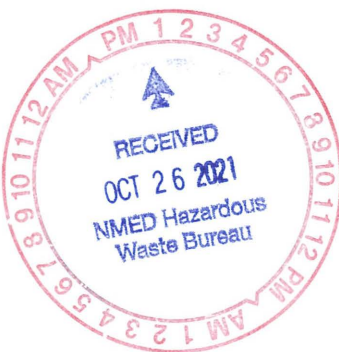**N3B** *Los Alamos*

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EM-LA

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Date: October 26, 2021
Refer To: N3B-2021-0387

Mr. Ricardo Maestas
Bureau Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6313

**Subject: Submittal of the Results from Extended Purging of Monitoring
Wells R-42 and R-28**

Dear Mr. Maestas:

Enclosed please find the "Results from Extended Purging of Monitoring Wells R-42 and R-28." The
U.S. Department of Energy Environmental Management Los Alamos Field Office (EM-LA) letter
to the New Mexico Environment Department (NMED) dated June 29, 2021, stated "After
completion of the pumping and sampling period, EM-LA will conduct an evaluation of the data
collected once the data have been received and validated. It is anticipated that data validation and
review will occur until the end of September. EM-LA will meet with NMED to discuss the data
results and the rehabilitation work plan. EM-LA will submit the well rehabilitation work plan to
NMED by October 26, 2021." As discussed in a presubmittal meeting held with NMED on
October 18, 2021, this report is being submitted in lieu of a well rehabilitation work plan for
regional aquifer wells R-28, R-42, and CrEX-3 because the recommendations provided in the report
are that rehabilitation of these wells is not the appropriate path forward for these wells.

If you have questions, please contact Christian Maupin at (505) 695-4281 (christian.maupin@em-
la.doe.gov) or Cheryl Rodriguez at (505) 414-0450 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Troy Thomson

Troy Thomson
Acting Program Manager
Environmental Remediation
N3B-Los Alamos

Sincerely,

**ARTURO
DURAN**

Digitally signed by ARTURO
DURAN
Date: 2021.10.25 17:59:34
-06'00'

Arturo Q. Duran
Compliance and Permitting Manager
U.S. Department of Energy
Environmental Management
Los Alamos Field Office

Enclosure(s): Two hard copies with electronic files –
Results from Extended Purging of Monitoring Wells R-42 and R-28 (EM2021-0715)

cc (letter and enclosure[s] emailed):
Laurie King, EPA Region 6, Dallas, TX
Chris Catechis, NMED-DOE-OB/-RPD
Steve Yanicak, NMED-DOE-OB
Patrick Longmire, NMED-GWQB
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RESULTS FROM EXTENDED PURGING
OF MONITORING WELLS R-42 AND R-28

1.0   BACKGROUND AND INTRODUCTION

In 2017, reductive amendments were deployed in pilot-scale tests in monitoring wells R-42 and R-28 to evaluate in situ reduction of hexavalent chromium [Cr(VI)] as a potential remedial action in the chromium plume area. These pilot-scale tests were conducted in accordance with the New Mexico Environment Department's (NMED's) approval of the "Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon" (LANL 2017, NMED 2017). Sodium dithionite was deployed in R-42 as a chemical reductant in late August 2017, and molasses was deployed in R-28 as a biostimulant in early September 2017. Before the amendment deployments, R-42 had the highest Cr(VI) concentration of any monitoring well in the chromium plume area (about 700 μg/L), and R-28 had the second highest Cr(VI) concentration (about 400 μg/L). Both amendment deployments were successful in demonstrating reduction of Cr(VI), with little indication of a rebound in Cr(VI) concentrations in either R-42 or R-28 through the end of 2019. Details of the deployments and subsequent observations in R-42 and R-28 through 2019 are documented in a series of eight quarterly progress reports, with the last being produced in June 2020 (LANL 2018a, 2018b; N3B 2018a, 2018b, 2019a, 2019b, 2019c, 2020).

In late 2020, R-42 and R-28 were both rehabilitated/redeveloped in an attempt to determine whether the continued observation of reducing conditions [and very low Cr(VI) concentrations] in both wells was a consequence of near-well geochemical conditions and/or permeability reduction close to the wells. The redevelopments resulted in significant increases in the specific capacities of both wells, and the R-42 redevelopment also resulted in an increasing trend in Cr(VI) concentrations (though not approaching pre-amendment concentrations), suggesting that reducing conditions in the vicinity of the well were slowly being exhausted. However, the R-28 redevelopment did not result in an increase in Cr(VI) concentrations, nor did it result in a significant change in other geochemical parameters that might suggest that reducing conditions were being exhausted. These observations were made during a series of sampling events conducted roughly every 2 weeks from mid-January 2021 through early April 2021.

In August and September 2021, both R-42 and R-28 were pumped nearly continuously (extended purge), with total withdrawals of approximately 104,000 gal. and 129,000 gal., respectively, to draw in prevailing oxidizing aquifer water in an attempt to exhaust local reducing conditions. The goal was to restore the wells to pre-amendment geochemical conditions so that they might accurately reflect the geochemistry in the surrounding aquifer, especially Cr(VI) concentrations. This report summarizes the results from this restoration effort. Some of the results from the earlier redevelopment effort are also presented, as these results are relevant for evaluating the effectiveness of the restoration effort.

2.0   EXTENDED PURGE OPERATIONS

Extended purging operations commenced around mid-day on August 24, 2021, at both R-42 and R-28, and they ended on September 22, 2021, at R-42 and on September 21, 2021, at R-28. Pumping was continuous with the exception of an unplanned interruption of approximately 17 hr at both wells from the evening of August 26, 2021, until just before noon on August 27, 2021, and planned interruptions of about 3 days at R-42 (September 4, 2021, to September 7, 2021) and about 4 days at R-28 (September 4, 2021, to September 8, 2021). There were also occasional brief interruptions of a few minutes at a time for operational activities such as wellhead filter changeouts or treatment system cartridge changeouts. Wellhead treatment systems were deployed at both R-42 and R-28 to remove dissolved iron and manganese to meet land-application criteria. These treatments also had the benefit of

avoiding adverse impacts to the downstream batch Cr(VI) treatment system. The performance of the wellhead treatment systems was monitored by daily sampling and Hach kit measurements at various locations in the systems, but these results are not presented or discussed in this report (they were made available to NMED in weekly reports). Daily samples were also collected at the R-42 and R-28 wellheads before any treatment, and these samples were analyzed for a standard suite of cations, trace metals, anions, pH, alkalinity, perchlorate, and total and dissolved organic carbon (R-28 only for organic carbon analysis). Two sets of samples were collected on the same day at the wellheads after the planned pumping interruptions, one after 50 gal. of pumping, and a second after 350 gal. of pumping. Additional samples were collected at R-42 after 50 and 300 gal. of pumping on both October 5, 2021, and October 12, 2021, 13 and 20 days, respectively after the extended purge had ended (these sampling events involved only 300 gal. of pumping). Hexavalent chromium concentrations were measured approximately once a week during the purge and were found to be in good general agreement with total chromium measurements. Daily measurements of total chromium were used to determine chromium trends, which were taken to reflect Cr(VI) concentrations. In the rest of this report, when Cr(VI) concentrations are mentioned, they actually reflect total chromium concentration measurements. Additionally, field parameters (temperature, dissolved oxygen [DO], oxidation-reduction potential [ORP], pH, specific conductance, and turbidity) were measured at the wellheads each day using a YSI, Inc., multiprobe system. Only two days of wellhead sampling during pumping were missed at both wells (August 24, 2021, the day pumping started, which was intentional, and August 27, 2021, the day that pumping was resumed after the unplanned interruption).

