Non-invasive flow path characterization in a mining-impacted wetland

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Abstract

Time-lapse electrical resistivity (ER) was used to capture the dilution of a seasonal pulse of acid mine drainage (AMD) contamination in the subsurface of a wetland downgradient of the abandoned Pennsylvania Mine workings in central Colorado. Data were collected monthly from mid-July to late October of 2013, with an additional dataset collected in June of 2014. Inversion of the ER data shows the development through time of multiple resistive anomalies in the subsurface, which corroborating data suggest are driven by changes in total dissolved solids (TDS) localized in preferential flow pathways. Sensitivity analyses on a synthetic model of the site suggest that the anomalies would need to be at least several meters in diameter to be adequately resolved by the inversions. The existence of preferential flow paths would have a critical impact on the extent of attenuation mechanisms at the site, and their further characterization could be used to parameterize reactive transport models in developing quantitative predictions of remediation strategies.

Keywords: Acid mine drainage, electrical resistivity, wetland

1. Introduction

Weathering of sulfide deposits creates a serious environmental water quality issue by generating acidic conditions and mobilizing heavy metals (see Da Rosa et al., 1997; Nordstrom, 2011b, for reviews). Although acid rock drainage forms naturally as a byproduct of sulfide oxidation, mining operations can increase the

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1 weathering rate by up to three orders of magnitude by increasing the reactive
2 mineral surface area (Alpers et al., 2007). The effects of acid mine drainage
3 (AMD) can persist for decades or even centuries after mining operations have
4 ceased through continued oxidation and dissolution of acid-releasing minerals
5 (Younger, 1997).

6 Effective remediation of AMD requires detailed knowledge of contaminant
7 transport through the subsurface, where longer retention times may allow for
8 extended contact with attenuating or neutralizing agents (Zhu et al., 2002).
9 Heterogeneity and preferential flow path development in AMD settings has been
10 shown to decrease the efficiency of contaminant attenuation (Malmström et al.,
11 2008), likely because preferential flow paths reduce the residence time of so-
12 lutes in the subsurface and contact with attenuating agents (Brusseau, 1994).
13 Preferential flow paths would be expected in mining-disturbed settings because
14 deposition of mining waste piles typically results in graded bedding with a wide
15 range of hydraulic conductivities (Morin & Hutt, 1994; Smith, 1995). Unfor-
16 tunately, the subsurface is rarely mapped to a sufficient extent to identify and
17 characterize flow paths, especially at historical mine sites, where efforts gen-
18 erally contend with a lack of site data and highly disturbed aquifer material
19 (e.g., Oram et al., 2010; Nordstrom, 2011a). Many AMD remediation projects
20 expend considerable effort quantifying flow and transport parameters through
21 tracer injections (Benner et al., 2002), hydrograph separation (Smith, 1995),
22 flow balance calculations (Gélinas et al., 1994), and aquifer permeability tests,
23 or are otherwise forced to make simplifying assumptions regarding subsurface
24 homogeneity.

25 The high pore fluid conductivity of AMD has been demonstrated to be a
26 useful tracer for mapping mining contamination (Gray, 1996), and an excellent
27 target for electrical geophysical methods (Merkel, 1972). Electrical resistivity
28 (ER) is a geophysical technique that measures the bulk electrical conductivity
29 of the subsurface by both establishing a potential gradient between a pair of
30 electrodes and measuring the potential drop across one or more pairs of other
31 electrodes (Binley & Kemna, 2005). The procedure is repeated for many differ-

ent electrode locations to develop a spatially distributed dataset of subsurface conductivity (See Loke et al., 2013, for a recent review). Where a consistent relationship exists between pore fluid and bulk conductivities, ER can be used to delineate the extent and magnitude of a contaminant plume (e.g., Spindler & Olyphant, 2004).

Time-lapse ER can circumvent the reliance on a consistent relationship between pore fluid and bulk conductivities by monitoring changes in subsurface electrical properties and attributing them to changes in pore fluid conductivity. Many time-lapse ER studies inject a conductive tracer to facilitate flow path imaging (e.g., Kemna et al., 2002; Ward et al., 2010; Pollock & Cirpka, 2012); however, the ‘first-flush’ behavior demonstrated by many mine sites creates an ideal natural electrical signal. The largest contaminant loads emanating from mine sites are typically coincident with large storms following prolonged dry conditions (Miller & Miller, 2007; Nordstrom, 2009). This results in a seasonal pulse of AMD that can be used in place of a traditional tracer study, allowing for the exploration of a greater support volume and the characterization of natural flow fields (Tiedeman & Hsieh, 2004).

The goals of this paper are twofold: (1) to demonstrate the use of time-lapse ER to map AMD flow paths with application to characterizing contaminant transport, and (2) to investigate the sensitivity of ER to different conductivity anomaly sizes and magnitudes. Inverting ER measurements using a standard L2-norm to calculate model resistance values necessarily involves smoothing, which may lead to some smaller features being difficult to resolve (Day-Lewis et al., 2005). An understanding of the capabilities of ER to resolve features of different sizes is crucial for quantitative analysis in AMD settings, where target anomaly sizes may not be easily constrained. ER has been previously used to characterize the extent of AMD contamination, but only using a single snapshot in time with application of rock physics relations (e.g., Oldenburg & Li, 1994; Rucker et al., 2009). Here, time-lapse ER is used to image the dilution of the natural AMD conductivity pulse to characterize subsurface flow.

1 **2. Field site description**

2 This research was conducted in a wetland between the historic Pennsylvania
3 Mine and Peru Creek, a headwater stream to the Colorado River in central
4 Colorado (Figure 1). The Peru Creek basin is bracketed on the north and east
5 by the Continental Divide, and drains west into the Snake River. Because 80%
6 of precipitation falls as snow, the hydrograph is dominated by a spring snowmelt
7 pulse (Crouch et al., 2013).

