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Rachelle Thorne
West Virginia University

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**Isotopic Composition of Dissolved Inorganic Carbon in Underground Mine
Discharges of the Northern Appalachian Basin**

Rachelle Thorne

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

Joseph J. Donovan, Ph.D, Chair
Shikha Sharma, Ph.D
Eberhard Werner

Department of Geology and Geography

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dissolved inorganic carbon

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ABSTRACT

Isotopic Composition of Dissolved Inorganic Carbon in Underground Mine Discharges of the Northern Appalachian Basin

Rachelle Thorne

This research examined the efficacy of using ^{13}C of dissolved inorganic carbon (DIC) to infer geochemical and microbiological processes in underground coal mine discharges. Groundwater samples from mines in two different coal seams (the Pittsburgh and Upper Freeport) and three different hydrogeologic settings (fully flooded, partially flooded, and free draining) were compared. Twenty mine discharges were sampled, fifteen from the Pittsburgh coal seam and five from the Upper Freeport. Sampling sites included mine portals and seeps. All sampling followed standard field protocols.

Results were evaluated for possible relationships between $\delta^{13}\text{C}_{\text{DIC}}$ and 1) mine hydrogeologic setting and 2) geochemical properties of the individual coal seams and their overlying rock strata. Isotopic results were used in conjunction with inorganic geochemistry to test if different sources of carbon could be discriminated, e.g. carbonate minerals, organic carbon from coal and shale, organic carbon from the soil zone, or biogenic methane.

Parameters describing hydrogeologic setting resulted in distinct statistical clusters separating fully-flooded, partially-flooded, and free-draining sites. Hydrogeochemical results show evidence of calcite dissolution, biogenic sulfate reduction, and CO_2 evasion in the sample set. However, no definitive correlation was observed between isotopic and geochemical results that would be useful for differentiating sources of dissolved inorganic carbon.

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1. Introduction

1.1 Problem

In light of rising atmospheric CO₂ concentrations, increased understanding of regional carbon cycling will, in turn, improve understanding of global carbon cycling. In the northern Appalachian region, much groundwater has been influenced by coal mining resulting in dissolved inorganic carbon (DIC) concentrations derived from a variety of sources. As a result, geochemical processes operating in mine waters may have significant impacts on carbon speciation, storage, and release. Establishing relationships between DIC isotopic signatures and mine settings and aquifers could elucidate these impacts. Additionally, on a local scale, determining the isotopic signatures of mine water can serve as a baseline for future hydrogeochemical research.

The Monongahela River flows north from West Virginia into Pennsylvania. Along its course it receives discharges of groundwater either directly from underground mines or from tributaries carrying mine water of either the Pittsburgh or the Upper Freeport coal seams. The abundance and variety of mine discharges to the Monongahela make it an ideal watershed to study their effects on the regional carbon cycle. If carbon isotopes are to be utilized towards understanding carbon cycling, it is necessary to determine appropriate applications for their use. Thus, the Monongahela River watershed serves as a useful location to assess the efficacy of various isotopic techniques.

1.2 Purpose

Principles of stable isotope geochemistry were applied to gain a better understanding of carbon sources and cycling in waters discharging from underground coal mines. The geochemical composition of groundwater in underground mine discharges is related to factors including geology, position with respect to the regional water table, and the identity of reactive minerals and gases. The goal of this research was to evaluate the applicability of carbon isotopic surveys as a tool for detecting correlations between $\delta^{13}\text{C}_{\text{DIC}}$ and inorganic geochemical composition of groundwater from underground mine discharges. In turn, potential correlations may reflect influences from the geology and hydrogeologic setting of those reservoirs. It is hypothesized that carbon isotopic surveys can detect significant correlations between $^{13}\text{C}_{\text{DIC}}$ signatures and geochemical composition.

1.3 Objectives

The sequence of objectives for the study was:

- 1) To identify and locate sampling sites based on previously-studied Pittsburgh and Upper Freeport coal mine discharges in the northern Appalachian Basin (McCoy, 2002; Donovan et al., 2004; Demchak, 2005; Thies, 2007; Mack, 2008; Denicola, 2013).
- 2) To collect and analyze groundwater samples for $\delta^{13}\text{C}_{\text{DIC}}$ and inorganic chemistry. Lab analysis was provided by West Virginia University Stable Isotope Laboratory (WVSIL) and National Research Center for Coal and Energy (NRCCE)

Analytical Laboratory. Inorganic chemistry data for Pittsburgh sites were incorporated from 2012 sampling by Denicola (2013).

- 3) To perform a statistical analysis of $\delta^{13}\text{C}_{\text{DIC}}$ and inorganic chemistry results.

Analysis was used to test whether or not carbon isotope signatures of DIC could detect differences in geology or hydrogeologic setting of the sampled mines.

1.4 Study area

The area of interest spans northern West Virginia and southwestern Pennsylvania; covering Tucker, Preston, Marion, Harrison, and Monongalia counties in West Virginia and Fayette and Greene counties in Pennsylvania (Figure 1). This area has a long history of coal mining, as well as current mining operations; thus it has been extensively studied with regard to impacts on watersheds as a result of various coal extraction practices.

All of the sampling locations are located in the Appalachian Plateau physiographic province which contains a large number of underground mine discharges. The Tucker and Preston county sampling locations are discharges from mines in the Upper Freeport coal seam. The rest of the sampled discharges are from mines in the Pittsburgh coal seam.

Spanning an area of 14,000 mi², the Upper Freeport coal ranges from 1 to 12 feet thick and is overlain by up to 2,000 feet of overburden. It has a mean sulfur content of 2.2±1.0% and a mean ash content of 12.3±4.0% (Figure 1; Rupert et al., 2001). It has been interpreted to mark the transition to a drier, but still humid, seasonal climate (Rupert et al., 2001).

Figure 1. Study area showing locations of sampling sites. Extent of the Pittsburgh and Upper Freeport coal seams within the study area are also shown. The Upper Freeport is shown in green; darker green indicates the portions that have been mined. Overlying the Upper Freeport is the Pittsburgh, shown in orange; darker orange indicates mined areas.

The Pittsburgh coal seam covers a 5,000 mi² area, ranges from 3.5 to 8 feet thick, and has up to 1,450 feet of overburden. It has a mean sulfur content of 2.8±1.1% and mean ash content of 9.0±2.9% (Figure 1; Tewalt et al., 2001). It has been interpreted as indicating the transition to a low rate of clastic sediment deposition marked by formation of peat bogs (Tewalt et al., 2001).

1.5 Stable carbon isotopes in groundwater

Evaluation of carbon isotopic signatures can be used to determine carbon sources and cycling in groundwater. As summarized by both Kendall and McDonnell (1998) and Clark and Fritz (1997), this is possible because although ¹³C and ¹²C have the same chemical behavior, variations in their atomic masses cause mass-dependent fractionation of the heavier versus lighter isotopes driven by various processes. The reactions responsible for fractionation may be broken into equilibrium and kinetic categories. In either category, lighter isotopes have weaker bonds and lower dissociation energies, therefore react more easily and faster.

Equilibrium fractionation partitions isotopes between various species or compounds with identical forward and backward reaction rates. Heavier isotopes preferentially accumulate in the species or compound with the higher energy state, such as aqueous and solid phases, while lighter isotopes are drawn to vapor/gas phases.

In non-equilibrium systems, kinetic fractionation partitions isotopes at dissimilar forward and backward reaction rates. Rates are dependent on ratios of isotopic masses and the energy required to break bonds. In these reactions, lighter isotopes with weaker bonds preferentially accumulate in products while heavier isotopes with stronger bonds

tend to remain in the residual reactants. Reactions may even be unidirectional in instances where products are physically removed from the reactant pool. This is most notable in biological reactions where microorganisms, acting as catalysts, prefer to break weaker bonds between lighter isotopes to form products than stronger bonds between heavier isotopes which are left behind in the substrate.

As a result, acid-base reactions, redox reactions, and bacterial metabolism may all influence dissolved inorganic carbon (DIC) concentrations in groundwater and cause variations in the ratio of aqueous ^{13}C to ^{12}C . For DIC species (aqueous CO_2 , carbonic acid, carbonate, and bicarbonate), $^{13}\text{C}_{\text{DIC}}$ signatures can give insight into what hydrogeochemical processes have occurred and what the sources of DIC are. Potential carbon sources in groundwater include carbonate mineral dissolution, oxidized organic carbon from coal/shale, organic carbon in soil through which recharge has passed, biogenic methane, and thermogenic methane. However, DIC is primarily produced from the weathering of carbonate minerals by carbonic acid or strong acids and silicate minerals by carbonic acid from the dissolution of biogenic soil CO_2 by infiltrating rain water. Additionally, the distribution of DIC species present is a function of pH.

There are several relevant equilibrium thermodynamic reactions that will affect DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ within coal mine aquifers (Table 1):

1. $\text{CO}_2(\text{g})$ dissolution: atmospheric CO_2 in the recharge area dissolves into the soil zone during weathering processes. This initiates the production of carbonic acid and subsequent decrease in pH.

2. Calcite dissolution: dissolution of calcite depends on its degree of saturation in groundwater. If the water is oversaturated, calcite will precipitate; and if the opposite holds true, the water will dissolve calcite until it reaches equilibrium.
3. Dolomite dissolution: dissolution of dolomite below the water table is slower than that of calcite and generally occurs while calcite is precipitating.
4. Silicate dissolution: quartz and aluminosilicates (i.e. feldspars and kaolinite) dissolve into solution producing DIC from CO_2 used in their alteration, increasing pH, and causing additional dissolution of CO_2 .
5. Gypsum dissolution: when influenced by the common ion effect, dissolution of gypsum may force calcite to precipitate, subsequently accumulating heavier carbon into the solid phase.

Dissolution of carbonates can be attributed either to dissolved CO_2 or to H_2SO_4 produced from pyrite oxidation. The combination of water and carbonates with dissolved CO_2 produces two bicarbonate ions and one calcium ion, whereas with H_2SO_4 two bicarbonate ions, two calcium ions, and one sulfate ion are produced. The isotopic composition of produced bicarbonate ions from the reaction using dissolved CO_2 will depend on the isotopic composition of both CO_2 and CaCO_3 while composition of only CaCO_3 will influence the reaction driven by H_2SO_4 (Lerman et al., 2007; Sharma et al., 2013).

Potential kinetic reactions include (Table 2):

1. Oxidation of organics in the soil zone, coal mine aquifer, and overburden-bacterial oxidation of organic carbon whereby microorganisms consume organics and produce isotopically lighter DIC species (Holland and Turekian, 2011).

