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Technical Article

Geochemical and Stable Isotope Evidence for Precipitation and Groundwater Sourcing of Recharge at the Green Valley Site, Vigo County, Indiana

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Abstract. We examined the recharge sources of acid mine drainage (AMD) seeps that form at the toe of the coal refuse (gob) pile at a site in Indiana, using traditional geochemistry and oxygen isotopes. AMD from this site has impacted local waterways, and reducing the volume of AMD is a priority. Our observations indicate that there are two main sources of recharge. The first is relatively dilute, isotopically homogenous, geochemically-reducing groundwater that flows up through pre-mining karst-like features beneath the gob pile due to localized, precipitation-induced, hydraulic head. This produces a perched water table above the regional water table. The second source of recharge is oxidizing and isotopically variable meteoric precipitation that percolates through the permeable capping material; a partially buried and abandoned railroad grade may also channel meteoric waters into the pile. During periods of low precipitation, oxygenated pore moisture in the unsaturated zone facilitates AMD generation. During periods of elevated precipitation, these metal-rich pore fluids are flushed through the system by isotopically variable, oxygenated, metal-poor meteoric waters. Each source contributes subequal but variable amounts of recharge waters. The hydraulic conductivity and permeability of the gob pile, as calculated by isotopic lag, is consistent with values for silty to clean unconsolidated sand.

Key Words: AMD; coal gob; geochemistry; hydrology; stable isotope

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Introduction

The Green Valley site is located in Vigo County, about 6.5 km northwest of Terre Haute, Indiana, USA (Figures 1 and 2). This study was undertaken to assess why previous reclamation efforts at the 92.3 ha (159 acres) site, comprising the abandoned Green Valley Mine and adjoining coal refuse (gob) pile, reduced but did not completely eliminate AMD. We used a broad range of traditional geochemistry techniques as well as oxygen isotope values. Many studies have used traditional geochemical methods, stable isotopes, or both to address the issue of AMD sourcing and recharge (e.g. Allen and Voormeij 2002; Hazen et al. 2002), setting a precedent for this type of multi-disciplinary approach. In particular, oxygen isotope ratios provide a conservative tracer that is uniquely intrinsic to the water molecule (Criss 1999). The use of stable isotope tracers has been successfully employed for hydrograph separation (e.g. Criss and Winston 2003), determination of flood water routing (e.g. Criss and Shock 2001; Winston and Criss 2003), groundwater tracing (e.g. Rose et al. 1996), and to determine oil field brine mixing with groundwater (Melchiorre et al. 1999).

The pre-mining topography was an undulating terrain with seasonal drainages and a total vertical relief of 18.3 m (60 ft) (Figure 2b). In the late 1940's, the Snow Hill Coal Corporation began underground coal-mining operations at the site via shafts sunk in the Springfield (Indiana V) and Seelyville (Indiana III) coal seams of the Petersburg and Staunton Formations, respectively. These coal seams are early Pennsylvanian in age and were located at depths of approximately 94.5 m (310 ft) (Springfield Coal) and

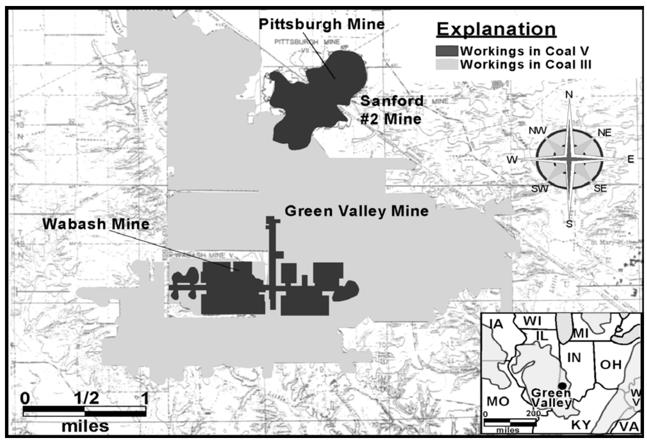

Figure 1. Location of underground mine workings in the vicinity of Green Valley, including the Wabash, Pittsburgh, Green Valley, and Sanford #2 mines (Indiana DNR file data, 1985); shaded area in index map indicates major coalfields of the Midwestern U.S., and the black dot identifies the Green Valley site.

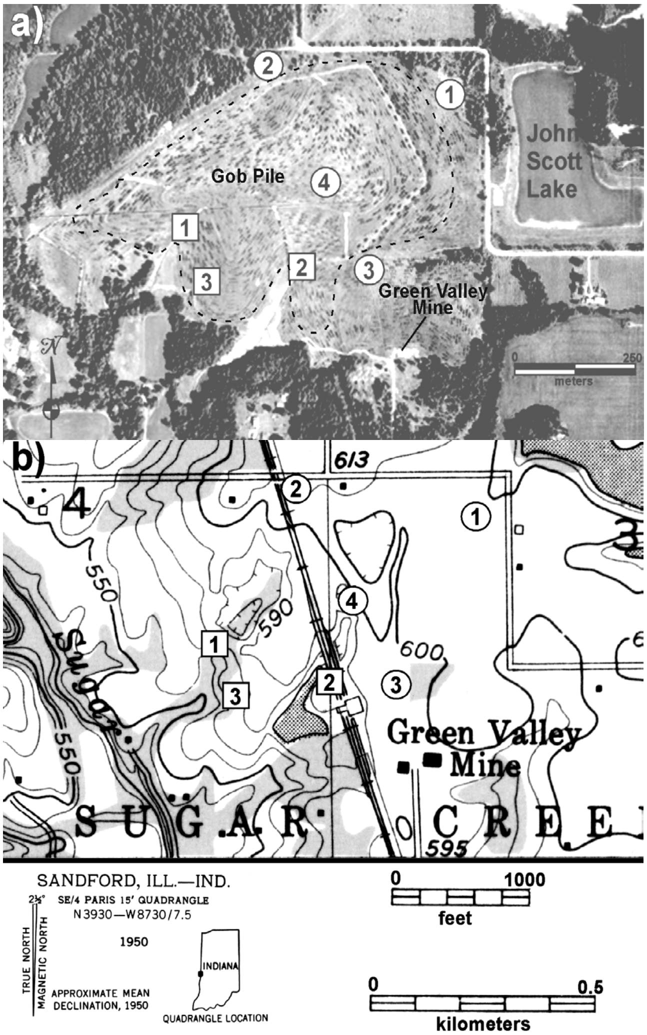

Figure 2. a) Air photograph of Green Valley in 2002, showing the location of the main gob pile (dashed outline), AMD seeps (numbered squares), and observation wells (numbered circles). b) Topographic map of the Green Valley site in 1950, shown at the same scale as a); note the deep sinkhole-like features to the northeast of AMD seep 1 and observation well DNR-4. The depression near AMD seep 1 had mature tree cover (shaded area) in 1950, indicating that these depressions are not related to recent mining.

152.4 m (500 ft) (Seelyville Coal) below the surface. Records show the mines employed as many as 342 men by 1956. Over 14 million t of coal were mined using the room and pillar method during a 15-year period (Figure 1). Mining was completed by 1963, and the site was abandoned without any reclamation. During the active phase of the mining operations (1948 to 1963), over 2,064,000 m^3 (2,700,000 yds^3) of coal refuse (gob and slurry) were deposited on the ground surface at the site. The refuse consists of coal fragments, limestone, shale, and pyrite. Scrap steel, rubber, and plastic from the mining operations also ended up in the gob piles.