8 The local geology includes part of a heavily mined Oligocene quartz mon-
9 zonite porphyry of the Montezuma district. The Montezuma stock intruded
10 Precambrian schist and gneiss, causing extensive fracturing and faulting and
11 widely disseminating pyrite (Fey et al., 2001). The mineral assemblage includes
12 abundant sulfides, in particular pyrite (FeS_2), sphalerite ($[\text{Zn},\text{Fe}]\text{S}$), and galena
13 (PbS) (Lovering, 1935). The Snake River contains ecologically toxic concentra-
14 tions of zinc, cadmium, and copper as a result of natural and anthropogeni-
15 cally induced pyrite weathering (Wood et al., 2005). A study of the nearby
16 Handcart Gulch, an unmined drainage near the edge of the Montezuma dis-
17 trict, found deposits of ferricrete (iron oxide) coating the streambed (Verplanck
18 et al., 2009), indicating that background metal concentrations are high even
19 in unmined drainages in the area, likely due to natural weathering of sulfide
20 minerals. Fracture flow associated with the Colorado Mineral Belt has been
21 suggested to enhance the rate of pyrite weathering in both mining impacted
22 and unimpacted areas, though the precise nature and cause of the fractures is
23 uncertain (Wood et al., 2005; Caine & Tomusiak, 2003).

24 Regionally, sulfate concentrations, which are a common proxy of mining con-
25 tamination, are highest in areas with extensive mining and hydrothermal alter-
26 ation (Fey et al., 2001). There are many abandoned mines scattered throughout
27 the region, but water and sediment chemistry analyses of the Snake River reveal
28 that one of the largest contributors of metals is the Pennsylvania Mine reach of
29 Peru Creek (Todd et al., 2005).

30 The Pennsylvania Mine was one of the largest mines in the region during

Figure 1: Map of study region with Peru Creek, ER array, and borehole sample locations.

1 its operation from 1885 to 1953 (Bird, 2003). The extensive underground mine
2 workings were historically accessed via six adits, two of which remain at least
3 partially open today (Lovering, 1935; Wood et al., 2005). A surface flow exits
4 the lower adit and discharges into Peru Creek approximately 100 m upgradient
5 from the wetland (Figure 1).

6 Because of its significant impact on local water sources, the surface water
7 chemistry of Peru Creek has been studied extensively (McKnight & Bencala,
8 1990; Sullivan & Drever, 2001; Fey et al., 2001; Runkel et al., 2013). There
9 is a large seasonality to both surface flow and contaminant concentration and
10 loading in Peru Creek (Sullivan & Drever, 2001). The peak flow occurs in late
11 May to early June and is typically 5-10 times as great as low flow during early
12 spring (Todd et al., 2005; Sullivan & Drever, 2001). Metals concentrations in
13 the mine outflow are highest during the high spring flows, consistent with the
14 first-flush behavior identified at other mine sites, although the spring concentra-
15 tion peaks are typically broader than those observed at some other mine sites

1 (Chapin & Todd, 2012). In September of 2009, synoptic sampling along the
2 Pennsylvania Mine reach of Peru Creek identified a diffuse contaminant source
3 emanating from the wetland area, where Peru Creek discharge was found to
4 increase from 60 L/s to 80 L/s in the wetland area, and sampled inflows did not
5 close the discharge or contaminant load budget (Runkel et al., 2013). Inflows
6 emanating from the wetland had higher metal concentrations than Peru Creek
7 indicating that the wetland is mining impacted (Runkel et al., 2013). In-stream
8 concentrations of specific metals were variable over the wetland reach: moving
9 downstream, concentrations of Cu, Zn, and Cd increased, while concentrations
10 of Fe and Pb decreased (Runkel et al., 2013). Chemical mixing and end-member
11 analyses indicated that the wetland samples are a mixture of Pennsylvania Mine
12 water and Cinnamon Gulch water, supporting the hypothesis that water is mov-
13 ing from the mine workings into the wetland (Runkel et al., 2013). Chemical
14 resemblance between the mine and wetland waters could also be a result of
15 contamination produced by tailing piles in the wetland (Runkel et al., 2013).

16 There are several pathways through which contamination could be reaching
17 the wetland area. The wetland has large deposits of potentially AMD-generating
18 waste rock. Using an average precipitation total of 91 cm/year, and estimating
19 the total waste rock area as 4,600 m², the Colorado Geological Society esti-
20 mated that an annual average of 0.5 m³/hr of flow could be passing through
21 waste rock and into groundwater each year (Wood et al., 2005). Water bud-
22 get calculations from Cinnamon Gulch (Figure 1) show that the vast majority
23 (>95%) of discharge to Peru Creek is from groundwater inflow (Wood et al.,
24 2005). Furthermore, a tracer injected directly into the mine was recovered in
25 boreholes in the wetland about 100 days after injection, indicating there is a
26 hydrological connection with the mine (Mark Rudolph, personal communica-
27 tion). Chemical analyses of groundwater sampled downgradient from the mine
28 suggest that the mine outflow is infiltrating into the wetland area (Rudolph,
29 2010). TDS levels are highest in the deeper wells, indicating that the wetland
30 connection with the mine workings or other tailings piles is through the deeper
31 fractured granite bedrock (Rudolph, 2010).

1 Flow through the wetland was previously studied to evaluate the site’s capac-
2 ity to naturally attenuate redirected mine effluent (Emerick et al., 1988). Bore-
3 holes near the area of interest include MW02, MW03, MW04, GW5, CGW1,
4 and GW3, which were installed to various depths and screened intervals across
5 the site. MW02 is screened into deeper granite bedrock (from 14-16.8 m below
6 ground surface, or bgs); MW03 is screened into a sandy gravel layer (5.5-8.5 m
7 bgs); GW5 is screened into peat and intermixed tailings (1.5-3 m bgs); MW04
8 and CGW1 are screened into clay and peat (1.5-3 m bgs and 0.3-1.4 m bgs,
9 respectively); and GW3 is screened into Peru Creek alluvium (1.5-4.6 m bgs).
10 Interpolation of the borehole logs suggests that the upper layer of clay and silt
11 in the wetland is bowl-shaped, roughly 5 m thick in the middle and tapering
12 out toward the edges (Emerick et al., 1988). The hydraulic conductivity of this
13 uppermost layer was found to be highly variable, with recovery rates from bail-
14 ing tests of the boreholes spanning orders of magnitude (Emerick et al., 1988).
15 The highly variable recovery rates were attributed to anomalous 5-8 cm thick
16 layers of fine-grained clayey sand encountered in multiple boreholes (Emerick
17 et al., 1988).

