

BIOGEOCHEMICAL CONTROLS ON NATURAL AND ANTHROPOGENIC GROUNDWATER CONTAMINANTS IN CALIFORNIA'S CENTRAL VALLEY

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INTRODUCTION

The Central Valley of California is one of the most agriculturally productive regions of the world, relying on groundwater to support its domestic, municipal, and agricultural water needs. More than one million people in the region rely on groundwater as their primary drinking water source, and the highly productive agricultural region relies heavily on groundwater pumping for crop irrigation (DeSimone et al., 2009). Groundwater contamination is a pervasive concern in the Central Valley as a result of anthropogenic, abiotic, and biotic processes. Elevated concentrations of trace elements in groundwater such as As, U, and Cr occur in Central Valley sediments, but are mobilized by both geologic and anthropogenic forcings (Rosen et al. 2019; McClain et al., 2019).

Recently, attention has been raised regarding groundwater quality in the Central Valley due to impacts from agricultural development. Nitrate (NO_3^-) is commonly applied to the land surface in the Central Valley to fertilize crop growth in agricultural regions (Nolan et al., 2014). Elevated concentrations of nitrates in groundwater have raised local concerns regarding human and ecological health as well as municipal water treatments costs (Burow et al., 2013). Additionally, the introduction of NO_3^- can have unforeseen consequences by changing aquifer biogeochemistry to promote the mobilization of some redox-sensitive trace elements that naturally exist in sediments derived from the igneous parent material (Davis et al., 1959), often leading trace metal concentrations in groundwater exceeding safe drinking water thresholds (He et al, 2010). In this study, we sought to elucidate geologic and anthropogenic

influences on the biogeochemical mechanisms that mobilize natural contaminants (e.g., arsenic, uranium, and hexavalent chromium) into groundwater in the Kings Groundwater Basin in the broader Central Valley of California.

METHODS

This study used a multifaceted approach of groundwater, sediment and microbiologic analyses in order to make a holistic assessment of the biogeochemical processes impacting trace elements in groundwater in the Central Valley. Publicly available groundwater chemistry data were accessed from the Groundwater Ambient Monitoring and Assessment Program (GAMA: <https://www.waterboards.ca.gov/gama/>). Data was downloaded for the Kings Groundwater Basin, a part of the greater Central Valley. Multiple chemical constituents, including arsenic, uranium, nitrate, iron, manganese, calcium, dissolved oxygen, total organic carbon, pH and alkalinity were compiled in both shallow and deep groundwater to evaluate the geospatial extent of groundwater contamination. Correlations of multiple groundwater chemicals were analyzed to infer geochemical mechanisms that mobilize groundwater contaminants from native sediments.

Sediments from the saturated and unsaturated zones collected by previous researchers were analyzed to characterize the geochemical and physical properties of sediment in the Central Valley. Analyses included sequential chemical extractions to target ion exchangeable, carbonate-bound, oxide-bound, and sulfide-bound fractions of major, minor, and trace elements. Bulk elemental abundances were also

to current and historic well concentrations of groundwater contaminants to evaluate the bacterial influence on water quality.

RESEARCH

Three projects were crafted to address questions related to the mobilization of elements in groundwater as a means to assess how these processes impact groundwater contamination. The different projects focused on expanding our process-based understanding to contaminants via biological, chemical, and observational/statistical tools. Each project was spearheaded by two to three nascent, second-year student scientists with our guidance. The project investigation took place over a five-week immersive summer research experience. The data and information gathered during the summer experience was compiled and synthesized into presentations at the Fall 2021 American Geophysical Union conference in New Orleans.

PROJECT SUMMARIES

Basin-wide Geospatial and Geostatistical Assessment

Geospatial and Statistical Analyses of Groundwater Contaminants in the San Joaquin River Valley During Drought and Non-Drought Periods

Nickels, M., Goudy, M., Ziegler, B.A., Mine, A.H.

