Applied Geochemistry 62 (2015) 84–95

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Temporal geochemical variations in above- and below-drainage coal mine discharge

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ARTICLE INFO

Article history:
Available online 24 February 2015

ABSTRACT

Water quality data collected in 2012 for 10 above- and 14 below-drainage coal mine discharges (CMDs), classified by mining or excavation method, in the anthracite region of Pennsylvania, USA, are compared with data for 1975, 1991, and 1999 to evaluate long-term (37 year) changes in pH, SO_4^{2-}, and Fe concentrations related to geochemistry, hydrology, and natural attenuation processes. We hypothesized that CMD quality will improve over time because of diminishing quantities of unweathered pyrite, decreased access of O_2 to the subsurface after mine closure, decreased rates of acid production, and relatively constant influx of alkalinity from groundwater. Discharges from shafts, slopes, and boreholes, which are vertical or steeply sloping excavations, are classified as below-drainage; these receive groundwater inputs with low dissolved O_2, resulting in limited pyrite oxidation, dilution, and gradual improvement of CMD water quality. In contrast, discharges from drifts and tunnels, which are nearly horizontal excavations into hillsides, are classified as above-drainage; these would exhibit less improvement in water quality over time because the rock surfaces continue to be exposed to air, which facilitates sustained pyrite oxidation, acid production, and alkalinity consumption. Nonparametric Wilcoxon matched-pair signed rank tests between 1975 and 2012 samples indicate decreases in Fe and SO_4^{2-} concentrations were highly significant ($p < 0.05$) and increases in pH were marginally significant ($p < 0.1$) for below-drainage discharges. For above-drainage discharges, changes in Fe and SO_4^{2-} concentrations were not significant, and increases in pH were highly significant between 1975 and 2012. Although a greater proportion of above-drainage discharges were net acidic in 2012 compared to below-drainage discharges, the increase in pH between 1975 and 2012 was greater for above- (median pH increase from 4.4 to 6.0) compared to below- (median pH increase from 5.6 to 6.1) drainage discharges. For cases where O_2 is limited, transformation of aqueous Fe^{II} species to Fe^{III} may be kinetically limited. In contrast, where O_2 is abundant, aqueous Fe concentrations may be limited by Fe^{III} mineral precipitation; thus, trends in Fe may not follow those for SO_4^{2-}. In either case, when the supply of alkalinity is sufficient to buffer decreased acidity, the pH could increase by a step trend from strongly acidic (3–3.5) to near neutral (6–6.5) values. Modeled equilibrium with respect to Fe^{III} precipitates varies with pH and Fe and SO_4^{2-} reconcentrations: increasing pH promotes the formation of ferrihydrite, while decreasing concentrations of Fe limit the formation of ferrihydrite, and decreasing Fe and SO_4^{2-} concentrations limit the precipitation of schwertmannite and favor formation of Fe^{III} hydroxyl complexes and uncomplexed Fe^{2+} and Fe^{3+}. The analysis of the long-term geochemical changes in CMDs in the anthracite field and the effect of the hydrologic setting on water quality presented in this paper can help prioritize CMD remediation and facilitate selection and design of the most appropriate treatment systems.

1. Introduction

Mining disturbance results in the rapid and extensive movement of water and air into mines and mine spoil, creating the aqueous and oxidizing environment required for acid and metals to leach from the remaining rock into nearby waterways. Coal mine drainage (CMD) commonly has elevated dissolved solids that originate from the oxidation of iron-bearing metal sulfides, e.g. pyrite, FeS_2, with the consequent release of sulfuric acid and dissolved and solid forms of Fe^{II} and Fe^{III} (Rose and Cravotta, 1998; Cravotta et al., 1999). Ochre forming Fe^{III} oxyhydroxide (ferrihydrite and goethite) and sulfate minerals (schwertmannite and jarosite) commonly are precipitated from mine drainage (Bigham

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http://dx.doi.org/10.1016/j.apgeochem.2015.02.010
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et al., 1996; Jonsson et al., 2006). CMD can also contain high concentrations of metal(loid)s such as Mn, Pb, Cu, As, Ni, Zn, Cr, and Al (Benner et al., 1997; Cravotta, 2008a). Thus, CMD can degrade the aquatic environment through chemical, physical, biological, and ecological pathways (Earle and Callaghan, 1998; MacCausland and McTammany, 2007). Discharge from mines and mining wastes may continue for decades to centuries following abandonment (Younger, 1997; Moncur et al., 2003; Gunsinger et al., 2006; Raymond and Oh, 2009).

Although many studies have focused on the downstream transport and transformations of Fe (Chapman, 1982; Fuller and Davis, 1989; McKnight and Bencala, 1989; Lee et al., 2002), few have evaluated the factors controlling Fe concentrations within abandoned underground mines. Data collected from various field studies indicate that CMD water quality gradually improves following the cessation of mining and the closure of a mine (Wood et al., 1999; Demchak et al., 2004; Thomas, 2013). In a study of 32 mine discharges in Scotland, Wood et al. (1999) found that mines abandoned for more than 50 years tended to have lower Fe and SO_4^{2-} concentrations compared to mines abandoned 20 years or less. However, this study had only limited data to evaluate how individual mine geochemistry changed over time, with only six sites having multiple samples analyzed over the period of record that was up to a maximum of approximately 20 years at one site and approximately 10 years at the other five, and discharge data were not evaluated.

In addition to mine age since closure, whether a mine is situated above- or below-drainage can affect the quality of the discharged water (e.g. Demchak et al., 2004). Generally, mines developed in the updip direction tend to be above-drainage with substantial volumes of unsaturated voids, whereas mines developed in the downdip direction tend to be below-drainage and saturated with groundwater after closure (Mentz and Warg, 1975). Two Pennsylvania bituminous coal mines on the same coal seam (Clarion A), one above-drainage and the other below-drainage, were reported by Mentz and Warg (1975) to have markedly different water qualities at the point of discharge. CMD from the above-drainage Shoff Mine that was 10% flooded at the time of the study had a mean pH of 2.6, mean total Fe concentration of 357 mg/L, and mean Fe^{II} concentration of 191 mg/L. Conversely, CMD from the below-drainage Yorkshire mine that was 90% flooded had a mean pH of 5.0, mean total Fe concentration of 46 mg/L, and mean Fe^{II} concentration of 45 mg/L. In a study by Lambert et al. (2004) of four abandoned coal mines also in the bituminous field in Pennsylvania, improvements in CMD water quality were greater at below-drainage mines than in above-drainage mines. Water from the one below-drainage mine was found to transition from acidic to alkaline within 25 years of mine closure, while water discharging from another below-drainage mine was circumneutral with high alkalinity at the initial sampling and exhibited an increase in alkalinity and no change in pH over the study period. Conversely, a partially flooded mine and unflooded mine exhibited much smaller improvements in water quality, and discharge from the unflooded mine remained net-acidic over the same time period.

We hypothesized that long-term improvements in CMD quality will result from diminishing quantities of unweathered pyrite, decreased access of O_2 to the subsurface after mine closure, decreased rates of acid production, and relatively constant influx of alkalinity from groundwater. Below-drainage discharges from coal seams situated below the water table would receive groundwater inputs with low dissolved O_2, resulting in limited pyrite oxidation and the gradual improvement of CMD water quality. In contrast, above-drainage discharges from coal seams situated above the water table would exhibit less improvement in CMD quality over time because the rock surfaces continue to be exposed to air, which facilitates sustained pyrite oxidation and alkalinity consumption. To evaluate these hypotheses, an extended study period with numerous sampling sites that evaluates discharge type, dissolved oxygen (DO), and alkalinity is necessary. This paper evaluates temporal variations in geochemistry at 24 CMDs in the anthracite coal region of Pennsylvania that were sampled in 1975 (Growitz et al., 1985), 1991 (Wood, 1996), 1999 (Cravotta, 2008a,b), and 2012 (this study). One goal of this study was to identify trends in CMD water quality over time in the anthracite coal region with respect to hydrologic setting (above/below drainage) of the mine. A second goal was to further develop the mechanistic understanding of the long-term potential of pollutants from abandoned CMD discharges to attenuate or continue impacting receiving waterways.

Understanding how these discharges evolve over time can be used to better inform watershed restoration plans and CMD treatment decisions. For example, one possible strategy is to monitor the evolution of the discharge as natural attenuation processes take place, and not install a treatment system for sites in which water quality does not far exceed relevant effluent goals. Conversely, for discharges that far exceed relevant water-quality criteria [e.g. pH between 6.0 and 9.0, negative net acidity concentration, and Fe and Mn less than an instantaneous maximum concentration of 7.0 or 5.0 mg/L, respectively (Commonwealth of Pennsylvania, 1998)] and in which the geochemistry is expected to evolve significantly over time, the construction of an active treatment system that can be readily adapted to changing chemistries, or a passive system with the capacity for modification, may be the optimal solution (Wood et al., 1999; Demchak et al., 2004). For sites in which the geochemistry is not expected to evolve significantly over time, passive systems may be the optimal solution due to the lower cost of implementation over a long time period compared to the cost of active chemical additions (Skousen et al., 2000; Johnson and Hallberg, 2005). The analysis of the long-term geochemical variations in CMDs in the anthracite field presented in this paper can help prioritize restoration activities and facilitate selection and design of the most appropriate treatment systems.

2. Methods

2.1. Site locations and available historical data

The anthracite coal region located in Northeastern Pennsylvania is comprised of four fields: the Northern, Eastern Middle, Western Middle, and Southern (Fig. 1). The Llewellyn and Pottsville Formations host most of the anthracite coal beds, which are primarily freshwater in origin (Brady et al., 1998). All of the sites sampled in this study discharge from underground mines on multiple coal seams in the Llewellyn Formation. Several CMD sources were sampled in each of the four fields.

Twenty-four sampling sites from prior studies were resampled for this investigation (Table 1 and Fig. 1) (Growitz et al., 1985; Wood, 1996; Cravotta, 2008a,b). Of those, four sites did not have pH or SO_4^{2-} measured in 1991, and five did not have Fe measurements in 1991. Of the 1975 samples, the Fe concentration for one sample was reported as >100 mg/L and two samples were reported as <1 mg/L.

