Arsenic Tracing in the Mississippi River Valley Aquifer

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Outline

- Arsenic
- Article Problem
- Locations
- Methods
- Modeling
- Article Output
- Article Conclusions
- Flow Path Modeling
- Conclusions

Arsenic

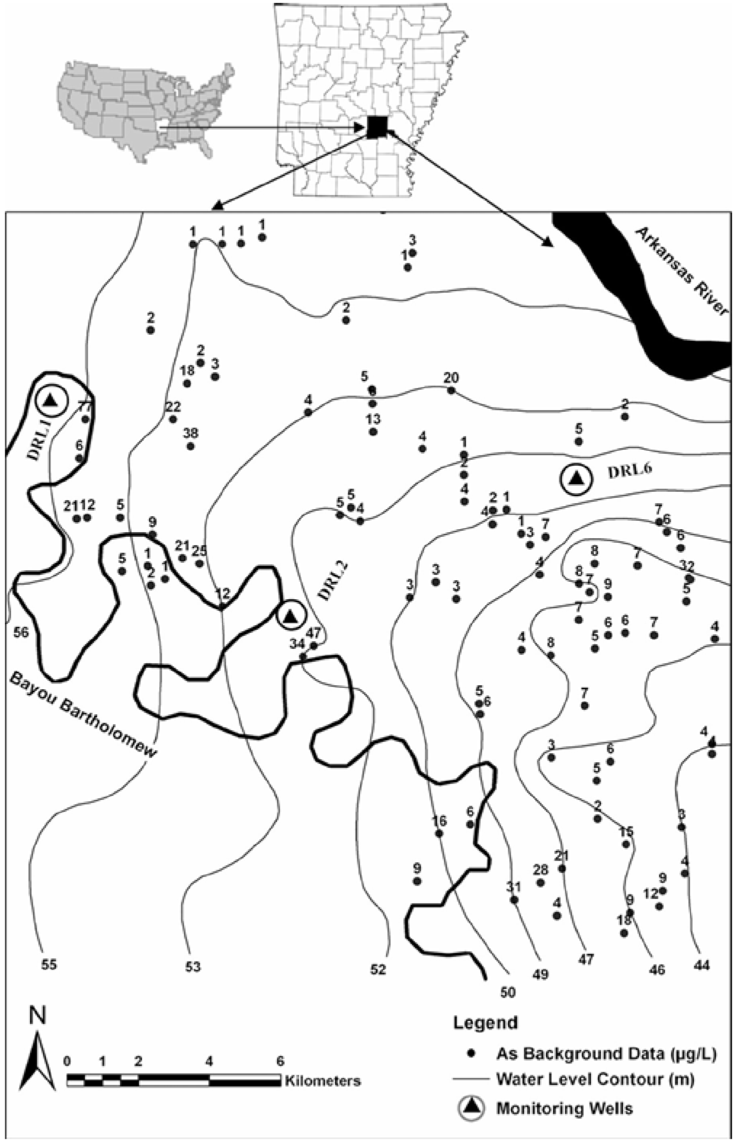
- Natural element found in soils
- As is recognized as a carcinogen
- Was once found in insecticides, pesticides, and herbicides
- Found today in pharmaceutical and glass industries
- Also used as a feed additive to increase weight gain and to treat diseases in swine and poultry
- Toxicity is linked to solubility, which is linked to pH and redox
- Sources of contamination for humans
  - Drinking water
  - Crops
  - Animal products

Article Problem

- Inverse modeling performed to analyze distribution of arsenic (As) in southeastern Arkansas
- Reductive dissolution of Fe oxyhydroxide suggested as the dominant release method
- Groundwater in this area heavily used for crop production
- Arsenic affects other areas of the world, especially in the Ganges-Brahmaputra-Meghna Delta region of Bangladesh
- US EPA and WHO safe level of 0.01 mg/L (10 ppb) in drinking water
  - Bangladesh water was found to have >0.05 mg/L from natural sources