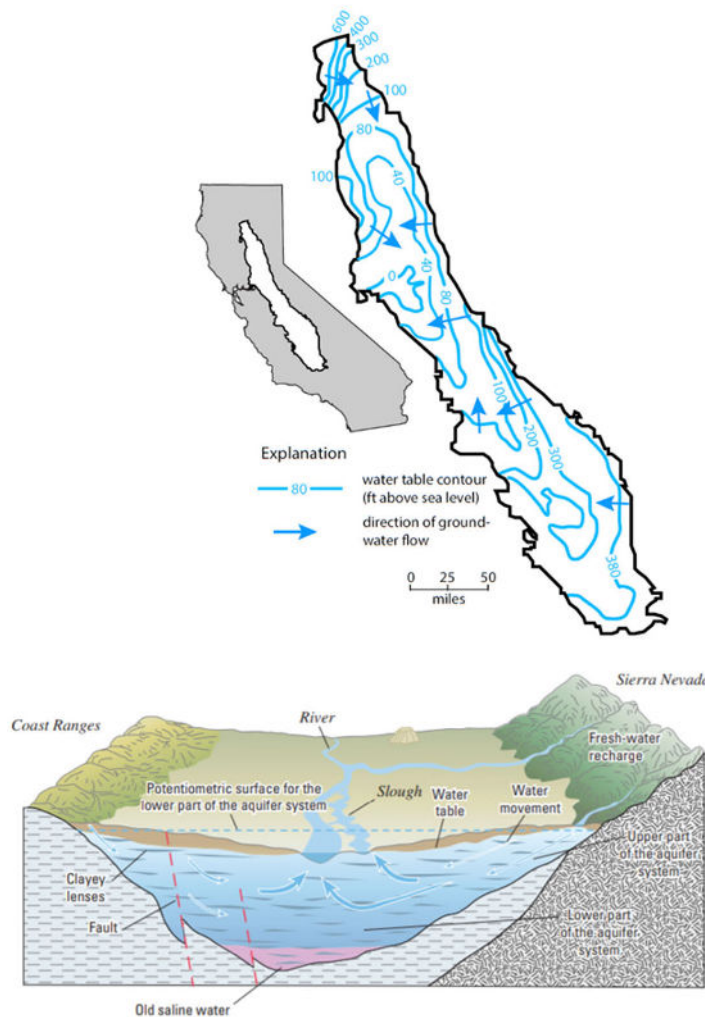


Figure 1. Water table contour map (top) showing the elevation of the water table and direction of groundwater flow in the Central Valley. The regional flow across the valley is shown in cross section (bottom); modified from Williamson et al., (1989) and DeSimone et al. (2009).

quantified using x-ray fluorescence. Particle size distributions were used to quantify the permeability of sediments. Fe(III)/Fe(II) extractions were performed to infer the redox state of the sediment.

We sampled both monitoring and pumping wells multiple times in summer 2021 to collect water for bacterial DNA analyses. Samples were filtered through a 0.2 μm Sterivex filter to concentrate microbial cells from a water sample. DNA extractions and purification was then performed using Qiagen DNeasy PowerWater Kit and a phenol-chloroform extraction method. Extracted DNA was amplified using PCR with 16s rDNA primers and analyzed using a MinIon benchtop sequencer to quantify bacterial community composition and relative abundances. These community compositions were then compared

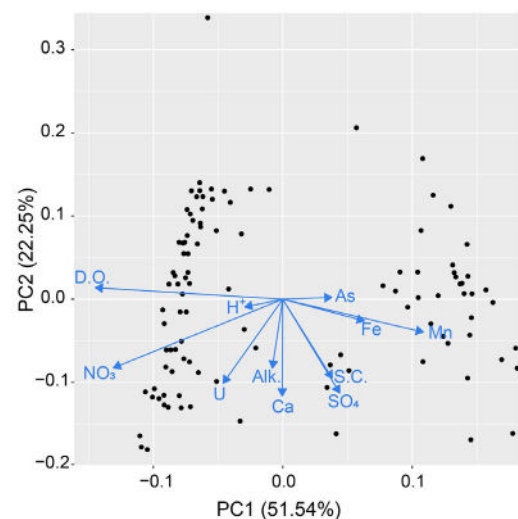


Figure 2. Principal component analysis for wells sampled in the Kings Groundwater Basin.

