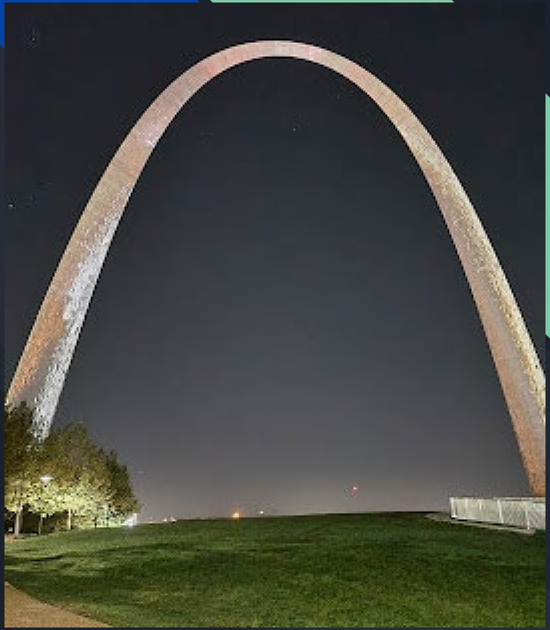


Point sources vs nonpoint sources and Inverse Modeling in the Lower Missouri River

By PJ McCurry

NDSU Geochemistry, Spring 2025

Baseline research

- Nonpoint Sources in the lower Missouri River by Robert E. Criss, M. Lee Davison, and James W. Kopp
  - Wanted to see how much of the Lower Missouri River water quality was influenced by nonpoint sources vs point sources.
  - Determine whether changes in solute loads were driven mainly by river flow from upstream or by local runoff, groundwater, and other nonpoint sources.
  - This required characterizing seasonal and event-driven changes in flow and water quality and separating the contribution of different sources

Nonpoint and point sources

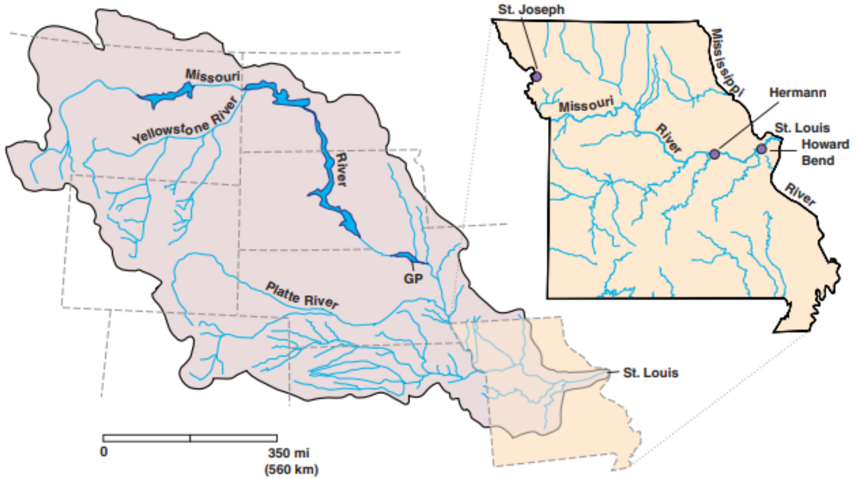
Fig 1: Urban Stormwater chart (Coa, 2023)

- Nonpoint sources
    - Water contamination from many dispersed sources, rather than a single identifiable point.
        - Agricultural runoff
        - Urban stormwater
        - Atmospheric deposition
- Point sources
    - Pollutants entering a waterway from a single, identifiable source like a pipe or ditch
        - Discharge from:
            - Sewage treatment plants
            - Factories
            - City storm drains.

