Exploration of sulfate, organic, and inorganic carbon on rare earth element mobility within Appalachian coal mine drainage

Authors: Eliza Siefert[1]; Dorothy Vesper[2]

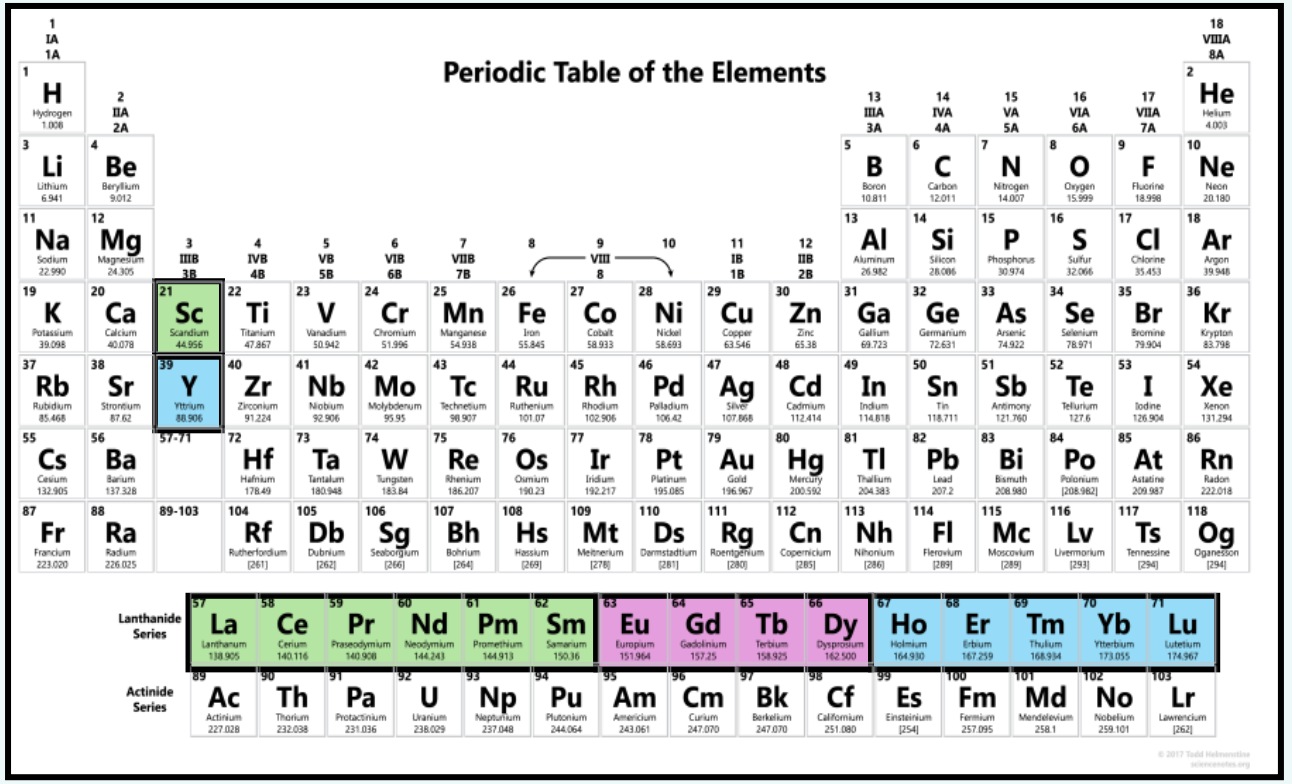
[1]West Virginia Water Research Institute, West Virginia University, Morgantown, WV

[2]Department of Geology and Geography, West Virginia University, Morgantown, WV

Maiden Mine Discharge into Robinson Run in Monongalia Co, WV (E. Siefert, WVWRI)

Appalachian CMD Geochemistry and REEs

- REEs have been found in CMD across Appalachia
- Y, Ce, Sc, Nd, La, Gd, Dy, Sm most abundant in REEs recorded in PA CMD
- Largely trivalent in solution
  - Ce(IV) oxidation anomaly
- Transport and fate associated with Fe and pH



Light Rare Earth Elements | Medium Rare Earth Elements | Heavy Rare Earth Elements

CMD – coal mine drainage
REE – rare earth elements + Y + Sc

Possible ions in CMD impacting REE speciation:

Organic Carbon

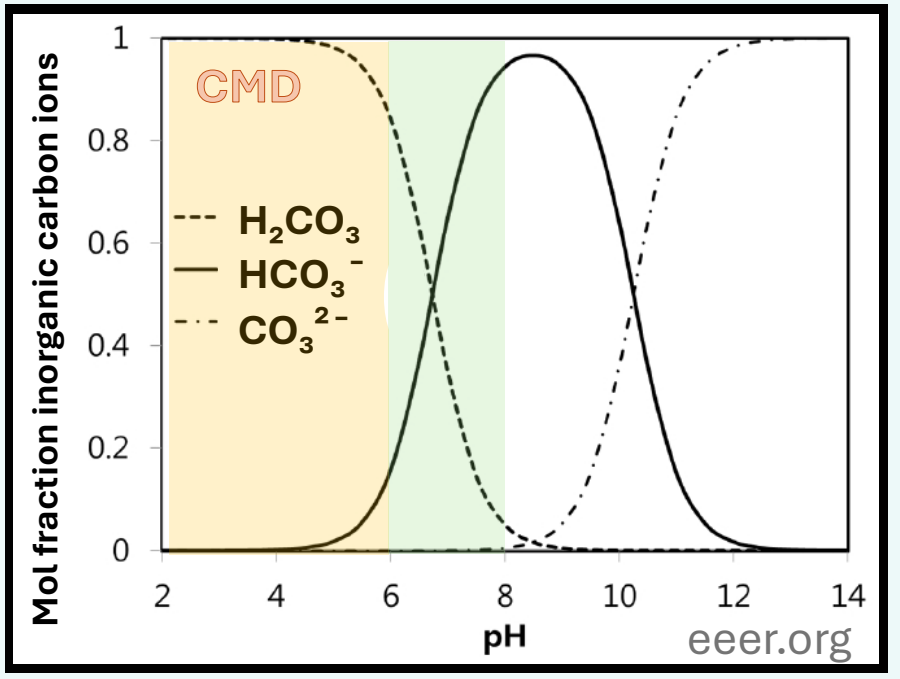
- Often low due to decreased biological activity
- OC in pit lakes up to 2 mg/L
  - Increases alongside pH
- Increase in treatment wetlands
- MREE associated with OC in alkaline waters

Inorganic Carbon

- CMD pH <6 Carbonate geology important source of dissolved metals (Ca, Fe, Mn, Ba, Pb, Zn)
- Marine Carbonate complexation increases with REE mass
  - Complexed ions prefer to remain in solution

Sulfate

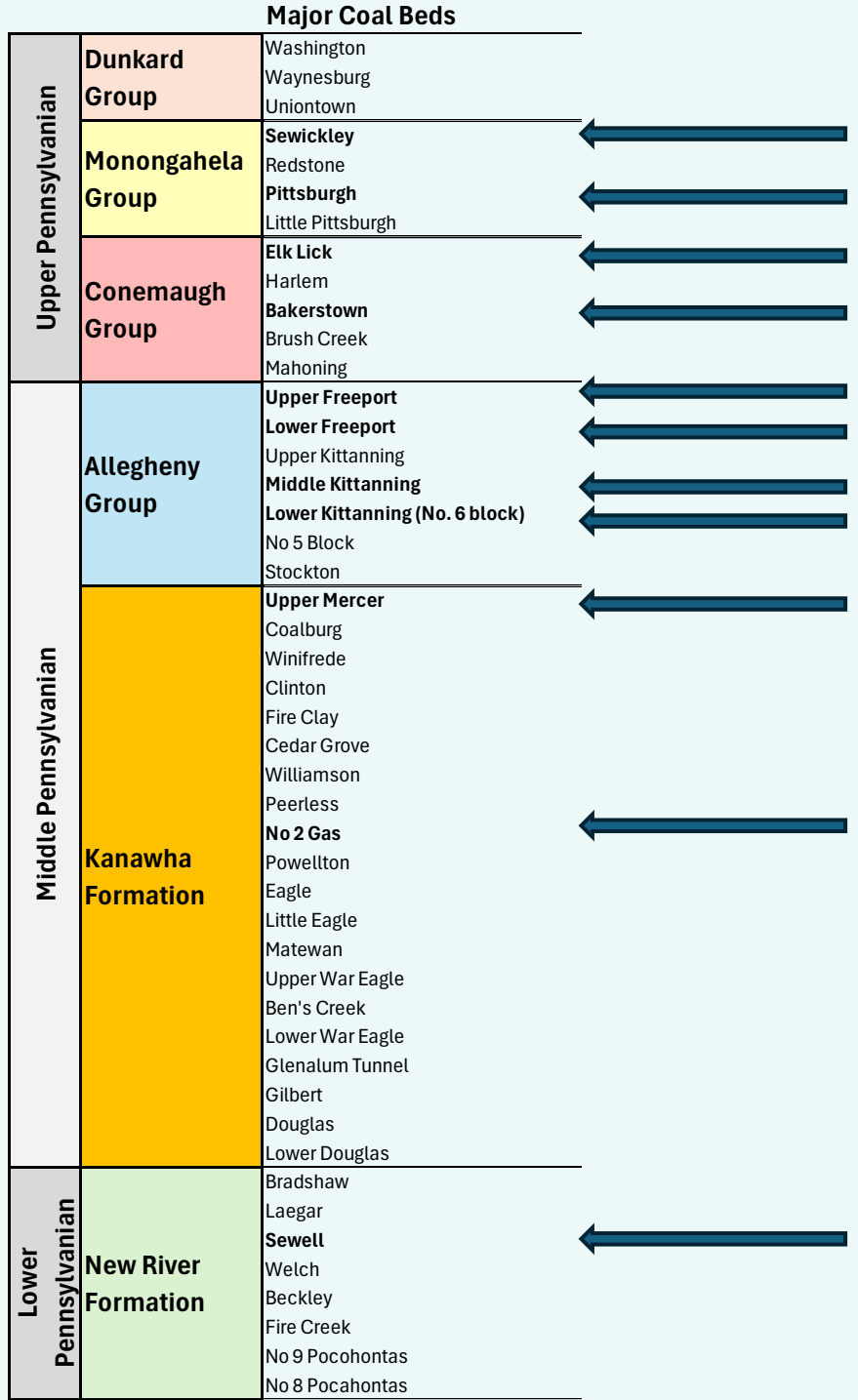
- Often dominant ion in CMD
- Lamberts Run, WV
  - Frequent REEs species are sulfate, free ion, and carbonate complexes

