Acidity Decay of Above-Drainage Underground Mines in West Virginia

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Acidity of water from abandoned underground mines decreases over time, and the rate of decrease can help formulate remediation approaches and treatment system designs. The objective of this study was to determine an overall acidity decay rate for above-drainage underground mines in northern West Virginia from a large data set of mines that were closed 50 to 70 yr ago. Water quality data were obtained from 30 Upper Freeport and 7 Pittsburgh coal seam mines in 1968, 1980, 2000, and 2006, and acidity decay curves were calculated. The mean decay constant, k, for Upper Freeport mines was 2.73×10^{-2} yr^{-1}, with a 95% confidence interval of ± 0.0052, whereas the k value for Pittsburgh mines was not significantly different at 4.26×10^{-2} yr^{-1} ± 0.017. Acidity from the T&T mine, which was closed 12 yr ago, showed a k value of 11.25×10^{-2} yr^{-1}. This higher decay rate was likely due to initial flushing of accumulated metal salts on reaction surfaces in the mine, rapid changes in mine hydrology after closure, and treatment. Although each site showed a specific decay rate (varying from 0.04×10^{-2} yr^{-1} to 13.1×10^{-2} yr^{-1}), the decay constants of 2.7×10^{-2} yr^{-1} to 4.3×10^{-2} yr^{-1} are useful for predicting water quality trends and overall improvements across a wide spectrum of abandoned underground mines. We found first-order decay models improve long-term prediction of acidity declines from above-drainage mines compared with linear or percent annual decrease models. These predictions can help to select water treatment plans and evaluate costs for these treatments over time.

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Extensive underground mining has taken place in West Virginia since the late 1800s (West Virginia Geological and Economic Survey, 2007), and Bennett (1991) estimated an area of about 610,000 ha with underground mining beneath the surface in West Virginia alone. This legacy of mining has changed groundwater quality and quantity due to intercepting and changing underground water flow paths (Da Silva et al., 2006). In areas of northern Appalachia where high sulfur coal exists and no limestone units are present for neutralization, the greatest environmental impact from underground mines has been on surface water quality from acid mine drainage (AMD) (Herlihy et al., 1990). Acid mine drainage is produced when sulfide minerals associated with coal seams react with oxygen and water to form low-pH, sulfate-rich, and high-iron solutions. The effects on surface water include high levels of acidity and metals that have detrimental effects on aquatic organisms (Gray, 1995; Monterroso and Macias, 1998; Stewart and Skousen, 2003), low pH conditions that accelerate weathering and release of aluminum and other toxic elements from minerals (Bigham et al., 1996; Kittrick et al., 1982), and orange-colored stream sediments from iron hydroxide precipitation (Rosseland et al., 1992; Winland et al., 1991; Younger, 1998).

Previous studies of water quality changes from underground mines have shown that acidity declines over time (Wood et al., 1999; Younger, 2000). Demchak et al. (2004) observed that changes in water chemistry over time differ between below-drainage (flooded) and above-drainage (not flooded) underground mines, with flooded mines rebounding to much better water quality within a decade and unflooded mines remaining acid for much longer. Lambert and Dzombak (2000) found that flooded underground mines in Pennsylvania change from very acid water to neutral or net alkaline water shortly after complete flooding (see also Brady et al., 1998; Capo et al., 2001; Donovan et al., 2000; Jones et al., 1994; Younger, 1997). Borch (2009) found similar results in the flooded Meigs mine in Ohio and suggested the following reasons for the dramatic water quality improvement within a few years after flooding at Meigs: (i) Pyrite oxidation ceased in the flooded sections; (ii) after the initial flush, there was less readily available iron sulfate salts to dissolve; (iii) alkaline

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Abbreviations: AMD, acid mine drainage; CD, cumulative difference.

strata in the roof rock of the mine pool provided some neutralization; (iv) dilution and influx of alkalinity occurred from groundwater inflows; (v) the groundwater flow path exhibited some short circuiting, so areas of rapid transport or flow exhibited better water quality than areas of restricted water movement; and (vi) geochemical reactions, such as sulfate reduction and cation exchange, occurred along the underground water flow path, thus improving the quality before discharge.

Above-drainage mines did not show the same dramatic improvement as below-drainage mines; they tended to improve slightly in water quality but remained acidic (Demchak et al., 2004; Lambert and Dzombak, 2000).