Fig 2: Diagram of a sewage treatment plant (Water Treatment Plant…)

Location

FIGURE 1 Missouri River basin showing the locations of the Howard Bend Waterworks (river mile 37.1) and the gauging stations at Hermann (river mile 97.9) and St. Joseph, Mo. (river mile 448.2)

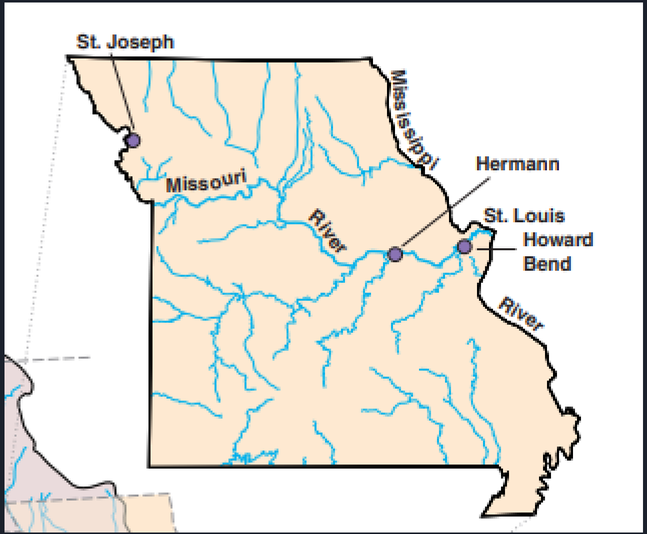


The last major impoundment on the main stem of the river is above the Gavins Point Dam (GP) near Yankton, S.D. Modified after maps by the US Army Corps of Engineers and Schroeder (1982).

- Missouri River water basin
  - Upper midwest - midwest
- Missouri
  - St. Joseph- St. Louis

Fig 3: showing the Missouri river/ Missouri River basin, as well as the Missouri river in Missouri (Criss et al, 2001)

samples



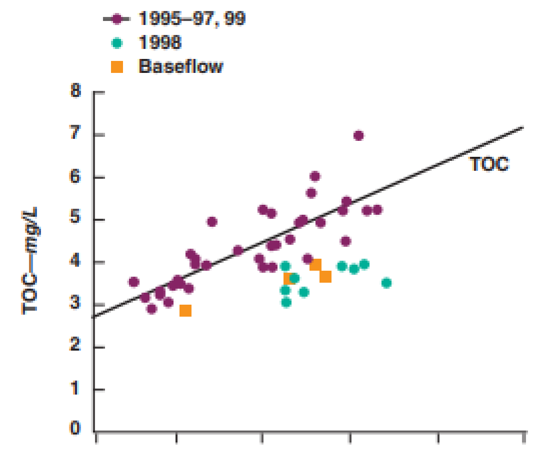
- Used composite samples from major water-treatment intakes
- Locations
    - St. Joseph, Herrmann, and Howards bend
- data collected over the years 1995-1999
    - Included both high flow and low flow years

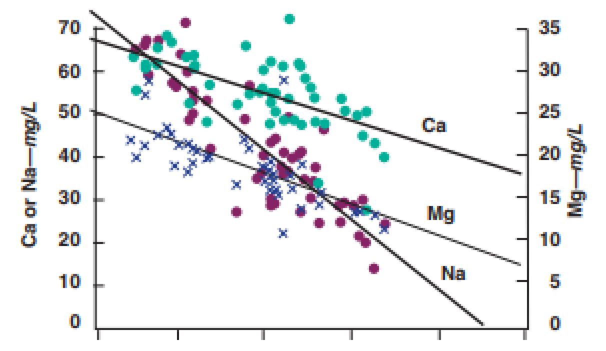
Fig 4: Map of Missouri showing the Missouri River)Criss et al. 2001)

