“Priority Pollutants” and Associated Constituents in Untreated and Treated Discharges from Coal Mines in Pennsylvania, U.S.A.

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with contributions from Keith Brady,
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Priority Pollutants in CMD

- Constituents in CMD have potential to be toxic or hazardous to humans and aquatic organisms.
- Concentrations of toxic metals in CMD tend to decrease as pH and alkalinity increase.
- Treatment of acidic effluents to pH > 6 with removal of Fe to < 7 mg/L and Mn to < 5 mg/L may provide a reasonable measure of protection for aquatic life.

Water-Quality Criteria: Protect Human Health and Freshwater Aquatic Organisms *(Tables IV, V, other)*

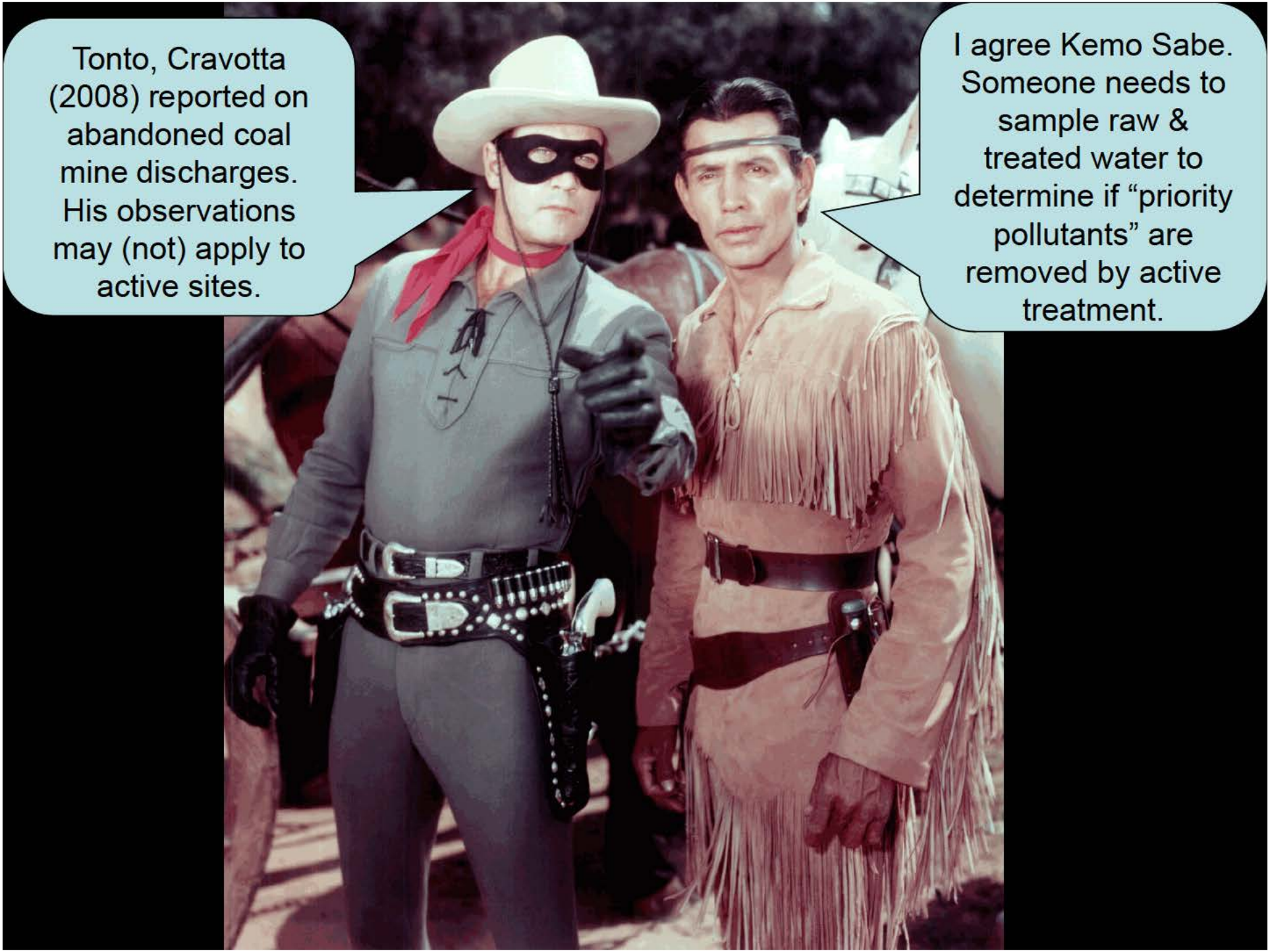
Constituent	Symbol	Units	Drinking Water (1)		Aquatic Criteria (2*, 3)		Mine Effluent (4)		NPDES 40CFR
			MCL	SCL	CMC	CCC	Max	Av30	122.21.D (5)
Aluminum	Al	µg/L	n.a.	200	750	87	750	variable	IV
Boron	B	µg/L	n.a.	n.a.	8,100	1,600	n.a.	n.a.	IV
Barium	Ba	µg/L	2,000	1,000	21,000	4,100	n.a.	n.a.	IV
Cobalt	Co	µg/L	n.a.	n.a.	95	19	n.a.	n.a.	IV
Fluoride	F	mg/L	4	2	n.a.	n.a.	n.a.	n.a.	IV
Iron	Fe	µg/L	n.a.	300	n.a.	1,000	7,000	3,000	IV
Manganese	Mn	µg/L	n.a.	50	n.a.	n.a.	5,000	2,000	IV
Nitrite	NO2N	mg/L	1	n.a.	n.a.	n.a.	n.a.	n.a.	IV
Nitrate	NO3N	mg/L	10	n.a.	n.a.	n.a.	n.a.	n.a.	IV
Sulfate	SO4	mg/L	500	250	n.a.	n.a.	250	n.a.	IV
Uranium	U	µg/L	30	n.a.	n.a.	n.a.	n.a.	n.a.	V
Vanadium	V	µg/L	n.a.	n.a.	510	100	n.a.	n.a.	V
Acidity, hot or net	ACIDH	mg/L	n.a.	n.a.	0	n.a.	n.a.	n.a.	n.a.
Chloride	Cl	mg/L	n.a.	250	860,000	230,000	n.a.	n.a.	n.a.
Oxygen	DOX	mg/L	n.a.	n.a.	4 minimum		n.a.	n.a.	n.a.
Ammonia	NH3N	mg/L	n.a.	20	37	6	n.a.	n.a.	n.a.
pH	pHF	units	n.a.	n.a.	6 minimum		6	n.a.	n.a.
Total Dissolved Solids	ROE	mg/L	n.a.	500	*2,000*	*500*	*2,000*	*1,000*	n.a.
Specific Conductance	SC25	µS/cm	n.a.	n.a.	*800*	*300*	n.a.	n.a.	n.a.
Temperature	TEMPC	C	n.a.	n.a.	31	n.a.	n.a.	n.a.	n.a.

Water-Quality Criteria: Protect Human Health and Freshwater Aquatic Organisms *(Table III)*

Constituent	Symbol	Units	Drinking Water (1)		Aquatic Criteria (2*, 3)		Mine Effluent (4)		NPDES 40CFR
			MCL	SCL	CMC	CCC	Max	Av30	122.21.D (5)
Silver *	Ag	µg/L	n.a.	100	15.56	15.56	n.a.	n.a.	III
Arsenic	As	µg/L	10	n.a.	340	150	n.a.	n.a.	III
Beryllium	Be	µg/L	4	n.a.	n.a.	n.a.	n.a.	n.a.	III
Cadmium *	Cd	µg/L	5	n.a.	4.90	0.46	n.a.	n.a.	III
Cyanide	CN	µg/L	200	140	22	5.2	n.a.	n.a.	III
Chromium III *	CrIII	µg/L	100	n.a.	1207	157	n.a.	n.a.	III
Chromium VI	CrVI	µg/L	3	n.a.	16	11	n.a.	n.a.	III
Copper *	Cu	µg/L	1,300	1,000	31.9	19.6	n.a.	n.a.	III
Mercury	Hg	µg/L	2	n.a.	1.40	0.77	n.a.	n.a.	III
Nickel *	Ni	µg/L	n.a.	n.a.	1017	113	n.a.	n.a.	III
Lead *	Pb	µg/L	15	n.a.	172	6.7	n.a.	n.a.	III
Phenols, total	PHENOL	mg/L	10	n.a.	n.a.	n.a.	n.a.	n.a.	III
Antimony	Sb	µg/L	6	n.a.	1,100	220	n.a.	n.a.	III
Selenium	Se	µg/L	50	n.a.	12.8	4.6	n.a.	n.a.	III
Thallium	Tl	µg/L	2.00	0.24	65	13	n.a.	n.a.	III
Zinc *	Zn	µg/L	7,400	5,000	255	255	n.a.	n.a.	III

*** Freshwater CMC and CCC for selected metals are expressed as a function of hardness. Values in table calculated for hardness of 250 mg/L $CaCO_3$. CMC and CCC will decrease with decreased hardness.**

**** CMC for selenium assumes all selenium is selenate (12.8), which is more toxic than selenite (185.9).**


Tonto, Cravotta (2008) reported on abandoned coal mine discharges. His observations may (not) apply to active sites.
I agree Kemo Sabe. Someone needs to sample raw & treated water to determine if “priority pollutants” are removed by active treatment.

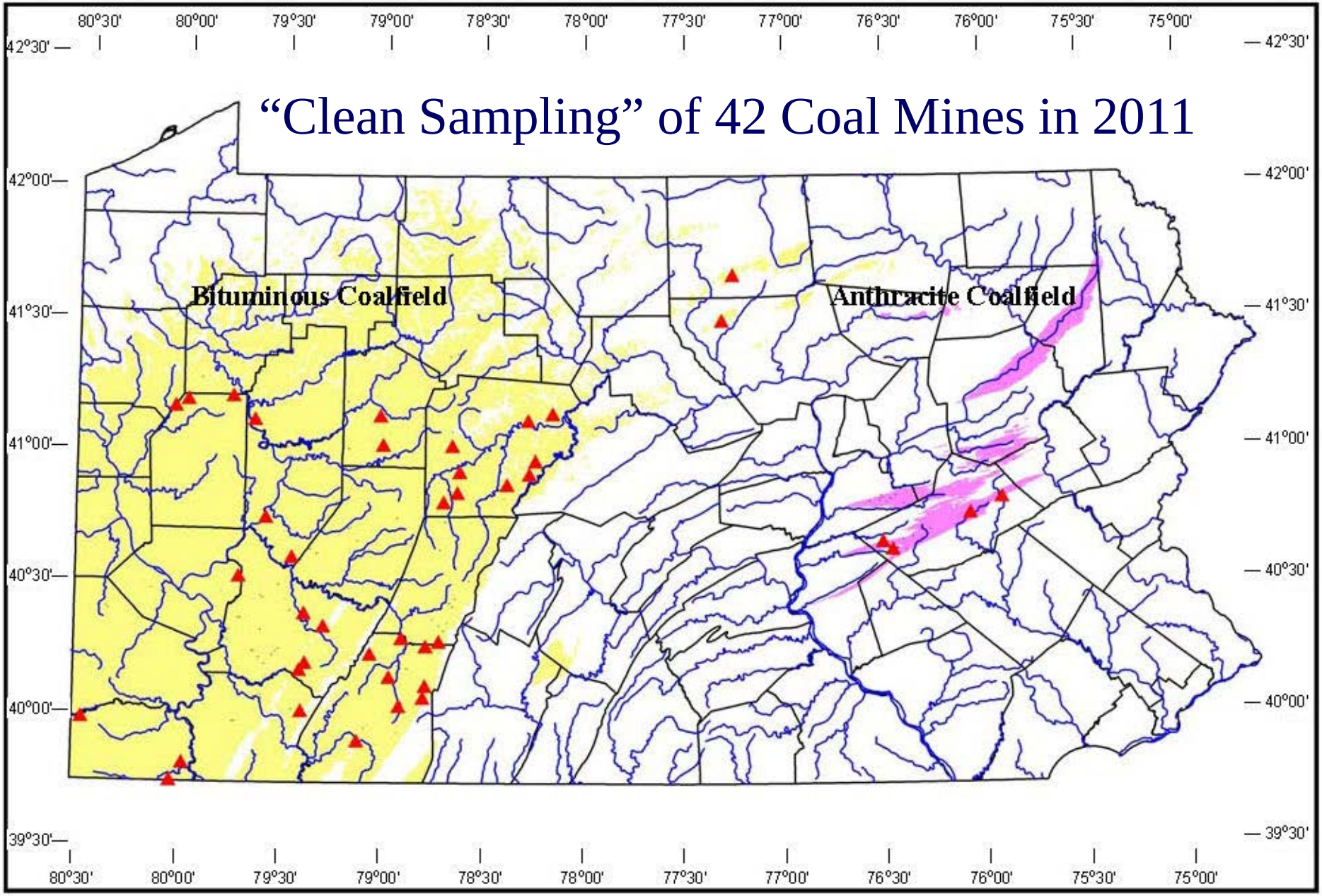


Fig. 1. Map of Pennsylvania showing locations of 42 coal-mining or coal-processing facilities in the Bituminous and Anthracite Coalfields where untreated and treated effluents were sampled in 2011.

42 Coal Mines or Refuse Facilities:
26 surface; 11 deep; 5 CRDA
28 % – no chemicals used (Ponds)
21 % – caustic soda (NaOH) used
40 % – lime (CaO; $Ca(OH)_2$) used
6 % – flocculent or oxidant used
4 % – limestone ($CaCO_3$) used

Field: flow, temperature, pH, redox potential (Eh), specific conductance (SC), dissolved oxygen (DOX), and alkalinity.

Laboratory: filtered and unfiltered samples analyzed for >70 constituents by ICP-MS, ICP-AES, IC, and other methods.

Split Samples: Actlabs, Ancaster, Ontario, CA

PaDEP Bureau of Laboratories, Harrisburg, PA

Relations among pH, Major Ions, Conductivity, and Total Dissolved Solids

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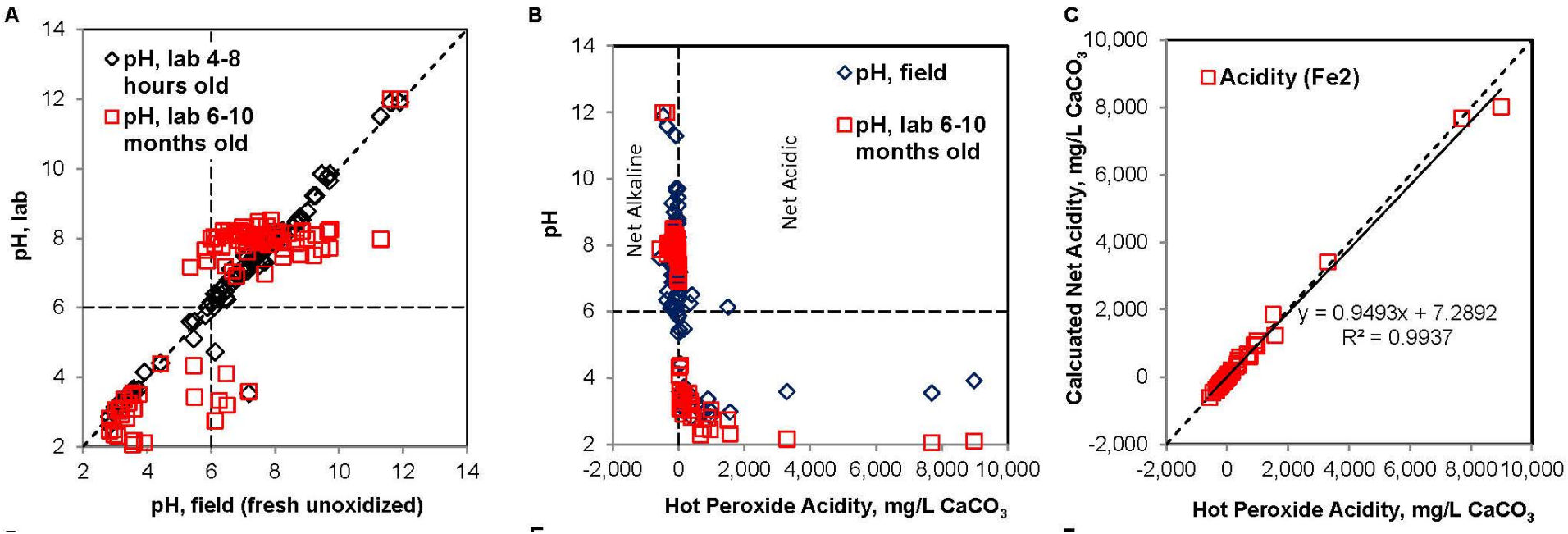
pH and Acidity (Untreated & Treated)



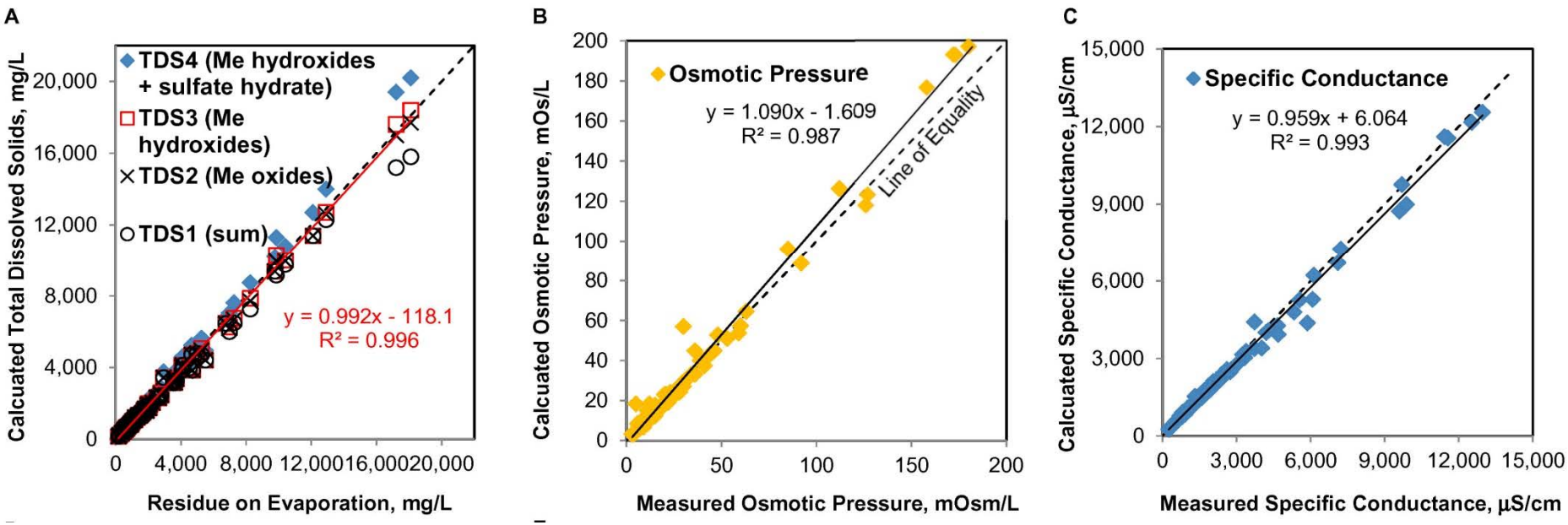
A. pH, fresh ≠ pH, lab (>8 hrs).

