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Quantification of acid loads and delineation of hydrochemical facies at a phreatic mine spoil aquifer

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**QUANTIFICATION OF ACID LOADS AND DELINEATION OF
HYDROCHEMICAL FACIES AT A PHREATIC MINE SPOIL AQUIFER**

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Thesis submitted
to the Eberly College of Arts and Sciences
at West Virginia University

in partial fulfillment of the requirements for the degree of

Masters of Science In
Geology

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Keywords: geochemistry, hydrogeology, coal, acid, hydrochemical facies, cubic spline

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ABSTRACT

QUANTIFICATION OF ACID LOADS AND DELINEATION OF HYDROCHEMICAL FACIES AT A PHREATIC MINE SPOIL AQUIFER

Mitchell A. McAdoo

Acid mine drainage geochemistry and *in situ* alkaline injection were investigated at the DLM coal mine, Alton West Virginia. These included spatial and temporal investigations into hydrochemical controls that were initiated with reclamation efforts. Approaches included the delineation of hydrochemical facies and analysis of time series data to develop a methodology for estimating acid loads.

Results of agglomerative hierarchical clustering were mapped to demonstrate spatial variations in response to reclamation efforts over time. Spatial patterns were determined and indicate that aquifer chemistry continued to evolve during the study period. Results confirmed that injection of alkalinity into the aquifer effected acid producing and neutralizing reactions in monitoring wells down gradient from the injection site.

Low-frequency water chemistry was interpolated with natural cubic splines, resampled and multiplied by high-frequency flow to produce estimates of acid loads at high-frequency. Cross-correlation between high-frequency and low-frequency datasets showed an exponential decrease in correlation as the number of days between flow measurements increased. Result confirmed that natural cubic splines can be used for resampling hydrochemical time series data and the frequency at which flow is measured limits the accuracy of acid load estimates.

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1: Introduction to the DLM Site and Surface Mine Drainage Geochemistry

1.1 Introduction

Surface mining for coal is prevalent throughout West Virginia and is an integral part of its economy. Surface mining can have adverse effects on downstream water quality and can change the hydrologic characteristics of the mined area (Kleinmann *et al*, 2000). After the coal is mined, the surface topography of the mine is required to be restored to its approximate original contour. To do this, mine operators use overburden removed during mining. These fills, often referred to as mine-spoil aquifers, can become resaturated and in some cases produce acidic discharges (Donovan, 1998). Aquifers of this type pose unique hydrogeological challenges due to their extreme degree of heterogeneity and unpredictable composition.

The hydraulic gradient and groundwater flow direction of these aquifers are driven primarily by the slope of the pit floor. Hydraulic conductivity and other hydrogeologic parameters vary spatially as well as temporally due to heterogeneity of fill material, subsidence and chemical alteration within the aquifer (Hawkins, 2004). Understanding the distribution of heterogeneity and groundwater flow can help in the formulation of effective remediation projects (Callaghan *et al*, 2000).

Among the strategies for the control and remediation of acid mine drainage (AMD), active methods are more widespread than passive ones. Active treatment systems commonly utilize chemicals such as lime or sodium hydroxide to raise pH and reduce metals concentrations. Drawbacks of active remediation include continuous maintenance and the need to handle sludge produced by the precipitation of metals. Passive systems

include the use of engineered or natural wetlands and often have high initial costs (Johnson and Hallberg, 2005).

One method to reduce sludge management problems is to employ *in situ* remediation techniques which introduce chemicals directly into the acid-producing material. There are two standard approaches to *in situ* remediation. One involves application of chemicals that reduce the amount of acid produced by inhibiting pyrite oxidation. The other involves the injection of alkalinity to precipitate metals directly within the aquifer (Werner *et al*, 2008). These methods can reduce treatment costs and environmental problems associated with sludge disposal. *In situ* remediation requires a firm understanding of the aquifers hydrogeologic framework as well as its baseline chemical composition (Canty and Everett, 2006).

1.2 Study Area and Remediation History

The DLM bond-forfeiture site, also known as the Alton project, is located in Upshur County, West Virginia (Fig. 1-1). It has been the focus of continued acid mine drainage remediation by the West Virginia Department of Environmental Protection (WVDEP) for the past 26 years. Coal of the Lower Kittanning seam (Pennsylvanian Age) was mined at this site from 1976 to 1983 (Sturm Environmental Services, 1986). The site is named after the DLM Coal Corporation, which forfeited its assets seized to the West Virginia Department of Energy in 1985. It is a large abandoned surface mine with three benches (X bench, Y bench, Z bench) that have been back filled with waste rock from overburden (Neumann, 2013).

The Alton project's three mine spoil aquifers (Fig. 1-2) have undergone many years of hydrogeochemical evolution and currently discharge AMD that is characteristically formed due to pyrite oxidation and aluminosilicate mineral dissolution in mine spoil. Multiple approaches have been used to neutralize the acidity, with the most successful being active treatment techniques. The aquifers are currently treated with sodium hydroxide at their discharges, producing sludge that is settled in a series of ponds. Sludge is pumped from the settling ponds to disposal ponds (Fig. 1-3) in the central portion of the spoil piles (Donovan *et al.*, 1997).

The spoil aquifer on which this study has focused, the X bench (Ketchum, 1998), comprises 97 acres. Multiple groundwater observation wells were drilled on the site, and trenches were excavated for injection of alkalinity (Fig. 1-4) at different times during the project's history. Water flows northwest from its recharge point until it discharges from a series of springs on the west side of the aquifer (Fig. 1-5).

In situ reclamation attempts began on the X bench in 1983 with the installation of three trenches filled with limestone and sodium carbonate briquettes. The trenches were installed up gradient from Springs C1 and C2 but failed to yield effective acid neutralization (Caruccio *et al.*, 1984). Following successful lime slurry experiments on the Y Bench in 1998 (Daly, 1998), injection of alkalinity began at the X bench with Trench T10 in a series of doses throughout 2000 (Neumann, 2013). Lime slurry injection resumed in 2010 with trenches T6, T7, T9 and T11 (Table 1-1). From 2000 to 2011 over 270 tons of lime was used for induced alkaline recharge into the X bench.

Figure 1-1: Map showing the location of the DLM site

Figure 1-2: Schematic cross section of a typical mine-spoil aquifer, after Daly (1998).

The alkaline injection process for these trenches utilized settling pond water pumped up to a mixing area near each trench where hydrated lime was dissolved to create a lime slurry (Fig. 1-6). In 2000 and early 2010 slurries were mixed by intermittent dumping from the bucket of either a bobcat or a front-end loader. Later, after December 2010, mixing was done using a continuous pneumatic jet of lime affording much more rapid mixing. Slurry flowed a short distance from here into a deep (5 m x 3 m x 15 m) infiltration trench cut with a long arm bucket excavator. The lime slurry infiltrated into macropores at the bottom of these trenches and was flushed deeper into the aquifer using clear settling pond water pumped into the trench for a number of hours after mixing.