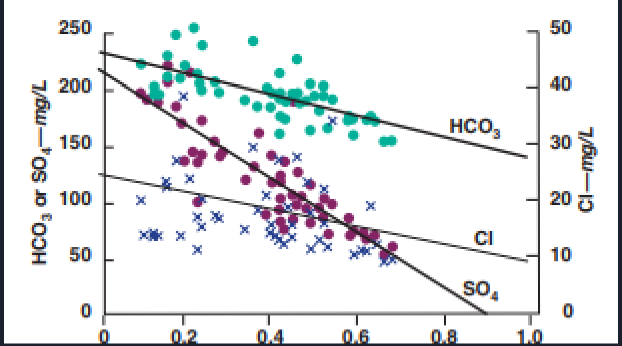
What they did

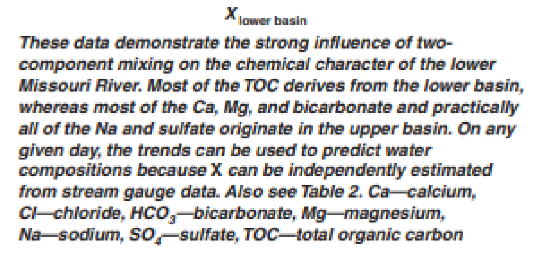
- Hydrologic Analysis
  - Using a mixing fraction (X) parameter that described the proportion of river flow coming from old (baseflow) vs. new (storm/runoff) water on each day
  - This fraction was used to relate streamflow to water chemistry
- Water chemistry and tracer measurements
  - Lab analyses measured:
    - Major ion concentrations
      - Ca, Mg, K, Na, Cl, SO4, ect.
    - Dissolved solids
    - Nutrients
    - Organic matter
- Data Analysis:
  - Examined correlations between water quality parameters and flow
    - EC and isotope ratios were compared with the mixing fraction X and river discharge
  - Mixing models were applied to estimate the relative contributions of baseflow and event water to the river chemistry

Monthly averages of several parameters versus the mixing factor X









$X_{\text{lower basin}}$

These data demonstrate the strong influence of two-component mixing on the chemical character of the lower Missouri River. Most of the TOC derives from the lower basin, whereas most of the Ca, Mg, and bicarbonate and practically all of the Na and sulfate originate in the upper basin. On any given day, the trends can be used to predict water compositions because X can be independently estimated from stream gauge data. Also see Table 2. Ca—calcium, Cl—chloride, HCO_3—bicarbonate, Mg—magnesium, Na—sodium, SO_4—sulfate, TOC—total organic carbon

Fig 5: Monthly averages of several parameters vs the mixing factor x (criss et al. 2001)

findings

- Flow controls on chemistry
  - Strong coupling between river discharge and water chemistry
    - High-flow events brought diluted, low-conductivity water
    - Low-flow conditions had more concentrated solutes
  - Many parameters varied with the mixing fraction X
    - Electrical conductivity was found to correlate well with X, confirming that EC largely reflected the mix of groundwater vs stormwater in the river
  - Most chemical variation could be explained by hydraulic changes rather than new pollutant
- Dominance of upstream water:
  - Quantitative mixing showed that the vast majority of lower Missouri flow was upstream water, not local runoff.
  - Only a small fraction of the daily flow ever came from local nonpoint inputs in the urban area.

Finding pt 2

- Relative Minor role of local Inputs
  - Nonpoint sources contributed only minor amounts of pollutants compared to the main river flow.
  - No evidence of large spikes of any pollutant purely from local runoff
  - As flow increased, river concentration of most constituents simply diluted
  - During drought periods, concentrations rose in a manner consistent with groundwater contributions.

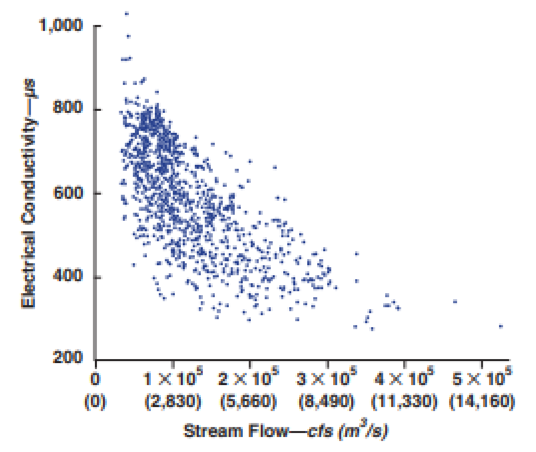
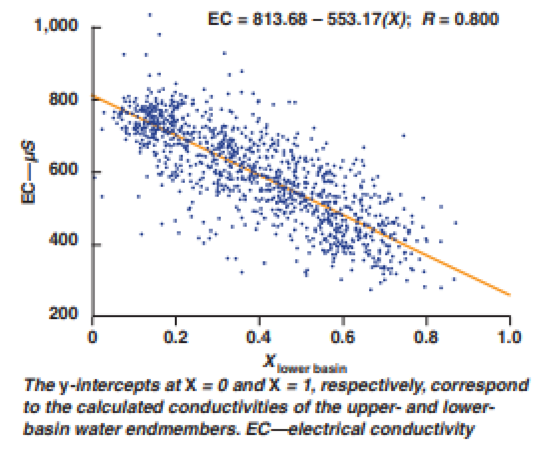