Acid mine drainage is unsightly, and treatment costs for abandoned underground mines are a public financial burden. Therefore, the length of time that these discharges continue to be a burden (aesthetically and financially) is important, and predicting their longevity is necessary to determine potential remediation strategies and cost projections. However, the physical setting in underground mines is difficult to study because abandoned mine maps may not be accurate and conditions below ground are always changing and unpredictable. Some sections or voids of abandoned above-drainage mines are flooded or partially flooded, which virtually removes those pyrite reaction surfaces from contributing acid products. Many other areas within the mine remain open to oxygen and water exchange and are susceptible to reaction. These exposed pyrite surfaces produce less acidity over time due to (i) weathering products forming an iron hydroxy sulfate coating, which reduces air and water contact and release of acid products (Younger, 1998), and (ii) the more morphologically reactive pyrite (framboidal) is depleted first, thereby leaving the less reactive pyrite (massive) for subsequent oxidation. Therefore, changes in pyrite reaction rate and availability of surfaces in these areas can result in drainage quality improvement. Only during roof or pillar collapse are fresh pyrite surfaces exposed to the mine atmosphere and water. Once mines are closed, ventilation systems cease, which greatly reduces the availability of oxygen for pyrite oxidation. Land surfaces over underground mines can be compacted or altered to reduce the amount of infiltration, or surface cracks can be clogged, thereby inhibiting direct inflow of surface water into the mine. Roof or pillar collapses within the mine can change flow paths or create pools of water in the mine. Although all of these factors presumably decrease acidity with time, most are difficult or impossible to validate. We are therefore left with empirical predictions of decline based on long-term data sets. Although site-specific models are unlikely, a regionally valid model would significantly improve our ability to plan and budget for treatment and could be useful for watershed-based water quality modeling and classification (Merovich et al., 2007).

Water quality improvements with time have been observed for parameters other than acidity. Typically, these improvements are modeled using percent decreases in one or more water quality parameters. For example, Demchak et al. (2001) found a linear relationship between sulfate and acidity with an R^2 value of 0.67 using data from Upper Freeport above-drainage underground mines. Using sulfate as an indicator, they calculated a 2.2% decrease in acidity per year for 40 mines between 1968 and 2000. Ziemkiewicz (1994) used a similar rate of 2% acidity decrease per year to estimate changes in AMD discharges over time (see also Koryak et al., 2004). Wood et al. (1999) calculated a slightly higher 3.3% acidity decrease per year in coal mine discharge chemistry over time in Scotland. Mack and Skousen (2008) found a 2.1% decrease per year in acidity from 40 underground mines in West Virginia.

The objective of this research was to determine the rate of acidity decline from above-drainage underground coal mines. Two distinct datasets were used: (i) a long-term data set for mines closed more than 50 yr ago for which data were only sporadically available and (ii) a 12-yr-old, recently closed Upper Freeport underground mine for which yearly data were available.

Materials and Methods

From a data set of previously sampled abandoned underground mines (Demchak et al., 2004), 37 sites were selected for sampling in 2006. These sites were selected because water quality data from 1968, 1980, and 2000 were available for these sites and approximate sizes and opening dates were known (Table 1). All sampling sites were located in Preston and Monongalia counties of West Virginia, and all sites discharged water from abandoned, above-drainage underground mines. This area in northern West Virginia receives an average of 115 cm of precipitation, which is somewhat evenly distributed throughout the year, and the average temperature is 11°C. Based on pumping and discharge rates of surrounding above-drainage mines, an average of about 20% of the precipitation on a year-round basis is discharged from underground mines in this area (Bruce Leavitt, Consulting Hydrologists, personal communication, 2009; GAI Consultants, 2001).

The Pittsburgh coal seam is the lowest stratum of the Monongahela Group in the Pennsylvanian System. The seam has 1.5 to 2% sulfur and an ash content of 6%, with seam thickness of about 3 m (Hennen and Reger, 1914). In this region, few overlying limestone materials are available within 30 m above the coal seam to neutralize the high amounts of acid-producing material in this coal and associated rocks.

The Upper Freeport coal seam is the topmost stratum of the Allegheny Formation in the Pennsylvanian System. Upper Freeport coal contains <1.5% sulfur and an ash content from 8 to 12% and averages 2 m in thickness (Hennen and Reger, 1914). The strata above the Upper Freeport coal contain massive sandstones and some shales, and no limestone or alkaline-bearing rock units are found within 50 m above the Upper Freeport coal in this area.

