Mineland Sulfate Release in the St. Louis River Watershed

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Presented to:
Minnesota Ground Water Association

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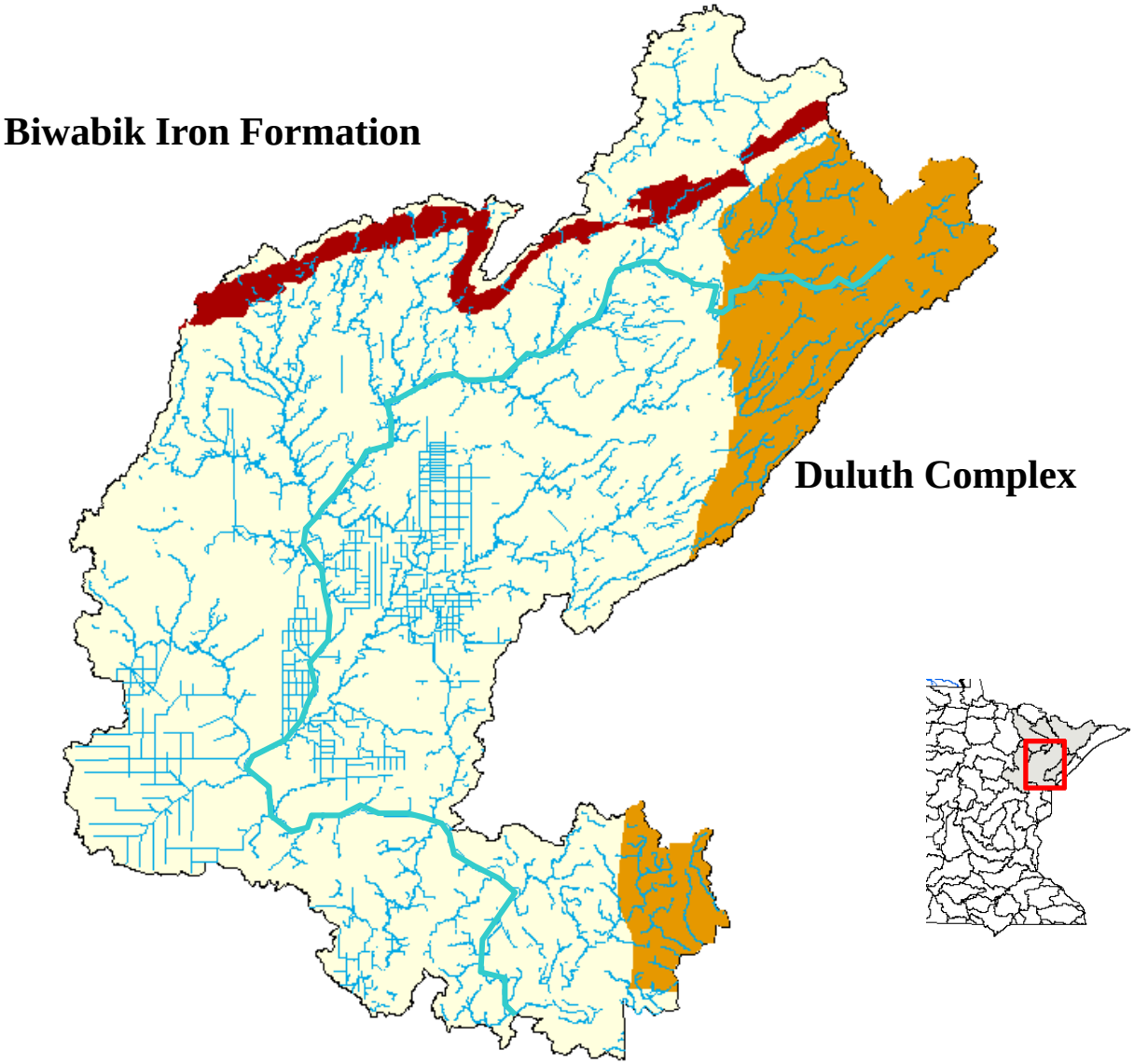
Outline

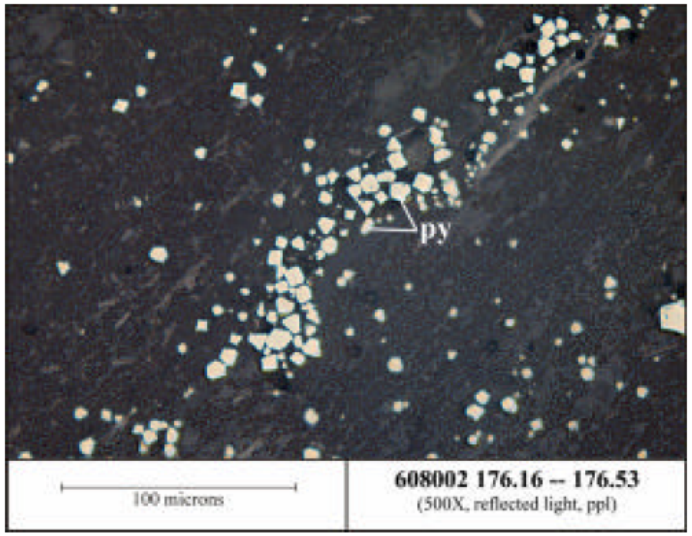
- Environmental concern
- SO_4 concentration and loading
- Geochemical processes
- Conclusions

Minnesota
DEPARTMENT OF NATURAL RESOURCES

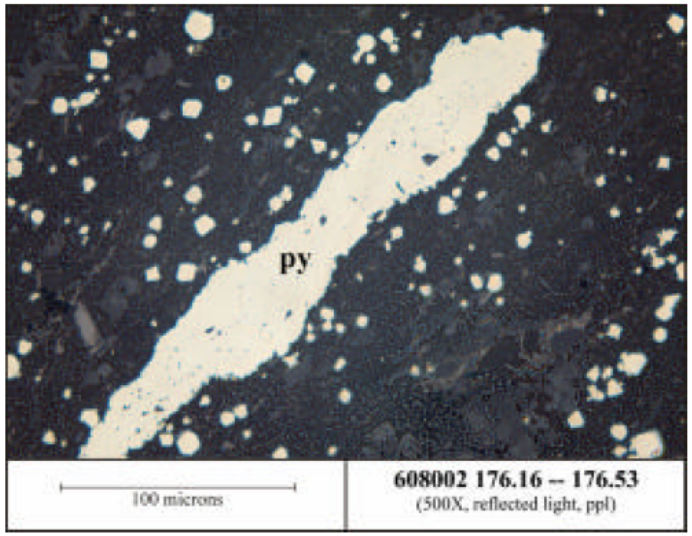
Ore hosts in the St. Louis River Basin



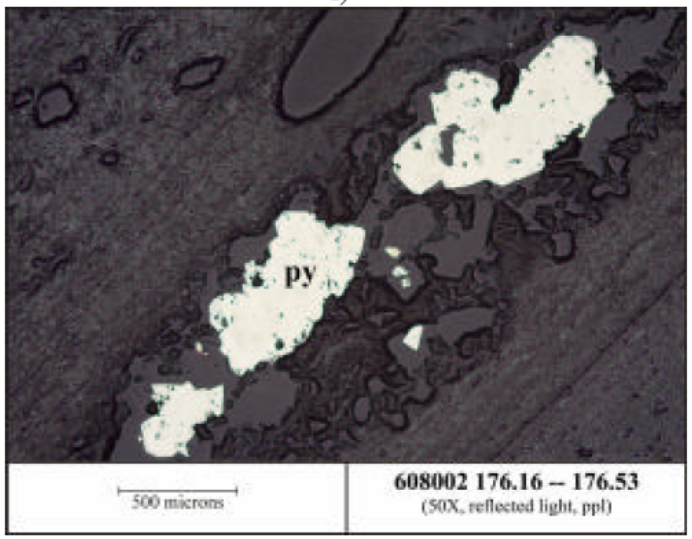
Pyrite in Biwabik Fe Formation



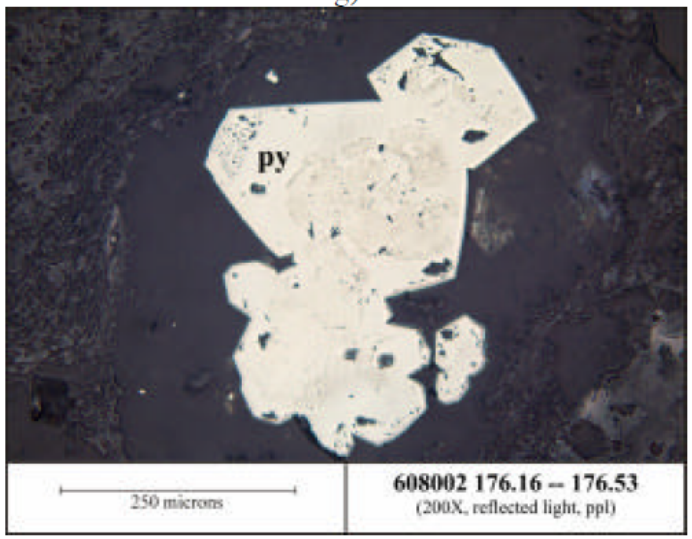
f)



g)



h)



i)

Photos from Rod Johnson and Associates (2009) Petrography Report for Mesabi Mining

