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DEPARTMENT OF ENERGY
Environmental Management Los Alamos Field Office (EM-LA)
Los Alamos, New Mexico 87544

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Mr. John E. Kieling
Bureau Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6303

Dear Mr. Kieling:

Subject: Submittal of the Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon

Enclosed please find two hard copies with electronic files of the "Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon." As discussed in a review meeting with New Mexico Environment Department–Hazardous Waste Bureau staff on July 19, 2018, because of the ongoing nature of the study, this document is being submitted as a progress report rather than as a completion report.

If you have any questions, please contact Steve White at (505) 309-1370 (steve.white@em-la.doe.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Arturo Q. Duran
Designated Agency Manager
Environmental Management
Los Alamos Field Office

Enclosures:
1. Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon (EM2018-0069)

cc (letter with enclosure[s]):
D. Katzman, N3B
S. White, N3B
C. Rodriguez, EM-LA

cc (letter with electronic enclosure[s]):
L. King, EPA Region 6, Dallas, TX
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EM-LA-40AD-00325

October 2018
EM2018-0069

Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon

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Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon

October 2018

Responsible program director:

Printed Name	Signature	Title	Organization	Date
Bruce Robinson	[signature]	Program Director	Water Program	10/23/2018

Responsible N3B representative:

Printed Name	Signature	Title	Organization	Date
Erich Evered	[signature]	Program Manager	N3B Environmental Remediation Program	10/23/2018

Responsible DOE EM-LA representative:

Printed Name	Signature	Title	Organization	Date
Arturo Q. Duran	[signature]	Designated Agency Manager	Office of Quality and Regulatory Compliance	10/30/18

CONTENTS

Figures

Attachment

1.0 INTRODUCTION

This fourth quarterly report presents results of two pilot-scale amendment tests conducted to evaluate feasibility for in situ treatment of hexavalent chromium [Cr(VI)] in the regional aquifer. The study is being conducted in accordance with the "Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon" (LANL 2017, 602505) as approved by the New Mexico Environment Department (NMED) (2017, 602546). The deployments occurred at regional groundwater monitoring wells R-42 and R-28. Sodium dithionite was injected into R-42 in late August 2017 and molasses was injected into R-28 in early September 2017 (Figure 1.0-1). The objectives of the tests are to evaluate (1) the ability of the amendments to reduce dissolved-phase Cr(VI) to insoluble and immobile trivalent chromium [Cr(III)] in the regional aquifer, (2) the longevity of the treatments in keeping Cr(VI) concentrations low (i.e., reduction capacity), (3) any adverse geochemical effects and their persistence, and (4) any adverse hydrological impacts of the treatments on hydraulic properties of the aquifer. The first quarterly report, issued at the end of January 2018 (LANL 2018, 602862), provided details of how the amendments were deployed and of the pumping and sampling strategies in each of the test wells, as well as the geochemistry data from the tests, through the end of calendar year 2017. The second quarterly report (LANL 2018, 603031) provided (1) an update of the geochemistry data from the two amendments tests, (2) the results of a borehole dilution tracer test that was conducted in R-42 in January 2018 to estimate the post-amendment ambient groundwater flow velocity through the R-42 screened interval, and (3) an analysis of pre- and post-amendment drawdown data from both R-42 and R-28 to evaluate the effects of the amendments on near-well hydraulic conductivity. The third quarterly report (N3B 2018, 700032) provided an update of the geochemistry data from the two amendments tests. The information provided in the three previous quarterly reports will not be repeated in this quarterly report. This quarterly report provides updated plots of geochemistry data from R-42 and R-28 that include results from additional samples collected during late June and through early September 2018. All of the new geochemistry data associated with these samples are included in Attachment 1 (on CD included with this document, plotted along with previously reported data).

2.0 UPDATE OF AMENDMENT TEST GEOCHEMISTRY RESULTS

2.1 Sodium Dithionite at R-42

Figure 2.1-1 shows an updated plot of the concentration trends of selected dissolved cations and metals, including chromium, measured in samples collected from R-42 as a function of time. Results are also shown in Figure 2.1-1 for the injection batches, which are plotted to the left of the vertical dashed line that indicates when pumping of the well was initiated. The vertical dashed lines shown in Figure 2.1-1 indicate when continuous pumping of R-42 stopped in September 2017, when net withdrawal of water from the well stopped in October 2017, and when 50-gal. biweekly purges were initiated after a dilution tracer test was conducted in January 2018, as described in the second quarterly report (LANL 2018, 603031). After the dilution tracer test, there has been no injection or circulation of water in R-42, and every sampling event has involved an approximately 50-gal. purge. As Figure 2.1-1 shows, there was a period that lacked purging/sampling that occurred from April 19 to June 13, 2018. This sampling hiatus is a result of the transition of environmental work conducted by the U.S. Department of Energy Environmental Management Los Alamos Field Office's (EM-LA's) contractor Los Alamos National Security, LLC to Newport News Nuclear BWXT – Los Alamos, LLC (N3B) beginning on April 30, 2018. Figure 2.1-2 shows concentration trends for some of the other elements of interest, including arsenic and selenium. Figure 2.1-3 shows concentration trends for selected anions. Concentrations of other elements or ions not shown in Figures 2.1-1 to 2.1-3 can be found in Attachment 1 (on CD included with this document).