B. Hot Acidity > 0, pH < 6.

C. Hot Acidity = Net Acidity =

$$50\cdot(10^{(3-pH)} + 2\cdot C_{Fe}/55.85 + 2\cdot C_{Mn}/54.94 + 3\cdot C_{Al}/26.98) - \text{Alkalinity}$$

Major Ions, Specific Conductance, Dissolved Solids



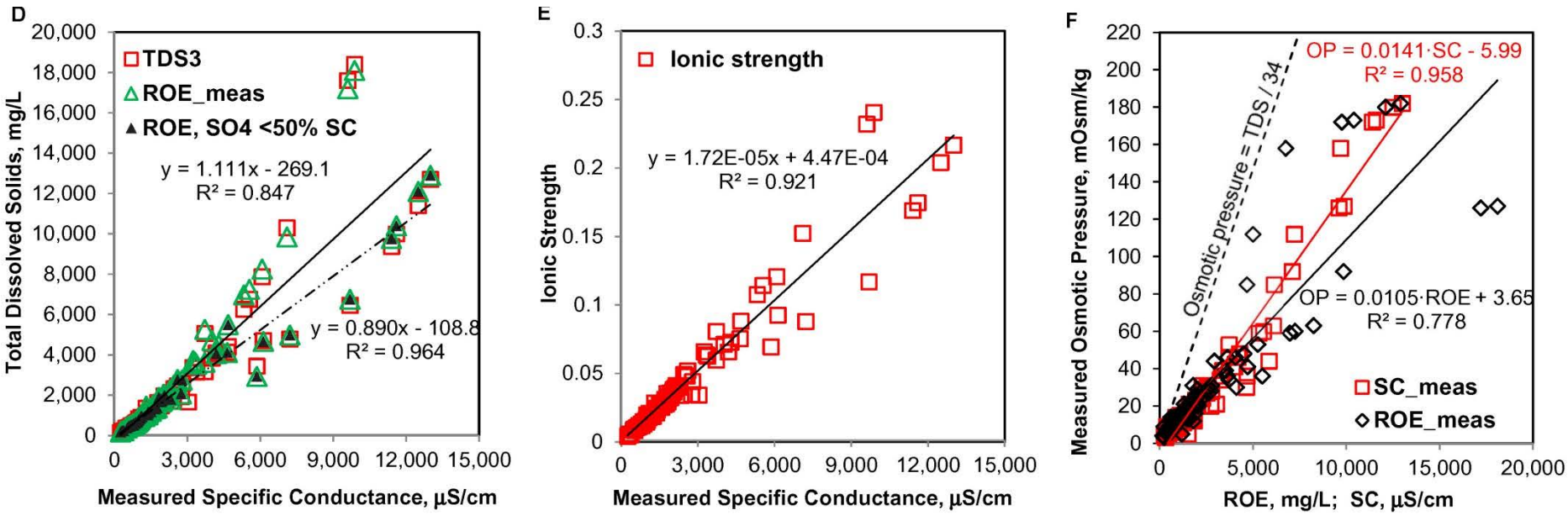
A. ROE = Total Dissolved Solids = Σ major ion concentrations (mg/L).

B. Osmotic Pressure = Σ major ion concentrations (mol/L).*

C. Conductivity = Σ ionic conductivities (µS/cm).*

* after speciation to account for ion complexation

Major Ions, Specific Conductance, Dissolved Solids



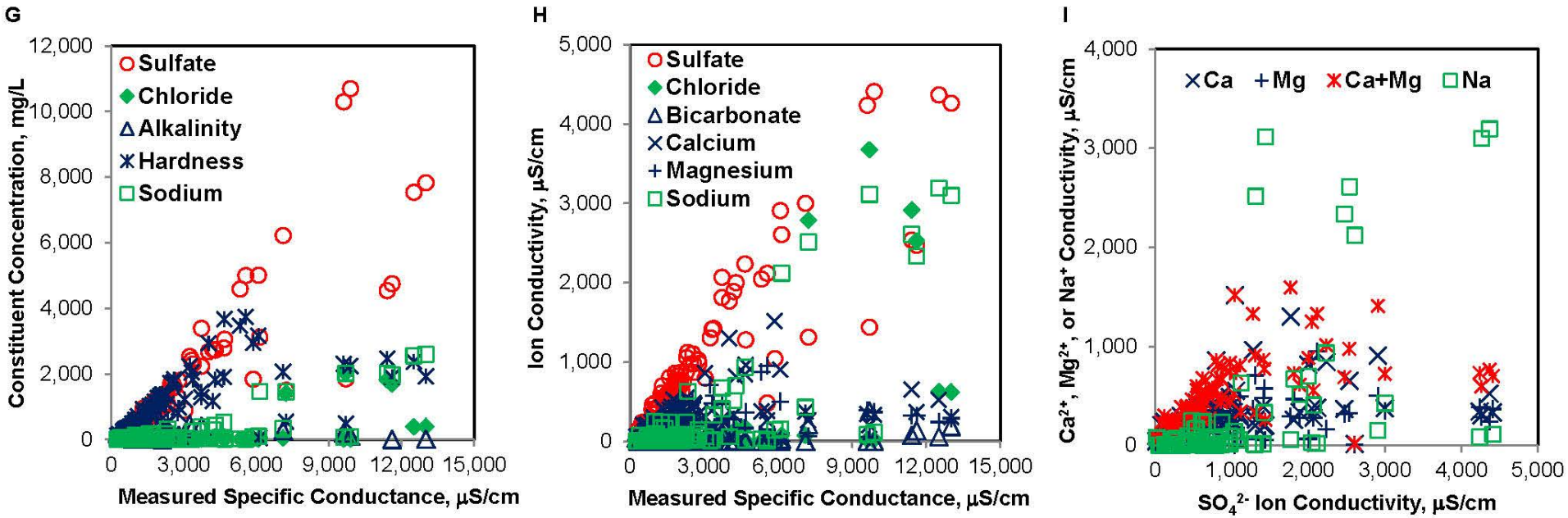
D. TDS = 0.89 to 1.11 × SC (greater slope for SO_4 dominant).

E. Ionic strength = $1.72 \times 10^{-5} \times$ SC (greater slope for SO_4 dominant).

F. Osmotic pressure = 0.0105 × TDS or 0.0141 × SC.*

* 50 mOsmol/kg ~ 5,000 mg/L ~ 4,000 µS/cm

Major Ions, Specific Conductance, Dissolved Solids

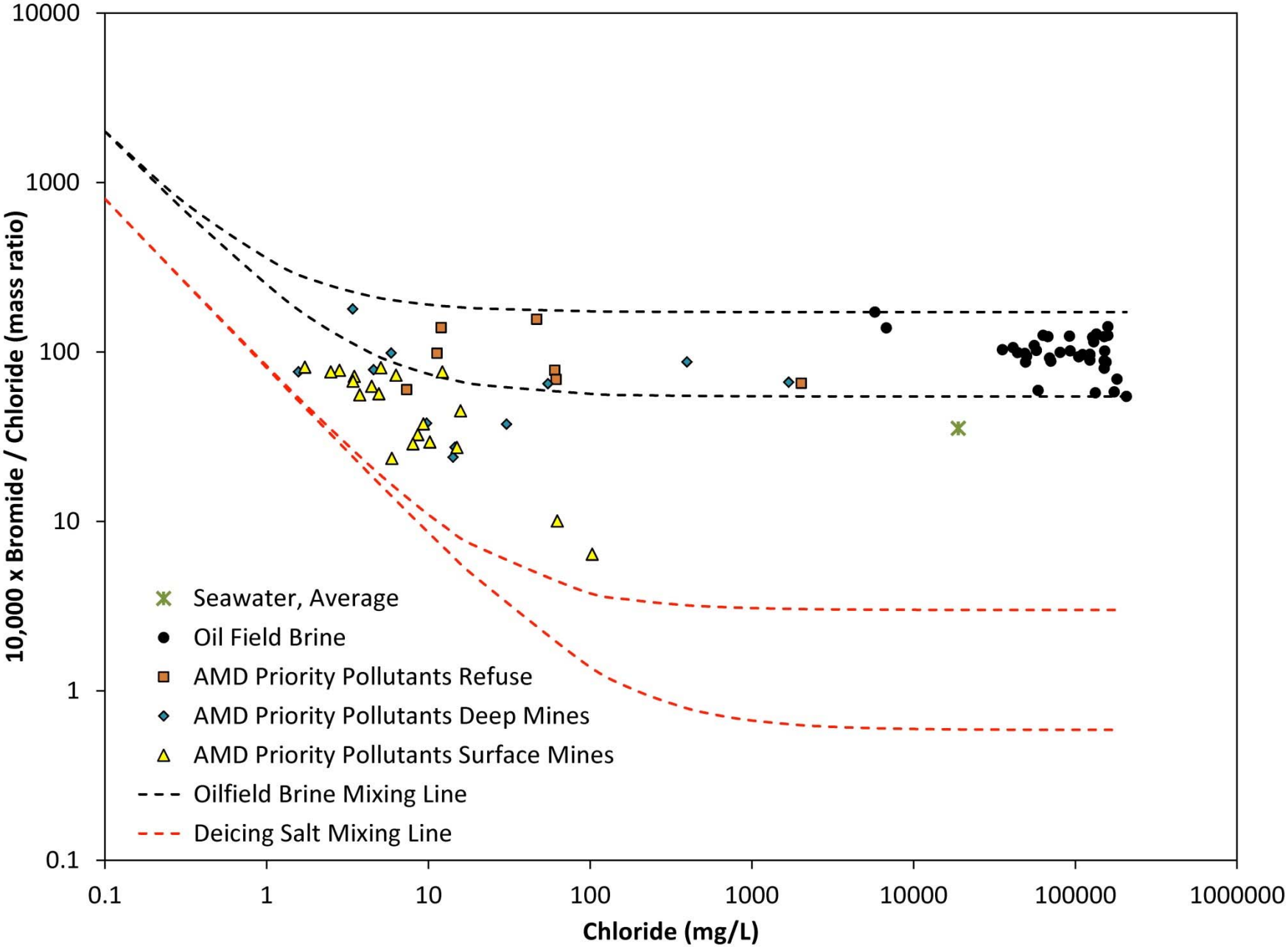


G. SC is strongly correlated with SO_4 and hardness (2.5·Ca + 4.1·Mg).

H. Ionic SC contributions are dominated by SO_4, Cl, Ca, Mg, and Na.

I. High ionic-strength waters are Ca-Mg-SO_4, Na-SO_4, and Na-SO_4-Cl type as indicated by ionic conductivities.

Chloride and Bromide in Deep Mine Effluents



Hydrochemical Correlations: Principal Components Analysis

Untreated Effluent (Influent)

Major Ions

Constituent Loadings:	pH PC1	TDS PC2	Salinity PC3	TIC PC4	Oxygen PC5
Cobalt (Co)	92 *	6	-14	-10	-7
Zinc (Zn)	90 *	22	-10	-14	-4
Nickel (Ni)	88 *	27	3	0	3
Manganese (Mn)	85 *	23	-16	-6	-13
Acidity, hot (ACIDH)	73 *	13	5	-55 *	6
Iron (Fe)	72 *	2	16	-10	-50 *
Uranium (U)	68 *	24	17	41 *	19
Redox potential (Eh)	66 *	-3	-14	-19	53 *
Titanium (Ti)	66 *	22	28	-23	-18
Aluminum (Al)	65 *	22	-2	-41 *	10
Alkalinity (ALK)	-66 *	1	7	64 *	-24
pH, fresh (pHF)	-92 *	12	6	-2	14
Residue on evaporation (ROE)	23	92 *	27	2	-8
Sulfate (SO4)	27	91 *	23	-6	-6
Specific conductance (SC25)	16	90 *	32	3	-8
Osmotic pressure (OSMP)	13	88 *	29	10	-10
Calcium (Ca)	0	81 *	10	9	-23
Magnesium (Mg)	49 *	73 *	-12	9	4
Potassium (K)	9	65 *	40 *	22	2
Strontium (Sr)	-8	51 *	35	22	-41 *
Barium (Ba)	-7	-63 *	24	17	-31
Chloride (Cl)	-6	17	84 *	-2	-3
Bromide (Br)	0	33	80 *	-5	3
Sodium (Na)	-16	49 *	69 *	-7	3
Total inorganic carbon (TIC)	-14	1	-5	82 *	-32
Total organic carbon (TOC)	-10	29	-4	64 *	17
Dissolved oxygen (DOX)	-10	-21	23	-4	71 *
Arsenic (As)	46 *	-4	34	14	-54 *
Eigenvalue:	9.803	6.205	2.415	2.002	1.245
Cumulative Percent Variance Explained:	35.01	57.17	65.79	72.94	77.39

Hydrochemical Correlations: Principal Components Analysis

Untreated Effluent (Influent)

Constituent Loadings:	pH PC1	TDS PC2	Salinity PC3	TIC PC4	Oxygen PC5
Significant Spearman Correlations ($p < 0.001$):					
Cadmium (Cd)	84	-	-	-	-
Beryllium (Be)	81	-	-	-	-
Acidity, net (ACIDN)	69	-	-	-50	-
Phenols, total (PHENOL)	66	-	-	-	-
Lead (Pb)	65	-	-	-	-
Thorium (Th)	63	-	-	-	-
Copper (Cu)	59	-	-	-	-
Chromium (Cr)	56	-	-	-	-
Chemical oxygen demand (COD)	53	36	-	-	-
Zirconium (Zr)	52	-	-	-	-
Thallium (Tl)	51	-	-	-38	-
Selenium (Se)	43	-	-	-	-
pH, oxidized (pHLox)	-74	-	-	-	-
Total dissolved solids (TDS3)	-	92	-	-	-
Hardness (HRD)	-	90	-	-	-
Temperature (TEMPC)	-	36	-	-	-
Fluoride (F)	-	34	-	-	-
Ammonia (NH3N)	-	-	44	-	-46
Molybdenum (Mo)	-	-	44	-	-

Constituents above were excluded from the PCA model (redundant parameter or substantial nondetects):

- ✓ Priority pollutant metals and phenols are correlated with PCA1.
- ✓ Hardness and TDS are correlated with PCA2.

Effects of Treatment on Priority Pollutants

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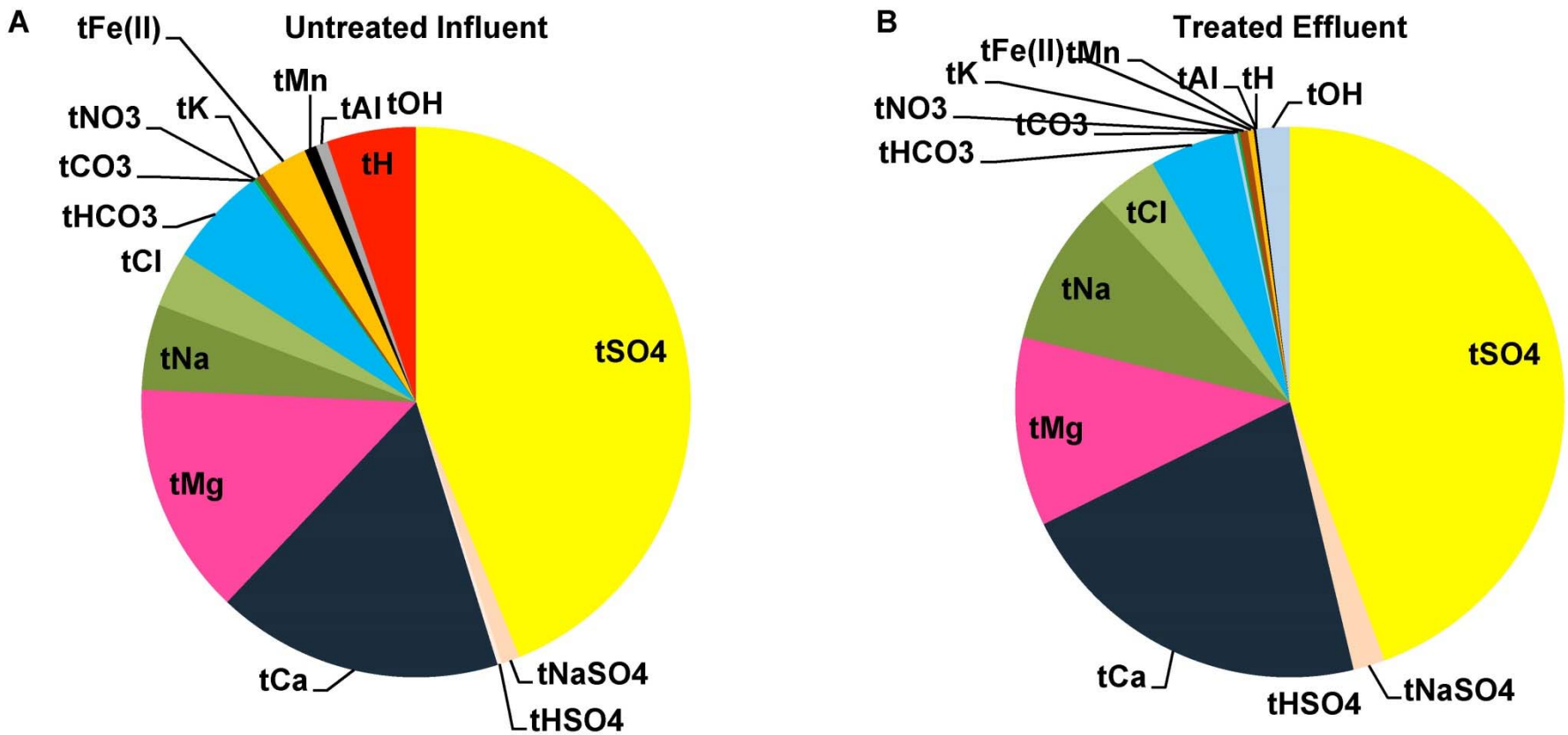
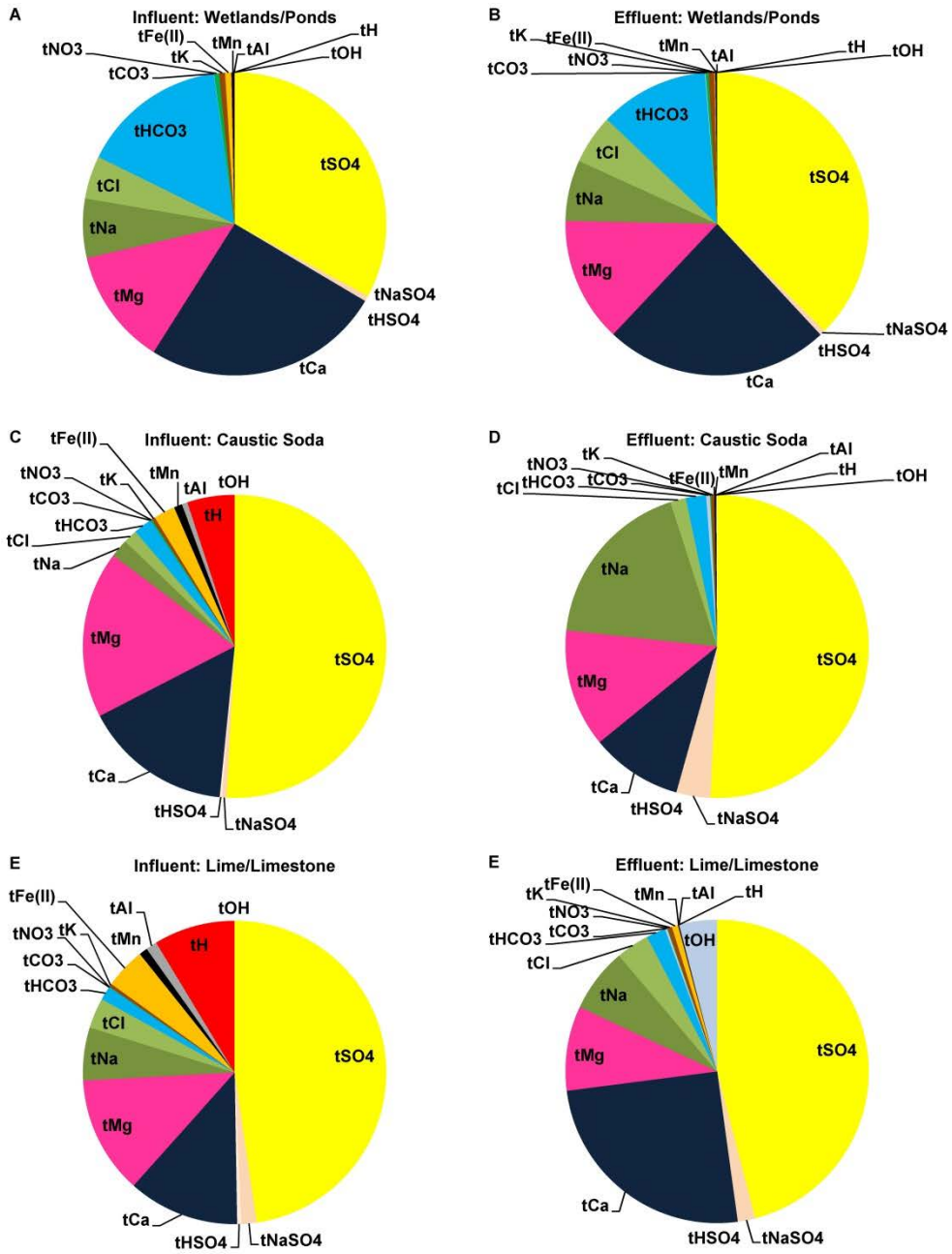
pH, Major Ions, Dissolved Solids, Specific Conductance