Figures 1 and 2 show the pumping rate and water-level histories at R-42 and R-28, respectively, during the extended purges. It is apparent that the pumping flow rate at R-42 slowly decreased during the purging, whereas the pumping rate remained relatively constant at R-28. The decrease at R-42 is believed to be mainly a result of increasing backpressure at the surface due to the slow clogging of an in-line filter; however, there was also evidence that the aquifer permeability near the well decreased somewhat during the purge as discussed below. Figures 3 and 4 show the specific capacities (gallons per minute [gpm]/ft of drawdown) in R-42 and R-28, respectively, dating back to before the amendments were deployed, with the last four points estimated from flow and drawdown data during the 2021 extended purges (the extended purge data are shown in more detail in the lower plots in each figure). The specific capacities during the extended purges were estimated by dividing the pump flow rates by the water-level changes after pumping commenced on August 24, 2021; August 27, 2021; and September 7, 2021 (R-42) and on September 8, 2021 (R-28), and also after pumping ceased on September 21, 2021 (R-28) and on September 22, 2021 (R-42). The water-level changes used for estimating specific capacities were considered accurate to within about $\pm10\%$, as the water levels were not corrected for barometric fluctuations or diurnal cycles, so there was no rigorous determination of when drawdowns or recoveries had stabilized (although previous measurements suggested that water levels stabilize quite rapidly in R-42 and R-28 at the low flow rates of the extended purges). It is apparent from Figures 3 and 4 that the late 2020 redevelopments resulted in significant increases in the specific capacity in both wells. While the relative decrease in specific capacity during the 2021 extended purges was greater in R-42 than in R-28, by the end of the purging the specific capacity of R-42 was only slightly lower than its pre-amendment value, whereas it was less than half of its pre-amendment value in R-28. However, the absolute specific capacity of R-28 at the end of the purging was still about 5 times greater than that of R-42 because the pre-amendment specific capacity of R-28 was about 10 times greater than pre-amendment specific capacity of R-42. At the end of purging, the flowmeter totalizers at the wellheads indicated that 104,463 gal. had been pumped from R-42 during the purge, and 129,093 gal. had been pumped from R-28.
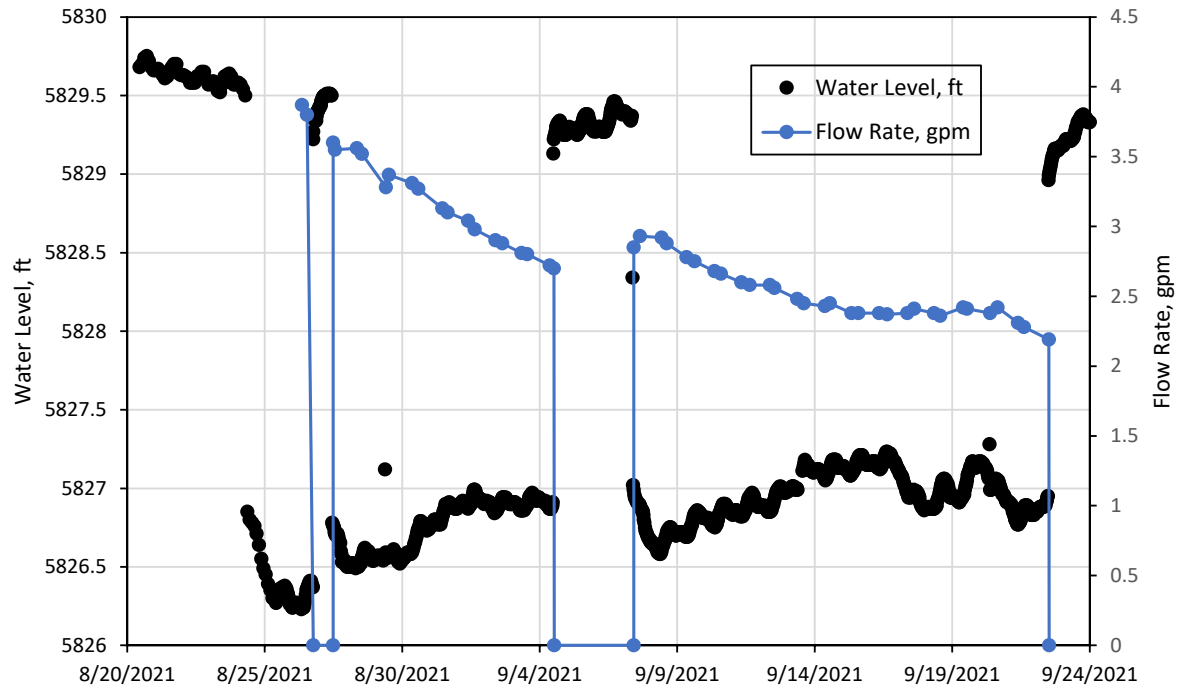
Figure 1   Pumping rate and water-level history for R-42 during 2021 extended purge. Note that flow-rate measurements were not recorded until August 26, 2021.
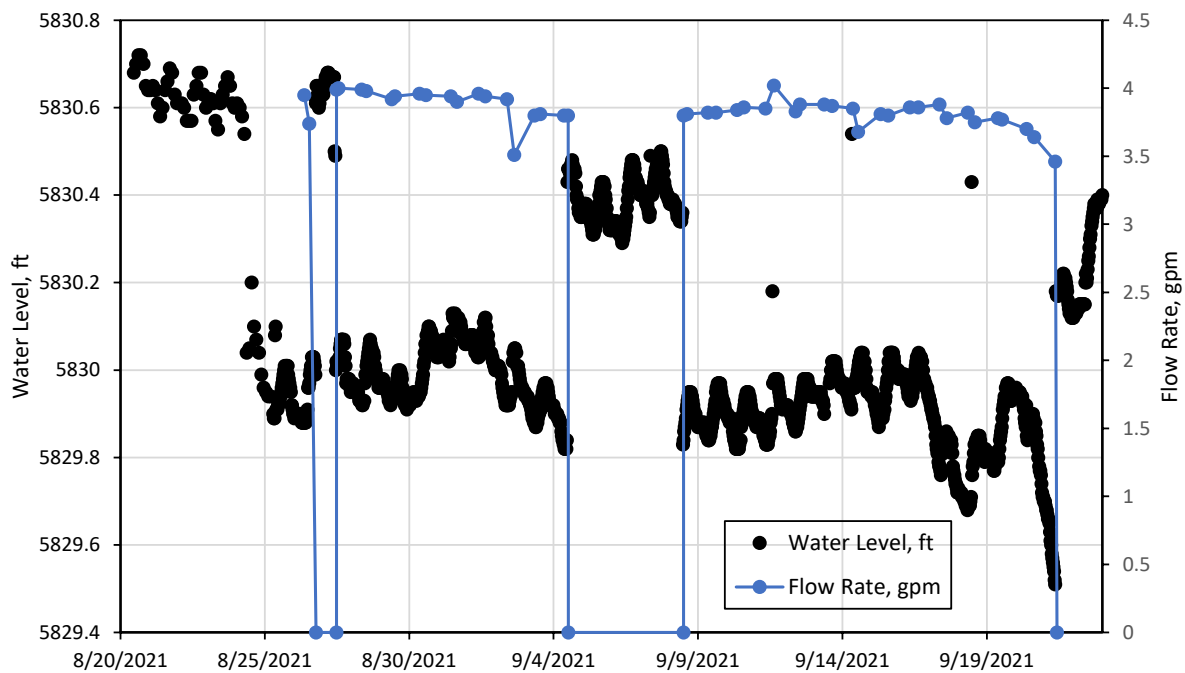