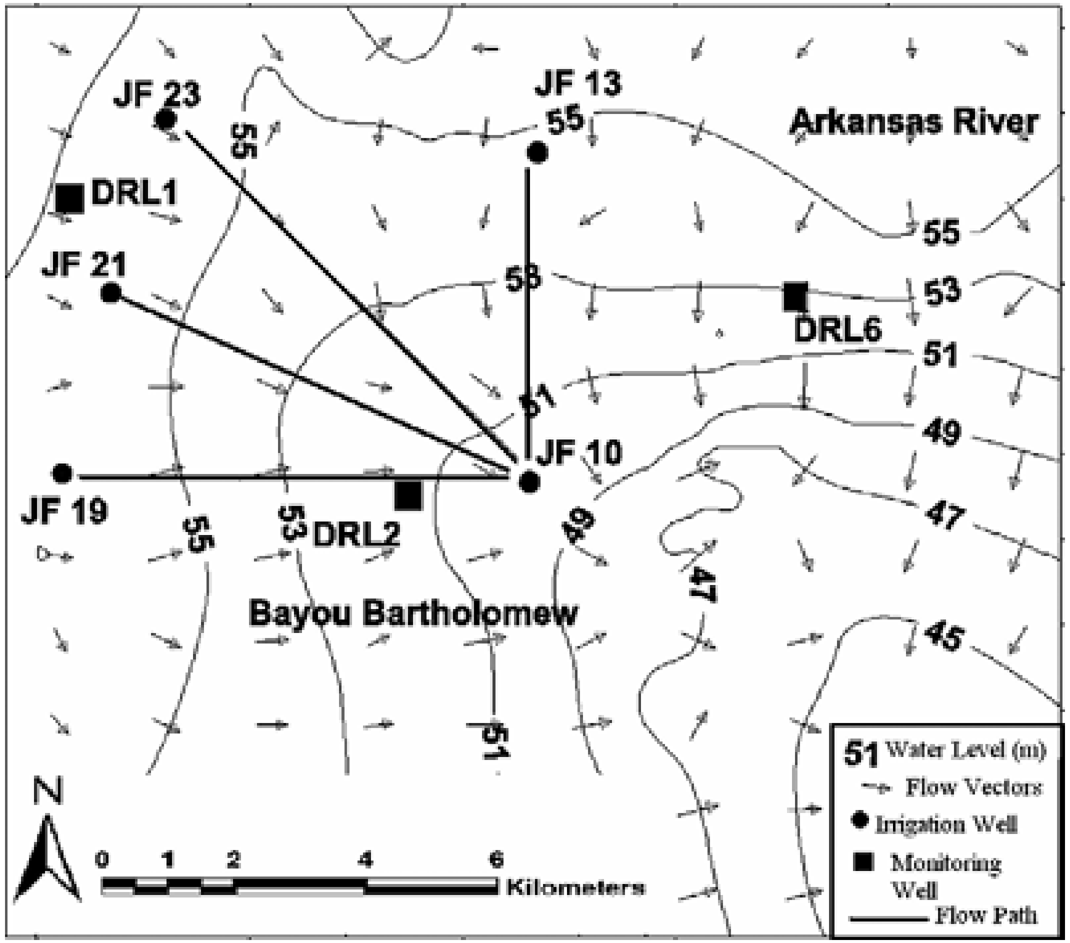
Location of study area

- As background data
- Water level contours
- Monitoring well sites



Modeled flow vectors and flow lines

- Irrigation wells (circles)
- Monitoring wells (squares)



Model Components

- 3 different sample areas
  - DRL1 – High As levels
  - DRL2 – Medium As levels
  - DRL6 – Low As levels
- Shallow level (10.6 m) and deep level (36.5 m) designations
- Analysis included field and well head measurements

