Inverse Modeling of Contaminated Groundwater in Thankavur City, India

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OUTLINE

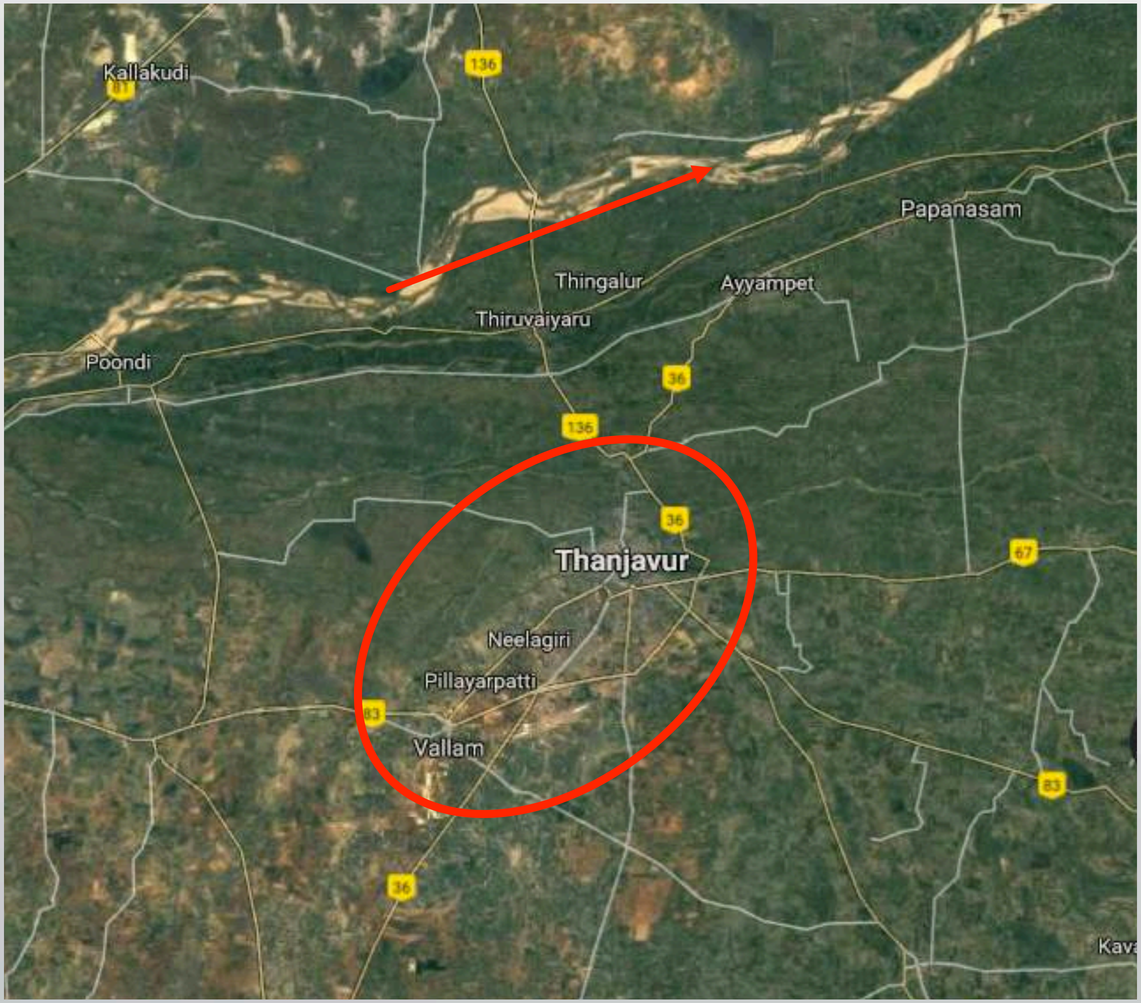
- Introduction
- Methodology
- Results and Conclusion of Initial Study
- Additional Modeling
- Conclusion of Additional Modeling

