



Priority pollutants and associated constituents in untreated and treated discharges from coal mining or processing facilities in Pennsylvania, USA



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ABSTRACT

Clean sampling and analysis procedures were used to quantify more than 70 inorganic constituents, including 35 potentially toxic or hazardous constituents, organic carbon, and other characteristics of untreated (influent) and treated (effluent) coal-mine discharges (CMD) 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 facilities sampled during 2011, 26 were surface mines, 11 were underground mines, and 5 were coal refuse disposal operations. Treatment of CMD with caustic soda (NaOH), lime (CaO or Ca(OH)₂), flocculent, or limestone was ongoing at 21%, 40%, 6%, and 4% of the facilities, respectively; no chemicals were added at the remaining facilities. All facilities with CMD treatment incorporated structures for active or passive aeration and settling of metal-rich precipitate.

The untreated influent samples had wide ranges of pH (2.8–7.6), hot acidity (–600 to 8000 mg/L as CaCO₃), specific conductance (SC; 253–13,000 μS/cm), total dissolved solids (TDS; 168–18,100 mg/L), and associated dissolved (<0.45-μm pore-size filter) constituents, including SO₄ (14.7–10,700 mg/L), Fe (<0.01 to 4100 mg/L), Mn (0.02–136 mg/L), Al (<0.01 to 128 mg/L), and Zn (<0.003 to 18.8 mg/L). Concentrations of Ag (<1 μg/L), Hg (<1 μg/L), Sn (<0.5 μg/L), and CN (<0.01 mg/L) were below detection limits. Only one influent sample met permitted mine effluent (PME) limits plus dissolved-constituent criteria maximum concentration (CMC) thresholds for the protection of freshwater aquatic organisms.

The pH of the treated effluent samples ranged from 5.5 to 11.9 and was greater than or equal to the pH of the corresponding influent at all sites. All the effluent samples met CMC levels for dissolved concentrations of Ag, As, Ba, Cd, Cl, Cr, Pb, Ni, Sb, Se, Tl, V, NH₃, NO₂, NO₃, and CN; however, nine violated one or more of the PME limits for pH (<6, *n* = 1), net acidity (>0, *n* = 3), Fe (>7 mg/L, *n* = 1), or Mn (>5 mg/L, *n* = 8), plus one or more exceeded CMC levels for Al (>0.75 mg/L, *n* = 2), Co (>95 μg/L, *n* = 5), Zn (>307 μg/L, *n* = 1), Cu (>7.4 μg/L, *n* = 1), or Se (>12.8 μg/L, *n* = 3). Although CMC exceedances for Co and Zn were attributed to samples also violating the PME limit for pH or Mn, the samples that exceeded the CMC for Al, Cu, or Se met applicable PME limits for pH, Fe, and Mn. Furthermore, many of the pH-compliant effluents did not meet reference criteria for SO₄ and related measures of ionic strength, including TDS, SC, and osmotic pressure.

The Wilcoxon matched-pair signed-ranks statistic was used to test if the overall difference between the effluent and influent pairs was equal to zero. Constituents that statistically were the same for effluent and influent (*p* > 0.05) included flow rate, SC, osmotic pressure, hardness, alkalinity, total organic carbon (TOC), K, Cl, NO₃, PO₄, Sb, Sr, Br, Se, Mo, and V. Although temperature, dissolved oxygen, pH, Ca, and Na were greater in the effluent than the influent, most constituents decreased as a result of treatment, including TDS, acidity, SO₄, Al, Fe, Mn, Mg, As, Ba, Be, Cd, Cr, Co, Cu, F, Pb, Ni, NH₃, Tl, Ti, U, Zn, Zr, total phenols, total inorganic carbon (TIC), biological oxygen demand (BOD), and chemical oxygen demand (COD). Nevertheless, some constituents that decreased, such as SO₄, still did not meet reference criteria.

Findings from this study suggest that typical chemical or aerobic treatment of CMD 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 from priority pollutant metals and other toxic or hazardous constituents in effluent but may not be effective for achieving permissible or background levels for TDS, SC, osmotic pressure, or concentrations of SO₄ and some other pollutants, including Se, Br, and Cl, if present.

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1. Introduction

Drainage from abandoned mines affects the quantity, quality, and potential uses of water supplies in coal and metal mining regions worldwide (Blowes et al., 2003; Feng et al., 2014; Nordstrom, 2000, 2011a,b; Wolkersdorfer and Howell, 2004). Metals and associated constituents in the drainage degrade the aquatic habitat and can be toxic to aquatic organisms in receiving water bodies (Cravotta, 2008a; Hyman and Watzlaf, 1997; Smith and Huyck, 1999). In Pennsylvania, abandoned coal-mine discharges (CMD) degrade more than 8800 km of streams (Pennsylvania Department of Environmental Protection, 2012) and result in lost revenues of approximately \$93 million annually from decreased opportunities for recreational fishing (Pennsylvania Department of Environmental Protection, 2009).

Although regulatory authorities in the USA routinely apply effluent limitations to dozens of inorganic and organic chemical pollutants in discharge permits for industrial facilities and wastewater treatment plants, only the pH and concentrations of acidity, alkalinity, Fe, Mn, and total suspended solids in CMD are routinely measured or regulated for permitted mine effluent (PME) from coal-mining operations in the USA.¹ For example, the Commonwealth of Pennsylvania (1998a,b) stipulates that CMD from active mines must be passed through a sedimentation pond or treatment facility and have pH 6.0–9.0 and alkalinity that exceeds its acidity concentration and must not have an instantaneous maximum concentration of Fe or Mn that exceeds 7.0 or 5.0 mg/L, respectively, before discharging. These PME criteria are less comprehensive than the National Pollutant Discharge Elimination System (NPDES) provisions of the Clean Water Act, which identifies numerous “priority pollutants” and associated conventional and non-conventional pollutants (summarized in Supplemental Table A.1) that have potential to be toxic or hazardous to humans and aquatic organisms (U.S. Code of Federal Regulations, 2013a; U.S. Environmental Protection Agency, 2012, 2013).

To gain an appreciation for potential impacts, the concentrations of the priority pollutants and other constituents that may be present in CMD can be compared to applicable limits for the protection of human health, including the drinking water maximum contaminant level (MCL) and the secondary contaminant level (SCL) (U.S. Environmental Protection Agency, 2012; World Health Organization, 2011). Concentrations in filtered samples (<0.45- μ m pore-size filter) also can be compared to values established for the protection of freshwater aquatic life, including the criterion continuous concentration (CCC) and criteria maximum concentration (CMC) levels (U.S. Environmental Protection Agency, 2013) (summarized in Supplemental Table A.1). Thus, if the CMD meets drinking water and aquatic criteria, downstream uses may be protected. Nevertheless, in addition to numerical water-quality criteria, the permitting authority may consider biological assessments, such as whole effluent toxicity (WET) tests and any other relevant data in characterizing the effluent (U.S. Environmental Protection Agency, 2002a,b, 2010a,b). Such information may be used in conjunction with characteristics of the receiving water body to establish site-specific NPDES limits.

On the basis of data for numerous inorganic chemicals in filtered (<0.45- μ m pore-size filter) samples of untreated CMD from abandoned coal mines in Pennsylvania (Cravotta, 2008a,b), one could hypothesize that 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 of aquatic life from dissolved trace

metals. The untreated CMD, which was sampled once at each of 140 sites during June to November 1999 (Cravotta, 2008a,b), exhibited a wide range of solute concentrations including numerous priority pollutant metals. For these samples: (1) pH ranged from 2.7 to 7.3 and had a bimodal distribution; (2) “net alkaline” CMD had pH > 6; (3) the concentrations of dissolved Fe were dominated by highly soluble Fe^{II} and were not correlated with pH; (4) the concentrations of SO₄, Fe^{III}, Al, Mn, Cu, Ni, Pb, Zn, Cd, and other transition metals were inversely correlated with pH; and (5) the concentrations of As and Ba were positively correlated with pH. Although many CMD samples that had pH > 6 did not meet reference PME criteria for Fe (7.0 mg/L) and Mn (5.0 mg/L), all such “pH-compliant” samples had concentrations of Al and priority pollutants (As, Cd, Cr, Cu, Pb, Ni, Se, V, and Zn) that were less than CMC levels after correcting for sample hardness. In contrast, effluents that had acidic pH (<6) commonly had elevated concentrations of priority pollutants compared to the aquatic CMC levels and drinking water MCLs or SCLs.

Aeration and the addition of caustic chemicals typically are used to increase the pH and decrease the concentrations of Fe, Mn, and Al by precipitating metal-rich solids from CMD at active, permitted facilities, whereas crushed limestone aggregate and/or aerobic wetlands are common treatments at decommissioned or abandoned mines (Skousen et al., 2000). At near-neutral and alkaline pH, trace metals tend to be attenuated by coprecipitation or adsorption to Fe^{III} oxides (Cravotta, 2008b; Dzombak and Morel, 1990; Kairies et al., 2005; Kooner, 1993; Lee et al., 2002; Webster et al., 1998), Mn^{III-IV} oxides (Loganathan and Burau, 1973), and Al oxides and silicates (Bigham and Nordstrom, 2000; Coston et al., 1995; Drever, 1997; Munk et al., 2002). Therefore, treatments that are effective for removing acidity, Fe, Mn, and Al also may decrease concentrations of potentially toxic constituents in CMD. Nevertheless, sparse data are available on the concentrations of trace metals and other pollutants in CMD, particularly after treatment.

In addition to potentially toxic trace elements, elevated total dissolved solids (TDS), specific conductance (SC), and other measures of ionic strength are commonly associated with waters discharged from coal mines (Bernhardt et al., 2012; Cravotta, 2008a,b; McAuley and Kozar, 2006; Pond et al., 2008; Stoner et al., 1987; Timpano et al., 2010;) and oil and gas wells (Dresel and Rose, 2010; Haluszczak et al., 2013; Hedin et al., 2005). CMD tends to have TDS concentrations that are greater than the background owing to accelerated weathering of minerals disturbed by mining and the release of Ca, Mg, HCO₃, and SO₄. Natural groundwaters and stream waters in some geologic settings also can have elevated TDS because concentrations of major dissolved ions may accumulate from dissolution of soluble carbonate, sulfate, and chloride minerals in aquifers and/or evapotranspiration processes (Hem, 1985; McAuley and Kozar, 2006). The concentrations of trace elements in solution may increase with TDS, not only because of the release of trace constituents with the major ions dissolved from minerals, but because of the potential for displacement of adsorbed trace ions from mineral surfaces by the major ions.

New regulatory limits on TDS and conductivity for waters discharged from coal mining, gas drilling, and wastewater treatment facilities in the Northern and Central Appalachian states recently have been proposed in the USA (Commonwealth of Pennsylvania, 2011b; U.S. Environmental Protection Agency, 2011). These limits attempt to protect certain freshwater organisms that are accustomed to low ionic-strength conditions and that can be stressed or killed by episodic or sustained increases in ionic strength (Bernhardt et al., 2012; Cormier et al., 2013; Pond et al., 2008). Generally, an aquatic biological response to TDS or SC may be attributed to physiological effects from osmotic (ionic) regulation by cells and tissues (Cormier et al., 2013). For example, Cormier

¹ Hereinafter, the use of an elemental or molecular formula without charge notation indicates the analytical concentration in filtered or unfiltered samples without regard to valence or the possible existence of various aqueous species or particulate forms

et al. (2013) demonstrated through causative analysis that increasing the concentration of Ca^{2+} , Mg^{2+} , HCO_3^- , and SO_4^{2-} , as measured by conductivity, is a common cause of extirpation of aquatic macroinvertebrates (e.g. Ephemeroptera, also known as mayflies) in Appalachia where surface coal mining is prevalent and where natural background concentrations of these major ions, Na^+ , and Cl^- are low (conductivity $<200 \mu\text{S}/\text{cm}$). However, our understanding of aquatic ecological impacts by excessive ambient concentrations of common major ions is confounded because elevated ionic strength rarely is independent of other stressors, and various constituents differ in their contributions to TDS, SC, and osmotic pressure.

This paper presents results of a study of the chemical characteristics of untreated (influent) and treated (effluent) discharges from 42 permitted coal-mining and coal-processing facilities in Pennsylvania. The primary objective was to test the hypothesis that treatment of coal-mine effluent to $\text{pH} > 6$ with removal of Fe to $<7 \text{ mg/L}$ and Mn to $<5 \text{ mg/L}$ will decrease concentrations of potentially toxic constituents to reference levels for protection of aquatic organisms or for drinking water. A secondary objective was to evaluate how treatment may affect TDS and associated relations among major and trace elements, hardness, SC, and osmotic pressure of effluents. Synoptic sampling of influent and effluent at each site was conducted in 2011 by the U.S. Geological Survey (USGS), in cooperation with the Pennsylvania Department of Environmental Protection (PaDEP).

2. Site selection, sampling, and analysis methods

The USGS and the PaDEP completed data collection for the study during April through December 2011. With input from the U.S. Office of Surface Mining, Reclamation and Enforcement (OSM), the PaDEP identified more than 40 CMD treatment facilities

with NPDES permits in the bituminous and anthracite coalfields of Pennsylvania. The proposed facilities included surface mines, underground mines, and coal refuse disposal operations. In addition to active permits, several abandoned mines with passive treatment systems also were identified for sampling. PaDEP mine inspectors typically provided information on the treatment operations, arranged for access, and accompanied USGS personnel to each facility during sampling.

Of the 42 sites sampled (Fig. 1), 26 were surface mines, 11 were deep mines, and 5 were coal refuse disposal facilities; 38 of the facilities processed bituminous coal, and 4 processed anthracite (Fig. 1). Caustic soda (NaOH), lime (CaO or $\text{Ca}(\text{OH})_2$), flocculent, or limestone was used at 21%, 40%, 6%, and 4% of the sites, respectively; no such chemicals were added at the other 28% of the sites. All the CMD treatment facilities incorporated structures for active or passive aeration and settling of solids. Untreated and treated effluent samples were collected at all sites except two of the surface mines that had standing water in the pit (untreated), but no discharge on the date visited. Although site visits attempted to obtain base-flow samples, a few samples were collected during or immediately following rain events. Two coal-refuse facilities that had been sampled initially during storm runoff conditions plus four surface mines that had elevated concentrations of acidity or other constituents were sampled a second time, 2–4 months after the first sample set had been collected. Because the influent characteristics and other conditions at a site generally will vary as mining and reclamation operations progress, the data for resampled sites were simply included with the data for all other sites. Thus, the resultant sample set consisted of 46 influent and effluent pairs (excluding the two sites where effluent was not discharged), mostly for different sites during stable base-flow conditions, and including a few samples representing changing or different hydrological conditions.

