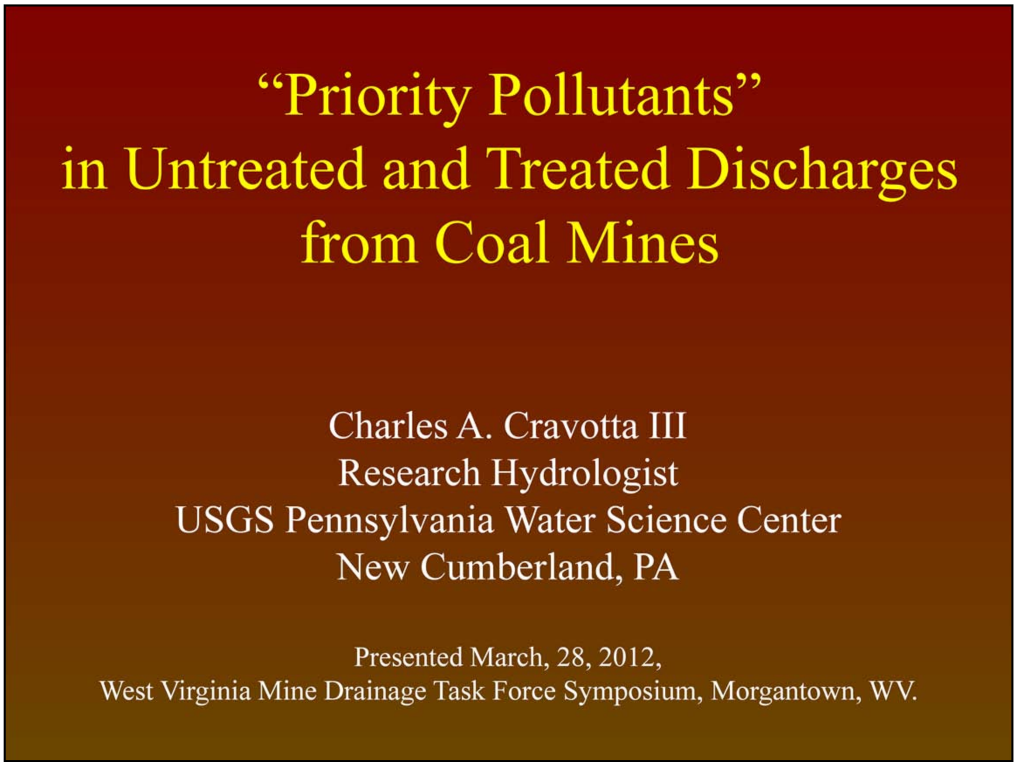

“Priority Pollutants” in Untreated and Treated Discharges from Coal Mines

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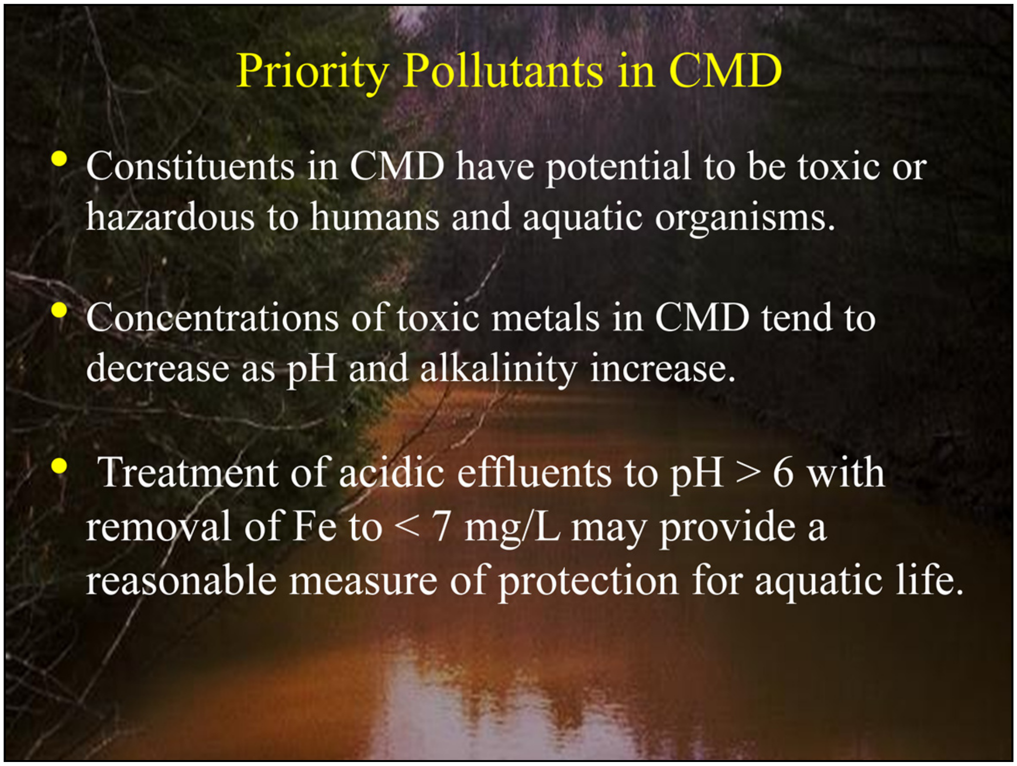
ABSTRACT: Clean sampling and analysis procedures were used to quantify more than 70 inorganic chemical constituents (including 36 priority pollutants), organic carbon and phenols, and other characteristics of untreated (influent) and treated (effluent) discharges at 38 permitted coal-mining or coal-processing facilities in the bituminous coalfield and 4 facilities in the anthracite coalfield of Pennsylvania. Of the 42 sites sampled, 26 were surface mines, 11 were deep mines, and 5 were coal refuse disposal facilities. No chemical additives were used at 28 percent of the sites; caustic soda (NaOH), lime (CaO; $Ca(OH)_2$), flocculent, or limestone was used at 21, 40, 6, and 4 percent of the sites, respectively. All the treatment facilities incorporated structures to promote aeration and settling of solids.

The influents had wide ranges of pH (2.8 to 7.6), specific conductance (253 to 13,000 mS/cm), dissolved solids (168 to 18,100 mg/L), hot acidity (-600 to 8,000 mg/L as $CaCO_3$), SO_4 (15 to 10,700 mg/L), Fe (0.01 to 4,100 mg/L), Mn (0.02 to 136 mg/L), Al (0.002 to 128 mg/L), Zn (0.002 to 18.8 mg/L), and associated constituents. The pH values of the effluents ranged from 5.5 to 11.9 and were greater than or equal to the pH of the corresponding influents. All but one of the effluents had pH $\geq$ 6; three had pH > 9. The measured hot acidity and computed net acidity were similar and were consistently lower for the effluent compared to the influent. Although most of the effluents were net alkaline (hot acidity and net acidity < 0), three were net acidic. None of the untreated influent met criteria maximum concentration (CMC) levels for the protection of freshwater aquatic organisms from toxic effects of priority pollutants. However, the treated effluents

met CMC levels for most pollutants, including Sb, As, Ba, Cd, Cl, Cr, Pb, Hg, Ni, Se, Ag, Tl, and V, and exceeded CMC levels only for Al (2 samples > 0.75 g/L), Fe (4 > 1.0 mg/L), Zn (1 > 0.255 mg/L), Cu (1 > 32 mg/L), and Co (5 > 95 mg/L).

The Wilcoxon matched-pair signed-ranks test was used to test the hypothesis that the difference between the effluent and influent pairs was equal to zero. Constituents that were the same for effluent and influent ($p > 0.05$) included flow rate, specific conductance (SC), osmotic pressure, hardness, alkalinity, total organic carbon (TOC), K, Cl, NO_3, PO_4, Sb, Sr, Br, Se, Mo, and V. However, most constituents decreased significantly as a result of treatment, including total dissolved solids (TDS), acidity, 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, total inorganic carbon (TIC), biological oxygen demand (BOD), and chemical oxygen demand (COD). Constituents that increased included temperature, dissolved oxygen (DO), pH, Ca, and Na.

Spearman's rank correlation and principal components analysis were used to evaluate the relations of priority pollutants to other chemical constituents in the influent and effluent. Most priority pollutants (Al, Fe, Mn, Co, Ni, Zn, Cd, Tl, U, As, Se) were negatively correlated with pH and positively correlated with acidity. Specific conductance was strongly correlated with TDS, hardness, SO_4, and major cations (Ca, Mg, Na, 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+}. The 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. Brine constituents were more strongly correlated with one another (Na, Cl, Br) than with other constituents and were not strongly associated with acidity or pH. In essence, increasing pH and decreasing Al, Fe, and Mn resulted in lower concentrations of priority pollutants but generally did not affect SC or osmotic pressure. These findings suggest that typical chemical or aerobic 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 SC or osmotic pressure.



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.

PRIORITY POLLUTANTS IN AMD:

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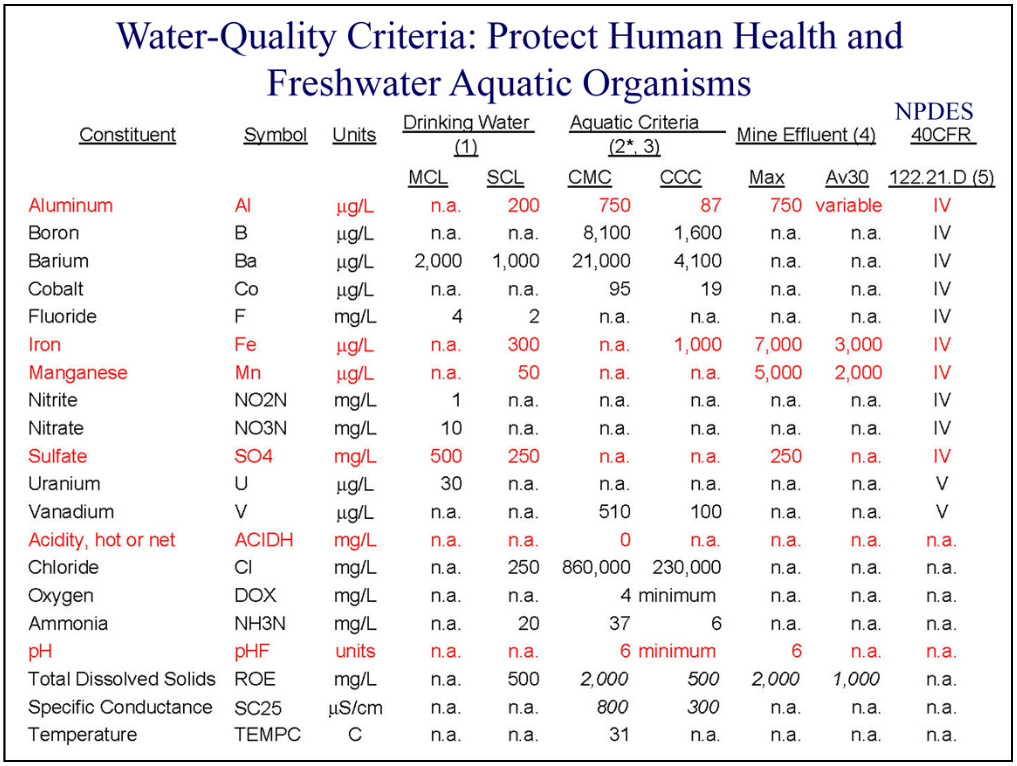
- Treatment of acidic effluents to pH > 6 with removal of Fe to < 7 mg/L may provide a reasonable measure of protection for aquatic life.



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.