Parameter	DRL1S	DRL1D	DRL2S	DRL2D	DRL6S	DRL6D
Water level (m bls)	5.6	5.7	6.9	6.8	8.4	8.3
Temperature (°C)	18.5	17.9	19.5	18.5	18.9	18.5
EC (μS/cm)	310	306	456	426	953	658
TDS (mg/L)	209	187	261	241	572	382
pH	6.11	6.13	6.87	6.81	6.84	6.68
Alkalinity (mg/L as $CaCO_3$)	108	135	215	189	437	300
ORP (RmV)	198	124	55	66	−247	−223
DO (mg/L)	0.4	0.08	0.06	0.06	0.08	0.08
Hardness (mg/L)	102	61	177	164	426	278
Total dissolved As (μg/L)	0.73	29.6	12.3	39.7	49.4	1.02
As(III) (μg/L)	<0.5	10.2	1.14	8.22	5.23	<0.5
As(V) (μg/L)	0.7	20.3	11.4	33.9	45.3	1.15
Particulate As (μg/L)	0.1	0	0	2.2	0	0.3
Total Fe (mg/L)	1.9	41	11.5	16.3	8.3	11
Fe^{2+} (mg/L)	0.04	9.2	7.3	8.5	4.6	5.8
Fe^{3+} (mg/L)	1.6	31.8	4.2	7.8	2.8	3.9
Particulate Fe (mg/L)	0.24	1.7	0.1	0	0.16	0.3
Ca^{2+} (mg/L)	25.4	17.4	55.6	48.8	130	80
Mg^{2+} (mg/L)	9.3	4.4	9.4	10.3	24.7	18.9
Na^{+} (mg/L)	16.3	11.7	16.3	17.1	41.8	18.7
K^{+} (mg/L)	2	2.6	1.1	1.4	1.5	1.2
Mn^{2+} (mg/L)	2.7	1.5	0.5	0.7	0.4	0.7
Cl^{-} (mg/L)	14.2	20.1	7.7	7.6	27.1	29.6
SO_4^{2-} (mg/L)	18	2	1	1.4	46	1.4
NO_3^{-}—N (mg/L)	2.25	<0.01	<0.01	<0.01	<0.01	<0.01
NH_4—N (mg/L)	0.03	0.21	0.9	0.35	1.1	0.72
PO_4—P (mg/L)	0.02	0.03	0.03	0.05	0.02	0.05
S^{2-} (μg/L)	2	6	11	51	27	27
SiO_2 (mg/L)	31.7	32.9	31.6	34	34.4	28.3
Br^{-} (mg/L)	0.08	0.08	0.06	0.06	0.14	0.12
Ba^{2+} (μg/L)	166	198	215	150	538	388
B^{3+} (μg/L)	25	13	35	30	42	44
Fl^{-} (mg/L)	0.4	0.3	0.3	0.4	<0.01	0.3
Zn^{2+} (μg/L)	2.7	5.2	2.4	3.8	1.7	1.4
V^{5+} (μg/L)	0.96	0.51	<0.50	<0.50	<0.50	<0.50
Co^{2+} (μg/L)	1.95	6.44	0.52	<0.50	<0.50	<0.50
Ni^{2+} (μg/L)	2.7	4.4	<0.50	<0.50	<0.50	<0.50
TOC (mg/L)	6.2	6.8	6	6.3	11	6.8
Volatile organic and inorganic compound (ppm)	<0.1	<0.1	0.3	0.5	1.4	0.7

Methods

- Collection was done in accordance with USGS methods
- The well was pumped for 30-45 min to collect temperature, electrical conductance (EC), pH, oxidation reduction potential (ORP), and dissolved oxygen (DO) readings
- Groundwater was collected in four 100 mL bottles
  - 1: Filtered (0.45 μm) and acidified
  - 2: Not-filtered and acidified
  - 3: Filtered (0.20 μm) and acidified
  - 4: Filtered (0.45 μm) and not-acidified
- Dissolved cations were measured on the acidified samples, dissolved anions were measured on the non-acidified samples

Statistics

- Data obtained from existing irrigation wells in the research area from 2002
- Metal analysis was done with a 0.45 µm membrane and preserved in nitric acid
- A plasma optical-emission mass spectrometer ran tests for trace metals
- These samples lacked Fe and As speciation, DO, dissolved H_2S, and ORP; these were supplemented using data from the DRL wells

