

The Past, Present, and Future of Pennsylvania's Anthracite Coal Mine Discharges

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Introduction

Pennsylvania has a long history of coal mining dating back to the 1700's has left a legacy on the landscape. Abandoned mines create the aqueous and oxidizing environment required to dissolve pyrite (FeS_2) and cause acid and metals to leach from the remaining rock and drain into nearby waterways (Figure 1).



Figure 1: An abandoned mine with visible Fe dissolution orange and green

Coal mine discharges (CMDs) can result in a trickle of contaminated water, or a gush of thousands of gallons a day (Figures 2 and 3). The amount of discharge can make a difference in the total amount (flux) of iron (Fe) and sulfate (SO_4) produced by these abandoned mines over time.



Figure 2: Low volume coal mine discharge

Pennsylvania has over 3,000 miles of streams contaminated by drainage from abandoned CMDs. Toxic metals in CMDs cause environmental impairment by killing plant and animal species, reducing biodiversity, disrupting the food chain, destroying the buffering capacity of water bodies, and altering vital habitats (Gray, 1997).

Fe is removed from solution through precipitation. There have been many studies on the downstream transformations and fate of contaminants such as Fe and pH, but few studies have focused on geochemistry at the point of discharge and how it has changed over time. Studies have also been limited by focusing only on concentration, and not including flux. To solve this gap in research, samples collected from CMDs in this study are compared to previous studies conducted in 1975, 1991, and 1999 to determine changes in water chemistry and mineralogy at CMDs (Growtitz et al., 1985; Wood, 1991; Cravotta, 2008a, 2008b).



Figure 3: High volume coal mine discharge

Methods

CMD sites were visited between July and October, 2012, and water samples and water quality data were collected on-site for anion and dissolved cation analysis. Water quality data collected on site included pH, Eh, dissolved oxygen, and discharge. These 23 discharges were identified based on GPS location and mine name as being sampled in previous studies.

