“Priority Pollutants” in Untreated and Treated Discharges from Coal Mines

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Presented March, 28, 2012,
West Virginia Mine Drainage Task Force Symposium, Morgantown, WV

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 may provide a reasonable measure of protection for aquatic life.

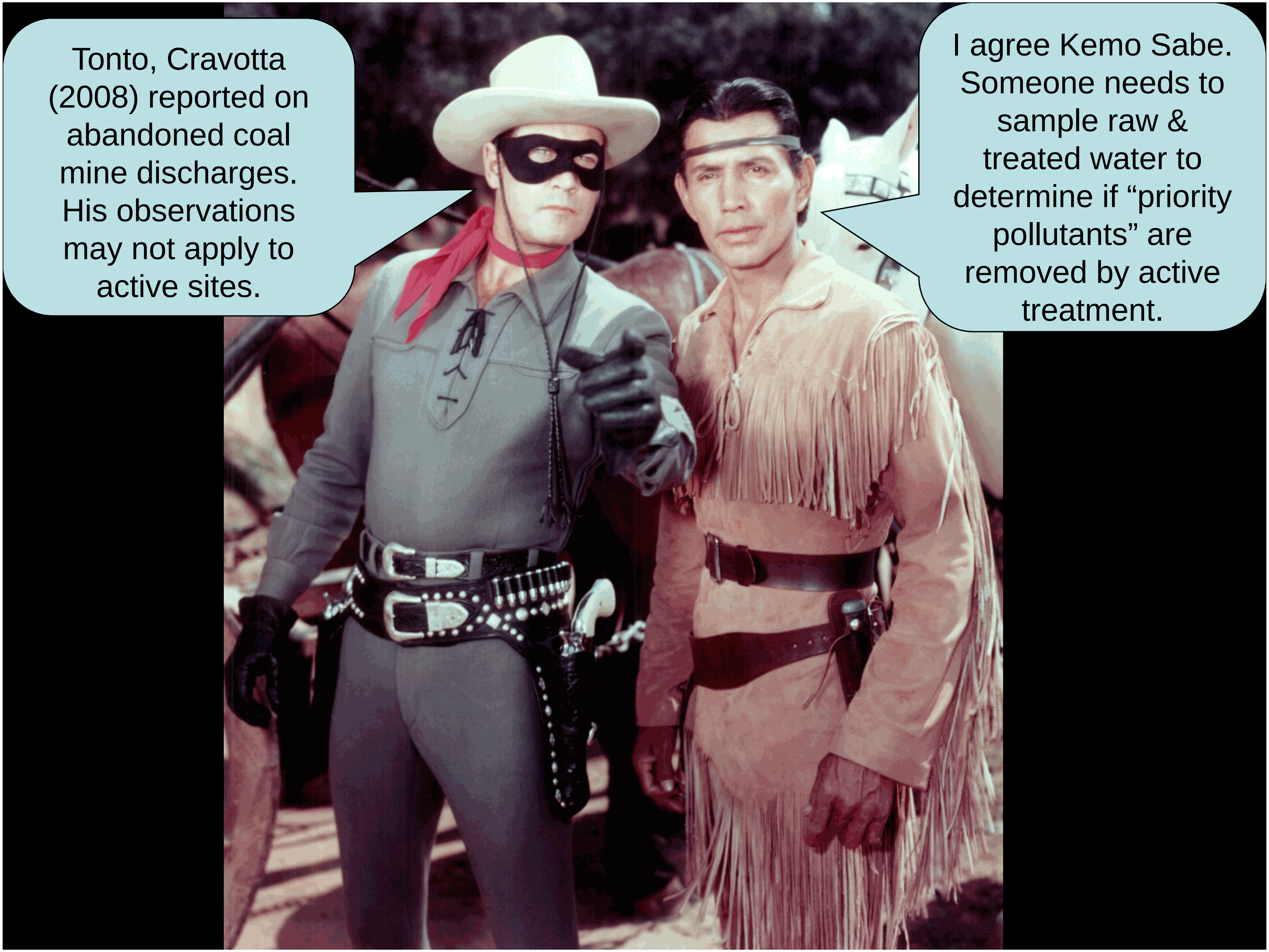
Water-Quality Criteria: Protect Human Health and Freshwater Aquatic Organisms

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

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 $CaCO_3$.**


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.

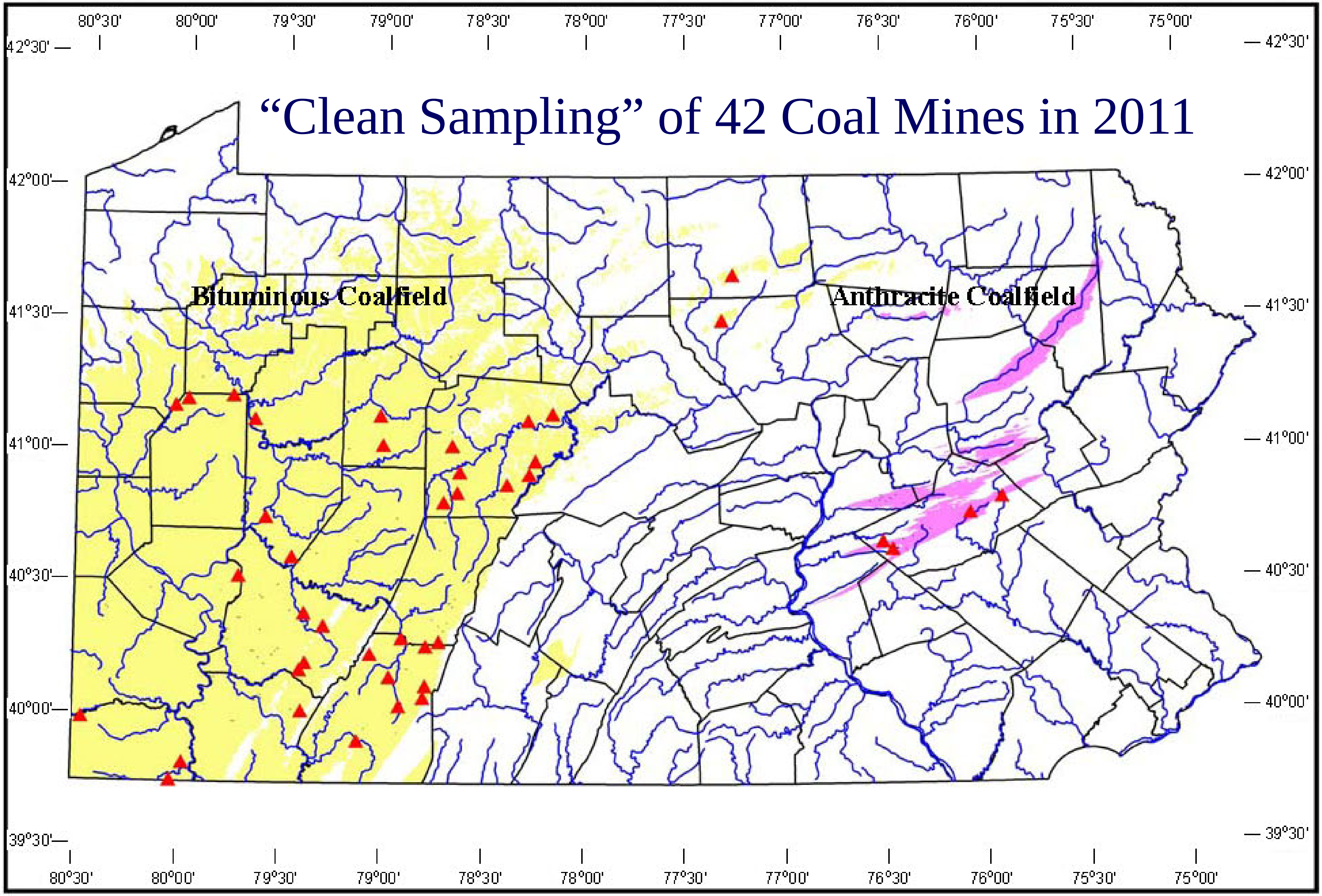
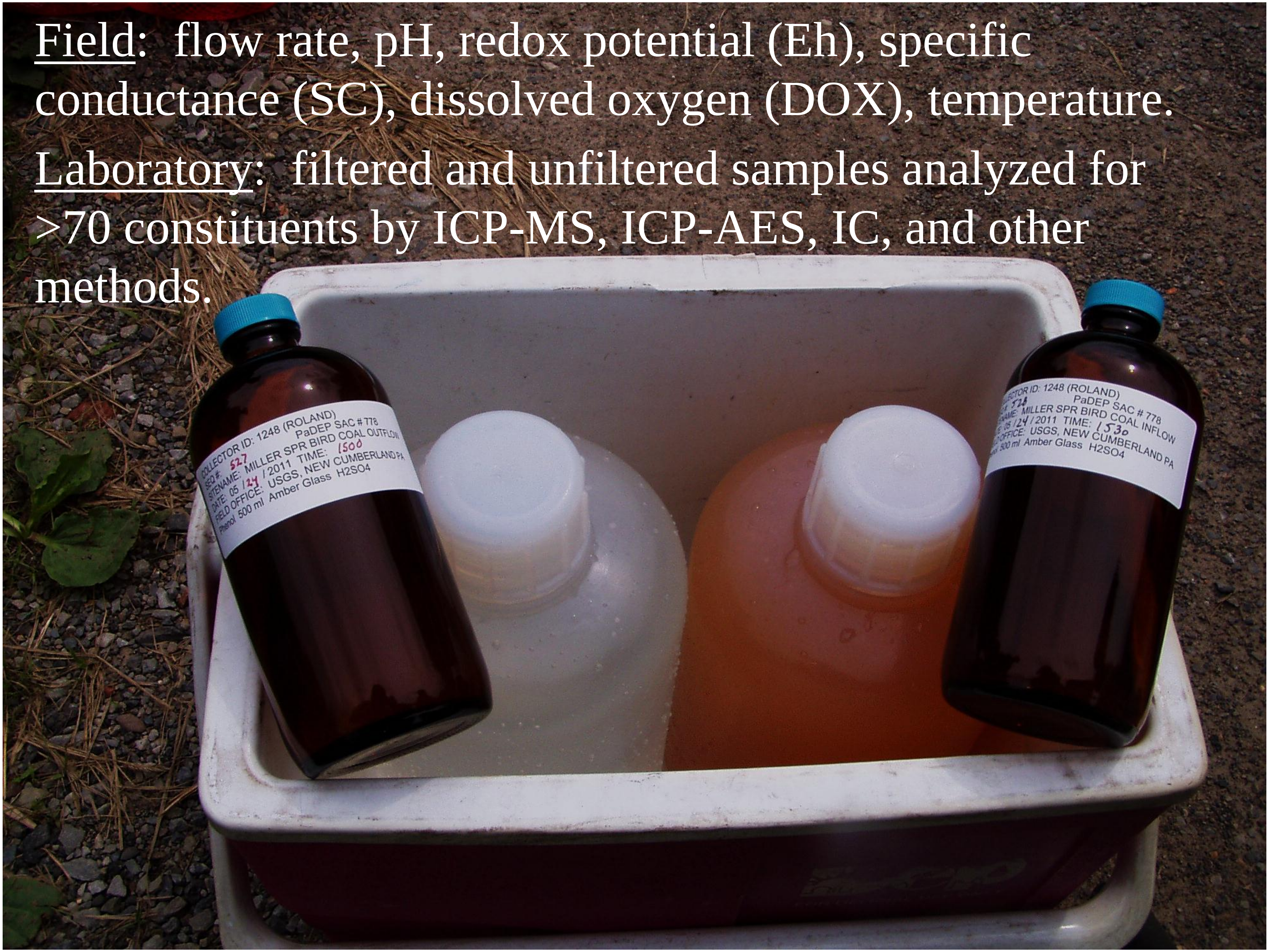


Fig. 1. Map of Pennsylvania showing locations of 42 coal-mining or coal-processing facilities in the Bituminous and Anthracite Coalfields where untreated and treated effluents were sampled in 2011.