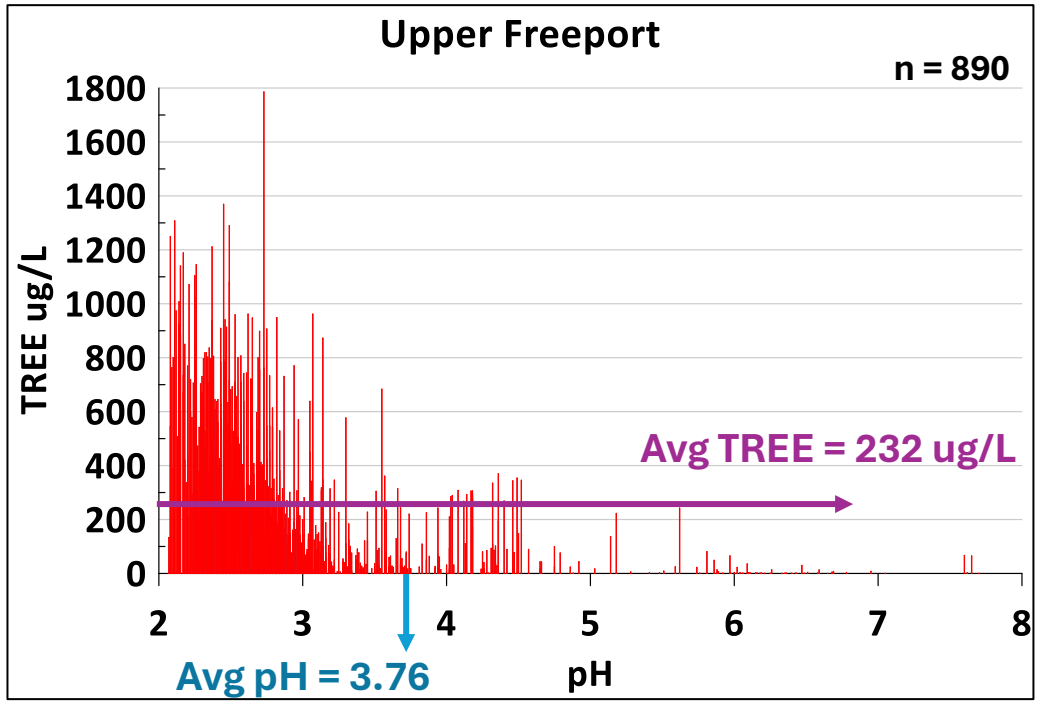


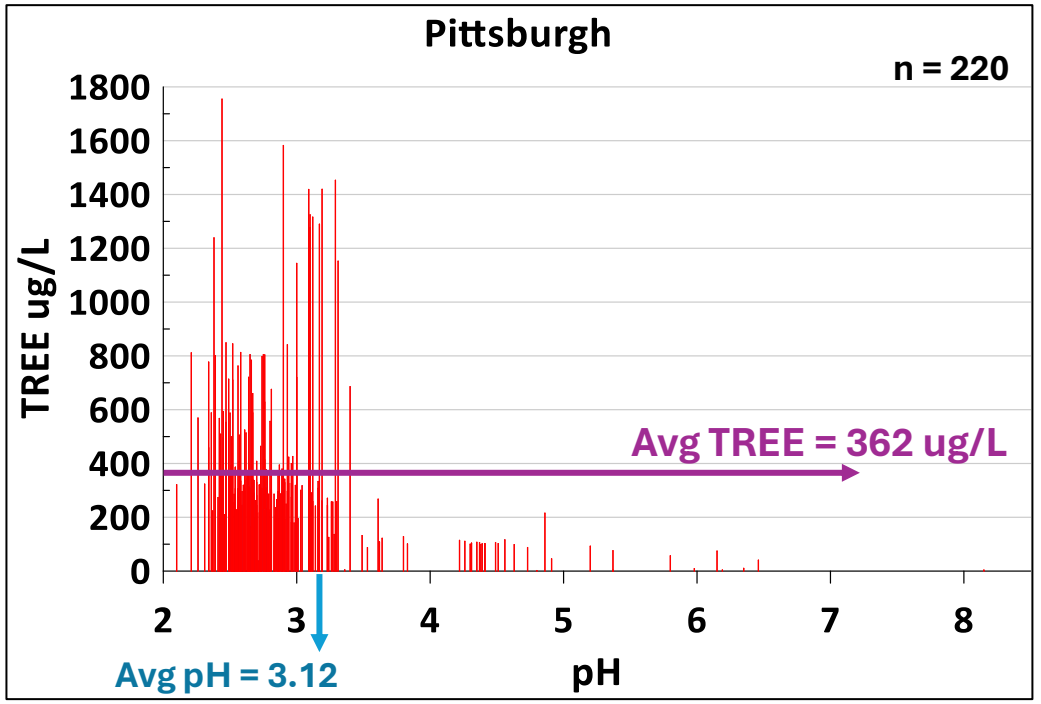
WVWRI CMD-REE Data

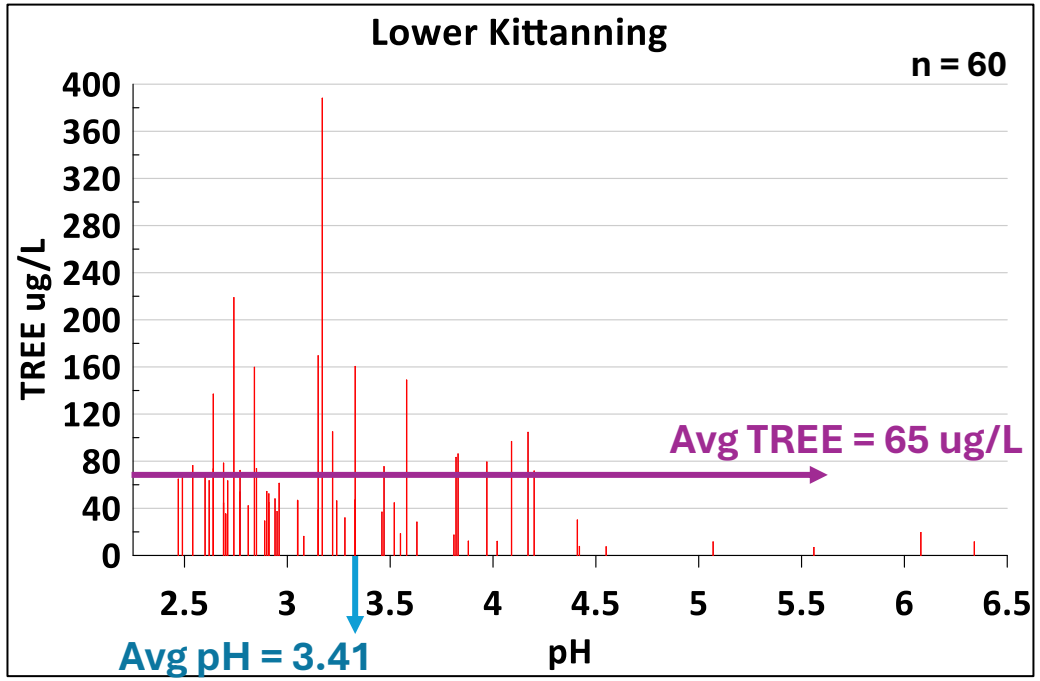
Seam	No Samples	Avg pH	Avg SO_4 (mg/L)	Avg TMM (mg/L)	Avg TREE (mg/L)
Upper Freeport	890	3.76	603	192	232
Pittsburgh	220	3.12	2100	740	362
Lower Kittanning	60	3.41	301	88	65
Bakerstown	34	4.66	329	90	33
Middle Kittanning	22	3.69	338	250	43
Sewickley	16	6.67	655	378	7
Lower Freeport	14	2.67	322	92	87
Upper Mercer	5	5.5	45	27	22
Elk Lick	3	3.16	537	211	66
No 2 Gas	3	4.13	416	27	22
Sewell	1	5.58	61	103	0.1

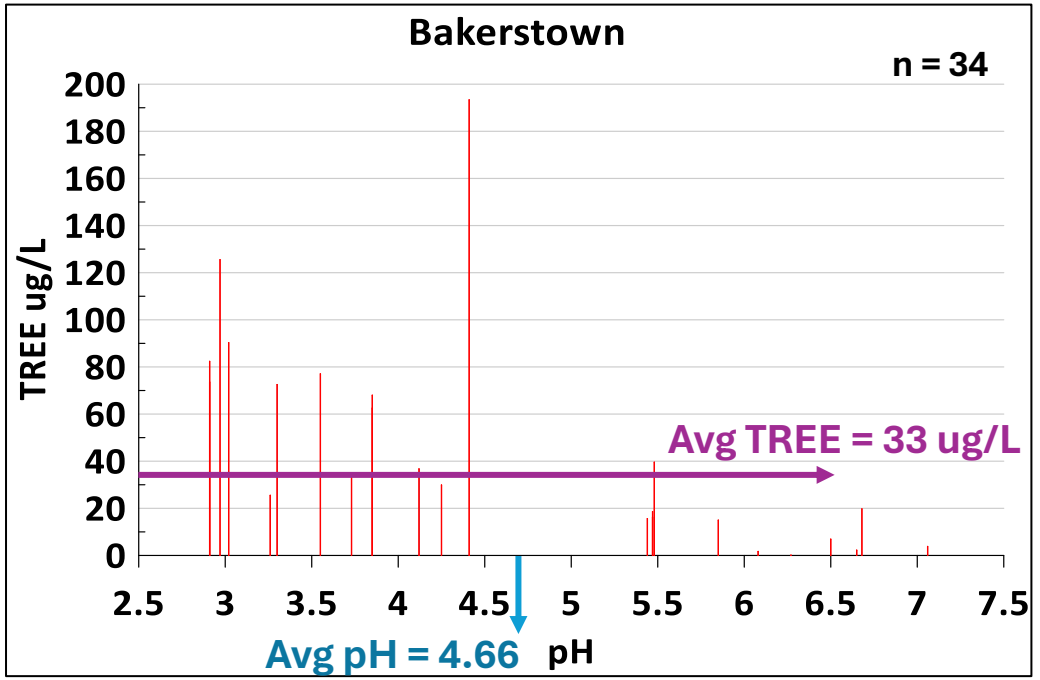
TMM – total major metals (Fe + Al + Mn + Mg)
TREE – total rare earth elements + Y + Sc



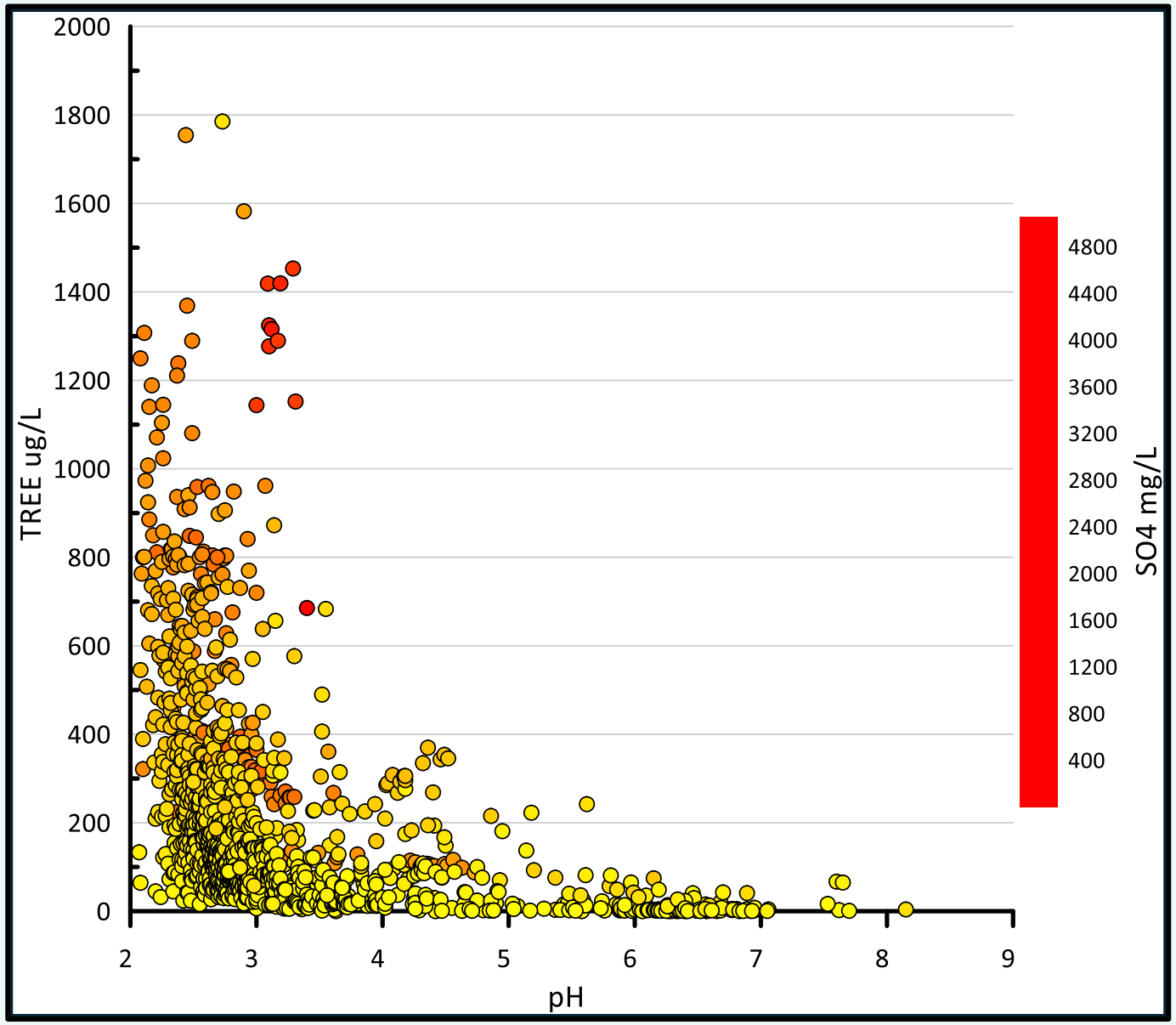

Upper Freeport
n = 890
TREE ug/L
1800
1600
1400
1200
1000
800
600
400
200
0
2
3
4
5
6
7
8
pH
Avg TREE = 232 ug/L
Avg pH = 3.76


Pittsburgh
n = 220
TREE ug/L
1800
1600
1400
1200
1000
800
600
400
200
0
2
3
4
5
6
7
8
pH
Avg TREE = 362 ug/L
Avg pH = 3.12