Cr(VI) concentrations (measured as total chromium) in R-42 have remained well below the New Mexico groundwater standard of 0.05 mg/L. Iron concentrations have remained elevated and at levels well above pre-deployment levels of approximately 10 µg/L, which suggests that groundwater in the well vicinity had not yet become oxidized (Figures 2.1-1 and 2.1-2). During sampling between mid-October 2017 and early January 2018, when well water was circulated instead of withdrawn for sampling, iron concentrations dropped dramatically and remained relatively low, probably because the well water was being oxygenated as it circulated between the surface and the aquifer (Figure 2.1-1). Once 50-gal. purges were initiated in January 2018, iron concentrations rose steadily, consistent with the reestablishment of reducing conditions in the wellbore. These reducing conditions apparently persisted during the nearly 2-mo sampling hiatus, indicating that the oxygen mass transfer rate into the water is predictably quite slow or that the turnover rate of reduced groundwater flowing through the wellbore is faster than the oxygen mass transfer rate. Figure 2.1-3 shows that concentrations of nitrate (NO_3^-) continued a declining trend from before the sampling hiatus and until recently. Low nitrate concentrations, approximately 1 mg/L, are well below pre-deployment levels of approximately 20 mg/L and are consistent with the persistence of reducing conditions in the aquifer around R-42. However, nitrate appeared to increase during the last sample within this report period, which may forecast a beginning of a return to oxidizing groundwater conditions. Continued slow declines in sulfate ($SO_4^{=}$, a dithionite reaction product) and bromide (the conservative tracer that was injected with dithionite) concentrations (Figure 2.1-3) suggest that groundwater was actively flowing through the well under natural flow conditions during the past several months. During this period, bromide concentrations also reached pre-amendment deployment concentrations of approximately 0.2 mg/L, indicating a return of native groundwater conditions with respect to conservative ions. While levels have been decreasing, sulfate concentrations have remained elevated above pre-test concentrations (at slightly greater than double pre-deployment levels of approximately 80 mg/L), which suggests that there has been a continuous generation of sulfate near R-42; this can probably be attributed to the slow oxidation of reduced sulfur species formed during and perhaps immediately after the dithionite deployment. Any sulfate generated during the period immediately following the deployment should have been removed by pumping in August through October of 2017, or as a result of natural groundwater flow since then (bromide tracer concentrations have decreased more rapidly than sulfate has since October 2017). The sulfate concentration is slowly declining.

Figure 2.1-1 illustrates that sodium levels peaked following amendment deployment. The sodium spike is associated with the sodium dithionite amendment. Sodium may be considered as an amendment tracer since, in this sense, it is similar to bromide. Initially, the sodium concentration decreased rapidly during pumping phases. Following cessation of pumping levels, the sodium concentration has continued to decrease more slowly. During this report period, like bromide, sodium reached pre-deployment levels. Sodium also appears to be continuing to trend further downward potentially towards the lower historically observed levels of approximately 20 mg/L.

Arsenic appears to be trending modestly downward from 7 to 4 µg/L over the last few months (Figure 2.1-2). There may also be a slight downward trend in iron and manganese. Concentrations of other constituents shown in Figures 2.1-1 through 2.1-3 appear to have remained at constant levels.

2.2 Molasses at R-28

Figure 2.2-1 shows the trends of selected cations and metals, including chromium, during the molasses test at R-28. Figure 2.2-2 shows concentration trends for some of the other elements of interest, including arsenic and selenium. Figure 2.2-3 shows trends for anions during the test. As with the R-42 dithionite test, there was a nearly 2-mo purging/sampling hiatus from April 19 to June 13, 2018. Figure 2.2-4 shows the bromide and total organic carbon (TOC) concentrations measured during the test. TOC concentrations are considered an indicator of molasses, although as the test has progressed, the concentrations may increasingly reflect molasses degradation products. During the first few months of the amendments study, naturally occurring concentrations of organic carbon in the aquifer were negligible compared with the levels of molasses introduced. Earlier TOC results likely also reflected the presence of ethanol that was used in the chase water introduced downhole following the molasses injection.

Figures 2.2-1 through 2.2-4 show recent trends and changes for anions, cations, metals, and TOC. A noticeable drop in concentration for a number of constituents including TOC and bromide was observed in late July 2018. TOC persists at approximately 120 mg/L, which is still well above the pre-deployment concentration of about 1 mg/L and which indicates a continuing amendment influence.

A similar step-like drop occurred in concentrations for several other constituents including iron, manganese, nickel, chromium, chloride, and bromide. The decrease observed in iron and manganese may indicate that the reduced ions are being employed as reducing agents.

During this reporting period, total chromium concentrations dropped below the 0.05 mg/L New Mexico groundwater standard. During the last couple of weeks of the period, concentration generally appeared to level out to around 0.025 mg/L. Supporting analyses were also performed to provide chromium speciation in July and August of this period; results indicate that the chromium in R-28 continues to predominantly be Cr(III) and not Cr(VI). The drop in chromium concentration relates to a decrease in the solubility of Cr(III). This may be because of a suspected increase in pH and resultant hydroxide precipitation, precipitation with iron, or precipitation as a metal sulfide.