ENVIRONMENTAL SIGNIFICANCE: Concentrations of dissolved metals and other constituents are regulated to minimize toxic or hazardouse effects and can be compared to:

(1) USEPA drinking water standards considering the maximum contaminant level (MCL) or secondary contaminant level (SCL);

(2,3) USEPA national aquatic water quality criteria for criteria maximum concentration (CMC) or criteria continuous concentration (CCC) limits, which may be corrected for hardness (blue shaded); or

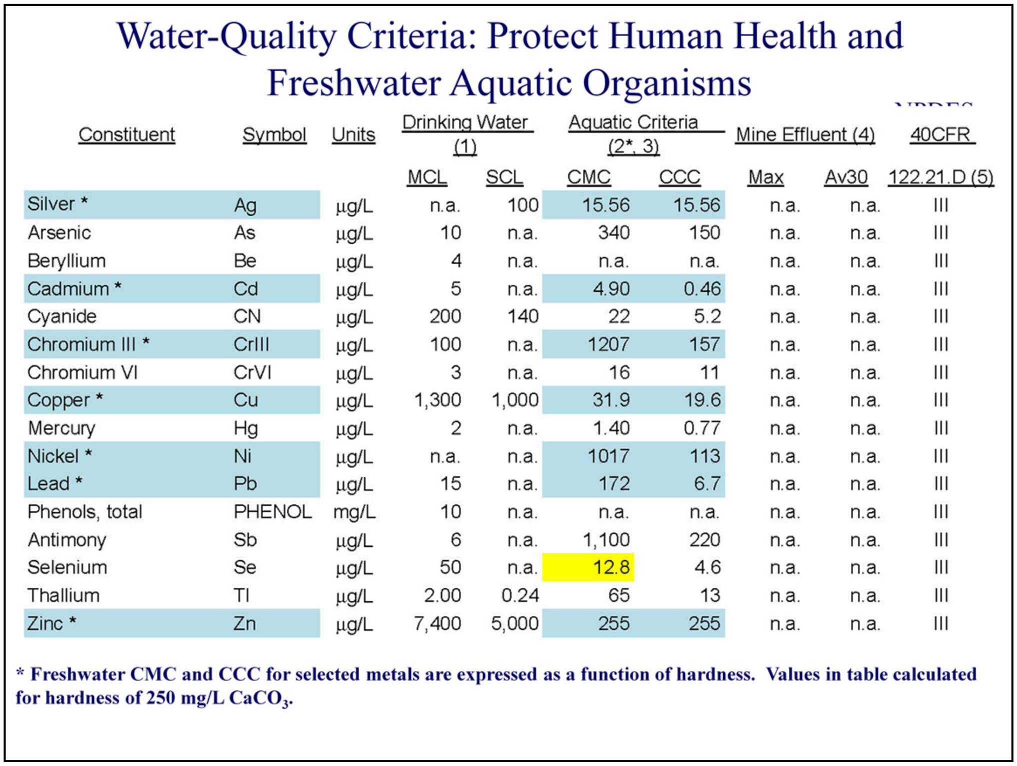
(4) Pennsylvania permitted mine effluent (PME) criteria establishing limits for the maximum allowable concentration (CPA) or 30-day average.

(5) USEPA 40CFR, Part 122.21, Appendix D, tables III, IV, and V —NPDES Permit Application Testing Requirements (40CFR 122.21):

Table III—Other Toxic Pollutants (Metals and Cyanide) and Total Phenols

Table IV—Conventional and Nonconventional Pollutants Required To Be Tested by Existing Dischargers if Expected to be Present

Table V—Toxic Pollutants and Hazardous Substances Required To Be Identified by Existing Dischargers if Expected To Be Present



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Constituent	Symbol	Units	Drinking Water (1)		Aquatic Criteria (2*, 3)		Mine Effluent (4)		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 $CaCO_3$.**

ENVIRONMENTAL SIGNIFICANCE: Concentrations of dissolved metals and other constituents are regulated to minimize toxic or hazardouse effects and can be compared to:

(1) USEPA drinking water standards considering the maximum contaminant level (MCL) or secondary contaminant level (SCL);

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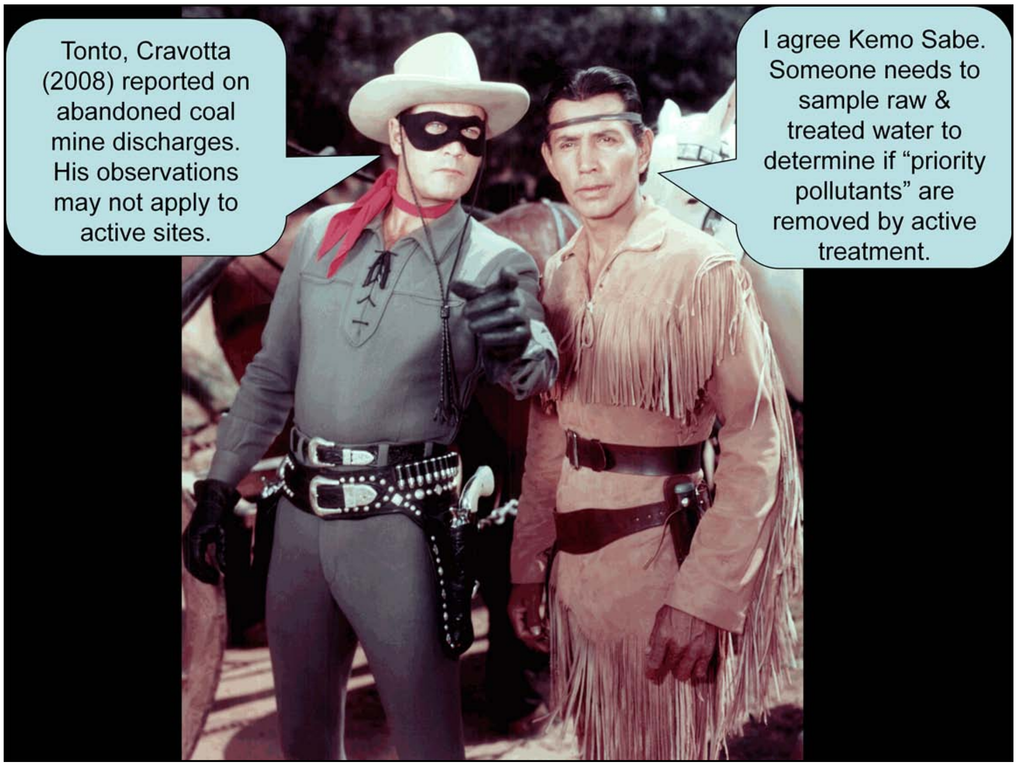


Tonto, Cravotta (2008) reported on abandoned coal mine discharges. His observations may not apply to active sites.

I agree Kemo Sabe. Someone needs to sample raw & treated water to determine if “priority pollutants” are removed by active treatment.

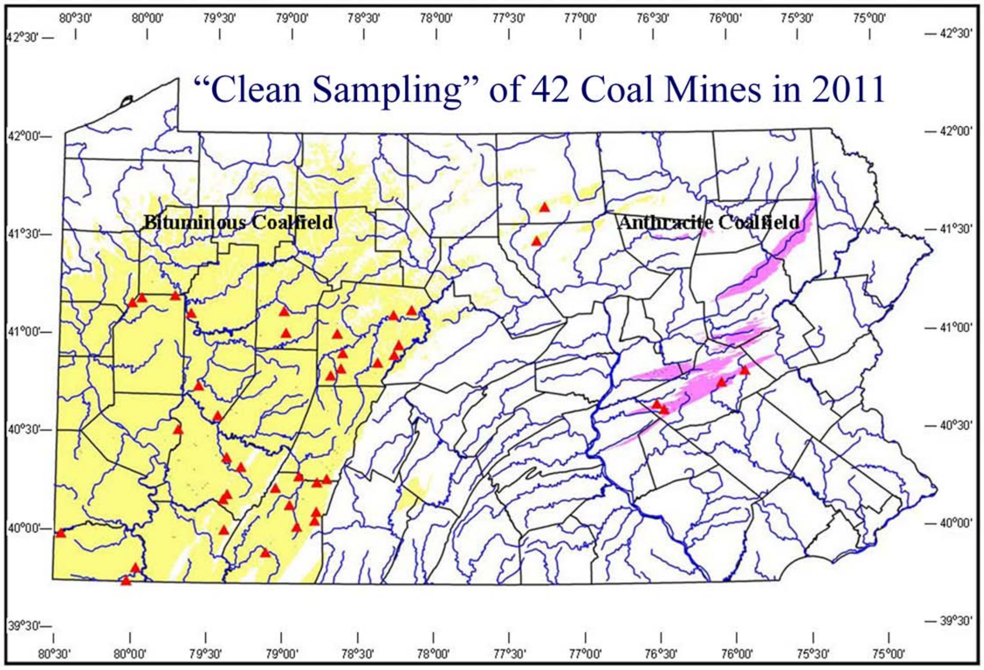


Fig. 1. Map of Pennsylvania showing locations of 42 coal-mining or coal-processing facilities in the Bituminous and Anthracite Coalfields where untreated and treated effluents were sampled in 2011.

COAL MAP: Clean sampling and analysis procedures were used to quantify more than 70 inorganic chemical constituents, including 36 "priority pollutants," organic carbon and phenols, and other characteristics of untreated (influent) and treated (effluent) discharges at 38 permitted coal-mining or coal-processing facilities in the bituminous coalfield and 4 facilities in the anthracite coalfield of Pennsylvania.

42 Coal Mines or Refuse Facilities:

26 surface; 11 deep; 5 CRDA

28 % – no chemicals used (Ponds)

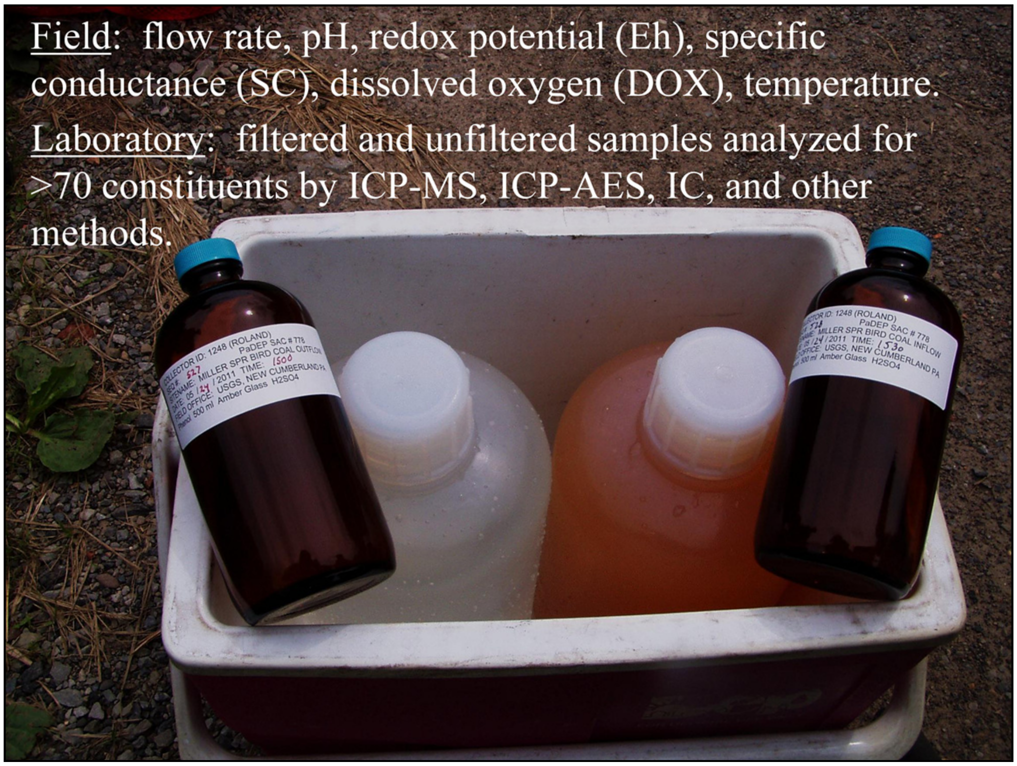
21 % – caustic soda (NaOH) used

40 % – lime (CaO; $Ca(OH)_2$) used

6 % – flocculent or oxidant used

4 % – limestone ($CaCO_3$) used

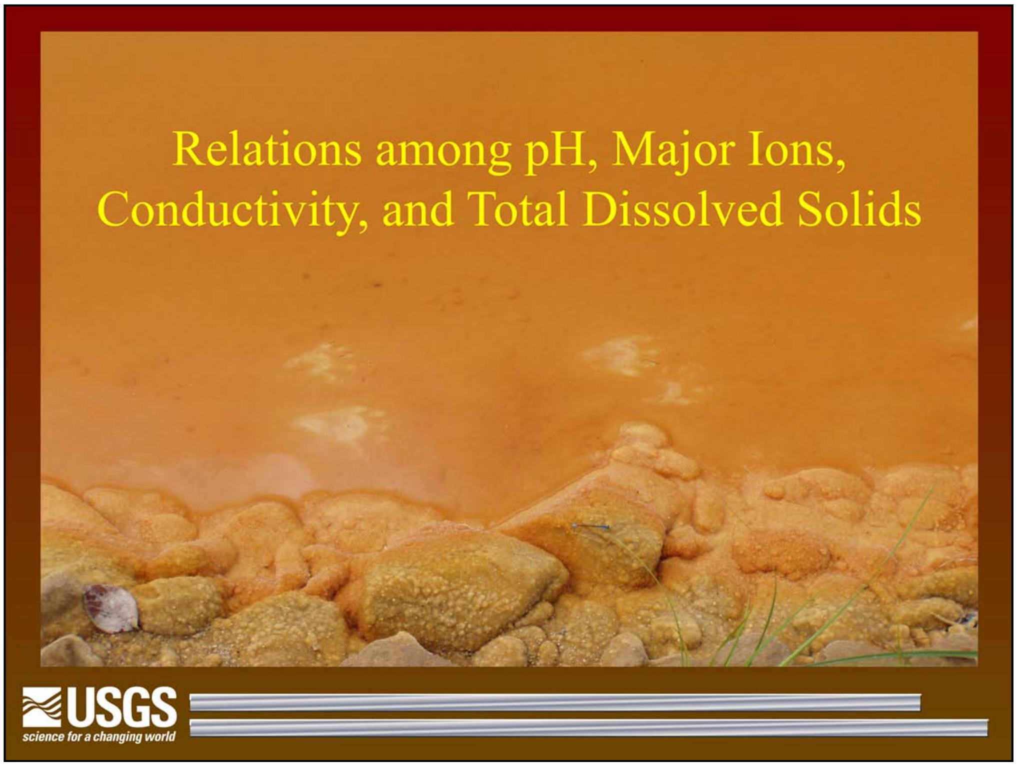
PRIORITY POLLUTANTS AT ACTIVE TREATMENT FACILITIES IN PENNSYLANIA: Of the 42 sites sampled, 26 were surface mines, 11 were deep mines, and 5 were coal refuse disposal facilities. No chemical additives were used at 28 percent of the sites; caustic soda (NaOH), lime (CaO or $Ca(OH)_2$), flocculent, or limestone was used at 21, 40, 6, and 4 percent of the sites, respectively. All the treatment facilities incorporated structures to promote aeration and settling of solids.