Parameters measured	Minimum	Maximum	Mean	Median	Std. deviation
Water level (m)	3.3	12.4	7.4	7	2.16
Temperature (°C)	17.3	19.5	17.9	18	0.47
Conductivity (µS/cm)	148	1353	528	421	309
TDS (mg/L)	168	746	327	261	157
pH	6.11	7.06	6.7	6.8	0.24
Alkalinity (mg/L as $CaCO_3$)	52	437	219	188	111
Hardness (mg/L)	43	491	203	164	127
As (µg/L)	0.73	50	14.1	7	15.3
Fe (mg/L)	1.87	41	11.9	10.5	8.1
Ca (mg/L)	10.6	143	58.7	48.6	37.6
Mg (mg/L)	4.1	33.5	13.8	10.3	8.3
Na (mg/L)	10.7	72	25.1	18.7	15.1
K (mg/L)	0.46	4.9	1.96	1.9	1.05
Mn (mg/L)	0.29	1.8	0.68	0.6	0.37
Cl (mg/L)	4.82	116	25.5	18	27.9
SO_4 (mg/L)	0.95	85.2	12.2	4	19.1
NO_3–N (mg/L)	<0.01	2.25	0.14	0.02	0.43
NH_3–N (mg/L)	0.04	1.06	0.29	0.23	0.25
PO_4–P (mg/L)	<0.005	0.1	0.03	0.02	0.03
Ni (µg/L)	<0.5	4.4	1.9	2	0.75
Cu (µg/L)	<5	46	7.2	5	7.8
SiO_2 (mg/L)	24.7	51.7	33.5	32.3	4.8
Br (mg/L)	<0.01	0.52	0.12	0.09	0.12
Ba (µg/L)	0.12	0.78	0.27	0.14	0.17
B (µg/L)	4.5	48.6	18.5	13.4	14.7
F (mg/L)	<0.01	0.4	0.24	0.23	0.08
Zn (µg/L)	<1	5	1.8	1.7	1
V (µg/L)	<0.5	1.9	1	1	0.33
Cr (µg/L)	<0.4	3	0.7	0.5	6.6
TOC (mg/L)	0.33	11	2.8	1.8	2.5

Article conclusions

- Common supersaturated phases
  - Quartz
  - Magnetite
  - Pyrite
  - $Ba_3(AsO_4)_2$ – Barium Arsenate
- Fe oxyhydroxide is dominant in releasing As
- Redox state is the main factor that affects the rate of Fe oxyhydroxide reduction

Phases	JF10	JF13	JF19	JF21	JF23
Sphalerite	−4.46	Supersaturated	−5.49	Supersaturated	−5.40
FeS (ppt)	−9.85	−2.29	−11.1	−2.65	−7.86
Ferrihydrite	−6.01	−6.01	−5.22	−5.78	−6.14
Goethite	−3.26	−3.25	−2.45	−3.02	−3.80
Hematite	−4.15	−4.14	−2.54	3.67	−4.39
Siderite	−0.29	Supersaturated	Supersaturated	−0.60	Supersaturated
Fluorite	−1.91	−1.60	−2.80	−2.25	−2.05
Halite	−8.26	−8.08	−8.06	−8.40	−8.26
Calcite	−0.58	−0.05	−0.40	−1.33	−0.92
Dolomite	−1.49	−0.47	−1.20	−2.94	−2.31
Gypsum	−3.25	−2.23	−3.30	−2.96	−2.92
Barite	−0.80	Supersaturated	−0.38	−0.28	−0.49
Manganite	−8.92	–	−9.83	–	−8.14
Magnesite	−1.84	−1.34	−1.72	−2.54	−2.34
Vivianite	−4.84	−5.97	−5.56	−5.01	−2.78
$FeAsO_4 \cdot 2H_2O$	−19.0	−19.0	−16.3	−17.7	−18.4