18 **3. Methods**

19 An array of 72 electrodes with 5-meter spacing was installed east to west,
20 through the wetland area and across the mine outlet, running roughly parallel
21 to the creek (Figure 1). Resistance data were collected on a 645 dipole-dipole
22 quadripole sequence, which was collected in 3 replicates each field session to
23 better estimate measurement error. Each stored quadripole measurement rep-
24 resents the average of a stack of 3-6 separate measurements, resulting in a total of
25 9-18 measurements collected per quadripole per field session. The dipole-dipole
26 geometry allows for up to 10 measurements to be collected simultaneously with
27 a 10-channel Syscal Pro resistivity meter (IRIS Instruments, Orleans, France),
28 resulting in a total collection time of approximately 15 minutes per sequence.
29 Initial conductivity data were collected on July 12th, 2013. Subsequent time-

1 steps were collected at approximately 2-week intervals, until the road was in-
2 accessible in late October 2013. An additional dataset was collected in June of
3 2014.

4 Electrodes were constructed from 75 cm X 1.27 cm schedule-40 PVC, wrapped
5 with 8 cm of conductive foil tape approximately 10 cm from one end. Each elec-
6 trode was installed to 20 cm bgs and connected to the ER meter using 18-gauge
7 tinned copper wire and prebuilt cables. Electrodes were left in place through-
8 out the field campaign, including over the winter season. Contact resistance was
9 checked at each electrode before each survey, and was consistently less than 1
10 kohm in the wetland, indicating excellent electrical connection with the ground.
11 Electrodes on the east side of the array had higher contact resistance, typically
12 between 10-20 kohm, and needed to be manually removed and replaced between
13 each survey because of their proximity to a road. Elevations of each electrode
14 were recorded using a Trimble XT6000 GPS unit, and post-corrected with GPS
15 Pathfinder Office 2, resulting in sub-decimeter accuracy in the horizontal direc-
16 tion, and 10-20 cm accuracy in the vertical direction.

17 Ancillary data that were collected to facilitate interpretation of the ER mea-
18 surements include: pore fluid conductivity, temperature, and water levels in 6
19 pre-existing wells (identified as MW02, MW03, MW04, CGW1, GW3, and GW5
20 in Figure 1) using a Solinst water level probe. In each borehole, temperature
21 and fluid conductivity data were collected at water level, as well as the top,
22 middle, and bottom of the screened interval, synchronous to, or immediately
23 following, ER measurements. Pressure transducers were left in four monitoring
24 wells (MW02, MW03, MW03, CGW1) over winter and spring to monitor water
25 level, temperature, and pore fluid conductivity. Peru Creek flow was gaged near
26 the center of the ER array using velocimeters on Oct 11th, 2013; thereafter,
27 flow was monitored continuously with two pressure transducers until Nov 4th,
28 2013.

1 3.1. Inversion

2 ER measurements were inverted using R2 (v2.7, Generalized 2-D Inversion
3 of Resistivity Data, (described in Binley & Kemna, 2005)). Inversions are inher-
4 ently non-unique and ill-posed because model unknowns typically greatly out-
5 number measurements (LaBrecque et al., 1996), and hence require additional
6 model constraints. To satisfy that requirement, R2 uses regularized optimiza-
7 tion, which seeks to minimize both data misfit and model roughness (Tikhonov
8 & Arsenin, 1977). The objective function, $\psi()$, takes the form:

$$\psi(m) = (W_d(m)[d - f(m)])^2 + \alpha(W_m[m - m_{ref}])^2 \quad (1)$$

9 where

m	model vector
d	measured resistance data, log transformed
W_d	data weighting matrix
$f(m)$	forward solution operating on the model
W_m	model weighting matrix that typically evaluates model roughness
α	weight that controls the relative importance of the two terms on the right side of the equation
m_{ref}	starting model guess

10 Conceptually, the W_m term of Equation 1 measures model roughness, the W_d
11 term measures misfit, and the α value controls their relative weights. Inversions
12 require an initial guess or model starting value, m_{ref} . In time-lapse ER, m_{ref}
13 refers to the inversion of the initial dataset.

14 A finite-element mesh was designed with 1 m x 1 m elements to 20 m depth,
15 below which depth element size gradually increased, resulting in 10,152 total
16 elements. Element sizes were slightly irregular, because nodes were placed at
17 each electrode location in the model.

1 Because of the regularization term in Equation 1, the resulting tomograms
2 represent smoothed depictions of the subsurface bulk electrical conductivity.
3 However, the degree of smoothing varies over the model space, resulting in an
4 inversion having less resolving power in some regions than in others. Resolution
5 matrices quantify the degree of smoothing associated with a given element (Day-
6 Lewis et al., 2005). The resolution matrix, $\mathbf{R}$, is quantified as:

$$\hat{m} \approx Rm_{true} \quad (2)$$

7 in which $\hat{m}$ is the model estimate, and m_{true} is the true conductivity value of
8 the measured domain. The diagonal of $\mathbf{R}$ quantifies the degree to which the
9 value of a given pixel in the inversion is informed by the data corresponding
10 to that pixel, as opposed to the smoothing influence of the regularization term.
11 To limit interpretation of results dominated by smoothing, inversion results
12 corresponding to values less than $10^{-2.5}$ in the diagonal of their resolution matrix
13 were filtered from the analysis.

14 *3.2. Evaluating Error*

15 Appropriately defining measurement and model error is vital to achieving
16 proper inversion fit. Error estimates that are too low result in a noisy inversion
17 model with artifacts, while error estimates that are too high result in an overly
18 smooth model with low resolving power (LaBrecque et al., 1996). The data
19 weighting term in Equation 1, $\mathbf{W}_d$, is typically of the form $\text{diag}(1/\epsilon_1, \dots, 1/\epsilon_n)$, in
20 which ϵ_i is the percent standard deviation associated with a stack of quadripole
21 resistance measurements.

