Geochemical Modeling of Acidity and Electrical Conductivity for Mine Water Treatment

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IMPORTANCE OF pH, ACIDITY, AND ELECTRICAL CONDUCTIVITY

- pH and "hot" acidity (or calculated "net" acidity) are used to indicate the severity of contamination and applicable strategies for treatment of acid mine drainage (AMD).

- In general, AMD that has low pH and high specific conductance (SC) tends to have elevated concentrations of acidity, sulfate, and dissolved metal(oid)s, including Fe, Al, Mn, Zn, Cu, and others.

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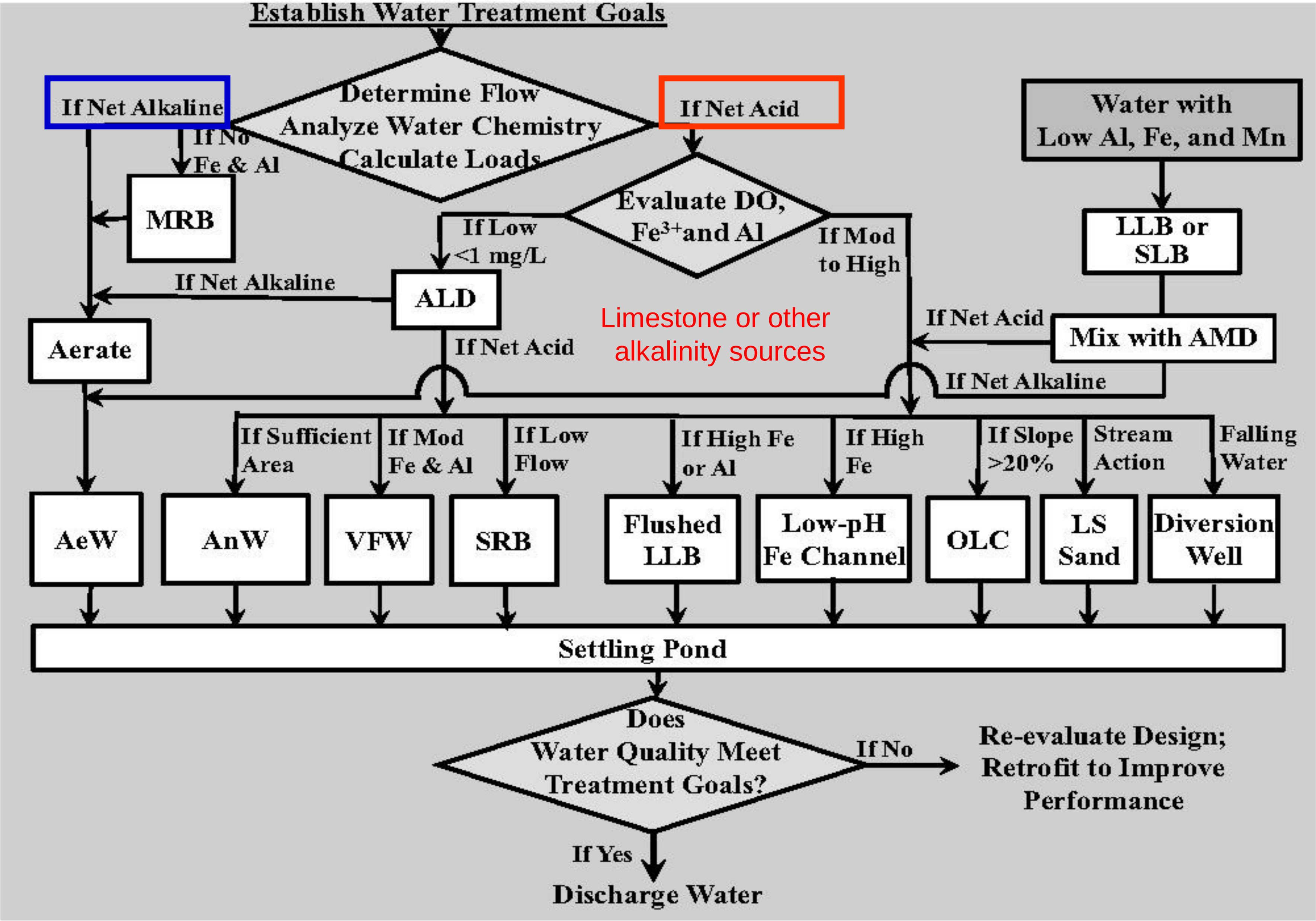
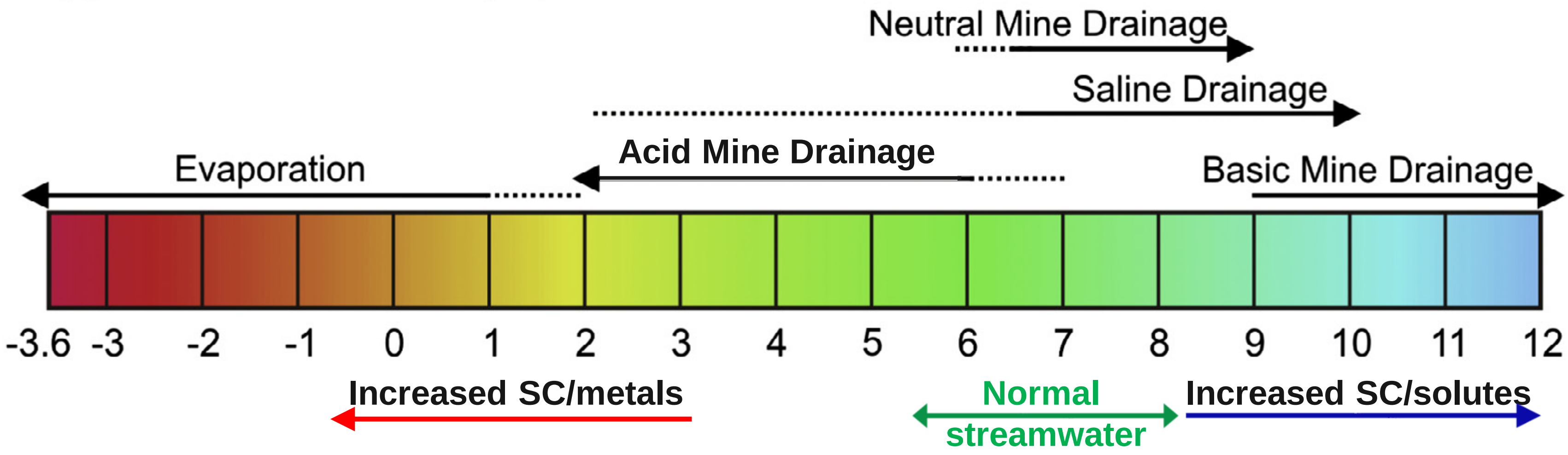


Skousen, J.G., Zipper, C.E., Rose, A.W., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., and Kleinmann, R.L., 2017. Review of passive systems for acid mine drainage treatment. Mine Water Environ. 36, 133-153.

RELATIONS AMONG pH, ALKALINITY, ACIDITY, AND DISSOLVED METALS

Typical relation to drainage pH:



Typical drainage characteristics:

Acid Mine Drainage

- acidic pH
- moderate to elevated metals
- elevated sulfate
- treat for acid neutralization and metal and sulfate removal

Neutral Mine Drainage:

- near neutral to alkaline pH
- low to moderate metals. May have elevated Zn, Cd, Mn, Sb, As or Se
- low to moderate sulfate
- treat for metal and sometimes sulfate removal

Saline Drainage:

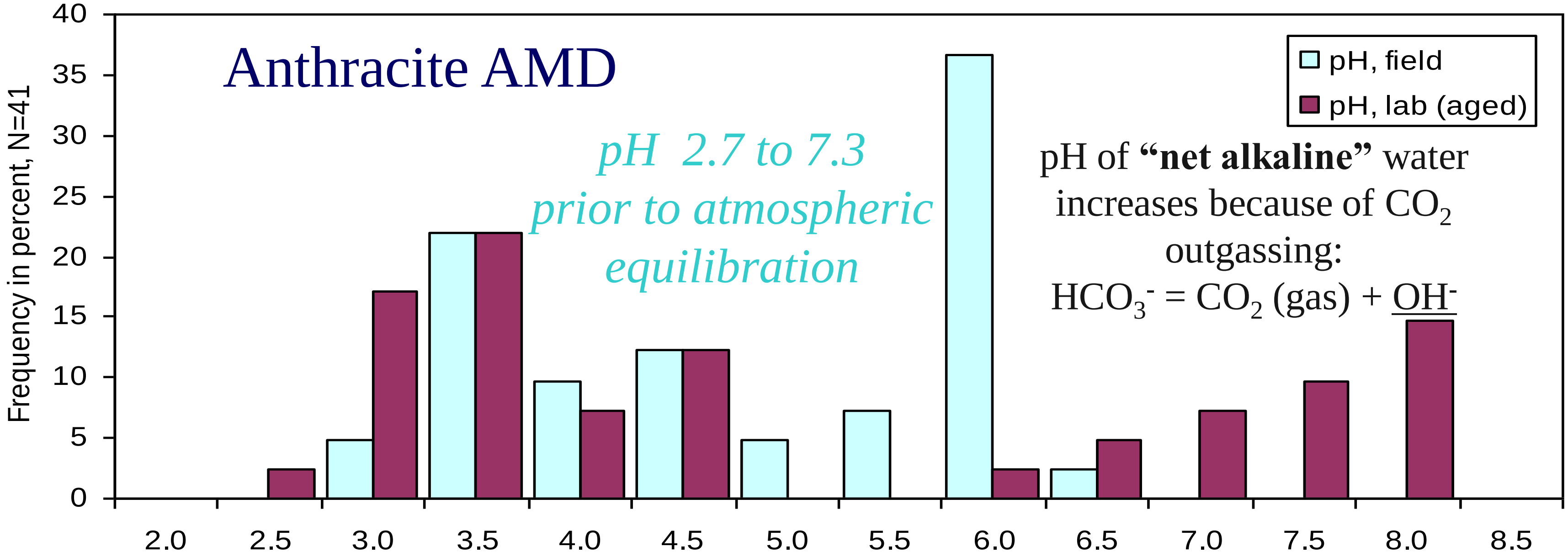
- acidic to alkaline pH
- low metals. May have moderate Fe
- moderate sulfate
- treat for sulfate and sometimes metal removal

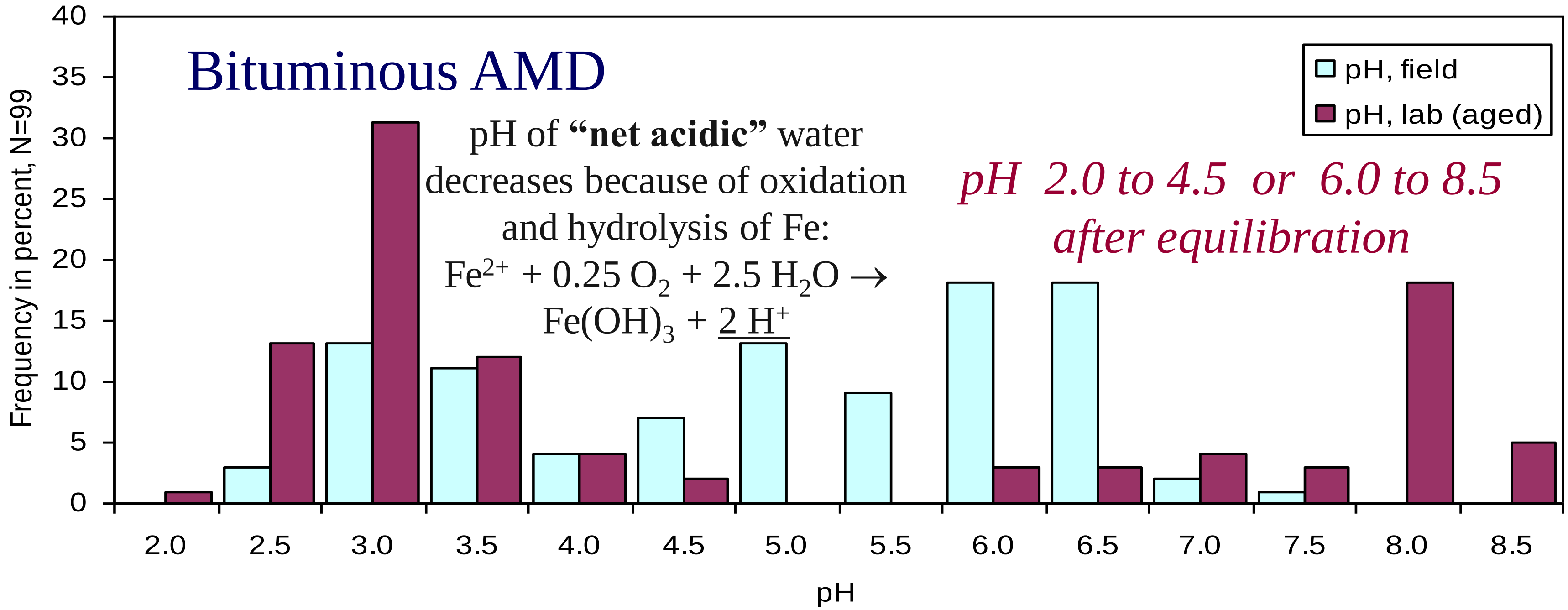
Nordstrom, D.K., Blowes, D.W., Ptacek, C.J. (2015) Hydrogeochemistry and microbiology of mine drainage: An update. Appl. Geochem. 57, 3-16. http://dx.doi.org/10.1016/j.apgeochem.2015.02.008

ACIDITY AND ALKALINITY — Definitions

- Neutrality – pH *near* 7.0 (effluent std 6.0 to 8.5).
- Alkalinity – capacity of sample to neutralize acid.
- Acidity – capacity of sample to neutralize base.
- Net acidity or net alkalinity – difference between computed acidity and alkalinity (sample neutral after complete oxidation?).