Treatment replaces conductivity contributions by H^+, Fe^{2+}, Mn^{2+}, Al^{3+} with OH^-, Na^+, Ca^{2+}. Conductivity contribution is indicated by decimal fraction of conductance from individual ions, or “transport number” (McCleskey et al., 2012. Geochim Cosmochim Acta 77:369–382).

pH, Major Ions, Dissolved Solids, Specific Conductance



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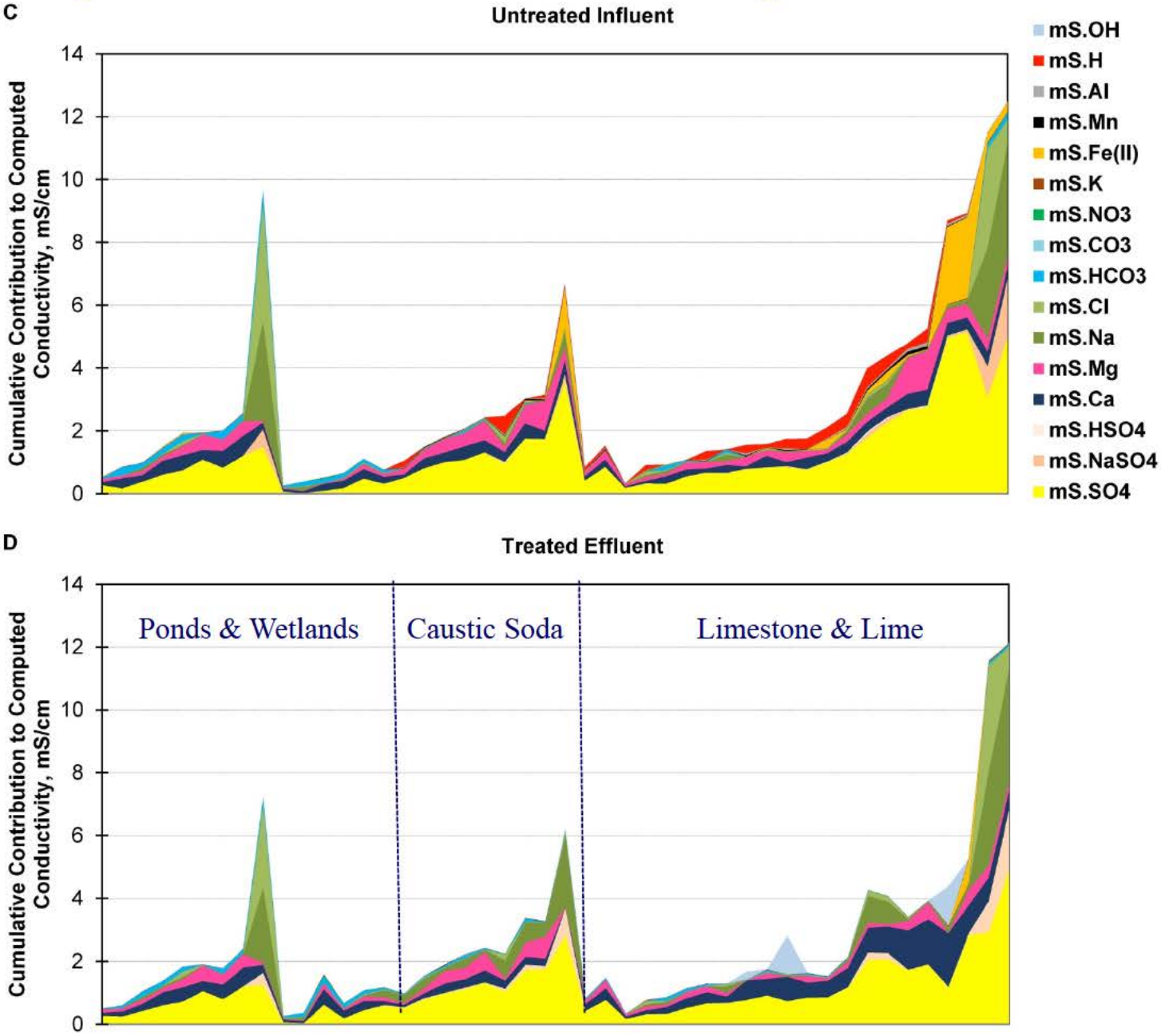
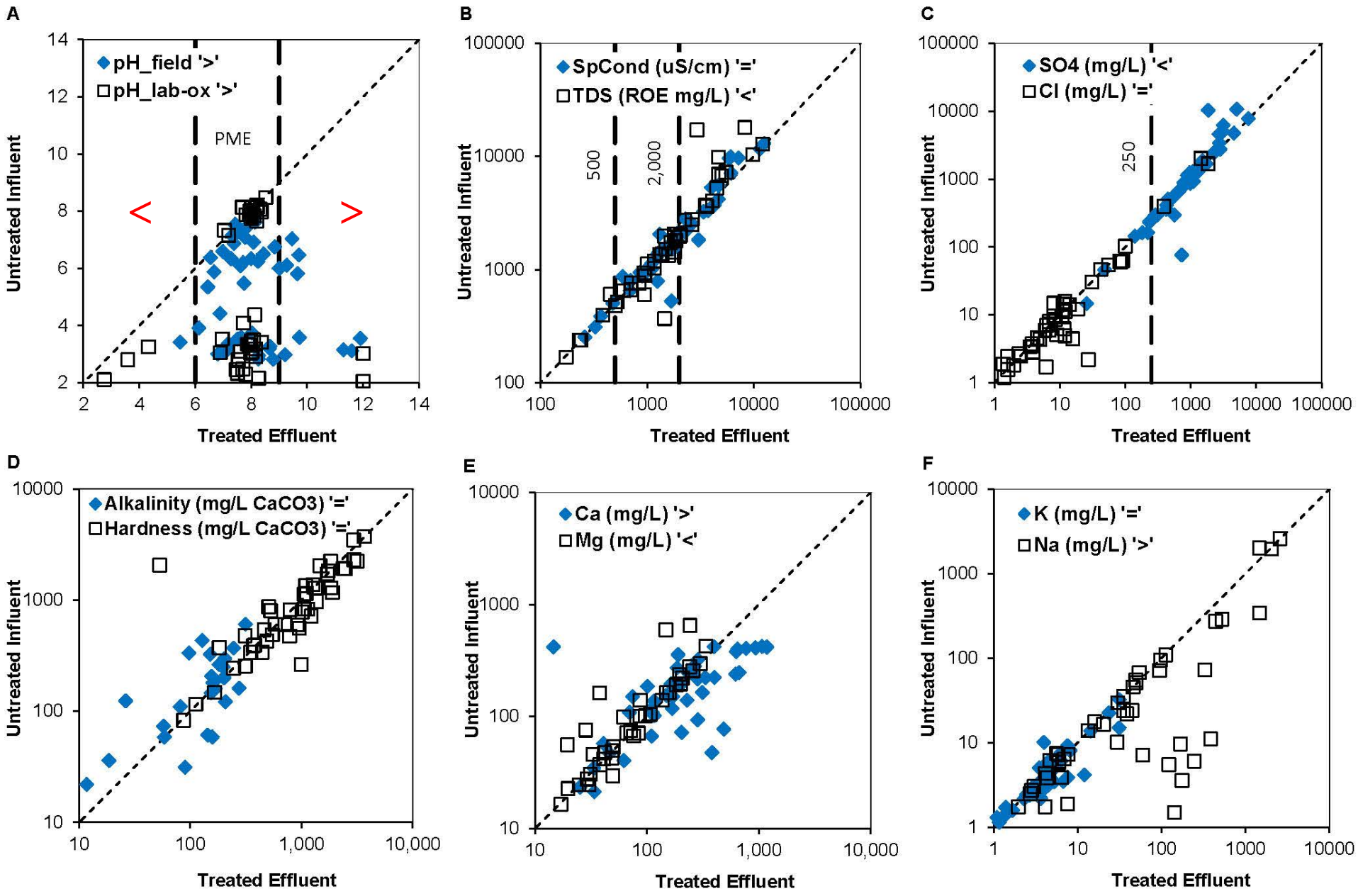


Effect of Treatment on pH and Solute Concentrations



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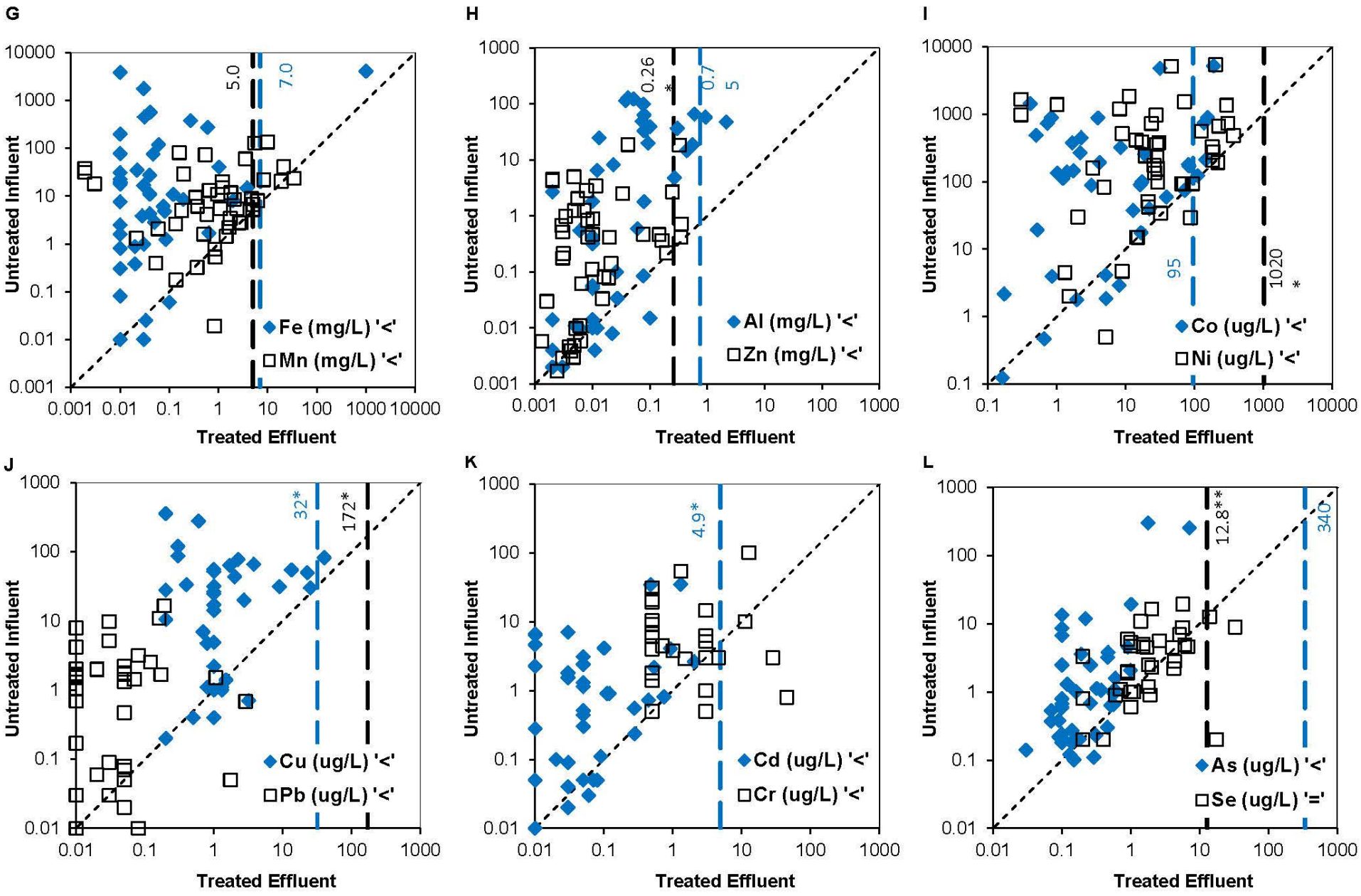

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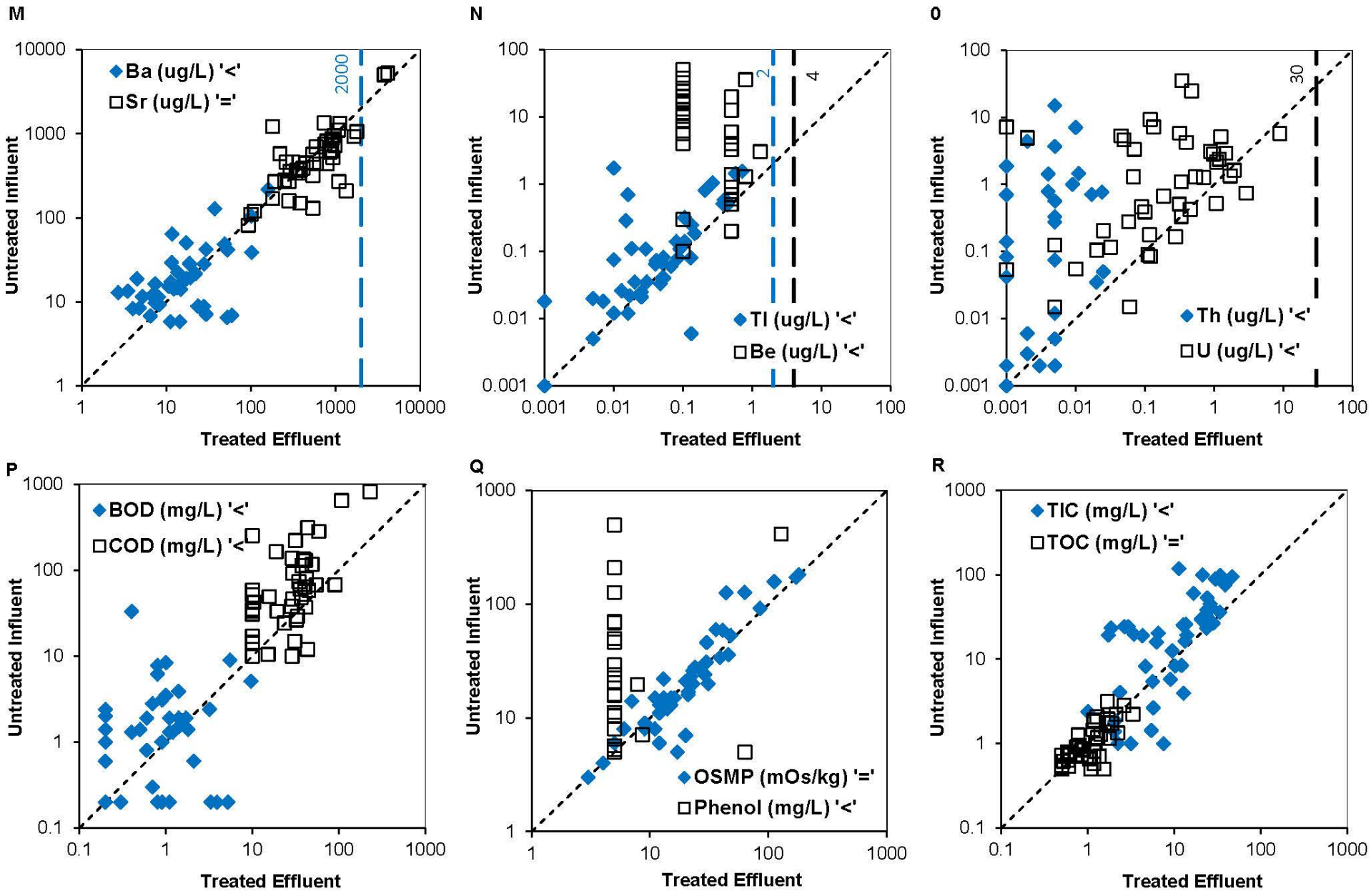
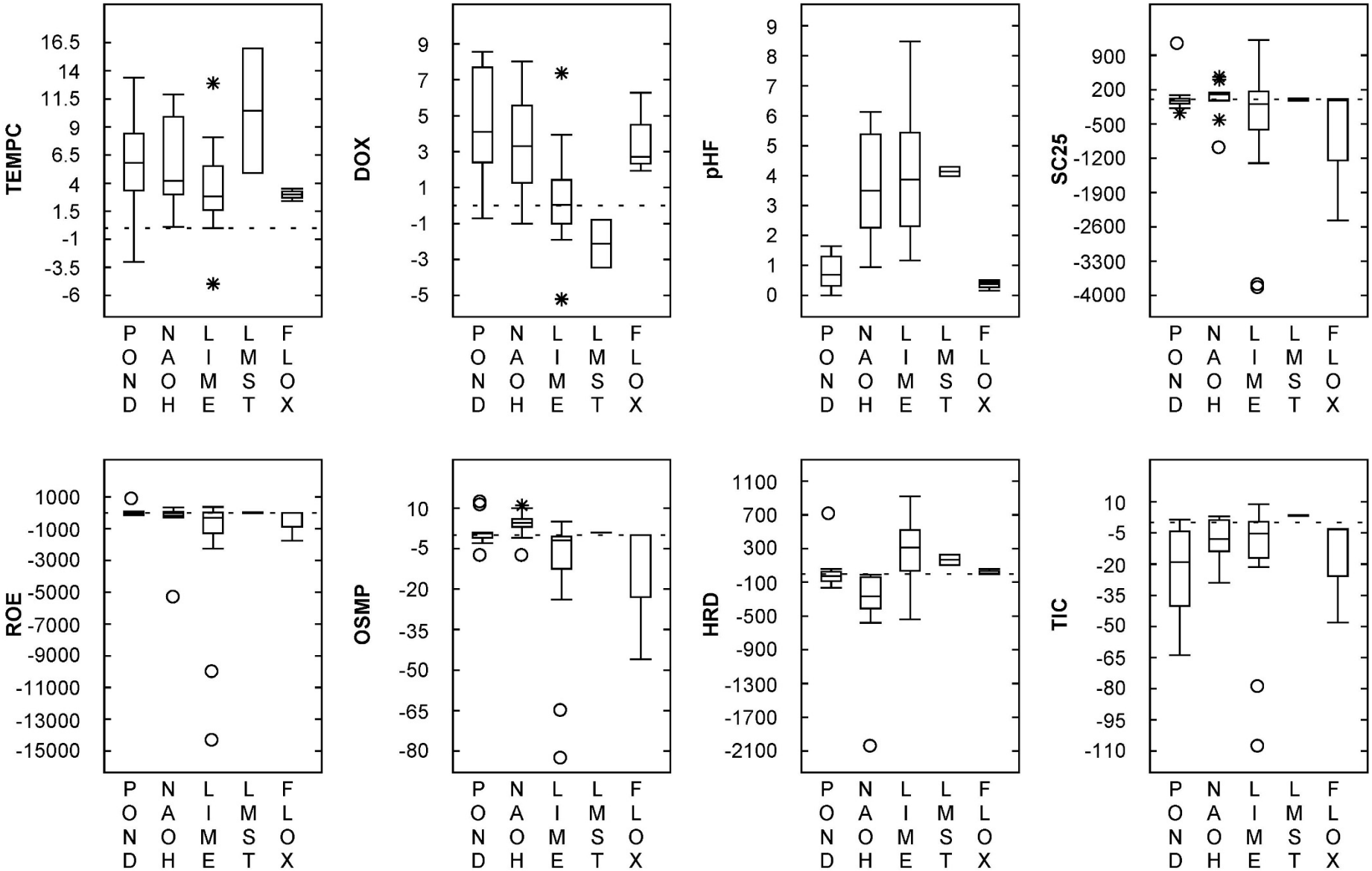


