Mine Water Environ (2015) 34:50–58
DOI 10.1007/s10230-014-0278-4

TECHNICAL ARTICLE

Effect of Flow Rate on Acidity Concentration from Above-Drainage Underground Mines

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Received: 23 June 2013 / Accepted: 19 March 2014 / Published online: 15 November 2014

Abstract High flows during spring runoff and snowmelt can increase the concentrations of contaminants in the discharge or dilute them. In the Appalachian region, March tends to be a time of high flows from underground mines, May has moderate flow rates, and July has low flows. The objective of this study was to determine the effect of flow rate on water quality from five acid-producing, above-drainage underground mines in West Virginia. We measured flow rates and acidity twice a week for 3 weeks in March, May, and July 2007. As expected, flow rates in March (average of five sites) were significantly higher at 32 L s^{-1} than flows in May and July at 18 and 6 L s^{-1}. Flows during weeks within months were not significantly different. Acidity concentrations for March and May (high and moderate flow months) were significantly lower at 342 and 400 mg L^{-1} (as $CaCO_3$) than those in July at 524 mg L^{-1} (as $CaCO_3$). Similar to flow, acidity concentrations during weeks within the same month were not significantly different. In general, this data supported the 'dilution' concept, where higher flow rates resulted in lower acidity concentrations from above-drainage underground mine discharges.

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Keywords Acid mine drainage · Dilution · Spring flush · Water quality

Introduction

Flow rates from underground mines are generally affected by seasonal variations in rain and snowmelt, infiltration, runoff, and evapotranspiration. Rainfall recharges the groundwater, which generally results in increased flows from discharge points. McDonough et al. (2005) found that the M-59 discharge in the Uniontown Syncline of Pennsylvania followed a seasonal variation in discharge volumes, with lower flows in the summer months and higher flows in the spring months. Wendland (2001) showed that groundwater reacted to rainfall with increased flow within a month or two, depending on the season. Highest flows from the above-drainage T&T mine in northern West Virginia occurred from March to June (400 L s^{-1}), with much lower flows on average from July to February (280 L s^{-1}; Demchak et al. 2004).

Such seasonal changes in flow can influence the water quality of acid mine drainage (AMD) emanating from underground mines. Yarnal and Draves (1993) studied the relationship between flow and water quality in streams of Huntingdon County, PA. They found that increased precipitation, especially from acid rain, generated higher concentrations of acidity and sulfates. Sarmiento et al. (2009) found that seasonal variations in mine discharge quality in the Odiel River basin in Spain were dependent on the quantity of precipitation, pollution concentration, and distance from the AMD sources. Byrne et al. (2012) observed significant flushing of metals during storm flow events at the abandoned Dylife metal mine in Wales, UK, resulting in very high concentrations of metals during high