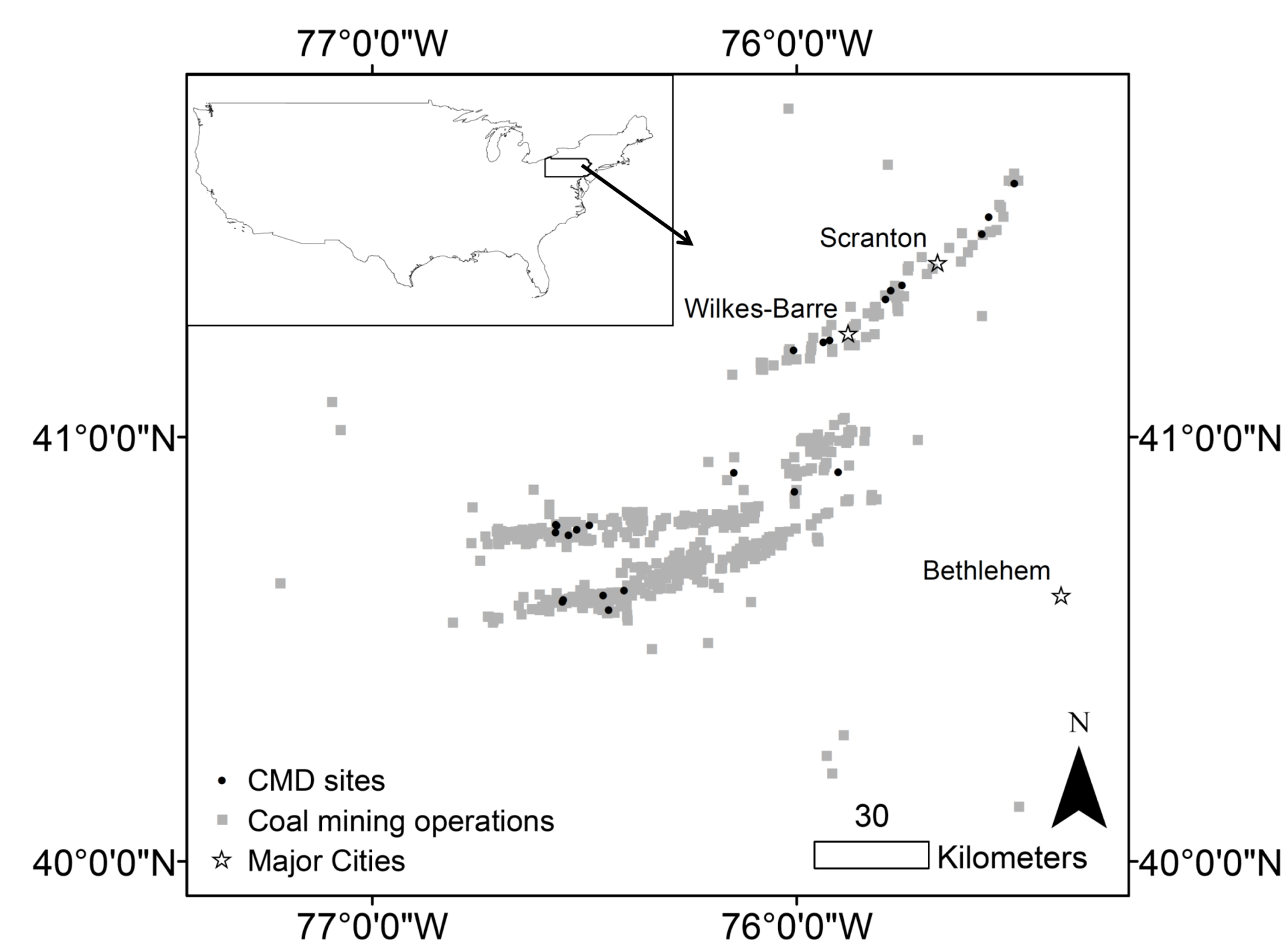


Figure 4: CMD sampling locations

Geochemical modeling was done using Phreeqc version 3.0.0 (Parkhurst and Appelo, 1999) and Geochemist's Workbench Act2 version 3.1 (Bethke, 2000).

How Have Iron, Sulfate, and pH Changed?

Fe and SO_4 concentrations decreased, and pH increased, indicating that the water quality in these CMDs has improved over time (Figure 5). However, according to the statistical analysis, the Fe concentration change between 1999 and 2012 was not statistically significant (Table 1).

The decrease in range of the Fe and SO_4 concentrations may indicate that over time these discharges are becoming more homogenous. This is consistent with the hydrology of the anthracite coalfield in that most discharges are sourced from large underground mine pools that receive water from multiple coal seams (Hornberger et al, 2004).

Over time, these various sources have mixed into a large homogenous body of water, and the data suggests these CMDs are becoming less affected by changing hydrological conditions.