INSTABILITY OF pH





ACIDITY AND ALKALINITY — Standard Practices

- Hot Acidity = Computed "Net Acidity"
- Standard Method "hot" acidity indicates *net acidity* for samples containing alkalinity *and* dissolved metals.
- A *positive value* of hot acidity or net acidity indicates (1) the potential for acidic pH (< 6.0) upon reaching atmospheric equilibrium, and
(2) the alkalinity deficiency (needed) to maintain pH ≥ 6.

The hot acidity generally does not change after sampling; however, the alkalinity may decrease owing to mineral precipitation while the pH may decrease or increase.

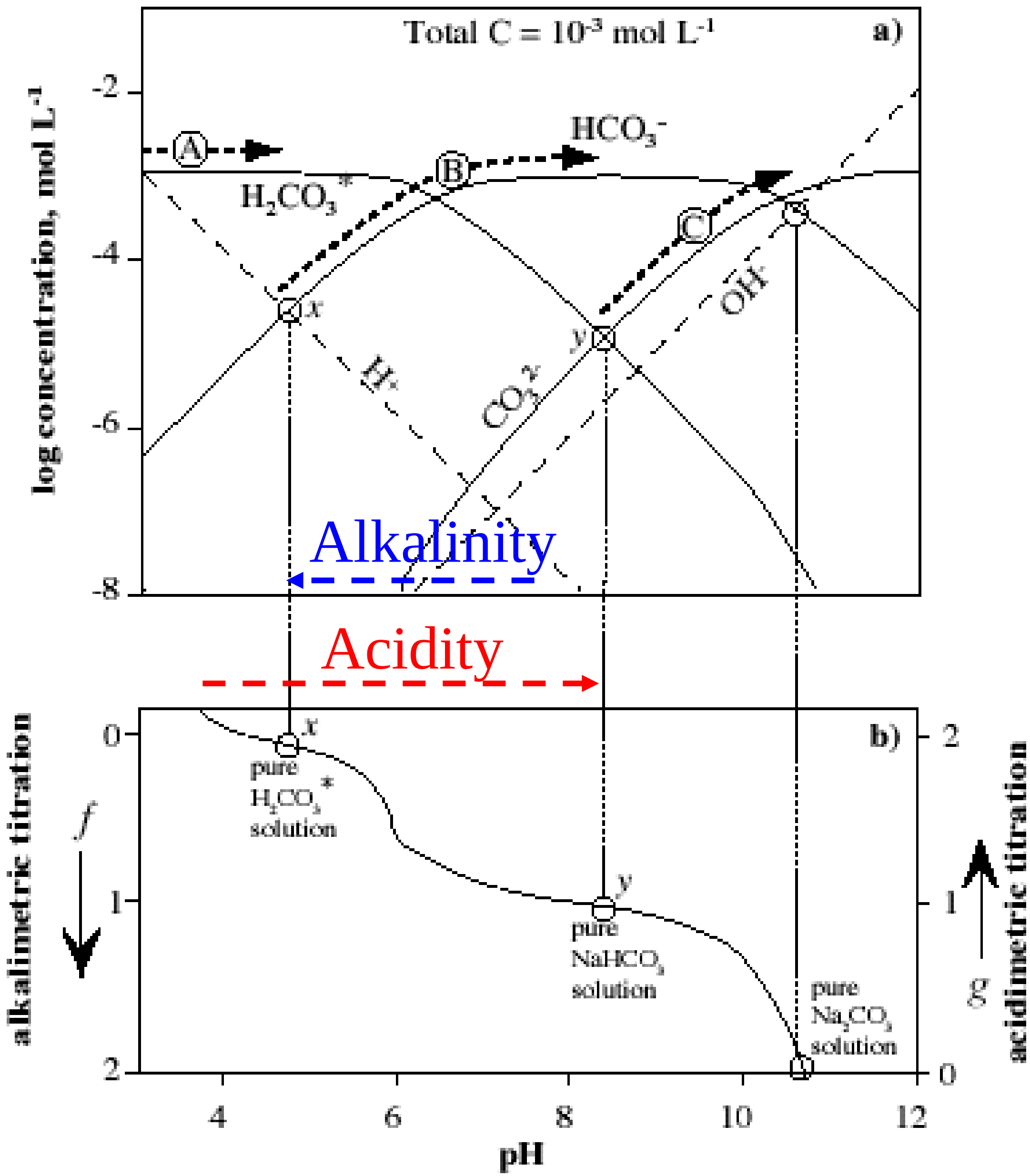
Alkalinity and Acidity Titration is Based on H_2O/CO_2 System

Alk to pH ~4.5:

$HCO_3^- + H^+ = H_2CO_3^*$

Acy to pH 8.3:

$H_2CO_3^* + OH^- = HCO_3^- + H_2O$



Standard Method “Hot H_2O_2” Acidity

1. Add H_2SO_4 to pH 4 (alkalinity titration)
2. Add H_2O_2 to oxidize Fe and Mn
3. Boil to facilitate oxidation and drive off CO_2
4. Cool to room temperature
5. Titrate to pH 8.3 with NaOH
6. Subtract equivalents of H_2SO_4 added from NaOH added
7. Calculate acidity as mg/L $CaCO_3$ (multiply equivalents by 50,044 mg/eq) and report positive or negative values.

Net Acidity Computations

$$\text{Net acidity (mg/L CaCO}_3\text{)} = \text{Acidity}_{\text{computed}} - \text{Alkalinity}$$

$$\text{Acidity}_{\text{computed}} \text{ (mg/L CaCO}_3\text{)} =$$

$$50 \cdot (10^{(3\text{-pH})}$$

$$+ 3 \cdot C_{Al} / 26.98$$

$$+ 2 \cdot C_{Fe}{}^{*} / 55.85$$

$$+ 2 \cdot C_{Mn} / 54.94\ )$$

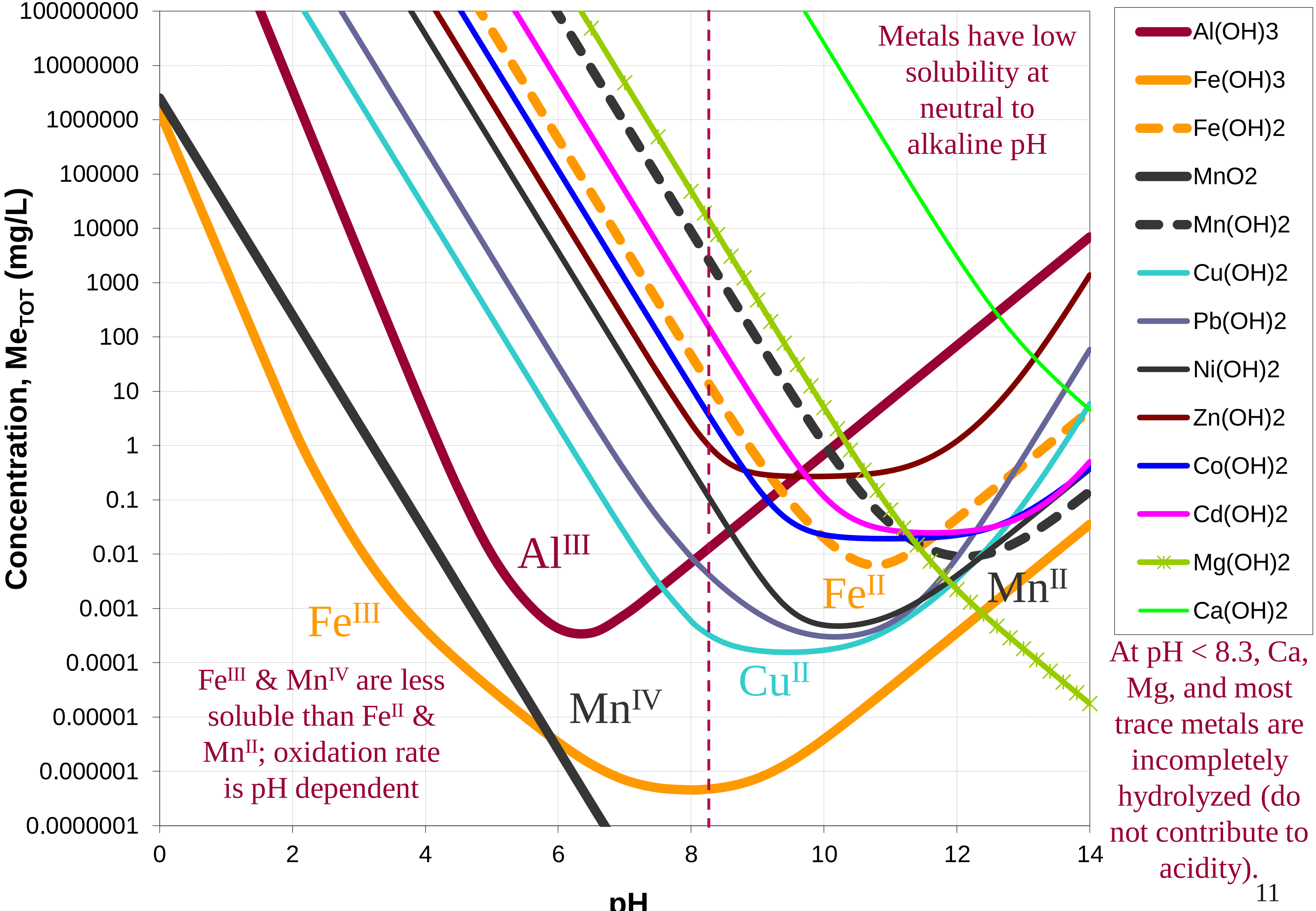
where C is Me concentration in mg/L

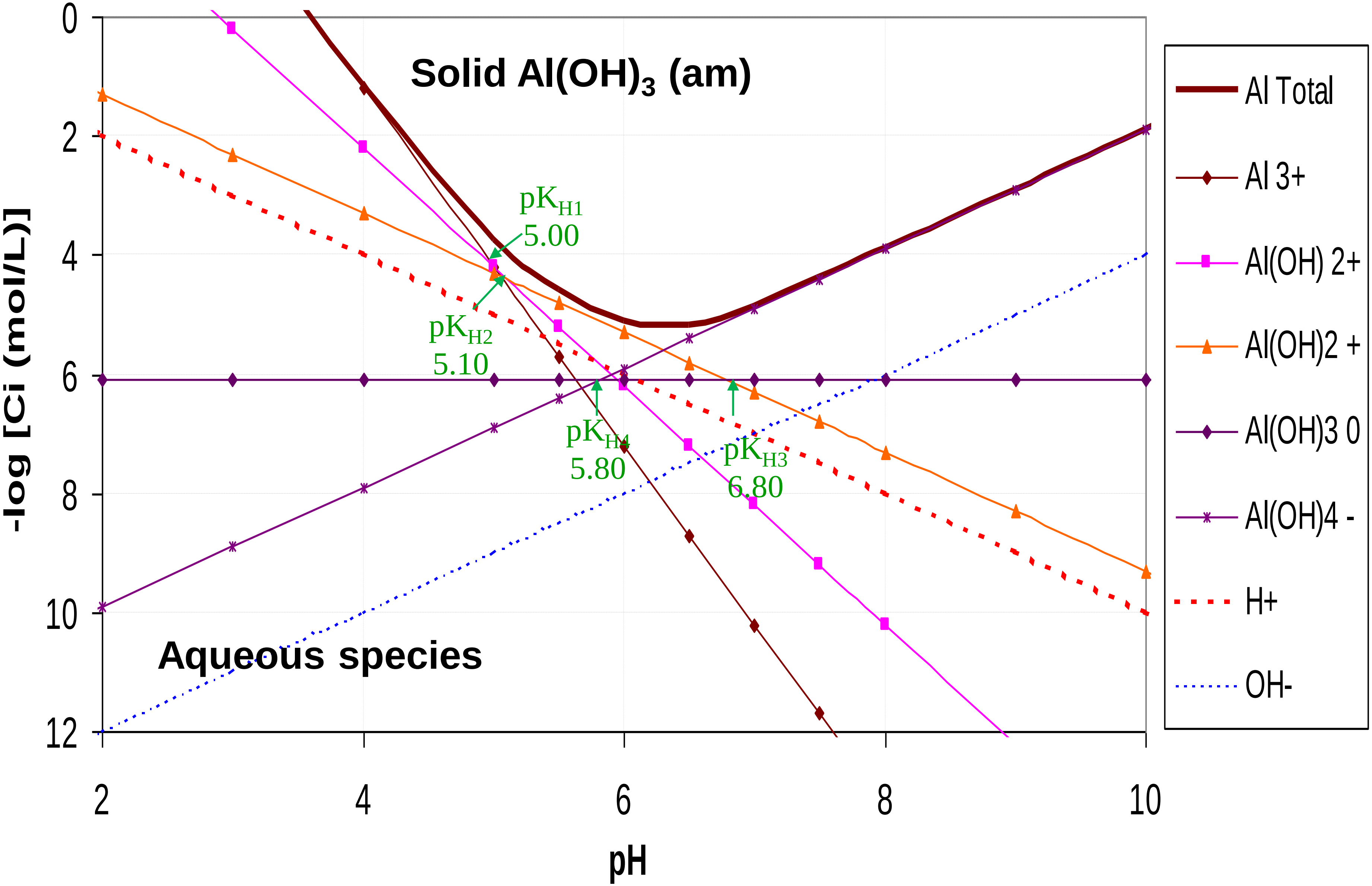
or

$$\text{Acidity}_{\text{computed}} \text{ (mg/L CaCO}_3\text{)} = 50 \cdot \Sigma\ (\varepsilon_i \cdot mM_i)$$