- a. Biogenic oxidation (i.e. methanotrophy) of carbon by dissolved O_2 -
carried out by aerobic bacteria
- b. Biogenic sulfate reduction- carried out by anaerobic bacteria
 - i. Oxidation of fixed carbon (CH_2O) by sulfate
 - ii. Oxidation of reduced carbon (CH_4) by sulfate

2. Methanogenesis

- a. Biogenic methanogenesis- anaerobic bacterial reduction of organic matter
that commonly occurs in shallow groundwater systems and results in ^{13}C
enrichment of DIC (Simpkins and Parkin, 1993; Scott et al., 1994; Botz et
al., 1996; Martini et al., 1998; Whiticar, 1999; Hellings et al., 2000;
Aravena et al., 2003; McIntosh et al., 2008; Sharma and Frost, 2008;
McLaughlin et al., 2011; Sharma and Baggett, 2011) and fractionation of
 $\sim 75 \pm 15\text{‰}$ between CO_2 and CH_4 (Whiticar et al., 1996)
 - i. Acetate fermentation- in fresh water methanogens use acetate food
source to produce CO_2 and methane
 - ii. CO_2 reduction- in marine water methanogens use hydrogen gas to
reduce CO_2 and produce methane

- 3. CO_2 evasion- CO_2 loss occurs when groundwater with a higher pCO_2 than
atmospheric discharges to the surface, switching from closed to open system
conditions. This process enriches the DIC pool and is dependent on temperature,
pH, the pCO_2 gradient between the water and the atmosphere, and turbulence of
flow. Although interactions between $CO_{2(g)}$ and $CO_{2(aq)}$ are considered
equilibrium reactions, depending on how open or closed the system is, it is widely

accepted that this type of scenario is best described as a kinetic process (Doctor et al., 2008).

In conjunction with the above reactions, there are several relevant carbon isotope values that were considered for this survey (Figure 2). Well known $\delta^{13}\text{C}$ values include:

1. atmospheric CO_2 (~ -8 ‰) (Keeling et al., 2010)
2. marine carbonates (~ 0 ‰, close to the reference VPDB which is also a marine carbonate) (Clark and Fritz, 1997)
3. freshwater carbonates (wide range, with most falling between -5 to -15 ‰) (Clark and Fritz, 1997)
4. soil CO_2 in temperate areas predominantly covered with C_3 plants (-23 ‰) (Aravena et al., 1992)
5. coal (~ -25 to -27 ‰), derived from peat, a C_3 plant, does not have much carbon isotopic variation, even under different depositional settings (Whiticar, 1996)
6. subsurface DIC (-5 to -25 ‰) (Kendall and McDonnell, 1998)
7. ambient groundwaters receiving equal contributions of carbon from carbonate rocks and soil CO_2 (-11 to -16 ‰) (Mook and Tan, 1991)

Several carbon isotope studies have been conducted on rock strata pertinent to the Pittsburgh and Upper Freeport coal seams. $\delta^{13}\text{C}$ signatures from these studies include:

1. two Pittsburgh Formation limestone units above the Pittsburgh coal were -2.5 and -1.7 ‰ (Sharma et al., 2013)
2. Pittsburgh coal, Little Pittsburgh coal, and Pittsburgh shale were -24.3 , -25.4 , and -21.6 ‰ respectively (Sharma et al., 2013)
3. coal carbonates in PA were -2.7 ‰ (Sack, 2012)

4. $\delta^{13}\text{C}$ of pedogenic carbonates in the sub-Ames interval range from -9.17 to -6.72
‰ PDB (Joeckel, 1995)

These values, when compared to results from this survey, were useful for interpreting carbon contributions to the individual sites.

Figure 2. Ranges and selected values for $\delta^{13}\text{C}$ of relevant compounds (For sources of data see p.15).

1.6 Geochemistry of underground coal mine discharges

The quality of water draining from underground mines will be influenced by the proportion of acid-producing minerals (pyrite) and acid-consuming minerals (carbonates) within and surrounding them (Skousen et al., 2002). Acid mine drainage (AMD) is caused by the oxidation of sulfur-containing minerals, such as pyrite, generating characteristic discharge water with low pH and high sulfate, iron, aluminum, and other metals (Equeenuddin et al., 2010). This results in a cyclic pattern of mineral dissolution and low pH water reacting with the surrounding strata (Equeenuddin et al., 2010). Oxidation of sulfide minerals is an important consideration for DIC because generation of H_2SO_4 results in subsequent neutralization by carbonates (Hendratta and Atekwana, 2011). Primary and secondary reactions influencing the geochemistry of mine waters are shown in Table 3. Overall, AMD generation will tend to enrich DIC in groundwater because the acidity formed neutralizes carbonates and dehydrates HCO_3^- causing $\text{CO}_{2(g)}$ evasion (Hendratta and Atekwana, 2011).

As summarized by Watzlaf et al. (2004), once pyrite oxidizes, acidity, alkalinity, carbonate dissolution, and sulfate reduction play a significant role in the chemical composition of underground coal mine drainage. Acidity represents the base neutralization capacity of water. There are four types: 1) organic acidity associated with dissolved organic carbon (DOC), 2) CO_2 acidity associated with dissolved CO_2 and carbonic acid, 3) proton acidity associated with free H^+ ions, and 4) mineral acidity associated with dissolved metals. Since mine water is generally low in DOC and much of CO_2 acidity is lost by degassing when exposed to the atmosphere, proton and mineral

acidity are the dominant contributors to acidity. Mineral acidity includes Fe, Al, and Mn because they produce H^+ during the following hydrolysis reactions:

- 1) $Fe^{2+} + 0.25O_2 + 1.5H_2O \rightarrow FeOOH + 2H^+$
- 2) $Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+$
- 3) $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$
- 4) $Mn^{2+} + 0.25O_2 + 1.5H_2O \rightarrow MnOOH + 2H^+$

From these reactions, total (metal + proton) acidity at low to circumneutral pH is calculated as follows:

$$\text{Acidity}_{\text{calc}} = 2[Fe^{2+}]/56 + 3[Fe^{3+}]/56 + 3[Al]/27 + 2[Mn^{2+}]/55 + 1000 \cdot 10^{-pH}$$

where acidity is in meq/L and metal concentrations (in square brackets) are in mg/L.

Alkalinity represents the acid neutralizing capacity for water of $pH > 4.5$. Hydroxyl ions (OH^-), carbonate, silicate, borate, organic ligands, phosphate, and ammonia may all contribute to alkalinity; however, the main sources of alkalinity in mine water are HCO_3^- or CO_3^{2-} . Due to the low to moderate pH of most coal mine discharges, HCO_3^- is the predominant source of alkalinity where present.

Carbonate dissolution increases aqueous concentrations of DIC, primarily as bicarbonate. Such dissolution is commonly driven by pCO_2 from decomposition of organic matter. Anoxic mine water environments will tend to have higher bicarbonate concentrations than in aerobic mines because there is limited oxygen for pyrite oxidation. Dissolution is further enhanced since carbonate surfaces are not coated in FeOOH.

Bacterial sulfate reduction involves oxidation of organic compounds via bacteria using sulfate as the terminal electron acceptor, precipitating metal sulfides and producing bicarbonate alkalinity. Sulfate-reducing bacteria (SRB) and fermentative bacteria are

most active in pH>~5 waters, but can proliferate in neutral-pH microenvironments and disperse as they continue to generate alkalinity. Requirements for sulfate reduction are: 1) high concentrations of sulfate, 2) available organic substrate such as lactate and acetate, and 3) absence of oxidizers such as O₂, Fe³⁺, Mn⁴⁺.

1.7 Geology of Pittsburgh and Upper Freeport coal seams and their overburden

Groundwater discharges from mines within the Upper Freeport and Pittsburgh seams were the focus of this survey. Consideration of coal and overburden composition is necessary to understand DIC isotopic signatures of underground mine discharges. Not only do the two coal seams vary in terms of composition, so do their overburden. The significance of this lies in distinguishing between calcareous (>10 % CaCO₃) and non-calcareous strata and high and low pyrite (FeS₂) strata, both of which relate to the paleoclimate and depositional environment at the time of formation (Perry, 2009). In general, the overlying rock layers above the Pittsburgh coal seam are known to have higher carbonate content than those above the Upper Freeport (Stone and Clapp, 1907; Hennen and Reger, 1913; Hennen and Reger, 1914).

1.7.1 Late Middle to Late Pennsylvanian

During the Alleghanian Orogeny, the Pittsburgh and Upper Freeport coal seams were deposited during the late Middle to Late Pennsylvanian (~290 Ma) in the northern Appalachian basin. In WV and PA, the Pennsylvanian is composed of the following groups, from oldest to youngest: Pottsville, Allegheny, Conemaugh, and Monongahela. The Upper Freeport coal seam marks the top of the Allegheny and the Pittsburgh marks the bottom of the Monongahela, with the Conemaugh between them (Figure 3).

System	Pennsylvanian		
Group	Monongahela		
Formation	Pittsburgh		
			Uniontown limestone
			Arnoldsburg sandstone
			Benwood limestone
			Sewickley coal
			Lower Sewickley sandstone
			Fishpot limestone
			Redstone coal
			Upper Pittsburgh sandstone
			Pittsburgh coal
	Conemaugh	Glenshaw	
			Ames limestone (M)
			Harlem coal
			Pittsburgh shale
			Saltsburg sandstone
			Bakerstown coal
			Pine Creek limestone
			Buffalo sandstone
			Brush Creek limestone (M)
			Brush Creek shale (M)
			Brush Creek coal
			Upper Mahoning sandstone
			Mahoning coal
			Upper Mahoning sandstone
			Lower Mahoning sandstone
			Uffington shale
	Allegheny	Freeport	
			Upper Freeport coal

Figure 3. Stratigraphic column showing pertinent rock strata overlying the Upper Freeport and Pittsburgh coal seams (Modified from McColloch et al., 2012 and Arkle et al., 1979). The Casselman Formation that occurs in the Upper Conemaugh Group, between the Glenshaw and Pittsburgh Formations, is not shown. (M) denotes marine deposits.

1.7.1a Allegheny Group

The Allegheny Group (~200-300 feet thick) is composed of claystone, siltstone, sandstone, conglomerate, coal, ironstone, and limestone, which are terrestrial to marine in origin (Rupert et al., 2001). The climate was moderately wet, but drying as the inland sea withdrew westward into Ohio allowing non-marine deposition (Fichter, 2000). However, for this survey, the only relevant portion of this group is the top-most non-marine layer, the Upper Freeport coal. Pod shaped coal bodies suggest that it formed in an upper delta-plain (Rupert et al., 2001; Horne et al., 1978).

1.7.1b Conemaugh Group

The Conemaugh Group (~400-900 feet thick) consists of red and green mudstone, siltstone, claystone, few thin coal beds, and several thin marine limestone beds (Rupert et al., 2001). It is divided into the Glenshaw and Casselman Formations, however the Glenshaw is the lower of the two and most relevant for consideration of overburden influence to the Upper Freeport coal seam. The lower quarter of the Glenshaw is non-marine because that environment continued from the upper Allegheny, while the upper three-fourths experienced marine transgressions that introduced shallow marine and lower delta-plain sediments (Fichter, 2000). This allowed for the formation of its characteristic laterally extensive marine units, including the Ames limestone which marks the top of the Glenshaw, as well as the transition to freshwater cyclothem (Fichter, 2000). Quartz-rich sandstone occurs in the lower portion of the Conemaugh, while calcareous sandstone is prevalent in the middle and upper portions (Brady et al., 1998).

Overall, the general trend of a drier climate continued from the late Allegheny through the Conemaugh.

