Geochemical Modeling for Evaluating Compatibility Issues in MAR Projects in CA

Brad Bessinger, Ph.D., PG

S.S. Papadopulos & Associates, Inc.
Environmental and Water-Resource Consultants

Tim Thompson, PG, CHG

GSI Water Solutions, Inc.

CWEMF
Folsom, CA
April 17, 2023

Objective

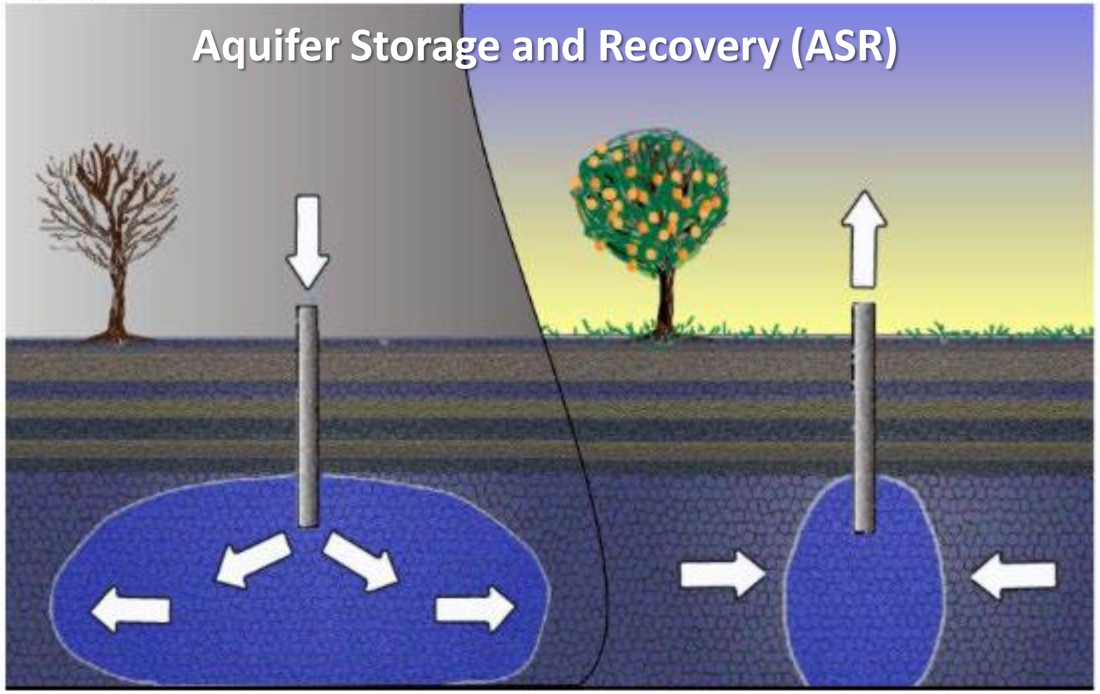
Demonstrate how geochemical modeling can be used to readily diagnose and **remedy** water quality issues in managed aquifer recovery (MAR)

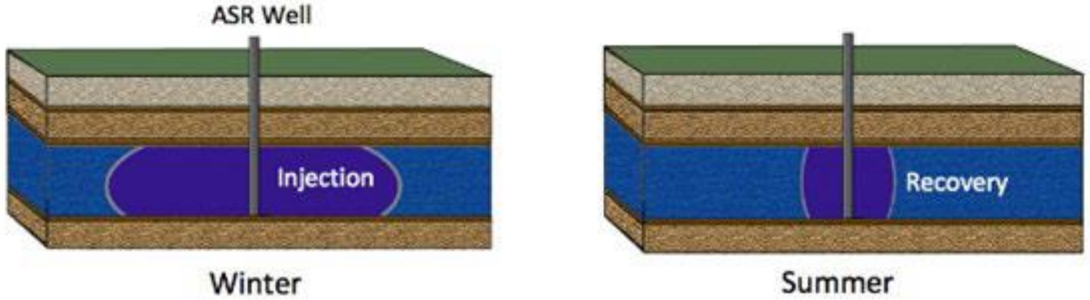
Outline

- Background on MAR and Modeling
- Case Study (City of Woodland ASR)
  - Project Description
  - Geochemical Issues
  - Model Development
  - Model Results
- Summary and Conclusions

Background on MAR & Modeling

Managed Aquifer Recharge (MAR)





ITRC (2023, in prep.)

Geochemical Issues in MAR

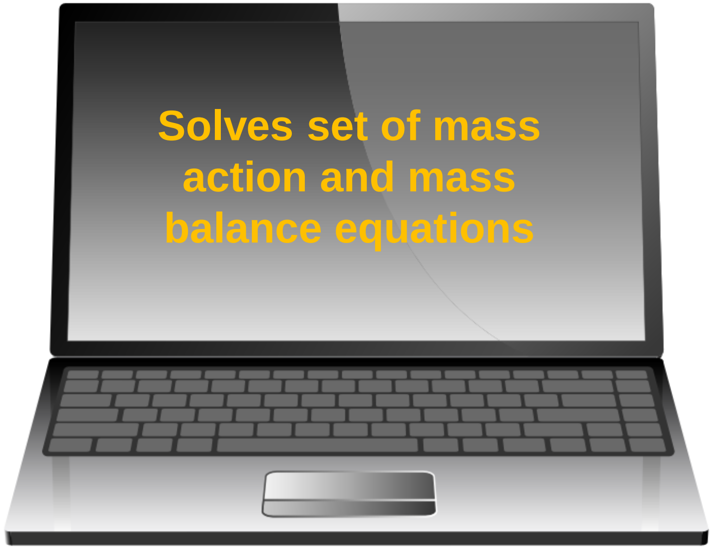
- Geochemical reactions occur during MAR projects due to differences between groundwater and recharge water chemistry
- Adverse consequences can occur (i.e., **geochemical incompatibility**):
  - **Water quality changes** that increase concentrations of regulated contaminants
  - **Mineral precipitation** and/or biofouling that clog aquifer or well
- Geochemical incompatibility regulated by SWRCB (primarily through anti-degradation rules)
  - Indirect Potable Reuse (IPR) projects comply w/ Groundwater Replenishment Reuse Project (GRRP) regulations
  - Modeling is a tool to evaluate potential geochemical incompatibility during planning phase of a project

What is Geochemical Modeling?

