Outline of Presentation

1. Problem Statement
2. Research Objectives
3. Methods
4. Conclusions and Future Work
Problem Statement

High Soil Salinity

Semi-arid agricultural areas:

- Excessive irrigation
- Seepage from earthen canals
- Inefficient drainage systems
- Consequent evaporative concentration

High soil salinity
High groundwater salinity

Reduction in crop yield
Example of Problem

Global Salt-Affected Soils

Wicke et al. (2011) *Energy and Environmental Science*

- 230 million ha of irrigated land → 20-25% severe salinity
- Salt-affected area increases by 1-1.5 million ha / year
Example of Problem
Global Salt-Affected Soils

Wicke et al. (2011) *Energy and Environmental Science*

- 27-28% off irrigated land $\rightarrow$ decline in crop productivity
- Principal water quality problem in semi-arid region

- Colorado River Basin
- Rio Grande Basin
- Central Valley, CA
- Yakima Basin, WA
- Snake River Basin, ID
- Arkansas River Valley, CO
- South Platte Basin, CO
Example of Problem

South Platte River Basin, Colorado

Northern Colorado Water Conservancy District (2004-2005):

- 13 Sampled Fields
- Electrical conductivity of soil water \((EC_e)\): 2.43 – 6.46 dS/m
Example of Problem
South Platte River Basin, Colorado

Soil salinity surveys (NCWCD)
Example of Problem

South Platte River Basin, Colorado

Groundwater Salinity

Observation Well Network
Example of Problem

South Platte River Basin, Colorado

Groundwater Salinity

April Values
Example of Problem
Arkansas River Valley, Colorado

- Irrigation since late 19th century
- 270,000 irrigated acres (14,000 fields)

**Soil salinity surveys** (Morway & Gates, 2012)
- 122,000 samples (electrical conductivity $EC_e$)
  - USR: 4.1 dS/m $\Rightarrow$ 6% crop yield reduction
  - DSR: 6.2 dS/m $\Rightarrow$ 17% crop yield reduction
- 42% of sampled area affected
Example of Problem
Arkansas River Valley, Colorado

Soil salinity surveys (Morway & Gates, 2012)
Example of Problem
Arkansas River Valley, Colorado

Soil salinity surveys (Morway & Gates, 2012)
Example of Problem
Arkansas River Valley, Colorado

Groundwater Salinity

Observation Well Network
Example of Problem

Arkansas River Valley, Colorado

Groundwater Salinity

Upstream Study Region

- 4 values greater than 20,000

Histogram showing the distribution of groundwater salinity measurements in the upstream study region.
Example of Problem
Arkansas River Valley, Colorado

Groundwater Salinity

Downstream Study Region

2 values greater than 20000
Example of Problem
Arkansas River Valley, Colorado

River Water Salinity

Upstream Study Region

Estimated Maximum to Prevent Crop Loss
Example of Problem
Arkansas River Valley, Colorado

River Water Salinity

~ 900 mg/L

Freshwater Limit (WHO)

Estimated Maximum to Prevent Crop Loss
Research Objectives

Arkansas River Valley, Colorado

Research Statement
Identify best managements practices (BMPs) that will remediate high salinity

- Higher irrigation efficiency
- Sealing earthen irrigation canals
- Land fallowing
- Subsurface drainage installation
- Increase pumping volumes
Research Objectives
Arkansas River Valley, Colorado

Research Statement
Identify best managements practices (BMPs) that will remediate high salinity

Project Phases
1. Model Development (soil-groundwater-river)
2. Model testing (soil, aquifer, basin scale)
3. Explore BMPs using model

[Map of Arkansas River Valley]
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   1. Model Development
   2. Model testing (field data)
   3. Model application (BMP assessment)
1. Model Development

Conceptual Model: $SO_4$ fate and transport

- Irrigation Water
- $NO_3, SO_4$
- Fertilizer
- $NH_4$

- Root Processes
- Water Table
- $NO_3, SO_4$

- $FeS_2$
- Shale Bedrock
- $SeO_4$

- Alluvial Aquifer
1. Model Development

Conceptual Model: $\text{SO}_4^-$ fate and transport

1. Mass inputs
2. Redox-sensitive (oxidation-reduction reactions) 
   Affected by $\text{O}_2$ and $\text{NO}_3$
3. Cycling in soil zone (similar to Nitrogen cycle) in agricultural settings