Sulfuric Acid

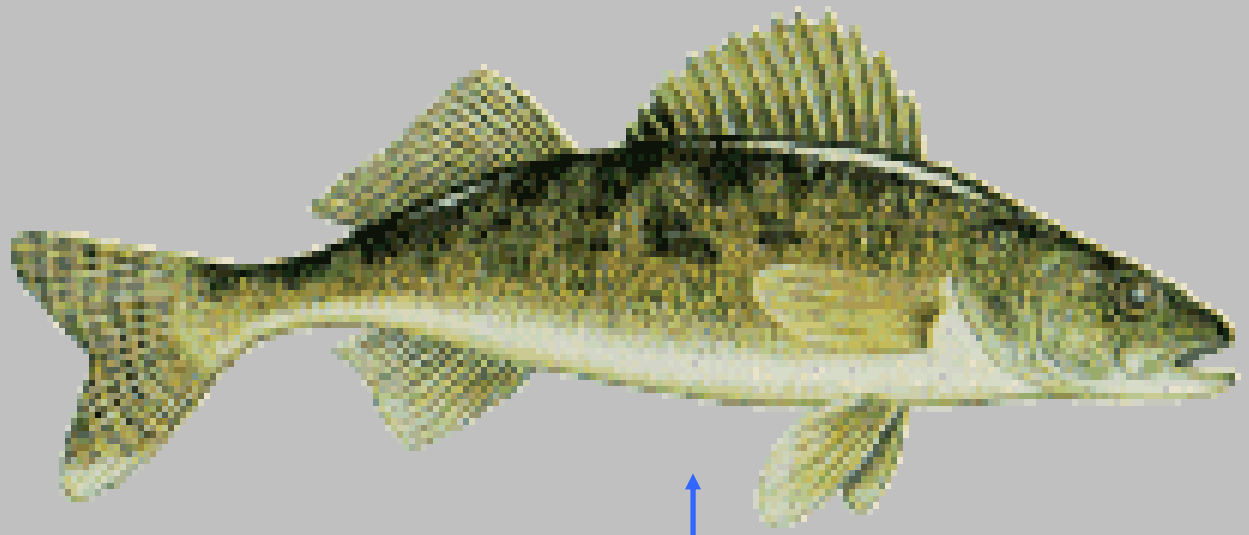
Pyrite Oxidation:

$$FeS_2 + 3.75O_2 + 3.5\ H_2O = Fe(OH)_3 + 2H_2SO_4$$

Calcium carbonate titration:

$$H_2SO_4 + 2CaCO_3 = 2Ca^{++} + SO_4^{=} + 2HCO_3^{-}$$

Methyl-Mercury: CH_3Hg^+



$SO_4^=$

CH_3Hg^+

Sulfate-reducing bacteria

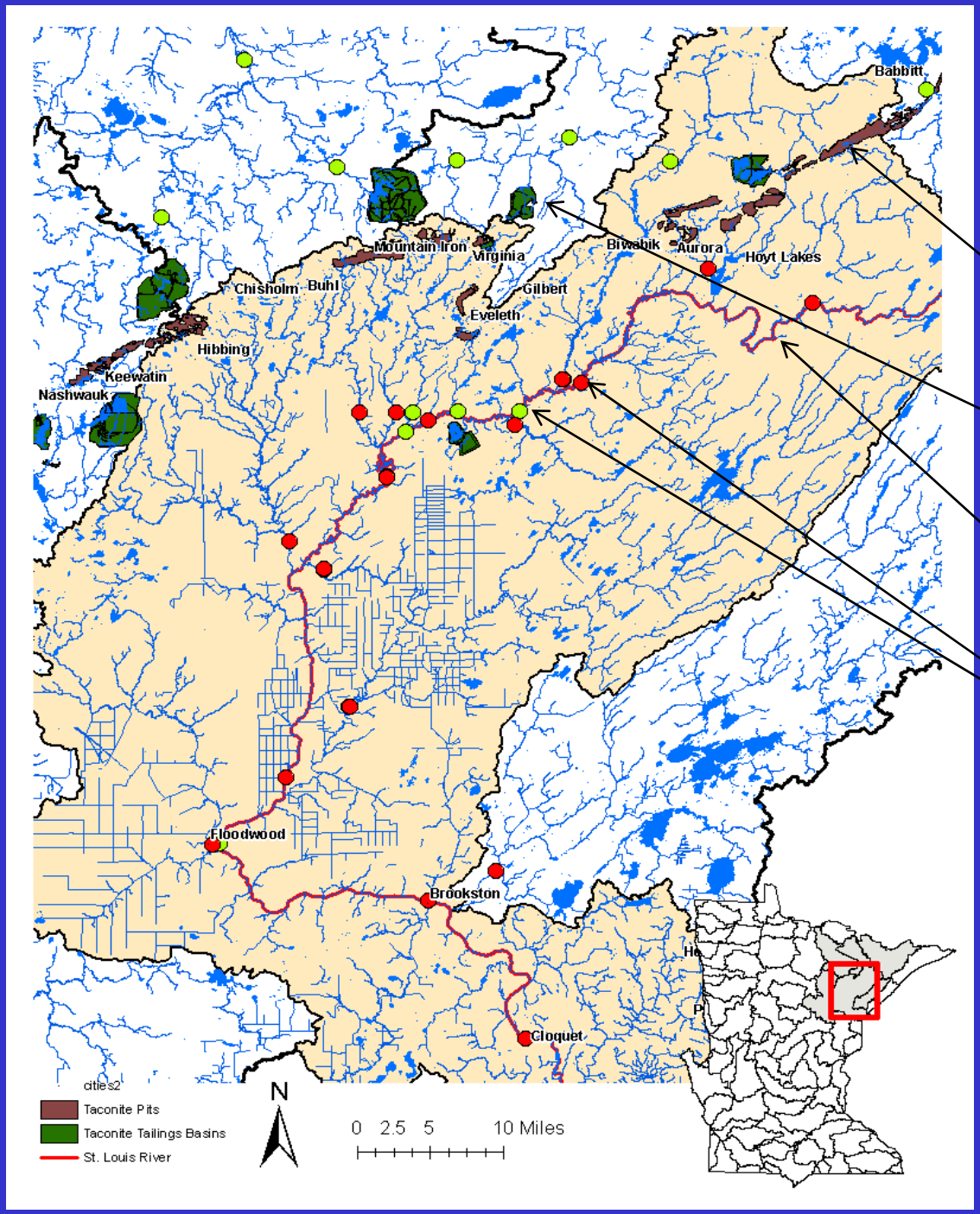
Hg^{++}

$C_{organic}$

$S^=$

Wild Rice SO_4 standard for producing waters during growing season is 10 mg/L.

(Photo: http://www.flickr.com/photos/esagor/513277768/page2/)



Location Slide:

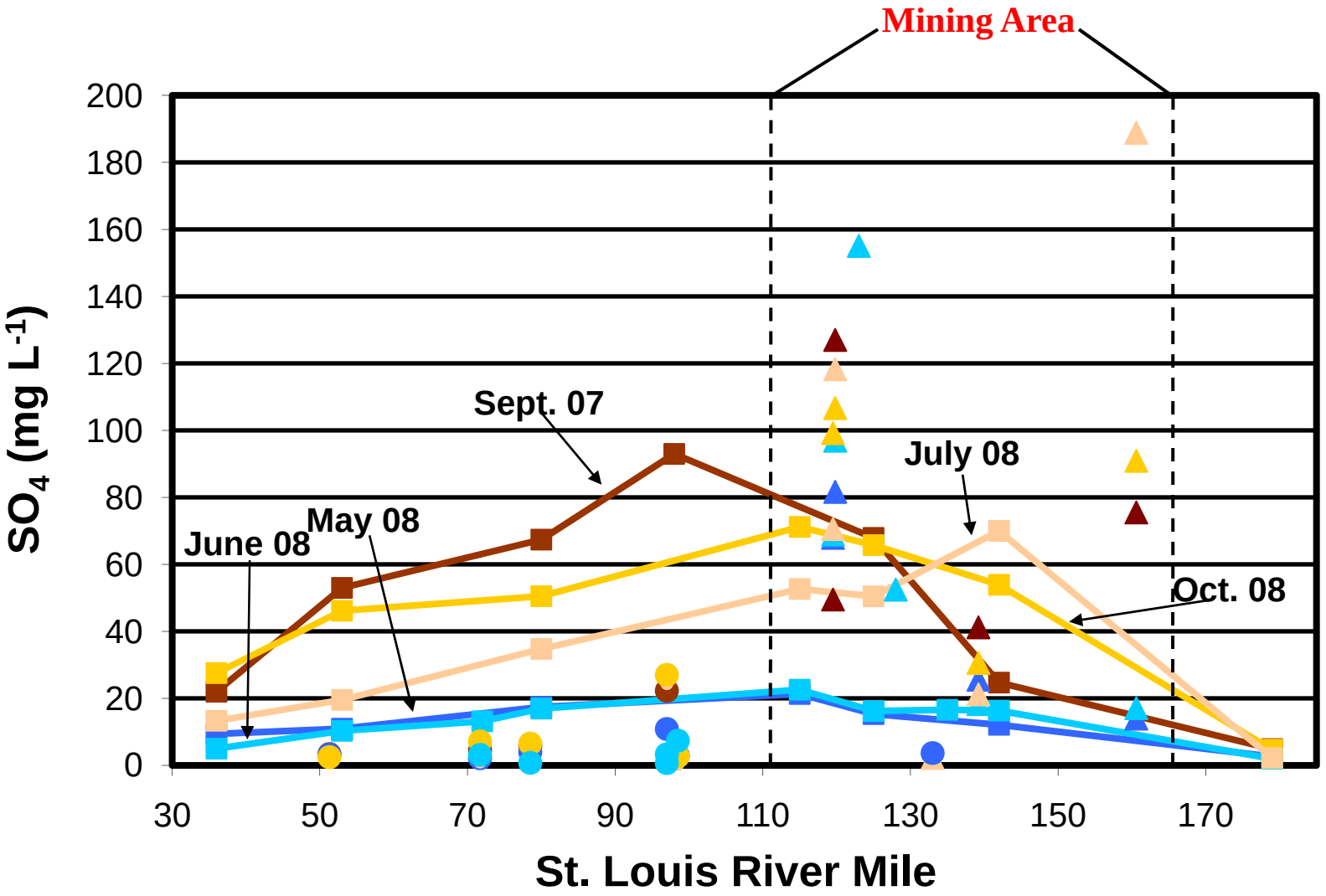
Taconite Pits

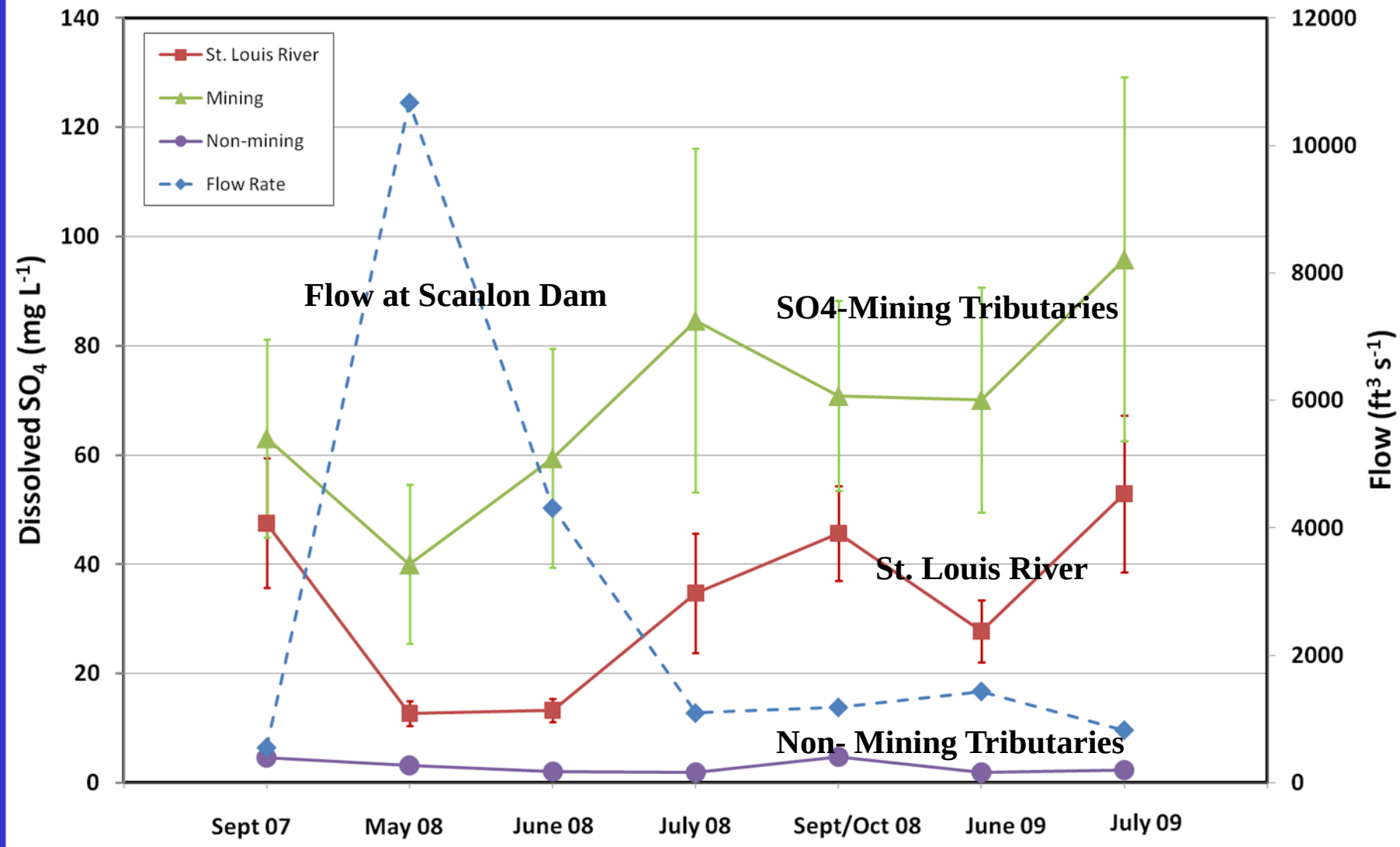
Tailings Basins

St. Louis River

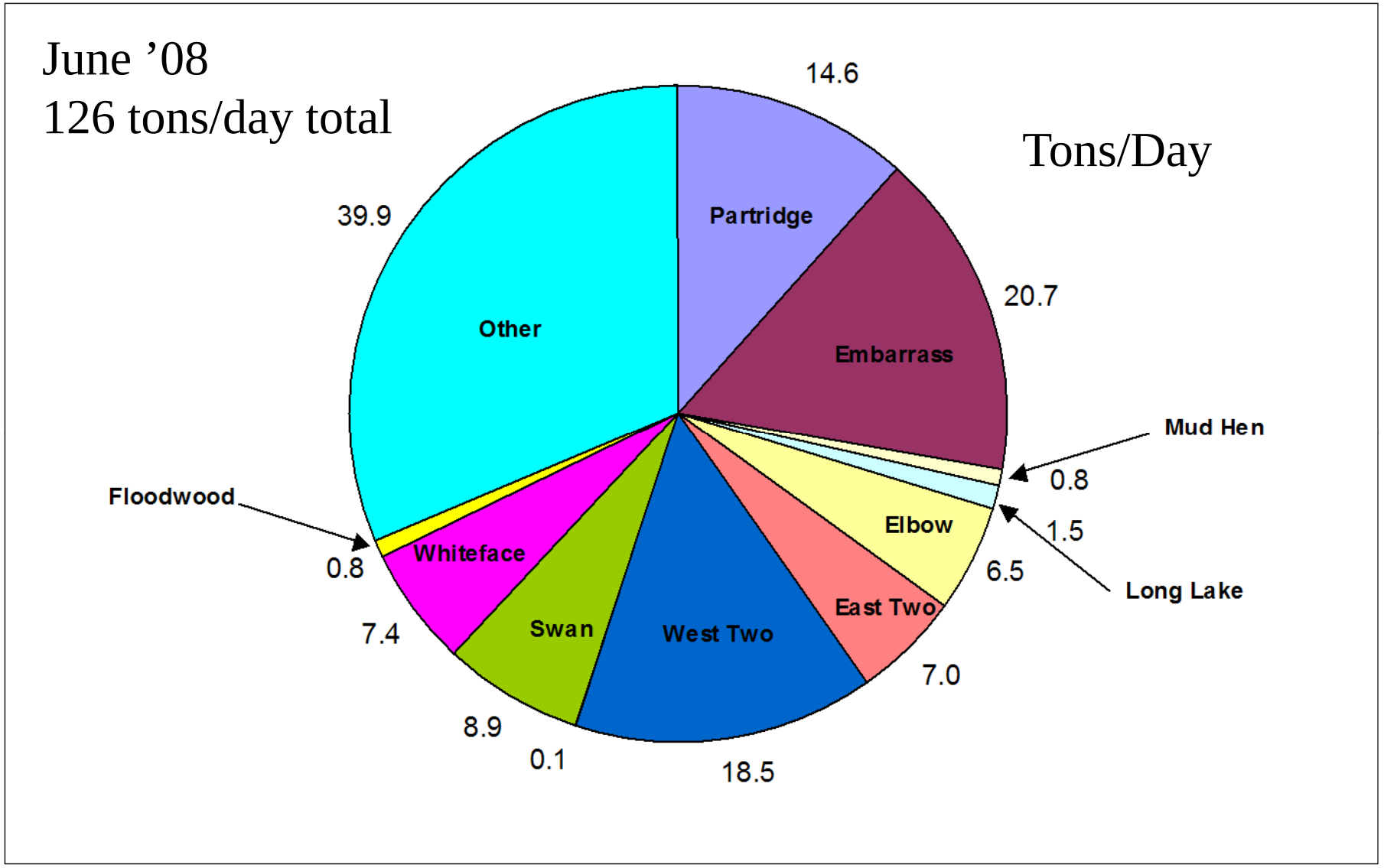
Sample points

Sulfate Concentrations in the St. Louis River and Tributaries

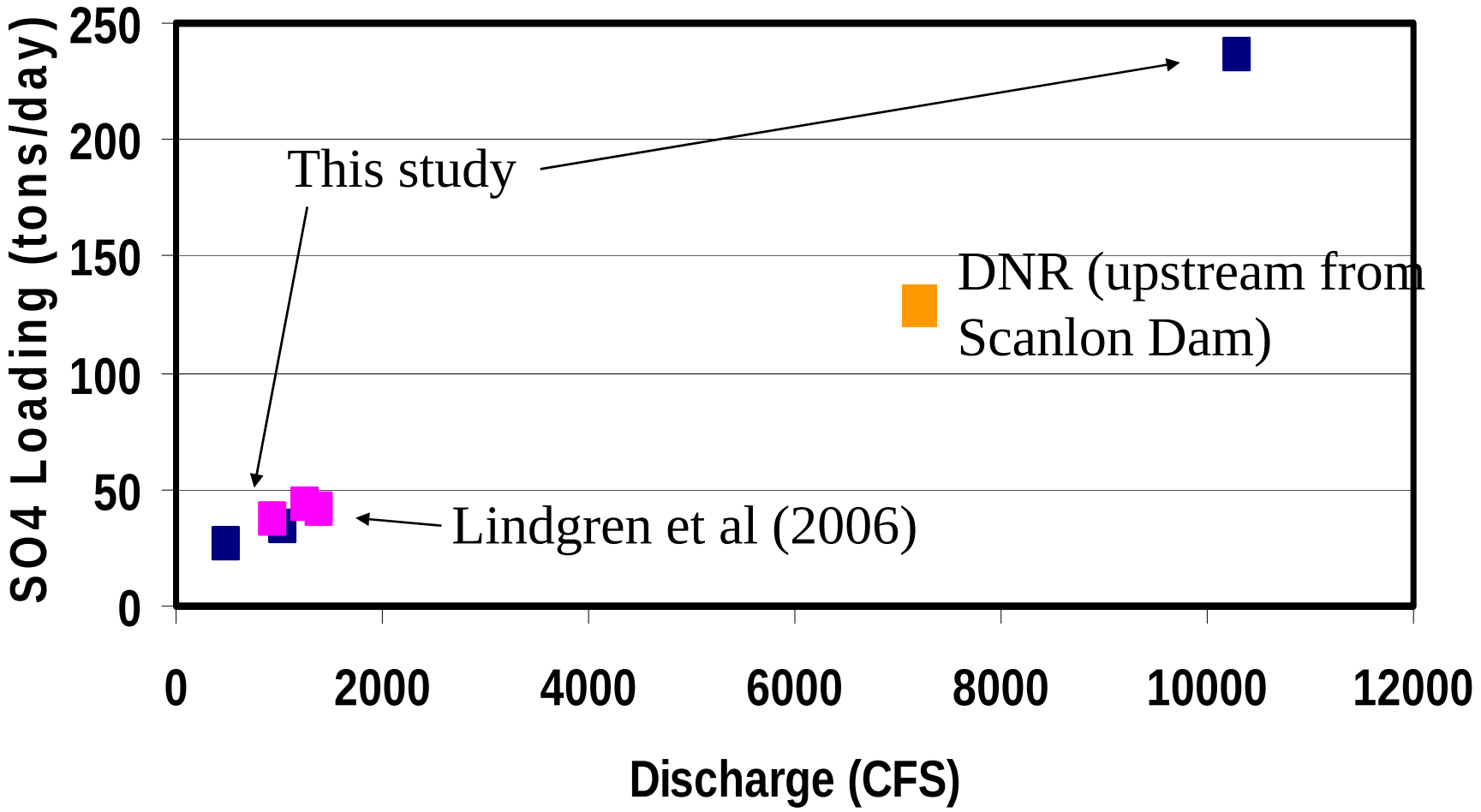



St. Louis River
Mining
Non-mining
Flow Rate
Flow at Scanlon Dam
SO4-Mining Tributaries
St. Louis River
Non- Mining Tributaries