INTRODUCTION

- Study area is suffering from acute shortage of good drinking water
- Groundwater is one of the main sources of water in study area
- **Objective of Initial Study:** Evaluate the groundwater quality and its suitability for domestic and agricultural activities

INTRODUCTION

- Study Area: Thanjavur City, India
- Surface Area of Aquifer: 36.31 km^2
- Total Population: 226,830 (2001 Census)
- Average Annual Rainfall: 1,114 mm *(Fargo, 574 mm)*
- Industry: Mostly agriculture
  - 400,000 ha of agricultural land
  - Irrigated through groundwater sources and Cauvery River



Source: Google Maps

METHODOLOGY

- Aquifer divided into 10 zones
- 102 wells selected for groundwater sampling
- Water sampled in 2008
- PHREEQC used to calculate distribution of aqueous species and mineral saturation indices
- Developed groundwater quality maps

RESULTS

1. Water Sampling Analysis
2. Mineral Dissolution
3. Contamination Sources

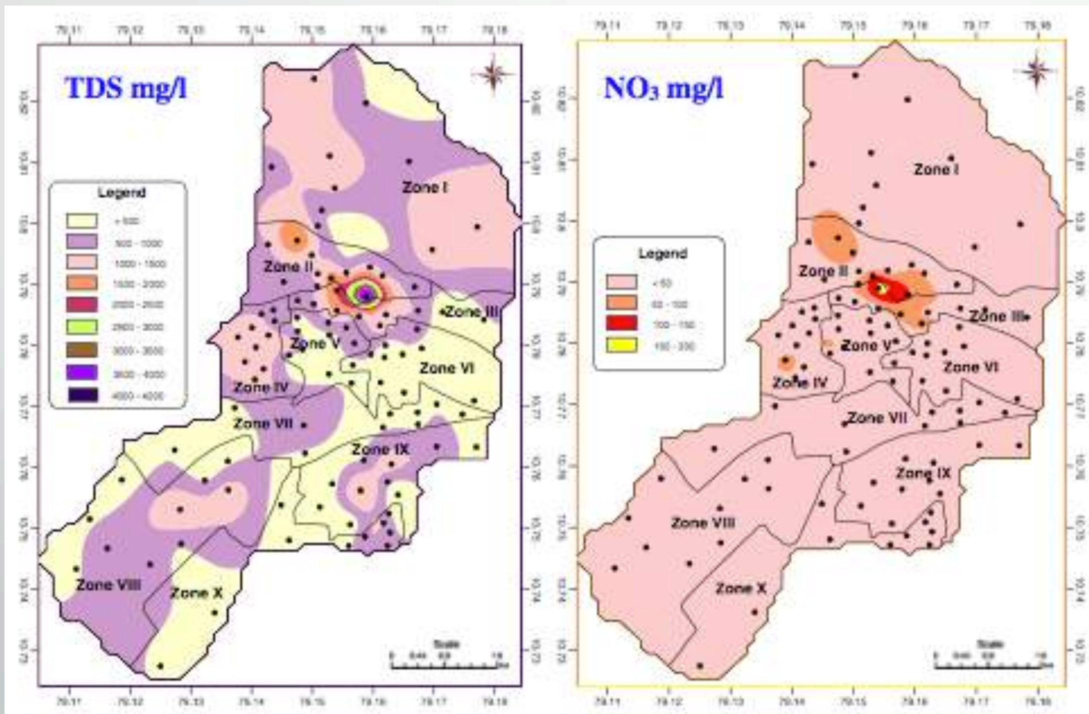
1. Water Sampling Analysis

- Initial conclusions of water sampling analysis:
  - Water chemistry in aquifer is not homogeneous
  - Chemical composition has a wide range of values
- **Research Question:** What causes the wide range of values?

1. Water Sampling Analysis

- 29.4% of samples are considered to be brackish water (TDS > 1000 mg/L)
- 96% of samples have the following distribution: Na > Ca > Mg > K
- 4% of samples have the following distribution: Ca > Na > Mg > K
- 13% of samples exceed 45 mg/L of Nitrate (EPA Standard: 10 mg/L)
- **Initial Conclusion:** A percentage of the groundwater is not safe for drinking or agricultural proposes without previous treatment.

