

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

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

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

Periodic Table of the Elements

The periodic table shows elements from Hydrogen (1) to Oganesson (118). The Lanthanide series (57-71) and Actinide series (89-103) are shown below the main table. Scandium (Sc) and Yttrium (Y) are highlighted in a darker blue box, indicating their classification as Heavy Rare Earth Elements.

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

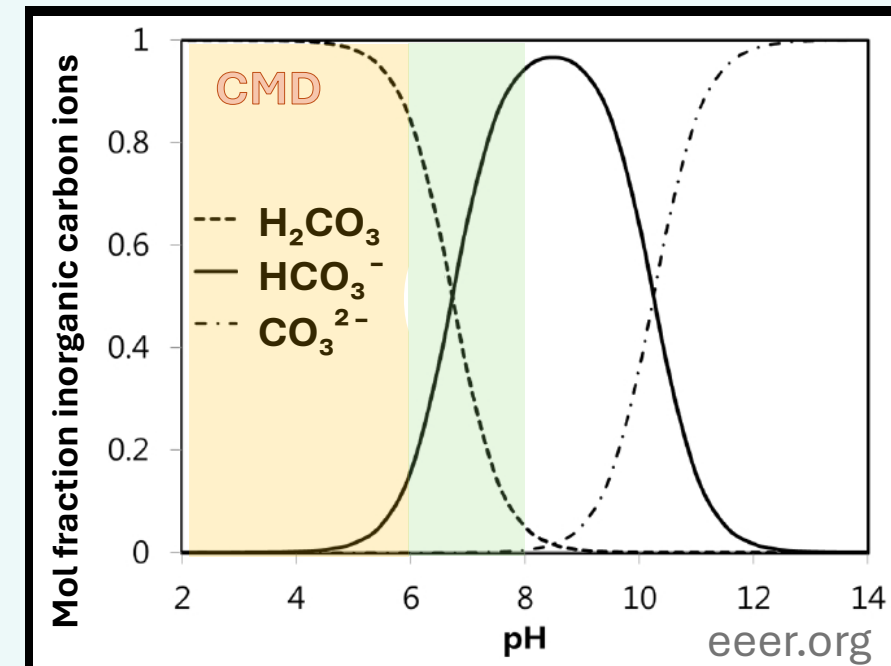
- Often low due to decreased biological activity
- OC in pit lakes up to 2 mg/L
 - Increases alongside pH
- Increase in treatment wetlands
- MREE associated with OC in alkaline waters

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



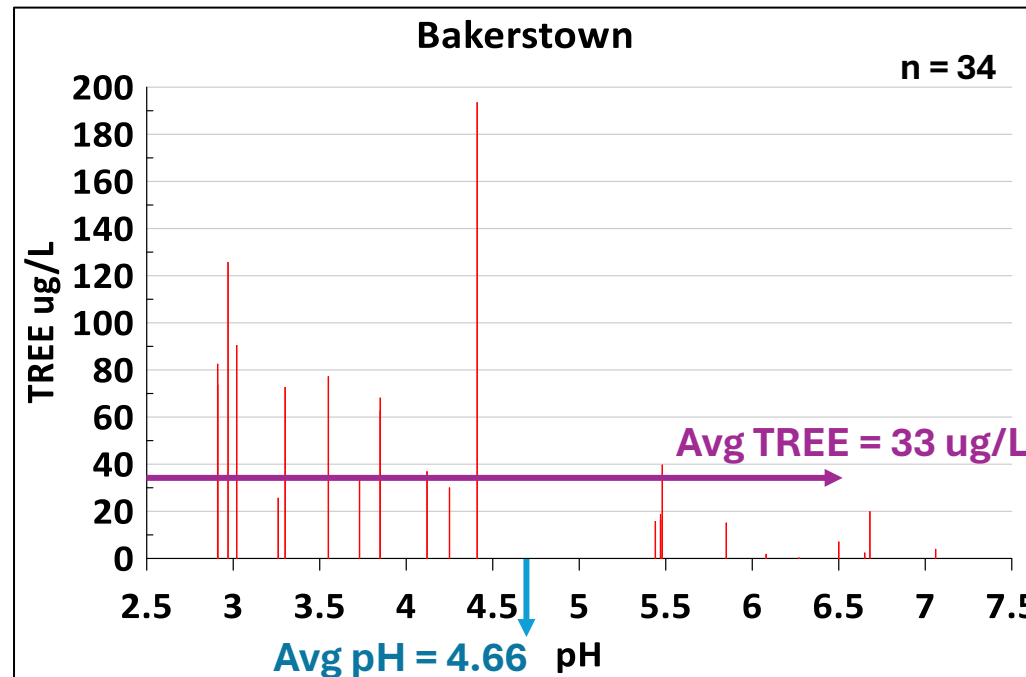
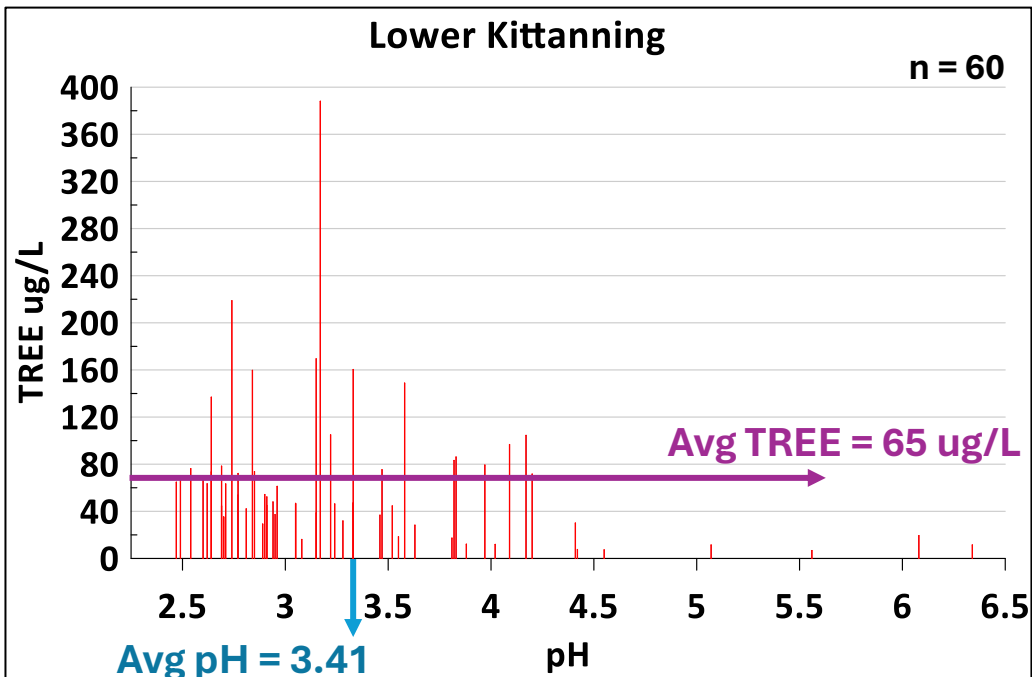
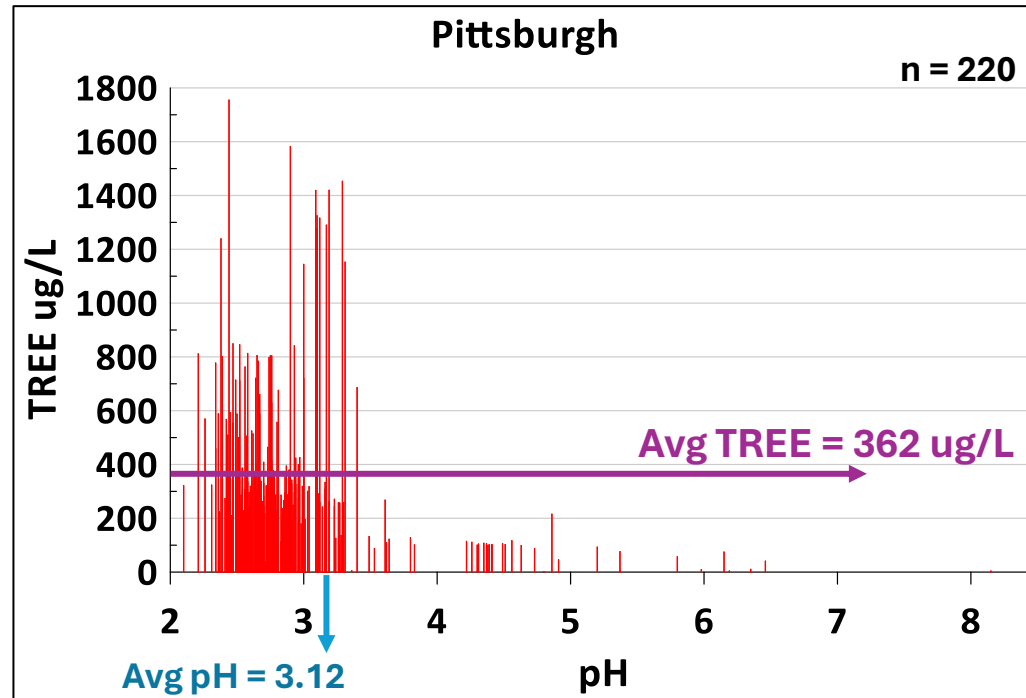
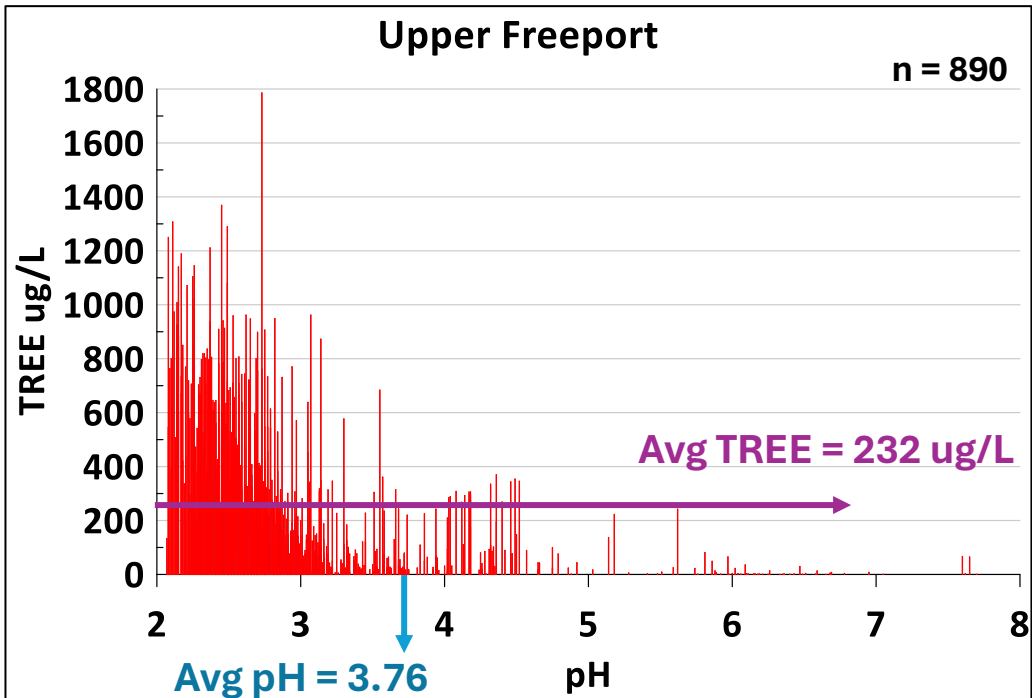
WWRI CMD-REE Data