Dissolved SO4 (mg L-1)
Flow (ft3 s-1)
140
120
100
80
60
40
20
0
12000
10000
8000
6000
4000
2000
0
Sept 07
May 08
June 08
July 08
Sept/Oct 08
June 09
July 09

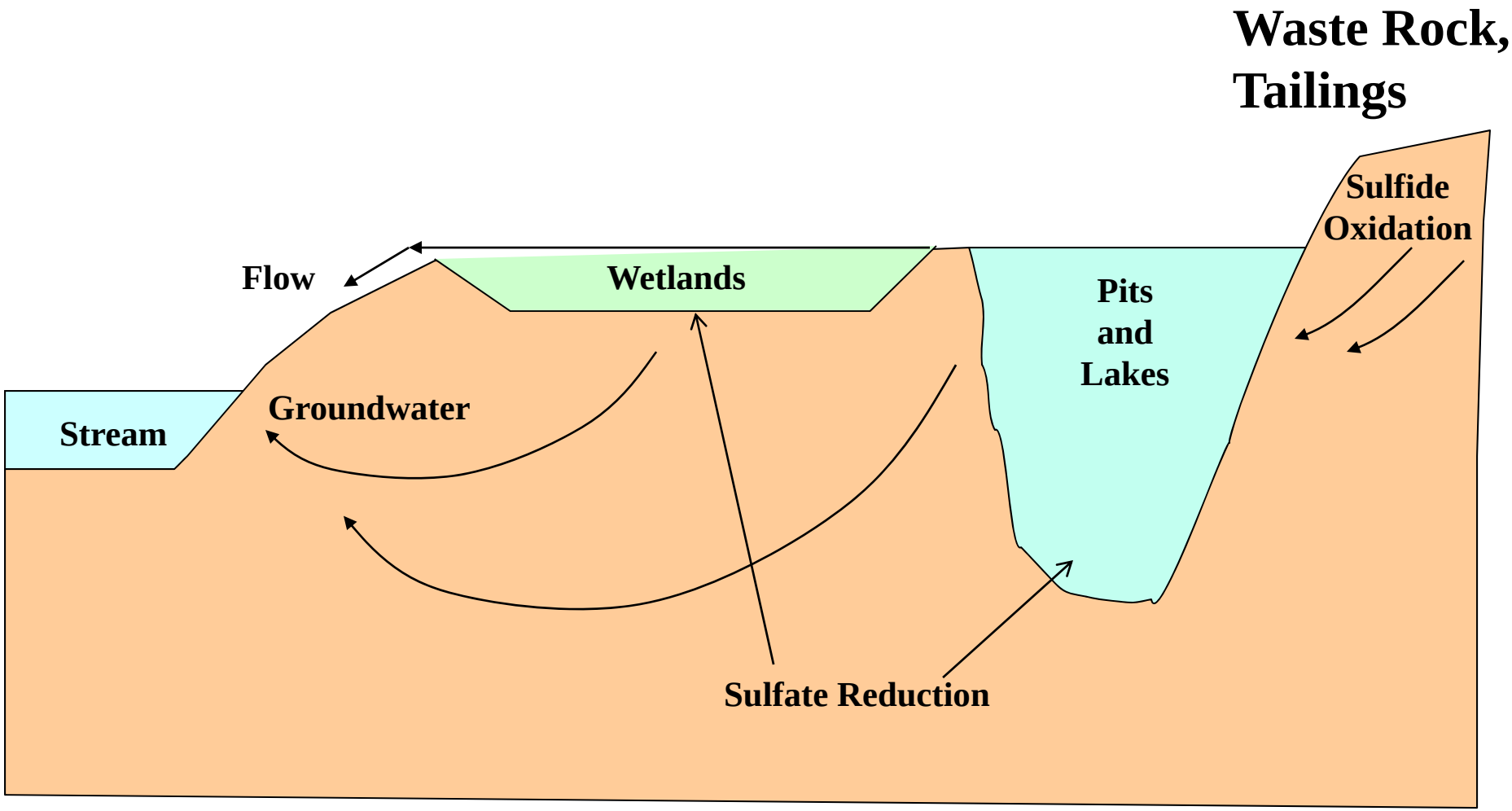
SO_4 Loading above Cloquet River



St. Louis River Discharge (USGS) vs. SO4 Loads at the Scanlon Dam



Sulfate Transport Schematic Diagram



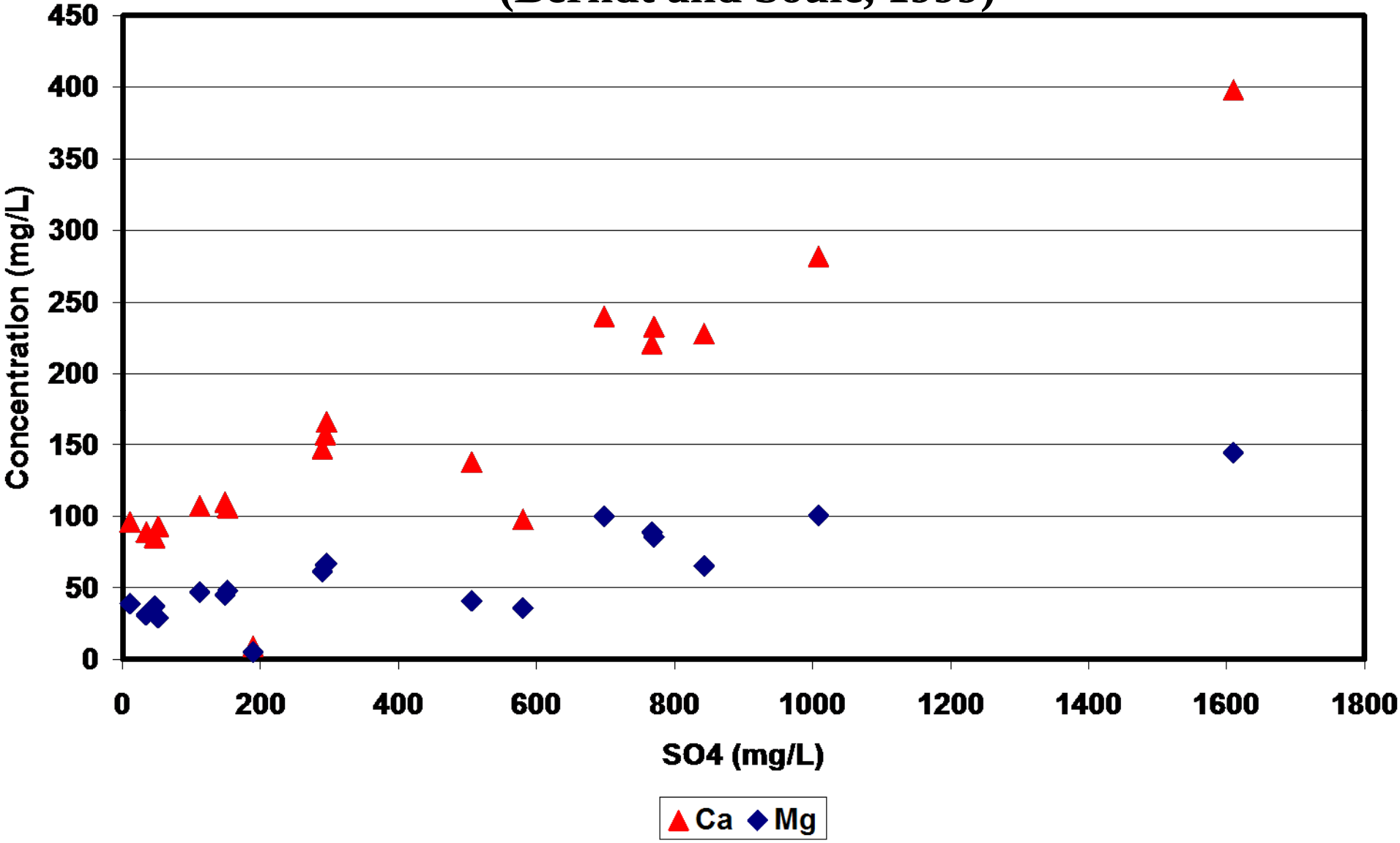
Pyrite Oxidation:

$$FeS_2 + 3.75O_2 + 3.5\ H_2O = Fe(OH)_3 + 2H_2SO_4$$

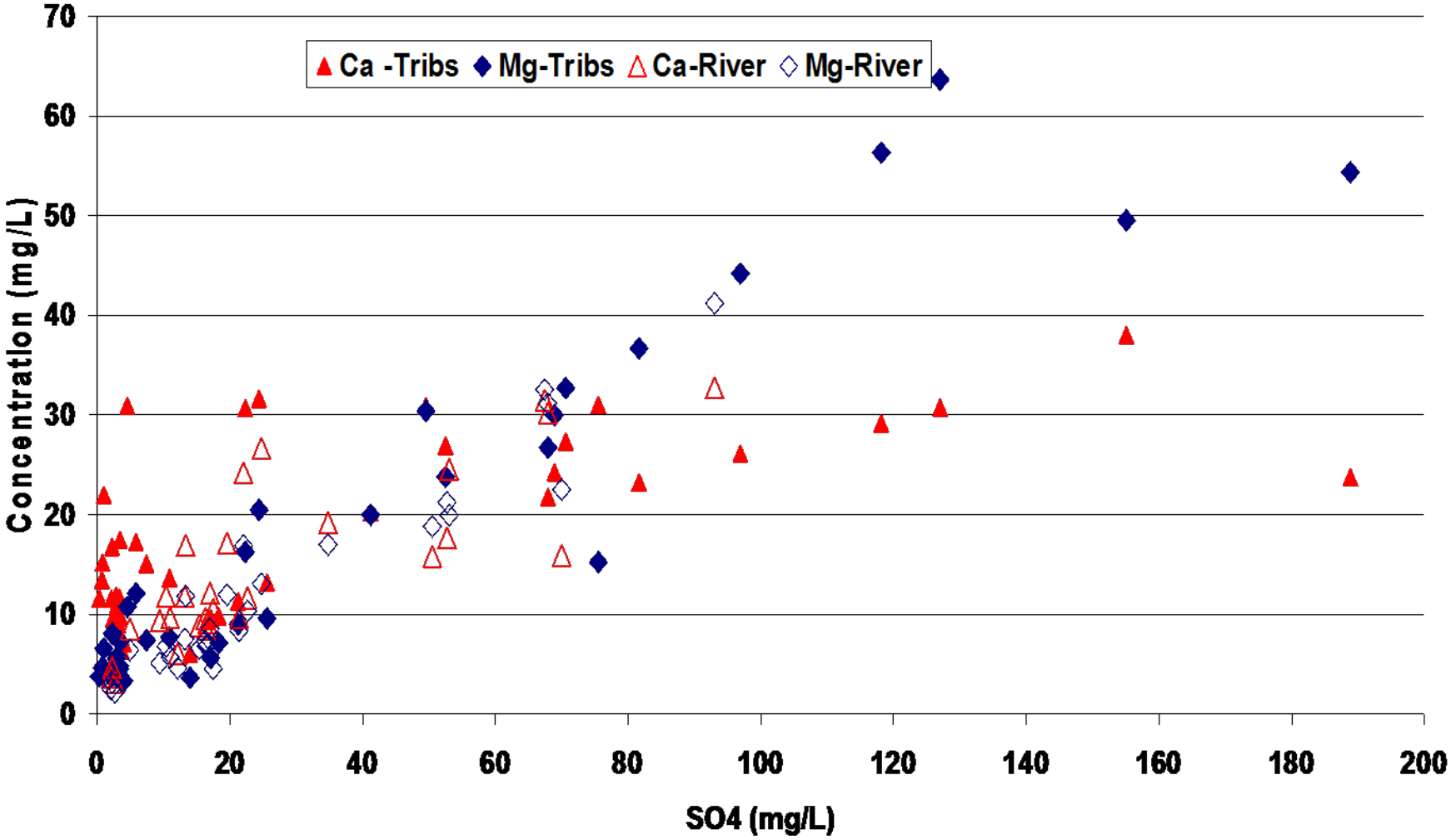
Calcium carbonate titration:

$$H_2SO_4 + 2CaCO_3 = 2Ca^{++} + SO_4^{=} + 2HCO_3^{-}$$

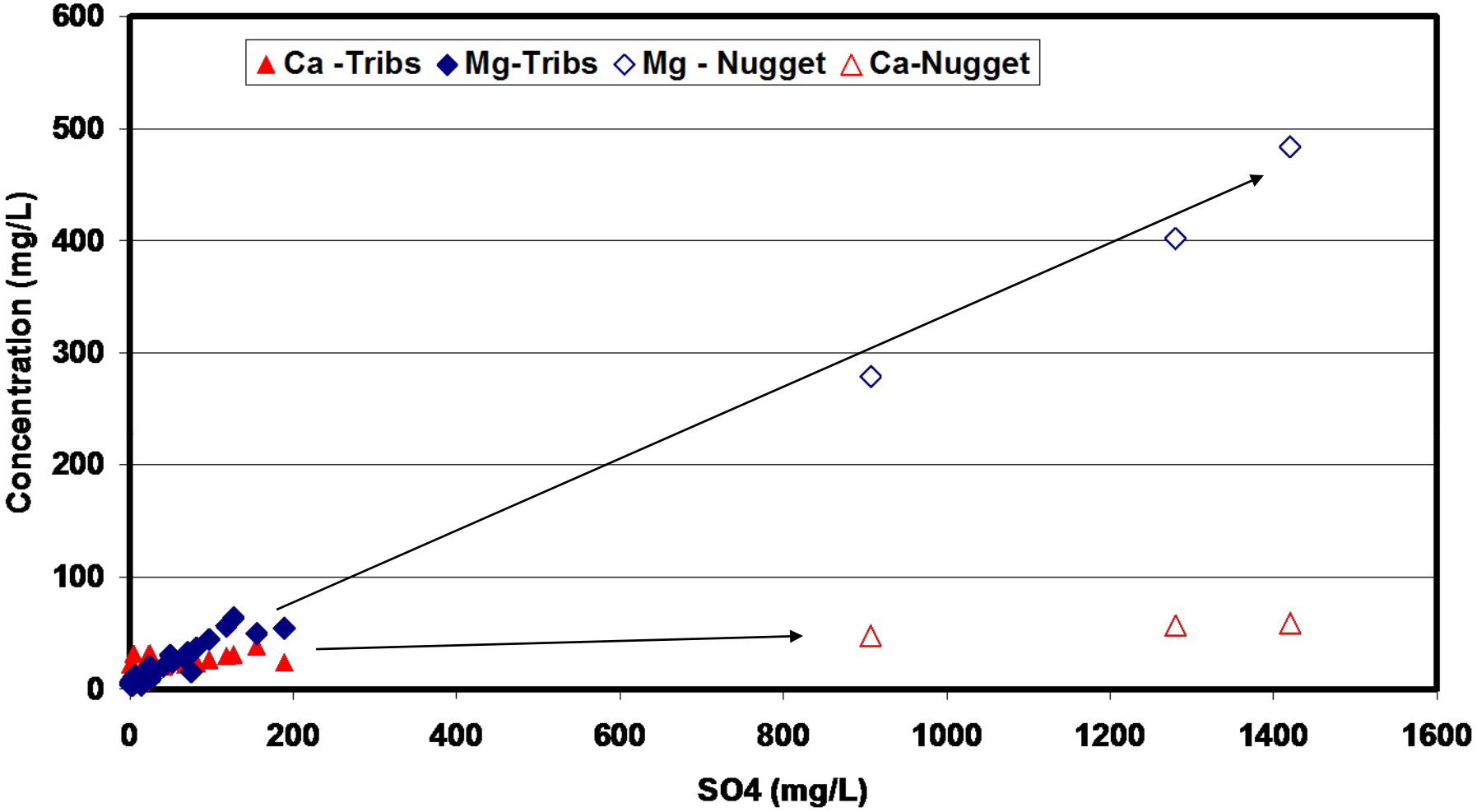
Ca and Mg vs SO_4 for Des Moines Lobe Aquifers (W. MN) (Berndt and Soule, 1999)



Ca and Mg values for Tributaries and the St. Louis River



Ca and Mg vs SO_4 for St. Louis River Tributaries



Dolomite titration:

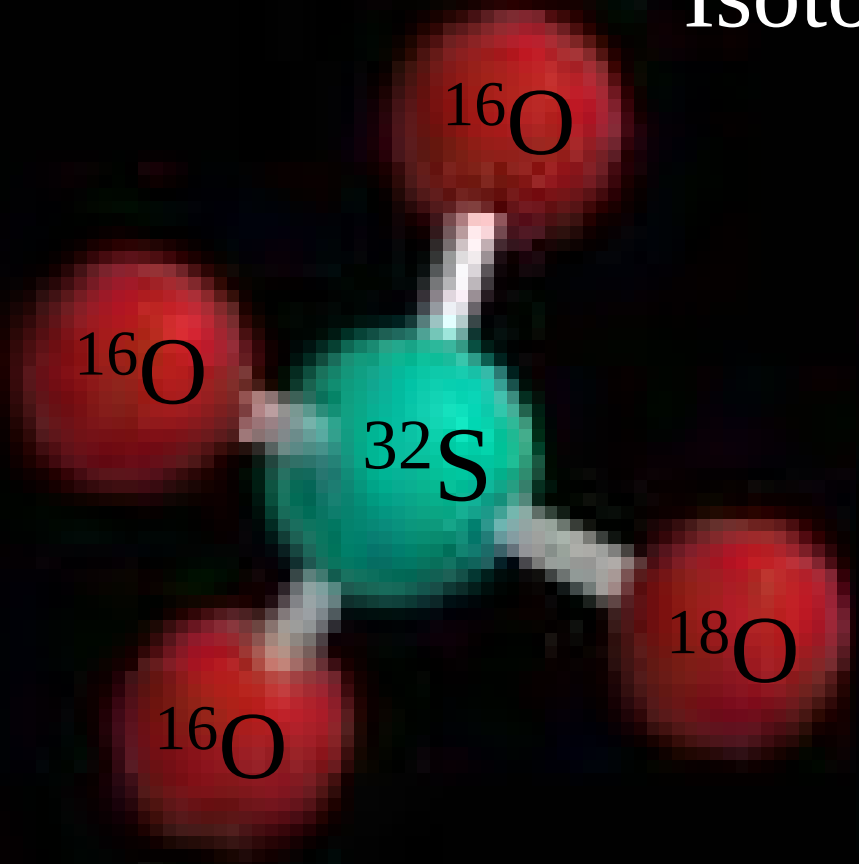
$$H_2SO_4 + 2CaMg(CO_3)_2 = 2Mg^{++} + 2CaCO_3 + SO_4^{=} + 2HCO_3^{-}$$

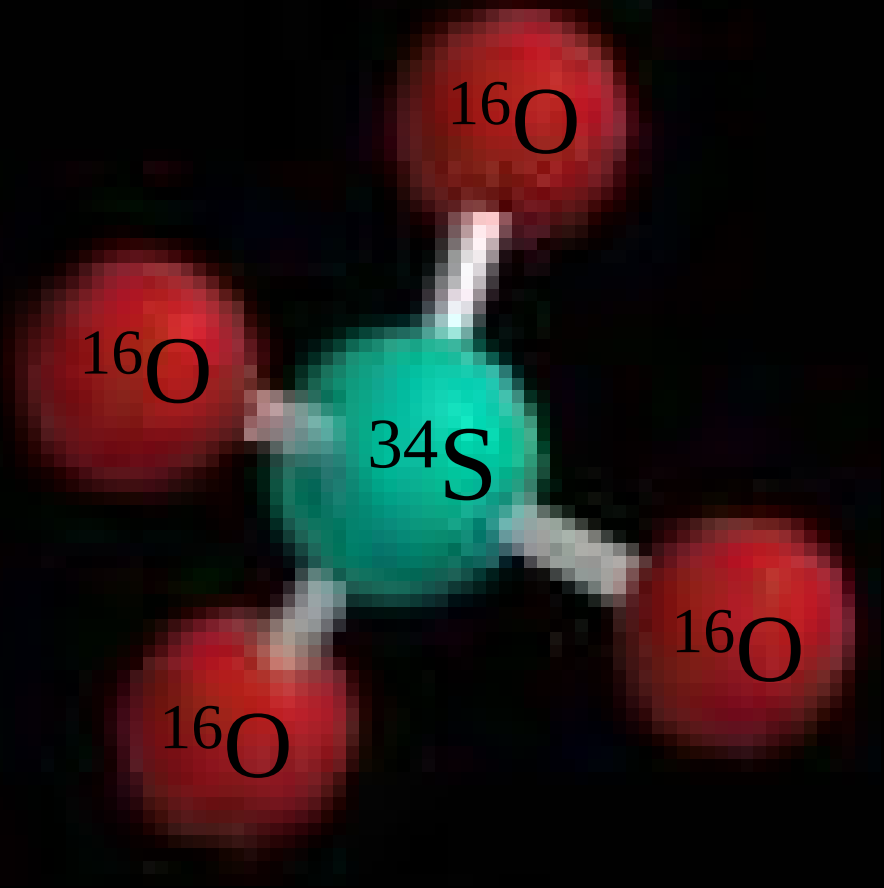
Overall Reaction in Fe Formation:
Acid titration by Mg-Siderite

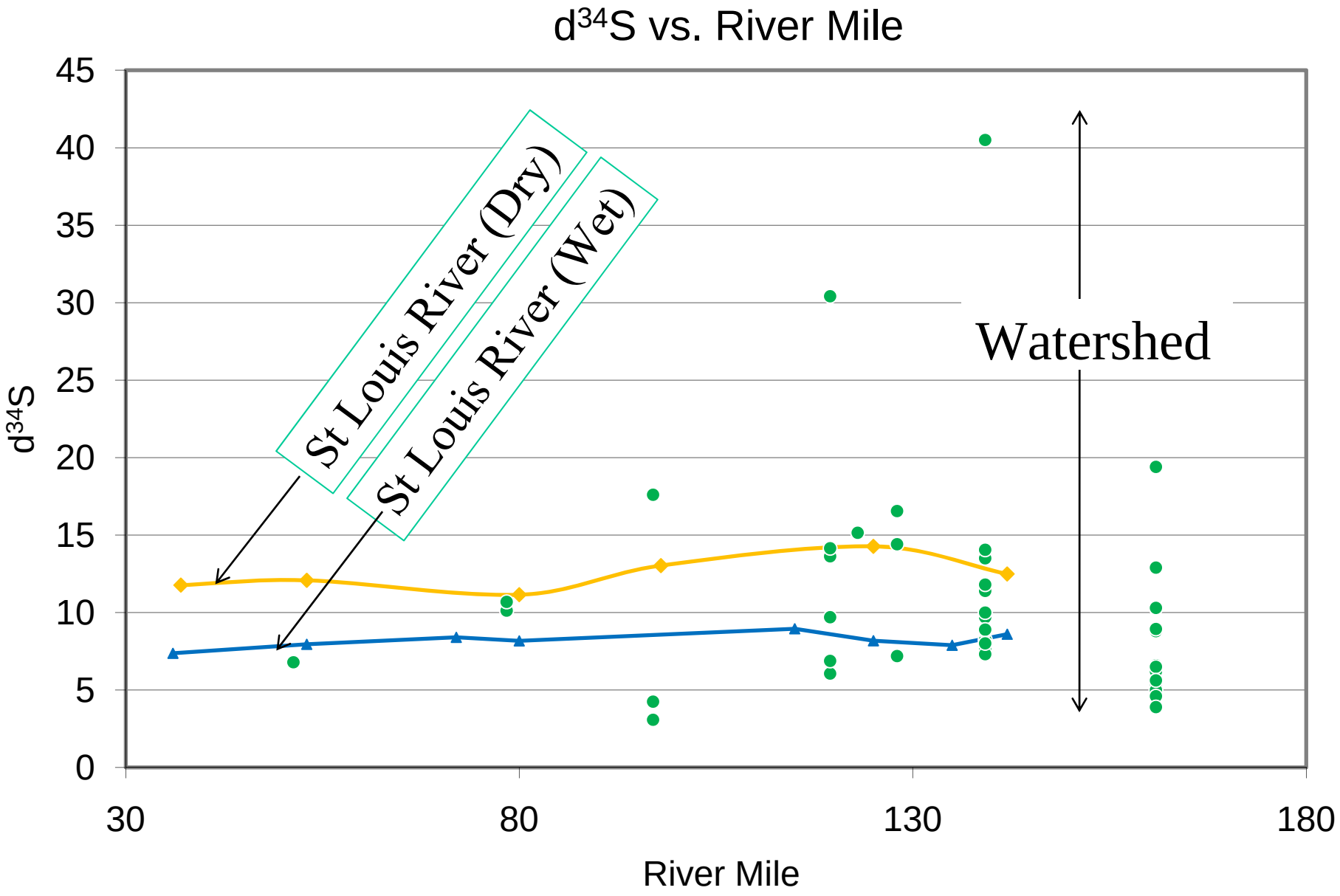
$$FeS_2 + 6O_2 + 16\ H_2O + 3(Ca,Mg)CO_3 + 9FeCO_3 =$$
$$10Fe(OH)_3 + 2(Ca,Mg)SO_4 + (Ca,Mg)(HCO_3)_2 + 10\ CO_2$$

Wetland SO_4 Reduction?