Model Input

1. **Chemical Description of System**
   - **Aqueous Composition**
   - **Minerals**
2. **Thermodynamic Database (log Ks)**
   - **Aqueous Species**
   - **Mineral Solubility**
   - **Surface Complexes**
3. **Reaction Rates (*optional*)**
4. **Groundwater Flow for Reactive Transport (*optional*)**

Model Calculations

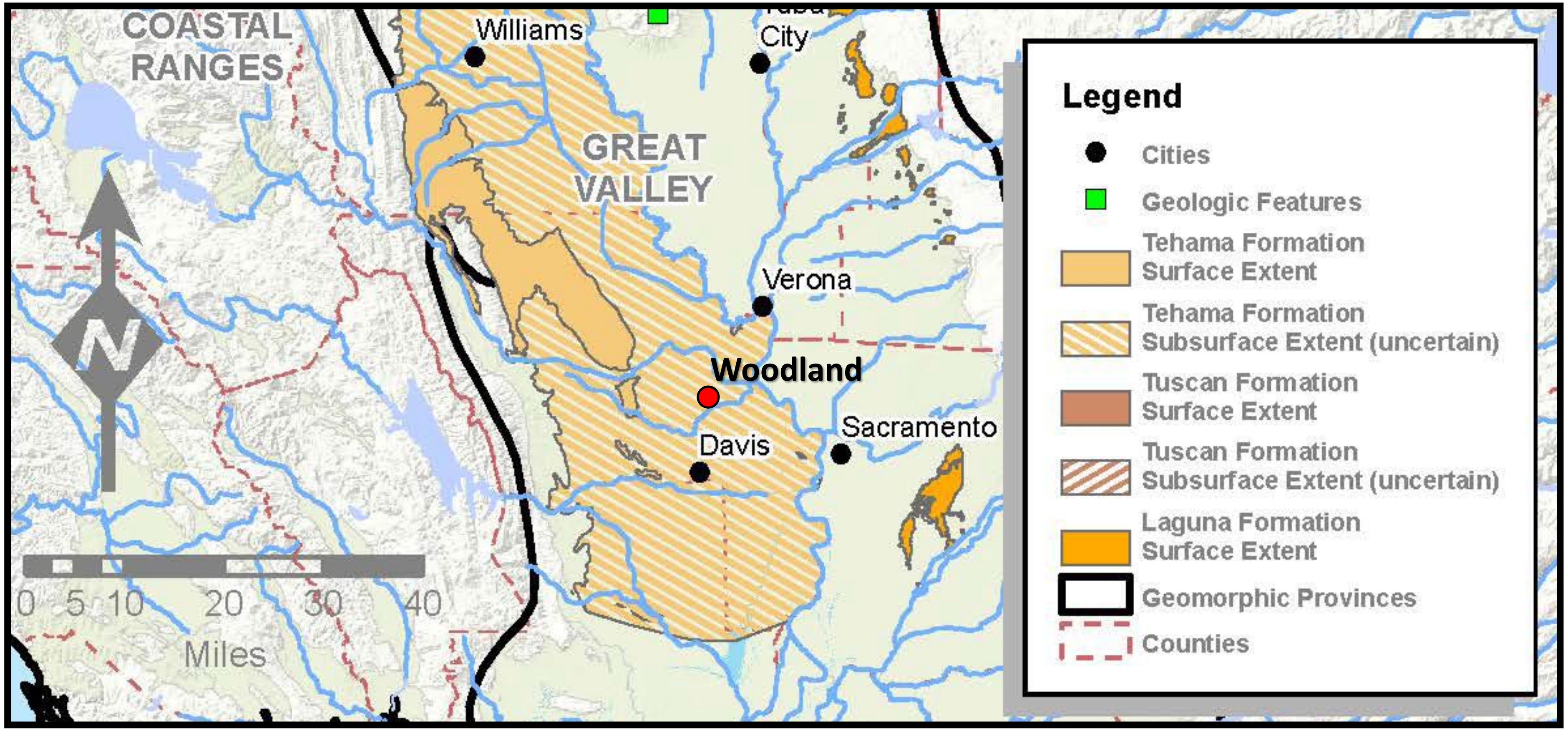


Model Output

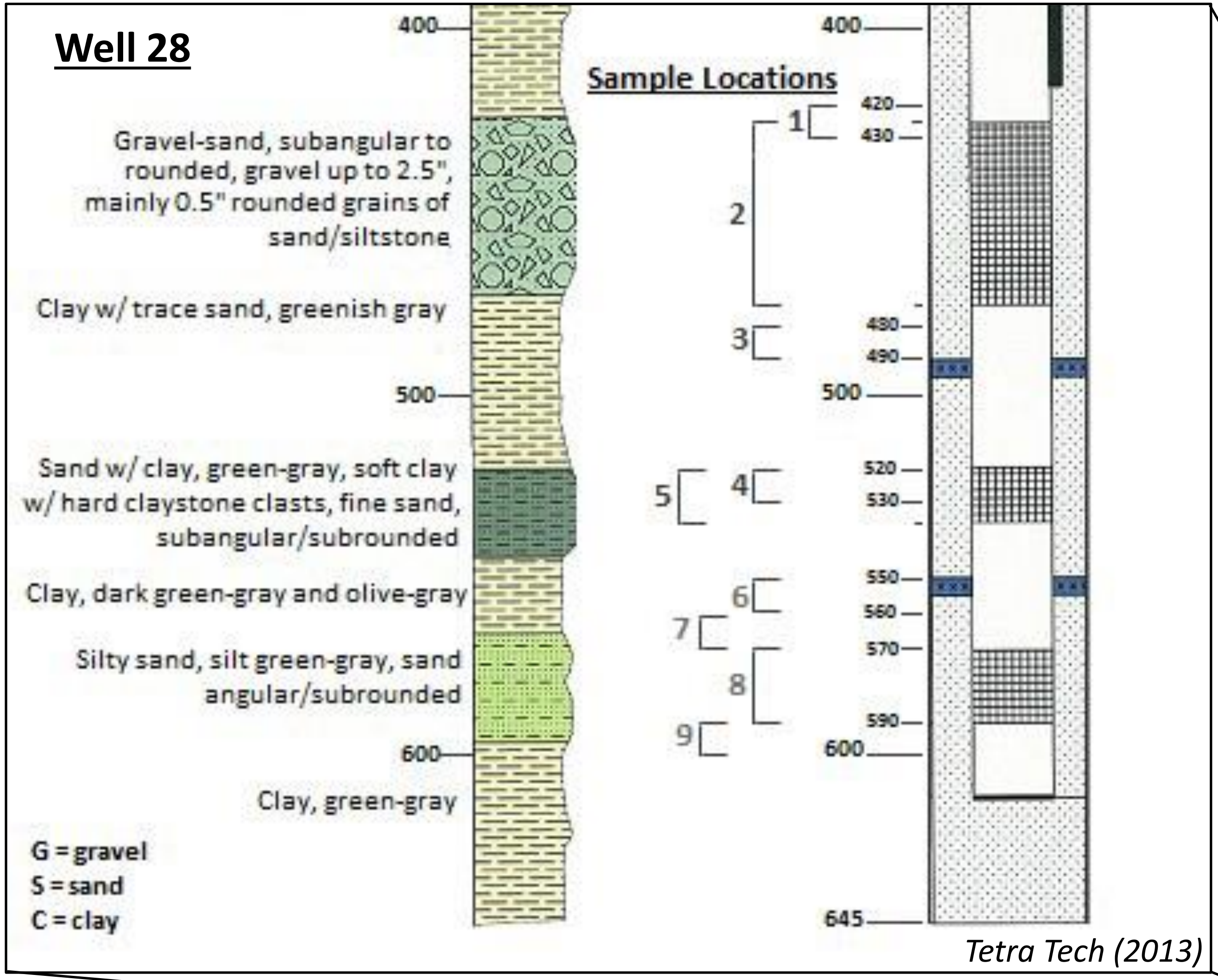
1. **Equilibrium distribution of elements between minerals, water, and gas (i.e., mobile/immobile)**
2. **To extent flow is included, model simulates fate and transport**
3. **Reactive transport model (RTM) can be used to simulate F&T during MAR and predict recovered water quality and potential mineral precipitation/clogging**