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 rate, pH, redox potential (Eh), specific conductance (SC), dissolved oxygen (DOX), temperature.

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



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

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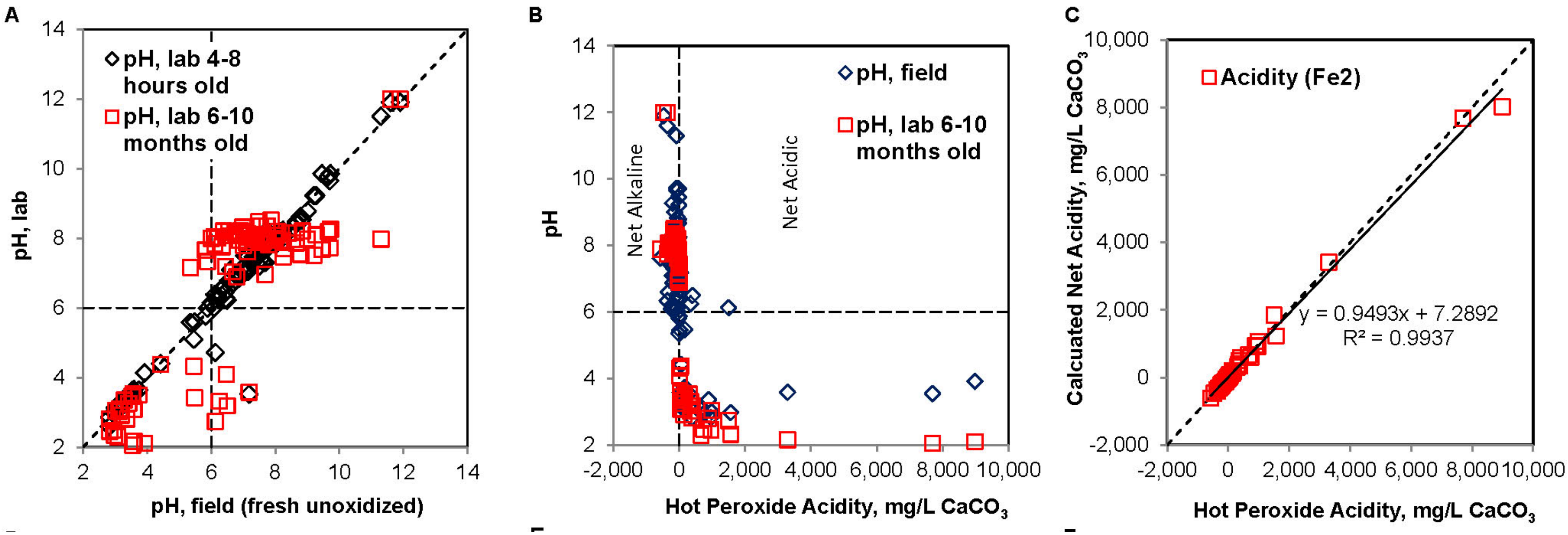
Hydrochemical Correlations: Principal Components Analysis

Constituent Loadings:	pH PCA1	TDS PCA2	TIC PCA3	Brine PCA4	Oxygen PCA5	BOD PCA6	TOC PCA7
Cobalt (Co)	90*	6	-19	-16	4	-11	-1
Zinc (Zn)	89*	19	-22	-10	-6	1	-1
Nickel (Ni)	87*	26	-13	2	-4	-10	11
Manganese (Mn)	86*	23	-8	-17	-2	-8	-7
Iron (Fe)	77*	6	0	12	25	35*	-20
Titanium (Ti)	68*	25	-17	26	7	4	-19
Acidity, hot (ACIDH)	68*	7	-61*	7	-10	8	-14
Uranium (U)	61*	25	-3	9	13	-19	56*
Redox potential (Ehmv)	54*	-13	-49*	-11	-26	-26	28
Chemical oxygen demand (COD)	48*	42*	-20	0	39*	3	24
Temperature (TEMPC)	-44*	37*	-39*	25	10	-7	37*
pH, oxidized (pHLox)	-73*	-17	47*	-11	-1	-8	-5
pH, fresh (pHF)	-93*	12	5	8	-8	-5	-5
Residual on evaporation (ROE)	22	92*	-10	21	-4	9	9
Specific conductance (SC25)	15	91*	-9	25	-1	10	10
Sulfate (SO4)	26	90*	-16	18	-8	9	4
Osmotic pressure (OSMP)	14	90*	-1	23	-1	10	12
Calcium (Ca)	0	87*	0	-1	18	-3	1
Potassium (K)	11	72*	14	34*	4	-23	8
Magnesium (Mg)	53*	70*	8	-10	-31	-4	1
Strontium (Sr)	-8	63*	10	19	51*	8	8
Total inorganic carbon (TIC)	-3	9	84*	-9	15	20	27
Acid neutralizing capacity (ANC)	-57*	10	72*	3	19	4	14
Aluminum (Al)	56*	14	-63*	-6	-2	14	8
Thallium (Tl)	41*	22	-69*	0	19	-16	10
Chloride (Cl)	-4	22	3	83*	9	5	-4
Bromide (Br)	2	37*	-5	79*	4	2	0
Sodium (Na)	-16	50*	-8	68*	-3	13	3
Barium (Ba)	-8	-47*	19	12	66*	-31	-7
Arsenic (As)	48*	4	8	23	52*	38*	6
Dissolved oxygen (DOX)	-13	-30	-10	37*	-49*	-31	16
Biological oxygen demand (BOD)	-2	6	15	8	2	78*	9
Total organic carbon (TOC)	-16	23	25	-5	-9	21	73*

pH and Acidity



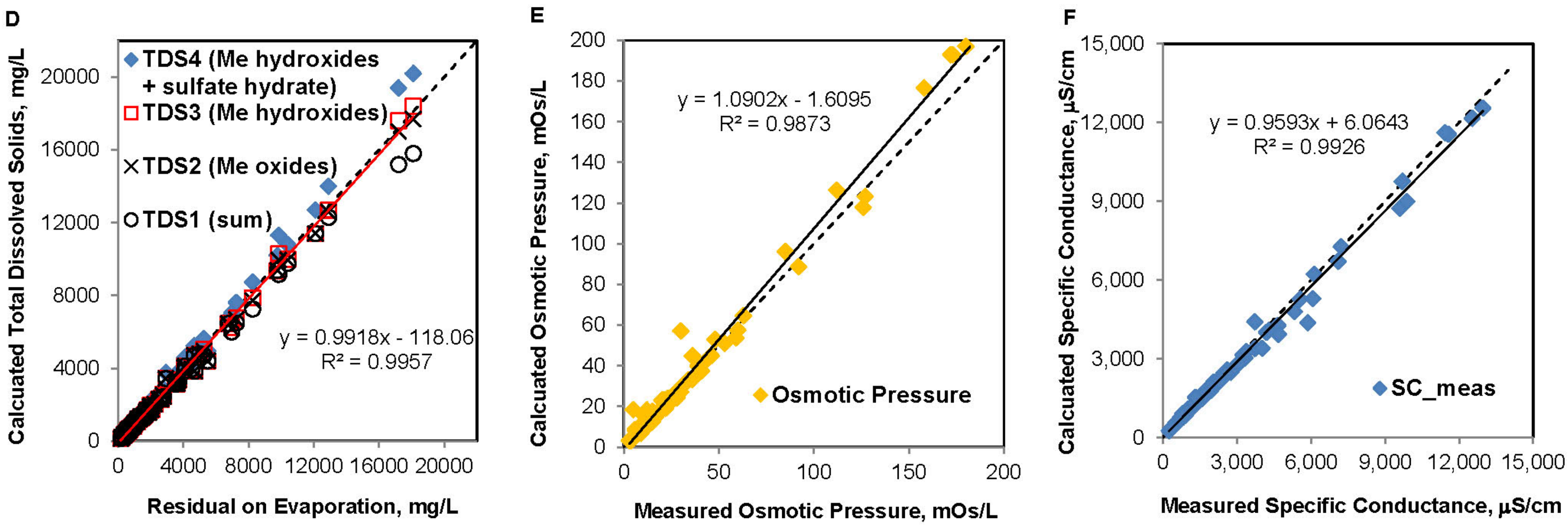
A. pH, fresh ≠ pH, lab.

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



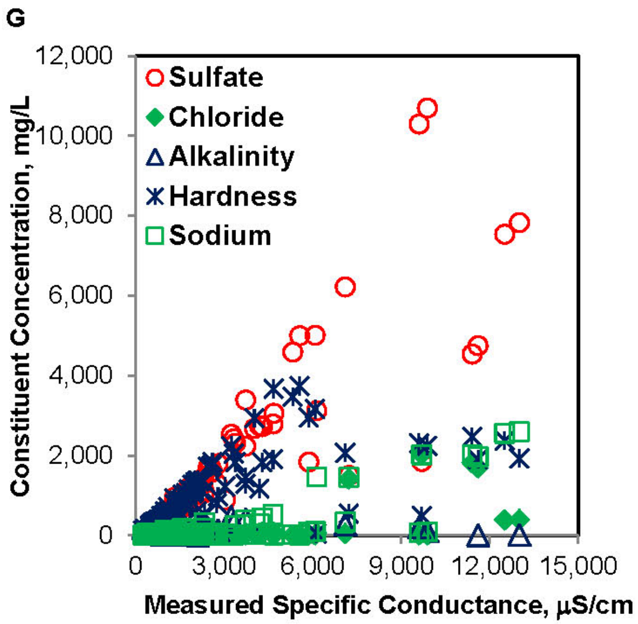
D. ROE = Total Dissolved Solids = Σ major ion concentrations (mg/L).

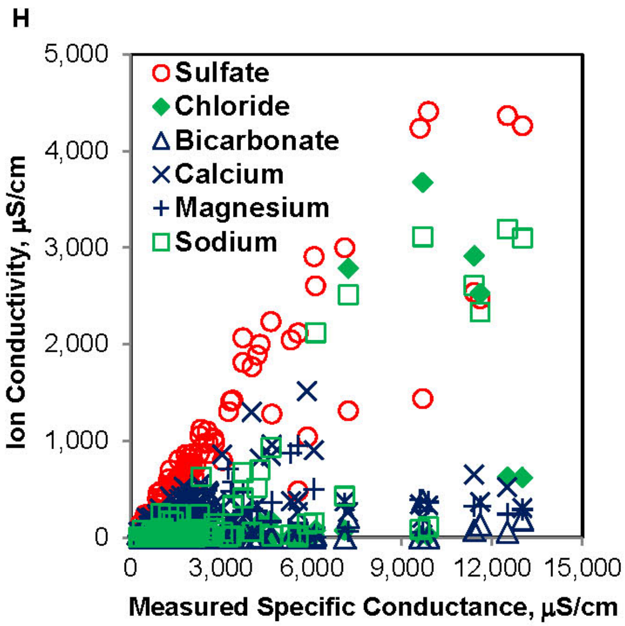
E. Osmotic Pressure = Σ major ion concentrations (mol/L).*