The site was first studied by Caserotti (1973), who noted that the polluted sections of West Little Sugar Creek and Sugar Creek were an "orange-rusty color". Caserotti and Marland (1974) reported that the AMD contained 56,000 mg/L of dissolved iron and 200,000 mg/L of dissolved sulfate. Another study by Watson (1976) concluded that sections of Sugar Creek near the site were "biologically dead" and that stream conditions would not improve until the gob pile was capped with a low-permeability cover. Also in 1976, Green Valley was designated as derelict mine land, and possible solutions with associated costs for dealing with the AMD were evaluated. During late Dec. 1984, at a time when a light snow blanketed much of the area, the surface of the gob pile was devoid of snow. Some of the areas were warm to the touch and in several places, there was enough heat generation that spontaneous combustion of the gob occurred (Geosciences Research Associates 1985).

In early 1985, the Abandoned Mine Land Section of the Indiana Department of Natural Resources (IDNR) began reclamation efforts, including grading and capping of the pile. The gob pile was successfully vegetated and AMD was significantly reduced, although some AMD still occurs and continues to affect local waterways. The site lies within the Wisconsin Glacial Boundary, and natural soils and unconsolidated deposits surrounding the site consist largely of silty loam topsoil and underlying sandy-clay till with local gravel and boulder horizons. The site was partially capped with similar materials removed from a borrow pit that is now John Scott Lake (Figure 2). The cap consists of a thin layer of clay-rich till atop coarse gravel, which comprises over 90% of the cover material. The gravel contains igneous, metamorphic, and glacially-striated sedimentary rocks (many >30 cm) and has a relatively high porosity and permeability, making it an inefficient capping material. Following the initial reclamation in 1985, additional work was performed to route on-site surface water and AMD towards ditches lined with >20 cm limestone riprap. These reactive channels are lined with brown, red, white, and rarely blue and green secondary minerals formed by AMD reacting with the limestone, the atmosphere, and organic debris. Microorganisms such as *Euglena mutabilis*, diatoms, fungi, and algae have been observed to form iron-rich stromatolite-like communities in the reactive drains (Brake 2003). Due to the limited surface area presented by the large limestone clasts and their armoring by non-reactive secondary minerals, these channels no longer provide their initial level of remediation.

AMD flows freely from three seeps located along the southern base of the gob pile (Figure 2). Seeps 1 and

2 have flowed for many years, while seep 3 first appeared in late April 2001 following a large rainfall, which produced several subsidence depressions. The water flowing from these seeps generally has a pH between 1.5 and 4, and an electrical conductivity (EC) as high as 25,000 μS/cm, reflecting elevated SO_4, Fe (up to 11,800 mg/L), Al (up to 1840 mg/L), Mn, Zn, and Ni. Chromium, Cu, Cd, and Pb are also present but at lower concentrations (Amt et al. 2003; Dale 2001; Eggert et al. 1981; Geosciences Research Associates 1985; Unger et al. 2003). Groundwater and surface waters from the site flow northeast to southwest towards Sugar Creek. Four monitoring wells have been completed for measuring static water levels and for sampling the shallow groundwater and water within the gob material (Figure 2).

Methods

Samples for this study were obtained between Sept. 2000 and Jan. 2002 at the two precipitation stations, four monitoring wells, and three AMD seeps at the site. Some of the wells and seeps were not sampled on days when precipitation or snowmelt increased the likelihood of sample contamination. Sampling at AMD seep 3 started later than the other seeps, as it did not exist at the start of this study. Measurements of EC, temperature, Eh, and pH of the natural waters and AMD were collected in-situ prior to sampling using portable meters (i.e. YSI 30 conductivity meter, Corning-Hanna 98/07 pH meter, YSI-6 Eh sonde). Sampling of wells included measurement of the depth of the static water level using a water depth probe. Three well volumes of water were hand-bailed using a stainless steel bailer to purge wells prior to sampling and measurements. Wells were allowed to recover to within 10% of the original static water level before 11.3 L (3 gallons) of water were bailed into an empty bucket for measurements and sampling. Isotope samples were collected in a borosilicate glass bottle with a polyseal cap. Sampling bailers and buckets were cleaned with distilled water between sampling of the various wells in order to avoid cross-contamination. The sampling of AMD seeps was similar, with conductivity, pH, and temperature measurements taken directly at the main orifice of the seeps, as were the isotope samples. Water samples for geochemistry were filtered to 0.5 μm and collected in glass bottles that were kept refrigerated until analysis. Samples were analyzed by ICP-MS at a licensed laboratory at Test America Inc., and in the geology department at Washington University in St. Louis. Alkalinity and acidity were measured by titration. Precipitation samples were collected from standard U.S. Forest Service style rain gauges, modified with a plastic float ball in the collection cone to minimize evaporation. Precipitation was recovered within several hours of the end of storms in order to minimize evaporation. All precipitation for each half-month time period at a station was collected, mixed, and stored within a large borosilicate glass bottle with a polyseal cap. At the end of each semi-monthly period, an aliquot of this bottle was removed for isotope analysis, providing a volume-weighted precipitation composite for the time period. Water samples were prepared for isotope analyses using the standard CO_2 equilibration method (Epstein and Mayeda 1953), and oxygen isotope values were measured using an automated sample equilibrator interfaced with an isotope ratio mass spectrometer at Washington University. Results are reported in the usual δ notation relative to Vienna Standard Mean Ocean Water (VSMOW) (Coplan 1995). Laboratory precision is ±0.04‰ for oxygen isotope values, based on duplicate analyses of internal laboratory standards.

Results

Precipitation

It was difficult to sample every precipitation event at the site, due to travel constraints and the possibility of vandalism to unattended equipment. Therefore, we examined the viability of using precipitation samples from a secure off-site locality as a proxy for Green Valley precipitation. The secure site we selected was located on the roof of Julian Science Center on the DePauw University campus, 50 km (31 miles) east of Green Valley. Composite precipitation samples were collected at Green Valley twice a month for a four-month period in the fall and winter of 2000 and three months during the summer of 2001 for a total of 14 dual-site samplings. The Green Valley rain gauge was located on a wooden post about 30 m (100 ft) north of observation well DNR-3. Supplemental precipitation information was collected at the DePauw University site continuously from Sept. 2000 to Jan. 2002.

A comparison of precipitation amounts and the $\delta^{18}O$ (VSMOW) values of rainwater from DePauw University and the Green Valley site show a general similarity in quantity and strong similarity in isotopic character (Figure 3a, b). Recorded precipitation at DePauw University was also similar to amounts recorded at Terra Haute airport, 3 km south of Green Valley (National Weather Service 2003) (Figure 3c). We assume that the DePauw University precipitation sampling station provides a reasonable proxy for direct sampling at Green Valley. Oxygen isotope measurements on precipitation from both the Green Valley and DePauw University sampling stations show a pronounced seasonal variation of higher $\delta^{18}O$ values in the summer and lower $\delta^{18}O$ values in the winter (Figure 4), similar to observations elsewhere in