1.3 Relevant previous research

Numerous hydrological and geochemical studies have focused on the X Bench as well as at similar mine-spoil aquifers in the region (Sturm, 1986; Frysinger, 1995; Maher, 1996; Avery, 1997; Donovan *et al.*, 1997; Ketchum, 1998; Ketchum *et al.*, 2000; Neuman, 2013). *In situ* chemical treatment of sodium hydroxide was attempted in numerous investigations (Aljoe and Hawkins, 1993; Canty and Everett, 2006; Werner *et al.*, 2008). Each study concluded that detailed hydrogeological and geochemical investigations should be conducted prior to injections.

Hydrogeological investigations of the X bench by Maher (1996) show heterogeneity in the aquifer in excess of three orders of magnitude. Frysinger (1995) and Avery (1997) used a preferred-flow-path conceptual model to simulate groundwater flow.

Figure 1-3: (1) The Cutright ponds, (2) sludge disposal pond and (3) Plant Hollow ponds at the DLM X bench. The red boundary represents the extent of the aquifer.

Figure 1-4: Map showing current well and trench locations at the DLM X bench

Figure 1-5: Map showing spring locations of the X bench and the extent of the aquifer

Date	Trench	Lime (tons)
7/17/2000	T10	6.1
7/24/2000	T10	6.1
8/7/2000	T10	7.6
8/14/2000	T10	7.6
8/21/2000	T10	6.1
8/28/2000	T10	6.1
8/30/2000	T10	3.0
8/31/2000	T10	6.1
9/5/2000	T10	6.1
9/8/2000	T10	3.0
9/11/2000	T10	6.1
9/12/2000	T10	3.0
9/20/2000	T10	6.1
9/25/2000	T10	6.1
9/20/2010	T6	9.0
9/21/2010	T7	10.0
10/18/2010	T9	6.0
10/19/2010	T11	6.0
10/27/2010	T6	12.5
10/27/2010	T11	12.5
3/28/2011	T6	12.0
3/28/2011	T11	12.0
4/27/2011	T7	12.5
4/27/2011	T9	12.5
8/23/2011	T9	12.0
8/23/2011	T7	12.0
8/29/2011	T6	12.0
8/29/2011	T11	12.0
10/31/2011	T7	24.5
12/21/2011	T6	14.0
Total		270.6

Table 1-1: Lime slurry injection dates and amounts

Figure 1-6: (1) View of the DLM X bench from south to north, (2) the mixing trench at T6, (3) the connector ditch at T6, (4) the infiltration trench T6.

Sincock (1998) found preferred flow paths in mine-spoil aquifers are similar to the interconnected workings of karst aquifers. Hawkins (2004) concluded that the driving force for groundwater flow in a mine-spoil aquifer is the geometry of the pit floor.

Donovan *et al* (1997) characterized the geochemistry of the X Bench and noted the effect of alkaline recharge from the sludge disposal pond. They concluded that the flux of alkalinity from sludge disposed in the pond was insufficient to neutralize the acidity generated in the aquifer. Daly (1998) conducted a geochemical investigation of the Y bench at the DLM site, where hydrated lime ($\text{Ca}(\text{OH})_2$) slurry was used to flood a low-lying sludge disposal area. While neutralization of acid and precipitation of metals was observed within the aquifer, the plume of alkalinity did not extend to the aquifer's discharges. This was attributed to rapid precipitation of calcite as a result of increased alkalinity and elevated CO_2 pressures. Barker (1997) monitored response to *in situ* injections at a West Virginia spoil aquifer into which sodium hydroxide was injected through wells. Carbonate precipitation, induced by CO_2 -induced carbonation of alkalinity, was also observed here. Barker also discussed how reaction products formed during injections play a role in buffering acidity and establishing pH plateaus.

1.4 Background

1.4.1 Geochemistry of Acid Mine Drainage

Due to heterogeneity in geochemical conditions found at coal mines, groundwater can vary both spatially and temporally (Cravotta and Hilgar, 2000). The initiation of acid conditions associated with coal mining comes from the oxidation of pyrite. The complex process, which involves chemical and biological reactions, begins with the oxidation of

pyrite by oxygen in the presence of water (Blowes *et al*, 2003). The products of the reaction are one mole of Fe^{2+} , two moles of SO_4^{2-} and two moles of H^+ (Eq. 1).

After the dissolution of pyrite, Fe^{2+} may be further oxidized to Fe^{3+} (Eq. 2).

Fe^{3+} can then further oxidize pyrite (Eq. 3) to produce 16 moles of H^+ or it can precipitate as a number of different hydrous ferric oxides (HFO). These include amorphous goethite, ferrihydrite and schwertmannite (Nordstrom, 2011).

Neutralization of acidity produced by pyrite oxidation and metal hydrolysis involves a series of reactions with mineral phases (Blowes and Ptacek, 1994; Jurjovec *et al.*, 2002). The sequence of phases may vary depending on the neutralizing minerals present, but generally begins with carbonate minerals which buffer the system to an approximate pH of 6.0. Equilibrium of water chemistry with amorphous aluminum hydroxide or gibbsite will buffer the pH between 4.0 and 4.5. At lower levels of alkalinity, hydrous ferric oxides such as goethite or ferrihydrite are favored and will maintain a pH of 2.5 to 3.5.

Aluminosilicate minerals such as chlorite, illite, smectite, kaolinite, muscovite and biotite may dissolve to some extent throughout the neutralization process (Blowes *et al.*, 2003). Silicate dissolution occurs most rapidly at lower pH and increases

concentrations of Al^{3+} , K^+ , Mg^{2+} , Ca^{2+} or Mn^{2+} . Although dissolution initially consumes H^+ , this hydrogen-ion acidity may be realized later in the water evolution through hydrolysis of Al^{3+} and Mn^{2+} to form precipitates (Rose and Cravotta, 1998).

Metal-laden water contains high concentrations of Fe^{2+} , Fe^{3+} , Al^{3+} and Mn^{2+} which contribute to the total aqueous acidity. Acidity is defined as the equivalent sum of acids titratable with a strong base (Stumm and Morgan, 1996). In metal rich mine water of near-neutral pH, metals can decrease the pH and add to the hydrogen-ion acidity upon hydrolysis (Kirby and Cravotta, 2005). Therefore, Equation 5 is used to incorporate acidity from metals and hydrogen where metal concentrations are in mg/l (Rose and Cravotta, 1998).

$$Acidity \left(\frac{mg}{l} \text{ as } CaCO_3 \right) = 50 \left[1000(10^{-pH}) + \frac{[2(Fe^{2+}) + 3(Fe^{3+})]}{56} + \frac{2(Mn)}{55} + \frac{3(Al)}{27} \right] \quad (5)$$

1.4.2 Chemistry of Lime Slurry

Hydrated lime ($Ca(OH)_2$), or portlandite, is a common alkaline mineral used for the neutralization of acid mine drainage (Johnson and Hallberg, 2005). It is produced by Hydration of CaO , formed by combustion of calcite (Whittington, 1996).

With enough water, $Ca(OH)_2$ is dissolved with two moles of OH^- and one mole of Ca^{2+} being released.

When added to AMD, strong caustic alkalinity (OH^-) increases pH and precipitates metals, neutralizing their acidity.