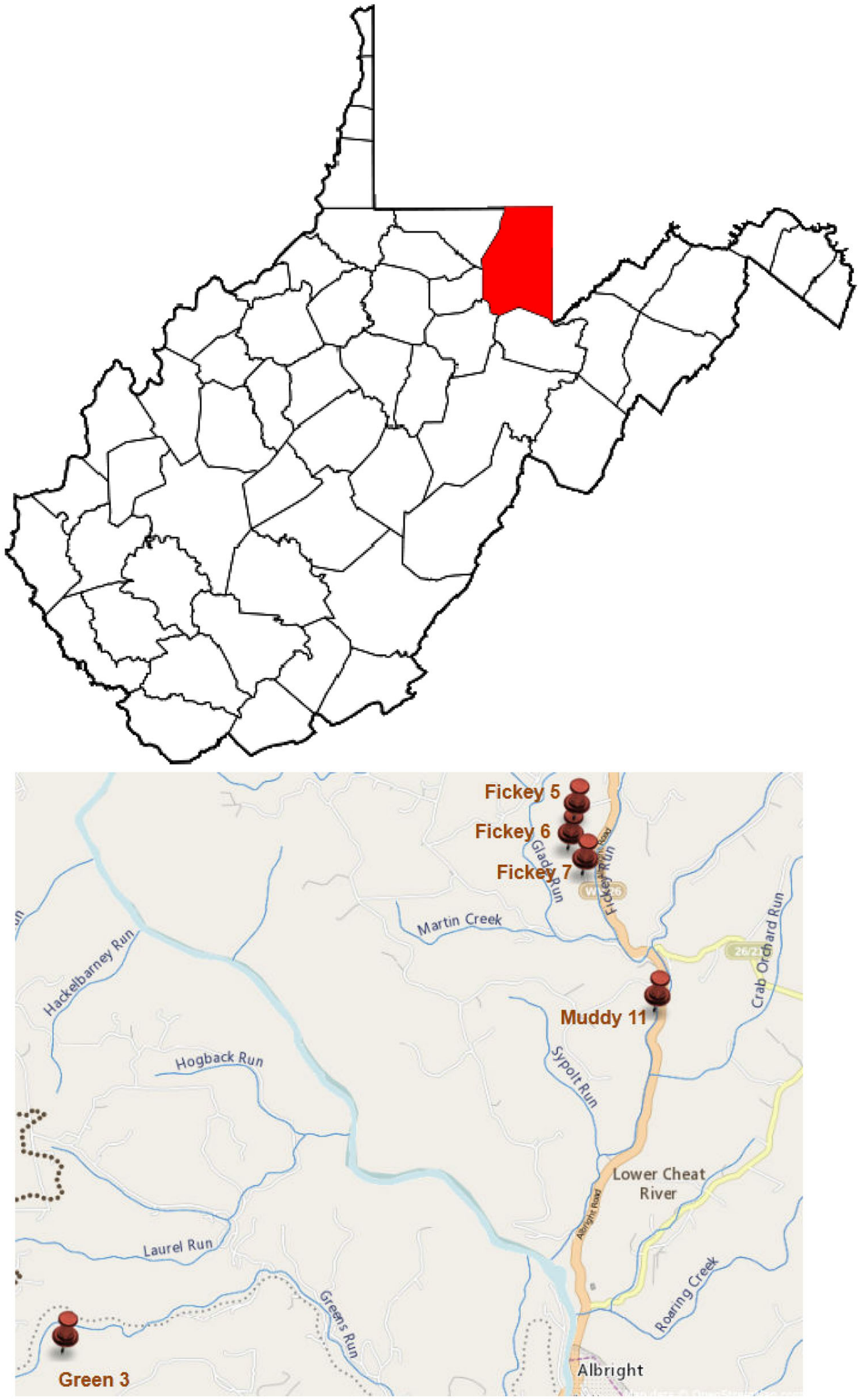

Fig. 1 Five sites used for this study

flows. Efflorescent metal sulfates on the surface of the mine spoil were shown to be the principal source of metals. A study of the 51-ha Majestic mine in Ohio by Pigati and Lopez (1999) reported that higher flows in the spring scoured metal salts from the interior of the mine and flushed them out with discharge, resulting in increased acidity and metal concentrations. Desbarats and Dirom (2007), during their study of the Maya mine in British Columbia, found small spikes in flow during the summer months after storm events. The highest spikes in metal concentrations at this mine were associated with the initial heavy rains in autumn.

The concept of a ‘spring flush’ can result from two processes. The first involves the flushing of accumulated metal salts from mine walls and ceilings that are only contacted by flowing waters during high flow times. During low flow, the metal salts accumulate on the surfaces, thereby storing high levels of acidity in the mine, which are released during high flows. The second process involves the filling and overflow of acidic water from disconnected, discrete mine pools that only discharge during high flows. Both processes could result in greater acidity in discharge waters. A similar phenomenon can occur at surface mines. Discrete pockets or pools of water held in the macropores of the overburden material may only contribute to the discharge when heavy rains in spring generate overflow and leach out stored acid products in mine spoils and cause high acidity in surface runoff and seeps. These discharges from surface mine spoils can thus also increase acidity during periods of high rainfall.

Further examples of the ‘spring flush’ idea can be found in two above-drainage mines in West Virginia. The Omega Mine had water samples taken continuously for 6 years. With higher flows from February to April, acidity values were consistently higher (roughly 4,500 mg L^{-1} as $CaCO_3$). In contrast, June to January showed lower flow values and lower acidities (roughly 3,500 mg L^{-1} as $CaCO_3$; Demchak et al. 2004). In contrast, during high flow months (March and April) the T&T mine showed only slightly higher acidities (900 mg L^{-1} as $CaCO_3$) compared to 850 mg L^{-1} as $CaCO_3$ during low flow months of July to September.