Figure 2   Pumping rate and water-level history for R-28 during 2021 extended purge. Note that flow-rate measurements were not recorded until August 26, 2021.
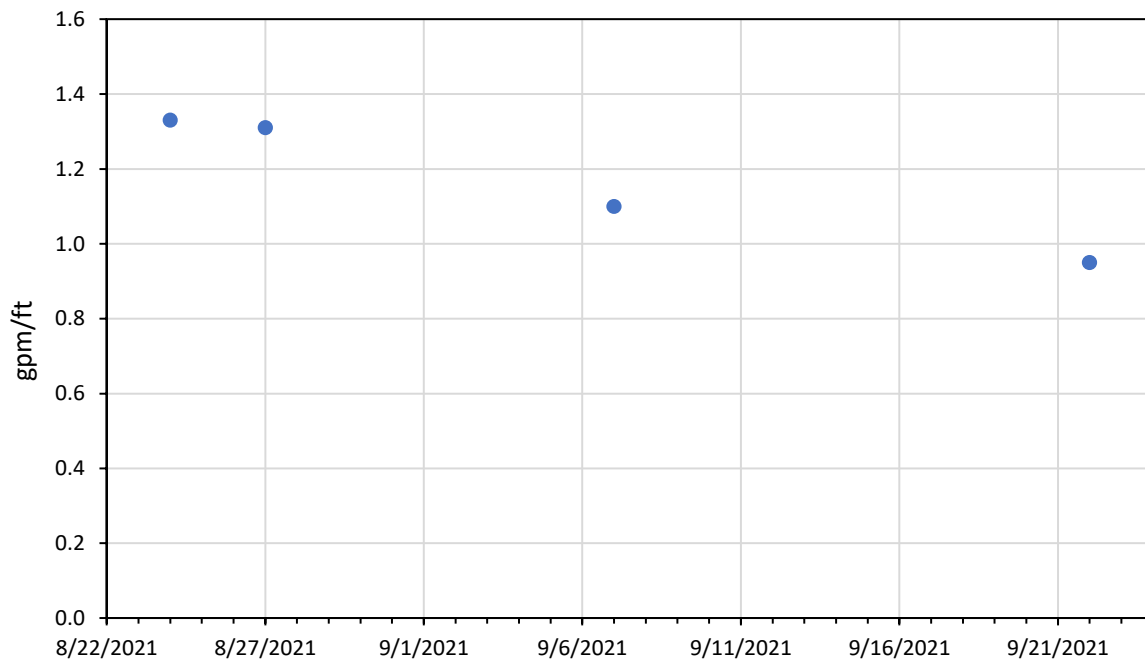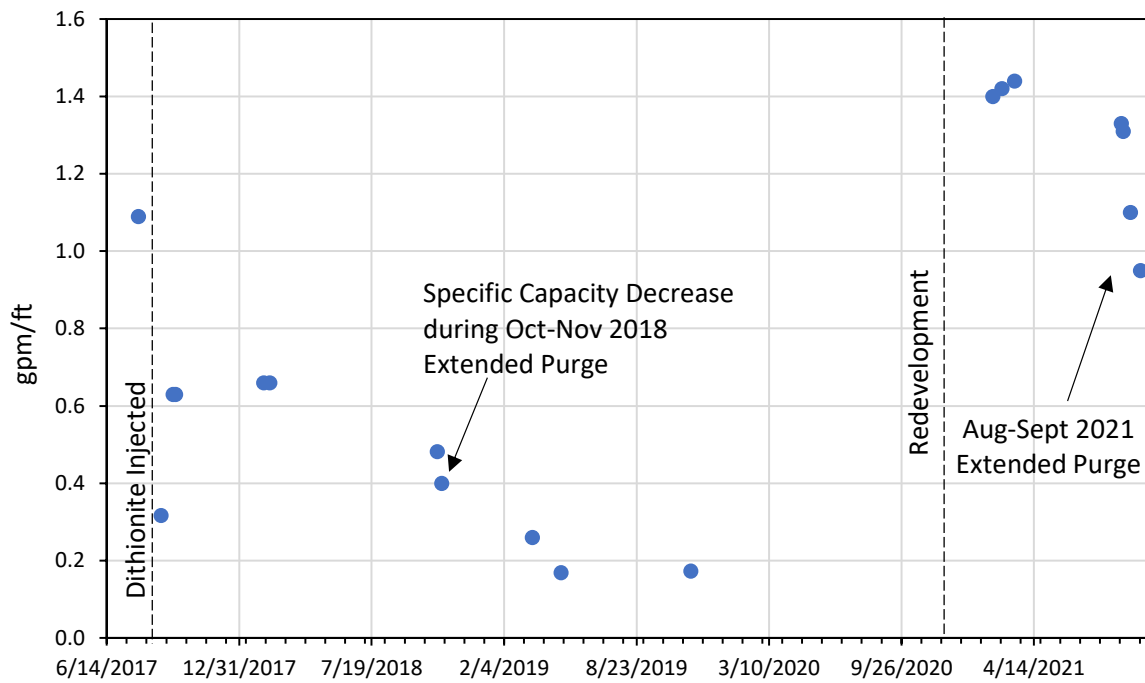
Figure 3 Estimated specific capacities of R-42 at various times from before the dithionite deployment to the end of the 2021 extended purge (upper plot) and during the extended purge only (lower plot).
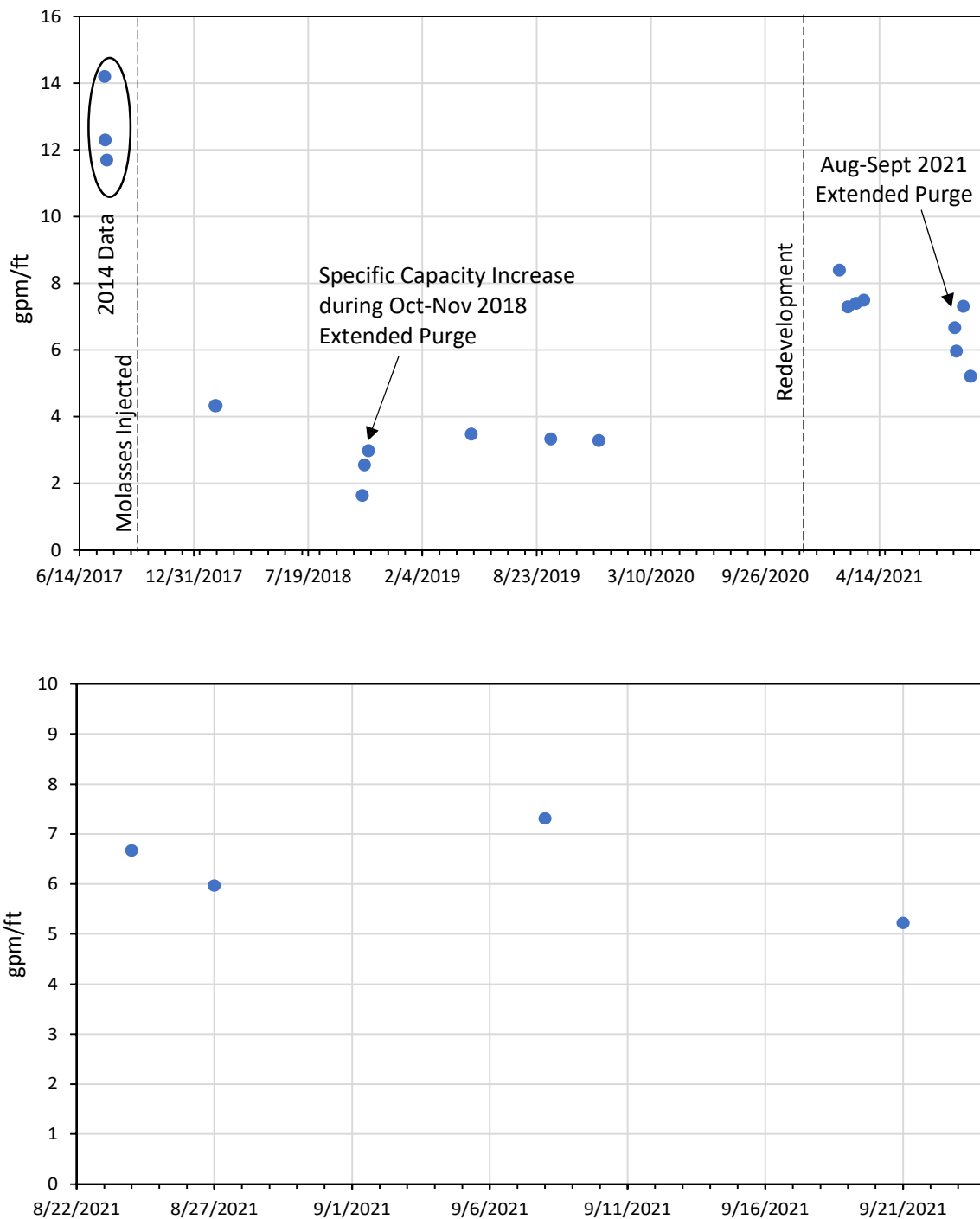
Figure 4   Estimated specific capacities of R-28 at various times from before the molasses deployment to the end of the 2021 extended purge (upper plot) and during the extended purge only (lower plot).

3.0 GEOCHEMICAL TRENDS DURING EXTENDED PURGING

Trends in key anions, redox-sensitive metals or cations, and selected field parameters for R-42 are shown in Figures 5, 6, and 7, respectively. In each figure, the upper plot of the figure shows trends since the fall of 2019, before the redevelopment of R-42, and the lower plot shows the trends during the 2021 extended purge only, including the samples collected on October 5, 2021, and October 12, 2021 (after 50 and 300 gal. pumped each day). The parameters selected for plotting are deemed to be the most important ones for evaluating how effective the extended purge was in restoring the wells to pre-amendment conditions.

Plots analogous to Figures 5, 6, and 7 are provided for R-28 in Figures 8, 9, and 10, with the main difference from the R-42 figures being that total organic carbon (TOC) is included in the anion plots (Figure 8) and potassium is included in the metal/cation plots (Figure 9). Also, there were no additional samples collected at R-28 on October 5, 2021, and October 12, 2021, as there were at R-42. TOC and potassium are of interest for R-28 because TOC was extremely high in the molasses amendment solution, and potassium was the primary cation in the molasses amendment solution.