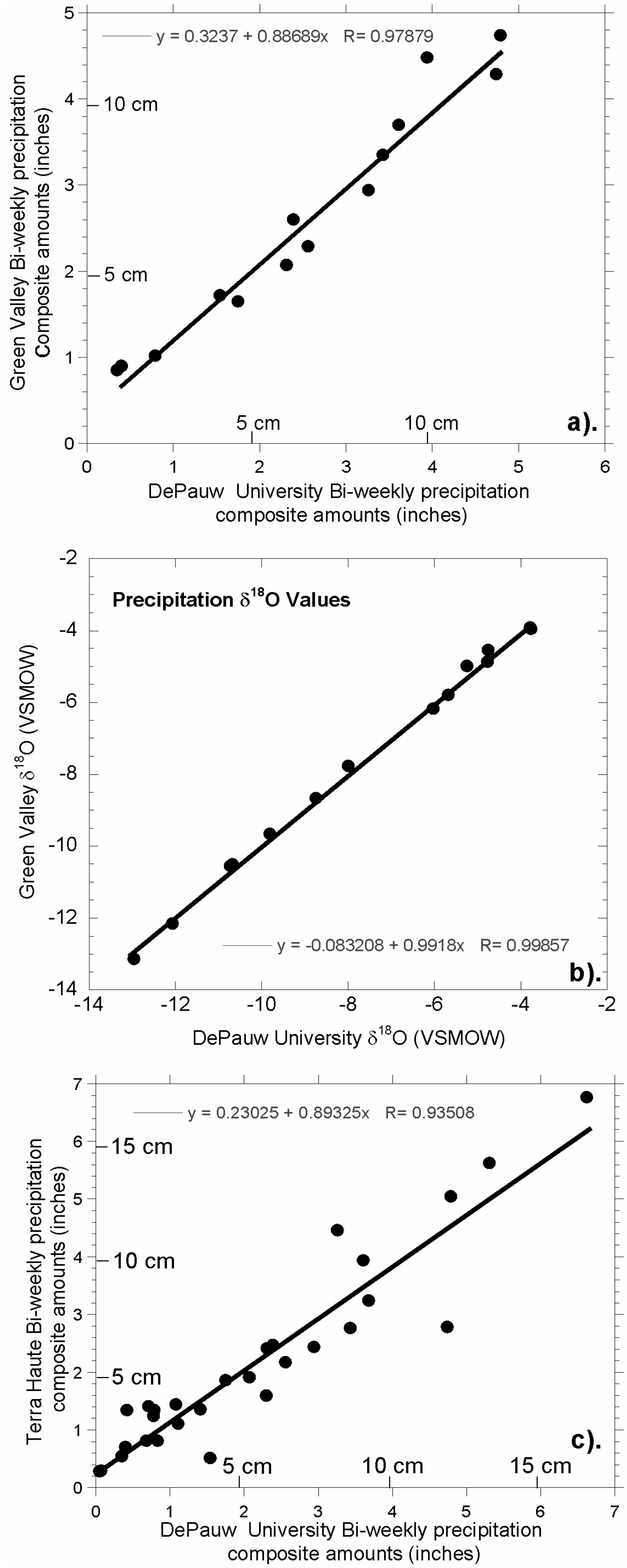

Figure 3. Relationship between: a) precipitation bi-monthly composites at Green Valley and DePauw University sites, b) $\delta^{18}O$ (VSMOW) values of precipitation at Green Valley and DePauw University sites, and c) precipitation bi-monthly composites at Terre Haute and DePauw University sites

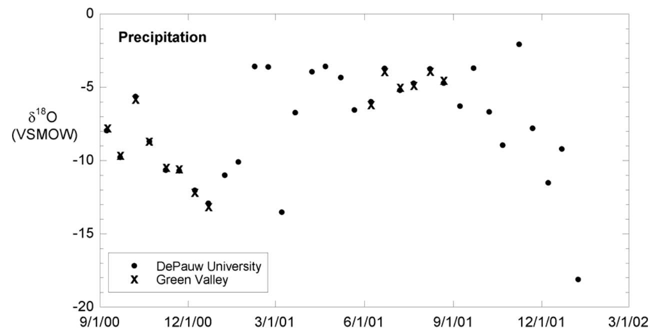

Figure 4. Seasonal variation of $\delta^{18}O$ (VSMOW) at Green Valley and DePauw University sites

the Midwestern U.S. (e.g. Missouri: Frederickson and Criss 1999; Wisconsin: Melchiorre and Criss, in review). Over the period of sampling, this seasonal $\delta^{18}O$ value variation ranged from -18.13‰ to -2.08‰, providing up to 16‰ seasonal variation in the $\delta^{18}O$ values of precipitation in west-central Indiana.

Static Water Levels

Static water levels were measured in the four monitoring wells between May and August of 2001 (Tables 1, 2). Three of these shallow wells (DNR-1, -2, -3) were drilled in undisturbed deposits adjoining the gob pile (Figure 2, Table 1), and have static water levels that behave similarly in response to precipitation (Figure 5a). Precipitation raises the static water level in 5 – 7 days; the pre-precipitation levels may represent local groundwater base flow. The static water elevations in these three wells indicate that groundwater flows across the site to the southwest.

Well DNR-4 is located at the top of the gob pile (Figure 2) and penetrates 11.7 m (38.5 ft) of refuse material. The behavior of the static water level (SWL) in well DNR-4 is different from the other wells, but is consistent with the different materials they penetrate over their full depth (Table 1). The static water level in well DNR-4 is poorly correlated with precipitation, and generally increased over the period of study (Figure 5b). While the SWL at wells DNR-1, -2, and -3 fluctuated by a maximum of 0.91 m, 1.04 m, and 2.38 m (3 ft, 3.4 ft, and 7.8 ft), respectively, the SWL of gob water, as measured at well DNR-4, fluctuated by only 0.24 m (0.8 ft). The poor correlation of well DNR-4 SWL with precipitation, and the very small fluctuation in SWL during a period when there were 69.2 cm (27.3 in) of precipitation suggest that precipitation may not directly influence the volume of water contained within the gob pile, and hints at a groundwater-moderated system. No estimates of discharge from AMD seeps were made. All precipitation amounts, static water levels, and geochemical data for this study can be accessed at http://dx.doi.org/10.1007/s10230-005-0066-2.

Table 1. Physical characteristics of the four observation wells at the Green Valley site

Well #	Surface Elevation (ft)	Surface Elevation (m)	Total Well Depth (m), (*ft*)	Average static water level (m), (*ft*)	Well Penetration Main Lithology
DNR-1	595.5	182	9, *2.7*	3.9, *1.2*	Mixed clay and sand
DNR-2	609.6	186	22, *6.7*	8.3, *2.5*	Mixed clay and sand
DNR-3	599.6	183	22, *6.7*	6.9, *2.1*	Mixed clay and sand
DNR-4	628.6	192	38.5, *11.7*	32.7, *10.0*	coal refuse

Table 2. All water chemistry data for AMD seeps and observation wells from this study

Sample Site	Date	TDS (ppm)	pH (field)	Acidity (mg/L)	Alkalinity (mg/L)	Fe^{+3} (mg/L)	Fe^{+2} (mg/L)	SO_4 (mg/L)	Al (mg/L)	Ca (mg/L)	Mn (mg/L)	Cl (mg/L)	Br (mg/L)
DNR-1[1]	4/16/2001	17,000	4.18	7,800	<1	18,000	30	16,000	3,600	2,700	290		
DNR-2[1]	4/16/2001	890	6.88	25	400	5.1	1.7	450	1.7	1,800	1.0		
DNR-3[1]	4/16/2001	5,900	6.32	240	1,100	8.5	2.1	3,700	4.2	4,000	3.8		
DNR-4[1]	4/16/2001	46,000	3.53	30,000	<1	33,000	21	16,000	9,600	2,800	450		
Seep 1[1]	4/16/2001	25,000	3.97	15,000	<1	4,400	24	15,000	8,400	1,800	120		
Seep 2[1]	4/16/2001	49,000	3.42	30,000	<1	7,500	22	22,000	15,000	4,000	520		
Seep 3[1]	5/4/2001	140,000	2.21	76,000	<1	31,000	16	95,000	7,500	600	48		
Seep 3[2]	8/15/2001	52,000	2.62	-	-	25,880	22	77,990	7,500	-	72	165	111

[1] Analyzed by ICP-MS at Test America, Inc.; [2] analyzed by ICP-MS at Washington University