An alternative effect of flow on acidity concentrations occurs when high flow results in decreased acidity and metal concentrations, or in other words ‘dilution’, and typically the converse: low flows result in high concentrations. Griffiths et al. (2001) found that higher flows at the Arnot underground mine in Pennsylvania resulted in low acidity concentrations. Stillings et al. (2006) found that concentrations of the major metal elements decreased at the Beatson mine in Alaska after major rain events due to dilution. Nilsson and Renöfält (2008) found that low flow periods increased water pollution in streams. The mechanism for this concept is that less water is available to dilute metals dissolved in the water, which results in higher acidity concentrations during low flow periods (Skousen and Ziemkiewicz 1996).

The studies reviewed here give no clear indication of which description (‘spring flush’ or ‘dilution’) is correct, and indeed imply that both ideas may be correct under different conditions and at different locations. The objectives of our study were to quantify the changes in flow and acidity for varying time scales, and to further evaluate the interaction between flow and acidity in underground mines.

Methods

Five abandoned, above-drainage, underground mine discharges were selected for water sampling (Fig. 1) because they represent a range of values in both flow and acidity. These sites were chosen from a large data set of underground discharges that we have monitored for several years (Demchak et al. 2004; Mack et al. 2010). These five sites are located in Preston County, WV, and all five removed coal from the Upper Freeport coal seam, and have been abandoned for more than 50 years. This area in northern West Virginia receives an average of 115 cm of precipitation, which is somewhat evenly distributed throughout the year. March receives an average of 11 cm of precipitation, May 8.5 cm, and July 7 cm. 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 2010; GAI Consultants 2001).

Water sampling was performed in 2007 to represent three time scales. All five sites were sampled two times a week for 3 weeks in March, and three times a week for 3 weeks in May and July. Flows were measured by stretching a measuring tape across the width of the discharge channel and dividing the channel into sections. Each section was between 10 and 20 % of the overall width

Table 1 ANOVA results for flow during weeks across 3 months for five sites

Model	n	*df*	*P* value
Site	5	4	<0.001
Month	3	2	<0.001
Site × month	15	8	<0.001
Week	8	5	0.007

Table 2 Mean flow values for each sampling month

Month	n	Mean flow (m^3 s^{-1})
March	30	0.032a
May	45	0.018b
July	45	0.006c

Values in columns with different letters are significantly different at $P < 0.001$