The solubility product (K_{sp}) of Ca(OH)_2 (4.68×10^{-6}) indicates it is slightly soluble (Whittington, 1996). Solubility may be increased or decreased depending on impurities present in solution. For example, SO_4^{2-} is known to dramatically decrease solubility while it can be doubled by organics. With alkaline injection, it is useful to dissolve the greatest amount of lime possible for incorporation of alkalinity into the aquifer. Therefore, efficiency would be dependent on effective dosing rates based on hydrated lime dissolution in a particular solution.

1.5 Organization of the Thesis

This document is divided into four sections with the first section covering study area history and background information. The second section includes an investigation into the DLM X bench to understand the post mining hydrochemical evolution of the mine-spoil. Section three includes the development of a methodology for estimating acid loads using natural cubic splines. Sections two and three have individual methods, results and conclusions and are treated as individual papers within the thesis. The final section outlines overall conclusions and recommendations for future research.

2: Delineation of Hydrochemical Facies at an Acid-Producing Mine-Spoil Aquifer

Abstract

Estimating post mining water quality at surface mines is complex, and influenced by the hydrochemical evolution of the mine spoil. Agglomerative hierarchical clustering was used to group hydrochemistry of the DLM X bench sampled in 1994, 1999, 2010 and 2012. Results were mapped to demonstrate spatial variations in response to reclamation attempts over time. Spatial patterns were discerned over multiple sampling periods and indicated that aquifer chemistry has continued to evolve over this period. The results show that induced alkaline recharge temporarily neutralized acidity and can have lasting effects on groundwater chemistry in mine spoil.

2.1 Introduction

The hydrochemical evolution of acid producing mine spoils has important implications for post mining water treatment (Cravotta and Hilgar, 2000). Chemical evolution of discharge from surface mines is dependent on many factors including overburden lithology. Calcareous lithologic units have greater acid neutralizing potential for post mining reclamation (Callaghan *et al.*, 2000). Pyrite (FeS_2) dissolution is primarily responsible for the initial acid production in coal overburden (Brady *et al.*, 2000). Although this mineral makes up only a small percentage of the mineralogy, it has a significant impact on water chemistry in the absence of neutralizing minerals. Therefore, the presence of carbonate minerals and mineralogy of the overburden are the most important factors controlling post mining water quality (Kleinmann *et al.*, 2000).

Mining reclamation practices and special handling of acid producing materials can also affect long term water quality. Alkaline amendments, such as limestone, are often used to increase the neutralizing potential of mine spoil (Kleinmann *et al.*, 2000). Applying undesirable mining practices such as improper handling of acid producing material and non-concurrent reclamation can further degrade post mining water quality (Callaghan *et al.*, 2000).

Mapping of “hydrochemical facies” is a method used to synthesize chemical characteristics of similar waters based on common geochemical processes (Back, 1966). Progressive reactions along groundwater flow paths can create spatial patterns in water chemistry useful in determining geochemical and transport processes (Freeze and Cherry, 1979; Glynn and Plummer, 2005). Statistical methods have been used to delineate geochemically-similar regions in aquifers and can be useful in determining chemical change over time (Mathes and Rasmussen, 2006).

2.2 Study Area and Background

To examine the spatial and temporal geochemical evolution of groundwater from the DLM X bench, a graphical time series was created for 1994 to 2012. Water samples were collected by different investigators from groundwater monitoring wells (Fig. 1-4) on the following dates 10/19/1994, 11/4/1994, 6/1/1999, 6/2/1999, 6/17/2010, 8/6/2010, 10/13/2012 and 10/25/2012. The 1994 samples indicated a complex system of preferential flow paths, acid-producing and acid-buffering reactions (Donovan *et al.*, 1996). The 2010 samples were interpreted to reflect a weathering environment that was

closed to atmospheric CO₂. Following alkaline injections occurring in 2000 (Table 1-1), improved water chemistry was observed in the vicinity of Trench T10 (Neuman, 2010).

Many protocols exist for graphical representation of geochemical data (Zaporozec, 1972). Standard plots used for displaying natural waters (i.e. Piper diagram) are less useful for acid-sulfate water (Kirby and Cravotta, 2005). Additionally, acid mine drainage can exhibit high concentrations of other cations due to acid buffering reactions that occur throughout the flow system (Blowes and Ptacek, 1994). Due to the complexity and number of important variables in these waters, a variation of the star plot (R Core Team, 2012) was chosen to graphically represent geochemistry.

2.3 Purpose and Objectives

The purpose of this investigation was to examine the spatial and temporal variability in groundwater chemistry at the DLM X bench from 1994 to 2012 and interpret groundwater evolution in response to remediation. It was chosen because it has been the focus of a variety of remediation efforts including the injection of lime slurry (Sturm, 1986; Avery, 1997; Donovan *et al.*, 1997; Neuman, 2013).

Specific objectives include:

1. Classification into clusters of water chemical analysis across all four sampling periods.
2. Mapping of hydrochemical facies for the four sampling periods.
3. Graphical representation of water chemical evolution during the study period.

2.4 Methodology

2.4.1 Classification of Water Types

Agglomerative hierarchical clustering by Ward's Minimum Variance Method (Han and Kamber, 2001) was used to classify groups according to water chemistry over different sampling periods. Cations used in the cluster analysis included Ca, Mg, Al, total Fe, and total Mn. Anions used for the cluster analysis included alkalinity and SO₄. Cation concentrations were determined by inductively coupled plasma-atomic emission spectrometry (USEPA, 1994) and SO₄ by ion chromatography (USEPA, 1993). Alkalinity was measured in the field by the H₂SO₄ standard titration method (ASTM, 2006). The measured values of all analytes were converted to units of milliequivalent per liter (meq/l) prior to clustering, and pH was used as measured in the field. Lab and field chemistry for all samples can be found in Appendix A.

Agglomerative hierarchical clustering is a “bottom-up” approach in which objects are sequentially merged into larger and larger clusters based on dissimilarity (Han and Kamber, 2001). Measurements were standardized by z-scores and Euclidean distance was used for dissimilarity between objects. Cluster analysis and dendrogram creation were performed using the `hclust()` function in R (R Core Team, 2012). An example script used for cluster analysis is presented in Appendix B. Standard boxplots were used to visualize the distribution of chemical constituents within clusters for normality and outliers (Han and Kamber, 2001). An example script for the creation of boxplots in R is found in Appendix B.

2.4.2 Graphical Representation of Water Chemistry

Star plots were used to graphically display chemical compositions of individual samples. The customizable stars() function in R was employed because of its ability of display any number of parameters (Murrell, 2006). Star plots created in this study incorporate pH, alkalinity, SO₄, Ca, Mg, Al, Fe, and Mn, the major chemical constituents in the aquifer. These plots, along with the sample's cluster group, were compiled for all available sampling periods.

Star plots display multiple variables for a single observation with each segment of the star representing one variable (Murrell, 2006). Chemical data were arranged into rows representing individual sample locations and columns representing chemical constituents. Each sample was identified by "X" (i.e., X-Bench), a 2 digit well I.D. and a 2 digit year ID. These data were imported into R as a matrix, normalized between 0 and 1, and the stars() function was applied (R Core Team, 2012). An example of script for star plots in R is located in Appendix B.