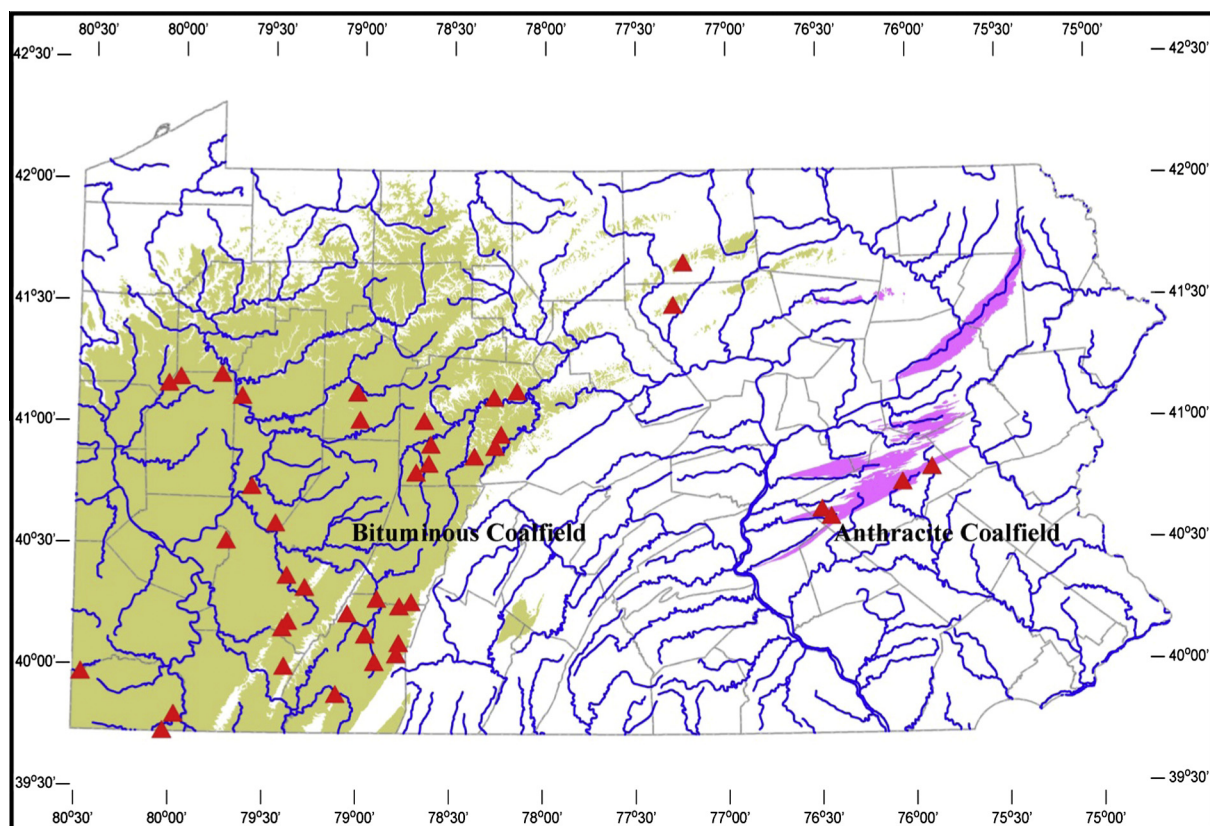


Fig. 1. Map of Pennsylvania showing locations of 42 coal mining or processing facilities in the Bituminous and Anthracite Coalfields where untreated and treated effluents were sampled in 2011.

At each site, global positioning system (GPS) coordinates were recorded, photographs of the treatment facilities were taken, and samples of influent and effluent were collected. Depending on site conditions, the instantaneous flow rate was measured with stopwatch and bucket, computed from wading measurements with a flow meter, computed from weirs or flumes, or estimated from pumping records. The pH, redox potential (Eh), DO, SC, and temperature were measured at the time of sample collection using meters and electrodes that had been calibrated daily (U.S. Geological Survey, variously dated). Field pH and Eh were determined using a gel-filled combination pH sensor with Pt and Ag/AgCl electrodes calibrated in pH 4.0, 7.0, and 10.0 buffer solutions and in Zobell's solution, and checked in pH 2.0 buffer. Values for Eh at 25 °C relative to the standard hydrogen electrode were computed from the field measured oxidation reduction potential (ORP) and temperature values in accordance with methods of Nordstrom (1977). Specific conductance was measured using a Wheatstone bridge calibrated in a KCl standard solution with a conductivity of 2500 $\mu\text{S}/\text{cm}$ and then checked in other KCl solutions with conductivities of 1000 and 25,000 $\mu\text{S}/\text{cm}$.

In addition to sampling of the untreated influent and treated effluent, empirical treatment titrations were conducted at one of the sampled sites (Nittany Mine) using procedures of Means and Hilton (2004) to demonstrate changes in potentially toxic constituent concentrations resulting from the progressive addition of a caustic chemical to the CMD. A Hach Digital Titrator[®] was used in the field with a cartridge containing 1.6 N NaOH to increase pH to endpoints of approximately 6.0, 7.5, 9.0, and 10.3. At each endpoint, the titrated sample was filtered and acidified (to pH < 2) for subsequent analysis of dissolved metals and associated solute concentrations.

To minimize contamination and produce reliable analytical data in the microgram per liter ($\mu\text{g}/\text{L}$) range, clean techniques were employed for collecting, handling, storing, preparing and analyzing influent and effluent samples. Grab samples were collected into acid-cleaned 3-L Teflon[®] bottles and then split into sample-rinsed polyethylene or glass bottles using a peristaltic pump with pre-cleaned tubing. Samples were split into filtered (0.45- μm Pall[®] AquaPrep 600 capsule filters) and unfiltered subsamples for analysis of dissolved and total concentrations, respectively (U.S. Environmental Protection Agency, 1996), preserved as appropriate (U.S. Environmental Protection Agency, 1979; HNO_3 for metals; H_2SO_4 for nutrients, phenols, and organic carbon; NaOH for cyanide), and stored in ice-filled coolers. Alkalinity of filtered samples, stored on ice and without headspace, was determined by USGS personnel within 8 h of sampling by titration with 0.16 N H_2SO_4 to the endpoint pH of 4.5 (American Public Health Association, 1998). The “hot” acidity was determined by titration with 0.16 N or 1.6 N NaOH to the endpoint pH of 8.3, after the addition of H_2SO_4 and H_2O_2 , boiling, and cooling (American Public Health Association, 1998). For comparison with the field-measured “fresh” pH, the laboratory pH was measured using a liquid-filled Orion[®] Ross electrode calibrated in pH 2.0, 4.0, 7.0, and 10.0 buffer solutions (1) when samples were titrated for alkalinity and (2), several months later, when samples that had equilibrated with the atmosphere under ambient conditions were titrated for acidity (“aged” pH).

Replicate samples for analysis of major anions and cations and trace elements were submitted to the PaDEP Laboratory, in Harrisburg, Pa., and the Actlabs Laboratory, in Ancaster, Ontario. Both labs quantified more than 70 inorganic constituents, including 15 priority pollutants, 20 additional toxic or hazardous constituents, and associated substances in filtered and unfiltered samples by inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma emission mass spectrometry (ICP-MS), and ion chromatography (IC) (Fishman

and Friedman, 1989; U.S. Environmental Protection Agency, 1979). Additional measurements at the PaDEP laboratory included total ammonia, total cyanide (CN), total inorganic carbon (TIC), total organic carbon (TOC), total phenols, biological oxygen demand (BOD), chemical oxygen demand (COD), pH, hot acidity, and residue on evaporation at 180 °C (ROE) (U.S. Environmental Protection Agency, 1979), plus osmotic pressure. The osmotic pressure was determined using freezing point depression, whereby an Osmol is defined as the number of moles of a solute required to lower the freezing point of 1 kg of water by 1.858 °C (Kiyosawa, 2003). For quality assurance, blanks and USGS standard reference water samples constituted 10% of the total number of samples processed. No problems were identified with the quality-control samples. Charge imbalances for the data generated by each laboratory routinely were less than 5% relative to the sum of cation and anion equivalents in each sample.

Results for replicate analyses by different methods or laboratories were similar and were averaged to obtain one value for each constituent in a sample before further evaluation. Because the different test methods (e.g. ICP-AES and ICP-MS) and laboratories had different limits for reporting detection of a constituent, the lowest non-censored (detected) value or the lowest censored (below detection) value, if all values were below detection limits, was retained as the average result for that sample. Before statistical evaluation, censored data and reported values less than the highest common reporting limit (HCRL) for a given constituent were censored to the HCRL, and the censored values were counted as 0.99 times the HCRL. For example, after averaging the three replicate results for dissolved Al per sample for all 46 samples, the retained values were <2 $\mu\text{g}/\text{L}$ for 7 samples, <10 $\mu\text{g}/\text{L}$ for 12 samples, 2–9 $\mu\text{g}/\text{L}$ for 12 samples, and 10 to 128,000 $\mu\text{g}/\text{L}$ for the remainder. Thus, the HCRL for dissolved Al is 10 $\mu\text{g}/\text{L}$, and the 19 censored values plus the 12 reported values from 2 to 9 were counted as 9.9 $\mu\text{g}/\text{L}$ before computing summary values, differences between influent and effluent, or ranks for use in statistical tests. The HCRL for each constituent was less than or equal to the applicable CMC and CCC thresholds.

Although NPDES regulations apply to “total recoverable” concentrations of metals in effluents (U.S. Code of Federal Regulations, 2013a), aquatic toxicity criteria are expressed in terms of the “dissolved” concentration in the water column (U.S. Environmental Protection Agency, 2013), which is assumed to be bioavailable and is operationally defined as that which passes through a 0.45 μm filter (U.S. Environmental Protection Agency, 1996). Therefore, unless otherwise specified, the data for filtered samples are used hereinafter to evaluate the effect of treatment pH on the removal of pollutants and reduction of toxicity, plus to compute aqueous speciation, mineral saturation indices, and estimates of ionic strength. The data for total concentrations in unfiltered samples were used primarily for data quality assurance with the expectation that concentrations in unfiltered samples would be greater than or equal to those in filtered samples. Charts showing the relation between dissolved (filtered) and total (unfiltered) concentrations in the influent and effluent samples, which are available online in Supplemental Fig. A1, showed that the total concentrations of Fe, Al, Pb, Zn, and several other metals generally were greater than the corresponding dissolved concentrations in the lower quartile concentration range, but the total and dissolved concentrations approached a common value for higher concentrations.

For quality assurance and to evaluate contributions from specific constituents, analytical concentrations of solutes were used to compute independent estimates of acidity and ionic strength. For comparison with measured hot acidity, the net acidity was computed considering positive acidity contributions by H^+ (indicated by field pH) and dissolved Fe, Mn, and Al concentrations and

negative contributions by alkalinity (Kirby and Cravotta, 2005). The hardness, as mg/L CaCO₃, was computed as the sum of concentrations of Ca (mg/L × 2.5) and Mg (mg/L × 4.1). Estimated TDS, as mg/L, was computed as the sum of major dissolved constituents (Ca, Mg, Na, K, SO₄, Cl, CO₃, NO₃, SiO₂) (Fishman and Friedman, 1989, p. 437–438) plus minor constituents (Sr, Ba, Fe, Al, Mn, Br) for comparison with the measured ROE. Because of uncertainty regarding the TDS estimate and the composition of solids weighed as ROE, several estimates of TDS were computed, assuming that Fe, Al, and Mn combined only with major anions (“TDS1”), formed only anhydrous oxides (Fe₂O₃, Al₂O₃, MnO₂) (“TDS2”), or formed only hydrous oxides (FeOOH, AlOOH, MnOOH) (“TDS3”). “TDS4” expanded on TDS3 assuming that SO₄ precipitated as hemihydrate (SO₄·0.5H₂O) instead of anhydrous compounds. Because of the inclusion of oxygen and water, the estimated mass of solid residue and, hence, the estimated TDS concentration increased progressively from TDS1 to TDS4. Finally, the molal concentrations of aqueous species, computed from dissolved concentrations by PHREEQC (Parkhurst and Appelo, 2013), were used to estimate the ionic contributions to specific conductance (McCleskey et al., 2012) and to estimate the osmotic pressure, where 1 mol/kg of each ion exerts approximately 1 mOsm/kg osmotic pressure (Haynes et al., 2013).

Graphical and statistical methods were used to investigate relations among the analytical and computed water-quality constituents and to identify effects of treatment. The concentrations of specific constituents in the untreated and treated CMD samples were plotted relative to the pH or hardness with reference lines for the applicable NPDES criteria for permitted mine effluent and U.S. Environmental Protection Agency (EPA) criteria for protection of human health and freshwater aquatic organisms. The Wilcoxon matched-pairs signed-rank test was used to indicate significant differences in water quality of influent and effluent. This nonparametric, rank-based statistical method accommodates non-normally distributed and/or censored data (Helsel and Hirsch, 2002). The matched-pair test computed the difference in compositions between the corresponding influent and effluent for each site (effluent - influent). 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. The treatment effects were considered significant if the mean rank difference was positive (“>”) or negative (“<”) at a probability level of 0.05 or smaller. The significance results were displayed as inequality ($p < 0.05$) or equality ($p > 0.05$) symbols in graphs showing the paired effluent and influent data and boxplots showing differences in values between effluent and influent by treatment type.

Principal components analysis (PCA), computed with SAS 9.4 (SAS Institute, Inc., 2012), was used to evaluate multivariate correlations among the constituents in the influent and effluent samples. The goal was to identify important hydrochemical processes or principal variables that could explain element associations and distributions (Joreskog et al., 1976; Thyne et al., 2004). The Spearman-rank correlation coefficient matrix provided the standardized input for the PCA. Because the PCA model would exclude the entire record for any sample with a missing value, those constituents that had missing values or those that were censored in more than 10% of the samples were excluded. The PCA model was optimized with varimax rotation, and only principal components (PCs) with eigenvalues greater than unity, equivalent to correlations with a probability greater than or equal to 0.995, were retained (Joreskog et al., 1976; Thyne et al., 2004). Loadings for each constituent included in the PCA model are equivalent to the Spearman-rank correlation coefficient between that constituent and the PC. To aid in interpretations, the scores for each PC in the PCA model were compiled and then evaluated by correlation analysis with those variables that had been excluded from the PCA.

Geochemical equilibrium modeling was used to evaluate potential for aqueous speciation to affect the constituent concentrations, SC, and osmotic pressure for the influent and effluent samples. The partial pressure of carbon dioxide (Pco₂) and mineral-saturation index (SI) values were calculated using the geochemical model PHREEQC (Parkhurst and Appelo, 2013) with the WATEQ4F database (Ball and Nordstrom, 1991) supplemented with thermodynamic data for schwertmannite, ferrihydrite, and goethite from Bigham et al. (1996) and for ettringite from Myneni et al. (1998). The activities of FeI and FeII species and other redox-sensitive elements were computed on the basis of the measured Eh, total dissolved element concentration, and temperature of the samples. Computed SI values for hydroxide, oxide, carbonate, sulfate, and silicate minerals were plotted as a function of pH to identify phases that could feasibly precipitate within treatment systems, possibly limiting dissolved solute concentrations and sequestering constituents in sludge.

Adsorption and desorption of anions and cations on hydrous ferric-oxide-coated surfaces were evaluated using a diffuse double-layer modeling approach with PHREEQC (Parkhurst and Appelo, 2013) and surface complexation data from Dzombak and Morel (1990). Supplemental aqueous speciation and solubility data for Cr^{III}, Cr^{VI}, Co, and V were obtained from the ThermoChimie data base (sit.dat; Duro et al., 2012) offered with PHREEQC. To be consistent with the modeling approach of Dzombak and Morel (1990), the hydrous ferric oxide (HFO) was specified as 90 mg/L, with a specific surface area of 600 m²/g consisting of 5×10^{-6} moles of strong binding sites and 2×10^{-4} moles of weak binding sites. The relevant anion or cation concentration was specified as 0.05 mmol/L in a matrix consisting of 5 mmol/L Cl, SO₄, and TIC plus Na to balance charge. Aqueous speciation and adsorption distribution for a range of pH values were computed, and the percentage of the total concentration distributed between the solution and sorbent was plotted as a function of pH. The sorption modeling results were illustrated as fractions of initial concentrations of ions that may be dissolved or adsorbed on a finite amount of HFO at 25 °C as a function of pH.

3. Results and discussion

Of the 46 matched influent-effluent pairs, the untreated influents represent a wide variety of flow (<1 to 702 L/s), pH (2.8–7.6), SC (253–13,000 µS/cm), acidity (about –600 to 8000 mg/L as CaCO₃), hardness (83–3740 mg/L as CaCO₃), and solute characteristics (Table 1). Dissolved concentrations of specific pollutants in the influents ranged over three orders of magnitude, as indicated by SO₄ (14.7 to 10,700 mg/L), Cl (0.84 to 2020 mg/L), Fe (<0.01 to 4100 mg/L), Mn (0.02 to 136 mg/L), Al (<0.01 to 128 mg/L), Zn (<3.0 to 18,800 µg/L), Ni (<2.0 to 5410 µg/L), Co (0.12 to 5180 µg/L), Cd (<0.5 to 34.8 µg/L), Pb (<0.05 to 16.6 µg/L), As (<0.1 to 298 µg/L), Se (<1.0 to 19.3 µg/L), and others (Table 1). Concentrations of Ag (<1 µg/L), Hg (<1 µg/L), Sn (<0.5 µg/L), and CN (<0.01 mg/L) in all samples were below detection limits. Although one influent sample (groundwater from a mine tunnel) had low concentrations of pollutants and met reference levels for protection of the aquatic environment, the vast majority contained many of the aforementioned priority and other potential pollutants at concentrations that exceeded reference levels for PME discharge limits, aquatic life CMCs, or drinking water MCLs (Table 1).