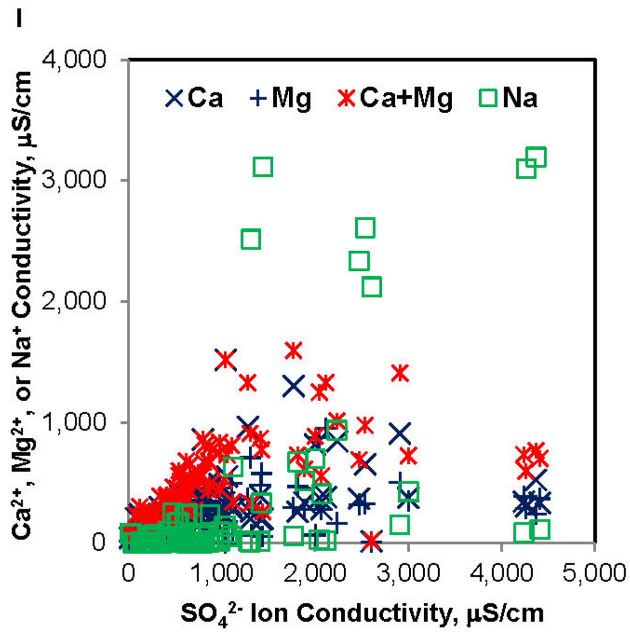
F. Conductivity = Σ ionic conductivities (µS/cm).*

* after speciation to account for ion complexation

Major Ions, Specific Conductance, Dissolved Solids





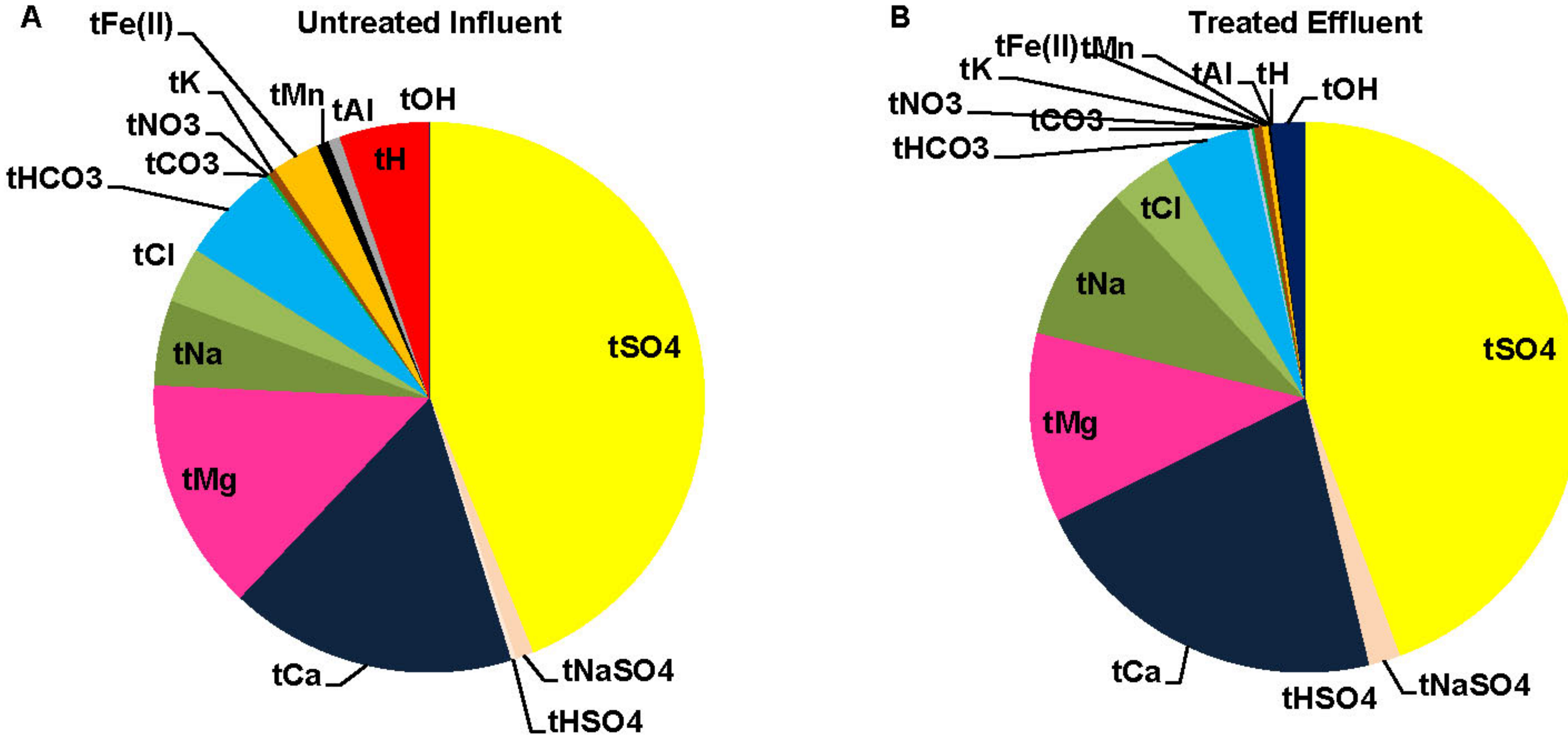


G. SC is strongly correlated with SO_4 and hardness (2.5·Ca + 4.1·Mg).

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

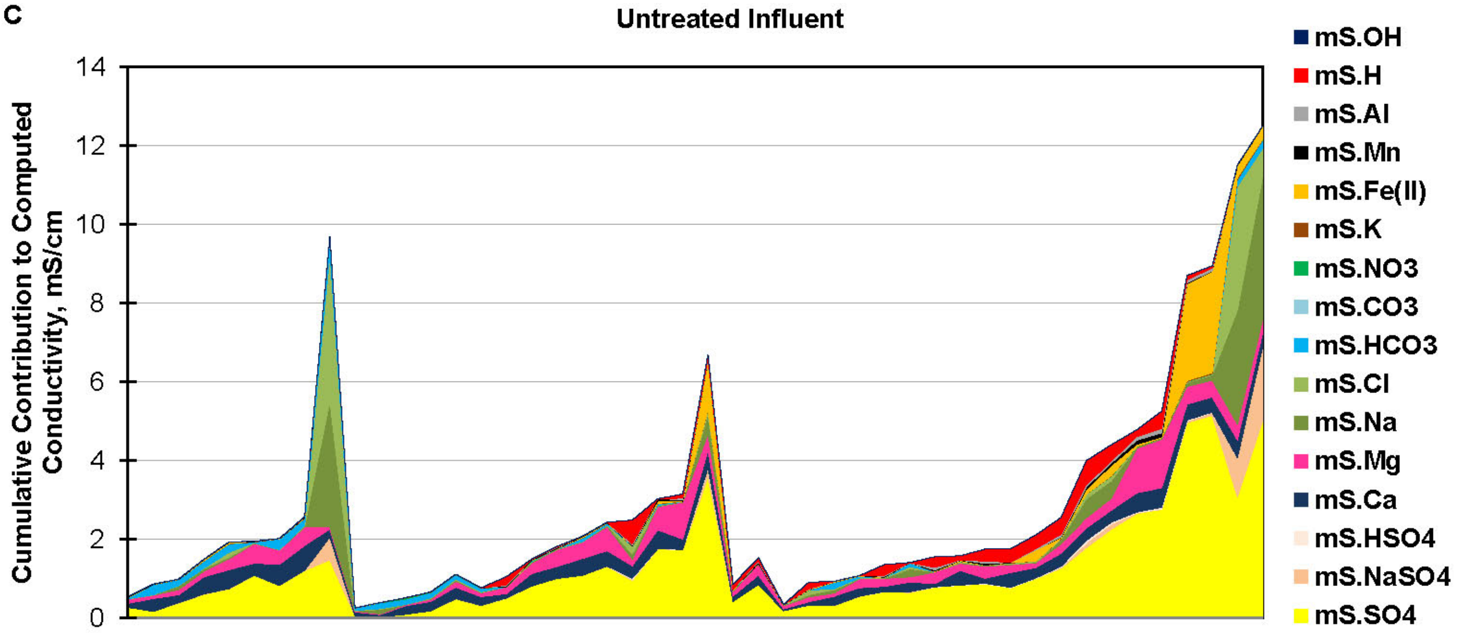
I. Ca-Mg-SO_4 and Na-SO_4 waters indicated by ionic conductivities.

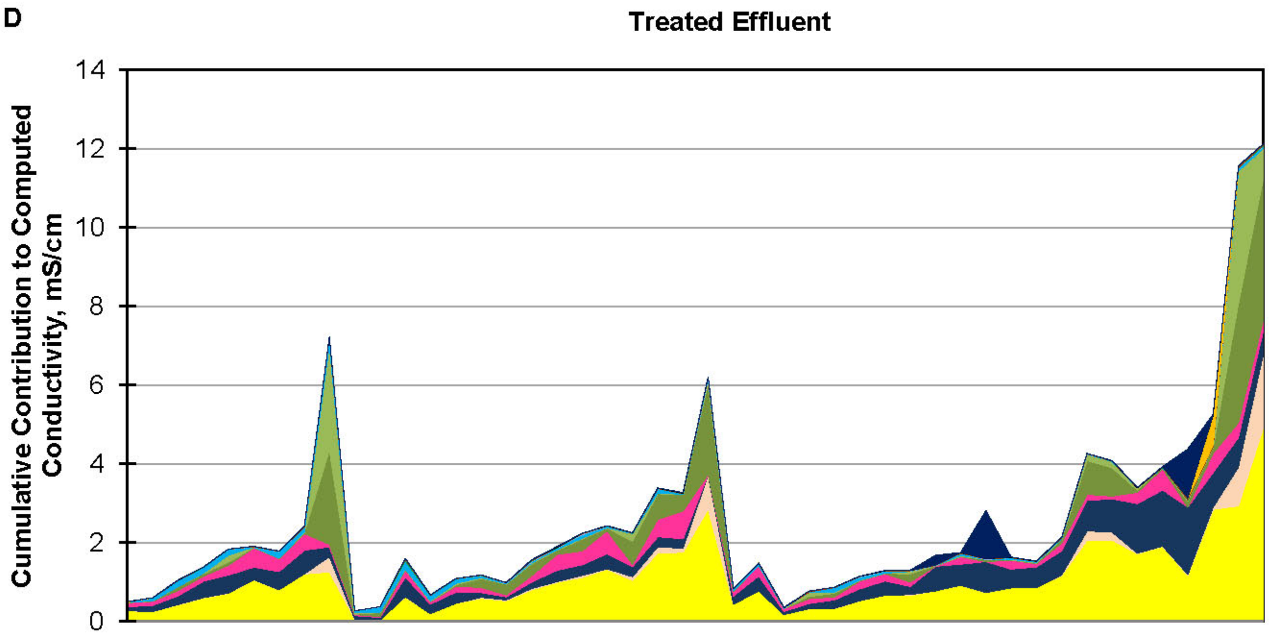
pH, Major Ions, Dissolved Solids, Specific Conductance



Conductivity contribution indicated by decimal fraction of conductance from individual ions, or "transport number" (McCleskey et al., 2012. A new method of calculating electrical conductivity with applications to natural waters: Geochimica et Cosmochimica Acta 77:369–382).