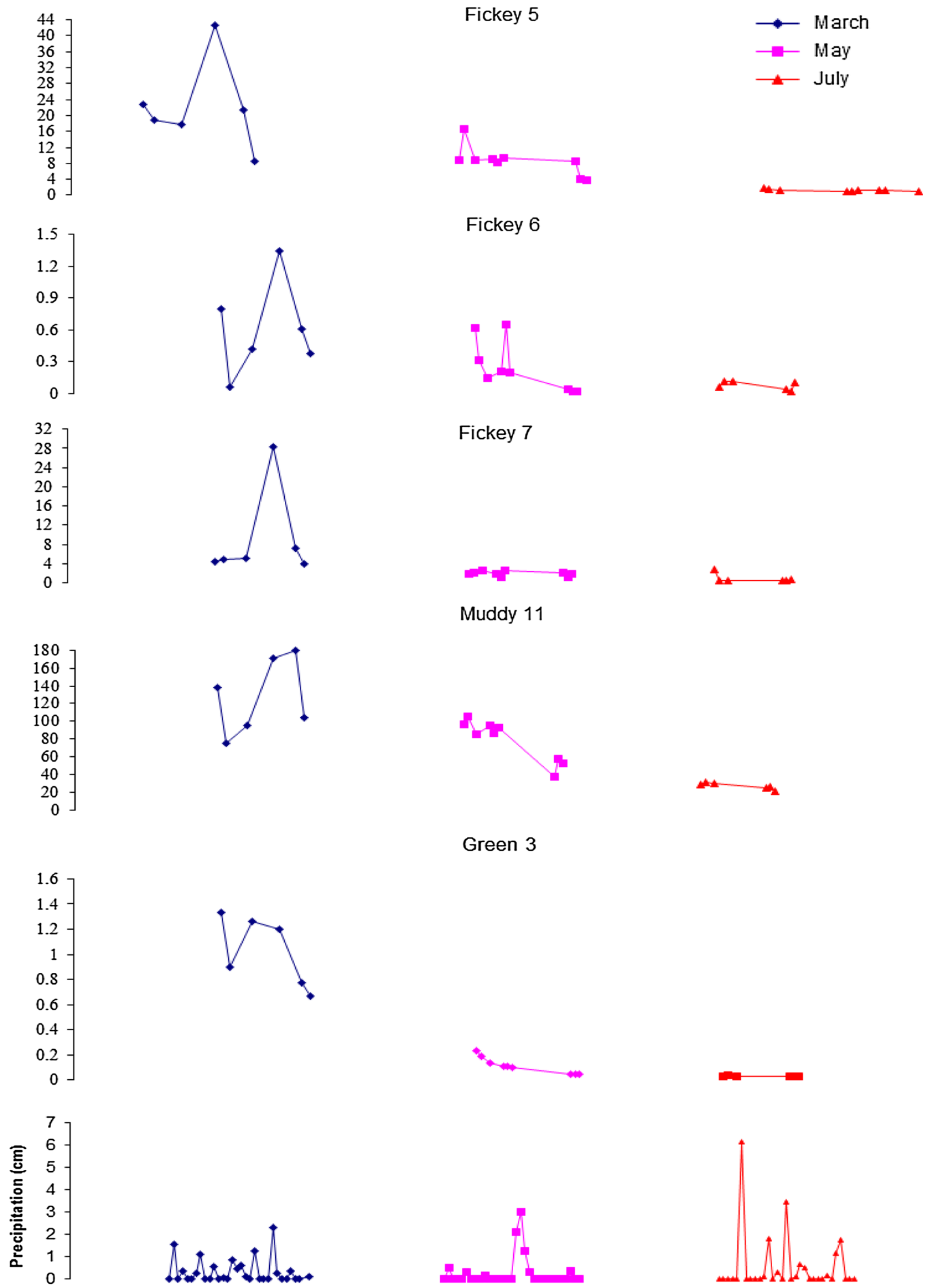

Fig. 2 Precipitation and flow for five sites. Precipitation values were taken from a rain gauge at Albright, WV. Flow values (in L s^{-1}) are shown on the y-axis for the five sites and vary in scale

of the discharge channel, so there were at least five measurements for each discharge channel. Depth at each sampling point was measured using the 0.6-depth method (Buchanan and Somers 1976). Velocity at each sampling point was determined using a Marsh-McBirney Flo-Mate 2000 (Marsh-McBirney, Frederick, MD, USA). The width interval, depth, and velocity were multiplied together at each point to compute flow, and total flow for the discharge was calculated as the sum of the flow values from each section. For discharges that were low and where the use of

Table 3 Mean flow values for entire sampling periods by site

Site	n	Mean flow (m^3 s^{-1})
Fickey 5	3	0.011b
Fickey 6	3	0.003c
Fickey 7	3	0.004bc
Muddy 11	3	0.078a
Green 3	3	4.0×10^{-4}c

Values in columns with different letters are significantly different at $P < 0.001$

Table 4 Basic statistics for flow values for five sites

Month	Site	n	Mean flow ($m^3 s^{-1}$)	Range of flow ($m^3 s^{-1}$)	Standard deviation
March	Fickey 5	6	0.022	0.008–0.043	0.011
	Fickey 6	6	0.001	6.0×10^{-5}–0.001	4.0×10^{-4}
	Fickey 7	6	0.009	0.004–0.028	0.009
	Muddy 11	6	0.127	0.076–0.180	0.042
	Green 3	6	0.001	7.0×10^{-4}–0.001	3.0×10^{-4}
May	Fickey 5	9	0.009	0.004–0.017	0.004
	Fickey 6	9	3.0×10^{-4}	1.0×10^{-5}–6.0×10^{-4}	2.4×10^{-4}
	Fickey 7	9	0.002	0.001–0.003	5.0×10^{-4}
	Muddy 11	9	0.079	0.038–0.106	0.023
	Green 3	9	1.0×10^{-4}	6.0×10^{-5}–3.0×10^{-4}	6.0×10^{-5}
July	Fickey 5	9	0.001	0.001–0.002	2.0×10^{-4}
	Fickey 6	9	5.0×10^{-5}	1.0×10^{-5}–1.0×10^{-4}	4.0×10^{-5}
	Fickey 7	9	0.001	4.0×10^{-4}–0.003	7.0×10^{-4}
	Muddy 11	9	0.029	0.022–0.036	0.004
	Green 3	9	3.0×10^{-5}	3.0×10^{-5}–3.0×10^{-5}	3.0×10^{-6}