Effect of Treatment Type on pH and Solute Concentrations



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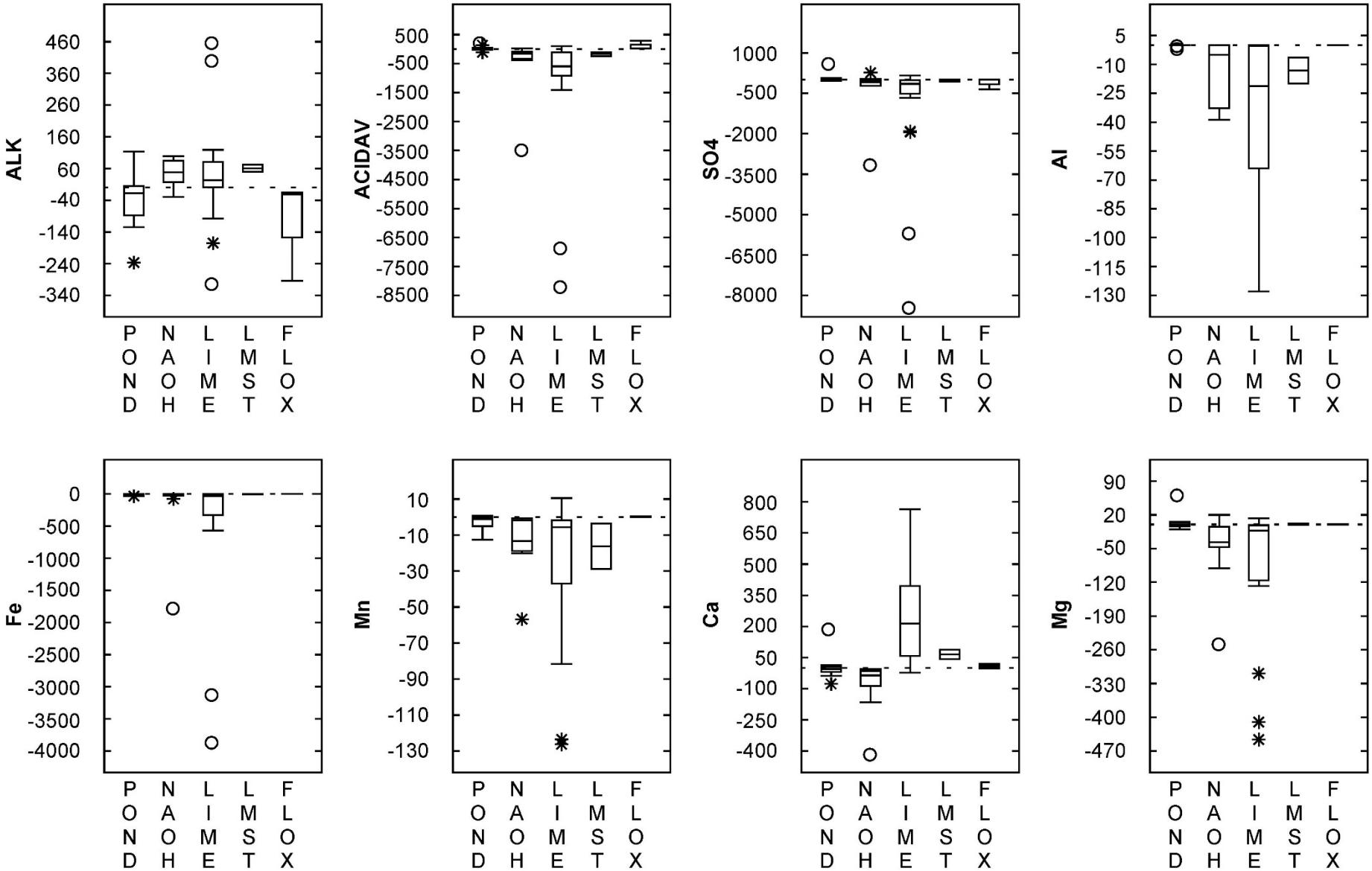

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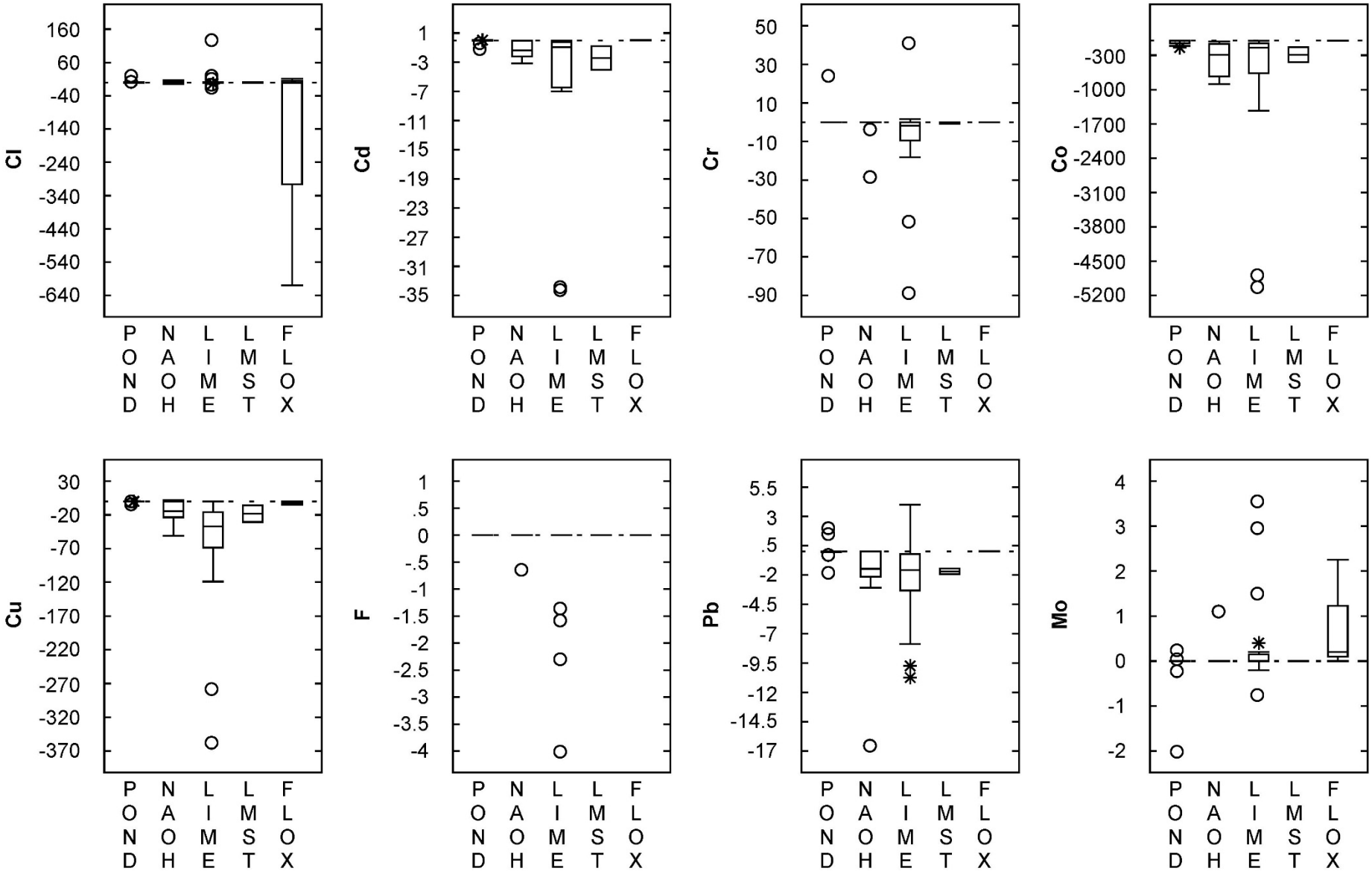

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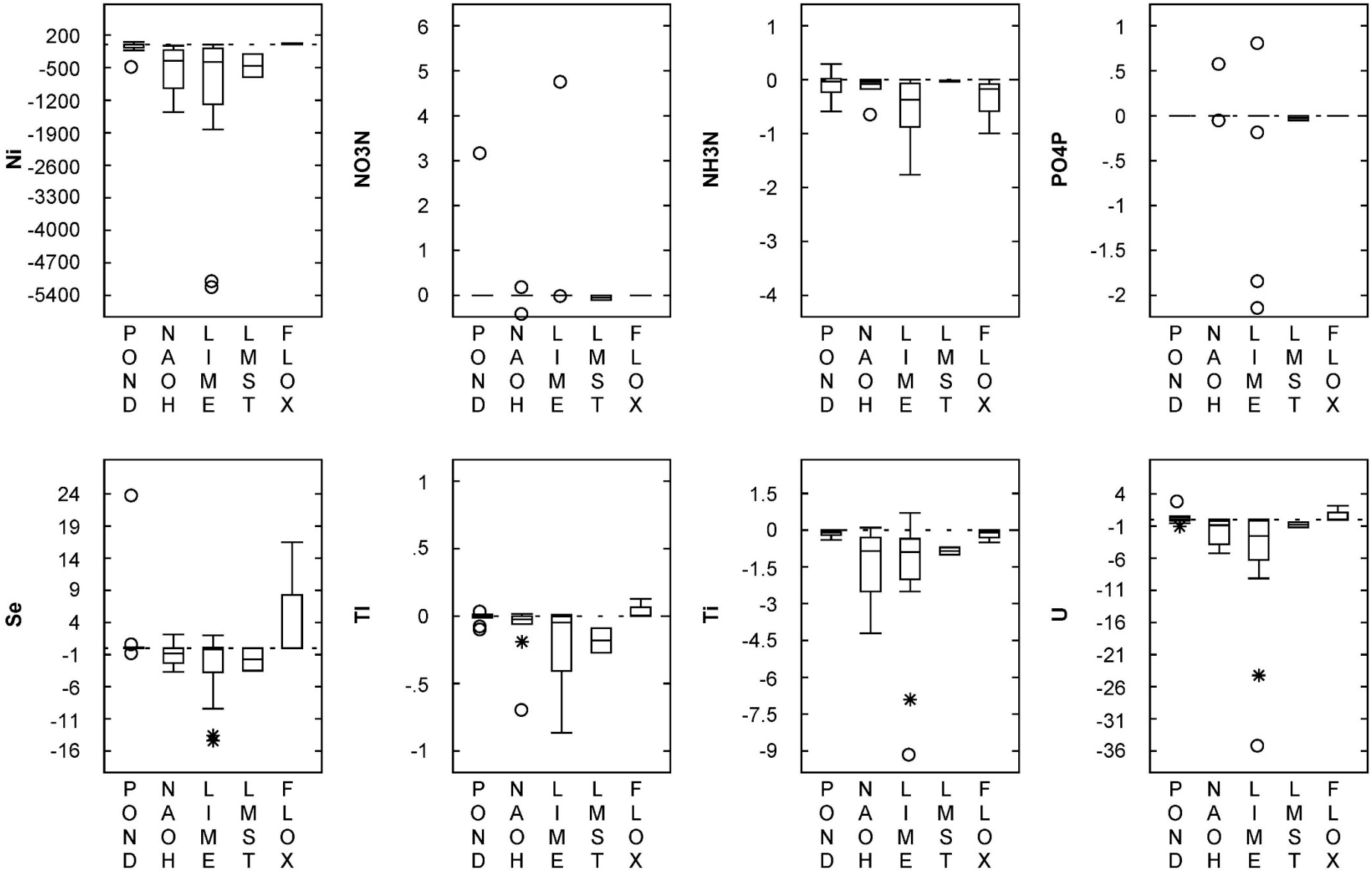
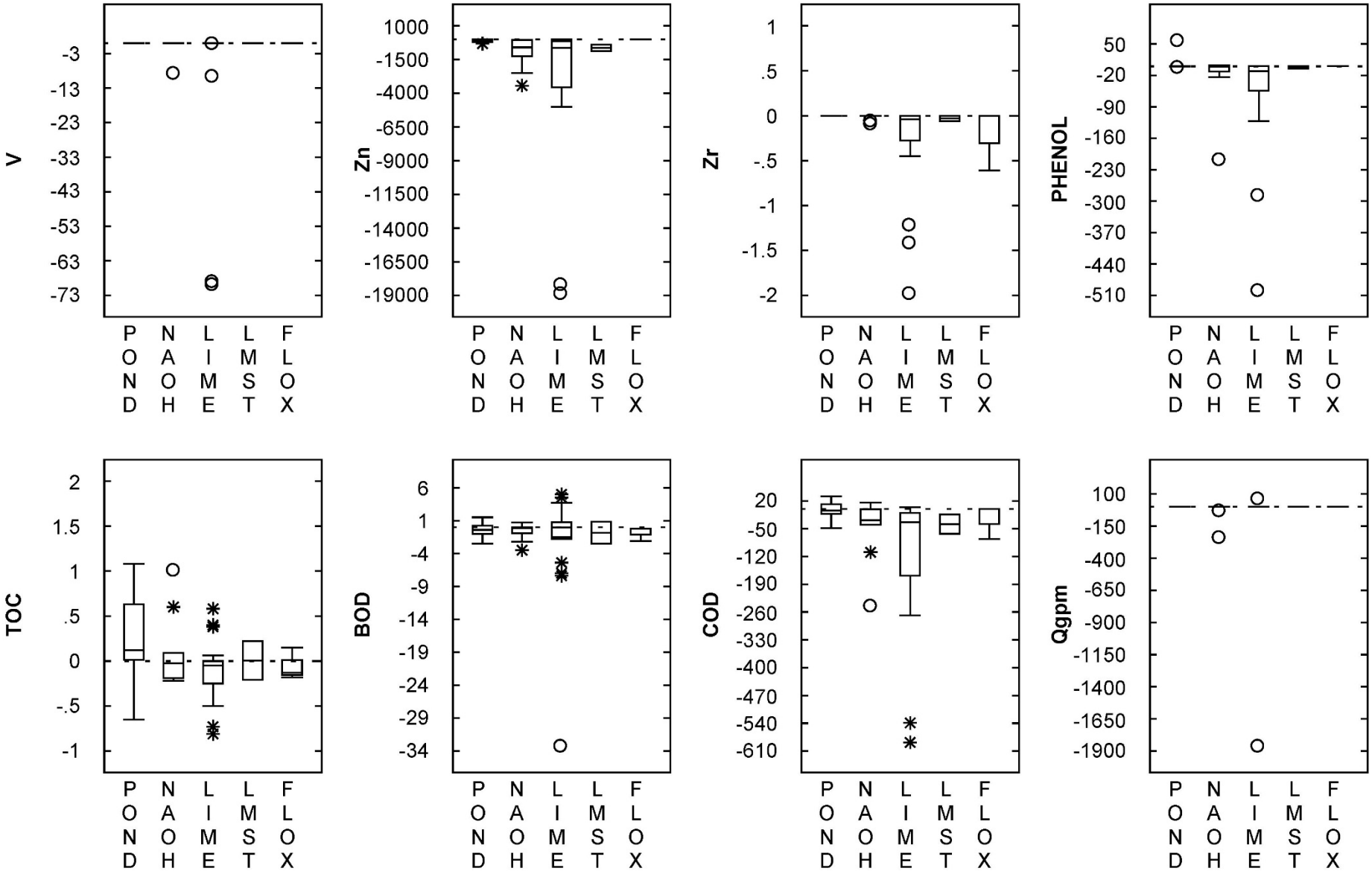