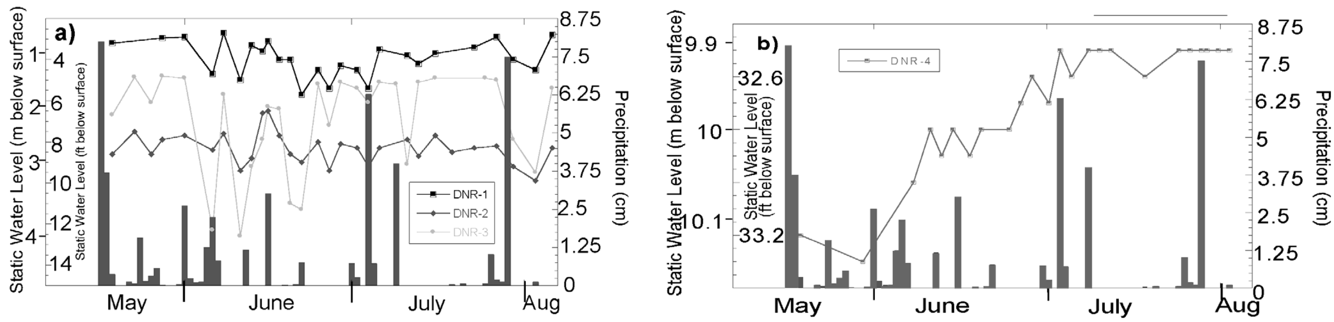

Figure 5. Relationship between precipitation and static water levels in: a) observation wells DNR-1, -2, and -3; b) Relationship between precipitation and static water level in observation well DNR-4. The histograms on both plots show precipitation amounts, with scaling on the right axes

Electrical Conductivity (EC)

Water from monitoring wells DNR-2 and -3 had the lowest EC values measured at the site, while water from wells DNR-1 and -4 had elevated EC. Wells DNR-1 and -3 varied minimally over time, while DNR-2 and -4 have pronounced variations that mirror local precipitation fluctuations (Figure 6). A plot of EC for water from well DNR-4 vs. the amount of precipitation on the day of the EC measurement shows a strong correlation between lower EC values and elevated precipitation amounts (Figure 7a).

The relationship suggests that every cm of precipitation will reduce the EC of water in well DNR-4 by 2205 μS/cm (5600 μS/in), and that during prolonged periods of drought, the maximum EC will be about 29000 μS/cm (Figure 7a). The regression line does not include storms where precipitation was less than 1.27 cm (0.5 in), as their conductivity values range widely due to a cumulative effect when small storms follow larger storms. The EC data for well DNR-4 indicate that precipitation has a very rapid dilution effect on gob waters (Figure 7a), but the dilution is transitory and relatively brief, with significant recovery within seven days (Figure 6).

A plot of EC for water from well DNR-2 vs. the amount of precipitation on the day of the EC measurement shows a strong correlation between lower EC values and elevated precipitation (Figure 7b). The relationship, which is similar to that observed for well DNR-4, suggests that every cm of precipitation will reduce the EC of water in well DNR-2 by 394 μS/cm and during prolonged periods of drought, the maximum EC will be about 14000μS/cm (Figure 7b). Again, the regression line does not include storms where precipitation was less than 1.27 cm (0.5 in). The EC data for well DNR-2 indicate precipitation produces a very rapid, localized dilution of groundwater (Figure 7b), but again the dilution is transitory and relatively brief with significant recovery

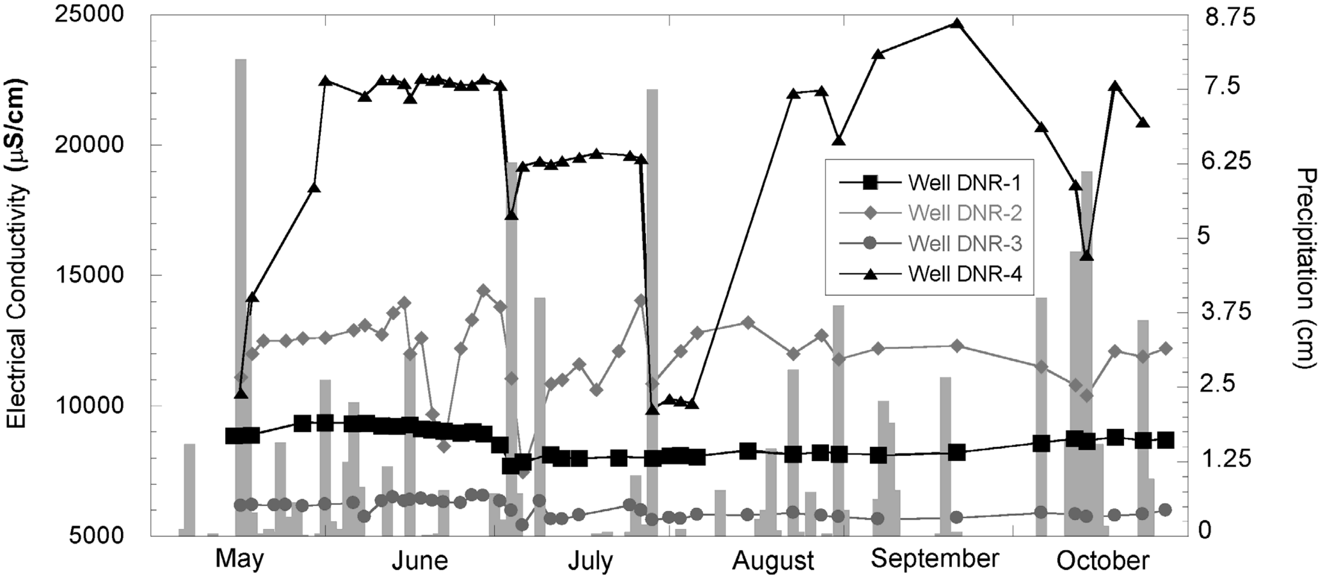

Figure 6. Relationship between precipitation and EC for water from observation wells DNR-1, -2, -3, and –4; the histogram on the plot shows precipitation amounts, with scaling on the right axes

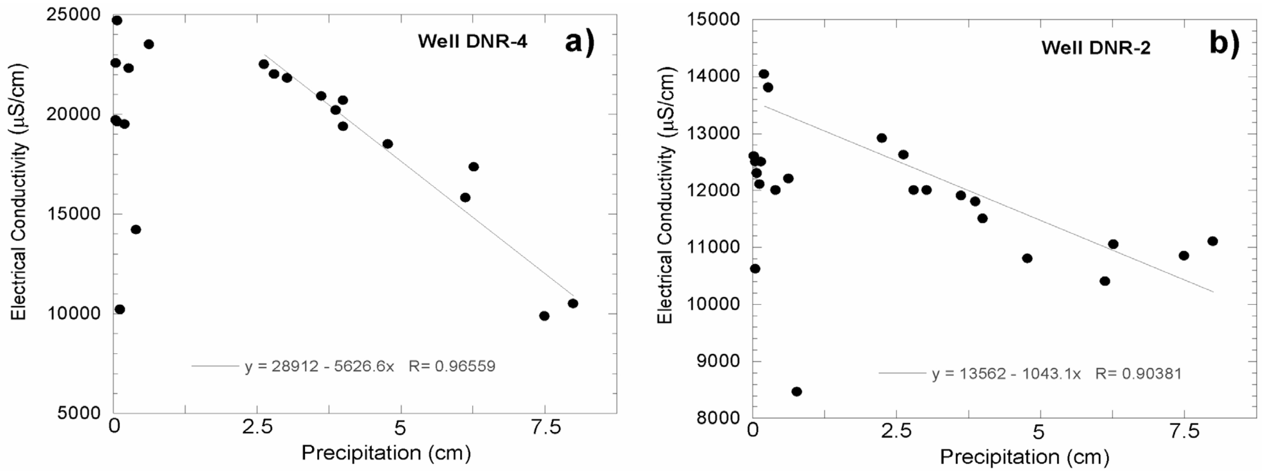

Figure 7. Relationship between large precipitation events and EC for water from observation well a) DNR-4, and b) DNR-2; these data represent conductivity measured within 24 hours of precipitation. Data for storms below 1.27 cm (0.5 in) are not included in the best-fit regressions. Note that the y-intercept at 0.0 cm precipitation for well DNR-4 (in gob) is nearly identical to the maximum EC for AMD water from the seeps 1-3.

within seven days (Figure 6). The dilution observed at well DNR-4 was five times greater than that observed for well DNR-2. As well DNR-2 is located in pre-mining deposits, this dilution may result from the localized influence of gob water on groundwater and/or surface runoff from the nearby refuse pile. Rip-rap ballast from the old railroad line (Figure 2), which is buried under the refuse pile, may also provide a permeable conduit for the introduction of precipitation into the pile. All three AMD seeps at the site show poor correlation between precipitation and EC, indicating that the AMD seeps do not have the near-instantaneous response times observed in some wells. If EC is plotted over time (time = actual day of measurement), along with precipitation amounts shifted forward by 30 days (time = actual day of measurement + 30 days), a good correlation is observed between precipitation and decreased EC of AMD seep waters (Figure 8).