2.5 Results

2.5.1 Classification of Clusters

The results of cluster analysis are graphically displayed by the dendrogram in Figure 2-1 and four different clusters were discriminated into groups. Figure 2-2 shows box plots for pH, alkalinity, and ion concentration within different cluster groups. The box represents the interquartile range from the 25th to 75th percentile, with the middle line representing the 50th percentile (median). The whiskers represent the high and low values

that fall within 1.5 times the interquartile range. Extreme values that fall outside the 1.5 X interquartile range are outliers and represented by dots (Han and Kamber, 2001).

Table 2-1 contains the average values of the four groups determined from cluster analysis and a brief description of their chemical compositions. Group 1 exhibits the highest pH, measurable alkalinity and also the lowest values for metals and sulfate. Group 2 has a low pH and little to no alkalinity. It also has low concentrations of metals, Ca, Mg and SO₄. Group 3 has similar pH and alkalinity as Group 2, but exhibits higher values for Ca, Mg and SO₄. Group 4 has the lowest pH and no measurable alkalinity. It also exhibits the highest concentrations for metals, Ca, Mg and SO₄.

2.5.2 Spatial Interpretation of Hydrochemical Facies

Hydrochemical facies created using the results of cluster analysis were mapped to examine spatial variations over time in response to reclamation attempts (Figure 2-3). The legend for this figure shows (a) the cluster group (symbol) and (b) the well ID (label in symbol). The 23 samples taken in 1994 are uniformly distributed across the aquifer, with the largest gap occurring in the south (Figure 2-3). The chemistry is dominated by Groups 3 and 4 with two anomalies (X24 and X15) from Group 1 showing localized sources of alkalinity. The 17 samples taken in 1999 (Figure 2-3) are more concentrated at the northern part of the aquifer. The predominant group in 1999 was Group 3, though Groups 1 and 2 increased in frequency from 1994. Localized areas of alkalinity occur at wells X9, X15 and X44. The 28 samples taken in 2010 are widely distributed although no wells were sampled near the sludge pond or on the west border. The predominant groups in 2010 were 1 and 2, with a higher frequency in Group 1 than in previous sampling

periods. In 2012, 16 samples were collected around and down gradient from areas that received alkaline injections in 2010 and 2011 (Table 1-1). Gaps in sampling distribution occur in the northeast, southeast and west areas of the aquifer. The predominant groups in 2012 are 1 and 3, which suggests that regions of alkaline and acidic water coexist in the aquifer.

2.5.2 Graphical Representation of Water Chemistry

Star plots were used as a visual times series for chemical evolution over different sampling dates (Fig. 2-4). Group 4 (highest metals and lowest pH) is not present after 1999. Some wells shifted groups between sampling dates; for example, X7 changed from Group 2 in 2010 to Group 3 in 2012. Also, Ca had its highest concentrations in 2012 and lowest in 2010. In 1994 and 1999, Ca was similar in concentration to Mg but greatly exceeded it in 2012. It is interpreted that these high Ca concentrations relate to reclamation activities between 2010 -2012.

2.6 Summary and Conclusion

Four distinct groups were discriminated based on cluster analysis of water chemistry (pH, alkalinity, Ca, Mg, SO₄, Al, Fe, and Mn). The clusters were used to map hydrochemical facies, analogous to the method of Robins *et al.* (2005). Spatial patterns over multiple sampling periods indicate that aquifer chemistry has continued to evolve over this period.

Figure 2-1: Dendrogram interpreted from cluster analysis with cluster groups

Figure 2-2: Box plots showing chemistry of cluster centroids by group. All concentrations are in meq/l and pH is in standard units.

Group	Average (meq/l)		Description
1	pH	6.55	Group 1 has the highest pH of all clusters. It has measurable alkalinity, low mineralization and low values for metal cations.
	Alk	2.18	
	Fe	0.38	
	Al	0.06	
	Mn	0.12	
	Ca	2.92	
	Mg	2.99	
	SO4	6.52	
2	pH	3.88	Group 2 is characterized by low mineralization and metals. What sets it apart from Group 1 is its low pH negligible alkalinity.
	Alk	0.04	
	Fe	0.19	
	Al	1.39	
	Mn	0.23	
	Ca	1.95	
	Mg	2.43	
	SO4	7.35	
3	pH	3.49	Group 3 is similar to Group 2 but has a greater mineralized component.
	Alk	0.18	
	Fe	1.06	
	Al	2.78	
	Mn	0.56	
	Ca	6.29	
	Mg	7.59	
	SO4	18.33	
4	pH	3.43	Group 4 is characterized by low pH and has the highest values for acidity, calcium, magnesium, and sulfate.
	Alk	0.00	
	Fe	3.52	
	Al	8.33	
	Mn	1.26	
	Ca	10.28	
	Mg	14.95	
	SO4	32.27	

Table 2-1: Description of cluster groups. pH is in standard units and all analytes are in meq/l.

Figure 2-3: Hydrochemical facies of the DLM X bench

Figure 2-4: Star plot matrix with cluster group number in the lower right corner

During 1994 and 1999, alkalinity was found at only a few locations and ascribed to either (a) dispersion of alkaline sludge leaking from the disposal pond (Frysinger, 1995; Donovan *et al.*, 1997), or (b) limestone amendment on the pit floor during mining and site reclamation (Kleinmann *et al.*, 2000). Clearly, alkalinity and pH substantially increased in a number of wells at some point after 1999, when Group 1 waters (highest pH and alkalinity) became more numerous and, in some portions of the spoil, ubiquitous. Wells in this group (X16, X17, X18, and X42) are especially prominent in the vicinity of the T10 trench, which received an estimated 79 tons of lime in 2000 (Neumann, 2013). These wells showed increases in pH and alkalinity as well as decreases in metals (Fig. 2-4).

Trench T7 received 4 lime slurry injections in 2010 and 2011 (Table 1-1) which influenced down gradient wells X9, X26 and X52. The highest values for pH, alkalinity, and Ca were observed at these wells in 2012, and equilibrium calculations show saturation with calcite (CaCO_3) and brucite (Mg(OH)_2) in X9. Although X52 remained in the same cluster group from 2010 to 2012, it underwent a large increase in Ca (Fig. 2-4). The results show that the alkaline injections of 2010-2011 influenced groundwater chemistry in downgradient wells.

3: Quantification of Acid Loads Discharging from a Phreatic Mine-Spoil Aquifer

Abstract

Quantifying acid loads is an important step in development and implementation of acid mine drainage remediation projects. This investigation develops a methodology for estimating acid loads discharging from surface mines using natural cubic splines. Low-frequency chemistry was interpolated, resampled and multiplied by higher-frequency datalogger-based flow measurements to produce high-frequency acid load datasets at five discharges. Cross-correlation of high-frequency datasets with sequentially lower-frequency datasets showed an exponential decrease in correlation as the number of days between flow measurements was increased by resampling. Results show that this method is useful for increasing the accuracy of acid load estimates using continuously-sampled flow measurements and automated data collection equipment.