Chloride is still above and approximately double its pre-deployment level of approximately 40 mg/L. Bromide is also still a few times above its pre-deployment level of approximately 0.2 mg/L. Both are approaching their respective pre-deployment levels. (Note that bromide was a conservative tracer with a low pre-deployment level that was added with the molasses.) Like bromide, persistent elevated concentrations of chloride, which was present in the molasses, is also an indicator that some components of the amendment solution continue to linger near R-28.

Other constituents (e.g., nitrate, nitrite, sulfate) also decreased in concentration over the period.

Sulfate has fallen to a couple of milligrams per liter and well below its pre-deployment level of approximately 60 mg/L. Potentially, under conditions where oxygen has been depleted in biologically active zones, sulfate may well have been employed by bacteria as an alternative electron acceptor. Nitrate and nitrite trends are similar to sulfate as these compounds are used by anoxic bacteria as electron acceptors prior to sulfate. Assuming that sulfate is being reduced, then precipitation of metal sulfides may also be occurring and consequently affecting metals such as nickel.

3.0 DISCUSSION AND RECOMMENDATIONS

As discussed above, the dithionite amendment test at R-42 still requires more time to determine Cr(VI) reduction capacity imparted to aquifer sediments because chromium concentrations have not yet begun to break through in R-42. The molasses amendment test at R-28 will also require more time to determine reduction capacity and also to confirm and analyze recent and ongoing changes in the chemistry there. Also, uncertainty remains at both locations regarding the effects of the amendment deployments on aquifer permeability near the wells. Obtaining current estimates of the groundwater flow velocity in the vicinity of the wells would help address the reduction capacity and questions regarding potential reductions in aquifer permeability. The groundwater flow velocity estimates would allow (1) the volume of aquifer water that has flowed through the treatment zones during the tests to be estimated (at R-42, it would be the volume since continuous pumping ended in October 2017) and (2) an assessment of whether changes to aquifer permeability are caused by the deployments. Pumping of both wells would provide faster and more definitive estimates of reduction capacity resulting from the amendments. Therefore, the next steps of the amendments testing will involve an effort to conduct long-duration continuous pumping at R-42 and R-28 with time-series sampling. The objectives are to (1) investigate the ability to clean the area in the aquifer around each well of amendments and amendment byproducts and (2) move more groundwater pore volumes through the treated zone to accelerate breakthrough and provide the basis for estimating reduction capacity. Before initiating long-duration continuous pumping, a short-duration (approximately 40,000 gal. per well) continuous pumping activity was conducted in late October 2018 to collect data that can be used to guide disposition of water pumped during the long-duration tests. Details of the work plan for the 40,000 gal. pumping were provided to NMED before initiation of the test.

4.0 REFERENCES AND MAP DATA SOURCES

4.1 References

The following reference list includes documents cited in this report. Parenthetical information following each reference provides the author(s), publication date, and ERID, ESHID, or EMID. This information is also included in text citations. ERIDs were assigned by the Laboratory's Associate Directorate for Environmental Management (IDs through 599999); ESHIDs were assigned by the Laboratory's Associate Directorate for Environment, Safety, and Health (IDs 600000 through 699999); and EMIDs are assigned by N3B (IDs 700000 and above). IDs are used to locate documents in N3B's Records Management System and in the Master Reference Set. The NMED Hazardous Waste Bureau and N3B maintain copies of the Master Reference Set. The set ensures that NMED has the references to review documents. The set is updated when new references are cited in documents.

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, 602505)

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 2018, 602862)

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 2018, 603031)

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 2018, 700032)

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, 602546)

4.2 Map Data Sources

Hillshade; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\Data\HYP\LiDAR\2014\Bare_Earth\BareEarth_DEM_Mosaic.gdb; 2014.

Unpaved roads; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder; \\slip\gis\GIS\Projects\14-Projects\14-0062\project_data.gdb\digitized_site_features\digitized_roads; 2017.

Drainage channel; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder; \\slip\gis\GIS\Projects\15-Projects\15-0080\project_data.gdb\correct_drainage; 2017.

Structures; Los Alamos National Laboratory, KSL Site Support Services, Planning, Locating and Mapping Section; 06 January 2004; as published 29 November 2010.

Paved Road Arcs; Los Alamos National Laboratory, FWO Site Support Services, Planning, Locating and Mapping Section; 06 January 2004; as published 29 November 2010.

Chromium plume > 50 ppb; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\13-Projects\13-0065\shp\chromium_plume_2.shp; 2018.

Regional groundwater contour May 2017, 4-ft interval; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\16-Projects\16-0027\project_data.gdb\line\contour_wl2017may_2ft; 2017.

Regional groundwater contour November 2017, 2-ft interval; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\16-Projects\16-0027\project_data.gdb\line\contour_wl2017nov_2ft; 2017.

Point features; As published; EIM data pull; 2017.

Technical Area Boundaries; Los Alamos National Laboratory, Site Planning & Project Initiation Group, Infrastructure Planning Office; September 2007; as published 13 August 2010.