Water Chemistry

The water chemistry of the wells and seeps varies across the site (Table 2). Water from wells DNR-2 and DNR-3 generally has lower total dissolved solids (TDS) and relatively neutral pH, while DNR-1 and DNR-4 have elevated TDS and low pH. Wells DNR-1, -2, and -3 are located adjacent to the gob pile, while well DNR 4 is located within the gob (Figure 2). The three AMD seeps have similarly elevated TDS and very low pH. Wells DNR-1 and -4 and the AMD seeps have elevated (Fe), (SO_4), (Al), and anomalous levels of other elements (Table 2).

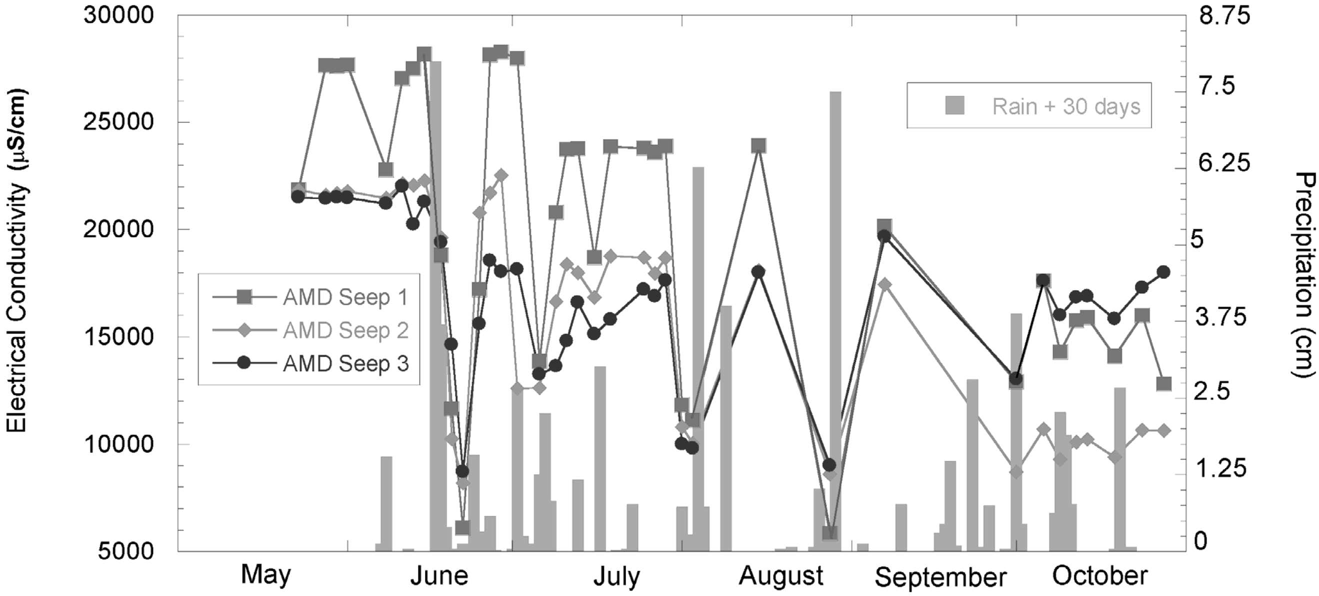

Figure 8. Relationship between precipitation and EC for water from AMD seeps 1, 2, and 3, with precipitation shifted +30 days. The histogram on the plot shows precipitation amounts, with scaling on the right axes. The relationship indicates that there is about 30 days lag-time between precipitation and decreased EC in the seeps.

These results are consistent with historical measurements at the site (Amt et al. 2003; Eggert et al. 1981; Geosciences Research Associates 1985; Unger et al. 2003). Of particular note, there are important dilution trends in the Eh-pH values of the water from different sites at Green Valley (Figure 9, Table 3). Wells DNR-2 and –3 have Eh-pH values that plot within the stability field (at 25°C) of $FeOH_3$ solids. Well DNR-1 has Eh-pH values that plot within the stability fields of both $FeOH_3$ solids and aqueous Fe^{+2}. Well DNR-4, and AMD seeps 1 and 2 have very similar Eh-pH values that plot within the field of aqueous $FeOH^{+2}$. AMD seep 3 has variable Eh-pH values that plot within the $FeOH^{+2}$, Fe^{+2}, and Fe^{+3} stability fields (Figure 9). Precipitation appears to dilute the seep water, raising pH and lowering Eh, moving the AMD water from Fe^{+3} stability to Fe^{+2} stability, allowing for a variety of unusual divalent and trivalent secondary iron mineral species, such as melanterite and xitieshanite, to precipitate in the AMD drainage (e.g. Melchiorre et al. 2005). The variability in Eh values is believed to result from mixing of reduced perched groundwater or gob waters with oxidized precipitation recharge waters. This important distinction is supported by isotopic evidence presented below.

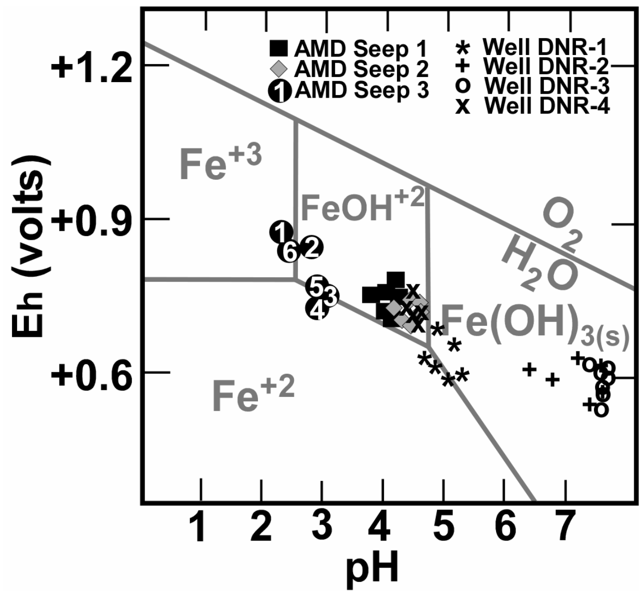

Figure 9. Eh-pH diagram (after Langmuir and Whittemore 1971; Brookins 1988), showing stability fields and water chemistry for a series of samples collected from observation wells and AMD seeps before and after a large precipitation event; samples are numbered youngest (1) to oldest (6)

Temperature

When ambient air temperature (National Weather Service 2003) is plotted against AMD seep or well water temperature (Figure 10a, b), one can infer a qualitative measure of circulation depth and residence time in the subsurface from examination of the slope and y-intercept of a linear regression through the data. On a plot of ambient air temperature versus water temperature, the y-intercept of a linear regression through the data should indicate the expected water temperature at an ambient air temperature of 0°C. For example, when water temperature equals ambient air temperature at 0°C, we may qualitatively infer a shallow circulation with strong groundwater thermal dependence upon ambient air temperature.

