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Date: JAN 29 2018
Refer To: ADEM-18-0009
LAUR: 18-20467

John Kieling, Bureau Chief
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Santa Fe, NM 87505-6303

Subject: Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater beneath Mortandad Canyon

Dear Mr. Kieling:

Enclosed please find two hard copies with electronic files of the first Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater beneath Mortandad Canyon. This submittal fulfills the Department of Energy (DOE) and Los Alamos National Security (LANS) recommendation to begin quarterly reporting beginning January 31, 2018. Subsequent reports will be submitted on a quarterly basis beginning April 30, 2018.

If you have any questions, please contact Stephani Swickley at (505) 606-1628 (sfuller@lanl.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@em.doe.gov).

Sincerely,

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Sincerely,

David S. Rhodes, Director
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Enclosures: Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater beneath Mortandad Canyon (EP2018-0011)

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LA-UR-18-20467
January 2018
EP2018-0011

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



Prepared by the Associate Directorate for Environmental Management

Los Alamos National Laboratory, operated by Los Alamos National Security, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC52-06NA253 and under DOE Office of Environmental Management Contract No. DE-EM0003528, has prepared this document pursuant to the Compliance Order on Consent, signed June 24, 2016. The Compliance Order on Consent contains requirements for the investigation and cleanup, including corrective action, of contamination at Los Alamos National Laboratory.
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EP2018-0011

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

January 2018

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1.0 INTRODUCTION

This report is the first quarterly report presenting results of two pilot-scale amendment deployments to evaluate feasibility for in situ reduction of chromium 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) (NMED 2017, 602546). The deployments occurred at existing regional groundwater monitoring wells R-42 and R-28. Sodium dithionite was deployed at R-42, and molasses was deployed at R-28 (Figure 1). The objectives of the tests were to evaluate (1) the ability of the amendments to reduce and immobilize Cr(VI) 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 of the treatments and their persistence, and (4) any adverse hydrological impacts of the treatments on the aquifer. This report provides details of the actual deployments, discussion of activities that have occurred since deployment including sampling activities, and results to date.

2.0 AMENDMENT DEPLOYMENT

2.1 Sodium Dithionite at R-42

On August 24–25, 2017, 9000 gal. of a 0.059 M sodium dithionite ($Na_2S_2O_4$) solution buffered with 0.057 M sodium sulfite (Na_2SO_3) was injected into well R-42. The sodium sulfite was added to buffer the solution to a pH around 7 during the injection, which helps stabilize the dithionite. As an additional measure to stabilize the dithionite, the water used for dissolution was also chilled using a commercial chilling unit before adding the solids. The 9000 gal. of dithionite solution was spiked with 0.00143 M sodium bromide (NaBr) so that bromide could serve as a tracer for the injection solution. Specifically, 300 kg of $Na_2S_2O_4$, 250 kg of Na_2SO_3, and 5 kg of NaBr were added to the 9000 gal. of water in 15 separate 600-gal. batches. Each batch was mixed into untreated R-42 water [pumped into holding tanks before testing, and containing approximately 740 μg/L Cr(VI)], and then it was immediately injected downhole after mixing. This procedure was intended to minimize the amount of time that dithionite solution remained on the surface because dithionite degrades rapidly in solution with exposure to air. The average holding time on the surface from the time of dithionite solid chemical addition to complete injection of a batch was typically about 1 h; the 15 batches took about 16.5 h to inject at an average injection rate of about 10 gal. per minute (gpm). On-site measurements of dithionite using an ultraviolet-visible (UV-Vis) spectrophotometer confirmed that each batch contained approximately the same concentration of dithionite and that the dithionite concentrations decreased very little, if at all, over the course of injecting each batch. The injections took place through a 2-in.-diameter high-density polyethylene pipe that was inserted downhole into the well casing to below the water table so that the dithionite solution would be minimally exposed to air as it was injected. The dithionite injection was followed with 1000 gal. of potable water to "chase" the injection solution out of the wellbore and into the formation. Following the injection, the injection pipe was removed from the well and a Grundfos electric submersible pump with stainless-steel riser was installed to allow for extraction of water. The test was designed as a push-pull test in which the injection solution was allowed to sit in the formation for about 3 d to react with aquifer sediments, and then the well was pumped to recover the injected solution and pull contaminated groundwater through the treated zone to the production well. The procedures and results of the post-injection phase of testing are discussed in Section 3.1.