1.7.1c Monongahela Group

The Monongahela Group (~200-430 feet thick) is composed of mainly limestones (non-marine to marginal marine), sandstones, shales, siltstones, with only a few coal seams (Tewalt et al., 2001). The climate at this time was wet, but drying, and mostly non-marine rocks are present with occasional marine beds caused from periodic coastal inflow into the floodplain (Cassle, 2005). It shows that the northern Appalachian basin was not connected to the sea, thus a widespread lake or system of lakes formed causing lateral transition from terrestrial red beds to lacustrine swamp deposits (Fichter, 2000). The Pittsburgh coal seam marks the beginning of the Monongahela Group which is subdivided into the Pittsburgh and Uniontown Formations. The entirely non-marine Pittsburgh Formation is the lower of the two and will be the focus of overburden influence for the Pittsburgh sites. It includes the Lower, Redstone, Fishpot, Sewickley, and Upper members and is characterized by thick carbonate accumulations of thin-bedded lacustrine limestone and associated thin mudstone (Fichter, 2000). The overburden varies from sandstone deposited in distributary channels to limestone deposited in lakes to shale deposited in mud flats. Calcareous sandstones are prevalent and shales may be a lateral less calcareous facies of the freshwater limestone (Brady et al., 1998).

1.8 Hydrogeologic setting

Coal seams can be situated at elevations either above or below major streams and rivers that control shallow regional groundwater flow (Figure 4). As explained by Donovan et al. (2000) and Demchak (2005), for those below drainage, once mining ceases, mine dewatering pumps are turned off and the mines begin to fill with water. For those above drainage, two post-mining scenarios are possible (Figure 4). If mined down-dip from a higher elevation, the mine will flood similar to below-drainage mines. If mined up-dip from a low elevation, infiltration will drain out of the mine rather than pooling, termed “free draining”.

Coal mine water chemistry is dependent on the extent and duration of flooding (Lambert et al., 2004). Most below-drainage mines, once flooded, will produce net-alkaline discharge (although still highly mineralized) because acid generation from pyrite oxidation is diminished (Demchak, 2005). Residence time of water in flooded mines and net alkalinity of resulting mine discharges are commonly positively correlated (Winters and Capo, 2004).

For mines sampled in this study, hydrogeologic setting was designated as fully flooded, partially flooded, or free draining. Fully flooded implies that the mine is situated below regional drainage and the discharge elevation is at or near the highest elevation of the mine. Mines that are partially flooded or free draining discharge from elevations below the highest part of the mine.

1.9 Hypothesis regarding $\delta^{13}\text{C}_{\text{DIC}}$

Many factors will contribute to $\delta^{13}\text{C}_{\text{DIC}}$ signatures in mine discharges: composition of rock strata (marine or non-marine, calcareous or non-calcareous); degree of atmospheric exposure; and amount of generated acidity. In considering the various hydrogeochemical processes that are influenced by geology and hydrogeologic setting, several hypotheses were formulated.

It is hypothesized that carbonate dissolution will produce more enriched values of ^{13}C compared to natural groundwaters. Anoxic environments attributed to fully flooded mines are hypothesized to have similar values to natural groundwaters because the pooled water should reach equilibrium with the surrounding rock. Likewise, it is anticipated that acid mine drainage will lead to carbonate dissolution and CO_2 evasion, consequently producing more enriched values when compared to natural groundwaters (Rose and Cravotta, 1998; Cravotta, 2008b; Kirby et al., 2009; Vesper and Smilley, 2010; Sharma et al., 2013).

Figure 4. General types of hydrogeologic settings for coal mines.

2. Methodology

2.1 Field methods

All sites were sampled during February 2013. Additionally, Pittsburgh sites were previously sampled during 2012 by Denicola (2013). Samples and field measurements, for both sampling events, were taken as close to discharge points as possible to minimize atmospheric contact. Sampling locations were selected on the basis of available chemical data, evidence of non-stagnant water, and ability to collect samples with little atmospheric exposure. Sample sites included seeps and mine portals. Upper Freeport sites were located using maps from Thies (2007) and Pittsburgh sites were located using GPS coordinates from Denicola (2013) (Table 4, Figures A1-A12,).

Sampling protocols followed those of Denicola (2013) for water chemistry and Sack (2012) for isotopes. Field parameters included temperature, pH, electrical conductivity (EC), oxidation-reduction potential (ORP), and alkalinity. Temperature (°C) and pH were measured by a Hanna HI 9025 pH meter calibrated using pH = 4 and pH = 7 buffer solutions. Electrical conductivity ($\mu\text{S}/\text{cm}$) was measured by a YSI EC 300 meter calibrated with a 1.413 mS/cm solution of 0.01 M KCl. Oxidation-reduction potential (mV) was measured by a YSI pH 100 meter calibrated using pH = 4 and pH = 7 buffer solutions.

All meters were calibrated at the start of each sampling day according to manufacturer protocol and checked at the end of the day for instrumental drift. Alkalinity ($\text{mg}/\text{L CaCO}_3$) measurements were determined through field titration to pH endpoint 4.5

using 1.6 N sulfuric acid in a 250 mL Erlenmeyer flask, a digital titrator, and the pH meter.

Samples were collected by inserting a 60 cc syringe into the discharge source and filtering through a 0.45 µm filter. The sample was split into 2 aliquots in 60 mL polyethylene bottles, stored on ice in the field, and refrigerated until analyzed. All bottles for cation analysis were acidified with 0.6 mL trace metal grade nitric acid, whereas the bottles for anion analysis were not preserved with acid. $^{13}\text{C}_{\text{DIC}}$ samples were collected using a 60 mL syringe with a Luer-Lok tip that was pre-rinsed three times with sample water and filtered through a 0.45 µm filter into a 10 mL Wheaton serum vial with 2 drops of benzalkonium chloride (17% w/w) added as an astringent. The vials were filled forming a meniscus at the top to ensure no headspace. 20 mm Teflon septa were placed in aluminum caps and sealed to the top of the vials using a crimper.

2.2 Chemical analysis

Major cations, metals, and anions were analyzed at the NRCCE Analytical Laboratory and $^{13}\text{C}_{\text{DIC}}$ sample analysis was conducted by WVSIL. Protocols and methods for geochemical collection and analysis followed Title 40, Code of Federal Regulations, Part 136 (40 CFR 136) by the U.S. Environmental Protection Agency. Lab analysis was conducted by a Varian Vista Pro CCD sequential inductively coupled plasma optical emission spectroscopy (ICP-OES) for determination of total Al, Fe, Mn, Na, K, Mg, Ca, Ba, S, and Sr. Concentrations of NO_3 , Br, Cl, and F (reported in mg/L) were determined by a Dionex GP40 gradient pump, AS40 automated sampler, LC20

chromatography enclosure, ED40 electrochemical detector, and AS4A column set using Na-CO₃-HCO₃ eluent.

Stable isotope analysis of DIC was carried out using a Finnigan Delta Advantage continuous-flow isotope-ratio mass spectrometer (IRMS) with the ThermoQuest Finnigan Gas Bench II device. Vienna Pee Dee Belemnite (V-PDB) is the International Atomic Energy Agency (IAEA) reference standard the lab standards were calibrated against. All $\delta^{13}\text{C}_{\text{DIC}}$ isotope values are calculated using Equation 1 (Appendix Table 1) and reported in per mil (‰) relative to the international standard, V-PDB. The precision for $\delta^{13}\text{C}_{\text{DIC}}$ is 0.1 ‰.

Equations used for all calculations made are presented in Table A1. They include: Eh from oxidation-reduction potential (ORP), electron potential (pe), charge balance (CBE), net alkalinity, DIC, total dissolved solids (TDS) as the sum of all major cations and anions, and sulfate from total sulfur. A Bjerrum plot of carbonate concentration vs. pH, in water under closed system conditions, and PHREEQC were used to determine carbonate speciation, alkalinity, net alkalinity, DIC, total anions, CBE, and TDS. PHREEQC was also used to determine pCO₂ and saturation indices. Equations used to construct the Bjerrum plot are also listed in Table A1.

3. Results

Fifteen groundwater discharges from 12 mines in the Pittsburgh seam were sampled and compared to 5 discharges from mines in the Upper Freeport seam. Results include field-measured, lab-measured, and calculated values. Comparisons were made on the basis of geology and hydrogeologic setting.

All analyses involving $\delta^{13}\text{C}_{\text{DIC}}$ values use DIC values based on February 2013 field measurements. Analyses not involving $\delta^{13}\text{C}_{\text{DIC}}$ values incorporate 2012 field measurements reported in Denicola (2013) for Pittsburgh sites. Geochemical analysis results for Pittsburgh sites are all taken from Denicola (2013) since the chemistry of underground mine discharges stays relatively the same throughout the year (Donovan et al., 1997).

3.1 Field results

Values of field parameters (temperature, pH, conductivity, and ORP), collected in February 2013, are presented in Table 5. Results for the Pittsburgh seam discharges also include those measured by Denicola (2013) in June-October 2012.

3.2 Calculated results

Calculated parameters (Eh, pe, alkalinity, net alkalinity, net acidity, sulfate, TDS, CBE, bicarbonate, carbonate, and DIC) are presented in Tables 6 and A1. Figure 5 displays observed Eh and pH for the 20 sites, superposed on iron speciation modeled after Hem (1971). Figure 6 shows carbonate species concentrations vs. pH used to estimate alkalinity for acidic ($\text{pH} < 4.5$) waters. HCO_3^- values for alkaline waters were fit

Figure 5. Eh versus pH diagram showing the ferric and ferrous equilibrium line showing the values for the sites sampled. Stability fields neglect aqueous species of ferrous and ferric iron (Modified from Hem, 1971). Gray squares indicate sites in the Pittsburgh coal seam, white squares indicate sites in the Upper Freeport.

Figure 6. Bjerrum plot showing distribution of carbonate species in water under closed system conditions. Bicarbonate equilibria were fitted to field alkalinity data from alkaline sites ($\text{pH} > 4.5$) to estimate alkalinity for acidic sites ($\text{pH} < 4.5$).

to closed system DIC equilibrium curves, with resulting average (fitted) total carbon of 0.016 and 0.0032 M for Pittsburgh and Upper Freeport sites, respectively (Table 7).

Using these DIC values for acidic waters and the measured alkalinities for waters with $\text{pH} > 4.5$, concentrations of Al^{3+} , Fe^{2+} , and Fe^{3+} ; pCO_2 ; and saturation indices of $\text{Al}(\text{OH})_3$, calcite, dolomite, $\text{Fe}(\text{OH})_3$, goethite, gypsum, and jarosite-k were determined using PHREEQC (Table 8).