pH, Major Ions, Dissolved Solids, Specific Conductance





Effects of Treatment on Priority Pollutants

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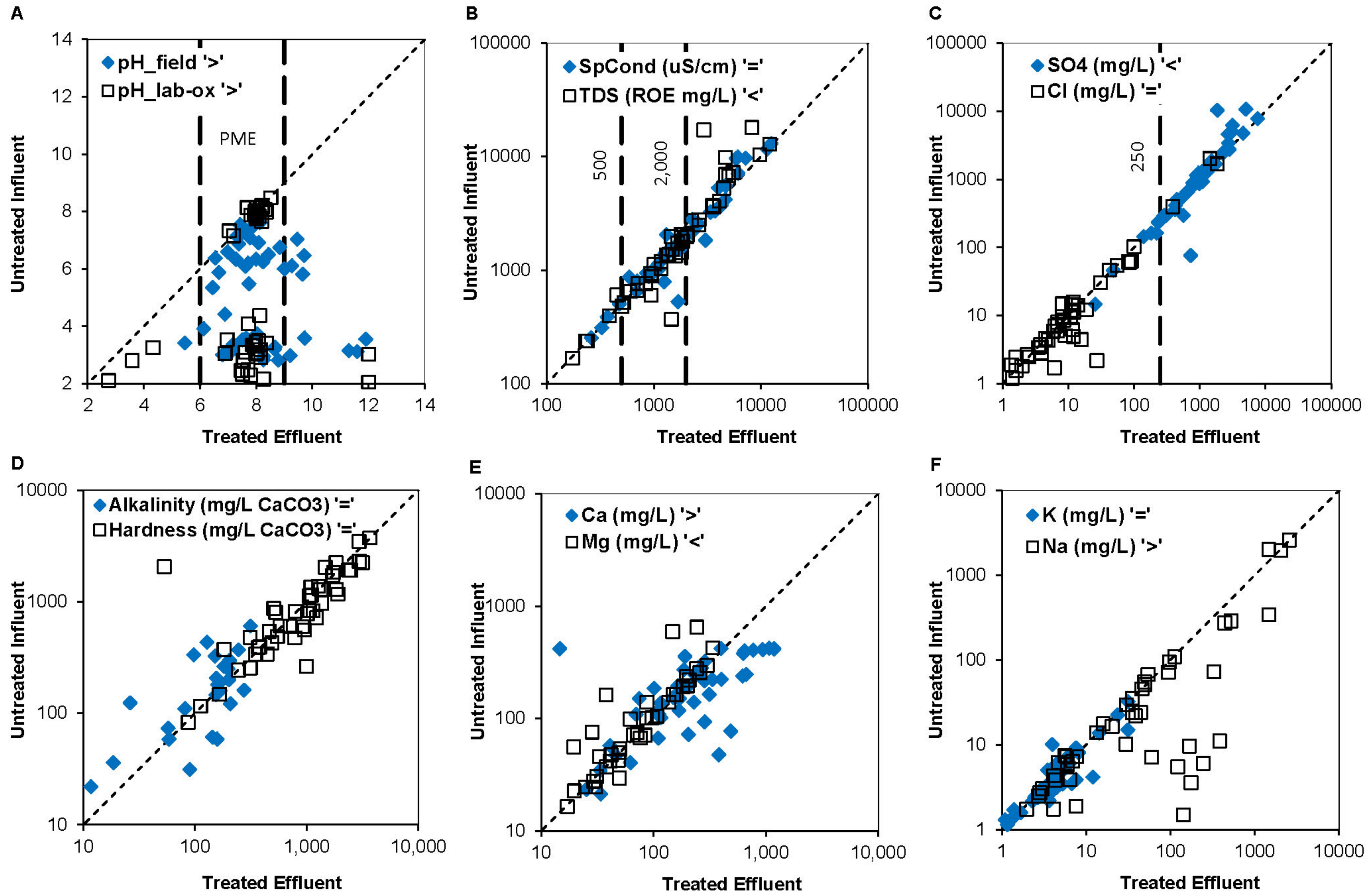
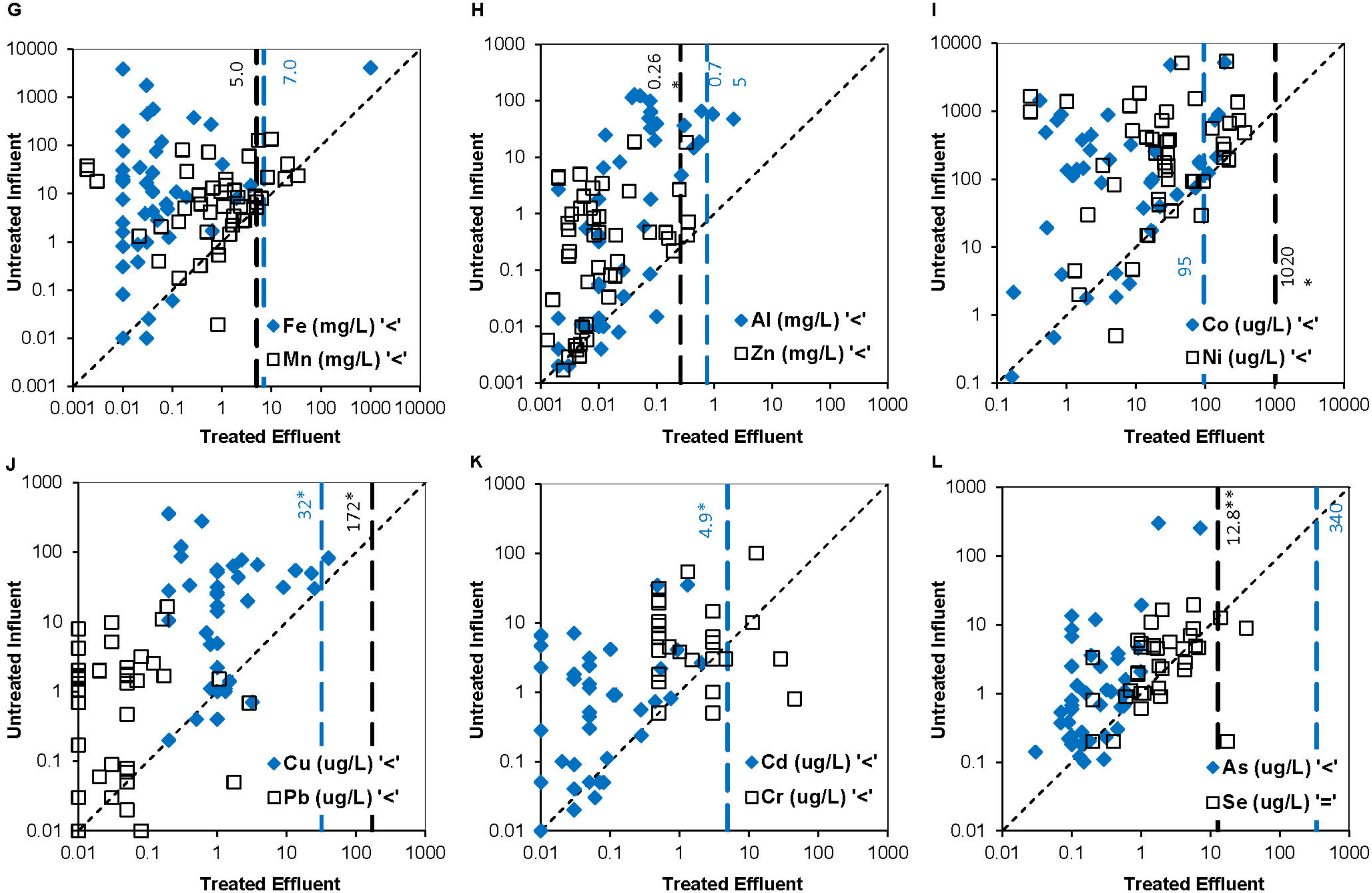
Effect of Treatment on pH and Solute Concentrations



Effect of Treatment on pH and Solute Concentrations



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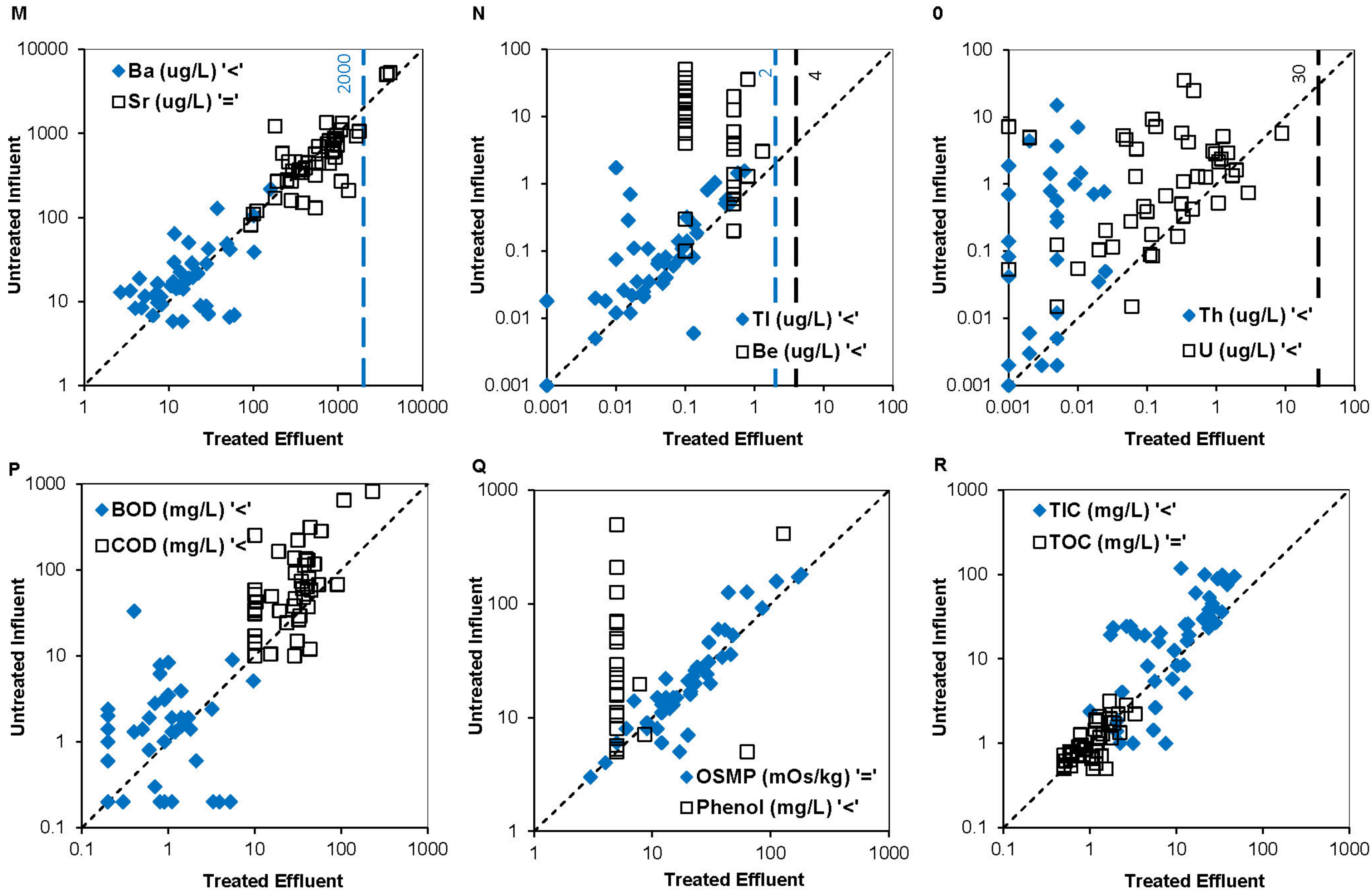