Fig 6: An approximately inverse relationship between the Ec at Howard Bend and the Stream flow measured at Hermann, Mo



The y-intercepts at X = 0 and X = 1, respectively, correspond to the calculated conductivities of the upper- and lower-basin water endmembers. EC—electrical conductivity

Fig 7: EC vs. mixing fraction X of lower basin water

Interpretation of findings

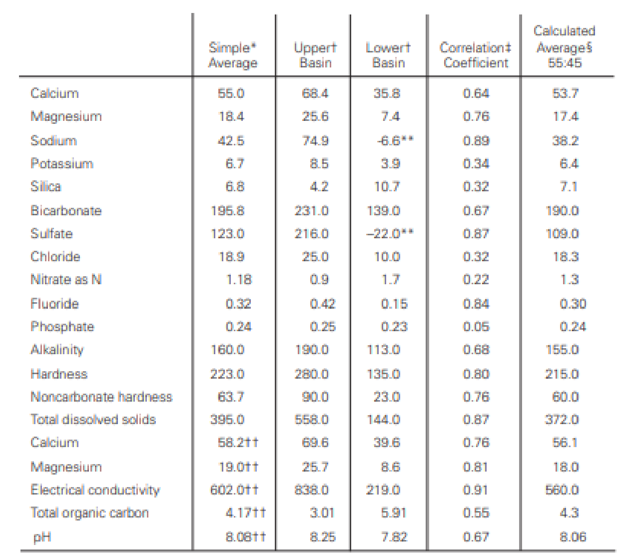
- Interpretation of Mixing relationships
    - EC-X relationship is evidence that the lower Missouri RIver behaves like a two-component system
    - Correlation of conductivity with X suggests that these solutions are largely conservative tracers of the mix
        - As more rainwater enters the river, conductivity drops
        - When flow recedes, more mineral-rich groundwater dominates and conductivity rises
- Isotopic evidence
    - High flows had isotopic values closer to precipitation
    - Low flows reflected more weathered groundwater values
- Implications for nonpoint pollution
    - Large nonpoint pollution sources were not present
        - Virtually all solute concentration changes could be explained by simple dilution and mixing
    - If they were
        - Expect anomalies or trends independent of flow

Conclusion

- River Hydrology dominates water quality in the lower missouri
- Variations in flow explained almost all chemical and isotopic variability
    - Nonpoint sources within st. louis area had only a marginal effect on overall river chemistry.
- Mixing analysis with tracers is a useful method for differentiating ravine sources and highlights the importance of accounting for flow variability in assessing nonpoint pollution.

What I did

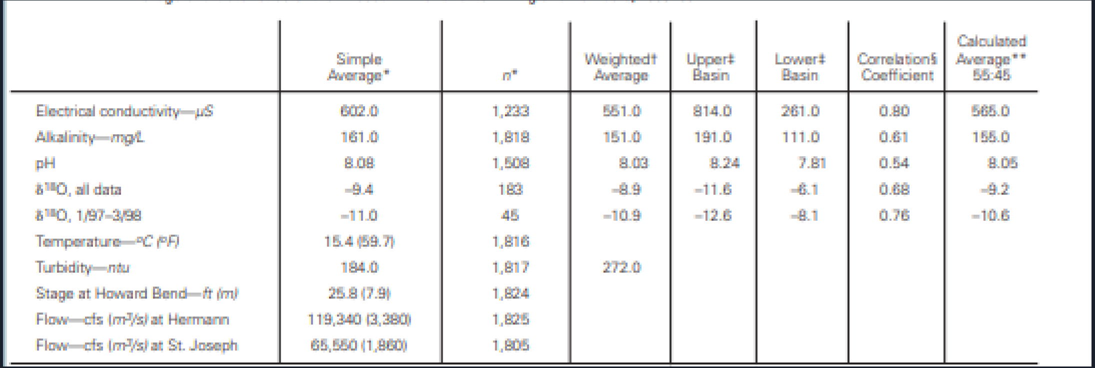
- Used the average concentrations that were found in “nonpoint sources in the lower Missouri River”
- Inverse modeling



