

Inadvertent Trace Metal Mobilization during Distributed Stormwater Collection-Managed Aquifer Recharge (DSC-MAR): Impacts of Alternating Wet-Dry Cycling, Subsurface Heterogeneity, and Carbon Availability

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Groundwater over-pumping and drought have depleted aquifers across California. One strategy to increase groundwater storage is DSC-MAR, where excess surface runoff is diverted into aquifers, typically through infiltration basins or spreading grounds. When alternative water sources are used (e.g., stormwater, agricultural runoff), infiltrating water can have high concentrations of nitrate. The use of carbon-based permeable reactive barriers (PRBs) within DSC-MAR basins can remove nitrate from recharge water by stimulating anaerobic microbial processes. However, these same conditions can enhance the mobilization of geogenic metals, like arsenic and manganese. Currently, the fate and transport of solubilized metals within redox fluctuating DSC-MAR systems is poorly understood. In this work we employ a novel synchrotron-based flow-through reactor system to investigate how repeat wet-dry cycling in the presence of PRB materials may alter solid phase metals release, distribution, and transformation within DSC-MAR basin soils, when compared to no PRB controls. Reactor systems were deployed at the Stanford Synchrotron Radiation Lightsource (X-ray fluorescence rapid-imaging beamline 7-2), allowing for the collection of coupled temporal effluent chemical and solid-phase metals speciation and spatial distribution data. Reactors were packed with active DSC-MAR basin soils, including a mixture of coarse and fine grains. Reactors underwent three cycles of 11-days flow with nitrate spiked synthetic stormwater followed by an 11-day dry-down. PRB added reactors released a pulse of dissolved organic carbon upon beginning the initial flow-cycle, accompanied by rapid nitrate removal. Control systems showed less efficient nitrate removal over the initial flow-cycle and

released pulses of elevated effluent nitrate upon initiating flow during each subsequent cycle. In both PRB and control systems, manganese and arsenic release demonstrated a cyclic increasing solubilization pattern throughout flow-cycles, reaching concentrations that exceed regulatory limits. Effluent arsenic and manganese concentrations were mostly comparable between treatments but were elevated in PRB systems throughout the initial flow-cycle. Study results have the potential to aid in methods development for reactor studies linking aqueous and solid phase data collection and generate mechanistic knowledge to inform application decisions regarding basin design and implementation. Additionally, results can enhance the capacity of predictive modeling regarding the potential for inadvertent metals release during DSC-MAR.