[Diagram showing mass inputs, uptake, and cycling processes involving $\text{SO}_4^-$, $\text{O}_2$, $\text{NO}_3$, $\text{Org. S}$, and $\text{FeS}_2$]
1. Model Development

- Dissolved Se and N
- Organic S and N
- Residual S (shale)

Irrigation Water, Seepage, Uptake, Reactions
Root and Stover Mass, Decomposition
Oxidized by $O_2$ and $NO_3$

Equilibrium Chemistry
- Complexation
- Cation exchange
- Precipitation-Dissolution

$SO_4$, Ca, Mg, Na, Cl, HCO$_3$

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$
$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 7N_2 + 10SO_4^{2-} + 2H_2O$$
1. Model Development

\[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \]

\[ 5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{Fe}^{2+} + 7\text{N}_2 + 10\text{SO}_4^{2-} + 2\text{H}_2\text{O} \]
1. Model Development

\[ 2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+ \]

\[ 5 \text{FeS}_2 + 14 \text{NO}_3^- + 4 \text{H}^+ \rightarrow 5 \text{Fe}^{2+} + 7 \text{N}_2 + 10 \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \]

Bedrock Shale
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry \( \text{SO}_4, \text{Ca}, \text{Mg}, \text{Na}, \text{Cl}, \text{HCO}_3 \)
3. Precipitation-Dissolution processes \( \text{CaSO}_4, \text{CaCO}_3, \text{MgSO}_4 \)

Base Numerical Model

UZF-RT3D
- Groundwater reactive transport in 3 Dimensions
- Transport in variably-saturated porous media
- Links with MODFLOW model results

Nitrogen Cycling module

Crop management parameters
- Plant, Harvest
- Fertilizer
- Root depth

System information
- Crop type distribution
- Irrigation solute concentration
- Shale bedrock and outcrop

Chemical Reaction Rates
- Nitrification
- Denitrification
- \( \text{FeS}_2 \) oxidation

Application to Study Region
- Tested against Groundwater concentrations, mass loadings to Arkansas River
- Explore BMPs for Nitrate remediation strategies
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

**Simulation set-up for SO₄**

250 m x 250 m grid:

- SO₄, Ca, Mg, Na, Cl, HCO₃
- CaSO₄, CaCO₃, MgSO₄

~10-20 m
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

Simulation set-up for $\text{SO}_4$

Crop Parameter Values
- Plant, Harvest Days
- Fertilizer
- Root depth
1. Model Development

1. Sulfur Cycling and Reaction Kinetics

2. Major Ion Chemistry
   - $\text{SO}_4$, Ca, Mg, Na, Cl, $\text{HCO}_3$

3. Precipitation-Dissolution processes
   - CaSO$_4$, CaCO$_3$, MgSO$_4$

Simulation set-up for $\text{SO}_4$

- Spin-up simulation: 40 years
- 2006-2009 simulation
- Flow model: MODFLOW (Morway et al., 2013)
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry  \( \text{SO}_4, \text{Ca}, \text{Mg}, \text{Na}, \text{Cl}, \text{HCO}_3 \)
3. Precipitation-Dissolution processes  \( \text{CaSO}_4, \text{CaCO}_3, \text{MgSO}_4 \)

Simulation Results

SO\(_4\) Groundwater concentration

Time Series (1 cell)
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
   - SO$_4$, Ca, Mg, Na, Cl, HCO$_3$
3. Precipitation-Dissolution processes
   - CaSO$_4$, CaCO$_3$, MgSO$_4$

Simulation Results

[Graph showing simulation results with bars for observed data and model predictions.

Map showing sulfate distribution in Layer 4 for July 2009.

Bar chart for $C_{NO_3}$ (mg L$^{-1}$) with relative frequency on the y-axis and $C_{NO_3}$ values on the x-axis.]
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

Equilibrium Chemistry Module

- Species interactions with each other:
  - Complexation
  - Cation exchange
  - Precipitation / dissolution

Equilibrium: no further tendency to change with time
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

Equilibrium Chemistry Module

Major Ions:
Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, SO$_4^{2-}$, CO$_3^{2-}$, NO$_3^-$

Precipitated solids:
CaCO$_3$(s) $\leftrightarrow$ Ca$^{2+}$(aq) + CO$_3^{2-}$(aq)
MgCO$_3$(s) $\leftrightarrow$ Mg$^+$ (aq) + CO$_3^{2-}$(aq)

Complexation: MgSO$_4^{0}$, NaSO$_4^-$, KSO$_4^-$
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