	Simple* Average	Upper† Basin	Lower† Basin	Correlation‡ Coefficient	Calculated Average§ 55:45
Calcium	55.0	68.4	35.8	0.64	53.7
Magnesium	18.4	25.6	7.4	0.76	17.4
Sodium	42.5	74.9	-6.6**	0.89	38.2
Potassium	6.7	8.5	3.9	0.34	6.4
Silica	6.8	4.2	10.7	0.32	7.1
Bicarbonate	195.8	231.0	139.0	0.67	190.0
Sulfate	123.0	216.0	–22.0**	0.87	109.0
Chloride	18.9	25.0	10.0	0.32	18.3
Nitrate as N	1.18	0.9	1.7	0.22	1.3
Fluoride	0.32	0.42	0.15	0.84	0.30
Phosphate	0.24	0.25	0.23	0.05	0.24
Alkalinity	160.0	190.0	113.0	0.68	155.0
Hardness	223.0	280.0	135.0	0.80	215.0
Noncarbonate hardness	63.7	90.0	23.0	0.76	60.0
Total dissolved solids	395.0	558.0	144.0	0.87	372.0
Calcium	58.2††	69.6	39.6	0.76	56.1
Magnesium	19.0††	25.7	8.6	0.81	18.0
Electrical conductivity	602.0††	838.0	219.0	0.91	560.0
Total organic carbon	4.17††	3.01	5.91	0.55	4.3
pH	8.08††	8.25	7.82	0.67	8.06

Fig 8: Missouri River Characteristics based on a monthly average (Criss et al, 2001)

Fig 9: Average characteristics of the missouri River and its mixing endmembers (Criss et al, 20010

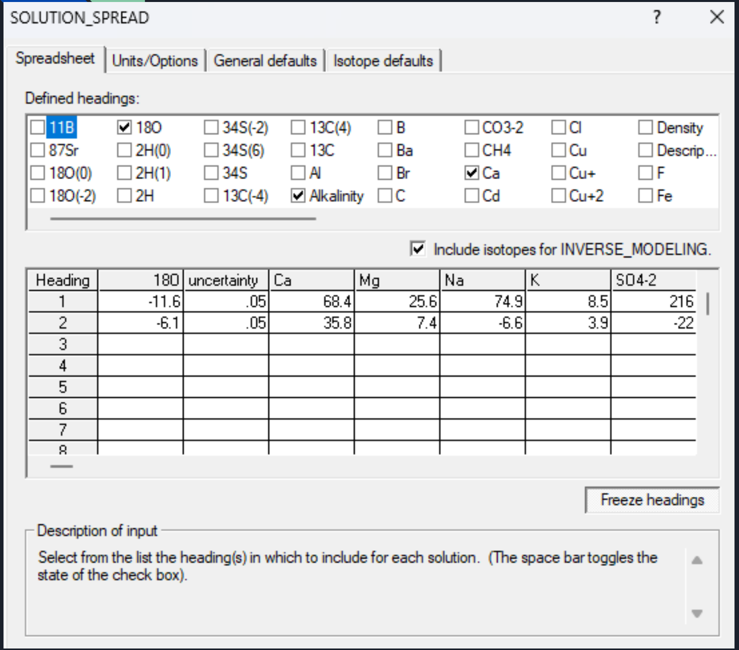


	Simple Average*	n*	Weighted† Average	Upper‡ Basin	Lower‡ Basin	Correlation§ Coefficient	Calculated Average** 55:45
Electrical conductivity—*μS*	602.0	1,233	551.0	814.0	261.0	0.80	565.0
Alkalinity—*mg/L*	161.0	1,818	151.0	191.0	111.0	0.61	155.0
pH	8.08	1,508	8.03	8.24	7.81	0.54	8.05
$\delta^{18}O$, all data	–9.4	183	–8.9	–11.6	–6.1	0.68	–9.2
$\delta^{18}O$, 1/97–3/98	–11.0	45	–10.9	–12.6	–8.1	0.76	–10.6
Temperature—°*C (°F)*	15.4 (59.7)	1,816					
Turbidity—*ntu*	184.0	1,817	272.0				
Stage at Howard Bend—*ft (m)*	25.8 (7.9)	1,824					
Flow—cfs *(m^3/s)* at Hermann	119,340 (3,380)	1,825					
Flow—cfs *(m^3/s)* at St. Joseph	65,550 (1,860)	1,805					