Kirby, C.S., Cravotta, C.A. III (2005) Net alkalinity and net acidity 2: Practical considerations: Applied Geochemistry 20, 1941-1964. https://doi.org/10.1016/j.apgeochem.2005.07.003

Hydrolysis/Precipitation of Fe, Mn, and Al Consumes "OH⁻"





Al(III) species distribution and solubility control by solid $Al(OH)_3$

HYDROLYSIS/SPECIATION

$H_2O \rightarrow H^+ + OH^-$ $K_W = 10^{-14}$ $pK_W = 14$

$+$

$Al^{+3} + OH^- \leftrightarrow AlOH^{+2}$ $pK_{OH1} = -9.00$

$=$

$Al^{+3} + H_2O \leftrightarrow AlOH^{+2} + H^+$ $pK_{H1} = 5.00$

pK_{H1} (= pK_{OH1} + pK_W) indicates pH where Al^{+3} = $AlOH^{+2}$

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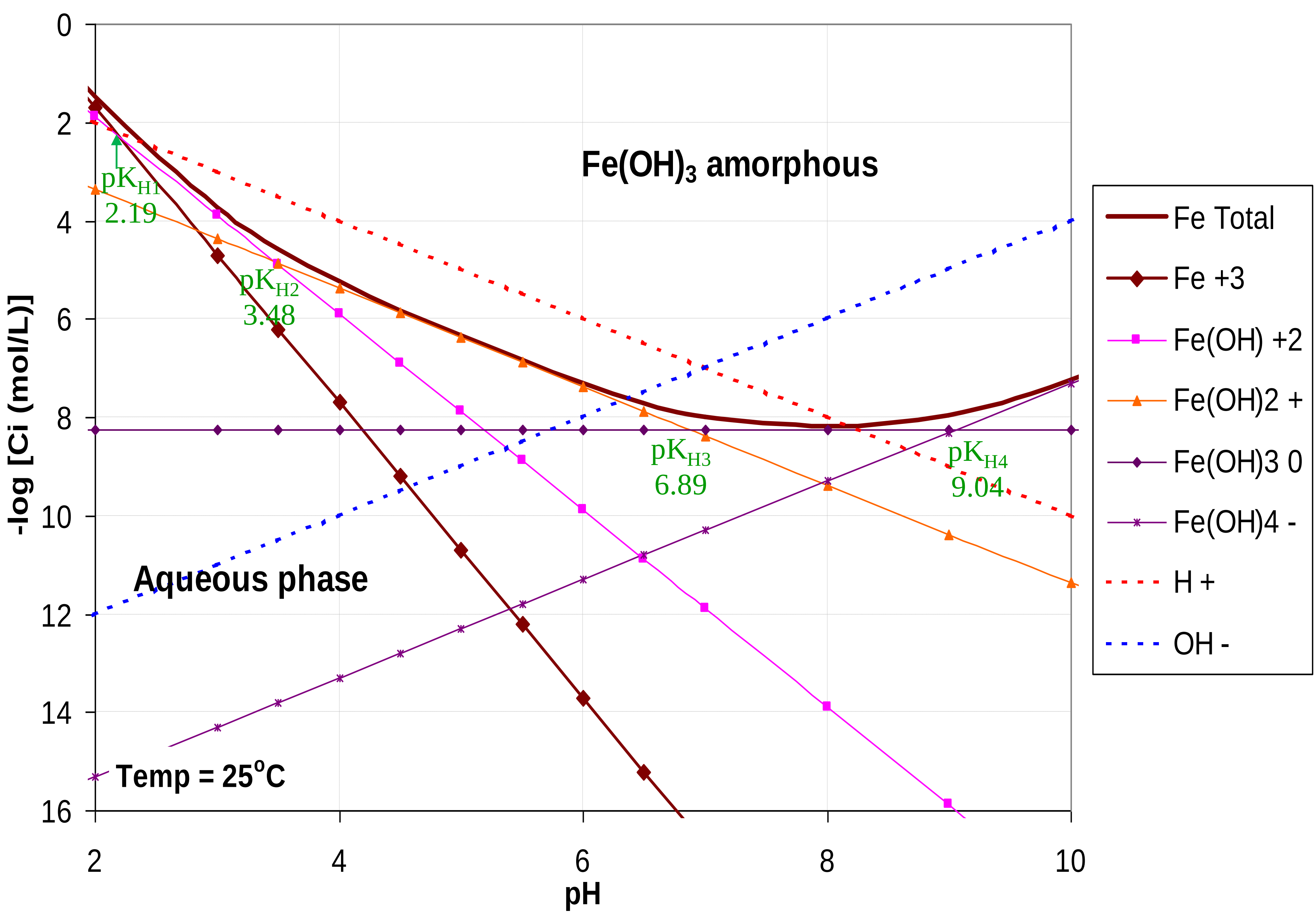
Aluminum Hydrolysis/Speciation

1) $Al^{+3} + H_2O \leftrightarrow AlOH^{+2} + H^+$ $pK_{H1} = 5.00$

2) $AlOH^{+2} + H_2O \leftrightarrow Al(OH)_2^+ + H^+$ $pK_{H2} = 5.10$

3) $Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3^0 + H^+$ $pK_{H3} = 6.80$

4) $Al(OH)_3^0 + H_2O \leftrightarrow Al(OH)_4^- + H^+$ $pK_{H4} = 5.80$



Fe(III) species distribution and solubility control by amorphous $Fe(OH)_3$

Ferric Iron
Hydrolysis/Speciation

1) $Fe^{+3} + H_2O \leftrightarrow FeOH^{+2} + H^+$ $pK_{H1} = 2.19$

2) $FeOH^{+2} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$ $pK_{H2} = 3.48$

3) $Fe(OH)_2^+ + H_2O \leftrightarrow Fe(OH)_3^0 + H^+$ $pK_{H3} = 6.89$

4) $Fe(OH)_3^0 + H_2O \leftrightarrow Fe(OH)_4^- + H^+$ $pK_{H4} = 9.04$

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Ferrous Iron and Manganese

Oxidation/Hydrolysis/Precipitation

1) $Fe^{+2} + H^{+} + 0.25\ O_2 = Fe^{+3} + 0.5\ H_2O$
2) $Fe^{+3} + 3\ H_2O = Fe(OH)_3 + 3\ H^{+}$
3) $Fe^{+2} + 0.25\ O_2 + 2.5\ H_2O = Fe(OH)_3 + 2\ H^{+}$

1) $Mn^{+2} + 2\ H^{+} + 0.5\ O_2 = Mn^{+4} + H_2O$
2) $Mn^{+4} + 2\ H_2O = MnO_2 + 4\ H^{+}$
3) $Mn^{+2} + 0.5\ O_2 + H_2O = MnO_2 + 2\ H^{+}$

ACIDITY COMPONENTS

$$\text{Acidity}_{\text{calculated}},\ \text{mg L}^{-1} = 50 \cdot \sum_{i}^{\text{all species}} \varepsilon_i \cdot mM_i$$

Acidity, ε_i, due to species, eq mol^{-1}

	+5	**+4**	**+3**	**+2**	**+1**	**0**	**-1**
Fe(II) complexes			$FeHSO_4^+$	Fe^{2+}, $FeSO_4^0$, $FeHCO_3^+$	$FeOH^+$, $FeCO_3^0$	**$Fe(OH)_2^0$**	
Fe(III) complexes	$Fe_3(OH)_4^{5+}$	$FeHSO_4^{2+}$, $Fe_2(OH)_2^{4+}$	Fe^{3+}, $FeSO_4^+$, $Fe(SO_4)_2^-$	$FeOH^{2+}$	$Fe(OH)_2^+$	**$Fe(OH)_3^0$**	$Fe(OH)_4^-$
Al complexes		$AlHSO_4^{2+}$	Al^{3+}, $AlSO_4^+$, $Al(SO_4)_2^-$	$AlOH^{2+}$	$Al(OH)_2^+$	**$Al(OH)_3^0$**	$Al(OH)_4^-$
Mn complexes				Mn^{2+}, $MnSO_4^0$	$MnOH^+$		
$H_2O/H_2S/CO_2$ species			***pH 2.5 → 8.3***		H^+, H_2CO_3*, H_2S	**H_2O, HCO_3^-, HS^-**	OH^-, CO_3^{2-}, S^{2-}
Non metal-bound SO_4				$H_2SO_4^0$	HSO_4^-	**SO_4^{2-}**	

Kirby, C.S., Cravotta, C.A. III (2005) Net alkalinity and net acidity 1: Theoretical considerations: Applied Geochemistry 20, 1920-1940. https://doi.org/10.1016/j.apgeochem.2005.07.002