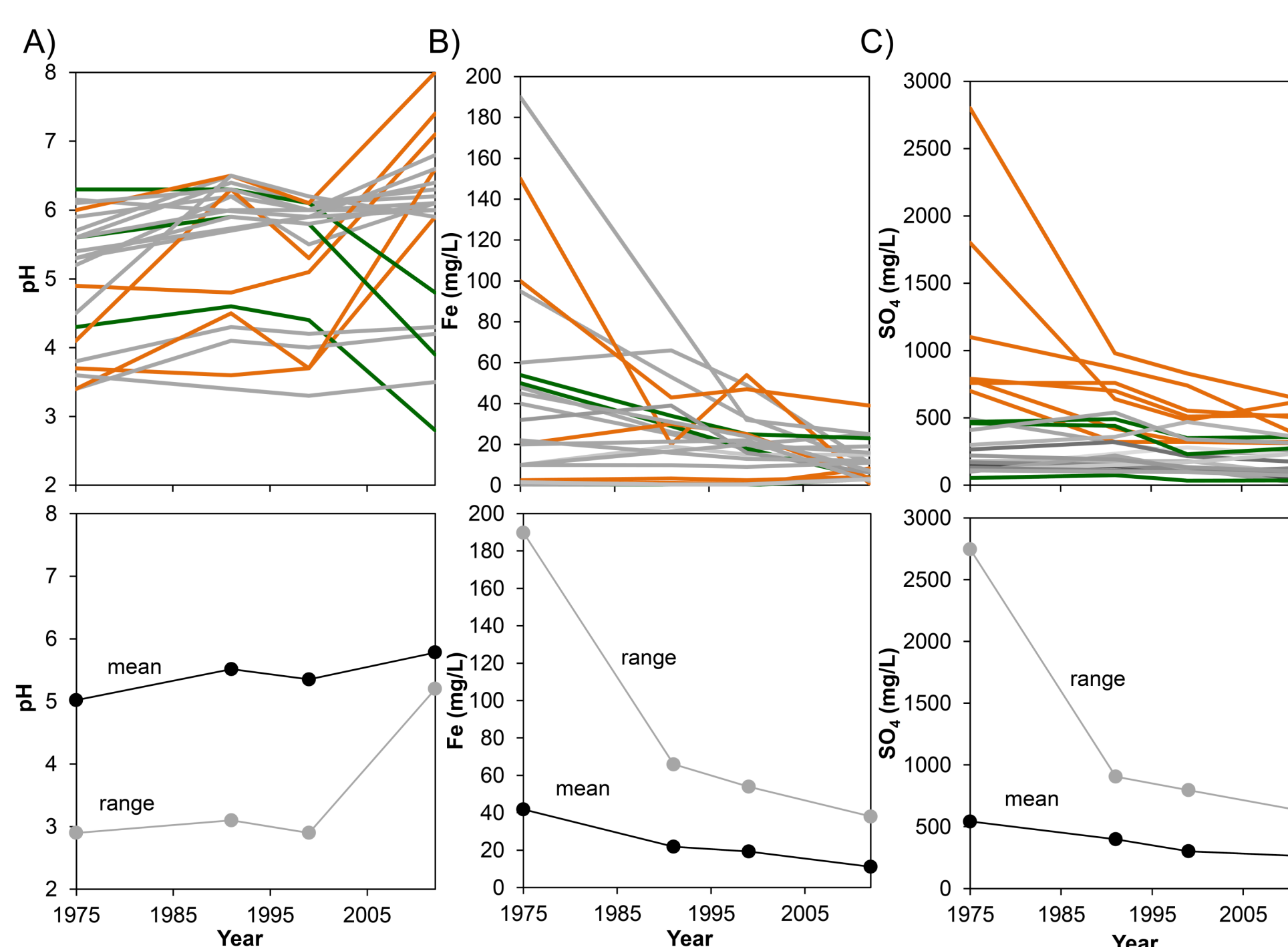


Figure 5: Boxplots of A) pH, B) Fe concentration (mg/L), and C) SO_4 concentration (mg/L) with mean and range values over time. CMDs have been grouped based on pH behavior: large pH increases (orange), modest increases (gray), and decreases (green)

Table 1: Results from a Wilcoxon matched pairs test. Bold values indicate the p-value is less than the significance level 0.05 and the distributions of the two samples are different

Parameter	Time Interval		
	'75-'91	'91-'99	'99-'12
Fe (mg/L)	0.038	0.005	0.709
SO_4 (mg/L)	0.457	0.001	0.048
pH	0.001	0.004	0.038

How Have Discharge and Flux Changed?

There was a decrease in discharge between 1975 and 1991, followed by increases between both 1991 and 1999, and 1999 and 2012 (Figure 6). However, since 1991 none of the changes have been significant (Table 2). Changes in Fe and SO_4 fluxes were not significant after 1991 as well.

This suggests that discharge has an influence on CMD geochemistry. However, studies have also shown that while CMDs are not as susceptible to storm events as streams are (Cravotta, 2008c), CMD receiving streams have been shown to exhibit increases in flow, SO_4 , and metal concentrations during storm events (Nordstrom, 2009). In contrast, the samples in this study were retrieved from the point of discharge and the lack of correlation of Fe to pH indicates they have a large

Fe(II) component which is not controlled by the solubility of hydroxide mineral species or SO_4 complexation.