Figures 5 through 10 each contain horizontal bars on the y-axis that match the colors of the plotted data points; these bars indicate the pre-amendment concentrations/values of the parameters plotted with that corresponding color. Some of the trends in the figures are muted by the log y axes, so lines connecting the data points are provided to help in visualizing increasing or decreasing trends.
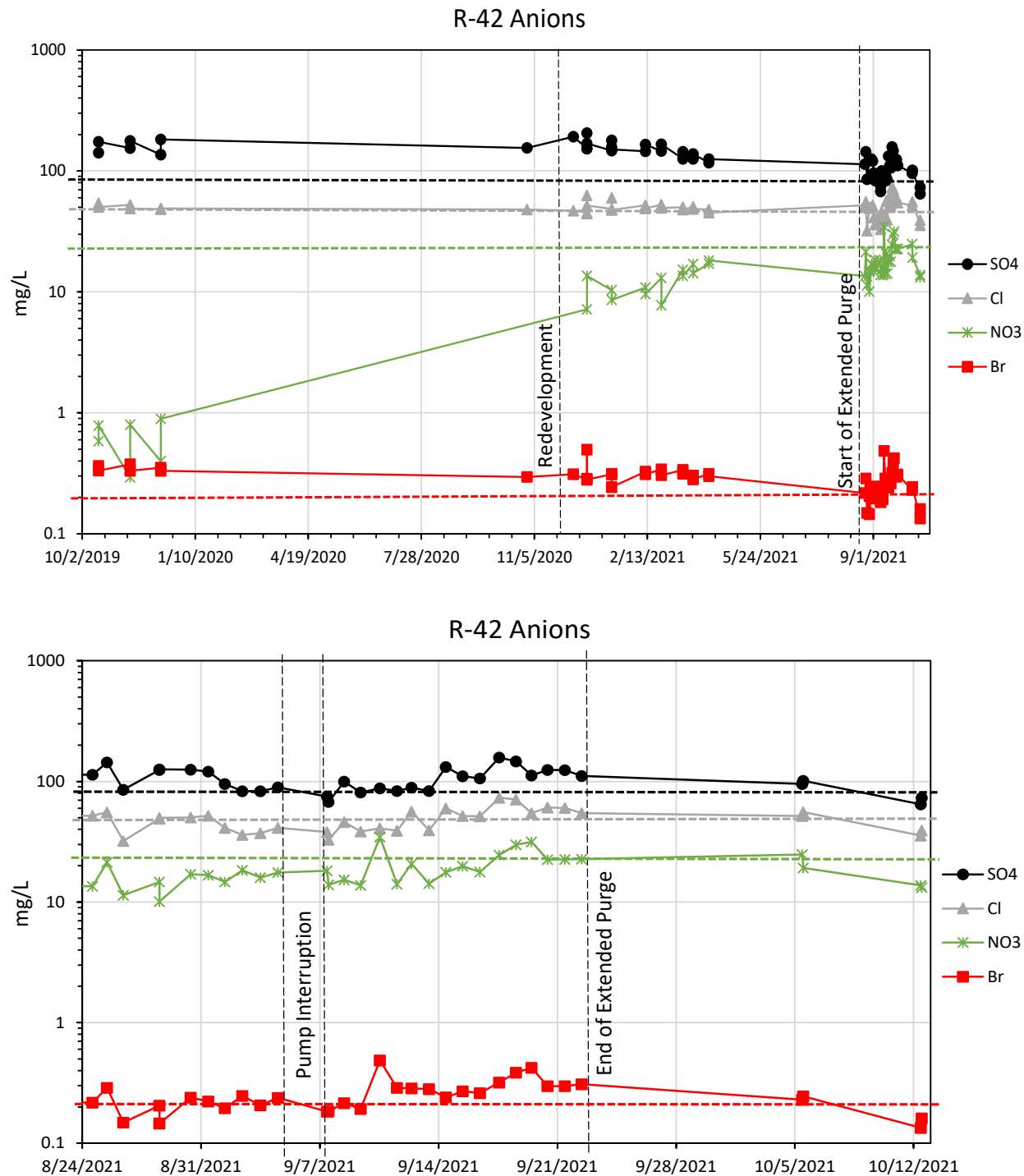
Figure 5 Concentration trends of selected anions in R-42 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Results from 10/5/2021 and 10/12/2021 samples are shown in both plots. Horizontal dashed lines indicate approximate pre-amendment concentrations of constituents with the same color symbols. Note that bromide was used as a tracer in the amendment solution.
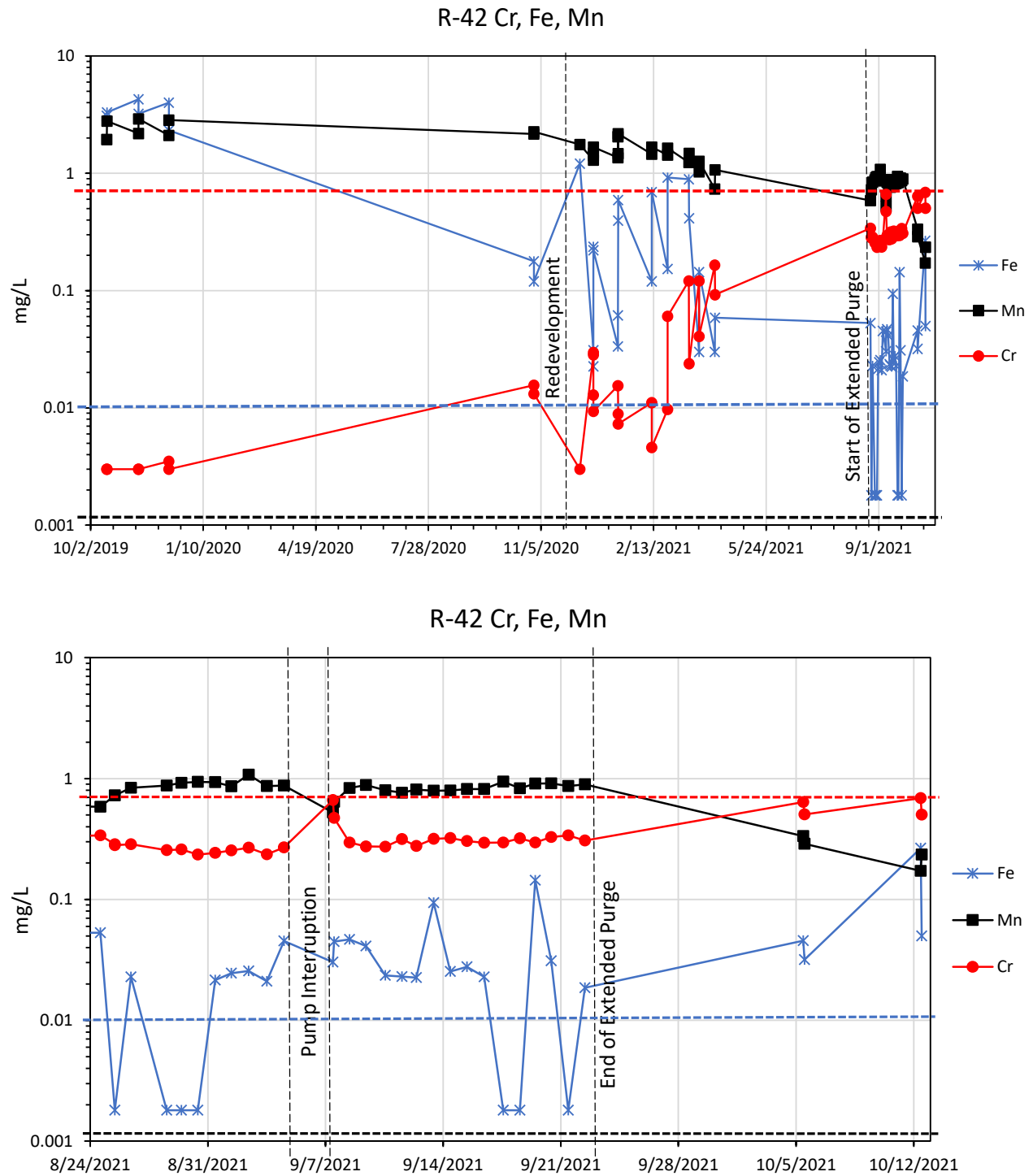
Figure 6 Concentration trends of iron, manganese, and chromium in R-42 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Results from 10/5/2021 and 10/12/2021 samples are shown in both plots. Horizontal dashed lines indicate approximate pre-amendment concentrations of constituents with the same color symbols.
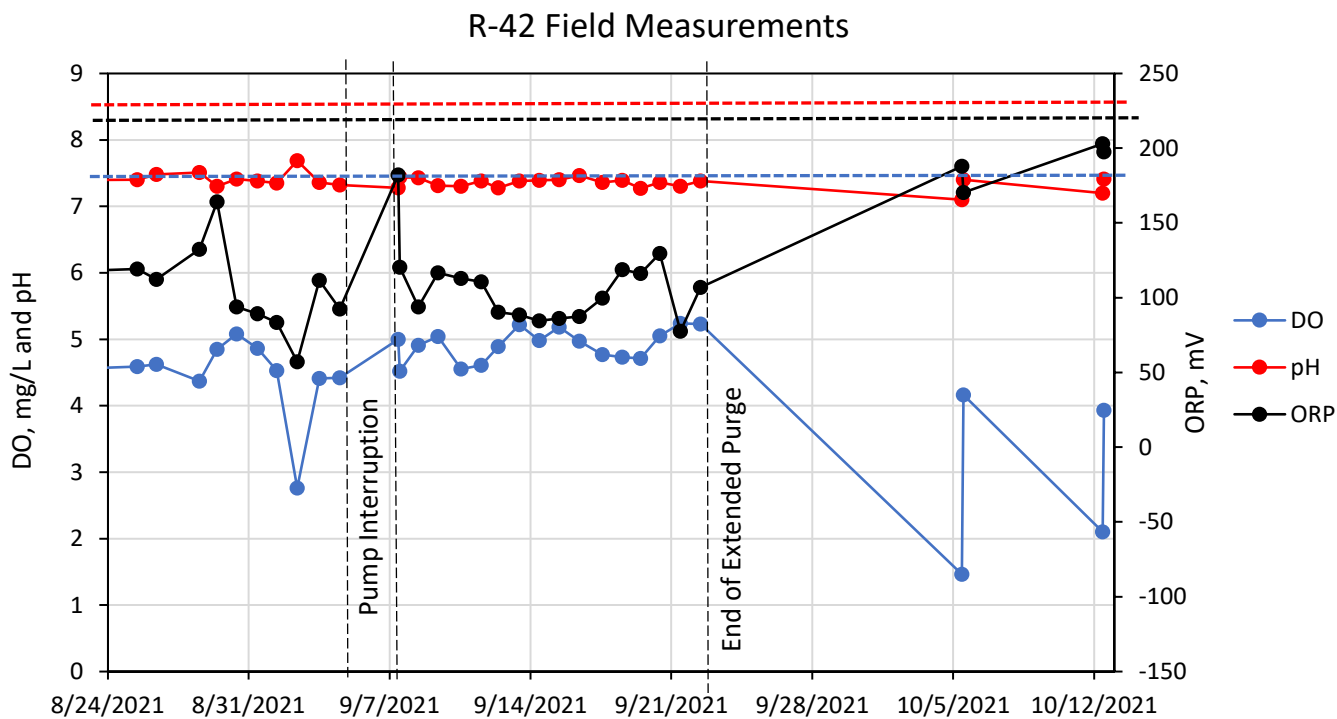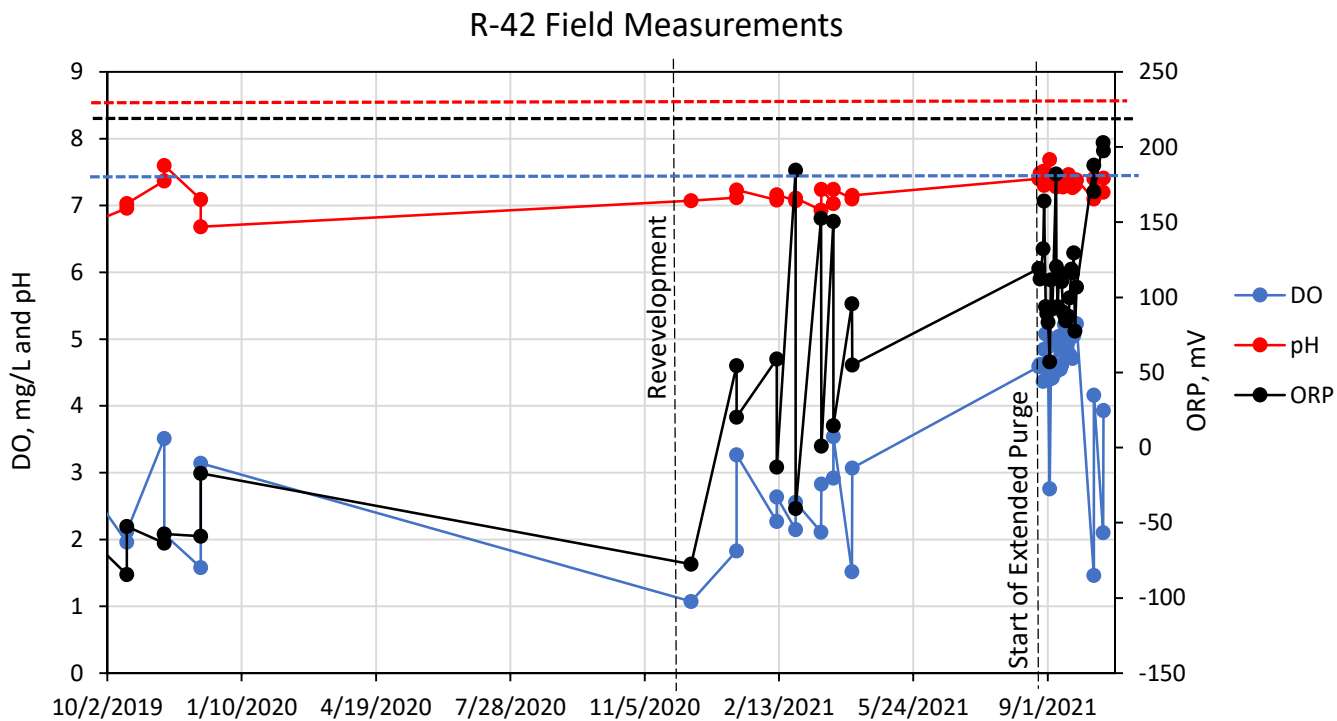