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

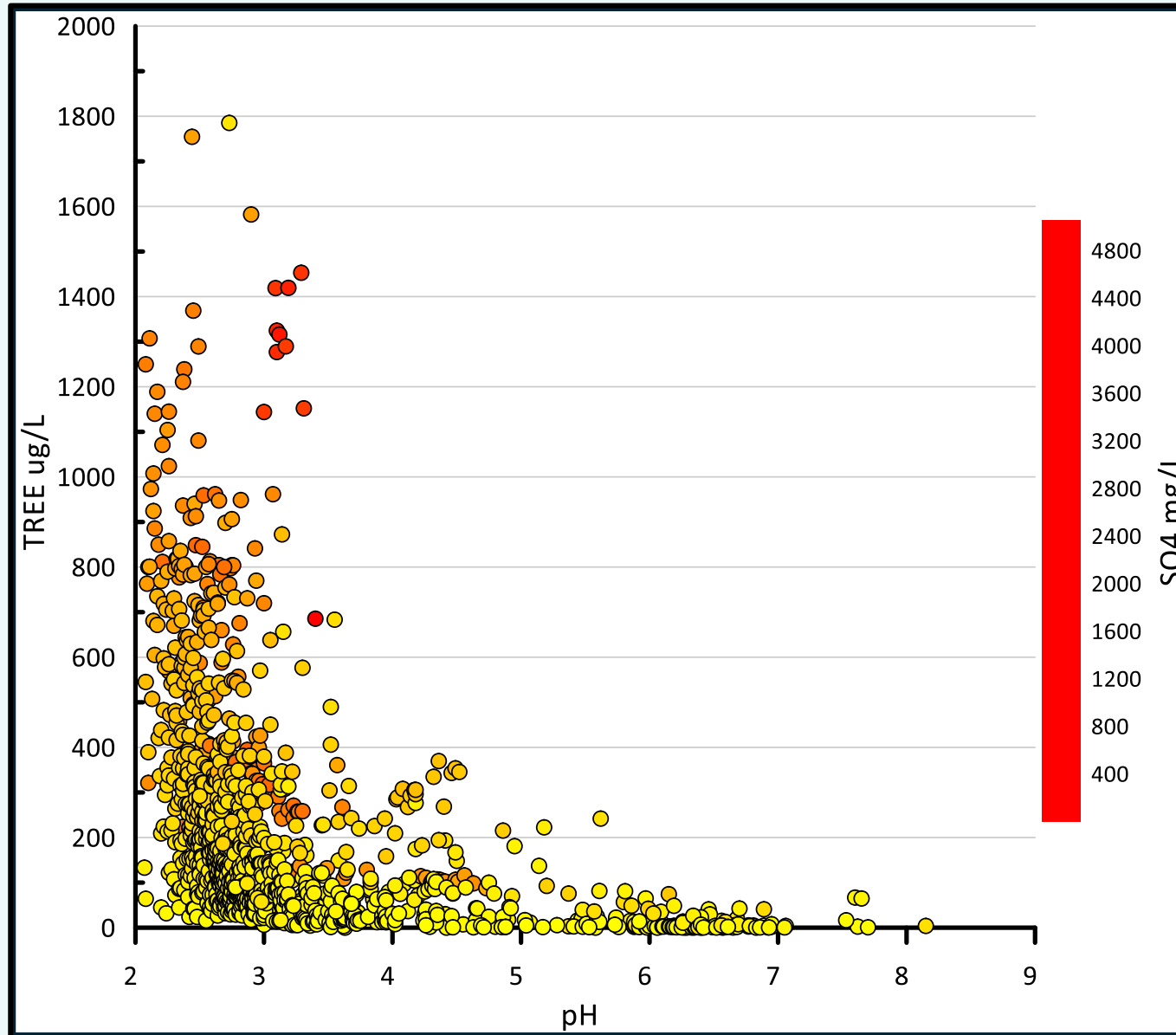
TMM – total major metals (Fe + Al + Mn + Mg)

TREE – total rare earth elements + Y + Sc

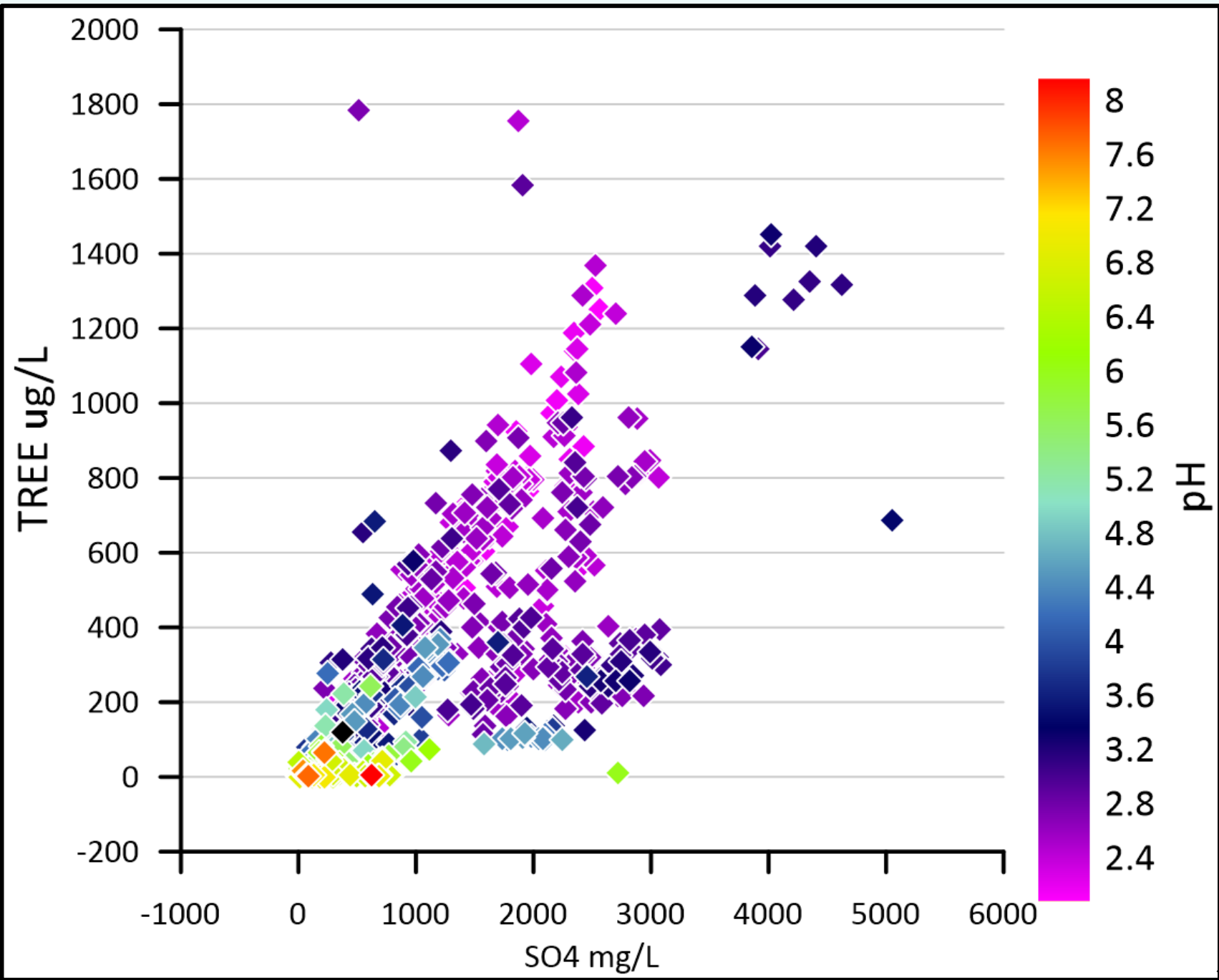
Major Coal Beds		
Upper Pennsylvanian	Dunkard Group	Washington Waynesburg Uniontown
	Monongahela Group	Sewickley Redstone Pittsburgh Little Pittsburgh
	Conemaugh Group	Elk Lick Harlem Bakerstown Brush Creek Mahoning
Middle Pennsylvanian	Allegheny Group	Upper Freeport Lower Freeport Upper Kittanning Middle Kittanning Lower Kittanning (No. 6 block) No 5 Block Stockton
	Kanawha Formation	Upper Mercer Coalburg Winifrede Clinton Fire Clay Cedar Grove Williamson Peerless No 2 Gas Powellton Eagle Little Eagle Matewan Upper War Eagle Ben's Creek Lower War Eagle Glenalum Tunnel Gilbert Douglas Lower Douglas
Lower Pennsylvanian	New River Formation	Bradshaw Laegar Sewell Welch Beckley Fire Creek No 9 Pocahontas No 8 Pocahontas