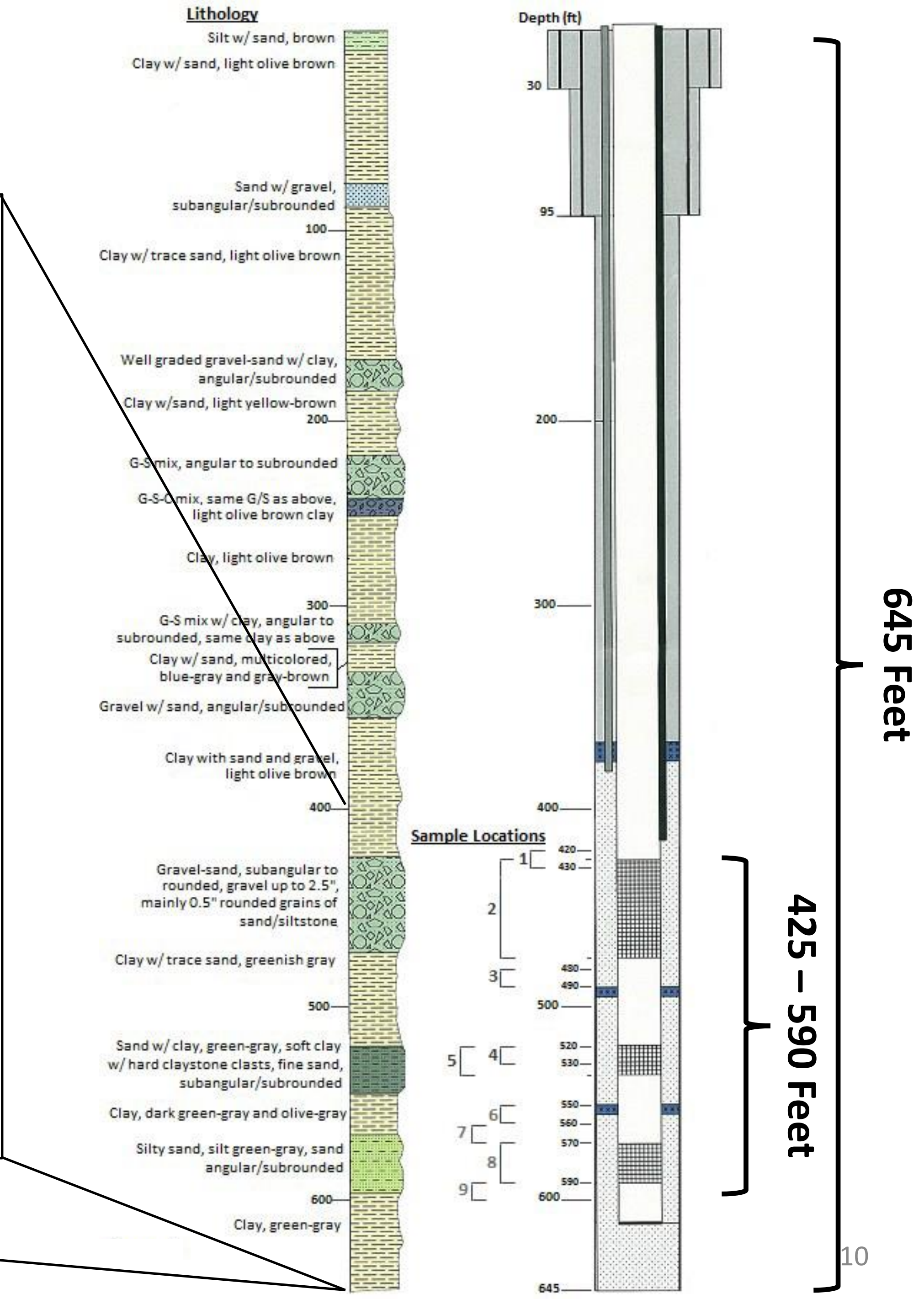
Case Study (City of Woodland ASR)