2.2 Molasses at R-28

On September 9, 2017, 30,000 gal. of a 3.3 wt% molasses solution (approximately 33 gal./L) spiked with 10 kg of NaBr (0.00085 M NaBr) was injected into well R-28. The injection solution was prepared by diluting 5000 gal. of a 20 wt% molasses solution into 25,000 gal. of untreated R-28 water in 20 separate 1500-gal. batches. The 20% molasses solution was delivered in a tanker truck and transferred to an on-site holding tank 2 d before injection. The Cr(VI) concentration in the R-28 water (pumped into holding tanks before the test) was approximately 310 µg/L. The injection hardware was the same as that used at R-42. The molasses injection was followed with 1500 gal. of potable water containing 10 vol% ethanol (specifically, 165 gal. of ethanol mixed into 1335 gal. of potable water) to help push the molasses solution into the formation and to kill or stun microbial growth within the well casing and filter pack as a measure to inhibit subsequent biofouling of the well. The injection pipe was removed from the well after injection was completed, and a Grundfos electric submersible pump with stainless-steel riser was installed to allow for extraction of water. The test was designed as a “push-drift” test in which R-28 was to be only passively sampled after injection. The passive sampling was accomplished using a closed-loop circulation system where water that was pumped to the surface was immediately injected back downhole, thus resulting in no net withdrawal other than the small amount needed for sampling. The rationale for the passive sampling strategy was threefold: (1) the lack of pumping (compared with ambient groundwater flow) allows for greater molasses contact time with the formation, which helps promote robust biomass growth, (2) the natural flow velocity at R-28 was known from previous testing to be among the highest anywhere in the Cr(VI) plume, with the expected time for the molasses solution to “drift” out of R-28 being about 2 mo, and (3) no management or treatment of extracted water was required. The procedures and results of the post-injection phase of testing are discussed in Section 3.2.

3.0 POST-INJECTION FIELD ACTIVITIES AND DISCUSSION OF RESULTS TO DATE

3.1 Sodium Dithionite Results

Pumping of R-42 at about 3 gpm was initiated approximately 80 h after completion of the chase water injection. However, after only a few hours of pumping, the pump tripped off because of excessive water-level drawdown in the well, so the pumping rate was reset to about 1.95 gpm, which was sufficient to maintain a stable head and eliminate drawdown, and the pump continued to operate at this rate more or less uninterrupted for 25 d. The productivity of the well was significantly lower after the dithionite injection than it had been when the holding tanks were filled with R-42 water before the test, which drew the water level down only 2–3 ft at about 3 gpm. However, the decrease in productivity is not attributed to the dithionite treatment because the injectivity/productivity of the well was already compromised during shakedown testing that preceded any amendment additions. In fact, the injection rate per unit of pressure applied increased during the dithionite injection. The most likely explanation for the decrease in well injectivity/productivity is that some air was injected into the filter pack and nearby formation in the injection interval during shakedown testing. The testing was initiated with a packer inflated above the injection interval, and this would have prevented air from escaping up the casing when it was pushed into the interval in front of the injected water. The packer was subsequently deflated for all further shakedown testing and for the entire dithionite injection (and the molasses injection at R-28), but the injectivity of the well never fully recovered. This point is raised because one of the test objectives was to evaluate the effects of the amendments on aquifer hydrology/permeability, and it is unlikely that the apparent decrease in permeability near R-42 is attributable to the dithionite treatment given that the condition was observed before any dithionite was deployed.