3.1 Introduction

The accurate determination of acidity and acid loads discharging from surface-mine backfills, is a practical tool for treatment and remediation. Acid-producing constituents that require treatment in addition to hydrogen ion include iron, aluminum and manganese (Skousen *et al*, 2000; Ziemkiewicz *et al*, 2003; Canty and Everet, 2006). The interval for sampling of water chemistry to estimate loads depends on the specific project requirements and desired accuracy, but generally ranges from daily to quarterly (Cravotta and Hilgar, 2000). Single samples cannot describe variations in geochemistry

related to seasonality. More informed estimates can be made only with higher frequency data for both flow and chemistry.

Acid loads (mg/s) are calculated by multiplying acidity (mg/l as CaCO_3) with flow (l/s). Very high-frequency flow estimates may be straightforwardly obtained with data-logger pressure transducers (Weight, 2004). High -frequency flow data is needed because flows may demonstrate higher variability than concentrations (Cravotta and Hilgar, 2000). Resampling the lower frequency chemistry to the frequency of the flows allows calculation of high-frequency acid loads.

3.2 Study Area and Background

Hydrochemical data were collected at the DLM X bench for this study from July 2010 to October 2012. The DLM X bench was chosen because it produces acid mine drainage and its flows are easily quantified. Five Parshall flumes equipped with pressure transducers (Fig. 1-4) were installed and used to estimate discharge from the aquifer. Aqueous chemistry was sampled at the flumes and acidity was calculated from analytical results.

Mathematical approximations can be used to create high frequency datasets to accommodate inconsistent sampling routines. Cubic splines have been successfully utilized in a number of applications (Bickley, 1968; Dougherty *et al*, 1989; Cao *et al*, 2006). Splines employ piece-wise, n th order polynomials to interpolate between data-points with continuous functions. The data points where adjacent polynomials converge are referred to as knots (Chapra and Canale, 1988). Applying cubic splines to low-

frequency acid concentrations allows for resampling and integration of high-frequency loads which can be used in remediation strategies.

3.3 Purpose and Objectives

The purpose of this investigation is to develop a methodology to approximate acid loads using widely-spaced sample intervals for chemistry but high-frequency measurement intervals for flow. This will be accomplished by (a) interpolating hydrochemical time-series data and re-sampling it to high-frequency and (b) numerically integrating acid loads on the higher-frequency interval.

Specific objectives include:

1. Collection of geochemical and hydrological data for the purpose of calculating acid loads
2. Approximate data using cubic splines to establish continuous flow and acid load datasets
3. Quantify acid loads over specified intervals with numerical integration techniques

3.4 Methodology

3.4.1 Collection of Geochemical and Hydrological Data

Acid Mine Drainage (AMD) was collected for chemical analysis at the intake of five Parshall flumes (Fig. 1-4) with a clean 60 cc syringe rinsed in the sample source prior to collection. The sample was then filtered through a 0.45 μm cellulose membrane filter and deposited in two 60 ml polyethylene sample bottles. One of the bottles contained 1 ml of concentrated nitric acid and was labeled as FA (filtered acidified),

while the other bottle was labeled FU (filtered un-acidified). The FA sample analyzed for dissolved cation concentrations by inductively coupled plasma-atomic emission spectrometry (USEPA, 1994). Anion concentrations were determined by ion chromatography using the FU sample (USEPA, 1993).

Field parameters measured at the intake of the flume included specific conductance, temperature, pH, Eh and alkalinity. Specific conductance ($\mu\text{S}/\text{cm}$) was measured with a YSI EC300 conductivity meter. Temperature ($^{\circ}\text{C}$) and pH were measured with a Hanna HI 9025 pH meter. Alkalinity was determined by the standard titration method (ASTM, 2006). Oxidation reduction potential (mv) was measured with a YSI pH/ORP meter. Eh was determined using Zobel's solution as a reference (Nordstrom and Wilde, 2005).

Discharge data was obtained from the 1-inch Parshall flumes using a sealed water level logger measuring absolute pressure to an accuracy of ± 0.12 psi and averaged on a daily interval. The absolute pressure is converted to hydraulic head by subtracting local atmospheric pressure and multiplying by 2.308 ft/psi. This head is then used to estimate flow using a rating equation :

$$Q = ch^n \quad (9)$$

where Q is the flow in ft^3/sec , h is head in feet, c is the Parshall flume coefficient and n is the Parshall flume exponent (Dodge *et al*, 2001). For the flumes used in this study the value of c equaled 0.338 and n equaled 1.55.

3.4.2 Resampling of Geochemical Data using Cubic Splines

Natural cubic splines were used in this study to resample unequally spaced water chemical samples that exhibited large variations from one point to the next. These conditions can induce oscillations in higher order polynomials where cubic splines can provide more acceptable approximations (Chapra and Canale, 1988). Natural cubic spline functions meet the following conditions: (1) the function values must be equal at their interior knots; (2) the first and last functions must pass through the endpoints; (3) the first derivatives at interior knots must be equal; (4) the second derivatives at interior knots must be equal; (5) the second derivative at the end knots must equal zero (Chapra and Canale, 1988). The `spline()` function in R was used to create natural cubic splines from the data (R Core Team, 2012). An example of script for cubic splines in R is located in Appendix B.

Cross-correlation was used to analyze the effect of decreasing flow measurement frequency. Cross-correlation is a measure of similarity between two datasets with values close to 1 identifying them as well correlated (Kachigan, 1986). Cubic splines were applied to sequentially lower frequency flow measurements, resampled at a daily interval, and cross-correlated with the daily flow dataset for Flume P9. Intervals between flow measurements included 1, 2, 3, 5, 7, 10, 14 and 30 days.

3.4.3 Numerical Integration to Determine Acid Loads

Cubic splines represent a series of continuous functions which may be integrated using a Gauss-Kronrod quadrature technique (Gander and Gautschi, 2000). Gaussian quadrature utilizes multiple x-values to discretize the area under the function. Such

integration can generate accurate integrated results within a specified tolerance (Chapra and Canale, 1988). Integration of acid loads was completed in R using the `quadgk()` function from the *pracma* package (R Core Team, 2012). An example of script for numerical integration in R is found in Appendix B.

3.5 Results

3.5.1 Continuous Flows and Acid Loads

Figure 3-1 shows acidity concentrations (mg/l as CaCO_3) for each flume resampled to a daily interval. This dataset was then multiplied by daily average flow (l/s) (Fig. 3-2) to calculate daily acid loads (mg/s). Gaps in the time series represent intervals when flow data were corrupt or not measured. The highest flows were at P10 and the lowest flows were at C1. Cubic splines were applied to daily acid loads (Fig. 3-3) to produce continuous acid loads for presentation and integration. These datasets follow a similar pattern to the flow datasets which shows that acid loads are directly influenced by flow volume.

Figure 3-1: Interpolated acid concentrations (mg/l as CaCO₃) at five flume sites.
Triangles represent dates of chemistry samples.

Figure 3-2 Flow (l/s) at five flume sites. Gaps represent intervals in which flow was not measured.

Figure 3-3: Acid loads (mg/s) for each flume.