Project Location



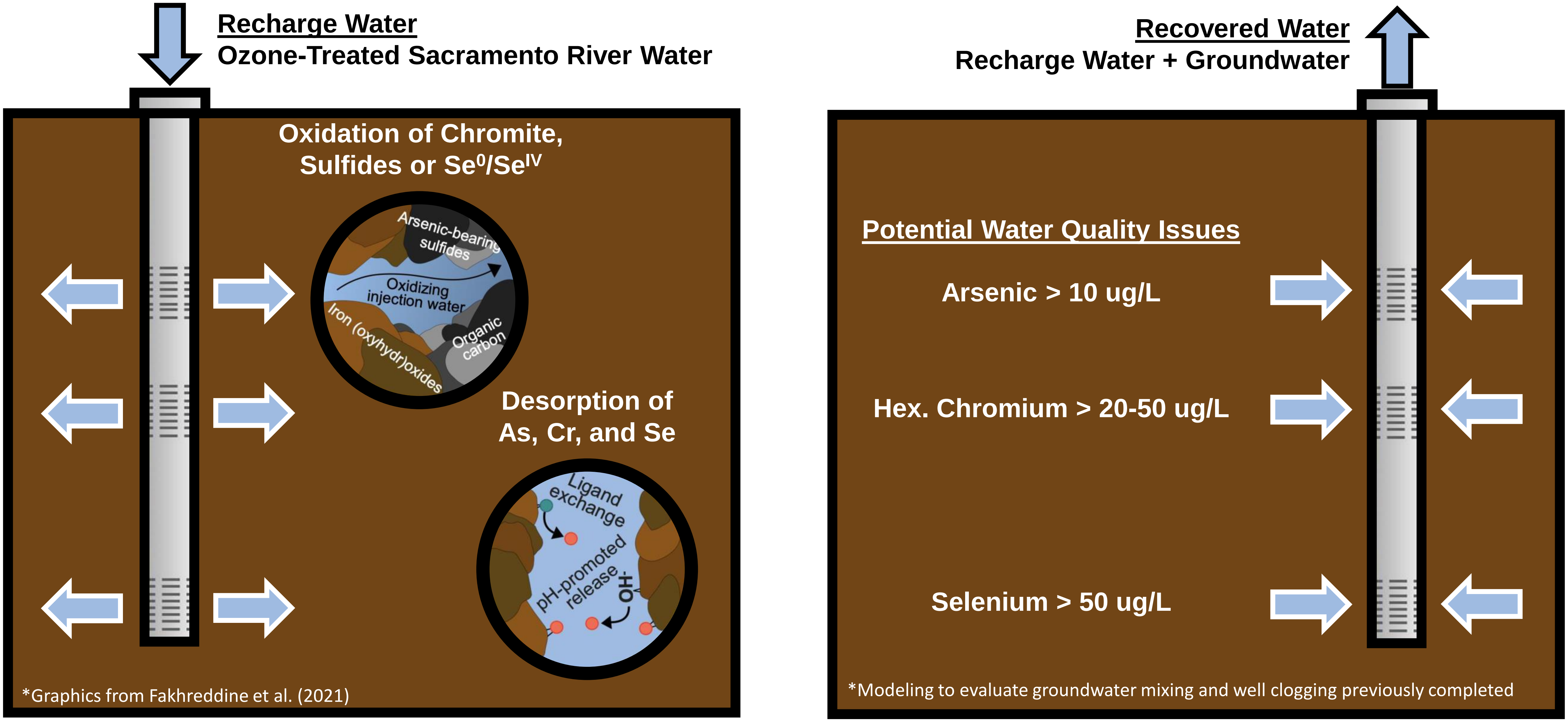
Project Description





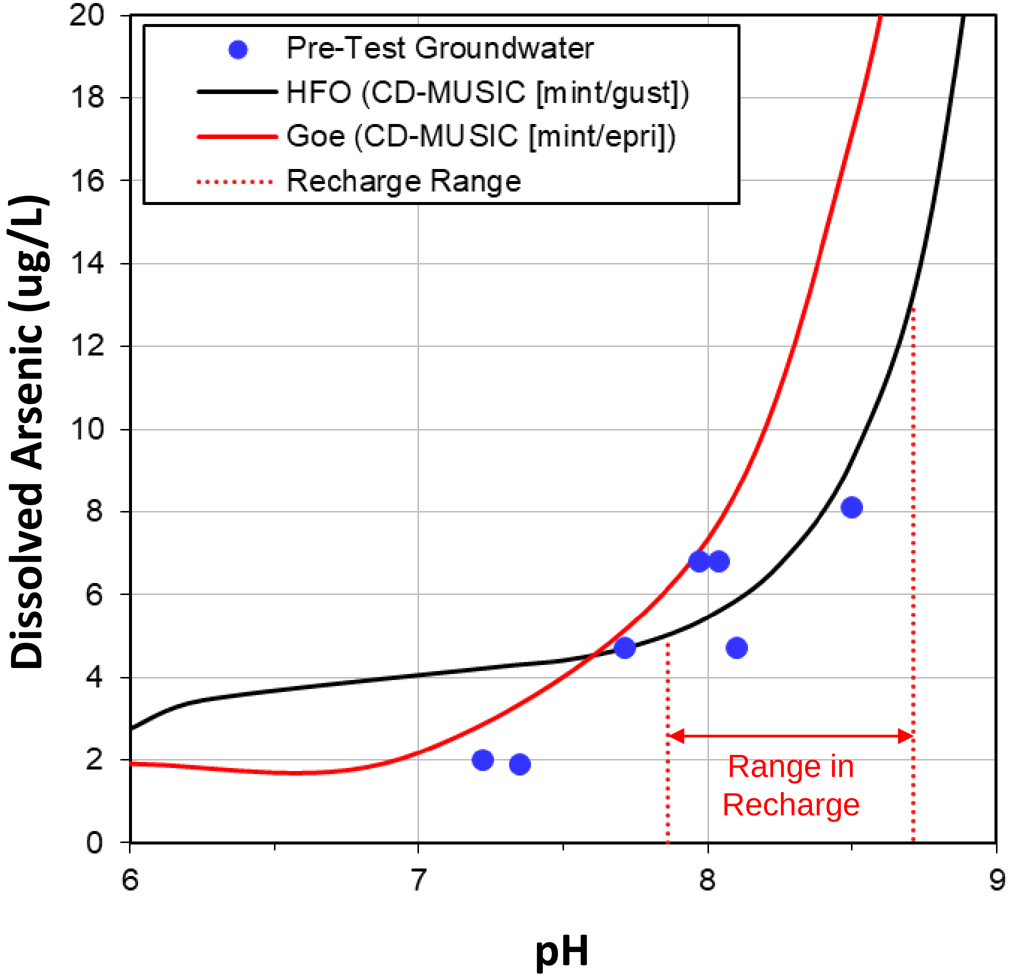
S.S. Papadopulos & Associates, Inc.
Environmental and Water-Resource Consultants

Geochemical Issues



Geochemical Issues

Measured Arsenic in Groundwater vs. Model Predicted Changes with pH



Predicted Arsenic Mobility in Groundwater

- Two surface complexation models (SCMs) compared to groundwater data
- Data and both SCMs predict increase in dissolved arsenic (i.e., desorption) with pH
- Predicted range in recharge (7.9-8.7) could cause enough desorption for As to be greater than MCL (10 ug/L) in recovered water