1968 Sampling

During June though September of 1968 through 1970, researchers sampled all mine discharges in the Monongahela River basin. In the Cheat River subbasin from Parsons, West Virginia to Pt. Marion, Pennsylvania, 555 AMD sources were found, with 315 of these being underground mines (USEPA, 1971). Maps and field sheets were completed for each site. A 1-L bottle was filled with discharge water, put on ice, and analyzed in the laboratory for acidity, alkalinity, conductivity, sulfate, and pH. Water samples were delivered to the laboratory each Friday and were analyzed using methodology from

standard methods (American Public Health Association, 1965). Water analyses were monitored for accuracy and precision by running periodic samples of reference standards.

1980 Sampling

The West Virginia Division of Water Resources also conducted sampling and analyses of underground mine discharges in this area during 1980 (West Virginia Division of Natural Resources, 1985). We accessed their data and found that some of their sample sites matched discharges sampled in 1968. Therefore, where sufficient information was available, we used their water quality analyses in 1980 to aid in estimating the rate of change in water quality. Water samples were collected, placed on ice, and taken to the laboratory, where acidity was measured by titration (Sheila Vukovich, West Virginia Division of Mining and Reclamation, personal communication, 2005).

2000 Sampling

We acquired the maps and field sheets from the 1968 study and located 40 of the underground mine discharge sites in 2000 (Demchak et al., 2004). A 250-mL water sample was taken at each sample point. The samples were not acidified. They were placed on ice and analyzed by West Virginia University's National Research Center for Coal Energy laboratory to determine pH, total acidity, and alkalinity by titration.

Table 1. Discharge name, the year the mine opened, coal seam mined, size of mine, and acidity values for each discharge.

Discharge	Year opened	Coal seam	Size	Acidity			
				1968	1980	2000	2006
			ha	mg L^{-1} as $CaCO_3$			
Bull 1	1955	UF†	21	2805		1401	780
Bull 2	1957	UF	923	1905		756	540
Bull 3	1957	UF	923	640		214	78
Bull 4	1955	UF	86	250	360	530	478
Bull 5	1955	UF	58	1370		336	334
Fickey 1	1945	UF	28	3270		961	486
Fickey 5‡	1950	UF	38	515	460	697	461
Fickey 6	1950	UF	75	1300	425	118	94
Fickey 7	1950	UF	60	1670		1086	490
Fickey 8	1952	UF	78	1505	625	390	420
Fickey 9	1945	UF	47	1920		498	636
Glade 1	1955	UF	26	1705		151	90
Glade 2	1950	UF	52	390		179	31
Glade 3	1950	UF	69	675		412	266
Glade 4	1950	UF	156	1660	1250	230	450
Glade 5	1950	UF	156	1765	1330	283	239
Greens 1	1945	UF	33	945	455	702	188
Greens 2§	1945	UF	42	8		4	6
Greens 3‡	1950	UF	88	1504	830	1732	1214
Martin 2	1955	UF	11	2315	545	135	110
Martin 3	1955	UF	11	490		253	35
Middle 1	1952	UF	310	917	515	291	290
Muddy 2	1940	UF	72	687	410	86	198
Muddy 3	1935	UF	278	170	110	45	72
Muddy 5	1950	UF	148	20		30	71
Muddy 6	1945	UF	98	4400		492	192
Muddy 7	1945	UF	86	520		57	27
Muddy 9	1952	UF	78	1515	1225	1050	800
Muddy 10	1940	UF	121	1440		487	414
Muddy 11	1943	UF	35	2140	634	550	444
Cheat PA 1	1935	P	63	2457		563	424
Cheat 2	1935	P	112	1061		1033	1048
Cheat 5	1935	P	55	1825	210	104	446
Cheat 6	1952	P	311	1450		488	214
Lynn 1	1943	P	34	1368	605	102	170
Lynn 2	1935	P	448	4690	3800	434	360
Lynn 3	1935	P	448	4988	1930	537	810

† P, Pittsburgh; UF, Upper Freeport.

‡ Not included in analyses because of surface disturbance.

§ Not included in analyses because of low acidity.

2006 Sampling

Using 37 of the sites from the 2000 data set (three sites from that study ceased to discharge water by 2006), sampling was performed quarterly in 2006 to establish water chemistry conditions across seasons. Although four samples were taken in 2006 for each site (Mack and Skousen, 2007), only the acidity values from summer 2006 were used to keep the sampling season consistent with all other sampling years. The sample collection procedure was the same as the 2000 sampling. Water samples were not acidified. They were placed on ice and analyzed by the laboratory as described previously.

