Office of Surface Mining Reclamation and Enforcement (OSMRE)
Mine Drainage Technology Initiative (MDTI)
Cooperative Agreement--S20AC20008

Final Technical Progress Report: May 1, 2020, to December 31, 2022

Title: *Quantifying the geochemical evolution of water discharged from a flooded mine pool to optimize mine drainage treatment strategies*

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Overview:

The overall objectives of this study were to identify and quantify major factors that lead to long-term changes in coal mine discharge (CMD) chemistry, and to develop models that allow prediction of CMD geochemical evolution and optimization of treatment for current and future conditions. This project focused on generally observed spatial and temporal variations in CMD water chemistry that must be considered for typical treatment strategies.

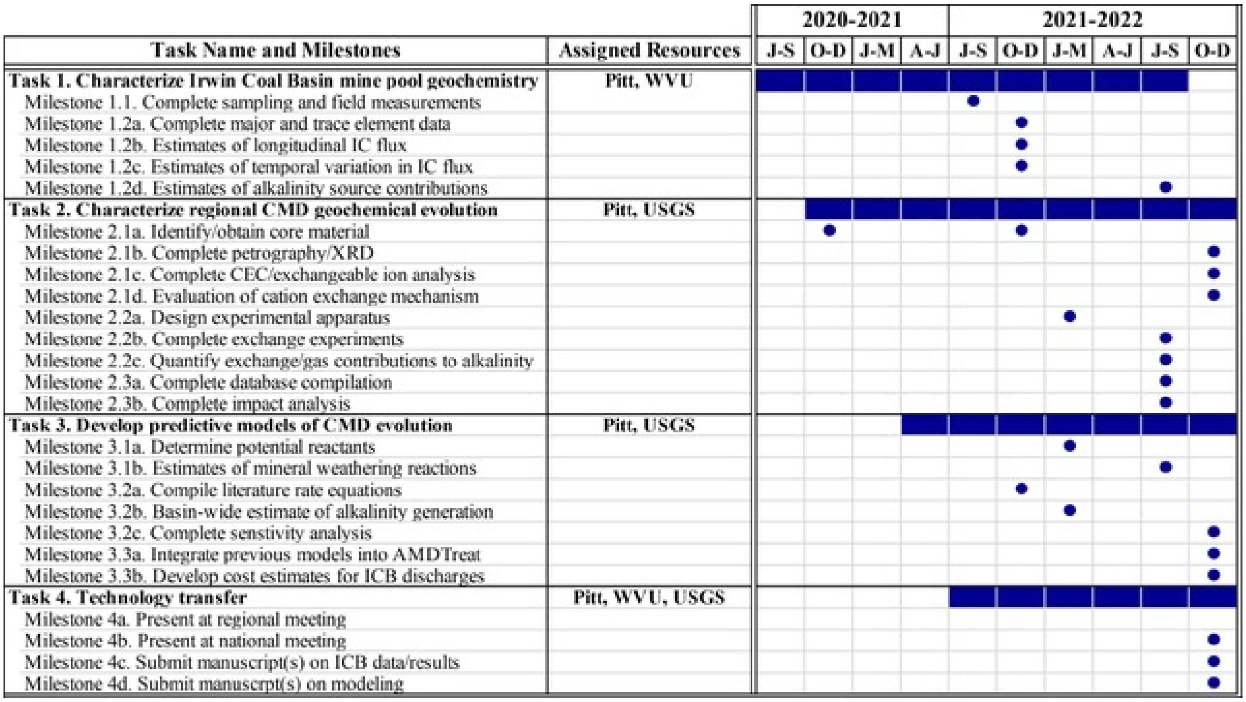
Hydrochemical and geochemical data for a field-based study of the Irwin Coal Basin (ICB), Pennsylvania, were obtained for CMD trend analysis and model development. Several large CMD sources in the ICB, which have a range of water-quality characteristics similar to regional Appalachian CMD, have evolved from acidic to net alkaline during the six to seven decades since their first post-mining expression. Sampling and field measurements of current water quality of the CMD were combined with archival data to assess trends in acidity, alkalinity, sulfate, iron, major cations, and carbon species concentrations. Archived drill core was sampled and analyzed to determine overburden and underclay mineralogy, cation exchange capacity, and exchangeable cation concentrations.

The hydrochemical and geochemical data were used to inform novel water-quality evolution models simulating the transition from net acidic to alkaline quality and permitting the extrapolation of long-term trends in pH, acidity, sulfate, iron, and other constituent concentrations. The start date and milestone end dates (Table 1) were modified over the course of the project because of COVID-related interruptions. Technology transfer includes two presentations and published abstracts at a regional and national meeting and generation of a manuscript with CMD evolution model to be submitted to a peer-reviewed journal. The project involved training and contributions of two graduate students and two undergraduate students.

Project Results

Three major tasks were designed to understand the acidity and alkalinity generating processes operating on decadal time scales in large coal mine pools. Task 1 focused on Irwin Coal Basin characterization, Task 2 involved characterization of regional CMD evolution, and Task 3 centered on predictive models of CMD evolution.

Table 1. Task chart for the project, including a no-cost extension through December of 2022. Completed end dates for the milestones are indicated by the blue circles.



		2020-2021				2021-2022					
Task Name and Milestones	**Assigned Resources**	**J-S**	**O-D**	**J-M**	**A-J**	**J-S**	**O-D**	**J-M**	**A-J**	**J-S**	**O-D**
Task 1. Characterize Irwin Coal Basin mine pool geochemistry	**Pitt, WVU**	■	■	■	■	■	■	■	■	■	
Milestone 1.1. Complete sampling and field measurements						●					
Milestone 1.2a. Complete major and trace element data							●				
Milestone 1.2b. Estimates of longitudinal IC flux							●				
Milestone 1.2c. Estimates of temporal variation in IC flux							●				
Milestone 1.2d. Estimates of alkalinity source contributions										●	
Task 2. Characterize regional CMD geochemical evolution	**Pitt, USGS**		■	■	■	■	■	■	■	■	■
Milestone 2.1a. Identify/obtain core material			●				●				
Milestone 2.1b. Complete petrography/XRD											●
Milestone 2.1c. Complete CEC/exchangeable ion analysis											●
Milestone 2.1d. Evaluation of cation exchange mechanism											●
Milestone 2.2a. Design experimental apparatus								●			
Milestone 2.2b. Complete exchange experiments										●	
Milestone 2.2c. Quantify exchange/gas contributions to alkalinity										●	
Milestone 2.3a. Complete database compilation										●	
Milestone 2.3b. Complete impact analysis										●	
Task 3. Develop predictive models of CMD evolution	**Pitt, USGS**				■	■	■	■	■	■	■
Milestone 3.1a. Determine potential reactants								●			
Milestone 3.1b. Estimates of mineral weathering reactions										●	
Milestone 3.2a. Compile literature rate equations							●				
Milestone 3.2b. Basin-wide estimate of alkalinity generation								●			
Milestone 3.2c. Complete senstivity analysis											●
Milestone 3.3a. Integrate previous models into AMDTreat											●
Milestone 3.3b. Develop cost estimates for ICB discharges											●
Task 4. Technology transfer	**Pitt, WVU, USGS**					■	■	■	■	■	■
Milestone 4a. Present at regional meeting											
Milestone 4b. Present at national meeting											●
Milestone 4c. Submit manuscript(s) on ICB data/results											●
Milestone 4d. Submit manuscrpt(s) on modeling											●

Task 1. Characterize ICB mine pool geochemistry.

Subtask Task 1.1 (Pitt/WVU): Bi-monthly sampling of Irwin Coal Basin discharges for one year

Nine coal mine discharges in the Irwin Coal Basin were sampled (Fig. 1). One discharge (#8 Banning) was sampled at a mine drainage treatment facility. After discussions regarding the analytical data from the first two sampling events, the Douglas Run discharge, near Banning but untreated since the 1970s was sampled instead of the Banning CMD.

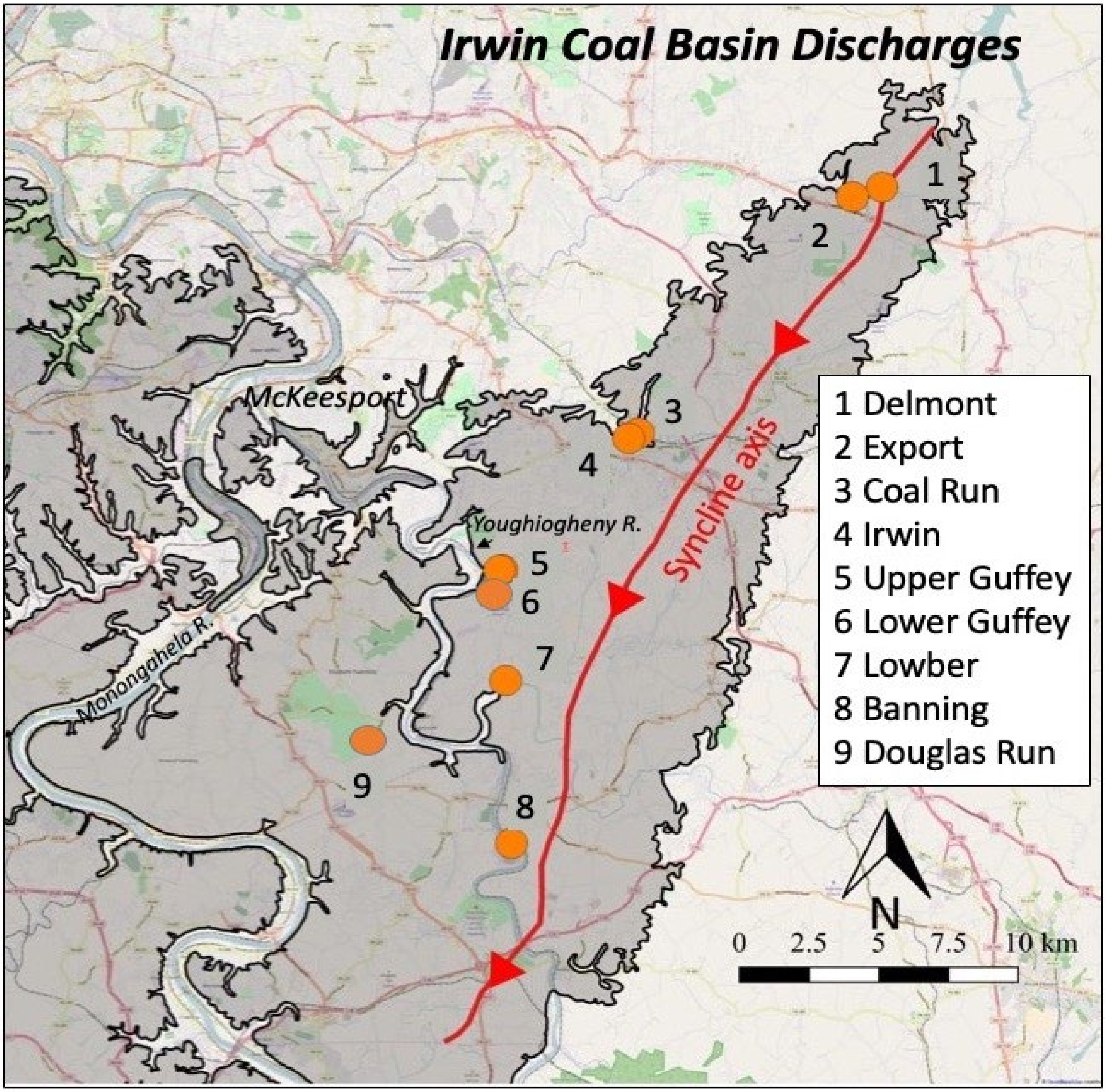


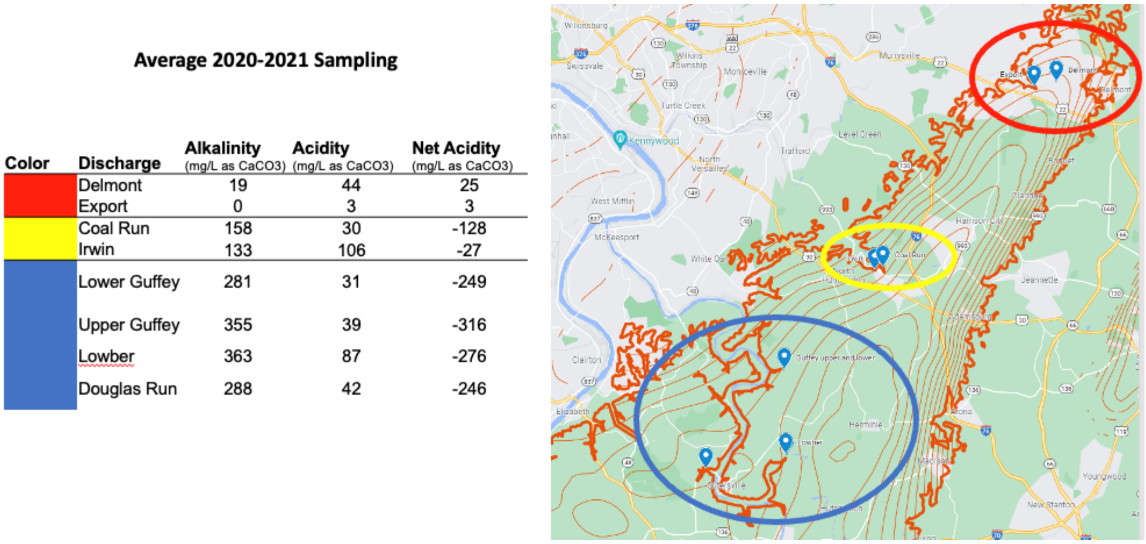
Figure 1. Map of Irwin Coal Basin, showing discharges sampled in this study.

The Pitt and WVU PIs coordinated on field measurement and sampling protocols for sampling the discharges for inorganic, CO_2 and associated carbon measurements and arranged for appropriate sampling bottles to be prepared (acid cleaned, pre-weighed) in advance. Sampling was carried out on October 17 and December 15, 2020, and April 19, June 23, and August 25, 2021, by Pitt co-Is and their grad students.

Subtask Task 1.2 (Pitt/WVU): Geochemical analysis of Irwin Coal Basin discharges.
Field parameters were measured using a flow meter and pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature, and electrical conductivity (EC) were determined using

a YSI Quatro Pro meter. Field alkalinity was determined using a Hach alkalinity kit and two-point titration. Flow data together with archival data are reported in Appendix A1. Bimonthly sampling data are reported in Appendices A2 (elemental data) A3 (anion data), A4 (dissolved inorganic carbon, DIC), and A5 (dissolved CO_2).

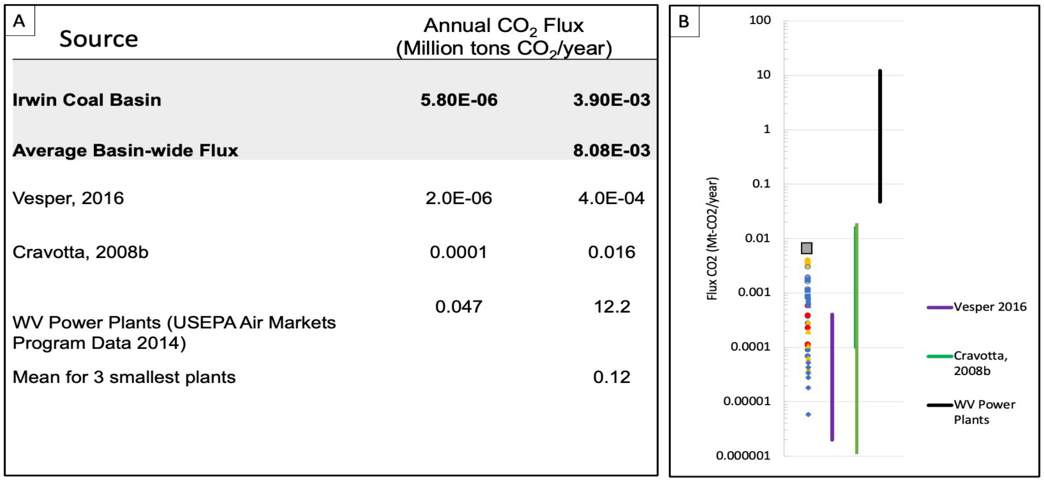
Spatial trends in acidity, alkalinity and net acidity are shown in Fig. 2.



Average 2020-2021 Sampling

Color	Discharge	Alkalinity (mg/L as CaCO3)	Acidity (mg/L as CaCO3)	Net Acidity (mg/L as CaCO3)
🟥	Delmont	19	44	25
	Export	0	3	3
🟨	Coal Run	158	30	-128
	Irwin	133	106	-27
🟦	Lower Guffey	281	31	-249
	Upper Guffey	355	39	-316
	Lowber	363	87	-276
	Douglas Run	288	42	-246

Figure 2. The six discharges can be divided into three main groups: net acidic (red); net alkaline (<250 mg/L) and >250 mg/L (blue).



A

Source	Annual CO_2 Flux (Million tons CO_2/year)	
Irwin Coal Basin	**5.80E-06**	**3.90E-03**
Average Basin-wide Flux		**8.08E-03**
Vesper, 2016	2.0E-06	4.0E-04
Cravotta, 2008b	0.0001	0.016
WV Power Plants (USEPA Air Markets Program Data 2014)	0.047	12.2
Mean for 3 smallest plants		0.12

Figure 3. A. Annual flux of carbon dioxide generated by discharges across the Irwin Coal Basin. B. Measured CO_2 flux (log scale) compared to other AMD discharges.

Estimates of longitudinal and temporal inorganic carbon flux and its contribution to alkalinity:

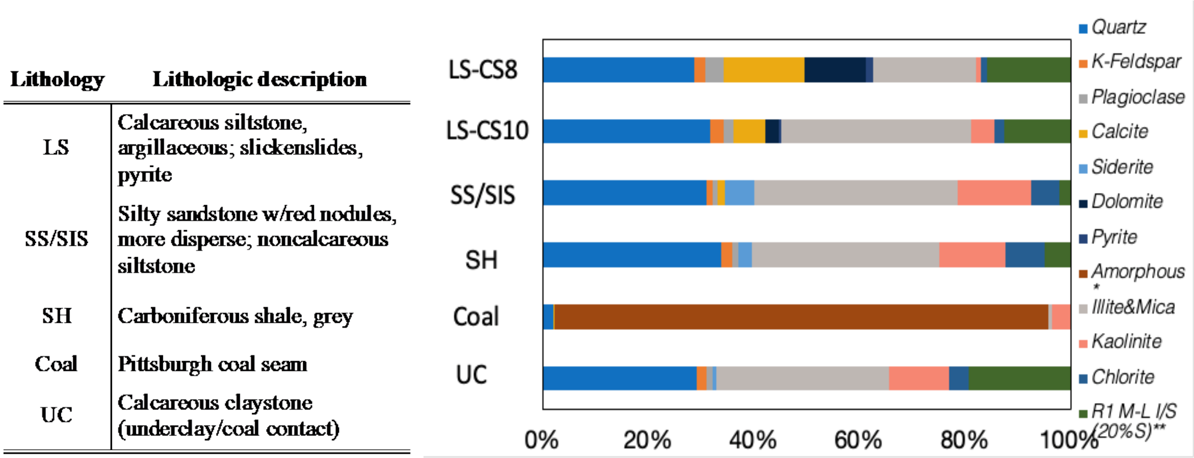
Assessing the role of CO_2 in alkalinity determinations requires determination of CO_2 flux in the ICB. Direct measurement of dissolved carbon dioxide from sampled discharges was determined at WVU using a Carbo-Q meter (Appendix A5). Figure 3 shows the annual CO_2 flux range for the six discharges as well as the basin wide annual flux, with a comparison to other CMD (data from Cravotta 2008 and Vesper 2016).

Task 2. Characterize regional CMD geochemical evolution.

Subtask Task 2.1: Characterization of ICB lithologies interacting with AMD.

Evaluation of mechanisms involved in ICB alkalinity generation involved identification of archived drill core material from the Pennsylvania DCNR Bureau of Topographic and Geologic Survey representative of coal overburden units of the Pittsburgh Formation. Core from Fayette County (FAY015-0225) was selected and shale, sandstone, siltstone and calcareous lithologies were sampled for CEC and XRD analysis.

XRD analysis (Fig. 4) indicated that alkalinity generating minerals included calcite, dolomite and siderite, and that clay minerals that could be involved in cation exchange reactions included illite, chlorite and other mica as well as mixed layer illite/smectite, present in all lithologies. These results were presented at the Northeast Section meeting of the Geological Society of America (NE GSA) meeting (Wallace et al., 2023).



Lithology	Lithologic description
LS	Calcareous siltstone, argillaceous; slickenslides, pyrite
SS/SIS	Silty sandstone w/red nodules, more disperse; noncalcareous siltstone
SH	Carboniferous shale, grey
Coal	Pittsburgh coal seam
UC	Calcareous claystone (underclay/coal contact)

Figure 4. Mineralogical composition of overburden lithologies based on XRD analysis of Fayette County Core FAY015-0225.

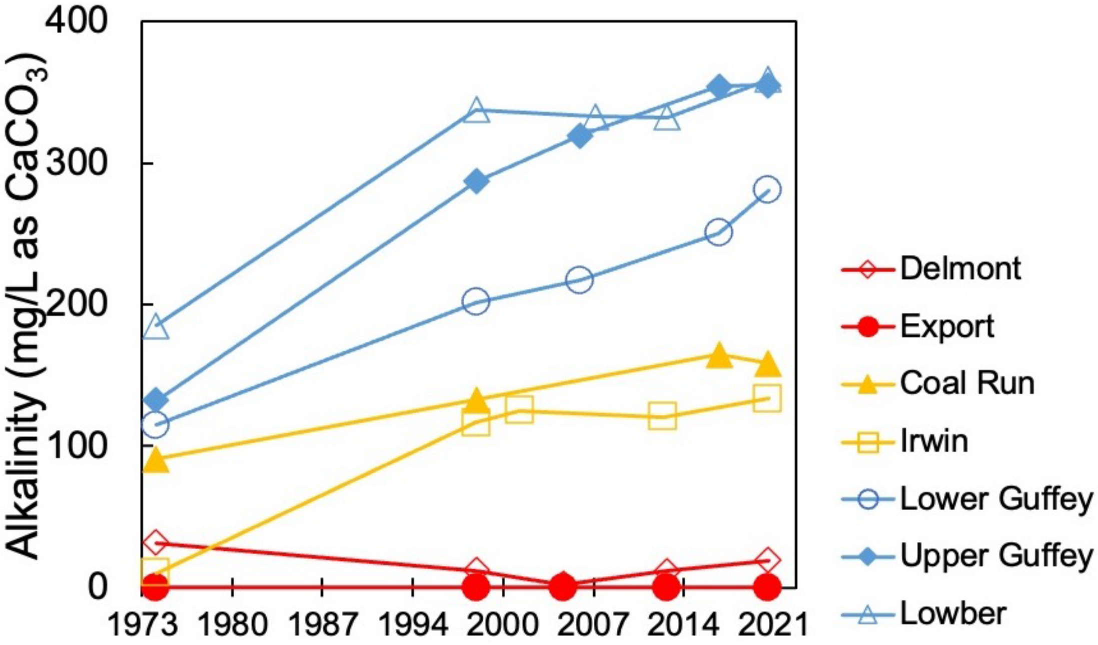


Figure 5. Alkalinity in ICB discharges, 1973-2021.

Long term (decadal) alkalinity trends indicate an overall increase in alkalinity in ICB discharges from the 1970s to the present. Archival data and data collected as part of Task 1 indicate, that with the exception of the Delmont and Export discharges near the perimeter of the ICB, alkalinity in the ICB discharges increased with time (Fig. 5).

Our results also confirm the positive correlation between alkalinity and increasing overburden thickness (Fig. 6).