Cross-correlation showed an exponential decrease as the number of days between flow measurements was increased (Fig. 3-4). At the high frequency interval (1 day) a correlation coefficient of 1.0 was obtained. At 10 days between measurements, the correlation drops to below 0.6. The correlation between daily acid loads and flow measurements also follows an exponential decay model (Fig. 3-5). At daily flow intervals, the acid loads and flow time-series correlate at 0.931. At flow measurement intervals of five days, the correlation between daily acid loads and flow drops to 0.699. The results show that flow influences acid loads, and as flow measurement frequency decreases the accuracy of acid load estimation decreases.

3.5.2 Monthly Acid Loads

Figure 3-6 shows the monthly mass flux of acidity discharging from the X bench over a two year period. Time periods in which loads were not computed are shown, and calculations that only included partial months are displayed by grey bars. Flume P10 had the highest flows the highest acid loads. The lowest acid loads are discharged from Flume C1-2, and Flume C6 has the most even distribution of loads over all months.

Table 3-1 shows the integrated acid loads for every month of the study at each flume. The grey areas represent averaged values, and were needed to compute an approximated acid load for the entire study period. January of 2012 had the highest acid load of the study period, followed by March 2011 and March 2012. The final value (41.9 tons of acid as CaCO_3) is equivalent to 7.61×10^5 hydrogen ion equivalents. Assuming ideal mixing conditions, it would take 31.1 tons of Ca(OH)_2 to neutralize the acidity discharged from the aquifer during the study period.

Figure 3-4: Correlation coefficients for high frequency flow and flow measured at decreasing frequency.

Figure 3-5: Correlation coefficients for high frequency acid loads and acid loads calculated with decreasing flow frequency

Figure 3-6: Monthly acid loads. Grey bars indicate partial months.

Year	Month	Acid Load (tons)					Total
		Flume C1	Flume C6	Flume P9	Flume P10	Flume T6	
2010	July	0.016	0.114	0.450	0.725	0.194	1.500
	Aug	0.016	0.114	0.450	0.256	0.194	1.031
	Sep	0.016	0.114	0.450	0.156	0.194	0.931
	Oct	0.016	0.114	0.450	0.725	0.141	1.446
	Nov	0.007	0.029	0.241	0.725	0.101	1.102
	Dec	0.060	0.066	0.316	0.725	0.071	1.238
2011	Jan	0.000	0.127	0.447	0.725	0.233	1.531
	Feb	0.000	0.141	0.334	0.725	0.352	1.552
	Mar	0.002	0.101	1.067	0.725	0.433	2.327
	Apr	0.012	0.139	0.720	0.725	0.194	1.790
	May	0.006	0.143	0.576	0.751	0.194	1.671
	June	0.002	0.148	0.210	0.788	0.194	1.342
	July	0.003	0.166	0.200	0.421	0.194	0.984
	Aug	0.022	0.162	0.236	0.454	0.194	1.069
	Sep	0.008	0.134	0.369	0.976	0.194	1.681
	Oct	0.016	0.114	0.450	0.725	0.194	1.500
	Nov	0.016	0.114	0.450	0.725	0.194	1.500
	Dec	0.016	0.114	0.450	0.725	0.194	1.500
2012	Jan	0.034	0.123	0.614	1.438	0.194	2.404
	Feb	0.014	0.117	0.526	0.924	0.194	1.775
	Mar	0.055	0.159	0.450	1.318	0.194	2.177
	Apr	0.016	0.123	0.450	0.664	0.194	1.448
	May	0.016	0.109	0.450	0.909	0.459	1.943
	June	0.016	0.085	0.450	0.368	0.149	1.068
	July	0.016	0.087	0.450	0.725	0.084	1.362
	Aug	0.016	0.069	0.450	0.725	0.062	1.322
	Sep	0.016	0.051	0.450	0.725	0.054	1.296
	Oct	0.016	0.114	0.450	0.725	0.194	1.500
Arithmetic Average		0.016	0.114	0.450	0.725	0.194	1.500
Total (tons)		0.451	3.191	12.611	20.294	5.444	41.991

Table 3-1: Acid discharged from the DLM X bench over the study period. Grey boxes represent values averaged from integrated loads. Acid loads are in units of tons as CaCO₃.

3.6 Summary and Conclusion

Chemical loads of acidity represent information commonly needed to design treatment plans for AMD. Acid loads requires estimates of both flow and total acidity. Flow (discharge rate) can be effectively sampled at high frequency using data-logger based pressure transducers and primary structures such as flumes (Weight, 2004). Water chemistry, however, is often observed to vary over much longer time intervals (Cravotta and Hilgar, 2000) and therefore is commonly sampled at much lower frequency. To calculate loads, resampling of water chemistry to higher frequency is needed.

This investigation was undertaken to give a case history of how these two datasets (flow and chemistry) might be paired to produce robust acidity estimates. It was also undertaken to show the loss of information resulting from coarsening the resampling interval from daily estimates to lower frequencies. Results show that natural cubic splines are useful in resampling hydrochemical time series data to estimate solute concentrations at higher frequencies than originally sampled. The frequency at which flow is measured limits the accuracy of acid load estimates, and high frequency measurements are needed to account for variability in discharge.

5: Conclusions and Future Research

5.1 Conclusions

1. Cluster analysis was useful for interpretation of hydrochemical facies and showed that DLM groundwater changed from primarily acidic in 1994 to more alkaline in 2012. Maps of hydrochemistry indicated that aquifer chemistry continued to evolve over the study period.
2. Wells down gradient from trenches T10 and T7 showed an increase in pH, alkalinity and Ca concentrations. It was clear that this change was influenced by alkaline injections which neutralized acidity in groundwater chemistry.
3. Natural cubic splines were useful for approximating hydrochemical time series. These functions provided a means of obtaining continuous, integrable functions that showed changes in acid concentrations. They further allowed for visualization of acid loads over time and numerical integration of loads.
4. High frequency flow measurements are needed to account for variability in discharge and the frequency at which flow is measured limits the accuracy of acid load estimates.

5.2 Future Research

1. A major contribution to the future of *in situ* injection of hydrated lime at DLM would be to understand the optimal dosage rate of $\text{Ca}(\text{OH})_2$. This would maximize the amount of dissolved alkalinity introduced to the aquifer.

2. The hydrogeology of the sludge disposal pond should be investigated to understanding the effect high density alkaline sludge has on local groundwater flow.
3. Current mineralogy is needed at the X bench for the confirmation of inverse modeling. A full vertical mineral profile, and in depth investigation into the role of the vadose zone, should be conducted for greater understanding of acid producing and consuming reactions.
4. A reaction-transport model should be implemented for the complete quantification of the system. This includes transient simulations of lime slurry injections and inclusion of preferred flow paths.