1. Water Sampling Analysis



2. Mineral Dissolution

- SI for carbonate (calcite, dolomite), sulfate (gypsum, anhydrite), and halite minerals were calculated using PHREEQC
- **Results:**
  - SI values for sulfate and halite minerals are highly understaturated
    - No known geological formation for these minerals in study area
  - SI values Calcite and Dolomite vary throughout aquifer
    - Dissolution of carbonate minerals caused by kankar formation

3. Contamination Sources

- High concentrations of Alkalinity, Potassium, Sulfate, Chloride and Nitrate
- High TDS concentration → Saline/Brackish water present
- **Reason?**
  - Wastewater Infiltration: Leaky septic systems and sewer system
  - Fertilizer Infiltration: Washed off agricultural fields and infiltrated with rain

INVERSE MODELING

1. Inverse Modeling 101
2. Solutions Chosen
3. SI Calculation
4. Model Input
5. Choosing Appropriate Output
6. Significance of Model Output

1. Inverse Modeling 101

- Finds the sets of minerals and gasses that, when reacted in appropriate amounts, account for the differences in composition between two solutions
- Typically used for a solution traveling along a flow path
- At least 2 solutions should be used
- **Assumptions:** Homogeneous water chemistry prior to aquifer contamination
- **What are we trying to achieve?** Put a numbers to contamination sources

2. Solutions Chosen

```
SOLUTION 1 - Zone 9 (Average Conditions)
    temp       25
    pH         7
    pe         4
    redox      pe
    units      ppm
    density    1
    Ca         45
    Mg         16
    Na         102
    K          5
    N(5)       9
    Alkalinity 123
    Cl         178
    S(6)       19
    water     1 # kg
EQUILIBRIUM_PHASES 1
      CO2(g)  -3.5
```

```
SOLUTION 2 - Zone 2 (Maximum Conditions)
    temp       25
    pH         9.6
    pe         4
    redox      pe
    units      ppm
    density    1
    Alkalinity 688
    Ca         240
    Cl         1660
    K          60
    Mg         154
    N(5)       102
    Na         740
    S(6)       113
    water     1 # kg
EQUILIBRIUM_PHASES 2
      CO2(g)  -3.5
```

3. SI Calculation

SOLUTION 1 - Zone 9 (Average Conditions)				
Phase	SI**	log IAP	log K(298 K, 1 atm)	
Anhydrite	-2.81	-7.09	-4.28	CaSO4
Aragonite	-0.79	-9.13	-8.34	CaCO3
Calcite	-0.65	-9.13	-8.48	CaCO3
CO2(g)	-1.84	-3.31	-1.47	CO2
Dolomite	-1.40	-18.49	-17.09	CaMg(CO3)2
Gypsum	-2.51	-7.09	-4.58	CaSO4:2H2O
H2(g)	-22.05	-25.15	-3.10	H2
H2O(g)	-1.50	-0.00	1.50	H2O
Halite	-6.31	-4.74	1.57	NaCl
O2(g)	-39.19	-42.08	-2.89	O2
Sylvite	-7.18	-6.28	0.90	KCl

SOLUTION 2 - Zone 2 (Maximum Conditions)				
Phase	SI**	log IAP	log K(298 K, 1 atm)	
Anhydrite	-1.93	-6.21	-4.28	CaSO4
Aragonite	2.36	-5.97	-8.34	CaCO3
Calcite	2.51	-5.97	-8.48	CaCO3
CO2(g)	-4.27	-5.74	-1.47	CO2
Dolomite	5.23	-11.86	-17.09	CaMg(CO3)2
Gypsum	-1.63	-6.21	-4.58	CaSO4:2H2O
H2(g)	-27.25	-30.35	-3.10	H2
H2O(g)	-1.50	-0.00	1.50	H2O
Halite	-4.59	-3.02	1.57	NaCl
O2(g)	-28.79	-31.68	-2.89	O2
Sylvite	-5.24	-4.34	0.90	KCl