Effect of Treatment Type on pH and Solute Concentrations



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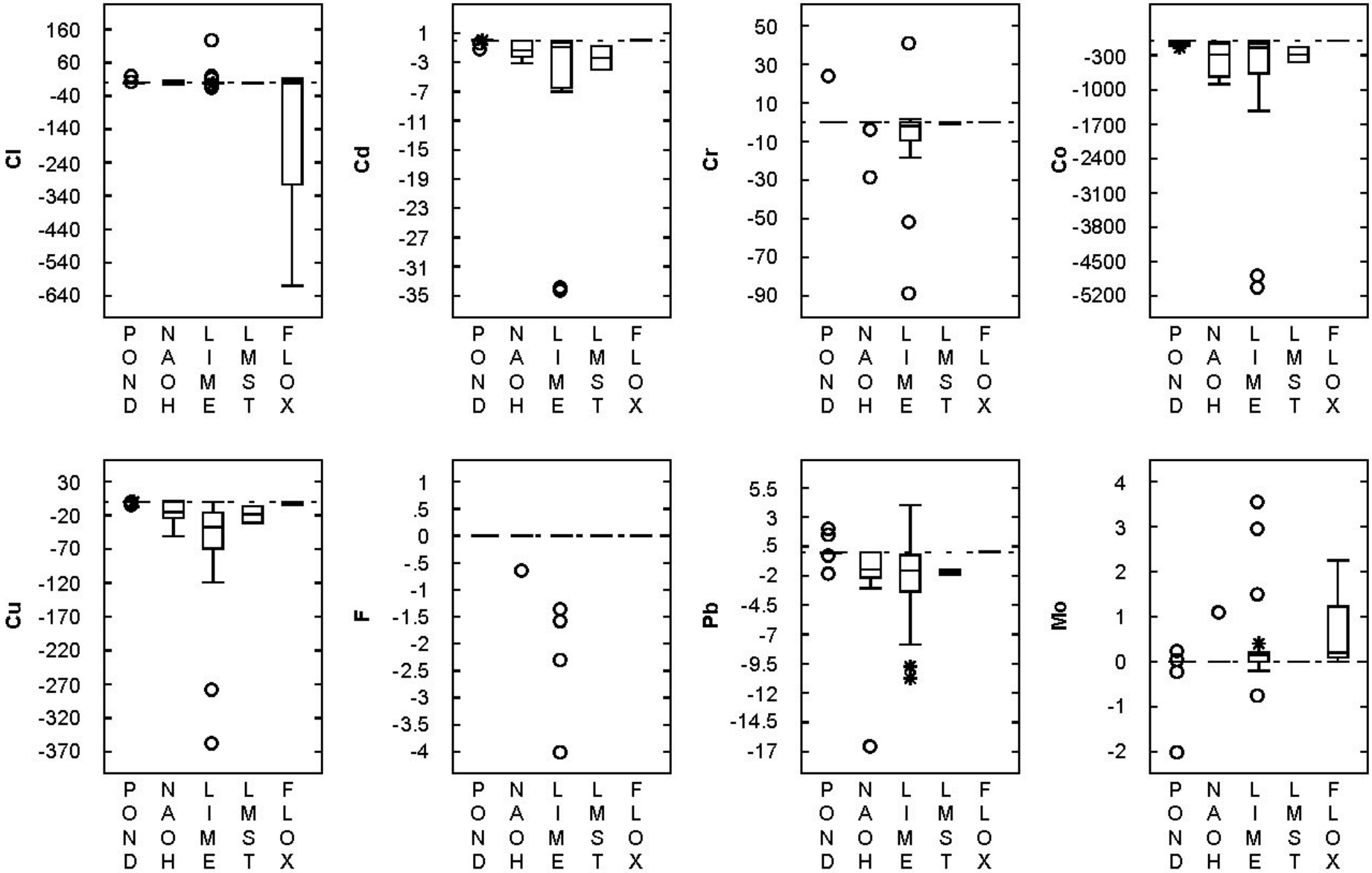

Implications for Aquatic and Terrestrial Organisms

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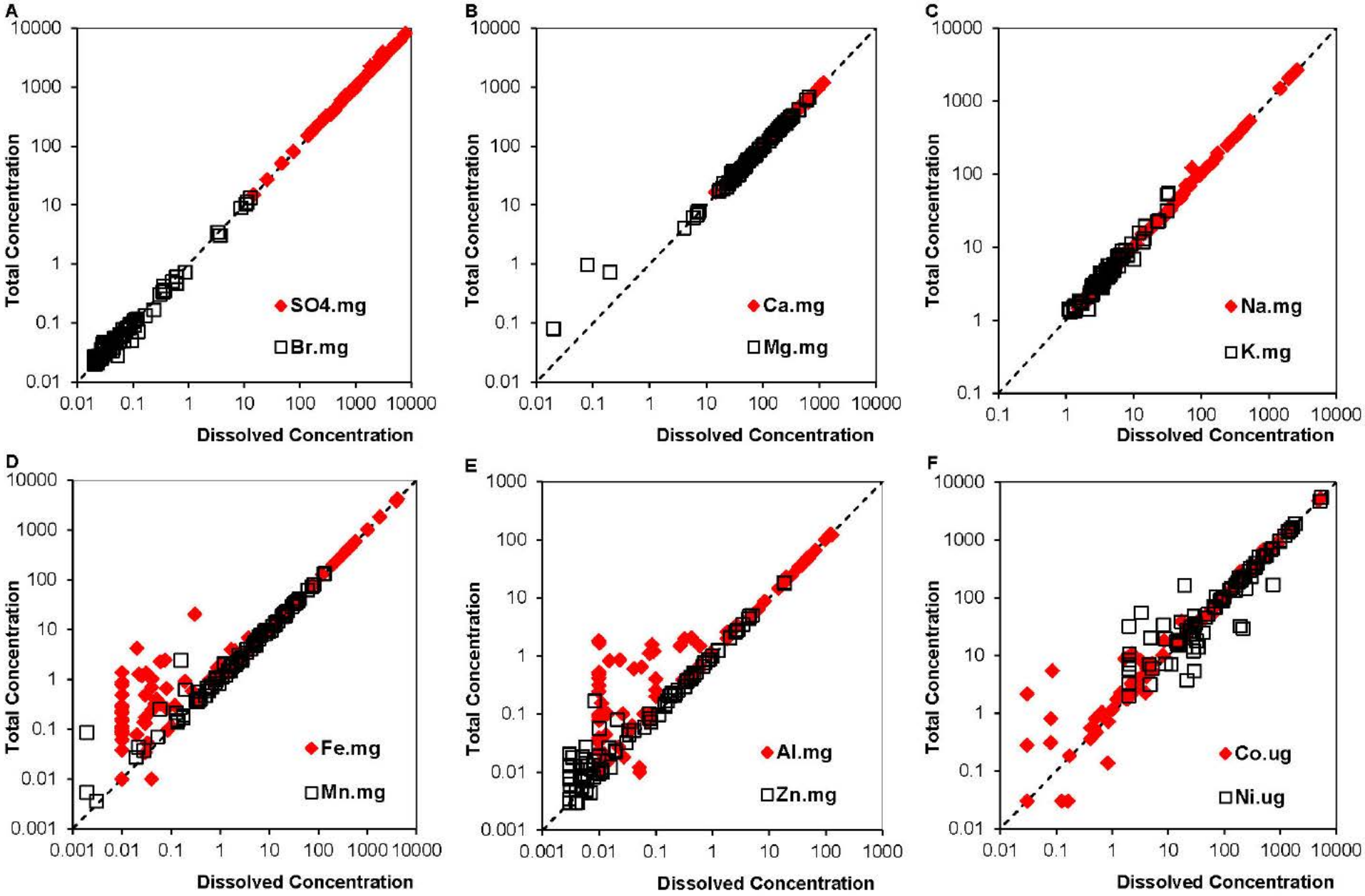
Dissolved Concentration ≤ Total Concentration



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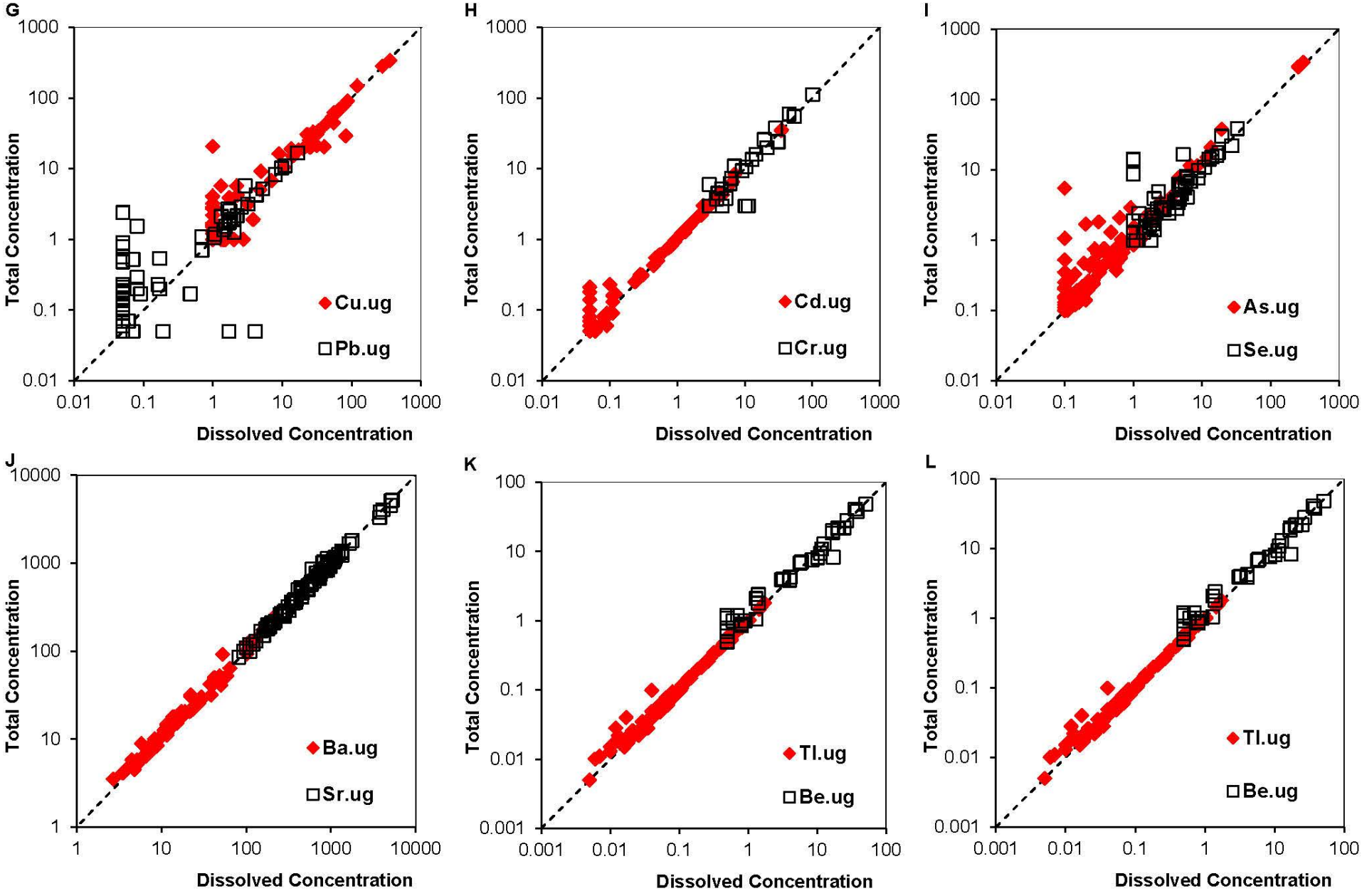
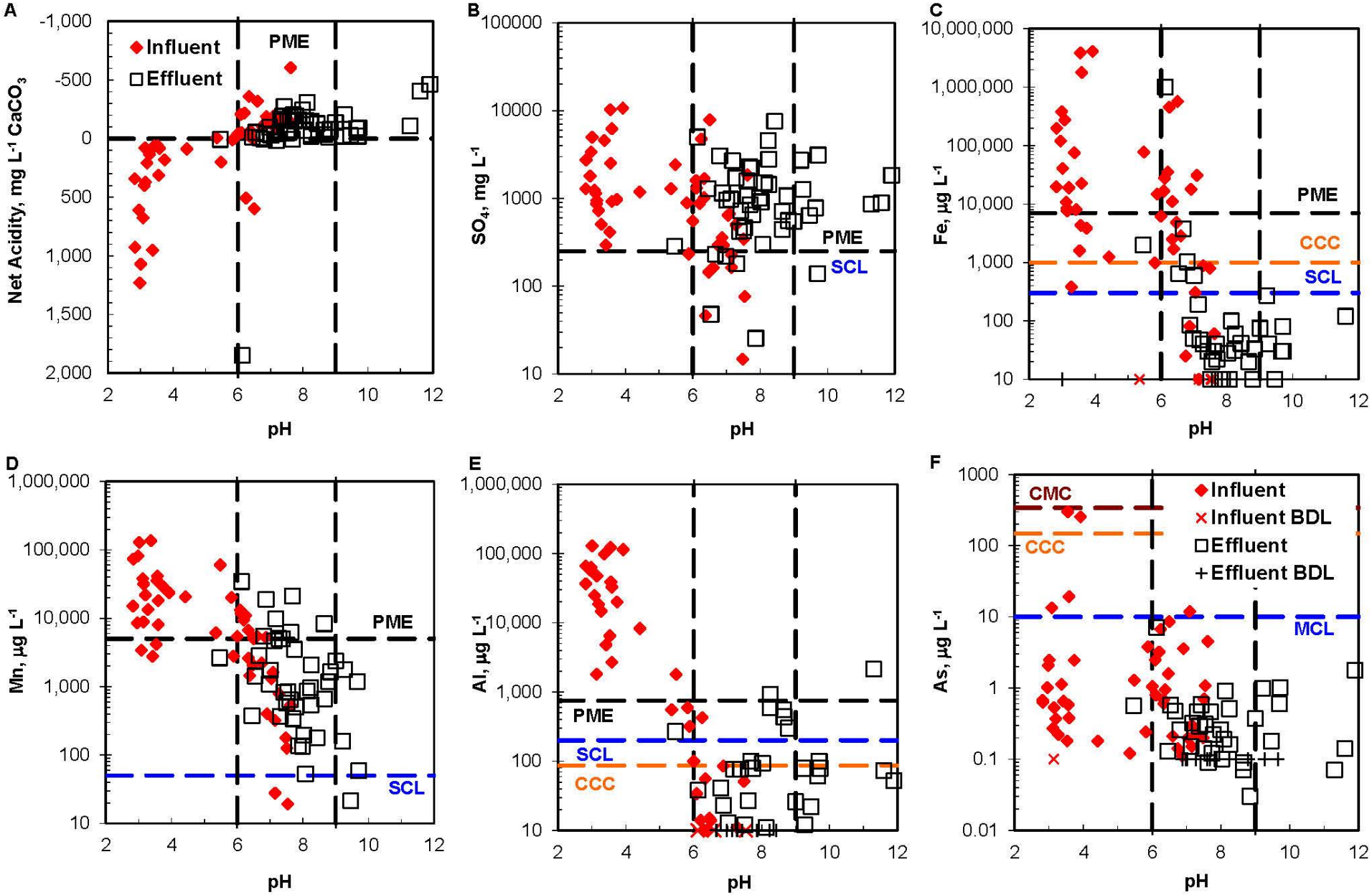


Concentrations Decrease with Increased pH (treatment)



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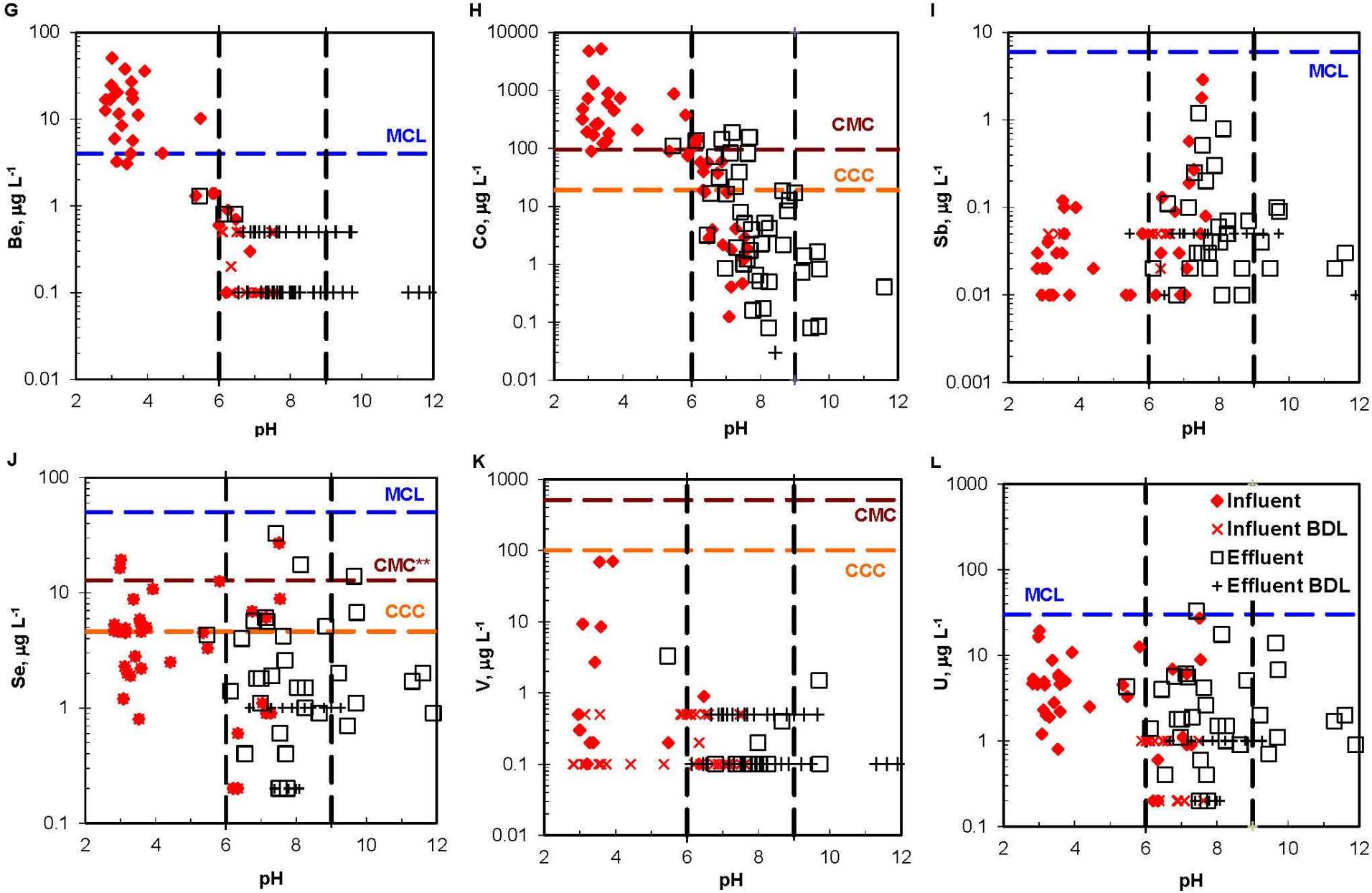