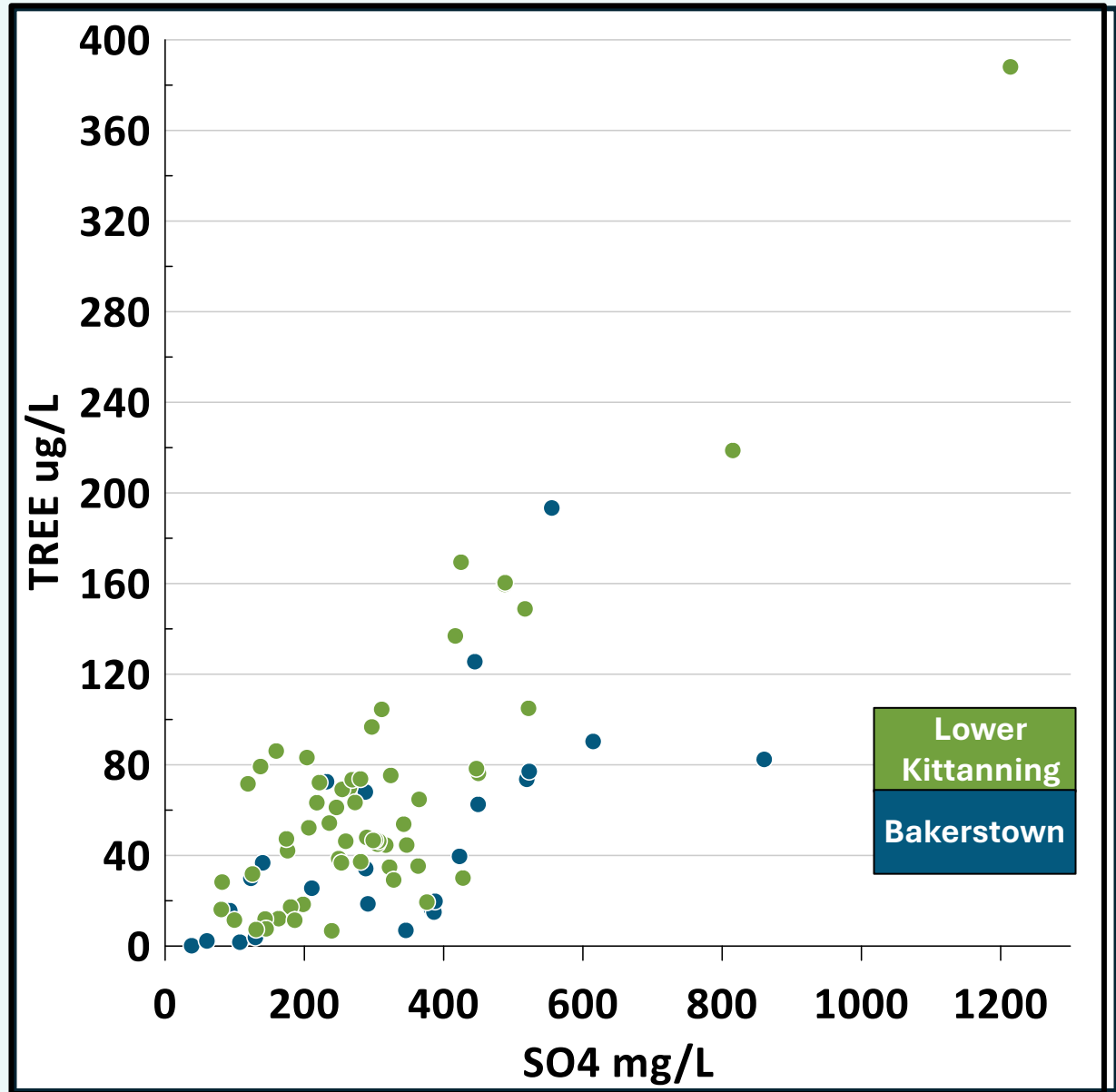
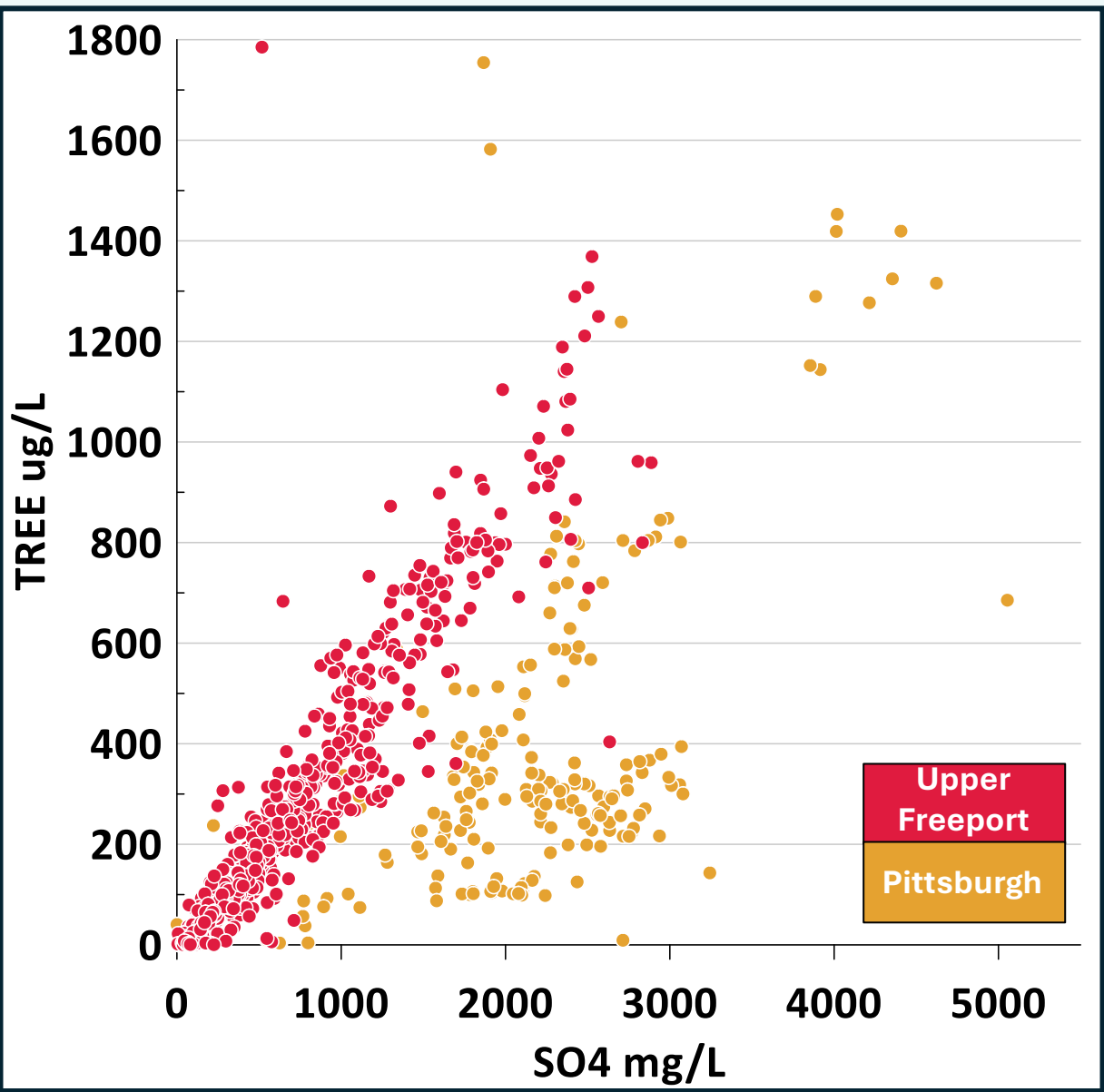
Association of [TREE] and pH with associated [SO4] in sampled sources