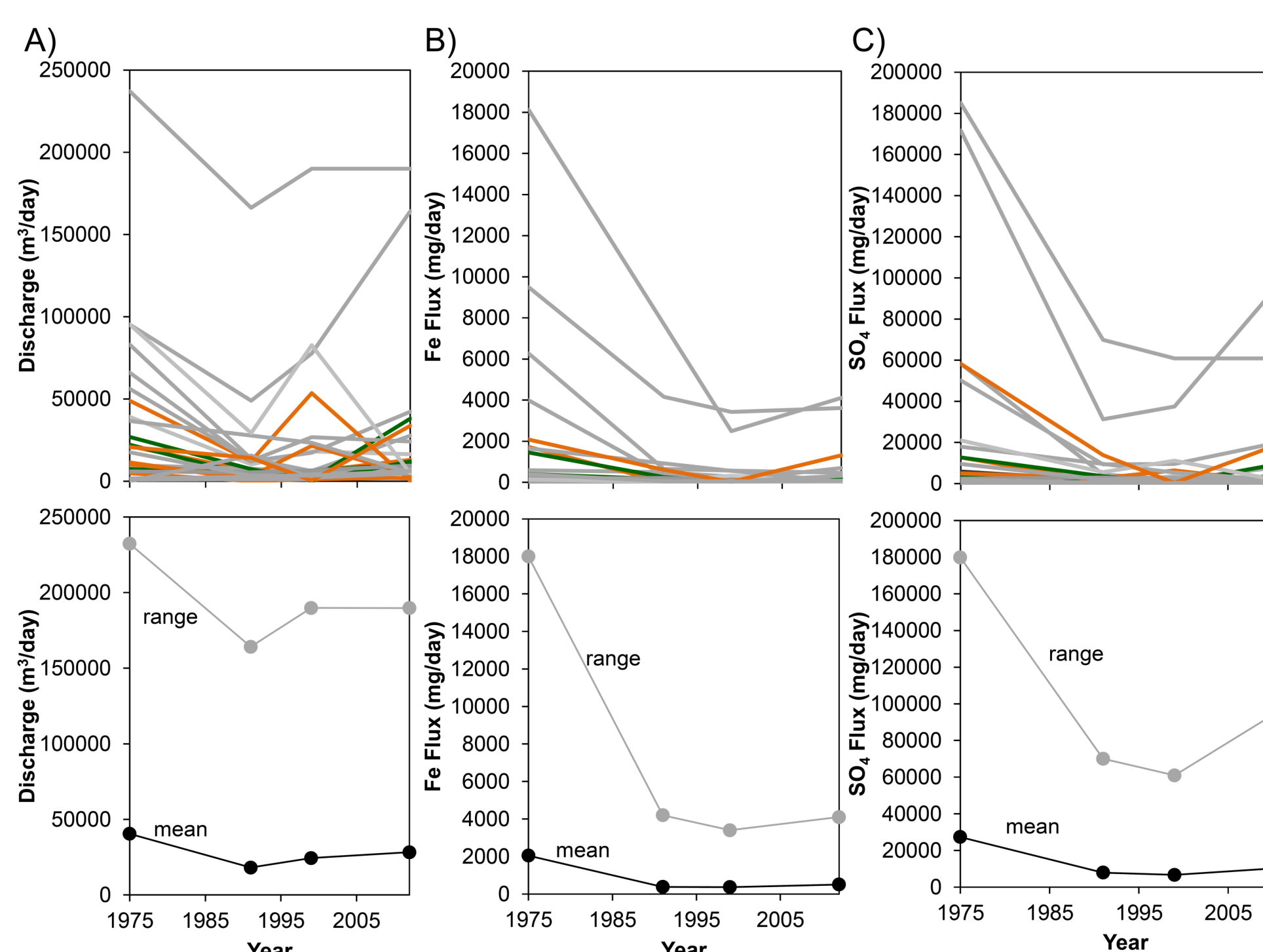


Figure 6: A) Discharge (m^3/day) B) Fe flux (mg/day) and C) SO_4 flux (mg/day) with range and mean values over time. CMDs have been grouped based on pH behavior: large pH increases (orange), modest increases (gray), and decreases (green)

Table 2: Results from a Wilcoxon matched pairs test: bold values indicate p-values less than the significance level 0.05 and that the distributions of the two samples are different

Parameter	Time Interval		
	'75-'91	'91-'99	'99-'12
Discharge (m^3/day)	< 0.0001	0.211	0.144
Fe (mg/day)	0.000	0.952	0.494
SO_4 (mg/day)	0.000	0.837	0.363

Shifts in Mineralogy

According to modeling, 0.05 to 4 moles of pyrite dissolves within 20 years (Figure 7), suggesting that all fresh pyrite surfaces exposed during mining operations would have dissolved quickly, and now these discharges are displaying steady-state dissolution of pyrite embedded in the remaining rock, the dissolution of other Fe phases slowly working their way out of the underground mine pool system, and the transition back to the long-term rock and mineral weathering rates for this landscape.