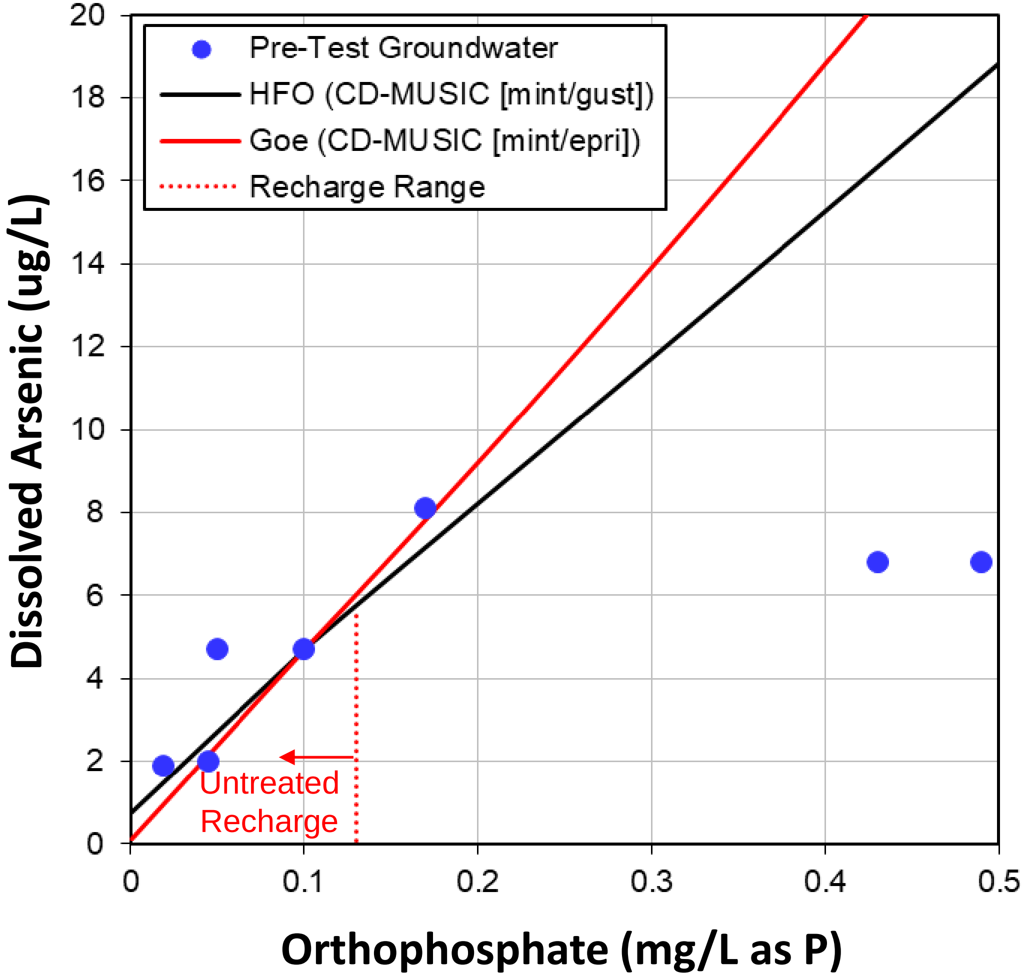
Note

- Cr(VI) and Se not shown but are similarly desorbed

S.S. PAPADOPULOS & ASSOCIATES, INC.
ENVIRONMENTAL AND WATER-RESOURCE CONSULTANTS

Geochemical Issues

Measured Arsenic in Groundwater vs. Model Predicted Changes with Orthophosphate



Predicted Arsenic Mobility in Groundwater

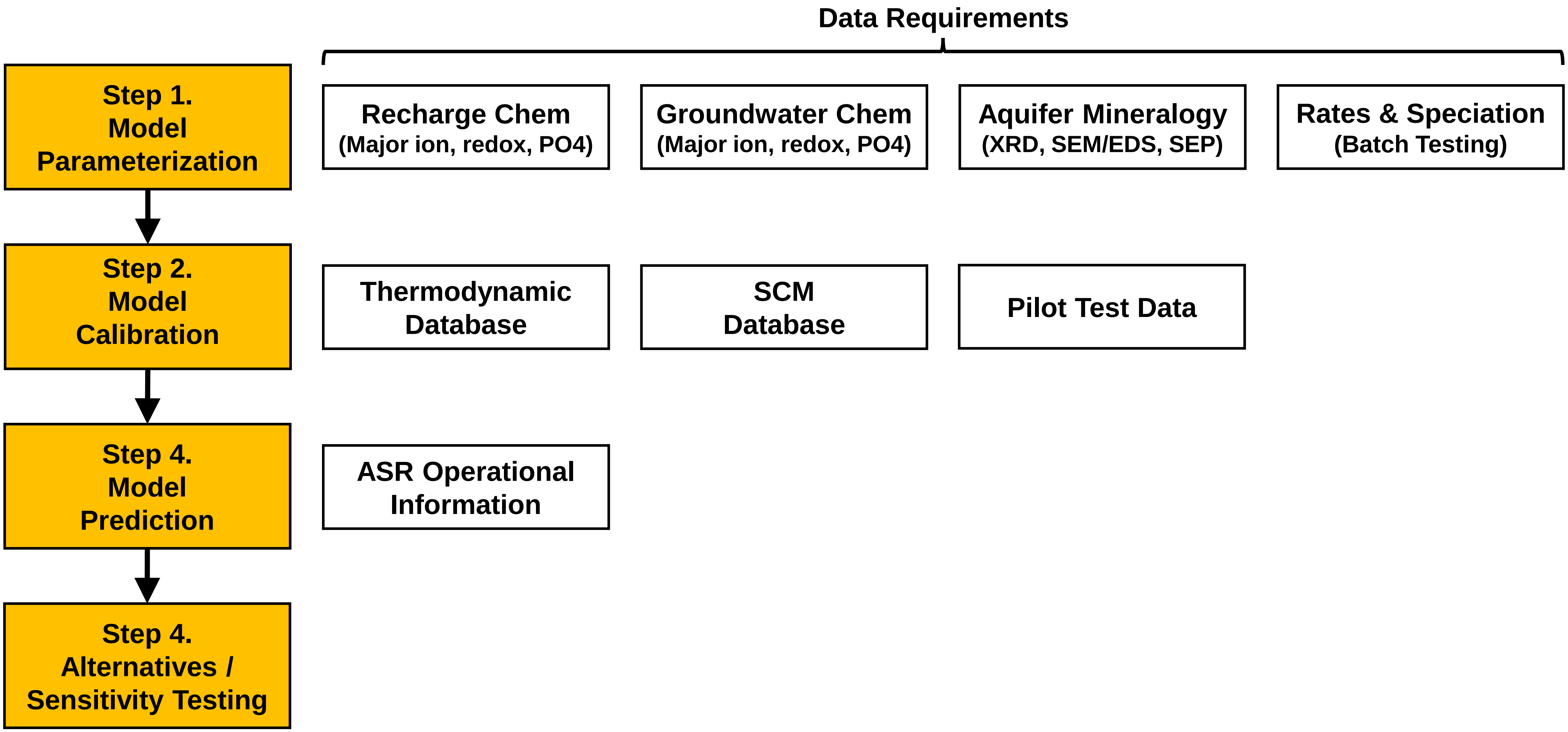
- Both SCMs and data predict increase in dissolved arsenic (i.e., desorption) with PO_4^{3-}
- Models do not replicate all groundwater data
- Predicted range in recharge (<0.13 mg/L) not sufficient to cause enough desorption for As to be greater than MCL (10 ug/L) in recovered water (assuming no phosphate added)

Implications

- Potential geochemical incompatibilities that could affect water quality
- Key variables that affect whether will occur include pH, PO_4^{3-}, sorption density, and quantity/dissolution rates of key minerals