Sulfate Speciation

Bisulfate (HSO_4^-) Contributes to Acidity at pH < 3

1) $HSO_4^- \leftrightarrow SO_4^{-2} + H^+$

$pK_{H1} = 1.988$

2) $[HSO_4^-] / [SO_4^{-2}] = K_{H1} \times [H^+]$

3) $[HSO_4^-] / [SO_4^{-2}] = 10^{(pK_{H1} - pH)}$

4) $[HSO_4^-] = [SO_4]_{TOT} \times 10^{(1.988 - pH)}$

where $[SO_4]_{TOT} = [HSO_4^-] + [SO_4^{-2}]$

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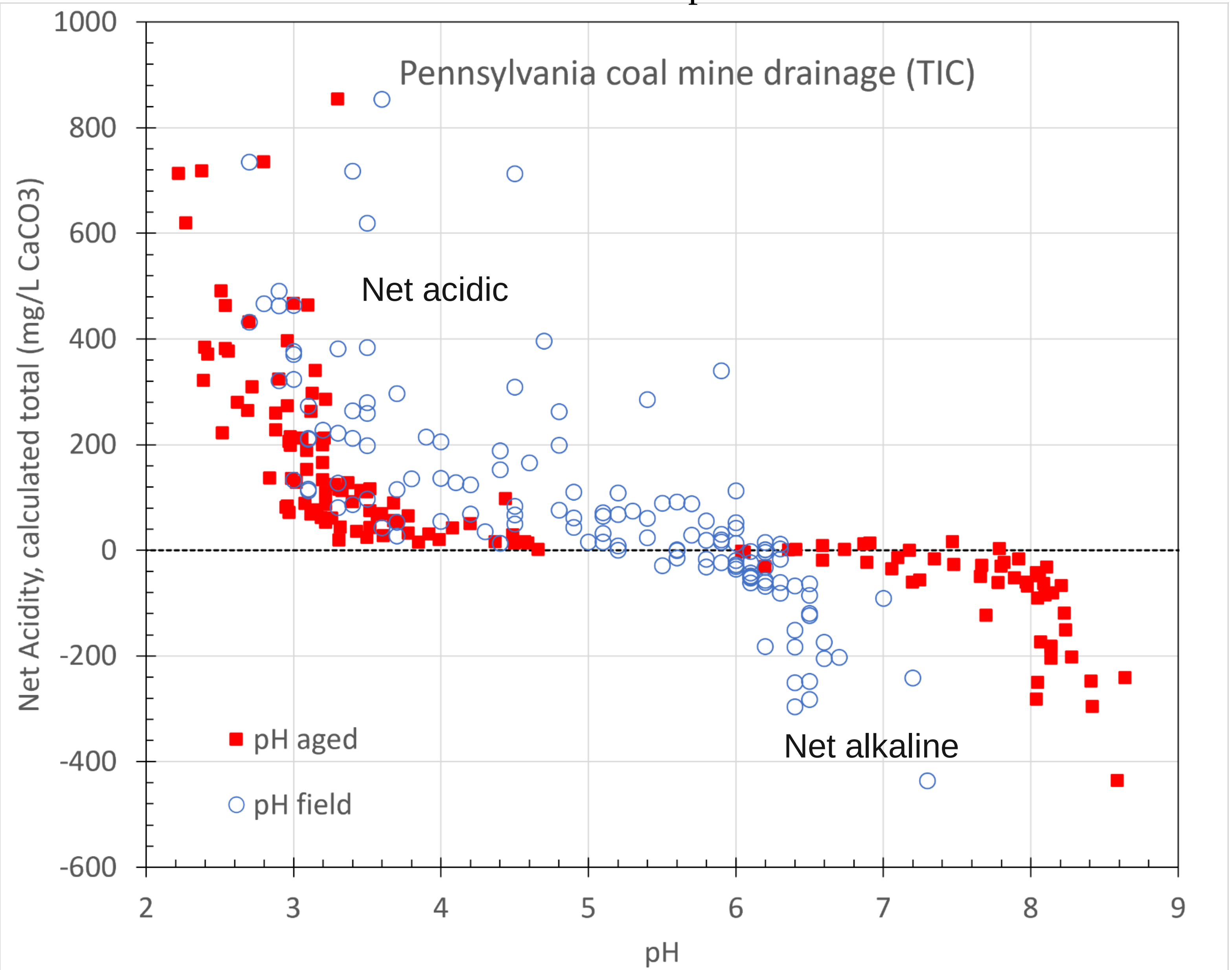
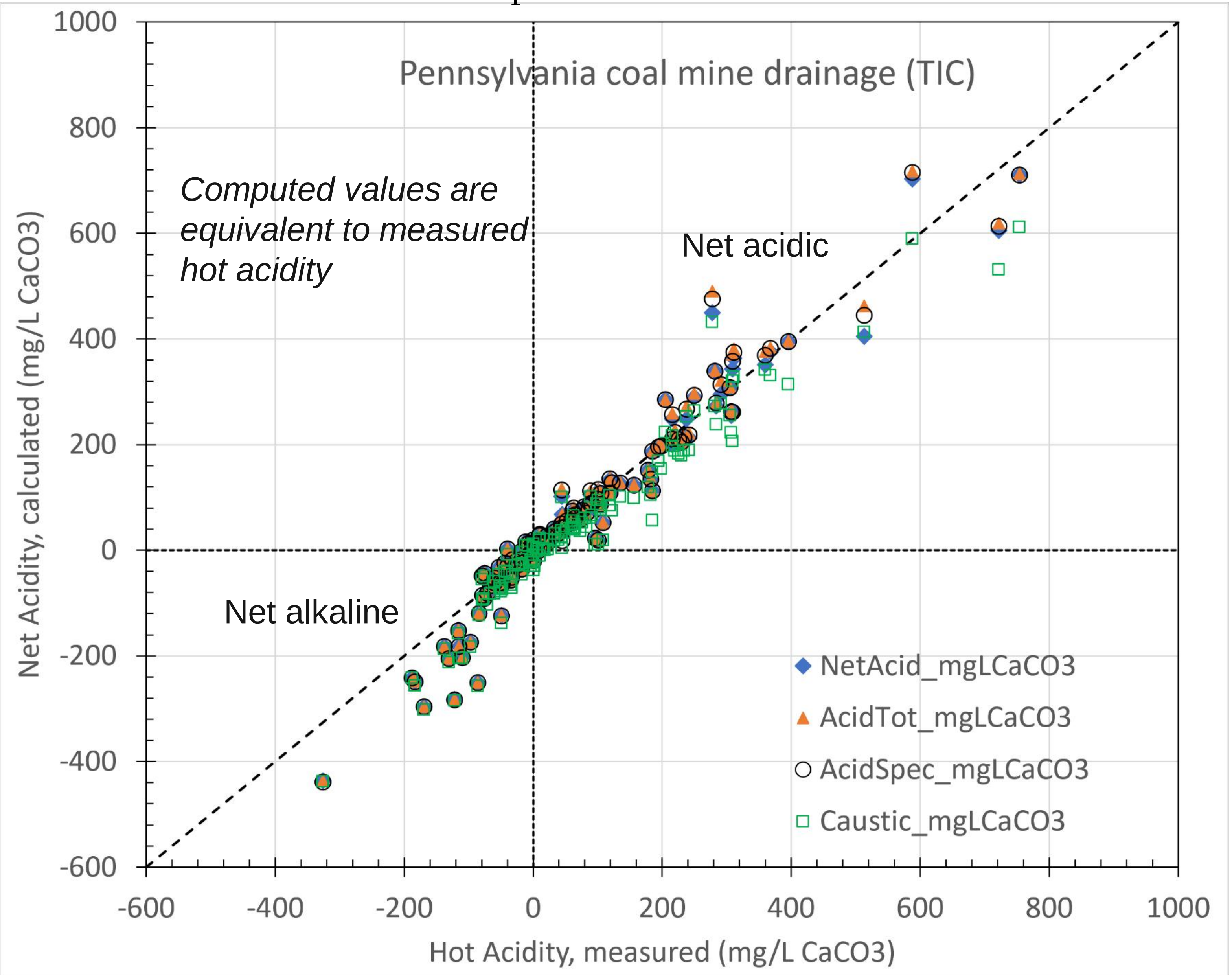
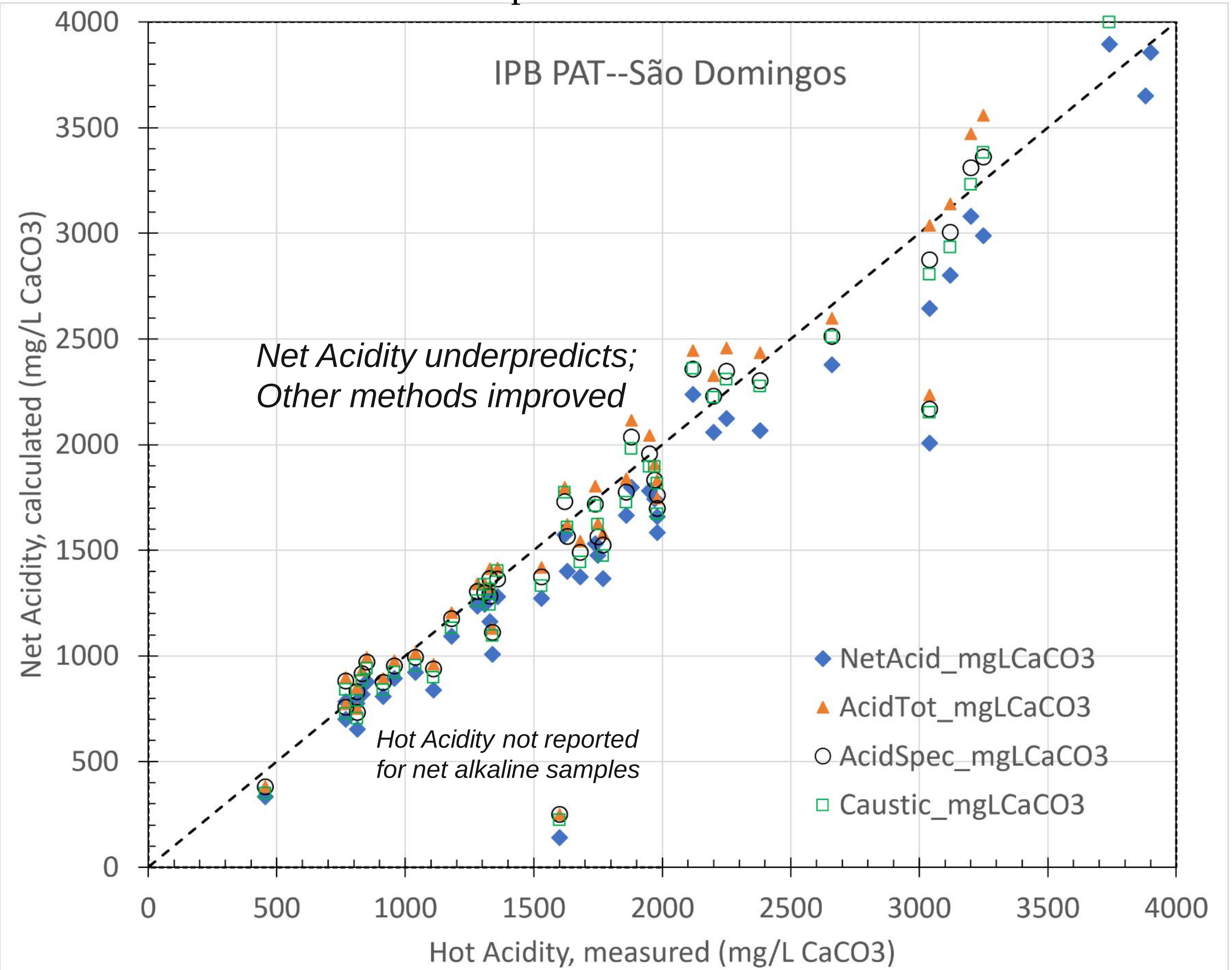
Bituminous and Anthracite AMD: Net Acidity$_{computed}$ vs. pH



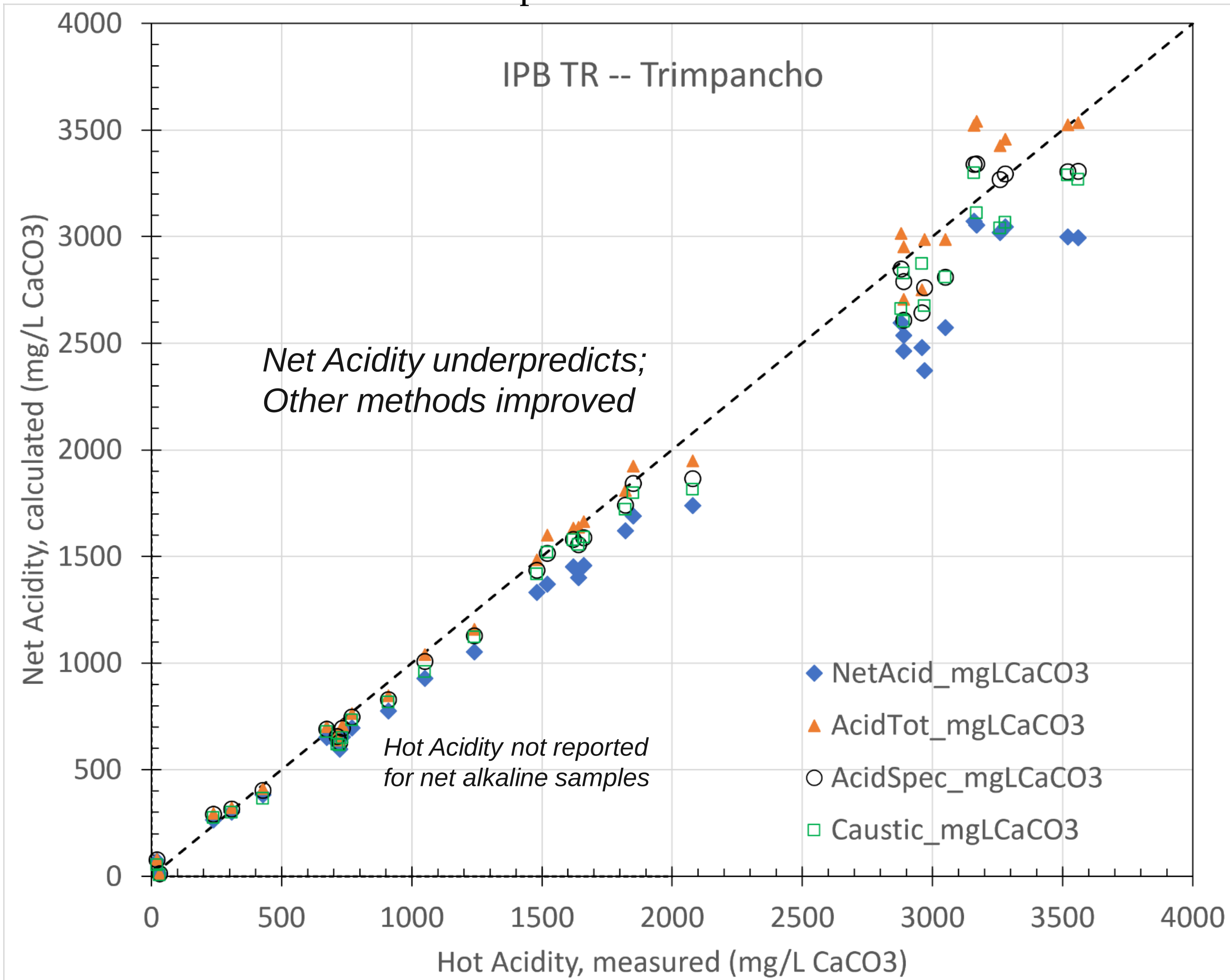
Bituminous and Anthracite AMD: Net Acidity$_{computed}$ vs. Hot Acidity$_{measured}$