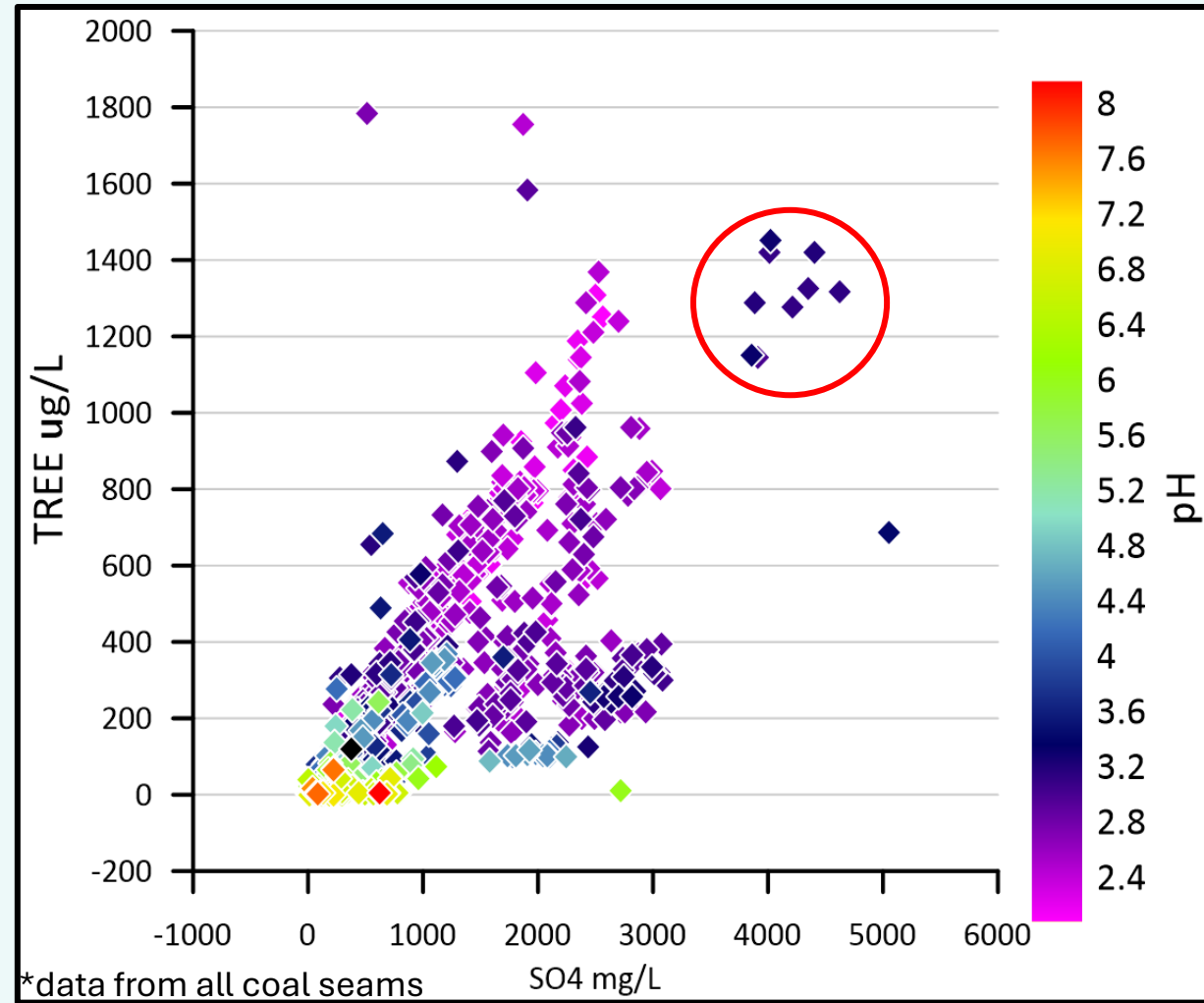
*data from all coal seams



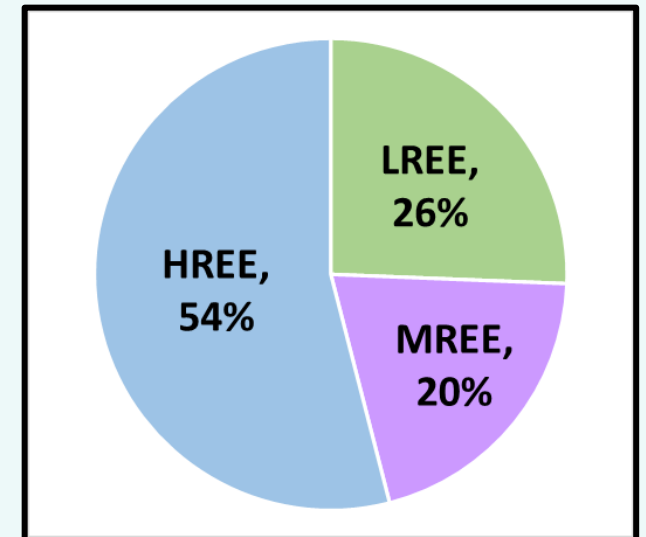
data from all coal seams



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

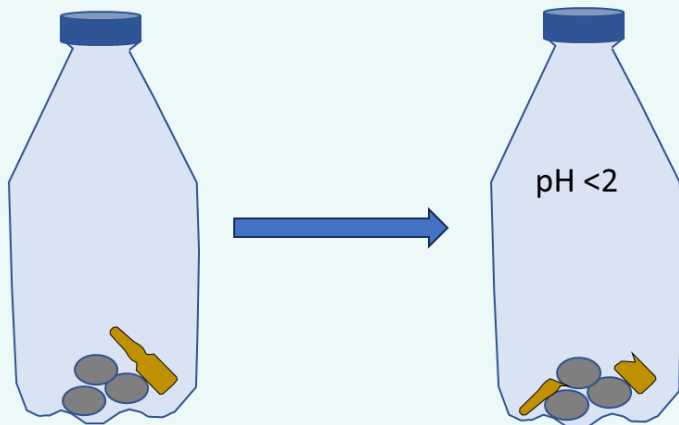
- REE mobility depends on aqueous speciation
- Relationship of sulfate, pH, and TREE concentrations
- Limited data on organic carbon
- Carbonates may lead to HREE to stay in solution
- Importance for:
 - Aquatic species
 - Extraction research
 - Sampling efforts



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

Methods – Sample Collection

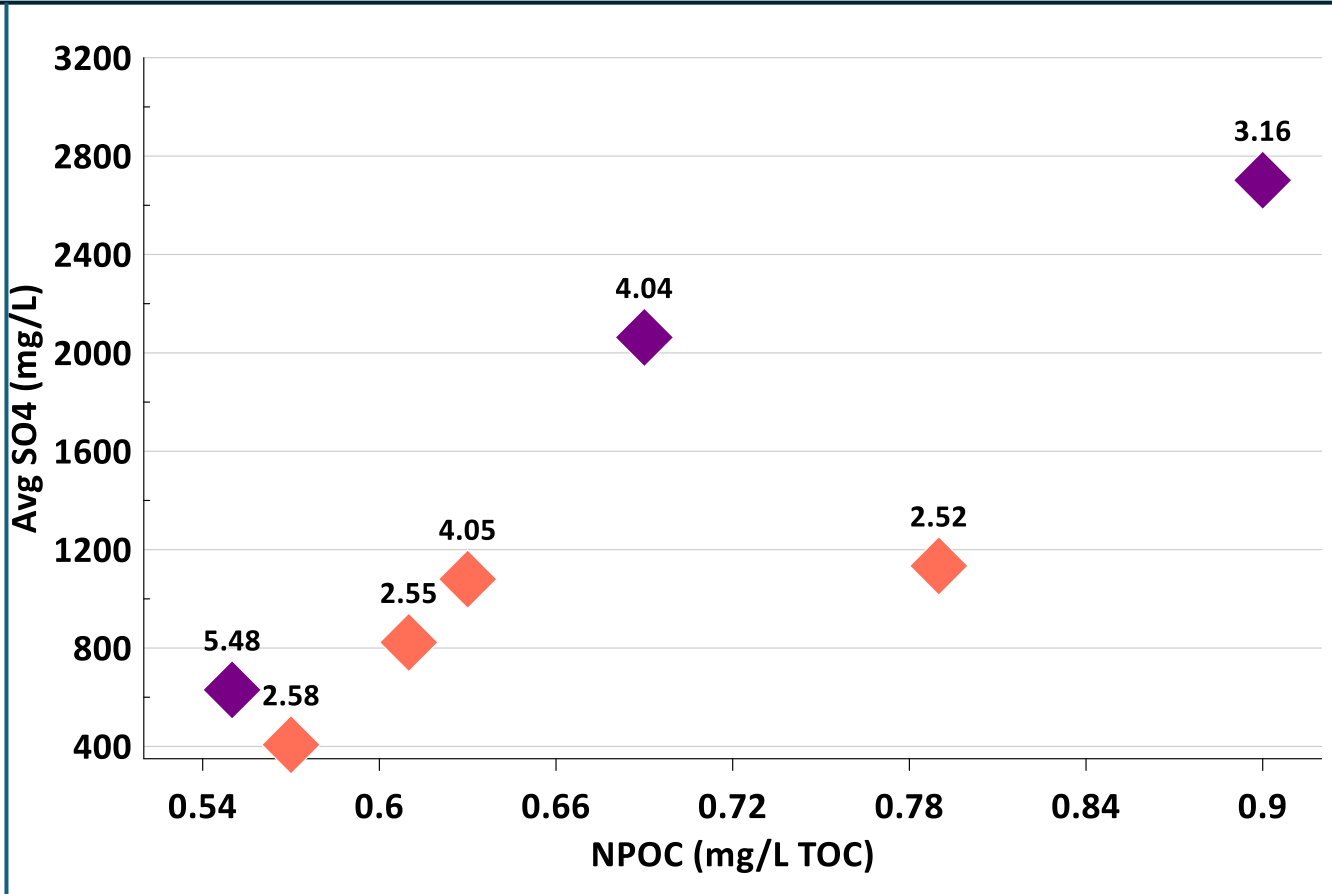
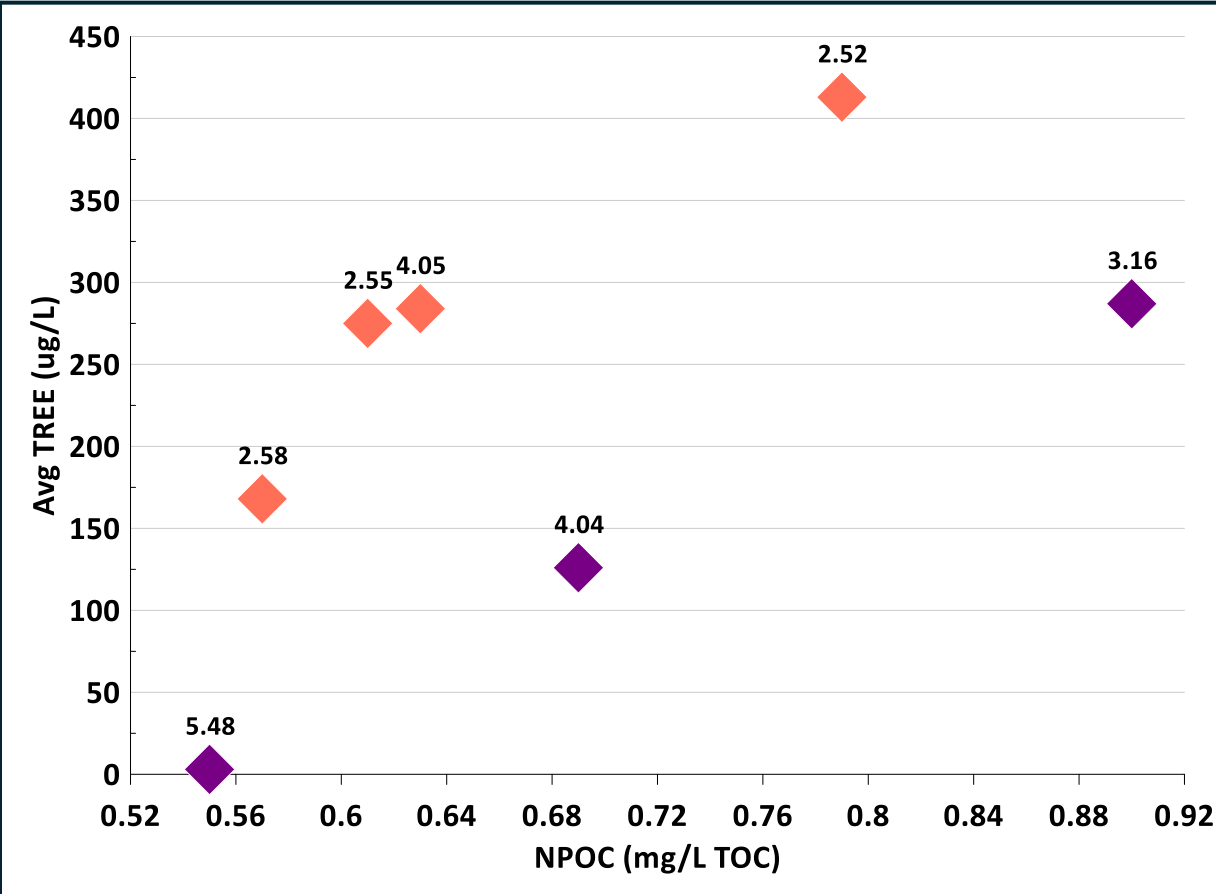
- Field
 - pH, spc, TDS, DO, ORP, flow
- Analytical
 - TMM, TREE, SO₄
- Organic carbon
 - NPOC via Shimadzu TOC/V
- Dissolved inorganic carbon (DIC)
 - Soda bottle with HCl ampule
 - Anton Paar CarbQC (Vesper et al., 2025)