4. Model Input

```
SOLUTION 1 - Zone 9 (Average Conditions)
    temp      25
    pH        7
    pe        4
    redox     pe
    units     ppm
    density   1
    Ca        45
    Mg        16
    Na        102
    K         5
    N(5)      9
    Alkalinity 123
    Cl        178
    S(6)      19
    water     1 # kg
EQUILIBRIUM_PHASES 1
      CO2(g)  -3.5
```

```
SOLUTION 2 - Zone 2 (Maximum Conditions)
    temp      25
    pH        9.6
    pe        4
    redox     pe
    units     ppm
    density   1
    Alkalinity 688
    Ca        240
    Cl        1660
    K         60
    Mg        154
    N(5)      102
    Na        740
    S(6)      113
    water     1 # kg
EQUILIBRIUM_PHASES 2
      CO2(g)  -3.5
```

```
INVERSE_MODELING 1
    solutions     1       2
```

→ Output: 158 possible models
→ Input needs to be adjusted

4. Model Input

```
INVERSE_MODELING 1
    solutions       1        2
    uncertainty     0.05     0.1
    phases
        Anhydrite          dis
        Aragonite          pre
        Calcite            pre
        CO2(g)             dis
        Dolomite           pre
        Gypsum
        H2(g)              dis
        H2O(g)             dis
        Halite
        O2(g)              dis
        Sylvite            dis
        H2S(g)
        N2(g)
        NH3(g)
        Sulfur
    balances
        K            0.05     0.05
    range              1000
    minimal
    tolerance          1e-10
    mineral_water      true
    multiple_precision      true
    mp_tolerance 1e-12
    censor_mp 1e-20
```

- **Uncertainty:** Sets uncertainty limits for solutions
- **Phases:** List of phases to be used during inverse modeling
- **Balances:** Includes mole balance for elements not contained in the phases
- **Range:** To display min. and max. ranges in phase transfers
- **Minimal:** To reduce models to the minimum number of phases that can satisfy all constrains
- **Tolerance:** Indicates the tolerance for optimizing solver
- **Mineral Water:** Identifier to include/exclude water derived from minerals in the balance calculations
- **Multiple Precision:** Invokes multiple-precision version Cl1
- **mp_tolerance:** Indicates tolerance of multiple precision method
- **Censor_mp:** Additional identifier of the multiple precision method

5. Choosing Appropriate Output

	Model #1	Model #3	Model #5	Model #7	Model #9
Solution Fraction					
Solution 1	1.26E+01	1.26E+01	1.23E+02	1.23E+01	1.23E+01
Solution 2	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Phase Mole Transfers					
Anhydrite	3.23E+02	3.23E+02	3.14E+02	3.14E+02	3.14E+02
Aragonite				-2.42E-02	-2.42E-02
Calcite	-2.48E-02	-2.48E-02	-2.42E-02		
CO2(g)					
Dolomite	-1.75E-03	-1.75E-03	-1.51E-03	-1.51E-03	-1.51E-03
Gypsum	-3.23E+02	-3.23E+02	-3.14E+02	-3.14E+02	-3.14E+02
H2(g)			7.64E-02		7.64E-02
H2O(g)					
Halite	-2.06E-02	-2.06E-02	-1.91E-02	-1.91E-02	-1.91E-02
O2(g)					
Sylvite					
H2S(g)	-1.95E-02		-1.91E-02	5.73E-02	-1.91E-02
N2(g)	-2.66E-02	-2.01E-02			
NH3(g)	5.27E-02	3.97E-02			
Sulfur		-1.95E-02		-7.64E-02	