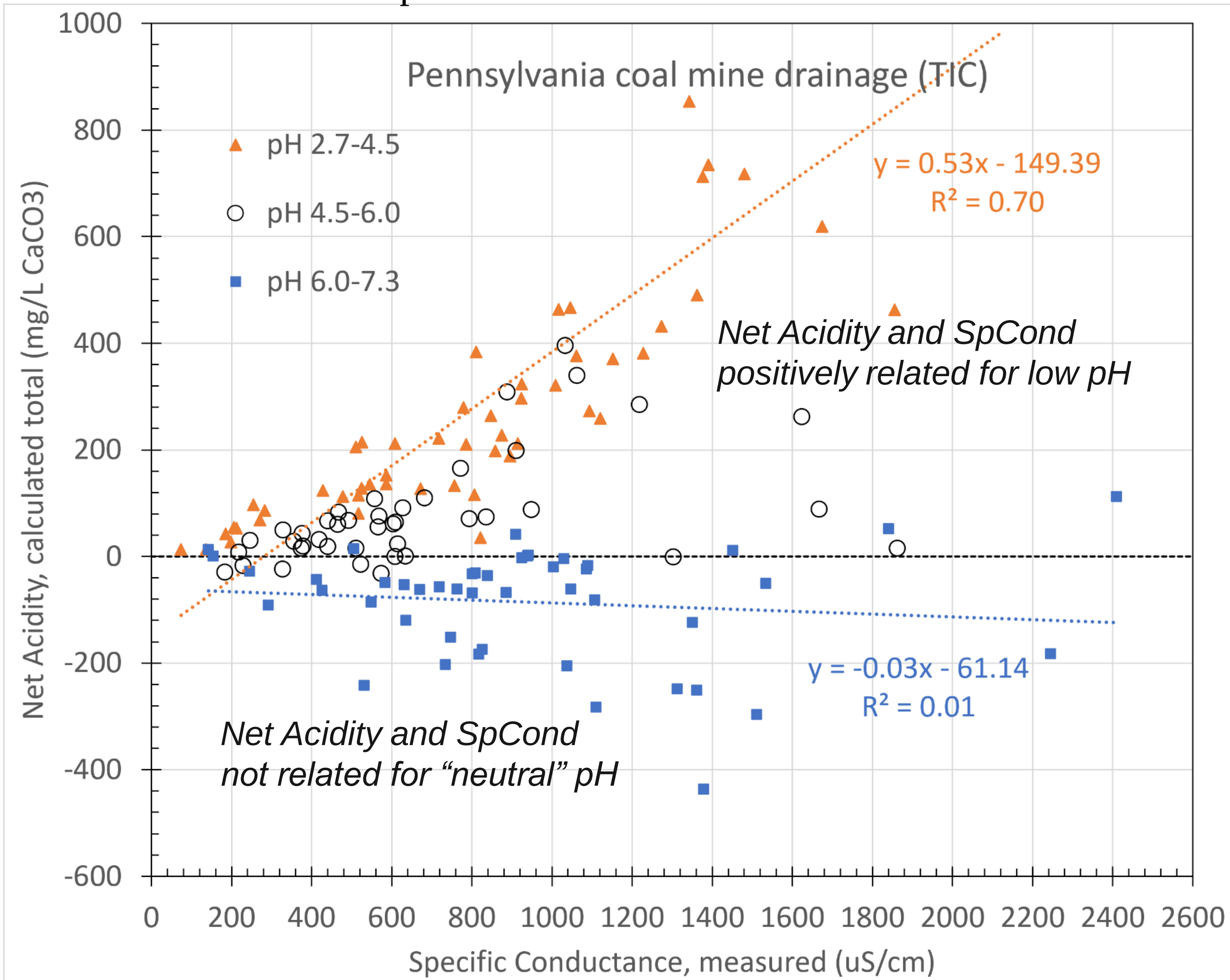
Iberian Pyrite Belt AMD:
Net Acidity$_{computed}$ vs. Hot Acidity$_{measured}$



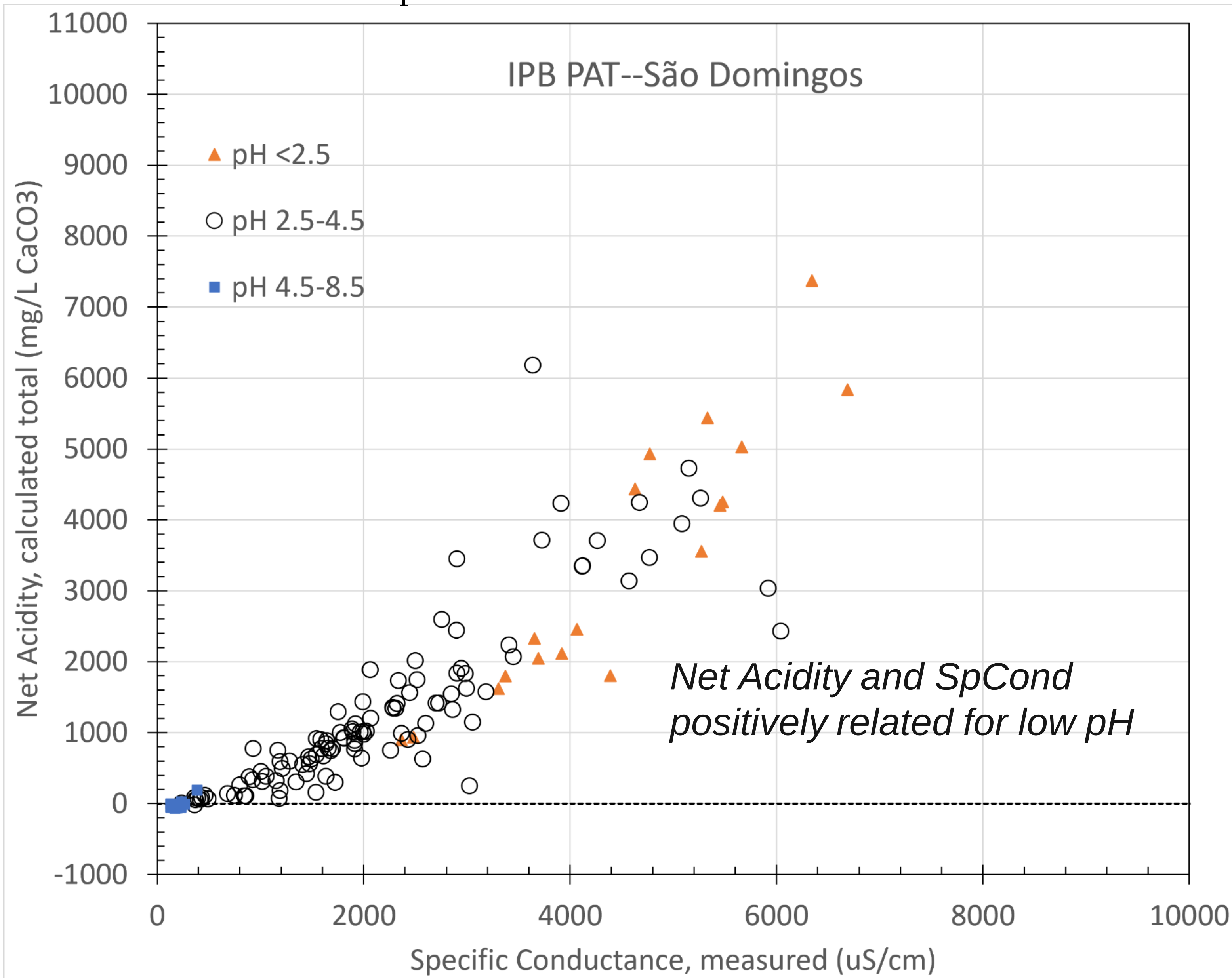
Iberian Pyrite Belt AMD: Net Acidity$_{computed}$ vs. Hot Acidity$_{measured}$



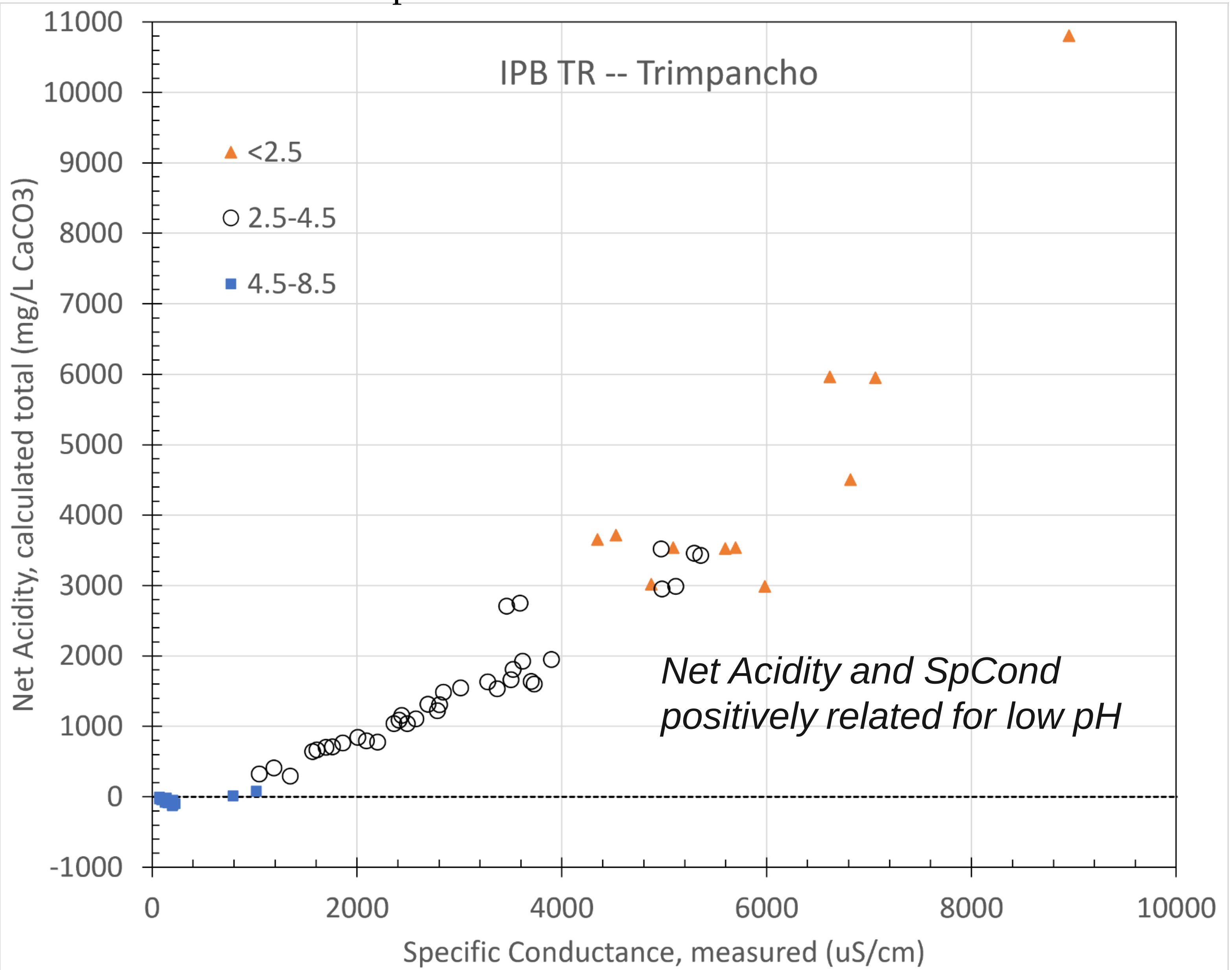
Bituminous and Anthracite AMD: Net $Acidity_{computed}$ vs. Specific $Conductance_{measured}$



Iberian Pyrite Belt AMD: Net Acidity$_{computed}$ vs. Specific Conductance$_{measured}$