The lack of correlation between Fe and pH may indicate that the transformation of Fe(II) to Fe(III) is kinetically limited by lack of oxygen, which has been reported as the rate limiting step to mine drainage treatment (Kirby et al., 1999). While Fe(III) precipitation appears to be oversaturated by goethite in almost all samples, schwertmannite, jarosite, and ferrihydrite transition into the more stable goethite over time (España, 2005). A decrease in SO_4 concentrations results in a higher pH required for K-jarosite and schwertmannite saturation.

The increase in pH seen in samples may contribute to an increase in saturation of ferrihydrite, jarosite, and schwertmannite; however, decreases in SO_4 concentration over time may limit the potential for saturation of jarosite and to a lesser extent schwertmannite, in the future (Figure 8). Lower Fe and SO_4 concentrations over time may lead to a decrease in jarosite formation and instead favor the formation of aqueous Fe complexes (Figure 9).

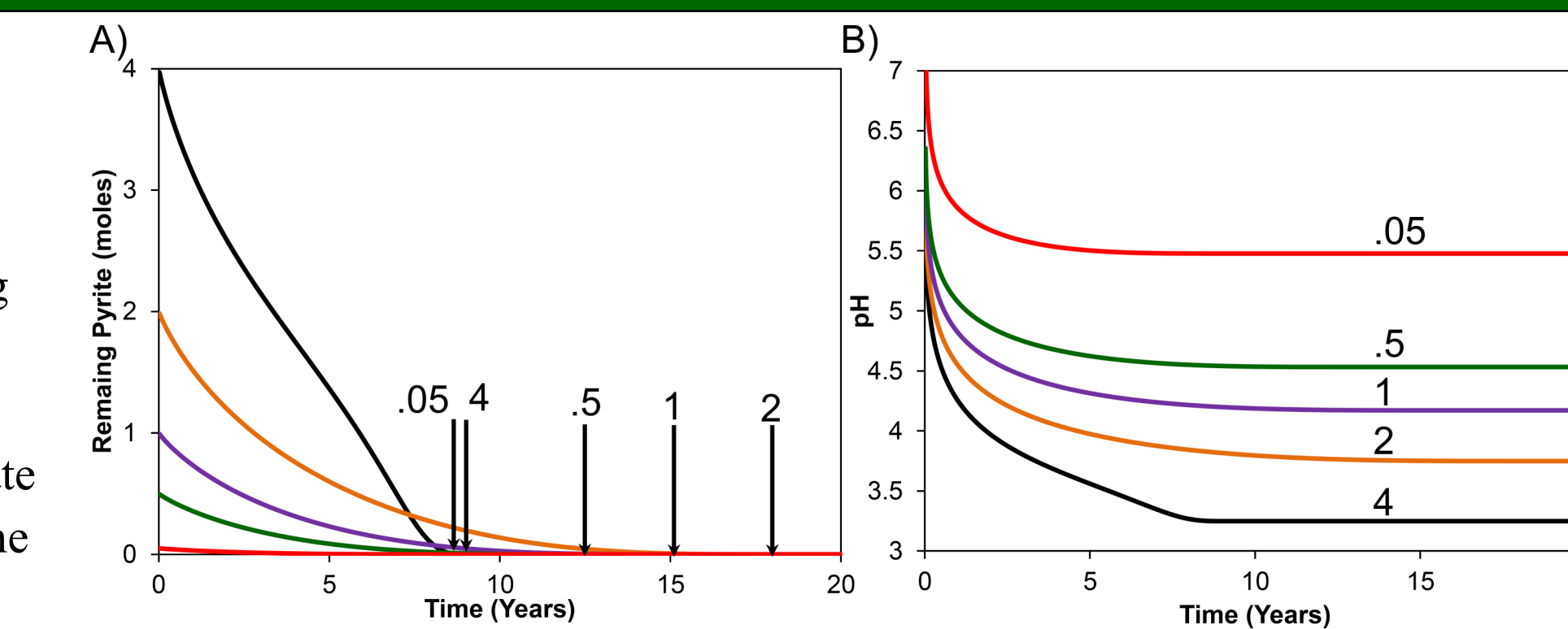


Figure 7: A) Inorganic dissolution of pyrite modeled in Phreeqc for .05, .5, 1, 2, and 4 initial moles of pyrite in 1 L and B) the resulting pH of the solution using dissolution rate equations by Williamson and Rimstidt, 1994