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Appendix A: Chemistry Results

Well Chemistry

Well ID	pH	Alkalinity (meq/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	SO ₄ ²⁻ (mg/l)	Fe Total (mg/l)	Al ³⁺ (mg/l)	Mn Total (mg/l)
X-03 93	3.53	0.00	210.00	119.00	1307.00	31.00	24.00	22.00
X-04 93	5.64	1.10	243.00	189.00	1372.00	15.00	1.00	18.00
X-05 93	3.52	0.00	288.00	202.00	1684.00	14.00	34.00	19.00
X-07 93	4.24	0.00	58.00	27.00	369.00	6.00	13.00	9.00
X-08 93	3.89	0.00	206.00	195.00	1757.00	98.00	62.00	58.00
X-09 93	4.34	0.00	150.00	121.00	944.00	2.00	25.00	12.00
X-11 93	3.04	0.00	167.00	117.00	1546.00	14.00	96.00	18.00
X-12 93	5.50	0.32	147.00	114.00	915.00	7.00	0.00	4.00
X-13 93	3.75	0.00	184.00	176.00	1920.00	94.00	80.00	35.00
X-14 93	3.88	0.00	177.00	114.00	1182.00	28.00	15.00	34.00
X-15 93	5.78	1.04	62.00	28.00	311.00	55.00	0.00	7.00
X-16 93	4.20	0.00	120.00	100.00	894.00	56.00	25.00	21.00
X-17 93	3.57	0.00	91.00	61.00	689.00	39.00	22.00	14.00
X-18 93	4.93	0.12	64.00	38.00	366.00	39.00	0.00	5.00
X-19 93	3.95	0.00	84.00	42.00	619.00	2.00	33.00	11.00
X-20 93	4.48	0.00	36.00	10.00	165.00	2.00	6.00	5.00
X-21 93	4.13	0.00	210.00	176.00	1588.00	26.00	28.00	23.00
X-22 93	3.75	0.00	269.00	261.00	2223.00	11.00	105.00	39.00
X-23 93	3.65	0.00	147.00	161.00	1710.00	93.00	77.00	28.00
X-24 93	6.83	2.38	155.00	157.00	856.00	1.00	0.00	2.00
X-26 93	3.15	0.00	141.00	88.00	1030.00	7.00	51.00	23.00
X-27 93	4.23	0.00	207.00	186.00	1677.00	111.00	13.00	22.00
X-03 94	3.46	0.00	196.70	131.70	1040.00	42.90	10.60	17.70
X-04 94	5.48	2.11	239.20	161.30	1030.00	9.84	0.50	12.40
X-07 94	3.71	0.00	203.50	173.30	1312.00	50.14	84.90	45.90
X-08 94	4.38	0.00	93.00	71.40	520.00	82.40	3.58	9.98
X-09 94	3.70	0.00	138.00	110.00	720.00	16.90	21.80	11.80
X-11 94	3.08	0.00	212.00	195.00	1604.00	46.70	97.50	25.90
X-12 94	4.18	0.00	156.00	134.00	1030.00	43.00	25.70	21.00
X-13 94	3.41	0.00	208.60	199.10	1632.00	107.41	91.00	40.00
X-14 94	3.67	0.00	150.10	75.50	890.00	11.58	11.20	24.30
X-15 94	5.52	1.18	81.20	36.20	328.00	55.30	0.05	6.45

Well Chemistry Continued

Well ID	pH	Alkalinity (meq/l)	Ca2+ (mg/l)	Mg2+ (mg/l)	SO42+ (mg/l)	Fe Total (mg/l)	Al3+ (mg/l)	Mn Total (mg/l)
X-16 94	3.86	0.00	117.00	85.70	708.00	49.40	19.80	19.50
X-17 94	2.56	0.00	96.90	67.70	448.00	46.40	19.90	12.80
X-19 94	3.25	0.00	79.10	48.70	580.00	48.00	26.20	12.20
X-20 94	3.26	0.00	123.00	78.30	1046.00	19.26	42.30	24.90
X-21 94	4.38	0.00	184.80	136.20	692.00	7.87	13.60	12.40
X-22 94	3.14	0.00	273.00	227.80	2000.00	43.81	91.20	35.20
X-23 94	3.22	0.00	160.80	162.20	1536.00	84.15	71.10	25.50
X-24 94	6.25	2.83	168.30	123.10	708.00	4.05	0.05	1.05
X-27 94	3.68	0.00	224.50	196.90	1872.00	172.70	24.20	27.00
X-41 94	2.90	0.00	204.50	146.40	890.00	6.74	75.20	24.70
X-42 94	3.40	0.00	93.60	83.70	640.00	48.00	30.40	12.20
X-31 94	5.16	0.01	105.00	48.90	352.00	105.00	0.49	17.10
X-45 94	3.63	0.00	94.12	58.50	556.00	77.63	49.10	28.50
X-46 94	3.90	0.00	204.30	161.40	1200.00	206.70	51.60	40.90
X-3 99	3.68	0.00	127.30	57.45	687.50	12.56	14.18	8.96
X-4 99	5.75	1.42	213.70	138.40	989.75	7.49	4.14	6.40
X-7 99	3.57	0.00	52.71	29.55	332.18	0.51	20.87	5.96
X-8 99	3.82	0.00	162.10	138.60	1246.05	76.04	87.41	37.41
X-9 99	6.36	2.88	66.46	19.49	191.39	0.12	1.79	0.35
X-15 99	6.11	1.08	34.56	7.86	75.22	11.64	1.05	1.66
X-16 99	3.94	0.00	112.90	82.39	883.07	50.99	22.11	16.56
X-17 99	3.71	0.00	88.51	63.51	709.04	36.52	24.77	10.64
X-18 99	4.45	0.54	63.98	41.19	297.72	9.69	2.30	3.95
X-19 99	4.08	0.00	56.32	32.70	364.32	1.64	20.53	6.54
X-20 99	3.26	0.00	94.10	63.16	546.00	9.47	33.70	15.40
X-21 99	5.20	0.00	159.10	103.70	816.30	5.66	4.99	7.22
X-23 99	3.00	0.00	115.00	114.30	959.46	59.39	66.87	17.92
X-27 99	4.78	0.04	169.90	121.40	876.53	7.60	17.28	12.85
X-42 99	3.48	0.00	48.62	36.35	442.87	15.64	31.69	9.27
X-44 99	6.08	1.86	54.29	17.26	135.70	55.72	1.89	9.86
X-46 99	3.73	0.00	134.80	95.89	896.70	52.59	28.25	22.58
X-03 10	4.24	0.00	29.30	17.10	253.00	0.19	4.19	0.00
X-04 10	5.80	1.78	39.50	76.80	722.00	10.80	0.05	0.00
X-05 10	3.41	0.00	35.00	41.70	572.00	0.87	31.30	0.00
X-07 10	3.94	0.00	23.80	15.80	302.00	0.07	14.80	0.00