Equilibrium Chemistry Module: Solution Algorithm

- Stoichiometric Algorithm
  - Solves simultaneous equations
  - Mass balance equations
  - Mass actions equations

- Non-Stoichiometric Algorithm
  - Finds equilibrium by minimizing Gibbs Free Energy (converges faster)

Currently: testing methods of including precipitation-dissolution into solution algorithm.
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

**Groundwater: Upstream Study Region**

- SO$_4$, Ca, Mg, Na, Cl, HCO$_3$ (mol/L)
- CaSO$_4$, CaCO$_3$, MgSO$_4$
1. Model Development

1. Sulfur Cycling and Reaction Kinetics
2. Major Ion Chemistry
3. Precipitation-Dissolution processes

SO_4, Ca, Mg, Na, Cl, HCO_3
CaSO_4, CaCO_3, MgSO_4

Groundwater: Downstream Study Region
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2. Model Testing

Applications, Methods of Testing

1. Soil profile scale
   - Measurements from CSU lysimeter
   - Irrigation Water, Drainage water
   - Soil water salt ion concentrations (with depth)

2. Regional scale
   - Soil salinity measurements
   - Groundwater solute concentrations \( \text{SO}_4, \text{HCO}_3, \text{Ca}, \text{Mg}, \text{Na}, \text{Cl}, \text{CO}_3 \)
   - Mass loadings to Arkansas River and tributaries
2. Model Testing

Lysimeter, AVRC

Irrigation / Drainage Water

Large Lysimeter
2. Model Testing

Lysimeter, AVRC

Irrigation / Drainage Water

Reference Lysimeter
2. Model Testing

Lysimeter, AVRC

Irrigation / Drainage Water

Large Lysimeter
2. Model Testing

Lysimeter, AVRC
Irrigation / Drainage Water

Reference Lysimeter

![Graph showing Mg (mg/L) over time with data points for Irrigation Water and Drainage Water](image)
2. Model Testing

Lysimeter, AVRC

Irrigation / Drainage Water

Large Lysimeter

![Graph showing EC (dS/m) over time for Irrigation Water and Drainage Water, with severe and moderate EC levels indicated.]
2. Model Testing

Lysimeter, AVRC
Irrigation / Drainage Water

Reference Lysimeter

![Graph showing EC (dS/m) over time for irrigation and drainage water.]
2. Model Testing

Lysimeter, AVRC

Soil Samples
2. Model Testing

Lysimeter, AVRC

Soil Samples

Samples every 1 ft.

- June 21
- September 11
- November 11
- April
2. Model Testing

Lysimeter, AVRC

Soil Samples
2. Model Testing

Lysimeter, AVRC

Soil Samples

![Graph showing NO₃-N concentration by depth](image)
2. Model Testing

Lysimeter, AVRC

Soil Samples
2. Model Testing

Regional Scale Data

Applications, Methods of Testing

1. Soil profile scale
   - Measurements from CSU lysimeter
   - Drainage water, soil water salt ion concentrations (with depth)

2. Regional scale
   - Soil salinity measurements
   - Groundwater solute concentrations $\text{SO}_4, \text{HCO}_3, \text{Ca}, \text{Mg}, \text{Na}, \text{Cl}, \text{CO}_3$
   - Mass loadings to Arkansas River and tributaries
Outline of Presentation

1. Problem Statement

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   1. Model Development
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   3. Model application (BMP assessment)
3. BMP Assessment

- Higher irrigation efficiency
- Sealing earthen irrigation canals
- Land fallowing
- Subsurface drainage installation
- Increase pumping volumes

**Performance Indicators**

- Decrease in soil salinity concentration
- Change in groundwater salinity
- Decrease in total salt loading to the Arkansas River
- Increase in average regional crop yield
Conclusions, Future Work

- Continue model development
- One more sampling event from Lysimeter site
- Model testing
- Apply model to BMPs in the Arkansas River Valley
QUESTIONS
First Method

Aqueous Component

Species

Precipitated Species
First Method (cont.)

![Diagram of aqueous component and precipitated species]
First Method (cont.)

Equilibrium State

Precipitated Species

Precipitated Species
Second Method

Precipitated Species

Aqueous Component

Species

Aqueous Component

Precipitated Species
Second Method (cont.)

Equilibrium State

Aqueous Component

Precipitated Species

Precipitated Species

Precipitated Species

Precipitated Species