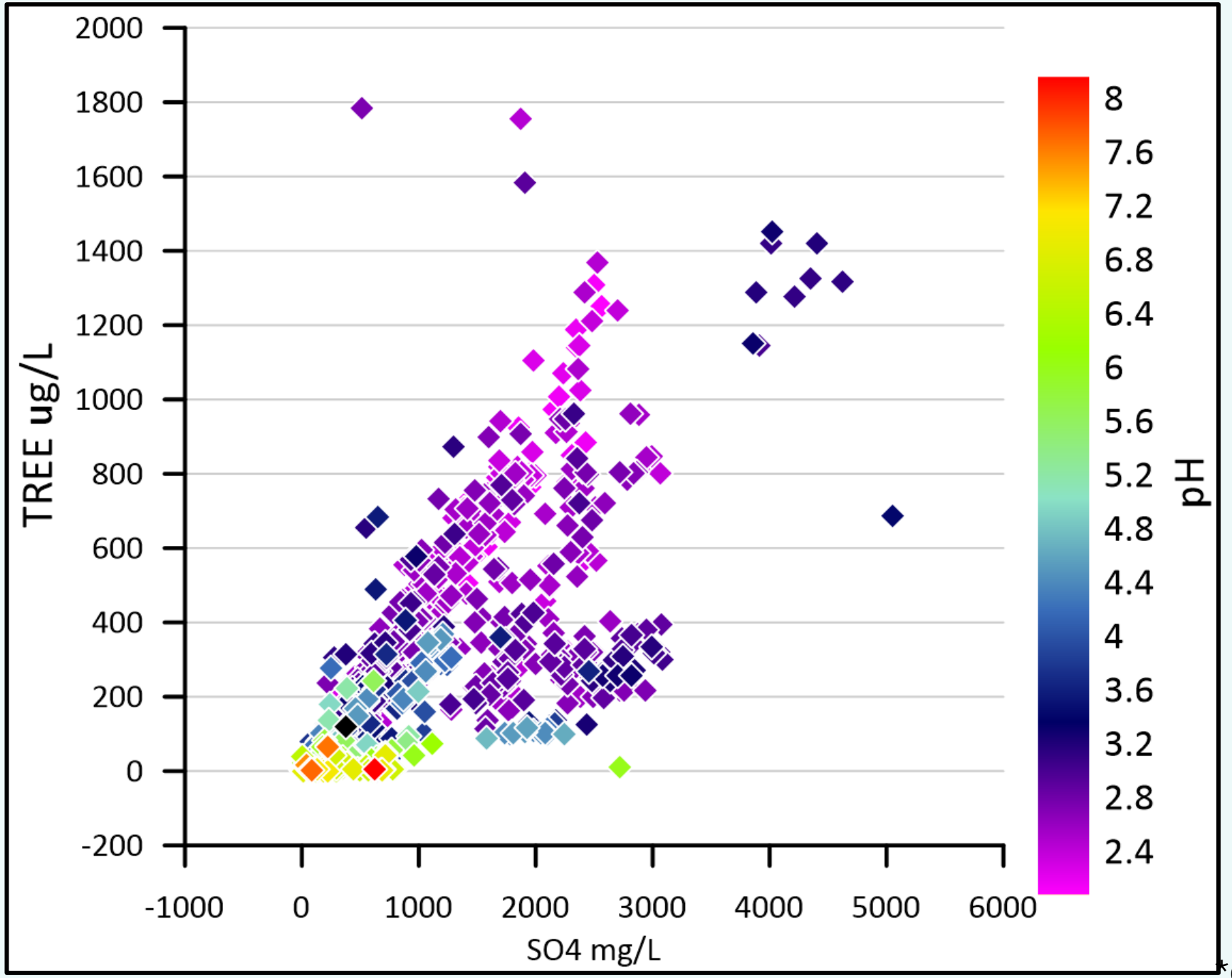

Lower Kittanning
n = 60
TREE ug/L
400
360
320
280
240
200
160
120
80
40
0
2.5
3
3.5
4
4.5
5
5.5
6
6.5
pH
Avg TREE = 65 ug/L
Avg pH = 3.41


Bakerstown
n = 34
TREE ug/L
200
180
160
140
120
100
80
60
40
20
0
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
pH
Avg TREE = 33 ug/L
Avg pH = 4.66

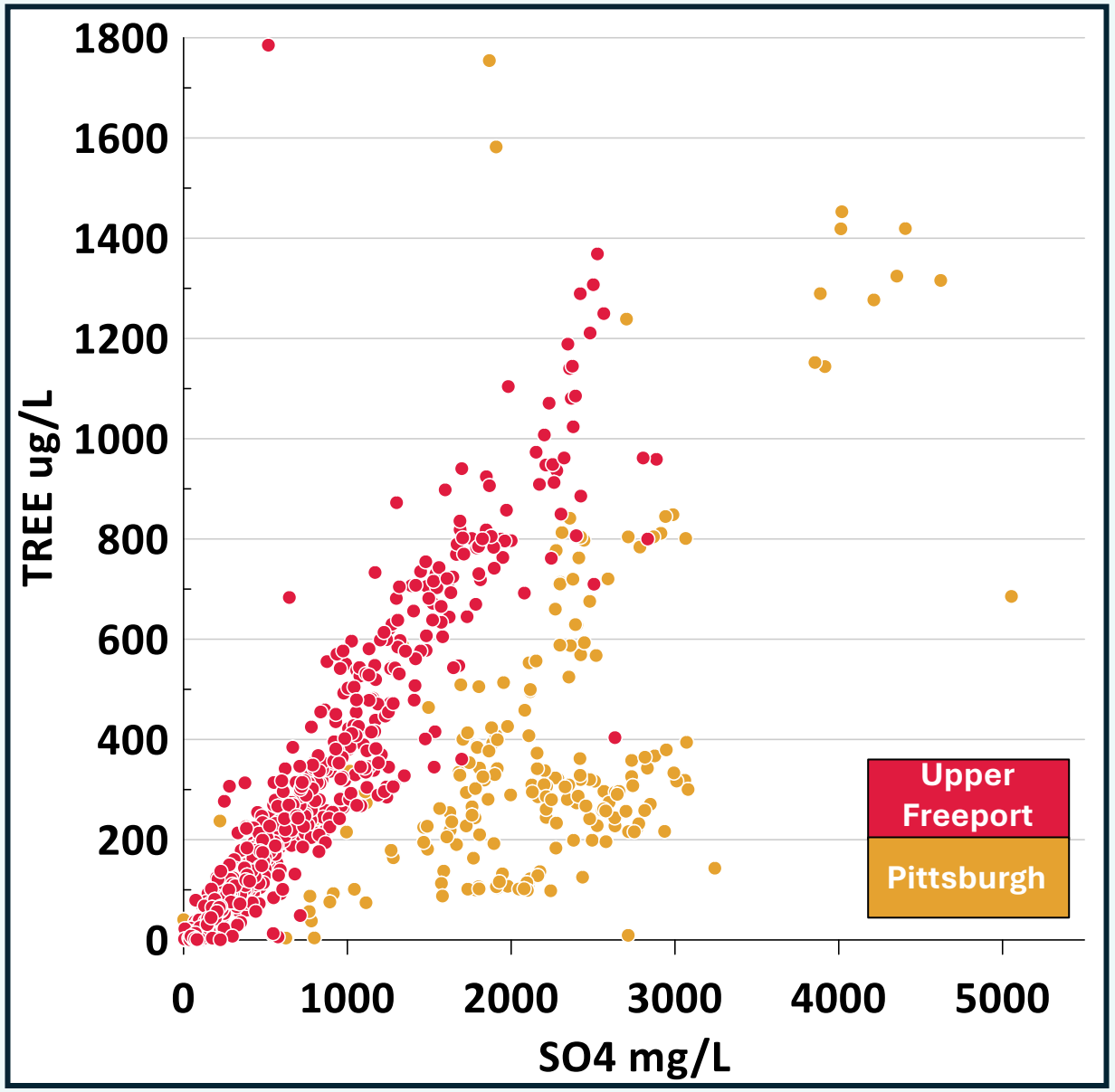
Association of [TREE] and pH with associated [SO4] in sampled sources