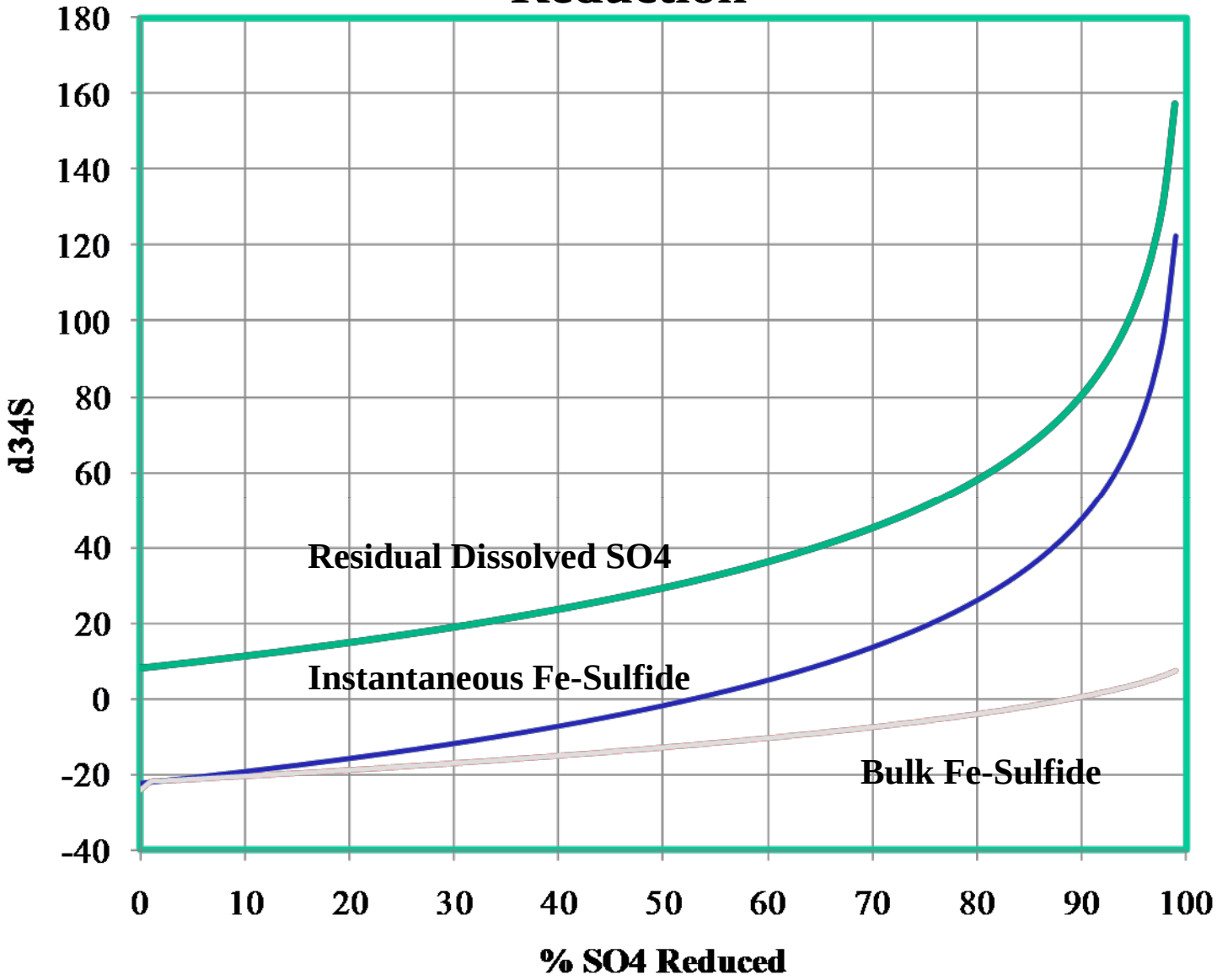
Sulfate Isotopes



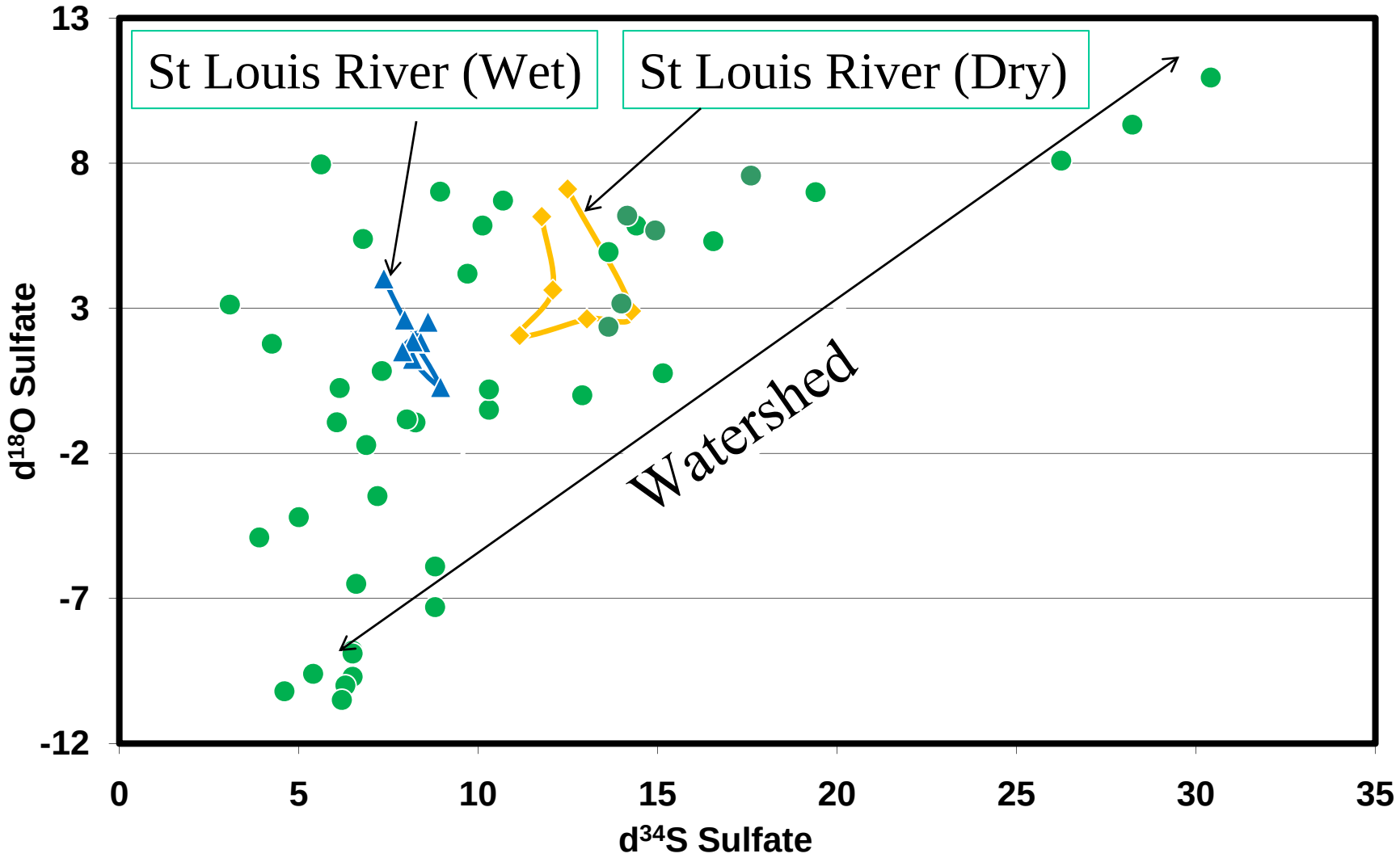



d34S vs. River Mile
45
40
35
30
25
20
15
10
5
0
d34S
30
80
130
180
River Mile
St Louis River (Dry)
St Louis River (Wet)
Watershed

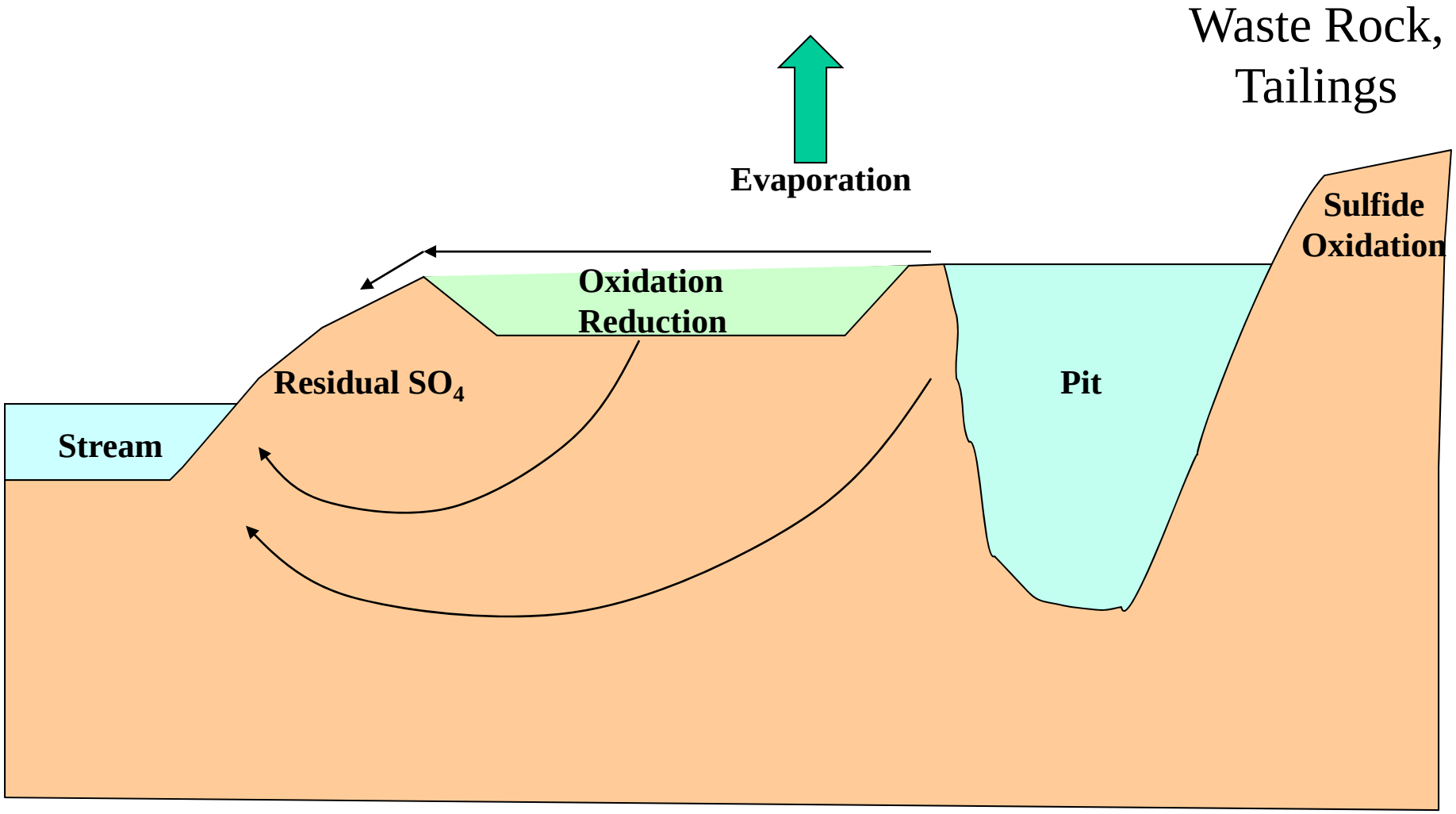
Rayleigh Distillation Process for Bacterial Sulfate Reduction