a flow meter was not practical (Fickey 6 and Green 3), flows were determined by the bucket and stopwatch method. The amount of time needed to fill a pre-marked 2 L bucket was recorded. This procedure was performed three times at each sampling time and the results were averaged.

Water pH in the field was measured with a Milwaukee Sharp pH meter and conductivity with a Milwaukee Sharp EC meter (Milwaukee Meters, Southport, Australia). Acidity and alkalinity were calculated by digital titration (HACH model AL-DT kit, HACH Company, Loveland, CO, USA). Concentrations of Al, Fe, Mn, Ca, and Mg were ascertained using a Plasma 400 inductively coupled spectrophotometer (Perkin Elmer, Norwalk, CT, USA). Sulfate was measured turbidimetrically by flow injection analysis using a Latchat Quik Chem FIA+ 8000 series (Latchat Instruments, Milwaukee, WI, USA). To evaluate titration accuracy, acidity was calculated using the mathematical equation for calculated acidity (Kirby and Cravotta 2004).

Table 5 Average flow values for each week

Week	n	Mean flow ($m^3 s^{-1}$)
March, #1	15	0.026b
March, #2	15	0.038a
May, #1	15	0.022b
May, #2	15	0.021b
May, #3	15	0.011c
July, #1	15	0.007c
July, #2	15	0.007c
July, #3	15	0.005c

Values in columns with different letters are significantly different at $P < 0.001$

Calculated acidity values were used in the final analysis. Precipitation data were collected from the nearest USGS rain gauge at Albright, WV.

Analysis of variance was used to determine significant differences among flow and acidity values over the time spans of a week and a month for these sampling sites. Flow and elemental concentrations were used in principal components analysis (PCA) to establish the number of eigenvalues to be used in factor analysis (FA). All eigenvalues greater than 1 were used in the FA for each of the five sites. The FA was then used to show relationships between flow, acidity, and other sampled parameters. Regression analyses were also used to evaluate relationships.

Table 6 ANOVA results for acidity during weeks across 3 months for five sites

Model	n	*df*	*P* value
Site	5	4	<0.001
Month	3	2	<0.001
Site × month	15	8	<0.001
Week	8	5	<0.001

Table 7 Mean acidity values for each sampling month

Month	n	Mean acidity (mg L^{-1} as $CaCO_3$)
March	30	342b
May	45	400b
July	45	524a

Values in columns with different letters are significantly different at $P < 0.001$

Table 8 Means, ranges, and deviations of acidity values for five sites during 3 months

Month	Site	n	Mean acidity (mg L^{-1} as $CaCO_3$)	Range of acidity (mg L^{-1} as $CaCO_3$)	Standard deviation
March	Fickey 5	6	329	284–370	37.7
	Fickey 6	6	48	31–56	9.6
	Fickey 7	6	311	276–330	19.6
	Muddy 11	6	359	312–444	47.6
	Green 3	6	663	500–761	92.0
May	Fickey 5	9	335	297–467	52.4
	Fickey 6	9	58	53–65	4.8
	Fickey 7	9	342	298–398	33.9
	Muddy 11	9	341	323–367	13.0
	Green 3	9	924	859–954	28.6
July	Fickey 5	9	516	374–635	113.6
	Fickey 6	9	89	75–102	8.7
	Fickey 7	9	510	379–634	87.7
	Muddy 11	9	409	343–488	58.9
	Green 3	9	1,094	805–1,318	178.1

Results and Discussion

Flow

Flow was significantly different among sites ($P < 0.001$), months ($P < 0.001$), and the interactions of sites with months ($P < 0.001$; Table 1). Average flows for sampling weeks within a month were also significantly different.