T&T Data Set

The West Virginia Department of Environmental Protection began treating the mine discharge at the T&T Mine in 1996. Water samples were collected weekly by agency personnel, and the samples were analyzed by WVU's National Research Center for Coal and Energy for pH, total acidity and alkalinity by titration, and sulfate. Mean acidity for each year was used in our analysis.

Data Analysis

Of the 30 Upper Freeport sampling sites, one site (Greens 2) was discarded because the 2006 acidity was <10 mg L^{-1}, and two (Fickey 5 and Greens 3) were discarded because of surface disturbance. Of the 27 remaining sites, 15 had three sampling dates (1968, 2000, 2006), and 12 had four sampling dates (1968, 1980, 2000, 2006). A calibration subset of 18 sites and nine validation sites was randomly selected six times, such that sites with four samplings and sites with three samplings were equally represented. Each calibration subset was fit to the following first-order decay model:

$$C_t = C_0 e^{-kt} \quad [1]$$

where C_t is acidity (mg L^{-1}) at time t, C_0 is acidity (mg L^{-1}) at time = 0, and k is the first-order decay constant (1/time), using nonlinear regression (PROC NLIN; SAS Inst., ver. 9.1, 2005). A single mean (n = 6) decay constant, k (yr^{-1}), was used to predict 2006 acidity at each validation subset site (n = 9) for each group. Cumulative difference (CD) was calculated as

$$\mathrm{CD} = \sum_{v=1}^{9}\left(\mathrm{Acidity}^{2006}_{v,\mathrm{predicted}} - \mathrm{Acidity}^{2006}_{v,\mathrm{actual}}\right) \quad [2]$$

and percent error (% Error) was calculated as

$$\%\ \mathrm{Error} = \frac{\sum_{v=1}^{9}\left(\dfrac{\mathrm{Acidity}^{2006}_{v,\mathrm{predicted}} - \mathrm{Acidity}^{2006}_{v,\mathrm{actual}}}{\mathrm{Acidity}^{2006}_{v,\mathrm{actual}}}100\right)}{9} \quad [3]$$

where v is a validation site, and summary statistics (mean, median, min, max) were calculated (n = 6). Upper and lower confidence intervals for k were calculated. This procedure was repeated with the calibration and validation subset reversed. In addition, first-order decay constants were adjusted so that the mean CD was zero and was calculated for all sites combined and for all sites individually. Because there is no physical reason to fit a first-order model to the data and because the 1968 data are potentially high influence points, sites with 1980 data were used to fit a linear model (1980–2006),

$$\frac{\mathrm{Acidity}_t}{\mathrm{Acidity}_{1980}} = b_0 + b_1(t) \quad [4]$$

where t is time and a first-order decay model. The results were compared as described previously. First-order decay constants were also calculated for the Pittsburgh and T&T data sets, but because there were insufficient sample numbers, all sites (Pittsburgh) and years (T&T) were used to fit a single first-order constant for each site.

Results

Acidity at the Upper Freeport sites decreased with time but not at all sites and not uniformly (Table 1). Four sites (Bull 4, Fickey 5, Greens 3, and Muddy 5) had higher acidity in at least one sampling compared with 1968, only two of which could be explained by surface reclamation (Fickey 5 and Greens 3, which were excluded from the analysis). Acidity increased from 2000 to 2006 at Fickey 8, Fickey 9, Glade 4, Muddy 2, Muddy 3, and Muddy 5.

General patterns of decline were difficult to discern at sites with only three sampling dates. Of the sites with four sampling dates, acidity decreased nearly linearly at Muddy 3 and Muddy 9 and concavely at Glade 4 and Glade 5. The largest decrease for many sites was between 1968 and 1980 (Fickey 6, Fickey 8, Martin 2, Middle 1, and Muddy 2), whereas others showed sharp declines from 2000 to 2006 (Glade 3, Muddy 9, and Bull 1).

Pittsburgh sites showed much more variable declines with time than did the Upper Freeport sites (Table 1). Acidity at Cheat 2 was essentially unchanged from 1968 to 2006; three sites had consistently decreasing acidity with time (Cheat PA 1, Cheat 6, and Lynn 2), whereas at three sites acidity decreased from 1968 to 2000 but increased between 2000 and 2006 (Cheat 5, Lynn 1, and Lynn 3). Therefore, acidity changes with time at the Pittsburgh sites were inconsistent.