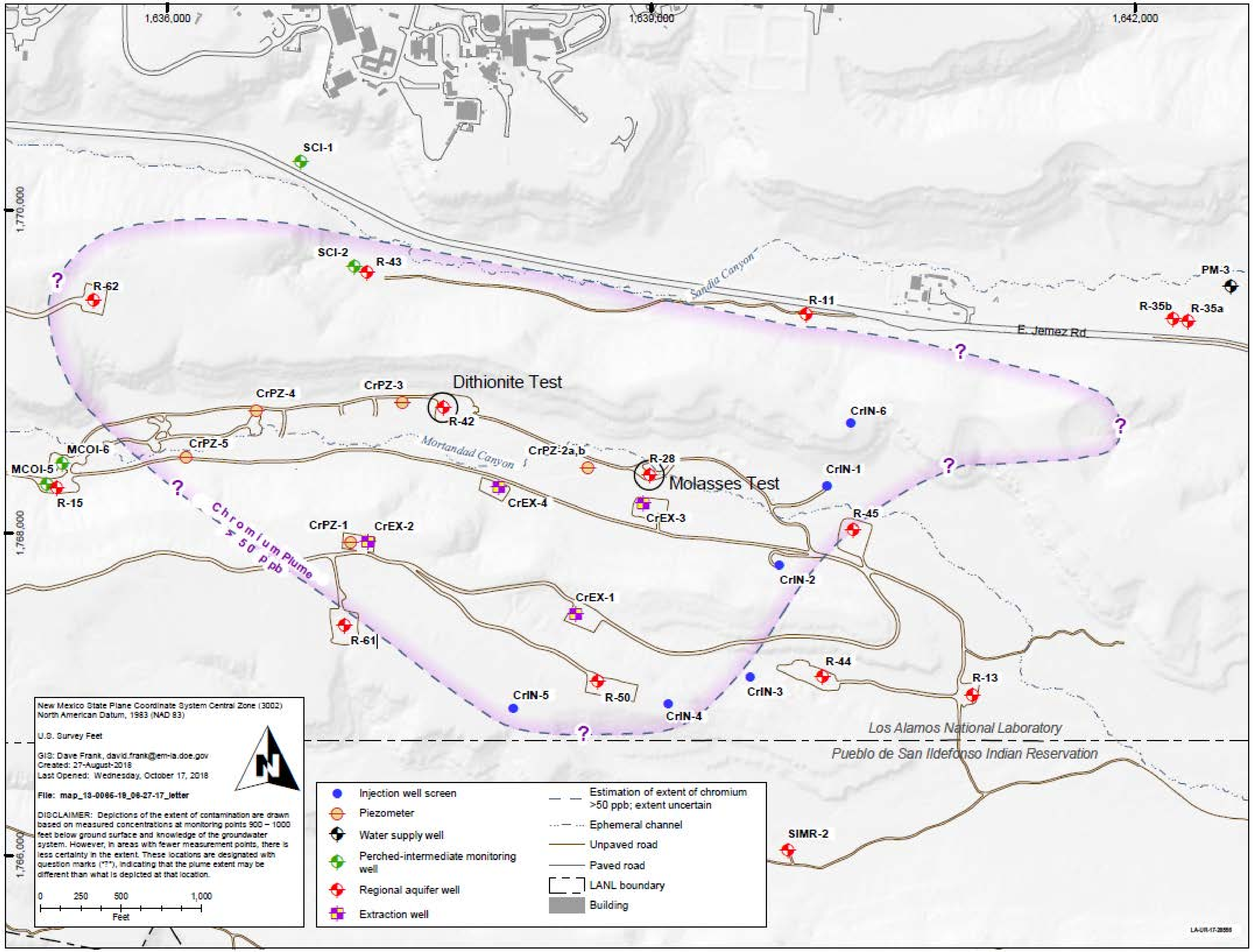
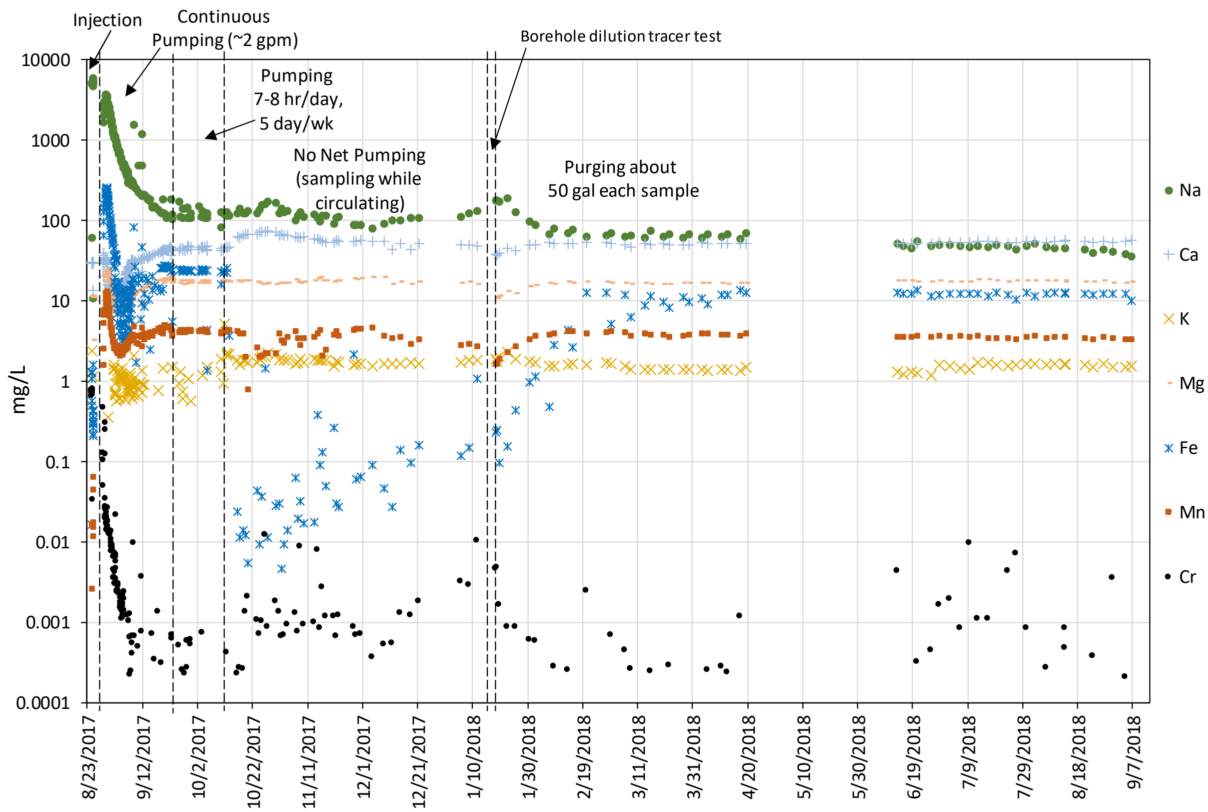