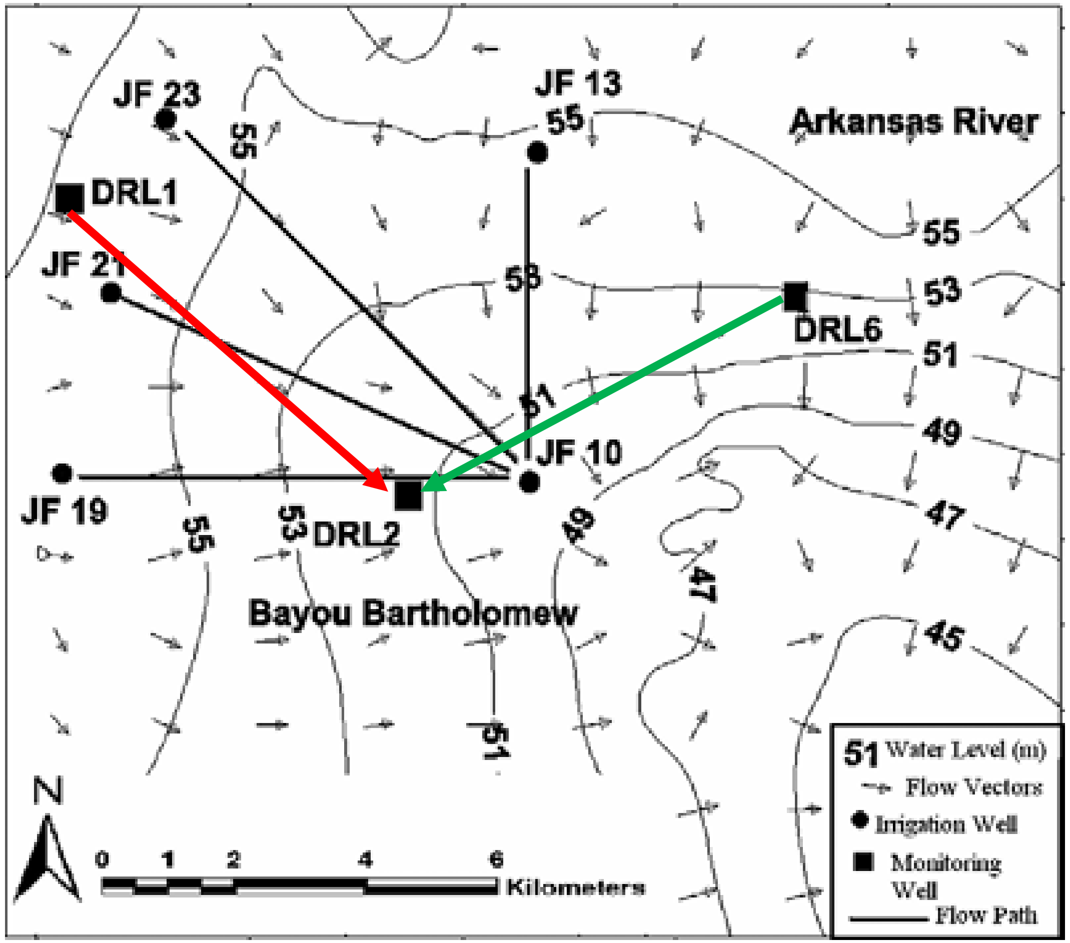
Comparison to Bangladesh As

- Sediment As concentrations and groundwater chemistry similar between Arkansas aquifer and Bangladesh, but aqueous As concentrations in this area are less than Bangladesh
- The biggest difference comes from the concentration of sulfate and its relationship with the reducing environment
- Sulfate reduction has not occurred in Bangladesh, so As has remained mobile in the reducing conditions
- Could be explained by concentration levels
  - Bangladesh: <3 mg/L
  - Arkansas: 1 to 46 mg/L

My analysis

- Flow path analysis
  - Red: DRL1S to DRL2S
  - Green: DRL6S to DRL2S

- Selected to compare to results found in the article
- MINTEQ.V4 database used, similar to the original MINTEQA2 database used in the article