Figure 7 Field measurements of pH, DO, and ORP in R-42 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Results from 10/5/2021 and 10/12/2021 are shown in both plots. Horizontal dashed lines indicate approximate pre-amendment values of parameters with the same color symbols.
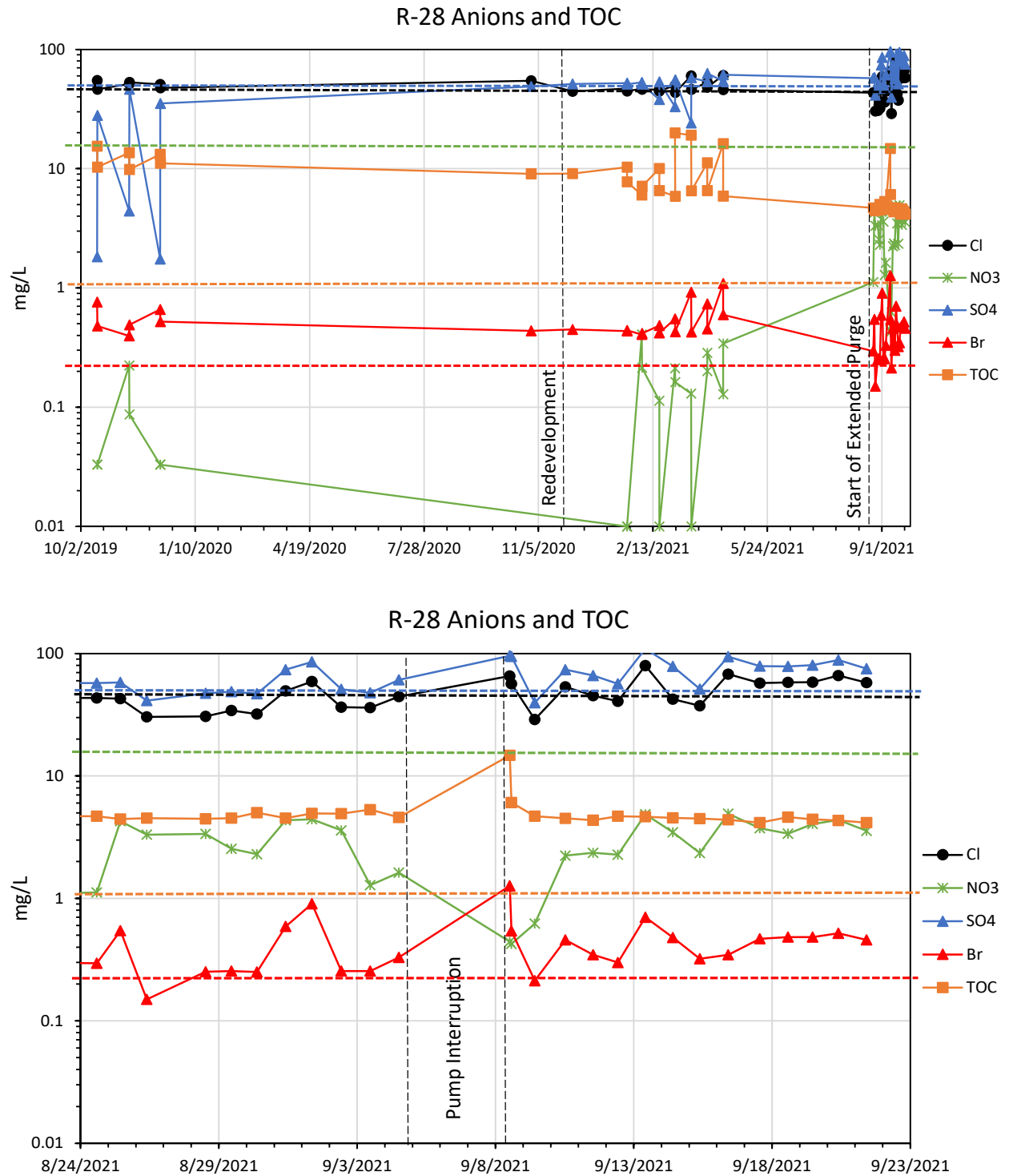
Figure 8   Concentration trends of selected anions and TOC in R-28 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Horizontal dashed lines indicate approximate pre-amendment concentrations of constituents with the same color symbols. Note that bromide was used as a tracer in the amendment solution.
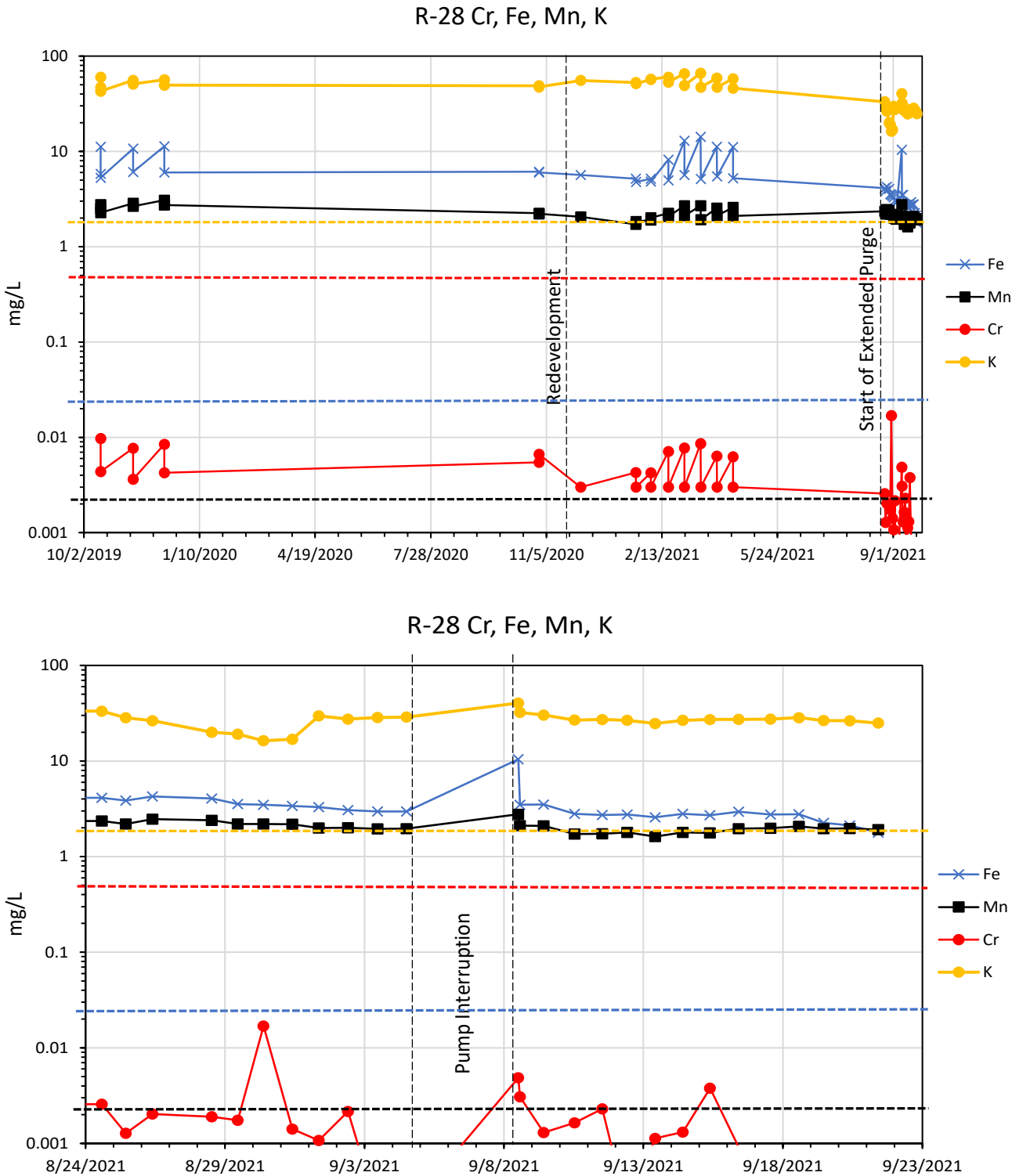
Figure 9 Concentration trends of iron, manganese, chromium, and potassium in R-28 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Horizontal dashed lines indicate approximate pre-amendment concentrations of constituents with the same color symbols.
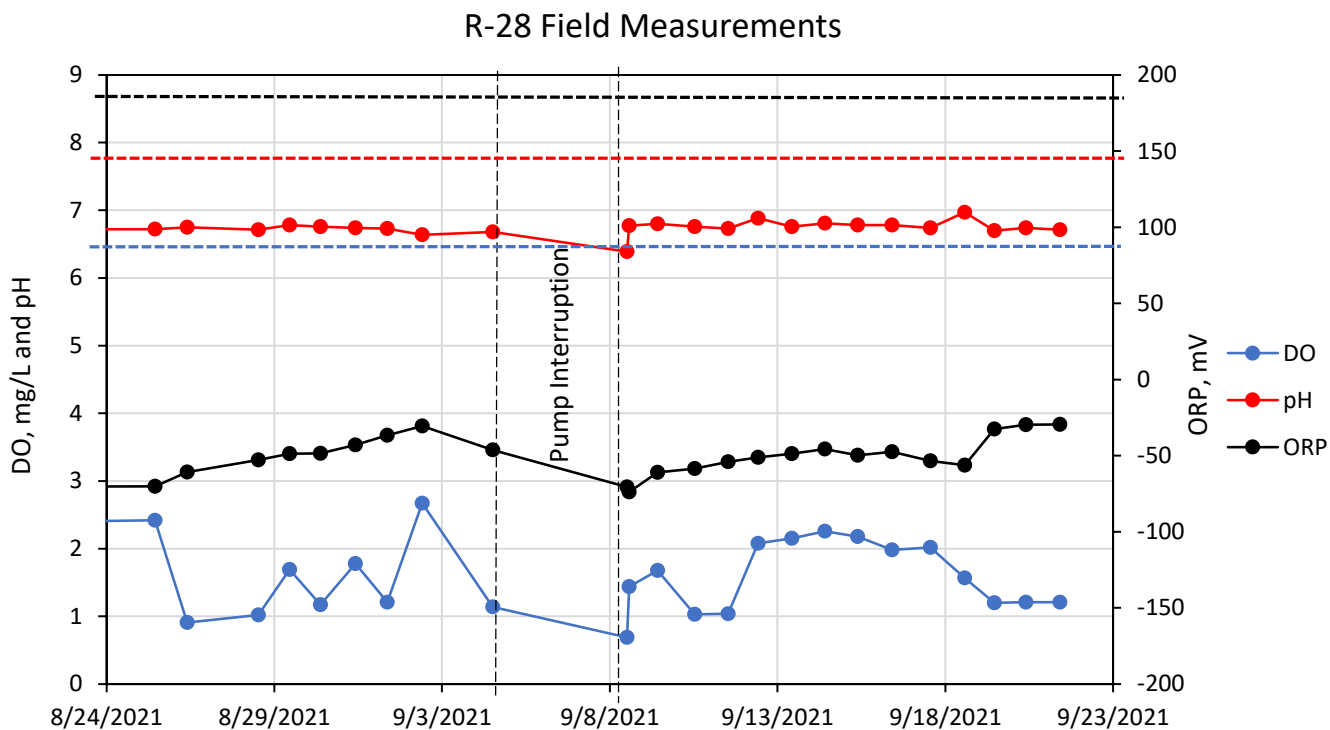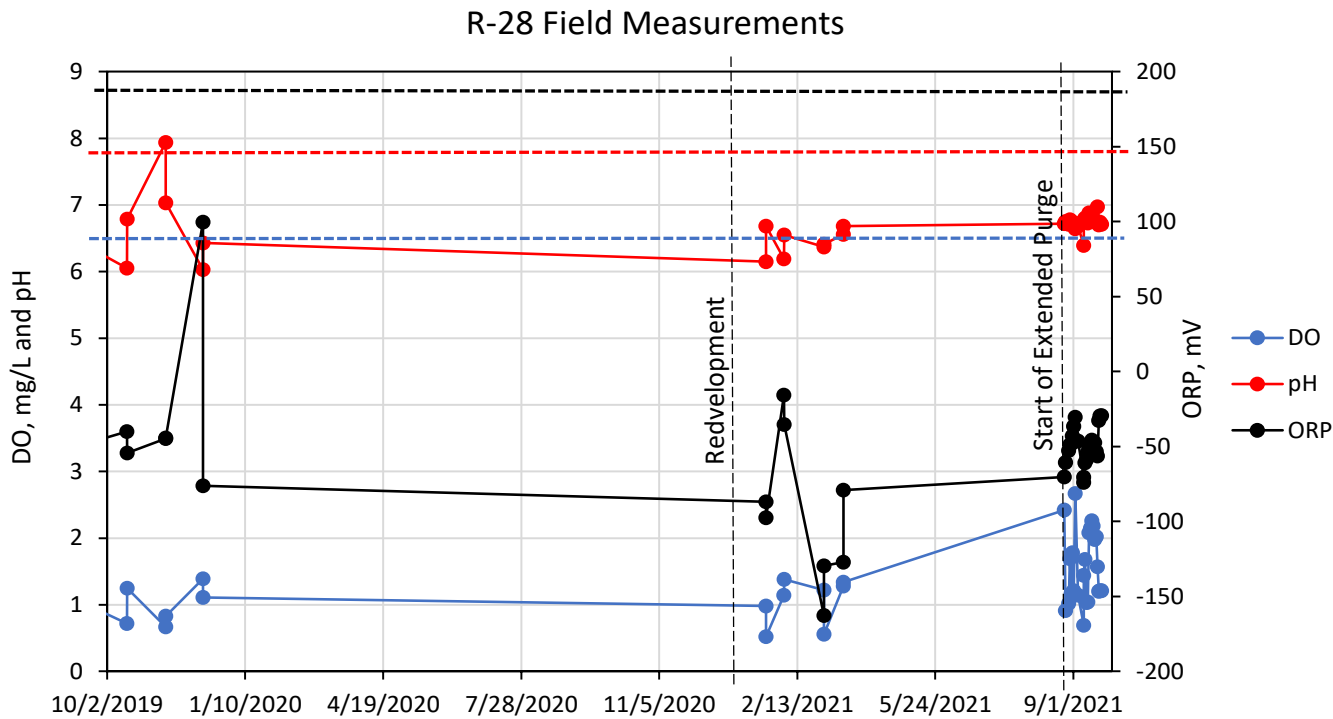
Figure 10 Field measurements of pH, DO, and ORP in R-28 from the fall of 2019 to the end of the extended purge (upper plot) and during the extended purge only (lower plot). Horizontal dashed lines indicate approximate pre-amendment values of parameters with the same color symbols.