22 R2 allows for measurement error to be calculated based on a generalized
23 error model, but this method not did adequately capture the measurement
24 variability between between data stacks, which was often much higher than
25 variability within individual stacks. To account for the inter-stack variability,
26 total measurement error for each quadripole was calculated as the global per-
27 cent standard deviation from the three replicate stacks. Final measurement
28 error was then either taken to be the total measurement error, or the reported

1 precision of the Syscal Pro unit (0.2%), whichever was greater. Throughout the
2 study period, instrumentation error was generally adopted as measurement er-
3 ror for quadripoles in the wetland because of the consistency between the stack
4 measurements.

5 Some quadripoles covering the far eastern part of the survey measured un-
6 reasonably large changes in resistance between time-steps, likely due to elec-
7 trode placement issues in resistive ground and local construction activities. To
8 make sure that these suspect quadripoles did not negatively affect the analysis,
9 quadripoles measuring resistance values with a coefficient of variation greater
10 than 1 over the survey duration were filtered out of the analysis.

11 Model error was assessed by comparing the apparent resistivities resulting
12 from a forward solution on an homogeneous model with a flat surface boundary
13 (Binley & Kemna, 2005). The average model error was 0.5%. Total error for
14 each quadripole was taken to be the sum of measurement error and model error.

15 **4. Results**

16 *4.1. Conductivity*

17 The background bulk conductivity data (Figure 2) conform to the lithological
18 interpretations made from borehole drilling logs (Emerick et al., 1988; Rudolph,
19 2010). There is a bowl-shaped, high conductivity (>10 mS/m, colors deep blue
20 and cooler on Figure 2) unit in the wetland with a maximum thickness of about
21 4-5 m that tapers out toward the edges of the wetland area. The conductivity of
22 this unit is typical of clays (Telford & Sheriff, 1990), and its interval corresponds
23 well with the wetland complex of interbedded clays and peat logged in boreholes
24 MW02-04 and CGW1. This unit appears to pinch out somewhat near the middle
25 of the structure. There is a less conductive unit extending from electrode 48,
26 located at $x=240$ m in Figure 2, at the surface down and to the west that
27 corresponds to the layer of sand and gravel observed in MW02, and the tailings
28 observed in GW5. Below the sand layer, conductivity decreases to less than 2
29 mS/m (colors bright yellow and warmer), typical of the granite bedrock with

Figure 2: Inversion of ER data collected on July 12th, 2013 showing the depth profile conductivity. Electrodes (E1-E72), model fitting parameter results, borehole logs, and the general character of vegetation are shown.

1 high fluid conductivity observed in the bottom of MW02, though this depth
 2 is approaching the resolution limit of this study. The low conductivity unit
 3 approaches the surface near electrode 48, where there is a small surface flow,
 4 consistent with the interpretation of a granite bedrock contact.

5 Resolution on the east side of the profile was impacted by local construc-
 6 tion activities and the complication of reinstalling electrodes with each survey
 7 (Figure 3). Consequently, the time-lapse data from the east side of the pro-
 8 file are difficult to interpret, and so only the results from the wetland will be
 9 shown here. In general, the high conductivities observed in the wetland area
 10 are absent on the east side of the profile, indicating a lack of clay deposits. The
 11 low conductivities under electrodes 68-72, located at $x = 325$ m to 350 m, likely
 12 correspond to dry granite bedrock.

13 Time-lapse ER data collected from July 2013 to June 2014 in the wetland
 14 area show the development of two resistive anomalies at approximately 5 m
 15 bgs, just under the interpreted boundary between the clay and peat layer and
 16 the sandy layer (Figure 4), and the development of a laterally extensive resistive
 17 feature in the near-surface (< 3 m) of the wetland. Both root-mean-square errors

Figure 3: Resolution of inversion of data collected on July 12th, 2013. Note, because of smoothing issues, only data for 1 m x 1 m pixels are shown.

1 between the modeled and measured data as well as the term controlling the
2 relative weights between the model and data misfit were consistent for inversion
3 results in the wetland throughout the study period, indicating that the degree of
4 smoothing in the inversion results is fairly consistent through time, and therefore
5 cannot explain the development of the temporal wetland anomalies. To confirm
6 that the anomalies were not artifacts of data noise in the initial dataset, the
7 resistance data were reanalyzed using the September inversion as the initial
8 model condition, which resulted in slightly muted, but persistent, resistivity
9 anomalies in the same locations, indicating that the anomalies represent real
10 changes in field site conditions. Note that because bulk background conductivity
11 decreases with depth at this site, absolute changes at depth produce a more
12 pronounced relative change; as a result, the apparent surficial resistive anomalies
13 in the data represent smaller relative conductivity changes than the anomalies
14 observed at greater depths.

15 4.2. Supporting Data

16 Three parameters most likely explain the development of the resistive anoma-
17 lies at depth: water content, temperature, and pore fluid conductivity. Field

Figure 4: Time-lapse percent change in conductivity, relative to background inversion of July 12, 2013 data.

1 observations suggested and water levels in the boreholes confirmed that the
 2 wetland stayed saturated throughout the field campaign, as the static water
 3 level was typically within 0.5 m of the ground surface. Furthermore, contact
 4 resistance measured between adjacent pairs of electrodes in the wetland was con-
 5 sistent throughout the study period, indicating that there was minimal change
 6 in saturation in the wetland. As a result, saturation differences cannot explain
 7 the development of the resistive anomalies, particularly beyond a meter or so
 8 below ground surface.

9 Seasonally driven temperature decreases would be expected between July
 10 and October, particularly in the very shallow subsurface. Furthermore, local-
 11 ized enhanced communication of groundwater with surface water could produce
 12 imagable temperature anomalies in the deeper subsurface, in effect acting as
 13 a temperature tracer (Musgrave & Binley, 2011). To explore the possibility of
 14 the anomalies being temperature based, the electrical conductivity response to
 15 changes in temperature was modeled (Schon, 2004):

$$\sigma(T) = \sigma(T_0)[1 + \beta(T - T_0)] \quad (3)$$

1 where

σ conductivity (mS/m)
 T temperature ($^{\circ}\text{C}$)
 T_0 initial temperature ($^{\circ}\text{C}$)
 β constant, equal to 0.025 ($^{\circ}\text{C}^{-1}$).