S.S. Papadopulos & Associates, Inc.
Environmental and Water-Resource Consultants

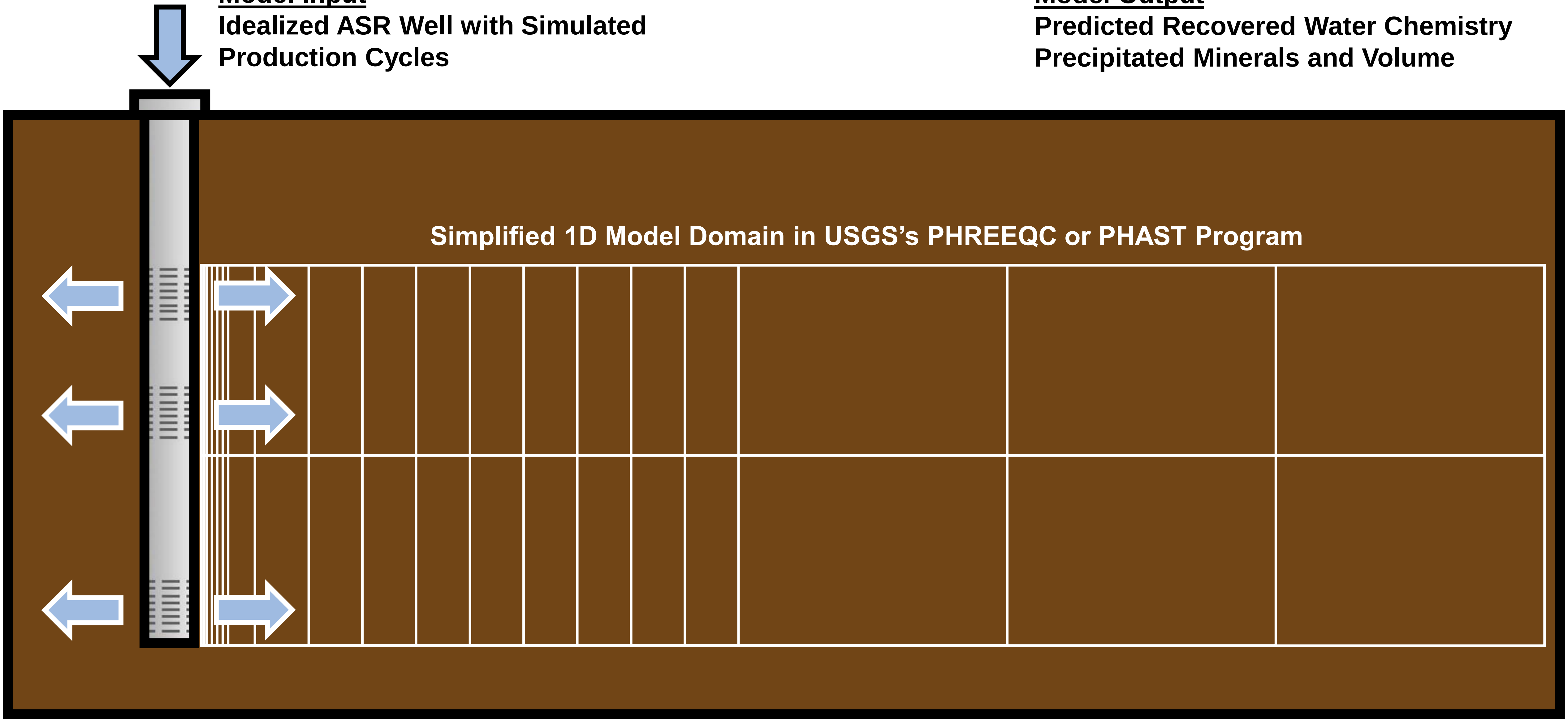
Model Development



Model Development

<u>Model Input</u>
Idealized ASR Well with Simulated Production Cycles

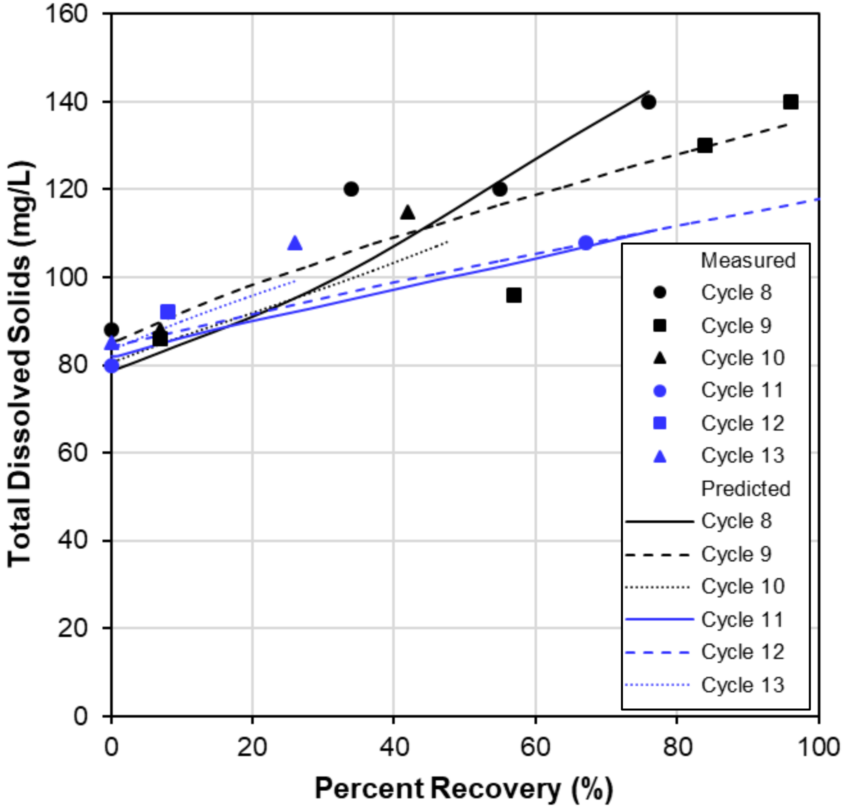
<u>Model Output</u>
Predicted Recovered Water Chemistry
Precipitated Minerals and Volume