3.1. Effects of treatment on water-quality characteristics and aquatic toxicity

The pH of the treated effluents ranged from 5.5 to 11.9 (Table 1, Fig. 2A “pH, fresh”). One sample had pH < 6; nine had pH > 9. The

Table 1

Summary values for 46 pairs of influent and effluent samples from coal mining or processing facilities, Pennsylvania, 2011, including counts of values exceeding reference levels for permissible effluent or protection of human health and freshwater organisms.

Constituent	Reporting units	Highest common reporting limit (HCRL) for censored data	Reference level		Untreated influent			Treated effluent		
			Value	Type	Median (minimum/maximum)	Number of values greater than or equal to HCRL	Number of values violating reference level	Median (minimum/maximum)	Number of values greater than or equal to HCRL	Number of values violating reference level
Flow rate (Q)	L/s	–	n.a.	n.a.	10.6 (0.14/702)	46	n.a.	10.3 (0.14/702)	46	n.a.
Temperature (TEMPC)	°C	–	30.6	CMC	12.7 (9.6/28.6)	46	0	19 (8.54/29.6)	46	0
Redox potential (Ehmv)	mV	–	n.a.	n.a.	402 (82/800)	46	n.a.	314 (90/521)	46	n.a.
pH, fresh (pHF)	Units	–	≥6.0	PME	5.65 (2.82/7.62)	46	25	7.82 (5.46/11.9)	46	1
pH, aged (pHLox)	Units	–	≥6.0	PME	3.82 (2.06/8.48)	46	25	8.00 (2.74/12.0)	46	1
Acidity, hot (ACIDH), as CaCO ₃	mg/L	–	0	PME	44.6 (–575/8980)	46	25	–74.4 (–475/1500)	46	3
Acidity, net (ACIDN), as CaCO ₃	mg/L	–	0	PME	63 (–605/8020)	46	26	–75.3 (–463/1850)	46	5
Alkalinity (ALK), as CaCO ₃	mg/L	0	≥20	PME	26.6 (0/606)	46	22	85.6 (0/464)	46	6
Iron (Fe)	µg/L	10	7000	PME	9660 (<10/4100000)	44	26	30 (<10/1000000)	36	1
Manganese (Mn)	µg/L	–	5000	PME	8300 (19.1/136000)	46	30	908 (0.3/34300)	46	8
Sulfate (SO ₄)	mg/L	–	250	PME	962 (14.7/10700)	46	39	934 (25.5/7540)	46	40
Residue on evaporation (ROE)	mg/L	–	2000	PME	1620 (168/18100)	46	17	1590 (174/12100)	45	17
Total dissolved solids (TDS3)	mg/L	–	2000	PME	1480 (153/18400)	46	15	1450 (155/11400)	46	15
Specific conductance (SC25)	µS/cm	–	300	BMK	1740 (253/13000)	46	45	1800 (261/12500)	46	45
Osmotic pressure (OSMP)	mOsm/kg	–	50	CMC	16.5 (3/182)	46	9	20 (3/180)	46	5
Dissolved oxygen (DOX)	mg/L	–	4	CMC	6.12 (0.24/11.7)	46	12	8.14 (0.23/12.8)	46	3
Ammonia (NH ₃ N)	mg/L	0.02	36.7	CMC	0.32 (0.04/11.2)	46	0	0.145 (<0.02/6.56)	43	0
Chloride (Cl)	–	–	860	CMC	6.69 (0.84/2020)	46	2	8.3 (0.99/1820)	46	2
Cyanide (CN)	µg/L	10	22	CMC	<1 (<1/<1)	0	0	<1 (<1/<1)	0	0
Aluminum (Al)	µg/L	10	750	CMC	572 (<10/128000)	36	22	22.5 (<10/2140)	28	2
Silver (Ag)*	µg/L	1	37.40	CMC	<1 (<1/<1)	0	0	<1 (<1/<1)	0	0
Arsenic (As)	µg/L	0.1	340	CMC	0.735 (<0.1/298)	45	0	0.155 (<0.1/7.1)	29	0
Barium (Ba)	µg/L	–	21000	CMC	15.5 (5.8/219)	46	0	14.4 (2.7/159)	46	0
Cadmium (Cd)*	µg/L	0.05	16.60	CMC	0.64 (<0.05/34.8)	34	2	<0.05 (<0.05/2.04)	19	0
Cobalt (Co)	µg/L	0.03	95	CMC	128 (0.12/5180)	46	26	2.7 (<0.03/188)	43	5
Chromium (Cr)*	µg/L	3	1708	CMC	<3 (<3/101)	17	0	<3 (<3/45.1)	5	0
Copper (Cu)*	µg/L	1	62.8	CMC	12.4 (<1/358)	32	12	<1 (<1/40.1)	17	1
Mercury (Hg)	µg/L	1	1.44	CMC	<1 (<1/<1)	0	0	<1 (<1/<1)	0	0
Nickel (Ni)*	µg/L	2	4573	CMC	239 (<2/5410)	44	5	26.7 (<2/363)	41	0
Lead (Pb)*	µg/L	0.05	281	CMC	0.865 (<0.05/16.6)	32	0	<0.05 (<0.05/4.05)	12	0
Antimony (Sb)	µg/L	0.05	1100	CMC	<0.05 (<0.05/2.88)	12	0	<0.05 (<0.05/1.2)	15	0
Selenium (Se as Se ^{VI})	µg/L	1	12.8	CMC	1.95 (<1/19.3)	26	2	1.05 (<1/32.8)	24	3
Thallium (Tl)	µg/L	0.005	65	CMC	0.074 (<0.005/1.73)	42	0	0.044 (<0.005/0.715)	40	0
Vanadium (V)	µg/L	0.5	510	CMC	<0.5 (<0.5/70)	7	0	<0.5 (<0.5/3.3)	2	0
Zinc (Zn)*	µg/L	3	370	CMC	417 (<3/18800)	44	25	6.78 (<3/349)	36	1
Beryllium (Be)	µg/L	0.5	4	MCL	1.4 (<0.5/50.7)	28	20	<0.5 (<0.5/1.3)	3	0
Fluoride (F)	mg/L	1	4	MCL	<1 (<1/5.04)	5	1	<1 (<1/1.55)	3	0
Nitrate (NO ₃ N)	mg/L	1	10	MCL	<1 (<1/6)	4	0	<1 (<1/9.17)	4	0
Phenols, total (PHENOL)	µg/L	5	5	MCL	<5 (<5/497)	21	21	<5 (<5/128)	4	4
Uranium (U)	µg/L	0.005	30	MCL	1.28 (0.015/35.4)	46	1	0.16 (<0.005/8.85)	41	0
Biological oxygen demand (BOD)	mg/L	0.2	n.a.	n.a.	1.3 (<0.2/33.2)	33	n.a.	0.8 (<0.2/9.6)	35	n.a.
Chemical oxygen demand (COD)	mg/L	10	n.a.	n.a.	48.8 (<10/818)	42	n.a.	29.4 (<10/230)	34	n.a.
Bromide (Br)	mg/L	0.02	n.a.	n.a.	0.038 (<0.02/12.8)	41	n.a.	0.054 (<0.02/10.6)	43	n.a.
Calcium (Ca)	mg/L	–	n.a.	n.a.	188 (21.4/422)	46	n.a.	196 (14.6/1180)	46	n.a.
Hardness (HRD)	mg/L	–	n.a.	n.a.	812 (82.7/3740)	46	n.a.	974 (53/3670)	46	n.a.
Potassium (K)	mg/L	–	n.a.	n.a.	3.66 (1.14/32.5)	46	n.a.	4.12 (1.09/31.3)	46	n.a.
Magnesium (Mg)	mg/L	–	n.a.	n.a.	87.4 (5.85/652)	46	n.a.	56.2 (0.02/335)	46	n.a.

(continued on next page)

Table 1 (continued)

Constituent	Reporting units	Highest common reporting limit (HCRL) for censored data	Reference level		Untreated influent			Treated effluent		
			Value	Type	Median (minimum/maximum)	Number of values greater than or equal to HCRL	Number of values violating reference level	Median (minimum/maximum)	Number of values greater than or equal to HCRL	Number of values violating reference level
Molybdenum (Mo)	µg/L	0.5	n.a.	n.a.	<0.5 (<0.5/7.95)	9	n.a.	<0.5 (<0.5/10.2)	14	n.a.
Sodium (Na)	mg/L	-	n.a.	n.a.	10.6 (1.5/2600)	46	n.a.	36.8 (1.95/2560)	46	n.a.
Phosphate (PO4P)	mg/L	0.02	n.a.	n.a.	<0.02 (<0.02/2.15)	5	n.a.	<0.02 (<0.02/0.85)	2	n.a.
Tin (Sn)	µg/L	0.5	n.a.	n.a.	<0.5 (<0.5/<0.5)	0	n.a.	<0.5 (<0.5/<0.5)	0	n.a.
Strontium (Sr)	µg/L	-	n.a.	n.a.	455 (81.6/5280)	46	n.a.	540 (92.8/4120)	46	n.a.
Thorium (Th)	µg/L	0.005	n.a.	n.a.	0.009 (<0.005/14.9)	24	n.a.	<0.005 (<0.005/0.025)	10	n.a.
Titanium (Ti)	µg/L	-	n.a.	n.a.	1.5 (0.4/10.3)	46	n.a.	0.95 (0.2/7.1)	46	n.a.
Total inorganic carbon (TIC)	mg/L	1	n.a.	n.a.	20.3 (<1/118)	42	n.a.	11.3 (<1/46.4)	44	n.a.
Total organic carbon (TOC)	mg/L	0.5	n.a.	n.a.	0.82 (<0.5/3.15)	40	n.a.	0.97 (<0.5/3.31)	39	n.a.
Zirconium (Zr)	µg/L	0.05	n.a.	n.a.	<0.05 (<0.05/2.01)	22	n.a.	<0.05 (<0.05/0.16)	8	n.a.

Concentrations in filtered (0.45-µm pore size) influent and effluent samples; reference level is maximum permissible value, unless indicated by “≥”, for which the level is minimum permissible; n.a., not applicable; PMF, permitted mine effluent (Commonwealth of Pennsylvania, 1998a,b, 2011b); MCL, maximum contaminant level in drinking water (Commonwealth of Pennsylvania, 2011a; U.S. Environmental Protection Agency, 2012); CMC, criterion maximum concentration for freshwater aquatic life (Commonwealth of Pennsylvania, 2011a; U.S. Environmental Protection Agency, 2013); BMK, benchmark (U.S. Environmental Protection Agency, 2011).

measured hot acidity and computed net acidity for each sample were equivalent in value (Fig. 2B). Before treatment, 25 of the 46 influents were net acidic (hot acidity and net acidity >0); however, after treatment, all but three of the effluents were net alkaline (hot acidity and net acidity <0) (Table 1).

All the effluent samples had higher pH and lower concentrations of acidity, plus most had significantly lower concentrations of Fe, Mn, and other potential pollutants than the corresponding influent samples (Fig. 2). As displayed in Fig. 2, the data distribution shifted to the right of the diagonal “line of equality” between influent and effluent for those constituents that increased by treatment and to the left for those that decreased. Boxplots, which are available online as Supplemental Fig. A2, illustrate the change in effluent constituent values relative to influent by treatment method. On the basis of the Wilcoxon matched-pair signed-ranks statistic for all treatment methods combined, concentrations of many dissolved solutes and associated constituents decreased after treatment, including TDS, acidity, SO₄, Al, Fe, Mn, As, Cd, Cr, Co, Cu, Ni, Tl, Ti, U, Zn, Zr, NH₃, F, Pb, Ba, Be, Mg, total phenols, total inorganic carbon (TIC), biological oxygen demand (BOD), and chemical oxygen demand (COD) (Fig. 2, “<”). Constituents that statistically were the same for influent and effluent included flow rate, SC, osmotic pressure, hardness, alkalinity, total organic carbon (TOC), K, Cl, Br, NO₃, PO₄, Sb, Sr, Se, Mo, and V (Fig. 2, “=”), and constituents that increased in effluent (Fig. 2, “>”) included pH, temperature, DO, Ca, and Na.

Constituents that were indicated to be the same in influent and effluent by the matched-pair test statistic exhibited a balanced distribution along both sides of the line of equality in Fig. 2. The widely observed increases in pH and DO (shift right in Fig. 2) and decreases in TIC, BOD, and COD (shift left in Fig. 2) for the effluents resulted from ingassing of O₂, outgassing of CO₂, and removal of Fe and Mn during aerobic treatment, commonly with the addition of caustic chemicals (CaO, Ca(OH)₂, or NaOH). Although COD is typically interpreted to indicate the amount of organic compounds in water (American Public Health Association, 1998), CMD typically has low organic carbon content, as indicated by the median TOC of 1 mg/L (Table 1). Thus, the COD for CMD may be more directly related to the quantities of Fe^{II} and Mn^{II}, which are reported to interfere with the COD analytical method and tend to be persistent until very high pH (>8.5) (American Public Health Association, 1998). The alkalinity did not change overall; it increased for many of the effluents where caustic soda, lime, or limestone were used and decreased for those where caustic chemicals were not used (as illustrated by Supplemental Fig. A2). At 28% of sites where treatment did not add chemicals, the effluent alkalinity decreased as Fe^{III} and Mn^{III-IV} oxides precipitated, while Na and Ca were unaffected. For the other sites, the added caustic chemicals or limestone accounted for overall increases in Ca and Na and typically generated sufficient alkalinity to offset or exceed its consumption by Fe and Mn hydrolysis reactions. Nevertheless, three effluents remained net acidic despite caustic treatment. Because of oxidation of Fe^{II} and Mn^{II} during sample storage, these net acidic effluent samples ultimately had pH < 6 (Fig. 2A “pH, aged”) and no remaining alkalinity.

The decreased concentrations of Fe, Mn, Al, and numerous associated trace elements in the chemically and/or aerobically treated effluents can be attributed to the precipitation of hydrous Fe, Mn, and Al oxides at near-neutral to alkaline pH with the concomitant adsorption and coprecipitation of trace cations and anions. Likewise, statistically significant, but relatively minor overall decreases in TDS of effluent can be attributed to the extensive removal of Fe, Mn, and Al plus partial removal of major constituents including SO₄, Mg, and aqueous CO₂ by treatment. The SC and osmotic pressure did not decrease by a constant ratio with TDS because as the solute concentrations decreased, the ionic

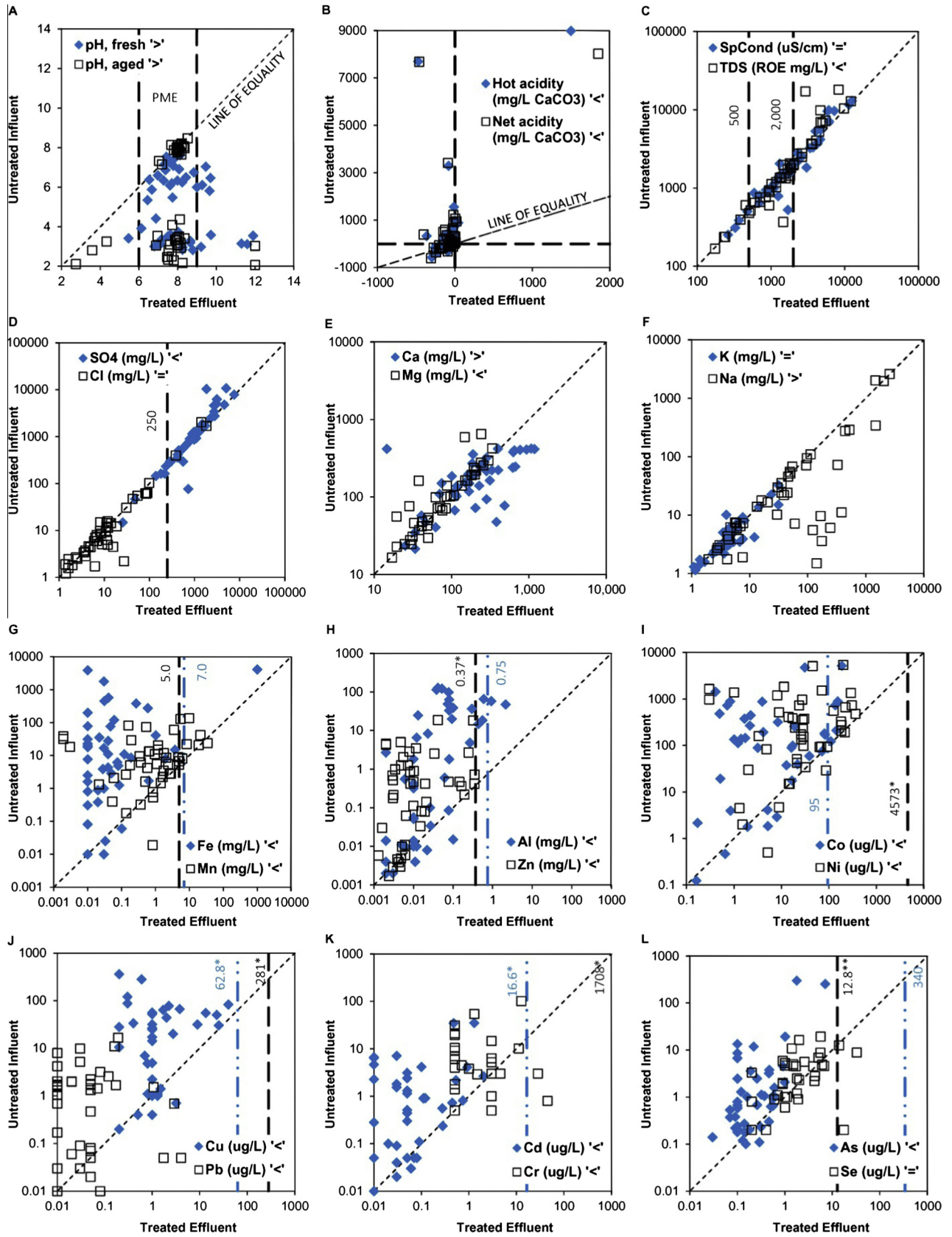


Fig. 2. Comparison of water-quality constituents for untreated influent and treated effluent at coal mining or processing facilities, Pennsylvania, 2011. Values below detection plotted at detection limit. Wilcoxon matched-pair signed-ranks test for difference (effluent–influent) used to indicate significant effect (p -value < 0.05) of treatment on increasing ($>$) or decreasing ($<$) constituent levels; treatment did not affect (p -value > 0.05) some constituents ($=$). Reference lines indicate the criteria (Table 1) for permitted mine effluent in Commonwealth of Pennsylvania (1998a,b), if applicable, or the contaminant levels for drinking water in the USA (U.S. Environmental Protection Agency, 2012), or criteria maximum concentration values for freshwater aquatic organisms (U.S. Environmental Protection Agency, 2013).