The PHREEQC output shows higher concentrations of Fe^{3+} than Fe^{2+} for T2BNE, COKE, and T&T2; higher concentrations of Fe^{2+} than Fe^{3+} for CLYD and TS10A; and higher Al^{3+} concentrations for MDVL, RB, and T&T2 than the rest of the sites. The poorly-crystalline mineral $\text{Al}(\text{OH})_3$ was close to equilibrium for VES12, ECL1, ECL3, BRWN, and CLYD and undersaturated for the rest, especially GRAY, T2BNE, MDVL, SM3A, COKE, RB, T&T2, and T&T3. Calcite was close to equilibrium for VES12, ECL1, ECL3, BRWN, CLYD, PALM, and GATE and undersaturated for the rest, especially GRAY, T2BNE, MDVL, SM3A, COKE, RB, T&T2, and T&T3. Dolomite was close to equilibrium for VES12 and ECL1 and was undersaturated for the rest, especially GRAY, T2BNE, MDVL, SM3A, COKE, RB, T&T2, and T&T3. $\text{Fe}(\text{OH})_3$ was close to equilibrium for BRWN, CLYD, PALM, MAD3B, MAD3A, SALT, and TS10A; undersaturated for GATE, GRAY, T2BNE, MDVL, SM3A, COKE, RB, T&T2, and T&T3; and oversaturated for VES12, ECL1, ECL3, and NORW. Goethite was oversaturated for all sites. Gypsum was close to equilibrium for ECL1, CLYD, GRAY, T2BNE, MAD3B, MAD3A, MDVL, NORW, SALT, and TS10A and undersaturated for the rest. Potassium-rich jarosite was close to equilibrium for CLYD, MAD3A, NORW, COKE, RB, T&T2, and T&T3 and undersaturated for the rest, especially GATE. pCO_2

values are only reported for sites with pH>4.5 where field alkalinity measurements were collected. They include VES12, ECL1, ECL3, BRWN, CLYD, PALM, GATE, MAD3B, NORW, and TS10A, all of which had values significantly higher than average atmospheric pCO₂ (10^{-3.5} atm).

3.3 Statistical analysis

Given the small sample set, a T-test (2 sample, equal variance, 1-tailed) was used on the field and lab data to test for significant differences between the means of aqueous constituents in the Pittsburgh and Upper Freeport mine discharges (Table 9). Using a 5% significance level, pH, Eh, and $\delta^{13}\text{C}_{\text{DIC}}$ reported p-values <0.05, indicating significant differences between the Pittsburgh and Upper Freeport for those parameters. The rest had p-values >0.05, indicating no significant differences between them for those parameters.

Bivariate correlation was calculated between: pH, Eh, Fe, Al, Mn, Na, K, Mg, Ca, Ba, SO₄, F, Cl, Br, TDS, net alkalinity, HCO₃, CO₃, DIC, and $\delta^{13}\text{C}_{\text{DIC}}$ (Table 10). Strong positive correlations are indicated by R-values greater than 0.90. No significant positive correlations are observed between $\delta^{13}\text{C}_{\text{DIC}}$ and any other constituent.

A cluster analysis (CA) dendrogram was developed using pH, Fe, Al, Mn, Na, K, Mg, Ca, Sr, SO₄, F, Cl, Br, TDS, and alkalinity for the 20 sites. CA was performed in R using hierarchical agglomeration and the single linkage method, also known as the nearest-neighbor method (Sibson, 1972; Figure 7). Hierarchical agglomeration is a function using a set of dissimilarities where dissimilarities between the clusters are the squared Euclidian distances between the cluster means. Essentially, each observation

Figure 7. Cluster analysis dendrogram (single linkage method) according to pH, Fe, Al, Mn, Na, K, Mg, Ca, Sr, SO₄, F, Cl, Br, TDS, and alkalinity. C1 represents Pittsburgh coal, fully flooded, net alkaline; C2 represents Pittsburgh, fully flooded, net alkaline, high total dissolved solids (TDS); C3 represents Pittsburgh and Upper Freeport, free draining, net acidic; and C4 represents Pittsburgh, partially flooded, alkaline.

begins as a separate group and groups close to one another are successively merged forming a dendrogram. Thus, relationships between observations and between clusters are displayed for interpretation. The resulting dendrogram shows a clear distinction between net-alkaline and net-acidic sites, as well as fully-flooded, partially-flooded, and free-draining sites. Four clusters can be differentiated and these are interpreted as follows: (C1) Pittsburgh coal, fully flooded, net alkaline; (C2) Pittsburgh coal, fully flooded, net alkaline, high TDS; (C3) Pittsburgh and Upper Freeport coal, free draining, net acidic; and (C4) Pittsburgh coal, partially flooded, net alkaline (Table 11). Averages for the clusters are shown in Table 12. Since C3 contains sites from both Pittsburgh and Upper Freeport, geology is not a controlling factor. However, CA detected differences in hydrologic setting.

3.4 Lab results

All 20 sites were analyzed for inorganic geochemistry (Fe, Al, Mn, Na, K, Mg, Ca, Ba, Sr, NO₃, S, F, Cl, and Br; Table 13). Since the geochemistry of mine discharges remains relatively consistent throughout the year (Donovan et al., 1997), chemical analysis results from Denicola (2013) were used in the dataset for the 15 Pittsburgh sites, while chemical analyses for the 5 Upper Freeport sites were based on February 2013 sampling. For results below the minimum detection level (MDL) a value of 0.5 times the MDL was employed in statistical calculations. A charge balance error (CBE) of up to 21.2% was considered to have passed quality control.

Hydrogeochemical variations between field samples are summarized in a Piper diagram (Figure 8, Table 14) presenting the relative abundance (in meq/L) of ions for

Figure 8. Piper diagram displaying hydrogeochemical results (meq/L) according to clusters. Arrows indicate shift in dominant ions from net acidic to net alkaline.

each sample. While Piper diagrams consider only Mg, Ca, Na, K, CO₃, HCO₃, SO₄, and Cl, they are useful for classifying waters and identifying evolution trends. The majority of the sample set can be discriminated into two categories: (1) Ca²⁺-SO₄²⁻ waters, typical of shallow and above-drainage mine water and (2) Na⁺-HCO₃⁻ waters, representing deeper groundwaters influenced by ion exchange. The dominant ions shift from net acidic to net alkaline as indicated by the arrows in Figure 8.

All 20 sites were analyzed for $\delta^{13}\text{C}_{\text{DIC}}$ with a precision of 0.1 ‰ (Table 15). Results range from -0.6 to -14.8 ‰ and were either within or above the normal groundwater range of -11 to -16 ‰. Net-alkaline samples all had DIC concentrations >240 mg/L versus net-acidic samples with concentrations of <42 mg/L.

A graph of $\delta^{13}\text{C}_{\text{DIC}}$ vs. DIC shows a clear distinction between net-alkaline and net-acidic samples (Figure 9). Per Table 15 and Figure 9, the samples can be broken into three groups that are (1) enriched above atmospheric $\delta^{13}\text{C}$; (2) enriched above normal groundwater range, but depleted below atmospheric $\delta^{13}\text{C}$; and (3) within normal groundwater range for $\delta^{13}\text{C}_{\text{DIC}}$.

Of the net-alkaline sites, ECL1 was the most enriched in ¹³C. Those most depleted in ¹³C were the fully-flooded mines, PALM and GATE, of which were the only two alkaline sites to plot in the normal groundwater range. Of the net-acidic sites, T2BNE was the most enriched with $\delta^{13}\text{C}_{\text{DIC}} = -0.6$ ‰ and TS10A was the most depleted with $\delta^{13}\text{C}_{\text{DIC}} = -14.8$ ‰.

Observations, regarding ¹³C_{DIC} composition, can also be made of the three mines that were sampled in two locations based on site-specific differences (Table 16). Within the Maiden #3 mine, MAD3B is strongly alkaline while MAD3A is not; ascribed to the

difference between discharge elevations (840 ft. vs. 900 ft., respectively). In this situation, water from MAD3B was isotopically heavier in ^{13}C than that from MAD3A. The Eclipse mine also has some differences between its two samples, ECL1 and ECL3. First, the coal bed is slightly lower in elevation at ECL1 (790 ft.) than at ECL3 (800 ft.). Second, ECL1 is at a slightly higher surface elevation (820 ft.) than ECL3 (800 ft.). Under these conditions, water from ECL1 was isotopically heavier in ^{13}C than that of ECL3. In contrast to the other mines with multiple sample locations, the two sites of the Maiden #1 mine, T2BNE and MDVL, are quite far apart, and have much different drainage elevations and mine catchments. T2BNE has a discharge elevation of 900 ft. and regional drainage elevation of 840 ft. for Dunkard Creek, to which it drains, whereas MDVL is situated at 890 ft. for both discharge and regional drainage (Robinson Run) elevations (Table 16). In this case, water from T2BNE was isotopically heavier in ^{13}C than water from MDVL.

Fractional contributions of carbonate dissolution vs. oxidation of organic C were estimated from the observed $\delta^{13}\text{C}_{\text{DIC}}$ using a two-end-member mixing model (Table A1, Equation 15; Table 17), similar to the approach of Sharma (2013). End-member values of $\delta^{13}\text{C}_{\text{carbonate}} = -2.5\text{‰}$ (Pittsburgh Formation freshwater limestone) and $\delta^{13}\text{C}_{\text{organic}} = -23\text{‰}$ VPDB (soil CO_2 in temperate regions dominated by C3 vegetation) were employed after the approaches of Sharma et al. (2013) and Aravena et al. (1992), respectively. The sample sites were broken into three groups as listed in Table 17.

Figure 9. $\delta^{13}C_{DIC}$ vs. dissolved inorganic carbon (DIC) for the study sites. Carbonate (Pittsburgh limestone) and organic matter (soil CO₂) end-members are shown. Upper Freeport sites are in bold to differentiate them from Pittsburgh sites.

4. Discussion

4.1 Effects of hydrogeologic setting on water chemistry

The hydrogeochemistry of each sample is interpreted to reflect its hydrogeologic setting. Cluster analysis resulted in four cluster groups (Figure 7) interpreted to be related to degree of flooding and, correspondingly, to alkaline versus acidic conditions. C3 waters are acidic with negligible alkalinity and come from “free draining” mines of both the Upper Freeport and Pittsburgh seams. C4 contains waters from “partially flooded” mines in the Pittsburgh seam. C1 and C2 waters are from “fully flooded” mines that are all in the Pittsburgh seam. Cluster analysis suggests that hydrogeologic setting has more of an impact on water chemistry than geology. This is perhaps attributed to the relatively minor differences in coal and overburden geology of the sampled mines.

This trend is demonstrated in Figure 10 (SI_{cal} vs. DIC) which emphasizes that the free-draining sites, regardless of geology, were strongly undersaturated with respect to calcite, while the partially-flooded and fully-flooded sites were close to equilibrium. The Piper diagram (Figure 8) also shows distinct grouping of sample sites according to hydrogeologic setting. C2 fully-flooded sites, PALM and GATE, plot as $Na^+HCO_3^-$ waters and contain the greatest concentration of alkalinity within the data set. The third fully-flooded mine, CLYD, fell in the Na^+Cl^- region with high TDS attributed to the fact that it is a recently developed discharge. Most of the C3 free-draining sites plot as $Ca^{2+}SO_4^{2-}$ waters. Additionally, the Eh–pH diagram (Figure 5) shows that although all waters

Figure 10. Saturation index of calcite versus dissolved inorganic carbon (DIC) according to clusters; illustrates behavior of sampled mines is dictated by hydrogeologic setting.

tend to straddle the Fe^{2+} - Fe^{3+} equilibrium line, C3 free-draining sites are all clustered together, with the exception of MAD3A and TS10A.