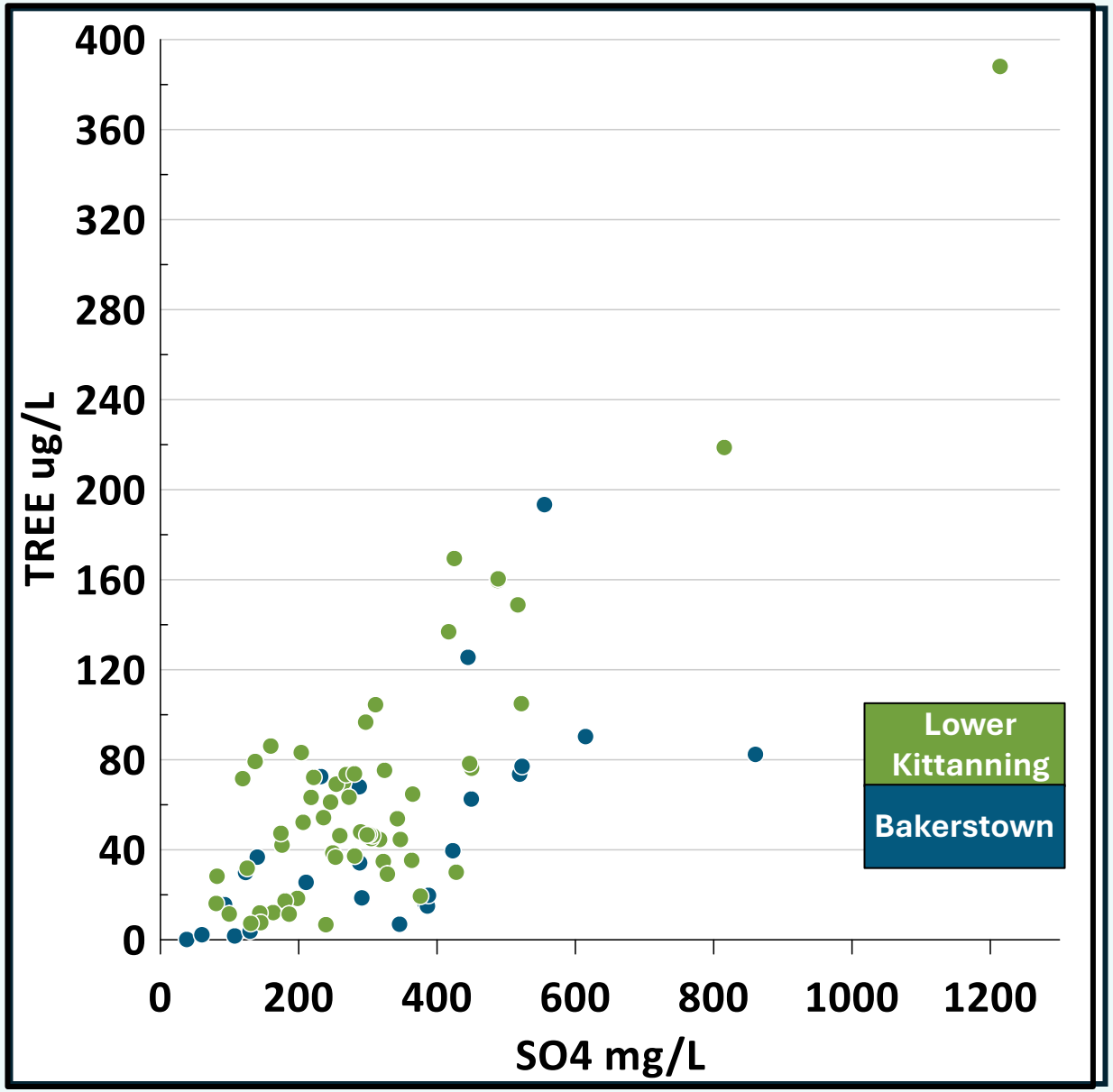


*data from all coal seams

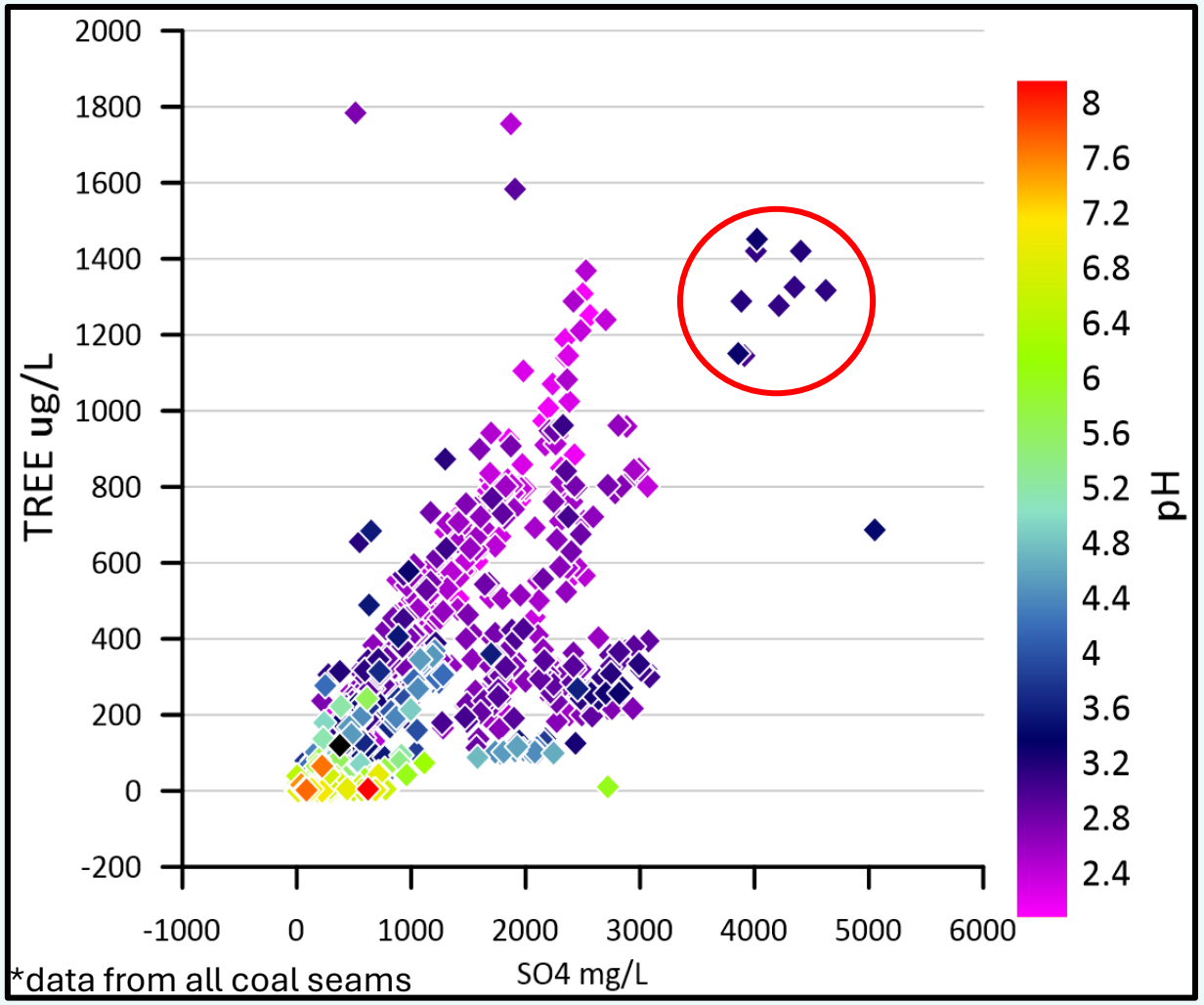


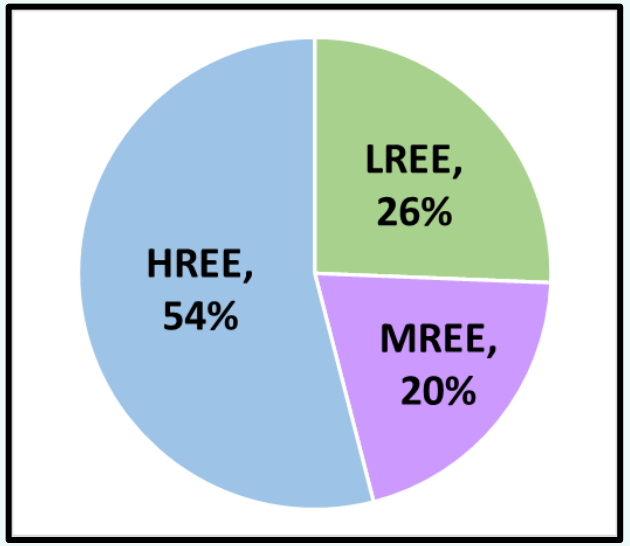
*data from all coal seams


1800
1600
1400
1200
1000
800
600
400
200
0
TREE ug/L
0
1000
2000
3000
4000
5000
SO4 mg/L
Upper Freeport
Pittsburgh


400
360
320
280
240
200
160
120
80
40
0
TREE ug/L
0
200
400
600
800
1000
1200
SO4 mg/L
Lower Kittanning
Bakerstown

RR Bethel Hollow Rd 1 - Pittsburgh





Avg pH	Avg SO4 (mg/L)	Avg TMM (mg/L)	Avg TREE (ug/L)
3.15	4143	1263	1310

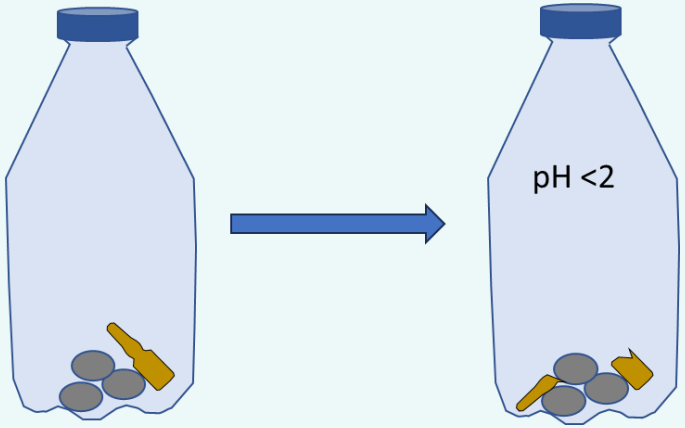
Research Focus

- REE mobility depends on aqueous speciation
- Relationship of sulfate, pH, and TREE concentrations
- Limited data on organic carbon
- Carbonates may lead to HREE to stay in solution
- Importance for:
    - Aquatic species
    - Extraction research
    - Sampling efforts

AML discharge into Lick Run in Preston Co, WV
(M. Shafer, WVWRI)

Methods – Sample Collection

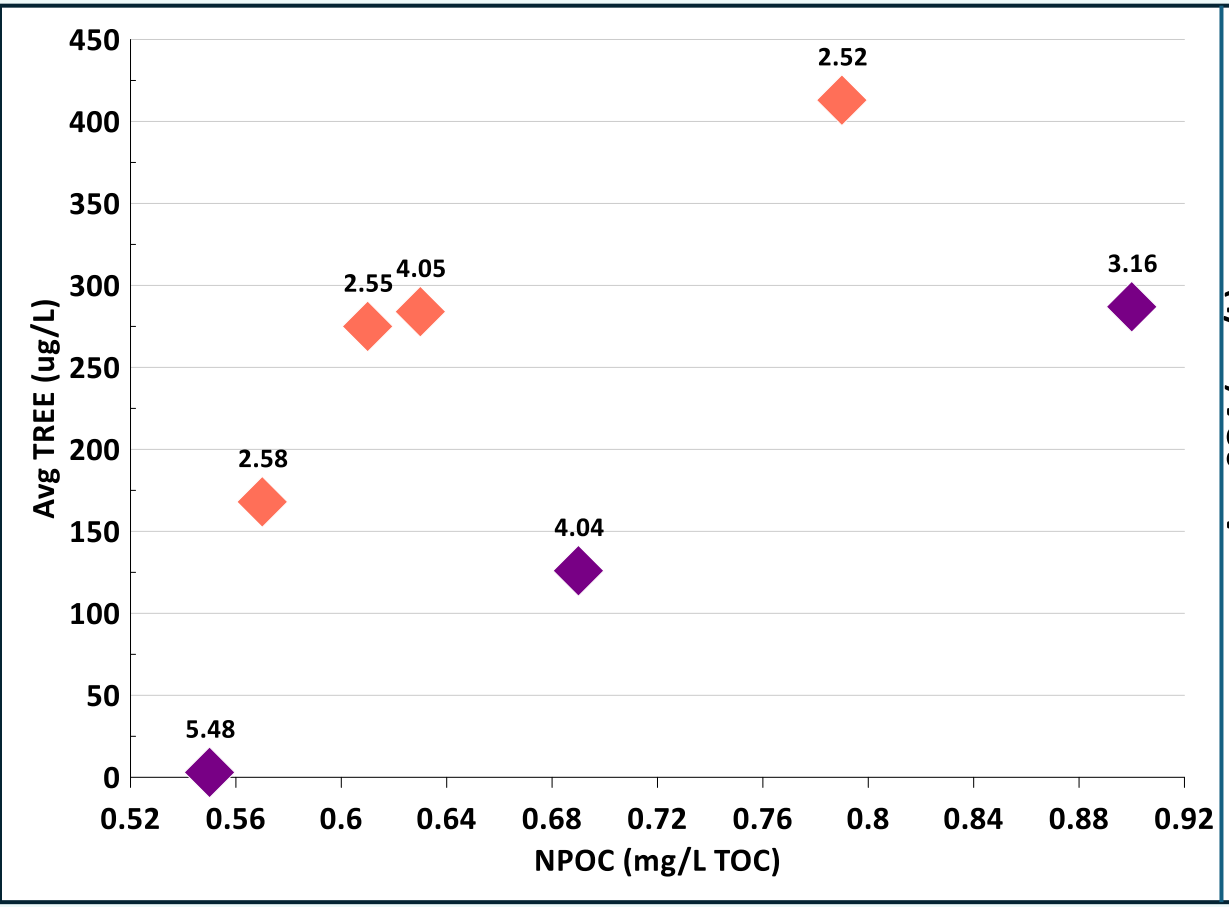
- Field
  - pH, spc, TDS, DO, ORP, flow
- Analytical
  - TMM, TREE, SO_4
- Organic carbon
  - NPOC via Shimadzu TOC/V
- Dissolved inorganic carbon (DIC)
  - Soda bottle with HCl ampule
  - Anton Paar CarbQC (Vesper et al., 2025)

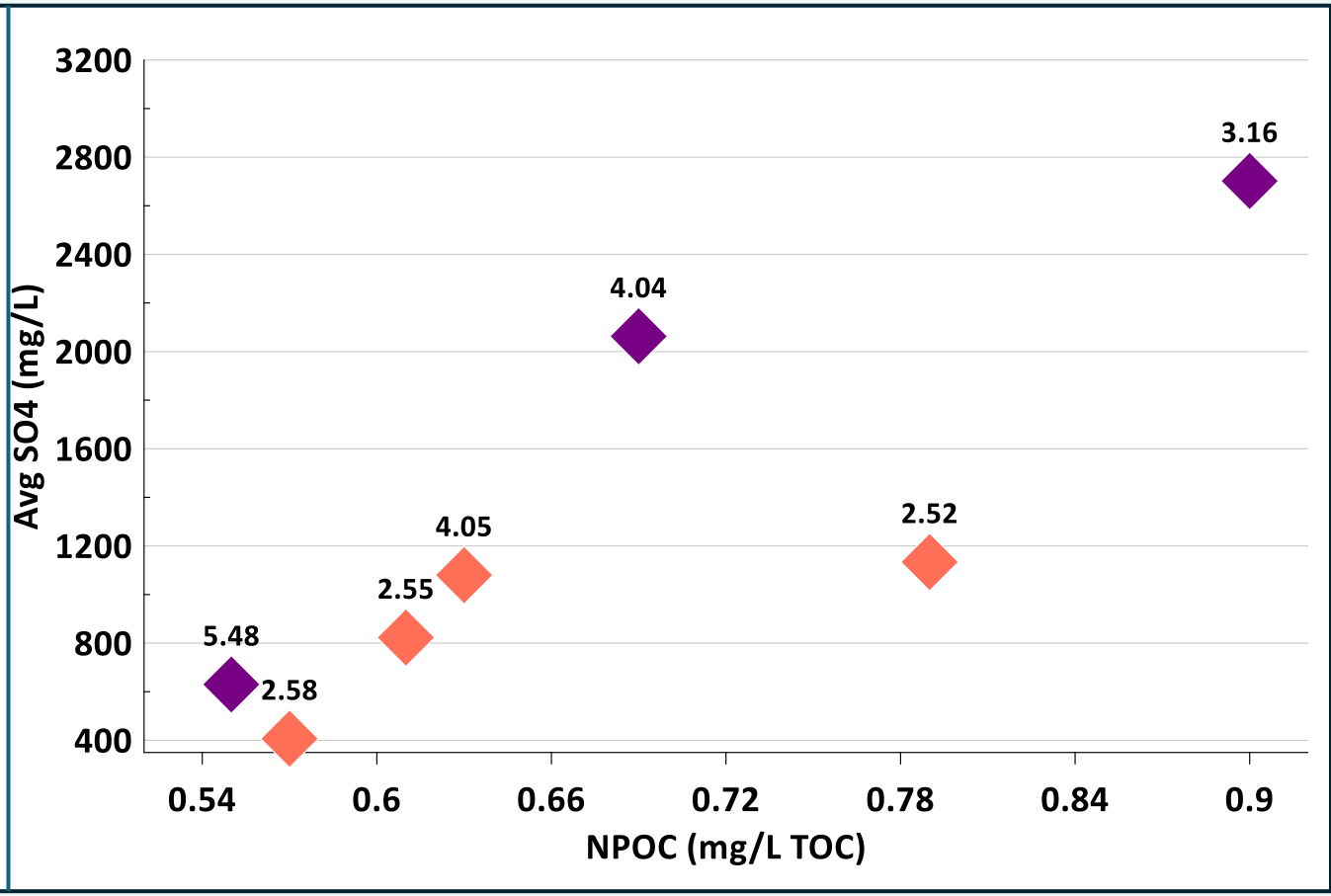


HCl glass ampule (J. Stewart, NBAC)