The discharges are classified as above- or below-drainage for this report based on the mining method used: drifts and tunnels, which are nearly horizontal excavations into hillsides above stream base level, are identified as above-drainage, while shafts, slopes, and boreholes, which are vertical or steeply sloping excavations into mine workings below stream base level, are below-drainage (Table 1). These classifications are consistent with the

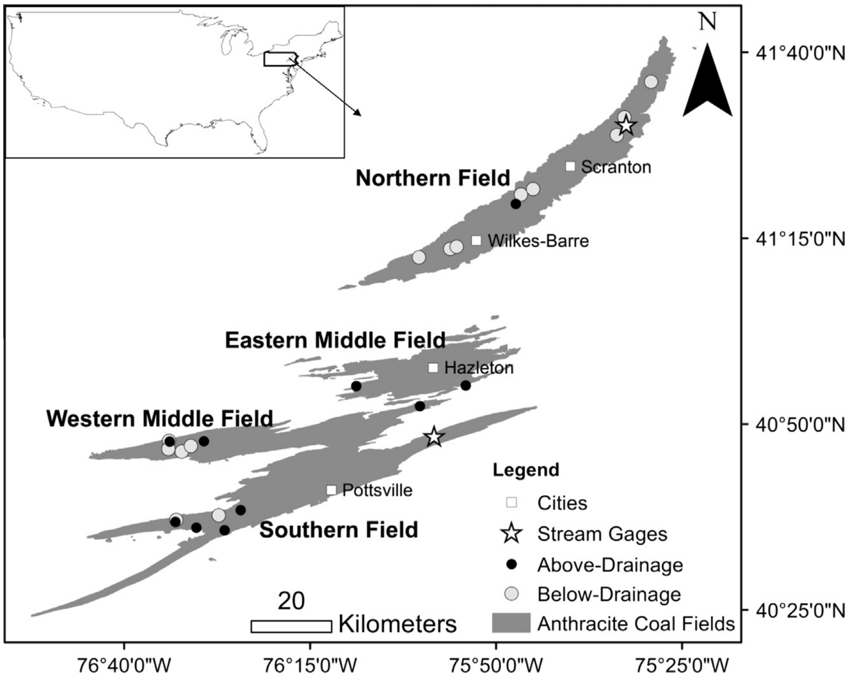

Fig. 1. Site map with sampling locations of above- (●) and below-(○) drainage discharges, coal fields (▨) (modified from PA DEP, 2013), stream gages (stars), and select cities (□).

Table 1
CMD location and drainage type.

Drainage type	Coal field	Discharge name	Latitude	Longitude
Above	Eastern middle	Beaver Meadow Outfall (Quakake)[a]	40.91925	−75.90159
		Oneida Tunnel	40.91842	−76.14688
	Northern	Butler Mine Tunnel (Pittston Water Level Tunnel)	41.32675	−75.78992
	Southern	Colket Mine[b,c]	40.64037	−76.40607
		Porter Tunnel[b,c]	40.60064	−76.50552
		Rowe Tunnel Discharge	40.59528	−76.44222
		Silverbrook Mine	40.87342	−76.00437
		Valley View Tunnel	40.61389	−76.55194
	Western middle	Scott Ridge Mine Tunnel[b,c]	40.79453	−76.48833
		Cameron Mine Drift	40.79361	−76.56528
Below	Northern	Buttonwood Outfall	41.22619	−75.93659
		Coalbrook Mine (Lower Wilson Creek Shaft)	41.60064	−75.48657
		Duryea Breech Seep	41.34758	−75.77797
		Gravity Slope (Peckville Shaft)	41.48119	−75.56296
		Honey Pot Outfall	41.20694	−76.00611
		Jermyn Mine Outfall Slope 1	41.52119	−75.54657
		Old Forge Borehole	41.36008	−75.75075
		South Wilkes-Barre Boreholes[c]	41.23064	−75.92186
	Southern	Markson Columnway	40.61861	−76.55000
		Tracy Airhole[b,c]	40.62889	−76.45528
	Western middle	Big Mountain Mine No.1 Slope	40.77138	−76.53762
		Cameron Mine Airshaft	40.79581	−76.56651
		Henry Clay Stirling Mine Pump	40.77728	−76.56805
		Maysville Mine Borehole at Ranshaw	40.78422	−76.51763

[a] Site resampled in 2014.
[b] pH and SO_4^{2-} concentration not reported in 1991.
[c] Fe concentration not reported in 1991.

hydrological characteristics described previously for updip and downdip mines, whereby the above-drainage and updip mine discharges tend to flow freely by gravity from unconfined, partly water-saturated zones, and the below-drainage and downdip mine discharges tend to flow from fully water-saturated zones under confined, artesian pressure conditions. The depth to which the drainage accesses the mine pool, or the effects that any other openings to the same mine may have on the water chemistry are not differentiated; rather, this study shows how knowledge of the physical setting and water-quality of singular major discharges can be used to estimate the long-term treatment strategy.

2.2. Sample collection and analysis

In 2012, field measurements and samples were collected at baseflow, which for use in this study is defined as flow below the 25th percentile of daily discharge on the sampling date for nearby streams (Fig. 1) that were considered representative of hydrologic conditions in the region. Discharge at eight of the CMD sites was determined by measuring channel depth and width and recording velocity at a minimum of 3 sections using an electromagnetic velocity meter (Marsh-McBirney, Loveland, CO). These discharges were deep enough (water depth greater than approximately 0.10 m) to allow for full immersion of the flow meter at approximately one-third depth from the bottom of the discharge. In discharges with shallower depths, velocity was estimated using a neutrally buoyant object traveling a measured distance. Discharges in which a weir was already in place were calculated using Eq. (1) for a rectangular weir:

$$Q = 1.84(b - 0.2H)H^{3/2} \tag{1}$$

where Q is discharge (m^3/s), H is head recorded in the field, and b is the width of a rectangular weir. At one site (Jermyn Mine Discharge) discharge was estimated visually as the flow emerged from an irregularly-shaped pipe directly into a large stream.

Samples and field data were collected as close as possible to the point of discharge to avoid possible variations in chemistry due to oxygenation, CO_2 degassing, or photoreduction that have been reported for several metals species including Fe (Brick and Moore, 1996; McKnight et al., 2001; Gammons et al., 2005). The pH, oxidation–reduction potential (ORP), and DO were measured in-situ using Manta II multiparameter sondes (Eureka Environmental). Probes were calibrated prior to use in the field, and calibrations were verified when all sampling was completed. All samples were stored on ice while in the field, and refrigerated at 4 °C upon return to Lehigh University. Samples were filtered on-site using a 0.45 μm filter (Whatman, P/P) for anion and dissolved cation analysis. Samples for cation analysis were acidified to a pH less than 2 in the field using HNO_3. For sites with pH greater than approximately 6, alkalinity was determined by titration using 0.1 or 0.01 N H_2SO_4 on the same day as sample collection and calculated using the gran function plot method. For samples with pH below approximately 6, alkalinity was calculated using charge balance and assuming samples with pH < 4.5 contain no measurable alkalinity. The charge balance method was assessed with the data from 1999 in which alkalinity was measured at each site and produced good correlation between measured and calculated values. Net acidity was calculated from data collected in 2012 using the equation:

$$\begin{aligned}\text{Net Acidity} = 50\{&1000(10^{-\text{pH}}) + [2(\text{Fe}^{\text{II}}) + 3(\text{Fe}^{\text{III}})]/56 \\ &+ 2(\text{Mn})/55 + 3(\text{Al})/27\} - \text{Alk}\end{aligned} \tag{2}$$

where net acidity and alk (alkalinity) are in the units of mg/L as $CaCO_3$ (Kirby and Cravotta, 2005). For net acidity calculations, all Fe is assumed to have an equivalent acidity of Fe^{II}. Net acidity was not calculated using the 1975 data because Mn concentration was not measured. The pCO_2 was determined based on pH, alkalinity, and temperature for 2012 and 1975.

Cation concentrations were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Thermo-Elemental X-Series, Winsford, UK) using conventional pneumatic nebulization. Cation concentrations were quantified using a six point external standard calibration curve with an absolute accuracy of 5–7% and a precision better than 3%. Anions were determined with ion chromatography using carbonate/bicarbonate eluent and an AS-14 column with suppressed conductivity detection (Dionex) with an accuracy of 5%.

On the day of field sampling at each site, streamflow data at the nearby U.S. Geological Survey (USGS) gages 01534500 Lackawanna River at Archbald, PA (lat 41.5044 N/long −75.5425 W), and 01469500 Little Schuylkill River at Tamaqua, PA (lat 40.8069 N/long −75.9722 W), were retrieved from the National Water Information System (NWIS) (U.S. Geological Survey, 2013) to assess whether the mine pool flows were likely to be near base-flow by comparing the mean daily discharge at each gage on the date sampled to gage statistics for the full record of data. All sampling in 2012 and 1991 coincided with daily mean discharge below the 25th percentile, indicating that the mine pools were at base-flow conditions as defined for this study. Daily mean discharge on all sampling dates in 1975 was below the mean discharge but above the 25th percentile discharge for both rivers. Daily mean discharge on all but one date in 1999 was below the mean discharge, and a majority of sampling dates in 1999 were also below the 25th percentile for both rivers (U.S. Geological Survey, 2013).

Cumulative distribution plots for pH, Fe, SO_4^{2-}, discharge, alkalinity, net acidity, DO, and pCO_2 (−log partial pressure of CO_2) were prepared to show the range and central tendency of data values. Such plots were used to indicate the probability that a given value will be exceeded, whether data are normally distributed, and whether data values differ among sample subsets such as above- and below-drainage hydrologic settings or different years.