After 25 d of continuous pumping at approximately 1.95 gpm, pumping was reduced to only 7–8 h per day, 5 d per week for about another 3 wk. During the continuous pumping period, samples were collected using an autosampler, initially at a frequency of one per hour, then one every 2 h, and eventually one every 8 h. When pumping was transitioned to 7–8 h per day, samples were collected manually at the beginning and end of each day. At the end of this period, about 77,000 gal. of water had been extracted, and four 20,000-gal. frack tanks had been almost completely filled. Net withdrawal of water was terminated at this point because the concentrations of dissolved iron and manganese in the extracted water remained above the limit that was allowed for land application of the water under discharge permit (DP)-1793, and there were no provisions for additional water storage for subsequent treatment or disposal. However, passive sampling of R-42 continued and was conducted from a sampling port in a closed-loop circulation system where water was circulated to the surface and downhole at a rate that did not affect static water level nor disrupt ambient flow through the well. Manual sampling frequency was reduced to 3–5 times per week, eventually decreasing to 2 times per week, with no sampling over the Laboratory's winter break.

Figure 2 shows the trends of selected cations and metals, including chromium, measured in samples collected from R-42 as a function of time, and Figure 3 shows the same data as a function of gallons pumped. Results are also shown in Figure 2 for the injection batches, which are plotted to the left of the vertical dashed line that indicates when pumping of the well was initiated. Vertical dashed lines are also shown in both figures for when continuous pumping stopped and when net withdrawal of water from the well stopped. Figure 4 shows trends for some of the other elements of interest, including arsenic and selenium. Figures 5 and 6 are similar to Figures 2 and 3 for selected anions measured in samples collected from R-42. Concentrations of other elements or ions can be found in Attachment 1 (on CD included with this document). Some results are still not available at the time of writing this report. Figure 7 shows the recoveries of the bromide tracer, along with sodium and sulfate, as a function of volume pumped during the test. In the case of sulfate, it was assumed that 2 M of sulfate would be generated for every mole of dithionite injected and 1 M of sulfate for every mole of sulfite injected, and the recovery calculation is based on these assumptions. Figure 8 shows the recoveries of iron and manganese (assumed to be Fe^{2+} and Mn^{2+} because of the exceedingly low solubilities of higher oxidation states of these elements) during the test.

Several points can be made concerning Figures 2–8. First, it is apparent that after pumping nearly 8 times as much water from R-42 as was injected during the dithionite injection and chase, Cr(VI) concentrations in R-42 remained very low. However, concentrations of many elements, including chromium, went through a peak as the dithionite solution was initially pumped back, and then they tailed off to relatively stable and generally low values. This result is attributed to a combination of two processes. The first is the aggressive reaction of the dithionite with aquifer sediments, which resulted in reduction and dissolution of iron- and manganese-bearing phases. These phases also contain large amounts of naturally occurring Cr(III). The second process is cation exchange, wherein the sodium from the dithionite solution displaces many other cations (e.g., Ca^{2+}, Mg^{2+}, K^{+}) from cation-exchange sites in the sediments. The high sodium concentrations likely also suppress the cation exchange of Fe^{2+}, Mn^{2+}, and even Cr^{3+} during the early portion of the test. Note that the pH of the produced water was never lower than about 6.8 during the entire time the high-concentration pulse was pumped back. Thus, the elevated cations/metals concentrations observed during this part of the test cannot be attributed to dissolution of mineral phases induced by low pH. The relatively high observed chromium concentrations during this part of the test, and in the injection batches themselves (Figure 1), suggest that the chromium is Cr(III), not Cr(VI), because Cr(VI) should not be compatible with dithionite. The fact that silica concentrations were not elevated significantly during the test (Figure 4) suggests that the dithionite selectively reacted with iron- and manganese-rich phases rather than indiscriminately dissolving silicate minerals that make up most of the rock matrix.

The cycling of iron concentrations between 10,000 and 30,000 gal. pumped (Figure 3) appears to reflect a daily periodicity that is unexplained but is likely related to some combination of daily temperature fluctuations and how long samples sat in the autosampler before being acidified. The highest concentrations tended to be in the early morning hours, 2:00–6:00 a.m., and the lowest concentrations were in the early afternoon hours, 2:00–6:00 p.m.