4.0   DISCUSSION OF GEOCHEMICAL TRENDS AND IMPLICATIONS FOR USE OF R-42 AND R-28 AS MONITORING WELLS

R-42

The geochemical trends in R-42 indicate that the reduction capacity induced by the 2017 dithionite deployment has eroded significantly since the fall of 2019, and R-42 is now much closer to reflecting pre-amendment geochemical conditions. Some redox-sensitive parameters, such as nitrate and iron, are essentially back to their pre-amendment concentrations. Also, sulfate, which had been highly elevated for most of the time since the dithionite deployment, has decreased nearly to its pre-amendment concentration. This is important because much of the remaining reduction capacity near R-42 is likely attributable to reduced sulfur species, including iron and manganese sulfides, so the fact that sulfate is now near its pre-amendment concentration suggests that these reduced sulfur species are mostly oxidized. Manganese remains the most elevated redox-sensitive constituent relative to its pre-amendment concentration, but this is not surprising because manganese is known to be quite slow to oxidize in the presence of DO and the absence of significant microbial activity (Morgan, 2005). Much of the persistent manganese might currently be coming from desorption of Mn^{2+} from cation exchange sites. However, there might also be a contribution from the oxidation of sulfide in manganese-sulfide precipitates, which then effectively mobilizes the Mn^{2+}. The same thing is likely happening to Fe^{2+}, but Fe^{2+} oxidizes much more rapidly in the presence of DO than Mn^{2+}, so it quickly converts to Fe^{3+} and precipitates as $Fe(OH)_3$ (Langmuir, 1997). The pH, ORP, and DO field parameters are still all lower than their pre-amendment values, but they have exhibited increasing trends, and ORP and DO are now basically consistent with pre-amendment values in terms of what oxidation states would be predicted to be dominant for most redox-sensitive elements. The pH field parameter may be lagging below pre-amendment values in part because of oxidation of residual sulfides or other reduced sulfur species, which generates protons and produces sulfate (SO_4^{2-}). (Sulfate still remains slightly elevated relative to pre-amendment concentrations.) The pH may also be lagging in part because of hydrolysis of Fe^{3+} to $Fe(OH)_3$, which occurs quickly after Fe^{2+} oxidizes to Fe^{3+}. However, note that the pre-amendment pH at R-42 was probably still artificially high from the lingering effects of a 2016 alkaline water injection that was conducted to promote desorption of hexavalent chromium from aquifer sediments.

Most importantly, Cr(VI) concentrations consistently remained at approximately half their pre-amendment values during the extended purge at R-42. However, immediately after the planned pumping interruption of 3 days on September 7, 2021, the first sample collected (after 50 gal. of pumping) had a Cr(VI) concentration of 663 μg/L, which is very close to the pre-amendment concentration of about 700 μg/L. Manganese was correspondingly lower in this sample as well, and both ORP and DO were higher, indicating that the water initially pumped from the well after the 3-day pause was more oxidized than what was being drawn from the well during sustained pumping before the pause. By the next day, concentrations of all constituents had effectively reverted to their values before the pumping interruption.