Inverse modeling (PHREEQC User manual, and Faure ch. 20)

- Taking a water sample, and working backwards to figure out what minerals dissolved, and in what proportion, to result in the water - bernie
- A technique to determine the geochemical reactions that account for changes in water chemistry along a flow path.
    - Calculating mole-balance models that describe the transfer of moles of phases and reactants,
    - Trying to reverse engineer the chemical evolution of water
- Identify the dominant reactions, like mixing, mineral dissolution/precipitation, and gas reactants, that are responsible for the observed changes in water composition.
- Need at least two solutions

How to inverse model in phreeqc



Defined headings:

- ☐ 11B
- ☐ 87Sr
- ☐ 18O(0)
- ☐ 18O(-2)
- ☑ 18O
- ☐ 2H(0)
- ☐ 2H(1)
- ☐ 2H
- ☐ 34S(-2)
- ☐ 34S(6)
- ☐ 34S
- ☐ 13C(-4)
- ☐ 13C(4)
- ☐ 13C
- ☐ Al
- ☑ Alkalinity
- ☐ B
- ☐ Ba
- ☐ Br
- ☐ C
- ☐ CO3-2
- ☐ CH4
- ☑ Ca
- ☐ Cd
- ☐ Cl
- ☐ Cu
- ☐ Cu+
- ☐ Cu+2
- ☐ Density
- ☐ Descrip...
- ☐ F
- ☐ Fe

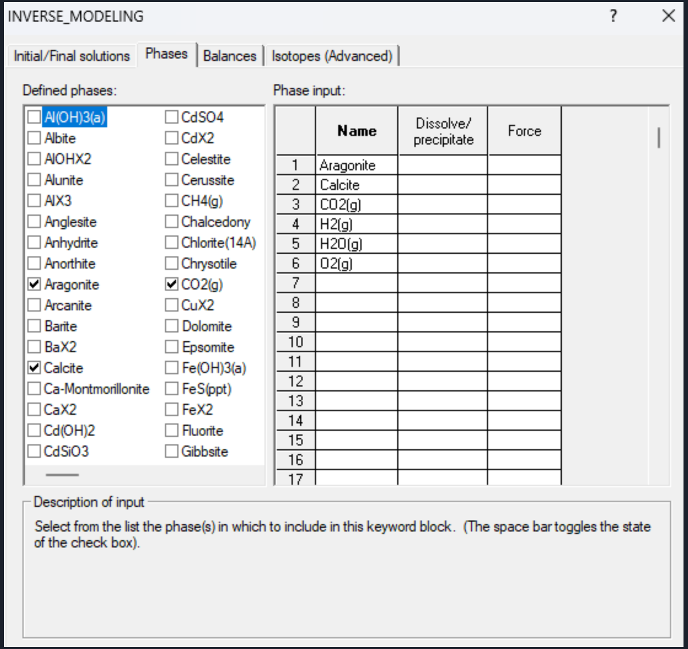
☑ Include isotopes for INVERSE_MODELING.

Heading	18O	uncertainty	Ca	Mg	Na	K	SO4-2
1	-11.6	.05	68.4	25.6	74.9	8.5	216
2	-6.1	.05	35.8	7.4	-6.6	3.9	-22
3							
4							
5							
6							
7							
8							

Description of input

Select from the list the heading(s) in which to include for each solution. (The space bar toggles the state of the check box).