The nonparametric Wilcoxon matched-pairs signed rank test (Helsel and Hirsch, 2002) was used to identify the statistical significance of differences in Fe and SO_4^{2-} concentrations and pH between the sampling years and by hydrologic setting. This nonparametric test ranks the values in the data sets being compared (for example, Fe concentration for 1975 and 2012) and ranks the absolute value of differences between pairs of values to determine the significance of the difference in median rank. Exact p-values were calculated using the statistical program GraphPad Prism version 6 (GraphPad software, San Diego, CA). A $p < 0.05$ is considered to be highly significant and a $p < 0.1$ is considered to be marginally significant. A comparison for the intervening years between 1975 and 2012 is not included because a portion of the sites were not sampled for every parameter in 1991, as discussed previously. Sites sampled in 1975 in which the exact Fe concentration is unknown were included in the signed rank test with the two censored values (<1 mg/L) and the two reported concentrations that were values less than 1 mg/L (0.32 and 0.22 mg/L) considered equivalent to 0.99, resulting in the same rank for use in the nonparametric Wilcoxon signed rank test. Likewise, the value reported as >100 mg/L was assigned the same rank as the only other site recorded at above 100 mg/L in below-drainage discharges in that sampling year. The Wilcoxon signed rank test is not sensitive to the precise value assigned to these two sites, and instead uses only their relative rank. For calculation of mean, median, and standard deviation, conservative values of 0.99 mg/L and 101 mg/L were used. These estimated values are denoted with dashed lines in Fig. 4. The arithmetic mean, median, standard deviation, and coefficient of variation (100 × standard deviation/mean) were also calculated to be able to compare to other studies. The mean value for pH was computed by two methods: (1) taking the negative log of the mean proton concentration, and (2) taking the mean of the pH value because the mean proton concentration does not clearly show whether a shift toward higher pH has occurred. The use of the proton concentration or pH value does not change the Wilcoxon signed rank test result.

The datasets were treated in aggregate first, and then divided into above- and below-drainage subsets for comparison. For each site, the overall significance of temporal changes in parameters (increase or decrease in pH or concentration) between 1975 and 2012 was tested using a Wilcoxon signed rank test, followed by an estimate of how much the parameters changed by comparing mean and median values. Fe and SO_4^{2-} concentrations were not adjusted for variations in discharge between 1975 and 2012. Finally, as a measure of variability of a parameter among all the sites in a given year, the standard deviation and coefficient of variation of the parameters were examined.

Sample collection procedures were similar among all the years studied, and the standards used for calibration of equipment were similar (e.g. pH buffers, chemical standards). Although analytical instruments and procedures have improved through time, these changes generally affected only the detection level and precision. Improvements in detection limits on more recent analyses would be more important for later samples in which concentration was lower and would be more important for trace metals as opposed to Fe and SO_4^{2-}, which tend to be found at easily measurable concentrations in CMDs. While instantaneous discharge measurements were useful to indicate the relative magnitude of CMD sources within the 2012 dataset, the discharge methods used in 2012 were less precise than those for previous studies and therefore were not ideal for a rigorous analysis of changes in long-term discharge over time or the effect of discharge on water quality trends.

2.3. Equilibrium geochemical modeling

Complete geochemical data for samples collected in 2012 were used with PHREEQC to calculate (1) pCO_2, (2) the redox distribution for dissolved Fe (Fe^{II} and Fe^{III}) on the basis of measured

Eh, and (3) the ratio of the uncomplexed, dissolved Fe^{2+} to total dissolved Fe (Fe^{II} and Fe^{III}, which includes the dissolved complexed and uncomplexed species) (PHREEQC version 3.0.6; Parkhurst and Appelo, 1999). Eh was calculated from ORP using the temperature correction method set forth in Nordstrom (1977), and an average temperature of 10 °C because temperature was not recorded at every site. For context, a 5 °C increase or decrease in temperature results in less than 1% change in calculated Eh value. Eh was converted to pe (where pe = Eh(V) × 16.9) for modeling purposes. Solubility curves for goethite (FeOOH), schwertmannite ($Fe_8O_8(OH)_{4.8}(SO_4)_{1.6}$), ferrihydrite ($Fe(OH)_3$), and siderite ($FeCO_3$), and an Eh–pH end member diagram of the equilibrium Fe species and minerals, were calculated using Geochemist's Workbench Act2 Student version 10.0.3 (Bethke and Yeakel, 2014) with a modified LLNLv8.R6+ database (electronic supplement). Fe mineral solubility curves were calculated using measured SO_4^{2-} ($pSO_4^{2-} = 2.5$) concentrations in the 2012 samples. Solubility of siderite was calculated under two conditions, $pCO_2 = 3.5$, based on the assumed concentration in ambient air, and $pCO_2 = 1.5$ to indicate potential conditions in the subsurface.

Eh–pH end-member diagrams were created based on measured high and low Fe concentrations (pFe = 3.01 and 4.28, respectively), and measured high and low SO_4^{2-} concentrations ($pSO_4^{2-} = 2.19$ and 4.10, respectively) from the 2012 samples at 25 °C. The stability of siderite was also calculated based on concentrations in 2012 samples with $pCO_2 = 3.5$. Calculations were done for 25 °C, at which the accepted thermodynamic properties of schwertmannite are valid. Fe-bearing minerals not expected to form in these discharges were suppressed: magnetite, hematite, jarosite, melanterite, and troilite. Assessments of mineralogy at mine drainages in anthracite coal region of Pennsylvania have not identified jarosite (Williams et al., 2002; Cravotta, 2005). However, jarosite has been identified as a plausible secondary sulfate mineral that may be dissolved in the first flush of hard-coal mine workings following abandonment (Gzyl and Banks, 2007). In a survey of the geochemistry of 140 mine discharges in Pennsylvania, Cravotta (2008b) shows melanterite to be undersaturated in all samples, but samples have varying degrees of saturation with respect to schwertmannite, ferrihydrite, and goethite. To account for variations in mineral assemblages occurring over time as solids age, two Eh–pH diagrams were created as representative of different environments: one with the meta-stable phases schwertmannite and ferrihydrite, and the other with goethite, the stable successor phase to ferrihydrite and schwertmannite (Bigham et al., 1996).

3. Results

3.1. Variations in water quality

Data on the pH, Fe and SO_4^{2-} concentrations, and discharge are summarized for the two different hydrologic settings in 1975 and 2012 in Figs. 2 and 3. Variations of these constituents and properties of CMD over time (1975–2012) are shown in Fig. 4. In general, the discharges displayed a bimodal distribution in pH (Fig. 2) which is consistent with other multi-site CMD characterizations, with near-neutral pH values resulting from carbonate buffering, and acidic pH values resulting from sulfate buffering and Fe^{III} hydrolysis reactions (Cravotta et al., 1999). Additionally, higher pH values were seen for below-drainage discharges compared to above-drainage discharges, and there were more sites with a higher pH value in 2012 compared to 1975 for both above- and below- drainage discharges.

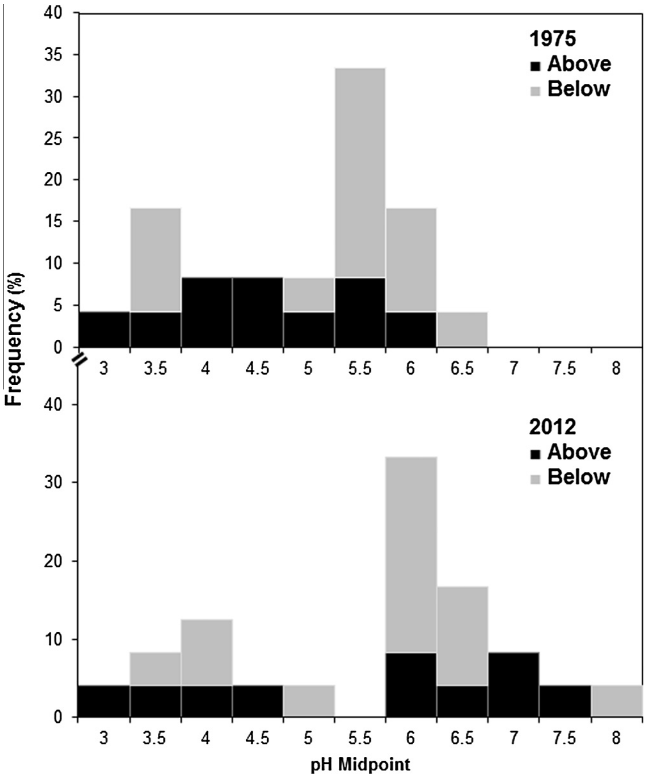

Fig. 2. Frequency distribution of pH values in 1975 (top) and 2012 (bottom) for above- (black) and below- (gray) drainage discharges.

The median pH for below-drainage discharges was higher than that for above-drainage discharges in 1975 (median pH = 5.6 and 4.4, respectively) and in 2012 (median pH = 6.1 and 6.0, respectively) (Fig. 3A). Similarly, Fe and SO_4^{2-} concentrations were also higher for below-drainage discharges compared to above-drainage discharges for both 1975 and 2012 (Fig. 3B and C). For example, in 2012 the median Fe concentration was 20 mg/L for below-drainage discharges, and 11 mg/L for above-drainage discharges (Fig. 3B). The median discharge for below-drainage discharges was greater than that for above-drainage discharges in both 1975 and 2012 (Fig. 3D), potentially due to a greater contributing area for recharge to mines identified with below-drainage discharges.