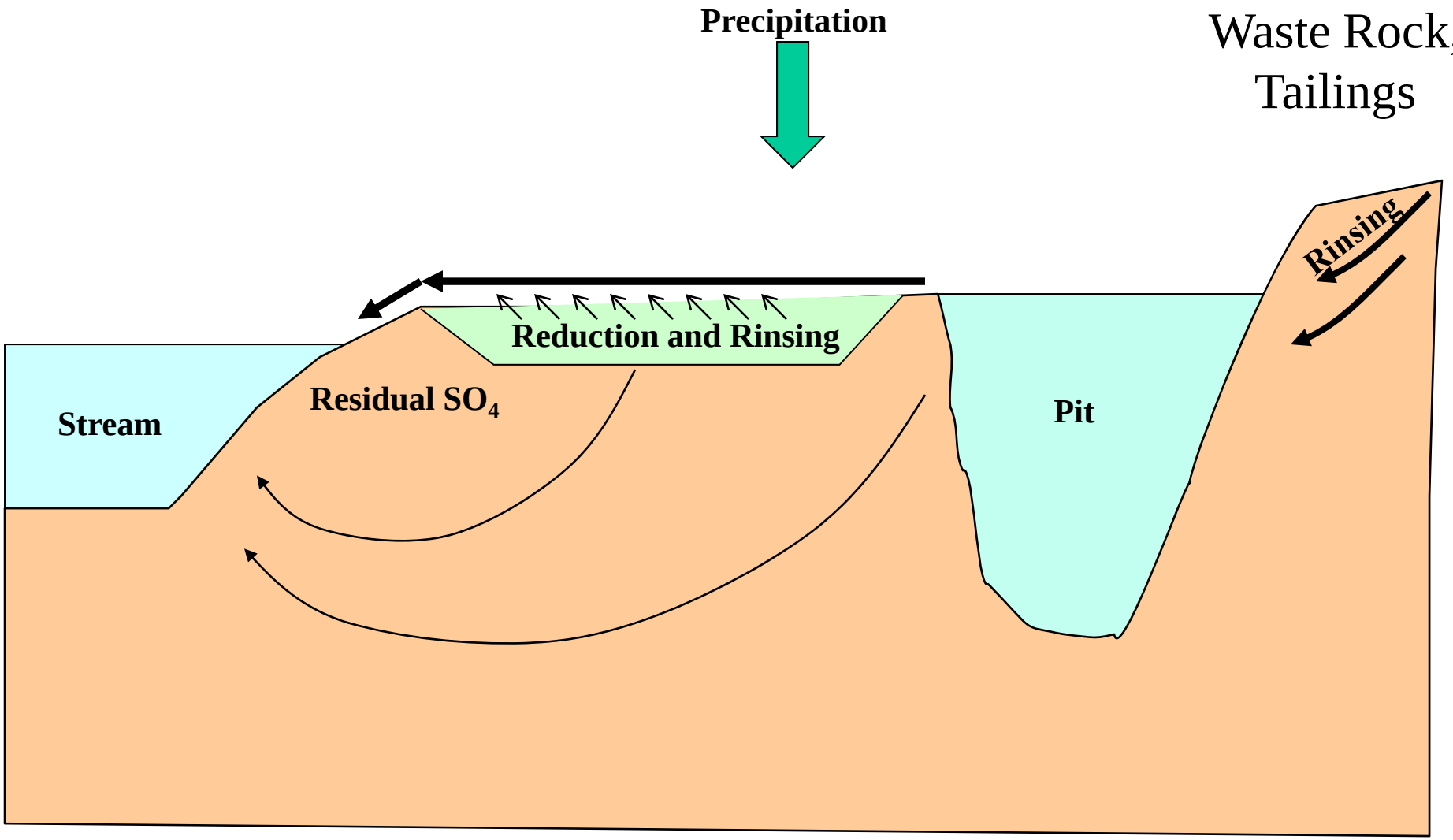
Sulfate Isotopes in the St. Louis River and Surrounding Watersheds



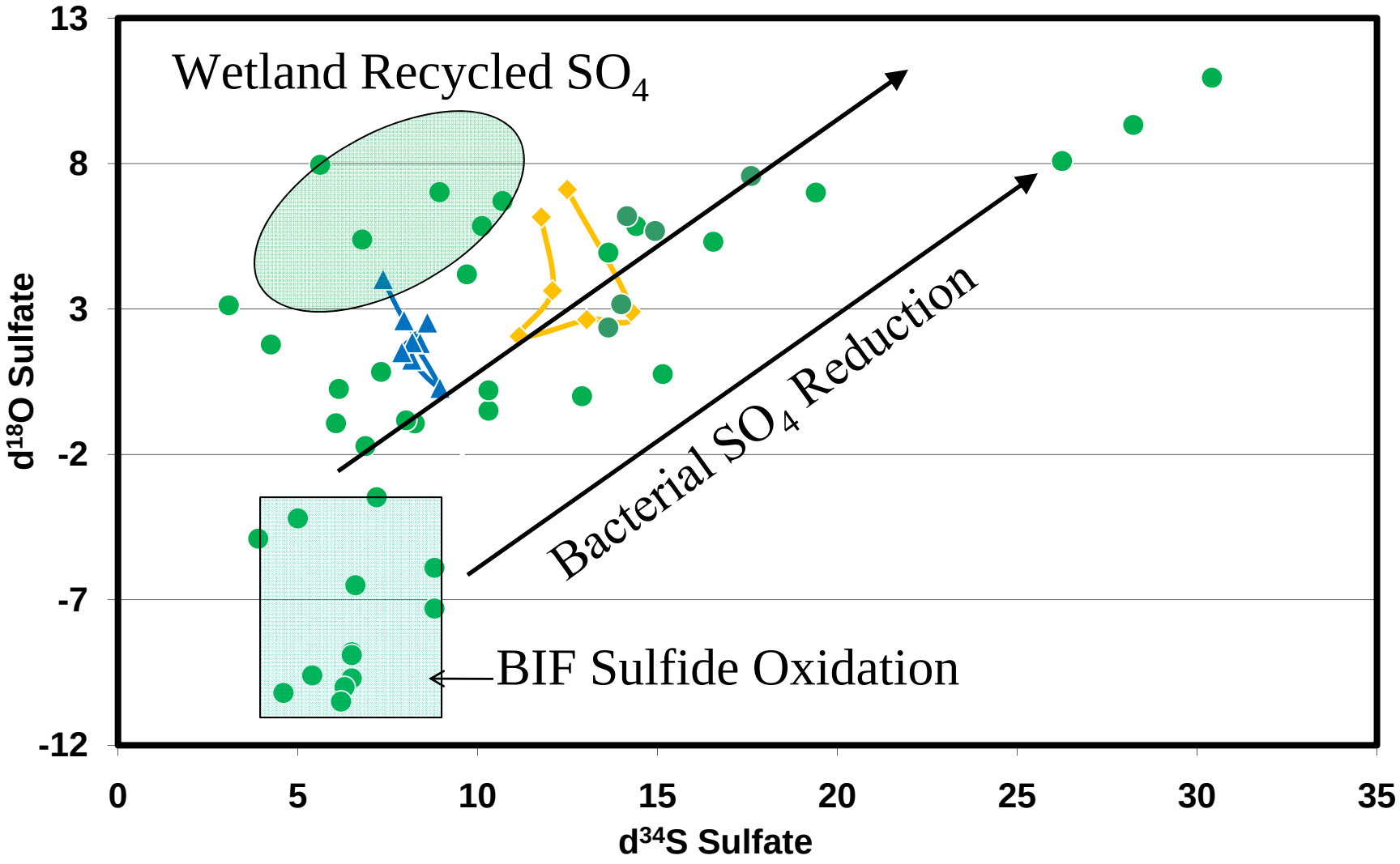
DRY CONDITIONS



WET CONDITIONS



Preliminary Interpretation of SO_4 Isotopes



Conclusions

(1) SO_4 concentrations elevated during dry seasons, but SO_4 loading is highest during wet seasons

(2) H_2SO_4 titration by Mg-siderite leads to high Mg/Ca ratio in mine land streams

(3) SO_4 isotopic data suggest sulfate reduction and reoxidation is important process in this region

THANK YOU!!