The range of acidity within any sampling year from these sites was large, with relative standard deviations of 60 to 82% for Upper Freeport sites and 64 to 98% for Pittsburgh sites (Table 2). For Upper Freeport sites, the trend was for mean acidity to decrease with time, with the largest absolute decrease (54%) occurring between 1968 and 1980; for the Pittsburgh sites, the largest absolute decrease (72%) occurred between 1980 and 2000, although the sample number for 1980 was small. Annual percent decreases varied between 1.7 and 4.9% per year, with an increase of 1.1% yr^{-1} between 2000 and 2006 at the Pittsburgh sites (Table 2). The overall annual percent decrease of 2.1% for both sites was similar to the 2% decrease per year used by Ziemkiewicz (1994) and the 3.3% decrease per year found by Wood et al. (1999).

The best-fit first-order decay constant, k, for the Upper Freeport sites was 2.73×10^{-2} yr^{-1} (95% confidence interval, ± 0.0052). This was comparable to the average k for all sites (2.62×10^{-2} yr^{-1} ± 0.0035) but led to large prediction errors in mean CD and % Error for acidity in 2006 in the validation data sets (Table 3). Although the prediction errors were large, they were positive and thus are very conservative (Fig. 1). The

Table 2. Mean acidity, summary statistics, percent decrease, and annual percent decrease for Upper Freeport and Pittsburgh coal seam underground mines in 1968, 1980, 2000, 2006, and overall.

Coal seam	Year(s)	*n*	Mean	SD	Min.	Median	Max.	Decrease	Annual decrease
					mg L^{-1}			%	% yr^{-1}
UF†	1968	27	1422	1003	20	1440	4400		
	1980	12	657	394	110	530	1330	54‡	4.5‡
	2000	27	434	357	30	336	1401	34‡	1.7‡
	2006	27	306	228	27	266	800	30‡	4.9‡
	overall	93	712		20	486	4400	78§	2.1§
P	1968	7	2548	1627	1061	1825	4988		
	1980	4	1636	1619	210	1268	3800	36‡	3.0‡
	2000	7	466	316	102	487	1033	72‡	3.6‡
	2006	7	496	320	170	424	1048	–6.5‡	–1.1‡
	overall	25	1245		102	605	4988	80§	2.1§

† UF, Upper Freeport; P, Pittsburgh.

‡ From previous data collection time.

§ From 1968 to 2006.

resulting constants were not different when the sample numbers in the calibration and validation data sets were reversed, suggesting that the results are robust. A k of 3.95×10^{-2} yr^{-1} resulted in a mean CD of zero and considerably better prediction errors (Table 3) and was closer to the mean k of all sites taken individually of 4.11×10^{-2} yr^{-1} (range, 2.68×10^{-2} yr^{-1} to 11.56×10^{-2} yr^{-1}). However, it also led to two sites (Muddy 5 and Bull 4) having large negative prediction errors (Fig. 2). The best fit k for the seven Pittsburgh sites was 4.26×10^{-2} yr^{-1} ± 0.017 (Fig. 3), a value not significantly different from either of the best-fit Upper Freeport constants. Although a better constant for Pittsburgh mines could be obtained with more data, a k of 0.03 to 0.04 yr^{-1} seems to be a reasonable estimate for both mines.

The first-order decay constant from 1980 forward was 2.62×10^{-2} yr^{-1} ± 0.008, which was not different from when the 1968 data were included. This suggests that the 1968 data were not potential high influence points. When simple linear regression from 1980 was used to predict acidity in 2006 in the Upper Freeport mines, the resulting prediction errors were smaller (Table 4) than when the 1968 data were used in a first-order model (Table 3). However, when extrapolating backward to 1940, the approximate time these mines opened, the simple linear regression predicts an acidity of approximately 1200 mg L^{-1}, a 2% decline per year predicts approximately 1700 mg L^{-1}, and the first-order model predicts between 2800 and 4000 mg L^{-1}. Communication with T&T company personnel (Larry Harris, personal communication, 2005) at the closure of the Upper Freeport T&T mine confirmed that water acidity was 5000 to 6000 mg L^{-1}. Another above-drainage Upper Freeport mine, Omega, was closed in 1998, and average water acidity after closure was 3800 to 5050 mg L^{-1} (GAI Consultants, 2001). Therefore, the first-order model predicted more accurately the original acidity at mine closure than either the linear or percent annual decrease models.