Fig. 3E–H show alkalinity and pCO_2 for above- and below-drainage discharges from water sampling conducted in 1975 and 2012, and DO and net acidity from water sampling conducted in only 2012. Above-drainage discharges displayed similar patterns in alkalinity in 1975 and 2012 with lower alkalinity values observed for above-drainage compared to below-drainage discharges. For example, in 2012 above-drainage discharges had a median alkalinity of 7.5 mg/L as $CaCO_3$, whereas the median alkalinity for the below-drainage discharges was 41 mg/L as $CaCO_3$ (Fig. 3E). In contrast, below-drainage discharges had a median concentration of DO that was much lower (1.1 mg/L) than that for the above-drainage discharges (9.9 mg/L) (Fig. 3F). While 57% of below-drainage discharges were net alkaline [net alkalinity = −net acidity (Kirby and Cravotta, 2005)], 80% of above-drainage discharges were net acidic (Fig. 3G). The pCO_2 exhibited a similar pattern as alkalinity: below-drainage discharges had higher pCO_2 concentrations than above-drainage discharges in both 1975 and 2012 (Fig. 3H). The median pCO_2 value decreased for both above- and below-drainage discharges between 1975 and 2012 while atmospheric pCO_2 has increased. This may be indicative of a decrease in weathering rates associated with pyrite oxidation and carbonate neutralization through which CO_2 is produced (Kirby and Cravotta, 2005). These results are consistent with water quality characterizations of above- and below-drainage discharges: above-drainage discharges contain greater DO and lower alkalinity due to exposure to air,

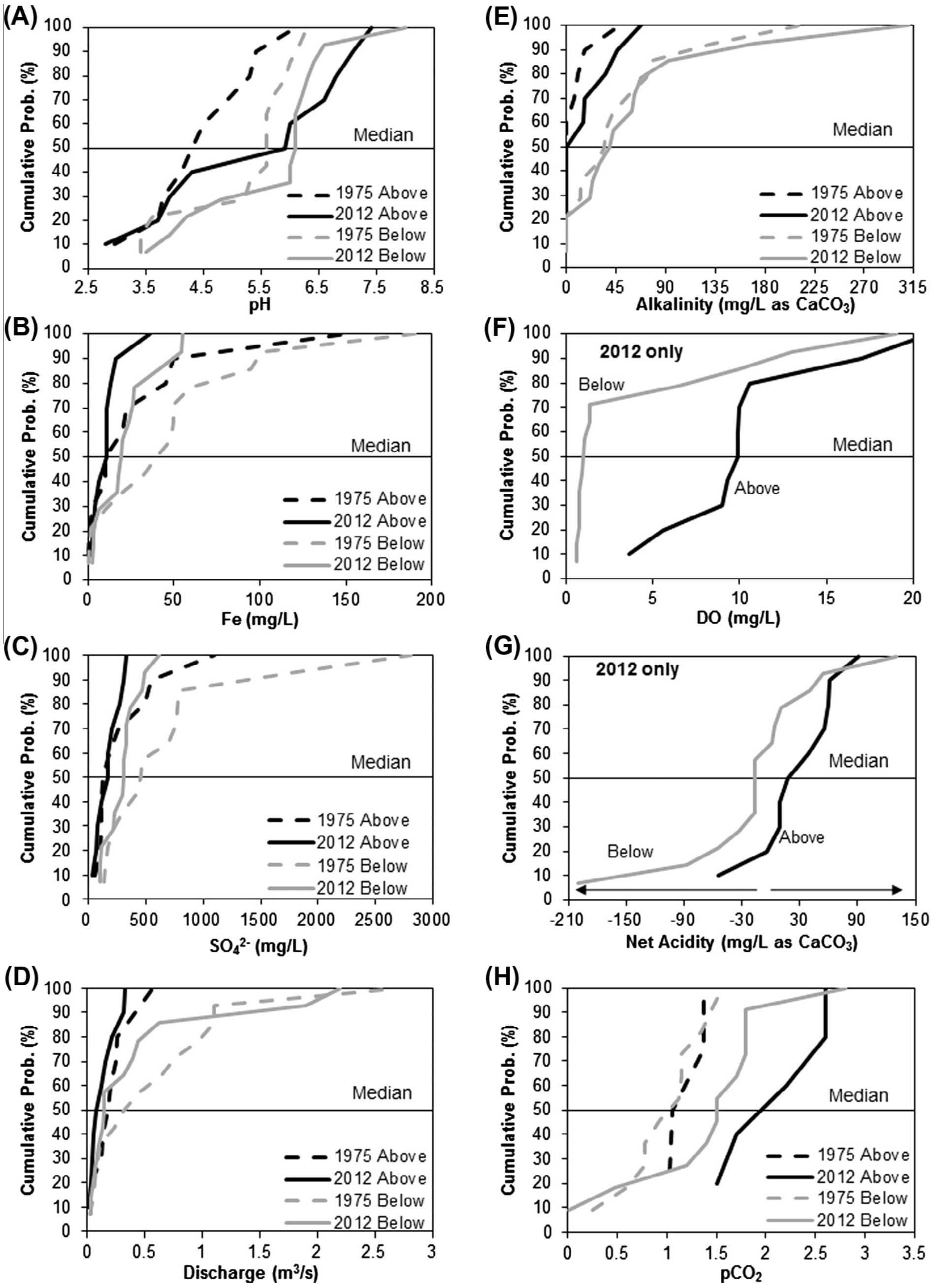

Fig. 3. Cumulative distribution plots comparing (A) pH, (B) Fe (mg/L), (C) SO_4^{2-} (mg/L), and (D) discharge (m^3/s), (E) alkalinity (mg/L as $CaCO_3$), (F) DO concentration (mg/L), (G) net acidity (mg/L as $CaCO_3$), and (H) pCO_2 in above- (black) and below- (gray) drainage discharges.

pyrite oxidation, and subsequent alkalinity consumption (Demchak et al., 2004; Lambert et al., 2004; McDonough et al., 2005).

On the basis of the nonparametric Wilcoxon matched-pairs signed rank test for all samples without differentiation by hydrologic setting, concentrations of Fe and SO_4^{2-} were lower and pH was higher in 2012 compared to 1975 (Wilcoxon signed rank test, $p = 0.029$, 0.0026, and 0.0044, respectively). However, above- and below-drainage CMDs exhibited differences in their overall hydro-chemical characteristics and tendency for water quality to change over time.

Overall, pH values increased in 2012 for 19 of 24 sites compared to 1975 data. The median pH of samples at all sites was 0.75 units higher in 2012 than in 1975. The median pH increased marginally significantly in below-drainage discharges (Wilcoxon signed rank test, $p = 0.070$, Table 2) with a median pH value of 5.6 in 1975, and 6.1 in 2012 (Fig. 4A and E), while the median pH in above-drainage sites increased highly significantly from 4.4 in 1975 to 6.0 in 2012 (Wilcoxon signed rank, $p = 0.047$, Table 2). While a slight decrease in the negative log of the mean proton concentration (equivalent to lower pH) was observed between 1975 and 2012 for the above-drainage discharges, this computational method obscures shifts toward a higher pH which are clearly indicated in Fig. 2. The Wilcoxon signed rank test result indicates the change in pH is significant because a greater number of sites exhibited a pH increase compared to the number of sites that exhibited a pH decrease.

The median Fe concentration decreased highly significantly at below-drainage sites between 1975 and 2012 (Wilcoxon signed rank test, $p = 0.019$, Table 2). The mean Fe concentration decreased

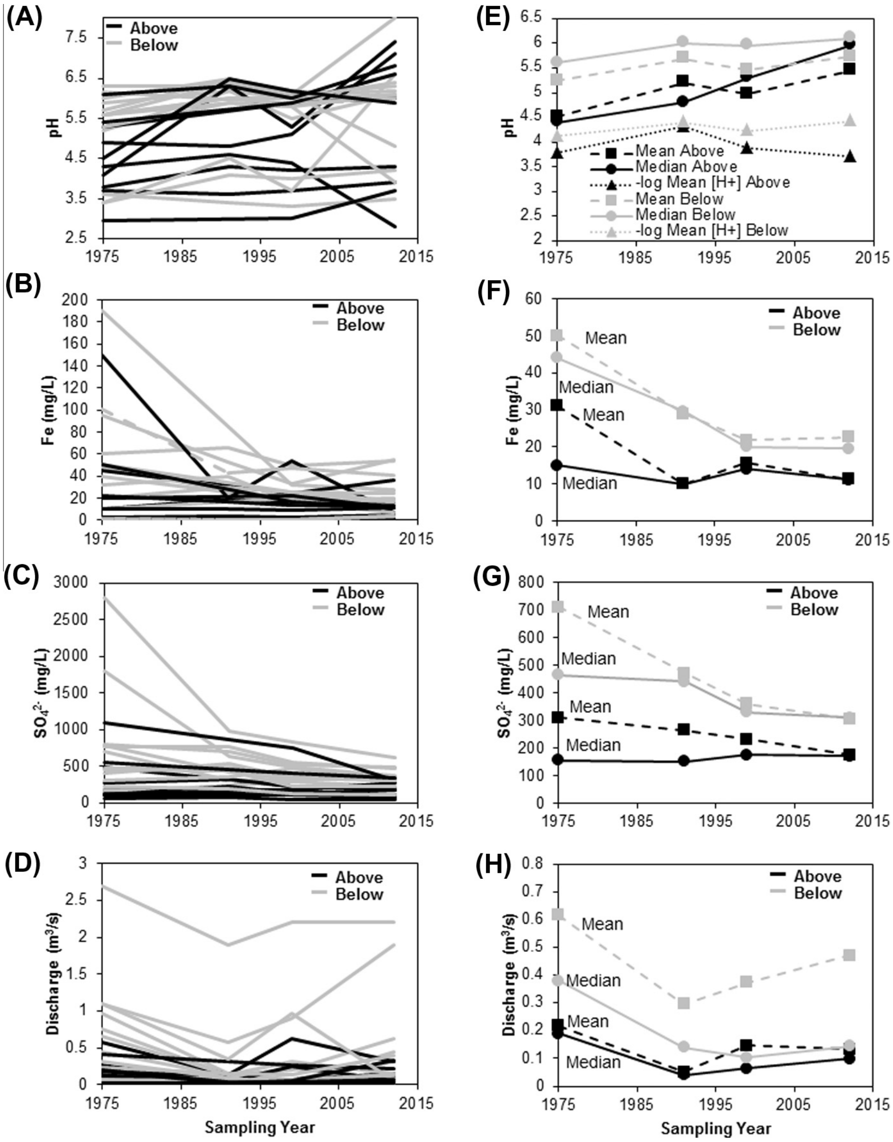

Fig. 4. Sampling results from 1975, 1991, 1999, and 2012 from anthracite CMDs for above- (black) and below- (gray) drainage discharges for (A) pH, (B) Fe concentration (mg/L) (dashed lines denote estimated values), (C) SO_4^{2-} concentration (mg/L), and (D) discharge (m^3/s), with the mean (■) and median (●) for E) pH with the mean also computed based on the proton concentration (▲), F) Fe (mg/L), G) SO_4^{2-} (mg/L), and H) discharge (m^3/s).