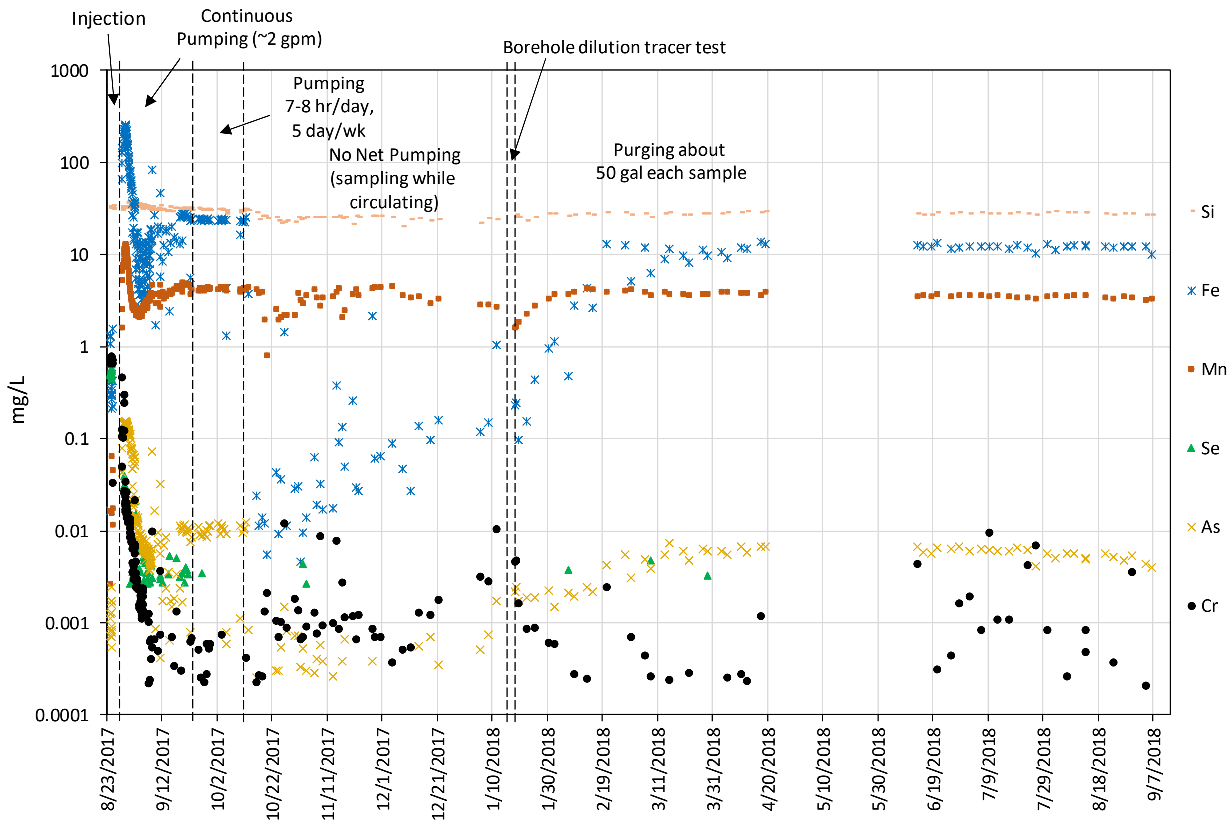