<u>Field</u>: flow rate, pH, redox potential (Eh), specific conductance (SC), dissolved oxygen (DOX), temperature.

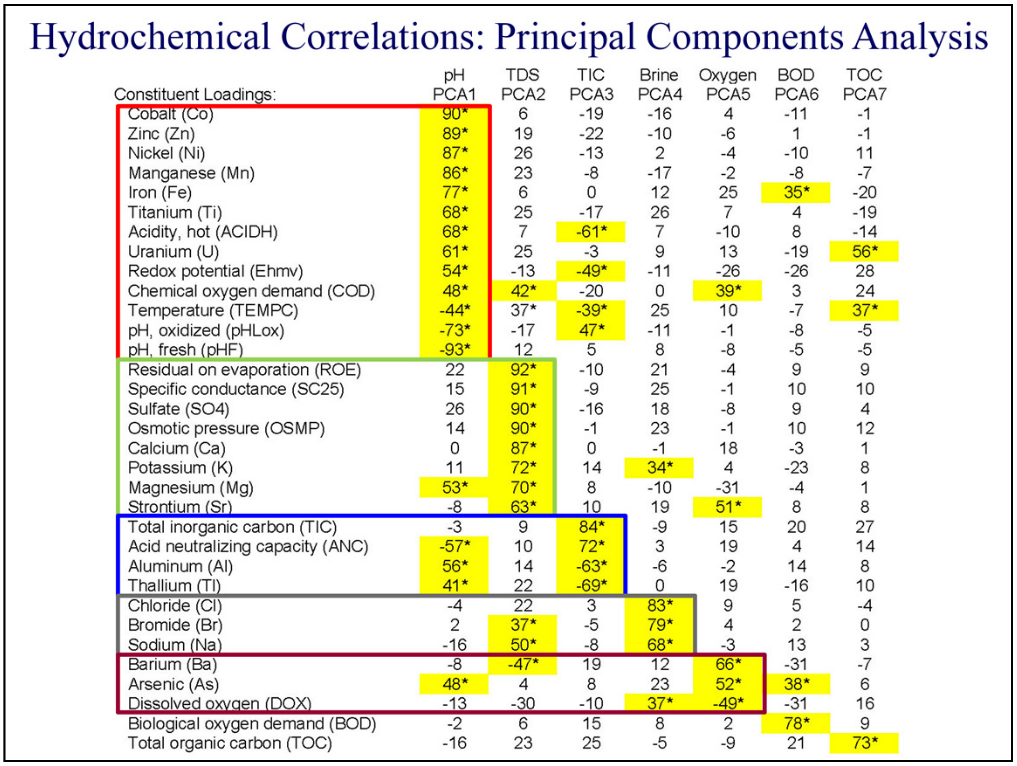
<u>Laboratory</u>: filtered and unfiltered samples analyzed for >70 constituents by ICP-MS, ICP-AES, IC, and other methods.

PRIORITY POLLUTANTS AT ACTIVE TREATMENT FACILITIES IN PENNSYLANIA: Data on flow rate, pH, redox potential (Eh), specific conductance, dissolved oxygen, and temperature were measured in the field when samples were collected. Samples for analysis of dissolved inorganic constituents were filtered using 0.45-um capsule filters inside a an enclosed glove box. Concentrations of major anions, major cations, and trace elements were determined using inductively coupled plasma emission mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and ion chromatography (IC) (Fishman and Friedman, 1989; Faires, 1993; Crock and others, 1999). Alkalinity and lab pH on filtered samples were determined in the laboratory within 8 hours of sampling. After 6 to 8 months of storage at ambient temperature, the samples were reanalyzed for “aged” pH and hot acidity.



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

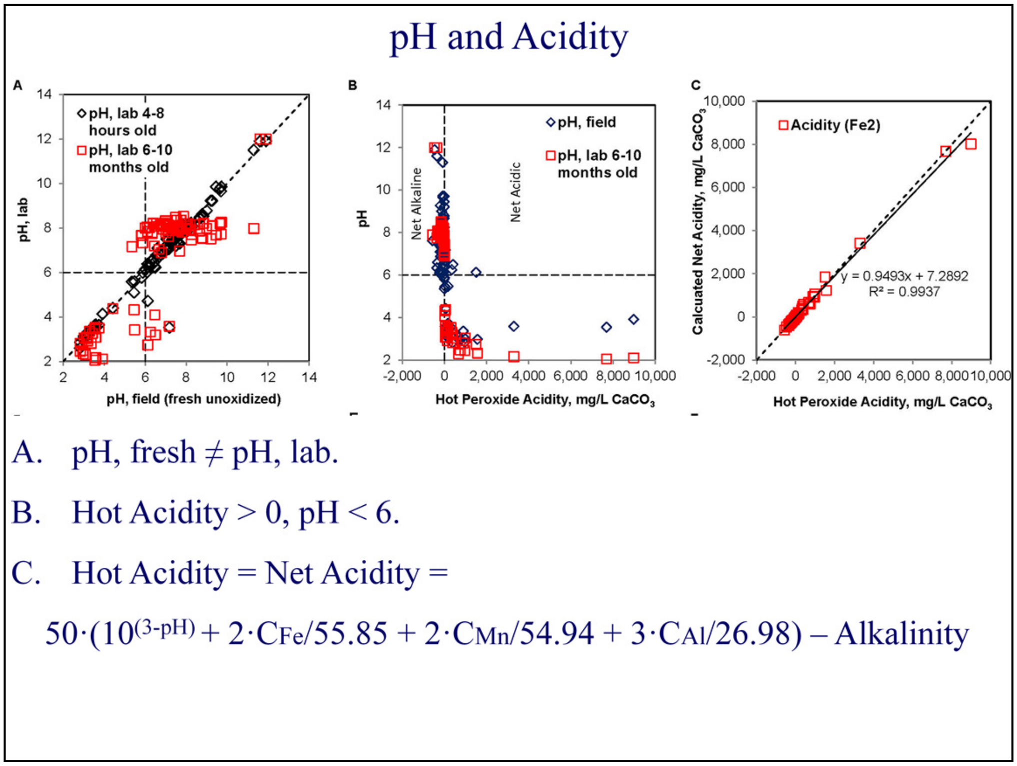
RELATIONS AMONG pH, MAJOR IONS, CONDUCTIVITY, TOTAL DISSOLVED SOLIDS:



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*

HYDROCHEMICAL CORRELATIONS: Spearman's rank correlation and principal components analysis were used to evaluate the relations of priority pollutants to other chemical constituents in the influent and effluent. Most priority pollutants (Al, Fe, Mn, Co, Ni, Zn, Cd, Tl, U, As, Se) were negatively correlated with pH and positively correlated with acidity. Specific conductance was strongly correlated with TDS, hardness, SO_4, and major cations (Ca, Mg, Na, 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+}. The 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. Brine constituents were more strongly correlated with one another (Na, Cl, Br) than with other constituents and were not strongly associated with acidity or pH. In essence, increasing pH and decreasing Al, Fe, and Mn resulted in lower concentrations of priority pollutants but generally did not affect SC or osmotic pressure.



pH and Acidity

A. pH, fresh ≠ pH, lab.

B. Hot Acidity > 0, pH < 6.

C. Hot Acidity = Net Acidity =

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

pH, ACIDITY:

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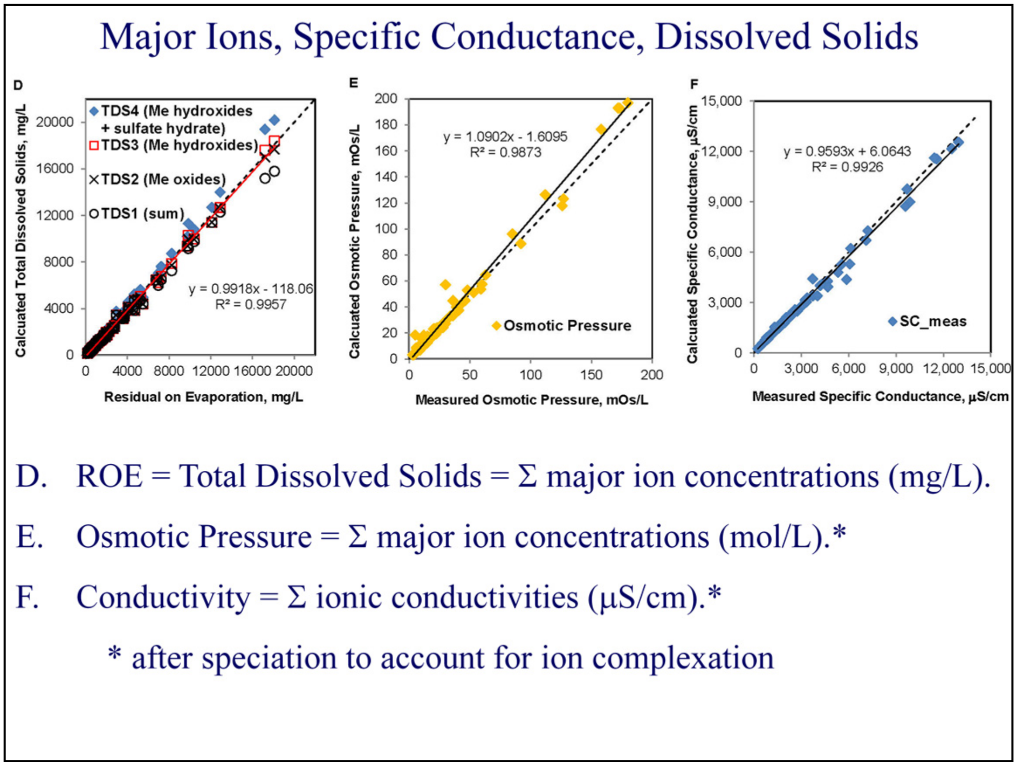
B. Hot Acidity > 0, pH < 6.