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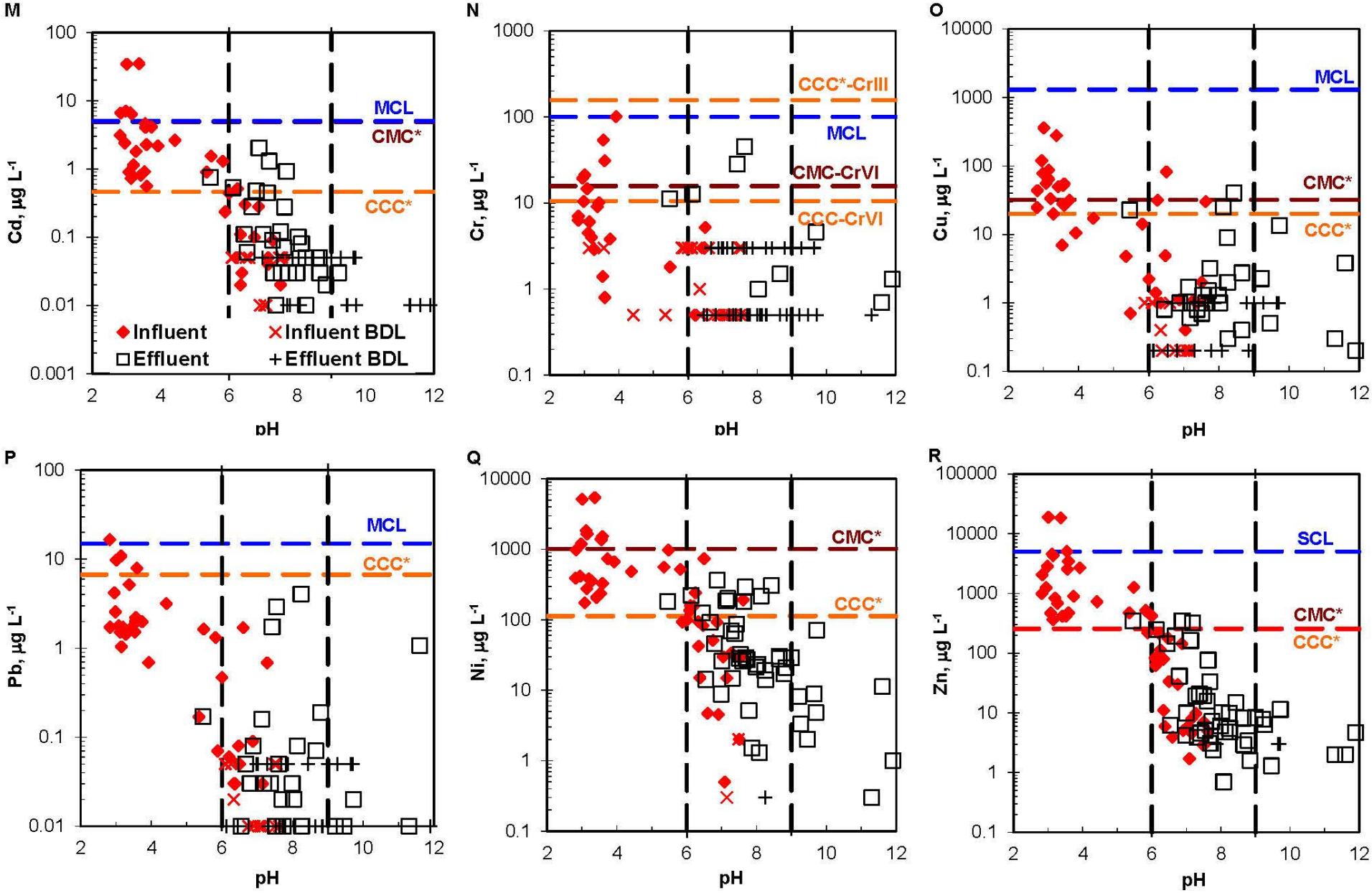
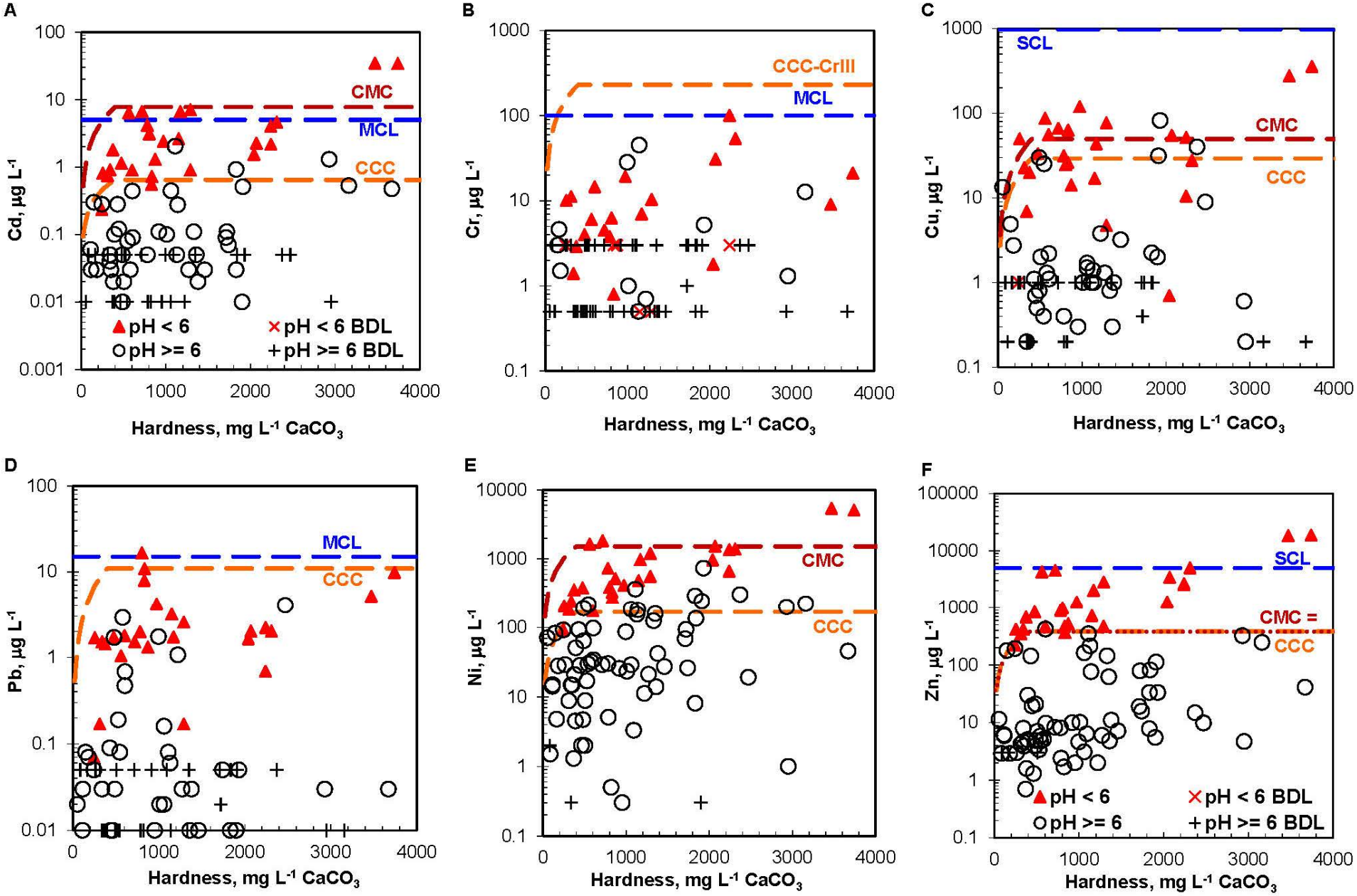


Metal* Toxicity Decreases with Hardness

$$Nickel = (Hardness)^{0.846} * 1.057$$

*Metals: Cd, Cr, Cu, Pb, Ni, Zn

Toxic Effects Decrease with Increased Hardness



Solubility and Sorption of Priority Pollutants

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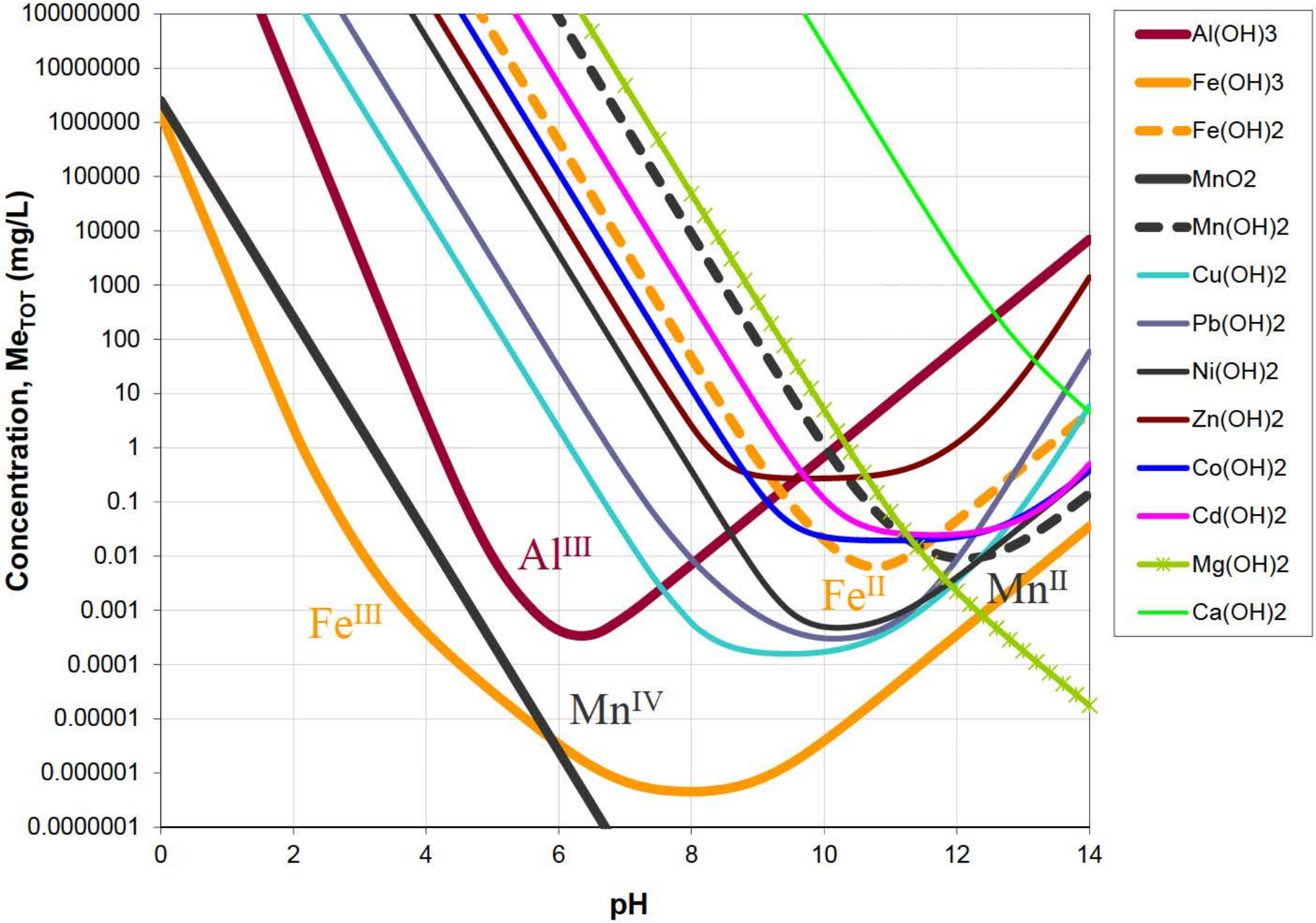
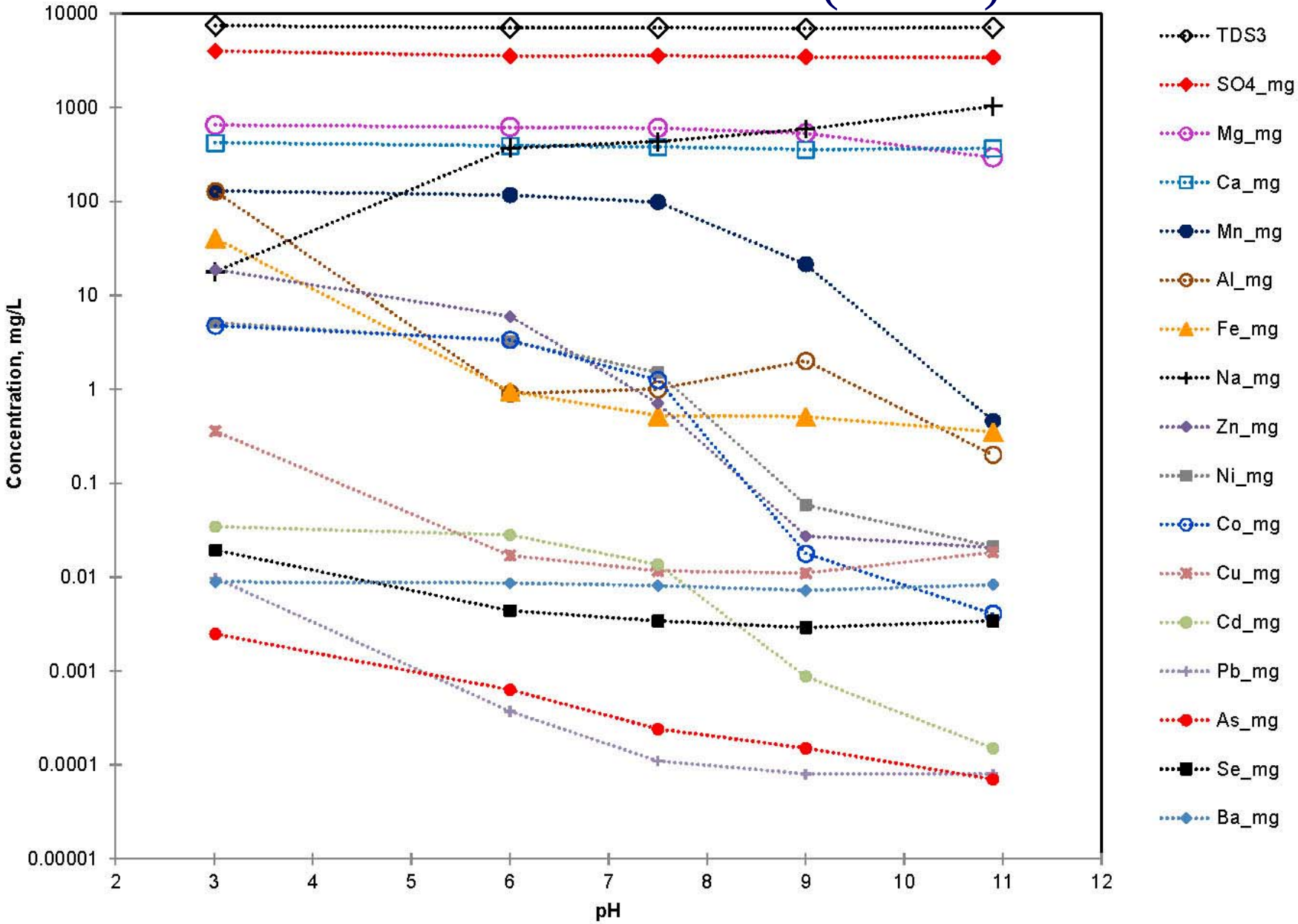
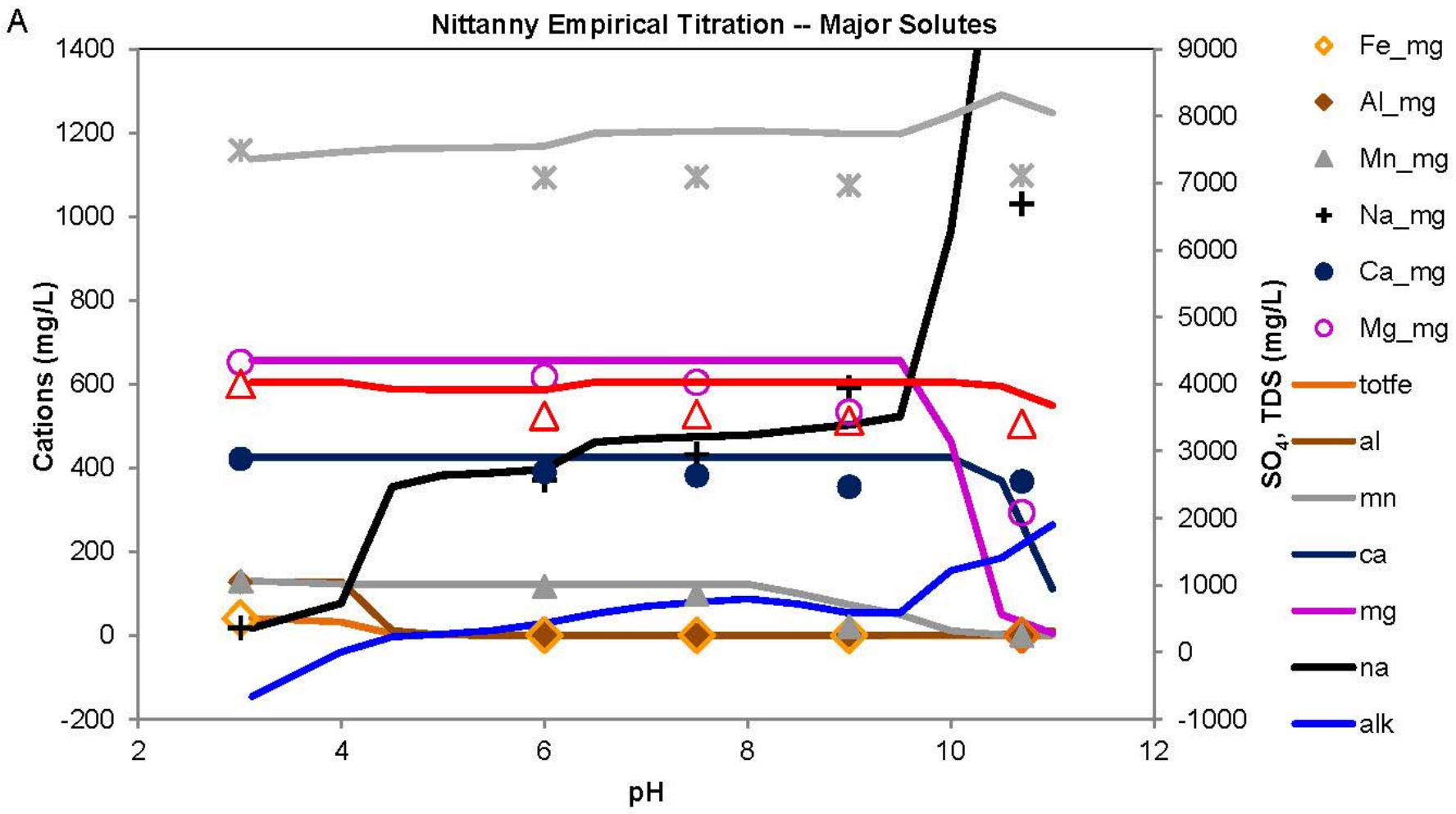
Solubilities of Metal Hydroxides