4.2 Effects of geology on water chemistry

Significant differences ($p < 0.05$) were determined between mean values of pH, Eh, and $\delta^{13}\text{C}_{\text{DIC}}$ in the Upper Freeport and Pittsburgh site groups (Table 9). However, there were no other significant mean differences between other geochemical parameters based on coal seam. Both Upper Freeport sites and Pittsburgh C3 sites show negligible DIC (Figure 9), so geology alone does not explain this observation. All Upper Freeport samples are from C3 sites and this is significantly different from the range of hydrogeologic settings in the Pittsburgh seam. Thus, the effect of geology on water chemistry is difficult to determine due to inherent bias within the sample set. Inorganic mine-water geochemistry is similar between the two formation sources.

4.3 ^{13}C evolution

The primary sources of DIC for most natural groundwater are decomposition of organic matter (e.g., in the soil zone) and dissolution of carbonate minerals (in the soil or in the aquifer). In “normal groundwater”, these two end-members contribute equally, producing $\delta^{13}\text{C}_{\text{DIC}}$ signatures ranging between about -11 to -16 ‰ (Mook and Tan, 1991). Dissolution of carbonate rocks can result from reaction with either carbonic or sulfuric acid. Carbonic acid weathering will incorporate atmospheric CO_2 ($\delta^{13}\text{C} \sim -8$ ‰) and release fossil carbon. Sulfuric acid weathering will only release fossil carbon. So while both produce HCO_3^- and release carbon isotopes reflecting the dissolved carbonate rocks, the increased amount of HCO_3^- containing fossil carbon produced from sulfuric acid

enhanced carbonate dissolution may result in different $\delta^{13}\text{C}_{\text{DIC}}$ values. Higher sulfate concentrations for all of the field sites suggest influence of sulfuric acid enhanced carbonate dissolution due to pyrite oxidation (Table 13). High sulfate concentrations also suggest that none of the sites are conducive for methanogenesis.

4.4 Differences in ^{13}C behavior among clusters

Correlation analysis showed no significant correlations between hydrogeochemical parameters and $\delta^{13}\text{C}_{\text{DIC}}$. Figure 9 shows no distinct differences between acidic and alkaline waters in terms of $\delta^{13}\text{C}_{\text{DIC}}$ values, however, there are systematic groupings of $\delta^{13}\text{C}_{\text{DIC}}$ vs. DIC in the dataset. Water chemistry in this plot can be discriminated into free-draining (C3, left), partially-flooded (C4, middle), and fully-flooded (C1, right) groups based on DIC alone. CLYD (the sole water in C2) is an apparent outlier given that this portal discharge is a relatively recent (began in 1996) discharge and has higher TDS than C1. PALM and GATE, discharges from the two fully-flooded highly-alkaline mines, are in fact isotopically lighter than the other alkaline waters of C4 (partially-flooded Pittsburgh seam mines). Another feature of these two C1 waters is that they discharge from wells in the deepest part of their flooded mines and give field evidence of sulfate reduction (detectable H_2S odor). The isotopically-enriched $\delta^{13}\text{C}_{\text{DIC}}$, as well as the extreme alkalinity in these waters, may be the result of biogenic sulfate reduction.

On average, C4 (alkaline, partially-flooded) sites show heavier $\delta^{13}\text{C}_{\text{DIC}}$ than C3 (acidic, free-draining) sites, excluding the outlier T2BNE (Table 12). This may be explained by dissolution of the isotopically-light (-1 to -3 ‰) Pittsburgh limestone, the

overburden unit that partially-flooded mine waters in the Pittsburgh seam would be exposed to. Thus, the C4 carbon isotopic signature may be ascribed to rock-water interaction contributing to carbonate dissolution. Depending on $p\text{CO}_2$ in the mines, corresponding to degree of mine saturation, CO_2 degassing may also influence $^{13}\text{C}_{\text{DIC}}$ concentration (Tables 8 and 12).

Of the C3 (acidic, free-draining) sites T&T3, RB, MAD3A, and TS10A fall within the normal groundwater range. The rest of the C3 sites are enriched above the normal groundwater range, excluding T2BNE, an outlier, due to potential surface water interaction from a subsided sinkhole capturing a small stream approximately 1km south of the discharge. As with fully- and partially-flooded mines, free-draining mines of C3 are likely influenced by a mixture of carbonate input, CO_2 evasion, and CO_2 from the soil zone. On average C3 sites show lighter $\delta^{13}\text{C}_{\text{DIC}}$ than C4 (alkaline, partially-flooded) sites which indicates larger organic carbon contributions for C3 sites than C4 (Tables 12 and 17).

4.5 Differences in ^{13}C within mines

The importance of hydrogeologic setting is well demonstrated in Maiden #3 mine which was sampled in two different locations, MAD3A and MAD3B. MAD3B is more enriched than MAD3A. Both are updip of the minimum mine elevation, but MAD3A has a discharge elevation higher than MAD3B (Table 16). Thus, MAD3A is discharging water from the beach portion of the mine versus MAD3B which is discharging water from the middle/back of the mine. MAD3A has a carbon isotope signature within the normal groundwater range. Although it is net acidic and would have been expected to

have a $^{13}\text{C}_{\text{DIC}}$ isotope signature more enriched than the range for normal groundwater, the mine water being discharged is coming off the top and that water may not have had enough time to interact with carbonates like the water coming out at MAD3B. This, in addition to oxidation of DOC driven by aerobic bacteria, may explain why MAD3A is not as enriched as MAD3B and also emphasizes the significance of hydrogeologic setting on the geochemistry of mine waters.

4.6 Data Limitations

Due to budget limitations, geochemical data for the Pittsburgh sites were taken from a previous study (Denicola, 2013). Thus, sampling times were different for geochemistry and isotopes at these Pittsburgh seam sites. Several of the sites had a pH too low (<4.5) to determine alkalinity in the field. For these sites, DIC was interpolated based on alkaline samples. Additionally, field sampling entailed some possibility of oxidation of water prior to ORP measurement and mixing of surface water (snowmelt). Finally, though pump intakes and probes/electrodes were submerged as deep as possible into the sampled mine discharges to avoid atmospheric exposure, CO_2 evasion was a potential factor.

5. Conclusions

Measured values for 20 sites showed no identifiable relationships in $^{13}\text{C}_{\text{DIC}}$ isotopic composition with respect to geology or hydrogeologic setting. Conversely, cluster analysis applied to inorganic geochemistry of the same waters resulted in four distinct clusters, each with sites whose chemical behavior was attributed to hydrogeologic setting. Cluster averages for $\delta^{13}\text{C}_{\text{DIC}}$ were -13.0, -8.2, -11.0, and -6.0 ‰ for C1-C4, respectively (Table 12). Using these clusters, the following are insights gained from this survey regarding the hydrogeochemical processes occurring in these underground mines:

- Biogenic sulfate reduction likely occurs in C1 net-alkaline, fully-flooded mines PALM and GATE as evidenced by high HCO_3^- concentrations and depleted $\delta^{13}\text{C}_{\text{DIC}}$ (Tables 5, 6, and 12).
- Sampled mines with higher pCO_2 than atmospheric will have a component of CO_2 evasion as evidenced by all C4 net-alkaline, partially-flooded sites.
- Sulfuric acid enhanced carbonate dissolution, due to pyrite oxidation, occurs in all sampled mines as evidenced by high SO_4 concentrations and the presence of Fe (Table 13).
- Methanogenesis is unlikely to occur in all sampled mines due to high SO_4 concentrations (Table 13).

Here, no strong positive relationships were evident between $\delta^{13}\text{C}_{\text{DIC}}$ and inorganic chemistry, possibly attributed to too many variables and too few sampling locations, leading to the conclusion that this is not an easy “quick look” technique for determining sources of carbon in DIC. However, although the study was inconclusive in evaluating

efficacy of using carbon isotope surveys to detect differences in geology and hydrogeologic setting, results suggest hydrogeologic setting and age of discharge play a key role in the amount of pyrite oxidized and subsequent calcite dissolution.

6. Recommended future work

To detect variations in $\delta^{13}\text{C}_{\text{DIC}}$, additional sampling of these sites is necessary, as well as increasing sample set size. Although the $^{13}\text{C}_{\text{DIC}}$ isotopic survey was not effective for this study, $^{13}\text{C}_{\text{DIC}}$ analysis may be effective if used on groundwater discharges from mines that have had log analysis conducted for the overburden and have access to the overlying rock strata in order to collect samples for ^{13}C isotopic analysis so that an end-member model analysis can be more accurately implemented. A better understanding of hydrogeochemical processes can also be gained through use of additional isotopes. Sharma et al. (2013) used $\delta^{34}\text{S}_{\text{SO}_4}$ to evaluate extent of bacterial sulfate reduction, as well as Sr isotopes to evaluate proportion of carbonate-derived DIC.

Tables

Carbon source	Equilibrium reactions	Effect on carbon isotopes
	CO_{2(g)} dissolution:	Enriches DIC*
Soil CO _{2(g)}	CO ₂ diffusion into water	$\delta^{13}\text{C} = -23\text{‰}$
↑	CO _{2(g)} ↔ CO _{2(aq)}	$^{13}\epsilon = 1.1\text{‰} \uparrow$
CO _{2(aq)}	CO ₂ hydration	$\delta^{13}\text{C}_{\text{DIC}} = -24.1\text{‰}$
↓	CO _{2(aq)} + H ₂ O ↔ H ₂ CO ₃	$^{13}\epsilon = 10.4\text{‰} \downarrow$
HCO ₃ ⁻ (bicarbonate)	1 st dissociation of carbonic acid	$\delta^{13}\text{C}_{\text{DIC}} = -13.7\text{‰}$
↓	H ₂ CO ₃ * ↔ H ⁺ + HCO ₃ ⁻	$^{13}\epsilon = 0.5\text{‰} \downarrow$
CO ₃ ²⁻ (carbonate)	2 nd dissociation of carbonic acid	$\delta^{13}\text{C}_{\text{DIC}} = -14.2\text{‰}$
↓	HCO ₃ ⁻ ↔ H ⁺ + CO ₃ ²⁻	$^{13}\epsilon = 0.3\text{‰} \downarrow$
CaCO ₃ (calcite)	Calcite dissolution: CaCO ₃ + H ₂ CO ₃ ↔ Ca ²⁺ + 2HCO ₃ ⁻	$\delta^{13}\text{C} = -14.5\text{‰}$
	Dolomite dissolution:	Enriches DIC
MgCa(CO ₃) ₂	Dissolution of magnesium MgCa(CO ₃) ₂ + 2H ⁺ ↔ Mg ²⁺ + Ca ²⁺ + 2HCO ₃ ⁻	Adds $\delta^{13}\text{C} \sim 0\text{‰}$ carbonate to DIC
	Silicate dissolution:	Enriches DIC
CO ₂	Dissolution of silicate (SiO ₂ , K/Na/Ca-AlSi ₃ O ₈) KAlSi ₃ O ₈ + 3H ₂ O + 3CO ₂ ↔ 2HCO ₃ ⁻ + 2K ⁺ Al ₂ Si ₂ O ₅ (OH) ₄ + SiO ₂	
	Gypsum dissolution:	Depletes DIC
HCO ₃ ⁻	Dissolution of gypsum under influence of the common ion effect Ca ²⁺ + HCO ₃ ⁻ + CaSO ₄ ·2H ₂ O ↔ Ca ²⁺ + SO ₄ ²⁻ + CaCO ₃ + H ⁺ + H ₂ O	
*Using average observed water temperature, 13°C.		