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

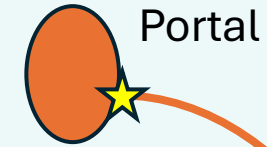
Lambert Run Site 3

- 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

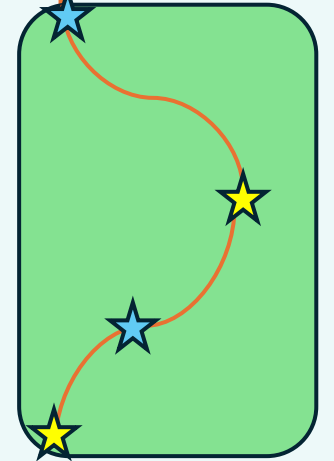


Portal



Open Channel

Altered Natural Wetland



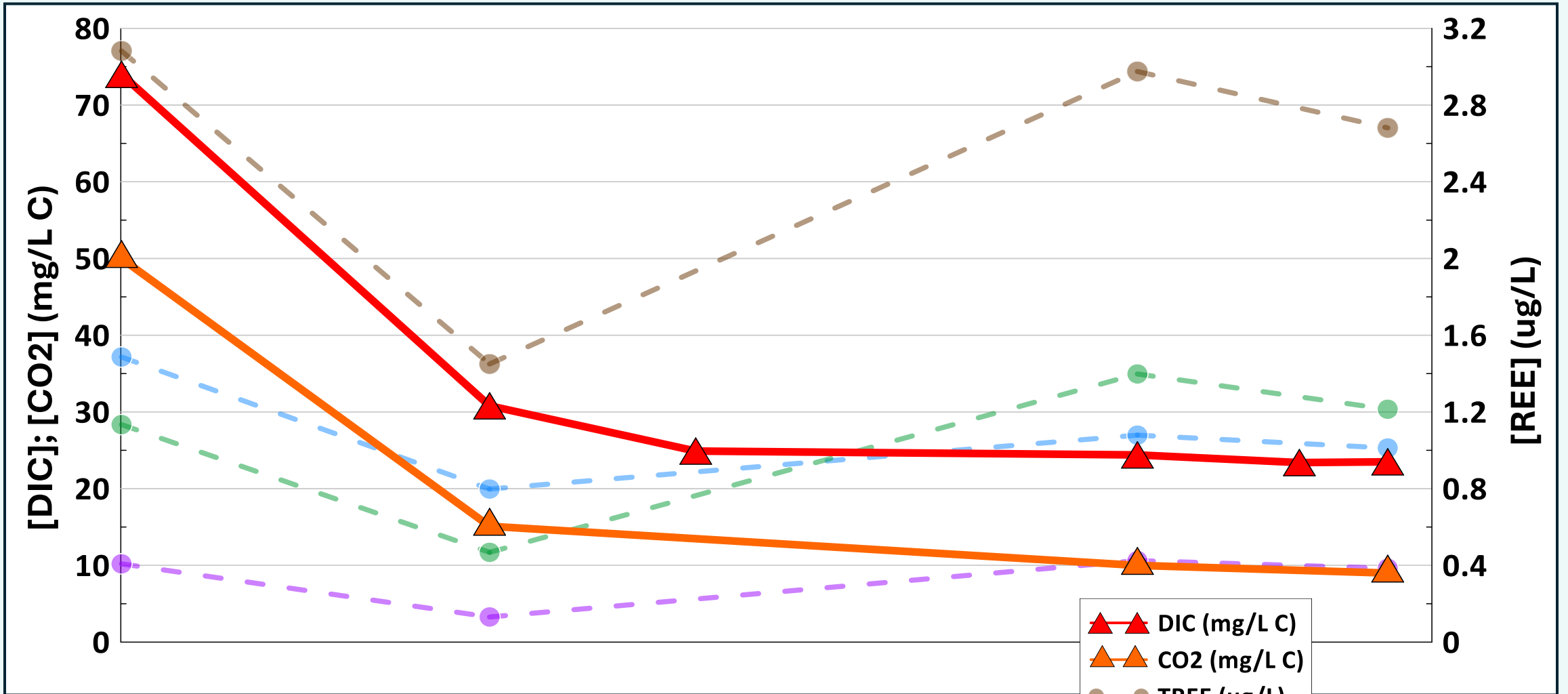
Exit

		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

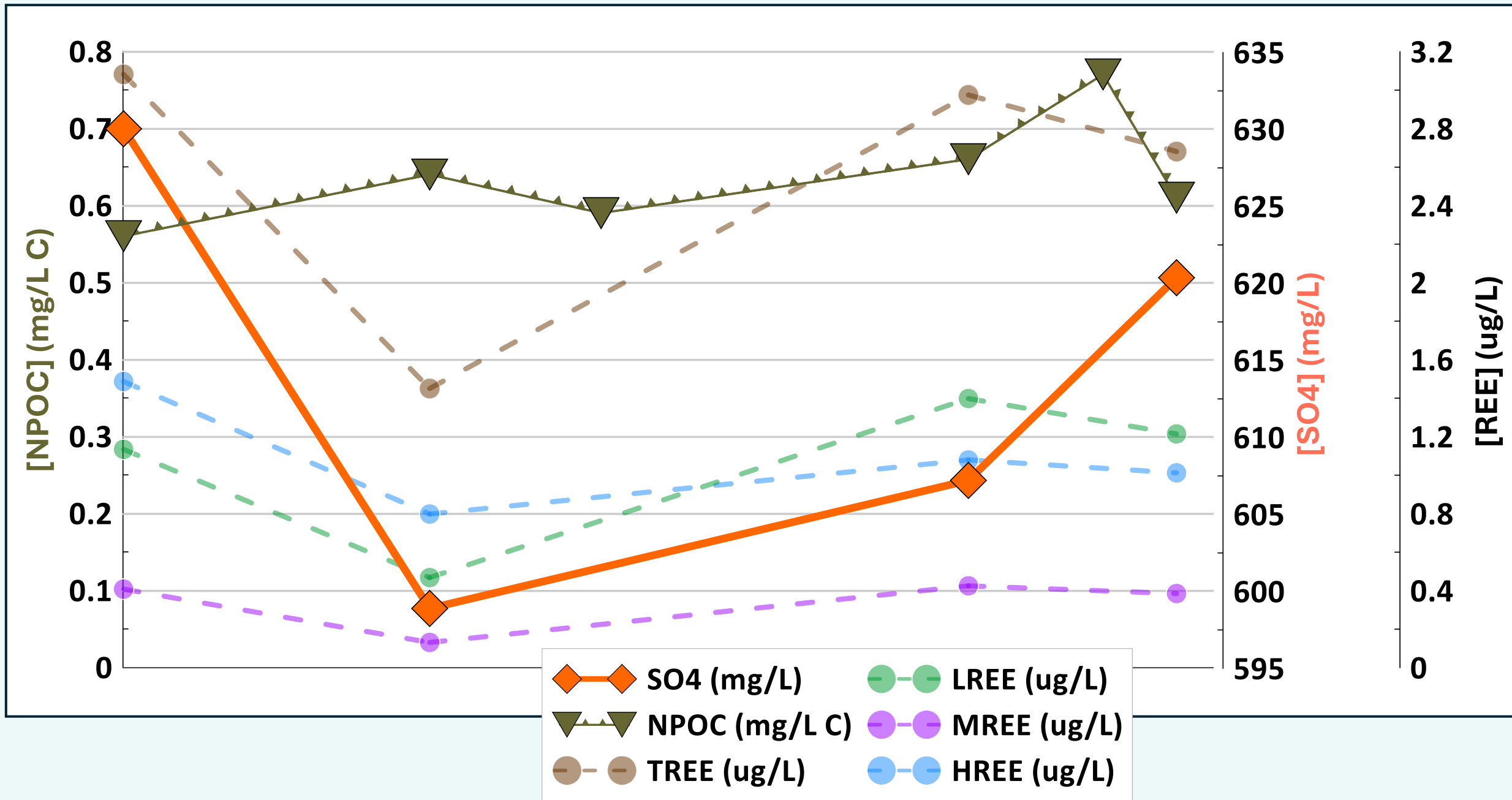


- ▲ DIC (mg/L C)
- ▲ CO2 (mg/L C)
- TREE (µg/L)
- LREE (µg/L)
- MREE (µg/L)
- HREE (µg/L)

Portal

Entrance to Wetland

Effluent



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

Periodic Table of the Elements

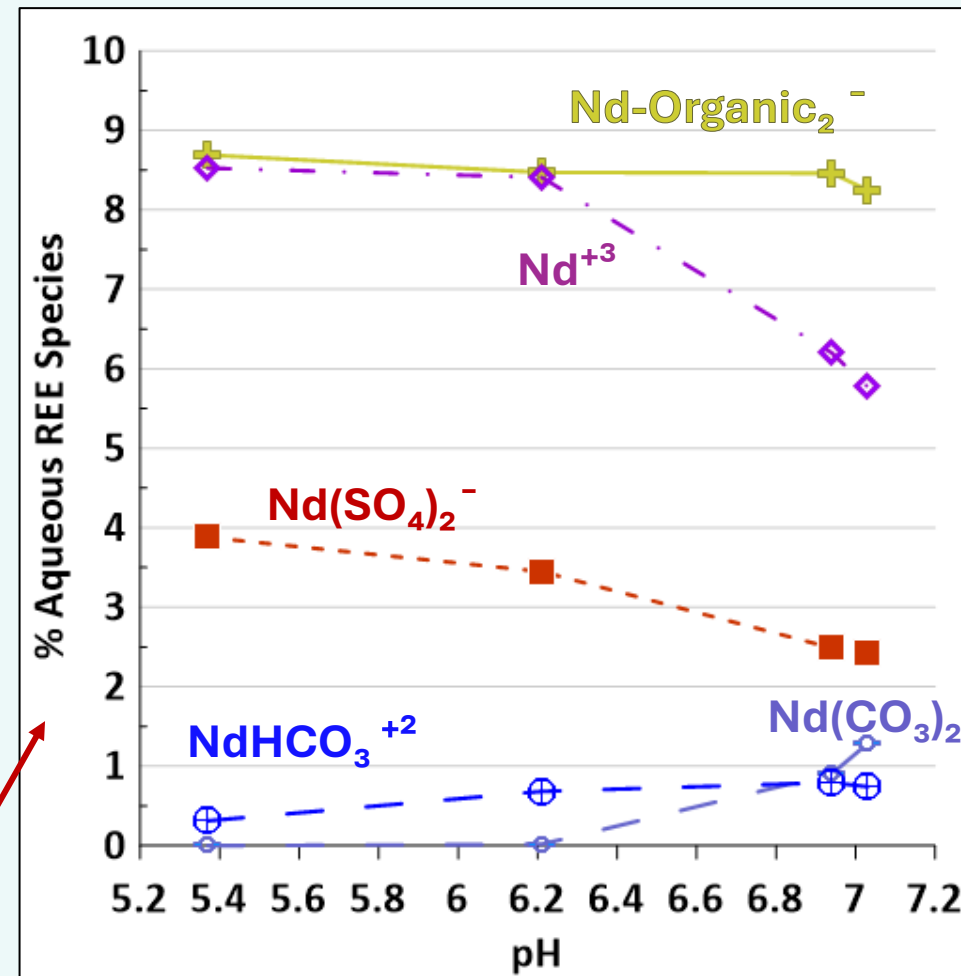
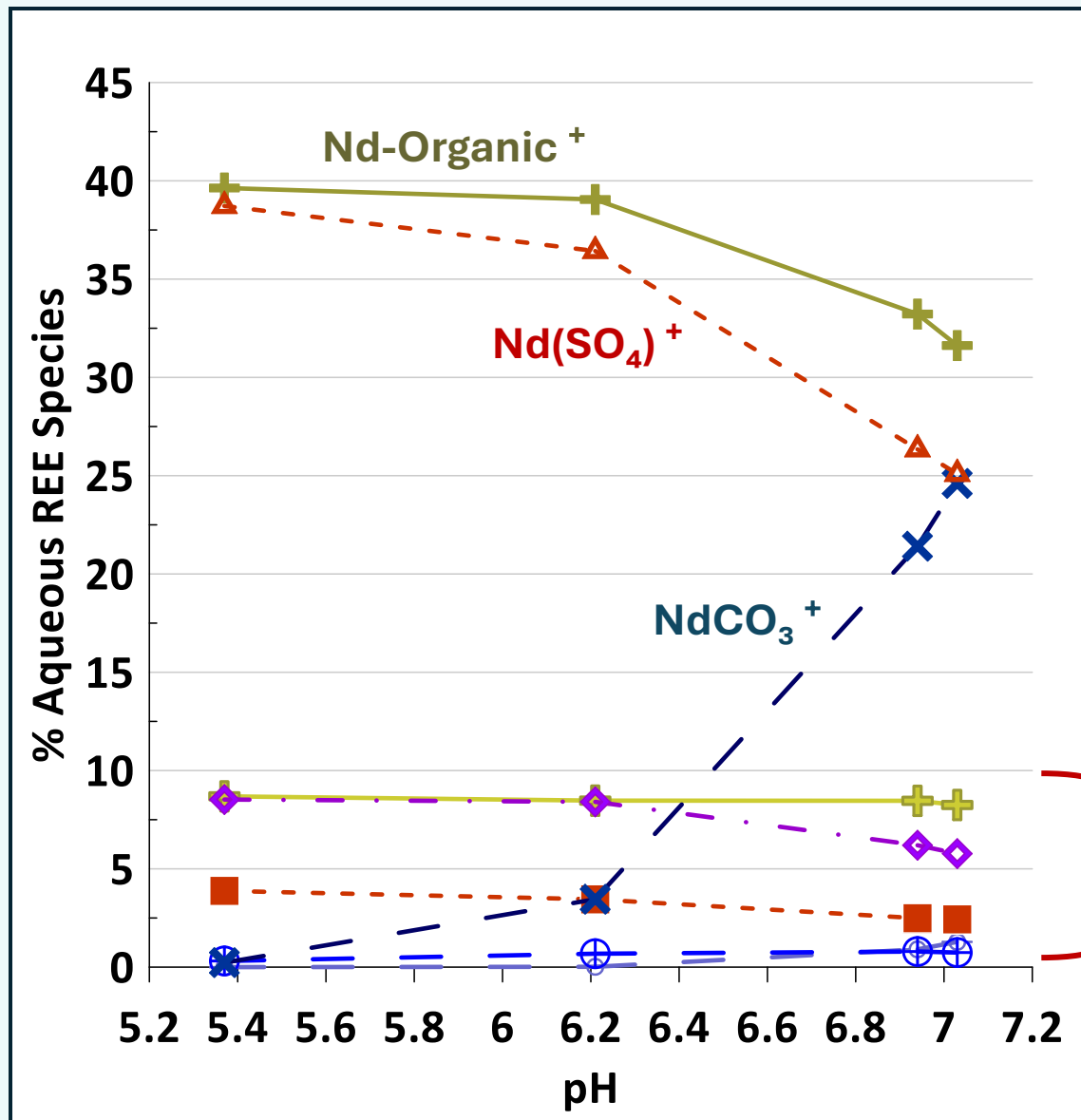
1 IA TA																	18 VIIIA 8A
1 H Hydrogen 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]
Lanthanide Series		57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967	
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]	