C. Hot Acidity = Net Acidity = Acidity (H^+, Fe^{2+}, Mn^{2+}, Al^{3+}) – ANC.

D. Net Acidity (mg/L $CaCO_3$) = $50 \cdot (10^{(3\text{-pH})} + 2 \cdot C_{Fe}/55.85 + 2 \cdot C_{Mn}/54.94 + 3 \cdot C_{Al}/26.98) - \text{Alkalinity}$



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, DISSOLVED SOLIDS, SPECIFIC CONDUCTANCE:

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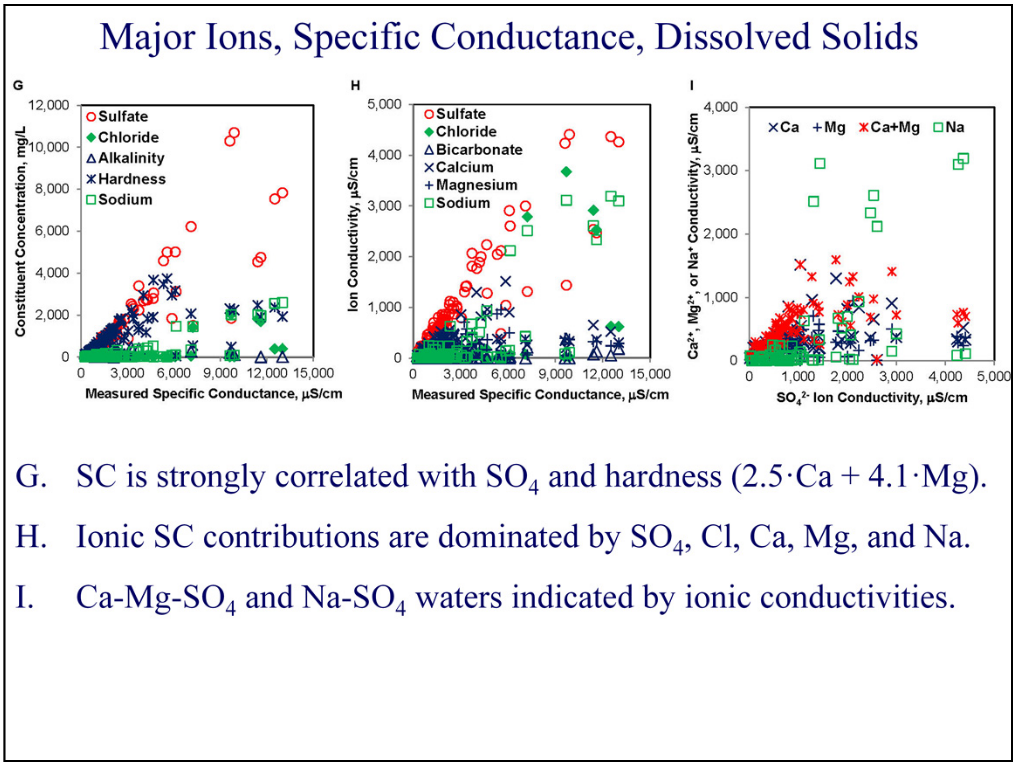

Major Ions, Specific Conductance, Dissolved Solids

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.

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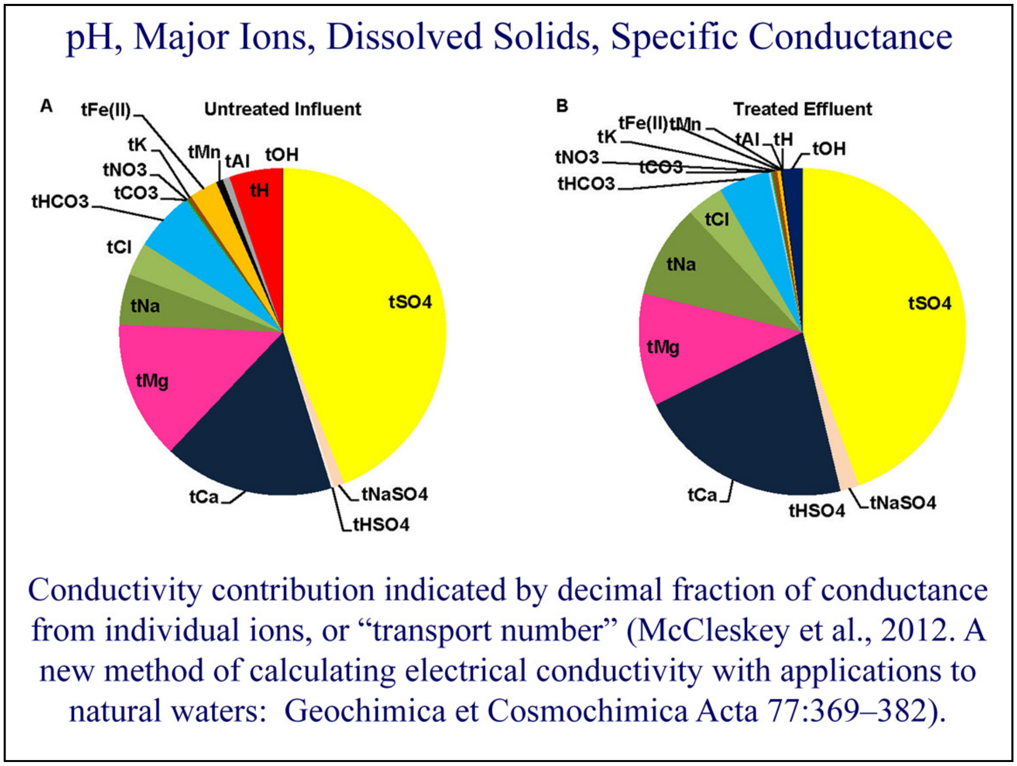
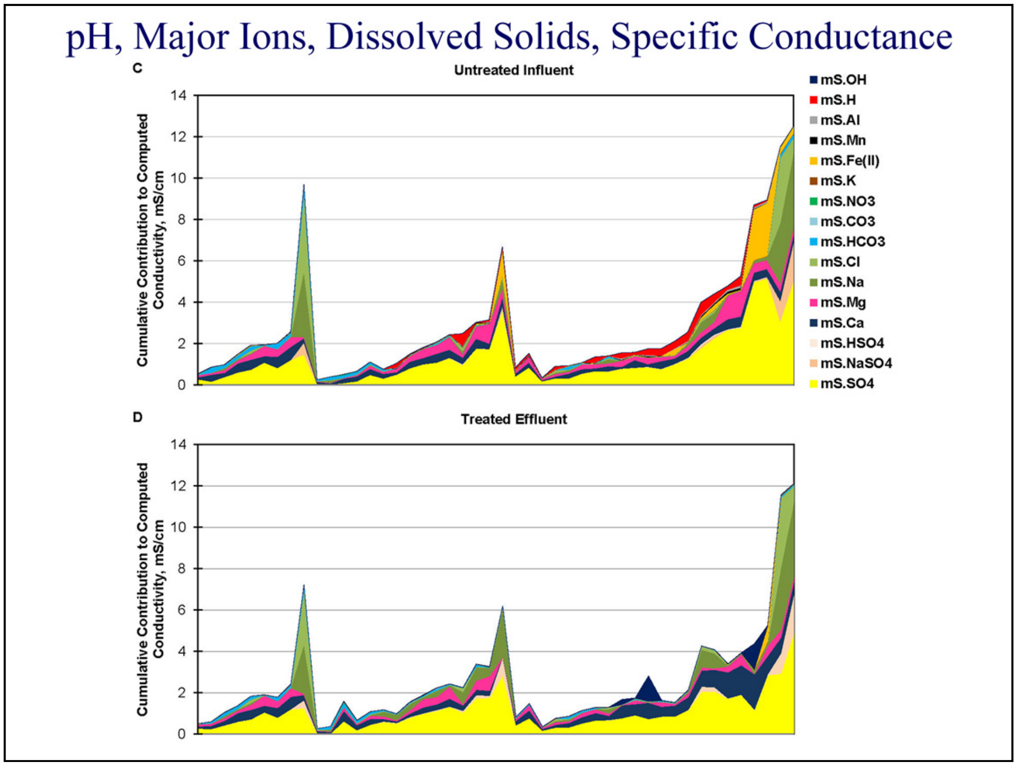


pH, Major Ions, Dissolved Solids, Specific Conductance

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, 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

pH, MAJOR IONS, DISSOLVED SOLIDS, SPECIFIC CONDUCTANCE:

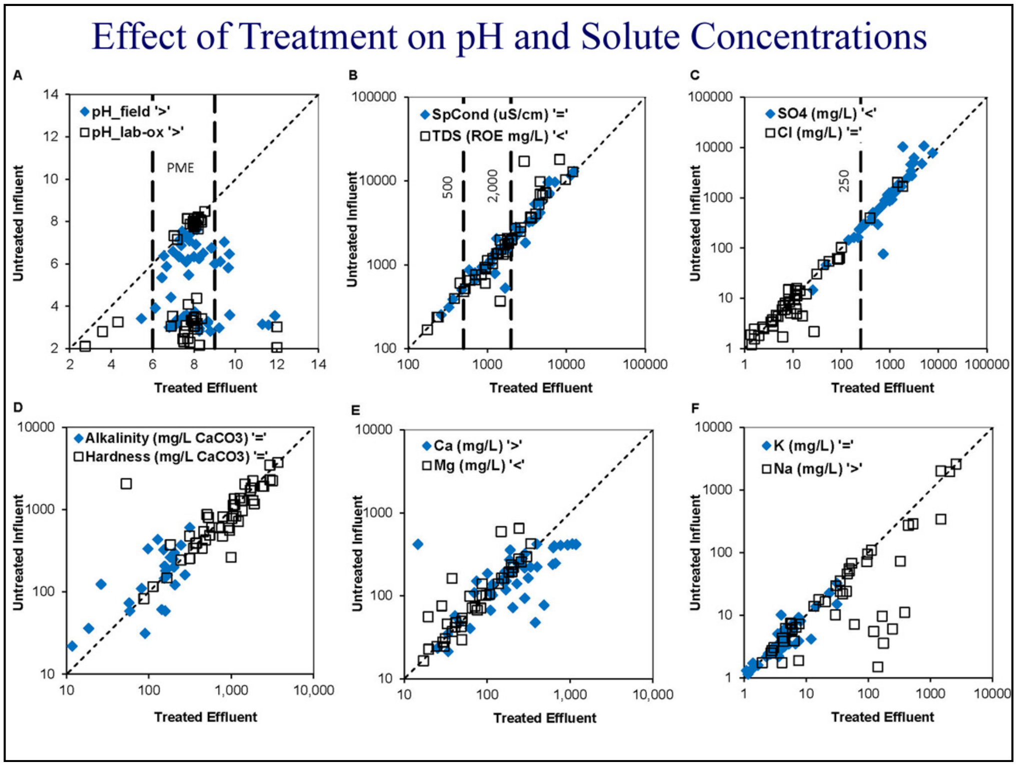
- Ionic contributions to SC were mainly from SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^-, and, to a lesser extent, H^+, Fe^{2+}, Mn^{2+}, and Al^{3+}.

- 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.

Effects of Treatment on Priority Pollutants

USGS
science for a changing world

EFFECT OF TREATMENT:



Effect of Treatment on pH and Solute Concentrations

EFFECT OF TREATMENT: The Wilcoxon matched-pair signed-ranks test was used to test the hypothesis that the difference between the effluent and influent pairs was equal to zero. The tests computed the difference in composition between the effluent and the corresponding influent for each site. The absolute values of the differences for all the sites combined were rank transformed, and then the sign of the differences was reapplied to the ranks

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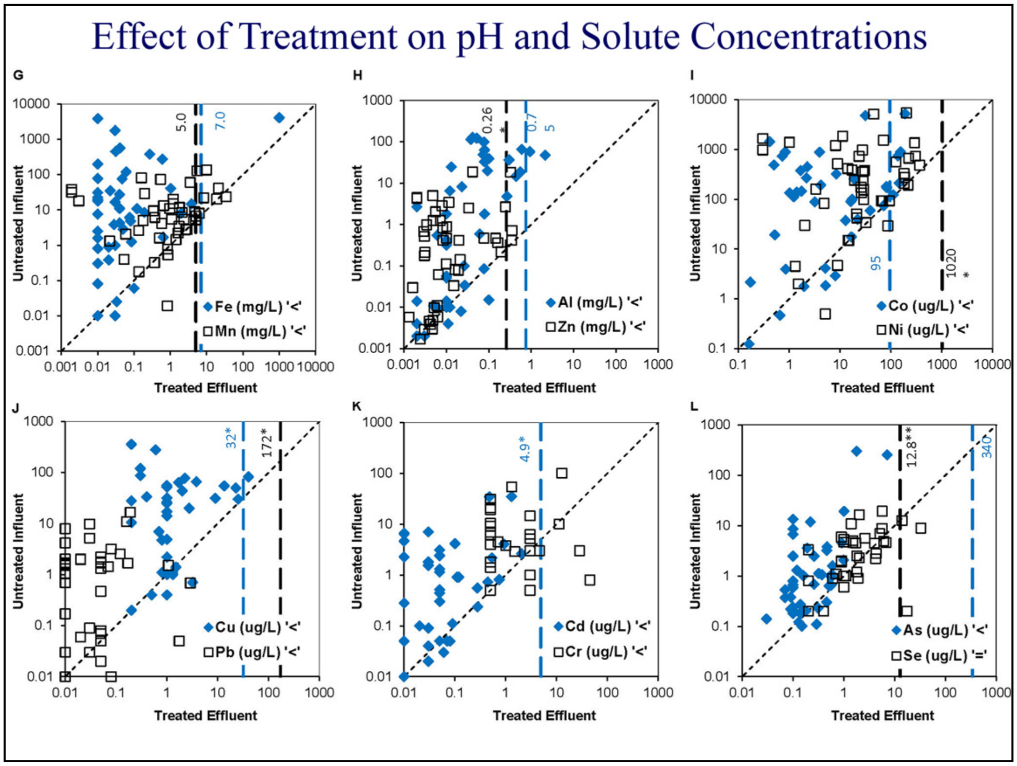