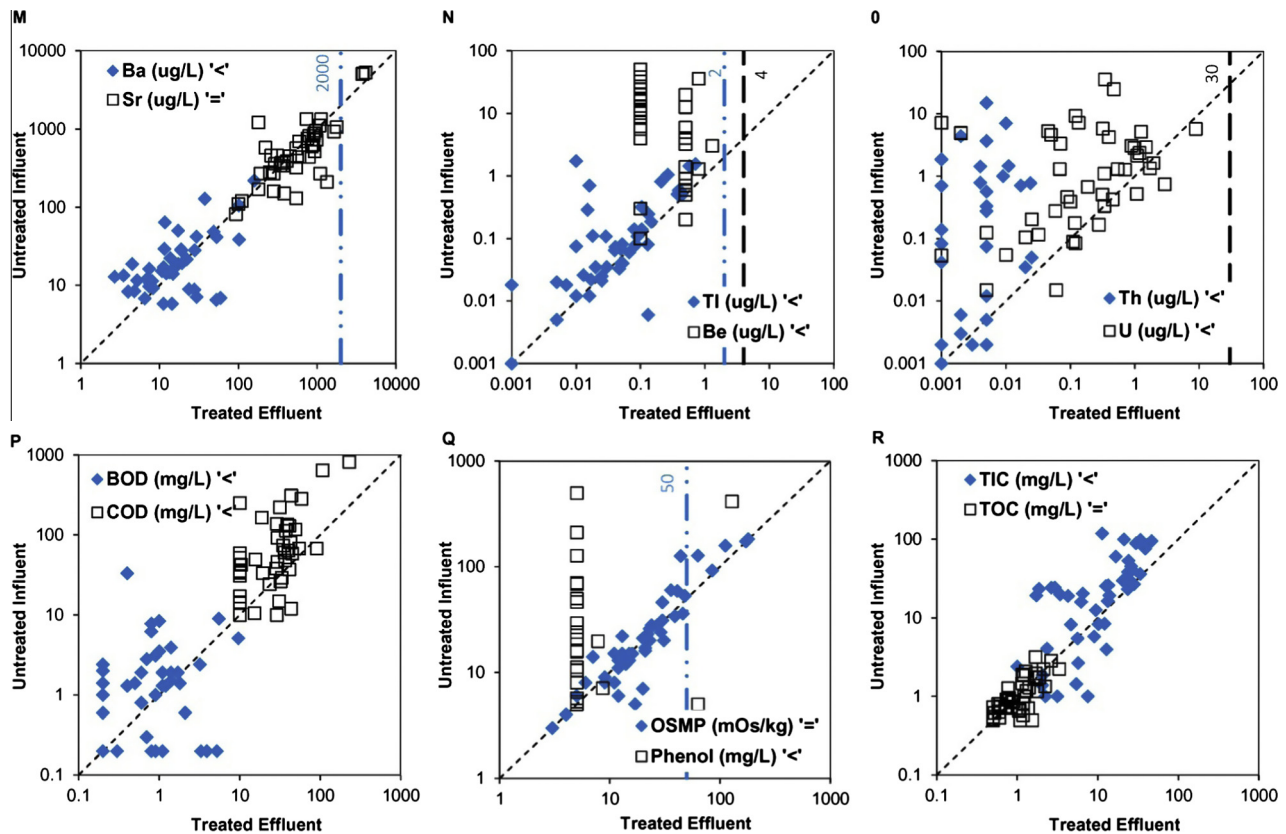


Fig. 2 (continued)

strength and tendency for ion complexation also decreased. With decreased ionic strength, the fraction of remaining solutes in the effluent that would be present as charged ions would tend to increase because of the dissociation of uncharged ion pairs (e.g. $\text{MgSO}_4^0 \rightarrow \text{Mg}^{2+} + \text{SO}_4^{2-}$) and other complexes. The uncomplexed ions ($\text{Mg}^{2+} + \text{SO}_4^{2-}$) contribute more to SC and osmotic pressure than the same mass of the complexed ions (MgSO_4^0) owing to the overall decreased charge and molar concentrations of the complexes.

Observed differences between the 46 influent and effluent pairs support the hypothesis that concentrations of Fe, Mn, Al, and other potentially toxic constituents will decrease to environmentally acceptable levels as the treatment pH is increased to values of 6 to 9; however, effective removal of Mn to <5 mg/L could require $\text{pH} > 9$. For example, during empirical titration of the Nittany Mine influent with NaOH, the concentrations of transition metals (Fe, Mn, Zn, Ni, Co, Ti, Cu, Cr, Cd, and Zr) and other metals (Al and Pb), which occur predominantly as cations in oxidizing aqueous systems (Langmuir, 1997), decreased by 2–3 orders of magnitude as the pH increased from 3 to 9 (Fig. 3). A few other transition metals, specifically V and Mo, as well as metalloids and nonmetals including As and Se, which occur as oxyanions (Langmuir, 1997), decreased to a lesser extent (Fig. 3), while concentrations of SO_4 , Tl, and most alkali earth (K, Li, Rb, Cs) and alkaline earth (Ca, Mg, Sr, Ba) elements remained relatively constant, within a factor of 1.25. As the pH increased from 9 to 10.3, concentrations of Mn and Mg decreased precipitously from 21.4 to 0.46 mg/L and 533 to 293 mg/L, respectively. Although some additional constituents decreased as pH increased to 10.3 (Al, Fe, Zn, Ni, Co, Cd, As, U, and Th), a few others increased (Si, Cu, and Zr) (Fig. 3). Thus, treatment to very high pH (>9), as practiced at some sites for Mn removal, could result in effluent that meets PME limits, but also could result in the remobilization of some pollutants and the

precipitation of non-target constituents, such as Mg (Means and Hilton, 2004; Cravotta et al., 2014). An alternative approach that was not investigated may consider treatment to pH 8–9 and the addition of a strong oxidant, such as potassium permanganate (KMnO_4) or calcium peroxide (CaO_2) (e.g. Lovett and Ziemkiewicz, 1991; Skousen et al., 2000), to remove Mn without precipitating Mg and remobilizing potential pollutants.

Although 45 of the 46 effluent samples had field-measured $\text{pH} > 6$, nine of the effluent samples violated one or more of the PME limits for net acidity (>0 , $n = 3$), Fe (>7 mg/L, $n = 1$), or Mn (>5 mg/L, $n = 8$), plus one or more exceeded reference CMC levels for Al (>0.75 mg/L, $n = 2$), Co (>95 $\mu\text{g/L}$, $n = 5$), Se (>12.8 $\mu\text{g/L}$, $n = 3$), Zn (>307 $\mu\text{g/L}$, $n = 1$), or Cu (>7.4 $\mu\text{g/L}$, $n = 1$) (Table 1, Figs. 2 and 4), after correcting the CMC for the latter two constituents by sample hardness (Fig. 5). Furthermore, many of the treated effluents did not meet reference criteria for SO_4 and related measures of ionic strength, including TDS, SC, and osmotic pressure (Table 1, Fig. 2). Nevertheless, all 46 effluent samples met CMC levels for Ag, As, Ba, Cd, Cl, Cr, Pb, Ni, Sb, Se, Tl, V, NH_3 , NO_2 , NO_3 , and CN (Table 1, Figs. 2 and 4). Although the CMC exceedances for Co and Zn were attributed to samples violating the PME limit for pH or Mn, the samples that exceeded the CMC for Al, Cu, or Se met the applicable PME limits for pH, Fe, and Mn.

The pH and hardness are considered by regulatory authorities as practical indicators of potential for toxic effects by Ag, Cd, Cr, Cu, Pb, Ni, and Zn in the effluent and receiving waters. As illustrated in Fig. 5 (and summarized in Supplemental Tables A.1 and A.2), the hardness-adjusted CMCs for this subset of priority pollutants increase with hardness to 400 mg/L as CaCO_3 , but remain unchanged thereafter (U.S. Code of Federal Regulations, 2013b; U.S. Environmental Protection Agency, 2013). More than 80% of the influents and effluents had hardness >400 mg/L (Fig. 5). All but one effluent sample had $\text{pH} > 6$. Although many

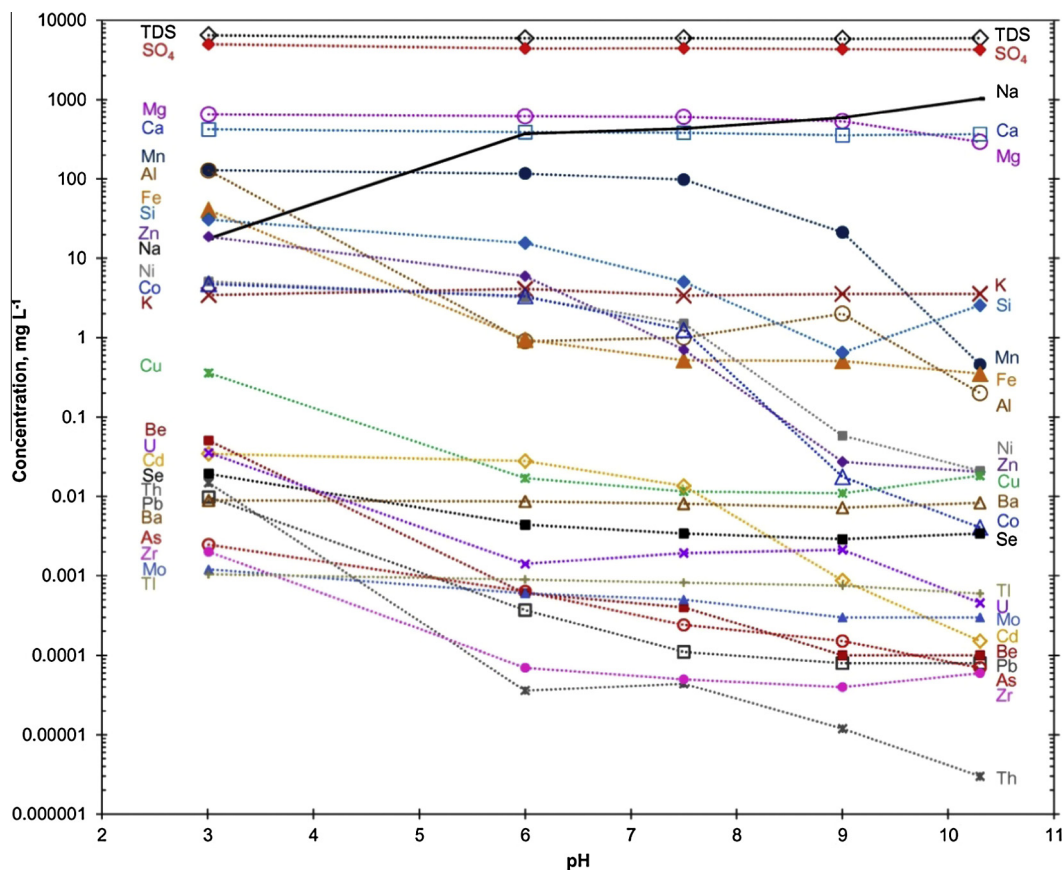


Fig. 3. Observed changes in pH and solute concentrations during field titration of metal-laden CMD at the Nittany Mine with caustic soda (1.6N NaOH).

of the influent samples had elevated concentrations of metals, the effluent samples that had pH > 6 met the aquatic hardness-adjusted CMC and CCC levels for Ag, Cd, Cr, Cu, Pb, Ni, and Zn (Fig. 5), with one exception.

The sole effluent sample that exceeded the CMC for Cu had a relatively high pH of 9.7, a low Cu concentration of 13.4 $\mu\text{g/L}$, and the lowest hardness of all samples. For this hardness of 53 mg/L, the adjusted CMC for Cu is 7.4 $\mu\text{g/L}$. If the hardness of this sample were >100 mg/L, the observed Cu concentration would meet the corresponding hardness-adjusted CMC. The corresponding influent sample, which had pH of 3.6, Cu of 54.8 $\mu\text{g/L}$, and hardness of 2070 mg/L, met the adjusted CMC for Cu of 62.8 $\mu\text{g/L}$ computed for hardness of 400 mg/L as CaCO_3 . The decrease in hardness of the effluent resulted from substantial decreases in Ca from 422 to 14.6 mg/L and Mg from 252 to 4.1 mg/L and was accompanied by an increase in Na (344–1470 mg/L) and decreases in SO_4 (6220 to 3120 mg/L), Fe (1780 to 0.03 mg/L), Mn (18.4 to <0.01 mg/L), and Al (32.9 to 0.08 mg/L). Despite very low concentrations of Ca and Mg, the NaOH-treated effluent was supersaturated with respect to calcite (SI = 0.5) and dolomite (SI = 0.1), but was undersaturated with gypsum (SI = -1.5) and brucite (SI = -2.0). Because of intermittent pumping (batch treatment) from the initial treatment pond to the settling pond and prolonged retention before discharge of the effluent, ample time (weeks) may be available for carbonate minerals to precipitate. Thus, precipitation of CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$ could explain the decrease in hardness and the corresponding increase in Cu toxicity. PHREEQC computations indicate that a lower pH (8.8 instead of 9.7) and a doubling of the concentrations of Ca and Mg (hardness >100 mg/L) in effluent could result in undersaturation with respect to carbonate minerals. Therefore, treatment to a lower pH (≤ 8.8)

potentially could mitigate Cu toxicity. The actual effect and justification of any change in treatment on pollutant concentrations warrants further study.