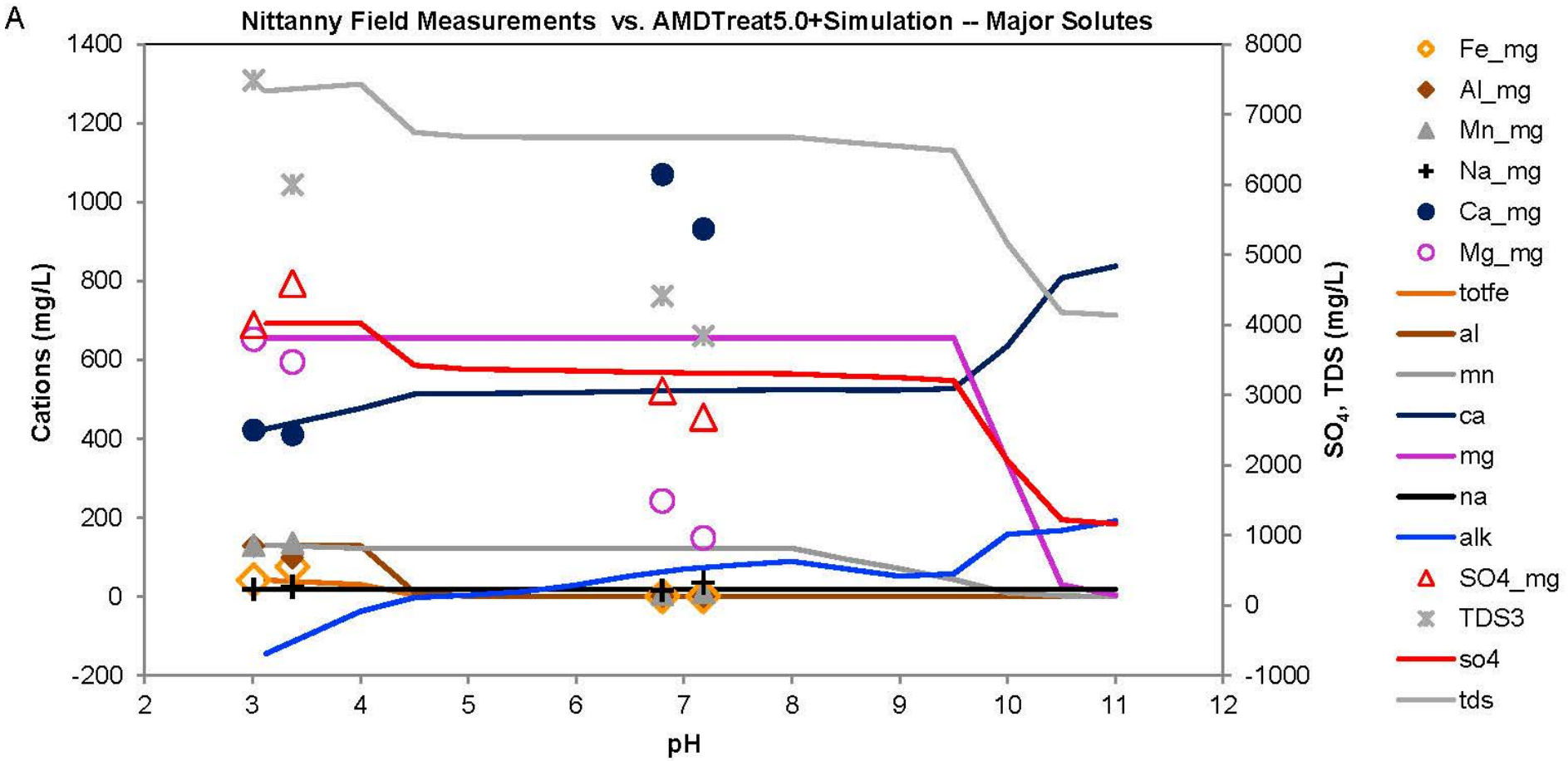
Changes in pH and Solutes during Treatment
Field Titration Results (NaOH)



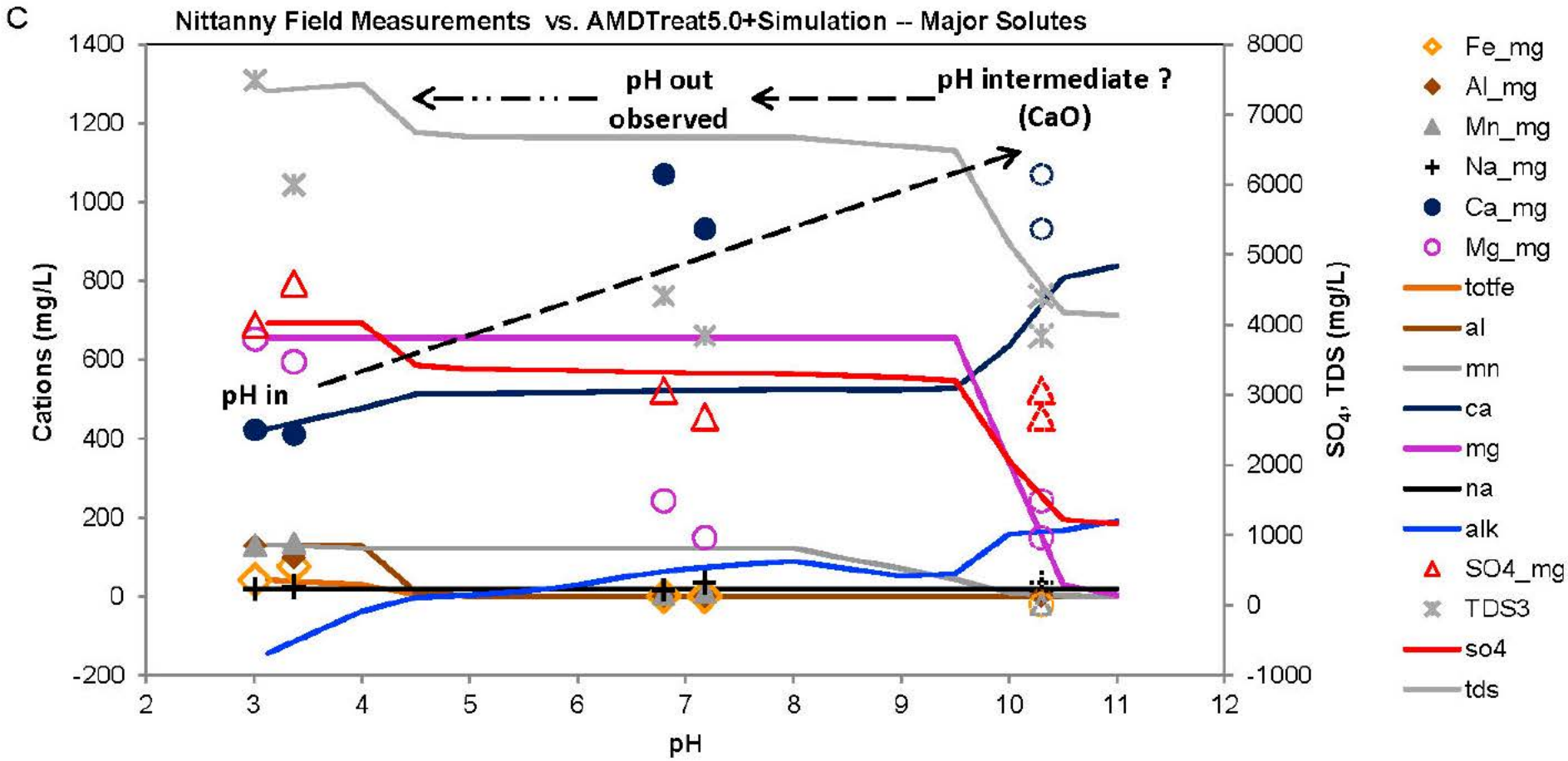
Changes in pH and Solutes during Treatment
Field Titration Results (NaOH) – AMDTreat 5.0+



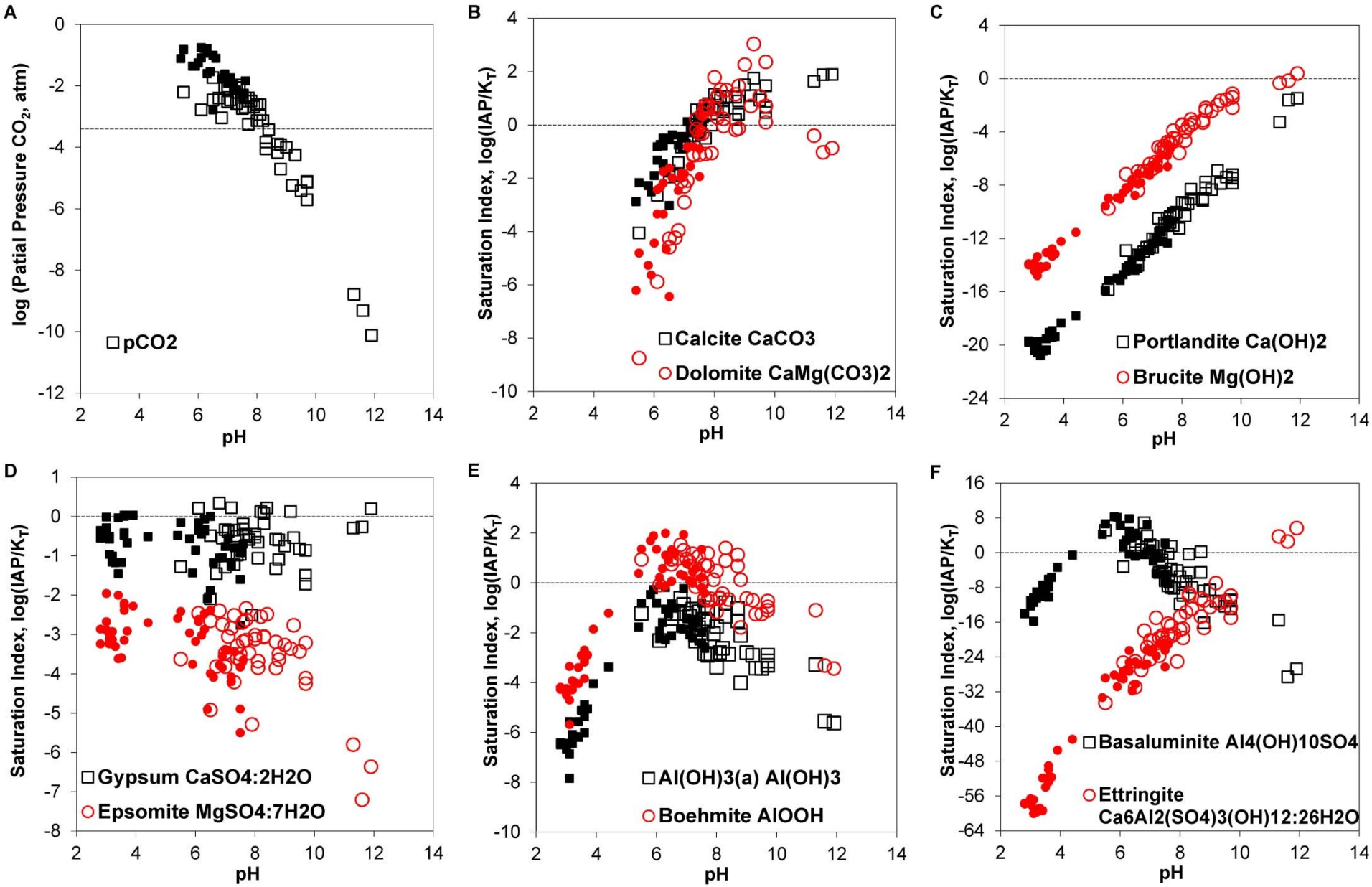
Changes in pH and Solutes during Treatment
Field Sampling Results (Lime) – AMDTreat 5.0+



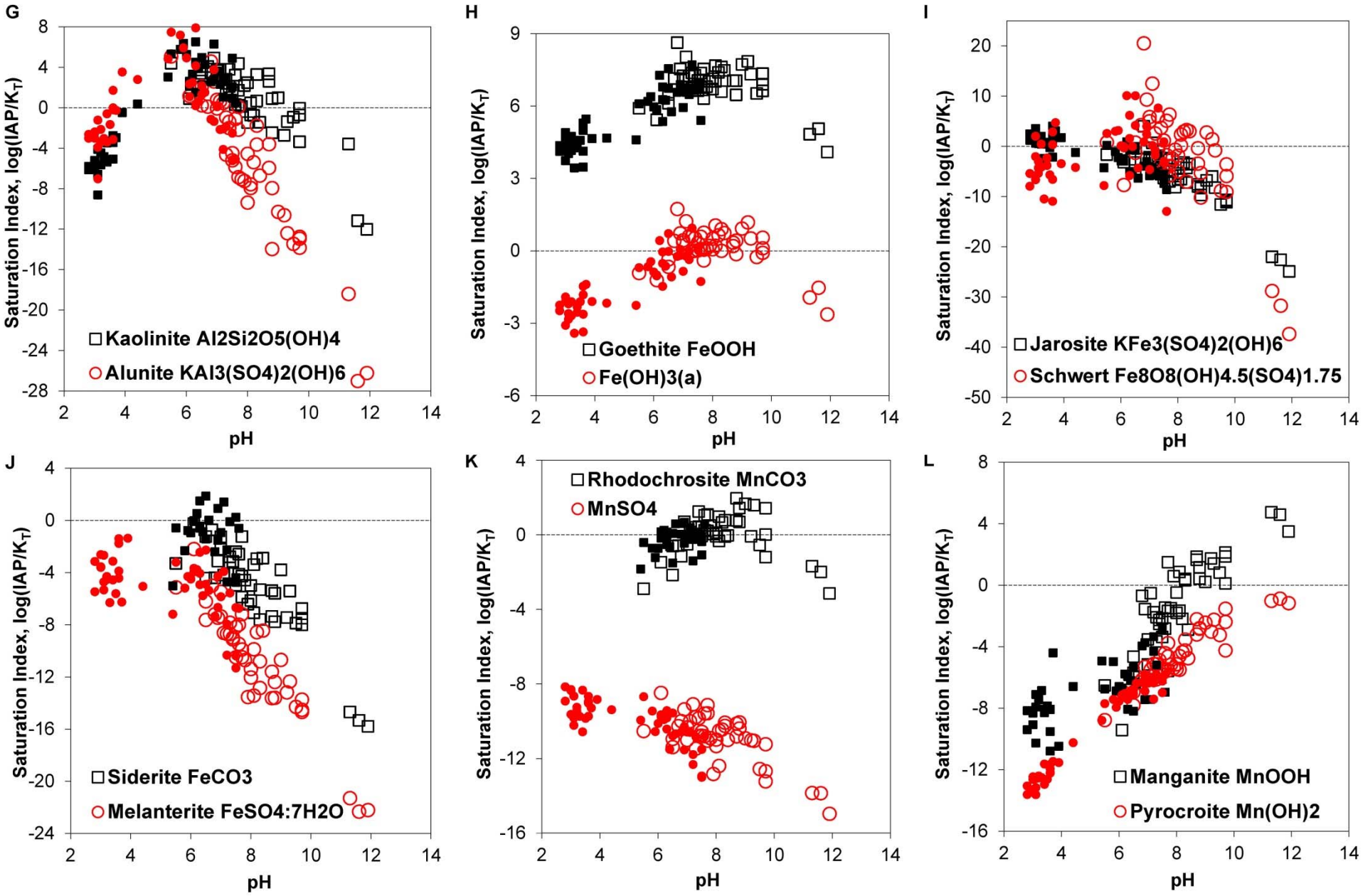
Changes in pH and Solutes during Treatment
Field Sampling Results (Lime) – AMDTreat 5.0+