Implications for Aquatic and Terrestrial Organisms

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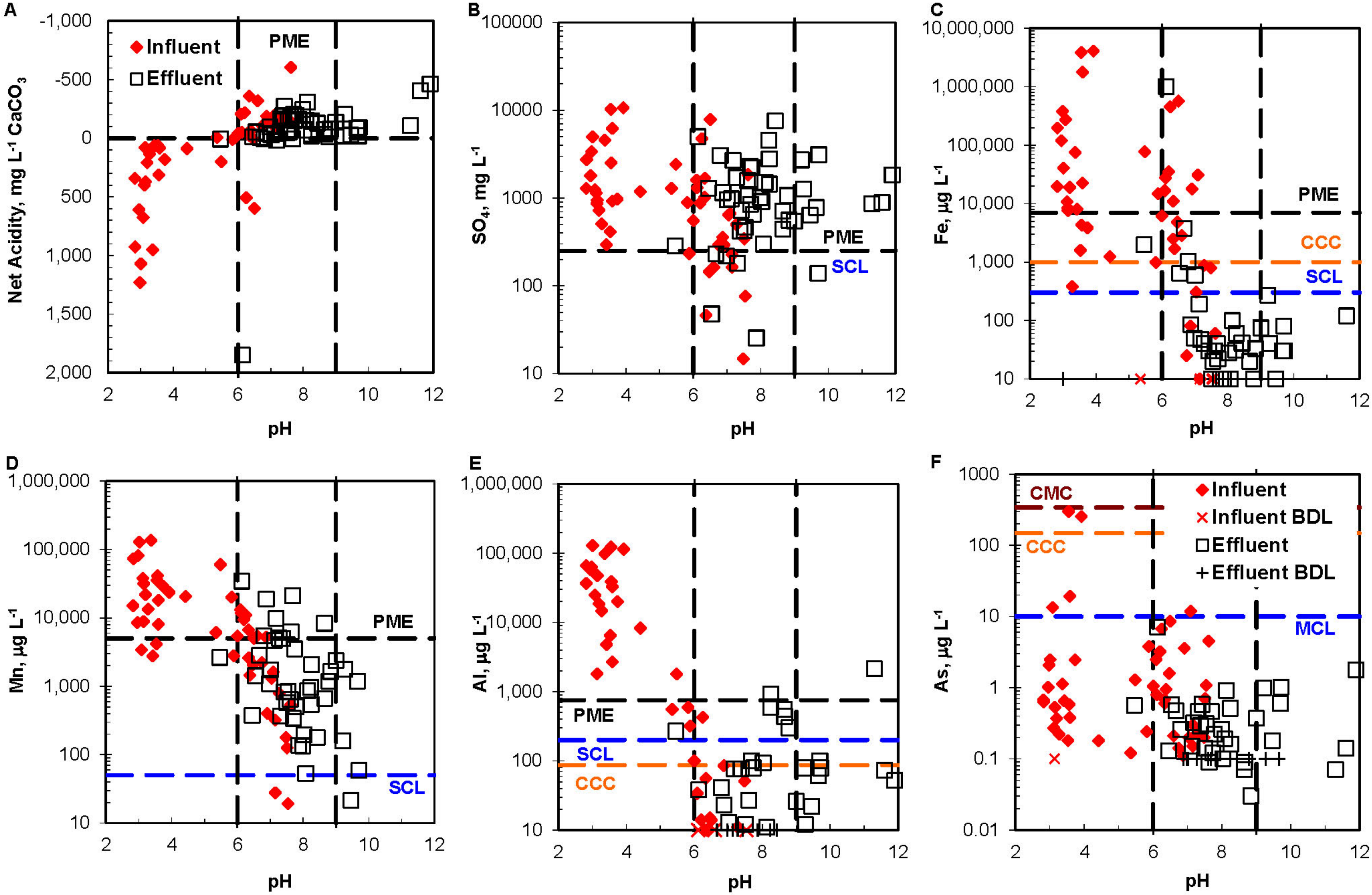
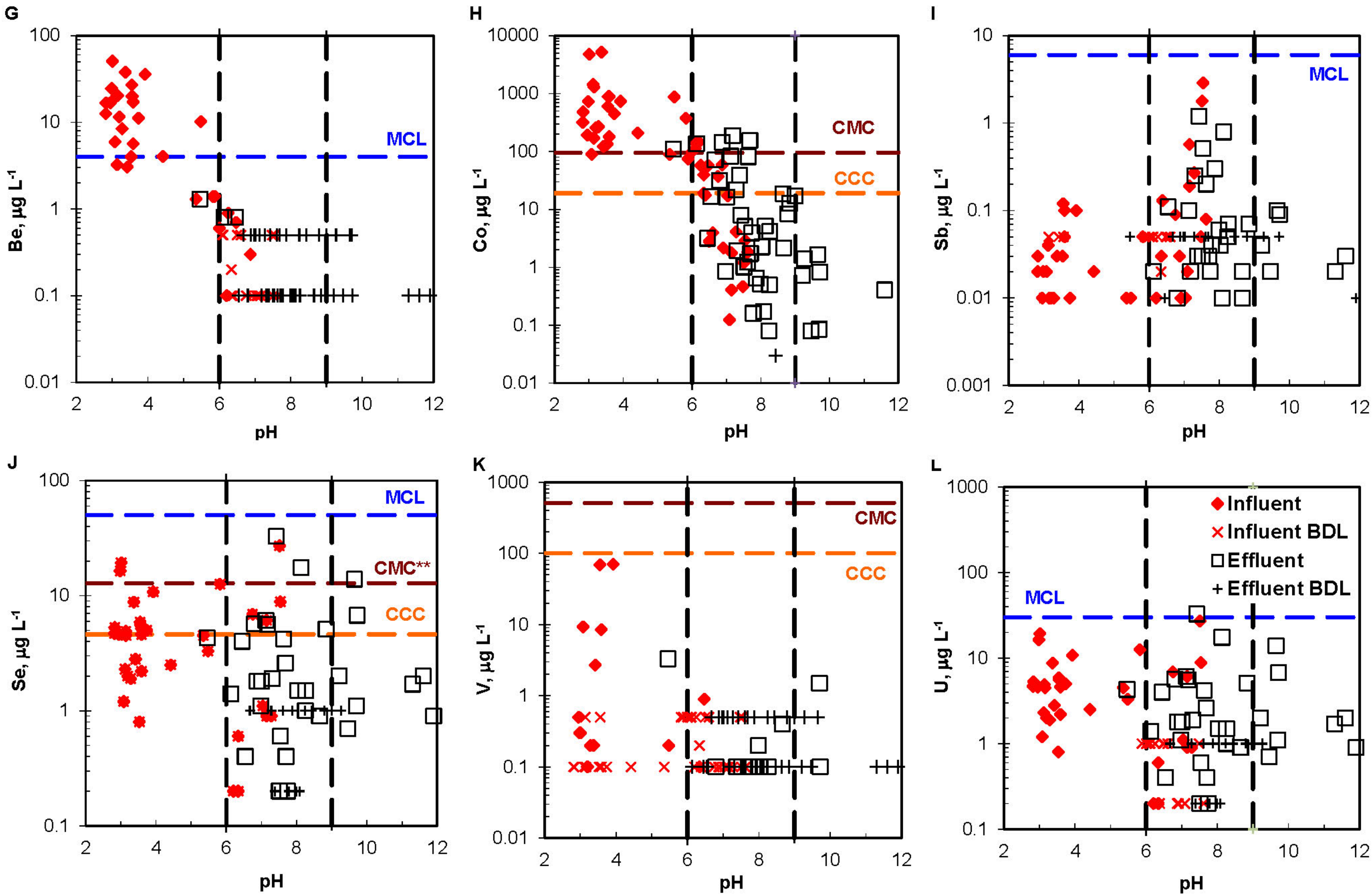
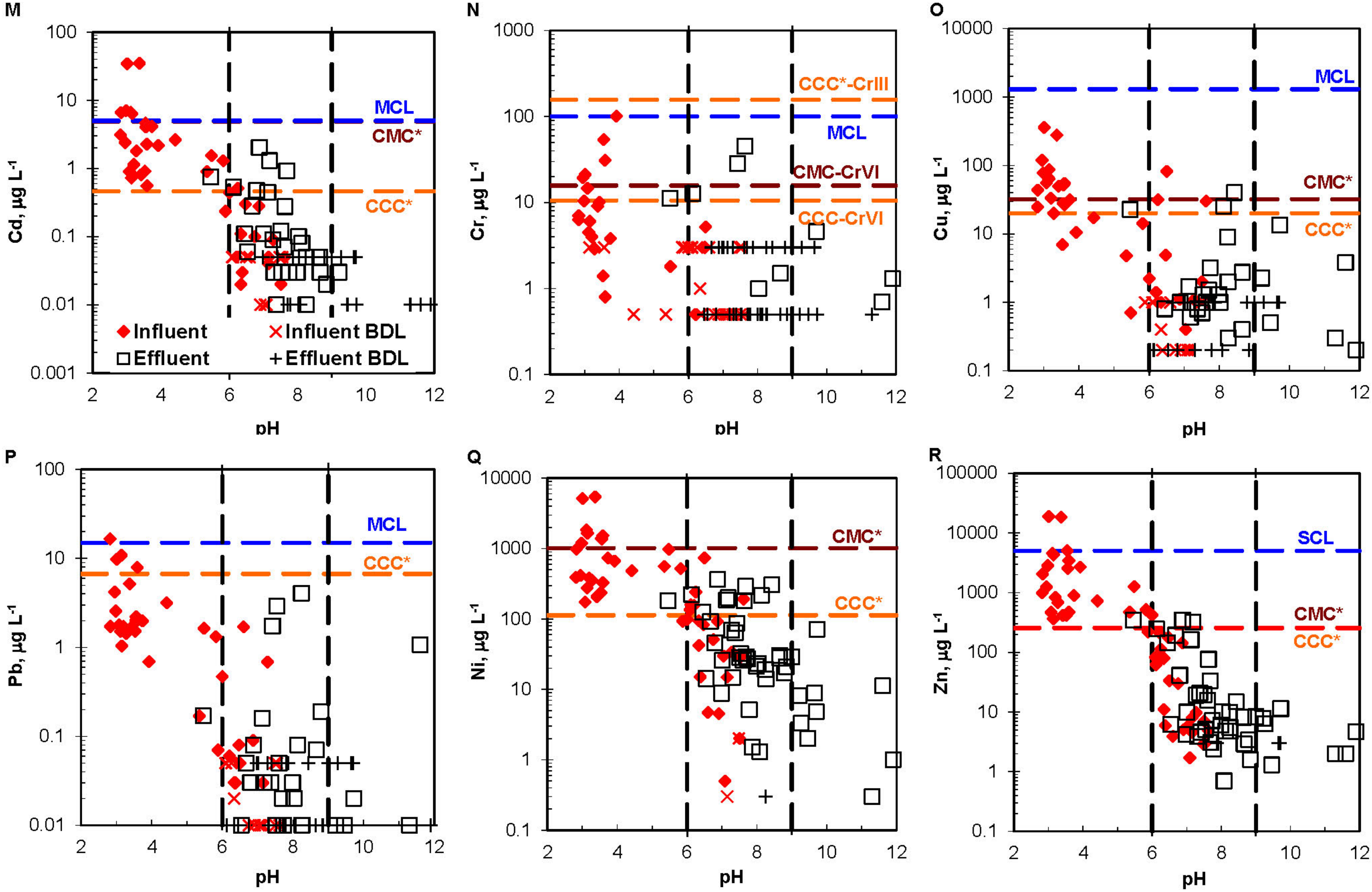
Concentrations Decrease with Increased pH ?



Concentrations Decrease with Increased pH ?



Concentrations Decrease with Increased pH ?