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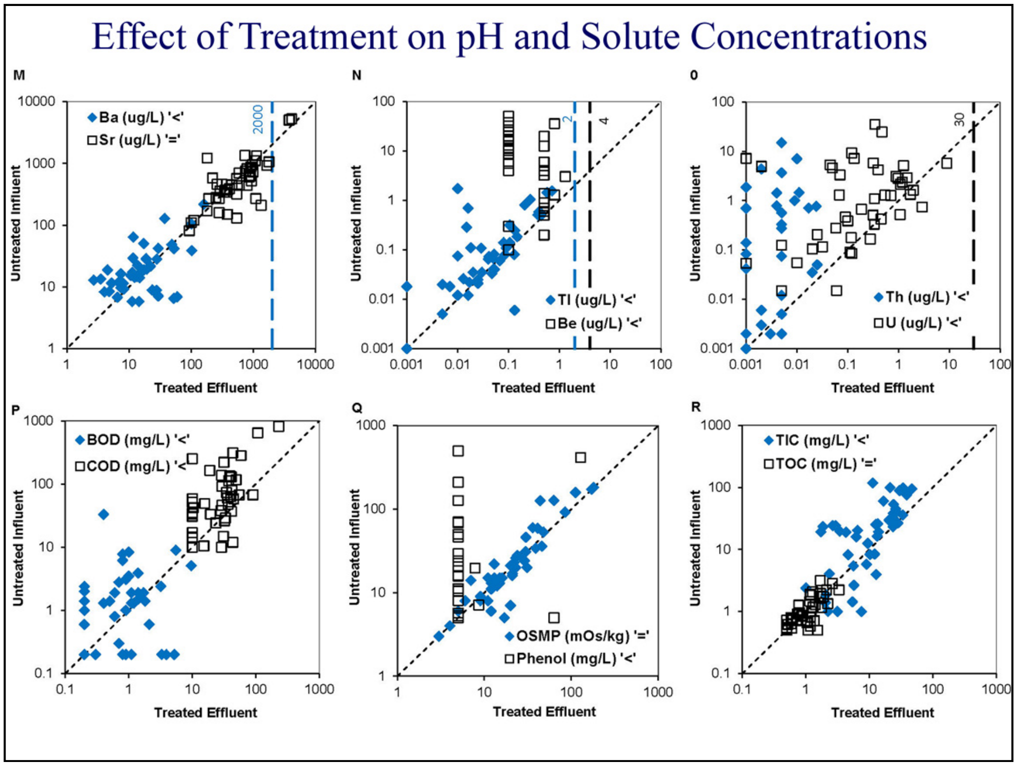

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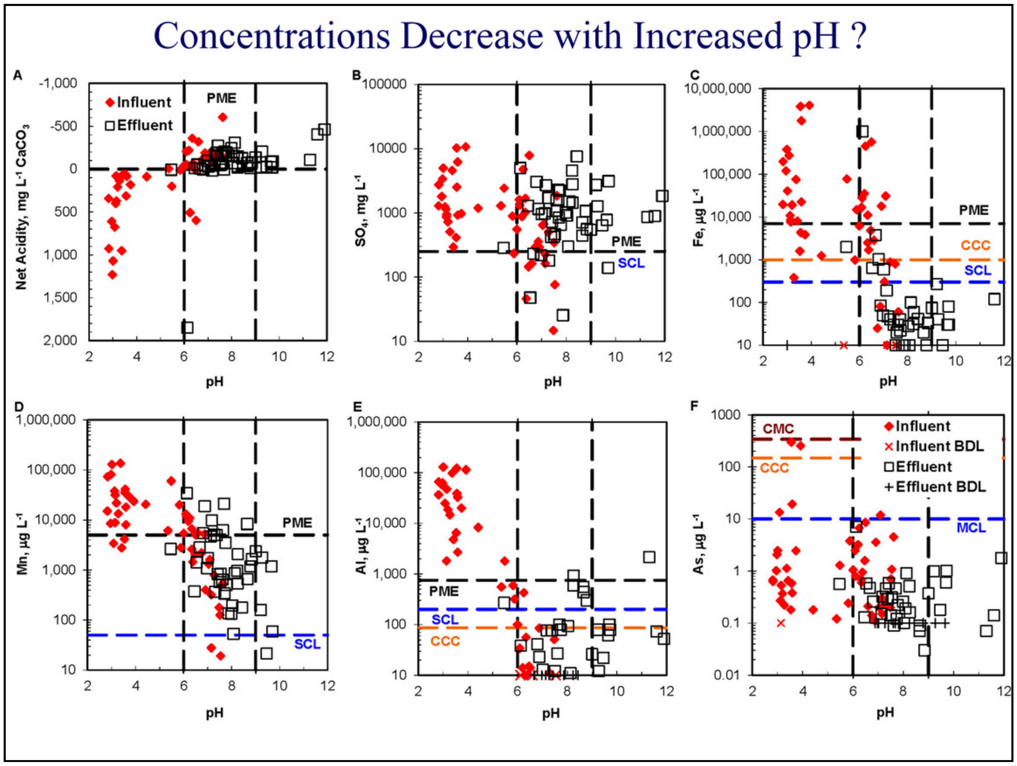
Implications for Aquatic and Terrestrial Organisms

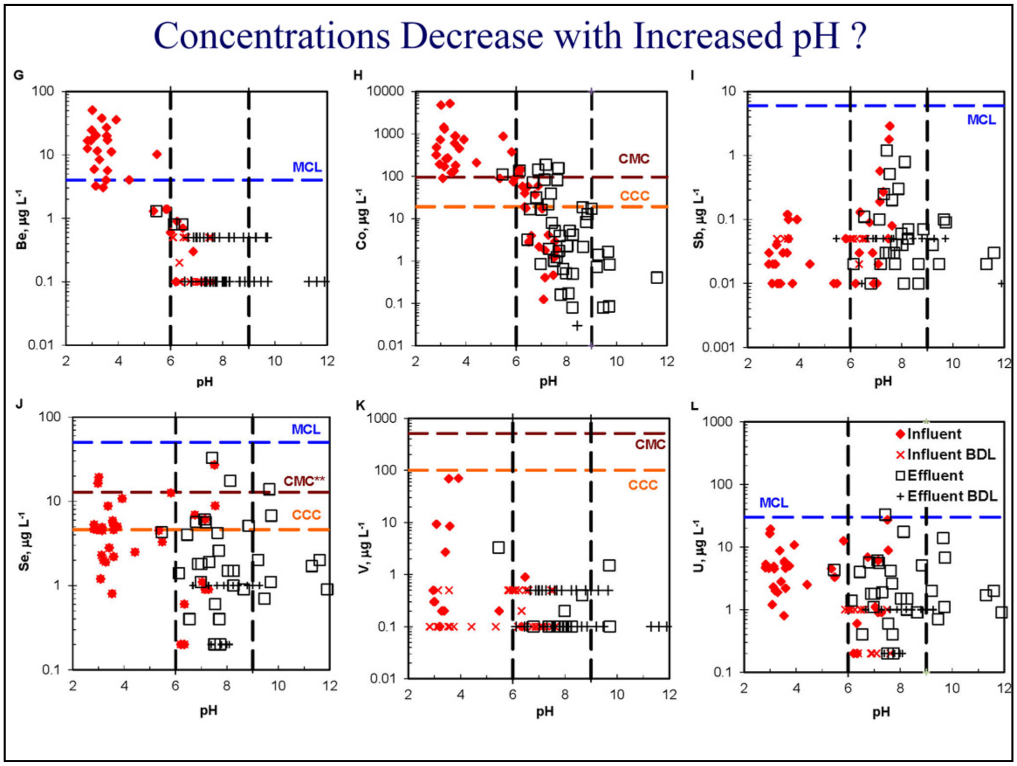
IMPLICATIONS FOR AQUATIC AND TERRESTRIAL ORGANISMS:



Concentrations Decrease with Increased pH ?

ENVIRONMENTAL SIGNIFICANCE: Permitted mine effluent must have pH 6 to 9. All but three effluents had net acidity concentrations greater than 0 (alkalinity > acidity) and pH ($\geq$ 6); some treated effluent had pH > 9. Although most of the treated effluents had greater than 250 mg/L SO4 threshold, only one sample had Fe greater than 7 mg/L. Several samples had Mn greater than 5 mg/L.

None of the untreated influent met all criteria maximum concentration (CMC) levels for the protection of freshwater aquatic organisms from toxic effects of priority pollutants. However, the treated effluents met CMC levels for most pollutants, including Sb, As, Ba, Cd, Cl, Cr, Pb, Hg, Ni, Se, Ag, Tl, and V, and exceeded CMC levels only for Al (2 samples > 0.75 mg/L), Fe (4 > 1.0 mg/L), Zn (1 > 255 ug/L), Cu (1 > 32 ug/L), and Co (5 > 95 ug/L).



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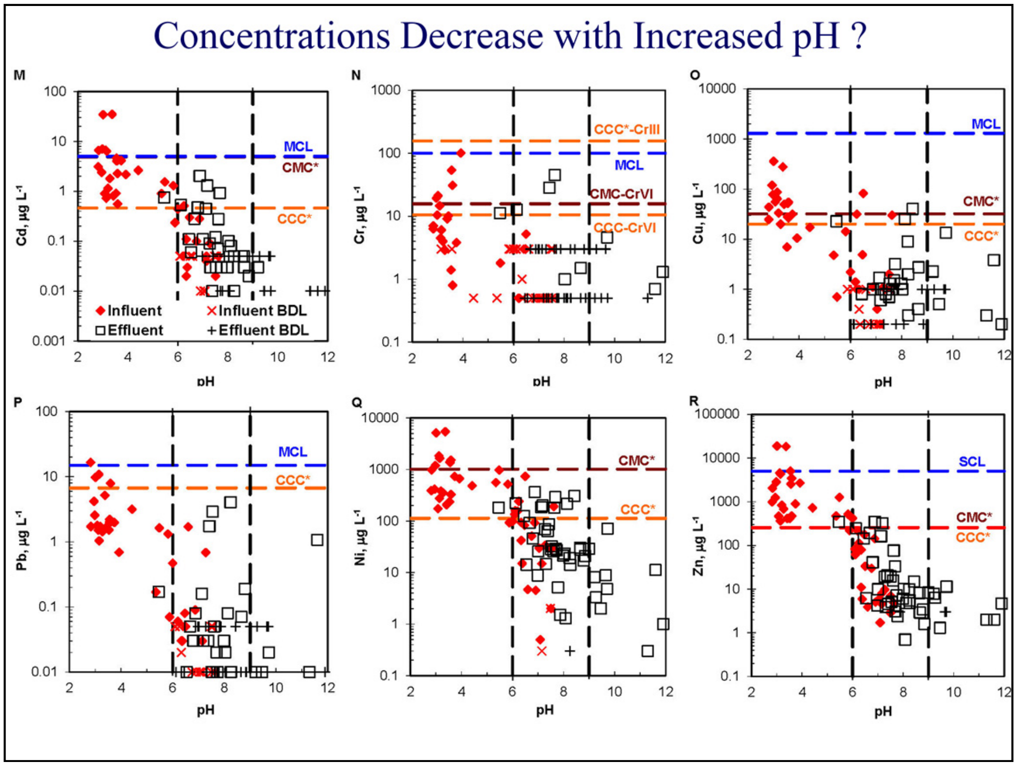


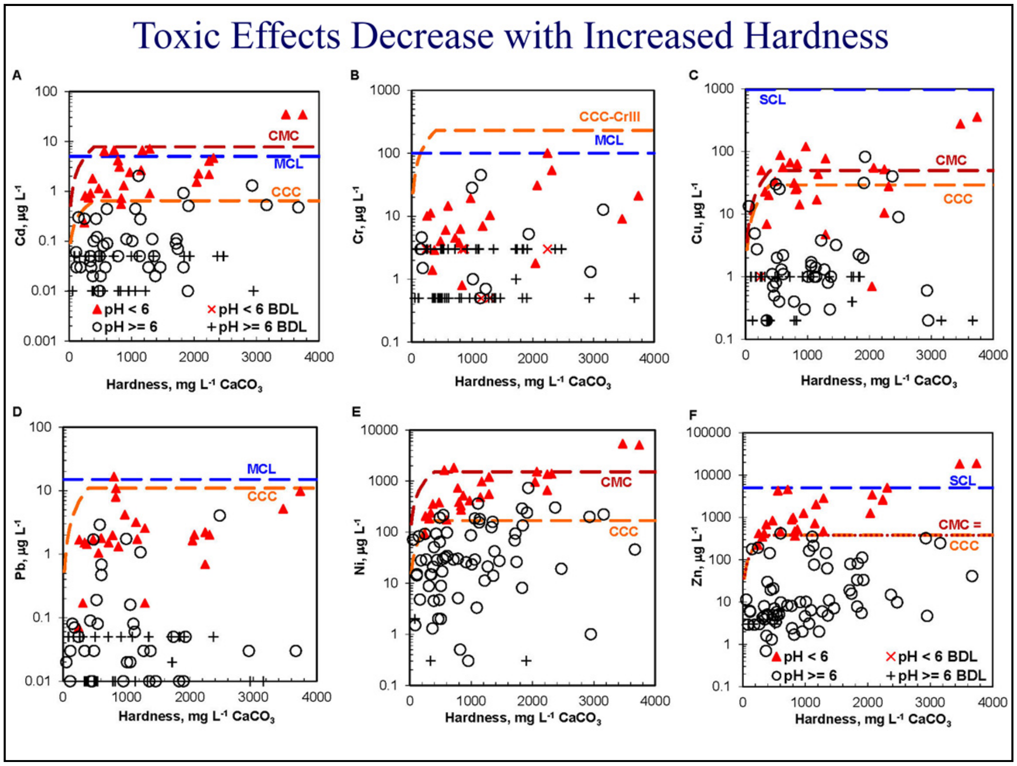
Concentrations Decrease with Increased pH ?