Fig 10: sequence spread inputs in phreeqc



Defined phases:

- ☐ Al(OH)3(a)
- ☐ Albite
- ☐ AlOHX2
- ☐ Alunite
- ☐ AlX3
- ☐ Anglesite
- ☐ Anhydrite
- ☐ Anorthite
- ☑ Aragonite
- ☐ Arcanite
- ☐ Barite
- ☐ BaX2
- ☑ Calcite
- ☐ Ca-Montmorillonite
- ☐ CaX2
- ☐ Cd(OH)2
- ☐ CdSiO3
- ☐ CdSO4
- ☐ CdX2
- ☐ Celestite
- ☐ Cerussite
- ☐ CH4(g)
- ☐ Chalcedony
- ☐ Chlorite(14A)
- ☐ Chrysotile
- ☑ CO2(g)
- ☐ CuX2
- ☐ Dolomite
- ☐ Epsomite
- ☐ Fe(OH)3(a)
- ☐ FeS(ppt)
- ☐ FeX2
- ☐ Fluorite
- ☐ Gibbsite

Phase input:

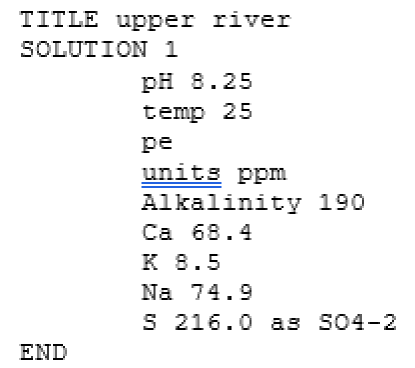
	Name	Dissolve/ precipitate	Force
1	Aragonite		
2	Calcite		
3	CO2(g)		
4	H2(g)		
5	H2O(g)		
6	O2(g)		
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			

Description of input

Select from the list the phase(s) in which to include in this keyword block. (The space bar toggles the state of the check box).

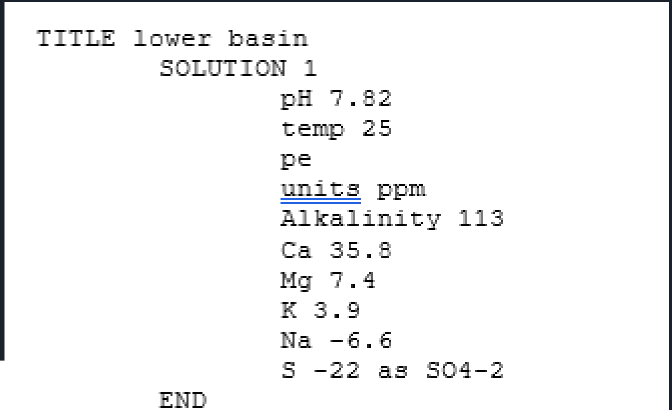
Fig 11: inverse modeling inputs in phreeqc

Possible errors in my PHREEQC



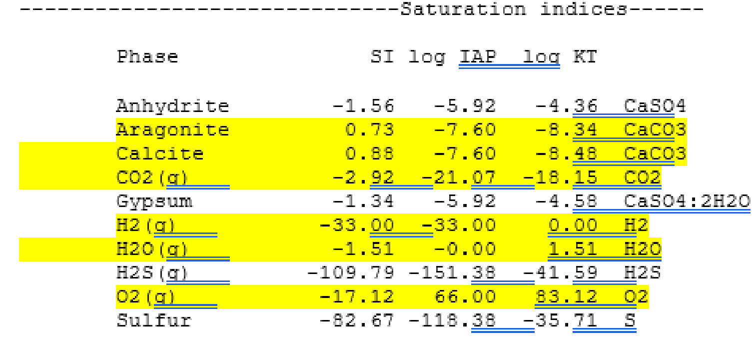
```
TITLE upper river
SOLUTION 1
        pH 8.25
        temp 25
        pe
        units ppm
        Alkalinity 190
        Ca 68.4
        K 8.5
        Na 74.9
        S 216.0 as SO4-2
END
```