Average flow for all sites was highest in March, followed by May, and then July (Table 2). This was expected since flows are higher in spring due to snowmelt and more rainfall (Stewart and Skousen 2003). Figure 2 shows flow for each site during the same time frame and precipitation from a nearby rain gauge station. March flows responded quickly to small precipitation events (Fig. 2). This was consistent with saturated soils and high water tables. Any precipitation or snowmelt received during this period either moved into groundwater supplies, which were already full, thereby causing more flow out of the mine to the discharge, or ran off as surface flow. Another obvious finding from Fig. 2 is that July flows remained consistently low despite storm events that would have increased discharge flow during March and May. During the July sampling time, the water soaked into soils and was held within pores, rather than moving into underground supplies; or if it did move into underground supplies, recharged the low mine pools and water tables, resulting in no additional flow to discharges from the precipitation event. Loss of water from evapotranspiration by plants and high July temperatures also prevented some of this water from moving into underground supplies or running off.

Muddy 11 had the highest average flows over all three sampling months (78 L s^{-1}; Table 3), as well as the greatest standard deviation (23 L s^{-1}, Table 4). Conversely, Fickey 6 had lower flows (0.3 L s^{-1}) and less standard deviation (0.24 L s^{-1}, Tables 3, 4). The least standard deviation in flow was generally in July when average flows were the lowest (Table 4; Fig. 2), and the opposite was found in March, with high flows and high standard deviation. This relationship between flow and standard deviation has a greater effect on the mean standard deviations when the number of samples is small. In this case, there were only six or nine water samples each month. Extrapolation of the effect of a larger sample set on standard deviation is difficult to establish without comparing the same months over several years due to annual differences in rainfall and snow melt.

The data were also analyzed to determine significant differences among mean flow values over the period of a week. Of the eight sampling weeks, the second sampling week in March was found to have the highest mean flow and the third week of July the lowest (Table 5).

Table 9 Mean acidity values for each week

Week	n	Mean acidity (mg L^{-1} as $CaCO_3$)
March, #1	15	342c
March, #2	15	341c
May, #1	15	401bc
May, #2	15	394bc
May, #3	15	406b
July, #1	15	441b
July, #2	15	518a
July, #3	15	612a

Values in columns with different letters are significantly different at $P < 0.001$