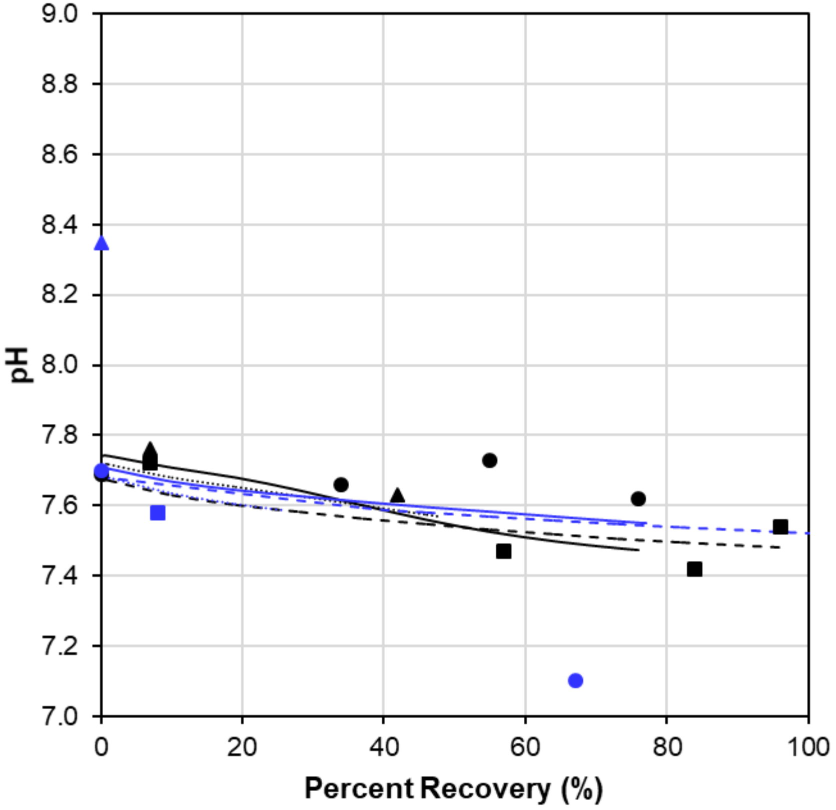
Model Development

Example of Model Calibration Results from Different Project Using ASR Performance/Pilot Test Data:

Recovered Water TDS



Recovered Water pH



General Approach

- Fit flow parameters to tracer
- Fit reaction rates to pH
- Fit As to rates/sorption density (*not shown*)

No Operational or Pilot Test Data for Woodland at time of the study (Jan. 2016)

S.S. Papadopulos & Associates, Inc.
Environmental and Water-Resource Consultants

Woodland Well 28 Model

Available Model Data

Step 1. Model Parameterization
- Recharge Chem (Major ion, redox, PO4)
- Groundwater Chem (Major ion, redox, PO4)
- Aquifer Mineralogy (XRD, SEM/EDS, ~~SEP~~)
- ~~Rates & Speciation (Batch Testing)~~

↓

Step 2. Model Calibration
- Thermodynamic Database
- SCM Database
- ~~Pilot Test Data*~~

↓

Step 4. Model Prediction
- ASR Operational Information

↓

Step 4. Alternatives / Sensitivity Testing

*Note: Pilot Test Data Available post-2016

Woodland Well 28 Model

Water Used for Base Case

Aquifer	pH	PO4 (mg/L)	As (ug/L)	Cr (ug/L)	Se (ug/L)
Groundwater	7.7	0.1	4.7	17	6.5
Recharge	8.0	0.13	1.0	0.5	2.5

Minerals Used

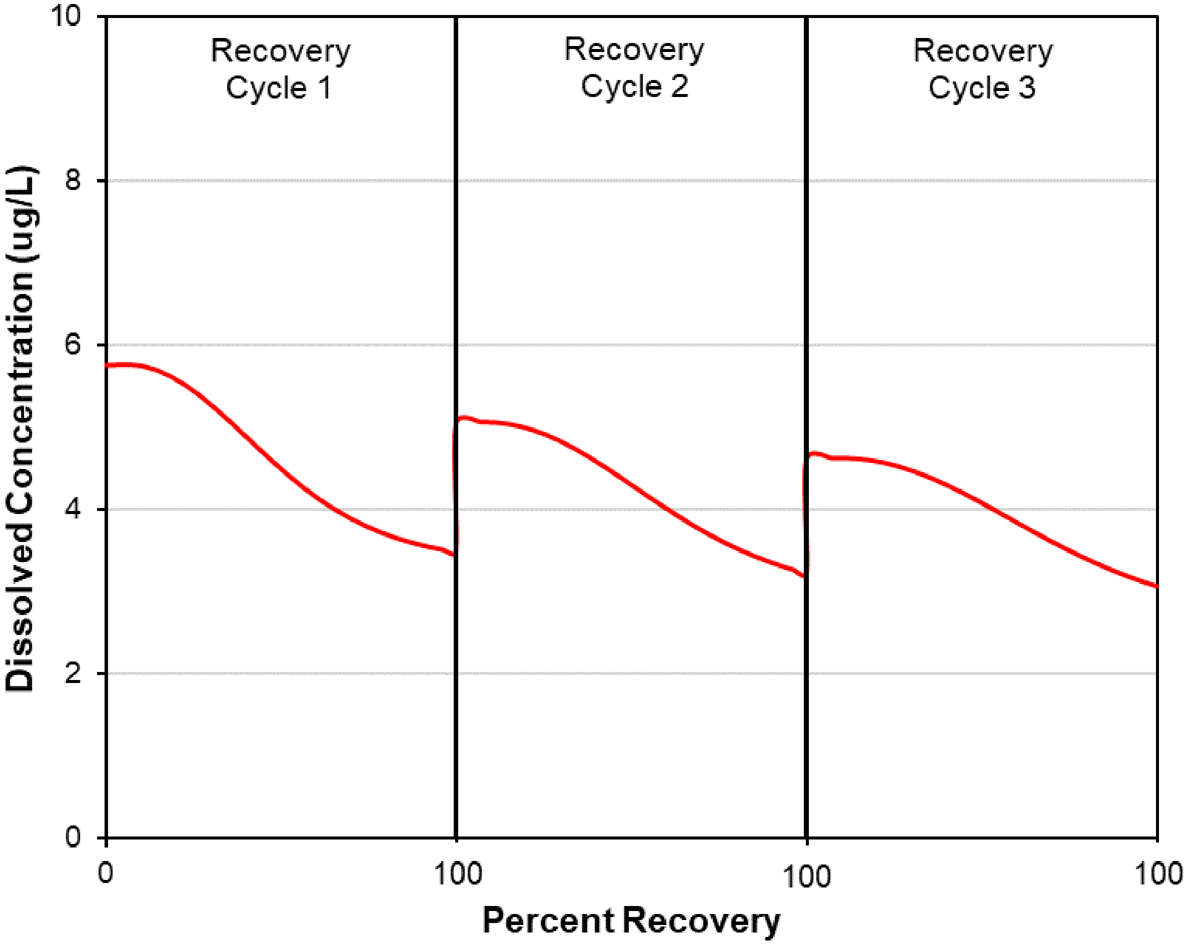
Major silicates not included (based on slow reaction rates and experience at other sites)
Goethite (based on field logs, thin sections, groundwater redox, and similarity to magnetite sorption)
Chromite (not identified by XRD or SE/EDS, but noted from USGS regional studies within XRF range [<300 ppm])
Organic carbon (identified in sediment and will compete with possible chromite for DO and ozone)