Acidity declines were greater at the T&T site (k = 11.25×10^{-2} yr^{-1}) (Fig. 4) than that predicted from the subset regression (Table 3). This could be because T&T is not representative of the other Upper Freeport mines. The decay constant from

Table 3. Prediction errors for first-order decay models.

	Subset regression ($k = 2.73 \times 10^{-2}$ yr^{-1})		Mean CD† = 0 ($k = 3.95 \times 10^{-2}$ yr^{-1})	
	CD	% Error	CD	% Error
	mg L^{-1}	%	mg L^{-1}	%
Mean	174	151	0	58
Median	159	138	–13	50
Min.	86	73	–80	9
Max.	296	224	77	104

† CD, cumulative difference.

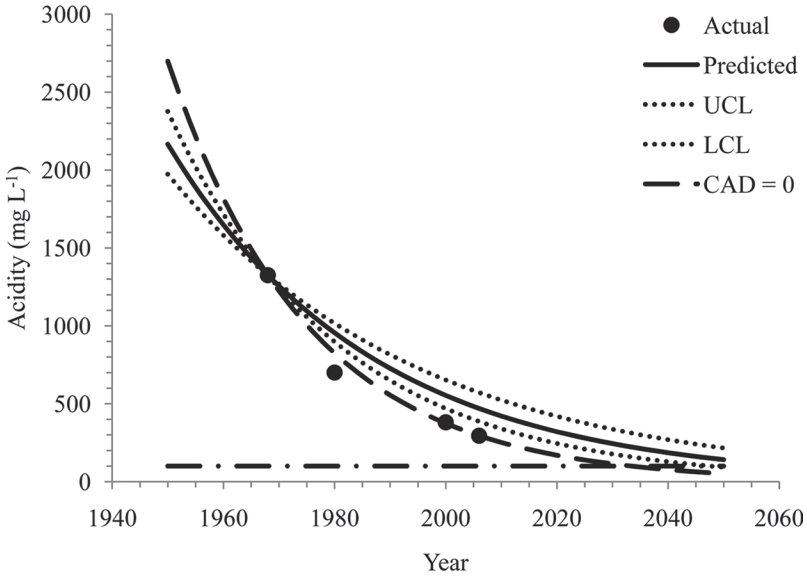

Fig. 1. Acidity (mg L^{-1}) for the Upper Freeport sites, best-fit first-order decay function (k = 0.0273), upper and lower confidence intervals, and, when adjusted so that mean cumulative difference = 0 (k = 0.0395), extrapolated to the year 2050. Horizontal dashed line represents the cutoff acidity to begin passive treatment (100 mg L^{-1}). CAD, cumulative average difference; LCL, lower confidence limit; UCL, upper confidence limit.

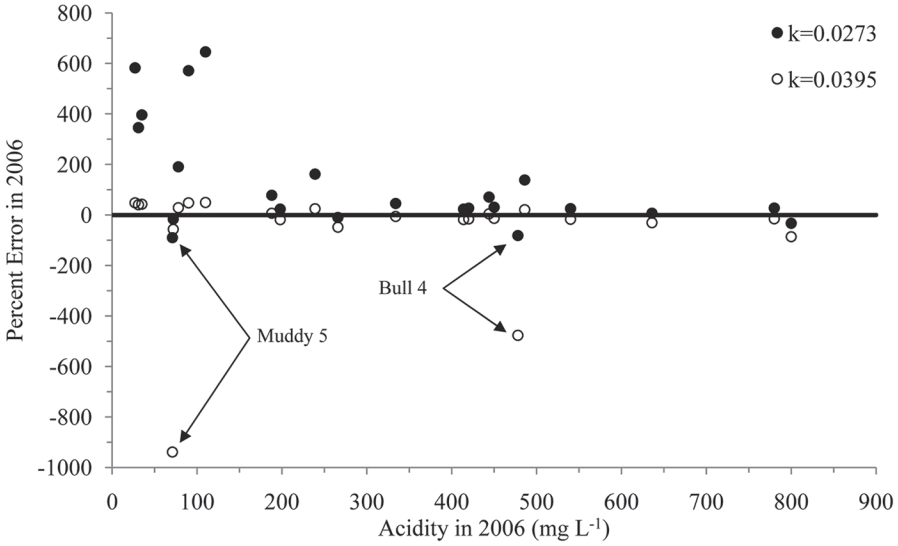

Fig. 2. Percent error for 2006 predicted acidity as a function of actual acidity in 2006 for Upper Freeport sites.