ENVIRONMENTAL SIGNIFICANCE: Without considering sample hardness, acidic samples (pH < 6) and some pH-compliant samples (pH ≥ 6) had elevated concentrations of Cd, Cr, Pb, Ni, and/or Zn compared to the aquatic CMC or CCC levels. However….

Metal* Toxicity Decreases with Hardness

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

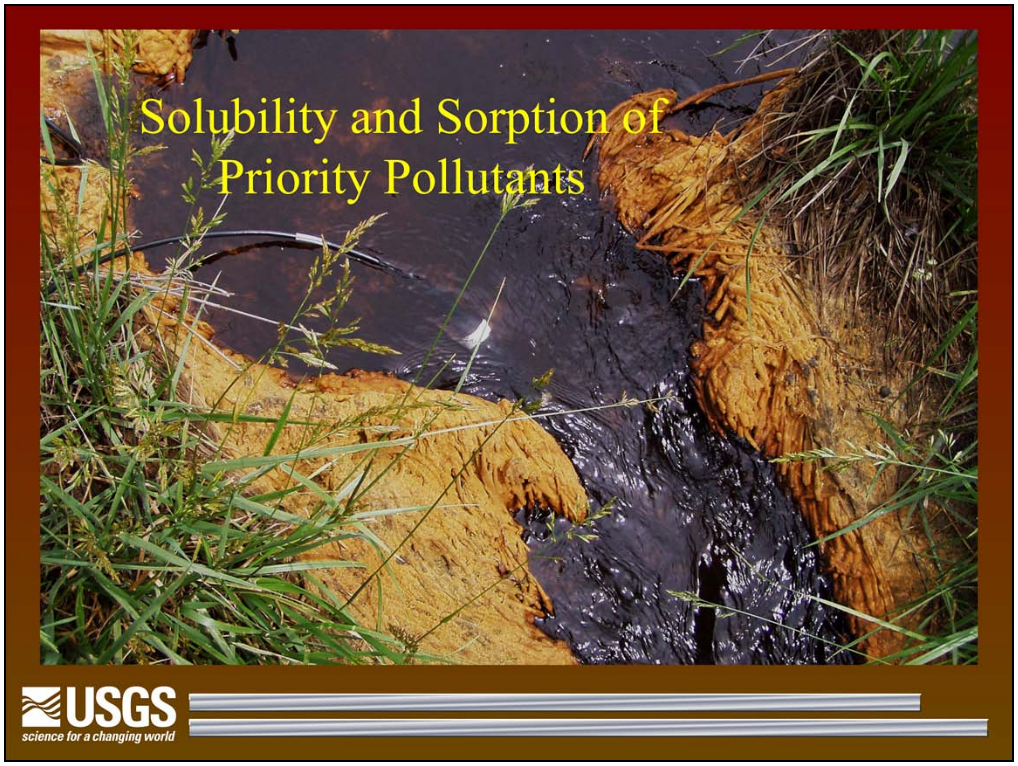
*Metals: Cd, Cr, Cu, Pb, Ni, Zn



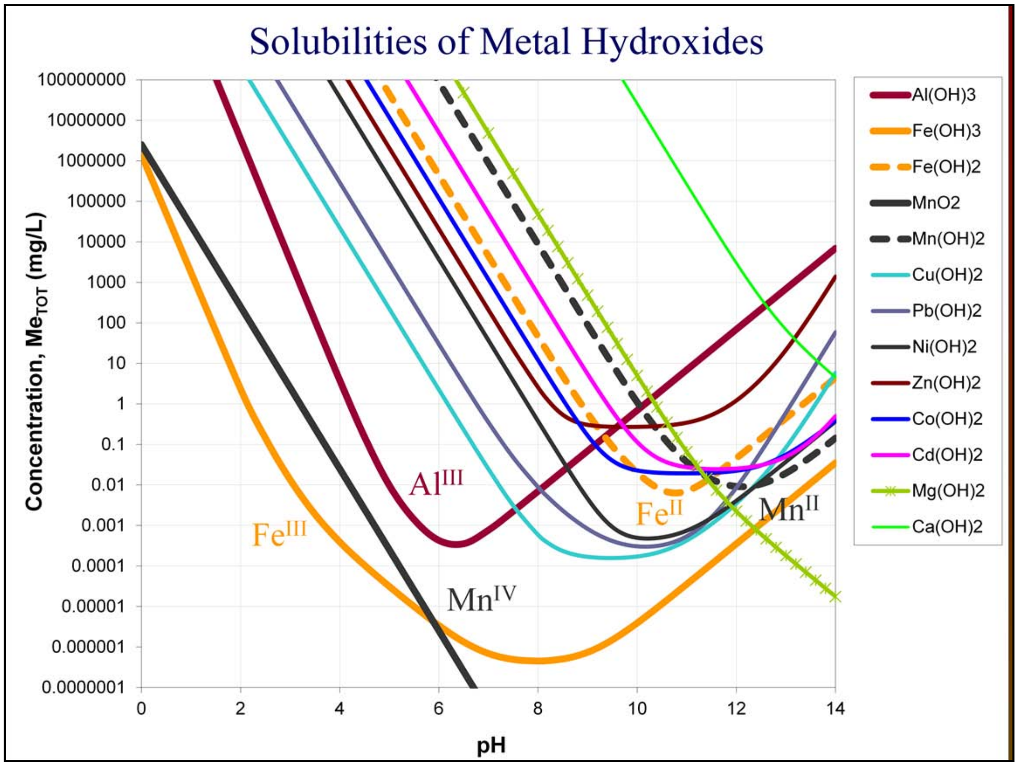
Toxic Effects Decrease with Increased Hardness

ENVIRONMENTAL SIGNIFICANCE: After correcting for sample hardness, all pH-compliant samples (pH ≥ 6) had concentrations of Cd, Cr, Pb, Ni, and Zn that were less than CMC levels. One pH-compliant sample exceeded the CMC value for Cu.

These findings suggest that 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.

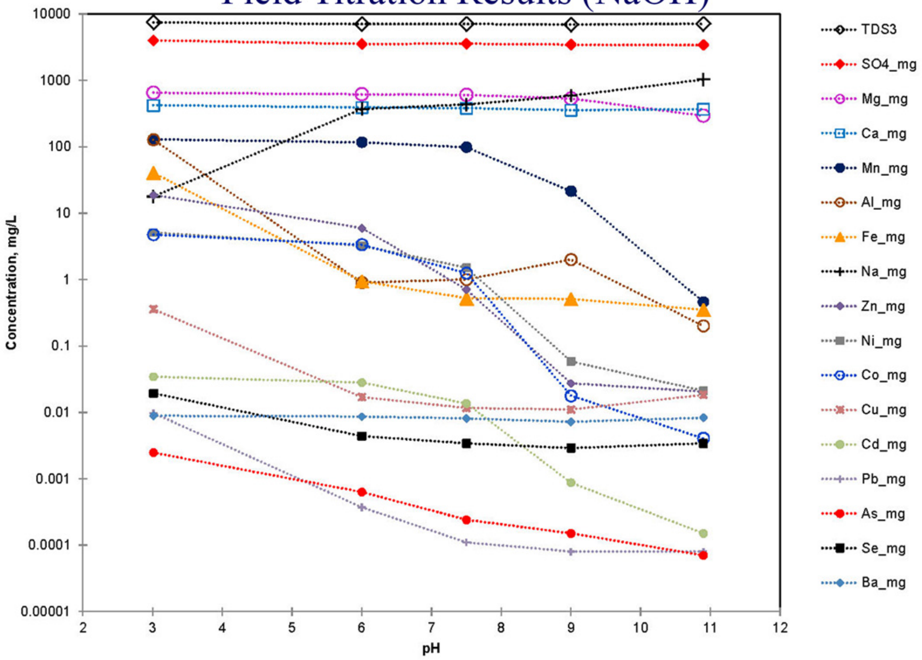


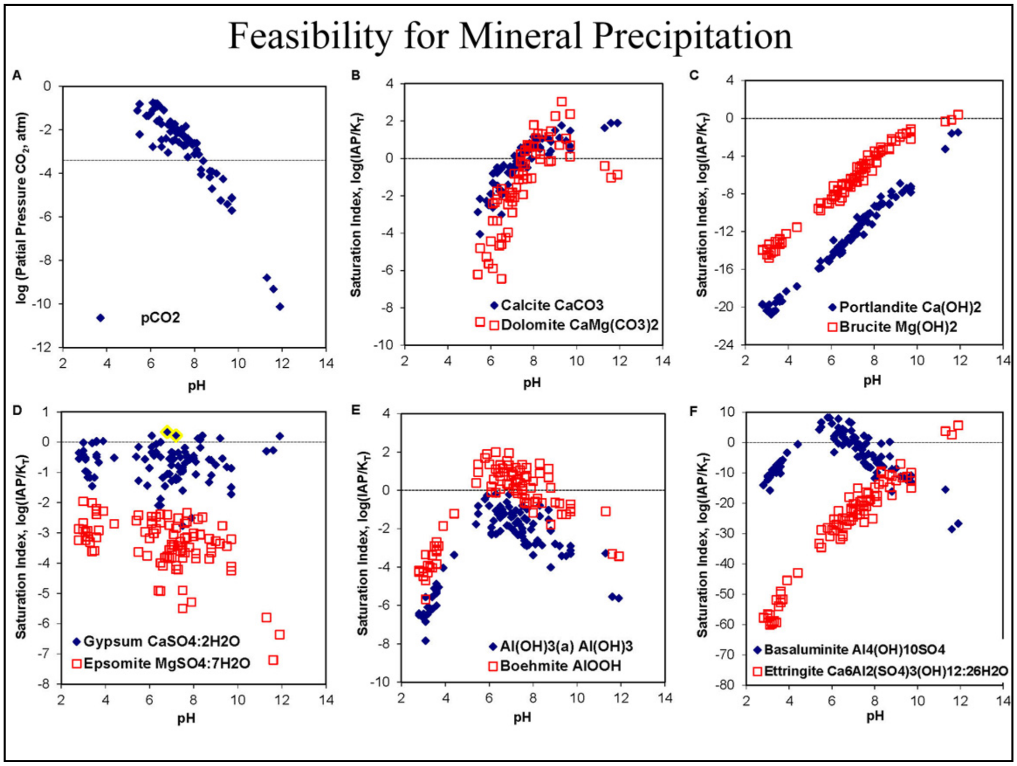
Solubility and Sorption of Priority Pollutants