The interpretation of the observations at R-42, particularly in light of the perturbations after the planned pumping interruption, are discussed in this and the next paragraph. During sustained pumping, the water being drawn into the well is likely a mixture of (1) fully oxidized aquifer water that reflects geochemical conditions outside the zone of influence of dithionite and (2) water that still has a reducing signature from the dithionite deployment. Conceptually, these waters are likely being contributed from different stratigraphic layers of different permeabilities, some of which have had all their reduction capacity exhausted and some of which have not. However, it is also possible that during pumping, the oxidized water is coming predominantly from a location upgradient of the well, while the reduced water is being drawn from a downgradient location. Conditions would be expected to remain reducing longer at downgradient than upgradient locations because oxidants were naturally flowing from upgradient to

downgradient locations during the vast majority of the time the well was not pumped. Either way, the Cr(VI) concentrations are likely being suppressed relative to pre-amendment concentrations because Cr(VI) is much lower in the reduced waters, and it is also possible that some Fe^{2+} from the reduced water is reacting with Cr(VI) in the oxidized water when the waters are mixed in the well. The Fe^{2+} reduction of Cr(VI) is very rapid (Eary and Rai, 1988, 1989; Fendorf and Li, 1996) and could potentially occur before the mixed waters are sampled at the surface. Given that Fe^{2+} concentrations are essentially at their pre-amendment concentrations in R-42, it is possible that the total equivalents per unit time of Cr(VI) entering the well during pumping exceed the total equivalents per unit time of Fe^{2+}, resulting in almost complete depletion of any Fe^{2+} entering the well, with the excess Cr(VI) being reflected in samples collected at the surface. If this is true, then total chromium concentration measurements at the wellhead may actually provide a better indication of Cr(VI) concentrations *entering the well* than Cr(VI) measurements.

Importantly, the results after the planned pumping interruption [i.e., Cr(VI) concentrations essentially matching pre-amendment concentrations] suggest that the water initially sampled from R-42 after the interruption did not reflect the influence of reduced waters that are drawn into the well during sustained pumping. This makes sense if most of the groundwater naturally flowing through the well is coming from higher permeability layers that are already oxidized, and it also makes sense (perhaps even more so) if reducing waters are coming mostly from locations downgradient of the well during pumping. The implication is that samples collected from R-42 using typical monitoring well protocols of sampling after one to three casing volumes may reflect Cr(VI) concentrations that are representative of the aquifer near R-42 outside the dithionite-affected zone. That is, R-42 may be restored to the point where it provides representative Cr(VI) concentrations provided the well is not pumped for an extended period before sampling. The results from the R-42 samples collected on October 5, 2021, and October 12, 2021, 13 and 20 days, respectively, after the end of the extended purge, seem to verify this. Chromium concentrations in the 50-gal. samples on these dates were 638 and 689 μg/L, respectively, and they were 505 and 504 μg/L, respectively, in the 300-gal. samples.

Figure 11 shows pre-amendment chromium concentrations in R-42 along with an extrapolation of an apparent trend that removes the influence of several perturbations from 2013 through 2016 that resulted from extended pumping (2013), and tracer and alkaline water injections (2014 and 2016, respectively). The chromium concentrations measured in the samples collected after the planned pumping interruption during the extended purge, and after the extended purge on October 5, 2021, and October 12, 2021, are also shown in Figure 11 as the red symbols. The 2013 to 2016 R-42 activities make the pre-amendment chromium trend somewhat uncertain, but nevertheless, the extrapolation shown in Figure 11 suggests that chromium concentrations, had the dithionite injection not occurred, should have dropped to below 600 μg/L by now, which is in relatively good agreement with the 2021 data points shown in red. Whether or not the extrapolated trend after the amendment deployment would have continued as shown in Figure 11, given the influence of the interim measure and uncertainties in how the plume would have evolved naturally, is impossible to determine. However, Figure 11 certainly shows that the chromium concentrations now being observed, after extraction volumes typically associated with routine monitoring, are plausibly reflecting concentrations near R-42 outside the zone of influence of the dithionite injection.
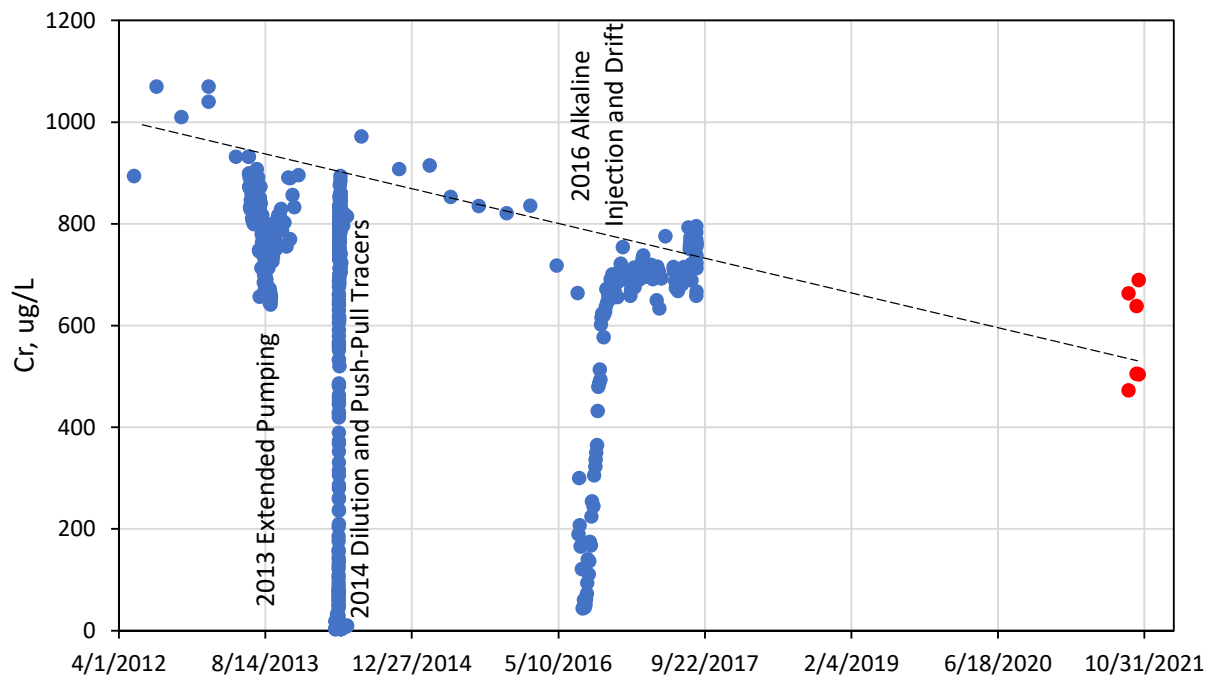
Figure 11 **Chromium concentrations in R-42 before the dithionite amendment deployment in August 2017 (blue symbols), and in samples collected in 2021 after the planned pumping interruption during the extended purge and 13 and 20 days after the end of the extended purge (red symbols). The dashed line is an arbitrary extrapolation of the pre-amendment trend after removing the influence of the field activities noted in the plot.**

Of course, even if Cr(VI) concentrations reflect pre-amendment levels in these recent R-42 samples, it is apparent (Figures 6 and 7) that there are still constituents, most notably manganese, that will likely not reflect pre-amendment concentrations for quite some time. Given that Cr(VI) is the primary constituent of concern in the chromium plume, this is considered an acceptable compromise for re-establishing R-42 as a monitoring location for evaluating Cr(VI) trends, including responses to interim measure operations. Monitoring persistent elevated concentrations of manganese in R-42 might even prove beneficial for validating predictions of manganese fate and transport coming out of the anticipated iron and manganese modeling exercise (N3B 2021).

Elevated Mn^{2+} concentrations should not be a concern with respect to representativeness of Cr(VI) concentrations. Unlike Fe^{2+}, which has both a thermodynamic and kinetic predisposition to reduce Cr(VI) (Eary and Rai, 1988, 1989; Fendorf and Li, 1996; Langmuir, 1997), Cr(VI) reduction by Mn^{2+} is neither thermodynamically nor kinetically favorable. The appendix provides some thermodynamic calculations showing that Mn^{2+} is not predicted to reduce Cr(VI). Mu et al. (2018) recently experimentally verified this and showed that Cr(VI) reduction in the presence of Mn^{2+} occurs only when an organic acid is also present (they studied oxalic acid), in which case Mn^{2+} acts as a catalyst for reduction, not as an electron donor.

The fact that the specific capacity of R-42 was close to its pre-amendment value after the extended purge (though somewhat decreased from its post-redevelopment value) suggests that the well was not hydraulically compromised by the purging and that flow bypassing of the well is not a significant concern.

However, specific capacity should be monitored during future sampling to ensure that hydraulic conditions do not significantly deteriorate, leading to questions of data representativeness.

R-28

The geochemical trends in R-28 indicate that neither the redevelopment nor the extended purge had much effect on the reducing conditions induced by the 2017 molasses deployment. Although the purge undoubtedly accelerated the exhaustion of reduction capacity in the vicinity of R-28, it did not come close to restoring the well to pre-amendment geochemical conditions. The most promising results were a significant increase in nitrate concentrations during the extended purge relative to post-redevelopment conditions and a slight uptick in DO concentrations during the extended purge. Other than that, all parameters remained essentially unchanged or only very slowly changing. Also, after the planned pumping interruption, it appeared that conditions in the well became more reducing, with decreases in ORP and DO and increases in TOC, iron, and manganese relative to before the interruption. Chromium concentrations remained very close to background, with no apparent trend upward. These observations have led to the conclusion that R-28 cannot be restored in a reasonable timeframe and that a new monitoring well should be installed in the vicinity of R-28.

Geochemically, the conditions in R-28 undoubtedly reflect the active influence of biomass generated as a result of the molasses injection, which have led to strongly reducing conditions because of the electron-donating characteristics of the biomass. However, at this point, a significant fraction of the remaining reduction capacity may be attributable to reduced species like Fe^{2+}, Mn^{2+}, and reduced sulfur that were generated by microbial processes and remain near the well. Most of the TOC that remains in the vicinity of R-28 is likely being produced by microbial processes, including the degradation of biomass, rather than being residual molasses or its direct degradation products. The increase in TOC and the strengthening of reducing conditions in the well during the planned pumping interruption suggest that biomass may have been accumulating in the filter pack and screen of the well during purging, and when the pumping stopped the influence of the biomass increased. However, it is also possible that TOC and reducing conditions were slightly depressed during pumping because the pumping established an altered steady-state balance between production and withdrawal of reducing constituents that favored withdrawal relative to unpumped conditions. The persistence of potassium as a dominant cation in water pumped from R-28 is likely due to the strong cation exchange characteristics of potassium, which have retarded its migration away from the well (in contrast, conservative anions present in the molasses solution, such as chloride and bromide, the latter of which was introduced as a tracer, have long since departed).