Once net withdrawal from R-42 ended, the concentrations of both iron and manganese in the samples dropped, although iron dropped almost immediately, and manganese was delayed by about 5 or 6 d and never dropped as much as the iron (Figure 2). These results indicate that the water in the well became oxygenated when it was no longer pumped, and perhaps this process was accelerated by circulating water to the surface, causing oxidation of first Fe^{2+} and then Mn^{2+}, followed by precipitation of the less-soluble, higher-oxidation states of these elements. The order of oxidation is consistent with thermodynamic expectations (Fe^{2+} is more easily oxidized than Mn^{2+}), and it is also consistent with observations of the oxidation/precipitation of these species in the large tanks used to hold the discharge water from R-42. Chromium concentrations do not appear to have increased, although not enough of the analytical results are yet available. Interestingly, concentrations of NO_3^-, which appeared to be relatively unaffected by the dithionite treatment, dropped significantly after pumping was stopped. This result is somewhat contradictory to what would be expected if the well became oxygenated, and it raises suspicions of increased microbial activity in the well after pumping was stopped (although this has not been evaluated). It is unknown how rapidly water is moving under natural-gradient flow conditions through the R-42 injection interval, but these results suggest that the rate is not fast enough to maintain reducing conditions in the well. A dilution tracer test is being planned for the first quarter of Calendar Year 2018 to determine how fast water is naturally moving through R-42, which will also help in interpreting the test when Cr(VI) concentrations eventually increase.

The bromide recovery curve in Figure 7 reflects the rate of recovery of the dithionite injection solution during the test. While the recovery is nearly complete after pumping back 8 times as much water as was injected, it is not as rapid as one might expect from a well-behaved injection pulse after only 3 d of aquifer drift. The recovery may also be artificially high by several percent because of the noticeable influence of one very high concentration sample that was collected after about 38,000 gal. pumped (Figure 7); this sample was re-analyzed twice and the high concentration of bromide was verified both times. The relatively low rate of bromide recovery could reflect a considerable amount of dispersion and/or aquifer drift during the test, but it may also reflect differences in the distribution of flow between the various stratigraphic layers in the screened test interval during injection and extraction. Such differences could have resulted from the significant differences in the injection and extraction flow rates and pressures, and there is also a possibility that air may have partially blocked some portions of the test interval during injection. Also, the injection solution was considerably more dense (on account of both more dissolved solids and a colder temperature) than the native groundwater, so some density-driven flow could have occurred in the formation that may have resulted in long tailing behavior.

The relatively low recovery of sulfate relative to bromide (Figure 7) suggests that a considerable amount of the dithionite and sulfite that was injected did not oxidize all the way to sulfate. Any sulfur species recovered in the samples should have appeared as sulfate because the samples were bubbled with air before analysis to ensure that they would be measured as sulfate. Although small amounts of dithionite were detected in the initial water that was pumped back, it was not nearly enough to account for the difference between the bromide and sulfate recoveries. This result is consistent with laboratory batch and column studies, where sulfur mass balance was seldom achieved, and it suggests that some of the dithionite is converted to reduced sulfur species that remain associated with the sediments. If this is occurring, the reduced sulfur species should provide more reduction capacity than just the reduced iron and manganese species that are generated by a treatment (and it may imply the formation of some iron and manganese sulfide species).

Figure 8 shows that the amounts of iron and manganese recovered during the test were very significant, with about 0.092 M of Fe^{2+} and 0.013 M of Mn^{2+} being produced per mole of dithionite injected. It is unknown how many moles of these reduced species may have been left behind in the formation. It is important to recognize that the removal of these considerable amounts of Fe^{2+} and Mn^{2+} would not occur during an actual full-scale deployment if it did not involve recovery of the injection solution. Leaving these constituents behind would increase the magnitude of the adverse short-term and local impact on aquifer water quality, but it would also, in principle, increase the Cr(VI) reduction capacity imparted by the treatment. The Fe^{2+} and Mn^{2+} concentrations following the dithionite deployment were the limiting factors in meeting applicable limits for land application of water pumped from the wellhead. Figure 4 indicates that arsenic and selenium were not problematic. However, in a field deployment with no withdrawal of water, sulfate and total dissolved solids might become the limiting long-term factors, as Fe^{2+} and Mn^{2+} will eventually oxidize and drop out of solution, providing Cr(VI) reduction benefits in the process.