	Model #2	Model #4	Model #6	Model #8	Model #10
Solution Fraction					
Solution 1	1.23E+01	1.26E+01	1.23E+01	1.26E+01	1.23E+01
Solution 2	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Phase Mole Transfers					
Anhydrite	3.14E+02	3.23E+02	3.14E+02	3.23E+02	3.14E+02
Aragonite		-2.48E-02	-2.42E-02	-2.48E-02	-2.42E-02
Calcite	-2.42E-02				
CO2(g)					
Dolomite	-1.51E-03	-1.75E-03	-1.51E-03	-1.75E-03	-1.51E-03
Gypsum	-3.14E-02	-3.23E+02	-3.14E+02	-3.23E+02	-3.14E+02
H2(g)			5.73E-02		5.73E-02
H2O(g)					
Halite	-1.91E-02	-2.06E-02	-1.91E-02	-2.06E-02	-1.91E-02
O2(g)					
Sylvite					
H2S(g)	5.73E-02	-1.95E-02			
N2(g)		-2.66E-02		-2.01E-02	
NH3(g)		5.27E-02		3.97E-02	
Sulfur	-7.64E-02		-1.91E-02	-1.95E-02	-1.91E-02

5. Choosing Appropriate Output

- Criteria for selecting the right model:
  - #1: Model must have calcite, dolomite, anhydrite, gypsum and halite
  - #2: Model should have least amount of automatically added phases
    - $H_2S(g)$, $N_2(g)$, $NH_3(g)$, and Sulfur

5. Choosing Appropriate Output

	Model #1	Model #3	Model #5	Model #7	Model #9
Solution Fraction					
Solution 1	1.26E+01	1.26E+01	1.23E+02	1.23E+01	1.23E+01
Solution 2	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Phase Mole Transfers					
Anhydrite	3.23E+02	3.23E+02	3.14E+02	3.14E+02	3.14E+02
Aragonite				-2.42E-02	-2.42E-02
Calcite	-2.48E-02	-2.48E-02	-2.42E-02		
CO2(g)					
Dolomite	-1.75E-03	-1.75E-03	-1.51E-03	-1.51E-03	-1.51E-03
Gypsum	-3.23E+02	-3.23E+02	-3.14E+02	-3.14E+02	-3.14E+02
H2(g)			7.64E-02		7.64E-02
H2O(g)					
Halite	-2.06E-02	-2.06E-02	-1.91E-02	-1.91E-02	-1.91E-02
O2(g)					
Sylvite					
H2S(g)	-1.95E-02		-1.91E-02	5.73E-02	-1.91E-02
N2(g)	-2.66E-02	-2.01E-02			
NH3(g)	5.27E-02	3.97E-02			
Sulfur		-1.95E-02		-7.64E-02	

	Model #2	Model #4	Model #6	Model #8	Model #10
Solution Fraction					
Solution 1	1.23E+01	1.26E+01	1.23E+01	1.26E+01	1.23E+01
Solution 2	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Phase Mole Transfers					
Anhydrite	3.14E+02	3.23E+02	3.14E+02	3.23E+02	3.14E+02
Aragonite		-2.48E-02	-2.42E-02	-2.48E-02	-2.42E-02
Calcite	-2.42E-02				
CO2(g)					
Dolomite	-1.51E-03	-1.75E-03	-1.51E-03	-1.75E-03	-1.51E-03
Gypsum	-3.14E-02	-3.23E+02	-3.14E+02	-3.23E+02	-3.14E+02
H2(g)			5.73E-02		5.73E-02
H2O(g)					
Halite	-1.91E-02	-2.06E-02	-1.91E-02	-2.06E-02	-1.91E-02
O2(g)					
Sylvite					
H2S(g)	5.73E-02	-1.95E-02			
N2(g)		-2.66E-02		-2.01E-02	
NH3(g)		5.27E-02		3.97E-02	
Sulfur	-7.64E-02		-1.91E-02	-1.95E-02	-1.91E-02

5. Significance of Model Output

I. Element Mole Transfers
II. Solution Fractions
III. Phase Mole Transfers

I. Element Mole Transfers

Solution 1: - Zone 9 (Average Conditions)