Table 2
Statistical significance (*p*-values) of nonparametric Wilcoxon matched-pairs signed rank test for difference between sample sets collected in 1975 and 2012 for above- and below-drainage discharges. Bold values indicate distributions of the two sample groups are different at the 95% confidence interval while italic values indicate distributions are different at the 90% confidence interval. The sign indicates whether the median rank has increased (+) or decreased (−).

Discharge type	Parameter	1975–2012
Above-drainage	pH	**+0.047**
	Fe	−0.52
	SO_4^{2-}	0.35
Below-drainage	pH	*+0.07*
	Fe	**−0.019**
	SO_4^{2-}	**−0.0011**

from 50 mg/L to 23 mg/L (Fig. 4F), and median concentration decreased from 44 mg/L to 20 mg/L during this time period. A below-drainage discharge exhibited the highest concentration of Fe with 190 mg/L in 1975 and while this site was not sampled in 1991, the concentration progressively decreased to 32 mg/L in 1999 and 27 mg/L in 2012. For above-drainage discharges as a group, there were no significant changes in Fe concentrations between 1975 and 2012. Overall, the standard deviation of Fe concentrations for above- and below-drainage discharges decreased by 78% and 66%, respectively.

Concentrations of SO_4^{2-} exhibited a highly significant decrease for below-drainage discharges between 1975 and 2012 (Wilcoxon signed rank test, $p = 0.0011$, Table 2, Fig. 4C and G). The median SO_4^{2-} concentration in these discharges decreased from 465 mg/L in 1975 to 310 mg/L in 2012 (Fig. 4G). The highest concentration of SO_4^{2-} in 1975 was 2800 mg/L; this same site still had the highest concentration in 2012, though the concentration had decreased to 620 mg/L. The above-drainage sites exhibited no significant change in SO_4^{2-} concentration, and the standard deviation decreased by 68% and 79%, respectively for above- and below-drainage discharges.

While there is variation in the instantaneous discharge over time (Figs. 3D and 4D, H), long-term changes in discharge would not be expected absent changes in the recharge to the mine. By project design, issues of discharge as an explanatory variable for changes in water chemistry were limited. Sampling was done at baseflow to avoid hydrologic conditions that could change water chemistry, such as the effects of dilution or salt dissolution due to storm events (Nordstrom, 2009; Cravotta et al., 2014).

A decrease in the coefficient of variation concurrent with a decrease in mean value indicates the range of values is decreasing, and the system is becoming more stable over time. While the coefficient of variation for Fe for above-drainage discharges in 1975 is much higher than that of the below-drainage discharges (146 versus 103, respectively), both decrease by 2012 (Fig. 5). The coefficient of variation for SO_4^{2-} also exhibits an overall decrease with higher values seen in 1975 compared to 2012. Conversely, the coefficient of variation for pH shows a small increase from 1975 to 2012, while the mean pH increased, indicating an increase in the range of values. Unlike pH and Fe and SO_4^{2-} concentrations, while the coefficient of variation for discharge is different for each year sampled for both discharge types, discharge is not expected to reach steady-state over time.

3.2. Modeled solid phases

To assess potential for various Fe minerals to limit concentrations of Fe and possibly SO_4^{2-}, the pH and −log activity of Fe^{II} and Fe^{III} for samples collected in 2012 are compared to the corresponding solubilities of Fe^{III} minerals (Fig. 6). Data reported for samples collected in 1975 and 1991 did not include major ions, and so were not sufficient for geochemical modeling. Data for samples collected in 1999 are not shown because variations in water quality parameters between 1999 and 2012 were not assessed. Sample composition that plots above the lines depicting the solid phase boundaries of minerals, which include Fe^{III} minerals: schwertmannite, goethite, and ferrihydrite, and a Fe^{II} mineral: siderite (Fig. 6), are oversaturated with respect to those minerals. With respect to Fe^{III}, almost all samples appear to be oversaturated with respect to goethite, while the meta-stable phases, schwertmannite and ferrihydrite, are at near to oversaturation levels across the pH range. Below approximately pH 6, schwertmannite is the dominant metastable phase, whereas ferrihydrite predominates at higher pH values. Above approximately pH 6, all samples are at near to oversaturation with respect to ferrihydrite. With respect to Fe^{II}, one sample is oversaturated with respect to siderite above approximately pH 7 for the modeled conditions of low concentration of CO_2 ($pCO_2 = 3.5$). For the modeled high concentration of CO_2 ($pCO_2 = 1.5$), a larger portion of the samples indicate potential for oversaturation above approximately pH 6.

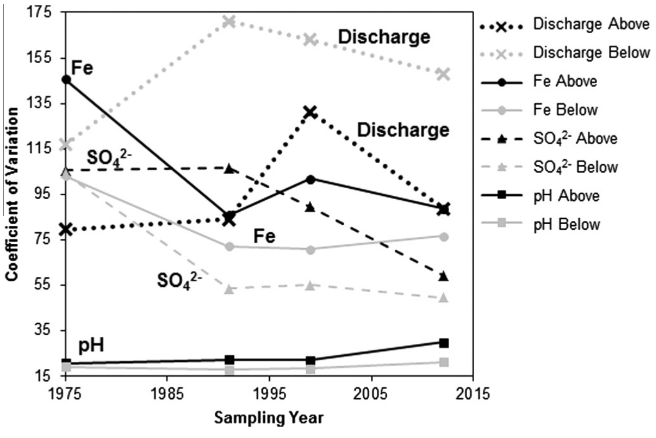

Fig. 5. Coefficient of variation during specified sampling year for pH in above- (■) and below- (■) drainage discharges, Fe in above- (●) and below- (●) drainage discharges, SO_4^{2-} in above- (▲) and below- (▲) drainage discharges, and discharge in above- (**x**) and below- (x) drainage discharges.

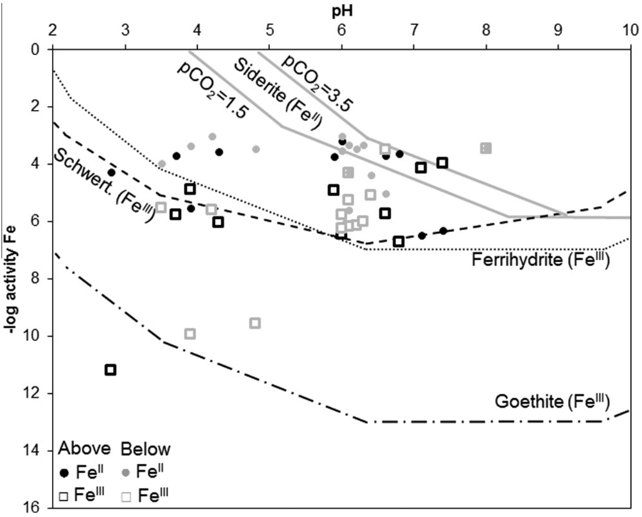

Fig. 6. Mineral solubility curves modeled in Geochemist's Workbench Act2 for goethite (-•-•), ferrihydrite (•••), schwertmannite (---), and siderite range ($pCO_2 = 1.5–3.5$) (—) with-log activity of Fe^{II} and Fe^{III} modeled using PHREEQC for above-drainage (black) and below-drainage (gray) discharges with $pSO_4^{2-} = 2.5$ at 25 °C.

Although Fe^{II} is the dominant aqueous species, there are not large differences in the calculated proportion of Fe as uncomplexed Fe^{2+} in above-compared to below-drainage discharges: the median Fe^{2+}:Fe_{total} ratio was 87% and 84% in 2012 for above- and below-drainage discharges respectively. The lack of correlation between aqueous Fe^{II} and pH indicates Fe^{II} is not limited by the solubility of hydroxide minerals at the conditions measured. However, Fe^{II} may be limited by siderite precipitation at approximately pH > 6.

As the mine drainage water quality evolves with age or elapsed time since mine closure, both the Fe and SO_4^{2-} concentrations decrease. This evolution prompts the evaluation of whether the discharges have become less favorable for the formation of certain solid phases. Fig. 7 shows the solid phase stability fields observed for high and low Fe and SO_4^{2-} end-member concentrations in water for a ferrihydrite and schwertmannite dominated system (Fig. 7A), and a system containing goethite, the stable phase formed by schwertmannite and ferrihydrite over time (Fig. 7B).

In Fig. 7A, for the high end-member ($pFe = 3.01$ and $pSO_4^{2-} = 2.19$, modeled phases indicated by bold lines) schwertmannite and ferrihydrite are indicated to form below and above approximately pH 6, respectively, in oxidized samples, while siderite forms above pH 7 in samples at lower oxidation states. For the low end-member, ($pFe = 4.28$ and $pSO_4^{2-} = 4.10$, modeled phases indicated by thin lines in Fig. 7A) below approximately pH 5 schwertmannite, $FeOH^{2+}$, and Fe^{3+} dominate, whereas ferrihydrite may predominate above approximately pH 5. Fe^{2+} and siderite are present at lower oxidation levels. In Fig. 7B, goethite is the dominant solid phase, with almost every sample falling within the thermodynamic stability field for this mineral under both end-member conditions.

To evaluate the effect of changes in water quality variables on potential for ferrihydrite to precipitate, the saturation index (SI) was calculated for a possible range of conditions at selected sites: decreased total H^+ (increased pH), Fe, and SO_4^{2-} concentration. For ferrihydrite, a decrease in Fe results in a decrease in SI, while a decrease in SO_4^{2-} results in a slight increase in SI due to lowering the potential for formation of aqueous sulfate complexes with Fe (Table 3). Compared to decreases in Fe and SO_4^{2-}, increases in pH result in a much larger change in SI of ferrihydrite.