Flow Path Modeling Inputs

```
SOLUTION 1
    temp        18.5
    pH          6.11
    pe          4
    redox       pe
    units       ppm
    density     1
    Alkalinity 108
    As          0.00073
    Ba          0.166
    Ca          25.4
    Cl          14.2
    Fe(2)       0.04
    Fe(3)       1.6
    Mg          9.3
    Mn(2)       2.7
    N(-3)       2.25
    N(5)        0.03
    Na          16.3
    P           0.02
    S(6)        0.002
    Si          31.7
    Zn          0.0027
    O(0)        0.06
    -water      1 # kg
```

```
SOLUTION 2
    temp        17.9
    pH          6.13
    pe          4
    redox       pe
    units       ppm
    density     1
    Alkalinity 135
    As          0.0296
    Ba          0.198
    Ca          17.4
    Cl          20.1
    Fe(2)       9.2
    Fe(3)       31.8
    Mg          4.4
    Mn(2)       1.5
    N(-3)       0.01
    N(5)        0.21
    Na          11.7
    O(0)        0.4
    P           0.03
    S(6)        0.006
    Si          32.9
    Zn          0.0052
    -water      1 # kg
```

```
SOLUTION 3
    temp        18.5
    pH          6.68
    pe          4
    redox       pe
    units       ppm
    density     1
    Alkalinity 300
    As          0.00102
    Ba          0.388
    Ca          80
    Cl          29.6
    Fe(2)       5.8
    Fe(3)       3.9
    Mg          18.9
    Mn(2)       0.7
    N(-3)       0.01
    N(5)        0.72
    Na          18.7
    P           0.05
    S(6)        0.027
    Si          28.3
    Zn          0.0014
    O(0)        0.08
    -water      1 # kg
```

- Solution 1: DRL1S
- Solution 2: DRL2S
- Solution 3: DRL6S

Modeling Challenges

- Uncertainties – had to be increased from the example observed
- Equalities/inequalities
  - Led to removing some elements given in the article
- Number of models
  - PHREEQC returned 1000-2000 models, reduced that to 409 and 820
- Transferring model data to excel
  - Required importing and formatting data to be interpreted
  - SI data was not transferred

```
-balance
      As(3) 0.45  0.25
      As(5) 0.45  0.25
      Ba    0.45  0.25
      Ca    0.45  0.25
      Cl    0.45  0.25
      Fe(2) 0.45  0.25
      Fe(3) 0.45  0.25
      Mg    0.45  0.25
      Mn(2) 0.45  0.25
      N(-3) 0.45  0.25
      N(5)  0.45  0.25
      Na    0.45  0.25
      P     0.45  0.25
      Si    0.45  0.25
      Zn    0.45  0.25
```

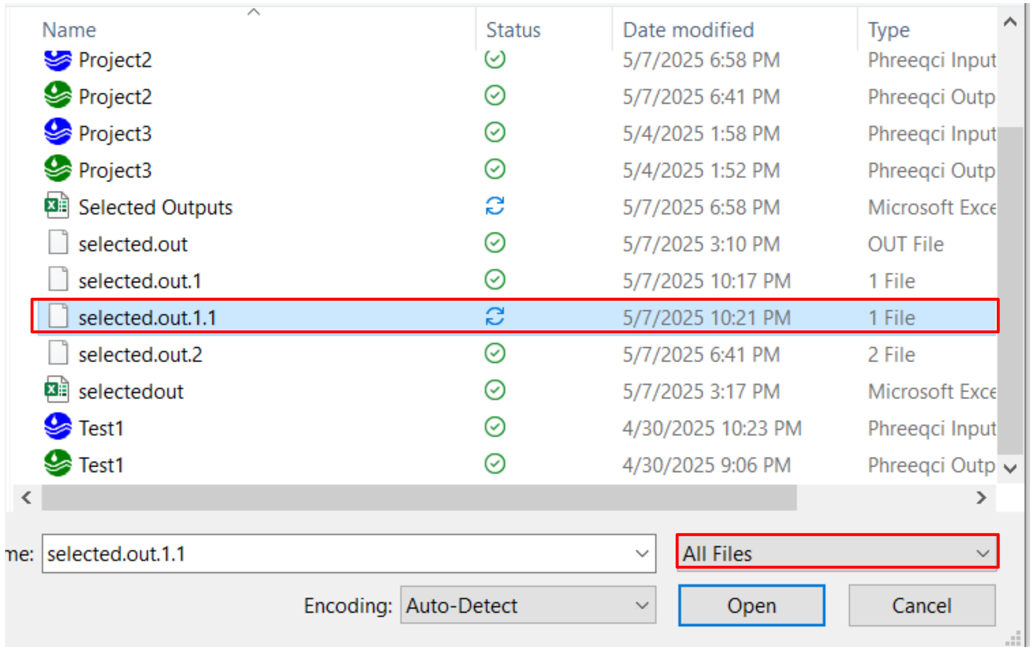
Simulation 1. Inverse 1. Models = 409.