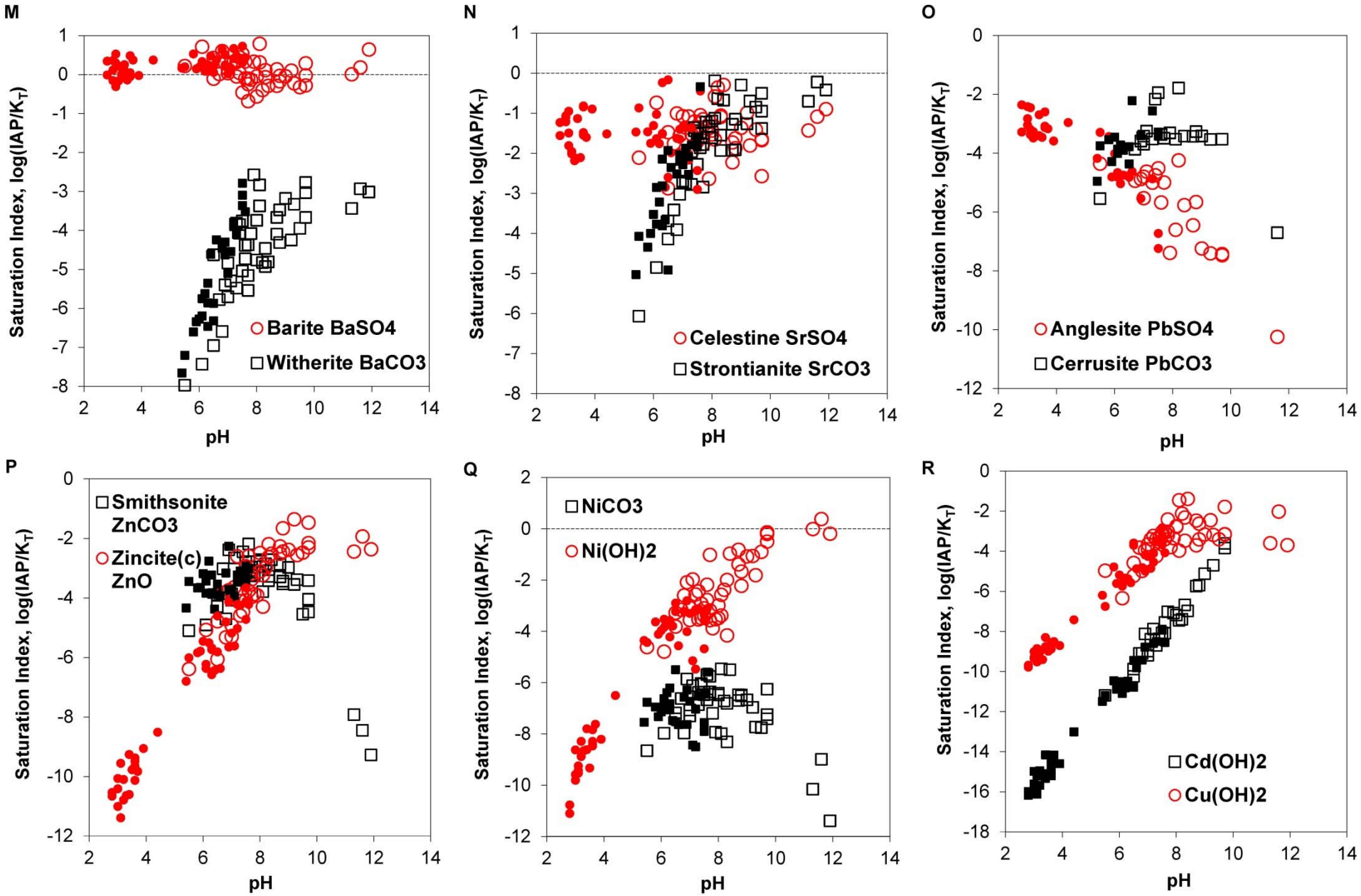
Feasibility for Mineral Precipitation



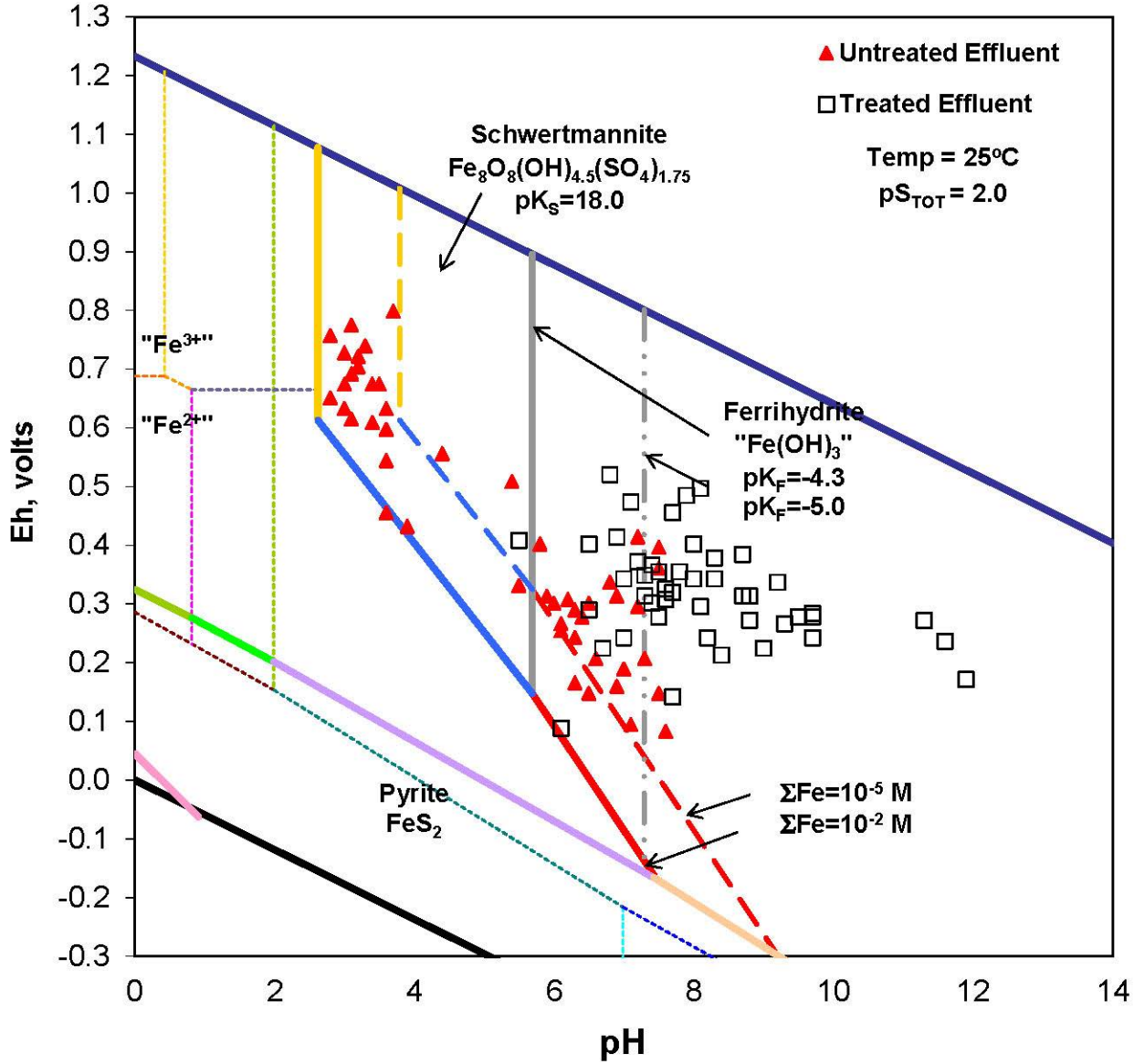
Feasibility for Mineral Precipitation



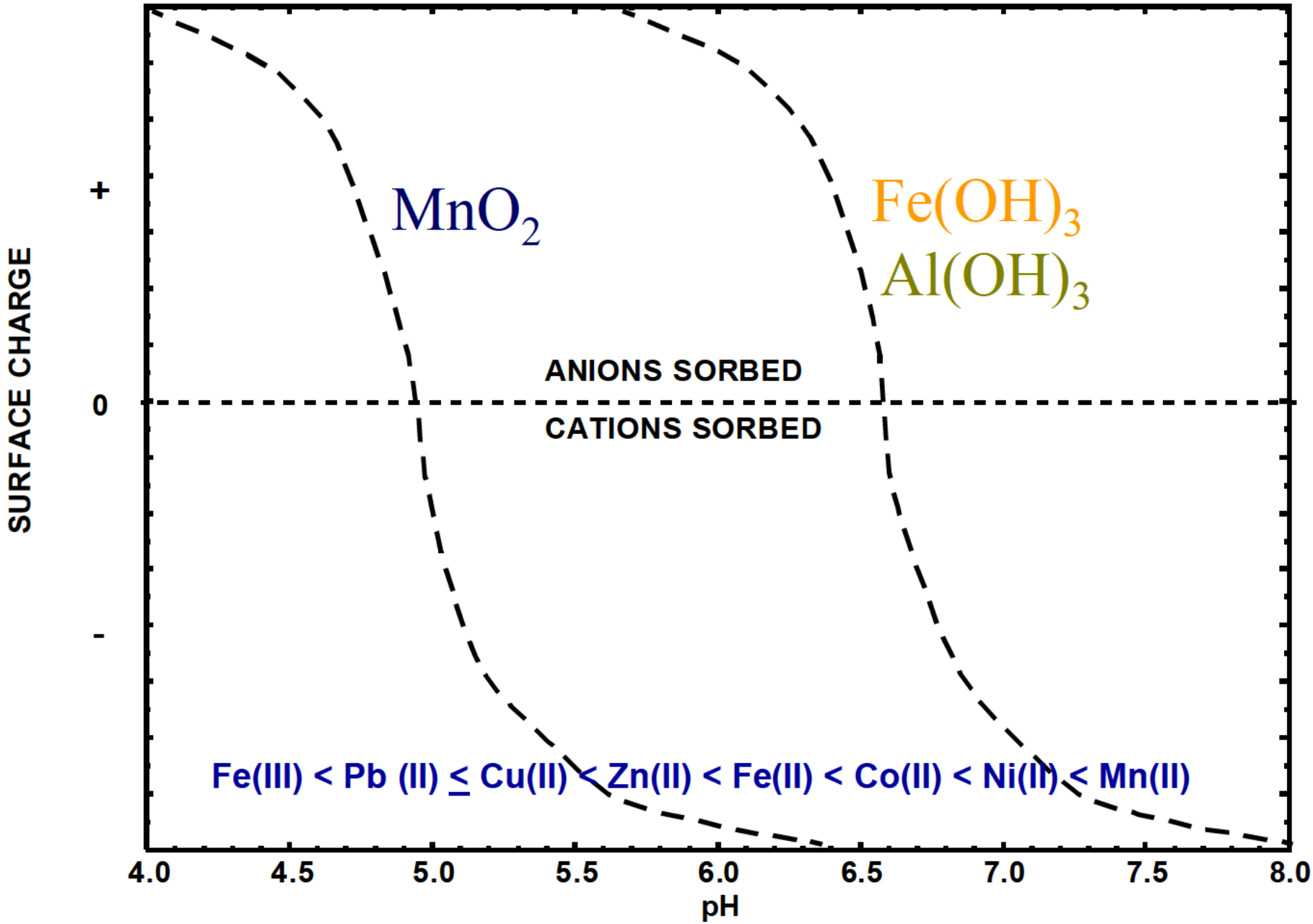
Feasibility for Mineral Precipitation



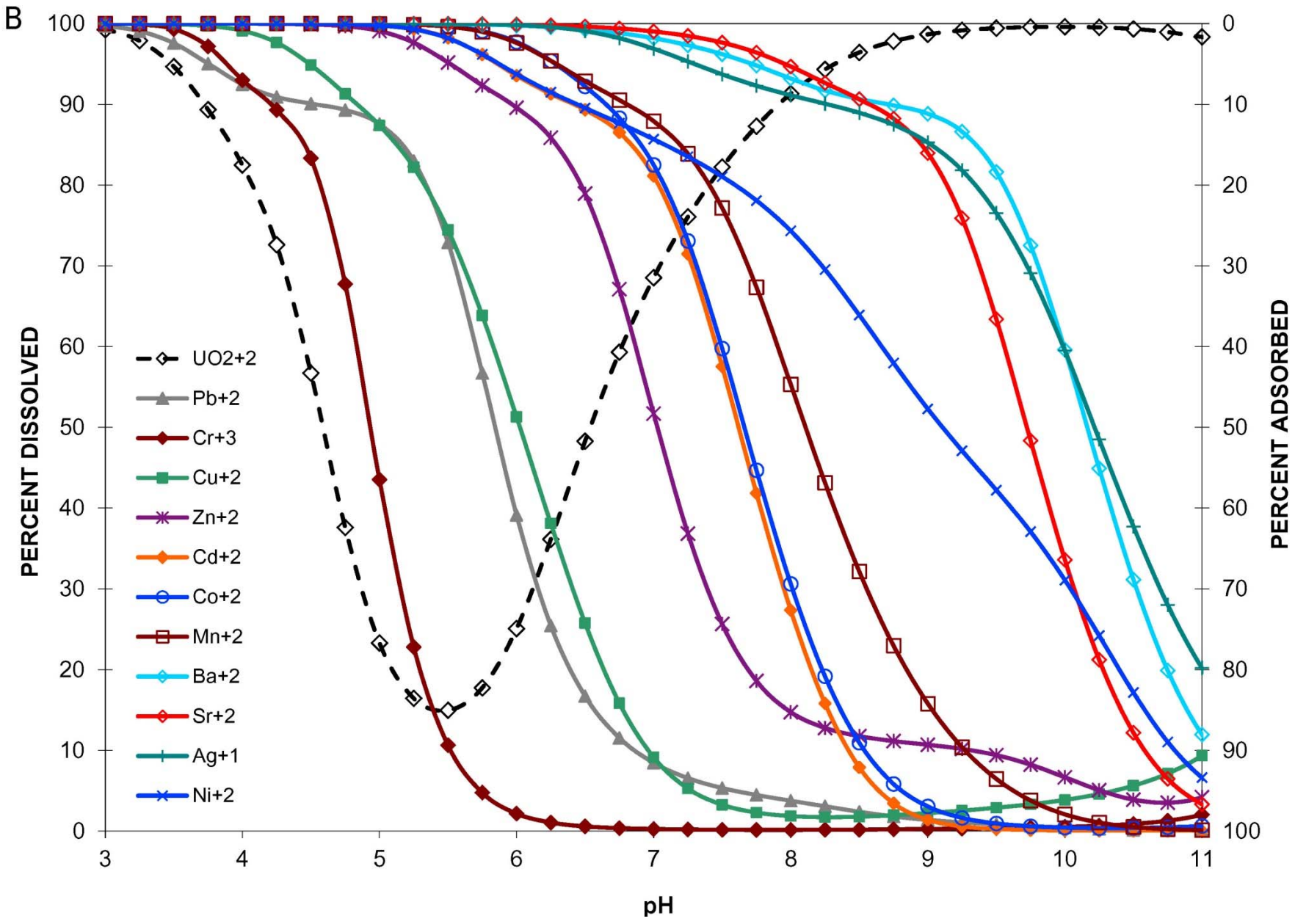
Hydrous Ferric Oxide (HFO) Stability



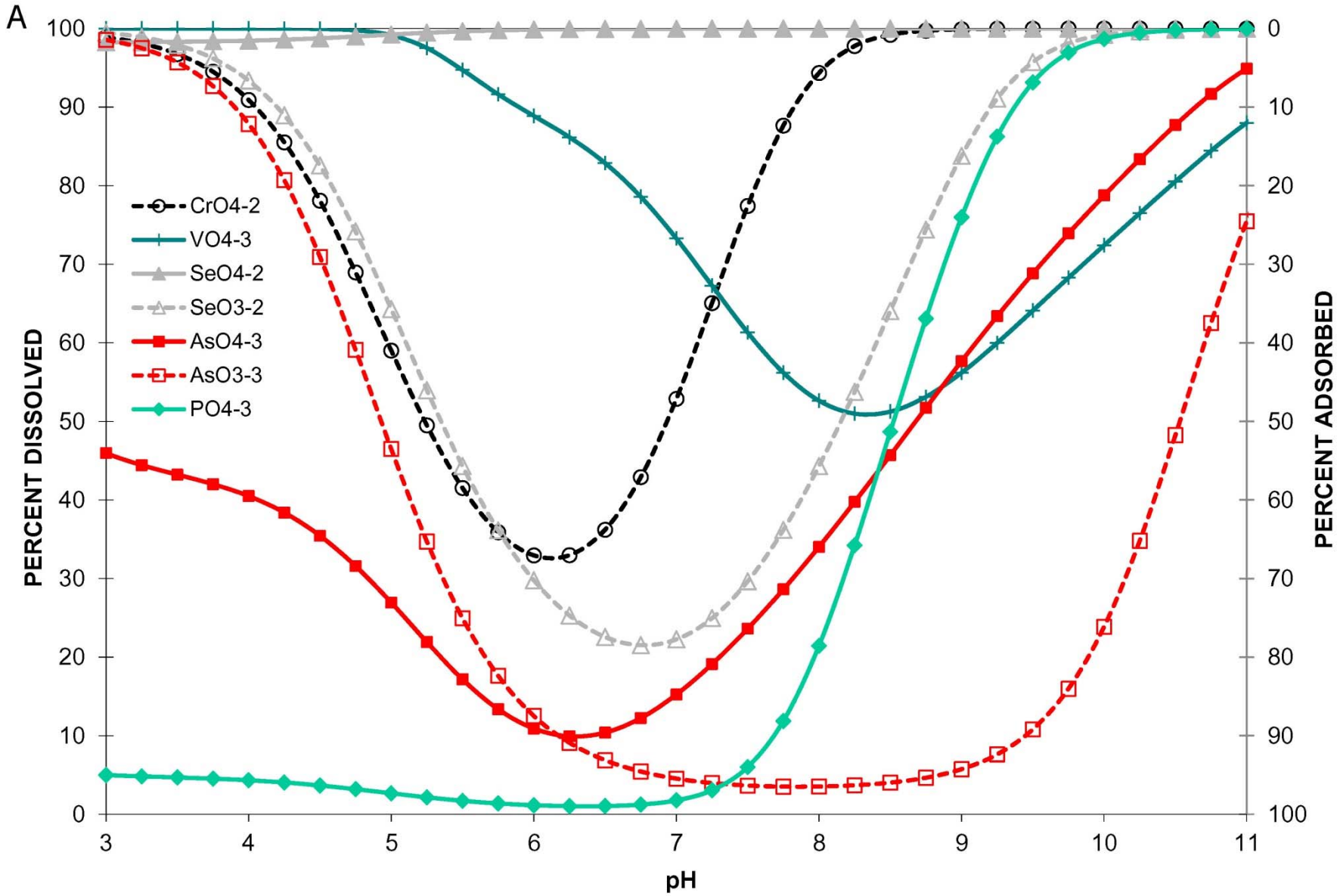
SORPTION AS AFFECTED BY "ZERO-POINT OF CHARGE"



Sorption of Cations on Hydrous Ferric Oxide (HFO)



Sorption of Anions on Hydrous Ferric Oxide (HFO)



CONCLUSIONS

- "Net alkaline" CMD maintained near-neutral pH ($\geq$ 6).
- Treatments as a whole:
  - ✓ increased pH ($\geq$ 6), temperature, DO, Ca, and Na;
  - ✓ decreased acidity, TDS, SO_4, Al, Fe, Mn, Mg, As, Ba, Be, Cd, Cr, Co, Cu, F, Pb, Ni, NH_3, Tl, Ti, U, Zn, Zr, total phenols, TIC, BOD, and COD;
  - ✓ did not affect flow rate, SC, osmotic pressure, hardness, alkalinity, K, Cl, Br, NO_3, PO_4, Sb, Sr, Se, Mo, V, or TOC.

CONCLUSIONS

- SC was strongly correlated with TDS, SO_4, hardness, Ca, Mg, Na, and K and was independent of pH.
- Ionic contributions to SC were mainly from SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, HCO_3^{-}, and, to a lesser extent, H^{+}, Fe^{2+}, Mn^{2+}, and Al^{3+}.
- Contributions to SC by H^{+}, Fe^{2+}, Mn^{2+}, and Al^{3+} in influent were replaced by additional contributions by Na^{+}, Ca^{2+}, and OH^{-} in treated effluent.

CONCLUSIONS

- Net alkaline CMD (pH $\geq$ 6) had concentrations of Al, As, Cd, Cr, Cu, Pb, Ni, Se*, V, and Zn that met CMC levels, but exceeded proposed thresholds for SO_4, SC, and TDS.
- Treatment of acidic effluents to pH > 6 with removal of Fe to < 7 mg/L and Mn to < 5 mg/L may provide a measure of protection for aquatic life from priority pollutant metals but may not be effective for decreasing SO_4, SC, and other measures of ionic strength.