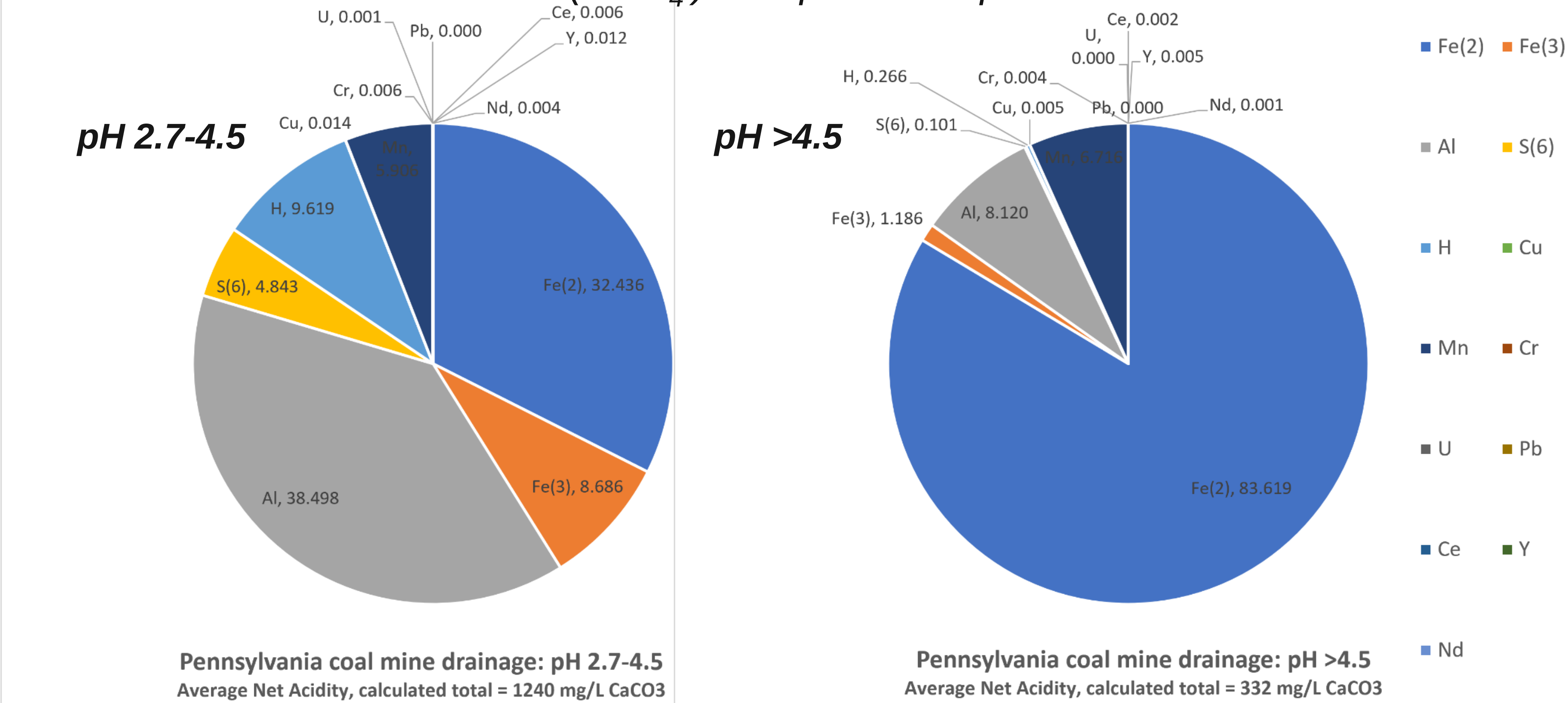


Iberian Pyrite Belt AMD: Net Acidity$_{computed}$ vs. Specific Conductance$_{measured}$



Bituminous and Anthracite AMD: Contributions to Net Acidity$_{computed}$ by Element

Bisulfate (HSO_4^-) is important at pH < 4.5



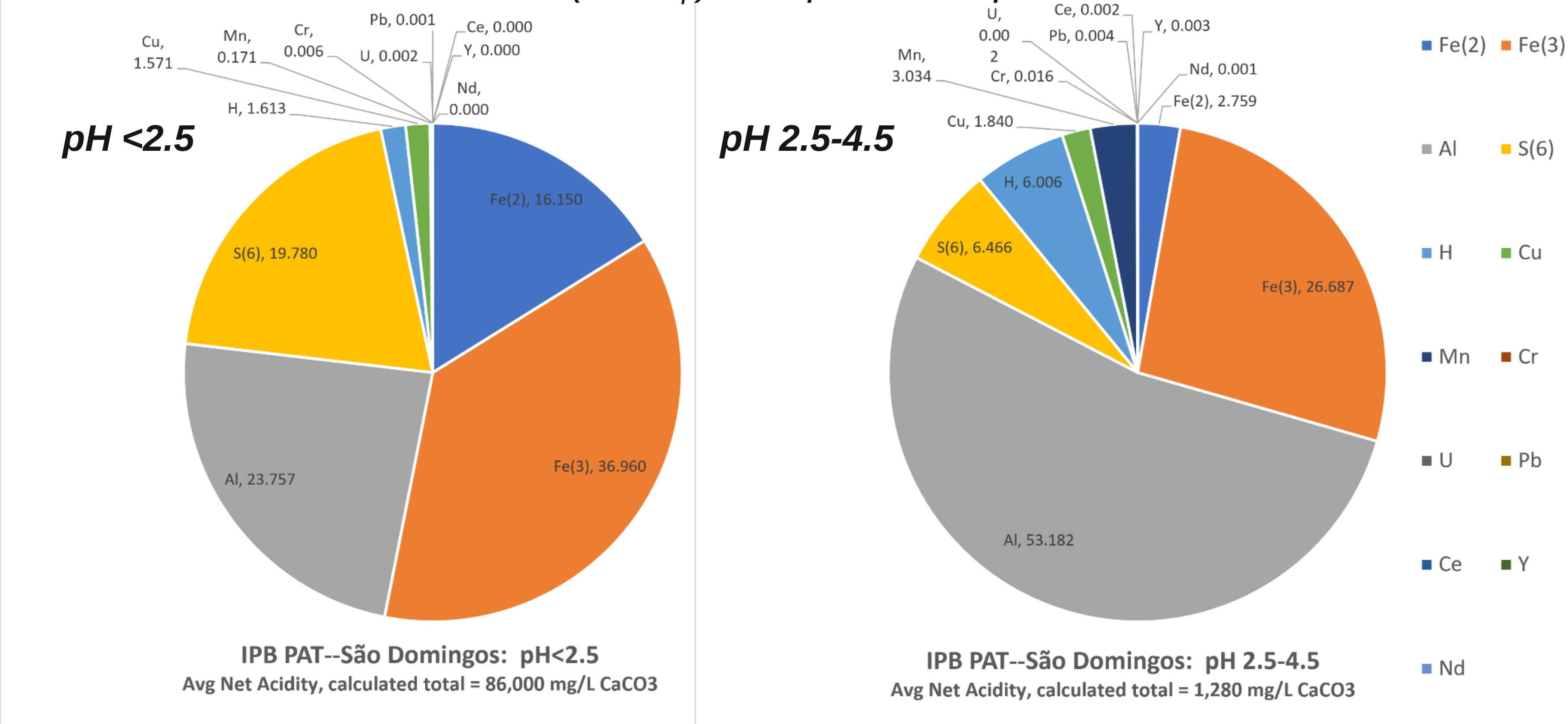
pH 2.7-4.5 had average acidity of 1,200 mg/L as $CaCO_3$ with major contributions from Al^{3+} (38.5%), H^+(9.6%), Fe^{2+} (32.4%) and Fe^{3+} (8.6%), and Mn^{2+} (5.9%) plus HSO_4^- (4.8%). Trace metals contributed less than 0.1%.

pH > 4.5 had average acidity of 332 mg/L as $CaCO_3$ with major contributions from Fe^{2+} (83.6%), Al^{3+} (8.1%), and Mn^{2+} (6.7%). Other components contributed ~1.2% together.

SpCond was comparable between the two pH classes, 1110 uS/cm for pH 2.7-4.5 and 1080 uS/cm for pH > 4.5

Iberian Pyrite Belt AMD: Contributions to Net Acidity$_{computed}$ by Element

Bisulfate (HSO_4^-) is important at pH < 4.5

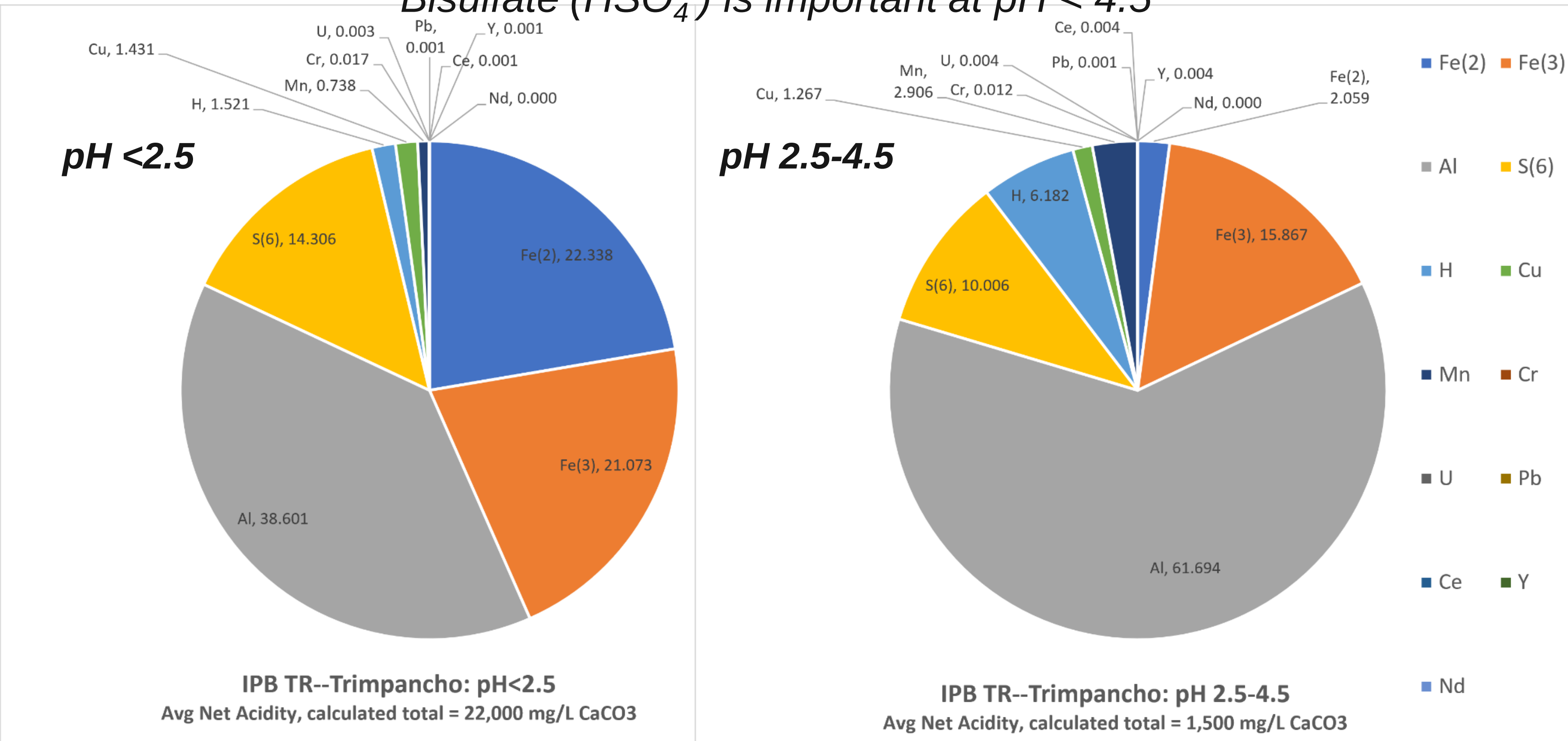


pH <2.5 had average acidity of 86,000 mg/L as $CaCO_3$ with major contributions from Fe^{2+} (16.1%) and Fe^{3+} (37.0%), Al^{3+} (23.7%), HSO_4^- (19.8%), H^+(1.6%), and Cu^{2+} (1.6%). Other trace metals and Mn^{2+} contributed less than 0.1%.

pH 2.5-4.5 had average acidity of 1,280 mg/L as $CaCO_3$ with major contributions from Al^{3+} (53.2%), Fe^{3+} (26.7%) and Fe^{2+} (2.8%), HSO_4^- (6.5%), H^+(6.0%), Mn^{2+} (3.0%), and Cu^{2+} (1.8%). Other components contributed less than 0.1%.