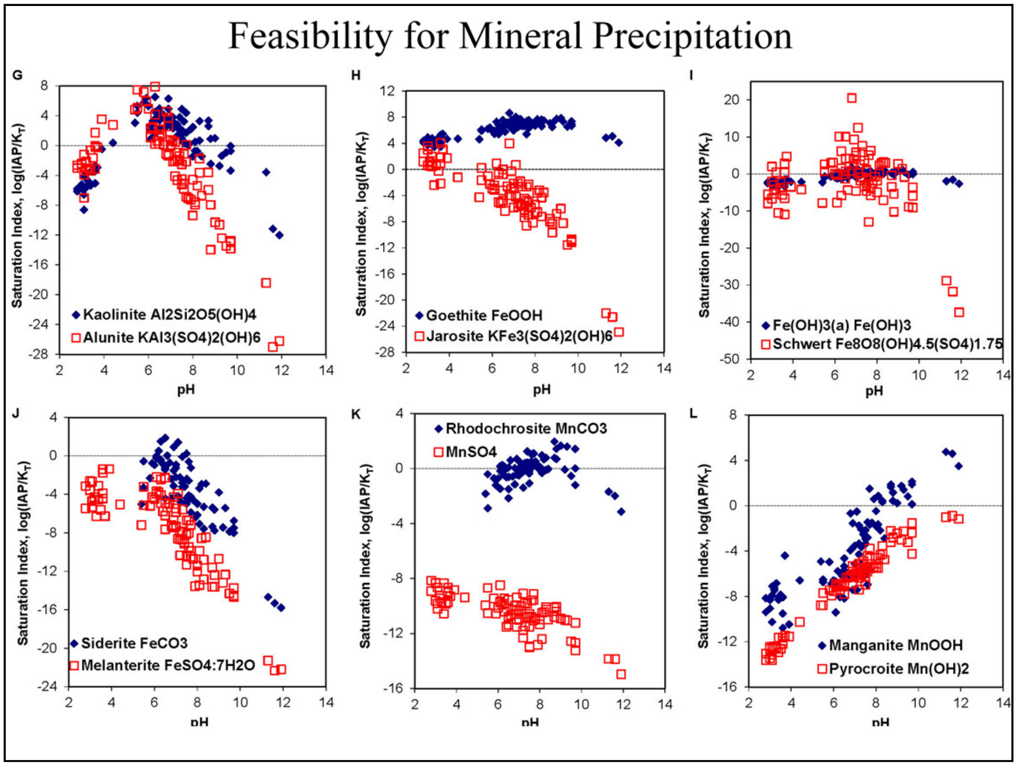
METAL HYDROXIDE SOLUBILITIES: A plot of various metal hydroxide solubilities as a function of pH generally shows “amphoteric” characteristics of the metals, where the solubility minimum for each metal ion occurs at “intermediate” pH; dissolved metal concentrations may increase at lower or higher pH relative to the minimum point. The solubility of hydrous Fe(II) oxide is significantly greater than that for Fe(III) at pH < 10.5. Hence, AMD may contain substantial concentrations of dissolved Fe^{2+}; however, upon its oxidation to Fe^{3+}, hydrous Fe(III) oxides tend to precipitate. Aeration of AMD typically causes pH to increase, initially, owing to the exsolution of CO_2 and H_2S. Hence, hydrous oxides of Fe(III) and Al commonly form where AMD discharges or mixes with alkaline sources. Generally, most other have minimum solubilities at alkaline pH range (pH>9). Nevertheless, these metals are readily adsorbed by hydrous Fe(III), Al, and Mn(IV) oxides, reducing their concentrations below the solubility of their respective hydrous oxide compounds.

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





Feasibility for Mineral Precipitation



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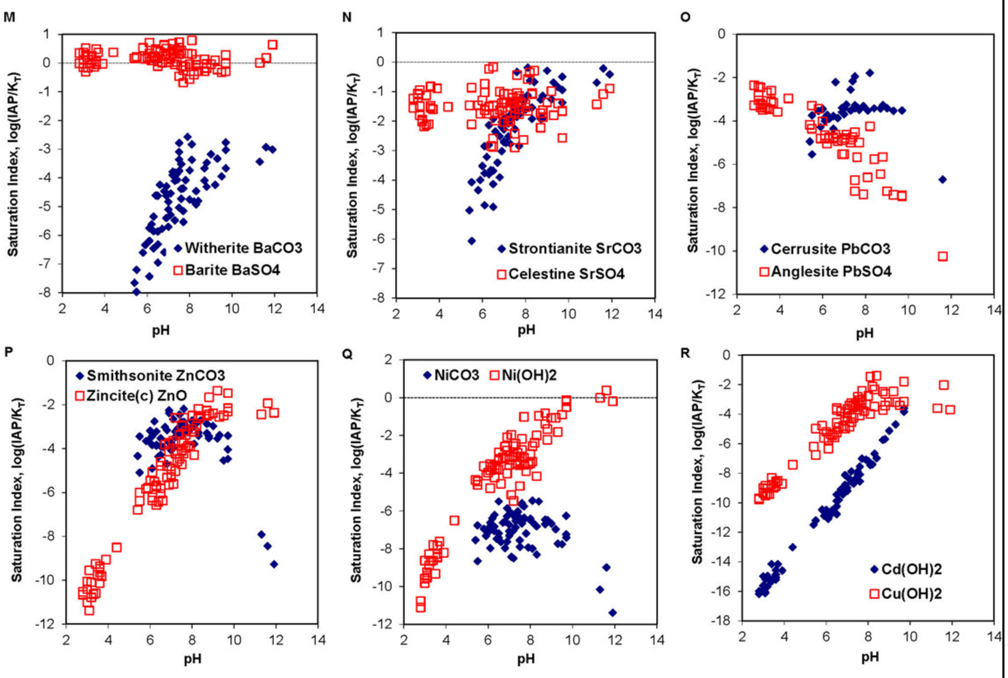
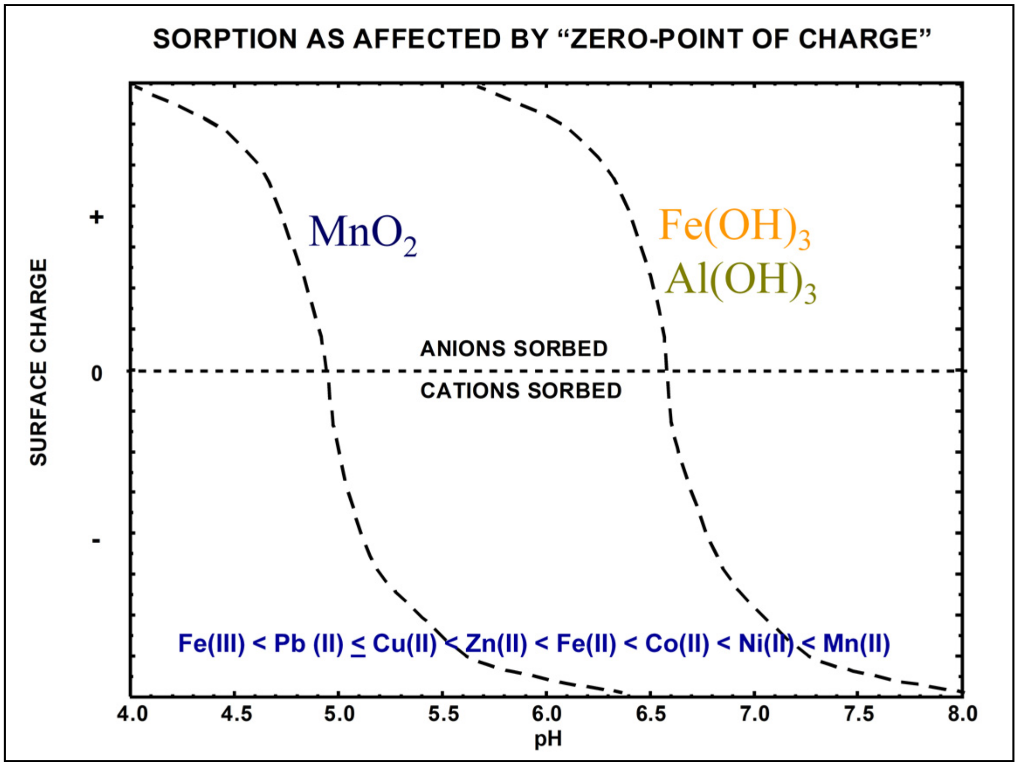
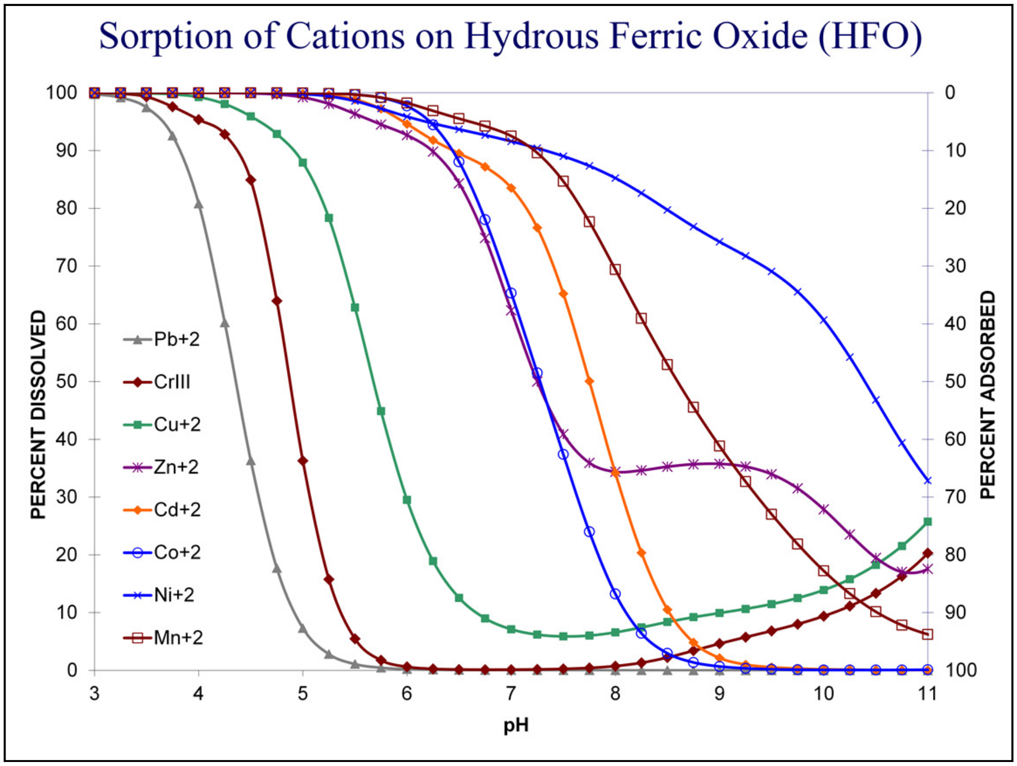
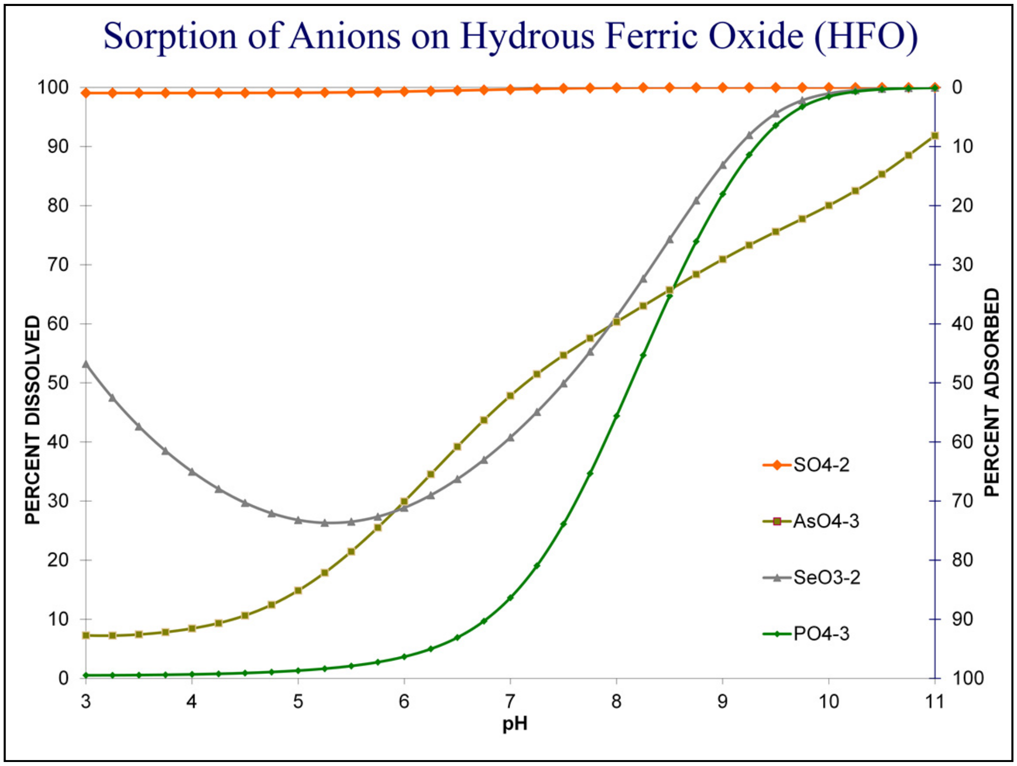