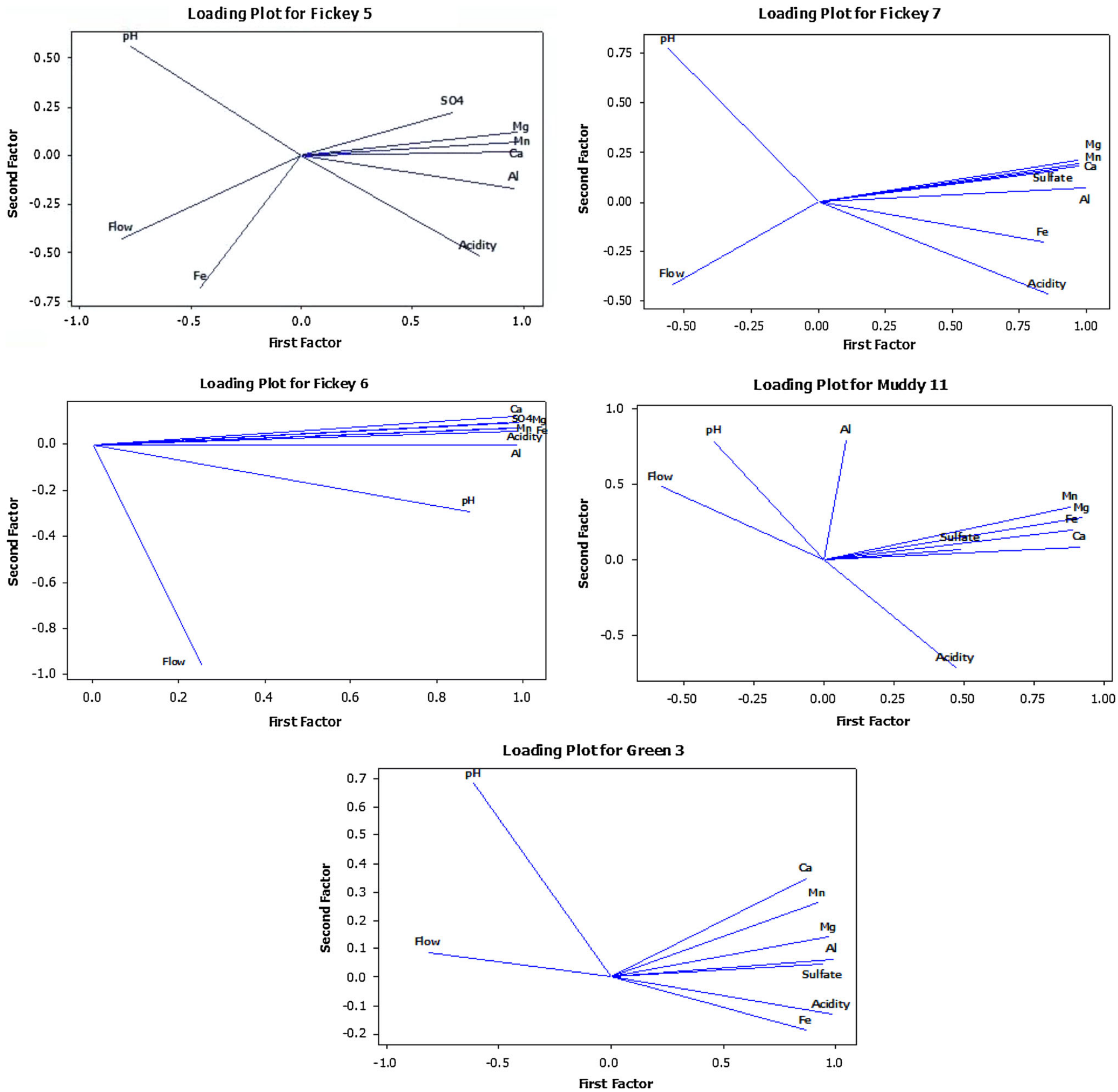

Fig. 3 Factor Analysis results for all five sites. Direction of lines indicated the loading of a parameter on the first or second principle component. *Length of the lines* indicated parameter magnitude

Acidity

Differences among sites ($P < 0.001$), month ($P < 0.001$), the interaction of sites with months ($P < 0.001$), and weeks within a month ($P < 0.001$) were all significant for acidity concentrations (Table 6). Acidity generally increased over the 3 month period for all sites and acidity was significantly higher in July than March and May (Table 7). With the exception of Fickey 6, the highest acidities and standard deviations were in July. Standard deviations in March and May showed no definite pattern, although acidity concentrations were greater in May than in March (Table 8).

Acidity was also significantly different among weeks, but not for weeks within the same month. The first and second weeks of March had the lowest acidity values, while the second and third weeks of July had the highest acidity concentrations (Table 9).