Well Chemistry Continued

Well ID	pH	Alkalinity (meq/l)	Ca2+ (mg/l)	Mg2+ (mg/l)	SO42+ (mg/l)	Fe Total (mg/l)	Al3+ (mg/l)	Mn Total (mg/l)
X-08 10	3.70	0.00	35.90	78.40	1052.00	35.80	53.30	0.00
X-11 10	3.11	0.00	36.90	63.20	842.00	4.12	38.80	0.00
X-13 10	3.49	0.00	40.80	123.00	1250.00	37.90	59.30	0.00
X-14 10	2.82	0.00	32.70	51.10	474.00	12.00	2.39	0.00
X-15 10	6.71	2.05	35.10	39.90	475.00	42.50	0.05	0.00
X-16 10	6.12	0.20	34.80	38.20	382.00	24.10	0.44	0.00
X-17 10	6.11	0.35	39.00	31.00	412.00	10.30	0.22	0.00
X-18 10	6.45	1.23	23.00	10.50	10.00	3.71	0.09	0.00
X-19 10	4.05	0.00	26.50	19.90	292.00	1.58	9.61	0.00
X-21 10	6.99	3.63	40.00	73.90	484.00	0.88	0.05	0.00
X-22 10	4.18	0.00	41.50	80.70	782.00	12.90	15.40	0.00
X-23 10	4.37	0.00	18.90	18.00	182.00	7.82	6.62	0.00
X-40 10	6.45	1.80	24.50	3.46	54.00	0.05	0.05	0.00
X-41 10	3.00	0.00	42.00	87.10	101.00	22.90	50.20	0.00
X-42 10	6.17	1.48	39.90	16.90	296.00	0.05	0.11	0.00
X-43 10	3.83	0.00	31.50	32.20	39.00	0.63	2.39	0.00
X-44 10	6.20	4.00	19.20	8.58	46.00	15.30	0.05	0.00
X-48 10	7.15	2.78	30.80	10.50	74.00	0.05	0.05	0.00
X-52 10	4.52	0.00	48.50	123.00	1360.00	26.40	19.20	0.00
X-53 10	3.32	0.00	41.10	82.40	908.00	14.10	13.10	0.00
X-55 10	4.36	0.00	31.00	25.20	351.00	8.06	9.43	0.00
X-58 10	6.06	1.50	39.90	74.40	600.00	4.76	0.11	0.00
X-59 10	4.10	0.00	41.10	70.60	9.40	2.40	35.20	0.00
X-60 10	6.20	0.39	32.50	31.80	328.00	3.93	0.05	0.00
X-7 12	5.51	1.02	168.00	81.20	924.00	1.08	1.27	15.90
X-8 12	3.69	0.00	100.00	75.40	996.00	34.30	40.70	17.10
X-9 12	11.43	7.06	170.00	0.32	97.00	0.08	6.44	0.00
X-12 12	6.96	2.61	65.30	84.50	600.00	0.02	0.03	0.02
X-19 12	3.95	0.00	57.70	22.90	336.00	10.20	6.48	4.59
X-21 12	6.38	4.25	127.00	76.10	481.00	0.01	0.01	0.29
X-22 12	3.63	0.00	164.00	104.00	1083.00	14.30	20.50	12.50
X-23 12	3.54	0.00	81.00	70.40	832.00	32.50	33.40	12.50
X-26 12	6.16	1.51	262.00	22.10	826.00	4.94	0.88	4.23
X-27 12	6.36	1.23	35.10	8.94	140.00	0.11	0.08	0.37
X-41 12	2.81	0.00	139.00	87.80	1137.00	6.33	48.80	10.70

Well Chemistry Continued

Well ID	pH	Alkalinity (meq/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	SO ₄ ²⁻ (mg/l)	Fe Total (mg/l)	Al ³⁺ (mg/l)	Mn Total (mg/l)
X-45 12	2.29	0.00	195.00	81.80	1150.00	79.80	8.38	23.80
X-52 12	5.38	1.08	315.00	114.00	1534.00	20.30	2.76	17.20
X-54 12	6.63	2.61	59.80	8.45	107.00	0.02	0.03	0.04
X-59 12	4.14	0.00	130.00	89.70	960.00	6.31	18.40	12.90
X-60 12	6.08	1.45	85.90	37.50	366.00	0.89	0.45	6.53

Appendix B: R Script

R Script for Cluster Analysis and Dendrogram

```
AllChem = read.delim('FILE NAME ',stringsAsFactors=FALSE) # reads the file
AllChem.use = AllChem[c(2,3,4,5,6,7,8,9)] #strips the text from the input file
means= apply(AllChem.use,2,mean) #vector of means
sds= apply(AllChem.use,2,sd) #vector of std deviations
AllChemScaled = scale(AllChem.use,center=means,scale=sds) #normalizes to z scores
AllChem.dist = dist(AllChemScaled) #euclidean similarity
AllChem.hclust = hclust(AllChem.dist, "ward") #clusters on the distance matrix
plot(AllChem.hclust,labels=AllChem$id, cex=.75, main='Well Chemistry Cluster
Analysis', xlab=") # plots the dendrogram
groups.4 = cutree(AllChem.hclust,4) #head counts for 4 clusters
table(groups.4)
rect.hclust(AllChem.hclust, k=4, border="red") # draws the red boxes around each cluster
```

R Script for Boxplots

```
#Boxplots for meq/l
AllChem4=cbind(AllChem,groups.4)
par(mfrow=c(4,1))
boxplot(subset(AllChem4[,2:8],AllChem4[,9]==1),horizontal=FALSE, ylim=c(0,40))
text(c(1.5),"cluster 1")
boxplot(subset(AllChem4[,2:8],AllChem4[,9]==2),horizontal=FALSE, ylim=c(0,40))
text(c(1.5),"cluster 2")
boxplot(subset(AllChem4[,2:8],AllChem4[,9]==3),horizontal=FALSE, ylim=c(0,40))
text(c(1.5),"cluster 3")
boxplot(subset(AllChem4[,2:8],AllChem3[,9]==4),horizontal=FALSE, ylim=c(0,40))
text(c(1.5),"cluster 4")
```

R Script for Star Plots

```
Allchem2 = read.csv(na.omit("FILENAME"))
Allchem2id = read.csv(na.omit("FILENAME"))
id <- as.vector(Allchem2id$id)
palette(gray(seq(0,1,len = 8)))
```

```
stars(Allchem2, labels = id, len = 1, nrow=7, key.loc = c(39,15), draw.segments =
+TRUE)
```

R Script for numerical Integration

```
# pracma Reference = http://cran.r-project.org/web/packages/pracma/pracma.pdf
```

```
library(pracma)
c6acidsec1=data.frame(c6acidflux1)
c6acidsec1=cbind(c6$c6sec[c(1:a)],c6acidsec1$X2)
c6flowsec1=cbind(c6$c6sec[c(1:a)], c6flowspline$y)
c6flowfun1=splinefun(c6flowsec1)
c6flowtot1=quadgk(c6flowfun1, 0, 32659200, tol = 1e-10)
c6flowtot1
c6acidfun1=splinefun(c6acidsec1)
c6acidtot1=quadgk(c6acidfun1, 0, 32659200, tol = 1e-10)
c6acidmg1=(c6acidtot1) #mg
c6acidmg1
c6acidkg1=(c6acidtot1/1000000)
c6acidkg1
c6acidmetricton1=(c6acidkg1/1000)
c6acidmetricton1
c6acidlb1=(c6acidkg1*2.20462)
c6acidlb1
c6acidshortton1=(c6acidlb1/2000)
c6acidshortton1

# Monthly integrated acid loads

c6acidOct10=quadgk(c6acidfun1, 0, 1209599, tol = 1e-10)
c6acidOct10
c6acidNov10=quadgk(c6acidfun1, 1209600, 3801599, tol = 1e-10)
c6acidNov10
c6acidDec10=quadgk(c6acidfun1, 3801600, 6479999, tol = 1e-10)
c6acidDec10
```