Elevated concentrations of Se (13.9–32.8 $\mu\text{g/L}$), with uncertain potential for toxicity, were documented for three effluent samples (Fig. 2L). The CMC threshold of 12.8 $\mu\text{g/L}$ (Table 1) applies if the measured Se consisted entirely of the more toxic selenate ($\text{Se}^{\text{VI}}\text{O}_4^{2-}$) species instead of the less toxic selenite ($\text{Se}^{\text{IV}}\text{O}_3^{2-}$) species with CMC of 185.9 $\mu\text{g/L}$ (U.S. Code of Federal Regulations, 2013a; U.S. Environmental Protection Agency, 2013). Without data on Se oxidation state, aqueous speciation computations with PHREEQC using the measured Eh were employed to estimate the potential equilibrium distribution of Se^{IV} and Se^{VI} . These computations indicated that the estimated fraction of Se^{VI} was a maximum of 25% of the total dissolved Se in samples containing at least 4 $\mu\text{g/L}$ Se. The corresponding CMC range would be 42.5–185.9 $\mu\text{g/L}$, which exceeds the highest measured Se concentration. At sites with elevated Se (>12.8 $\mu\text{g/L}$), direct measurement of concentrations of Se^{IV} and Se^{VI} in the influent and effluent (e.g. Wolf et al., 2011) could be helpful to ascertain the environmental significance of aqueous Se data, and strong oxidizing agents such as permanganate should be avoided to prevent oxidation of Se^{IV} to Se^{VI} .

3.2. Correlations among priority and other potential pollutants, dissolved major ions, TDS, and conductivity

Spearman's rank correlation and PCA were used to identify significant correlations potential pollutants, pH, and other water-quality variables. The reported PCA model consists of five PCs that explain 77% of the variance among 28 variables for undifferentiated influent and effluent (Table 2). The PCA model indicates that

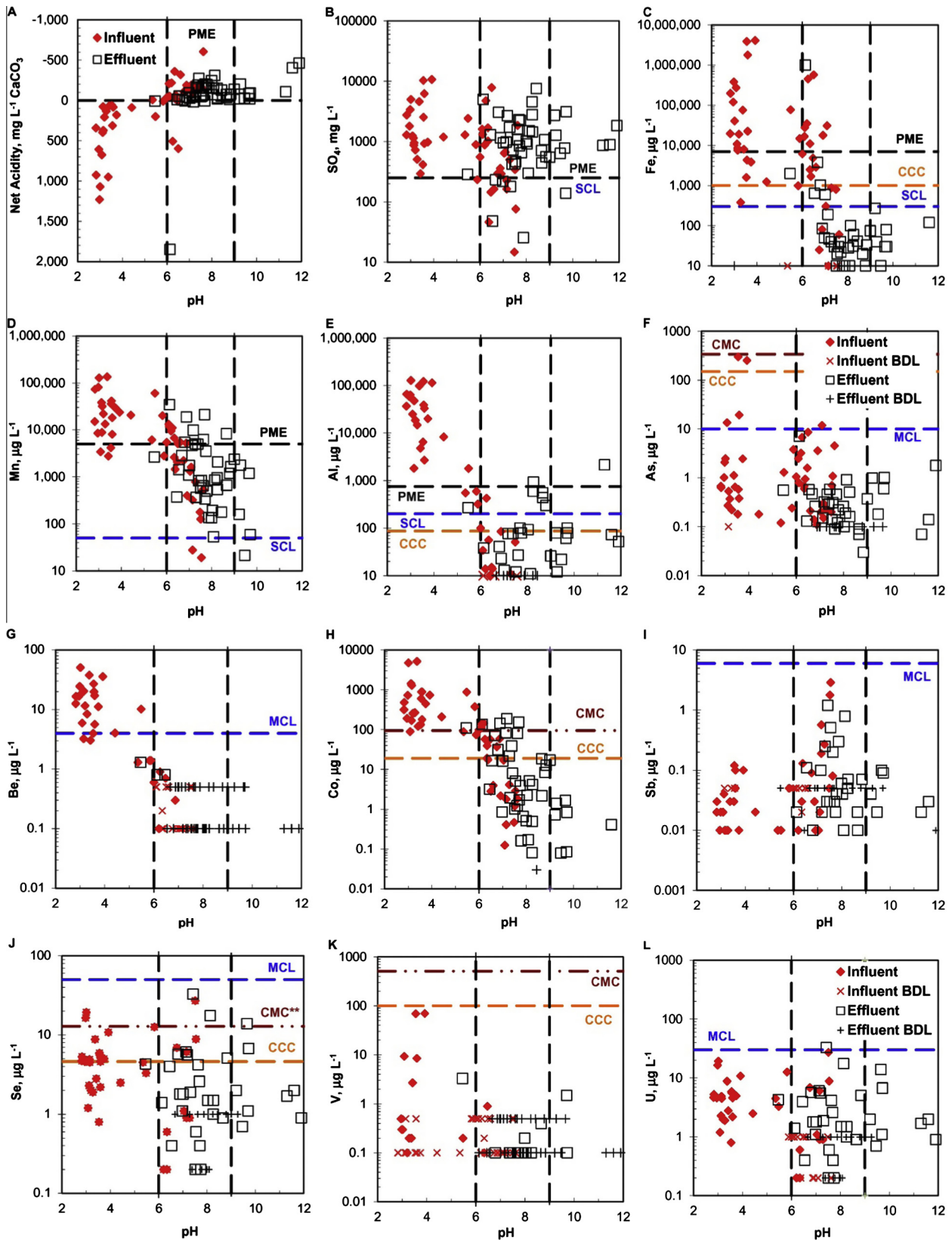


Fig. 4. Contaminant concentration and pH of untreated influent and treated effluent from coal mining or processing facilities, Pennsylvania, 2011, with reference to criteria for permitted mine effluent (PME) in Commonwealth of Pennsylvania (1998a,b), maximum contaminant level (MCL) or secondary contaminant level (SCL) for drinking water (U.S. Environmental Protection Agency, 2012), and criteria maximum concentration (CMC) and criterion continuous concentration (CCC) for freshwater aquatic organisms (U.S. Environmental Protection Agency, 2013). Values below detection limit (BDL) plotted at detection limit. *CMC and CCC computed for hardness of 400 mg/L as CaCO₃. **CMC of 12.8 µg/L for Se assumes all Se is selenate.

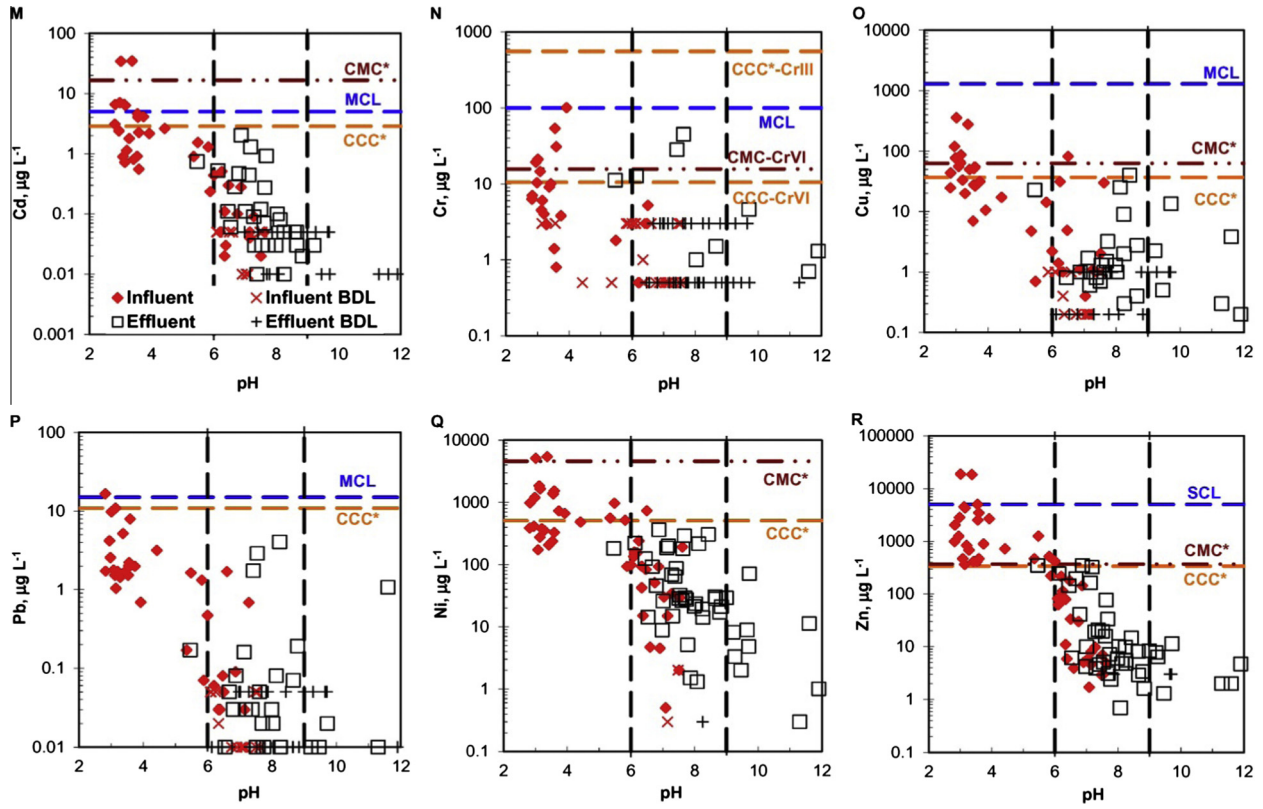


Fig. 4 (continued)

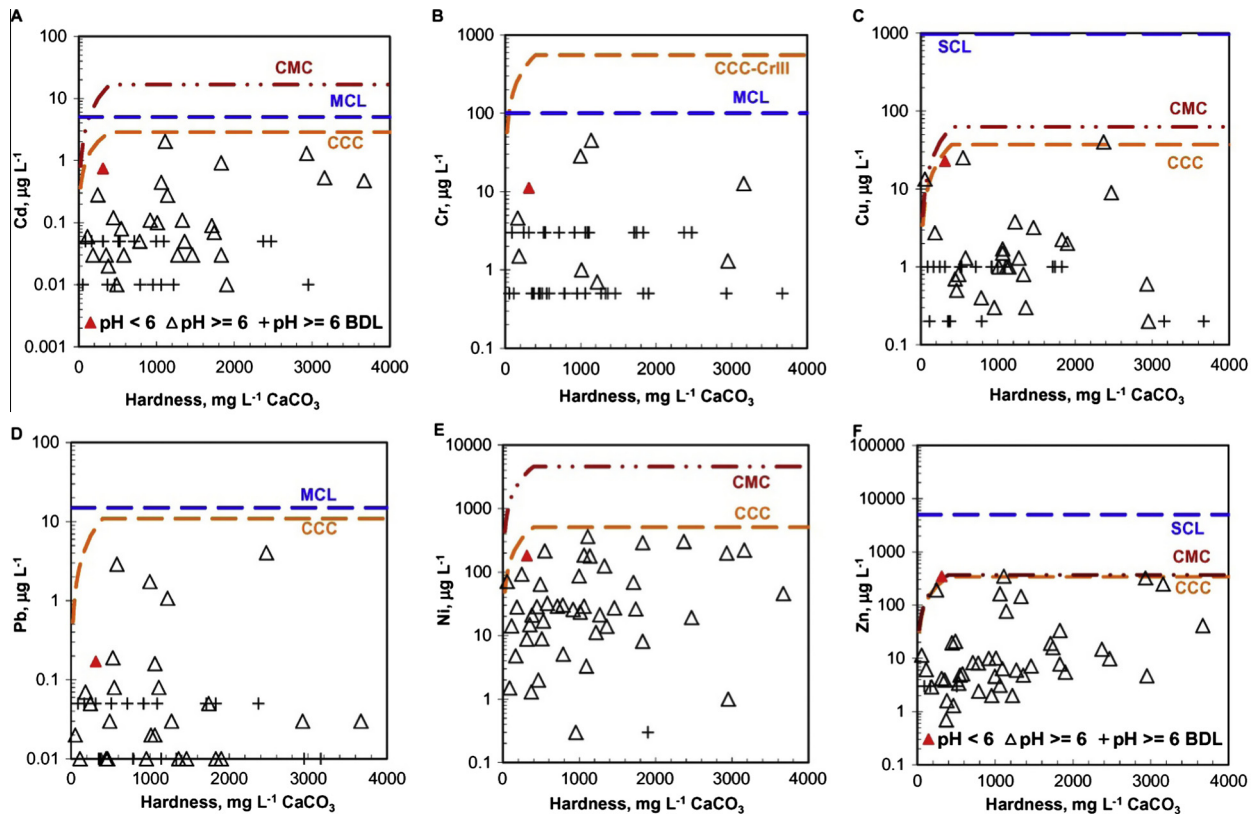


Fig. 5. Contaminant concentration, hardness, and pH classification of effluent samples from coal mining or processing facilities, Pennsylvania, 2011, with reference to hardness-based criteria maximum concentration (CMC) and continuous concentration (CCC) for protection of freshwater aquatic organisms (U.S. Environmental Protection Agency, 2013) and maximum contaminant level (MCL) or secondary contaminant level (SCL) for U.S. drinking water (U.S. Environmental Protection Agency, 2012). Values below detection limit (BDL) plotted at detection limit.

Table 2
Principal components analysis (PCA) model of factors controlling chemistry of untreated and treated CMD from coal mining or processing facilities, Pennsylvania, 2011.

Constituent loadings:	pH PC1	TDS PC2	Salinity PC3	TIC PC4	Oxygen PC5	Communality
Cobalt (Co)	92*	6	-14	-10	-7	0.888
Zinc (Zn)	90*	22	-10	-14	-4	0.896
Nickel (Ni)	88*	27	3	0	3	0.850
Manganese (Mn)	85*	23	-16	-6	-13	0.818
Acidity, hot (ACIDH)	73*	13	5	-55*	6	0.855
Iron (Fe)	72*	2	16	-10	-50*	0.793
Uranium (U)	68*	24	17	41*	19	0.754
Redox potential (Eh)	66*	-3	-14	-19	53*	0.775
Titanium (Ti)	66*	22	28	-23	-18	0.643
Aluminum (Al)	65*	22	-2	-41*	10	0.647
Alkalinity (ALK)	-66*	1	7	64*	-24	0.906
pH, fresh (pHF)	-92*	12	6	-2	14	0.889
Residue on evaporation (ROE)	23	92*	27	2	-8	0.968
Sulfate (SO4)	27	91*	23	-6	-6	0.965
Specific conductance (SC25)	16	90*	32	3	-8	0.951
Osmotic pressure (OSMP)	13	88*	29	10	-10	0.905
Calcium (Ca)	0	81*	10	9	-23	0.730
Magnesium (Mg)	49*	73*	-12	9	4	0.790
Potassium (K)	9	65*	40*	22	2	0.645
Strontium (Sr)	-8	51*	35	22	-41*	0.608
Barium (Ba)	-7	-63*	24	17	-31	0.582
Chloride (Cl)	-6	17	84*	-2	-3	0.743
Bromide (Br)	0	33	80*	-5	3	0.754
Sodium (Na)	-16	49*	69*	-7	3	0.738
Total inorganic carbon (TIC)	-14	1	-5	82*	-32	0.793
Total organic carbon (TOC)	-10	29	-4	64*	17	0.532
Dissolved oxygen (DOX)	-10	-21	23	-4	71*	0.614
Arsenic (As)	46*	-4	34	14	-54*	0.639
Eigenvalue:	9.803	6.205	2.415	2.002	1.245	21.671
Cumulative percent variance explained:	35.01	57.17	65.79	72.94	77.39	
<i>Significant spearman correlations (p < 0.001):</i>						
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 (NH3 N)	-	-	44	-	-46	
Molybdenum (Mo)	-	-	44	-	-	

Varimax rotation factor pattern for rank-transformed data (SAS, 1988); minimum eigenvalue >1; loading values for constituents included and Spearman correlations coefficients for constituents excluded from model multiplied by 100 and rounded.

* Significant loadings ($p < 0.005$).

variations in most constituents were related to one or more specific chemical factors such as pH, TDS, salinity, TIC, and DO. Significant Spearman rank correlation coefficients for 19 constituents excluded from the PCA because of censoring or redundancy are displayed beneath the model loadings (Table 2). None of the chemical constituents was correlated (positively or negatively) with flow rate, implying that dilution was not a major factor affecting constituent values for the data as a whole. However, as previously explained, dilution may have affected the effluent characteristics at a few sites.