Table 1. Potential equilibrium reactions affecting DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ within coal mine aquifers (Fetter, 2001; Brady et al., 1998; Clark and Fritz, 1997; Pankow, 1991).

Carbon source	Kinetic reactions	Effect on carbon isotopes
CH ₂ O	Oxidation of fixed carbon by sulfate: Biogenic sulfate reduction $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$	Depletes DIC*
CH ₄	Oxidation of reduced carbon by sulfate: Biogenic sulfate reduction $\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$	Depletes DIC*
Organic Matter (i.e. CH ₂ O, CH ₄)	Oxidation of carbon by dissolved O₂: Ex: Biogenic methanotrophy $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	Depletes DIC*
CH ₃ COO ⁻	Acetate fermentation: Biogenic methanogenesis $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_4 + \text{CO}_2$	Enriches DIC
CO ₂	CO₂ reduction: Biogenic methanogenesis $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	Enriches DIC
---	CO₂ evasion: CO ₂ loss to atmosphere $\text{CO}_{2(\text{aq})} \rightarrow \text{CO}_{2(\text{g})}$ *May cause subsequent carbonate dissolution which enriches DIC	Enriches DIC

Table 2. Potential kinetic reactions affecting DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ within coal mine aquifers (Fetter, 2001; Brady et al., 1998; Clark and Fritz, 1997; Pankow, 1991).

PRIMARY REACTIONS
<p><u>Abiotic, pH>4</u></p> <p>Sulfur oxidation $\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$</p> <p>Iron oxidation & iron hydrolysis $\text{Fe}^{2+} + 2.5\text{H}_2\text{O} + 0.25\text{O}_2 \rightarrow \text{Fe}(\text{OH})_{3(\text{s})} + 2\text{H}^+$</p> <p><u>Biotic, pH<4</u></p> <p>Bacterial oxidation of Fe²⁺ $\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ \rightarrow 0.5\text{Fe}^{3+} + 0.5\text{H}_2\text{O}$</p> <p>Fe³⁺ reduction by pyrite $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$</p>
SECONDARY REACTIONS
<p>Contact with clays/aluminosilicates Releases: Al, Na, K, Mg Produces: circumneutral pH, ↑ sulfate, ↓ metals</p> <p>Contact with carbonate minerals Releases: Ca, Mg, Mn, Fe (siderite) Produces: circumneutral pH, ↑ Fe & Mn, can become acidic (pH~3) upon oxidation & precipitation of Fe</p> <p>Contact with non-alkaline material Produces: acidic drainage with ↑ Fe, Al, & Mn</p>

Table 3. Primary and secondary reactions, associated with pyrite oxidation, affecting DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ within coal mine aquifers (Fetter, 2001; Brady et al., 1998; Clark and Fritz, 1997; Pankow, 1991).

Site ID	Site	Mine	Coal Seam	Hydrogeologic Setting	Easting 27	Northing 27	County	State
VES12	Vesta 1&2	Vesta #1 & #2	Pittsburgh	Partially Flooded	595076	4437154	Fayette	PA
ECL1	Eclipse 1	Eclipse	Pittsburgh	Partially Flooded	594823	4437180	Fayette	PA
ECL3	Eclipse 3	Eclipse	Pittsburgh	Partially Flooded	593835	4437033	Fayette	PA
BRWN	Brownsville	Chamoni	Pittsburgh	Partially Flooded	595284	4432718	Fayette	PA
CLYD	Clyde	Clyde	Pittsburgh	Fully Flooded	582347	4425741	Greene	PA
PALM	Palmer	Palmer	Pittsburgh	Fully Flooded	592120	4419309	Fayette	PA
GATE	Gates	Gates	Pittsburgh	Fully Flooded	592378	4415805	Fayette	PA
GRAY	Grays Landing	Odonald 1 & 2	Pittsburgh	Free-Draining	592619	4409660	Fayette	PA
T2BNE	Taylorstown 2B	Maiden #1	Pittsburgh	Free-Draining	587590	4399227	Greene	PA
MAD3B	Maiden 3B	Maiden #3	Pittsburgh	Partially Flooded	587953	4402037	Greene	PA
MAD3A	Maiden 3A	Maiden #3	Pittsburgh	Free-Draining	588219	4402006	Greene	PA
MDVL	Maidsville	Maiden #1	Pittsburgh	Free-Draining	586294	4394599	Monongalia	WV
SM3A	Smith 03A	Peacock	Pittsburgh	Free-Draining	595133	4389706	Monongalia	WV
NORW	Norway	Mine #26	Pittsburgh	Partially Flooded	568612	4369498	Marion	WV
SALT	Saltwell	Nixon #5	Pittsburgh	Free-Draining	563148	4356844	Harrison	WV
COKE	Coketon	Kempton	Upper Freeport	Free-Draining	628635	4332867	Tucker	WV
TS10A	Tri-State 10A	Tri-State 10	Upper Freeport	Free-Draining	611202	4368438	Preston	WV
RB	Ruthbell #3	Ruthbell #3	Upper Freeport	Free-Draining	617760	4377641	Preston	WV
T&T2	T&T#2&RB#1	T&T #2 & Ruthbell #1	Upper Freeport	Free-Draining	617461	4377849	Preston	WV
T&T3	T&T #3	T&T #3	Upper Freeport	Free-Draining	615491	4378506	Preston	WV

Table 4. General information and locations for sampling sites.

Site ID	Sample Date	Temperature (°C)	pH	Specific Conductivity (µS/cm)	Oxidation Reduction Potential (mV)	Alkalinity (mg/L CaCO ₃)
VES12	02/2013	13.1	6.42	1009	123	330
ECL1	02/2013	13.6	7.06	1027	245	254
ECL3	02/2013	11.9	6.46	1047	174	232
BRWN	02/2013	13.2	6.59	1354	49	485
CLYD	02/2013	14.9	6.24	7110	75	450
PALM	02/2013	16.6	7.06	1599	183	720
GATE	02/2013	16.4	7.00	1755	97	760
GRAY	02/2013	16.4	3.10	1944	368	0
T2BNE	02/2013	11.9	3.89	1190	471	0
MAD3B	02/2013	13.6	6.18	1435	19	197
MAD3A	02/2013	10.2	4.03	1720	248	0
MDVL	02/2013	15.2	2.87	2756	467	0
SM3A	02/2013	14.8	2.78	2305	408	0
NORW	02/2013	13.9	6.22	1000	97	232
SALT	02/2013	13.9	5.30	721	324	26
COKE	02/2013	10.4	3.20	650	542	0
TS10A	02/2013	12.2	5.87	1024	5	43.6
RB	02/2013	13.0	2.84	1316	449	0
T&T2	02/2013	13.3	2.52	1746	587	0
T&T3	02/2013	9.3	2.93	757	512	0
VES12	07/2012	15.4	7.11	1450	241	449
ECL1	07/2012	13.6	7.00	1806	310	378
ECL3	07/2012	12.1	6.70	1510	251	323
BRWN	06/2012	12.8	6.62	1573	20	558
CLYD	10/2012	14.9	6.33	9100	-38	536
PALM	06/2012	16.9	6.51	1993	-30	853
GATE	06/2012	16.3	6.41	2205	-192	923
GRAY	06/2012	14.7	2.71	2965	310	0
T2BNE	06/2012	15.0	2.69	2442	558	0
MAD3B	06/2012	13.8	6.02	2147	27	202
MAD3A	06/2012	14.3	4.92	2490	172	12.5
MDVL	06/2012	14.8	2.83	3885	396	0
SM3A	06/2012	14.3	2.84	2486	392	0
NORW	07/2012	13.5	6.25	1480	60	240
SALT	07/2012	13.6	3.93	995	445	0

Table 5. Field parameters collected. Included are results from 2012 sampling conducted by Denicola (2013).

Site ID	Sample Date	Eh (V)	pe	CBE(%)	TDS (mg/L)	Net Alkalinity (mg/L CaCO ₃)
VES12	02/2013	0.36	6.27	4.82	1051	330
ECL1	02/2013	0.48	8.38	0.20	1337	254
ECL3	02/2013	0.41	7.24	-2.21	1087	232
BRWN	02/2013	0.28	4.96	4.90	1343	482
CLYD	02/2013	0.29	4.99	-2.57	7552	32.3
PALM	02/2013	0.39	6.73	21.69	1556	718
GATE	02/2013	0.32	5.58	19.21	1734	758
GRAY	02/2013	0.59	10.29	-9.60	956	-207
T2BNE	02/2013	0.70	12.42	-15.77	856	-53.8
MAD3B	02/2013	0.25	4.34	-9.26	1824	102
MAD3A	02/2013	0.48	8.59	-10.03	1564	-103
MDVL	02/2013	0.67	11.73	-9.33	1099	-296
SM3A	02/2013	0.64	11.13	-19.97	653	-163
NORW	02/2013	0.33	5.71	-5.62	1274	212
SALT	02/2013	0.55	9.69	-22.56	848	1.1
COKE	02/2013	0.77	13.66	3.19	305	-76.0
TS10A	02/2013	0.23	4.11	-1.13	1127	-192
RB	02/2013	0.67	11.80	2.28	597	-205
T&T2	02/2013	0.81	14.29	4.68	612	-337
T&T3	02/2013	0.74	13.19	3.40	413	-105
VES12	07/2012	0.48	8.10	-3.05	1197	449
ECL1	07/2012	0.55	9.33	-5.78	1489	378
ECL3	07/2012	0.50	8.39	-7.49	1198	323
BRWN	06/2012	0.25	4.29	0.77	1432	555
CLYD	10/2012	0.19	3.28	-3.34	7657	118
PALM	06/2012	0.19	3.26	14.60	1718	851
GATE	06/2012	0.03	0.54	11.49	1932	921
GRAY	06/2012	0.54	9.09	-5.25	956	-265
T2BNE	06/2012	0.79	13.30	-7.25	853	-152
MAD3B	06/2012	0.26	4.37	-9.44	1830	107
MAD3A	06/2012	0.40	6.80	-10.61	1576	-89.9
MDVL	06/2012	0.62	10.54	-8.90	1099	-303
SM3A	06/2012	0.62	10.49	-21.25	653	-152
NORW	07/2012	0.29	4.96	-6.05	1283	220
SALT	07/2012	0.68	11.50	-20.37	819	-28.2

Table 6. Calculated results. Included are results from 2012 sampling conducted by Denicola (2013).

Site ID	pH	Estimated alkalinity (mg/L CaCO ₃)	Total carbon (M)
GRAY	2.71	0.15	0.016
T2BNE	2.69	0.14	0.016
MDVL	2.83	0.20	0.016
SM3A	2.84	0.20	0.016
MAD3A	4.03	3.10	0.016
SALT	3.93	2.46	0.016
COKE	3.20	0.09	0.0032
RB	2.84	0.04	0.0032
T&T2	2.52	0.02	0.0032
T&T3	2.93	0.05	0.0032

Table 7. Estimated alkalinity for sites with pH<4.5 from Bjerrum plot.