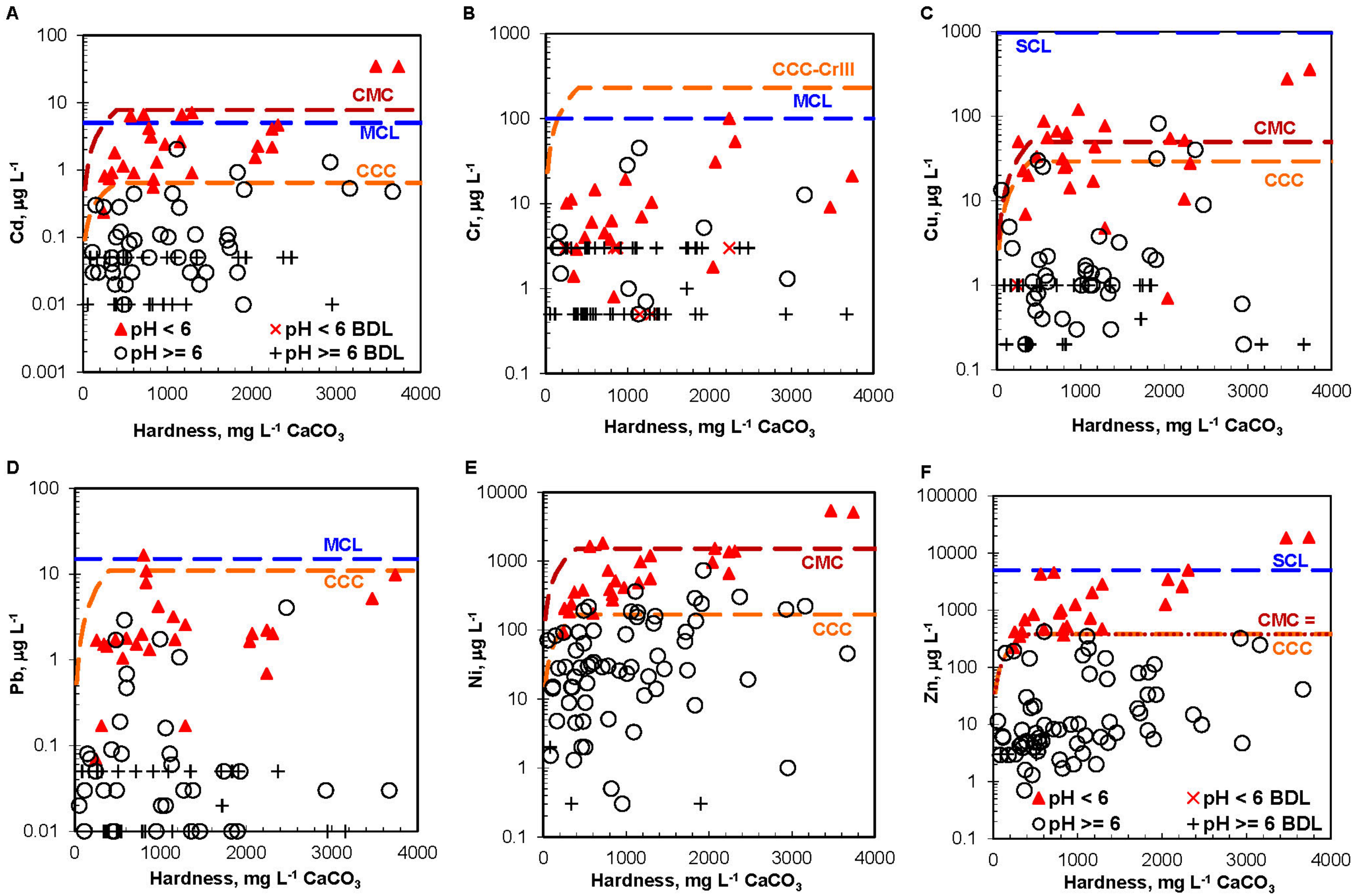


Metal* Toxicity Decreases with Hardness

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

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

Toxic Effects Decrease with Increased Hardness



Solubility and Sorption of Priority Pollutants

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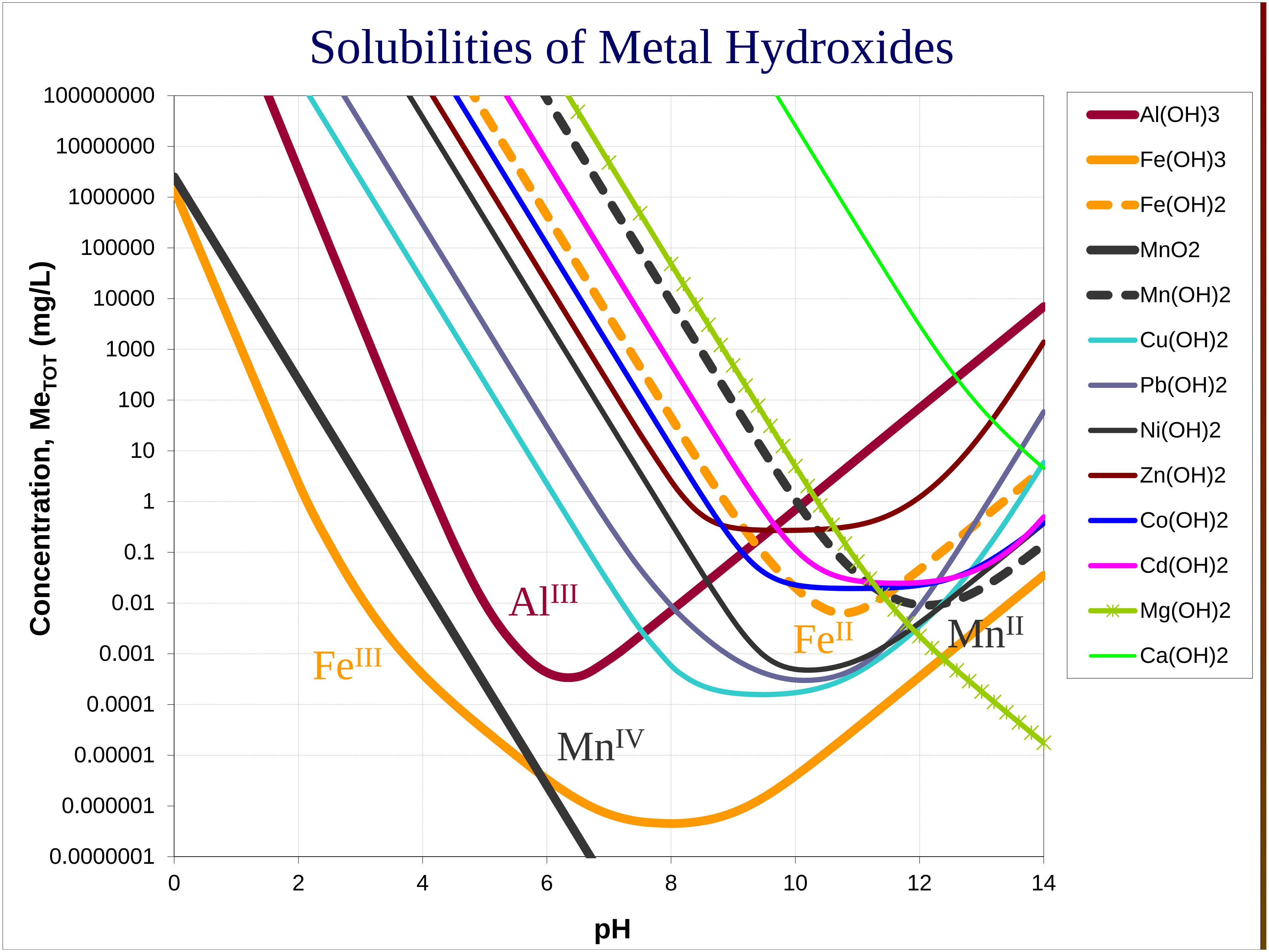
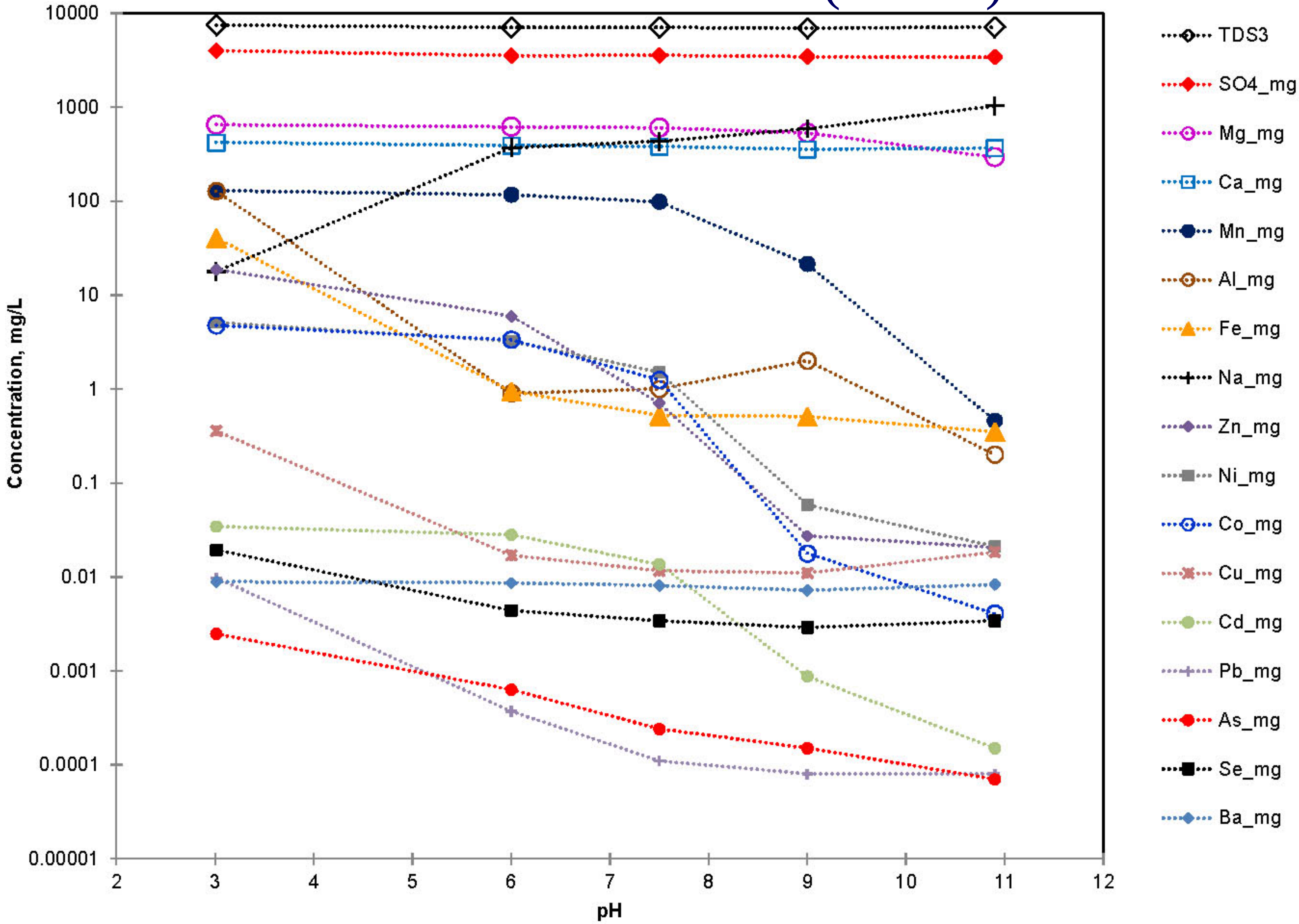
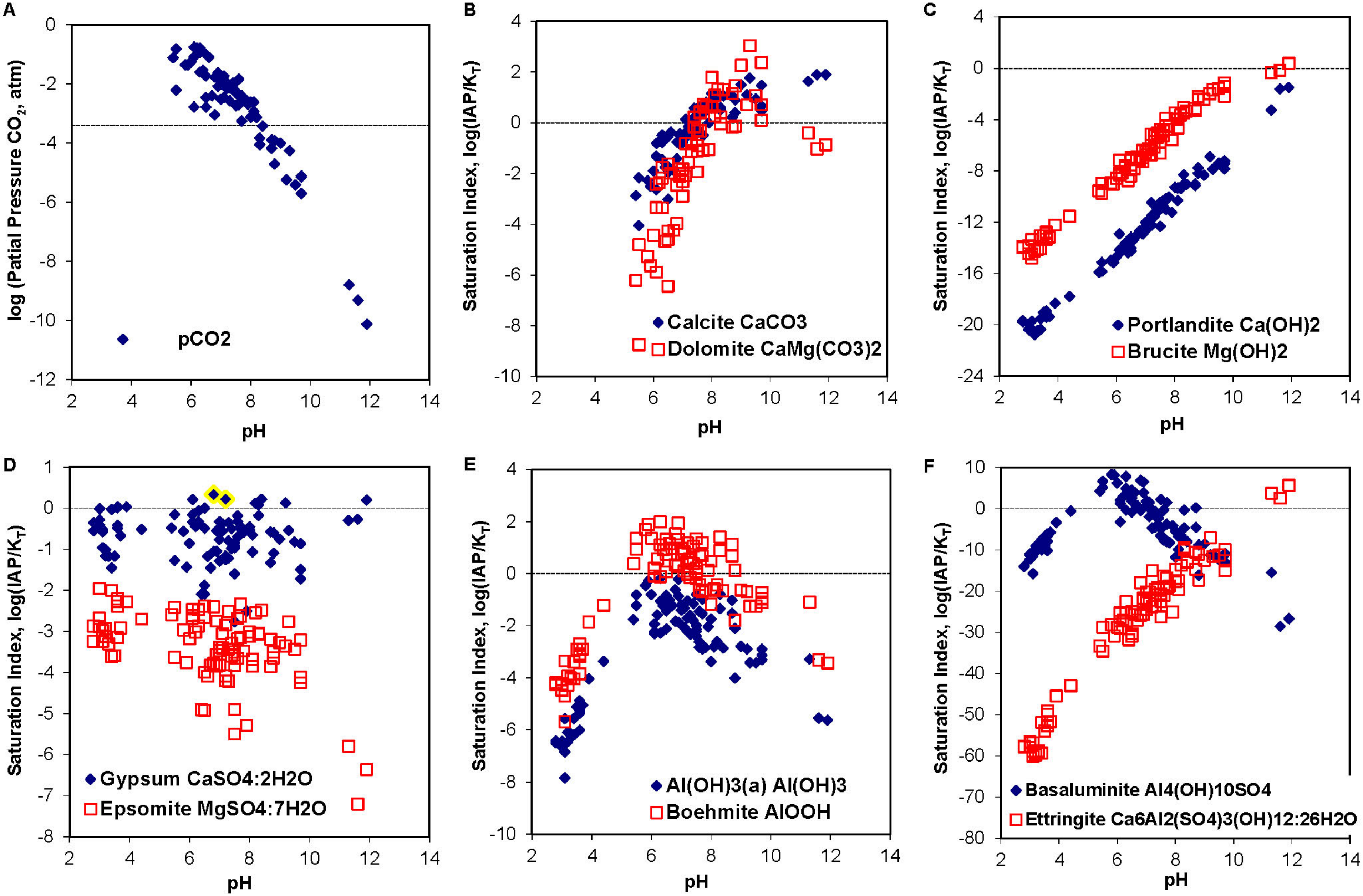