Table 3. 2001 pH and Eh values (in volts) for AMD seeps and observation wells; seep 3 measurements correspond to Figure 9, from youngest (7/25/01, #1) to oldest (8/15/01, #6)

Day	Rain (cm)	Seep 1 pH	Seep 2 pH	Seep 3 pH	DNR 1 pH	DNR 2 pH	DNR 3 pH	DNR 4 pH	Seep 1 Eh	Seep 2 Eh	Seep 3 Eh	DNR-1 Eh	DNR-2 Eh	DNR-3 Eh	DNR-4 Eh
7/23					5.2	7.6						0.65	0.56		
7/25	0.08	4.2	4.3	2.5			7.7	4.4	0.77	0.70	0.88			0.58	0.72
7/26	1.04														
7/27	0.20	4.4	4.6	3		6.8	7.7	4.6	0.75	0.71	0.86		0.58	0.60	0.71
7/28	0.13														
7/29	7.62	4.2	4.5	3.1	4.9	6.4	7.6	4.6	0.72	0.69	0.78	0.60	0.60	0.55	0.69
8/1		4.3	4.6	3	4.7		7.4	4.5	0.71	0.73	0.76	0.62		0.61	0.75
8/3	0.13	4.3	4.5	3	4.9	7.2	7.6	4.5	0.78	0.74	0.79	0.68	0.62	0.60	0.71
8/6					5.1	7.4	7.6					0.58	0.53	0.56	
8/10	0.79														
8/15		3.9	4.2	2.6	5.3	7.6	7.6.		0.76	0.72	0.85	0.59	0.61	0.52	

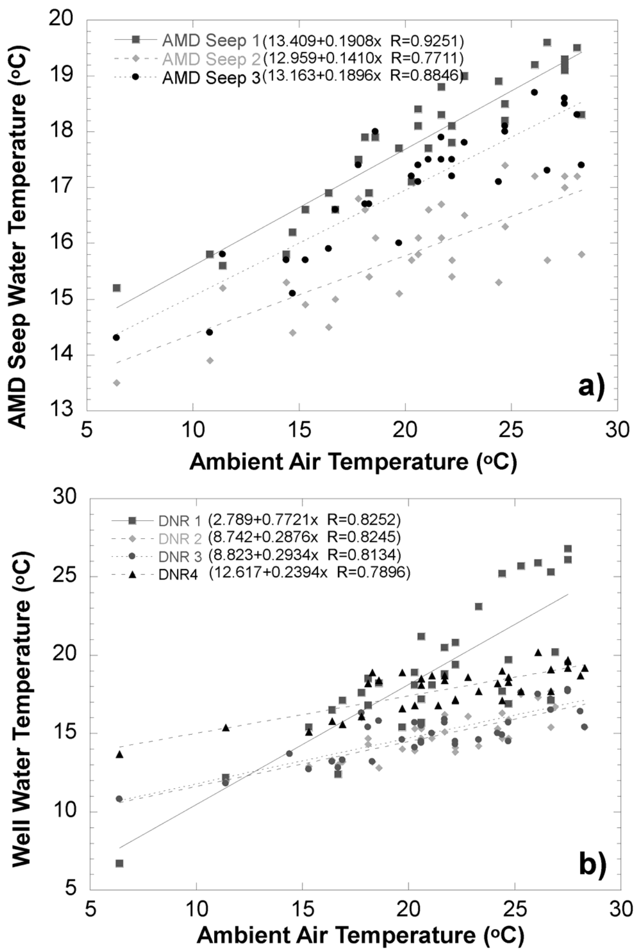

Figure 10. Relationship between: a) AMD seep water and ambient air temperature, and b) observation well water and ambient air temperature

Conversely, if extrapolation of the water temperature exceeds the ambient air temperature when air temperature is 0° C, we may qualitatively infer a deeper circulation path that reflects sourcing from a thermally moderated depth. For Green Valley AMD seep water, the extrapolated y-intercept average when air temperature is 0° C is 13.1° C (Figure 10a), which is very close to the average cave, groundwater, and annual air temperature in Indiana of about 12.7° C (e.g. Doerr 1992; Lee and Krothe 1998). This suggests that water from the AMD seeps have a sufficient subsurface residence time to impart a thermal behavior similar to groundwater. For the monitoring wells, a similar plot (Figure 10b) yields y-intercept values that have a general relation with well depth. Well DNR-1 is the shallowest well (2.7 m, 9 ft) and has the lowest y-intercept value (2.7), while well DNR-4 is the deepest well (11.7 m, 38.5 ft) and has the highest y-intercept value (12.6). Well DNR-4 has a y-intercept value very close to the average cave and groundwater temperature in Indiana. Wells DNR-2 and -3 both have intermediate depths (6.7 m, 22 ft) and intermediate y-intercept values (8.7 and 8.8). If AMD seep or well water temperature is controlled exclusively by air temperature, a best-fit linear regression through such data should have a slope near 1.0. Conversely, slopes significantly above or below 1.0 would indicate that air temperature does not strongly control water temperature. Slopes for AMD seep temperature data (Figure 10a) are significantly below 1.0, suggesting that daily ambient air temperature does not greatly influence the temperature of seep waters. Temperature data for the monitoring wells yield a range of slopes that correlate with well depth. Well DNR-4 is the deepest well and has the lowest slope, while the shallow well DNR-1 has the slope closest to 1.0, in keeping with the decreasing effect of ambient air temperature on groundwater with increasing depth. It may also reflect heat generation by exothermic decomposition of sulfide minerals within the refuse pile. The observed trends in water temperature relative to air temperature suggest that the water in all AMD seeps and observation well DNR-4 have sufficient subsurface residence times and depths of origin to impart a thermal behavior similar to groundwater. Wells DNR-1, -2, and -3 are shallower in depth, and have thermal behavior that is more significantly influenced by ambient air temperature. It must be noted that these thermal behaviors may represent or be influenced by, to an unknown degree, the exothermic decomposition or burning of gob sulfide minerals.

Oxygen Isotope Values and Hydraulic Conductivity

As discussed above, a pronounced cyclicity in the $\delta^{18}O$ values of precipitation composites is observed at Green Valley over time (Figure 4), similar to that observed for other locations throughout the Midwestern U.S. In a fortuitous set of circumstances, a mild February 2001 produced very enriched $\delta^{18}O$ precipitation, followed by an Arctic front in early March 2001 that produced very depleted $\delta^{18}O$ precipitation event, resulting in a 10‰ $\delta^{18}O$ shift over a 15-day period. This extreme fluctuation in precipitation $\delta^{18}O$ values provides a convenient, conservative tracer spike that is a property of the precipitation water molecules. This natural isotope spike is observed in all AMD seep and observation well waters within 105 days of the precipitation (Figures 11 and 12).

The similarity between isotopic variation of precipitation and AMD seep and observation well waters is offset minimally in wells DNR-1, -2, and -3 (less than 8 days), with more significant lag-times observed for well DNR-4 (27 days) and AMD seeps 1, 2, and 3 (60, 90, and 105 days, respectively). A buried utility line near DNR-2 may provide more rapid infiltration, and DNR-3 is in proximity to a drainage channel that may also enhance infiltration in the near vicinity.

A model using a damped running average of local meteoric precipitation has been used by other workers to successfully predict the $\delta^{18}O$ values of rivers (e.g. Frederickson and Criss 1999; Melchiorre and Criss, in review).