Light Rare Earth Elements

Medium Rare Earth Elements

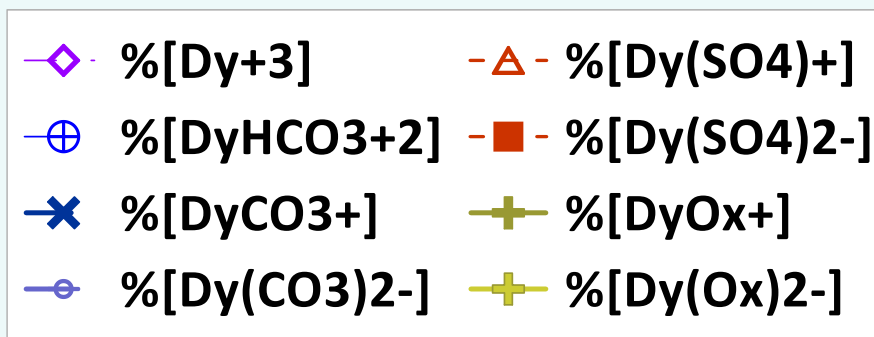
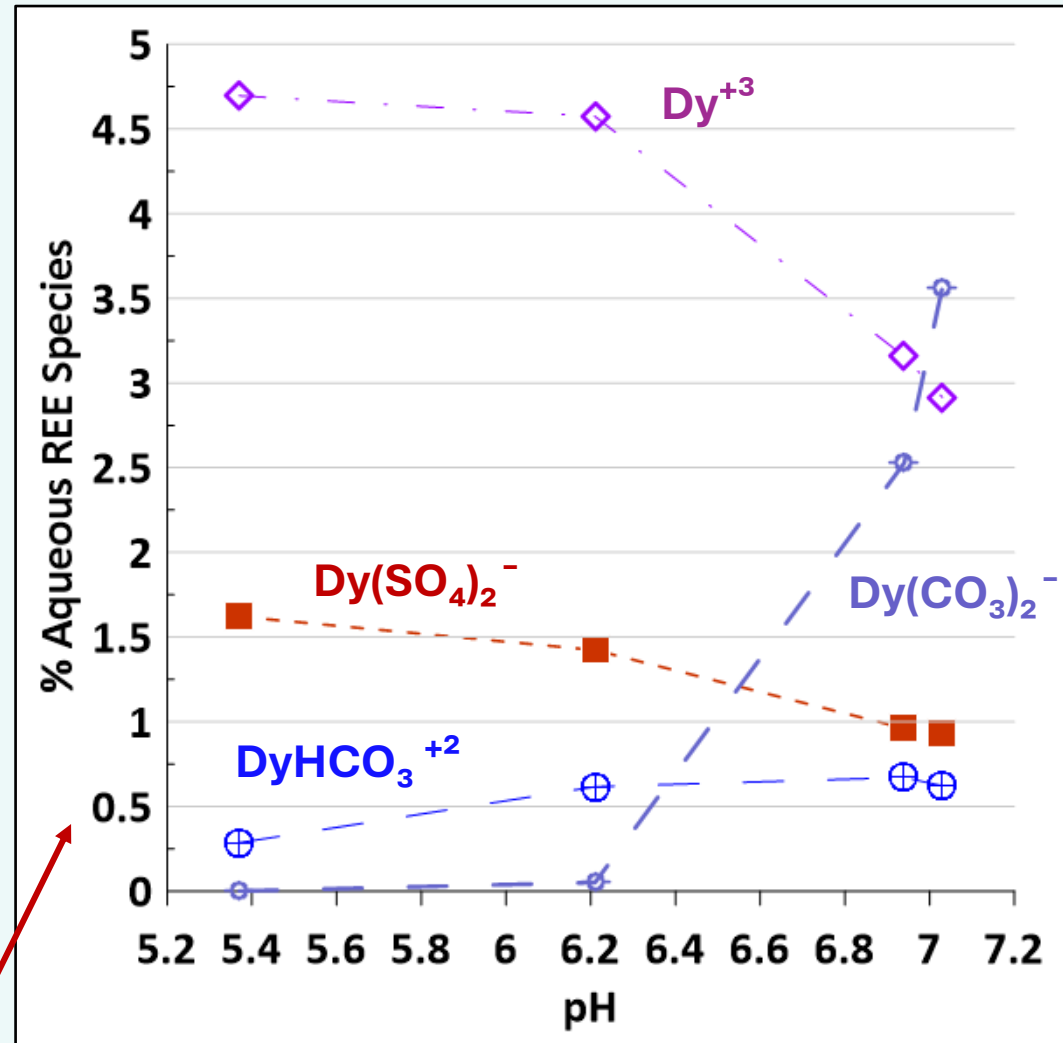
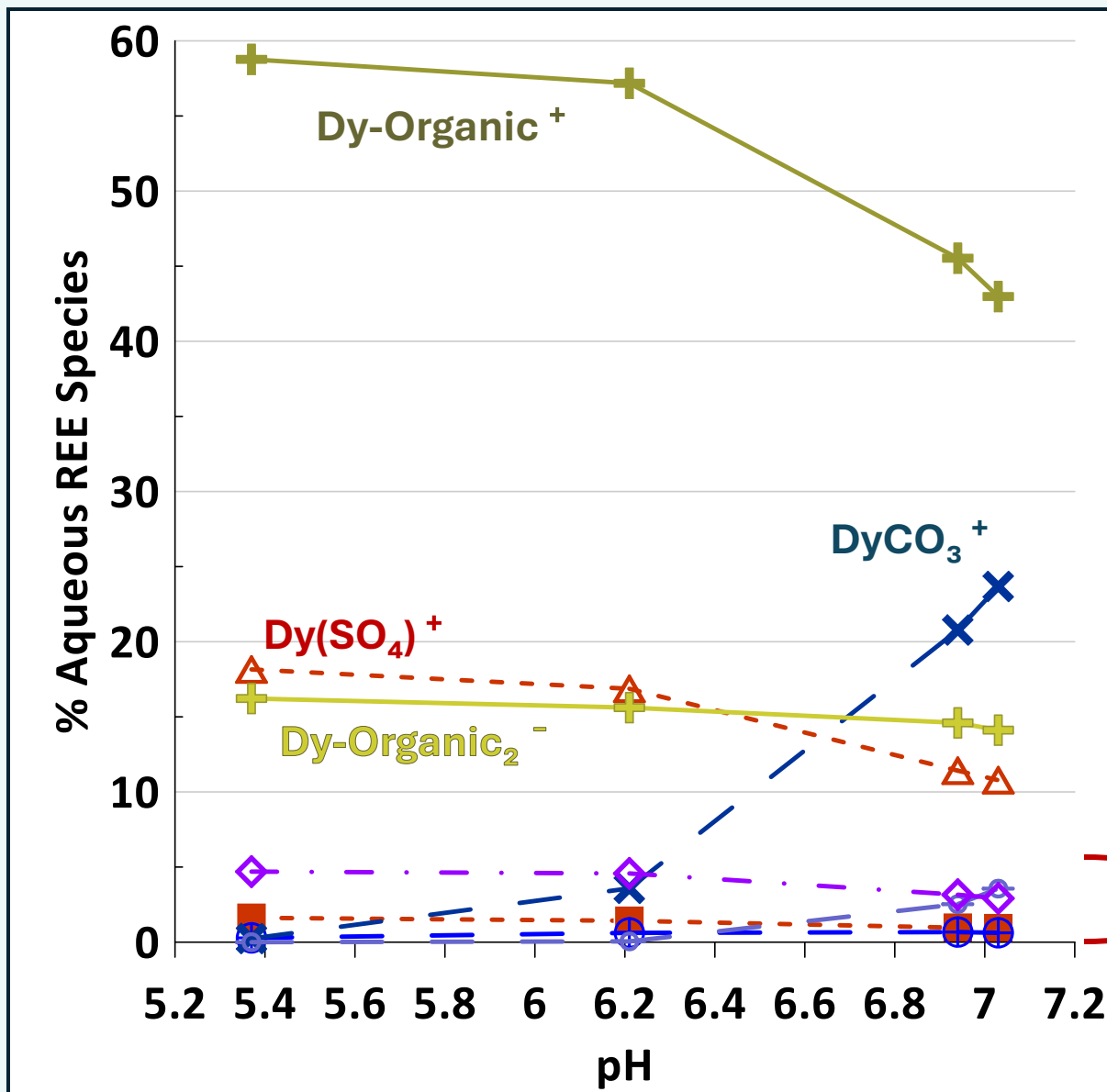
Heavy Rare Earth Elements