Solubilities of Metal Hydroxides
Concentration, Me_{TOT} (mg/L)
100000000
10000000
1000000
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0.0000001
0
2
4
6
8
10
12
14
pH
Al^{III}
Fe^{III}
Fe^{II}
Mn^{IV}
Mn^{II}
Al(OH)3
Fe(OH)3
Fe(OH)2
MnO2
Mn(OH)2
Cu(OH)2
Pb(OH)2
Ni(OH)2
Zn(OH)2
Co(OH)2
Cd(OH)2
Mg(OH)2
Ca(OH)2

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



Feasibility for Mineral Precipitation



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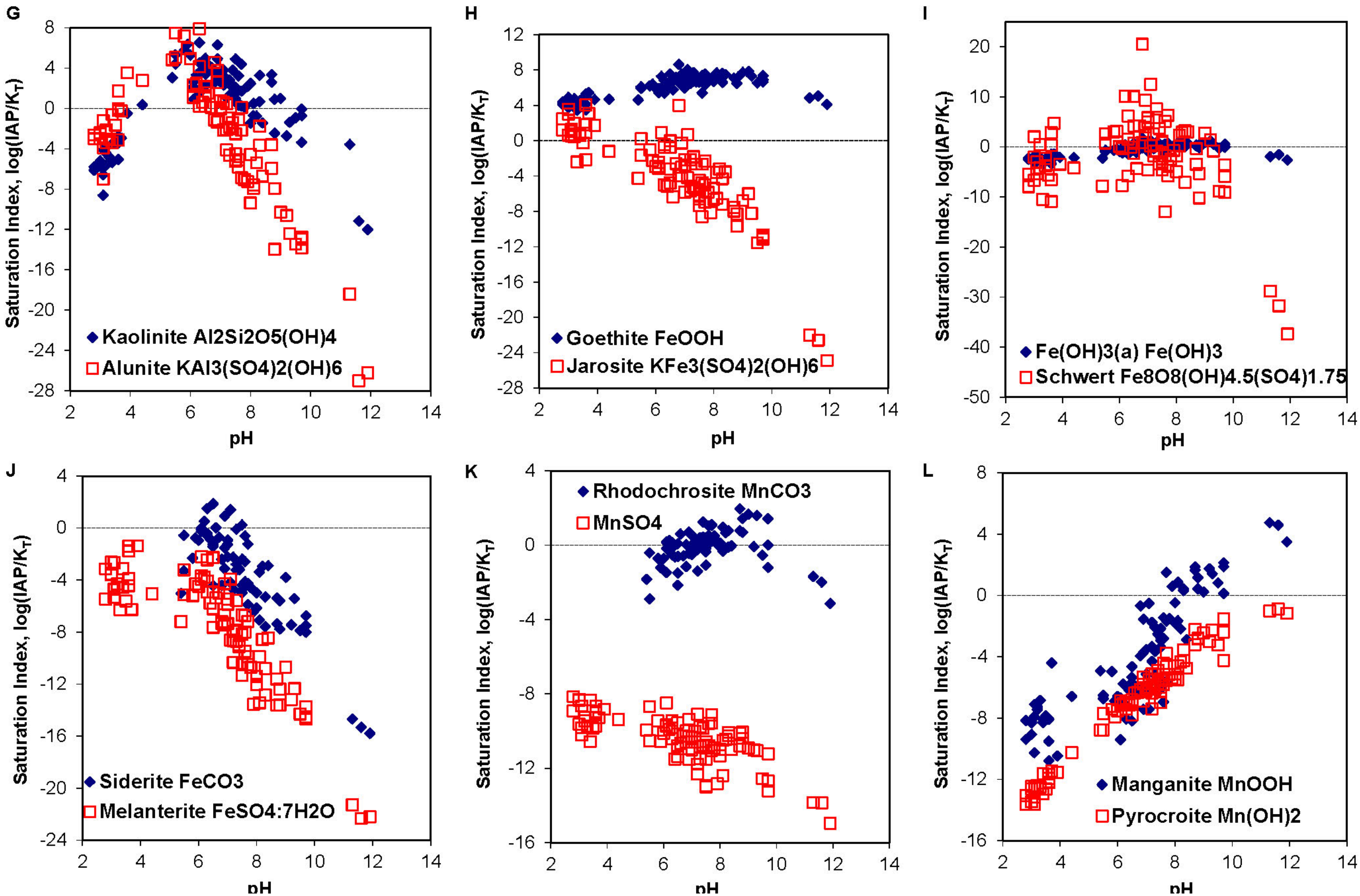
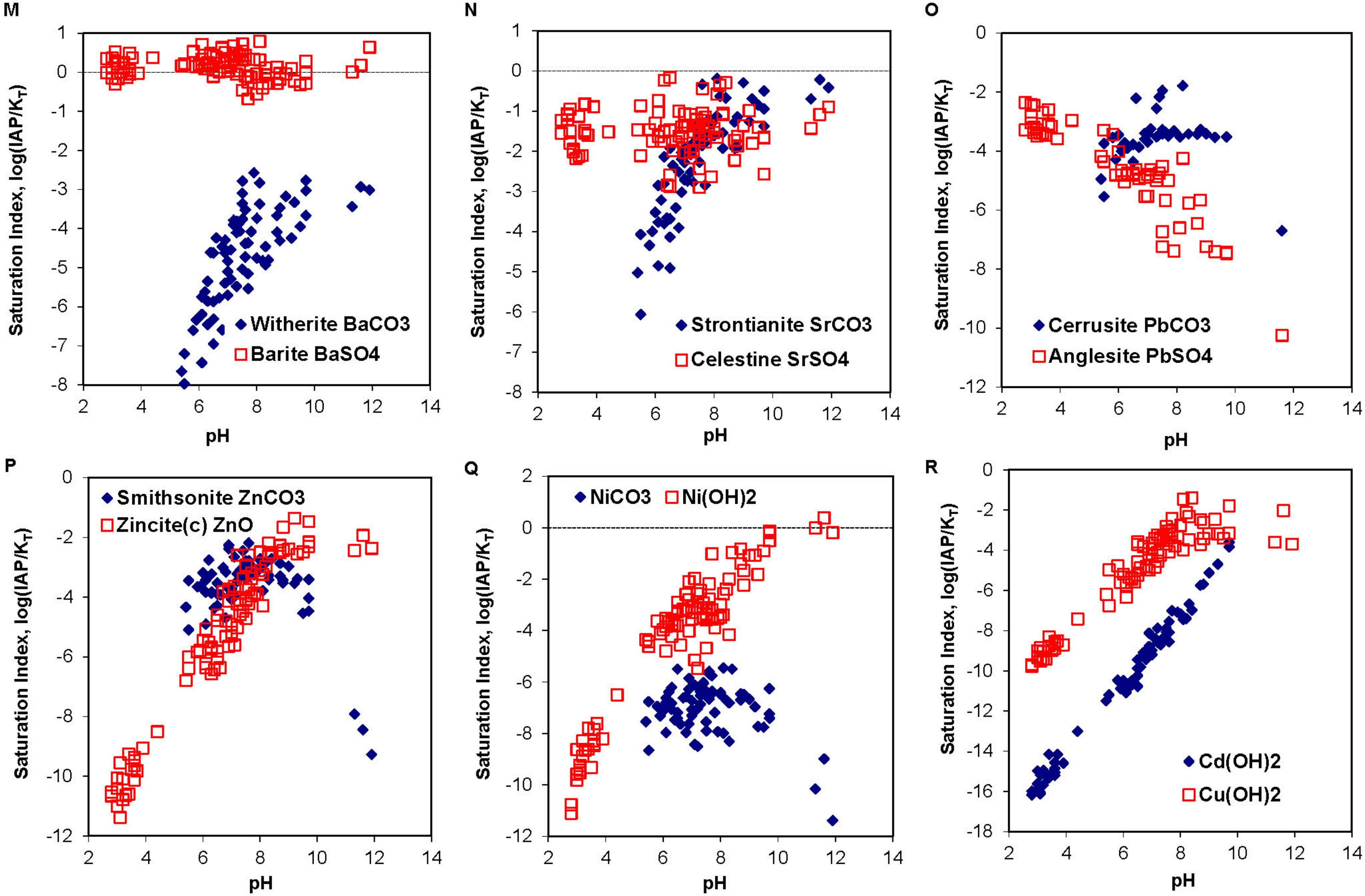
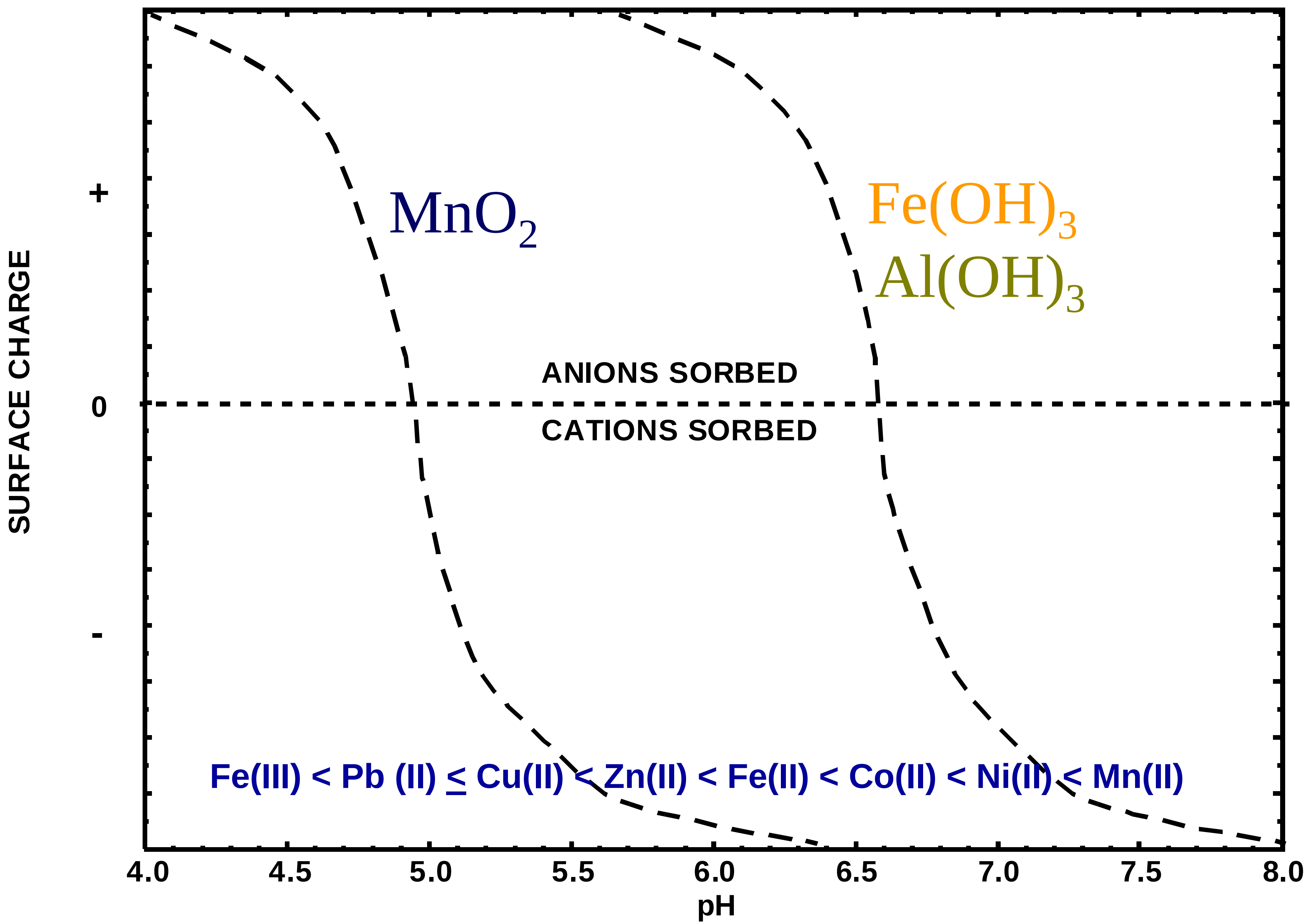