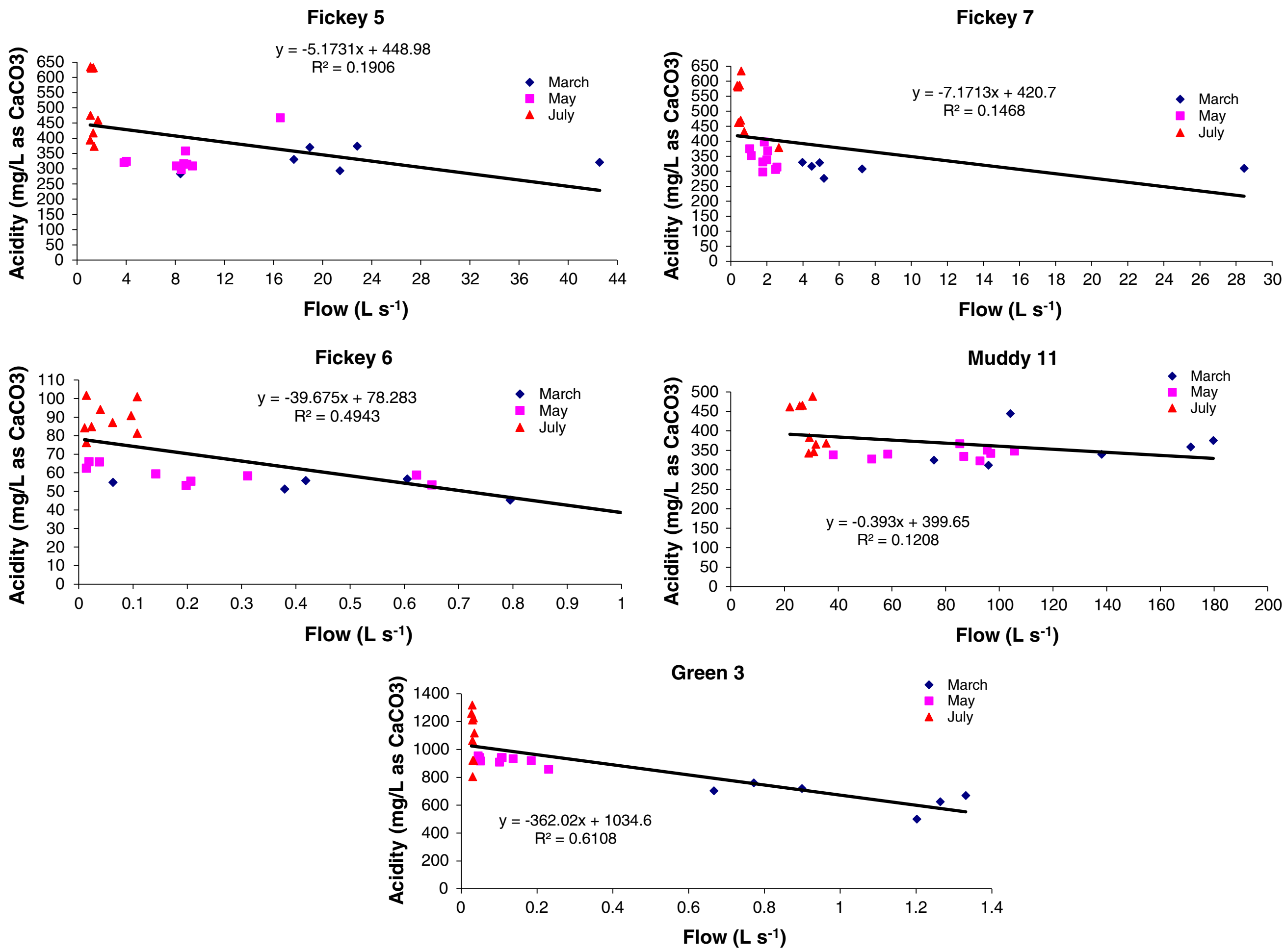

Fig. 4 Relationship between flow and acidity for all 5 sites. The *regression line slope* is negative, showing an inverse relationship between flow and acidity

Analyses of Flow and Acidity

Factor analysis (FA) results for all five sites were similar to one another when comparing flow and acidity (Fig. 3). Flow and acidity consistently showed opposite loading values on Factor 1, but they did not load similarly on Factor 2. Fickey 6 and Muddy 11 both loaded differently on Factor 2 from the other three sites for flow and acidity. The lines of these two parameters were widely spaced, meaning that flow and acidity were not strongly related to one another, especially on Factor 1. However, the magnitudes of the lines for each of these parameters were similar, even if the directions were not.

All sites showed similar regression relationships between flow and acidity, although the correlation coefficients were not high (0.12–0.61). Flow was highest in March and lowest in July, while acidity showed the opposite pattern. The slopes of the regression trend lines for all sites were negative, meaning that as flow increased, acidity decreased (Fig. 4). Three of the five regressions were significant (Table 10), while sites with the lowest r^2 values (Fickey 7 and Muddy 11) were not significant. These five discharges would need to be sampled for several years to determine if this trend will continue over a longer period of time.

Table 10 *P* values for flow vs acidity for five sites

Sample site	*P* value
Fickey 5	<0.03
Fickey 6	<0.001
Fickey 7	0.06
Muddy 11	0.10
Green 3	<0.001

The discharge flow and acidity results from these five underground mine sites support the ‘dilution’ description where high flows yield low concentrations (Skousen and

Ziemkiewicz 1996). Similar results were found by Stillings et al. (2006) in Alaska and Griffiths et al. (2001) in Pennsylvania.

Acknowledgments The authors acknowledge the staff of Friends of the Cheat for their help with site identification. We also thank the property owners at the sample sites for allowing access for collection of water samples.

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