Reactions Used

Surface Complexation Model: CD-MUSIC for goethite (EPRI 2009) with recent sensitivity testing with Gust. (2022)
Surface Site Density: Goethite with total abundance used as a sensitivity parameter (base case use typical value)
Oxygen and ozone oxidation rates: Scientific literature accounting for reduction in reactivity with sediment age

Model Results

Predicted Arsenic Concentrations in Recovered Water for Multiple ASR Cycles

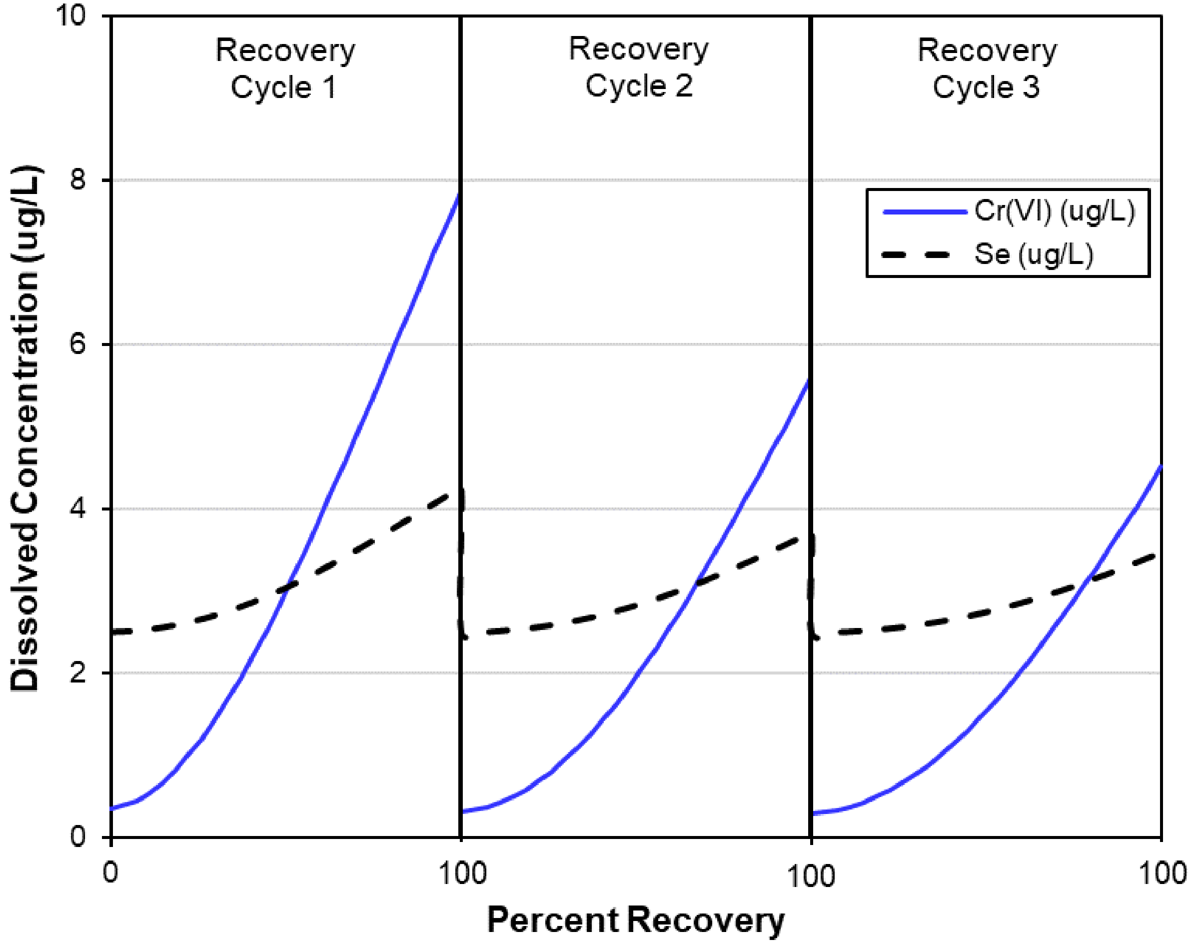


Results

- Arsenic concentrations greater than recharge concentration (1 ug/L) due to geochemical incompatibility / desorption
- Recovery Cycle 1: Arsenic concentrations highest
- Recovery Cycles 2-3: Aquifer conditioning occurs (consisting of equilibration between recharge and aquifer sediments); this reduces As concentrations in recovered water
- Key finding: Arsenic concentrations are predicted to be less than the MCL (10 ug/L) during operations

Model Results

Predicted Cr(VI) and Se Concentrations in Recovered Water for Multiple ASR Cycles



Results

- Hexavalent chromium and selenium concentrations highest during Recovery Cycle 1 but decrease with aquifer conditioning
- Hexavalent chromium and selenium concentrations increase during individual cycles due to mixing with groundwater but remain relatively low
- Key finding: Concentrations affected by (1) conditioning and overall decrease over time and (2) mixing with groundwater
- **Final recommendation: Perform pilot testing to confirm results**

Model Accuracy

Constituent	Groundwater (ug/L)	Recovered Water (ug/L)	Predicted Cycle 3 (ug/L)	MCL or PHG (ug/L)
Hex. Chromium	18	1.7 – 4.1	0.3 – 4.5	50 (MCL); 20 (PHG)
Arsenic	<2	<2 – 3.2	3.1 – 4.6	10
Selenium	5	4.9 – 5.5	2.5 – 3.5	50

Summary and Conclusions

Summary

1. Geochemical modeling can be used to predict geochemical compatibility between recharge water, groundwater, and aquifer sediments in MAR
    - Changes in water quality
    - Significant mineral precipitation that can lead to well clogging
2. City of Woodland was concerned about potential issues associated with arsenic, hexavalent chromium, and selenium
3. Modeling demonstrated that incompatibility should cause an increase in arsenic concentrations over recharge water or groundwater but at levels below MCLs (and that reduce over time due to aquifer conditioning)
4. Model results were based on limited data but proved accurate with subsequent data collected at Well 28 (no issues reported after 5 years of operations and City looking to expand with two additional ASR wells)

Conclusions

1. Geochemical modeling requires a complete description of the system being modeled; however, geochemical inference based on experience can be **readily** employed in the absence of a complete dataset
2. Recharge water and groundwater chemistry are the primary data required for preliminary modeling to **diagnose** potential issues
3. Pilot testing required to verify geochemical reactive transport model results and have confidence as seek to **remedy** any water quality issues

Questions?