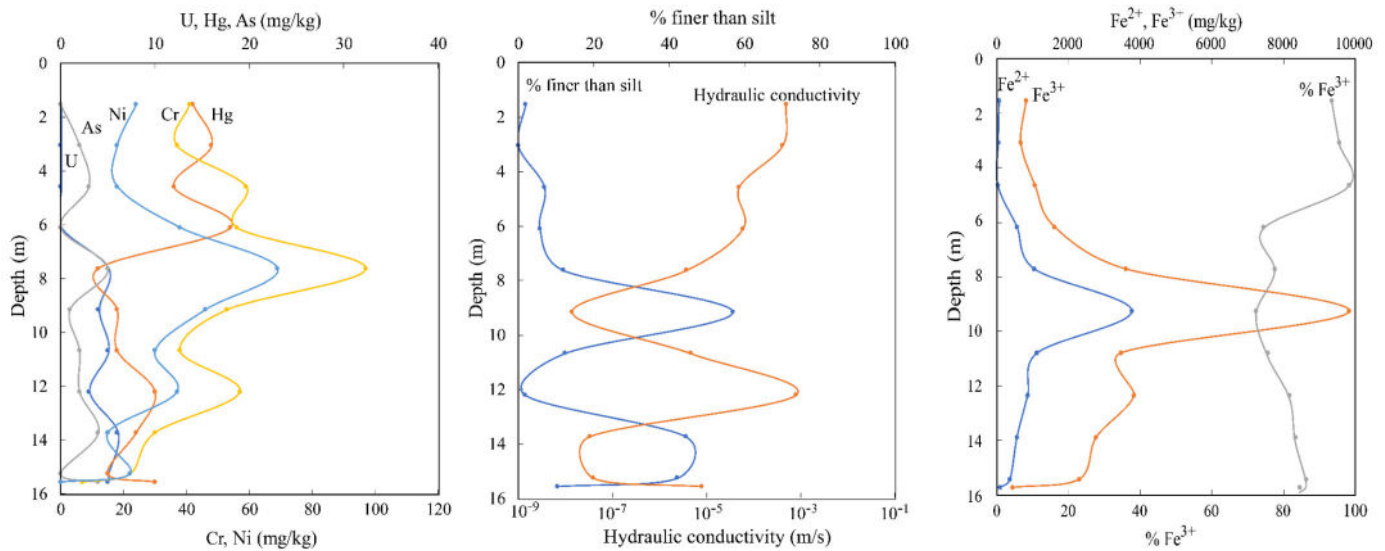


Figure 3. Unsaturated zone depth profiles for bulk concentrations of some trace elements (left), the percent finer than silt and calculated hydraulic conductivity (middle), and the iron redox speciation (right).

Groundwater analyses from the GAMA database show that there are regions in the Kings Groundwater Basin that contain unsafe levels of arsenic and uranium. In particular, shallow groundwater has elevated uranium. Using a principal component analysis (Figure 2), we show that the majority of the variation in the groundwater dataset (51.54% for principal component 1) appears to be related to redox, with dissolved oxygen and nitrate juxtaposed against Fe and Mn in the principal component 1 dimension. Elevated uranium in shallow groundwater was attributed to the more oxidizing conditions associated with nitrate and dissolved oxygen from groundwater recharging from the surface. These electron acceptors can oxidize reduced U(IV) in minerals that comprise the aquifer matrix to U(VI), which is soluble in groundwater as the UO_2^{2+} ion. Elevated U concentrations were concomitant with elevated alkalinity levels, likely due to the formation of uranium-carbonate complexes, which can inhibit the ability of dissolved uranium species to interact with mineral surfaces and be removed from groundwater.

Sedimentary Geochemistry

Mobilization of Trace Elements from Sediments into Groundwater in California's Central Valley

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Comparisons of sediments collected from the saturated and unsaturated zones show that most elements with statistically significant differences were higher in the saturated zone than the unsaturated zone. These elements included Ti, V, Mn, Cu, Zn, As, Rb, Sr, Ba, Th, and U. Only Au was statistically higher in the unsaturated zone than the saturated zone. However, Hg, W, and Co were also highly enriched in surface sediments, and decreased rapidly in concentration. We hypothesize that the elevated levels of Hg and Au in surface sediments might stem from the California Gold Rush, where Au-rich rocks in the Sierra Nevada experienced enhanced weathering during mining operations, and Hg was commonly used to amalgamate Au.

Depth profiles (Figure 3) in the unsaturated zone sediment show that near-surface sediments (zero to six m below land surface) have non-detectable levels of U (<1 mg/kg). Below six m, U concentrations increase to a consistent concentration of ~6 mg/kg to a depth of 16 m. Analyses of Fe(III)/Fe(II) show that near-surface sediments are highly oxidized (>95% Fe(III)) and have a high permeability. These findings, coupled with elevated U in shallow groundwater and nitrate from agricultural runoff, suggest that U from surface sediments are likely oxidatively dissolved and transported downward through the unsaturated zone and recharge into shallow groundwater.