Figure 1.0-1 The Cr(VI) plume showing locations of the R-42 dithionite test and the R-28 molasses test



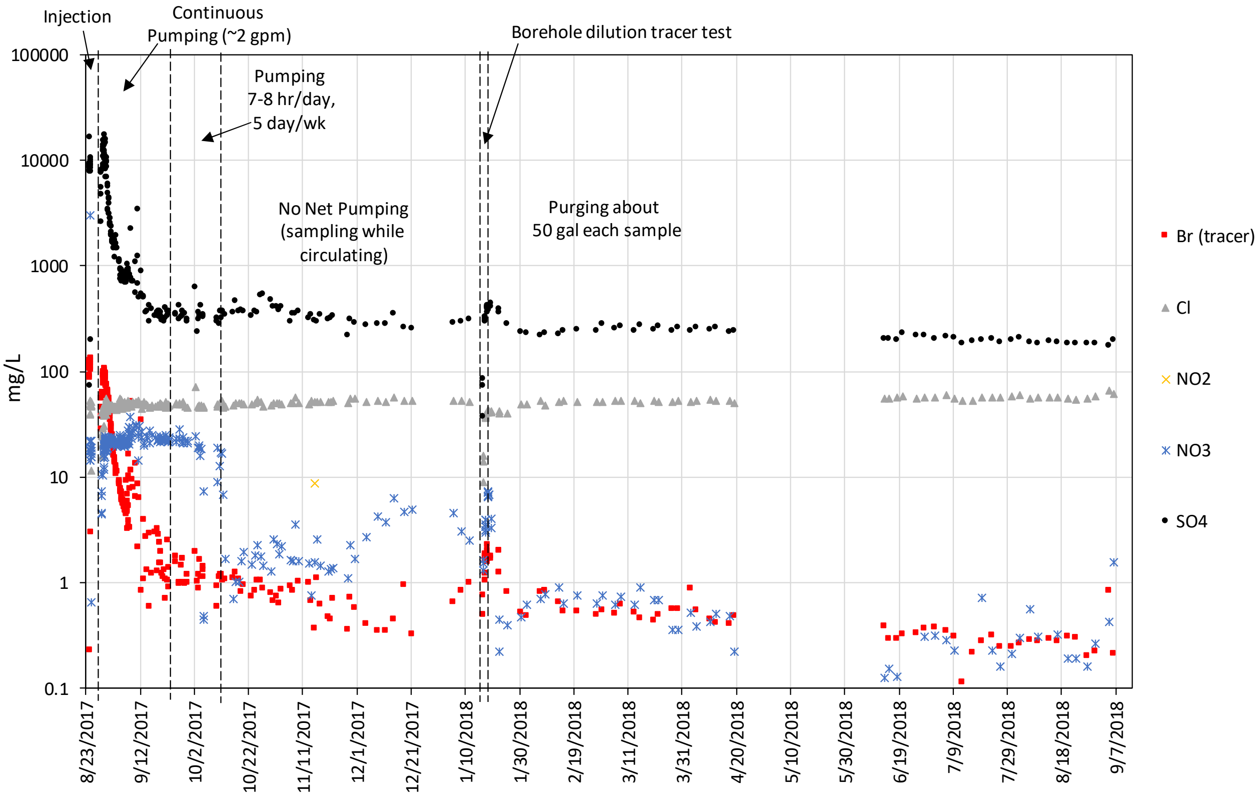
Notes: The pre-test concentration of chromium (Cr) was approximately 0.8 mg/L, and pre-test concentrations of iron (Fe) and manganese (Mn) were negligible. The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.1-1 Concentrations of selected cations and metals in R-42 dithionite test as a function of time



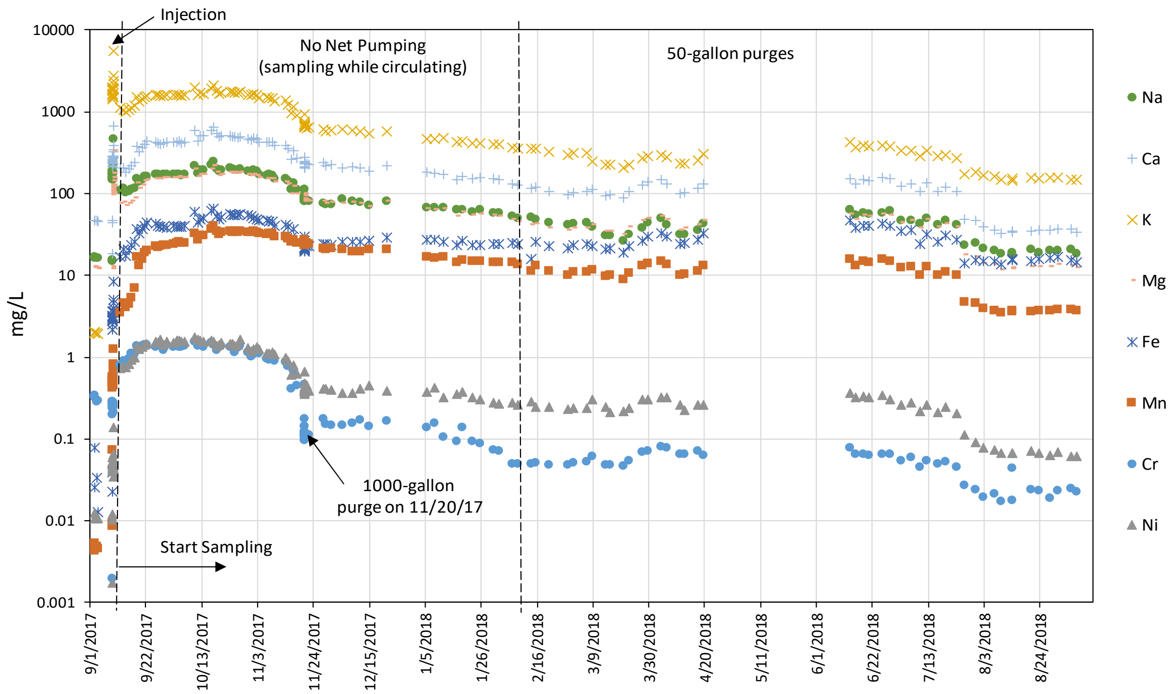
Notes: The pre-test concentration of Cr was approximately 0.8 mg/L, and pre-test concentrations of Fe and Mn were negligible. The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.1-2 Concentrations of selected constituents during R-42 dithionite test as a function of time