Data Transfer

1. Data block for exporting results into a table

```
SELECTED_OUTPUT
        -file selected.out.1.1
        -user_punch true
        -inverse_modeling true
```

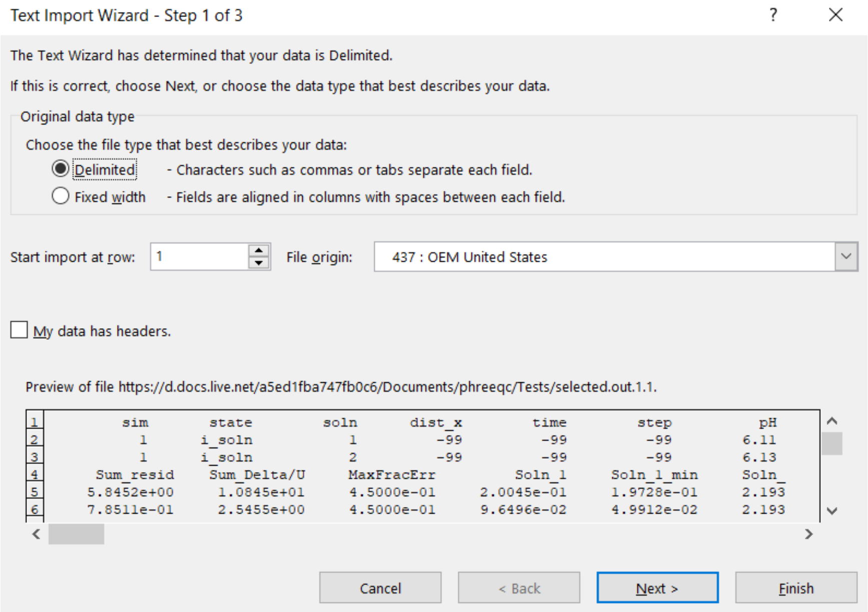
2. Access output through Notepad



Data Transfer cont.

3. Use Notepad to open data in Excel

4. Save and format Excel data



			Solution 3			Solution 2			Calcite			Gypsum		
Sum_res	Sum_Del	MaxFrac	Soln_3	Soln_3_n	Soln_3_n	Soln_2	Soln_2_n	Soln_2_n	Calcite	Calcite_r	Calcite_r	Gypsum	Gypsum	Gypsum
4.00E+00	5.37E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2.77E+00	5.13E+00	4.50E-01	4.68E-01	3.51E-01	5.29E-01	1.00E+00	1.00E+00	1.00E+00	1.05E+00	9.33E-01	1.29E+00	-1.05E+00	########	-9.33E-01
3.63E+00	4.76E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	4.74E+00	3.75E+00	4.74E+00
3.63E+00	4.76E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	2.69E+01	2.12E+01	2.69E+01
2.90E+00	5.91E+00	4.50E-01	4.31E-01	3.51E-01	5.29E-01	1.00E+00	1.00E+00	1.00E+00	1.02E+00	8.43E-01	1.16E+00	-1.02E+00	########	-8.43E-01
4.00E+00	5.37E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
4.06E+00	5.48E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3.63E+00	4.76E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	4.74E+00	3.75E+00	4.74E+00
3.83E+00	5.10E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-2.77E+00	########	########
2.61E+00	5.25E+00	4.50E-01	4.31E-01	3.51E-01	5.29E-01	1.00E+00	1.00E+00	1.00E+00	-1.58E+01	########	########	1.58E+01	1.31E+01	1.80E+01
4.43E+00	5.96E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-7.90E-01	-7.90E-01	-6.25E-01
7.07E+00	8.86E+00	4.50E-01	6.67E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
4.43E+00	5.96E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-2.46E+00	########	########
3.63E+00	4.76E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-2.44E-03	-2.92E-03	-1.52E-03
3.83E+00	5.10E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-7.14E-01	-7.14E-01	-5.64E-01
7.57E+00	9.36E+00	4.50E-01	6.67E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-1.90E-07	-2.28E-07	-1.42E-07
6.93E+00	8.56E+00	4.50E-01	6.71E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
4.00E+00	5.37E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2.61E+00	5.25E+00	4.50E-01	4.31E-01	3.51E-01	5.29E-01	1.00E+00	1.00E+00	1.00E+00	-3.74E+01	########	########	3.74E+01	3.10E+01	4.27E+01
6.10E+00	7.40E+00	4.50E-01	6.67E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	1.11E+01	1.05E+01	1.33E+01
4.00E+00	5.37E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
4.06E+00	5.48E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3.63E+00	4.76E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	1.96E-03	8.77E-04	2.48E-03	-2.44E-03	-2.92E-03	-1.52E-03
4.06E+00	5.48E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
3.83E+00	5.10E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	-2.77E+00	########	########
3.83E+00	5.10E+00	4.50E-01	6.01E-01	6.01E-01	6.85E-01	1.00E+00	1.00E+00	1.00E+00	0.00E+00	0.00E+00	0.00E+00	1.11E+01	8.75E+00	1.11E+01