PC1, which explains 35.01% of the data variability, has negative loadings by pH and alkalinity, and positive loadings by Co, Zn, Ni, Mn, Fe, U, Ti, Al, Mg, As, acidity, and Eh (Table 2). Numerous trace elements, including Cd, Be, Pb, Th, Cu, Cr, Zr, Tl, and Se, plus total phenols and COD, are positively correlated with PC1 scores,

indicating potential pollutant concentrations tend to be greatest for acidic, oxidizing conditions and least for conditions with elevated pH and alkalinity (Fig. 4). Thus, the constituent associations on PC1 are consistent with (1) the release of Fe, Mn, Al, and trace elements at low pH, and (2) coprecipitation or adsorption reactions by trace metals on Fe, Mn, and Al solids at near-neutral and alkaline pH. Although the low pH of untreated CMD can be attributed to the release of sulfuric acid from the oxidation of pyrite, SO₄ and other major ions, except Mg, were not loaded on PC1 because, once dissolved, SO₄ and associated major ion concentrations vary only moderately, if at all, with pH.

PC2, which explains 22.16% of the data variability, identifies constituents that vary with, or contribute to, ionic strength and that are poorly correlated with pH. PC2 has positive loadings by ROE, SC, osmotic pressure, SO₄, Ca, Mg, Sr, K, and Na, with a

negative loading by Ba (Table 2). Scores on PC2 were correlated with the computed TDS and hardness and measured COD, temperature, and F. The negative loading of Ba on PC1 results because of solubility control by barite (BaSO_4) at high SO_4 concentrations. As explained in more detail below, the major ion concentrations directly account for the measured and computed values for TDS, SC, and osmotic pressure. Positive correlations by Mg and COD on both PC2 and PC1 indicate potential for ionic strength and pH to affect these constituents. Concentrations of Mg and COD (Fe^{II} and Mn^{II}) tend to be elevated for low pH, high ionic strength samples and remain elevated as pH increases to near-neutral values; however, at very high pH (>8.5), the concentrations of Mg, Fe^{II} , and Mn^{II} decrease as pH increases. Likewise, positive loadings of K and Na on PC2 and PC3 indicate more than one environmental factor could explain variations in these cations.

PC3, which explains 8.62% of the data variability, has positive loadings by Cl, Br, Na, and K, with positive correlations by NH_3 and Mo. The halogen and alkali earth elements are typically associated with saline waters such as oil and gas brines or connate fluids (e.g. Dresel and Rose, 2010; Haluszczak et al., 2013). As indicated by their loading only on PC3, Cl and Br were more strongly correlated with one another than with other major ions and were not strongly associated with acidity, pH, or ionic strength. The coal-bearing rocks of the Appalachian Plateau were once deeply buried and saturated with saline waters (Brady et al., 1998; Reed et al., 2005). Shallow rocks are more fractured and thus allow for greater flushing by meteoric water than deeper portions of the flow system (Wyrick and Borchers, 1981; Stoner et al., 1987). Thus, CMD samples with high positive scores on PC3 tend to originate from deep mines or from associated waste rock piles. Although the Cl, Br, and Na concentrations in CMD are dilute compared to oil and gas brines or other sources of salinity, the Br/Cl ratios (as illustrated by Supplemental Fig. A3) indicate many of the deep mine waters have enriched Br compositions that are consistent with residual brine diluted with meteoric water. Similar correlations among Cl, Br, and Na were reported for natural groundwaters used for domestic supplies in the eastern USA (Chapman et al., 2013).

PC4, which explains 7.15% of the data variability, has positive loadings by TIC, alkalinity, TOC, and U and negative loadings or correlations by acidity, Al, and TI. High positive scores on PC4 may be interpreted to indicate conditions favoring increased mobility of U and decreased mobility of Al and TI where dissolved carbon species are elevated. Positive loadings by U on PC1 and PC4 are consistent with the presence of U^{VI} as the uranyl (UO_2^{2+}) oxyanion in CMD. The uncomplexed oxyanion and other cations (dissolved metals) generally have high mobility at low pH and decreased mobility at near-neutral and alkaline pH, as indicated by PC1. With increased alkalinity, however, the uranyl ion may form negatively charged carbonate complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$; $\text{UO}_2(\text{CO}_3)_3^{4-}$) that are mobile at high pH (e.g. Langmuir, 1997). As implied by PC4 and explained in more detail below, the formation of these negatively charged carbonate complexes can enhance the mobility of U at pH values typical of treated CMD. Similar relations among alkalinity, pH, and U were reported for natural groundwaters in the eastern USA (Chapman et al., 2013).

PC5, which explains 4.45% of the data variability, has positive loadings by DO and Eh with negative loadings and correlations by As, Fe, Sr, and NH_3 . PC5 is interpreted to indicate the effect of redox environment on Fe and As mobility. Samples with very low DO and strongly negative scores on PC5 are consistent with reducing conditions that could result in the reductive dissolution of Fe^{III} -oxides, reductive desorption of As (reduction of As^{V} to As^{III}), or dissimilatory reduction of NO_3 to NH_3 (e.g. Welch et al., 2000). Although some influents were anoxic ($\text{DO} < 0.5$ mg/L), with chemical characteristics consistent with Mn^{IV} and Fe^{III} reducing conditions as defined by McMahon and Chapelle (2008; $\text{NO}_3 < 0.5$ mg/

L, $\text{Mn} > 0.05$ mg/L, $\text{Fe} > 0.1$ mg/L, and $\text{SO}_4 > 0.5$ mg/L), low concentrations of electron donors, such as TOC, generally would limit the development of strongly reducing conditions and the consequent reductive dissolution of Fe^{III} and Mn^{IV} oxides. Aerobic treatment of the CMD would favor the development of oxidizing conditions, corresponding to positive scores on PC5, and the formation of HFO and associated oxides, whose charged surfaces may attract As and other trace ions.

3.3. Control of dissolved metal concentrations by precipitation and adsorption processes

The influent samples had elevated Pco_2 values ($10^{-2.8}$ to $10^{-0.7}$ atm; median $10^{-1.6}$ atm) compared to the effluent Pco_2 ($10^{-10.1}$ to $10^{-1.7}$ atm; median $10^{-2.8}$ atm) and the ambient atmosphere Pco_2 ($10^{-3.4}$ atm) (Fig. 6). Although most influent samples had acidic pH (median 5.85) and were undersaturated with carbonate minerals, those with near-neutral pH (6 to 7) were frequently saturated with respect to siderite (FeCO_3) and rhodochrosite (MnCO_3), and a subset of those also was saturated with calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Fig. 6B, J and K). In contrast, most effluent samples had alkaline pH (median 7.85); effluents with $\text{pH} > 7.4$ were frequently saturated or supersaturated with calcite, dolomite, and rhodochrosite, but were undersaturated with siderite. All the influents and effluents were undersaturated with smithsonite (ZnCO_3), cerussite (PbCO_3), strontianite (SrCO_3), witherite (BaCO_3) (Fig. 6N, M, O and P), otavite (CdCO_3) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) (not displayed in Fig. 6). Undersaturation with respect to these trace carbonate minerals indicates that their precipitation would not be feasible and therefore unlikely to limit the constituent concentrations in the effluent. Furthermore, frequent supersaturation with respect to calcite, dolomite, siderite, and rhodochrosite may indicate kinetic limitations (slow rate) for the precipitation of more common carbonate minerals from effluent. Thus, observed concentrations of Ca, Mg, Fe, Mn, and associated trace metals in most effluent samples probably are not limited by carbonate precipitation.

On the basis of SI values > 0 , concentrations of Ca and Ba in many effluents appear to be limited by the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and barite (BaSO_4), while those of Al, Fe, and Mn appear to be limited by the precipitation of hydrous oxide or hydroxysulfate minerals (Fig. 6). Generally, gypsum saturation and the consequent removal of SO_4 were indicated where Ca compounds were added to increase pH (Fig. 2D and Supplemental Fig. A.2). Likewise, the increased pH of most effluents resulted in saturation or supersaturation with respect to gibbsite ($\text{Al}(\text{OH})_3$), boehmite (AlOOH), ferrihydrite or amorphous $\text{Fe}(\text{OH})_3$, goethite (FeOOH), and various $\text{Mn}^{\text{III-IV}}$ minerals including manganite (MnOOH) and todorokite ($\text{Mn}_7\text{O}_{12} \cdot 3\text{H}_2\text{O}$). Additionally, effluent samples were frequently saturated with basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$), alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{4.5}(\text{SO}_4)_{1.75}$), but were undersaturated with most other sulfate minerals (Fig. 6). SI values < 0 for melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), zincosite (ZnSO_4), $\text{CdSO}_4 \cdot 2.7\text{H}_2\text{O}$, chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), anglesite (PbSO_4), celestite (SrSO_4), and other trace sulfate compounds indicate such phases were unlikely to limit associated trace element concentrations. With few exceptions (e.g. $\text{Ni}(\text{OH})_2$, cuprous ferrite (CuFeO_2), and cupric ferrite (CuFe_2O_4)), hydroxide and oxide compounds of Zn, Cd, Cu, Pb, Sr, and other trace metals remained below saturation. Nevertheless, most trace element concentrations typically decreased with increased pH (Fig. 4).

The effluent sample that had the highest concentration of dissolved Al (2.14 mg/L) had the highest pH (11.9) of all samples in this study (Fig. 4). In the alkaline pH range, dissolved Al

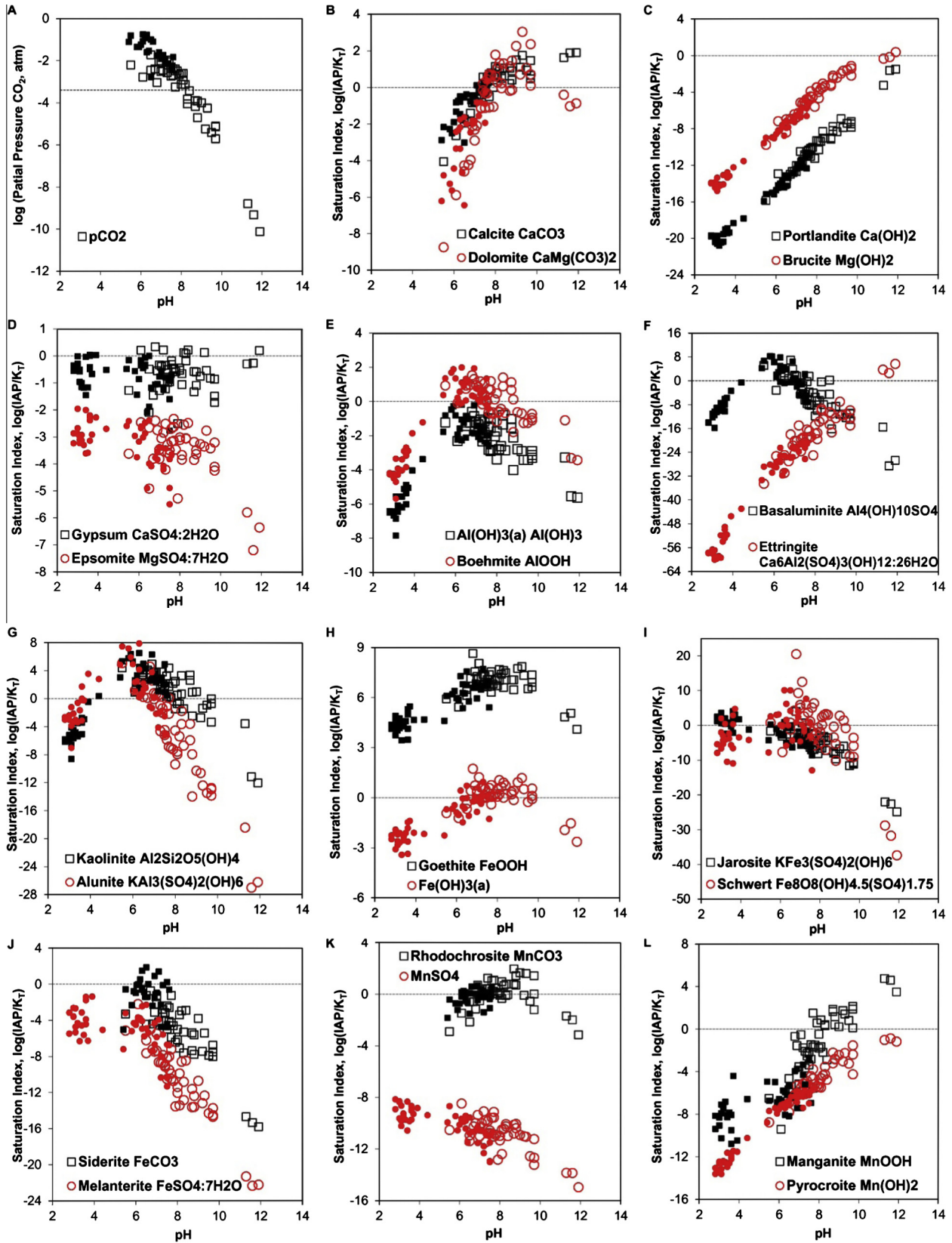


Fig. 6. Partial pressure of CO₂ and saturation indices for minerals and other solids as a function of pH for treated effluent at coal mining or processing facilities, Pennsylvania, 2011. Computations with PHREEQC (Parkhurst and Appelo, 2013) using the WATEQ4F data base (Ball and Nordstrom, 1991) with supplemental thermodynamic data for schwertmannite, ferrihydrite, and goethite (Bigham et al., 1996) and ettringite (Myneni et al., 1998). Open symbols indicate treated effluent; filled symbols indicate untreated influent.

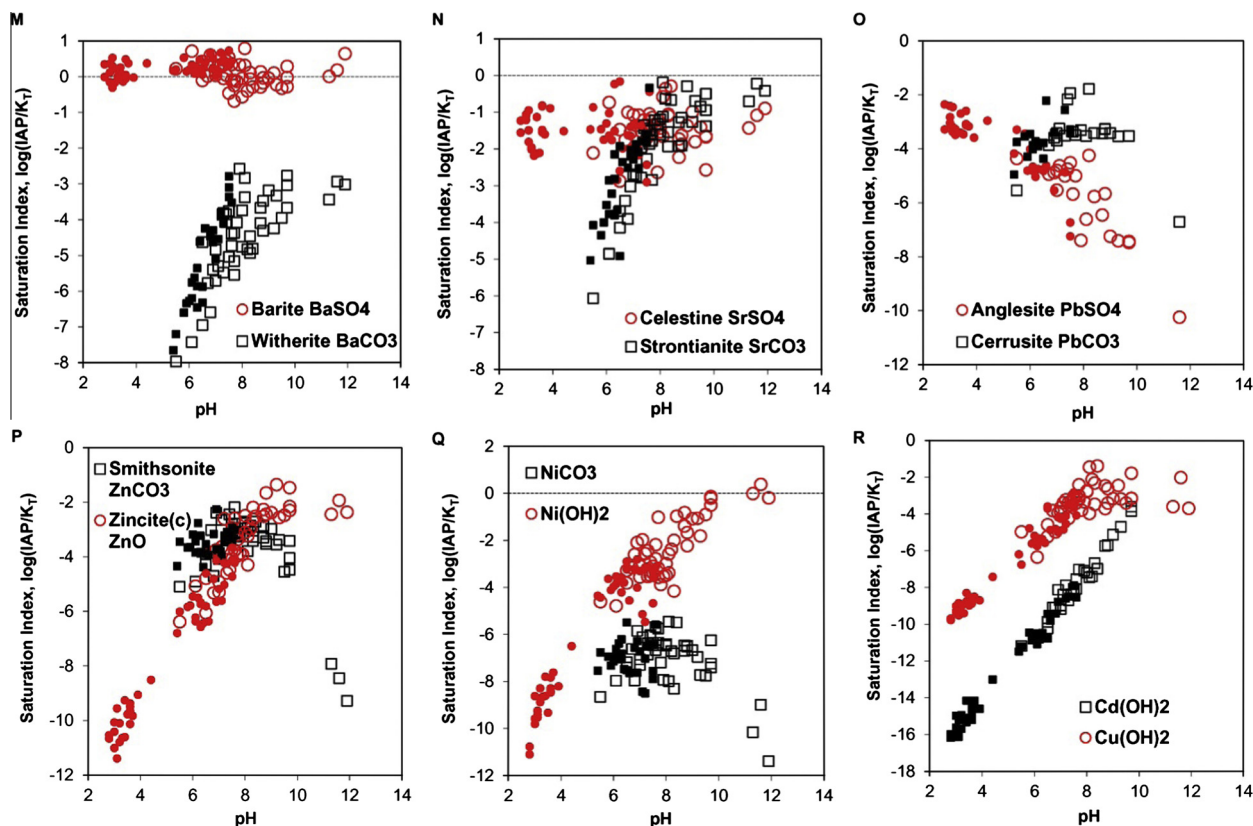


Fig. 6 (continued)

concentration may increase with pH because of the formation of aqueous $\text{Al}(\text{OH})_4^-$ that adds to the total dissolved Al concentration at equilibrium with hydroxide and hydroxysulfate compounds (e.g. Cravotta, 2008b; Bigam and Nordstrom, 2000). However, where liming agents or compounds containing Ca are added, concentrations of Al and SO_4 may be limited at high pH values (>9) by the precipitation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) (Loop et al., 2004; Myneni et al., 1998), which can lead to undersaturation with respect to Al hydroxides or silicates. Nevertheless, high pH values (>9) are typically temporary and/or local because the high-pH effluents tend to be undersaturated with respect to atmospheric CO_2 and supersaturated with respect to CaCO_3 (Fig. 6A and B). In general, after absorbing CO_2 from the atmosphere, precipitating CaCO_3 , and/or mixing with a receiving water body, the pH would tend to decrease to target values ($6 < \text{pH} < 9$) and the corresponding concentration of Al also may decrease as $\text{Al}(\text{OH})_3$ and associated solids become saturated and precipitate.