The input and output of web phreeqc to find the phases

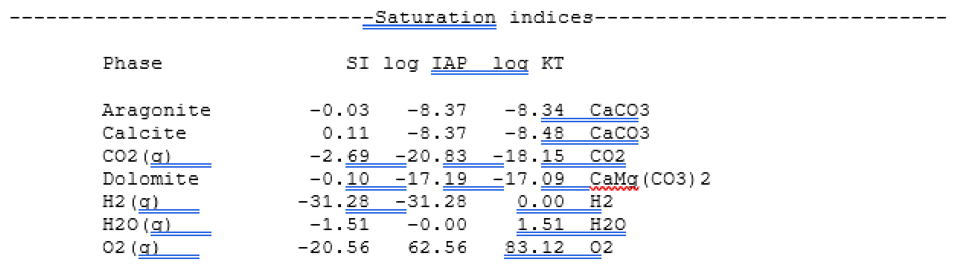


```
TITLE lower basin
        SOLUTION 1
                pH 7.82
                temp 25
                pe
                units ppm
                Alkalinity 113
                Ca 35.8
                Mg 7.4
                K 3.9
                Na -6.6
                S -22 as SO4-2
        END
```

- Average data samples
- Percent uncertainty
- Not all elements/ minerals were counted
- Not all phases were counted



```
------------------------------Saturation indices------

        Phase               SI  log IAP  log KT

        Anhydrite        -1.56   -5.92   -4.36  CaSO4
        Aragonite         0.73   -7.60   -8.34  CaCO3
        Calcite           0.88   -7.60   -8.48  CaCO3
        CO2(g)           -2.92  -21.07  -18.15  CO2
        Gypsum           -1.34   -5.92   -4.58  CaSO4:2H2O
        H2(g)           -33.00  -33.00    0.00  H2
        H2O(g)           -1.51   -0.00    1.51  H2O
        H2S(g)         -109.79 -151.38  -41.59  H2S
        O2(g)           -17.12   66.00   83.12  O2
        Sulfur          -82.67 -118.38  -35.71  S
```

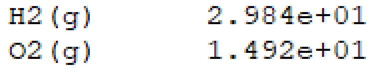


```
-----------------------------Saturation indices-----------------------------

      Phase               SI  log IAP  log KT

      Aragonite        -0.03   -8.37   -8.34  CaCO3
      Calcite           0.11   -8.37   -8.48  CaCO3
      CO2(g)           -2.69  -20.83  -18.15  CO2
      Dolomite         -0.10  -17.19  -17.09  CaMg(CO3)2
      H2(g)           -31.28  -31.28    0.00  H2
      H2O(g)           -1.51   -0.00    1.51  H2O
      O2(g)           -20.56   62.56   83.12  O2
```

My findings

Phase mole transfers

Major



```
H2(g)          2.984e+01
O2(g)          1.492e+01
```

Minor

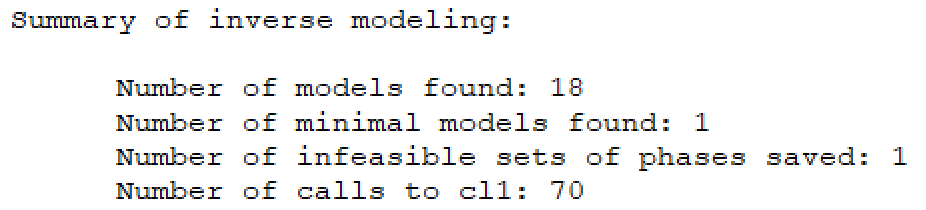
```
Calcite          1.769e-02
```

```
Aragonite          1.769e-02
```

Fig 12: the major and minor minerals that were dissolved into the system

- All shown to be dissolving, If negative then it would mean precipitation.

- Minimal models = models with a minimum number of phases)
- Number of calls to cll = number of calls to the inequality equations solver



```
Summary of inverse modeling:

      Number of models found: 18
      Number of minimal models found: 1
      Number of infeasible sets of phases saved: 1
      Number of calls to cl1: 70
```

Fig 13: summary of the inverse modeling done by phreeqc

references

Cao, A., 2023, Saving for a rainy day: How rain barrels help with urban stormwater pollution & water quality (3/28/2023): Sabai Design, https://sabai.design/blogs/the-green-house/rain-barrels-urban-stormwater-pollution-water-quality (accessed April 2025).

Criss, R.E., Lee Davisson, M., and Kopp, J.W., 2001, Nonpoint sources in the lower missouri river: Journal AWWA, v. 93, p. 112–122, doi: 10.1002/j.1551-8833.2001.tb09131.x.

Wastewater Treatment Plant Safety & productivity - saferack, https://saferack.com/industries/wastewater/ (accessed April 2025).

Thank you for your time!