the subset regression is meant to be an overall representation of 27 sites; individual sites had decay constants greater and less than the mean. It is also possible that treatment and remediation efforts by the company and state agencies at T&T are improving water quality faster than would be predicted from untreated mines. The remediation efforts at T&T involve (i) pumping limestone slurry into the mine in 2000 to neutralize the acidity and (ii) continual injection of AMD treatment sludge back into the mine since 2002. Finally, it is possible that acidity declined faster during the first decade after mine closure than in subsequent decades (Borch, 2009). Younger (1997) stated that this rapid decline in acidity after closure is related to initial flushing of stored acid products (vestigial acidity), with lower acidity emanating from the mine with time. The underground mines we sampled were closed more than 10 yr before our first sample date in 1968, so presumably much of their stored acid products were flushed before our first sampling. This may also explain why the backward prediction to 1940 was a little lower than expected.

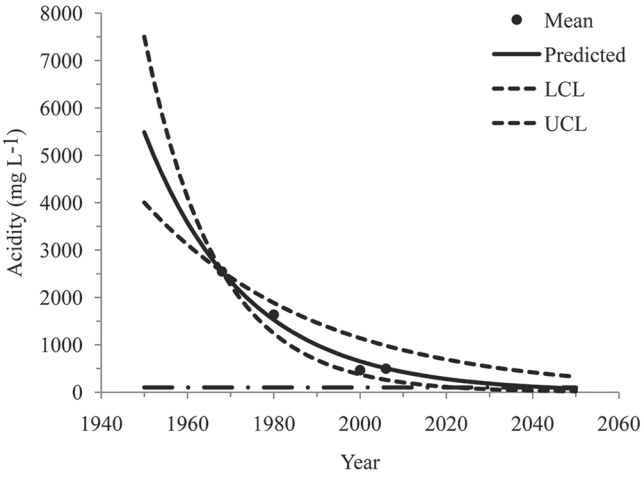

Fig. 3. Acidity (mg L^{-1}) for the seven Pittsburgh sites, best-fit first-order decay function (k = 0.0.0426), and upper and lower confidence intervals. Horizontal dashed line represents the cutoff acidity to begin passive treatment (100 mg L^{-1}). LCL, lower confidence limit; UCL, upper confidence limit.

Discussion

It is probable that the discharges from underground mines would not follow a consistent decay rate throughout their history due to initial rapid changes in the mine environment immediately after mine closure. The time between mine closure and the first sampling could be very important to the assessment of water quality changes from the mine. Although we were able to determine the mine opening dates (Table 1), it is nearly impossible to determine the closure date because there was no requirement for operators to report closure dates. We do, however, know that these mines were closed in the 1950s to early 1960s because the USEPA field sheets, which were filled out in the late 1960s, denoted that the mines were already closed. Pyrite oxidation rate, availability of pyrite surface area, and mine geochemistry could change rapidly once the mine is closed due to a lack of new pyrite exposure from further mining. It is also possible that the accumulated and stored metal salts within the mine could be flushed out soon after mine closure, which would show an initial high acidity with rapid declines. Periodic changes within the mine, like random physical alterations due to high rainfall and inflow, make prediction of water chemistry at any given time difficult.

Although studies on the longevity of acid mine drainage have calculated annual percent decreases, this approach is not the best for prediction because it is sensitive to the time interval used (i.e., it decreases as time increases if acidity changes are small or zero). Depending on the initial conditions and time period, a 2% rate of acidity decline for decline could be essentially indistinguishable from a first-order decay constant of 0.04, but the forward and backward predictions would be vastly different. Given that similar first-order decay constants were obtained with and without the 1968 data and that the backward predictions using the first-order model were closer to what would be expected at mine closure, we conclude that the first-order approach is preferred over simple linear or percent decline functions. Although there is no a priori reason to fit a first-order function to the data, the advantages are that it allows for simple forward and backward estimation, and, if a valid constant is known, similar predictions could be made for other areas with limited data sets. The disadvantage of first-order (and percent decline) functions is that they asymptotically approach zero acidity. We are not aware of any above-drainage acid mine drainage site that has naturally attenuated to zero acidity; therefore, some modified version of the first-order function could be considered, for example:

$$C_t = C_\infty + (C_0 - C_\infty)e^{-kt} \quad [5]$$

where C_∞ is the long-term, steady-state acidity. Much more research is needed to determine what to use for C_∞, but presumably it is a function of the geology, including sulfur content, pyrite forms, limestone layers, and perhaps the area of disturbance.