PHREEQ LREE: Neodymium

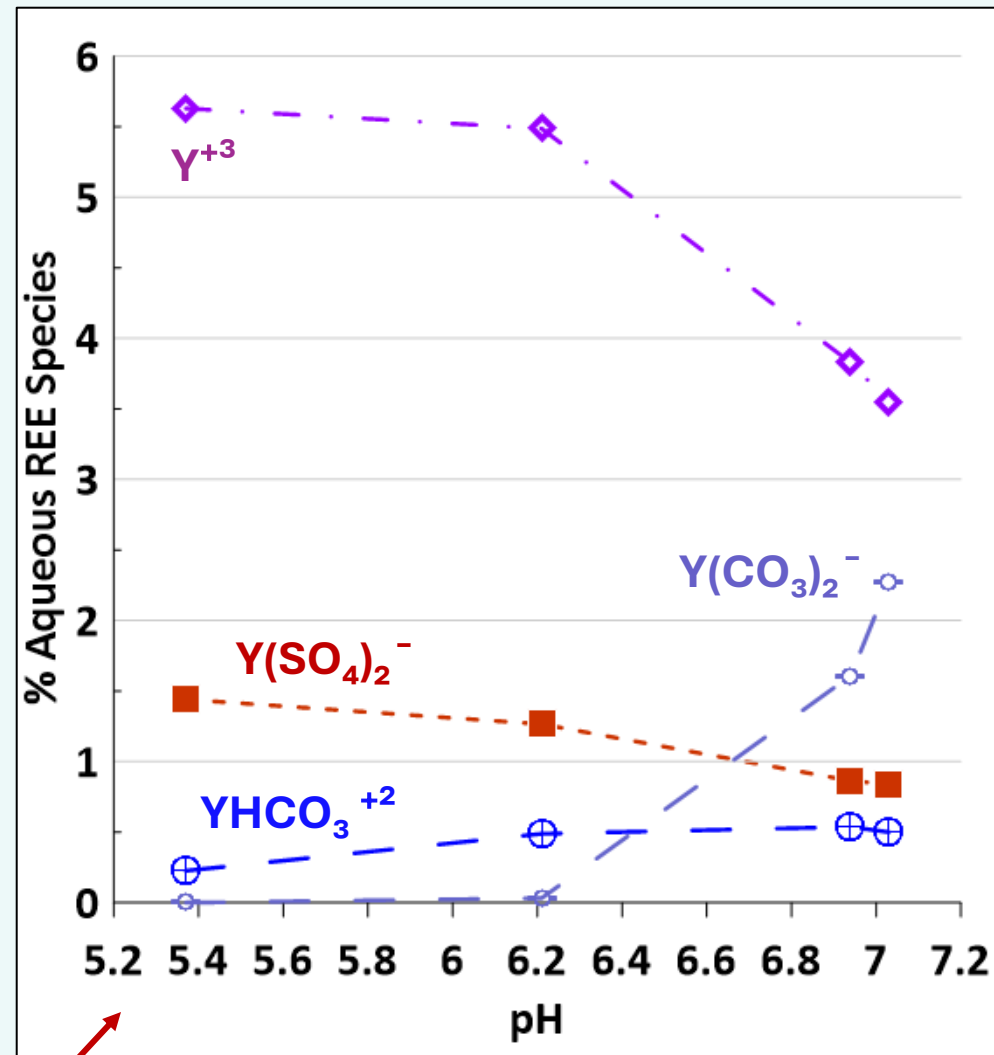
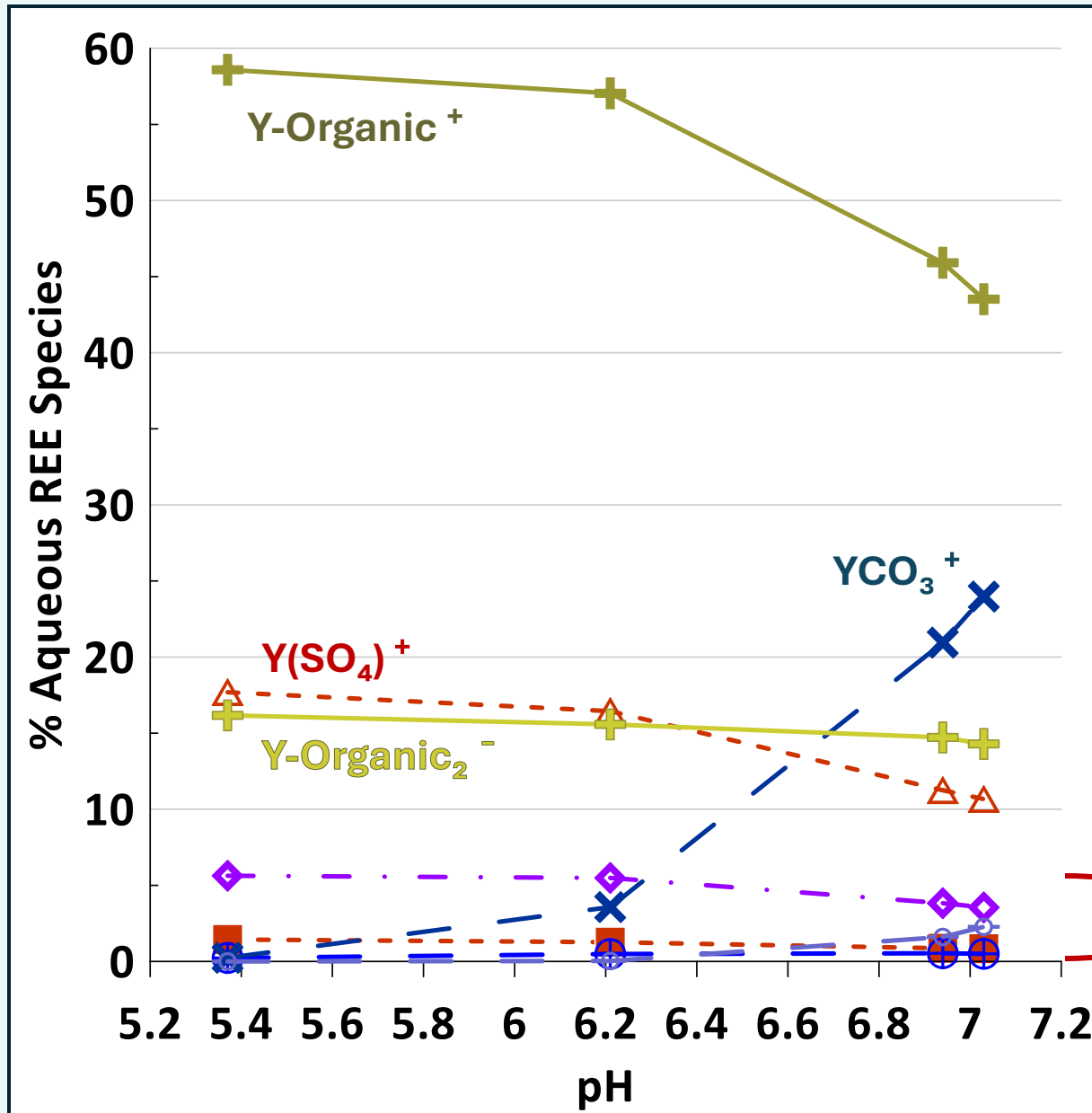


- ◆ · % [Nd³⁺]
- ⊕ % [NdHCO₃⁺²]
- × % [NdCO₃⁺]
- ⊖ % [Nd(CO₃)₂⁻]
- △- % [Nd(SO₄)⁺]
- % [Nd(SO₄)₂⁻]
- + % [NdOx⁺]
- + % [Nd(Ox)₂⁻]