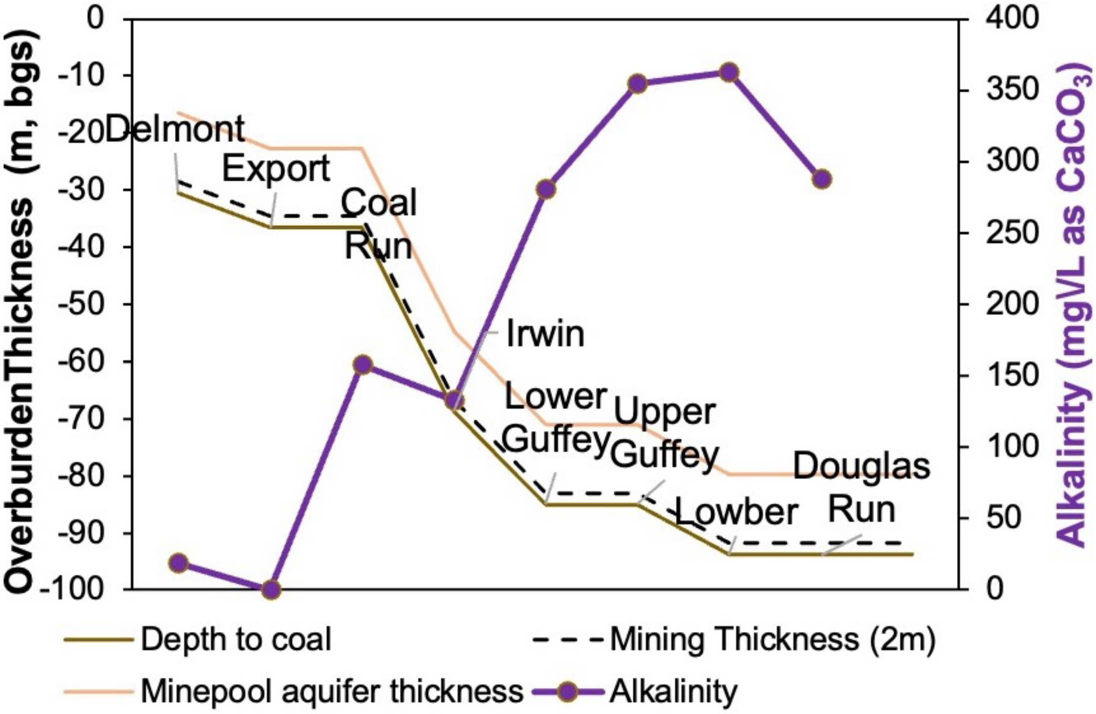


Figure 6. Relationship between overburden thickness and alkalinity of discharges in the ICB.

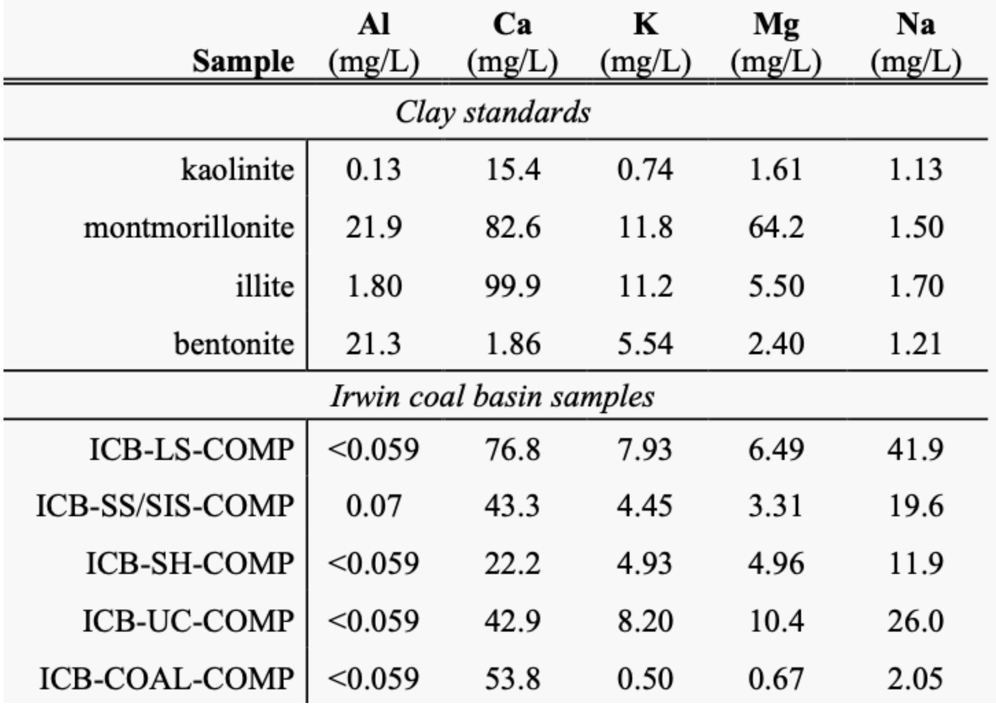
Geochemical processes that could influence the observed trends in alkalinity include (1) cation exchange-enhanced carbonate dissolution and (2) siderite ($FeCO_3$) equilibrium. Elevated pCO_2 across the basin (measured as part of this study) and calculated saturation index (SI) for calcite are indicative of acid neutralization, with the positive correlation between sodium and alkalinity consistent with cation exchange. These results were presented at the national GSA Meeting in Denver (Schaffer et al. 2022).

Subtask Task 2.2: Benchtop reactor experiments

Cation exchange capacity (CEC) experiments were conducted at WVU to aid in the quantification of the contribution of cation exchange and gas conditions to alkalinity generation that informed Task 3 modeling efforts. Samples of unweathered core material representing major overburden lithologies (described in Fig. 4) were compared with clay standards. This work was presented at the NE GSA in Reston, Virginia (Wallace et al., 2023).

Samples of underclay and argillaceous limestone/calcareous siltstone had the highest CEC (14 and 11 meq/100g, respectively) and significant exchangeable Na (1.13 and 1.82 meq/100g, respectively). The data indicate the potential for significant sodium release from exchange sites on overburden minerals (Table 1 and Fig. 7) . The results also confirm that the elevated dissolved Na concentrations observed in the net alkaline ICB discharges is the result of interaction of overburden lithologies with Ca-rich fluids in the mine pool. Cation exchange reactions would release Na and remove Ca, which drives further carbonate mineral dissolution, resulting in increased pH and alkalinity generation.

Table 1. Exchangeable cation content of ICB



Sample	Al (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)
Clay standards					
kaolinite	0.13	15.4	0.74	1.61	1.13
montmorillonite	21.9	82.6	11.8	64.2	1.50
illite	1.80	99.9	11.2	5.50	1.70
bentonite	21.3	1.86	5.54	2.40	1.21
Irwin coal basin samples					
ICB-LS-COMP	<0.059	76.8	7.93	6.49	41.9
ICB-SS/SIS-COMP	0.07	43.3	4.45	3.31	19.6
ICB-SH-COMP	<0.059	22.2	4.93	4.96	11.9
ICB-UC-COMP	<0.059	42.9	8.20	10.4	26.0
ICB-COAL-COMP	<0.059	53.8	0.50	0.67	2.05

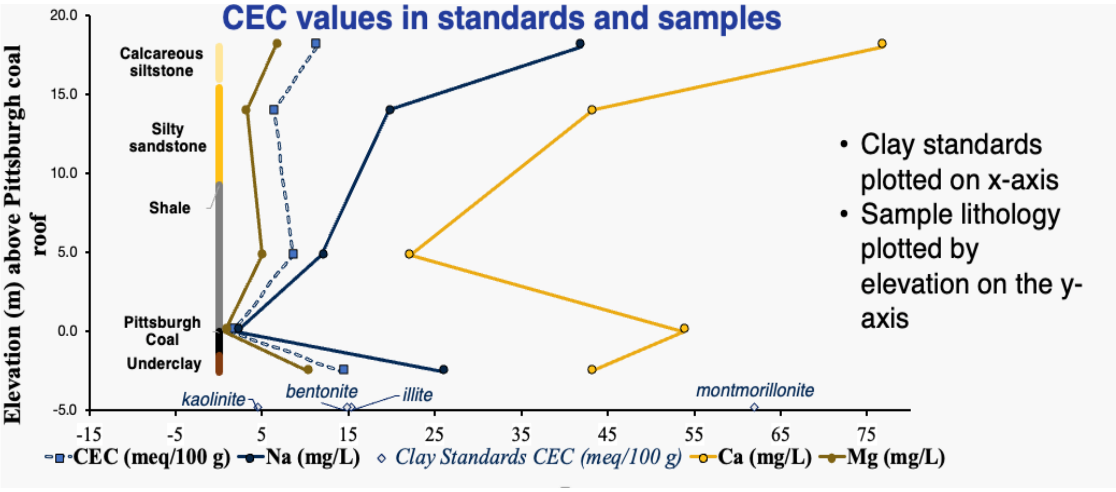


Figure 7. CEC values and exchangeable cation content of ICB overburden lithologies.

These results were used in Task 3 inverse and forward modeling of cation exchange reactions (together with pyrite oxidation, calcite dissolution, etc.) to simulate the evolution of acidic, Ca/SO_4 minewaters to alkaline $Na/HCO_3 + SO_4$ type minewaters.

Subtask 2.3 (Pitt/USGS): Database compilation and analysis of Appalachian CMD

A database of Appalachian CMD discharges with long temporal chemical records was compiled as part of an analysis of the actual vs. modeled evolution of Appalachian CMD through time. The database incorporates information from Scarlift Reports and published data; it will be published in Supplementary Information in a manuscript in preparation and is attached as Appendix A1.

Task 3. Develop predictive models of CMD evolution

Potential effects of water-quality evolution on the management of water resources, including treatment system design and operation, and long-term (decadal) changes in mine pool geochemistry were evaluated using PHREEQC aqueous speciation models. Task 3 modeling efforts aimed to put constraints on the contributions of reactions involving carbonate mineral dissolution, sulfate reduction and cation exchange reactions that can explain the trends observed in both the bimonthly sampling and archival data.

This work focused on two subtasks: (1) *Model equilibrium relationships and mineral interactions affecting the geochemical mass-balance through the Irwin Coal Basin using PHREEQC* and (2) *supplemental modeling to identify critical variables affecting rates of water-mineral interaction and long-term evolution*.

Equilibrium relationships in Irwin Coal Basin CMD were modeled with PHREEQC, using information on mineral occurrence and computed saturation indices to identify potential reactants. Data from Tasks 1 and 2 (including historical data) were used together with mine pool residence time and geometry to generate field estimates of the rates of important mineral weathering reactions. This forward model demonstrated the interaction of hydrological and geochemical processes over decadal time scales and indicated potential for extrapolation of future water-quality trends.

Figure 8 shows the first-flush forward reaction simulations compared to historical water-quality data from the Lowber discharge, which represents a typical deep minepool that has evolved from net-acidic to net-alkaline over time. These models demonstrate the dominant reactions that take place after pyrite is oxidized and initial AMD is produced by near instantaneous dissolution of soluble oxidation products (sulfate salts). After this initial flush of AMD, water in the mine pool is progressively diluted and neutralized over time by inflows of alkaline groundwater coupled with the dissolution of carbonate minerals, while progressively less pyrite oxidation takes place.

Alkalinity is generated and cation exchange and mineral dissolution and precipitation occur as overburden minerals react with an evolving mine pool fluid. Overall, the measured iron concentrations from the Lowber discharge are only approximately 1/5 of the value required to match FeS_2 stoichiometry, which indicates substantial Fe attenuation over time (Fig. 8A). In addition, the poor fit of the observed data with the simple dilution model, indicate that there is a continued release of oxidation products originating from sulfate salts or active oxidation of pyrite in the subsurface (Fig. 8B).

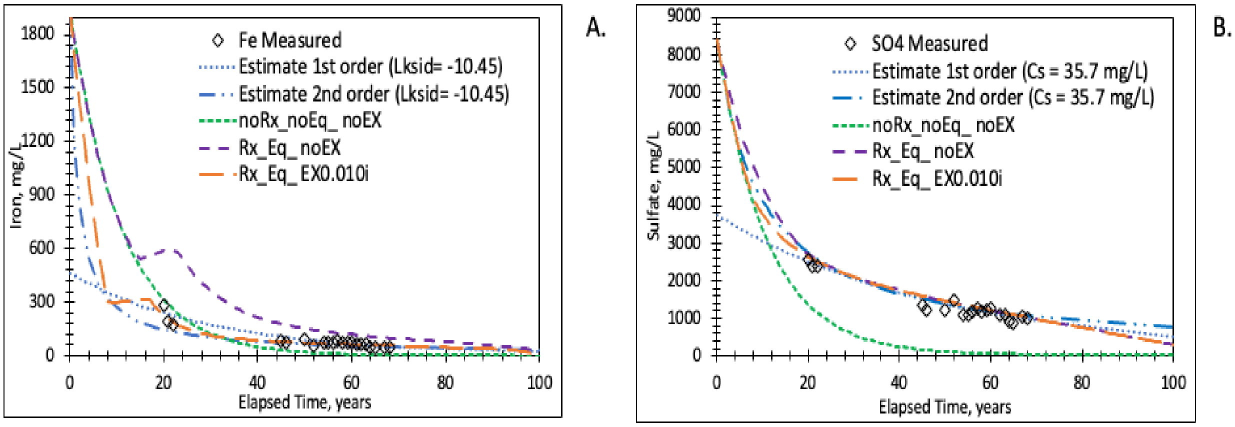


Figure 8. First-flush evolution model compared to observed water-quality data for the Lowber discharge. (A) dissolved iron. (B) sulfate. The green curve represents progressive mixing of mine pool water with groundwater without additional reactions or cation exchange .

The PHREEQC model indicates that cation exchange reactions are not necessary to explain the observed changes in sulfate or iron, but must be considered to explain observed pH, alkalinity, calcium, magnesium and sodium concentrations, which are related to the transition from net acidic to net alkaline conditions.

The model also indicates potential importance of siderite, an iron carbonate mineral, as a sink for iron during the early stages of development of net alkaline water quality, but also as a potential source of Fe during later stages. Modeling with PHREEQC and Geochemist's Workbench suggested that siderite is stable in the ICB mine pools with net alkaline discharges. Siderite dissolution under equilibrium conditions could explain the commonly observed dissolved Fe content (~20 mg/L) in circumneutral CMD in the Appalachian Basin.

This is graphically shown in Figure 9, using Eh-pH stability diagrams that were constructed with Geochemists Workbench software. The diagrams use the median log activity values of $Fe^{2+,}$ SO_4^{2-}, and pCO_2 that were calculated from PHREEQC for two conditions. Data from the Irwin Basin discharges represents end-member mineral phase distribution under first flush conditions (Fig. 9A), with the second (Fig. 9B) showing the effect that increasing Fe, SO_4 and pCO_2 with depth has on increasing the siderite stability field.

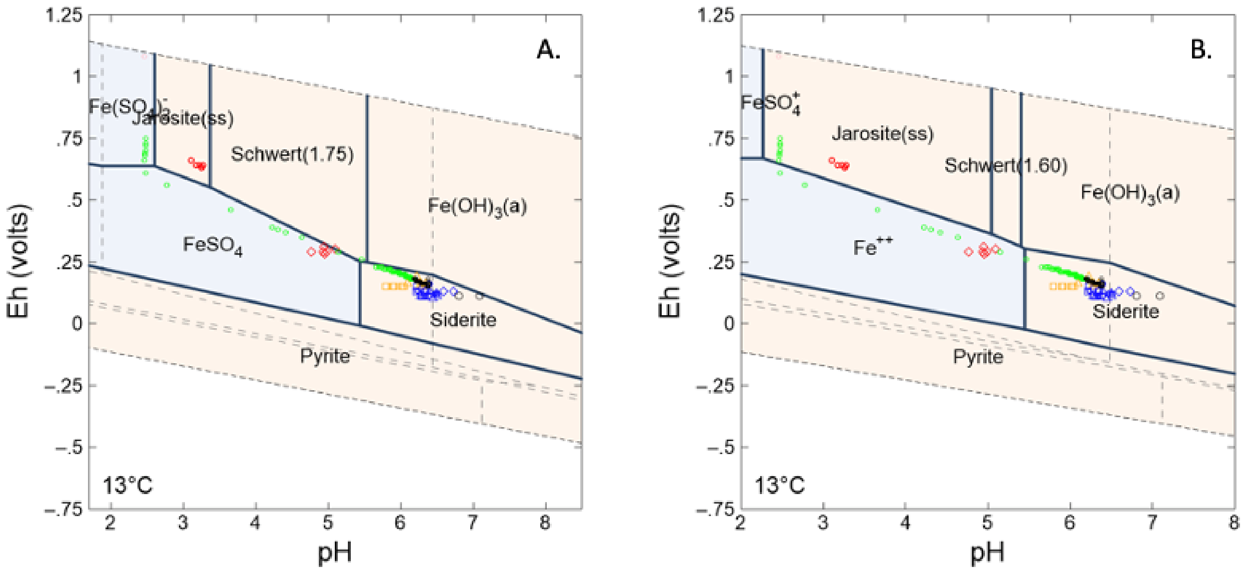


Figure 9. Eh-pH diagram of the Irwin Coal basin sampling sites constructed with Geochemists Workbench using the median log activity values of Fe^{2+}, SO$_4^{2-}$, and pCO$_2$ calculated from PHREEQC of the first flush conditions(A) and deeper, net alkaline Lowber mine pool (B). The forward reaction (and CEC) first flush model results are shown in green(0-68 years) and black (68-100 years).

Subtask 3.3 (Pitt/USGS): Application of OSMRE AMDTreat for cost analysis of adaptive treatment strategies.

A task of this study was to provide guidance on the application of new modeling tools for evaluation of optimized, cost-effective treatment strategies. AMDTreat 6.0 Beta and the included PHREEQ-N-AMDTreat tool are now available for cost estimation and post-treatment water-quality prediction. For this study, these new tools were used with the current net-alkaline, Fe-laden water quality at Lowber discharge (2,000 gal/min, net acidity -250 mg/L, pH 6.3, Fe 45 mg/L) to estimate the possible size and net-present cost of (1) a passive aerobic treatment wetland similar to that now in place or (2) an active treatment system that uses hydrogen peroxide to remove dissolved Fe, both meeting the same discharge limit of 1.5 mg/L. The PHREEQ-N-AMDTreat tool was used, first, to indicate an adequate (optimum) retention time for system sizing and the chemical quantities needed, if any. Next, cost calculations were conducted *using default unit cost values* for the estimated system size for the specified retention time from the water-quality model. Finally, the same technologies were considered, but with future predicted water quality that had increased pH of 6.9 and decreased Fe concentration of 5.8 mg/L, consistent with siderite equilibrium, but unchanged 2,000 gal/min flow rate and net acidity of -250 mg/L.

The PHREEQ-N-AMDTreat model results indicate that for 2021 water-quality conditions, a passive treatment wetland with 16-hour retention time could feasibly treat the Lowber discharge to meet Fe discharge limits. AMDTreat sizing and cost summaries indicate such a passive system may require 7 acres and $816 thousand to construct. Assuming 75 years lifetime, the net present value cost for construction and operation of this system is estimated to be $1.876 million. In contrast, for the same 2021 influent water quality, an active treatment system using hydrogen peroxide followed by a settling pond may require less than 1 acre and $521 thousand for construction, but because of high annual costs for chemicals has a net present value cost of $16.627 million.

Given the projected 2070 water-quality conditions (5.8 mg/L Fe and pH 6.9), PHREEQ-N-AMDTreat model results indicate a passive treatment wetland with 8-hour retention time that occupies 3.6 acres could feasibly treat the Lowber discharge to meet Fe discharge limits. AMDTreat cost summaries indicate such a passive system may require $410 thousand to construct. Assuming 75 years lifetime, the net present value cost for construction and operation of this system is estimated to be $0.939 million. An active treatment system using hydrogen peroxide followed by a settling pond may occupy less than 1 acre but still require $239 thousand for construction with a net present value cost of $2.531 million. Thus, although the projected lower Fe concentration results in lower treatment costs, the net-present value costs are significant after more than a century has elapsed from the first flush.

Task 4 (Pitt/WVU/USGS): **Technology transfer *via* dissemination of study results to the scientific and user community**.

Workshop*:*

Co-PI Cravotta presented a workshop on the AMDTreat and the PHREEQ-N-AMDTreat tool with Brent Means at the West Virginia Task Force meeting in October 2022.

Research presentations*:* Results of this project were presented at national and regional meetings; published abstracts include:

Schaffer CR, Capo RC, Stewart BW, Hedin BC, Vesper DJ, Cravotta III CA, 2022, Multidecadal geochemical evolution of acid mine drainage in an Appalachian coal basin. Geological Society of America Annual Meeting Abstracts with Programs 54(5), Denver, CO; doi: 10.1130/abs/2022AM-381086

Wallace M., Schaffer CR, Vesper DJ, Stewart BW, Capo RC, 2023, Experimental evidence for generation of net alkaline mine drainage via cation exchange-enhanced limestone dissolution, Irwin Coal Basin, Pennsylvania. Geological Society of America Northeastern/Southeastern Regional meeting, Reston, VA.

Publications*:* A journal manuscript is in preparation

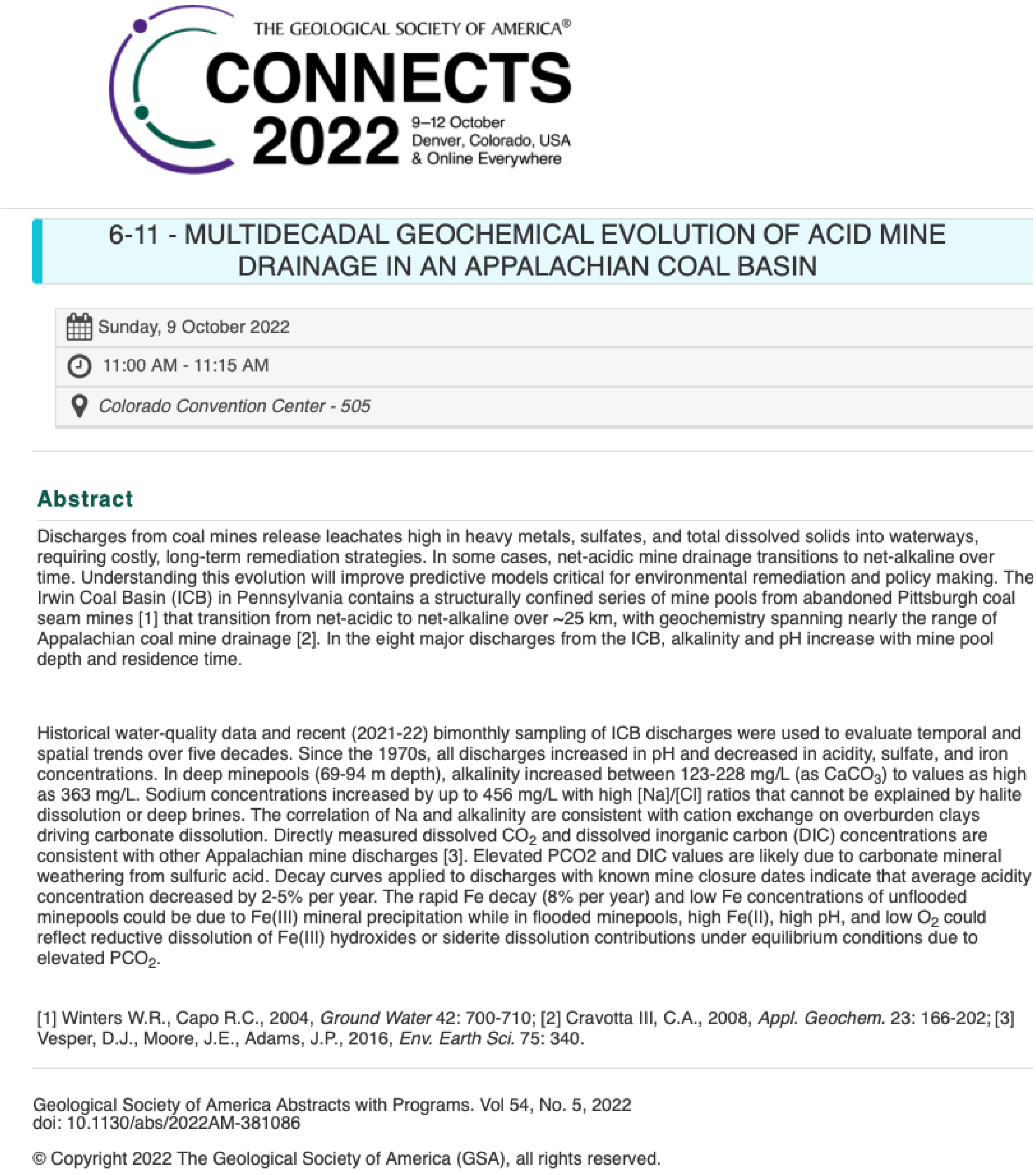
Schaffer CR, Cravotta III, CA, Capo RC, Hedin, BC, Stewart BW, Vesper DJ, 2023, Multi-decadal geochemical evolution of coal mine drainage in an Appalachian coal basin (to be submitted to Science of the Total Environment).