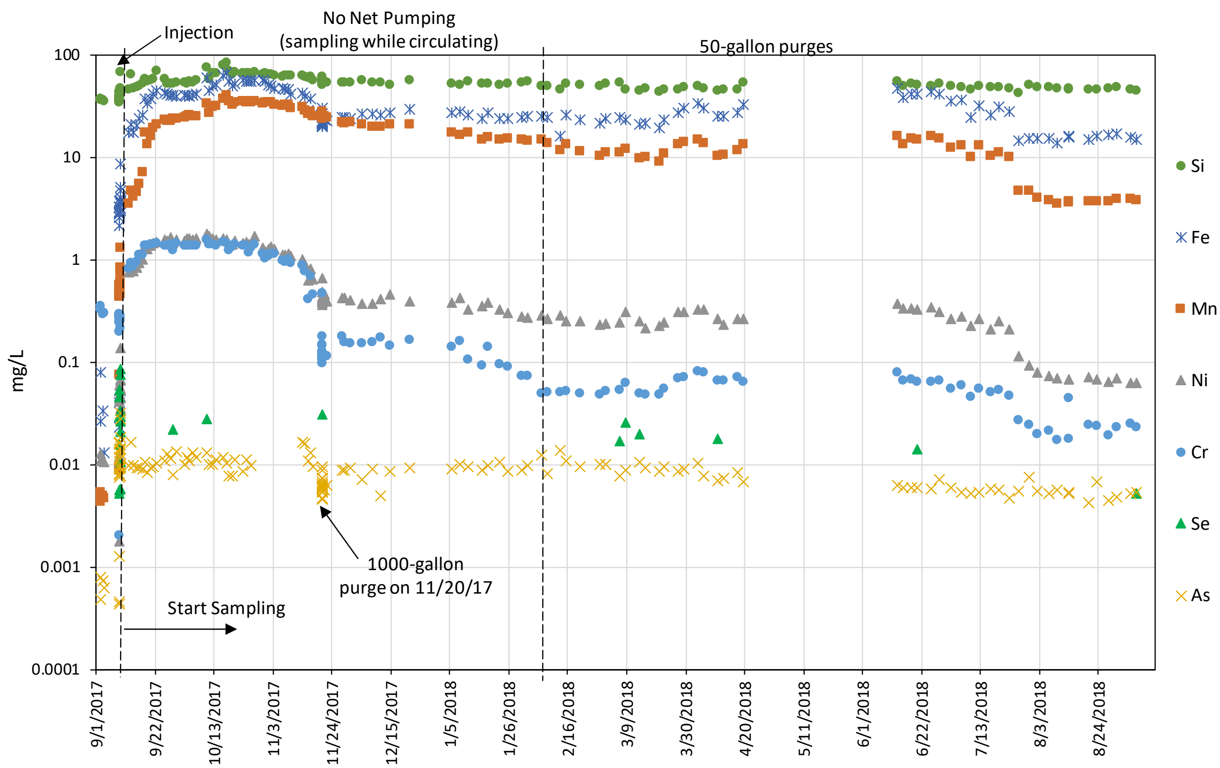
Note: The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.1-3 Concentrations of anions in R-42 dithionite test as a function of time



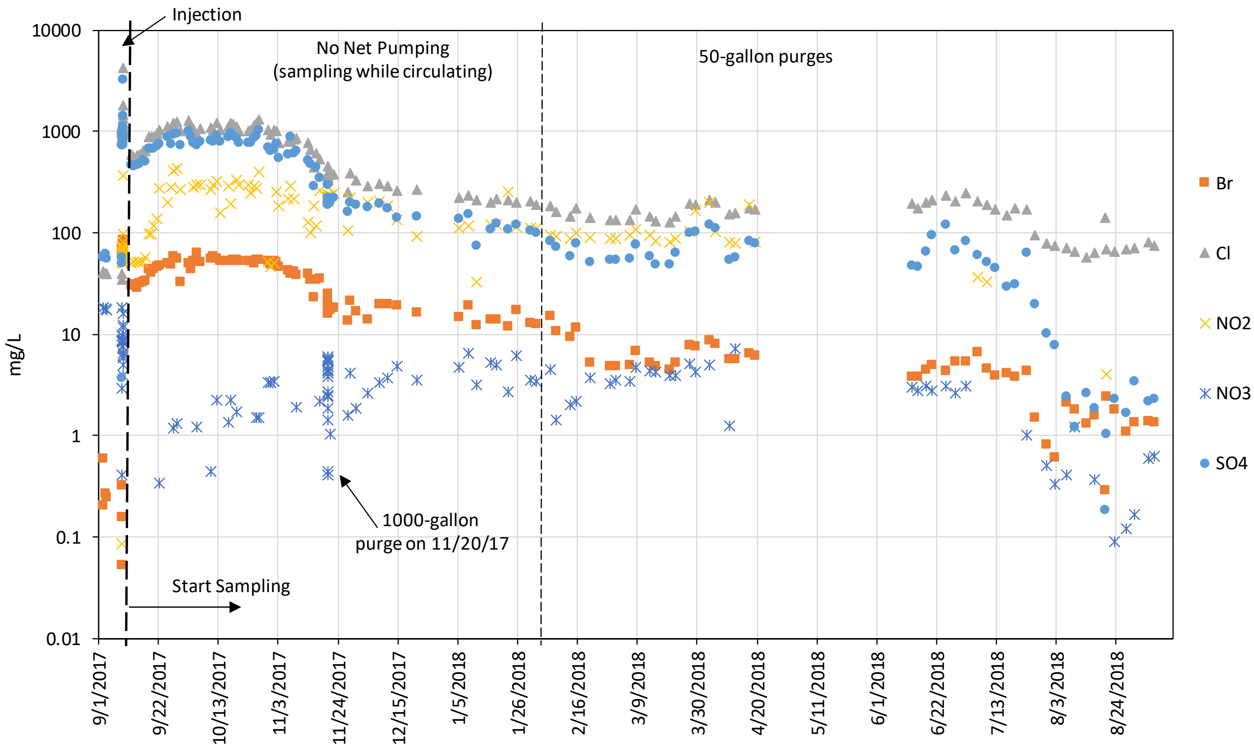
Notes: The pre-test concentration of Cr was approximately 0.4 mg/L, and pre-test concentrations of Fe and Mn were negligible. The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.2-1 Concentrations of selected cations and metals in R-28 molasses test as a function of time



