

Biotransformation of copper along redox gradients in polluted wetland sediments

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Knowledge of copper (Cu) biotransformation along redox gradients in polluted wetland sediments is scarce. We evaluated the impact of biogeochemical processes on the Cu cycle in wetland sediments for 520 days in Winogradski columns.

Photosynthetic algae released dissolved oxygen in the water overlying the sediments while sulfide and ferrous iron concentrations increased with depth in the sediments. Sequential extraction revealed that the chemical composition of the sediments, including Cu distribution, changed with depth and could be related to TEAPs. Cu partitioning into the residual phases of the wetland sediments increased over time from <39% to >90%. Cu became enriched at the 6-8cm sediment depth and the stable isotope ratios changed compared to the initial sediment conditions ($\delta^{65}\text{Cu}_{\text{initial}} - \delta^{65}\text{Cu}_{6-8\text{cm}} = -0.19\text{‰}$). This suggests that isotopically heavier Cu was released and accumulated during sediment ageing, which will be confirmed with porewater analysis.

Together, the results highlight the reductive dissolution of Fe oxy(hydr)oxides with concomitant release of Cu bound to Fe-bearing phases, although re-oxidation of reduced Cu^+ species at the oxic water-anoxic sediment interface cannot be excluded. Microbially mediated processes altered the geochemical composition of aged anoxic sediments, thereby highlighting the dominant role of microorganisms in controlling the biogeochemistry of trace metals. Analysis of the microbial composition using high-throughput sequencing techniques in the future will help to elucidate the relationship between biogeochemical processes, Cu transformation and bacterial community change along the redox gradients.