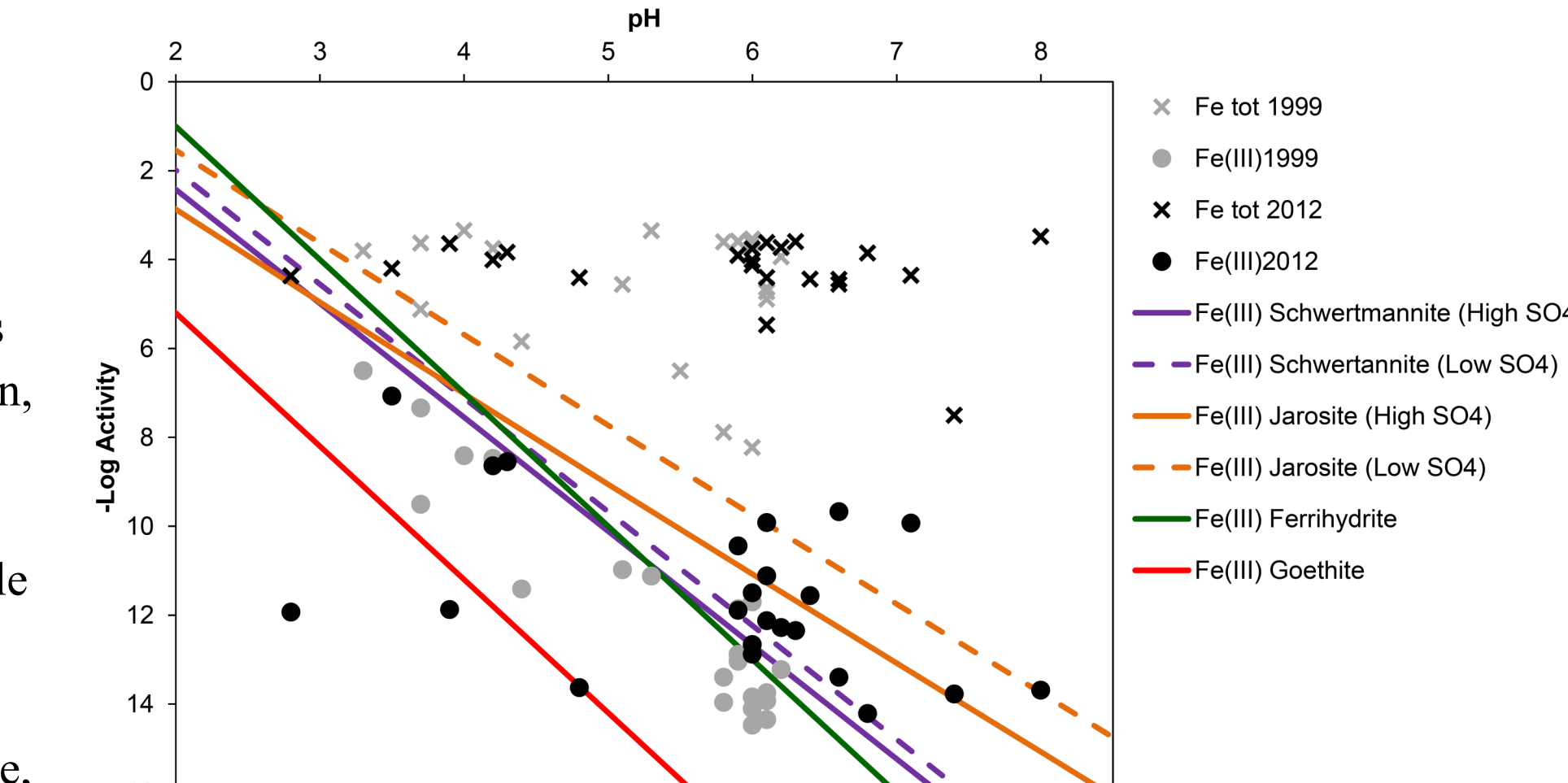


Figure 8: Calculated Fe(III) solubility curves for goethite, ferrihydrite, schwertmannite, and K-jarosite with $-\log$ activity of total Fe (X) and Fe(III) (●) concentrations modeled using Phreeqc for 1999 (gray) and 2012 samples (black)