2 Over the course of the field campaign, temperatures in the top 2 m bgs gener-
3 ally increased by about 2.5 $^{\circ}\text{C}$ by the end of September, before decreasing by
4 about 2.5 $^{\circ}\text{C}$ by the end of October. According to Equation 3, a temperature
5 decrease of 2.5 $^{\circ}\text{C}$ would produce a 6.8 % decrease in conductivity, which would
6 not completely explain the resistive anomalies. However, the development of a
7 localized layer of ice, which is much more resistive than water, at the site in
8 October indicates that some areas had more pronounced cooling than others.
9 A temperature decrease of 8 $^{\circ}\text{C}$ would produce a conductivity decrease of 25% ,
10 which is entirely within the range of the observed data. It therefore likely that
11 the resistive anomalies that developed on the surface were primarily tempera-
12 ture driven. However, water temperatures in the boreholes remained relatively
13 constant (± 1 $^{\circ}\text{C}$) at depths greater than 1.5 m bgs. At the outset of the
14 study, the average temperature at depth was approximately 3.5 $^{\circ}\text{C}$, indicating
15 that a highly improbable phase change would need to occur to produce the resis-
16 tive anomalies at depth. Therefore, it is unlikely that the resistivity anomalies
17 at depth could be completely explained by temperature changes.

18 This leaves fluid conductivity change as the most likely explanation for the
19 development of the wetland anomalies. Conductivity decreases could have oc-
20 curred if preferential flow paths in the wetland allow for the flushing of high
21 pore fluid salinity following the first-flush pulse. Because the contamination is
22 typically produced during the dry season, additional flow through the system
23 after the spring snowmelt pulse has flushed out the accumulated TDS would
24 have lower TDS concentrations and produce a more resistive signal.

1 There are multiple lines of evidence in the borehole data to suggest that such
2 preferential flow paths exist in the wetland: (1) Initial TDS values were more
3 variable and changes were more localized than they were for temperature. (2)
4 There was little consistency between boreholes screened into the same aquifer;
5 for example, CGW1 had TDS concentrations that were nearly an order of mag-
6 nitude higher than MW02, even though they are 100 m apart and both screened
7 into the surface aquifer. The borehole measurements indicate that preferential
8 flow is most likely to be occurring in the sandy layer at intermediate depth, be-
9 cause boreholes screened into this layer demonstrated much greater pore fluid
10 conductivity variation. Standard deviations of the conductivities of boreholes
11 screened into the sandy or tailing material were $GW3 = 10.5 \text{ mS/m}$, $GW5 = 6.6$
12 mS/m , and $MW03 = 6.6 \text{ mS/m}$; while standard deviations were much smaller
13 for the boreholes screened into the surface layer, $MW04 = 3.6 \text{ mS/m}$, $CGW1$
14 $= 3.6 \text{ mS/m}$; and into the deeper bedrock well $MW02 = 3.2 \text{ mS/cm}$.

15 Two of the most variable wells, GW3 and GW5, show trends of decreasing
16 fluid conductivity in the early field season (Figure 5). GW3 displayed a con-
17 sistent decrease in fluid conductivity throughout the field season, starting at 42
18 mS/m and ending near 18 mS/m . GW5 decreased initially, from 89 mS/m to
19 73 mS/m , before rising in late September and October back up to 84 mS/m . No
20 other wells showed consistent trends in fluid conductivity, though conductivity
21 in MW03 did increase slightly over the study period.

22 Petrophysical relationships allow for examination of the feasibility that the
23 observed pore fluid conductivity change could produce the development of the
24 resistive anomalies at depth. Archie's Law relates pore fluid conductivity to
25 bulk conductivity (Archie, 1942; Yuval & Oldenburg, 1996):

$$\sigma_w = \frac{\sigma}{a\theta^m} \quad (4)$$

26 where

σ_w pore fluid conductivity mS/m
 σ bulk conductivity mS/m

a constant
 θ porosity (-)
 m cementation factor.

Equation 4 was used to calculate the pore fluid conductivity change necessary to produce the observed bulk conductivity decreases of 15%. This analysis is limited in that it assumes a consistent relationship between bulk conductivity and pore fluid conductivity (Day-Lewis et al., 2005), which, due to heterogeneities in the aquifer and in the resolution of the inversion, can be difficult to quantify precisely (Singha & Gorelick, 2006). However, for the purposes of examining feasibility and possible ranges, standard parameter values from the literature suffice. Parameters were $a = 1.2$, $\theta = 0.3$ and $m = 2$, all values consistent with clay-free unconsolidated rock reported in AMD literature (Yuval & Oldenburg, 1996). Note that this calculation would not hold in the very near surface, where starting conductivities are drastically higher and where there are abundant clays with variable surface charge. The results of the calculation depend on initial conductivity, but near the center of the anomalies, where starting bulk conductivity is approximately 7.7 mS/m, a decrease in pore fluid conductivity of about 10.6 mS/m would be required to produce a 15% decrease in bulk conductivity. This value is consistent with the range of observed decreases in conductivities in the wetland (up to a decrease of 16 mS/m pore fluid conductivity at GW5); therefore, TDS flushing likely explains the development of resistive anomalies at depth.

4.3. Flow conditions

The proposed mechanism of flushing TDS from preferential flow paths in the wetland to create localized resistive anomalies indicates that the initial July 12th baseline ER dataset captured the spring pulse of contamination, which is consistent with other measurements of spring flush timing. Time-lapse chemistry data show that mine outflow concentrations are highest roughly coincident

Figure 5: Pore fluid conductivity measurement trends over time collected in the site boreholes.

1 with peak Snake River flow (Chapin & Todd, 2012), which annually occurs in
2 early summer (Figure 6). Unlike some other mines, concentrations from the
3 Pennsylvania Mine do not show a traditional first-flush, but instead rise quickly
4 to roughly 2-4 times their winter low values, before slowly dropping back down
5 to baseline over the next several months (Chapin & Todd, 2012). A similar
6 trend was observed in the pore fluid conductivity measured in a monitoring well
7 GW3, adjacent to the mine outflow (Figure 5).