Site ID	Al ³⁺	Fe ²⁺	Fe ³⁺	log pCO _{2(g)}	Al(OH) ₃	Calcite	Dolomite	Fe(OH) ₃	Goethite	Gypsum	Jarosite-K
	(mol/kg)			(atm)	(Saturation indices)						
VES12	7.48E-11	7.09E-10	8.37E-15	-1.46	-0.69	0.06	-0.81	1.91	7.45	-1.24	-2.3
ECL1	3.30E-10	1.14E-10	2.16E-14	-1.45	-0.55	-0.04	-0.43	1.94	7.41	-0.91	-1.54
ECL3	3.84E-09	6.15E-09	1.18E-13	-1.22	-0.46	-0.44	-1.19	1.82	7.23	-1.07	-1.49
BRWN	2.75E-09	1.32E-05	2.10E-14	-0.89	-0.8	-0.66	-2.2	0.82	6.26	-1.39	-4.21
CLYD	4.83E-08	2.05E-03	4.92E-13	-0.7	-0.61	-0.54	-1.39	0.99	6.51	-0.1	-0.13
PALM	1.38E-09	8.11E-06	1.57E-15	-0.58	-1.16	-0.73	-1.25	-0.65	4.94	-2.15	-9.01
GATE	1.40E-09	6.00E-06	2.17E-18	-0.45	-1.51	-0.93	-2.07	-3.83	1.75	-2.04	-17.8
GRAY	7.81E-05	8.12E-04	9.07E-08	-	-7.93	-11.51	-23.25	-4.26	1.25	-0.89	-8.81
T2BNE	4.91E-05	3.50E-06	6.35E-06	-	-8.16	-11.56	-23.28	-2.46	3.06	-0.9	-3.36
MAD3B	5.01E-09	5.76E-04	1.27E-12	-0.76	-2.34	-1.33	-2.9	0.73	6.21	-0.58	-1.51
MAD3A	7.26E-07	6.58E-04	3.95E-10	-	-3.43	-3.63	-7.5	-0.06	5.43	-0.59	-0.61
MDVL	1.66E-04	7.16E-04	2.30E-06	-	-7.25	-11.08	-22.46	-2.51	3	-0.77	-3.81
SM3A	7.67E-05	2.51E-04	6.44E-07	-	-7.51	-11.33	-22.93	-2.96	2.54	-1.3	-5.71
NORW	5.36E-09	1.22E-04	9.65E-13	-0.89	-1.58	-1.05	-2.42	1.36	6.83	-0.8	-0.64
SALT	2.65E-05	1.49E-06	3.89E-08	-	-4.79	-4.77	-9.79	-0.94	4.53	-0.84	-1.23
COKE	7.84E-05	1.06E-06	2.93E-06	-	-6.62	-11.2	-22.37	-1.14	4.2	-1.61	-0.59
TS10A	1.58E-09	1.74E-03	1.79E-12	-1.3	-3.34	-2.17	-4.77	0.49	5.91	-0.71	-2.35
RB	1.32E-04	3.20E-04	1.55E-05	-	-7.37	-11.89	-24.11	-1.58	3.87	-1.11	-0.19
T&T2	2.19E-04	4.64E-06	7.02E-05	-	-8.08	-13.02	-26.43	-1.87	3.58	-1.25	-0.85
T&T3	4.85E-05	2.01E-05	1.82E-05	-	-7.75	-11.74	-23.91	-1.19	4.11	-1.22	0.05

Table 8. PHREEQC results.

	pH	Cond	Eh	Fe	Al	Mn	Na	K	Mg	Ca	Ba	Sr	NO ₃	SO ₄	F	Cl	Br	$\delta^{13}\text{C}_{\text{DIC}}$
p-value	0.026	0.058	0.035	0.372	0.068	0.366	0.081	0.182	0.079	0.155	0.134	0.064	0.196	0.216	0.265	0.127	0.228	0.029

Table 9. P-values from T-test (2 sample, equal variance, 1-tailed) on field and lab data. Values less than 0.05 indicate significant differences between Pittsburgh and Upper Freeport sites.

	pH	Eh	Fe	Al	Mn	Na	K	Mg	Ca	Sr	SO ₄	F	Cl	Br	TDS	NetAlk	HCO ₃	CO ₃	DIC	$\delta^{13}\text{C}_{\text{DIC}}$
pH	1.00																			
Eh	-0.78	1.00																		
Fe	0.06	-0.32	1.00																	
Al	-0.80	0.64	0.00	1.00																
Mn	0.00	-0.22	0.88	-0.18	1.00															
Na	0.50	-0.61	0.62	-0.39	0.56	1.00														
K	0.47	-0.48	0.76	-0.39	0.72	0.92	1.00													
Mg	0.27	-0.28	0.75	-0.28	0.76	0.64	0.82	1.00												
Ca	0.29	-0.28	0.83	-0.22	0.76	0.64	0.86	0.95	1.00											
Sr	0.53	-0.50	0.71	-0.41	0.64	0.91	0.98	0.85	0.87	1.00										
SO₄	0.13	-0.27	0.89	-0.11	0.85	0.77	0.90	0.90	0.92	0.88	1.00									
F	-0.23	-0.03	-0.22	0.07	-0.15	-0.02	-0.24	-0.40	-0.49	-0.27	-0.27	1.00								
Cl	0.33	-0.22	0.63	-0.26	0.61	0.79	0.87	0.71	0.77	0.88	0.78	-0.26	1.00							
Br	0.27	-0.43	0.65	-0.20	0.56	0.89	0.81	0.61	0.56	0.78	0.72	0.11	0.70	1.00						
TDS	0.38	-0.49	0.80	-0.28	0.72	0.95	0.97	0.82	0.84	0.96	0.93	-0.17	0.85	0.86	1.00					
NetAlk	0.79	-0.68	-0.30	-0.65	-0.32	0.45	0.20	-0.12	-0.17	0.25	-0.17	0.15	0.10	0.28	0.18	1.00				
HCO₃	0.76	-0.76	-0.04	-0.54	-0.15	0.65	0.39	0.03	0.00	0.43	0.05	0.18	0.27	0.51	0.41	0.95	1.00			
CO₃	0.68	-0.43	0.30	-0.45	0.20	0.76	0.71	0.40	0.46	0.75	0.45	-0.15	0.71	0.63	0.68	0.58	0.69	1.00		
DIC	0.76	-0.76	-0.04	-0.54	-0.15	0.65	0.39	0.03	0.00	0.43	0.05	0.18	0.27	0.51	0.41	0.95	1.00	0.69	1.00	
$\delta^{13}\text{C}_{\text{DIC}}$	0.16	0.29	-0.22	-0.13	-0.21	-0.01	0.10	0.24	0.23	0.23	0.05	-0.23	0.30	-0.10	0.06	0.05	-0.02	0.32	-0.02	1.00

Table 10. Pearson's correlation matrix. Positive correlations with R-values greater than 0.80 are shaded in gray.

Cluster 1	Cluster 2	Cluster 3	Cluster 4
PALM	CLYD	TS10A	BRWN
GATE		MAD3A	MAD3B
		COKE	NORW
		T&T3	VES12
		SM3A	ECL1
		RB	ECL3
		T&T2	
		T2BNE	
		MDVL	
		SALT	
		GRAY	

Table 11. Clusters resulting from cluster analysis (single linkage method) of pH, Fe, Al, Mn, Na, K, Mg, Ca, Sr, SO₄, F, Cl, Br, TDS, and alkalinity.

	C1	C2	C3	C4
pH	6.5	6.3	3.5	6.6
Cond	2099.0	9100.0	1831.4	1661.0
Eh	0.1	0.2	0.6	0.4
HCO₃	1083.4	653.9	7.2	437.2
Fe	0.8	225.4	38.9	10.4
Al	0.1	0.1	9.4	0.1
Mn	0.1	7.2	1.6	0.5
Na	549.5	1596.9	22.5	203.4
K	3.2	26.7	1.2	4.3
Mg	18.5	103.5	29.4	36.6
Ca	27.3	352.6	88.2	113.5
Ba	0.1	0.0	0.0	0.0
Sr	1.2	7.8	0.5	1.8
NO₃	0.0	0.2	0.2	0.3
SO₄	132.6	4159.0	598.9	521.9
F	0.6	0.3	0.4	0.3
Cl	6.3	519.4	17.1	74.3
Br	1.4	3.9	0.2	0.1
δ¹³C_{DIC}	-13.0	-8.2	-11.0	-6.0

Table 12. Averages for clusters with units for specific conductance as $\mu\text{S}/\text{cm}$, Eh as volts, cations and anions as mg/L , and $\delta^{13}\text{C}_{\text{DIC}}$ as permil (‰). C3 averages exclude T2BNE, an outlier.

Site ID	Fe	Al	Mn	Na	K	Mg	Ca	Ba	Sr	NO ₃	SO ₄	F	Cl	Br	HCO ₃
VES12	<0.1	<0.1	<0.1	196.8	4	25.34	92.37	0.021	1.451	<0.065	256.21	0.316	71.871	0.168	548
ECL1	<0.1	<0.1	<0.1	215.36	4.71	38.78	136.5	0.012	2.354	<0.065	454.98	0.262	173.706	0.156	461
ECL3	<0.1	<0.1	<0.1	141.35	4.12	40.59	119.44	0.017	1.855	1.446	314.51	0.189	180.387	<0.088	394
BRWN	1.34	<0.1	0.11	332.71	2.692	18.23	50.504	<0.012	1.5	<0.004	340.24	0.3602	3.64	<0.129	681
CLYD	225.37	0.13	7.19	1596.9	26.67	103.51	352.57	0.029	7.776	0.163	4159.00	0.264	519.35	3.879	654
PALM	0.922	<0.1	<0.1	504.89	3.115	28.26	30.57	0.076	1.28	<0.004	99.27	0.5643	5.639	2.3626	1041
GATE	0.705	<0.1	<0.1	594.14	3.271	8.69	24.016	0.038	1.12	<0.004	165.91	0.5863	6.954	0.5343	1126
GRAY	58.088	11.072	1.31	18.3	<0.1	35.3	96.241	<0.012	0.64	<0.004	728.08	0.6207	5.642	0.5784	0.18
T2BNE	5.173	6.871	1.17	24.36	<0.1	40.39	96.472	<0.012	0.72	0.723	670.93	0.4019	5.649	<0.129	0.17
MAD3B	8.329	4.57	0.95	13.99	<0.1	26.98	106.719	<0.012	0.62	0.376	1116.46	0.8408	5.734	<0.129	246
MAD3A	50.464	<0.1	2.16	181.5	4.969	59.14	158.971	<0.012	1.97	<0.004	1151.99	0.3814	7.108	<0.129	15.3
MDVL	51.805	0.429	3.61	136.37	3.745	53.9	146.299	<0.012	1.4	<0.004	861.00	0.3267	10.709	<0.129	0.24
SM3A	54.294	23.538	0.46	5.07	<0.1	35.3	116.95	<0.012	0.53	0.012	392.25	<0.088	1.302	<0.129	0.25
NORW	17.078	8.23	2.12	22.97	<0.1	17.03	49.663	<0.012	0.09	<0.004	649.21	0.5075	142.309	<0.129	293
SALT	10.48	<0.1	0.53	152.48	5.43	37.66	123.4	0.016	1.844	<0.065	658.33	0.325	9.143	<0.088	3.01
COKE	0.22	4.1	0.79	12.11	1.03	35.5	101.14	<0.012	0.619	<0.065	229.48	0.239	2.006	<0.088	0.11
TS10A	127.56	<0.1	3.69	25.11	3.44	35.25	141.44	0.012	0.907	<0.065	733.13	0.244	2.673	0.165	41.4
RB	30.56	13.77	0.72	1.82	1.39	22.86	75.07	<0.012	0.353	0.076	447.75	0.419	2.122	0.198	0.05
T&T2	37.01	21.39	0.46	0.59	0.3	15.32	58.48	<0.012	0.247	0.208	477.16	0.588	<0.44	0.285	0.02
T&T3	10.458	4.646	1.01	0.4	1.01	18.44	65.58	<0.012	0.21	0.654	309.65	0.365	<0.44	<0.088	0.06

Table 13. Raw geochemical lab data (mg/L) including values below minimum detection limits. Pittsburgh results used are from Denicola (2013).