Although concentrations of major cations and anions in natural waters are generally controlled by acid-base and precipitation-dissolution reactions, the concentrations and mobilities of most trace ions are commonly controlled by surface-complexation (adsorption) reactions on hydrous Fe^{III} oxides, $\text{Mn}^{\text{III-IV}}$ oxides, and aluminum oxides and silicates (Coston et al., 1995; Drever, 1997; Kooner, 1993; Webster et al., 1998). The effluents were supersaturated with various such sorbent phases (Fig. 6) and, as shown in the online Supplemental Fig. A4, the Eh and pH data for effluent consistently plotted within the stability fields for goethite and ferrihydrite, which are referred to generically as HFO. The HFO was a major component of the rust-colored solids (sludge) that precipitated at the treatment facilities.

Generally, as the pH increases, the predominance of negatively charged surface sites on HFO and negatively charged aqueous species increases. At acidic pH (<6), abundant protons attracted to the

negatively charged oxide atoms at HFO surfaces yield an effective positive charge that adsorbs anions, such as selenite ($\text{Se}^{\text{IV}}\text{O}_3^{2-}$), arsenate ($\text{As}^{\text{V}}\text{O}_4^{3-}$), and phosphate (PO_4^{3-}) (Fig. 7A), and repels cations, such as chromium (Cr^{+3}), copper (Cu^{+2}), cadmium (Cd^{+2}), lead (Pb^{+2}), nickel (Ni^{+2}), and zinc (Zn^{+2}) (Fig. 7B). As pH increases to alkaline values (>7.5), the HFO surfaces acquire a more negative charge that adsorbs cations and repels anions (Fig. 7). However, the potential for sorption of various constituents is complicated by changes in the aqueous species in response to pH and Pco_2 (alkalinity, TIC). For example, selenite ($\text{H}_{2-x}\text{Se}^{\text{IV}}\text{O}_3^x$), arsenate ($\text{H}_{3-x}\text{As}^{\text{V}}\text{O}_4^x$), phosphate ($\text{H}_{3-x}\text{PO}_4^x$), and chromate ($\text{H}_{2-x}\text{Cr}^{\text{VI}}\text{O}_4^x$) species tend to transform from predominantly uncharged ions at very low pH to more negatively charged species as the pH increases (e.g. $\text{H}_2\text{SeO}_3^0 = \text{HSeO}_3^- + \text{H}^+ = \text{SeO}_3^{2-} + 2\text{H}^+$). The negatively charged HSeO_3^- and H_2AsO_4^- species, which predominate at pH values of approximately 3 to 7 (e.g. Takeno, 2005), are attracted to positively charged HFO surface sites that are abundant at acidic pH (<6). However, as the pH increases to alkaline values, where SeO_3^{2-} and HAsO_4^{2-} species predominate, the HFO surface takes on a negative charge, which repels such anions and attracts cations.

Likewise, some cations that are mobile at low pH (e.g. UO_2^{+2} , Zn^{+2} , Ni^{+2}) and could be anticipated to adsorb on HFO at alkaline pH, tend to form negatively charged carbonate complexes (e.g. $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$; $\text{Zn}(\text{CO}_3)_2^{2-}$; and $\text{Ni}(\text{CO}_3)_2^{2-}$). The negatively charged complexes are repelled by negatively charged HFO surfaces at high pH (Fig. 7B). Lastly, sorbed cations or anions may be displaced by other ions such as magnesium (Mg^{+2}), chloride (Cl^-), and sulfate (SO_4^{2-}) through ion exchange or competition for sorption sites. Thus, concentrations of trace elements in solution may increase with TDS, not only because of the release of trace constituents with the major ions dissolved from minerals, but because of the displacement of trace ions from surface-complexation sites by the major ions. For the trace elements that form

aqueous complexes, the increase in soluble major ion concentrations also increases the likelihood of the formation of variously charged ion complexes that can affect the potential for sorption.

3.4. Influence of major ions on total dissolved solids, conductivity, and osmotic pressure

The computed values for TDS, SC, and osmotic pressure, estimated from measured solute concentrations in the samples, were equivalent to the corresponding measured values for ROE, SC, and osmotic pressure (Fig. 8A–C). Close agreement among the measured and computed values for TDS, ROE, SC, and osmotic pressure plus the ionic strength (Fig. 8A–F) generally validates the computation methods and the analytical results. Although expressed by different units, these measures are proportional to the solute concentrations and therefore are closely related to one another. However, the different measures of ionic strength are affected to different extents by variations in major ion concentrations as explained in more detail below.

The measured ROE and computed TDS, in milligrams per liter, consider only the total mass of solutes and are not sensitive to aqueous speciation or ionic charge. The TDS concentration ordinarily is measured in the laboratory as ROE, from the weight of the dry residue remaining after evaporation of water and other volatile components of a sample at 180 °C and/or is estimated as the sum of major ion concentrations (Fishman and Friedman, 1989). However, Hem (1985, p. 156–157) cautioned that, “although evaporating the water from an aliquot and weighing the residue seems about as simple and direct a way of measuring the solute content as could be devised, the results of such a determination can be difficult to interpret.” The problem mainly arises from incomplete volatilization of water and organic compounds that may be retained in the residue. Water retained in the crystal structure of solids formed by Fe, Mn, and Al and possibly SO_4 , literally gives more weight to these constituents for the measurement or computation of TDS, but does not have an effect on the SC or osmotic pressure calculations. Likewise, estimating TDS as the sum of constituents also has limitations because the standard method of

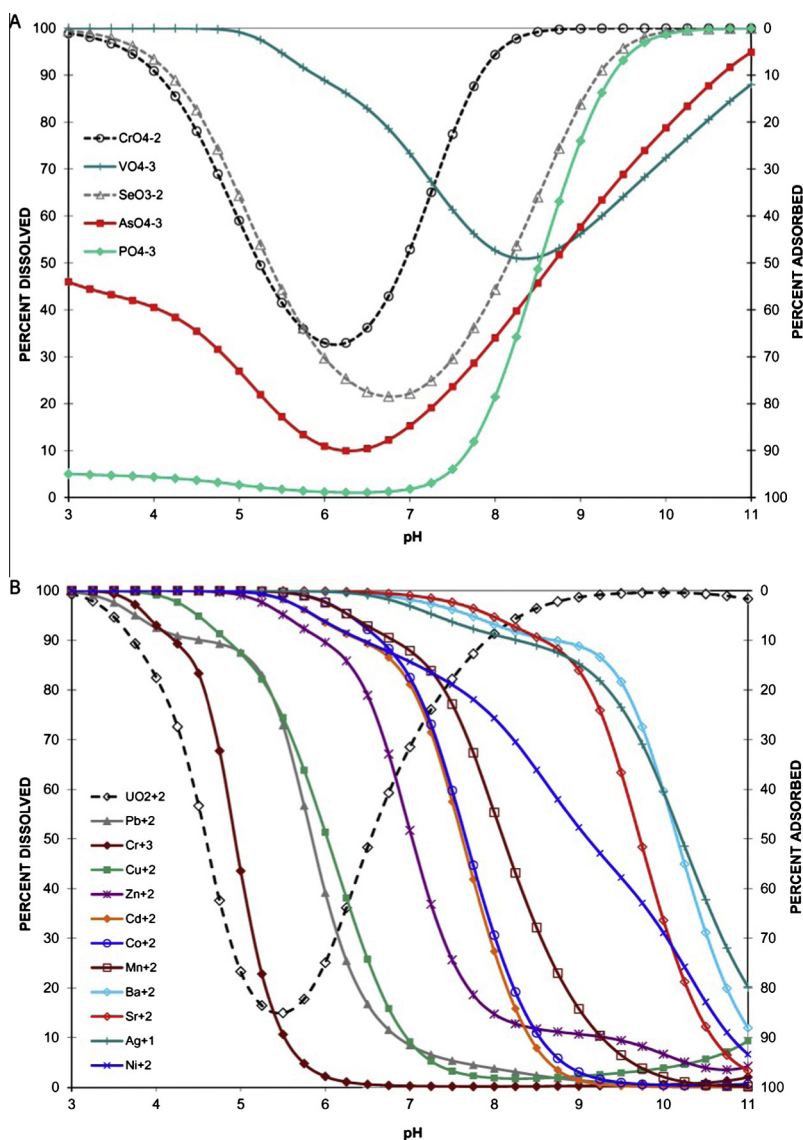


Fig. 7. Equilibrium fractions of initial concentrations of ions that may be dissolved or adsorbed on a finite amount of hydrous ferric oxide (HFO) at 25 °C as a function of pH: (A) anions; (B) cations. Area below curve indicates fraction that is not adsorbed; area above curve indicates fraction adsorbed. Simulations conducted using PHREEQC (Parkhurst and Appelo, 2013) with thermodynamic data from Ball and Nordstrom (1991), Duro et al. (2012), and Dzombak and Morel (1990). HFO was specified as 90 mg/L, with a specific surface area of 600 m²/g consisting of 5×10^{-6} moles of strong binding sites and 2×10^{-4} moles of weak binding sites. Relevant anion or cation was specified as 0.05 mmol/L in matrix consisting of 5 mmol/L Cl⁻, SO₄²⁻, and TIC plus Na to balance charge.

computation requires a complete analysis of major ions (Ca, Mg, Na, K, SiO₂, SO₄, CO₃, Cl, and NO₃) for summation (Fishman and Friedman, 1989) but does not consider additional ions, such as Fe, Mn, and Al, which could form hydrous oxides in residue. Although the measured ROE was strongly correlated with all variations of the computed TDS (Fig. 8A), the best agreement was achieved by assuming Fe, Mn, and Al precipitated as FeOOH, AlOOH, and MnOOH, respectively (TDS3). The SO₄ and “hardness” (Ca and Mg) were predominant sources of TDS in the influent and effluent; however, many samples with high ionic strength included substantial contributions by HCO₃, Cl, Na, and Fe (Fig. 8G). Because of the removal of Fe, Mn, Al, and CO₂ by treatment, the TDS of effluent was significantly (statistically) less than that of influent; however, the SC and osmotic pressure were not affected by treatment (Fig. 2C).

For the calculated SC values displayed in Fig. 8C, the new method of computation by McCleskey et al. (2012) was used, which considers the ionic molal conductivities of free cations and anions (H⁺, Li⁺, Na⁺, K⁺, Cs⁺, NH₄⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Al³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Zn²⁺, F⁻, Cl⁻, Br⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, NO₃⁻, and OH⁻) and ion pairs (HSO₄⁻, NaSO₄⁻, NaCO₃⁻, and KSO₄⁻). Uncharged aqueous species (e.g. H₂CO₃, FeSO₄, MgSO₄, and CaSO₄) and dissolved gases (O₂, N₂) have negligible ionic conductivities and thus were excluded. More than 90% of the calculated SC values were within 10% of the measured SC (Fig. 8C), compared to an average excess of 60% for estimated SC computed as the sum of the analytical concentrations multiplied by a constant factor for each major ion, without considering aqueous speciation (e.g. Compton and Sander, 1996; Robinson and Stokes, 1968). Generally, this simplified estimation method, which is strictly valid for fully dissociated

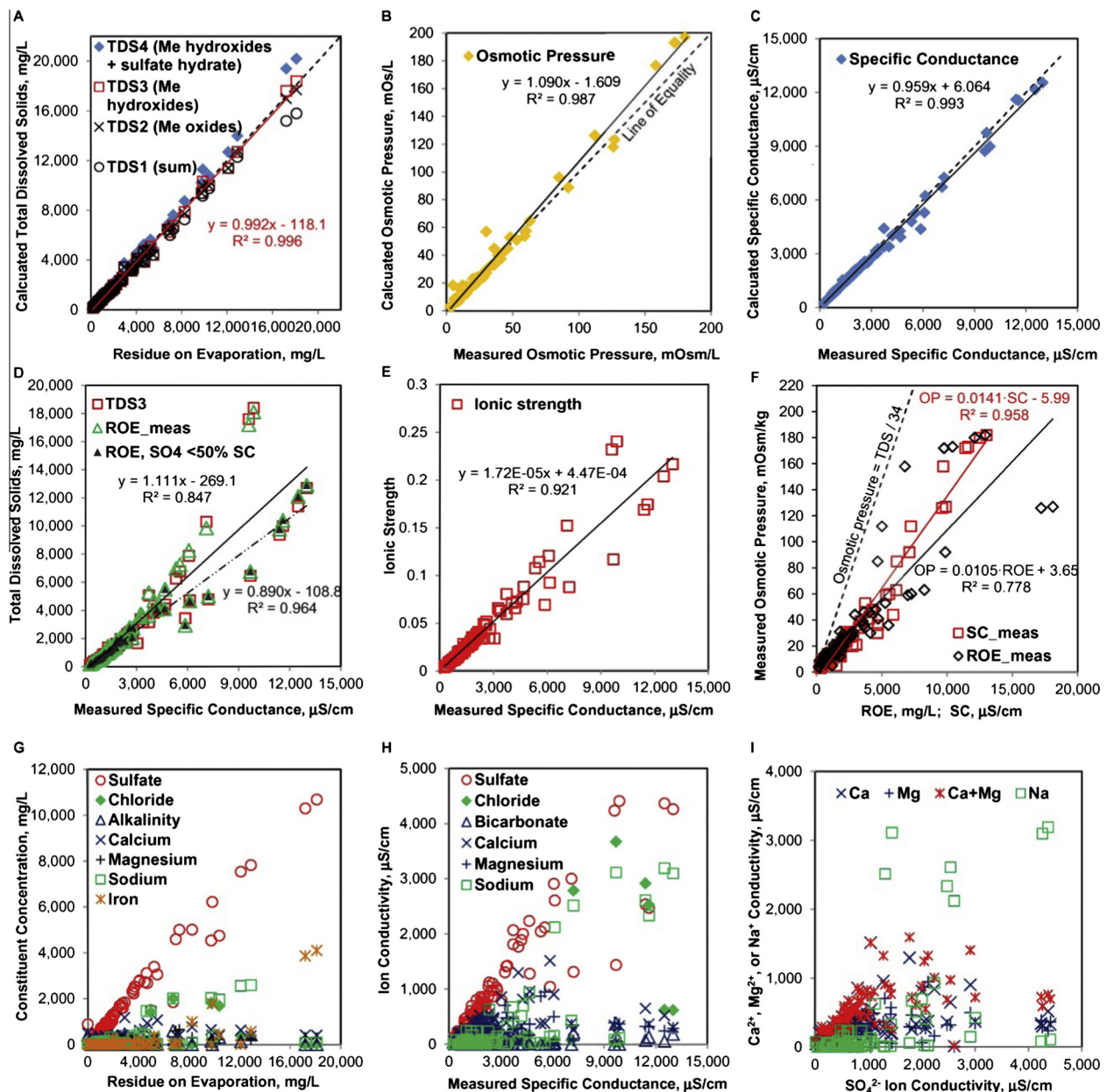


Fig. 8. (A–C) Comparisons of measured and computed values for total dissolved solids (TDS), residue on evaporation (ROE), osmotic pressure, and specific conductance (SC) for untreated influent and treated effluent at coal mining or processing facilities, Pennsylvania, 2011. Osmotic pressure estimated as the sum of molal concentrations of ions after aqueous speciation (Haynes et al., 2013), and SC estimated as the sum of ionic conductivity contributions (McCleskey et al., 2012); (D and E) relation between measured SC and calculated TDS and ionic strength; (F–H) relation between measured SC and (or) ROE and measured osmotic pressure, ion concentration, and conductivity; and (I) relation between SO₄ ion conductivity and major cation conductivity.