Training:

This project also provided partial support to Ph.D. students Camille Schaffer and Tashane Boothe (Pitt), MS student Morgan Wallace (WVU) and two undergraduate research assistants (Pitt).

Attachment 1. Published abstracts.

Schaffer CR, Capo RC, Stewart BW, Hedin BC, Vesper DJ, Cravotta III CA (2022) Multidecadal geochemical evolution of acid mine drainage in an Appalachian coal basin. Geological Society of America Annual Meeting Abstracts with Programs 54(5), Denver, CO; doi: 10.1130/abs/2022AM-381086



THE GEOLOGICAL SOCIETY OF AMERICA®
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2022
9–12 October
Denver, Colorado, USA
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6-11 - MULTIDECADAL GEOCHEMICAL EVOLUTION OF ACID MINE DRAINAGE IN AN APPALACHIAN COAL BASIN

Sunday, 9 October 2022

11:00 AM - 11:15 AM

Colorado Convention Center - 505

Abstract

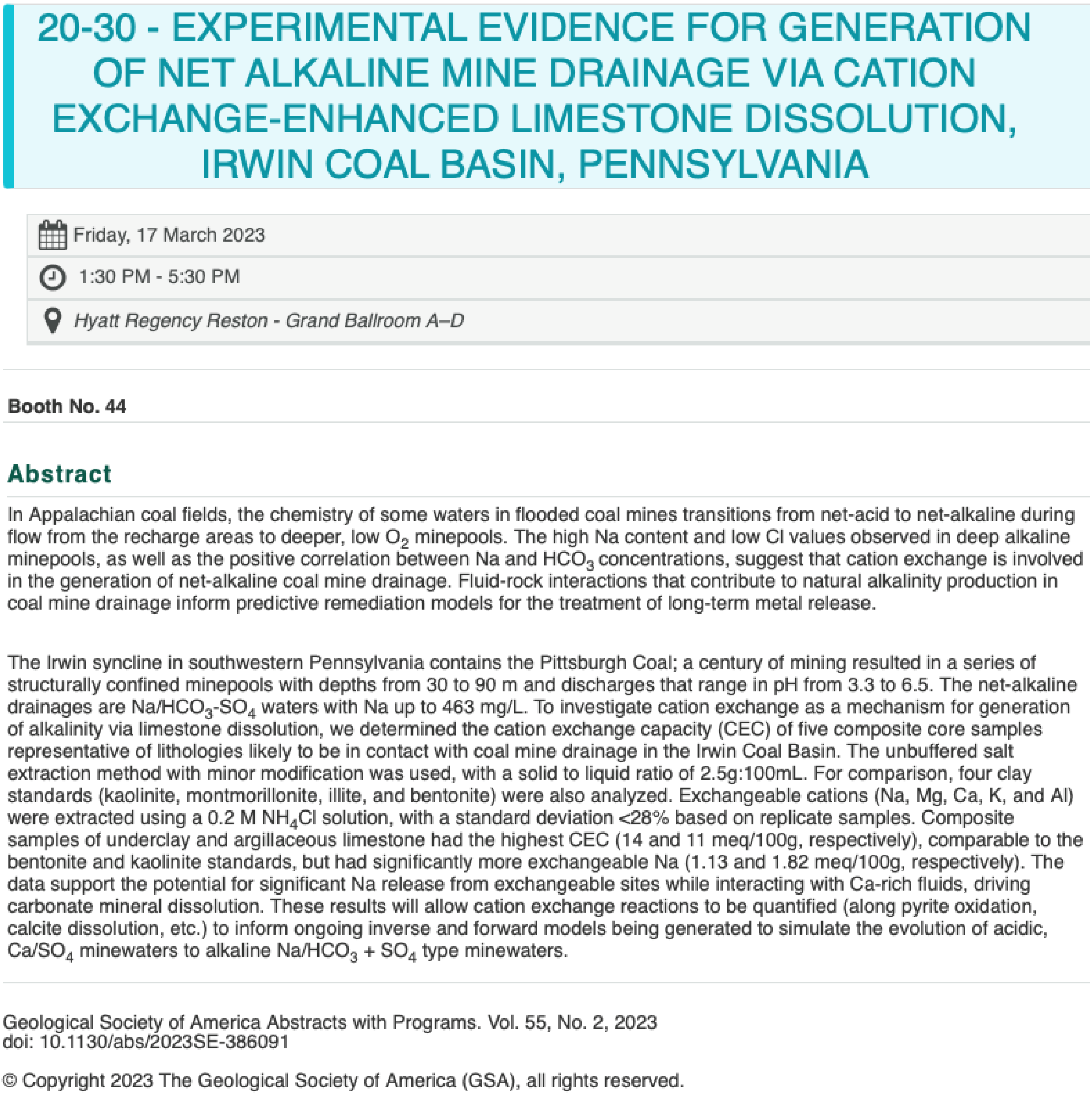
Discharges from coal mines release leachates high in heavy metals, sulfates, and total dissolved solids into waterways, requiring costly, long-term remediation strategies. In some cases, net-acidic mine drainage transitions to net-alkaline over time. Understanding this evolution will improve predictive models critical for environmental remediation and policy making. The Irwin Coal Basin (ICB) in Pennsylvania contains a structurally confined series of mine pools from abandoned Pittsburgh coal seam mines [1] that transition from net-acidic to net-alkaline over ~25 km, with geochemistry spanning nearly the range of Appalachian coal mine drainage [2]. In the eight major discharges from the ICB, alkalinity and pH increase with mine pool depth and residence time.

Historical water-quality data and recent (2021-22) bimonthly sampling of ICB discharges were used to evaluate temporal and spatial trends over five decades. Since the 1970s, all discharges increased in pH and decreased in acidity, sulfate, and iron concentrations. In deep minepools (69-94 m depth), alkalinity increased between 123-228 mg/L (as $CaCO_3$) to values as high as 363 mg/L. Sodium concentrations increased by up to 456 mg/L with high [Na]/[Cl] ratios that cannot be explained by halite dissolution or deep brines. The correlation of Na and alkalinity are consistent with cation exchange on overburden clays driving carbonate dissolution. Directly measured dissolved CO_2 and dissolved inorganic carbon (DIC) concentrations are consistent with other Appalachian mine discharges [3]. Elevated PCO2 and DIC values are likely due to carbonate mineral weathering from sulfuric acid. Decay curves applied to discharges with known mine closure dates indicate that average acidity concentration decreased by 2-5% per year. The rapid Fe decay (8% per year) and low Fe concentrations of unflooded minepools could be due to Fe(III) mineral precipitation while in flooded minepools, high Fe(II), high pH, and low O_2 could reflect reductive dissolution of Fe(III) hydroxides or siderite dissolution contributions under equilibrium conditions due to elevated PCO_2.

[1] Winters W.R., Capo R.C., 2004, *Ground Water* 42: 700-710; [2] Cravotta III, C.A., 2008, *Appl. Geochem.* 23: 166-202; [3] Vesper, D.J., Moore, J.E., Adams, J.P., 2016, *Env. Earth Sci.* 75: 340.

Geological Society of America Abstracts with Programs. Vol 54, No. 5, 2022
doi: 10.1130/abs/2022AM-381086

Wallace M., Schaffer CR, Vesper DJ, Stewart BW, Capo RC, 2023, Experimental evidence for generation of net alkaline mine drainage via cation exchange-enhanced limestone dissolution, Irwin Coal Basin, Pennsylvania. Geological Society of America Northeastern/Southeastern Regional meeting, Reston, VA.



20-30 - EXPERIMENTAL EVIDENCE FOR GENERATION OF NET ALKALINE MINE DRAINAGE VIA CATION EXCHANGE-ENHANCED LIMESTONE DISSOLUTION, IRWIN COAL BASIN, PENNSYLVANIA

📅 Friday, 17 March 2023

🕘 1:30 PM - 5:30 PM

📍 *Hyatt Regency Reston - Grand Ballroom A–D*

Booth No. 44

Abstract

In Appalachian coal fields, the chemistry of some waters in flooded coal mines transitions from net-acid to net-alkaline during flow from the recharge areas to deeper, low O_2 minepools. The high Na content and low Cl values observed in deep alkaline minepools, as well as the positive correlation between Na and HCO_3 concentrations, suggest that cation exchange is involved in the generation of net-alkaline coal mine drainage. Fluid-rock interactions that contribute to natural alkalinity production in coal mine drainage inform predictive remediation models for the treatment of long-term metal release.

The Irwin syncline in southwestern Pennsylvania contains the Pittsburgh Coal; a century of mining resulted in a series of structurally confined minepools with depths from 30 to 90 m and discharges that range in pH from 3.3 to 6.5. The net-alkaline drainages are Na/HCO_3-SO_4 waters with Na up to 463 mg/L. To investigate cation exchange as a mechanism for generation of alkalinity via limestone dissolution, we determined the cation exchange capacity (CEC) of five composite core samples representative of lithologies likely to be in contact with coal mine drainage in the Irwin Coal Basin. The unbuffered salt extraction method with minor modification was used, with a solid to liquid ratio of 2.5g:100mL. For comparison, four clay standards (kaolinite, montmorillonite, illite, and bentonite) were also analyzed. Exchangeable cations (Na, Mg, Ca, K, and Al) were extracted using a 0.2 M NH_4Cl solution, with a standard deviation <28% based on replicate samples. Composite samples of underclay and argillaceous limestone had the highest CEC (14 and 11 meq/100g, respectively), comparable to the bentonite and kaolinite standards, but had significantly more exchangeable Na (1.13 and 1.82 meq/100g, respectively). The data support the potential for significant Na release from exchangeable sites while interacting with Ca-rich fluids, driving carbonate mineral dissolution. These results will allow cation exchange reactions to be quantified (along pyrite oxidation, calcite dissolution, etc.) to inform ongoing inverse and forward models being generated to simulate the evolution of acidic, Ca/SO_4 minewaters to alkaline $Na/HCO_3 + SO_4$ type minewaters.

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Appendix A1. Archival and sampling data, including flow measurements.

Site	Date Collected	Sample Source	Field Data						Major Elements									
			Flow	pH	Conductivity	ORP	Alkalinity	Discharge T	Na	K	Ca	Sr	Mg	Mn	Fe	Al	Si	S
			gal/min		uS/cm	mV	mg/l as CaCO3	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Douglas Run	25-Feb-1994	Capo		6.7			279		222	4.4	79		27	0.4	17	0.10		154
Douglas Run	2-Mar-1995	Capo		6.4			304		222	4.7	85	1.6	28	0.4	13	0.10	7.4	137
Douglas Run	13-Jul-1995	Capo		6.0			278		204	4.2	79	1.3	27	0.5	18	0.10	6.0	143
Douglas Run	1-Mar-1999	Capo		6.4			304		222			1.6			13	0.10	7.4	
Douglas Run	1-Jul-1999	Capo		6.0			278		204			1.3			25	0.10	6.0	
Douglas Run	19-Apr-2021	MDTI	2505.00	6.7	1423	-80	479	12	188	3.3	75	1.2	22	0.3	9	<0.004	4.6	98
Douglas Run	23-Jun-2021	MDTI	1936.41	6.4	1344		286	12	192	3.6	83	1.3	25	0.4	15	0.01	5.1	116
Douglas Run	25-Aug-2021	MDTI	4032.00	6.6	1363	-80	280.5	13	191	3.5	83	1.4	25	0.5	16	<0.005	9.4	121
Banning	3-May-2017	Hedin	2,310	6.8			490		393	2.7	90	1.5	25	0.2	8	ND	7.1	206
Banning	16-Oct-2020	MDTI	2,310	7.1	2182		296		390	4.7	84	1.6	23	0.2	6	< 0.010	7.6	207
Banning	15-Dec-2020	MDTI	2,310	6.8	2581	-100.9	325	11.2	440	3.7	91	1.8	25	0.2	7	<0.010	8.1	222
Banning	24-Feb-2021	MDTI	N/A-no site access															
Lowber	15-Aug-1973	Scarlift	1,790	5.8			0								310			
Lowber	15-Sep-1973	Scarlift	1,858	5.8			0								290			
Lowber	15-Oct-1973	Scarlift	1,790	5.8			254								280			
Lowber	15-Nov-1973	Scarlift	1,722	5.9			214								153			
Lowber	15-Jan-1974	Scarlift	1,722	5.9			400								247			
Lowber	15-Feb-1974	Scarlift	1,858	5.8			188								311			
Lowber	15-Mar-1974	Scarlift	1,722	5.6			344								302			
Lowber	15-Apr-1974	Scarlift	1,722	5.6			308								212			
Lowber	15-May-1974	Scarlift	1,722	5.5			224								216			
Lowber	15-Jun-1974	Scarlift		5.1			160								193			
Lowber	15-Jul-1974	Scarlift	1,460	4.8			46								191			
Lowber	15-Aug-1974	Scarlift	1,722	5.3			158								72			
Lowber	15-Sep-1974	Scarlift	1,460	5.4			126								81			
Lowber	15-Oct-1974	Scarlift	1,722	5.5			140											
Lowber	15-Nov-1974	Scarlift	1,858	5.7			226								188			
Lowber	15-Dec-1974	Scarlift	1,946	5.1			44								113			
Lowber	15-Jan-1975	Scarlift	1,998	5.4			90								150			
Lowber	15-Feb-1975	Scarlift	2,213	6.1			150								151			
Lowber	15-Mar-1975	Scarlift	2,286	6.2			200								105			
Lowber	15-Apr-1975	Scarlift	2,213	6.0			102								144			
Lowber	15-May-1975	Scarlift	1,858	6.2			102								164			
Lowber	15-Jun-1975	Scarlift	2,140	5.9			174								178			
Lowber	15-Jul-1975	Scarlift	1,858	6.1			270								191			
Lowber	15-Aug-1975	Scarlift	1,790	6.3			266								188			
Lowber	15-Sep-1975	Scarlift	1,928	5.8			396								285			
Lowber	15-Oct-1975	Scarlift	1,928	5.8			224								183 .			
Lowber	25-Feb-1994	Capo		6.3			320		481	7.0	153		44	1.2	79	0.09		445
Lowber	2-Mar-1995	Capo		6.1			332		483	8.2	163	2.6	42	1.3	78	0.10	11.0	444
Lowber	13-Jul-1995	Capo		6.0			360		426	7.2	149	1.9	41	1.3	75	0.10	9.5	439
Lowber	1-Mar-1999	Capo		6.1			332		483			2.6			78	0.10	11.0	
Lowber	1-Jul-1999	Capo		6.0			360		426			1.9			75	0.20	9.5	
Lowber	3-May-2017	Hedin	1,372	6.4			357		379	3.4	139	1.7	35	0.9	43	0.01	7.6	305
Lowber	16-Oct-2020	MDTI	1,842	6.3	2805		352	14	451	5.9	150	1.9	37	1.0	50	0.03	9.8	374
Lowber	15-Dec-2020	MDTI	1,652	6.2	3037	-83	382	13.7	456	4.8	152	2.0	37	1.0	50	0.01	9.5	357
Lowber	24-Feb-2021	MDTI	1,659	6.2	2947	-61.1	340	13.7	463	6.0	149	2.0	37	1.1	53	0.02	8.7	399
Lowber	19-Apr-2021	MDTI	1,652	6.3	2811	-103	312	13.7	404	5.5	139	1.9	40	1.0	49	0.02	8.3	325
Lowber	23-Jun-2021	MDTI	1,896	6.36	2737		361	14	446	5.8	148	1.9	38	0.9	45	0.04	8.9	339
Lowber	25-Aug-2021	MDTI	2,058	6.3	2537	-101.8	350.5	14	440	5.4	145	2.0	37	1.0	46	0.01	5.6	120
Guffey Upper	15-Aug-1973	Scarlift	1,858	5.7			56								98			
Guffey Upper	15-Sep-1973	Scarlift	1,524	5.6			70								110			
Guffey Upper	15-Oct-1973	Scarlift	1,722	5.5			72								94			
Guffey Upper	15-Nov-1973	Scarlift	1,460	5.7			82								76			
Guffey Upper	15-Jan-1974	Scarlift	1,212	5.8			142								89			
Guffey Upper	15-Feb-1974	Scarlift	1,036	5.9			130								90			
Guffey Upper	15-Mar-1974	Scarlift	1,397	5.7			182								49			
Guffey Upper	15-Apr-1974	Scarlift	1,524	5.4			150								67			
Guffey Upper	15-May-1974	Scarlift	1,858	5.6			170								73			
Guffey Upper	15-Jun-1974	Scarlift	1,722	5.5			160								66			

Appendix A1, cont.

			Field Data						Major Elements									
Site	Date Collected	Sample Source	Flow	pH	Conductivity	ORP	Alkalinity	Discharge T	Na	K	Ca	Sr	Mg	Mn	Fe	Al	Si	S
			gal/min		uS/cm	mV	mg/l as CaCO3	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Guffey Upper	15-Jul-1974	Scarlift	1,524	5.7			160								69			
Guffey Upper	15-Aug-1974	Scarlift	1,227	5.6			162											
Guffey Upper	15-Sep-1974	Scarlift	983	5.5			112											
Guffey Upper	15-Oct-1974	Scarlift	1,656	5.5			124											
Guffey Upper	15-Nov-1974	Scarlift	906	5.7			136								70			
Guffey Upper	15-Dec-1974	Scarlift	1,103	5.8			112								30			
Guffey Upper	15-Jan-1975	Scarlift	1,103	5.9			104								53			
Guffey Upper	15-Feb-1975	Scarlift	1,144	6.4			118								40			
Guffey Upper	15-Mar-1975	Scarlift	2,097	6.3			164								39			
Guffey Upper	15-Apr-1975	Scarlift	1,944	6.1			134								44			
Guffey Upper	15-May-1975	Scarlift	1,902	6.4			138								56			
Guffey Upper	15-Jun-1975	Scarlift	1,531	6.1			140								48			
Guffey Upper	15-Jul-1975	Scarlift	1312	6.1			194								54			
Guffey Upper	15-Aug-1975	Scarlift	1,103	6.3			0								47			
Guffey Upper	15-Sep-1975	Scarlift	1,063	5.8			148								82			
Guffey Upper	15-Oct-1975	Scarlift		5.7			144								70			
Guffey Upper	25-Feb-1994	Capo		6.2			224		257	3.5	65		22	0.7	33	0.10		190
Guffey Upper	13-Jul-1995	Capo		6.2			350		281	3.8	51	1.1	16	0.5	22	0.20	7.3	155
Guffey Upper	17-May-2017	Hedin	92	6.5			354		287	2.2	112	1.2	19	0.4	19	ND	5.9	147
Guffey Upper	16-Oct-2020	MDTI	43	6.5	2036		367	13	355	4.0	64	1.2	18	0.4	25	0.01	7.3	184
Guffey Upper	15-Dec-2020	MDTI	14	6.3	2060	-105.6	349	13	330	3.1	68	1.3	19	0.5	28	<0.008	6.9	174
Guffey Upper	24-Feb-2021	MDTI	64	6.4	1855	-79.5	352	12.6	302	3.7	68	1.3	20	0.4	23	<.004	6.4	170
Guffey Upper	19-Apr-2021	MDTI	99	6.5	1655	-86.2	353	12.1	269	3.3	62	1.2	18	0.3	14	0.01	6.0	132
Guffey Upper	23-Jun-2021	MDTI	124	6.3	1841		367	13	322	3.8	63	1.3	18	0.4	21	0.00	6.6	157
Guffey Upper	25-Aug-2021	MDTI	80	6.5	1672	-108.8	352	13	297	3.5	63	1.3	18	0.4	18	<0.004	6.8	152
Guffey Lower	15-Aug-1973	Scarlift	1,524	5.5			0								71			
Guffey Lower	15-Sep-1973	Scarlift	1,111	5.7			66								60			
Guffey Lower	15-Oct-1973	Scarlift	1,334	5.7			162								54			
Guffey Lower	15-Nov-1973	Scarlift	1,212	5.8			100								55			
Guffey Lower	15-Jan-1974	Scarlift	1,036	5.8			176								71			
Guffey Lower	15-Feb-1974	Scarlift	1,152	5.6			156								56			
Guffey Lower	15-Mar-1974	Scarlift	1,094	5.5			154								87			
Guffey Lower	15-Apr-1974	Scarlift	924	5.4			138								41			
Guffey Lower	15-May-1974	Scarlift	1,152	5.7			204								47			
Guffey Lower	15-Jun-1974	Scarlift	1,212	5.3			102								47			
Guffey Lower	15-Jul-1974	Scarlift	1,036	5.6			96								50			
Guffey Lower	15-Aug-1974	Scarlift	1,036	5.7			144								0			
Guffey Lower	15-Sep-1974	Scarlift	1,036	5.6			98								25			
Guffey Lower	15-Oct-1974	Scarlift	1,152	5.7			114								0			
Guffey Lower	15-Nov-1974	Scarlift	979	6.4			146								39			
Guffey Lower	15-Dec-1974	Scarlift	713	6.3			110								24			
Guffey Lower	15-Jan-1975	Scarlift	1,094	6.0			140								36			
Guffey Lower	15-Feb-1975	Scarlift	1,212	6.1			94								29			
Guffey Lower	15-Mar-1975	Scarlift	1,212	6.2			106								35			
Guffey Lower	15-Apr-1975	Scarlift	1,208	6.4			80								44			
Guffey Lower	15-May-1975	Scarlift	1,212	6.2			76								58			
Guffey Lower	15-Jun-1975	Scarlift	1,152	6.0			76								38			
Guffey Lower	15-Jul-1975	Scarlift	979	6.0			82								35			
Guffey Lower	15-Aug-1975	Scarlift	924	6.2			102								39			
Guffey Lower	15-Sep-1975	Scarlift	924	6.0			128								66			
Guffey Lower	15-Oct-1975	Scarlift		5.8			128								53			
Guffey Lower	25-Feb-1994	Capo		6.3			211		191	3.6	62		21	0.6	26	0.10		136
Guffey Lower	5-Mar-1995	Capo		6.3					235	3.9	66	1.4	20	0.5	22	0.10	8.5	
Guffey Lower	13-Jul-1995	Capo		6.0			192		133	2.8	61	1.2	21	0.6	24	0.10	7.1	95
Guffey Lower	3-May-2017	Hedin		6.4			250		199	2.0	71	1.3	21	0.5	18	ND	6.0	95
Guffey Lower	16-Oct-2020	MDTI	6,916	6.5	1533		271	12	230	3.2	63	1.4	19	0.5	16	0.02	6.7	116
Guffey Lower	15-Dec-2020	MDTI	3,649	6.4	1629	-97.4	298	12	235	2.8	62	1.5	19	0.5	17	0.01	6.7	114
Guffey Lower	24-Feb-2021	MDTI	2,648	6.4	1626	-65.5	289		250	3.4	63	1.5	19	0.6	20	0.01	6.5	134
Guffey Lower	19-Apr-2021	MDTI	4,402	6.5	1534	-92.6	290	13	227	3.1	60	1.4	19	0.5	17	0.02	6.3	113
Guffey Lower	23-Jun-2021	MDTI	2,772	6.2	1483		268	14	222	3.2	63	1.4	20	0.5	19	0.02	6.6	111
Guffey Lower	25-Aug-2021	MDTI	4,558	6.4	1398	-101.6	265	13	218	3.1	62	1.5	19	0.4	16	0.02	6.8	109