Iberian Pyrite Belt AMD: Contributions to Net Acidity$_{computed}$ by Element

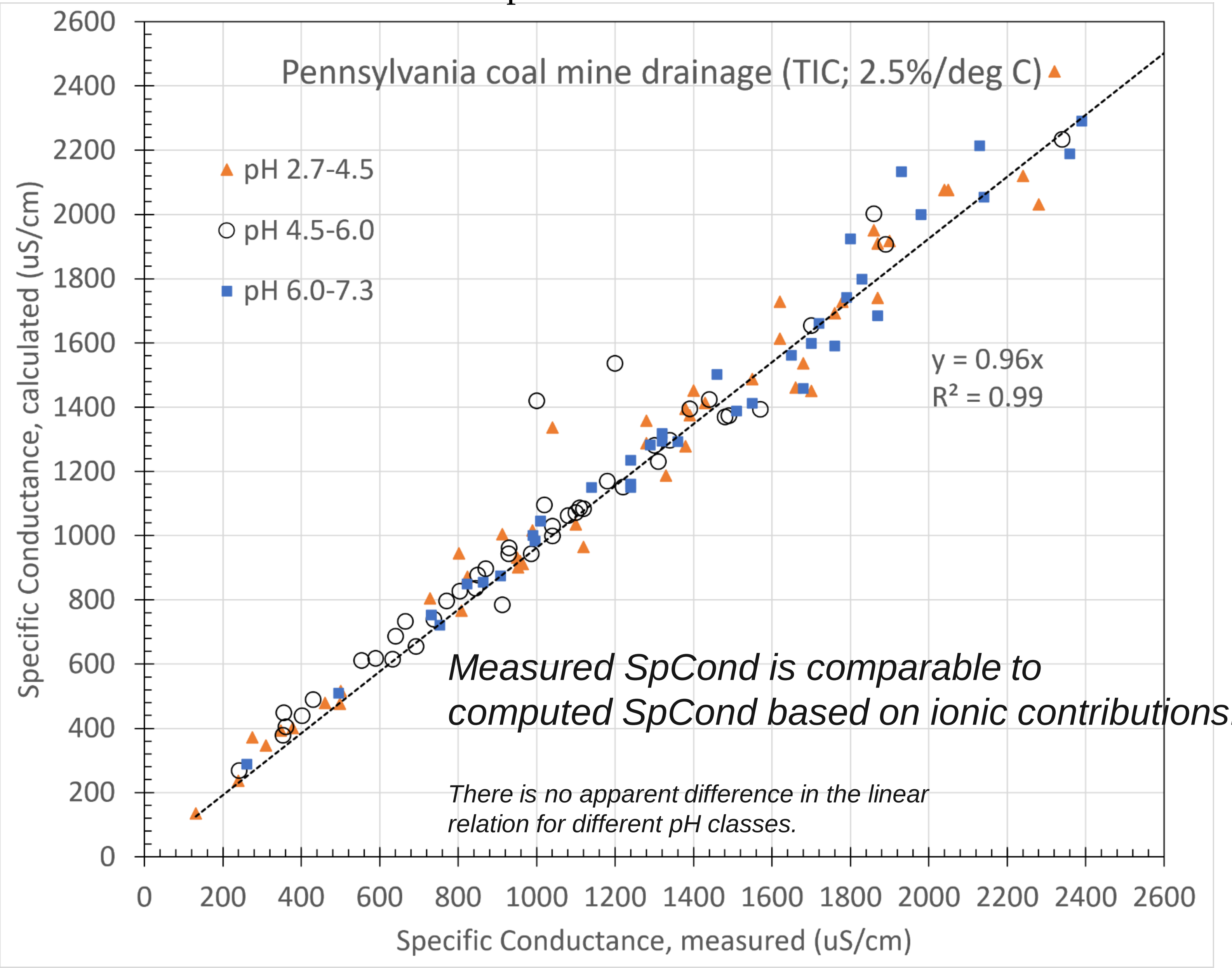
Bisulfate (HSO_4^-) is important at pH < 4.5



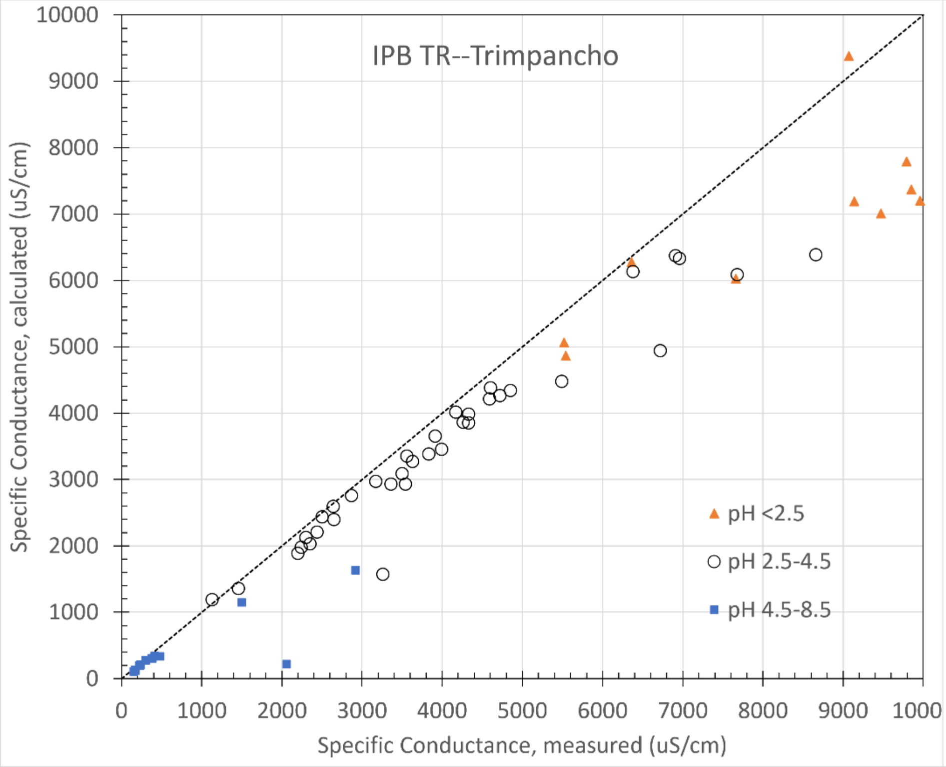
pH <2.5 had average acidity of 22,000 mg/L as $CaCO_3$ with major contributions from Fe^{2+} (22.3%) and Fe^{3+} (21.0%), Al^{3+} (38.6%), HSO_4^- (14.3%), H^+ (1.5%), and Cu^{2+} (1.4%). Other trace metals and Mn^{2+} contributed less than 1%.

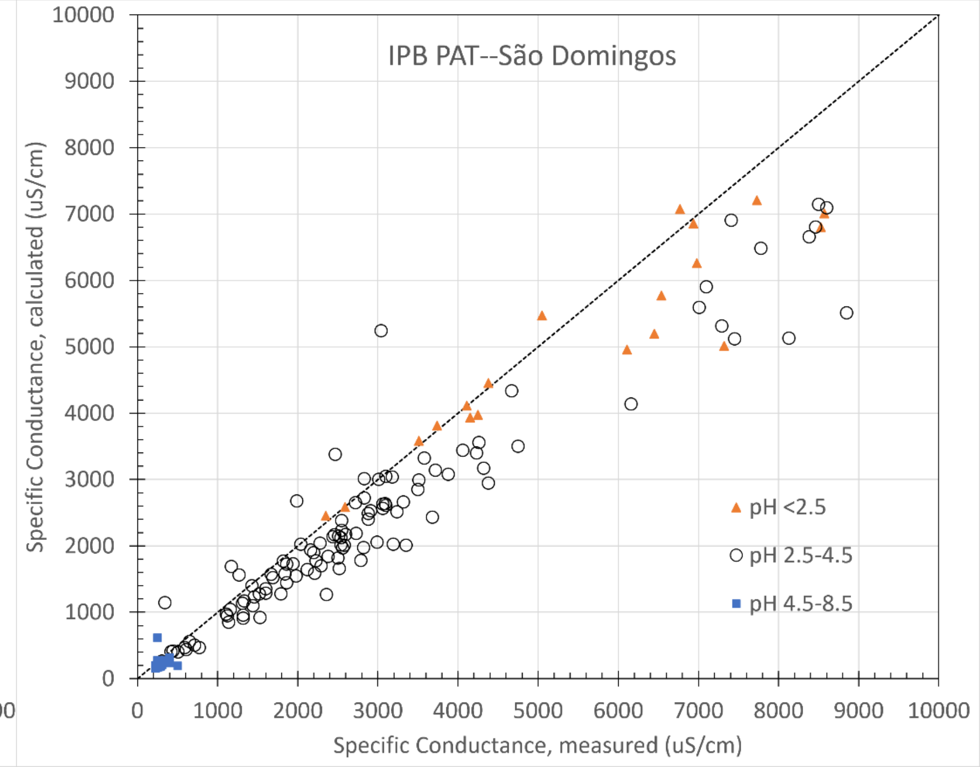
pH 2.5-4.5 had average acidity of 1,500 mg/L as $CaCO_3$ with major contributions from Al^{3+} (61.7%), Fe^{3+} (15.8%) and Fe^{2+} (2.1%), HSO_4^- (10.0%), H^+ (6.2%), Mn^{2+} (2.9%), and Cu^{2+} (1.3%). Other components contributed less than 1%.

Bituminous and Anthracite AMD: $SpCond_{computed}$ vs. $SpCond_{measured}$



Iberian Pyrite Belt AMD: $SpCond_{computed}$ vs. $SpCond_{measured}$



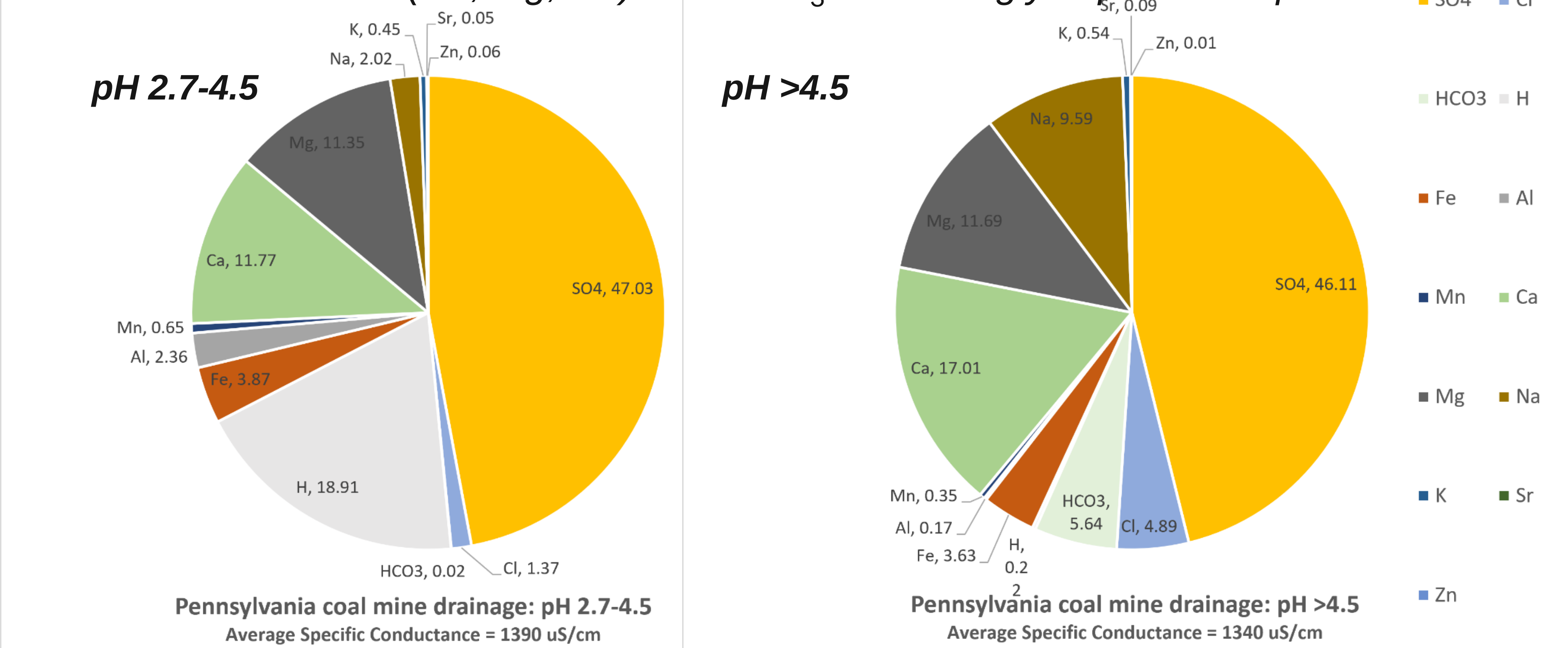


Measured SpCond is comparable to computed SpCond based on ionic contributions.