NPOC – Non-purgeable organic carbon
DIC – dissolved inorganic carbon

Collected at-source NPOC





Upper Freeport

Pittsburgh

***site average pH displayed above**

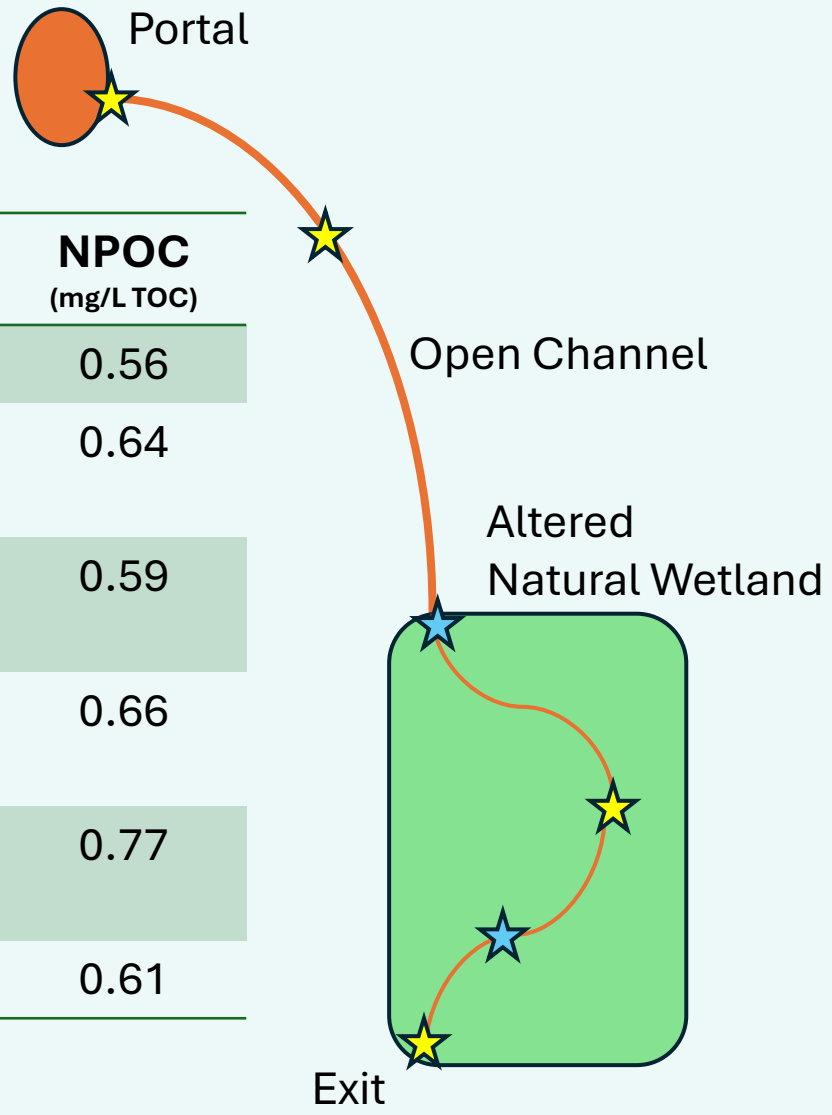
Lambert Run Site 3

- Near neutral CMD source
  - Pittsburgh seam
- Passive treatment location
- Previous sampling efforts
  - Sulfate, free ion, carbonate complexes
  - As pH rises, carbonates become significant for HREE
  - Vesper and Smilley, 2010

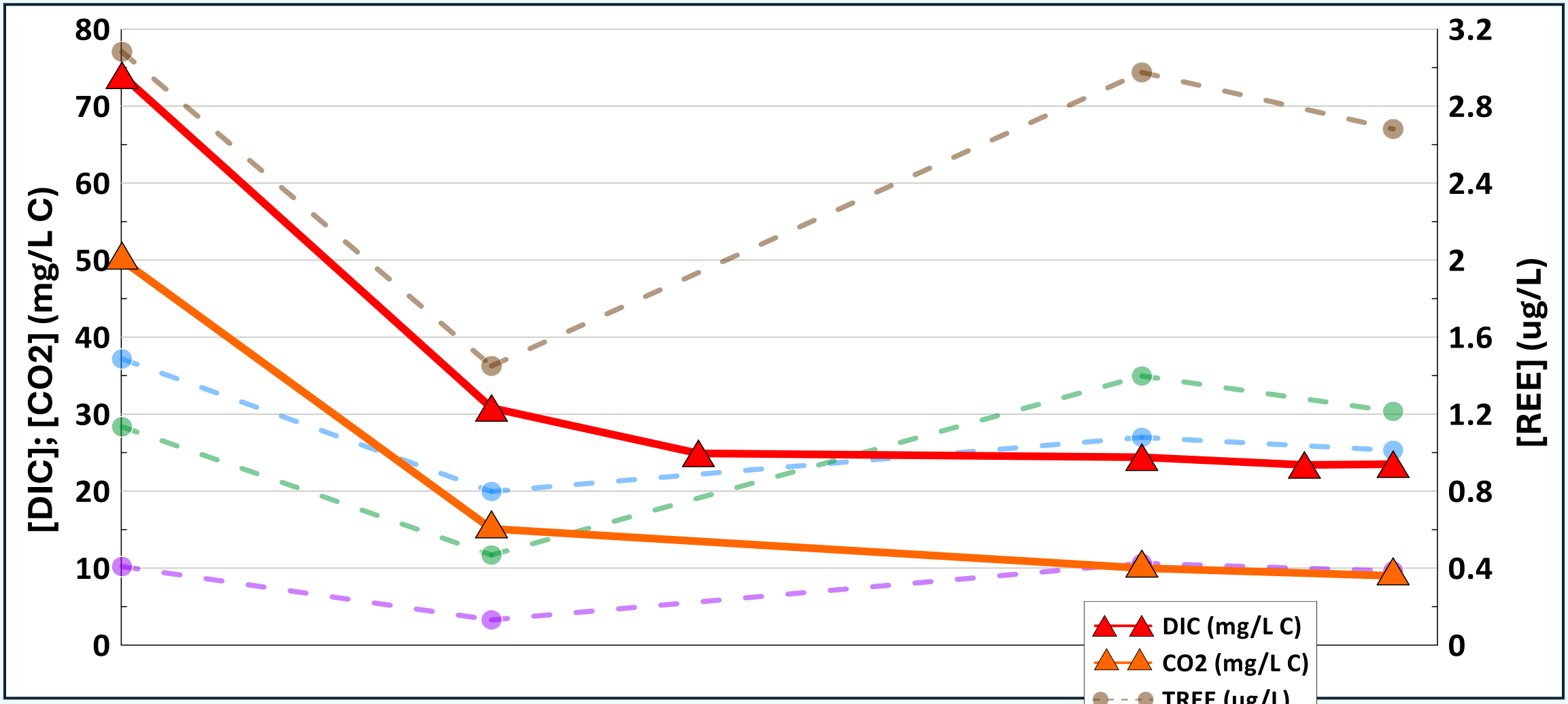
Lambert 3 site portal, April 2026 (J. Stewart, NBAC)

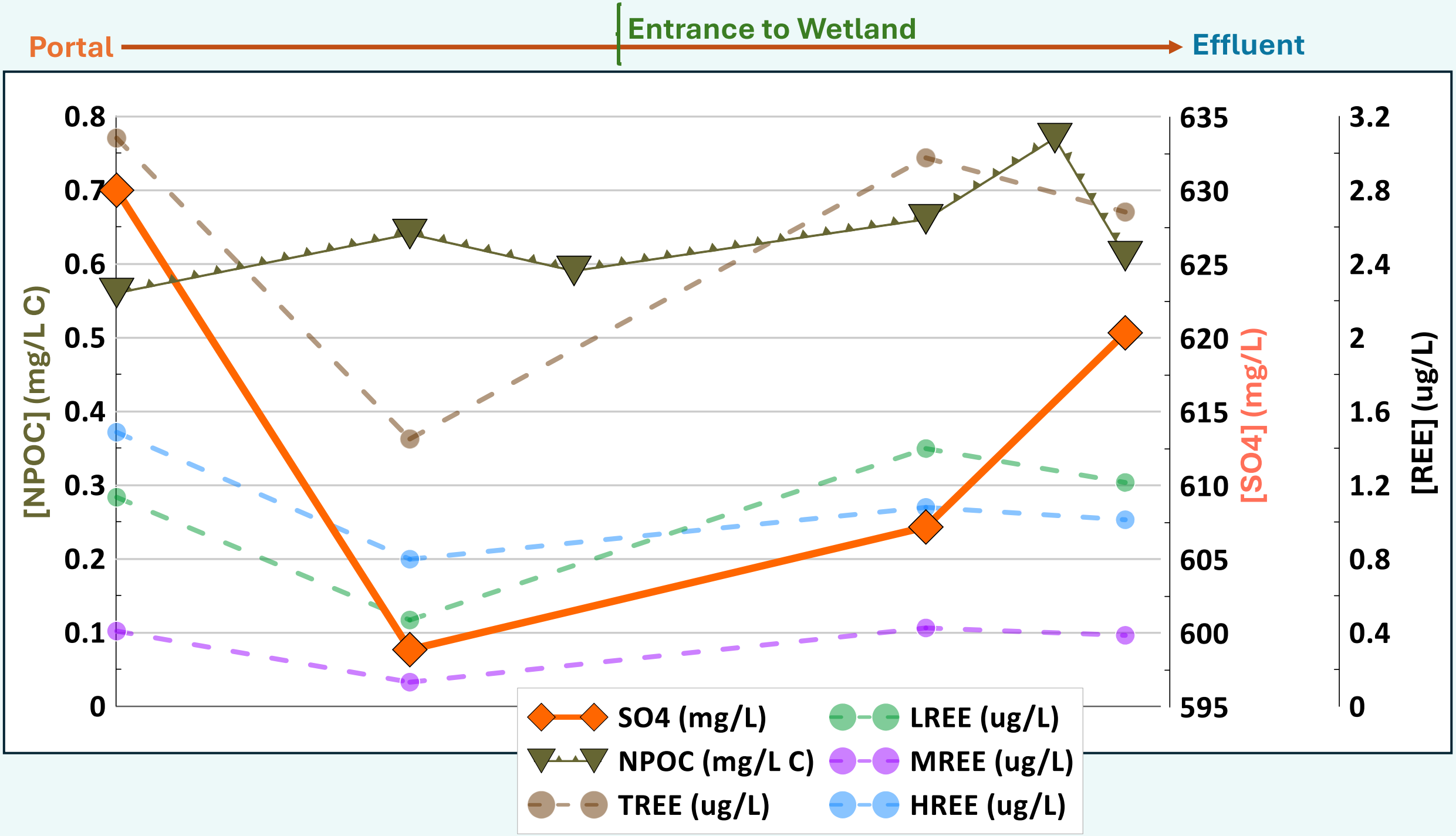
Lambert 3 Collected Data

	pH	TMM (mg/L)	TREE (ug/L)	SO4 (mg/L)	DIC (mg/L C)	CO2 (mg/L C)	NPOC (mg/L TOC)
Portal	5.48	238	3	630	74.0	50.0	0.56
Open Channel	6.21	238	1.5	599	30.8	15.1	0.64
Entrance to Wetland	6.66	--	--	--	24.9	--	0.59
Wetland Flowing	6.80	236	2.9	607	24.4	10.0	0.66
Swampy Wetland	6.93	--	--	--	23.4	--	0.77
Exit	7.01	236	2.7	620	23.5	9.0	0.61



Portal → Entrance to Wetland → Effluent

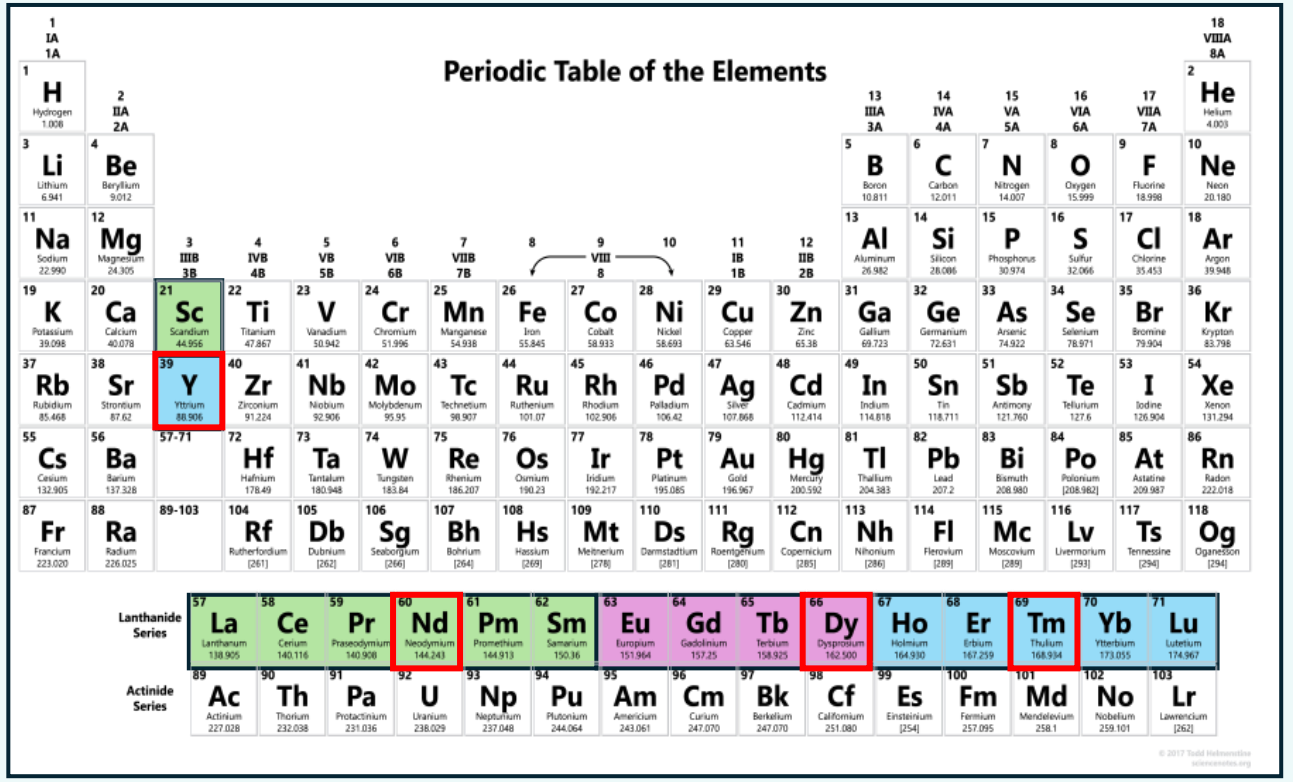



Portal
Entrance to Wetland
Effluent
[NPOC] (mg/L C)
[SO4] (mg/L)
[REE] (ug/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
635
630
625
620
615
610
605
600
595
3.2
2.8
2.4
2
1.6
1.2
0.8
0.4
0
SO4 (mg/L)
NPOC (mg/L C)
TREE (ug/L)
LREE (ug/L)
MREE (ug/L)
HREE (ug/L)