Appendix A1, cont

			Field Data						Major Elements									
Site	Date Collected	Sample Source	Flow	pH	Conductivity	ORP	Alkalinity	Discharge T	Na	K	Ca	Sr	Mg	Mn	Fe	Al	Si	S
			gal/min		uS/cm	mV	mg/l as CaCO3	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Irwin	15-Aug-1973	Scarlift	6,285	4.0			0								190			
Irwin	15-Sep-1973	Scarlift	4,361	4.1			0								195			
Irwin	15-Oct-1973	Scarlift	2,875	3.2			0								173			
Irwin	15-Nov-1973	Scarlift	2,236	3.4			0								107			
Irwin	15-Dec-1973	Scarlift	3,125	4.0			6								172			
Irwin	15-Jan-1974	Scarlift	3,708	3.5			0								174			
Irwin	15-Feb-1974	Scarlift	6,854	3.1			0								184			
Irwin	15-Mar-1974	Scarlift	7,208	5.0			42								179			
Irwin	15-Apr-1974	Scarlift	8,049	3.2			0								129			
Irwin	15-May-1974	Scarlift	8,201	3.0			0								124			
Irwin	15-Jun-1974	Scarlift	9,583	2.8			0								118			
Irwin	15-Jul-1974	Scarlift		3.2			0								122			
Irwin	15-Aug-1974	Scarlift	8,188	3.6			0								63			
Irwin	15-Sep-1974	Scarlift	8,285	4.7			14								77			
Irwin	15-Oct-1974	Scarlift	7,756	4.5			0								76			
Irwin	15-Nov-1974	Scarlift	8,076	3.9			0								106			
Irwin	15-Dec-1974	Scarlift		3.4			0								49			
Irwin	15-Jan-1975	Scarlift	11,190	3.2			0								90			
Irwin	15-Feb-1975	Scarlift	13,194	5.2			22								80			
Irwin	15-Mar-1975	Scarlift	15,667	4.1			0								85			
Irwin	15-Apr-1975	Scarlift	12,556	2.6			0								56			
Irwin	15-May-1975	Scarlift	9,847	3.9			0								119			
Irwin	15-Jun-1975	Scarlift	8,774	4.4			6								127			
Irwin	15-Jul-1975	Scarlift	7,533	5.6			48								150			
Irwin	15-Aug-1975	Scarlift	6,490	5.6			34								155			
Irwin	15-Sep-1975	Scarlift	6,849	5.5			72								165			
Irwin	15-Oct-1975	Scarlift		5.9			24								140			
Irwin	1-Jun-1974	Scarlift		4.0											126			
Irwin	25-Feb-1994	Capo		6.0			109		172	4.4	111		31	1.7	56	0.20		261
Irwin	2-Mar-1995	Capo		6.0			109		125	5.9	122	1.6	35	1.9	70	0.10	12.7	237
Irwin	13-Jul-1995	Capo		7.0			132		137	5.1	107	1.2	32	1.7	62	0.20	10.7	197
Irwin	3-May-2017	Hedin	8,451	6.1			148		145	3.2	119	1.2	30	1.4	45	0.04	9.4	174
Irwin	16-Oct-2020	MDTI	7,344	6.1	1703		131	13	154	5.1	140	1.5	36	1.9	57	0.07	10.4	246
Irwin	15-Dec-2020	MDTI	8,299	6.0	1759		128	12.8	149	4.6	143	1.6	37	1.9	58	0.06	10.3	229
Irwin	24-Feb-2021	MDTI	8,120	5.9	1736		132	13	153	5.1	138	1.6	37	2.3	68	0.05	10.3	263
Irwin	19-Apr-2021	MDTI	9,866	6.0	1686	-54.2	135	14.8	152	5.0	125	1.5	35	1.7	53	0.05	9.4	223
Irwin	23-Jun-2021	MDTI	9,327	5.8	1645		144	14	156	5.0	126	1.5	35	1.7	60	0.06	10.1	215
Irwin	25-Aug-2021	MDTI	8,415	5.9	1517	-55.7	132	13.4	152	4.8	125	1.5	34	2.0	61	0.05	10.4	221
Coal Run	15-Sep-1973	Scarlift	1,008	5.7			36								32			
Coal Run	15-Oct-1973	Scarlift	299	5.5			-								11			
Coal Run	15-Nov-1973	Scarlift	347	5.7			72								29			
Coal Run	15-Jan-1974	Scarlift	421	5.7			104								22			
Coal Run	15-Feb-1974	Scarlift	1,018	5.6			114								24			
Coal Run	15-Mar-1974	Scarlift	1,065	5.6			108								18			
Coal Run	15-Apr-1974	Scarlift	1,448	5.6			118								19			
Coal Run	15-May-1974	Scarlift	463	5.8			132								18			
Coal Run	15-Jun-1974	Scarlift	569	5.4			108								22			
Coal Run	15-Jul-1974	Scarlift		5.6			96								15			
Coal Run	15-Aug-1974	Scarlift	222				122								0			
Coal Run	15-Sep-1974	Scarlift	229	5.7			80											
Coal Run	15-Oct-1974	Scarlift	463	5.7			94											
Coal Run	15-Nov-1974	Scarlift	300	5.9			128								11			
Coal Run	15-Dec-1974	Scarlift	849	5.8			80								11			
Coal Run	15-Jan-1975	Scarlift	849	6.3			84								17			
Coal Run	15-Feb-1975	Scarlift	890	6.5			98								17			
Coal Run	15-Mar-1975	Scarlift	979	6.5			78								20			
Coal Run	15-Apr-1975	Scarlift	482	5.7			66								23			
Coal Run	15-May-1975	Scarlift	540	6.4			66								26			
Coal Run	15-Jun-1975	Scarlift	494	6.0			74											
Coal Run	15-Jul-1975	Scarlift	385	5.9			70											
Coal Run	15-Aug-1975	Scarlift	385	6.3			72											
Coal Run	15-Sep-1975	Scarlift	925	5.8			96								20			

Appendix A1, cont.

			Field Data						Major Elements									
Site	Date Collected	Sample Source	Flow	pH	Conductivity	ORP	Alkalinity	Discharge T	Na	K	Ca	Sr	Mg	Mn	Fe	Al	Si	S
			gal/min		uS/cm	mV	mg/l as CaCO3	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Coal Run	15-Oct-1975	Scarlift	611	5.8			84								15			
Coal Run	1-Jun-1974	Scarlift	674	5.9			91								178			
Coal Run	25-Feb-1994	Capo		6.2			128		115	2.7	78		27	0.7	17	0.30		123
Coal Run	2-Mar-1995	Capo		5.8			121		83	3.4	78	1.5	28	0.7	16	0.20	8.6	99
Coal Run	13-Jul-1995	Capo		6.2			148		91	3.0	75	1.1	26	0.8	19	0.20	6.0	102
Coal Run	3-May-2017	Hedin	1,482	6.4			165		112	2.0	82	1.2	24	0.7	16	0.03	5.2	88
Coal Run	16-Oct-2020	MDTI	92	6.4	968		159	12.1	98	2.7	67	1.0	21	0.5	12	0.06	5.7	86
Coal Run	15-Dec-2020	MDTI	145	6.3	1092	-52.5	172	11.9	100	2.5	66	1.1	21	0.4	12	0.06	5.6	76
Coal Run	24-Feb-2021	MDTI	1,015	6.2	1002	-37.6	157		96	2.7	68	1.1	22	0.5	13	0.09	5.6	87
Coal Run	19-Apr-2021	MDTI	452	6.3	1000	-64.6	153	12.6	92	2.8	70	1.1	22	0.4	12	0.10	5.7	77
Coal Run	24-Jun-2021	MDTI	258	6.1	998		154	13.2	99	2.9	70	1.1	23	0.5	14	0.09	5.8	76
Coal Run	25-Aug-2021	MDTI	690	6.3	945	-59.5	155	12.7	99	2.9	69	1.2	22	0.5	13	0.07	5.8	77
Delmont	15-Aug-1973	Scarlift																
Delmont	15-Sep-1973	Scarlift																
Delmont	15-Oct-1973	Scarlift																
Delmont	15-Nov-1973	Scarlift																
Delmont	15-Dec-1973	Scarlift																
Delmont	15-Jan-1974	Scarlift																
Delmont	15-Feb-1974	Scarlift																
Delmont	15-Mar-1974	Scarlift																
Delmont	15-Apr-1974	Scarlift																
Delmont	15-May-1974	Scarlift	911	3.0			0								0			
Delmont	15-Jun-1974	Scarlift	960	3.3			0								28			
Delmont	15-Jul-1974	Scarlift	655	3.3			0								28			
Delmont	15-Aug-1974	Scarlift	508	3.1			0								0			
Delmont	15-Sep-1974	Scarlift	542	2.9			0											
Delmont	15-Dec-1974	Scarlift	841	4.9			10								19			
Delmont	15-Jan-1975	Scarlift	364	3.4			0								26			
Delmont	15-Feb-1975	Scarlift	1,048	3.7			0								26			
Delmont	15-Mar-1975	Scarlift	224	3.3			0								22			
Delmont	15-Apr-1975	Scarlift		3.0			0								22			
Delmont	15-May-1975	Scarlift	628	3.4			0								38			
Delmont	15-Jun-1975	Scarlift	5	3.3			0											
Delmont	15-Jul-1975	Scarlift	443				0											
Delmont	15-Aug-1975	Scarlift	371				0											
Delmont	15-Sep-1975	Scarlift	417				0											
Delmont	15-Oct-1975	Scarlift	571	3.1			0								25			
Delmont	25-Feb-1994	Capo		5.0			13		30	3.5	88		28	1.8	31	1.40		164
Delmont	2-Mar-1995	Capo		3.4			0		23	3.5	82	0.7	27	1.9	38	1.30	13.8	135
Delmont	13-Jul-1995	Capo		5.2			22		23	3.3	86	0.6	28	2.2	31	0.70	10.5	125
Delmont	3-May-2017	Hedin	665	5.1			16		30	2.3	86	0.6	25	1.7	28	0.67	8.6	124
Delmont	16-Oct-2020	MDTI	160	5.1	720		12	12.6	26	2.7	67	0.5	21	1.4	22	0.41	9.0	103
Delmont	15-Dec-2020	MDTI	200	5.0	740	70.6	11	12	26	2.8	70	0.5	21	1.4	23	0.47	8.9	97
Delmont	24-Feb-2021	MDTI	835	5.0	760	84.1	14	11.8	27	2.8	68	0.5	22	1.7	28	0.55	8.7	115
Delmont	19-Apr-2021	MDTI	859	5.0	750	96.1	22	11.9	27	2.8	68	0.5	22	1.7	28	0.55	8.7	115
Delmont	23-Jun-2021	MDTI	634	4.8	772		25	12	29	3.1	77	0.6	24	1.8	27	0.58	9.4	116
Delmont	25-Aug-2021	MDTI	594	4.9	736	83.7	18	12	29	3.0	75	0.6	23	1.7	27	0.46	9.5	112
Export	15-Aug-1973	Scarlift	694	2.6			0								56			
Export	15-Sep-1973	Scarlift	310	2.8			0								47			
Export	15-Oct-1973	Scarlift	310	2.8			0								38			
Export	15-Nov-1973	Scarlift	521	2.9			0								46			
Export	15-Jan-1974	Scarlift	899	3.1			0								40			
Export	15-Feb-1974	Scarlift	537	2.7			0								32			
Export	15-Mar-1974	Scarlift	708	3.0			0								38			
Export	15-Apr-1974	Scarlift	610	2.9			0								28			
Export	15-May-1974	Scarlift	889	2.9			0								31			
Export	15-Jun-1974	Scarlift	868	2.7			0								27			
Export	15-Jul-1974	Scarlift		2.8			0								25			
Export	15-Aug-1974	Scarlift	686	2.7			0								13			
Export	15-Sep-1974	Scarlift	715	2.8			0								15			
Export	15-Oct-1974	Scarlift	692	3.1			0								16			

			Field Data						Major Elements									
Site	Date Collected	Sample Source	Flow	pH	Conductivity	ORP	Alkalinity	Discharge T	Na	K	Ca	Sr	Mg	Mn	Fe	Al	Si	S
			gal/min		uS/cm	mV	mg/l as CaCO3	°C	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Export	15-Nov-1974	Scarlift	690	2.8			0								25			
Export	15-Dec-1974	Scarlift	792	3.0			0								13			
Export	15-Jan-1975	Scarlift	765	3.0			0								18			
Export	15-Feb-1975	Scarlift	906	3.1			0								20			
Export	15-Mar-1975	Scarlift	838	3.0			0								19			
Export	15-Apr-1975	Scarlift	1,000	2.8			0								21			
Export	15-May-1975	Scarlift	1,001	3.2			0								25			
Export	15-Jun-1975	Scarlift	929	3.0			0								18			
Export	15-Jul-1975	Scarlift	856	2.4			0								17			
Export	15-Aug-1975	Scarlift	810	3.1			0								19			
Export	15-Sep-1975	Scarlift	126	2.8			0								18			
Export	15-Oct-1975	Scarlift	1,424	2.9			0								26			
Export	1-Jun-1974	Scarlift	792	2.9			0								27			
Export	2-Mar-1995	Capo		2.8			0		19	1.4	101	0.7	34	1.9	1.3	13.40	24.3	182
Export	13-Jul-1995	Capo		3.2			0		22	1.3	107	0.7	38	2.3	1.5	18.20	22.3	200
Export	3-May-2017	Hedin	3,917	3.3			0		22	0.8	94	0.6	29	1.5	2.6	12.08	15.0	161
Export	16-Oct-2020	MDTI	264	3.3	945		0	12.7	23	1.5	78	0.5	25	1.3	0.7	9.12	16.8	138
Export	15-Dec-2020	MDTI	248	3.2	985	426.4	0	12.1	25	1.6	81	0.6	26	1.2	0.8	9.72	16.6	129
Export	24-Feb-2021	MDTI	525	3.3	988	425.7	0	12.2	23	1.6	82	0.6	26	1.4	0.8	10.67	17.7	151
Export	19-Apr-2021	MDTI	1,313	3.1	988	452.9	0	12.1	21	1.3	79	0.5	26	1.2	1.1	11.37	16.9	138
Export	23-Jun-2021	MDTI	884	3.2	978		0	12	22	1.5	82	0.6	27	1.4	0.9	11.51	17.2	140
Export	25-Aug-2021	MDTI	520	3.3	914	420	0	12.3	23	1.5	81	0.6	26	1.2	0.7	8.72	17.7	140

Appendix A1, cont.

Appendix A2 (bimonthly sampling elemental data)

October 17 2020

Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PA- BA -201016	< 20	< 0.1	4.6	22.2	0.22	7.5	< 5	< 30	< 2	< 20	82.0	< 2	< 30	< 2	< 20	5.60	< 2	0.06	< 5	382	6	< 0.02	< 10
PA- LOW -201017	< 20	< 0.1	5.8	36.3	1.02	9.6	< 5	< 30	< 2	< 20	148	4	< 30	3	< 20	49.2	< 2	0.08	< 5	444	8	0.03	10
PA- CM -201017	< 20	8.5	1.5	25.0	1.25	16.9	< 5	< 30	2	< 20	78.8	< 2	< 30	31	< 20	0.67	6	0.12	< 5	22.7	88	< 0.02	< 10
PA- UG -201017	< 20	< 0.1	3.9	17.5	0.43	7.2	< 5	< 30	< 2	< 20	62.5	< 2	< 30	3	< 20	24.9	< 2	0.05	< 5	349	9	0.09	< 10
PA- LG -201017	< 20	< 0.1	3.1	18.7	0.46	6.6	< 5	< 30	< 2	< 20	61.6	< 2	< 30	2	< 20	16.2	< 2	< 0.05	< 5	226	8	0.11	< 10
PA- IR -201017	< 20	< 0.1	5.0	35.6	1.85	10.2	< 5	< 30	< 2	< 20	138	4	< 30	6	< 20	55.8	< 2	0.07	< 5	152	15	0.03	10
PA- CR -201017	< 20	< 0.1	2.7	20.2	0.47	5.6	< 5	< 30	< 2	< 20	65.4	< 2	< 30	2	< 20	12.2	< 2	< 0.05	< 5	96.5	9	0.02	< 10
PA- DEL -201017	< 20	0.4	2.7	20.5	1.35	8.9	< 5	< 30	< 2	< 20	65.5	< 2	< 30	5	< 20	21.4	< 2	0.05	< 5	25.8	20	< 0.02	< 10
PA- EX -201017	< 20	8.5	1.5	24.9	1.25	16.5	< 5	< 30	2	< 20	77.0	< 2	< 30	31	< 20	0.66	6	0.12	< 5	22.6	87	< 0.02	< 10
PA- GA -201017	< 20	< 0.1	5.8	36.2	1.01	9.5	< 5	< 30	< 2	< 20	150	4	< 30	2	< 20	49.2	< 2	0.08	< 5	449	9	0.03	10
BLANK	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10

December 16, 2020

Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PA-BA-201215	< 20	< 0.1	4.4	24.3	0.23	7.9	< 5	< 30	< 2	< 20	89.5	< 2	< 30	< 2	< 20	6.67	< 2	0.07	< 5	432	< 5	0.03	< 10
PA-LOW-201215	< 20	< 0.1	5.6	36.1	0.99	9.3	< 5	< 30	< 2	< 20	149	4	< 30	3	< 20	49.5	< 2	0.08	< 5	447	6	0.04	< 10
PA-GA-201215	< 20	< 0.1	2.5	20.2	0.44	5.5	< 5	< 30	< 2	< 20	65.0	< 2	< 30	< 2	< 20	11.6	< 2	< 0.05	< 5	97.4	5	0.03	< 10
PA-UG-201215	< 20	< 0.1	3.6	19.0	0.45	6.8	< 5	< 30	< 2	< 20	67.0	2	< 30	5	< 20	27.1	< 2	0.05	< 5	324	9	0.09	< 10
PA-LG-201215	< 20	< 0.1	2.9	18.6	0.45	6.6	< 5	< 30	< 2	< 20	61.3	< 2	< 30	< 2	< 20	16.3	< 2	< 0.05	< 5	231	5	0.12	< 10
PA-IR-201215	< 20	< 0.1	4.8	36.0	1.88	10.1	< 5	< 30	< 2	< 20	140	4	< 30	7	< 20	57.4	< 2	0.08	< 5	146	14	0.04	< 10
PA-CR-201215	< 20	< 0.1	2.5	20.4	0.44	5.5	< 5	< 30	< 2	< 20	64.5	< 2	< 30	< 2	< 20	11.7	< 2	< 0.05	< 5	97.7	6	< 0.02	< 10
PA-DEL-201215	< 20	0.4	2.6	20.9	1.38	8.7	< 5	< 30	< 2	< 20	68.2	< 2	< 30	4	< 20	22.3	< 2	< 0.05	< 5	25.5	16	< 0.02	< 10
PA-EX-201215	< 20	8.1	1.4	25.2	1.16	16.3	< 5	< 30	< 2	< 20	79.4	< 2	< 30	32	< 20	0.75	6	0.12	< 5	24.6	83	< 0.02	< 10
PA-BL-201215	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10

February 24, 2021

Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
IB-CM-20210224	< 20	0.5	2.8	21.9	1.45	8.8	< 5	< 30	< 2	< 20	67.6	< 2	< 30	5	< 20	23.3	< 2	0.05	< 5	26.3	16	< 0.02	< 10
IB-LOW-20210224	< 20	< 0.1	5.9	36.8	0.95	8.6	< 5	< 30	< 2	< 20	147	3	< 30	4	< 20	46.8	< 2	0.08	< 5	456	< 5	< 0.02	< 10
IB-GA-20210224	20	< 0.1	3.5	19.7	0.38	6.2	< 5	< 30	< 2	< 20	66.2	< 2	< 30	4	< 20	19.5	< 2	< 0.05	< 5	295	< 5	< 0.02	< 10
IB-UG-20210224	20	< 0.1	3.6	20.0	0.38	6.3	< 5	< 30	< 2	< 20	66.8	< 2	< 30	4	< 20	19.7	< 2	< 0.05	< 5	297	< 5	0.02	< 10
IB-LG-20210224	< 20	< 0.1	3.3	19.1	0.47	6.4	< 5	< 30	< 2	< 20	62.1	< 2	< 30	< 2	< 20	16.3	< 2	< 0.05	< 5	246	< 5	0.10	< 10
IB-IR-20210224	< 20	< 0.1	5.0	36.9	1.88	10.1	< 5	< 30	< 2	< 20	136	4	< 30	5	< 20	55.8	< 2	0.08	< 5	151	9	< 0.02	10
IB-CR-20210224	< 20	0.1	2.7	21.6	0.42	5.5	< 5	< 30	< 2	< 20	66.9	< 2	< 30	2	< 20	11.6	< 2	< 0.05	< 5	94.2	< 5	< 0.02	< 10
IB-DEL-20210224	< 20	0.5	2.8	21.8	1.42	8.6	< 5	< 30	< 2	< 20	67.0	< 2	< 30	5	< 20	23.1	< 2	0.05	< 5	26.1	16	< 0.02	< 10
IB-EX-20210224	< 20	9.2	1.6	25.5	1.24	17.4	< 5	< 30	2	< 20	80.4	< 2	< 30	36	< 20	0.64	14	0.11	< 5	22.5	92	< 0.02	< 10
IB-BL-20210224	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10

Appendix A2, cont.