PHREEQ MREE: Dysprosium

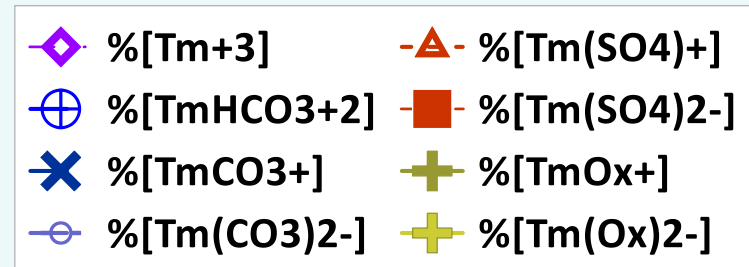
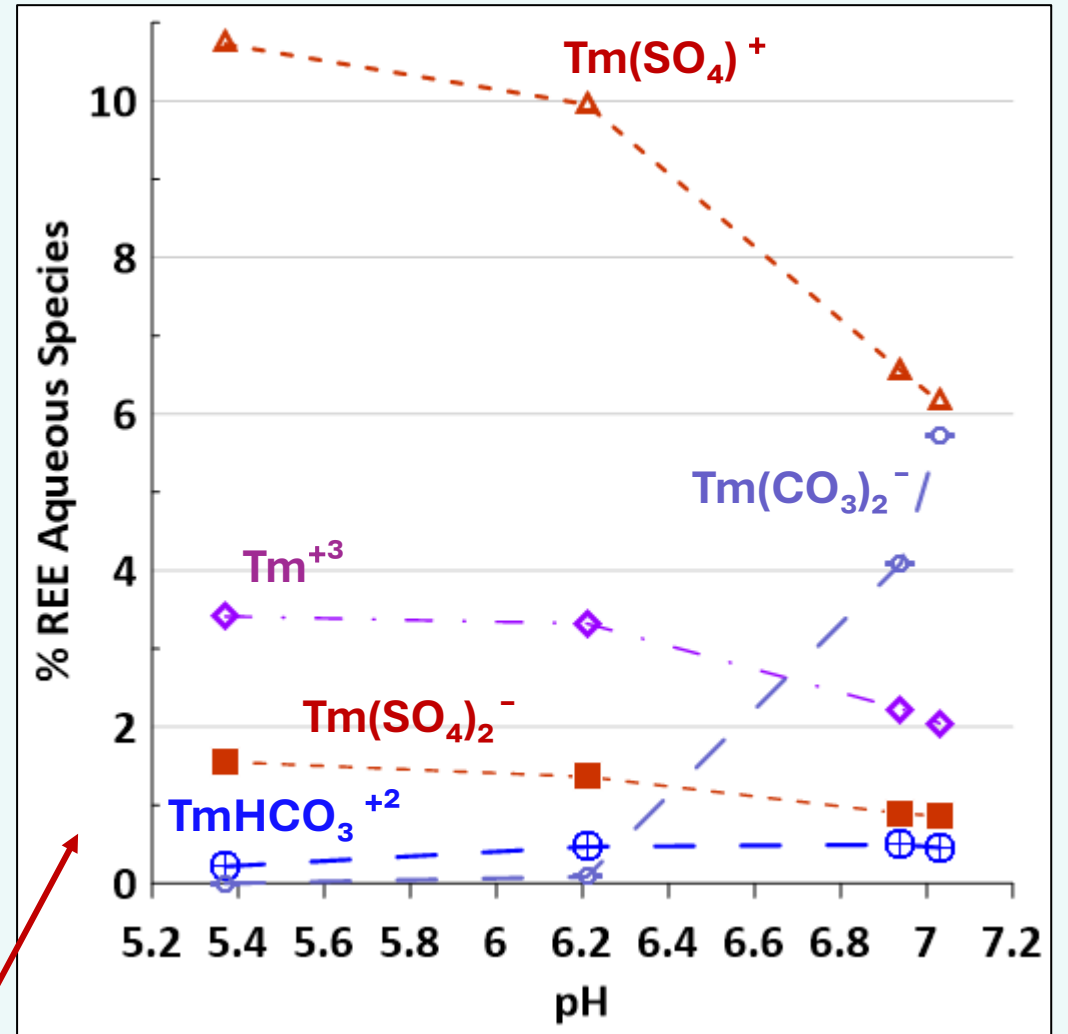
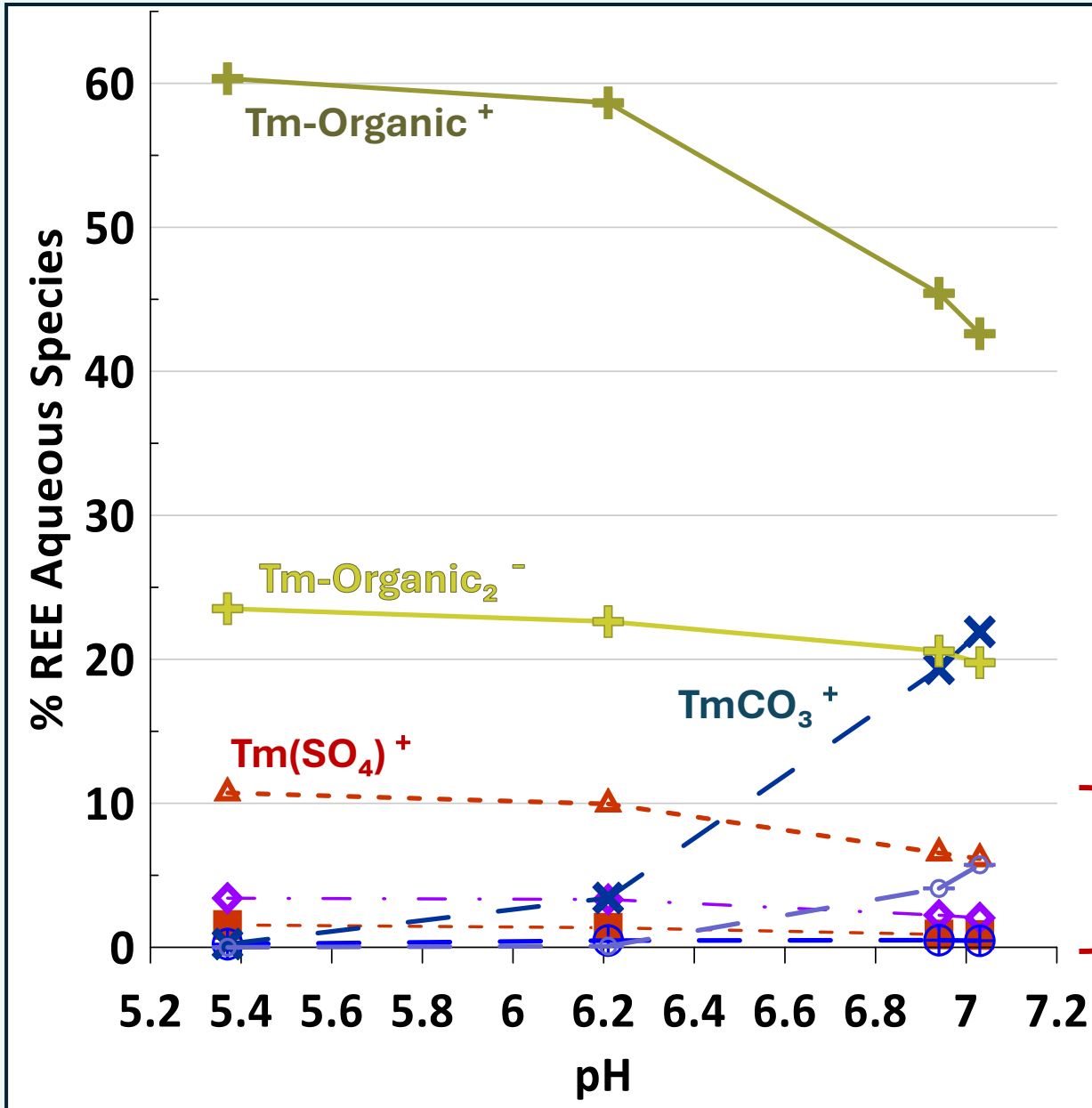


PHREEQ HREE: Yttrium



- ◆ · % [Y⁺³]
- ⊕ % [YHCO₃⁺²]
- × % [YCO₃⁺]
- ⊖ % [Y(CO₃)₂⁻]
- △- % [Y(SO₄)⁺]
- % [Y(SO₄)₂⁻]
- + % [YO_x⁺]
- + % [Y(O_x)₂⁻]

PHREEQ HREE: Thulium



Discussion

- Relationship of pH, sulfate and TREE concentrations
 - Potentially related to coal seam
- Potential relationship of organic carbon in CMD and coal seam
- CO₂ degassing from portals
- < 10% of REEs modeled as free ions
- SO₄⁻² 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, WVVRI)

Acknowledgments

CMD metals data access:

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

Assistance:

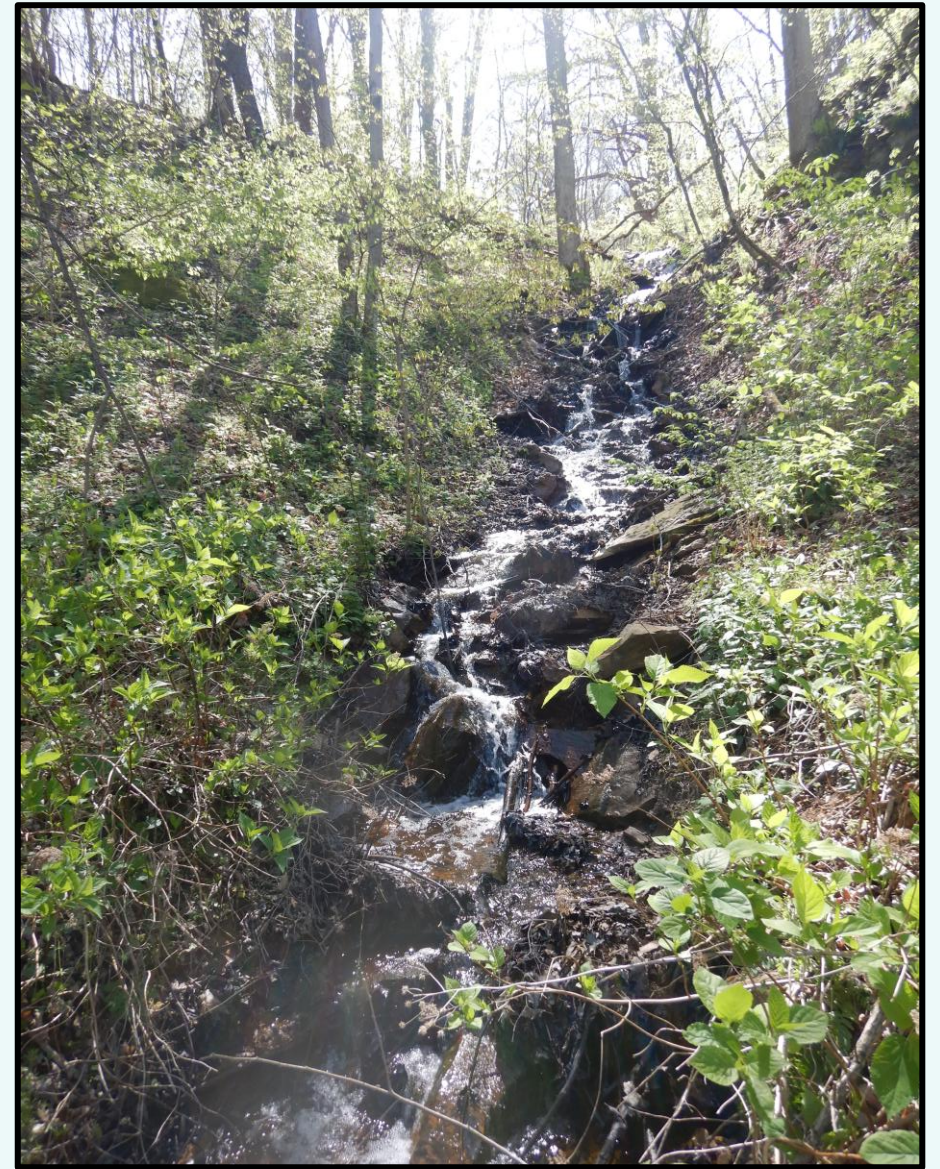
- Chuck Cravotta, PhD
- Office of Surface Mining Reclamation and Enforcement
- WV Geologic and Economic Survey
- Friends of the Cheat
- Friends of Deckers Creek
- Save the Tygart Watershed Association
- Garrett College
- Kara Meadows and Jared Stewart

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Questions?

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