5.0   SUMMARY OF FINDINGS AND RECOMMENDATIONS

The data from R-42 indicate a likelihood that representative chromium concentrations from the centroid of the plume are currently being measured at R-42 in samples collected after relatively small volumes are pumped. Although some constituents, most notably manganese, have not fully returned to pre-amendment concentrations, none of these appear to be adversely affecting the representativeness of chromium data. Monthly sampling using the standard groundwater monitoring well sampling protocol will be conducted for 9 months at R-42 to assess longer-term trends and potential rebound back to more reducing conditions. Additionally, a dilution tracer test will be conducted during the same 9-month sampling period to collect data on hydraulic conditions in the aquifer near R-42. These additional data will provide further insight into the conditions surrounding R-42 and inform the appropriate path forward with respect to the need for an additional monitoring well in the vicinity of R-42.

R-28 is unlikely to provide representative data in the near term, so the recommendation is to install a new monitoring well in the vicinity of R-28. The specific location and objective, including the general design

concept, will be provided in a separate drilling work plan. Periodic sample collection from R-28 may take place on a quarterly basis to continue to track geochemical evolution in the aquifer around R-28.

The extraction well, CrEX-3, underwent rehabilitation beginning in December 2020 and was completed in January 2021. It is currently integrated into the set of extraction wells operating for the interim measure. No additional rehabilitation is anticipated or necessary at this time.

6.0   REFERENCES

Eary, L. E., and D. Rai, "Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion," *Environ.Sci. Technol,.* **22**, pp. 972–977, 1988. (Eary and Rai, 1988)

Eary, L. E., and D. Rai, "Kinetics of Chromate Reduction by Ferrous Ions Derived from Hematite and Biotite at 25°C," *Am. J. Sci,.* **289**, pp. 180–213, 1989. (Eary and Rai, 1989)

Fendorf, S. E., and G. Li, "Kinetics of Chromate Reduction by Ferrous Iron," *Environ. Sci. Technol.,* **30**, pp. 1614–1617, 1996. (Fendorf and Li, 1996)

Langmuir, D., *Aqueous Environmental Geochemistry*, Prentice-Hall, Upper Saddle River, NJ, 1997. (Langmuir, 1997)

LANL (Los Alamos National Laboratory), July 2017. "Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-17-25406, Los Alamos, New Mexico. (LANL 2017)

LANL (Los Alamos National Laboratory), January 2018. "Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-18-20467, Los Alamos, New Mexico. (LANL 2018a)

LANL (Los Alamos National Laboratory), April 2018. "Second Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Los Alamos National Laboratory document LA-UR-18-23418, Los Alamos, New Mexico. (LANL 2018b)

Morgan, J.J., "Kinetics of Reaction between O_2 and Mn(II) Species in Aqueous Solution," *Geochimica et Cosmochimica Acta*, **69**(1), pp. 35–48, 2005. (Morgan, 2005)

Mu, Y., X. Jiang, Z. Ai, F. Jia, and L. Zhang, "Mn^{2+} Promoted Cr(VI) Reduction with Oxalic Acid: The indispensable role of in-situ generated Mn^{3+}," *J. Hazard. Mater.*, **343**, pp. 356–363, 2018. (Mu et al. 2018)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), July 2018. "Third Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2018-0019, Los Alamos, New Mexico. (N3B 2018a)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), October 2018. "Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2018-0069, Los Alamos, New Mexico. (N3B 2018b)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), January 2019. "Fifth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2019-0011, Los Alamos, New Mexico. (N3B 2019a)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), April 2019. "Sixth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2019-0133, Los Alamos, New Mexico. (N3B 2019b)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), December 2019. "Seventh Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon, April to September 2019," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2019-0427, Los Alamos, New Mexico. (N3B 2019c)
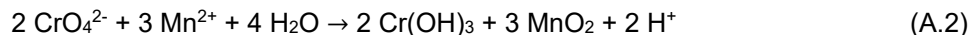
N3B (Newport News Nuclear BWXT-Los Alamos, LLC), June 2020. "Eighth Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon, October 2019 to March 2020," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2020-0253, Los Alamos, New Mexico. (N3B 2020)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), September 2021. "Work Plan for Groundwater Modeling for Contaminant Migration from Wells R-42 and R-28, Revision 1," Newport News Nuclear BWXT-Los Alamos, LLC, document EM2021-0570, Los Alamos, New Mexico. (N3B 2021)

NMED (New Mexico Environment Department), July 31, 2017. "Approval, Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon," New Mexico Environment Department letter to D. Hintze (DOE-EM) and B. Robinson (LANL) from J.E. Kieling (NMED-HWB), Santa Fe, New Mexico. (NMED 2017)

Appendix: Thermodynamic Calculations Showing the Inability of Mn²⁺ to Reduce Cr(VI) at R-42

The following reactions can be written to describe the reduction of Cr(VI) by Mn²⁺:

$$2 \; CrO_4^{2-} + 3 \; Mn^{2+} + 4 \; H^+ \rightarrow 2 \; Cr^{3+} + 3 \; MnO_2 + 2 \; H_2O \qquad \text{(A.1)}$$

$$2 \; CrO_4^{2-} + 3 \; Mn^{2+} + 4 \; H_2O \rightarrow 2 \; Cr(OH)_3 + 3 \; MnO_2 + 2 \; H^+ \qquad \text{(A.2)}$$

Using free energies of formation taken from literature sources (Table A-1), equilibrium constants can be estimated for these reactions from (Langmuir, 1997):

$$\Delta G^o_{reaction} = \Sigma_{products} \, aG^o_f - \Sigma_{reactants} \, aG^o_f = -RTlnK_{eq} \qquad \text{(A.3)}$$

where, *a* is the stoichiometric coefficient of the product or reactant in the reaction expression (e.g., 3 for Mn²⁺ in both reactions), *R* is the universal gas constant, and *T* is absolute temperate. Assuming activity coefficients of 1 for all species, the equilibrium constant expressions for reactions A.1 and A.2, respectively, are

$$K_{eq} = \frac{[Cr^{3+}]^2}{[CrO_4^{2-}]^2[Mn^{2+}]^3[H^+]^4} \text{ for reaction A.1} \qquad \text{(A.4)}$$

$$K_{eq} = \frac{[H^+]^2}{[CrO_4^{2-}]^2[Mn^{2+}]^3} \text{ for reaction A.2} \qquad \text{(A.5)}$$

where, [x] designates a molar concentration for species x, $Cr(OH)_3$ and MnO_2 are assumed to be solid precipitates with unit activity, and H_2O is also assumed to have unit activity.

Inserting the free energies of formation from Table A-1 into eq. A.3 for both reactions and solving for K_{eq} yields equilibrium constants at 25°C of 2.3×10^{26} and 344.6 for reactions A.1 and A.2, respectively. Ignoring activity coefficients, and assuming a pH of 7 ($[H^+] = 10^{-7}$ M) and a Mn²⁺ concentration of 1 mg/L or 1.8×10^{-5} M, we can estimate a $[Cr^{3+}]/[CrO_4^{2-}]$ ratio from the equilibrium expression for reaction A.1 (eq. A.4), and we can estimate an equilibrium CrO_4^{2-} concentration from the equilibrium expression for reaction A.2 (eq. A.5). The results are 1.2×10^{-8} for the $[Cr^{3+}]/[CrO_4^{2-}]$ ratio from reaction A.1 and 0.07 M or 3680 mg/L for the equilibrium CrO_4^{2-} concentration from reaction A.2. Both results indicate that Mn²⁺ is not predicted to appreciably reduce Cr(VI) at the prevailing pH and Mn²⁺ concentrations observed in R-42. Similar predictions can be obtained using geochemical models, such as PHREEQC (Parkhurst and Appelo, 1999).

Table A-1
Free Energies of Formation (kJ/mol) for Species in Reactions A.1 and A.2

Species	G^o_f, kJ/mol	Reference
Cr^{3+}	-225.5	Schmidt (1984)
CrO_4^{2-}	-731.4	Schmidt (1984)
$Cr(OH)_{3(s)}$	-869.1	Schmidt (1984)
Mn^{2+}	-227.6	Latimer (1952)
$MnO_{2(s)}$	-456.9	Tye (1976)
H_2O	-237.2	Naumov et al. (1974)
H^+	0	By standard convention

REFERENCES

Langmuir, D., *Aqueous Environmental Geochemistry*, Prentice-Hall, Upper Saddle River, NJ, 1997.

Latimer, W.M., *Oxidation Potentials,* 2nd ed., Prentice-Hall, New York, 1952.

Naumov, G.B., Ryzhenko, B.N., Khodakovsky, I.L., Barnes, I., and Speltz, V. *Handbook of Thermodynamic Data*, U.S. National Technical Information Service, PB226 722, U.S. Geological Survey, Water Resources Division, Menlo Park, CA, 1974.

Parkhurst, D.L. and Appelo, C.A.J. User's guide to PHREEQC (V2), *Water-Resources Investigations Report 99-4259*, U.S. Geological Survey, Denver, CO, 1999.

Schmidt, R.L. *Thermodynamic Properties and Environmental Chemistry of Chromium*, PNL-4881, Pacific Northwest Laboratory, Richland, WA, 1984.

Tye, F.L., Manganese dioxide electrode - III relationship between activities and stoichiometry for compositions near to MnO2, *Electrochimica Acta*, 21(6):415-420, 1976.