April 19, 2021

Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PA-DR-20210419	< 20	< 0.1	3.2	21.9	0.33	4.5	< 5	< 30	< 2	< 20	73.9	< 2	< 30	< 2	< 20	8.59	< 2	< 0.05	< 5	185	< 5	< 0.02	< 10
PA-LOW-20210419	< 20	< 0.1	5.4	39.6	0.99	8.2	< 5	< 30	< 2	< 20	137	3	< 30	4	< 20	48.4	< 2	0.08	< 5	398	< 5	0.03	< 10
PA-GA-20210419	< 20	< 0.1	3.2	22.6	0.32	4.7	< 5	< 30	< 2	< 20	73.0	< 2	< 30	< 2	< 20	7.53	< 2	< 0.05	< 5	191	< 5	< 0.02	< 10
PA-UG-20210419	< 20	< 0.1	3.3	18.1	0.34	5.9	< 5	< 30	< 2	< 20	60.7	< 2	< 30	4	< 20	13.9	< 2	< 0.05	< 5	265	< 5	< 0.02	< 10
PA-LG-20210419	< 20	< 0.1	3.1	18.5	0.48	6.2	< 5	< 30	< 2	< 20	59.5	< 2	< 30	2	< 20	17.1	< 2	< 0.05	< 5	224	< 5	0.11	< 10
PA-IW-20210419	< 20	< 0.1	4.9	34.8	1.70	9.3	< 5	< 30	< 2	< 20	123	4	< 30	7	< 20	51.9	< 2	0.07	< 5	150	14	0.03	< 10
PA-CR-20210419	< 20	< 0.1	2.8	21.8	0.44	5.6	< 5	< 30	< 2	< 20	69.3	< 2	< 30	4	< 20	11.4	< 2	< 0.05	< 5	90.5	7	< 0.02	< 10
PA-DEL-20210419	< 20	0.5	2.7	21.7	1.42	8.9	< 5	< 30	< 2	< 20	64.8	< 2	< 30	6	< 20	22.6	< 2	0.05	< 5	25.9	17	< 0.02	< 10
PA-EX-20210419	< 20	9.8	1.3	25.3	1.14	16.6	< 5	< 30	2	< 20	77.8	< 2	< 30	35	< 20	1.09	17	0.10	< 5	21.1	89	< 0.02	< 10
PA-BL-20210419	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10
PA-CB-20210419	< 20	< 0.1	2.7	21.7	0.43	5.9	< 5	< 30	< 2	< 20	68.4	< 2	< 30	3	< 20	11.4	< 2	< 0.05	< 5	90.8	8	< 0.02	< 10

June 23, 2021

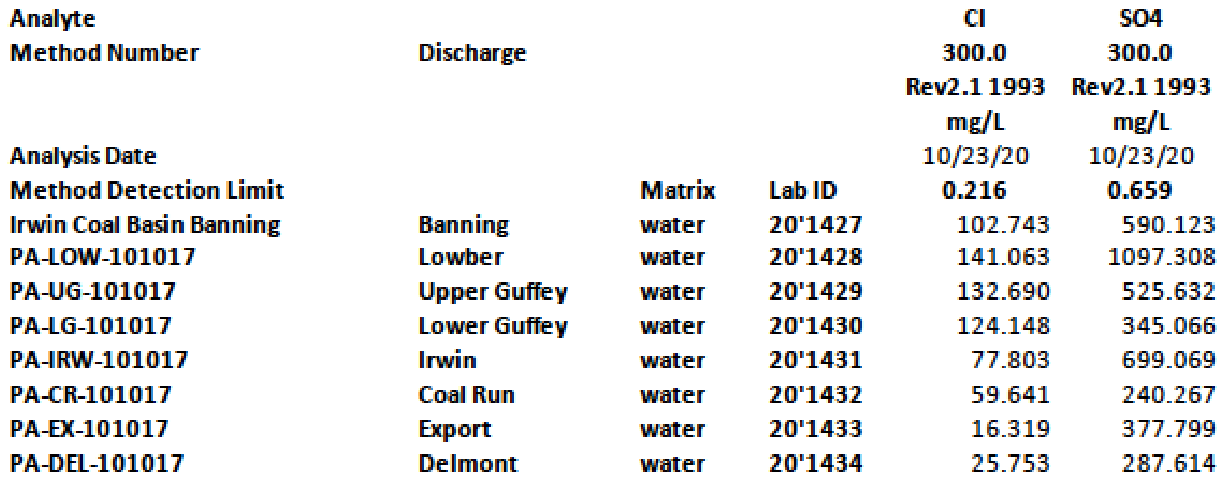
Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PA-DR-20210623	< 20	< 0.1	3.5	24.9	0.39	5.0	< 5	< 30	< 2	< 20	81.3	< 2	< 30	< 2	< 20	12.7	< 2	< 0.05	< 5	188	< 5	< 0.02	< 10
PA-LOW-20210623	< 20	< 0.1	5.7	36.8	0.93	8.7	< 5	< 30	< 2	< 20	145	< 2	< 30	4	< 20	44.2	< 2	0.07	< 5	438	9	0.03	< 10
PA-GA-20210623	< 20	9.3	1.4	26.5	1.16	16.9	< 5	< 30	2	< 20	80.4	< 2	< 30	34	< 20	0.82	10	0.11	< 5	21.7	88	< 0.02	< 10
PA-UG-20210623	< 20	< 0.1	3.7	18.1	0.36	6.5	< 5	< 30	< 2	< 20	62.2	< 2	< 30	3	< 20	17.6	< 2	< 0.05	< 5	316	6	0.02	< 10
PA-LG-20210623	< 20	< 0.1	3.1	19.5	0.45	6.5	< 5	< 30	< 2	< 20	61.6	< 2	< 30	< 2	< 20	15.9	< 2	< 0.05	< 5	218	6	0.12	< 10
PA-IR-20210623	< 20	< 0.1	4.9	34.4	1.64	9.9	< 5	< 30	< 2	< 20	124	< 2	< 30	6	< 20	50.1	< 2	0.07	< 5	153	13	0.04	< 10
PA-CR-20210623	< 20	< 0.1	2.8	22.3	0.49	5.7	< 5	< 30	< 2	< 20	68.9	< 2	< 30	3	< 20	12.1	< 2	< 0.05	< 5	97.2	8	0.03	< 10
PA-DEL-20210623	< 20	0.5	3.0	24.0	1.51	9.2	< 5	< 30	< 2	< 20	75.5	< 2	< 30	6	< 20	23.7	< 2	0.05	< 5	28.6	20	< 0.02	< 10
PA-EX-20210623	< 20	9.3	1.5	26.5	1.17	16.9	< 5	< 30	2	< 20	80.5	< 2	< 30	34	< 20	0.83	10	0.11	< 5	22.0	87	< 0.02	< 10
PA-BL20210623	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10
PA-CB-20210623	< 20	< 0.1	8.0	37.0	0.93	8.7	< 5	< 30	< 2	< 20	142	< 2	< 30	2	< 20	44.5	< 2	0.07	< 5	430	7	< 0.02	< 10

August 25, 2021

Analyte Symbol	Ba	Al	K	Mg	Mn	Si	Ag	As	Be	Bi	Ca	Cd	Ce	Co	Cr	Fe	Cu	Li	Mo	Na	Ni	P	Pb
Unit Symbol	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L	mg/L	ug/L
Lower Limit	20	0.1	0.1	0.1	0.01	0.1	5	30	2	20	0.1	2	30	2	20	0.01	2	0.05	5	0.1	5	0.02	10
Method Code	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES
PA-DR-20210825	< 20	< 0.1	3.4	25.0	0.44	5.5	< 5	< 30	< 2	< 20	81.7	< 2	< 30	< 2	< 20	16.1	< 2	< 0.05	< 5	187	< 5	< 0.02	< 10
PA-LOW-20210825	< 20	< 0.1	5.3	36.1	0.95	9.2	< 5	< 30	< 2	< 20	142	< 2	< 30	4	< 20	46.0	< 2	0.07	< 5	431	< 5	0.04	< 10
PA-GA-20210825	< 20	< 0.1	3.4	24.9	0.44	5.5	< 5	< 30	< 2	< 20	81.8	< 2	< 30	< 2	< 20	16.1	< 2	< 0.05	< 5	187	< 5	< 0.02	< 10
PA-UG-20210825	< 20	< 0.1	3.4	17.9	0.37	6.7	< 5	< 30	< 2	< 20	61.7	< 2	< 30	4	< 20	17.6	< 2	< 0.05	< 5	291	< 5	0.03	< 10
PA-LG-20210825	< 20	< 0.1	3.0	19.1	0.45	6.7	< 5	< 30	< 2	< 20	60.9	< 2	< 30	< 2	< 20	16.3	< 2	< 0.05	< 5	215	< 5	0.12	< 10
PA-IR-20210825	< 20	< 0.1	4.7	33.4	1.67	10.2	< 5	< 30	< 2	< 20	123	< 2	< 30	5	< 20	51.3	< 2	0.07	< 5	149	11	0.06	< 10
PA-CR-20210825	< 20	< 0.1	2.8	21.3	0.51	5.7	< 5	< 30	< 2	< 20	67.4	< 2	< 30	2	< 20	12.6	< 2	< 0.05	< 5	96.8	< 5	0.02	< 10
PA-DEL-20210825	< 20	0.5	2.9	22.9	1.50	9.3	< 5	< 30	< 2	< 20	73.4	< 2	< 30	5	< 20	23.8	< 2	0.06	< 5	28.7	20	< 0.02	< 10
PA-EX-20210825	< 20	8.9	1.5	25.9	1.21	17.4	< 5	< 30	2	< 20	79.5	< 2	< 30	33	< 20	0.60	8	0.10	< 5	22.5	83	< 0.02	< 10
PA-BL-20210825	< 20	< 0.1	< 0.1	< 0.1	< 0.01	< 0.1	< 5	< 30	< 2	< 20	< 0.1	< 2	< 30	< 2	< 20	< 0.01	< 2	< 0.05	< 5	< 0.1	< 5	< 0.02	< 10
PA-SH-20210825	< 20	< 0.1	2.7	21.4	0.51	5.8	< 5	< 30	< 2	< 20	67.0	< 2	< 30	2	< 20	12.6	< 2	< 0.05	< 5	97.0	< 5	0.03	< 10

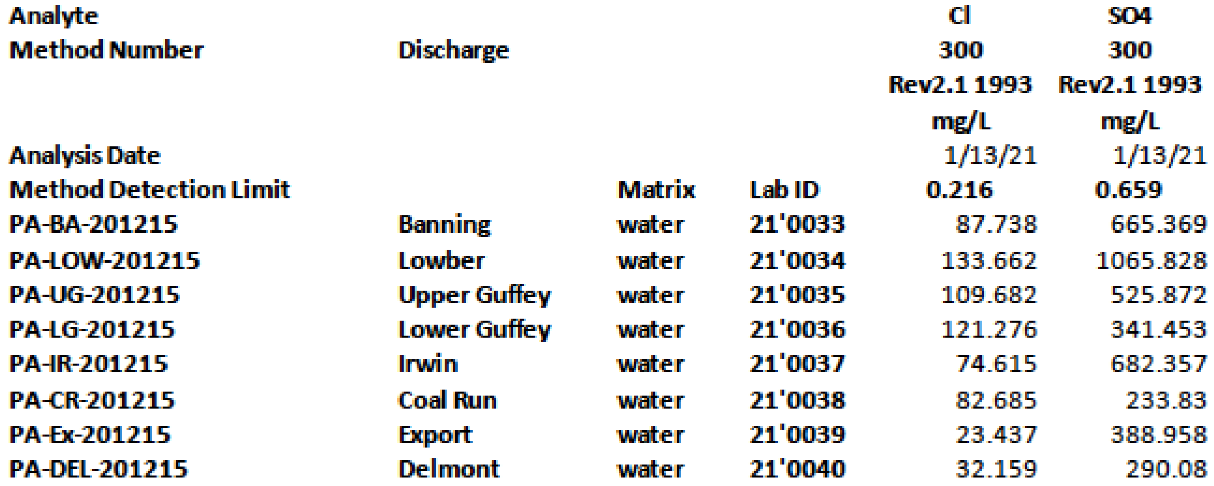
Appendix A3 (bimonthly sampling anion data)

October 17 2020



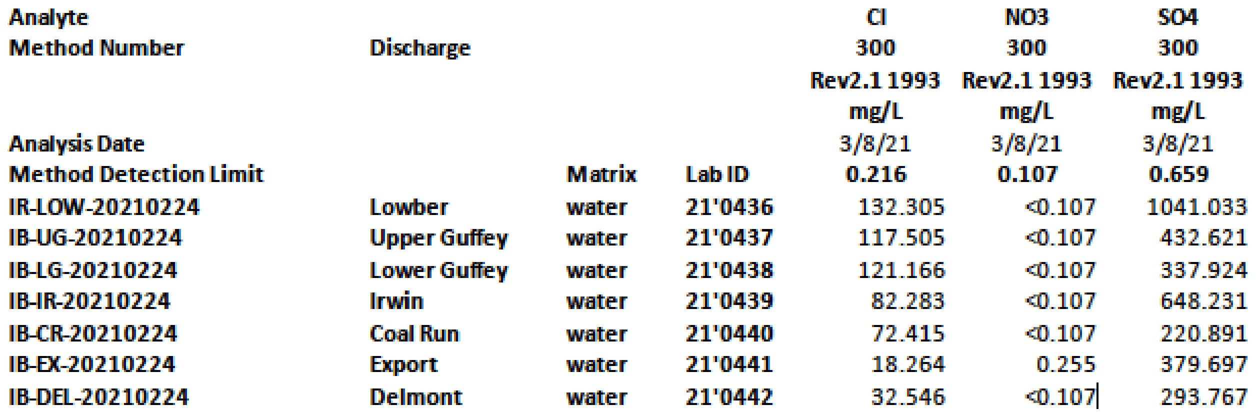
Analyte				**Cl**	**SO4**
Method Number	**Discharge**			**300.0**	**300.0**
				Rev2.1 1993	**Rev2.1 1993**
				mg/L	**mg/L**
Analysis Date				10/23/20	10/23/20
Method Detection Limit		**Matrix**	**Lab ID**	**0.216**	**0.659**
Irwin Coal Basin Banning	**Banning**	**water**	**20'1427**	102.743	590.123
PA-LOW-101017	**Lowber**	**water**	**20'1428**	141.063	1097.308
PA-UG-101017	**Upper Guffey**	**water**	**20'1429**	132.690	525.632
PA-LG-101017	**Lower Guffey**	**water**	**20'1430**	124.148	345.066
PA-IRW-101017	**Irwin**	**water**	**20'1431**	77.803	699.069
PA-CR-101017	**Coal Run**	**water**	**20'1432**	59.641	240.267
PA-EX-101017	**Export**	**water**	**20'1433**	16.319	377.799
PA-DEL-101017	**Delmont**	**water**	**20'1434**	25.753	287.614

December 16, 2020



Analyte				**Cl**	**SO4**
Method Number	**Discharge**			**300**	**300**
				Rev2.1 1993	**Rev2.1 1993**
				mg/L	**mg/L**
Analysis Date				1/13/21	1/13/21
Method Detection Limit		**Matrix**	**Lab ID**	**0.216**	**0.659**
PA-BA-201215	**Banning**	**water**	**21'0033**	87.738	665.369
PA-LOW-201215	**Lowber**	**water**	**21'0034**	133.662	1065.828
PA-UG-201215	**Upper Guffey**	**water**	**21'0035**	109.682	525.872
PA-LG-201215	**Lower Guffey**	**water**	**21'0036**	121.276	341.453
PA-IR-201215	**Irwin**	**water**	**21'0037**	74.615	682.357
PA-CR-201215	**Coal Run**	**water**	**21'0038**	82.685	233.83
PA-Ex-201215	**Export**	**water**	**21'0039**	23.437	388.958
PA-DEL-201215	**Delmont**	**water**	**21'0040**	32.159	290.08

February 24, 2021



Analyte				**Cl**	**NO3**	**SO4**
Method Number	**Discharge**			**300**	**300**	**300**
				Rev2.1 1993	**Rev2.1 1993**	**Rev2.1 1993**
				mg/L	**mg/L**	**mg/L**
Analysis Date				3/8/21	3/8/21	3/8/21
Method Detection Limit		**Matrix**	**Lab ID**	**0.216**	**0.107**	**0.659**
IR-LOW-20210224	**Lowber**	**water**	**21'0436**	132.305	<0.107	1041.033
IB-UG-20210224	**Upper Guffey**	**water**	**21'0437**	117.505	<0.107	432.621
IB-LG-20210224	**Lower Guffey**	**water**	**21'0438**	121.166	<0.107	337.924
IB-IR-20210224	**Irwin**	**water**	**21'0439**	82.283	<0.107	648.231
IB-CR-20210224	**Coal Run**	**water**	**21'0440**	72.415	<0.107	220.891
IB-EX-20210224	**Export**	**water**	**21'0441**	18.264	0.255	379.697
IB-DEL-20210224	**Delmont**	**water**	**21'0442**	32.546	<0.107	293.767

Appendix A3, cont.

April 19, 2021

Analyte				Cl	NO3	SO4
Method Number	Discharge			300	300	300
				Rev2.1 1993	Rev2.1 1993	Rev2.1 1993
				mg/L	mg/L	mg/L
Analysis Date				4/29/21	4/29/21	4/29/21
Method Detection Limit		Matrix	Lab ID	0.216	0.107	0.659
PA-LOW-20210419	Lowber	water	21'1134	125.939	0.221	997.523
PA-DR-20210419	Douglas Run	water	21'1135	97.559	0.514	291.579
PA-UG-20210419	Upper Guffey	water	21'1136	148.225	0.234	387.004
PA-LG-20210419	Lower Guffey	water	21'1137	120.341	0.405	336.92
PA-IW-20210419	Irwin	water	21'1138	97.421	0.718	658.545
PA-CR-20210419	Coal Run	water	21'1139	94.256	0.262	239.686
PA-EX-20210419	Export	water	21'1140	18.733	0.222	388.395
PA-DEL-20210419	Delmont	water	21'1141	31.214	<0.107	292.836

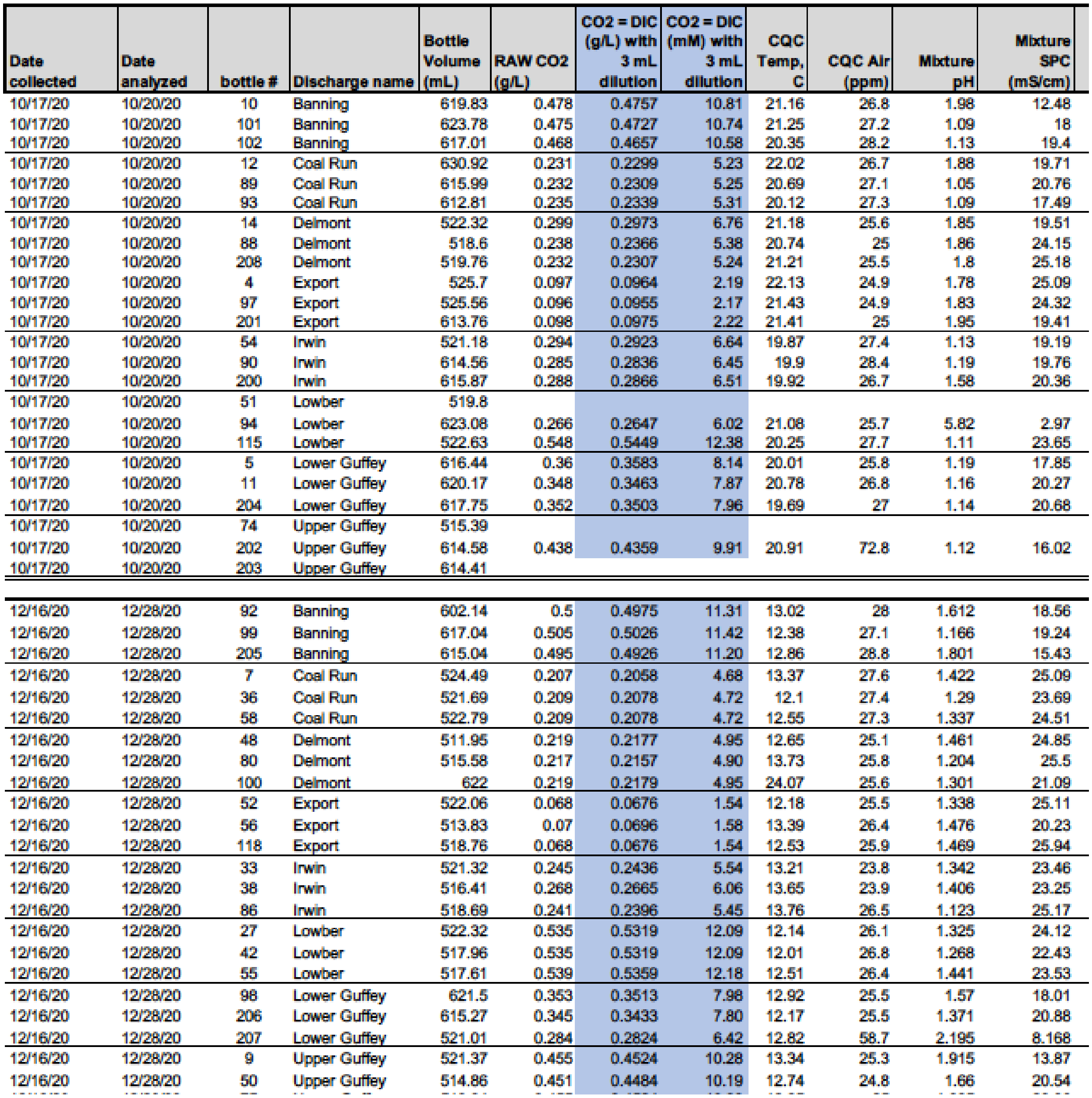
June 23, 2021

Analyte				Cl	NO3	PO4	SO4
Method Number	Discharge			300	300	300	300
				Rev2.1 1993	Rev2.1 1993	Rev2.1 1993	Rev2.1 1993
				mg/L	mg/L	mg/L	mg/L
Analysis Date				6/25/21	6/25/21	6/25/21	6/25/21
Method Detection Limit		Matrix	Lab ID	0.216	0.107	0.101	0.659
PA-IR-DR 20210623	Douglas Run	water	21'1798	95.983	0.418	<0.101	378.430
PA-IR-LOW 20210623	Lowber	water	21'1799	131.094	<0.107	<0.101	1,021.172
PA-IR-UG 20210623	Upper Guffey	water	21'1800	121.163	<0.107	<0.101	451.845
PA-IR-LG 20210623	Lower Guffey	water	21'1801	126.053	<0.107	<0.101	305.676
PA-IR-IR 20210623	Irwin	water	21'1802	96.839	<0.107	<0.101	610.939
PA-IR-CR 20210623	Coal Run	water	21'1803	94.531	<0.107	<0.101	230.393
PA-IR-EX 20210623	Export	water	21'1804	19.812	0.350	<0.101	356.449
PA-IR-DEL 20210623	Delmont	water	21'1805	30.512	<0.107	<0.101	316.067

August 25, 2021

Analyte				Cl	NO3	SO4
Method Number	Discharge			300	300	300
				Rev2.1 1993	Rev2.1 1993	Rev2.1 1993
				mg/L	mg/L	mg/L
Analysis Date				9/2/21	9/2/21	9/2/21
Method Detection Limit		Matrix	Lab ID	0.495	0.334	0.14
PA-IR-DR 20210825	Douglas Run	water	21'2554	98.499	0.486	342.503
PA-IR-LOW 20210825	Lowber	water	21'2555	133.499	<0.334	1039.181
PA-IR-UG 20210825	Upper Guffey	water	21'2556	114.481	<0.334	430.236
PA-IR-LG 20210825	Lower Guffey	water	21'2557	133.520	0.423	304.191
PA-IR-IR 20210825	Irwin	water	21'2558	102.877	<0.334	621.665
PA-IR-CR 20210825	Coal Run	water	21'2559	94.403	0.367	219.759
PA-IR-EX 20210825	Export	water	21'2560	21.887	0.351	383.888
PA-IR-DEL 20210825	Delmont	water	21'2561	34.847	<0.334	321.380

Appendix A4 (DIC data)