This isotopic relationship between precipitation and river base flow is modeled on the assumption the influence of precipitation $\delta^{18}O$ values for specific events results from mixing and diminishes over time. It is possible to estimate the time of homogenization using the model of Frederickson and Criss (1999):

$$\delta^{18}O_{flow} = (\Sigma\delta_i P_i e^{-ti/\tau})/(\Sigma P_i e^{-ti/\tau}) \quad (1)$$

where δ_i and P_i are the $\delta^{18}O$ value and amount for a given precipitation event, t_i is the time interval between precipitation and sampling of the river, and τ is the time constant for the site. A large value for τ indicates that the river base flow has been homogenized for a long period of time in a large groundwater reservoir. For a small value of τ, the $\delta^{18}O$

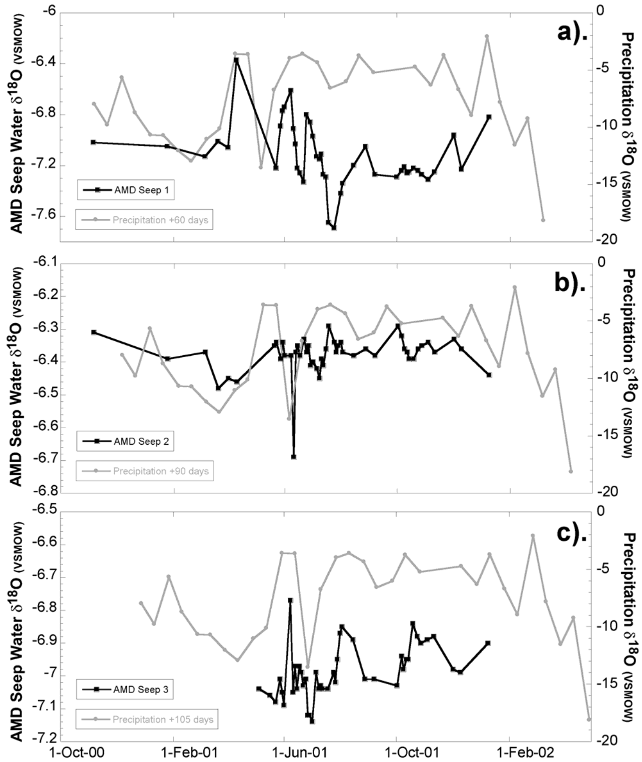

Figure 11. Plots of precipitation and AMD seep water composite $\delta^{18}O$ (VSMOW) values over time for: a) AMD seep 1, with precipitation shifted +60 days, b) AMD seep 2, with precipitation shifted +90 days, and c) AMD seep 3, with precipitation shifted +105 days

value of river flow is very similar to recent precipitation, because storage is small and all but the most recent events are damped out by the exponential term. Application of this model does not produce a good fit to the observed data from AMD seeps and observation wells (Figure 13), regardless of the value of τ that is used. This is most likely not a failing of the Frederickson and Criss (1999) model, but results from a combination of factors including the relatively small reservoir size of the gob pile, water sources other than precipitation that recharge the gob pile, and a lack of mixing and homogenization of water within the gob pile. The failure to model the behavior by a traditional model that works well for single, well-homogenized reservoirs is therefore significant, as it qualitatively indicates the AMD source water originates from either multiple reservoirs and/or is not well homogenized.

Using the oxygen stable isotope lag time (Figures 11, 12) and the distance traveled, it is possible to estimate the minimum hydraulic conductivity (K) and permeability (k) of the gob pile and pre-mining deposits at the Green Valley site (Table 4). While the use of Darcy's law is not strictly valid for advective transport, we nevertheless use it here in an attempt to estimate K and k. For these estimates at observation

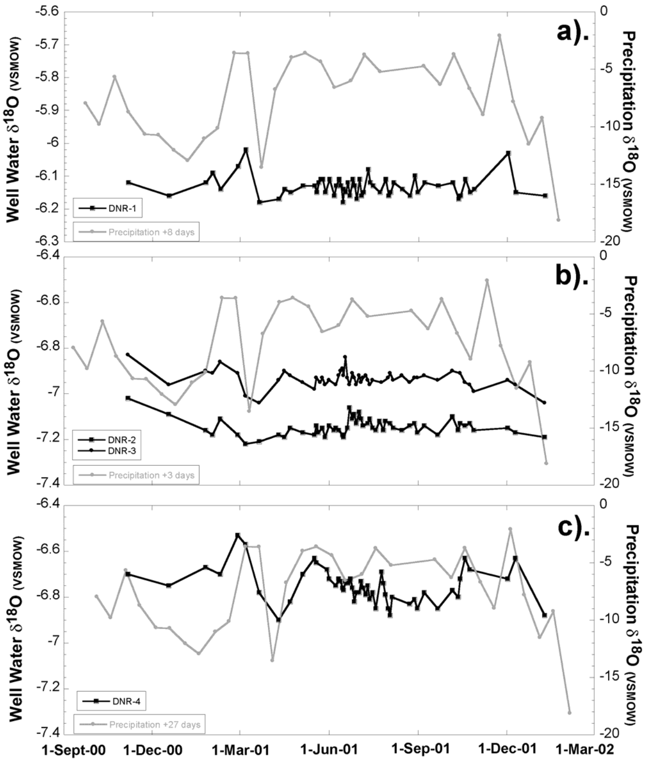

Figure 12. Observation well water and precipitation composite $\delta^{18}O$ (VSMOW) values over time for: a) well DNR-1, with precipitation shifted +8 days, b) wells DNR-2 and -3, with precipitation shifted +3 days, and c) well DNR-4, with precipitation shifted +27 days

wells, we assumed the precipitated water travels from the surface to the bottom of the well over the period of isotope lag. For the AMD seeps, we assumed that the precipitated water travels from the surface at the center of the gob pile to the AMD seep orifice over the period of isotope lag. These will only be minimum values of K, as any lateral transport will make K smaller. These estimates of K and k for the four observation wells range from 2.6 x 10^{-5} to 3.9 x 10^{-6} m/s and 2.7 to 0.41 darcies, respectively. These are consistent with reported values for silty to clean unconsolidated sand (e.g. Freeze and Cherry 1979).

For the AMD seeps, estimates of K and k range from 5.8 x 10^{-5} to 2.6 x 10^{-5} m/s and 6.0 to 2.7 darcies, respectively. These slightly higher hydraulic conductivity and permeability estimates are consistent with widely reported values for silty to clean unconsolidated sand, and coarse to fine coal refuse. Though all of these estimates incorporate several assumptions, they are relatively consistent with each other and compatible with local deposits. Assuming that these estimates of K and k approximate the true conditions of pre-mining deposits and gob, it indicates that the gob pile materials have similar to higher hydraulic conductivity and permeability values than the unmined unconsolidated materials surrounding it. This suggests that a high priority should

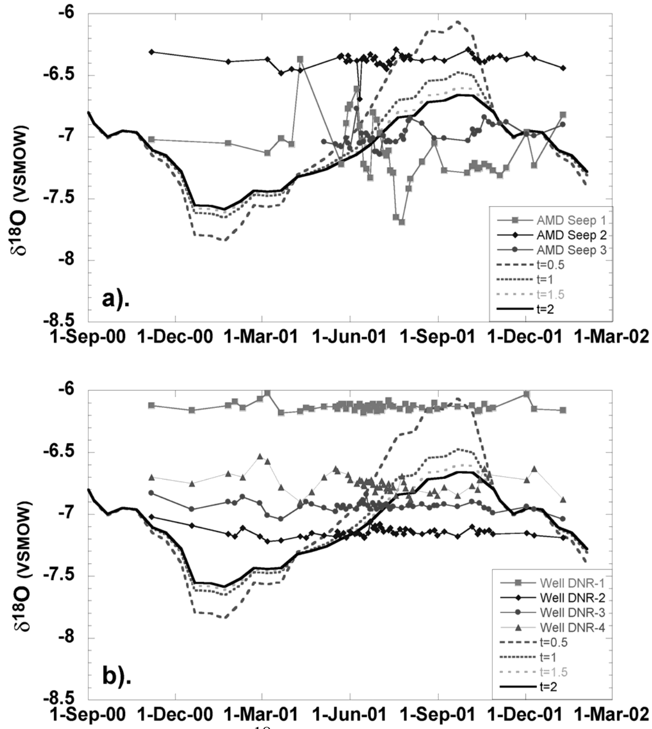

Figure 13. Plots of $\delta^{18}O$ (VSMOW) values over time for: a) AMD seep water and b) observation well water, showing calculated $\delta^{18}O$ (VSMOW) values for different values of τ, using the Frederickson and Criss (1999) model

be given to reducing the permeability of the capping materials on the Green Valley gob pile.