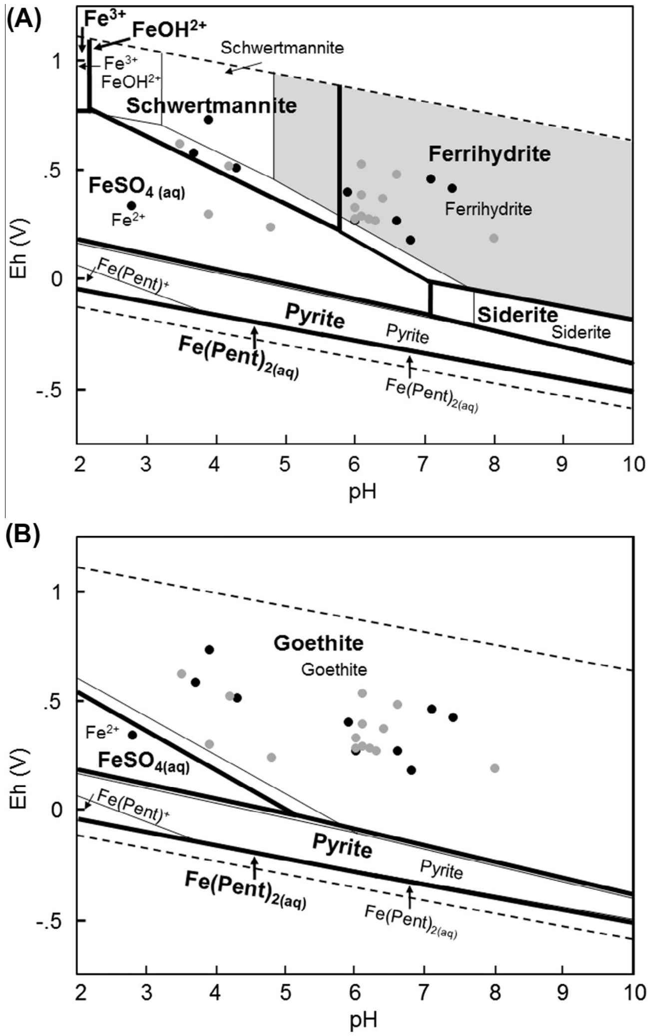

Fig. 7. Eh–pH diagram of Fe dominant species fields calculated by Geochemist's Workbench Act2 with results from above-drainage sites (●) and below-drainage sites (●) in 2012. Bold lines refer to high Fe and SO_4^{2-} concentrations (pFe = 3.01 and pSO_4^{2-} = 2.19) while thin lines refer to low Fe and SO_4^{2-} concentrations (pFe = 4.28 and pSO_4^{2-} = 4.10) at 25 °C with pCO_2 = 3.5 for a (A) schwertmannite and ferrihydrite system in which the shaded region corresponds to the low end-member of ferrihydrite, and (B) goethite system.

Table 3
Computed saturation indices for select samples near saturation with ferrihydrite in 2012 under individually modified water quality conditions: initial conditions and a 50% (0.5×) decrease in H^+, Fe, and SO_4^{2-} concentrations, with bold values indicating the difference.

Site	SI Ferrihydrite		
	Beaver meadow outfall	Silverbrook mine	Cameron mine airshaft
H^+	−0.82	−1.4	−1.1
0.5 H^+	−0.3	−0.48	−0.24
$\Delta SI_{(0.5H^+ - H^+)}$	**0.52**	**0.9**	**0.9**
Fe	−0.82	−1.4	−1.1
0.5 Fe	−1.1	−1.7	−1.4
$\Delta SI_{(0.5Fe - Fe)}$	**−0.3**	**−0.3**	**−0.3**
SO_4^{2-}	−0.82	−1.4	−1.1
0.5 SO_4^{2-}	−0.78	−1.3	−1.1
$\Delta SI_{(0.5SO_4^{2-} - SO_4^{2-})}$	**0.038**	**0.049**	**0.05**

4. Discussion

In a comparison of 1975 and 2012 CMD samples, Wilcoxon signed rank statistical tests show that decreases in Fe and SO_4^{2-} concentrations were highly significant and increases in pH were marginally significant (H^+ decreased) for below-drainage discharges, while above-drainage discharges exhibited highly significant increases in pH, and no significant change in Fe or SO_4^{2-} concentrations during the 37 years evaluated (Fig. 4 and Table 2). Median Fe and SO_4^{2-} concentrations and pH in the 1991 and 1999 samples support the apparent trends indicated in comparison tests between 1975 and 2012. The decrease in the coefficient of variation of the Fe and SO_4^{2-} concentrations in both above- and below-drainage discharges (Fig. 5) may indicate that over time these discharges are becoming less variable in composition which can reflect a slow approach toward steady-state conditions. These results indicate the water quality has gradually improved at below-drainage discharges, and is consistent with results presented for other time-series studies (Wood et al., 1999; Lambert et al., 2004; Sams and Beers, 2000; Demchak et al., 2004; Gzyl and Banks, 2007; Perry and Rauch, 2013). While updip mining practices may be beneficial in that water does not need to be pumped out to access the coal seam, updip mining is consistent with above-drainage hydrologic conditions as previously described in that the potential for pyrite oxidation is enhanced. In contrast, for below-drainage discharges, because of limited availability of O_2 in water compared to air, the rate of pyrite oxidation is slowed exponentially compared to that in air (Schuring et al., 1997).

As illustrated by the time-series plots showing the mean and median concentrations of Fe and SO_4^{2-} (Fig. 4), it is apparent that the above- and below-drainage discharges continue to yield the products of pyrite oxidation in 2012, but in lower amounts than in 1975. For both discharge types, Fe and SO_4^{2-} will continue to be discharged until pyrite is exhausted and residual oxidation products are removed. The marginally elevated but decreasing concentrations of SO_4^{2-} for both discharge types (Fig. 4G) imply that pyrite oxidation continues to be active or the oxidation products continue to be available. Nevertheless, insignificant to minor changes in Fe and SO_4^{2-} concentrations for above-drainage discharges during 1975 to 2012 indicate these sites may be approaching steady-state water-quality conditions. These changes for above-drainage discharges are consistent with high availability of O_2, decreasing quantities of available pyrite, and aqueous Fe concentrations that are limited by Fe^{III} mineral precipitation (Figs. 6 and 7). In contrast, highly significant long-term decreases in the Fe and SO_4^{2-} concentrations for below-drainage discharges (Table 2) and the limited access of O_2 in the flooded mine workings suggest the potential for kinetic limitations on the oxidation of pyrite and the oxidation of aqueous Fe^{II} and the consequent precipitation of Fe^{III} minerals. For example, the homogeneous oxidation rate model of Stumm and Morgan (1996) indicates the Fe^{II} oxidation rate is proportional to O_2 concentration. The apparent lack of steady-state conditions for below-drainage discharges implies greater elapsed time would be needed until pyrite is exhausted and residual oxidation products are removed. A more complete dataset for this time series including sampling over different hydrologic conditions and into the future would be useful to confirm this hypothesis.

Different trends for Fe concentrations in above- and below-drainage discharges result from differences in geochemical conditions that may favor Fe mineral formation. A lack of correlation between dissolved Fe and pH in both above- and below-drainage discharges indicates that Fe^{II} is the predominant aqueous species and that pH has not increased sufficiently to favor the precipitation of Fe^{II} minerals or the rapid oxidation of Fe^{II} to Fe^{III}. PHREEQC modeling supports this interpretation in that the Fe^{II}/Fe ratio is similar for the two discharge types. Relatively high pH (>6) and P_{CO_2} ($>10^{-3.5}$ atm) would be needed to precipitate Fe^{II} as siderite, whereas oxic conditions (DO > 0.5 mg/L) would be needed to transform Fe^{II} to Fe^{III} and precipitate ferrihydrite or schwertmannite

(Fig. 7). Although precipitation of Fe^{III} minerals may account for the relatively low Fe concentrations compared to SO_4^{2-} concentrations in above-drainage discharges, relatively low DO in below-drainage discharges may account for less extensive Fe^{II} oxidation and higher median dissolved Fe concentration in below-drainage discharges compared to above-drainage discharges, despite the pH for the above- and below-drainage discharges being almost the same (median 6.0–6.1) in 2012 (Fig. 3).

The bimodal distribution in pH for both above- and below-drainage discharges (Fig. 2) and the increase in pH values in the near-neutral mode suggests that a step change in pH (as opposed to the gradual changes seen in Fe and SO_4^{2-} concentrations) could occur over time as the discharges shift from buffering in the acidic pH range (3–3.5) to the near-neutral pH range (6–6.5), with the shift to near-neutral pH representing the new, long-term steady state. This shift may be anticipated with a decrease in the rate of acid production, due to progressively decreasing oxidation of pyrite, while the alkalinity supply remains constant. Although increases in pH were highly significant for above-drainage discharges, a majority of these discharges were still net acidic in 2012 (Fig. 3G). The implication is that pyrite oxidation is still active and that many samples have marginal alkalinity and are poorly buffered. The pH of the net acidic samples will decrease to acidic pH range as Fe^{II} oxidation releases protons (Kirby and Cravotta, 2005). For example, in 1975, only 21% of the discharges had $pH > 5.75$, including 4% that were above-drainage and 17% that were below-drainage. In 2012, 67% of the discharges had $pH > 5.75$, including 25% as above-drainage discharges, and 42% as below-drainage discharges, indicating a shift toward the near-neutral steady state for a majority of discharges.

The increase in pH for above- and below-drainage discharges in this study may cause a shift from schwertmannite formation to ferrihydrite formation (Fig. 7A). This is supported by water quality results from this study and solid phase analyses at Colket Mine by Cull et al. (2014) in which the dominant solid phase transitioned from schwertmannite to ferrihydrite over a 15 year period, during which time pH increased from 5.9 to 6.6. Lower Fe concentrations over time may also lead to a decrease in solid phase formation and instead favor the formation of aqueous Fe^{2+}, Fe^{3+}, and Fe^{III} hydroxyl complexes (Fig. 7A and Table 3).

