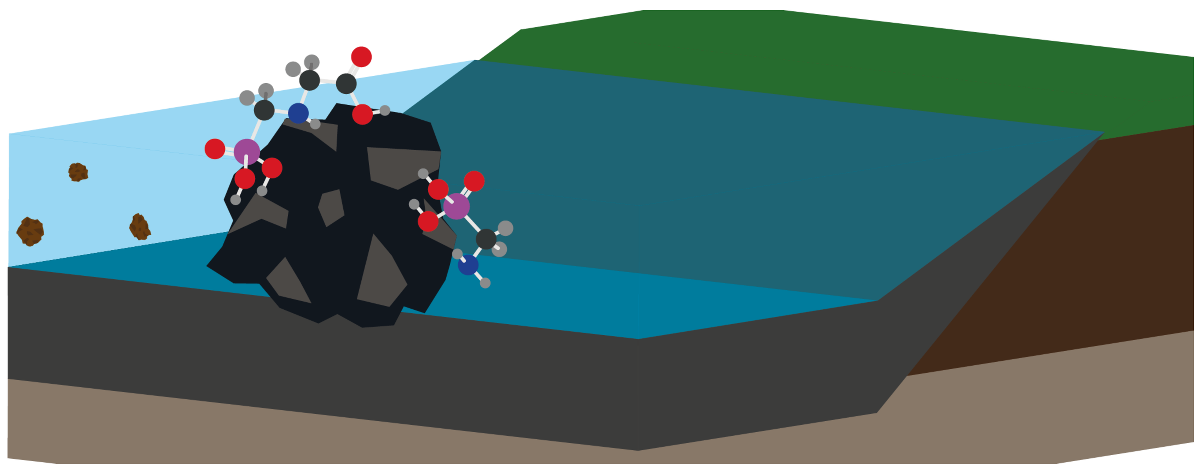
- sediments from Neckar-tributaries around Tübingen
- sediment cores from inlet and outlet in an artificial pond in Tübingen





- 4 of 7 river sediments tested positive
- bottom sediment layer from pond may originate from the 1970s

→ **GLP and AMPA are potential legacy compounds**



Universität Tübingen · Faculty of Science; **Chemistry Department – Institute of Physical and Theoretical Chemistry**; Auf der Morgenstelle 18 · 72076 Tübingen · Germany · Phone: +49 7071 29-75656
benedikt.wimmer@uni-tuebingen.de

Universität Stuttgart · TUM · HelmholtzZentrum münchen Deutsches Forschungszentrum für Gesundheit und Umwelt · HELMHOLTZ ZENTRUM FÜR UMWELTFORSCHUNG UFZ · DFG