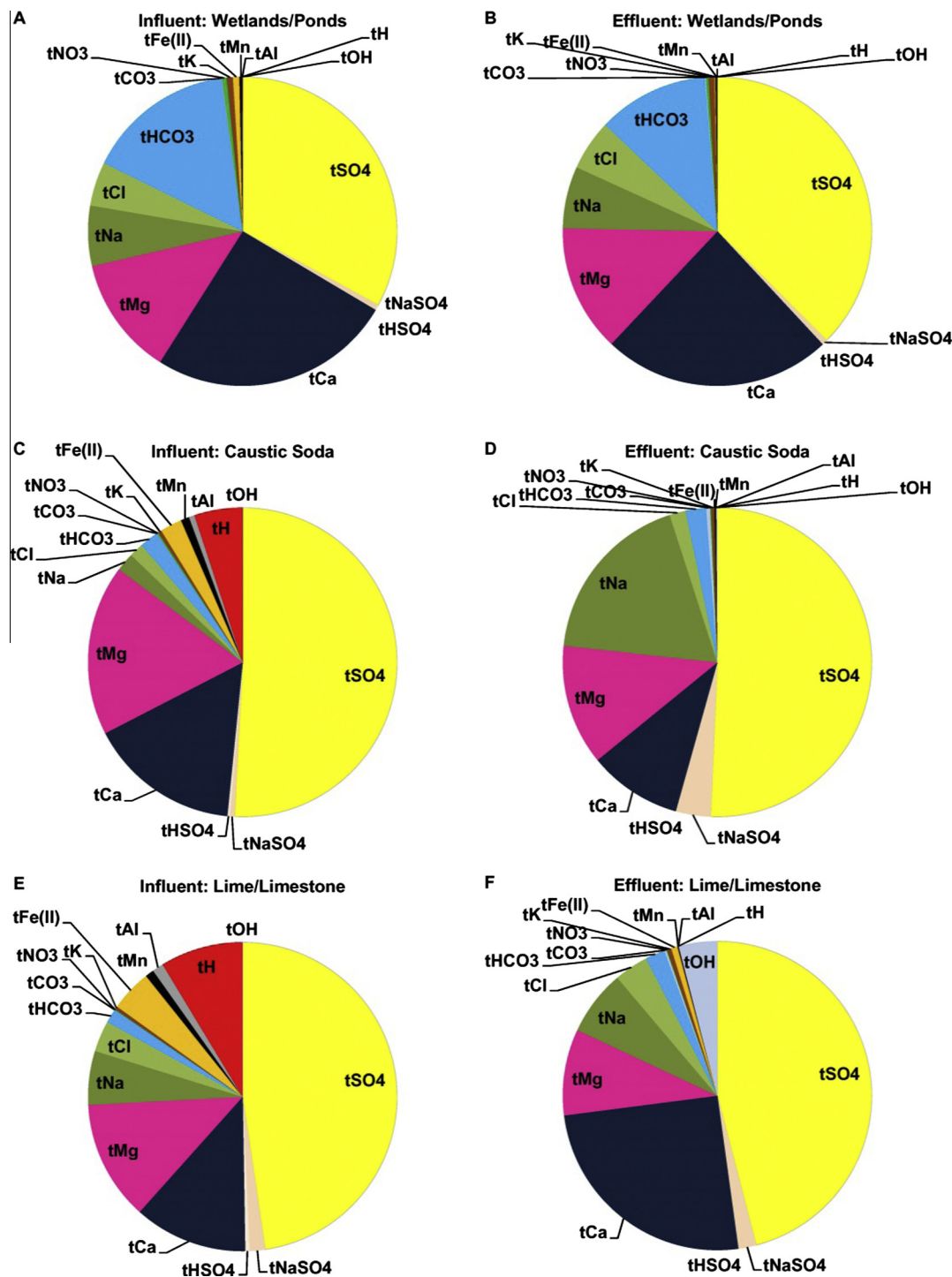


Fig. 9. Ionic contributions to specific conductance for untreated influent and treated effluent at coal mining or processing facilities, Pennsylvania, 2011. Contribution fractions are averages for: (A and B) wetlands and ponds without caustic chemicals ($N = 14$); (C and D) caustic soda addition ($N = 10$); and (E and F) lime or limestone addition ($N = 22$). Ion contributions estimated as “transport number” (relative contribution of a given ion to the overall conductivity) after aqueous speciation calculations with PHREEQC using methods of McCleskey et al. (2012).

ions at infinite dilution, overestimated SC because as ionic strength increases, aqueous complexation causes a decrease in the overall ionic charge distribution and the corresponding conductivity of the solution. Hence, the method of McCleskey et al. (2012) is superior for estimating the SC of CMD and other mineralized or saline waters.

As shown in Fig. 9, the ionic contributions to SC of the influent for each of the three general treatment methods were mainly from

SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , HCO_3^- , H^+ , Fe^{2+} , and, to a lesser extent, NaSO_4^- , Mn^{2+} , and Al^{3+} . For those treatments that did not utilize caustic agents (wetlands, ponds; Fig. 9A and B), the SC contribution by HCO_3^- decreased because alkalinity is consumed by the oxidation and hydrolysis of Fe^{2+} and Mn^{2+} . Although the predominance of SO_4^{2-} was not affected by treatment, the contributions to SC of influent by H^+ , Fe^{2+} , Mn^{2+} , and Al^{3+} were replaced by additional contributions by Na^+ , Ca^{2+} , HCO_3^- , and OH^- in effluent from the

caustic soda or lime/limestone treatments. Obviously, for the treatments involving caustic soda (NaOH) (Fig. 9C and D), the SC contribution by Na⁺ in the effluent increased and, for those involving lime (CaO, Ca(OH)₂) or limestone (CaCO₃) that from Ca²⁺ increased (Fig. 9E and F). Because Fe²⁺, Mn²⁺, and Al³⁺ ions that oxidized and/or precipitated were replaced by Na⁺ or Ca²⁺ from added chemicals, the SC of the effluent from the caustic soda or lime/limestone treatments was not generally affected by treatment (Fig. 2C and Supplemental Fig. A2). Nevertheless, because of the changed composition and contributions of different ions to the SC, influent and effluent or other waters having the same SC value could have significantly different chemical and toxicological characteristics.

The osmotic pressure was computed, after aqueous speciation, as the sum of the molal concentrations of the same cations, anions, and ion pairs considered for the calculated SC, described above. The ions with low atomic weight and that tend to be dissociated are emphasized for the osmotic pressure estimate. For example, Na and Cl, which have relatively low atomic weights and predominate as free ions, will contribute more to the osmotic pressure than the same concentration, in milligrams per liter, of SO₄ or TIC (CO₃), which have greater molecular weights and form ion pairs with major cations. Thus, the osmotic pressure may be more sensitive than TDS to changes in salinity components associated with brines. Furthermore, because they consider the same aqueous species, the osmotic pressure and SC are more closely related to one another than to TDS (Fig. 8F), which does not consider the molecular weight or ionic charge.

The direct measurement of SC requires little cost or effort compared to other quantitative measures of electrolyte concentration and, thus, may be a practical surrogate for analytical TDS, osmotic pressure, or the formally defined ionic strength of a solution:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (1)$$

where c_i is the molal concentration of ion i (mol/kg), z_i is the charge of that ion, and the sum is taken over all ions in the solution (e.g. Hem, 1985; Langmuir, 1997). The major solute concentrations are typically used to compute I , such as the values shown in Fig. 8E, computed with PHREEQC (Parkhurst and Appelo, 2013). As an alternative, Langmuir (1971, 1997) reported that for carbonate groundwaters, the SC, in microsiemens per centimeter at 25 °C multiplied by a factor of 1.88×10^{-5} , approximates I ($=1.88 \times 10^{-5} \times \text{SC}$ (μS/cm)), which is similar to the linear regression estimate based on the data considered in this study ($I = 1.72 \times 10^{-5} \times \text{SC}$; Fig. 8E). Likewise, for many natural waters, the SC, multiplied by a factor of 0.65, is reported to approximate the TDS in milligrams per liter (Fishman and Friedman, 1989). Nevertheless, because of variations in the types and total quantities of ions in natural waters, the factor relating SC and TDS may be as low as 0.54 or as high as 0.96 (Hem, 1985). As shown in Fig. 8D, a factor of 1.11 was computed to estimate TDS from SC for the undifferentiated influent and effluent for this study. However, the samples appeared to bifurcate along two major trends. The samples that had less than 50% contribution to the SC by SO₄ (SO₄²⁻ and NaSO₄) exhibited a lesser slope of 0.89, which is in the upper range reported by Hem (1985). However, the samples that had greater than 50% contribution to the SC by SO₄ exhibited a much steeper slope. For the same sample pairs, the correlation coefficient for SC and TDS (Fig. 8D) was less than that for SC and I (Fig. 8E). Thus, the use of SC to estimate I and osmotic pressure may be useful. However, the use of SC with a typical factor such as 0.65 to compute TDS of CMD may underestimate the actual TDS and be misleading without other analytical data.

Guidance on new TDS limits on discharges (Commonwealth of Pennsylvania, 2011b) requires historical data on osmotic pressure and acknowledges that such data may not be available.

Therefore, the guidance suggests using available data on TDS as a surrogate for estimation of osmotic pressure:

$$\text{Osmotic pressure (mOsm/kg)} \times 34 = \text{TDS (mg/L)} \quad (2)$$

As shown in Fig. 8F, a few CMD samples with less than 50% contribution to the SC by SO₄ had values approaching this proportionality factor of 34; however, for most of the CMD samples, the measured osmotic pressure was much less than would be estimated from the TDS using the recommended proportionality factor. For theoretical and practical reasons already discussed, SC may be a more useful surrogate measure than TDS to estimate osmotic pressure, plus the correlation between osmotic pressure and SC is stronger than that with ROE or TDS. The empirical relation for CMD samples in this study (Fig. 8F) is:

$$\text{Osmotic pressure (mOsm/kg)} = 0.0141 \times \text{SC (}\mu\text{S/cm)} - 5.99 \quad (3)$$

Rearranging this equation and solving for SC at the osmotic pressure CMC of 50 mOsm/kg (Table 1), an equivalent SC value of 4000 μS/cm is obtained (after rounding to two significant digits). This SC value is comparable to the reported salinity tolerance for early life stages of non-native rainbow trout and brown trout (TDS 3000 mg/L, ~SC 4400 μS/cm, using 0.68 conversion) (James et al., 2003) but is an order of magnitude larger than the proposed benchmark for SC of 300 μS/cm intended to protect native aquatic organisms in Appalachia from impacts of mining discharges (U.S. Environmental Protection Agency, 2011) and approximately double that for TDS of 2000 mg/L at new mines or gas drilling operations in Pennsylvania (Commonwealth of Pennsylvania, 2011b). Although different benchmarks may be applicable to account for natural variability in SC or TDS among different geologic settings or ecoregions, the order-of-magnitude disparities (inconsistencies) in criteria for SC, TDS, and osmotic pressure and potential implications for interpretation and minimization of aquatic ecological effects from changes in ionic strength may warrant review.

Strong intercorrelations among Na, K, Cl, and Br (Table 2) suggest a common origin of these constituents in CMD. In a few cases, these constituents contributed substantially to the elevated ionic strength indicated by the measured and computed SC and osmotic pressure (Fig. 8). Generally, the Na and Cl, with maximum values 2630 mg/L and 2030 mg/L, respectively, were major contributors to TDS and, to a greater extent, the SC of these influent samples (Fig. 8G and H). Saline ground water associated with oilfield brines has been documented in western Pennsylvania (Dresel and Rose, 2010), and discharges of CMD and brines from abandoned oil and gas exploration holes is a serious problem in some localities (Hedin et al., 2005). Elevated salinity at some of the sites sampled, particularly the underground mines and associated refuse disposal facilities, could be attributed to mixing with connate waters or brines that are relatively enriched in Br compared to road deicing salts that have low concentrations of Br (as illustrated by Supplemental Fig. A3).

4. Conclusions

Although a large majority of the *untreated influent* samples exceeded freshwater CMC values for Al, Fe, Co, Ni, and/or Zn, most of the *treated effluent* samples met these criteria for protection of freshwater aquatic organisms. Likewise, all 46 of the treated effluent samples met CMC levels for Ag, As, Ba, Cd, Cl, Cr, Pb, Ni, Sb, Se, Ti, V, NH₃, NO₂, NO₃, and CN. Nevertheless, 9 of the effluent samples violated one or more of the PME limits for pH (<6, $n = 1$), net acidity (>0, $n = 3$), Fe (>7 mg/L, $n = 1$), or Mn (>5 mg/L, $n = 8$), plus one or more exceeded CMC levels for Al (>0.75 mg/L, $n = 2$), Co

(>95 µg/L, *n* = 5), Zn (>307 µg/L, *n* = 1), Cu (>7.4 µg/L, *n* = 1), or Se (>12.8 µg/L, *n* = 3). All CMC exceedances for Co and Zn were attributed to samples violating the PME limit for pH or Mn; however, the samples that exceeded the CMC for Al, Cu, or Se met applicable PME limits for pH, Fe, and Mn. Furthermore, many of the pH-compliant effluents did not meet reference criteria for SO₄ and related measures of ionic strength, including TDS, SC, and osmotic pressure.

Most priority pollutants, including Al, Fe, Mn, Cd, Cr, Co, Cu, Pb, Ni, Zn, Tl, U, and Se, were negatively correlated with pH and positively correlated with acidity. TDS was strongly correlated with SC, osmotic pressure, hardness, SO₄, Ca, Mg, and K, and was negatively correlated with pH. Brine constituents were more strongly correlated with one another (Na, Cl, and Br) than with other constituents and were not strongly associated with acidity or pH.

Of the various measures of ionic strength, the ROE and calculated TDS emphasized those constituents that were present in the greatest mass concentration (SO₄, HCO₃, Ca, and Mg), whereas constituents such as Na and Cl, which tend to be mainly present as free ions, were given greater weight in SC and osmotic pressure. Concentrations of SO₄ and hardness contributed more than half of the dissolved solids and SC for most samples. Nevertheless, because of the changed composition and contributions of different ions to the SC, influent and effluent or other waters having the same SC value could have significantly different chemical and toxicological characteristics.

Observed differences between the 46 influent and effluent pairs support the hypothesis that concentrations of Fe, Mn, Al, and most other potentially toxic constituents will decrease to environmentally acceptable levels as the treatment pH is increased to values of 6–9. On the basis of the Wilcoxon matched-pair statistic, treatment did not affect flow rate, SC, osmotic pressure, hardness, alkalinity, TOC, K, Cl, NO₃, PO₄, Sb, Sr, Br, Se, Mo, and V. Treatment increased the temperature, dissolved oxygen, pH, Ca, and Na values. However, most constituents decreased as a result of treatment, including TDS, acidity, SO₄, Al, Fe, Mn, Mg, As, Ba, Be, Cd, Cr, Co, Cu, F, Pb, Ni, NH₃, Tl, Ti, U, Zn, Zr, total phenols, TIC, BOD, and COD. These findings suggest that typical chemical or aerobic treatment of CMD 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 from priority pollutant metals but may not be effective for decreasing TDS, SC, osmotic pressure, or concentrations of SO₄ and some other pollutants, if present, including Se, Br, and Cl, to background levels. Whole effluent toxicity (WET) testing of the effluent may be considered on a case-by-case basis to evaluate the potential for aquatic biological effects from constituents in the effluent.

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Appendix A. Supplementary material

Supplemental material includes extensive data for the influent and effluent samples, in spreadsheet format (Tables A.4–A.6), plus summaries of water-quality criteria for permitted mine effluents and for the protection of human health and freshwater aquatic life (Tables A.1–A.3). Additionally, Figs. A.1–A.4 are available for the online version of the paper. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apgeochem.2015.03.001>.

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