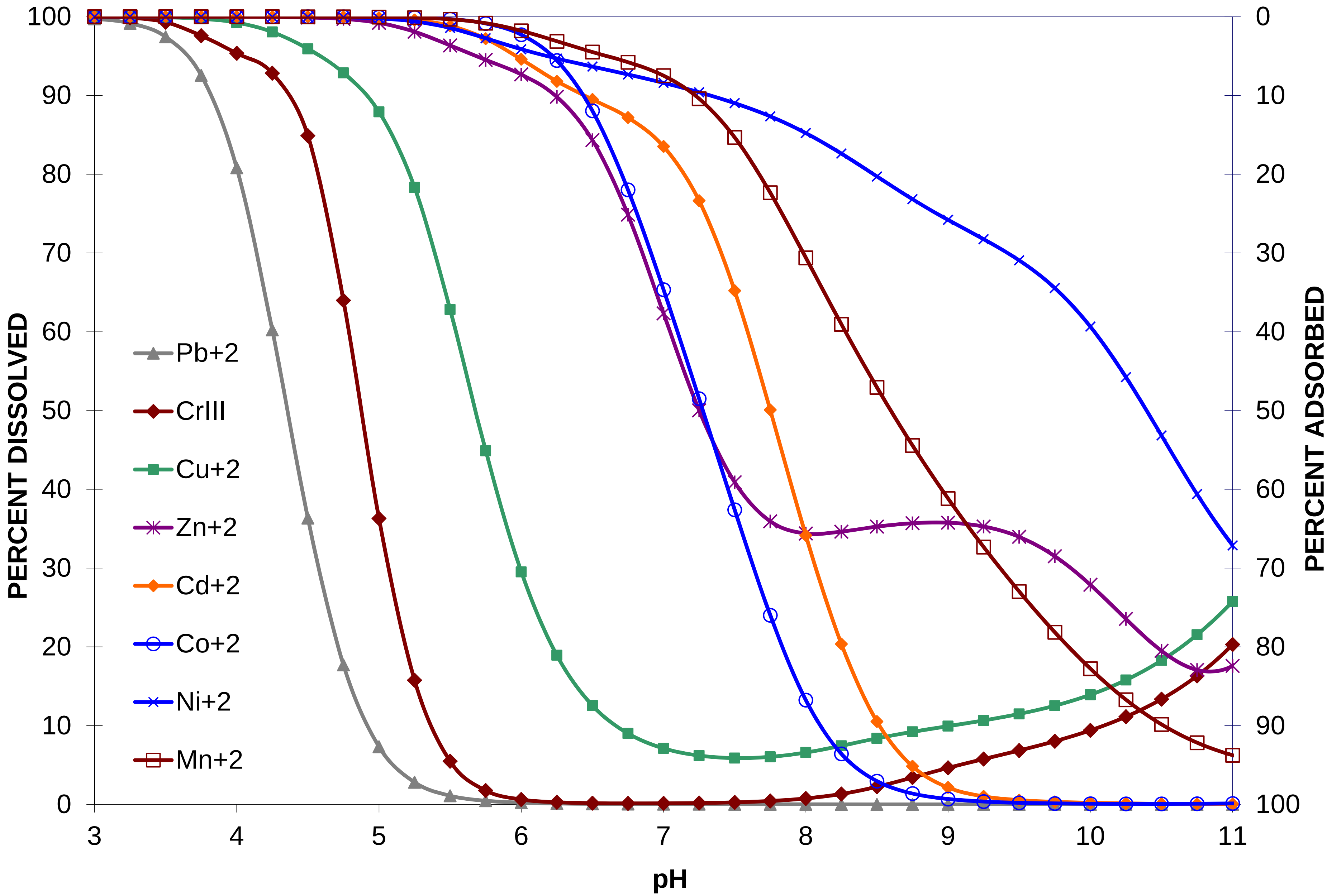
Feasibility for Mineral Precipitation



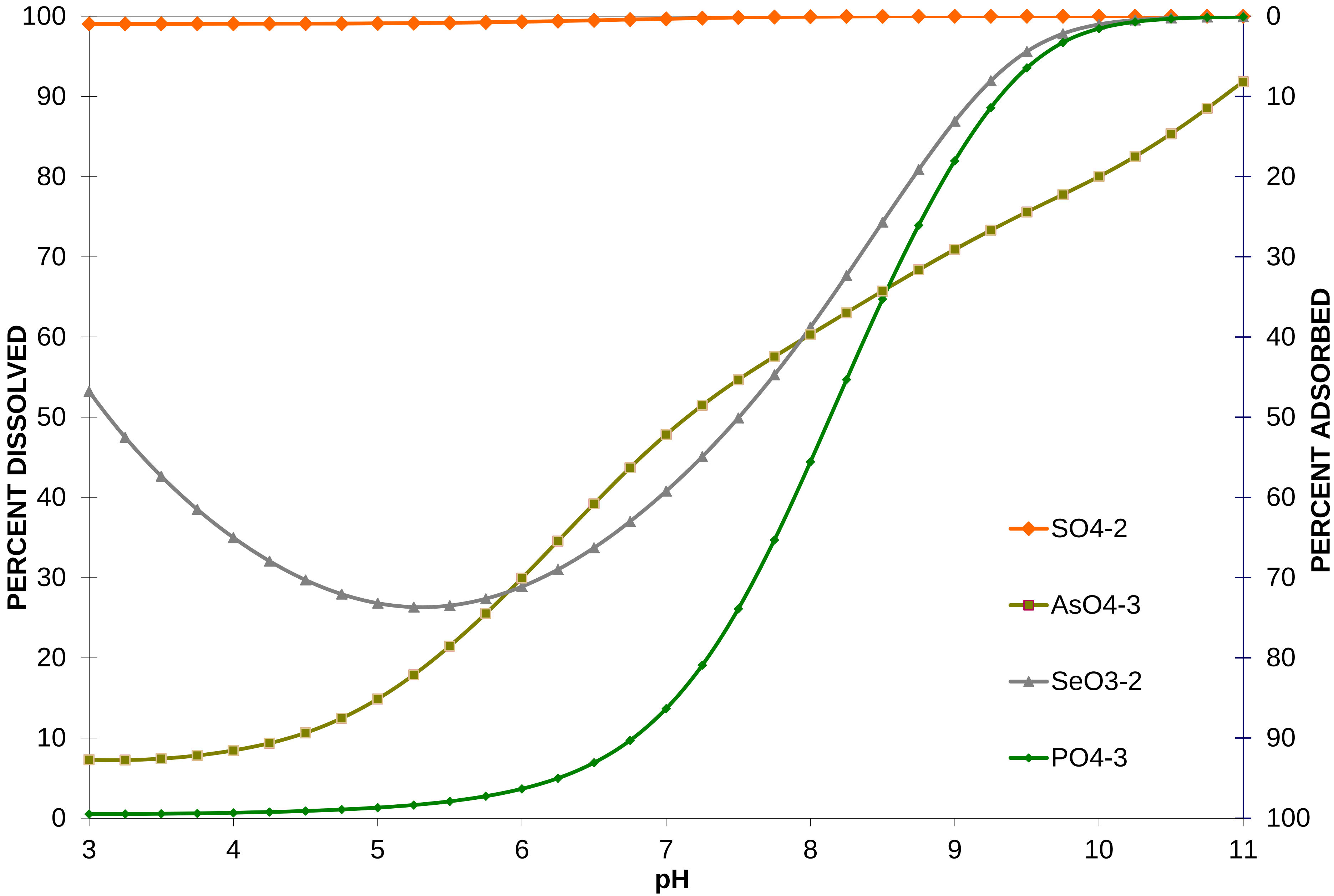
SORPTION AS AFFECTED BY "ZERO-POINT OF CHARGE"



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.

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CONCLUSIONS

- Relations among pH and solutes indicate:
  - ✓ solubility control of Al and Fe^{III} by hydroxide or hydroxysulfate minerals;
  - ✓ solubility control of Fe^{II} and Mn by carbonate or hydroxide minerals;
  - ✓ solubility control of Ba by barite ($BaSO_4$);
  - ✓ adsorption of Pb, Cu, Zn, Cd, Ni, and Cr^{III} by Fe^{III} minerals at neutral pH;
  - ✓ adsorption of As and Se by Fe^{III} minerals at low pH.

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.

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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 may provide a reasonable 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.

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