Although this study has demonstrated that water quality of coal-mine discharges has improved and will continue to improve over time, many sites will continue to discharge unacceptably high concentrations of Fe and SO_4^{2-}, and in some cases, low pH, and may require remediation to reach acceptable effluent quality. Knowledge of how the geochemical composition of these discharges naturally evolves over time can be used to better inform treatment decisions. Differences in the rates of change by above- and below-drainage discharges, where the former is approaching steady state, while the latter continues to change, warrant consideration in development of the long-term treatment strategy for a given CMD type.

Treatment may be designed to accommodate the anticipated changes in chemistry and the end-user of the water (e.g. water supply, aquatic life). For example, both discharge types in this study indicate potential to improve over time. A no-treatment action plan may be acceptable for discharges that have water quality that meets or approaches effluent criteria for active mines (e.g. $pH \geq 6$; net acidity < 0; Fe < 7 mg/L; and Mn < 5 mg/L) or other appropriate goals. Nevertheless, approximately 79% of the below-drainage discharges did not meet effluent criteria. For such discharges, treatment options could include the addition of alkaline material or the installation of limestone beds with a finite lifetime (approximately 20 year supply), which may be adequate to neutralize the remaining release of acid flushed from the flooded mine workings until the pH of the raw water increases due to decreases in oxygen transport and pyrite oxidation in the mine and additions of alkalinity from groundwater. In 2012, 50% of the below-drainage discharges met the criteria for pH and alkalinity levels, whereas only 21% met relevant criteria for pH, alkalinity and Fe. At this stage of net-alkaline discharge, aerobic wetlands or active aeration and degassing supersaturated CO_2 from these low oxygen CMDs will promote the oxygenation of Fe^{II} (Johnson and Hallberg, 2005; Geroni et al., 2012). While the storage capacity of wetlands is generally limited, the gradual decrease in loading of Fe and increase in pH over time will require less capacity as the system ages. As pH increases, the detention time of the system will not need to be as large because the Fe oxidation rate generally will increase with pH (e.g. Stumm and Morgan, 1996).

Above- and below-drainage discharges that have positive net acidity and low pH tend to lack alkalinity and may benefit from alkaline addition to increase pH and promote Fe precipitation under alkalinity buffered conditions (e.g. Cravotta, 2003; Johnson and Hallberg, 2005). For example, in 2012, 50% of above-drainage sites were below the acceptable range for pH, and 80% did not meet acceptable alkalinity levels. Above-drainage sites also tend to have lower Fe and SO_4^{2-} concentrations and pH than below-drainage sites (Fig. 3), and may benefit from the installation of passive treatment systems capable of functioning in the long-term that require low maintenance and therefore lower cost of implementation over a long time period compared to costs of active chemical additions (Skousen et al., 2000; Johnson and Hallberg, 2005). For example, vertical flow wetlands contain organic material and limestone that add alkalinity and reduce Fe^{III} to form metal sulfides (Demchak et al., 2001). Anaerobic wetlands have also been identified in improving water quality in net acidic discharges; however, depending on the discharge installation can require a large land area to sufficiently reduce acid and metal concentrations (Ziemkiewicz et al., 2003).

5. Conclusions

Many regions of the world have a legacy of extensive coal mining and regional environmental degradation similar to the anthracite coalfields of Pennsylvania, USA. Understanding how the different hydrologic settings of abandoned mines will affect their water quality from the time of closure and in the future is important for identifying restoration and treatment strategies because some mines, particularly those with above-drainage discharges, are expected to continue to produce acidic, metal-laden waters for decades to come, while others (such as below-drainage discharges) may improve over time. For the 14 below-drainage mines evaluated in this study, concentrations of Fe and SO_4^{2-} decreased between 1975 and 2012 while the coefficient of variation in these constituents also decreased, indicating the water quality is improving and stabilizing over time, but may not have reached steady-state conditions yet. In contrast, for the 10 above-drainage mines evaluated, no significant change in Fe or SO_4^{2-} concentrations were identified in a comparison of 1975 and 2012 samples, indicating that these discharges may be approaching steady-state conditions characterized by sustained weathering and depletion of pyrite and efficient flushing of oxidation products. The bimodal pH distribution in both above- and below-drainage samples in 1975 and 2012, with a greater frequency of near-neutral pH in 2012, suggests a step change in pH over time as opposed to the gradual changes seen in Fe and SO_4^{2-} concentrations. The near-neutral pH favors the precipitation of Fe^{II} minerals or the oxidation of Fe^{II} and the precipitation of Fe^{III} minerals, thus limiting Fe concentrations. In contrast, changes in pH may have little if any effect on concentrations of SO_4^{2-}, which is likely to reflect the delivery of pyrite oxidation products from the mined rock. A more complete sampling record conducted across different hydrologic conditions (i.e. capturing flushing events in addition to base flow) might allow for the calculation of SO_4^{2-} and other solute loads that would be required for a thorough examination of pyrite and associated mineral weathering rates. Such an evaluation may focus on trends in the transport and concentrations of SO_4^{2-} and net acidity, which tend to be conservative, rather than focus on Fe concentration, which is nonconservative. Future studies that include sampling across different hydrologic conditions and collecting precise instantaneous and continuous discharge measurements may also be suitable to qualify the relationship between discharge and water quality based on the hydrologic setting.

Although mean and median Fe and SO_4^{2-} concentrations for above-drainage discharges were lower than those for below-drainage discharges, the above-drainage sites were typically net acidic and had lower pH, which may exacerbate transport of Al and other potentially toxic metals. Given the persistent acidic conditions of above-drainage discharges, they may be considered a higher priority for intervention and remediation than the below-drainage discharges that have a tendency for improvement. The treatment strategy may consider designs that include alkaline addition and aeration. Ideally, a long-term treatment strategy may be adjusted to changing conditions, which may be anticipated based on the hydrologic setting and past characteristics of the discharge.

Long-term treatment strategies could benefit from an understanding of the manner and rate of change in the discharge chemistry. Different treatment methods may be anticipated as the chemistry of CMD evolves over time, gradually becoming less acidic and less mineralized, and with higher pH that eventually may not warrant intervention. In the interim, treatment options that increase pH through aeration and CO_2 degassing, or alkaline addition may be effective in promoting the oxidation of Fe^{2+} and the precipitation of Fe^{III} solids.

Acknowledgments

The authors would like to thank Lisa Senior and Curtis Schreffler, of the USGS, James I. Sams III of the USDOE, J. Donald Rimstidt of Virginia Tech, and an anonymous reviewer for their helpful suggestions for improving this manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2015.02.010.

References

Benner, S.G., Blowes, D.W., Ptacek, C.J., 1997, A full-scale porous reactive wall for prevention of acid mine drainage. Ground Water Monit. Remediat., Fall 1997 Ed., 99–107. http://dx.doi.org/10.1111/j.1745-6592.1997.tb01269.x.

Bethke, C.M., Yeakel, S., 2014, The Geochemist's Workbench Release 10.0: GWB essentials guide. Aqueous Solutions, LLC, Champagin, IL, 149p.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim. Cosmochim. Acta 60 (12), 2111–2121. http://dx.doi.org/10.1016/0016-7037(96)00091-9.

Brady, K.B.C., Hornberger, R.J., Fleeger, G., 1998. Influence of geology on postmining water quality: Northern Appalachian Basin. In: Brady, K.B.C., Smith, M.W., Schueck, J., (Eds.) Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Harrisburg, PA, PA Dep. Environ. Prot. 5600-BK-DEP2256, pp. 8.1–8.92.

Brick, C.M., Moore, J.M., 1996. Diel variation of trace metals in the Upper Clark Fork River, Montana. Environ. Sci. Technol. 30 (6), 1953–1960. http://dx.doi.org/10.1021/es9506465.

Chapman, B.M., 1982. Numerical simulation of the transport and speciation of nonconservative chemical reactants in rivers. Water Resour. Res. 18 (1), 155–167. http://dx.doi.org/10.1029/WR018i001p00155.

Commonwealth of Pennsylvania, 1998. Underground mining of coal and coal preparation facilities. PA Code, Title 25. Environ. Prot. 25 PA. Code §89 (Chapter 89).

Cravotta III, C.A., 2003. Size and performance of anoxic limestone drains to neutralize acidic mine drainage. J. Environ. Qual. 32 (4), 1277–1289. http://dx.doi.org/10.2134/jeq2003.1277.

Cravotta III, C.A., 2005. Effects of Abandoned Coal-mine Drainage on Streamflow and Water Quality in the Mahanoy Creek Basin, Schuylkill, Columbia, and Northumberland Counties, Pennsylvania, 2001. U.S. Geol. Surv. Sci. Investig. Rep., 2004-5291.

Cravotta III, C.A., 2008a. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: constituent quantities and correlations. Appl. Geochem. 23 (2), 166–202. http://dx.doi.org/10.1016/j.apgeochem.2007.10.011.

Cravotta III, C.A., 2008b. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: geochemical controls on constituent concentration. Appl. Geochem. 23 (2), 203–226. http://dx.doi.org/10.1016/j.apgeochem.2007.10.003.

Cravotta, C.A., III, Brady, K.B.C., Rose, A.W., Douds, J.B., 1999, Frequency distribution of the pH of coal-mine drainage in Pennsylvania. In: Morganwalp, D.W., Buxton, H. (Eds.), U.S. Geological Survey Toxic Substances Hydrology Program – Proceedings of the Technical Meeting, Charleston, SC, March 8–12, 1999. U.S. Geol. Surv. Sci. Investig. Rep. 99-4018A, pp. 313–324.

Cravotta III, C.A., Goode, D.J., Bartles, M.D., Risser, D.W., Galeone, D.G., 2014. Surface water and groundwater interactions in an extensively mined watershed, upper Schuylkill River, Pennsylvania, USA. Hydrol. Process. 28 (10), 3574–3601. http://dx.doi.org/10.1002/hyp.9885.