PHREEQC Modeling

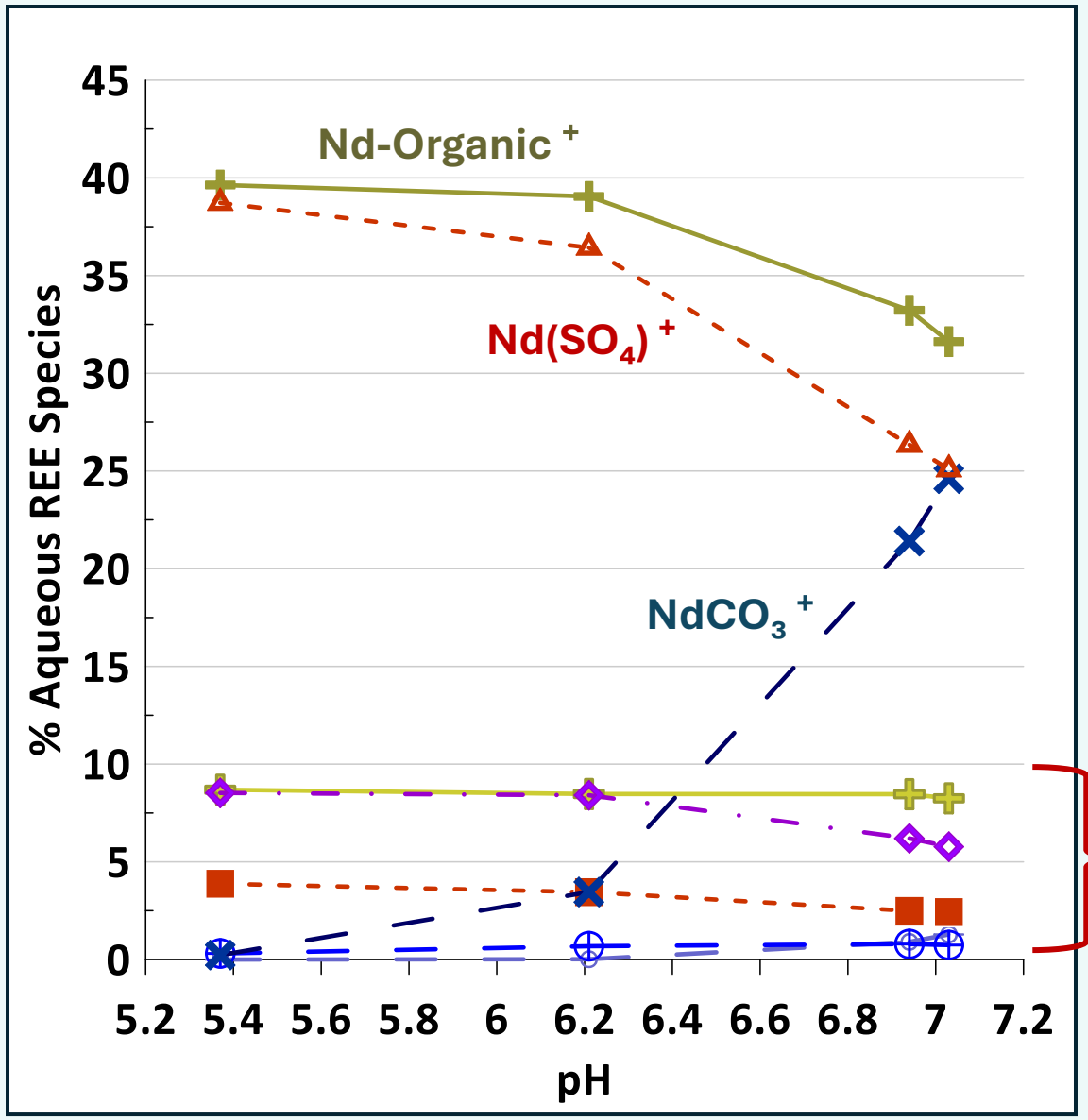
- Light REE – Neodymium (Nd)
- Medium REE – Dysprosium (Dy)
- Heavy REE – Thulium (Tm) and Yttrium (Y)

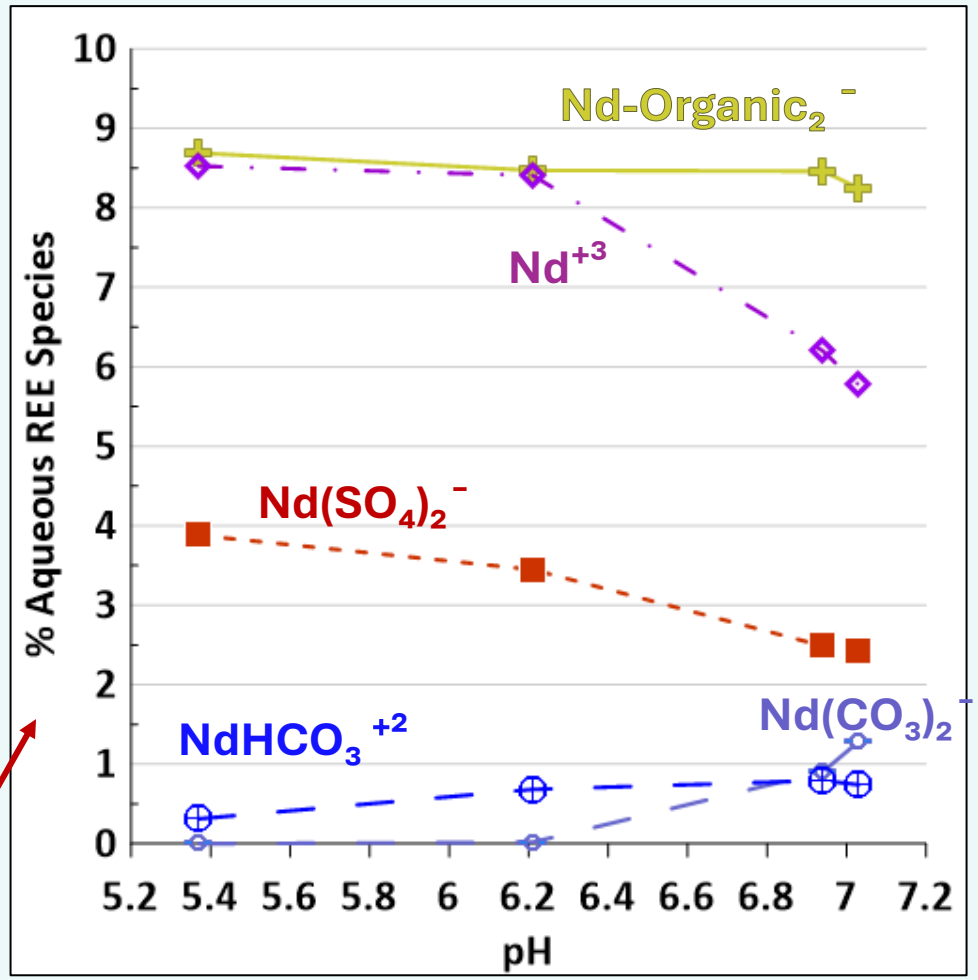
- Kinetics data
- Assumptions
  - Organic carbon as oxalate
  - No surface interactions
  - No additional ligands
  - <MDL



Light Rare Earth Elements | Medium Rare Earth Elements | Heavy Rare Earth Elements