8 The travel time from the mine to the wetland is complicated by seasonal vari-
9 ability in groundwater head gradients, but tracer studies have shown the travel
10 time to be approximately 100 days during winter low flow (Mark Rudolph, per-
11 sonal communication). Because groundwater head gradients would be expected
12 to be lower during winter and therefore produce slower flow, 100 days can be
13 taken to be a maximum travel time. Therefore the pulse of contamination would
14 be expected to reach the wetland sometime between peak flow in early June and
15 100 days later in early September, with a more likely arrival time in July or Au-
16 gust, consistent with our background and early time-lapse measurements. The
17 contrasting magnitudes and trends in the site borehole measurements indicate
18 that movement of mining impacted water through the site is heterogeneous, and
19 that arrival times are likely to be variable across the site (Figure 5).

20 The local flow maximum in mid-September of 2013 is the result of a storm
21 in the middle of the study period. Storm events of this magnitude (>1 -2 cm
22 precipitation) have been demonstrated to cause concentration increases in the
23 Pennsylvania Mine outflow (Chapin & Todd, 2012). This would be expected
24 to present a secondary pulse, observable in our data as a conductivity increase
25 and subsequent decrease. Pore fluid conductivity did increase in borehole GW5,
26 about 100 m upgradient of the ER array. It is proposed that this pulse had not
27 yet reached the ER array by the end of the survey. An arrival time of mid-
28 November to late January would be consistent with the travel times discussed
29 in the preceding paragraph, but no geophysical measurements were collected
30 during this time due to road conditions being impassable in the winter.

Figure 6: Snake River hydrograph. ER background (D*) and time-lapse (D) collection dates are shown.

Figure 7: Flow diagram of the sensitivity modeling process.

5. Sensitivity Analysis

As a result of the non-uniqueness of the inverse problem, a large number of potential solutions exist that fit the data sufficiently well. The sensitivity of the inversion to changes in the ER model was investigated with synthetic data to develop an understanding of how regularization impacts the inversion's ability to resolve features of different sizes and contrasts, and to constrain the range of possible features that would be expected to produce the tomograms in Figure 4. Synthetic data parameters were chosen to mimic the electrical properties of this study, such that the results inform on real-world, non-uniform settings and geometries. The below process (schematically depicted in Figure 7) was followed:

1. Total resistivity change was calculated in a region encompassing the two anomalies at depth that developed between the background and final datasets, respectively collected on July 12th and Oct 28th.
2. The recovered resistivity was then split into two anomalies and added onto the background resistivity model in locations that replicated the observed

- 1 anomalies. The anomalies were emplaced at $y = -5$ m with circular ge-
2 ometries that had variable radii. Total mass remained constant and equal
3 to the original anomaly mass, such that an anomaly larger in area would
4 have lower contrast against the background.
- 5 3. A forward solution was computed for the synthetic anomalies using the
6 same quadrupole sequence that was used to collect field data.
- 7 4. The resulting forward model data were given 1% random noise to replicate
8 the noise of field data. The same error parameters that were used to
9 evaluate the field data were assigned to the forward model data.
- 10 5. The inverse solution was then computed in R2 (Figure 8).

11 In short, a forward and inverse solution was computed for the observed
12 anomalies to test the inversion's ability to resolve anomalies of different sizes
13 and contrasts. As was expected, results show that the model is more sensitive
14 to larger anomaly structures (Figure 8). The inversion was unable to detect
15 anomalies with radii of 0.5 to 1 m at relatively shallow depths of 5 m, even
16 though the contrasts of these anomalies are much larger. The analysis also
17 shows that the left anomaly more easily resolved than the right anomaly, likely
18 because of the greater average depth of the right anomaly. It is important to
19 note that the inversions of the field data had different error fitting parameters,
20 making a quantitative comparison to the inversions of the field data difficult.

21 6. Discussion & Conclusions

22 Application of time-lapse ER allowed for non-invasive location and character-
23 ization of the resistive anomalies in an AMD-impacted wetland. Corroborating
24 borehole measurements indicate that the resistive anomalies developed in re-
25 sponse to localized decreases in pore fluid salinity, which are hypothesized to be
26 driven by flushing of mining contamination through preferential flow paths in
27 the wetland. The timing of the observed anomalies agrees well with the produc-
28 tion of the seasonal first-flush and associated travel times. Because of smoothing
29 inherent in inversions, the exact geometry of the flow paths is unknown, but the

Figure 8: Cross sections of sensitivity modeling results for anomalies of different radii, denoted ‘r’ on each subfigure, units in meters. Also shown are the anomaly contrasts and inversion fitting results.

1 sensitivity tests reveal that they must be at least several meters in diameter.
2 Petrophysical relationships suggest that the localized changes in pore fluid con-
3 ductivity within the flow paths are on the order of hundreds of $\mu\text{g/L}$, which is
4 within the temporal variability of the conductivities in the boreholes as well as
5 of the mine outflow (Chapin & Todd, 2012).

6 The results of this study indicate that contamination may be discharging
7 from the wetland to Peru Creek that would have been missed by spatially local-
8 ized borehole sampling. Furthermore, this study shows that the wetland metals
9 contributions would be expected to change over time as the pulse of contamina-
10 tion travels through the wetland. If the pore fluid changes are driven by leakage
11 from the mine workings, there may be substantially more flow leaking from the
12 mine workings than previously thought, which would have substantial impli-
13 cations for the hydrogeology of the mine workings and proposed remediation
14 efforts.

15 Reactive transport models are an important tool for developing quantitative
16 predictions of remediation activities (for AMD examples, see Walton-Day et al.,
17 2012; Benner et al., 2002); however, collecting sufficient data in the field to pa-

parameterize these models in AMD-impacted regions can be difficult, especially considering that heterogeneous distributions of either potentially contaminant-retarding agents or hydraulic conductivity can dramatically complicate interpretation of contaminant breakthrough curves (Malmström et al., 2008). In particular, preferential flow can cause separation of downstream breakthrough concentration peaks that mimic the effects of heterogeneous geochemical conditions in reactive transport (Malmström et al., 2008). Not differentiating the between the two conditions could lead to overestimates of the total amount of attenuation taking place (Malmström et al., 2008). Therefore, by offering preliminary contaminant pathway identification and characterization, the type of time-lapse geophysical data collected here may provide a valuable parameterization tool for reactive transport models, especially at sites with limited subsurface data.