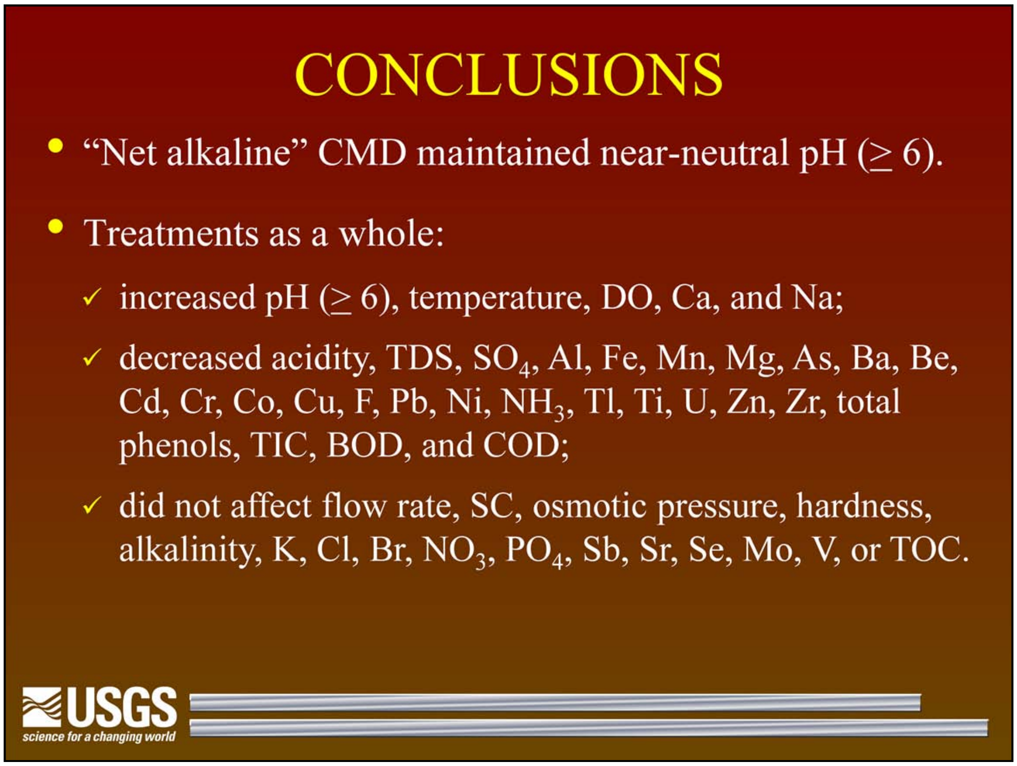
ADSORPTION: The adsorption of metals by Fe(III), Al, and Mn(IV) hydroxides accounts for the attenuation of most trace metals. Cations are adsorbed at high pH. Anions, such as SO4 and AsO3, are adsorbed at low pH.



CATION SORPTION: Equilibrium fractions of initial concentrations of cations and anions that are dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 °C as a function of pH. Cations—lead, chromium-III, copper, zinc, cadmium, cobalt, manganese, and nickel. Area below curve indicates fraction that is not adsorbed; area above curve indicates fraction adsorbed. Simulations conducted using PHREEQC (Parkhurst and Appelo, 1999) with thermodynamic data from Ball and Nordstrom (1991) and surface complexation data from Dzombak and Morel (1990).



ANION SORPTION: Equilibrium fractions of initial concentrations of cations and anions that are dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 ^{o}C as a function of pH. Anions– sulfate, arsenic (arsenate), selenium (selenite), and phosphate. Area below curve indicates fraction that is not adsorbed; area above curve indicates fraction adsorbed. Simulations conducted using PHREEQC (Parkhurst and Appelo, 1999) with thermodynamic data from Ball and Nordstrom (1991) and surface complexation data from Dzombak and Morel (1990).



CONCLUSIONS

- "Net alkaline" CMD maintained near-neutral pH (≥ 6).
- Treatments as a whole:
  - ✓ increased pH (≥ 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;
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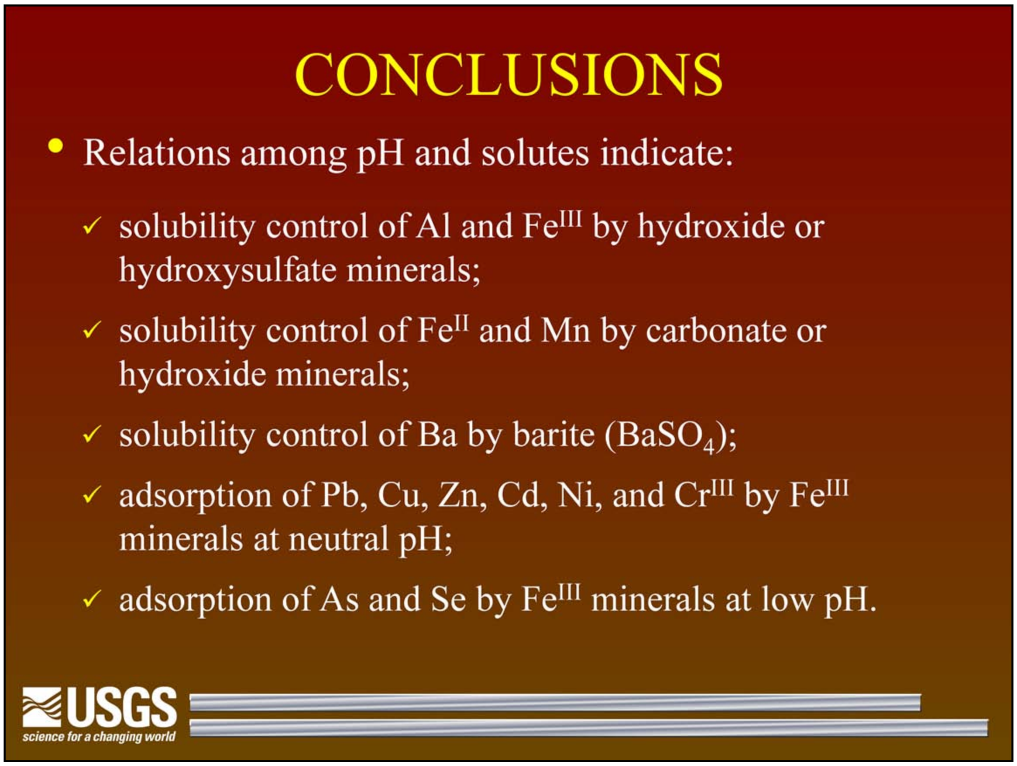

CONCLUSIONS

- 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.

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CONCLUSIONS:

- Relations among pH and solutes indicate—

✓ dissolved Fe^{II} >> Fe^{III} over range of pH;

✓ sulfate complex formation can increase the total dissolved concentrations of Al and Fe^{III}.

✓ solubility control of Al and Fe^{III} by hydroxide or hydroxysulfate minerals;

✓ solubility control of Fe^{II} and Mn by carbonate minerals;

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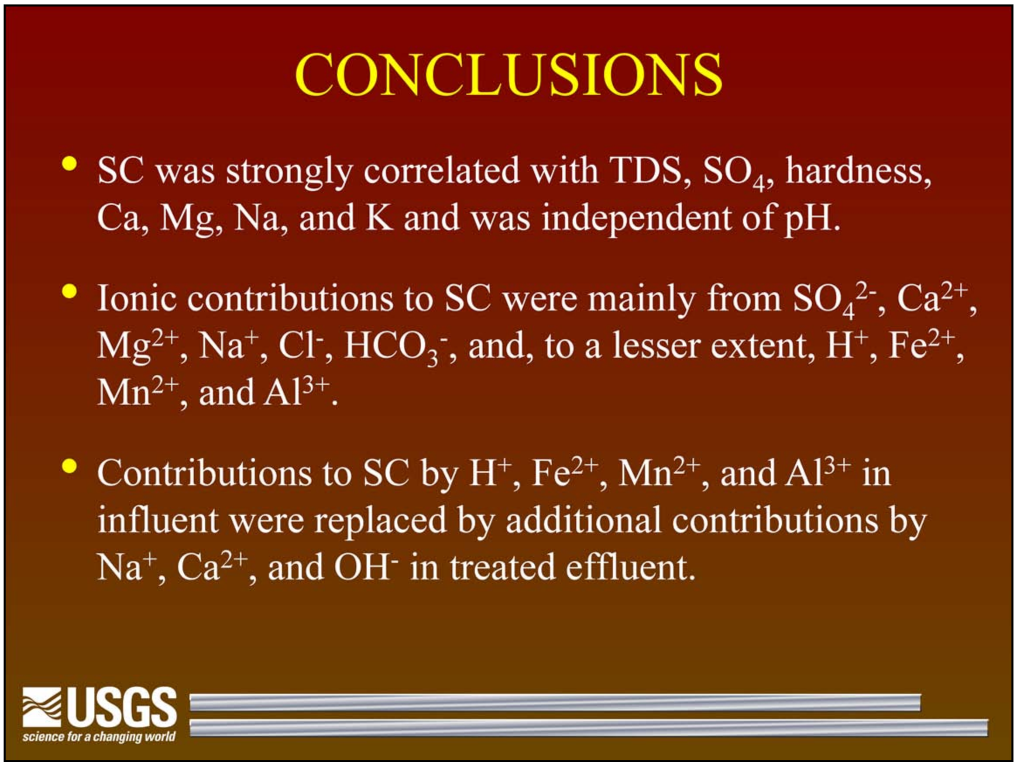

CONCLUSIONS

- 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+}.
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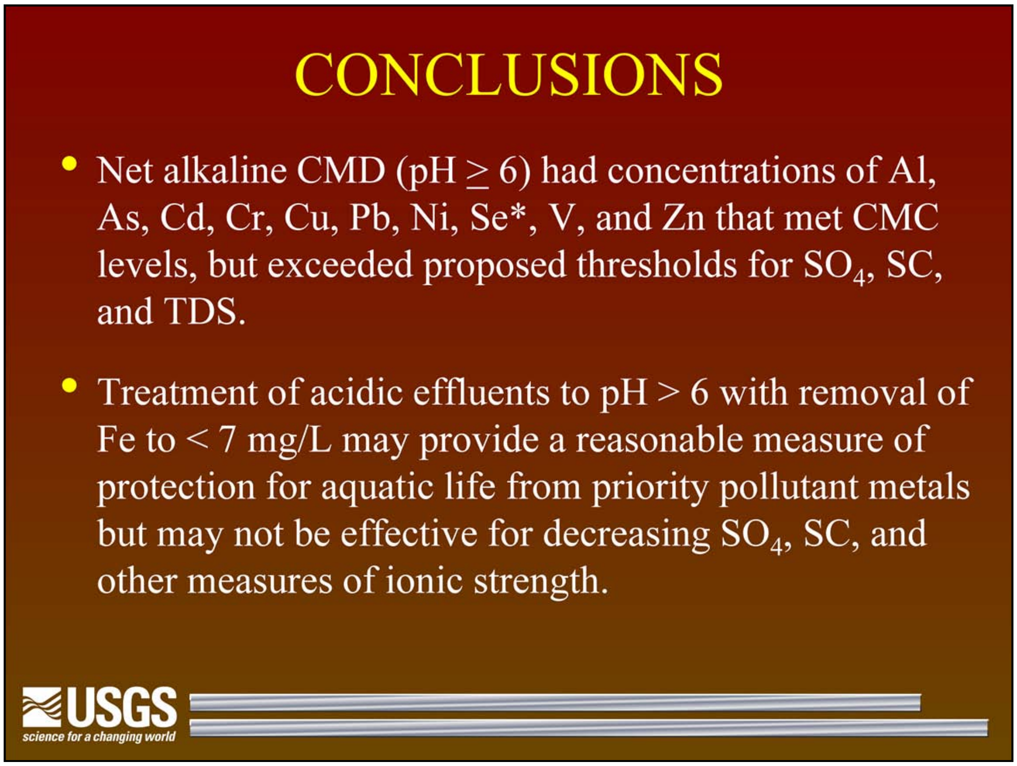

CONCLUSIONS

- 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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