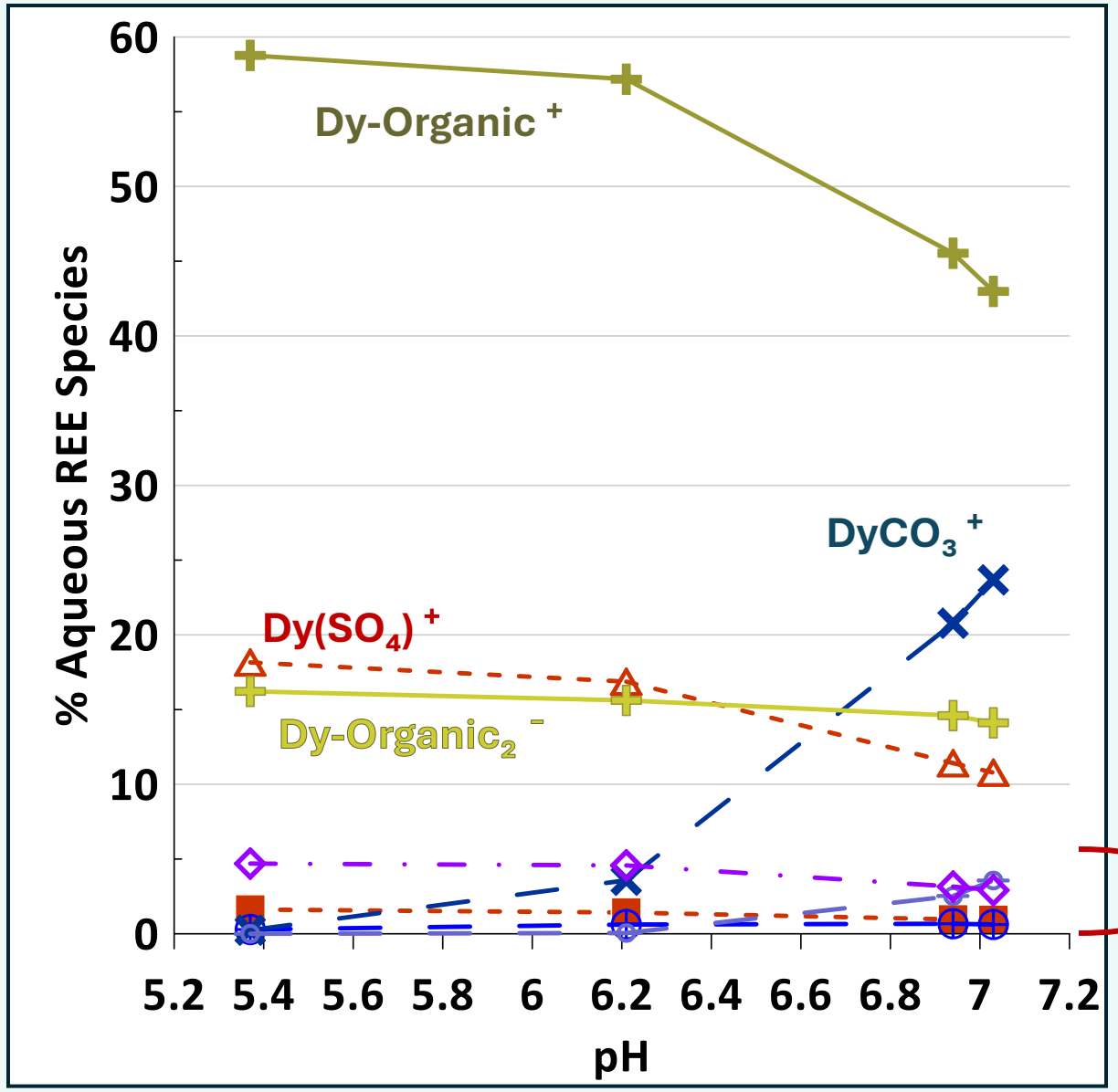
PHREEQ LREE: Neodymium

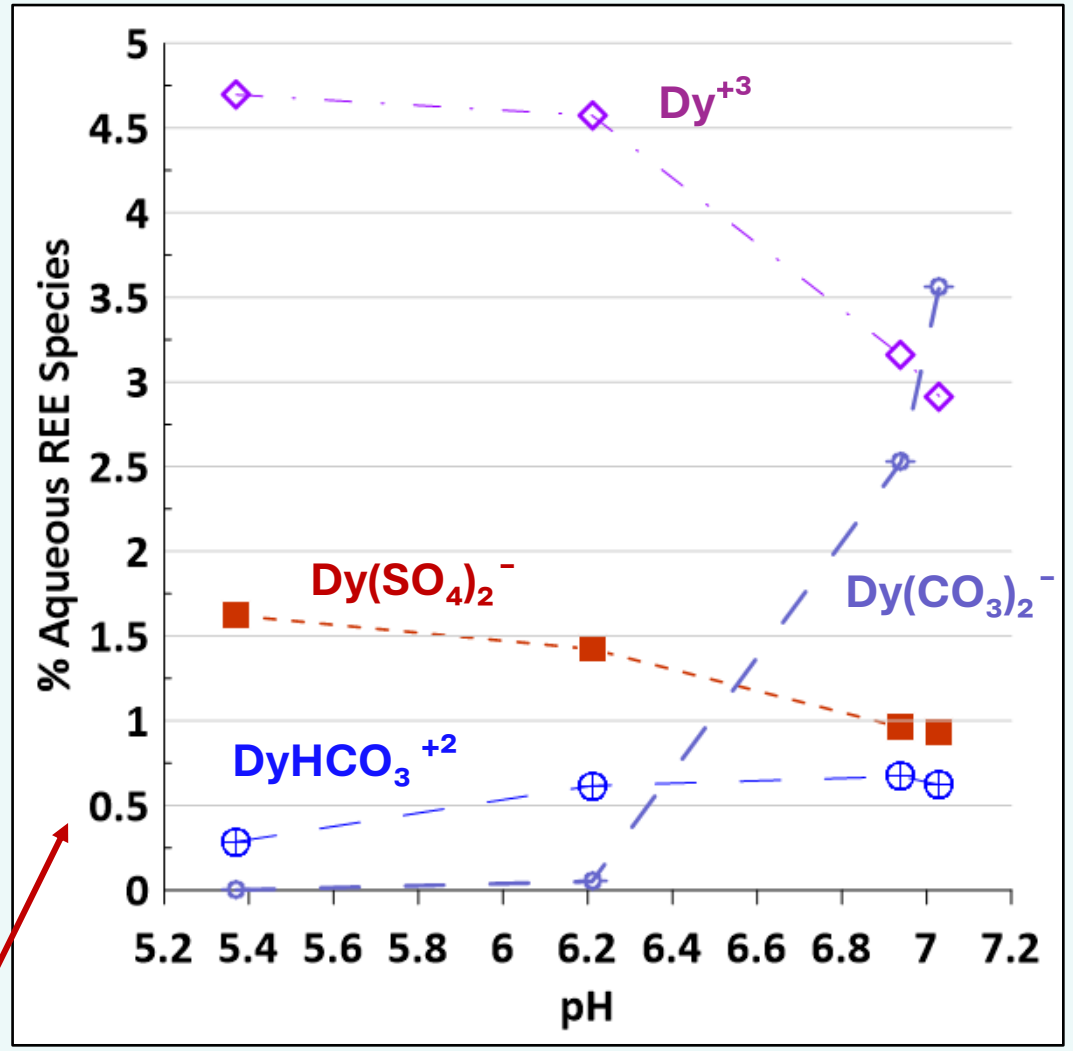




%[Nd+3]
%[Nd(SO4)+]
%[NdHCO3+2]
%[Nd(SO4)2-]
%[NdCO3+]
%[NdOx+]
%[Nd(CO3)2-]
%[Nd(Ox)2-]

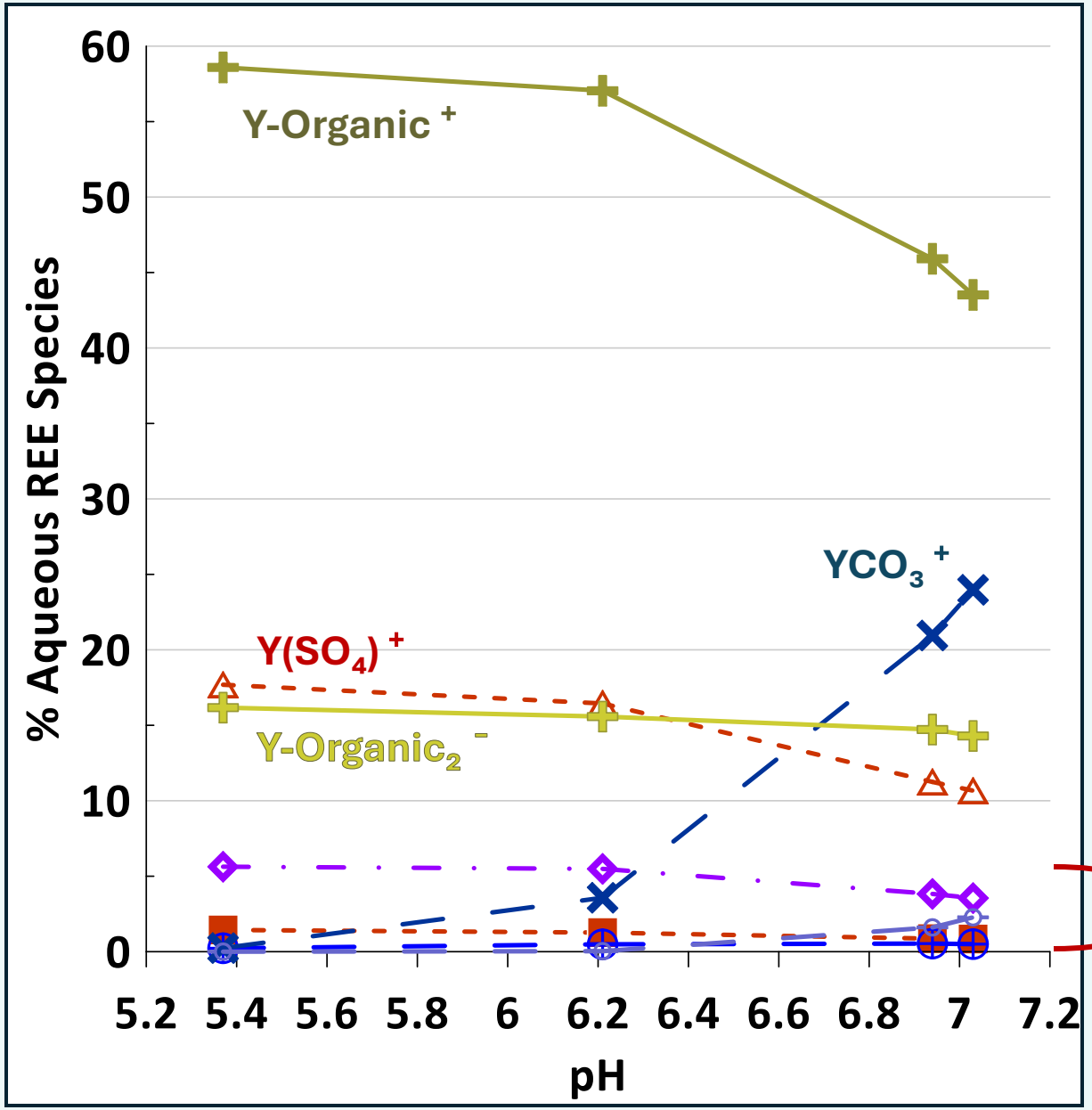
PHREEQ MREE: Dysprosium

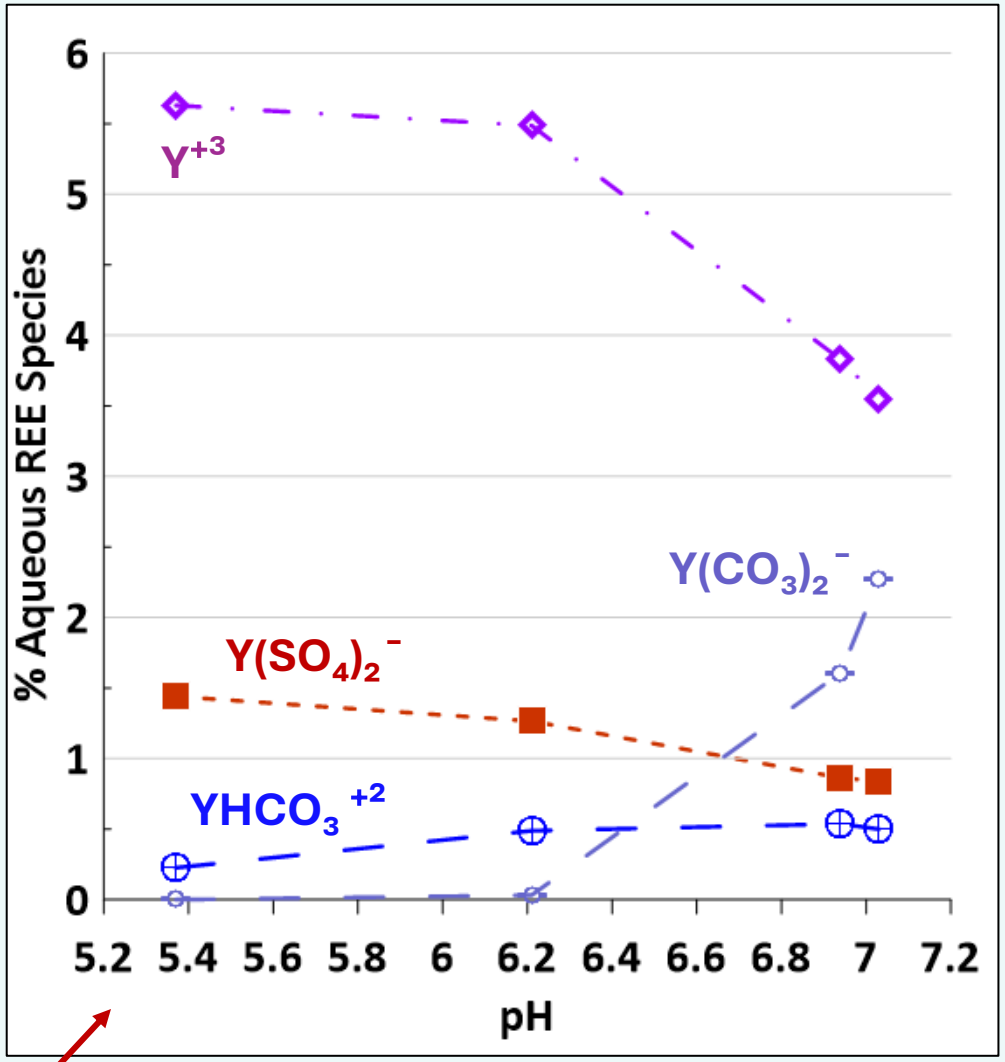


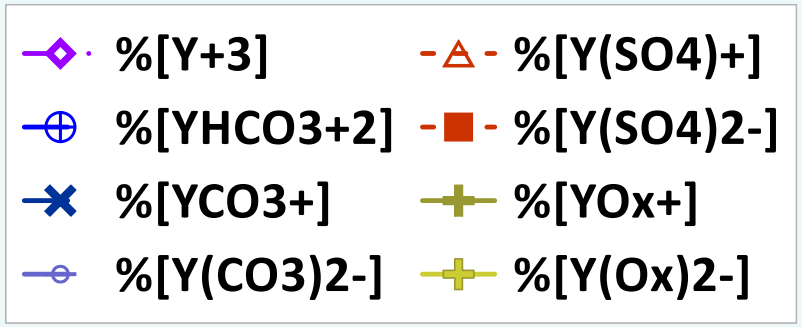


%[Dy+3] %[Dy(SO4)+]
%[DyHCO3+2] %[Dy(SO4)2-]
%[DyCO3+] %[DyOx+]
%[Dy(CO3)2-] %[Dy(Ox)2-]