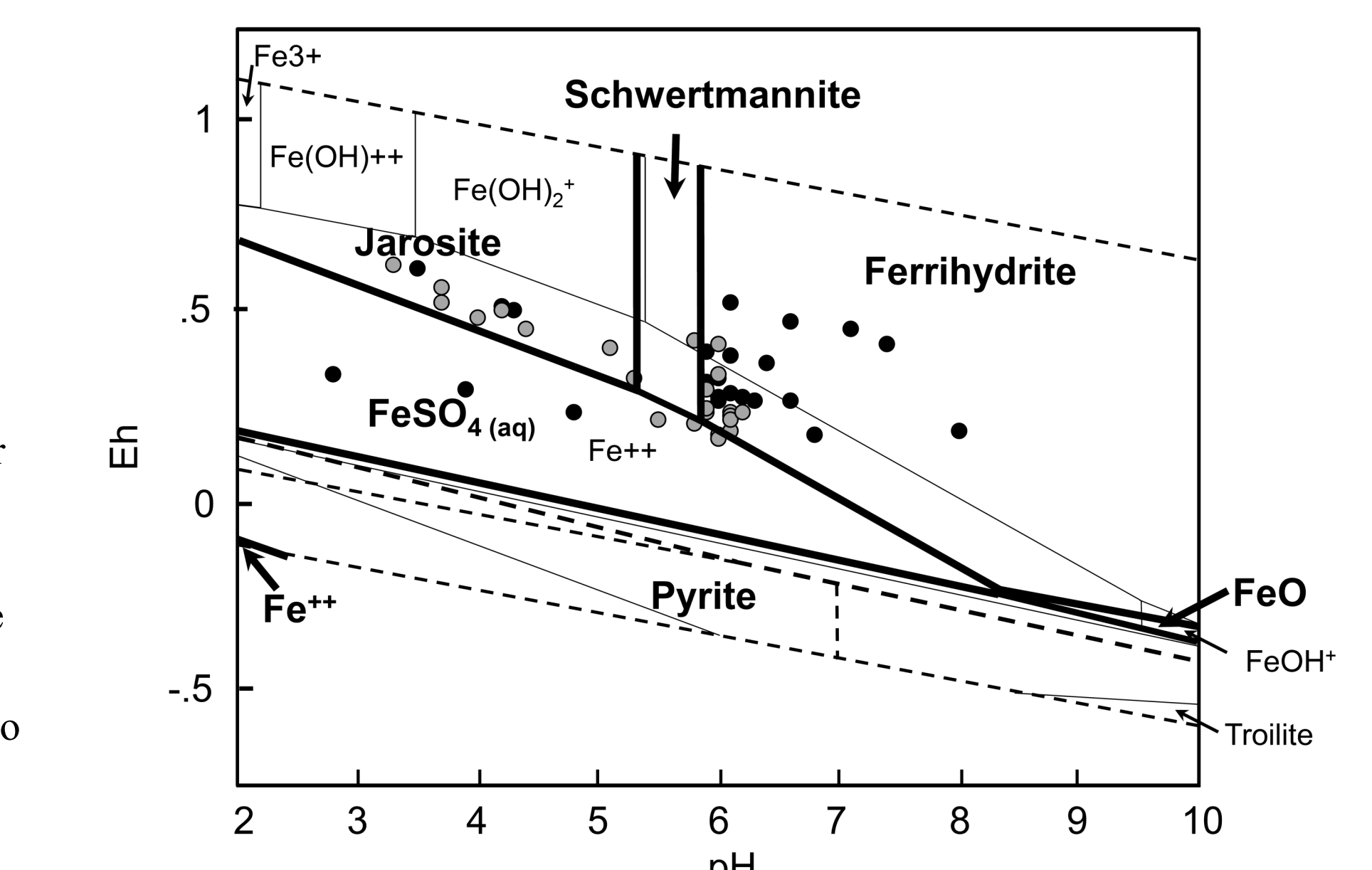


Figure 9: Eh pH diagram of Fe(III) dominant species fields calculated by Geochemist's Workbench Act2 with results from the 2012 (●) and 1999 (●) samples. Bold lines refer to elevated Fe(III) and SO_4 concentrations (pK = 3.01 and 2.06, respectively) while thin lines refer to low Fe(III) and SO_4 concentrations (pK = 6.06 and 4.05, respectively) at 25 °C with pK K+ = 3.67

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