Microbiological Characterization

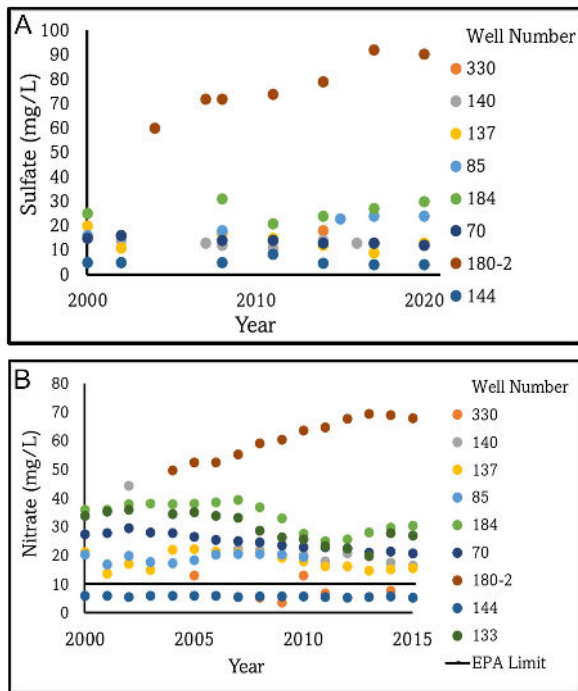


Figure 4. Sulfate (a) and nitrate (b) concentrations over a fifteen year period are shown for the array of wells sampled.

Microbial Community Response to Changing Groundwater Chemistry in The San Joaquin Valley

Peterson, T.M., Kron, E.J., O'Rourke, L.E., Goodman, J.D., Mine, A.H., Ziegler, B.A.

Heterogeneous trends were observed in well contaminants in the City of Fresno, which lies within the Kings Groundwater Basin, and more broadly in the city municipal well network. This suggests that the aquifer environment is a dynamic system where sediment, water, and biological interactions are highly variable in space and time. Trends in contaminants at specific wells appear to be a result of aquifer sediment geochemistry, anthropogenic forcing, and microbial activity. As an example, Well 180-2, has both increasing sulfate and nitrate (Figure 4), likely due to fertilizer and gypsum applications in farming activities. Microbiological community analyses completed at a hydrogen sulfide producing well were not coupled to elevated levels of redox sensitive elements (e.g. Fe, Mn, Cr), although microbes capable of redox metabolisms coupled to those elements were observed (Figure 5). This suggests sulfate reduction occurring in the aquifer is not tied to microbially-mediated reduction and mobilization of sediment-derived redox-sensitive elements, or that this coupling

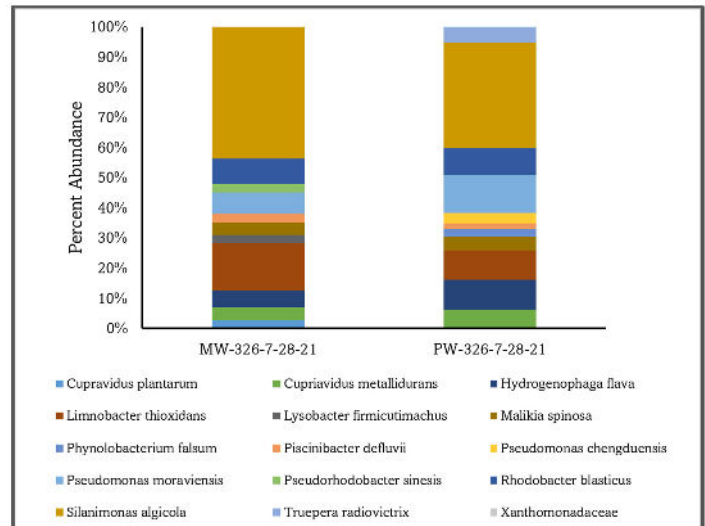


Figure 5. Relative abundance of bacterial groups in production well 326 (PW326) compared against its associated monitoring well (MW326).

varies in time and wasn't captured in our snapshot time sampling. The most abundant bacterial groups in both the monitoring and production wells tested, metabolize either sulfates or nitrates highlighting the significance of redox in well contamination. Differences in community composition between the monitoring and production well highlight the subsurface complexity; these wells are only 25ft apart.

IMPLICATIONS

More recent attention has been raised regarding groundwater quality in the Central Valley due to the impact of agricultural development. However, the introduction of NO_3^- can have unforeseen consequences by changing aquifer biogeochemistry promoting the mobilization of some redox-sensitive trace elements that naturally exist in sediments derived from the igneous parent material. Elevated concentrations of nitrates and organic contaminants from industrial and agricultural activity appear to be important controls on groundwater contamination and likely biological community in the subsurface. Sustaining and providing clean drinking water will require a multi-faceted approach to water purification and groundwater pumping. Current observations of changes in the Central Valley include: groundwater level declines, subsidence, and the pervasiveness of groundwater contamination.

ACKNOWLEDGMENTS

This material is based upon work supported by the Keck Geology Consortium and the National Science Foundation under Grant No. 2050697.

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