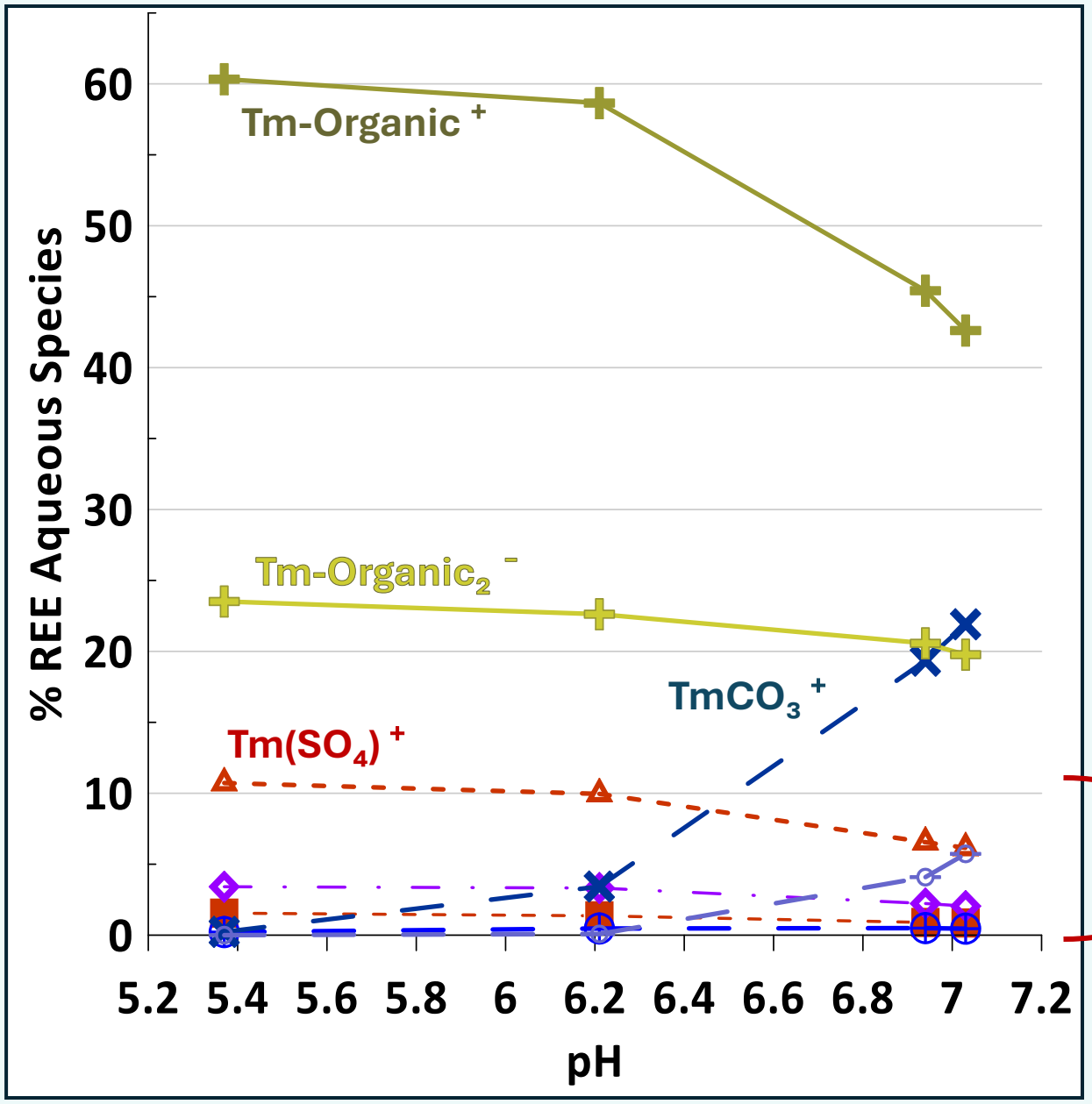
PHREEQ HREE: Yttrium

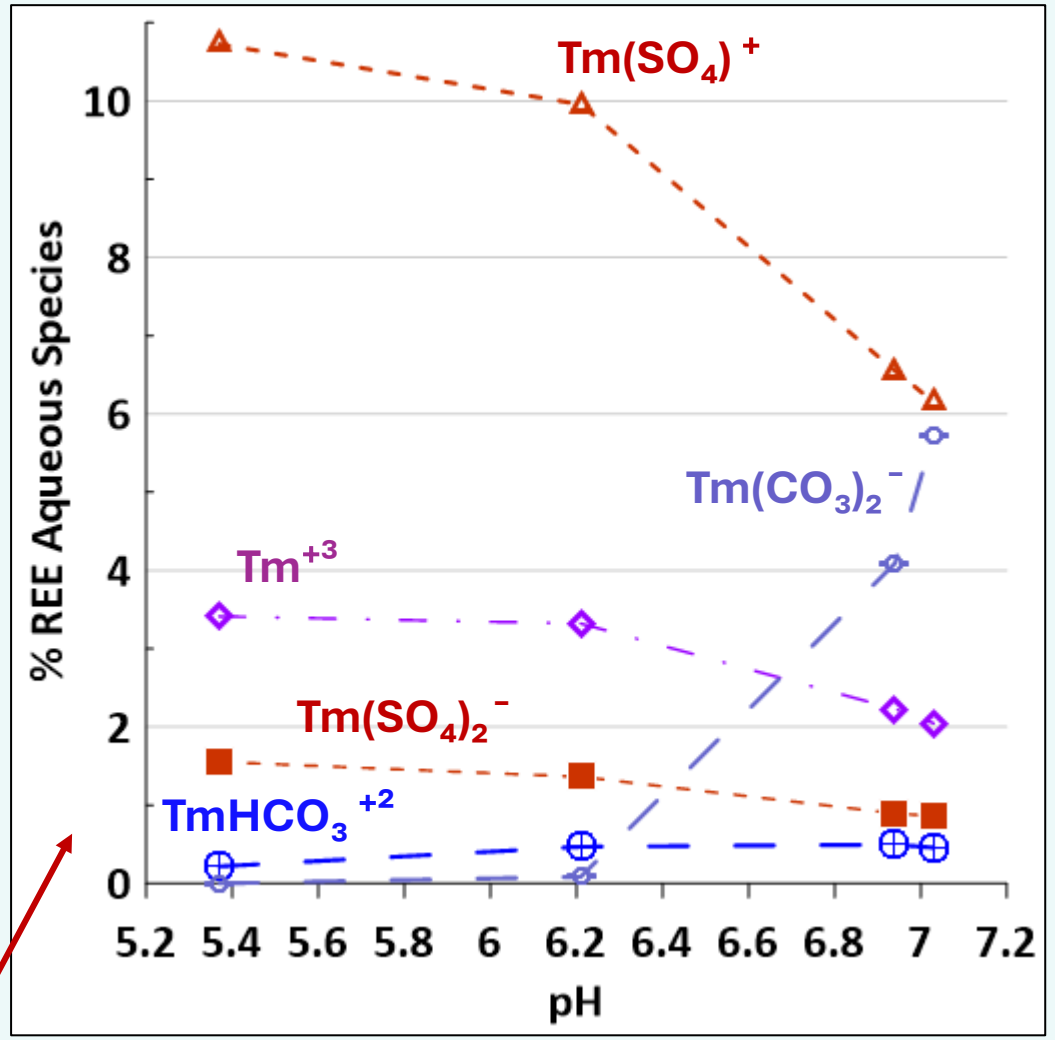


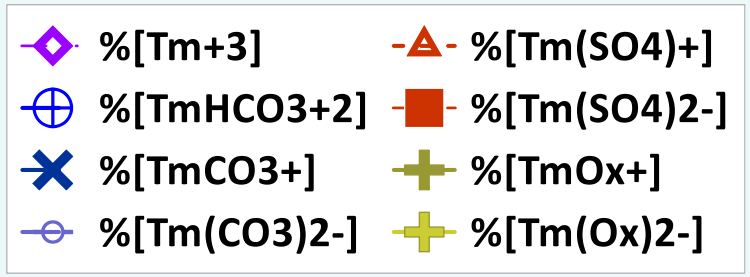




PHREEQ HREE: Thulium







Discussion

- Relationship of pH, sulfate and TREE concentrations
  - Potentially realted to coal seam
- Potential relationship of organic carbon in CMD and coal seam
- CO_2 degassing from portals
- < 10% of REEs modeled as free ions
- SO_4^{-2} aqueous complexation most important for Nd (LREE)
- Carbonates REE aqueous speciation at higher pH

Maiden borehole in Robinson Run, WV (E. Siefert)

Next Steps

- Continued NPOC, DIC sampling efforts
- Continue comparisons with other published data
  - Aqueous
  - CMD precipitates
- PHREEQC Sensitivity modeling
- Considerations of phosphate
- Considerations of surface v underground CMD

Discharge from Kittle Flats in Randolph Co, WV
(R. Spirnak, WVWRI)

Acknowledgments

CMD metals data access:

- National Energy Technology Laboratory CORECM
- WV Department of Environmental Protection
    - Infrastructure Investment and Jobs Act

Assistance:

- Chuck Cravotta, PhD
- Office of Surface Mining Reclamation and Enforcement
- WV Geologic and Economic Survey
- Friends of the Cheat
- Friends of Deckers Creek
- Save the Tygart Watershed Association
- Garrett College
- Kara Meadows and Jared Stewart

References

Bau M. (1999). Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta* 63, 67-77.

Cravotta CA. (2008a). Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations. *Applied Geochemistry* 23, 166-202.

Cravotta CA. (2008b). Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: Geochemical controls of constituent concentrations. *Applied Geochemistry* 23, 293-226.

Cravotta CA. (2026). Interactive PHREEQ-N-AMDTreat+REYs water-quality modeling tools to evaluate potential attenuation of rare-earth elements and associated dissolved constituents by aqueous-solid equilibrium processes. United States Geological Survey and Cravotta Geochemical Consulting LLC.

Leybourne MI. and Johannesson KH. (2008). Rare earth elements (REE) and yttrium in stream waters, stream sediments, and Fe-Mn oxyhydroxides: Fractionation, speciation, and controls over REE+Y patterns in the surface environment. *Geochimica et Cosmochimica Acta* 72, 5962-5983.

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., https://doi.org/10.3133/tm6A43

She Z., Wang J., He C., Jiang Z., Pan X., Wang M., Ma D., Shi Q., Yue Z. (2023). Molecular insights into the impacts of acid mine drainage on dissolved organic matter dynamics in pit lakes. *Science of the Total Environment.* 888, 164097.

Vass CR., Noble A., Ziemkiewicz PF. (2019). The occurrence and concentration of rare earth elements in acid mine drainage and treatment by-products: Part 1 – Initial survey of the Northern Appalachian coal basin. *Mining, Metallurgy & Exploration* 36, 903-916.

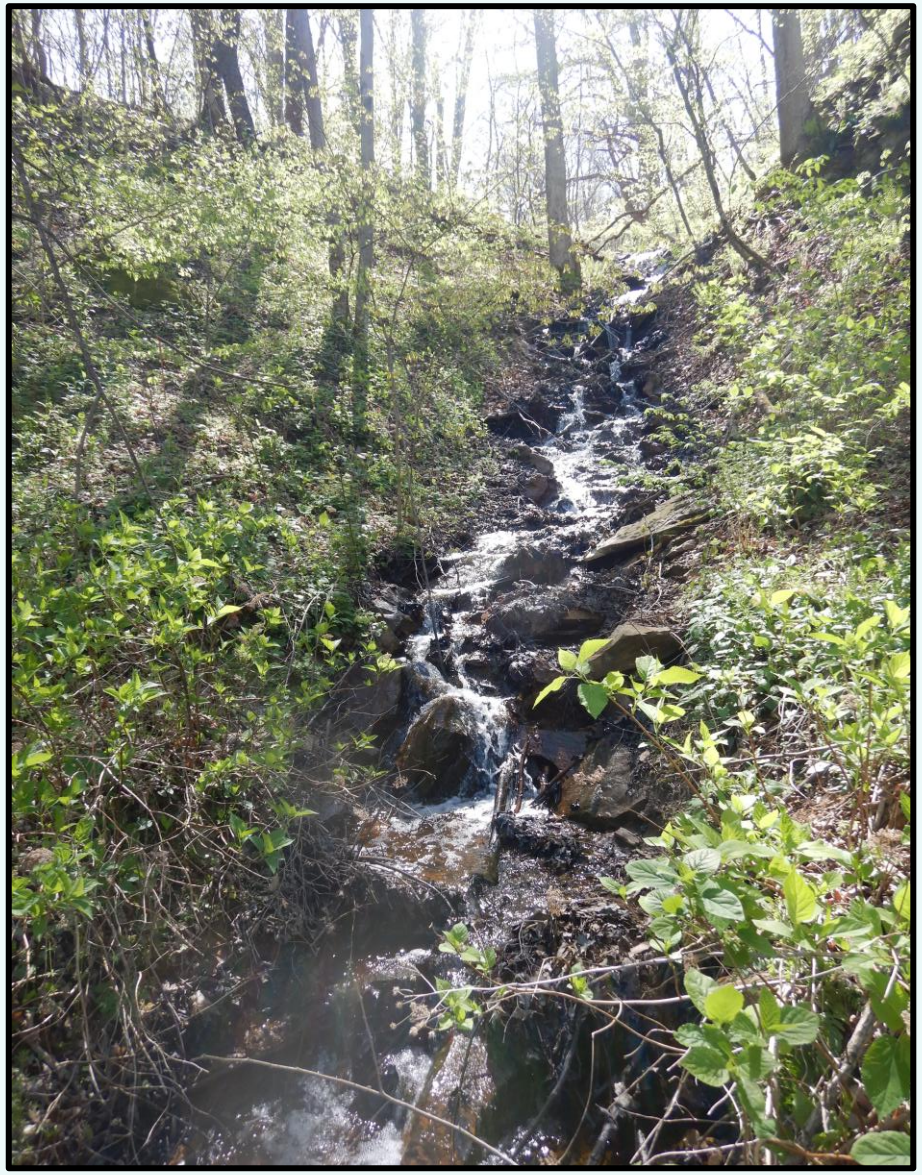
Verplanck PL., Nordstrom DK., Taylor HE., Kimball BA. (2004). Rare earth element partitioning between hydrous ferric oxides and acid mine drainage during iron oxidation. *Applied Geochemistry* 19, 1339-1354.

Vesper DJ., Cravotta CA., Lei L., Wallace M., Schaffer CR. (2025). Determination of CO2 and DIC in high-CO3 waters: an application for the analysis of coal mine drainage. *Applied Geochemistry* 183, 106336.

Vesper DJ. and Smilley MJ. (2010). Attenuation and diel cycling of coal-mine drainage constituents in a passive treatment wetland: A case study from Lambert Run, West Virginia, USA. *Applied Geochemistry* 25, 795-808.

Questions?

eliza.siefert@mail.wvu.edu



Surface mine discharge into Crafts Run in Monongalia Co, WV
(E. Siefert, WVWRI)

West Virginia University
DEPARTMENT OF
GEOLOGY AND GEOGRAPHY

West Virginia University
WEST VIRGINIA
WATER RESEARCH INSTITUTE