	Input		Delta		Input+Delta
pH	7.000e+00	+	0.000e+00	=	7.000e+00
Alkalinity	2.459e-03	+	-1.229e-04	=	2.336e-03
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	2.945e-03	+	0.000e+00	=	2.945e-03
Ca	1.123e-03	+	5.617e-05	=	1.179e-03
Cl	5.023e-03	+	-3.486e-05	=	4.988e-03
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	1.279e-04	+	2.535e-06	=	1.305e-04
Mg	6.584e-04	+	3.292e-05	=	6.914e-04
N(-3)	0.000e+00	+	0.000e+00	=	0.000e+00
N(0)	0.000e+00	+	0.000e+00	=	0.000e+00
N(3)	0.000e+00	+	0.000e+00	=	0.000e+00
N(5)	6.429e-04	+	-3.214e-05	=	6.107e-04
Na	4.439e-03	+	0.000e+00	=	4.439e-03
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	1.979e-04	+	-9.894e-06	=	1.880e-04

Solution 2: - Zone 2 (Maximum Conditions)

	Input		Delta		Input+Delta
pH	9.600e+00	+	0.000e+00	=	9.600e+00
Alkalinity	1.380e-02	+	-1.380e-03	=	1.242e-02
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	8.970e-03	+	0.000e+00	=	8.970e-03
Ca	6.011e-03	+	6.011e-04	=	6.612e-03
Cl	4.700e-02	+	-4.700e-03	=	4.230e-02
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
K	1.540e-03	+	6.476e-05	=	1.605e-03
Mg	6.358e-03	+	6.358e-04	=	6.994e-03
N(-3)	0.000e+00	+	0.000e+00	=	0.000e+00
N(0)	0.000e+00	+	0.000e+00	=	0.000e+00
N(3)	0.000e+00	+	0.000e+00	=	0.000e+00
N(5)	7.310e-03	+	2.033e-04	=	7.513e-03
Na	3.231e-02	+	3.231e-03	=	3.554e-02
O(0)	0.000e+00	+	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	1.181e-03	+	-1.181e-04	=	1.063e-03

Concentration (mol/kg water) or (pH)

Input + Uncertainty

Added Uncertainty

II. Solution Fractions

Solution fractions:			Minimum	Maximum
Solution	1	1.230e+01	1.227e+01	1.232e+01
Solution	2	1.000e+00	1.000e+00	1.000e+00

- Solution #1 (Zone 9) must be concentrated 12.3 fold to produce solution #2 (Zone 2)
- 12.3 kg of water in solution #1 is reduced to 1 kg of water in solution #2
- Look into phase mole transfers in order to find out where the 12.3 times concentration is coming from

III. Phase Mole Transfers

Phase mole transfers:		Minimum	Maximum	
Anhydrite	3.137e+02	3.129e+02	3.143e+02	CaSO4
Calcite	-2.424e-02	-2.701e-02	-2.146e-02	CaCO3
Dolomite	-1.511e-03	-1.525e-03	-1.491e-03	CaMg(CO3)2
Gypsum	-3.137e+02	-3.143e+02	-3.129e+02	CaSO4:2H2O
Halite	-1.907e-02	-2.189e-02	-1.627e-02	NaCl
H2S(g)	5.732e-02	4.905e-02	6.556e-02	H2S
Sulfur	-7.642e-02	-8.741e-02	-6.540e-02	S

Optimized Phase Transfers
(mol/12.3 kg water)

(-) Precipitation → Out of solution

(+) Dissolution → Into solution

Optimized Phase Transfers
(mol/kg water)

Anhydrite	2.55E+01
Calcite	-1.97E-03
Dolomite	-1.23E-04
Gypsum	-2.55E+01
Halite	-1.55E-03
H2S(g)	4.66E-03
Sulfur	-6.21E-03

Conclusions

- Inverse modeling shows that within the given uncertainty limits precipitation of calcite, dolomite, gypsum, halite and sulfur, and dissolution of anhydrite can $H_2S(g)$ can explain the changes in major ion composition
- Confirms that contamination is occurring

REFERENCES

- Nagaragan, R., Rajmohan, N., Mahendran, U., and Senthamilkumar, S. (2010). Evaluation of Groundwater Quality and its Suitability for Drinking and Agricultural use in Thanjavur City, Tamil Nadu, India. *Environmental Monitoring and Assessment.* 171: 289-308

Thank you!
Questions?