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References

Alpers, C. N., Nordstrom, D. K., Verosub, K. L., & Helm-Clark, C. (2007). Paleomagnetic Determination of Pre-Mining Metal Flux Rates at the Iron

- 1 Mountain Superfund Site, Northern California. *Eos, Trans. AGU*, 88, Suppl.
- 2 Archie, G. E. (1942). The electrical resistivity log as an aid in determining some
3 reservoir characteristics. *Transactions of the American Institute of Mining,*
4 *Metallurgical, and Petroleum Engineers*, 146, 54–62.
- 5 Benner, S., Blowes, D., Ptacek, C., & Mayer, K. (2002). Rates of sulfate reduc-
6 tion and metal sulfide precipitation in a permeable reactive barrier. *Applied*
7 *Geochemistry*, 17, 301–320.
- 8 Binley, A. M., & Kemna, A. (2005). DC resistivity and induced polarization
9 methods. In Y. Rubin, & S. Hubbard (Eds.), *Hydrogeophysics* (pp. 129–156).
10 N.Y.: Springer.
- 11 Bird, D. A. (2003). Characterization of anthropogenic and natural sources of
12 acid rock drainage at the Cinnamon Gulch abandoned mine land inventory
13 site, Summit County, Colorado. *Environmental Geology*, 44, 919–932.
- 14 Brusseau, M. (1994). TRANSPORT OF REACTIVE CONTAMINANTS ME-
15 DIA IN HETEROGENEOUS POROUS MEDIA. *Reviews of Geophysics*, (pp.
16 285–313).
- 17 Caine, J. S., & Tomusiak, S. R. (2003). Brittle structures and their role in
18 controlling porosity and permeability in a complex Precambrian crystalline-
19 rock aquifer system in the Colorado Rocky Mountain Front Range. *Geological*
20 *Society of America Bulletin*, 115, 1410.
- 21 Chapin, T. P., & Todd, A. S. (2012). MiniSipper: a new in situ water sampler
22 for high-resolution, long-duration acid mine drainage monitoring. *The Science*
23 *of the Total Environment*, 439, 343–53.
- 24 Crouch, C. M., McKnight, D. M., & Todd, A. S. (2013). Quantifying sources
25 of increasing zinc from acid rock drainage in an alpine catchment under a
26 changing hydrologic regime. *Hydrological Processes*, 27, 721–733.

1 Da Rosa, C. D., Lyon, J. S., Hocker, P. M., & Udall, S. L. (1997). *Golden*
2 *dreams, poisoned streams: how reckless mining pollutes America's waters,*
3 *and how we can stop it.* Washington, DC: Mineral Policy Center.

4 Day-Lewis, F. D., Singha, K., & Binley, A. M. (2005). Applying petrophysical
5 models to radar travel time and electrical resistivity tomograms: Resolution-
6 dependent limitations. *Journal of Geophysical Research*, 110, B08206.

7 Emerick, J., Huskie, W., & Cooper, D. (1988). Treatment of discharge from a
8 high elevation metal mine in the Colorado Rockies using an existing wetland.
9 *Proceedings from a conference at the annual meeting of the American Society*
10 *for Surface Mining and Reclamation*, (pp. 345–350).

11 Fey, D. L., Church, S. E., Unruh, D. M., & Bove, D. J. (2001). *U.S. Geological*
12 *Survey Open-File Report 02-0330 Water and Sediment Study of the Snake*
13 *River Watershed, Colorado.* Technical Report.

14 Gélinas, P., Lefebvre, R., Choquette, M., & Isabel, D. (1994). *Monitoring and*
15 *Modeling of Acid Mine Drainage from Waste Rock Dumps.* Technical Report
16 June Report GREGI 12.

17 Gray, N. F. (1996). Field assessment of acid mine drainage contamination in
18 surface and ground water. *Environmental Geology*, 27, 358–361.

19 Kemna, A., Kulesa, B., & Vereecken, H. (2002). Imaging and characterisation
20 of subsurface solute transport using electrical resistivity tomography (ERT)
21 and equivalent transport models. *Journal of Hydrology*, 267, 125–146.

22 LaBrecque, D. J., Miletto, M., Daily, W., Ramirez, A., & Owen, E. (1996).
23 The effects of noise on Occams inversion of resistivity tomography data. *Geo-*
24 *physics*, 61, 538–548.

25 Loke, M. H., Chambers, J. E., Rucker, D. F., Kuras, O., & Wilkinson, P. B.
26 (2013). Recent developments in the direct-current geoelectrical imaging
27 method. *Journal of Applied Geophysics*, 95, 135–156.

- 1 Lovering, T. (1935). *Geology and ore deposits of the Montezuma Quadrangle,*
2 *Colorado*. Technical Report Professional Paper 178 Geological Survey.
- 3 Malmström, M. E., Berglund, S., & Jarsjö, J. (2008). Combined effects of spa-
4 tially variable flow and mineralogy on the attenuation of acid mine drainage
5 in groundwater. *Applied Geochemistry*, 23, 1419–1436.
- 6 McKnight, D. M., & Bencala, K. E. (1990). The Chemistry of Iron, Aluminum,
7 and Dissolved Organic Material in Three Acidic, Metal-Enriched, Mountain
8 Streams, as Controlled by Watershed and in-Stream Processes. *Water Re-*
9 *sources Research*, 26, 3087.
- 10 Merkel, R. H. (1972). The use of resistivity techniques to delineate acid mine
11 drainage in ground water. *Groundwater*, 10.
- 12 Miller, J. R., & Miller, S. O. (2007). The water column-concentration and load.
13 In *Contaminated Rivers* (pp. 103–126). Springer Netherlands.
- 14 Morin, K., & Hutt, N. (1994). An empirical technique for predicting the chem-
15 istry of water seeping from mine-rock piles. In *Proceedings of the Third In-*
16 *ternational Conference on the Abatement of Acidic Drainage*.
- 17 Musgrave, H., & Binley, A. (2011). Revealing the temporal dynamics of sub-
18 surface temperature in a wetland using time-lapse geophysics. *Journal of*
19 *Hydrology*, 396, 258–266.
- 20 Nordstrom, D. K. (2009). Acid rock drainage and climate change. *Journal of*
21 *Geochemical Exploration*, 100, 97–104.
- 22 Nordstrom, D. K. (2011a). Hydrogeochemical processes governing the origin,
23 transport and fate of major and trace elements from mine wastes and miner-
24 alized rock to surface waters. *Applied Geochemistry*, 26, 1777–1791.
- 25 Nordstrom, D. K. (2011b). Mine Waters: Acidic to Circumneutral. *Elements*,
26 7, 393–398.