Site ID	Classification
VES12	Na-HCO ₃
ECL1	No dominant type
ECL3	No dominant type
BRWN	Na-HCO ₃
CLYD	Na-SO ₄
PALM	Na-HCO ₃
GATE	Na-HCO ₃
GRAY	Ca-SO ₄
T2BNE	Ca-SO ₄
MAD3B	SO ₄
MAD3A	SO ₄
MDVL	Ca-SO ₄
SM3A	Ca-SO ₄
NORW	SO ₄
SALT	Ca-SO ₄
COKE	Mg-SO ₄
TS10A	Ca-SO ₄
RB	Ca-SO ₄
T&T2	Ca-SO ₄
T&T3	Ca-SO ₄

Table 14. Classification of sampled mine discharges according to a Piper diagram.

Group	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	DIC (mg/L)	Net- acidic	Net- alkaline	Carbonate contribution	Organics contribution
1	-0.65	2.74	T2BNE		1.09	-0.09
	-1.07	310		ECL1	1.07	-0.07
	-4.07	283		ECL3	0.92	0.08
	-5.11	403		VES12	0.87	0.13
	-6.24	283		NORW	0.82	0.18
2	-8.16	549		CLYD	0.72	0.28
	-8.26	0.45	GRAY		0.72	0.28
	-8.68	31.72	SALT		0.70	0.30
	-9.04	240		MAD3B	0.68	0.32
	-9.87	0.02	T&T2		0.64	0.36
	-10.38	592		BRWN	0.62	0.38
	-10.4	0.21	SM3A		0.61	0.39
	-10.78	0.26	MDVL		0.60	0.40
	-10.79	0.11	COKE		0.60	0.40
3	-11.55	0.06	T&T3		0.56	0.44
	-12.37	0.05	RB		0.52	0.48
	-12.67	3.8	MAD3A		0.50	0.50
	-12.77	879		PALM	0.50	0.50
	-13.15	928		GATE	0.48	0.52
	-14.78	41.4	TS10A		0.40	0.60

Table 15. $\delta^{13}\text{C}_{\text{DIC}}$, carbon contributions, and DIC. Sample sites are grouped according to proximity to atmospheric $\delta^{13}\text{C}$ (~ -8 ‰; Keeling et al., 2010) and natural groundwater range for $\delta^{13}\text{C}_{\text{DIC}}$ (Mook and Tan, 1991). Group 1 sites were enriched above atmospheric $\delta^{13}\text{C}$; Group 2 sites were enriched above normal groundwater range, but depleted below atmospheric $\delta^{13}\text{C}$; and Group 3 sites were within the natural groundwater range for $\delta^{13}\text{C}_{\text{DIC}}$.

Site ID	Maximum mine elevation (ft)	Minimum mine elevation (ft)	Discharge elevation (ft)	Elevation of regional drainage (ft)	Regional drainage
VES12	1020	790	830	744	Monongahela River
ECL1	1040	790	820	744	Monongahela River
ECL3	1040	800	800	744	Monongahela River
BRWN	780	730	760	744	Monongahela River
CLYD	720	380	800	780	Ten Mile Creek
PALM	660	500	770	763	Monongahela River
GATE	560	470	790	763	Monongahela River
GRAY	970	810	790	763	Monongahela River
T2BNE	1100	890	900	840	Dunkard Creek
MAD3B	920	780	840	820	Dunkard Creek
MAD3A	920	780	900	820	Dunkard Creek
MDVL	1010	810	890	890	Robinson Run
SM3A	1250	1230	1210	1240	West Run
NORW	1000	770	880	860	West Fork River
SALT	1240	1040	1040	990	Shinns Run
COKE	3240	2600	2960	2940	North Fork of the Blackwater
TS10A	1799	1700	1710	1710	Morgan Run
RB	1700	1500	1510	1420	Muddy Creek
T&T2	1900	1500	1580	1420	Muddy Creek
T&T3	2100	1900	1810	1740	Martin Creek

Table 16. Site specific information.

Greater carbonate contribution	Greater organic contribution	Equal contributions
VES12	TS10A	PALM
ECL1		GATE
ECL3		MAD3A
BRWN		RB
CLYD		T&T3
GRAY		
T2BNE		
MAD3B		
MDVL		
SM3A		
NORW		
SALT		
COKE		
T&T2		

Table 17. Sample sites grouped according to carbonate and organic contributions using a two end-member mixing model.

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Appendix

EQUATIONS	
1	$\delta^{13}\text{C}_{\text{DIC}} (\text{‰}) = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} \right] \times 1000$ $\text{where } R = \frac{^{13}\text{C}}{^{12}\text{C}}$
2	$Eh (V) = (ORP_{\text{sample}} (mV) \times 0.001) - (ORP_{\text{lab standard zobell}} (mV) \times 0.001) + Eh_{\text{theoretical zobell}} (V)$ $\text{where } Eh_{\text{theoretical zobell}} = 0.428 - 0.0022(T - 25^{\circ}\text{C})$
3	$pe (V) = \frac{Eh(V)}{0.059}$
4	$CBE (\%) = \left[\frac{(\sum \text{anions} (\frac{eq}{L}) - \sum \text{cations} (\frac{eq}{L}))}{(\sum \text{anions} (\frac{eq}{L}) + \sum \text{cations} (\frac{eq}{L}))} \right] \times 100$
5	$\text{net alkalinity} \left(\frac{mg}{L} \text{CaCO}_3 \right) = \text{alkalinity}_{\text{field}} \left(\frac{mg}{L} \text{CaCO}_3 \right) - \text{acidity}_{\text{calc}} \left(\frac{mg}{L} \text{CaCO}_3 \right)$
6	$\text{acidity}_{\text{calc}} \left(\frac{mg}{L} \text{CaCO}_3 \right) = 50 \times [(1000(10^{-\text{pH}})) + 2 \left(\frac{C_{\text{Fe}}}{55.8} \right) + 2 \left(\frac{C_{\text{Mn}}}{54.9} \right) + 3 \left(\frac{C_{\text{Al}}}{27.0} \right)]$
7	$DIC \left(\frac{mg}{L} \text{CaCO}_3 \right) = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
8	$TDS \left(\frac{eq}{L} \right) = \sum \text{anions} \left(\frac{eq}{L} \right) + \sum \text{cations} \left(\frac{eq}{L} \right)$
9	$\text{SO}_4^{2-} \left(\frac{mg}{L} \right) = \frac{\text{sulfur}}{0.3338}$
Bjerrum plot equations for estimated concentrations and calculated concentrations from field titrated alkalinity: Given 13°C, K ₁ = 3.63E-07, K ₂ = 3.47E-11	
10	$\text{Estimated alkalinity} \left(\frac{mg}{L} \text{CaCO}_3 \right) = [[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]] * 1000 * 50$
11	$\text{Estimated HCO}_3^- \left(\frac{mg}{L} \right) = (10^{[\text{HCO}_3^-]}) * 1000 * 61$
12	$\text{Estimated CO}_3^{2-} \left(\frac{mg}{L} \right) = 2[\text{CO}_3^{2-}] * 1000 * 60$

13	$\text{Calculated } \text{HCO}_3^- \left(\frac{\text{mg}}{\text{L}} \right) = \left[\frac{\text{field alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ CaCO}_3 \right)}{(1000 * 50)} \right] * 1000 * 61$
14	$\text{Calculated } \text{CO}_3^{2-} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{K_1 * \text{field alkalinity} \left(\frac{\text{eq}}{\text{L}} \right) * \gamma_1}{([H^+] * \gamma_2)} * 1000 * 60$ <p>where $\gamma_1 = 10^{-0.51 * \frac{\sqrt{I}}{1 - \sqrt{I}}}$, $\gamma_2 = 10^{-0.51 * 4 * \frac{\sqrt{I}}{(1 - \sqrt{I})}}$, and $I = 0.5 * \left(10^{-pH} + \Sigma iz^2 \left(\frac{\text{eq}}{\text{L}} \right) \right)$</p>
15	$\delta^{13}\text{C}_{\text{mix}} = \delta^{13}\text{C}_{\text{carbonate}} f_1 + \delta^{13}\text{C}_{\text{organic}} (1 - f_1)$ <p>where $\delta^{13}\text{C}_{\text{mix}}$ = isotopic signature of DIC in water sample, $\delta^{13}\text{C}_{\text{carbonate}}$ (-2.5‰) = isotopic composition of limestone, $\delta^{13}\text{C}_{\text{organic}}$ (-23‰) = average isotopic composition of organic matter, and f_1 = fractional contribution from carbonate dissolution</p>
16	$^{13}\epsilon = 10^3 \ln \alpha$ $10^3 \ln \alpha = a \left(\frac{10^6}{T_k^2} \right) + b \left(\frac{10^3}{T_k} \right) + c$ <p>at $T = 286K$ (13°C)</p>

Table A1. Equations used.

Figure A1. Index of sampling site locations.

Figure A2. Hydrogeology of ECL1, ECL3, VES12, and BRWN of the Pittsburgh coal seam.

Figure A3. Hydrogeology of CLYD within the Pittsburgh coal seam.

Figure A4. Hydrogeology of PALM and GATE of the Pittsburgh coal seam.

Figure A5. Hydrogeology of GRAY, MAD3A, and MAD3B of the Pittsburgh coal seam.

Figure A6. Hydrogeology of T2BNE, MDVL, MAD3A, and MAD3B of the Pittsburgh coal seam.

Figure A7. Hydrogeology of SM3A within the Pittsburgh coal seam.

Figure A8. Hydrogeology of NORW within the Pittsburgh coal seam.

Figure A9. Hydrogeology of SALT within the Pittsburgh coal seam.

Figure A10. Hydrogeology of T&T2, T&T3, and RB of the Upper Freeport coal seam.

Figure A11. Hydrogeology of TS10A within the Upper Freeport coal seam.

Figure A12. Hydrogeology of COKE within the Upper Freeport coal seam.