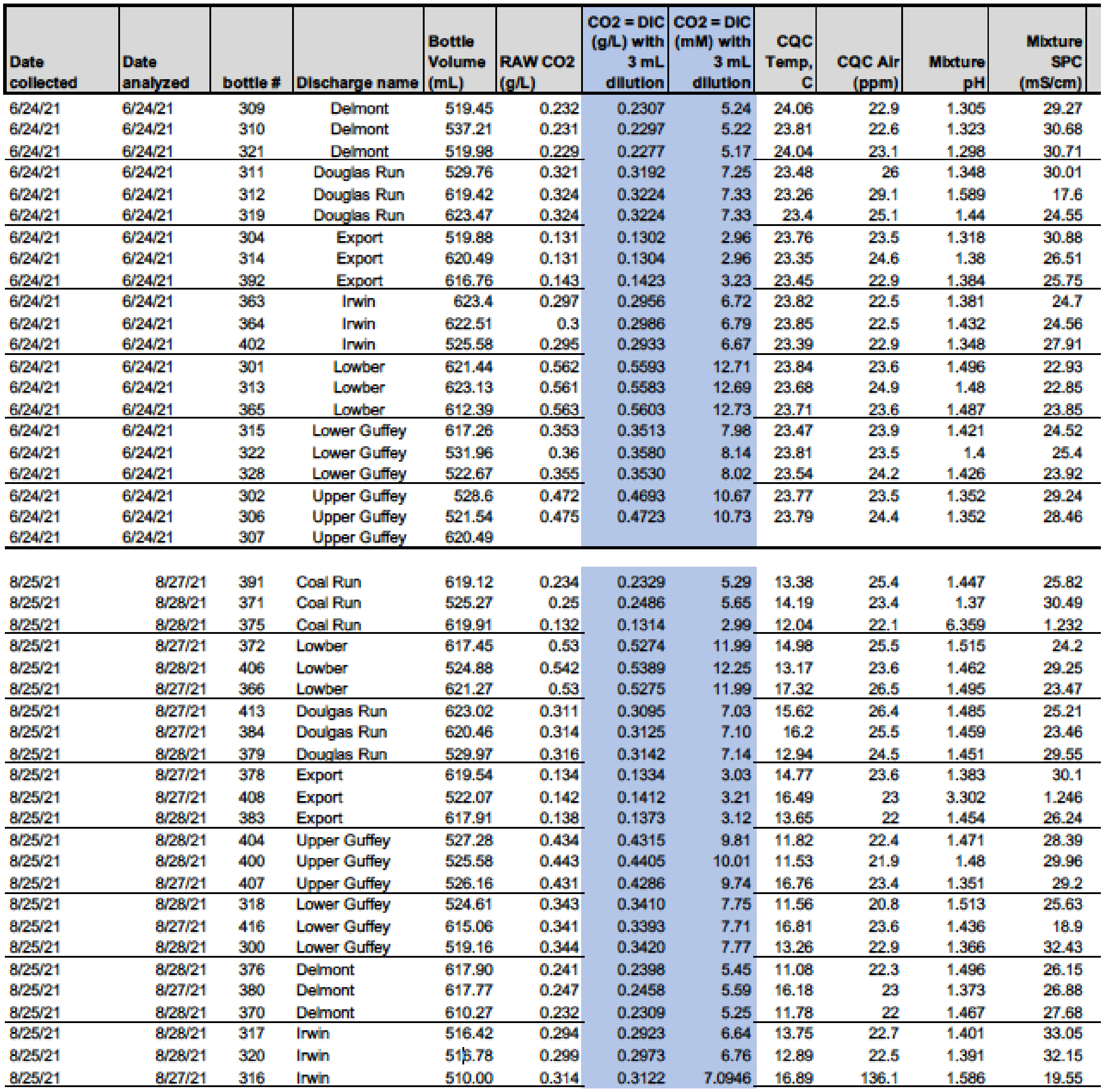


Date collected	Date analyzed	bottle #	Discharge name	Bottle Volume (mL)	RAW CO2 (g/L)	CO2 = DIC (g/L) with 3 mL dilution	CO2 = DIC (mM) with 3 mL dilution	CQC Temp, C	CQC Air (ppm)	Mixture pH	Mixture SPC (mS/cm)
10/17/20	10/20/20	10	Banning	619.83	0.478	0.4757	10.81	21.16	26.8	1.98	12.48
10/17/20	10/20/20	101	Banning	623.78	0.475	0.4727	10.74	21.25	27.2	1.09	18
10/17/20	10/20/20	102	Banning	617.01	0.468	0.4657	10.58	20.35	28.2	1.13	19.4
10/17/20	10/20/20	12	Coal Run	630.92	0.231	0.2299	5.23	22.02	26.7	1.88	19.71
10/17/20	10/20/20	89	Coal Run	615.99	0.232	0.2309	5.25	20.69	27.1	1.05	20.76
10/17/20	10/20/20	93	Coal Run	612.81	0.235	0.2339	5.31	20.12	27.3	1.09	17.49
10/17/20	10/20/20	14	Delmont	522.32	0.299	0.2973	6.76	21.18	25.6	1.85	19.51
10/17/20	10/20/20	88	Delmont	518.6	0.238	0.2366	5.38	20.74	25	1.86	24.15
10/17/20	10/20/20	208	Delmont	519.76	0.232	0.2307	5.24	21.21	25.5	1.8	25.18
10/17/20	10/20/20	4	Export	525.7	0.097	0.0964	2.19	22.13	24.9	1.78	25.09
10/17/20	10/20/20	97	Export	525.56	0.096	0.0955	2.17	21.43	24.9	1.83	24.32
10/17/20	10/20/20	201	Export	613.76	0.098	0.0975	2.22	21.41	25	1.95	19.41
10/17/20	10/20/20	54	Irwin	521.18	0.294	0.2923	6.64	19.87	27.4	1.13	19.19
10/17/20	10/20/20	90	Irwin	614.56	0.285	0.2836	6.45	19.9	28.4	1.19	19.76
10/17/20	10/20/20	200	Irwin	615.87	0.288	0.2866	6.51	19.92	26.7	1.58	20.36
10/17/20	10/20/20	51	Lowber	519.8							
10/17/20	10/20/20	94	Lowber	623.08	0.266	0.2647	6.02	21.08	25.7	5.82	2.97
10/17/20	10/20/20	115	Lowber	522.63	0.548	0.5449	12.38	20.25	27.7	1.11	23.65
10/17/20	10/20/20	5	Lower Guffey	616.44	0.36	0.3583	8.14	20.01	25.8	1.19	17.85
10/17/20	10/20/20	11	Lower Guffey	620.17	0.348	0.3463	7.87	20.78	26.8	1.16	20.27
10/17/20	10/20/20	204	Lower Guffey	617.75	0.352	0.3503	7.96	19.69	27	1.14	20.68
10/17/20	10/20/20	74	Upper Guffey	515.39							
10/17/20	10/20/20	202	Upper Guffey	614.58	0.438	0.4359	9.91	20.91	72.8	1.12	16.02
10/17/20	10/20/20	203	Upper Guffey	614.41							
12/16/20	12/28/20	92	Banning	602.14	0.5	0.4975	11.31	13.02	28	1.612	18.56
12/16/20	12/28/20	99	Banning	617.04	0.505	0.5026	11.42	12.38	27.1	1.166	19.24
12/16/20	12/28/20	205	Banning	615.04	0.495	0.4926	11.20	12.86	28.8	1.801	15.43
12/16/20	12/28/20	7	Coal Run	524.49	0.207	0.2058	4.68	13.37	27.6	1.422	25.09
12/16/20	12/28/20	36	Coal Run	521.69	0.209	0.2078	4.72	12.1	27.4	1.29	23.69
12/16/20	12/28/20	58	Coal Run	522.79	0.209	0.2078	4.72	12.55	27.3	1.337	24.51
12/16/20	12/28/20	48	Delmont	511.95	0.219	0.2177	4.95	12.65	25.1	1.461	24.85
12/16/20	12/28/20	80	Delmont	515.58	0.217	0.2157	4.90	13.73	25.8	1.204	25.5
12/16/20	12/28/20	100	Delmont	622	0.219	0.2179	4.95	24.07	25.6	1.301	21.09
12/16/20	12/28/20	52	Export	522.06	0.068	0.0676	1.54	12.18	25.5	1.338	25.11
12/16/20	12/28/20	56	Export	513.83	0.07	0.0696	1.58	13.39	26.4	1.476	20.23
12/16/20	12/28/20	118	Export	518.76	0.068	0.0676	1.54	12.53	25.9	1.469	25.94
12/16/20	12/28/20	33	Irwin	521.32	0.245	0.2436	5.54	13.21	23.8	1.342	23.46
12/16/20	12/28/20	38	Irwin	516.41	0.268	0.2665	6.06	13.65	23.9	1.406	23.25
12/16/20	12/28/20	86	Irwin	518.69	0.241	0.2396	5.45	13.76	26.5	1.123	25.17
12/16/20	12/28/20	27	Lowber	522.32	0.535	0.5319	12.09	12.14	26.1	1.325	24.12
12/16/20	12/28/20	42	Lowber	517.96	0.535	0.5319	12.09	12.01	26.8	1.268	22.43
12/16/20	12/28/20	55	Lowber	517.61	0.539	0.5359	12.18	12.51	26.4	1.441	23.53
12/16/20	12/28/20	98	Lower Guffey	621.5	0.353	0.3513	7.98	12.92	25.5	1.57	18.01
12/16/20	12/28/20	206	Lower Guffey	615.27	0.345	0.3433	7.80	12.17	25.5	1.371	20.88
12/16/20	12/28/20	207	Lower Guffey	521.01	0.284	0.2824	6.42	12.82	58.7	2.195	8.168
12/16/20	12/28/20	9	Upper Guffey	521.37	0.455	0.4524	10.28	13.34	25.3	1.915	13.87
12/16/20	12/28/20	50	Upper Guffey	514.86	0.451	0.4484	10.19	12.74	24.8	1.66	20.54

Appendix A4 cont.

Date collected	Date analyzed	bottle #	Discharge name	Bottle Volume (mL)	RAW CO2 (g/L)	CO2 = DIC (g/L) with 3 mL dilution	CO2 = DIC (mM) with 3 mL dilution	CQC Temp, C	CQC Air (ppm)	Mixture pH	Mixture SPC (mS/cm)
2/24/21	2/26/21	330	Coal Run	529.23	0.229	0.2277	5.18	14.01	27.4	1.04	23.01
2/24/21	2/26/21	337	Coal Run	527.66	0.226	0.2247	5.11	14.77	27.8	1.184	31.85
2/24/21	2/26/21	338	Coal Run	624.11	0.224	0.2229	5.07	14.65	26.9	1.476	23.24
2/24/21	2/26/21	350	Export	520.81	0.087	0.0865	1.97	15.81	37.9	1.487	17.1
2/24/21	2/26/21	358	Export	522.67	0.087	0.0865	1.97	14.16	25.4	1.52	32.19
2/24/21	2/26/21	359	Export	617.91	0.097	0.0965	2.19	15.36	24.6	1.315	21.45
2/24/21	2/26/21	331	Irwin	625.29	0.275	0.2737	6.22	13.84	26	0.95	22.89
2/24/21	2/26/21	345	Irwin	624.37	0.27	0.2687	6.11	15.21	26.3	1.47	16.39
2/24/21	2/26/21	352	Irwin	620.18	0.277	0.2757	6.27	15.78	26.3	1.407	19.82
2/24/21	2/26/21	347	Lowber	612.12	0.551	0.5483	12.46	14.87	26.9	1.257	28.47
2/24/21	2/26/21	354	Lowber	623.1	0.552	0.5494	12.49	15.15	27.6	1.81	10.75
2/24/21	2/26/21	360	Lowber	616.65	0.56	0.5573	12.67	14.97	26.6	1.369	18.94
2/24/21	2/26/21	333	Lower Guffey	522.61	0.367	0.3649	8.29	14.67	26.4	1.096	30.89
2/24/21	2/26/21	340	Lower Guffey	617.43	0.373	0.3712	8.44	15.26	26.5	1.466	21.6
2/24/21	2/26/21	353	Lower Guffey	518.17	0.371	0.3689	8.38	14.15	25.7	1.053	30.46
2/24/21	2/26/21	332	Upper Guffey	625.39	0.441	0.4389	9.97	15.45	25	1.345	25.73
2/24/21	2/26/21	346	Upper Guffey	617.11	0.429	0.4269	9.70	13.85	25.5	0.434	24.51
2/24/21	2/26/21	361	Upper Guffey	529.69	0.436	0.4335	9.85	15.02	25.7	1.935	18.87
4/19/21	4/22/21	45	Coal Run	514.61	0.218	0.2167	4.93	14.02	25	1.059	33.58
4/19/21	4/22/21	84	Coal Run	517.88	0.219	0.2177	4.95	15.06	24.7	0.94	30.18
4/19/21	4/22/21	105	Coal Run	607.54							
4/19/21	4/22/21	61	Delmont	519.21	0.194	0.1929	4.38	13.5	28	1.138	34
4/19/21	4/22/21	329	Delmont	520.49	0.203	0.2018	4.59	14.26	23.5	1.165	33.5
4/19/21	4/22/21	348	Delmont	618.56	0.205	0.2040	4.64	13.63	22.8	1.16	29.13
4/19/21	4/22/21	349	Douglas Run	520.53	0.329	0.3271	7.43	14.82	27.5	1.092	31.89
4/19/21	4/22/21	356	Douglas Run	523.23	0.325	0.3231	7.34	15.79	28.4	1.148	29.69
4/19/21	4/22/21	81	Douglas Run	519.14	0.329	0.3271	7.43	17.88	27.7	1.6	30.46
4/19/21	4/22/21	35	Export	518.9	0.142	0.1412	3.21	15.37	124	1.418	17.8
4/19/21	4/22/21	59	Export	521.52	0.126	0.1253	2.85	12.51	23.8	1.029	33.47
4/19/21	4/22/21	64	Export	514.18	0.129	0.1283	2.91	14.45	24	1.348	34.26
4/19/21	4/22/21	324	Irwin	519.32							
4/19/21	4/22/21	336	Irwin	517.75	0.276	0.2744	6.24	13.08	22.2	1.019	30.3
4/19/21	4/22/21	351	Irwin	519.51	0.285	0.2834	6.44	13.71	28.2	1.61	16.6
4/19/21	4/22/21	325	Lowber	512.1	0.55	0.5468	12.43	14.86	25.9	1.085	30.36
4/19/21	4/22/21	355	Lowber	523.1	0.553	0.5498	12.50	15.36	26	1.2	30.46
4/19/21	4/22/21	357	Lowber	517.62	0.558	0.5548	12.61	17.29	24.8	1.221	30.09
4/19/21	4/22/21	334	Lower Guffey	521.08	0.362	0.3599	8.18	13.37	24	0.99	31.67
4/19/21	4/22/21	341	Lower Guffey	617.77	0.357	0.3553	8.07	13.03	23.6	1.111	27.7
4/19/21	4/22/21	342	Lower Guffey	512.1	0.347	0.3450	7.84	15.74	25.3	1.148	32.05
4/19/21	4/22/21	327	Upper Guffey	518.34	0.407	0.4047	9.20	13.05	26.1	1.358	25.75
4/19/21	4/22/21	335	Upper Guffey	621.89	0.415	0.4130	9.39	13.71	24.9	1.138	24.59
4/19/21	4/22/21	339	Upper Guffey	534.67	0.419	0.4167	9.47	13.08	24.6	1.747	31.51
6/24/21	6/24/21	362	Coal Run	625.3	0.224	0.2229	5.07	23.31	23.8	1.405	24.55
6/24/21	6/24/21	390	Coal Run	622.88	0.227	0.2259	5.13	23.33	24.9	1.44	21.97

Appendix A4 cont.



Date collected	Date analyzed	bottle #	Discharge name	Bottle Volume (mL)	RAW CO2 (g/L)	CO2 = DIC (g/L) with 3 mL dilution	CO2 = DIC (mM) with 3 mL dilution	CQC Temp, C	CQC Air (ppm)	Mixture pH	Mixture SPC (mS/cm)
6/24/21	6/24/21	309	Delmont	519.45	0.232	0.2307	5.24	24.06	22.9	1.305	29.27
6/24/21	6/24/21	310	Delmont	537.21	0.231	0.2297	5.22	23.81	22.6	1.323	30.68
6/24/21	6/24/21	321	Delmont	519.98	0.229	0.2277	5.17	24.04	23.1	1.298	30.71
6/24/21	6/24/21	311	Douglas Run	529.76	0.321	0.3192	7.25	23.48	26	1.348	30.01
6/24/21	6/24/21	312	Douglas Run	619.42	0.324	0.3224	7.33	23.26	29.1	1.589	17.6
6/24/21	6/24/21	319	Douglas Run	623.47	0.324	0.3224	7.33	23.4	25.1	1.44	24.55
6/24/21	6/24/21	304	Export	519.88	0.131	0.1302	2.96	23.76	23.5	1.318	30.88
6/24/21	6/24/21	314	Export	620.49	0.131	0.1304	2.96	23.35	24.6	1.38	26.51
6/24/21	6/24/21	392	Export	616.76	0.143	0.1423	3.23	23.45	22.9	1.384	25.75
6/24/21	6/24/21	363	Irwin	623.4	0.297	0.2956	6.72	23.82	22.5	1.381	24.7
6/24/21	6/24/21	364	Irwin	622.51	0.3	0.2986	6.79	23.85	22.5	1.432	24.56
6/24/21	6/24/21	402	Irwin	525.58	0.295	0.2933	6.67	23.39	22.9	1.348	27.91
6/24/21	6/24/21	301	Lowber	621.44	0.562	0.5593	12.71	23.84	23.6	1.496	22.93
6/24/21	6/24/21	313	Lowber	623.13	0.561	0.5583	12.69	23.68	24.9	1.48	22.85
6/24/21	6/24/21	365	Lowber	612.39	0.563	0.5603	12.73	23.71	23.6	1.487	23.85
6/24/21	6/24/21	315	Lower Guffey	617.26	0.353	0.3513	7.98	23.47	23.9	1.421	24.52
6/24/21	6/24/21	322	Lower Guffey	531.96	0.36	0.3580	8.14	23.81	23.5	1.4	25.4
6/24/21	6/24/21	328	Lower Guffey	522.67	0.355	0.3530	8.02	23.54	24.2	1.426	23.92
6/24/21	6/24/21	302	Upper Guffey	528.6	0.472	0.4693	10.67	23.77	23.5	1.352	29.24
6/24/21	6/24/21	306	Upper Guffey	521.54	0.475	0.4723	10.73	23.79	24.4	1.352	28.46
6/24/21	6/24/21	307	Upper Guffey	620.49							
8/25/21	8/27/21	391	Coal Run	619.12	0.234	0.2329	5.29	13.38	25.4	1.447	25.82
8/25/21	8/28/21	371	Coal Run	525.27	0.25	0.2486	5.65	14.19	23.4	1.37	30.49
8/25/21	8/28/21	375	Coal Run	619.91	0.132	0.1314	2.99	12.04	22.1	6.359	1.232
8/25/21	8/27/21	372	Lowber	617.45	0.53	0.5274	11.99	14.98	25.5	1.515	24.2
8/25/21	8/28/21	406	Lowber	524.88	0.542	0.5389	12.25	13.17	23.6	1.462	29.25
8/25/21	8/27/21	366	Lowber	621.27	0.53	0.5275	11.99	17.32	26.5	1.495	23.47
8/25/21	8/27/21	413	Doulgas Run	623.02	0.311	0.3095	7.03	15.62	26.4	1.485	25.21
8/25/21	8/27/21	384	Doulgas Run	620.46	0.314	0.3125	7.10	16.2	25.5	1.459	23.46
8/25/21	8/28/21	379	Douglas Run	529.97	0.316	0.3142	7.14	12.94	24.5	1.451	29.55
8/25/21	8/27/21	378	Export	619.54	0.134	0.1334	3.03	14.77	23.6	1.383	30.1
8/25/21	8/27/21	408	Export	522.07	0.142	0.1412	3.21	16.49	23	3.302	1.246
8/25/21	8/28/21	383	Export	617.91	0.138	0.1373	3.12	13.65	22	1.454	26.24
8/25/21	8/28/21	404	Upper Guffey	527.28	0.434	0.4315	9.81	11.82	22.4	1.471	28.39
8/25/21	8/28/21	400	Upper Guffey	525.58	0.443	0.4405	10.01	11.53	21.9	1.48	29.96
8/25/21	8/27/21	407	Upper Guffey	526.16	0.431	0.4286	9.74	16.76	23.4	1.351	29.2
8/25/21	8/28/21	318	Lower Guffey	524.61	0.343	0.3410	7.75	11.56	20.8	1.513	25.63
8/25/21	8/27/21	416	Lower Guffey	615.06	0.341	0.3393	7.71	16.81	23.6	1.436	18.9
8/25/21	8/28/21	300	Lower Guffey	519.16	0.344	0.3420	7.77	13.26	22.9	1.366	32.43
8/25/21	8/28/21	376	Delmont	617.90	0.241	0.2398	5.45	11.08	22.3	1.496	26.15
8/25/21	8/27/21	380	Delmont	617.77	0.247	0.2458	5.59	16.18	23	1.373	26.88
8/25/21	8/28/21	370	Delmont	610.27	0.232	0.2309	5.25	11.78	22	1.467	27.68
8/25/21	8/28/21	317	Irwin	516.42	0.294	0.2923	6.64	13.75	22.7	1.401	33.05
8/25/21	8/28/21	320	Irwin	516.78	0.299	0.2973	6.76	12.89	22.5	1.391	32.15
8/25/21	8/27/21	316	Irwin	510.00	0.314	0.3122	7.0946	16.89	136.1	1.586	19.55

Appendix A5 (CO_2 data)

Data collected	Date analyzed	Sample name	CO2 (g/L)	CO2 (mM)	Temp C)	Air (ppm)
10/17/20	10/19/20	Banning	0.094	2.14	18.08	23.9
10/17/20	10/19/20	Banning	0.093	2.11	17.39	23.7
10/17/20	10/19/20	Banning	0.091	2.07	17.73	23.7
10/17/20	10/19/20	Lower Guffey	0.141	3.20	16.63	24.4
10/17/20	10/19/20	Lower Guffey	0.143	3.25	17.26	24.3
10/17/20	10/19/20	Lower Guffey	0.141	3.20	16.53	24.5
10/17/20	10/19/20	Upper Guffey	0.185	4.20	16.56	22.5
10/17/20	10/19/20	Upper Guffey	0.185	4.20	17.1	24.2
10/17/20	10/19/20	Upper Guffey	0.183	4.16	16.54	22.6
10/17/20	10/19/20	Irwin	0.183	4.16	17.32	26.5
10/17/20	10/19/20	Irwin	0.185	4.20	17.08	25.8
10/17/20	10/19/20	Lowber	0.249	5.66	17.14	24.9
10/17/20	10/19/20	Lowber	0.246	5.59	17.16	25.2
10/17/20	10/19/20	Lowber	0.245	5.57	17.92	25.2
10/17/20	10/19/20	Export	0.096	2.18	18.41	24.8
10/17/20	10/19/20	Export	0.094	2.14	17.76	24.6
10/17/20	10/19/20	Export	0.096	2.18	17.47	24.5
10/17/20	10/19/20	Coal Run	0.111	2.52	18.47	25.5
10/17/20	10/19/20	Coal Run	0.112	2.55	18.65	25.7
10/17/20	10/19/20	Coal Run	0.108	2.45	18.75	25.7
10/17/20	10/19/20	Delmont	0.217	4.93	18.19	24.9
10/17/20	10/19/20	Delmont	0.213	4.84	18.41	24.9
10/17/20	10/19/20	Delmont	0.217	4.93	18.47	24.9
12/16/20	12/21/20	Irwin	0.162	3.68	25.4	15.54
12/16/20	12/21/20	Irwin	0.173	3.93	9.75	NA
12/16/20	12/21/20	Coal Run	0.105	2.39	25.9	14.09
12/16/20	12/21/20	Coal Run	0.106	2.41	24.9	14.89
12/16/20	12/21/20	Coal Run	0.101	2.30	26.1	14.13
12/16/20	12/21/20	Delmont	0.216	4.91	23.7	14.12
12/16/20	12/21/20	Delmont	0.203	4.61	24.9	13.9
12/16/20	12/21/20	Delmont	0.21	4.77	24.7	14.84
12/16/20	12/21/20	Export	0.074	1.68	25.1	14.52
12/16/20	12/21/20	Export	0.068	1.55	25.8	14.23
12/16/20	12/21/20	Export	0.07	1.59	25.6	14.99
12/16/20	12/21/20	Lowber	0.244	5.55	24.3	15.04
12/16/20	12/21/20	Lowber	0.241	5.48	24.5	14.72
12/16/20	12/21/20	Lowber	0.252	5.73	24.4	15.15
12/16/20	12/21/20	Banning	0.096	2.18	24.2	15.65
12/16/20	12/21/20	Banning	0.095	2.16	24.2	15.04
12/16/20	12/21/20	Banning	0.097	2.20	24.2	15.5
12/16/20	12/21/20	Lower Guffey	0.148	3.36	24.6	16.22
12/16/20	12/21/20	Lower Guffey	0.146	3.32	24	15.69
12/16/20	12/21/20	Lower Guffey	0.147	3.34	23.9	15.85
12/16/20	12/21/20	Upper Guffey	0.183	4.16	22.6	16.93
12/16/20	12/21/20	Upper Guffey	0.179	4.07	23.6	16.71
12/16/20	12/21/20	Upper Guffey	0.196	4.45	22.6	16.67
2/24/21	2/26/21	Irwin	0.186	4.23	24.7	12.42
2/24/21	2/26/21	Irwin	0.181	4.11	25.1	12.32
2/24/21	2/26/21	Irwin	0.18	4.09	25.5	12.94
2/24/21	2/26/21	Upper Guffey	0.155	3.52	29.2	13.09
2/24/21	2/26/21	Upper Guffey	0.154	3.50	26.7	12.16
2/24/21	2/26/21	Upper Guffey	0.163	3.70	25.9	12.35
2/24/21	2/26/21	Lower Guffey	0.147	3.34	26.7	10.94