- 1 Oldenburg, D. W., & Li, Y. (1994). Inversion of induced polarization data.
2 *Geophysics*, 59, 1327–1341.
- 3 Oram, L. L., Strawn, D. G., Morra, M. J., & Möller, G. (2010). Selenium
4 biogeochemical cycling and fluxes in the hyporheic zone of a mining-impacted
5 stream. *Environmental Science & Technology*, 44, 4176–83.
- 6 Pollock, D., & Cirpka, O. A. (2012). Fully coupled hydrogeophysical inver-
7 sion of a laboratory salt tracer experiment monitored by electrical resistivity
8 tomography. *Water Resources Research*, 48, W01505.
- 9 Rucker, D. F., Glaser, D. R., Osborne, T., & Maehl, W. C. (2009). Electrical
10 Resistivity Characterization of a Reclaimed Gold Mine to Delineate Acid Rock
11 Drainage Pathways. *Mine Water and the Environment*, 28, 146–157.
- 12 Rudolph, M. (2010). *Dye injection and sampling and analysis plan Cinnamon*
13 *Gulch/Pennsylvania Mine site 2009 fluorescent dye tracer study*. Technical
14 Report COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVI-
15 RONMENT.
- 16 Runkel, R. L., Walton-day, K., Kimball, B. A., Verplanck, P. L., & Nimick,
17 D. A. (2013). Estimating instream constituent loads using replicate synoptic
18 sampling, Peru Creek, Colorado. *Journal of Hydrology*, 489, 26–41.
- 19 Schon, J. H. (2004). *Physical Properties of Rocks: Fundamentals and Principles*
20 *of Petrophysics*. Elsevier Science & Technology Books.
- 21 Singha, K., & Gorelick, S. M. (2006). Effects of spatially variable resolution on
22 field-scale estimates of tracer concentration from electrical inversions using
23 Archie's law. *Geophysics*, 71, G83–G91.
- 24 Smith, L. (1995). *Hydrogeology of waste rock dumps*. Technical Report July
25 British Columbia Ministry of Energy, Mines and Petroleum Resources and
26 CANMET.

1 Spindler, K., & Olyphant, G. (2004). Geophysical investigations at an aban-
2 doned mine site subjected to reclamation using a fixated scrubber sludge cap.
3 *Environmental & Engineering Geoscience*, *X*, 243–251.

4 Sullivan, A. B., & Drever, J. I. (2001). Spatiotemporal variability in stream
5 chemistry in a high-elevation catchment affected by mine drainage. *Journal*
6 *of Hydrology*, *252*, 237–250.

7 Telford, W. M., & Sheriff, R. E. (1990). *Applied Geophysics* volume 1. Cam-
8 bridge University Press.

9 Tiedeman, C. R., & Hsieh, P. A. (2004). Evaluation of longitudinal disper-
10 sivity estimates from simulated forced- and natural-gradient tracer tests in
11 heterogeneous aquifers. *Water Resources Research*, *40*, 1–15.

12 Tikhonov, A., & Arsenin, V. (1977). *Solutions of ill-posed problems*.

13 Todd, A. S., McKnight, D. M., & Duren, S. M. (2005). *Water quality charac-*
14 *teristics for the Snake River, North Fork of the Snake River, Peru Creek, and*
15 *Deer Creek in Summit county, Colorado: 2001 to 2002*. Technical Report
16 University of Colorado, Institute of Arctic and Alpine Research.

17 Verplanck, P. L., Nordstrom, D. K., Bove, D. J., Plumlee, G. S., & Runkel,
18 R. L. (2009). Naturally acidic surface and ground waters draining porphyry-
19 related mineralized areas of the Southern Rocky Mountains, Colorado and
20 New Mexico. *Applied Geochemistry*, *24*, 255–267.

21 Walton-Day, K., Runkel, R. L., & Kimball, B. A. (2012). Using Spatially De-
22 tailed Water-Quality Data and Solute-Transport Modeling to Support Total
23 Maximum Daily Load Development. *JAWRA Journal of the American Water*
24 *Resources Association*, *48*, 949–969.

25 Ward, A. S., Gooseff, M. N., & Singha, K. (2010). Characterizing hyporheic
26 transport processes - Interpretation of electrical geophysical data in coupled
27 stream-hyporheic zone systems during solute tracer studies. *Advances in Wa-*
28 *ter Resources*, *33*, 1320–1330.

- 1 Wood, R. H. I., Bird, D. A., & Sares, M. A. (2005). *Mine site history and water-*
2 *shed characterization of the Cinnamon Gulch Area, Dillon Ranger District,*
3 *White River National Forest, Summit County, Colorado.* Technical Report
4 Colorado Geological Survey, Department of Natural Resources.
- 5 Younger, P. L. (1997). The longevity of minewater pollution: a basis for decision-
6 making. *The Science of the Total Environment*, 194-195, 457–66.
- 7 Yuval, D., & Oldenburg, W. (1996). DC resistivity and IP methods in acid mine
8 drainage problems: results from the Copper Cliff mine tailings impoundments.
9 *Journal of Applied Geophysics*, 34, 187–198.
- 10 Zhu, C., Anderson, G., & Burden, D. (2002). Natural Attenuation Reactions at
11 a Uranium Mill Tailings Site, Western U.S.A. *Groundwater*, 40, 5–13.