Cull, S., Cravotta III, C.A., Klinges, J.G., Weeks, C., 2014. Spectral masking of goethite in abandoned mine drainage systems: implications for Mars. Earth Planet. Sci. Lett. 403, 217–224. http://dx.doi.org/10.1016/j.epsl.2014.06.045.

Demchak, J., Morrow, T., Skousen, J., 2001. Treatment of acid mine drainage by four vertical flow wetlands in Pennsylvania. Geochem. Explor. Environ. Anal. 2, 1–13. http://dx.doi.org/10.1144/geochem.1.1.71.

Demchak, J., Skousen, J., McDonald, L.M., 2004. Longevity of acid discharges from underground mines located above the regional water table. J. Environ. Qual. 33 (2), 656–668. http://dx.doi.org/10.2134/jeq2004.6560.

Earle, J., Callaghan, T., 1998. Impacts of mine-drainage on aquatic life, water uses, and man-made structures. In: Brady, K.B.C., Smith, M.W., Schueck, J. (Eds.), Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Harrisburg, PA, PA Dep. Environ. Prot. 5600-BK-DEP2256, pp. 4.1–4.10.

Fuller, C.C., Davis, J.A., 1989. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. Lett. Nat. 340, 52–54. http://dx.doi.org/10.1038/340052a0.

Gammons, C.H., Nimick, D.A., Parker, S.R., Cleasby, T.E., McClesky, R.B., 2005. Diel behavior of iron and other heavy metals in a mountain stream with acidic to neutral pH. Fisher Creek, Montana, USA. Geochim. Cosmochim. Acta 69 (10), 2505–2516. http://dx.doi.org/10.1016/j.gca.2004.11.020.

Geroni, J.N., Cravotta III, C.A., Sapsford, D.J., 2012. Evolution of the chemistry of Fe bearing waters during CO_2 degassing. Appl. Geochem. 27 (12), 2335–2347. http://dx.doi.org/10.1016/j.apgeochem.2012.07.017.

Growitz, D.J., Reed, L.A., Beard, M.M., 1985. Reconnaissance of mine drainage in the coal fields of Eastern Pennsylvania. U.S. Geol. Surv. Water-Resour. Investig. Rep., 83-4274.

Gunsinger, M.R., Ptacek, C.J., Blowes, D.W., Jambor, J.L., 2006. Evaluation of long-term sulfide oxidation processes within pyrrhotite-rich tailings, Lynn Lake, Manitoba. J. Contam. Hydrol. 83 (3–4), 149–170. http://dx.doi.org/10.1016/j.jconhyd.2005.10.013.

Gzyl, G., Banks, D., 2007. Verification of the "first flush" phenomenon in mine water from coal mine in the Upper Silesian Coal Basin, Poland. J. Contam. Hydrol. 92 (1–2), 66–86. http://dx.doi.org/10.1016/j.jconhyd.2006.12.001.

Helsel, D.R., Hirsch, R.M., 2002. Statistical Methods in Water Resources. U.S. Geol. Surv., Tech. Water-Resour. Investig. 04-A3, 523p.

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338 (1–2), 3–14. http://dx.doi.org/10.1016/j.scitotenv.2004.09.002.

Jonsson, J., Jonsson, J., Lovgran, L., 2006. Precipitation of secondary Fe(III) minerals from acid mine drainage. Appl. Geochem. 21 (3), 437–445. http://dx.doi.org/10.1016/j.apgeochem.2005.12.008.

Kirby, C.S., Cravotta III, C.A., 2005. Net alkalinity and net acidity 1: theoretical considerations. Appl. Geochem. 20 (10), 1920–1940. http://dx.doi.org/10.1016/j.apgeochem.2005.07.002.

Lambert, D.C., McDonough, K.M., Dzombak, D.A., 2004. Long-term changes in quality of discharge water from abandoned underground coal mines in Uniontown Syncline, Fayette County, PA, USA. Water Res. 38 (2), 277–288. http://dx.doi.org/10.1016/j.watres.2003.09.017.

Lee, G., Bigham, J.M., Faure, G., 2002. Removal of trace metals by coprecipitation with Fe, Al, and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. Appl. Geochem. 17 (5), 569–581. http://dx.doi.org/10.1016/S0883-2927(01)00125-1.

MacCausland, A., McTammany, M.E., 2007. The impact of episodic coal mine drainage pollution on benthic macroinvertebrates in streams in the Anthracite region of Pennsylvania. Environ. Pollut. 149 (2), 216–226. http://dx.doi.org/10.1016/j.envpol.2006.12.030.

McDonough, K.M., Lambert, D.C., Mugunthan, P., Dzombak, D.A., 2005. Processes governing flow and chemical characteristics of discharges from free-draining, underground coal mines. J. Environ. Eng. 131 (10), 1361–1368. http://dx.doi.org/10.1061/(ASCE)0733-9372(2005) 131:10(1361).

McKnight, D.M., Bencala, K.E., 1989. Reactive transport in an acidic mountain stream in Summit County, Colorado: a hydrologic perspective. Geochim. Cosmochim. Acta 53 (9), 2225–2234. http://dx.doi.org/10.1016/0016-7037(89)90346-3.

McKnight, D.M., Kimball, B.A., Runkel, R.L., 2001. PH dependence of iron photoreduction in a rocky mountain stream affected by acid mine drainage. Hydrol. Process. 15 (10), 1979–1992. http://dx.doi.org/10.1002/hyp.251.

Mentz, J.W., Warg, J.B., 1975. Up-dip Versus Down-dip Mining – An Evaluation. U.S. Environ. Prot. Technol. Series EPA- 670/2-75-047, 74p.

Moncur, M.C., Ptacek, C.J., Blowes, D.W., Jambor, J.L., 2003. Fate and transport of metals from an abandoned tailings impoundment after 70 years of sulfide oxidation. In: Proc. of Sudbury '03, Min. Environ. III, pp. 238–247.

Nordstrom, D.K., 1977. Thermochemical redox equilibria of ZoBell's solution. Geochim. Cosmochim. Acta 41 (12), 1835–1841. http://dx.doi.org/10.1016/0016-7037(77)90215-0.

Nordstrom, D.K., 2009. Acid rock drainage and climate change. J. Geochem. Explor. 100 (2–3), 97–104. http://dx.doi.org/10.1016/j.gexplo.2008.08.002.

PA DEP, 2013. Coal mining operations. Harrisburg, PA: Pennsylvania Spatial Data Access. Web 19 December, 2013. <http://www.pasda.psu.edu/uci/MapService.aspx?Dataset=271>.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, one-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geol. Surv. Water Investig. Rep. 99-4259, Denver CO.

Perry, E.F., Rauch, H., 2013. Estimating water quality trends in abandoned coal mine-pools. In: Presented at WV Mine Drain. Task Force Meet., March 26-27, 2013, Morgantown, WV.

Raymond, P.A., Oh, N.-H., 2009. Long-term changes of chemical weathering in rivers heavily impacted from acid mine drainage: insights on the impact of coal mining on regional and global carbon and sulfur budgets. Earth Planet. Sci. Lett. 284 (1–2), 50–56. http://dx.doi.org/10.1016/j.epsl.2009.04.006.

Rose, A.W., Cravotta, C.A., III, 1998. Geochemistry of coal-mine drainage, In: Brady, K.B.C., Smith, M.W., Schueck, J. (Eds.), Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Harrisburg, PA, PA Dep. Environ. Prot., 5600-BK-DEP2256, pp. 1.1–1.22.

Sams III, J.I., Beers, K.M., 2000. Effects of Coal-Mine Drainage on Stream Water Quality in the Allegheny and Monongahela River Basins – Sulfate Transport and Trends. U.S. Geol. Surv. Water-Resour. Investig. Rep., 99-4208.

Schuring, J., Kolling, M., Schulz, H.D., 1997. The potential formation of acid mine drainage in pyrite-bearing hard-coal tailing under water-saturated conditions: an experimental approach. Environ. Geol. 31 (1–2), 59–65. http://dx.doi.org/10.1007/s002540050164.

Skousen, J.G., Sexstone, A., Ziemkiewicz, P.F., 2000. Acid mine drainage control and treatment. In: Reclam. Drastically Disturb. Lands, Am. Soc. Agron. Am. Soc. Surf. Min. Reclam., Agron. No. 41.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, 3rd ed. John Wiley & Sons Inc., NY.

Thomas, L., 2013. Coal Geology, 2nd ed. Wiley-Blackwell, West Sussex, UK.

U.S. Geological Survey, 2013. USGS Current Water Data for Pennsylvania. National Water Information System: Web Interface <http://waterdata.usgs.gov/pa/nwis/rt>.

Williams, D.J., Bigham, J.M., Cravotta III, C.A., Traina, S.J., Anderson, J.E., Lyon, J.G., 2002. Assessing mine drainage pH from the color and spectral reflectance of chemical precipitates. Appl. Geochem. 17 (10), 1273–1286. http://dx.doi.org/10.1016/S0883-2927(02)00019-7.

Wood, C.R., 1996. Water Quality of the Large Discharges from Mines in the Anthracite Region of Eastern Pennsylvania. U.S. Geol. Surv. Water-Resour. Investig. Rep., 95-4243.

Wood, S.C., Younger, P.L., Robins, N.S., 1999. Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland. Quart. J. Eng. Geol. 32, 69–79. http://dx.doi.org/10.1144/GSL.QJEG.1999.032.P1.05.

Younger, P.L., 1997. The longevity of minewater pollution: a basis for decision-making. Sci. Total Environ. 194–195, 457–466. http://dx.doi.org/10.1016/S0048-9697(96)05383-1.

Ziemkiewicz, P.F., Skousen, J.G., Simmons, J., 2003. Long-term performance of passive acid mine drainage treatment systems. Mine Water Environ. 22 (3), 118–129. http://dx.doi.org/10.1007/s10230-003-0012-0.