Small-scale spatial variability of phenoxy acid mineralization potentials in transition zones with a multidisciplinary approach

The phenoxy acid group of herbicides is widely used to control broadleaf weeds, and it contaminates groundwater and surface water by leaching from agricultural soil or landfills. Due to the distinct vertical and horizontal gradients in nutrients and hydrologic exchange in transition zones, the challenge of small-scale spatial variability occurs in terms of microbiological and physicochemical properties.

We used genomic- and metagenomic-based approaches to reveal the effects of long-term phenoxy acid in situ exposure on the small-scale spatial variability of herbicide mineralization potentials in two transition zones, (1) the interfaces of unsaturated and saturated zones and (2) groundwater and surface water. Small-scale spatial variability of phenoxy acids was previously shown in topsoil; however, such small-scale studies are scarce in subsurface environments. We therefore studied the factors shaping the centimetre-scale vertical variability of phenoxy acid degradation in the interface of unsaturated and saturated zones. We demonstrated more even centimetre-scale vertical distribution of MCPA mineralization potential than that of 2,4-D at the concentration of 1 mg kg⁻¹, and the mineralization activity was linked to the abundance of tfdA genes involved in phenoxy acid degradation depending on the MCPA leaching from the overlying agricultural soil expressed as long-term in situ MCPA exposure. Knowledge on the small-scale variability of mineralization potential is very important to predict the fate and transport of herbicides in aquifer sediments. Due to a more widespread mineralization potential, we used MCPA as a model herbicide to determine the effects of herbicide concentration and additional carbon source on the centimetre-scale vertical distribution of mineralization potential along the unsaturated-saturated zone interface. We determined higher MCPA degradation activity at environmentally relevant concentrations (~15 μg kg⁻¹) compared to high concentrations (10 mg kg⁻¹) indicating the greater number of bacteria adapted to low MCPA concentration. We further showed that the addition of external carbon sources such as soil extract and benzoic acid could stimulate cometabolic degradation in the ring structure rather than the carboxyl group of MCPA. These findings might be important to develop bioremediation strategies for slightly contaminated subsurface environments. Old landfills are major sources of multiple contaminants detected in groundwater and surface water. In this PhD thesis, the mineralization potentials of phenoxy acids in landfill-impacted groundwater-surface water interface were determined. The phenoxy acids were mineralized to different extents in response to changing herbicide mass discharges determined by multiplying the specific groundwater discharge with herbicide concentrations. The differences in mineralization potentials were linked to the initial abundance of tfdA gene classes. The Monod-based kinetic model confirmed the role of initial abundance of tfdA gene classes in the different mineralization potentials of discharge zones. Understanding of the natural attenuation potential of groundwater-surface water transition zones is important for stream water protection. In landfill-impacted groundwater-surface water interface, we further analyzed bacterial communities with a combined genomic-metagenomic approach. Principal component analysis disclosed the clustering of bacterial diversity determined by terminal restriction length polymorphism and 16S rRNA amplicon pyrosequencing according to discharge zones. This comprehensive analysis indicated that specific phenoxy acid degraders proliferated in the streambed sediments in response to changing discharge rates of landfill-phenoxy acids; and the bacterial communities differentiated after mineralization at environmentally relevant and higher concentrations. Our results suggested that the clustering of bacterial communities depending on the landfill impact could be used as microbial ecological indicators for more advanced risk assessment analysis. In conclusion, this PhD thesis provided information about the mineralization potential of phenoxy acids depending on the long-term in situ herbicide exposure and bacterial ecology. The findings based on our multidisciplinary approach including engineering, genomics/metagenomics, bioinformatics and multivariate statistics could contribute to develop novel bioremediation strategies in the future.