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# Cycling of major and trace elements in an irrigated dryland critical zone: redox, solubility and soil texture

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Dryland ecosystems are characterized by water scarcity, and their soil development is dominated by formation of secondary phases like pedogenic carbonate and salts. Irrigation modifies not only water and carbon dynamics of the dryland critical zone when natural fields are converted to agroecosystems, but also the mobility of major and trace elements. This study focused on a typical flood-irrigated pecan orchard at far west Texas in the Rio Grande valley to investigate the hydrological, geochemical and biological controls on transport and retention of salts, nutrients and trace metals. We combined chemistry of major and trace elements in the soils (sequential extraction for the water-soluble salt fraction and acid leachable pedogenic carbonate fraction) and in water samples along the flow paths (irrigation water, soil water and shallow groundwater), and employed sensors to monitor the soil conditions (soil moisture, salinity, $pO_2$, temperature), and fluctuation of groundwater levels, and its salinity (as EC).

Our results identified that both geochemical factors (mineral solubility, redox) and extrinsic factors (soil texture, water availability) are important in governing the elemental mobility. For example, irrigation water is high in TDS and at equilibrium with respect to calcite. Intensive evaporation especially in clayey soils concentrates the soil solution and drives the formation of pedogenic carbonate, sequestering dissolved $Ca^{2+}$ preferentially relative to soluble $Na^{+}$. Interestingly, $Mn^{2+}$, $Zn^{2+}$ and phosphate ($PO_4^{3-}$) co-precipitate with $CaCO_3$ limiting bioavailability of these nutrients in soils. Coupled flood irrigation and slow infiltration of soil water in clayey soils created a “perched” water table and temporally led to $O_2$ depletion and reducing conditions, controlling the mobility of redox sensitive elements such as Fe and V, and even promoting anaerobic respiration. Our study highlights that agriculture in drylands has modified the water cycles by not only diverting river water for irrigation at the watershed scales but also modifying the water quality of river water through return flow. However, mobility and retention of many chemical elements is uniquely different depending on geochemical and hydrological conditions with important agroecosystem implications on soil salinity, nutrient uptake and groundwater quality.