Flow Path Observations

- Many changes and variations within the different models found
- Consistently no Fluorite
- Most models did not have Dolomite
- Barium Arsenate had higher average phase mole transfers between DRL1S and DRLS2S than DRL6S
- Scorodite ($FeAsO_4$ $2H_2O$) was comparable between the flow paths

	Barium Arsenate		Scorodite	
	DRL1S-DRL2S	DRL6S-DRL2S	DRL1S-DRL2S	DRL6S-DRL2S
Max	2.93E+01	4.66E+01	2.51E+01	1.91E+01
Avg	7.14E-01	2.70E+00	-5.41E+00	-1.43E+00
Min	-9.57E+00	-1.25E+01	-9.32E+01	-5.86E+01

Comparison of Results

- 21-10 compared to DRL1S-DRL2S
- 13-10 compared to DRL6S-DRL2S
- Differences in results may come from uncertainties and some elements being neglected

Mineral phases	Phase state	Phase mole transfers JF23—JF10	Phase mole transfers JF21—JF10	Phase mole transfers JF19-JF10	Phase mole transfers JF13-JF10
Calcite	Dissolving	2.74E − 04	1.40E − 03	1.35E − 03	—
Gypsum	Dissolving	2.33E − 04	—	—	8.80E − 06
CH_2O	Dissolving	5.92E − 04	3.11	2.07	2.88
Halite	Dissolving	1.35E − 04	2.13E − 04	—	1.56E − 04
Fluorite	Dissolving	5.32E − 07	4.15E − 06	3.43E − 06	3.04E − 06
$Fe(OH)_3$(a)	Dissolving	1.79E − 04	1.25E + 01	8.29	—
FeS (ppt)	Precipitating	−2.72E − 04	−9.34	−7.68	−8.65
H_2S(g)	Dissolving	—	9.34	7.68	8.65
Siderite	Precipitating	—	−3.11	−6.12E − 01	−2.88
Sphalerite	Dissolving	−2.44E − 08	1.11E − 08	—	9.78E − 09
Barite	Dissolving	5.11E − 07	8.15E − 07	4.69E − 07	−2.03E − 07
Vivianite	Precipitating	−1.61E − 07	−2.64E-07	−7.09E − 07	−2.27E − 07
NaX	Dissolving		2.51E − 04	2.09E − 04	—
CaX_2	Precipitating	−2.27E − 04	−4.93E-04	−4.77E − 04	—
CO_2(g)	Precipitating	—	—	−1.46	—
NH_3(g)	Dissolving	6.43E − 06	—	—	—

Overall Conclusions

- Inverse modeling is a powerful tool in examining how groundwater may evolve over different flow paths
- It is important to know as much about the different solutions to get accurate models
- Arsenic levels in this study area are affected by Fe and Mn oxyhydroxides, which are affected by the redox environment
- As levels are also affected by sulfate concentration levels
- As compounds, such as Barium Arsenate and Scorodite, are also affected by the concentration levels of As and other elements in them, as well as temperature and pH

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Questions?