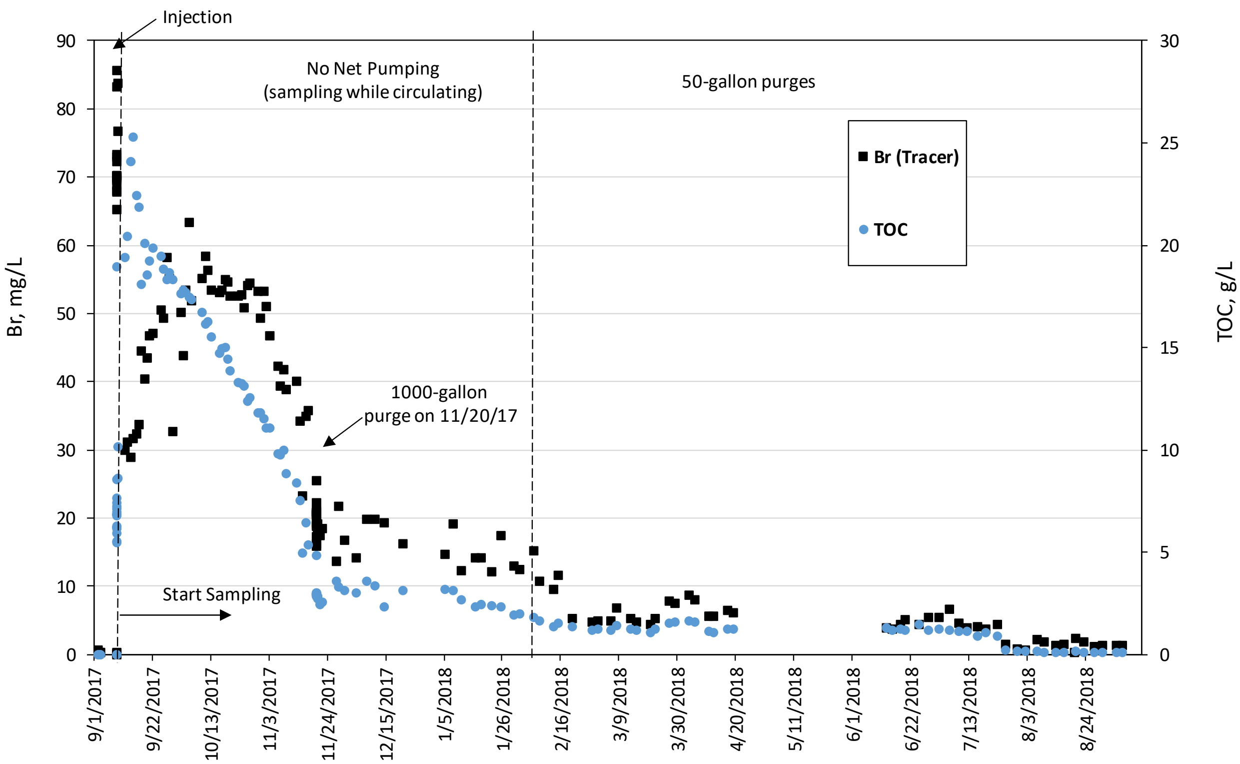
Notes: The pre-test concentration of Cr was ~0.4 mg/L, and pre-test concentrations of Fe and Mn were negligible.
The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.2-2 Concentrations of selected constituents during R-28 molasses test as a function of time



Note: The sampling hiatus from April to June 2018 is a result of the transition of environmental work from EM-LA's previous contractor, Los Alamos National Security, LLC, to N3B.

Figure 2.2-3 Concentrations of anions in R-28 molasses test as a function of time



Note: Unlike other plots, concentrations scales are not logarithmic.

Figure 2.2-4 Concentrations of bromide and TOC in R-28 molasses test as a function of time

Attachment 1

Data Associated with Fourth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon (on CD included with this document)