Bituminous and Anthracite AMD: Ionic Contributions to Electrical Conductivity$_{computed}$

Sulfate is a major contributor to electrical conductivity

Base cations (Ca, Mg, Na) and HCO_3 increasingly important at pH >4.5

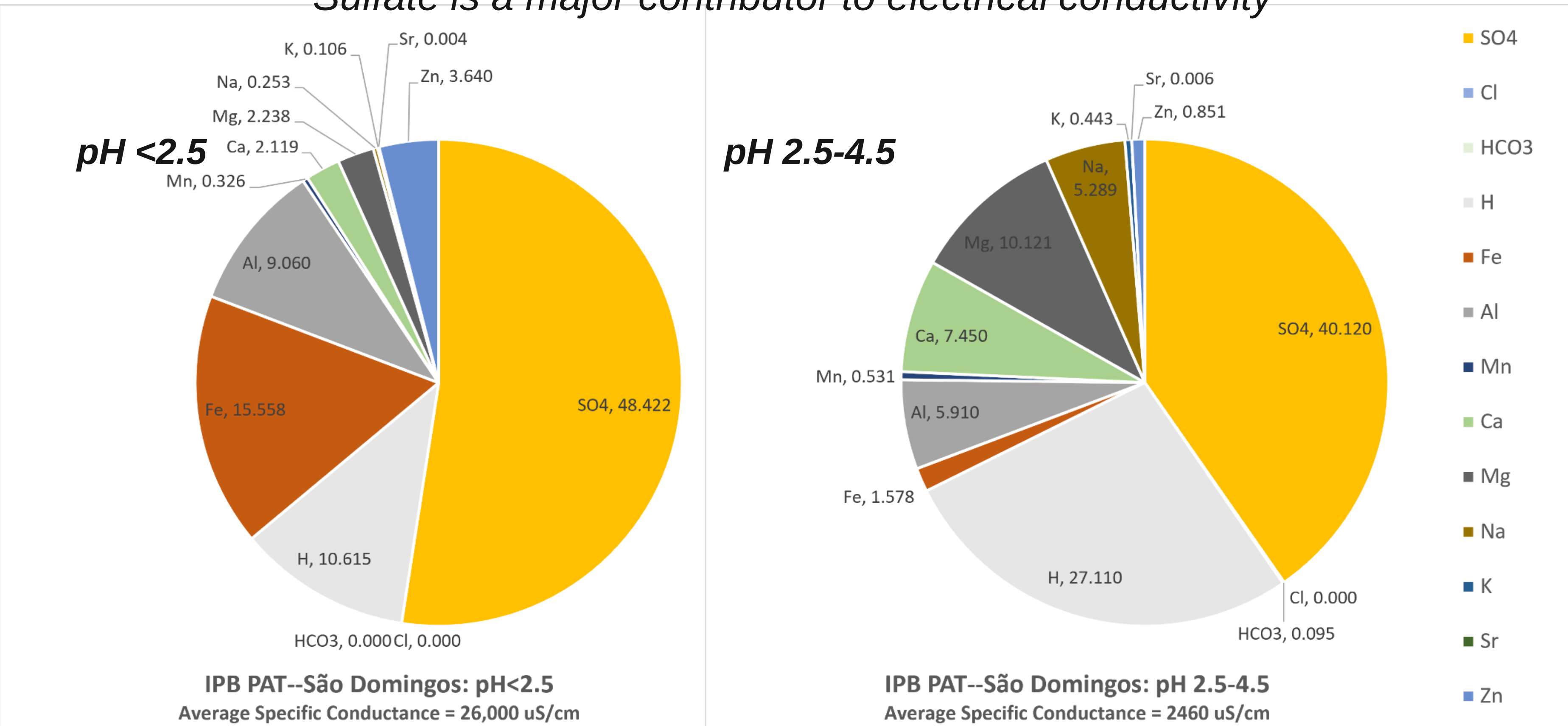


pH 2.7-4.5 had average SpCond of 1,390 uS/cm with major contributions from SO_4 (47.0%), H^+ (18.9%), Ca (11.8%), Mg (11.4%), Fe (3.9%), Na (2.0%), and Cl (1.4%). Mn, K, and trace metals contributed < 1%.

pH > 4.5 had average SpCond of 1,340 uS/cm with major contributions from SO_4 (46.1%), Ca (17.0%), Mg (11.7%), Na (9.6%), HCO_3 (5.6%), Cl (4.8%), and Fe (3.6%). Al, Mn, K, and trace metals contributed < 1%.

Iberian Pyrite Belt AMD: Ionic Contributions to Electrical Conductivity$_{computed}$

Sulfate is a major contributor to electrical conductivity

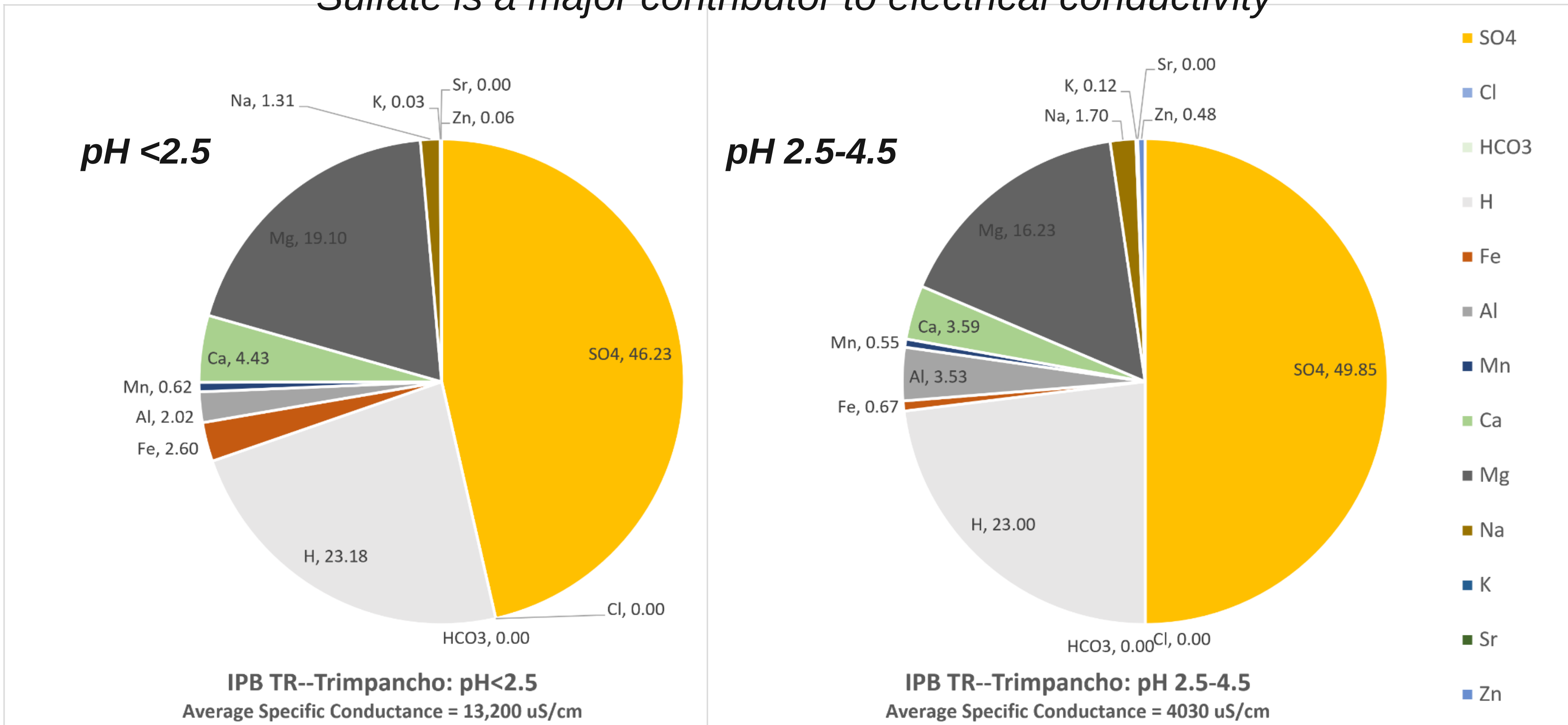


pH <2.5 had average SpCond of 26,000 uS/cm with major contributions from SO_4 (48.4%), H^+ (10.6%), Fe (15.6%), Al (9.1%), Zn (3.6%), Ca (2.1%), and Mg (2.2%). Cl, K, Mn, and trace metals contributed < 1%.

pH 2.5-4.5 had average SpCond of 2,460 uS/cm with major contributions from SO_4 (40.1%), H^+ (27.1%), Fe (1.6%), Al (5.9%), Ca (7.5%), Mg (10.1%), and Na (5.3%). Cl, K, Mn, Zn, and trace metals contributed < 1%.

Iberian Pyrite Belt AMD: Ionic Contributions to Electrical Conductivity$_{computed}$

Sulfate is a major contributor to electrical conductivity



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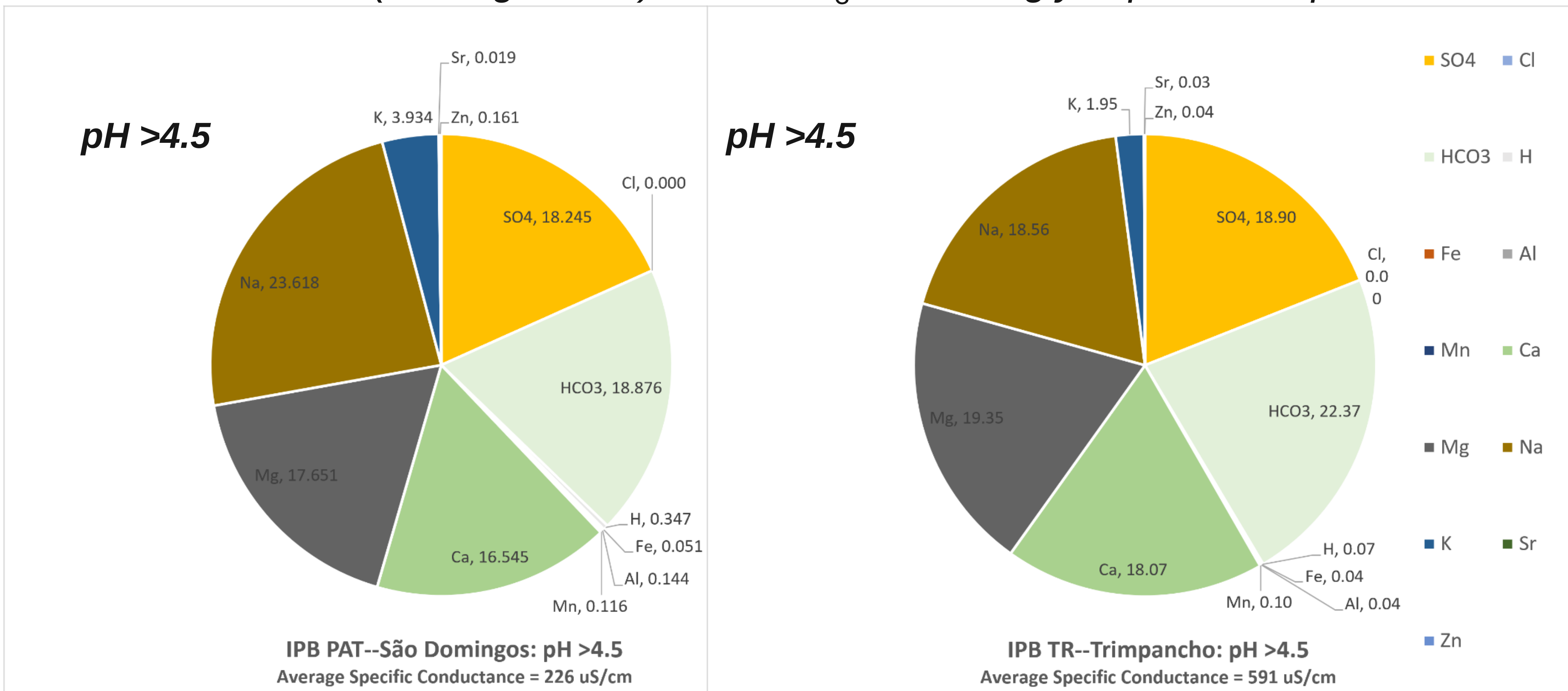
pH 2.5-4.5 had average SpCond of 2,460 uS/cm with major contributions from SO_4 (40.1%), H^+ (27.1%), Fe (1.6%), Al (5.9%), Ca (7.5%), Mg (10.1%), and Na (5.3%). Cl, K, Mn, Zn, and trace metals contributed < 1%.

Iberian Pyrite Belt AMD: Ionic Contributions to Electrical Conductivity$_{computed}$

Base cations (Ca, Mg, Na, K) and HCO_3 increasingly important at pH >4.5



pH >4.5 had average SpCond of 226 uS/cm with major contributions from SO_4 (18.2%), HCO_3 (18.9%), Ca (16.5%), Mg (17.7%), Na (23.6%), and K (3.9%).

pH >4.5 had average SpCond of 591uS/cm with major contributions from SO_4 (18.9%), HCO_3 (22.4%), Ca (18.7%), Mg (19.4%), Na (18.6%), and K (2.0%).

Many of the pH >4.5 samples are streamwater downstream of AMD, which is diluted and neutralized.

SUMMARY/CONCLUSIONS

- Aqueous speciation calculations are helpful to understand the ionic contributions to acidity and electrical conductivity.
- “Extreme” AMD such as that of the Iberian Pyrite Belt can have low pH with very high acidity, SC, and concentrations of sulfate.
- The conventional computation of net acidity that uses pH and analytical concentrations of Fe, Al, Mn, and alkalinity underestimates the hot acidity of extreme AMD.
- An improved computation of “total” acidity considers additional elements, including sulfate, with a contribution from 0 to 1 depending on how much is present as HSO_4^-.

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- Dr. Patrícia Gomes patriciagomes@dct.uminho.pt
- Dr. Charles A. Cravotta cravottageochemical@gmail.com
- Dr. Mehrez Hermassi mehrez.hermassi@uqat.ca

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