An acidity of 100 mg L^{-1} is often used as the cutoff for where passive treatment becomes a viable treatment option. Predictions from the first-order model indicate that acidity will be 100 mg L^{-1} from the Upper Freeport and Pittsburgh sites somewhere between 2030 and 2060 (Fig. 1 and 3) and between 2015 and 2020 at the T&T site (Fig. 4). We are not suggesting that acidity at every site will be <100 mg L^{-1}; rather, we suggest that the combined contribution from all these sites to the region would be <100 mg L^{-1}.

Table 4. Prediction errors for simple linear decline models.

	Subset regression ($b_1 = -1.81 \times 10^{-2}$ yr^{-1})		Mean CD† = 0 ($b_1 = 2.04 \times 10^{-2}$ yr^{-1})	
	CD	% Error	CD	% Error
	mg L^{-1}	%	mg L^{-1}	%
Mean	115	119	0	58
Median	95	107	–13	50
Min.	29	51	–79	9
Max.	221	183	77	104

† CD, cumulative difference.

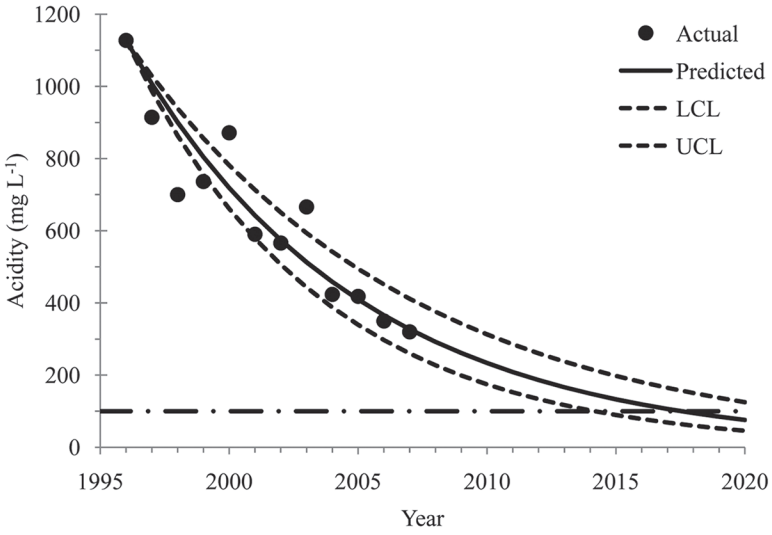

Fig. 4. Acidity (mg L^{-1}) at the T&T site for the first 11 yr after closure, best-fit first-order decay function (k = 0.1125), and upper and lower confidence intervals. Horizontal dashed line represents the cutoff acidity to begin passive treatment (100 mg L^{-1}). LCL, lower confidence limit; UCL, upper confidence limit.

Conclusions

Given that the average acidity of Upper Freeport underground mines was 1422 mg L^{-1} in 1968 and 306 mg L^{-1} in 2006, a significant improvement in regional water quality from above-drainage underground mines has occurred in the last 50 to 70 yr. A similar trend was found for Pittsburgh underground mines: Acidity was 2548 mg L^{-1} in 1968 and 496 mg L^{-1} in 2006. Even with this large decline in discharge acidity, there is still a large quantity of stored acidity in these watersheds, which apparently will continue to be gradually released over time. First-order decay curves show an improvement in prediction over the long-term compared with linear declines and percent annual decreases and provide an important prediction tool for future water quality. Such a tool could be extremely beneficial when a discharge is being considered for passive or active treatment. By more accurately estimating future acidity, treatment systems can be designed to more efficiently neutralize AMD discharges and predict when active treatment systems are necessary and when less costly passive treatment techniques may be used as the acidity declines over time. In addition, cost projections for treatment based on acidity and flow could be evaluated, and future benefits for improved water quality conditions in receiving streams could be assessed. The analysis of decay curves could be improved by more data sets where water samples were taken from mines at a greater frequency, at least annually, as well as beginning to take samples at the time of mine closure to obtain baseline acidity.

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