Data collected	Date analyzed	Sample name	CO2 (g/L)	CO2 (mM)	Temp C)	Air (ppm)
2/24/21	2/26/21	Lower Guffey	0.149	3.39	24.9	11.37
2/24/21	2/26/21	Lower Guffey	0.159	3.61	25.1	11.22
2/24/21	2/26/21	Coal Run	0.107	2.43	26.1	11.34
2/24/21	2/26/21	Coal Run	0.11	2.50	25.6	10.44
2/24/21	2/26/21	Coal Run	0.108	2.45	25.1	11.96
2/24/21	2/26/21	Export	0.089	2.02	25.3	11.99
2/24/21	2/26/21	Export	0.093	2.11	25.1	11.95
2/24/21	2/26/21	Export	0.089	2.02	26.2	12.3
2/24/21	2/26/21	Delmont	0.231	5.25	24	11.52
2/24/21	2/26/21	Delmont	0.226	5.14	25.2	11.75
2/24/21	2/26/21	Delmont	0.232	5.27	24.9	12.03
2/24/21	2/26/21	Lowber	0.247	5.61	24.8	13.52
2/24/21	2/26/21	Lowber	0.257	5.84	23.9	13.31
2/24/21	2/26/21	Lowber	0.257	5.84	24.2	13.52
4/19/21	4/24/21	Douglas Run	0.098	2.2273	9.82	24.7
4/19/21	4/24/21	Douglas Run	0.101	2.2955	11.53	23.7
4/19/21	4/24/21	Douglas Run	0.103	2.3409	13.24	23.7
4/19/21	4/24/21	Lowber	0.258	5.8636	9.6	22.3
4/19/21	4/24/21	Lowber	0.262	5.9545	11.35	22
4/19/21	4/24/21	Lowber	0.252	5.7273	13.28	22.1
4/19/21	4/24/21	Lower Guffey	0.157	3.5682	8.15	21
4/19/21	4/24/21	Lower Guffey	0.162	3.6818	13.08	23.1
4/19/21	4/24/21	Lower Guffey	0.167	3.7955	13.05	21.5
4/19/21	4/24/21	Delmont	0.204	4.6364	13.09	23.9
4/19/21	4/24/21	Delmont	0.202	4.5909	13.47	23.7
4/19/21	4/24/21	Delmont	0.191	4.3409	13.33	23.7
4/19/21	4/24/21	Irwin	0.226	5.1364	12.09	20.4
4/19/21	4/24/21	Irwin	0.218	4.9545	13.13	21.4
4/19/21	4/24/21	Irwin	0.223	5.0682	13.63	21.1
4/19/21	4/24/21	Export	0.121	2.7500	12.26	24.3
4/19/21	4/24/21	Export	0.126	2.8636	12.88	23.6
4/19/21	4/24/21	Export	0.128	2.9091	13.61	23.8
4/19/21	4/24/21	Upper Guffey	0.172	3.9091	12.25	21.4
4/19/21	4/24/21	Upper Guffey	0.169	3.8409	12.98	21.9
4/19/21	4/24/21	Upper Guffey	0.173	3.9318	14.3	21.7
4/19/21	4/24/21	Coal Run	0.116	2.6364	12.34	23.1
4/19/21	4/24/21	Coal Run	0.118	2.6818	14.14	24.2
4/19/21	4/24/21	Coal Run	0.113	2.5682	14.28	23.7
6/24/21	6/24/21	Lower Guffey	0.167	3.7955	23.81	21.8
6/24/21	6/24/21	Lower Guffey	0.165	3.7500	24	20.5
6/24/21	6/24/21	Lower Guffey				
6/24/21	6/24/21	Delmont	0.212	4.8182	24	22.4
6/24/21	6/24/21	Delmont	0.23	5.2273	23.91	21.3
6/24/21	6/24/21	Delmont	0.214	4.8636	23.94	22.1
6/24/21	6/24/21	Export	0.141	3.2045	23.81	21.4
6/24/21	6/24/21	Export	0.136	3.0909	23.9	23.4
6/24/21	6/24/21	Export	0.137	3.1136	23.82	19.8
6/24/21	6/24/21	Upper Guffey	0.199	4.5227	23.78	19.8
6/24/21	6/24/21	Upper Guffey	0.189	4.2955	23.83	22.1
6/24/21	6/24/21	Upper Guffey				
6/24/21	6/24/21	Coal Run	0.115	2.6136	23.81	23.3
6/24/21	6/24/21	Coal Run	0.118	2.6818	23.77	22.2
6/24/21	6/24/21	Coal Run				

Appendix A5 cont.

Appendix B. Geochemical “First-flush” Mixing and Reaction Models

To be published as Supplemental Information in “Multi-decadal geochemical evolution of drainage from coal mines in the Appalachian basin” by CR Schaffer, CA Cravotta III, RC Capo, BC Hedin, DJ Vesper, BW Stewart

A “first-flush” forward reaction model was developed using PHREEQC version 3.6.2 (Parkhurst and Appelo, 2013) with the wateq4f thermodynamic database (Ball and Nordstrom, 1991) to quantify hydrogeochemical processes involved in the long-term evolution of mine-water quality. Goals of the model were (1) to identify processes that explain widely reported long-term changes in CMD chemistry and (2) to estimate trends in CMD quality decades into the future, constrained by known hydrology and geochemistry. The model objective was to explain the initial development of extremely acidic mine-pool water; the exponential decay of SO4 and Fe concentrations to near steady-state elevated values over a decadal time scale; the transition from net-acidic to net-alkaline conditions; and Na enrichment.

The model was designed and calibrated to simulate observed changes in chemistry of the Lowber CMD, which is representative of evolved, mineralized mine-pool water that had undergone net-acidic to net-alkaline transition, while also exhibiting persistent elevated concentrations of SO4, Fe, and major ions, including Na. The Lowber mine was closed in 1950; CMD first occurred in 1953. The initially acidic mine-pool water in 1953 (year 0), is simulated by instantaneous reaction of ambient groundwater (Table S4) with accumulated pyrite oxidation products, represented by coquimbite (Fe2(SO4)3:9H2O, ideal formula) formed by pyrite oxidation in humid air prior to mine flooding, plus carbonate aluminosilicate, and oxide minerals (Table S5). The ambient groundwater is a Ca/HCO3 water type represented by sample WE-315 of McAuley and Kozar (2006), having pH and solute concentrations near the median composition of “unmined” samples reported by those authors. Thereafter, progressive evolution of the Lowber CMD over 100 years is simulated as 100 sequential reaction steps (1 year each). At each step, a constant fraction of groundwater was mixed with the evolving mine-pool water. Given the 11.4-year mine-pool residence time reported by Winters and Capo (2004), the groundwater fraction mixed with the mine-pool water each year was calculated as 8.8% (1 year/11.4 years); by 2021 (year 68), the total groundwater influx equated to six mine-pool volumes. A consistent mineral assemblage, including pyrite, carbonates, aluminosilicates, and exchanger having the composition of core samples (Tables S5 and S6), was reacted in each step, but in progressively decreasing quantities. A 1% per year decay rate was assumed, such that all reactants would be depleted after 100-years. Using available water-quality data from 1970’s to 2021, the model was calibrated by adjusting the total quantities of specified mineral reactants until simulation results were comparable to the historical sample dataset to 2021 (year 68). Calcite, dolomite, gypsum, Fe(OH)3(a), jarosite, schwertmannite, siderite, manganite, Al(OH)3(a), hydrobasaluminite, illite, and chalcedony were specified to precipitate upon reaching equilibrium (saturation index, SI = 0), except for siderite, jarosite, and schwertmannite specified to precipitate at SI = 0.3 (Table S5).

To evaluate the effects of dilution, mineral dissolution, and exchange processes on the evolving mine pool water, three model scenarios considered the mixing of the groundwater and mine-pool water: (1) without mineral dissolution or cation exchange; (2) with mineral dissolution but without cation exchange; and (3) with mineral dissolution and cation exchange. On-screen graphs display simulation results compared to annual median values computed for observed values (Fig. B1)

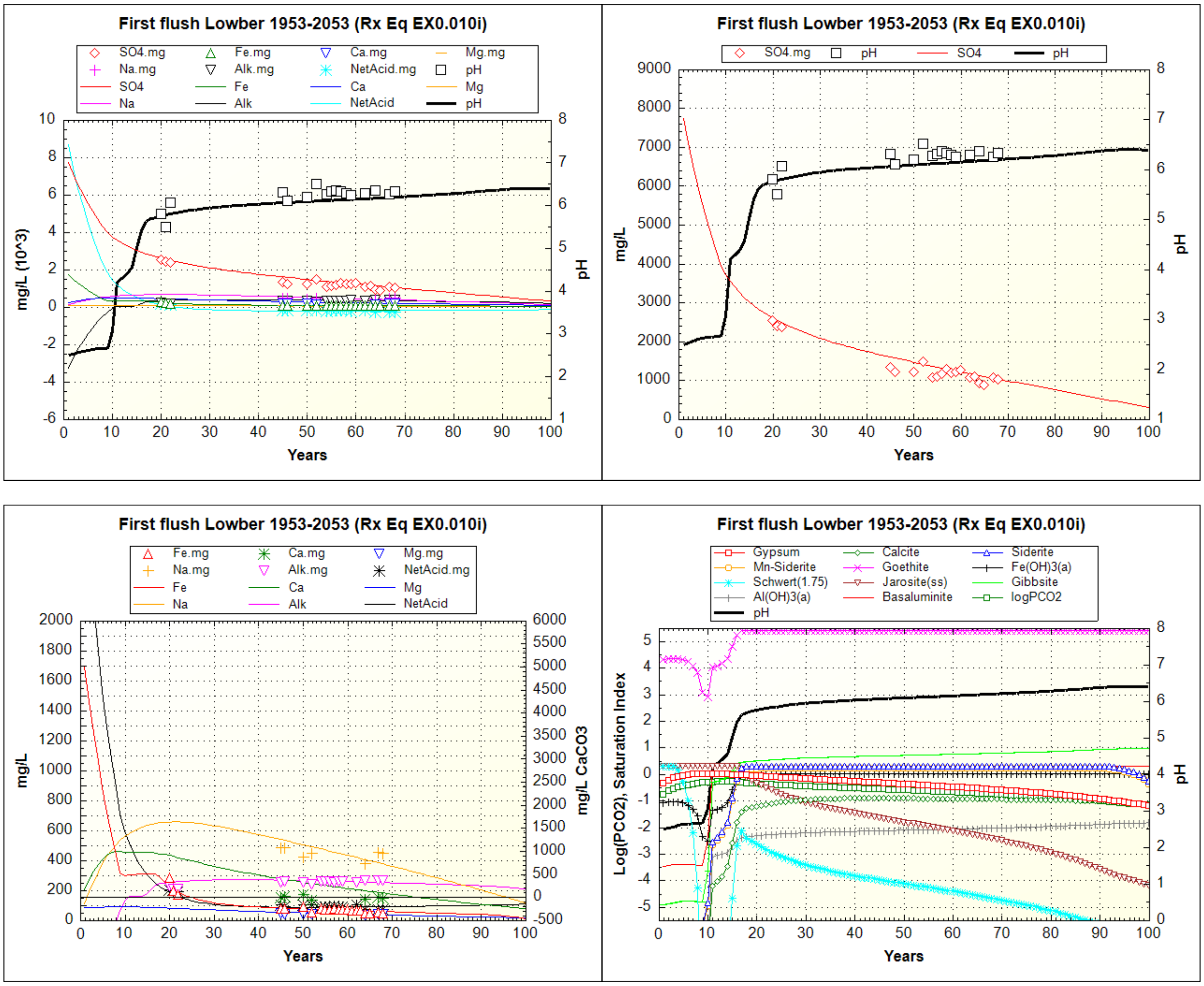


Figure B1. On-screen graphs generated by "first-flush" CMD evolution model of Lower mine simulating mixing of alkaline groundwater combined with mineral dissolution and cation exchange. Points are annual medians for observed data; curves are model results.

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Appendix C. PHREEQC forward reaction model

To be published as Supplemental Information in "Multi-decadal geochemical evolution of drainage from coal mines in the Appalachian basin" by CR Schaffer, CA Cravotta III, RC Capo, BC Hedin, DJ Vesper, BW Stewart

The PHREEQC program below is an example of a forward-reaction model developed to quantify the relative importance and effects of mineral dissolution, cation exchange, and mixing with ambient groundwater as potential mechanisms affecting the pH, acidity, alkalinity, sulfate, iron, and other major cation concentrations in CMD. Phreeqc Interactive version 3 software, which is needed to run the program, can be accessed at https://www.usgs.gov/software/phreeqc-version-3. For general instructions on the PHREEQC program, the user is referred to Parkhurst and Appelo (2013) and Appelo and Postma (2005).

This specific model uses thermodynamic data from Ball and Nordstrom (1991), groundwater-quality data from McAuley and Kozar (2006), plus long-term monitoring data for CMD from the Lowber Mine (this report). To run the model, the PHREEQC script (shown below, "fwd_icb_FirstFlush_Lowber_230625.pqi") plus five additional data files with this supplemental zip file (wateq4f+schwert+EX.dat; Lowber_QW.txt; Lowber_SO4_pH.txt; Lowber_Fe_NAcid_Ca.txt; Lowber_Eh_pH.txt) must be unzipped and present in a single folder. Graphical displays of selected output as a function of elapsed time plus a tab-delimited selected output file "Forward_firstflush_loop.sel" containing those data plus additional data will be generated. The selected output can be opened with Excel or another spreadsheet to examine the simulated water-quality values as a function of elapsed time, in years, since the first flush. Specific instructions or options are provided within the program as comment lines (identified by # at the beginning of the comment). Many lines have been deactivated with a single #, but retained for reference or future activation by deleting any preceding #. Lines with ##, ###, #### are for information only and not intended to be activated.

The "first-flush" computations begin after the heading line: ##### First flush, repeat prior computation of initial composition, then proceed with looping of mixing and reactions ##### After this heading, # is mainly used to document changes in values for mineral quantities or other variables considered during calibration of the model. The lines of code with same mineral name or line number that have not been commented out are the "final" calibrated results that display in the graphs and output file. A comprehensive Excel file "speciation.FeIIplusDataEquilibriumAsymptote_Lowber1953_coquimbite_230625_cac.xlsx" showing the results of different simulations plus associated information is included with the zip file.

DISCLAIMER: This software is preliminary or provisional and is subject to revision. It is being provided to meet the need for timely best science. The software has not received final approval by the U.S. Geological Survey (USGS). No warranty, expressed or implied, is made by the USGS or the U.S. Government as to the functionality of the software and related material nor shall the fact of release constitute any such warranty. The software is provided on the condition that neither the USGS nor the U.S. Government shall be held liable for any damages resulting from the authorized or unauthorized use of the software.

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Appendix D. PHREEQC “First-flush” geochemical model of long-term evolution from initially net-acidic to net-alkaline water quality—Script, only