Discussion

The multidisciplinary approach to recharge sourcing proved useful, and revealed the limitations of each technique. Geochemical tracers can mark the expulsion of pore water, temperature can provide qualitative suggestions on the depth of water circulation, static water level changes mark head changes, and natural oxygen isotope values are inherent characteristics of the water molecules itself, providing a conservative tracer of discrete parcels of water. Together, the apparent discrepancies between the results of each technique provided valuable insight into the recharge at Green Valley.

When the characteristics of observation wells DNR-1, -2, and -3 were examined (Table 5), there was little difference noted in the observed lag time estimates from the various methods, with all responses occurring within eight days of precipitation. This suggests that the wells located in the shallow unconfined aquifer of unmined alluvial deposits quickly receive meteoric recharge. This recharge is rapidly homogenized with existing groundwater with respect to the oxygen isotope and EC values of the precipitation. When the values for observation well

Table 4. Calculations of hydraulic conductivity and permeability, using oxygen stable isotope transmission times

	DNR-1	DNR-2, -3	DNR-4	AMD Seep 1	AMD Seep 2	AMD Seep 3
Well Depth (m)	2.74	6.71	11.73			
Distance from center of gob pile (m)				300	200	350
Isotope lag time (days)	8	3	27	60	90	105
Isotope lag time (seconds)	691200	259200	2332800	5184000	7776000	9072000
K (m/s)	3.96E-06	2.59E-05	5.03E-06	5.79E-05	2.57E-05	3.86E-05
K (cm/s)	3.96E-04	2.59E-03	5.03E-04	5.79E-03	2.57E-03	3.86E-03
k (darcy)	4.12E-01	2.69E+00	5.23E-01	6.02E+00	2.67E+00	4.01E+00
k (cm^2)	4.04E-09	2.64E-08	5.13E-09	5.90E-08	2.62E-08	3.94E-08

Table 5. Summary table for AMD seep and observation well characteristics and interpretation

	Observation Well DNR-1	Observation Well DNR-2	Observation Well DNR-3	Observation Well DNR-4	AMD Seep 1	AMD Seep 2	AMD Seep 3
Static water level variation and lag time	0.9 m (3 ft) 5 to 7 days	1.04 m (3.4ft) 5 to 7 days	2.4 m (7.8 ft) 5 to 7 days	0.2 m (0.8 ft) Unknown			
Water temperature data trend	Shallow circulation depth, significant ambient air temp. influence	Moderate circulation depth, moderate ambient air temp. influence	Moderate circulation depth, moderate ambient air temp. influence	Significant circulation depth, little ambient air temp. influence	Significant circulation depth, little ambient air temp. influence	Significant circulation depth, little ambient air temp. influence	Significant circulation depth, little ambient air temp. influence
Electrical conductivity max/min (µS/cm) and lag time	9360/7700 1 to 3 days	14420/7470 1 to 3 days	6580/5420 1 to 3 days	24700/9880 1 to 3 days	28280/5850 30 days	22530/8200 30 days	22030/8700 30 days
Isotope lag time	8 days	3 days	3 days	27 days	60 days	90 days	105 days

DNR-4 and all AMD seeps are examined (Table 5), a discrepancy is noted between the lag time estimates by static water level, conductivity, and isotopic methods. The similarity of lag time observation estimates by various methods for the observation wells within the undisturbed deposits suggest that the discrepancies between lag time estimates for gob are not due to method-induced errors. Rather, these discrepancies reveal flow and recharge conditions within the gob pile that are quite different from the local undisturbed deposits, and bear directly upon remediation efforts at the Green Valley site.

The EC of the observation well DNR-4 responds to precipitation within 3 days, while all AMD seeps respond after 30 days. The oxygen isotope response to precipitation occurs much later at observation well DNR-4 and all AMD seeps. It is impossible for dilute precipitation to reduce EC without changing the isotopic character of the water, as the oxygen isotope signature is a conservative tracer inherent to the molecules of the recharge water itself. The only way that this dual response can be produced is through the addition of two recharge water sources. It has been demonstrated that gaining rivers often rise following precipitation due to the change in head, followed by a dampened isotopic response as precipitation homogenizes within the aquifer (e.g. Frederickson and Criss 1999; Rose et al. 1999; Winston and Criss 2002). The rapid dilutional conductivity response to precipitation at well DNR-4 in the center of the gob pile, followed 30 days later by a similar response at the AMD seeps on the edges of the gob pile imply that a water source within the pile has oxygen isotope values that are seasonally homogenous and close to the values of the local groundwater. Examination of the 1950 topographic map (Figure 2) reveals a potential source for this water. The unusual deep, wooded, pre-mining depressions that lie under the gob pile may be the surface expression of karst features within the Alum Cave limestone or other carbonate unit. These depressions are suspiciously located just up-gradient along the pre-mining topography from the present AMD seeps (Figure 2). These pre-mining topographic features and the old railroad grade may serve as conduits that facilitate the formation of either perched gob water or groundwater mounding within the gob pile. Precipitation may increase local groundwater or perched gob water head and force relatively dilute and isotopically homogenous gob water or groundwater into the gob pile, reducing EC without a significant isotopic shift. This diluted water would then flow down-gradient within the pile to emerge 30 days later at the AMD seeps. A ‘groundwater’ (regional ground water or perched gob water) base flow component to the AMD seeps would also explain their fairly constant flow rate during periods of minimal precipitation. This mounded groundwater would emerge within the pile under reducing conditions and would not contribute significantly to oxidation of pyrite in the gob pile.

The second source of water is meteoric precipitation. The relationship between the $\delta^{18}O$ value of precipitation and water from well DNR-4 and the AMD seeps is convincing (Figures 11 and 12). This precipitation recharge moves into and through the gob pile more slowly than, and does not mix appreciably with, the head-driven expulsion of groundwater described above. These oxidizing meteoric waters would percolate slowly down through the unsaturated portion of the gob pile, acquiring a low pH and elevated EC while retaining their oxygen isotope signature. This would produce the observed isotopic lag time without significant change to conductivity, assuming stratification or channeling, and minimal mixing with gob water.

Conclusions

The combined methodology of using traditional water chemistry and light stable isotope values appears to work well, reflecting limitations presented by each technique when used independent of each other. The combined observations at Green Valley indicate that there are two main sources of recharge to the AMD seeps at the toe of the gob pile. The first is relatively dilute, isotopically homogenous, reducing perched gob water or groundwater that results from localized precipitation-induced head that is expelled through pre-mining karst features to create a groundwater mound within the gob. The second source of recharge is oxidizing and isotopically variable meteoric precipitation that infiltrates through the gob pile, leaching the unsaturated zone. The magnitude of effect observed for both sources indicate that they contribute subequal but variable amounts of the recharge waters that ultimately emerge as AMD seeps. The hydraulic conductivity and permeability of the gob pile, as calculated by isotopic lag, is consistent with reported values for silty to clean unconsolidated sand.

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