To be published as Supplemental Information in “Multi-decadal geochemical evolution of drainage from coal mines in the Appalachian basin” by CR Schaffer, CA Cravotta III, RC Capo, BC Hedin, DJ Vesper, BW Stewart

```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.7.3-15968\database\wateq4f.dat

TITLE “First-flush” geochemical model of long-term evolution from initially net-acidic to net-alkaline water quality

# Program written by C.A. Cravotta III describes the transition from net-acidic to alkaline quality and long-term trends in pH, acidity, sulfate, iron, and major cation concentrations.

# Select \database\wateq4f.dat

# In addition to wateq4f.dat, a supplemental thermodynamic database file is needed, wateq4f+schwert+EX.dat, that includes hydroxysulfate minerals using unit formulas.

# Additionally, four external data files are needed for observed water-quality data points to display in on-screen graphs: Lowber_QW.txt; Lowber_SO4_pH.txt; Lowber_Fe_NAcid_Ca.txt; Lowber_Eh_pH.txt.

# Data for ambient groundwater at WE-315 of McAuley and Kozar (2006) are specified for the sole input solution to the first-flush model.

# Median composition of the Lowber CMD is also specified as input for comparison to first-flush model  results for speciation and saturation indices.

INCLUDE$ wateq4f+schwert+EX.dat

SELECTED_OUTPUT 1

   -file               Forward_firstflush_loop.sel

   -reset               false

   -simulation           false

   -ph                 false

   -reaction             false

   -solution            true

   -user_punch           true
```

```
USER_PUNCH 1

-headings Years Year Descrip ChrgBal TempC pH pe Eh.v peSato EhSato.v O2.mg Alk.mgCaCO3 NetAcid_mgCaCO3 Ca.mg Mg.mg Na.mg K.mg

-headings HCO3.mg SO4.mg Cl.mg SiO2.mg Sr.mg Fe.mg Al.mg Mn.mg Hardness.mg TDS.mg SC25.uScalc

-headings si_Calcite si_Dolomite si_Gypsum si_Celestite si_Strontianite

-headings si_Microcline si_Adularia si_Albite si_Anorthite si_Chlorite7A si_Beidellite si_Illite si_Kaolinite

-headings si_Gibbsite si_Al(OH)3(a) si_Kmica si_Quartz si_Chalcedony si_SiO2(a)

-headings si_Goethite si_Fe(OH)3(a) si_Schwert1.75 si_Schwert1.50 si_Schwert1.00 si_JarositeSS si_FerCopiapite si_Coquimbite si_Melanterite si_Siderite(d) si_Mn-Siderite

-headings si_Rhodochrosite si_Todorokite si_Manganite logpCO2 CO2_mmol/L CO2_mg/L CO2_logK

-headings Na.CatEQ CaMg.CatEQ Na.ClMRATIO

-headings CaX2 MgX2 NaX KX HX MnX2 FeX3 AlX3

-headings Jarosite_Femol Schwert1.75_Femol Fe(OH)3_Femol Siderite_Femol

-start

  01  YEARS = GET(1)

  02  YEAR0 = 1953

  03  YEAR  = YEAR0 + YEARS

  04 PUNCH YEARS

  05 PUNCH YEAR

  10 PUNCH DESCRIPTION

  20 PUNCH PERCENT_ERROR

  30 PUNCH TC

  40  pH = -LA("H+")

  50 PUNCH pH

  60  pe = -LA("e-")

  70 PUNCH pe

  80  nernst = 8.314e-3*TK*LOG(10)/96.42
```

```
  90 PUNCH pe*nernst

 100 REM  pe and Eh computed from O(-2)/O(0):  2 H2O = O2 + 4 H+ + 4 e-

 110  logo2 = LA("O2")

 120  satolgkt = (-45.54+(134.79/(LOG(10)*0.001987))*(1/298.15-1/TK))

 130  pesato = (logo2-4*pH-satolgkt-2*LA("H2O"))/4

 140 PUNCH pesato

 150 PUNCH pesato*nernst

 160 REM Concentrations converted from moles to milligrams per liter

 170 PUNCH TOT("O(0)")*GFW("O")*1000

 180 PUNCH ALK*GFW("Alkalinity")*1000

 185 PUNCH (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)

 190 PUNCH TOT("Ca")*GFW("Ca")*1000

 200 PUNCH TOT("Mg")*GFW("Mg")*1000

 210 PUNCH TOT("Na")*GFW("Na")*1000

 220 PUNCH TOT("K")*GFW("K")*1000

 230 PUNCH ALK*GFW("Alkalinity")*1000*1.22

 240 PUNCH TOT("S(6)")*(GFW("S")+4*GFW("O"))*1000

 250 PUNCH TOT("Cl")*GFW("Cl")*1000

 260 PUNCH TOT("Si")*(GFW("Si")+2*GFW("O"))*1000

 270 PUNCH TOT("Sr")*GFW("Sr")*1000

 280 PUNCH TOT("Fe")*GFW("Fe")*1000

 290 PUNCH TOT("Al")*GFW("Al")*1000

 300 PUNCH TOT("Mn")*GFW("Mn")*1000

 310  Hardness = 1000*(2.5*TOT("Ca")*GFW("Ca"))+(4.1*TOT("Mg")*GFW("Mg"))

 320 PUNCH Hardness

 330  TDS =
1000*(TOT("Ca")*GFW("Ca")+TOT("Mg")*GFW("Mg")+TOT("Na")*GFW("Na")+TOT("K")
*GFW("K")+TOT("Si")*(GFW("SiO2"))+TOT("S(6)")*(GFW("SO4"))+TOT("Cl")*GFW("Cl"
```

```
)+ALK*GFW("Alkalinity")*0.6+TOT("Fe")*GFW("FeOOH")+TOT("Al")*GFW("AlOOH")+T
OT("Mn")*GFW("MnOOH"))

 340 PUNCH TDS

 350 REM Calculate Electrical Conductivity using McCleskey, R.B., Nordstrom, D.K., Ryan,
J.N., and Ball, J.W., 2012, A New Method of Calculating Electrical Conductivity With
Applications to Natural Waters: Geochimica et Cosmochimica Acta, v. 77, p. 369-382

 360  ec_ca = ((0.007647*TC^2+2.204*TC+59.11)-
(0.03174*TC^2+2.334*TC+132.3)*((MU^0.5)/(1+(2.8*MU^0.5))))*MOL('Ca+2')

 370  ec_mg = ((0.01068*TC^2+1.695*TC+57.16)-
(0.02453*TC^2+1.915*TC+80.50)*((MU^0.5)/(1+(2.1*MU^0.5))))*MOL('Mg+2')

 380  ec_na = ((0.003763*TC^2+0.877*TC+26.23)-
(0.00027*TC^2+1.141*TC+32.07)*((MU^0.5)/(1+(1.7*MU^0.5))))*MOL('Na+')

 390  ec_k = ((0.003046*TC^2+1.261*TC+40.70)-
(0.00535*TC^2+0.9316*TC+22.59)*((MU^0.5)/(1+(1.5*MU^0.5))))*MOL('K+')

 400  ec_cl = ((0.003817*TC^2+1.337*TC+40.99)-
(0.00613*TC^2+0.9469*TC+22.01)*((MU^0.5)/(1+(1.5*MU^0.5))))*MOL('Cl-')

 410  ec_so4 = ((0.01037*TC^2+2.838*TC+82.37)-
(0.03324*TC^2+5.889*TC+193.5)*((MU^0.5)/(1+(2.6*MU^0.5))))*MOL('SO4-2')

 420  ec_hco3 = ((0.000614*TC^2+0.9048*TC+21.14)-(-
0.00503*TC^2+0.8957*TC+10.97)*((MU^0.5)/(1+(0.1*MU^0.5))))*MOL('HCO3-')

 430  ec_feii = ((0.009939*TC^2+1.878*TC+54.80)-
(0.03997*TC^2+3.217*TC+164.5)*((MU^0.5)/(1+(4.0*MU^0.5))))*MOL('Fe+2')

 440  ec_feiii = ((0.02077*TC^2+4.390*TC+82.42)-(-0.09676*TC^2+20.76*TC-
22.18)*((MU^0.5)/(1+(4.0*MU^0.5))))*MOL('Fe+3')

 450  ec_co3 = ((-0.000326*TC^2+2.998*TC+64.03)-(-
0.00181*TC^2+5.542*TC+120.2)*((MU^0.5)/(1+(2.3*MU^0.5))))*MOL('CO3+2')

 460  ec_oh = ((0.003396*TC^2+2.925*TC+121.3)-
(0.00933*TC^2+0.1086*TC+35.90)*((MU^0.5)/(1+(0.01*MU^0.5))))*MOL('OH-')

 470  ec_nh4 = ((0.003341*TC^2+1.285*TC+39.04)-
(0.00132*TC^2+0.6070*TC+11.19)*((MU^0.5)/(1+(0.3*MU^0.5))))*MOL('NH4+')

 480  ec_naco3 = ((0.00336*TC^2+3.845*TC+89.51)-
(0.00061*TC^2+6.387*TC+141.7)*((MU^0.5)/(1+(2.0*MU^0.5))))*MOL('NaCO3-')

 490  ec_naso4 = ((0.002309*TC^2+5.459*TC+219.2)-
(0.01454*TC^2+5.193*TC+253.6)*((MU^0.5)/(1+(0.5*MU^0.5))))*MOL('NaSO4-')
```

```
500  ec_kso4 = ((-0.002439*TC^2+4.253*TC+129.7)-(-
0.01576*TC^2+6.21*TC+146.8)*((MU^0.5)/(1+(1.3*MU^0.5))))*MOL('KSO4-')

510  ec_cs = ((0.003453*TC^2+1.249*TC+43.94)-
(0.00646*TC^2+0.7023*TC+21.79)*((MU^0.5)/(1+(1.3*MU^0.5))))*MOL('Cs+')

520  ec_al = ((0.02376*TC^2+3.227*TC+90.24)-
(0.06484*TC^2+5.149*TC+76.79)*((MU^0.5)/(1+(3.0*MU^0.5))))*MOL('Al+3')

530  ec_f = ((0.002764*TC^2+1.087*TC+26.66)-
(0.00178*TC^2+0.6202*TC+19.34)*((MU^0.5)/(1+(0.5*MU^0.5))))*MOL('F-')

540  ec_hso4 = ((0.000927*TC^2+0.8337*TC+29.56)-
(0.02887*TC^2+0.87304*TC+36.25181)*((MU^0.5)/(1+(7.0*MU^0.5))))*MOL('HSO4-')

550  ec_h = ((-0.01414*TC^2+5.355*TC+224.2)-(-
0.00918*TC^2+1.842*TC+39.23)*((MU^0.5)/(1+(0.3*MU^0.5))))*MOL('H+')

560  ec_li = ((0.002628*TC^2+0.7079*TC+19.20)-
(0.00412*TC^2+0.4632*TC+13.71)*((MU^0.5)/(1+(0.2*MU^0.5))))*MOL('Li+')

570  ec_no3 = ((0.001925*TC^2+1.214*TC+39.90)-
(0.00118*TC^2+0.5045*TC+23.31)*((MU^0.5)/(1+(0.1*MU^0.5))))*MOL('NO3-')

580  ec_sr = ((0.006649*TC^2+2.069*TC+61.63)-
(0.00702*TC^2+0.9009*TC+33.41)*((MU^0.5)/(1+(0.1*MU^0.5))))*MOL('Sr+2')

590  ec_ba = ((0.01059*TC^2+2.090*TC+68.10)-
(0.03127*TC^2+2.248*TC+93.91)*((MU^0.5)/(1+(1.9*MU^0.5))))*MOL('Ba+2')

600  ec_br = ((0.000709*TC^2+1.477*TC+40.91)-
(0.00251*TC^2+0.5398*TC+12.01)*((MU^0.5)/(1+(0.1*MU^0.5))))*MOL('Br-')

610  ec_mn = ((0.01275*TC^2+2.109*TC+46.19)-
(0.1071*TC^2+9.023*TC+135.4)*((MU^0.5)/(1+(7.6*MU^0.5))))*MOL('Mn+2')

620  ec_cu = ((0.00818*TC^2+1.939*TC+53.26)-
(0.0292*TC^2+6.745*TC+151.5)*((MU^0.5)/(1+(8.0*MU^0.5))))*MOL('Cu+2')

630  ec_zn = ((0.01249*TC^2+1.912*TC+48.20)-
(0.08284*TC^2+5.188*TC+75.73)*((MU^0.5)/(1+(7.0*MU^0.5))))*MOL('Zn+2')

640  ec_haso4 = ((2.829*TC+54.80)-
(4.251*TC+103.4)*((MU^0.5)/(1+(1.63*MU^0.5))))*MOL('HAsO4-2')

650  ec_h2aso4 = ((0.8291*TC+16.35)-
(0.2673*TC+14.07)*((MU^0.5)/(1+(0.39*MU^0.5))))*MOL('H2AsO4-')

660  ec_calc =
1000*(ec_ca+ec_mg+ec_na+ec_k+ec_cl+ec_so4+ec_hco3+ec_feii+ec_feiii+ec_co3+ec_oh+ec_
```

```
nh4+ec_naco3+ec_naso4+ec_kso4+ec_cs+ec_al+ec_f+ec_hso4+ec_h+ec_li+ec_no3+ec_sr+ec_
ba+ec_br+ec_mn+ec_cu+ec_zn+ec_haso4+ec_h2aso4)
 670 REM NLF Temperature Compensation (ISO 7888)
 680  sc_nlf = ec_calc/(1+(((0.00000030*(TC^2)+0.00005757*TC+0.0193))*(TC-25)))
 690 PUNCH sc_nlf
 700 REM Saturation indices
 710 PUNCH SI("Calcite")
 720 PUNCH SI("Dolomite")
 730 PUNCH SI("Gypsum")
 740 PUNCH SI("Celestite")
 750 PUNCH SI("Strontianite")
 760 PUNCH SI("Microcline")
 770 PUNCH SI("Adularia")
 780 PUNCH SI("Albite")
 790 PUNCH SI("Anorthite")
 800 PUNCH SI("Chlorite7A")
 810 PUNCH SI("Beidellite")
 820 PUNCH SI("Illite")
 830 PUNCH SI("Kaolinite")
 840 PUNCH SI("Gibbsite")
 850 PUNCH SI("Al(OH)3(a)")
 860 PUNCH SI("Kmica")
 870 PUNCH SI("Quartz")
 875 PUNCH SI("Chalcedony")
 880 PUNCH SI("SiO2(a)")
 890 PUNCH SI("Goethite")
 900 PUNCH SI("Fe(OH)3(a)")
 910 PUNCH SI("Schwert(1.75)")/8
 920 PUNCH SI("Schwert(1.50)")/8
```

```
 930 PUNCH SI("Schwert(1.00)")/8
 940 PUNCH SI("Jarosite(ss)")/3
 950 PUNCH SI("Ferricopiapite")/4.78
 955 PUNCH SI("Coquimbite")/1.47
 960 PUNCH SI("Melanterite")
 970 PUNCH SI("Siderite(d)(3)")
 975 PUNCH SI("Mn-Siderite")
 980 PUNCH SI("Rhodochrosite")
 990 PUNCH SI("Todorokite")/7
1000 PUNCH SI("Manganite")
1010 PUNCH SI("CO2(g)")
1020 PUNCH MOL('CO2')*1000
1030 PUNCH MOL('CO2')*1000*(GFW('CO2'))
1040 PUNCH LK_PHASE("CO2(g)")
1050  NaEQ = TOT('Na')
1060  CaEQ = TOT('Ca')*2
1070  MgEQ = TOT('Mg')*2
1080  KEQ  = TOT('K')
1090  SrEQ = TOT('Sr')*2
2000  HEQ = MOL('H+')
2010  CatEQ = NaEQ + CaEQ + MgEQ + KEQ + SrEQ + HEQ
2020  NaRATIO = NaEQ / CatEQ
2030 PUNCH NaRATIO
2040 PUNCH (CaEQ+MgEQ)/CatEQ
2050 REM Molar ratio [Na]/[Cl]
2060 PUNCH TOT("Na")/TOT("Cl")
## Include the exchanger composition in output ##
5000 PUNCH MOL("CaX2")
```

```
5010 PUNCH MOL("MgX2")

5020 PUNCH MOL("NaX")

5030 PUNCH MOL("KX")

5080 PUNCH MOL("HX")

5090 PUNCH MOL("MnX2")

6000 PUNCH MOL("FeX2")

6100 PUNCH MOL("AlX3")

6200 PUNCH EQUI("Jarosite(ss)")*3

6210 PUNCH EQUI("Schwert(1.75)")*8

6220 PUNCH EQUI("Fe(OH)3(a)")

6230 PUNCH EQUI("Siderite(d)(3)")

-end

END


# The solution spread option allows input of data copied as rows from Excel.

# Data must be converted to default units specified as mg/L or other units.


SOLUTION_SPREAD

   -units    mg/kgw

 Number                 Description     temp  O(0)     pe       pH       S(6)     Cl      Si          Ca
Mg          Na      K        Fe       Mn       Al     Alkalinity

                                                                                                   charge


    0     GW_McCauley-Kozar_WE315         11.8     5.5        4       6.9          36       12    7.63
52         10.2       7.3    1.37    0.074   0.004   0.003         127

    112    PAIB_LOW_MDTI_MEDIAN      13.85   0.01     2.20    6.32    1040.11          132.91
          9.13     148.55           39.90   448.91           4.90    48.35   1.03    0.02          360

END


REACTION 0 #NO REACTIONS
```

```
EXCHANGE 0 #NO CATION EXCHANGE

EQUILIBRIUM_PHASES 0 #NO EQUILIBRIUM


##### First flush, repeat prior computation of initial composition, then proceed with looping of
mixing and reactions #####

REACTION 1 ## High SO4, Fe, low pH first flush ##

        Calcite               1

        Dolomite              0.5

        Mn-Siderite           0.6

        Microcline            0.1 #0.5

        Plagioclase           0.1 #0.5

        #Fe(OH)3(a)           0

        #Illite       1

        #Beidellite   1

        Chlorite7A    0.5

        Halite        0.05 #0.01

        #CH2O             10

#       Pyrite        21 #19.9 #22

#       Coquimbite            13.5 #2 mol Fe1.5Al0.5(SO4)3 ~ 3 mol FeS2

#       O2(g)      78.5 #75 #70 #77 #68 #70

## To model flushing of efflorescent salt, can react coquimbite+NoO2 instead of pyrite+O2

        Coquimbite            30 #35 #45 #2 mol Fe1.5Al0.5(SO4)3 ~ 3 mol FeS2

        O2(g)      0 #Coquimbite instead of pyrite

0.001 moles in 1 steps

END


EQUILIBRIUM_PHASES 1

 Calcite       0       0

 Dolomite      0       0
```

```
 Gypsum         0       0
 Fe(OH)3(a)     0       0
#Goethite       0       0
 Manganite      0       0
 Siderite(d)(3) 0.3     0
#Siderite       0       0
#Mn-Siderite    0       0
 Illite   0     0
#Kaolinite      0       0
 Al(OH)3(a)     0       0
#Gibbsite       0       0
 Chalcedony     0       0
#CO2(g)         -0.82   1
#CO2(g)         -0.82   0
## Added hydrobasaluminite, jarosite and schwertmannite as possible precipitates
 Hydrobasaluminite      0       0
 Jarosite(ss)   0.3     0
 Schwert(1.75)0.3       0
END

USE SOLUTION 0 BACKGROUND Ca/HCO3
USE REACTION 1
#USE EQUILIBRIUM_PHASES 0
USE EQUILIBRIUM_PHASES 1
USE EXCHANGE 0
SAVE SOLUTION 1 Lowber First Flush
END
```

```
#! save initial conditions
COPY cell 1 1000
END

#!Write firstflush
SOLUTION 100
SELECTED_OUTPUT 2
 -file firstflush
 -reset false
USER_PUNCH 2
  10 FOR i = 1 to 100 STEP 1
  20 YEARS = 0 + i
  30 IF (YEARS > 100) THEN END
  40 GWfrac = 1/11.4 #11.4 yr residence time
  50 MDfrac = 1.0-GWfrac
  60 iDECAY = (i-1) / 100 * 1
  70 MOLES = 1.0e-6
  80 iMOLES = MOLES * (1.0 - iDECAY)
  90 EXCHANGE = 1.0
#100  NaXeq =           0.3830
#110  CaX2eq =          0.2080
#120  MgX2eq =          0.0630
#130  KXeq = 0.0750
#140  AlX3eq =          0.0004
 100  NaXeq =           0.3740
 110  CaX2eq =          0.2355
 120  MgX2eq =          0.0460
 130  KXeq =  0.0618
```

```
 140  AlX3eq =          0.0004
 150 EXCHfrac = 0.010 * (1.0 - iDECAY)
#150 EXCHfrac = 0.004
#150 EXCHfrac = 0.006
#150 EXCHfrac = 0.010
 160 a$ = EOL$ + "USE SOLUTION 0 " + CHR$(59) + "USE SOLUTION " + STR$(i) + EOL$
 175 a$ = a$ + "MIX " + STR$(i) + EOL$
 180 a$ = a$ + STR$(0) + STR$(GWfrac) + EOL$
 190 a$ = a$ + STR$(i) + STR$(MDfrac) + EOL$
#200 a$ = a$ + "USE REACTION 0" + CHR$(59) + " USE EQUILIBRIUM_PHASES 0" +
CHR$(59) + " USE EXCHANGE 0" + EOL$
#200 a$ = a$ + "USE REACTION 2" + CHR$(59) + " USE EQUILIBRIUM_PHASES 1" +
CHR$(59) + " USE EXCHANGE 0" + EOL$
 200 a$ = a$ + "USE REACTION 2" + CHR$(59) + " USE EQUILIBRIUM_PHASES 1" +
CHR$(59) + " USE EXCHANGE 2" + EOL$
 210 a$ = a$ + "REACTION 2" + EOL$
 220 a$ = a$ + "  Calcite       1140    " + EOL$
 230 a$ = a$ + "  Dolomite      418     " + EOL$
 240 a$ = a$ + "  Mn-Siderite 228       " + EOL$
 250 a$ = a$ + "  Microcline    0       " + EOL$
 260 a$ = a$ + "  Plagioclase   0       " + EOL$
 270 a$ = a$ + "  Fe(OH)3(a) 0          " + EOL$
 280 a$ = a$ + "  Illite 0         " + EOL$
 290 a$ = a$ + "  Beidellite    0       " + EOL$
 300 a$ = a$ + "  Chlorite7A  0         " + EOL$
 310 a$ = a$ + "  Pyrite        494     " + EOL$
 320 a$ = a$ + "  Coquimbite 380        " + EOL$
 350 a$ = a$ + "  Halite        684     " + EOL$
 360 a$ = a$ + "  CH2O                  912     " + EOL$
```

```
 370 a$ = a$ + "  O2(g)                    2489    " + EOL$

 380 a$ = a$ + STR$(iMOLES) + " moles in 1 steps " + EOL$

 550 a$ = a$ + "EXCHANGE 2" + EOL$

 560 a$ = a$ + " NaX " + STR$(NaXeq*EXCHfrac) + EOL$

 570 a$ = a$ + " CaX2 " + STR$(CaX2eq*EXCHfrac) + EOL$

 580 a$ = a$ + " MgX2 " + STR$(MgX2eq*EXCHfrac) + EOL$

 590 a$ = a$ + " KX " + STR$(KXeq*EXCHfrac) + EOL$

 600 a$ = a$ + " AlX3 " + STR$(AlX3eq*EXCHfrac) + EOL$

 610 a$ = a$ + "SAVE SOLUTION " + STR$(1+i) + EOL$

 620 a$ = a$ + "END" + EOL$

 630 PUNCH a$

 640 NEXT i


END


#! Don't write more to firstflush

SELECTED_OUTPUT 2

-active false

END


#==================================================================

# firstflush is written, now run it

#==================================================================

#! Initialize time

SOLUTION 100 # need to do a calculation to invoke SELECTED_OUTPUT

USER_PRINT

10 PUT(0, 1)

END
```

```
SOLUTION 100 # need to do a calculation to invoke SELECTED_OUTPUT
USER_PRINT
10 PUT(GET(1) + 1, 1)
END
#
# Time series
USER_GRAPH 1
 -chart_title "First flush Lowber 1953-2053 (Rx Eq EX0.010i)"
 -headings YEARS SO4 Fe Ca Mg Na Alk NetAcid pH
 -axis_titles "Years" "mg/L" "pH"
 -axis_scale x_axis 0 100 10 1.0
#-axis_scale y_axis -500 7000 500 100
 -axis_scale sy_axis 1 8 1 0.5
##Empirical data plotted as symbols over simulation curves#
 -plot_concentration_vs          x
 -plot_tsv_file Lowber_QW.txt
 -start
 10  YEARS = GET(1)
 20  SO4_mgL = TOT("S(6)")*GFW("SO4")*1000
 30  Fe_mgL = TOT("Fe")*GFW("Fe")*1000
 40  Al_mgL = TOT("Al")*GFW("Al")*1000
 50  Mn_mgL = TOT("Mn")*GFW("Mn")*1000
 60  Ca_mgL = TOT("Ca")*GFW("Ca")*1000
 70  Mg_mgL = TOT("Mg")*GFW("Mg")*1000
 80  Na_mgL = TOT("Na")*GFW("Na")*1000
 90  pH = -LA("H+")
100  pe = -LA("e-")
110  nernst = 8.314e-3*TK*LOG(10)/96.42
```

```
120 EhV = pe*nernst
130  Alkalinity_mgL = ALK*GFW("Alkalinity")*1000
140  NetAcid_mgL = (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)
150 GRAPH_X YEARS
160 GRAPH_Y SO4_mgL Fe_mgL Ca_mgL Mg_mgL Na_mgL Alkalinity_mgL NetAcid_mgL
170 PLOT_XY YEARS, pH, color = Black, line_w = 3, symbol = None, y-axis = 2
 -end
#
# Time series SO4 pH
USER_GRAPH 2
 -chart_title "First flush Lowber 1953-2053 (Rx Eq EX0.010i)"
 -headings YEARS SO4 pH
 -axis_titles "Years" "mg/L" "pH"
 -axis_scale x_axis 0 100 10 1.0
#-axis_scale y_axis 0 7000 500 100
 -axis_scale sy_axis 1 8 1 0.5
 -connect_simulations true
##Empirical data plotted as symbols over simulation curves#
 -plot_concentration_vs          x
 -plot_tsv_file Lowber_SO4_pH.txt
 -start
 10  YEARS = GET(1)
 20  SO4_mgL = TOT("S(6)")*GFW("SO4")*1000
 30  Fe_mgL = TOT("Fe")*GFW("Fe")*1000
 40  Al_mgL = TOT("Al")*GFW("Al")*1000
 50  Mn_mgL = TOT("Mn")*GFW("Mn")*1000
 60  Ca_mgL = TOT("Ca")*GFW("Ca")*1000
 70  Mg_mgL = TOT("Mg")*GFW("Mg")*1000
```

```
 80  Na_mgL = TOT("Na")*GFW("Na")*1000
 90  pH = -LA("H+")
100  pe = -LA("e-")
110  nernst = 8.314e-3*TK*LOG(10)/96.42
120 EhV = pe*nernst
130  Alkalinity_mgL = ALK*GFW("Alkalinity")*1000
140  NetAcid_mgL = (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)
150 GRAPH_X YEARS
160 GRAPH_Y SO4_mgL
170 PLOT_XY YEARS, pH, color = Black, line_w = 3, symbol = None, y-axis = 2
 -end
#
# Time series Fe Ca Mg Na Alkalinity NetAcidity
USER_GRAPH 3
 -chart_title "First flush Lowber 1953-2053 (Rx Eq EX0.010i)"
 -headings YEARS Fe Ca Mg Na Alk NetAcid
 -axis_titles "Years" "mg/L" "mg/L CaCO3"
 -axis_scale x_axis 0 100 10 1.0
 -axis_scale y_axis 0 2000 100 50
 -axis_scale sy_axis -500 6000 500 100
#-axis_scale sy_axis 0 8 1 0.5
 -connect_simulations true
##Empirical data plotted as symbols over simulation curves#
 -plot_concentration_vs          x
 -plot_tsv_file  Lowber_Fe_NAcid_Ca.txt
 -start
 10  YEARS = GET(1)
 20  SO4_mgL = TOT("S(6)")*GFW("SO4")*1000
```

```
 30  Fe_mgL = TOT("Fe")*GFW("Fe")*1000
 40  Al_mgL = TOT("Al")*GFW("Al")*1000
 50  Mn_mgL = TOT("Mn")*GFW("Mn")*1000
 60  Ca_mgL = TOT("Ca")*GFW("Ca")*1000
 70  Mg_mgL = TOT("Mg")*GFW("Mg")*1000
 80  Na_mgL = TOT("Na")*GFW("Na")*1000
 90  pH = -LA("H+")
100  pe = -LA("e-")
110  nernst = 8.314e-3*TK*LOG(10)/96.42
120 EhV = pe*nernst
130  Alkalinity_mgL = ALK*GFW("Alkalinity")*1000
140  NetAcid_mgL = (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)
150 GRAPH_X YEARS
160 GRAPH_Y Fe_mgL Ca_mgL Mg_mgL Na_mgL
170 GRAPH_SY Alkalinity_mgL NetAcid_mgL
 -end
#
# Time series Saturation Indices
USER_GRAPH 4
 -chart_title "First flush Lowber 1953-2053 (Rx Eq EX0.010i)"
 -headings YEARS Gypsum Calcite Siderite Mn-Siderite Goethite Fe(OH)3(a) Schwert(1.75)
Jarosite(ss) Gibbsite Al(OH)3(a) Basaluminite logPCO2 pH
 -axis_titles "Years" "Log(PCO2), Saturation Index" "pH"
 -axis_scale x_axis 0 100 10 1.0
 -axis_scale y_axis -5.5 5.5 1 0.5
#-axis_scale sy_axis -500 4000 500 100
 -axis_scale sy_axis 0 8 1 0.5
 -connect_simulations true
```

```
 -start
 10  YEARS = GET(1)
 20  SO4_mgL = TOT("S(6)")*GFW("SO4")*1000
 30  Fe_mgL = TOT("Fe")*GFW("Fe")*1000
 40  Al_mgL = TOT("Al")*GFW("Al")*1000
 50  Mn_mgL = TOT("Mn")*GFW("Mn")*1000
 60  Ca_mgL = TOT("Ca")*GFW("Ca")*1000
 70  Mg_mgL = TOT("Mg")*GFW("Mg")*1000
 80  Na_mgL = TOT("Na")*GFW("Na")*1000
 90  pH = -LA("H+")
100  pe = -LA("e-")
110  nernst = 8.314e-3*TK*LOG(10)/96.42
120 EhV = pe*nernst
130  Alkalinity_mgL = ALK*GFW("Alkalinity")*1000
140  NetAcid_mgL = (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)
150 GRAPH_X YEARS
160 GRAPH_Y SI("Gypsum") SI("Calcite") SI("Siderite(d)(3)") SI("Mn-Siderite")
SI("Goethite") SI("Fe(OH)3(a)") SI("Schwert(1.75)") SI("Jarosite(ss)") SI("Gibbsite")
SI("Al(OH)3(a)") SI("Basaluminite") SI("CO2(g)")
170 PLOT_XY YEARS, pH, color = Black, line_w = 3, symbol = None, y-axis = 2
 -end
#
# Time series Eh pH
USER_GRAPH 5
 -chart_title "First flush Lowber 1953-2053 (Rx Eq EX0.010i)"
 -headings YEARS Eh pH
 -axis_titles "Years" "Eh, volts" "pH"
 -axis_scale x_axis 0 100 10 1.0
```

```
#-axis_scale y_axis 0 7000 500 100
 -axis_scale sy_axis 1 8 1 0.5
 -connect_simulations true
##Empirical data plotted as symbols over simulation curves#
 -plot_concentration_vs          x
 -plot_tsv_file Lowber_Eh_pH.txt
 -start
 10  YEARS = GET(1)
 20  SO4_mgL = TOT("S(6)")*GFW("SO4")*1000
 30  Fe_mgL = TOT("Fe")*GFW("Fe")*1000
 40  Al_mgL = TOT("Al")*GFW("Al")*1000
 50  Mn_mgL = TOT("Mn")*GFW("Mn")*1000
 60  Ca_mgL = TOT("Ca")*GFW("Ca")*1000
 70  Mg_mgL = TOT("Mg")*GFW("Mg")*1000
 80  Na_mgL = TOT("Na")*GFW("Na")*1000
 90  pH = -LA("H+")
100  pe = -LA("e-")
110  nernst = 8.314e-3*TK*LOG(10)/96.42
120 EhV = pe*nernst
130  Alkalinity_mgL = ALK*GFW("Alkalinity")*1000
140  NetAcid_mgL = (10^-pH + TOT("Fe")*2 + TOT("Al")*3 +
TOT("Mn")*3)*GFW("Alkalinity")*1000 - (ALK*GFW("Alkalinity")*1000)
150 GRAPH_X YEARS
160 GRAPH_Y EhV
170 PLOT_XY YEARS, pH, color = Black, line_w = 3, symbol = None, y-axis = 2
 -end
#
INCLUDE$ firstflush
```

```
#! Closeout USER_GRAPHS
USER_GRAPH 1
 -detach
USER_GRAPH 2
 -detach
USER_GRAPH 3
 -detach
USER_GRAPH 4
 -detach
USER_GRAPH 5
 -detach
#! Don't add to SELECTED_OUTPUT
SELECTED_OUTPUT 1
-active false
END
```