Based on laboratory test results, it has been estimated that it would take up to 180,000 gal. of pumping of R-42 to exhaust the reduction capacity imparted by the dithionite treatment and see Cr(VI) concentrations increase in the well water. About 80,000 gal. of water were pumped during the test, and Cr(VI) reduction capacity is now being exhausted only by natural gradient flow. Until the dilution tracer test is conducted, it is difficult to predict how long it may take until Cr(VI) concentrations begin to increase.

3.2 Molasses Results

Passive sampling of R-28 began 3 d after the molasses injection/chase ended. Samples were collected manually 1 time per day, initially 7 d per week, then omitting weekends after 17 d, and eventually decreasing to 2 d per week. However, an approximate 1000-gal. purge of R-28 at approximately 2.5 gpm was conducted after about 10 wk to determine whether samples being collected were providing good representation of water chemistry in the aquifer or if sample data were being influenced by processes occurring in the wellbore. During this purge, samples were collected manually every 20 min (for 7 h) to evaluate trends as the well was pumped.

Figure 9 shows the trends of selected cations and metals, including chromium, during the molasses test so far. Figure 10 shows trends for anions during the test. Figure 11 shows the bromide and total organic carbon (TOC) concentrations during the test. TOC is being used as a surrogate for molasses, as background concentrations of organic carbon in the aquifer are negligible compared with the levels of molasses introduced. However, TOC will reflect ethanol and molasses breakdown products as well. The decrease in concentrations of many constituents on November 20, 2017, is associated with the 1000-gal. purge that was conducted that day. Figure 12 shows a plot of the selected metals concentrations on that day alone, and Figure 13 shows the anions and TOC concentrations on that day.

An unexpected result of the test so far has been the observation of higher concentrations of chromium after introducing molasses than had ever previously been observed in R-28 (by a factor of 3 or more). This result was particularly surprising given that laboratory testing had shown that molasses is capable of rapidly and abiotically reducing Cr(VI) to Cr(III), so measureable concentrations of Cr(VI) were not expected to be seen until all molasses had drifted out of the well. Indeed, UV-Vis spectroscopic measurements confirmed that all the chromium measured in well-water samples is Cr(III) [or at least it is not Cr(VI)]. The high chromium concentrations have been attributed to leaching from the stainless-steel casing in R-28, as concentrations of nickel are also elevated well above background concentrations. Chromium and nickel are the two main additives (to iron) in stainless steel. The post-injection pH in the well water has been consistently in the range of 4.6 to 4.8, which is expected for molasses breakdown and has been observed in laboratory experiments. While this is a relatively low pH, it is not thought to be low enough to cause such elevations of chromium and nickel concentrations from stainless steel. It is suspected that very local-scale microbial corrosion/leaching processes could be contributing to the

observations, and it is also possible that something in the molasses is complexing Cr(III) and possibly Ni(II) to increase their effective solubility.

The relatively steady decline in molasses concentrations shown in Figure 11, even during the time when bromide concentrations were relatively constant, suggests that the molasses is being consumed at a rate of about 1% per day by microbial processes in the formation. This estimate does not account for other potential contributions to TOC made by molasses degradation/consumption products, so the actual molasses consumption rate could be somewhat higher.

The rapid decrease in concentrations of most constituents at the beginning of the 1000-gal. purge on November 20, 2017 (Figures 12 and 13), followed by the relatively steady concentrations for the remainder of the purge, suggests that there was a skin effect in the very near vicinity of R-28 (likely in the well screen or filter pack). This skin effect apparently caused diversion of flow around the wellbore such that there was a delay in the concentrations observed in the wellbore relative to what was present in the formation just outside the wellbore at any given time. The dramatic drop in chromium concentrations is particularly telling in that it suggests that the high chromium concentrations observed before the purge were indeed an artifact of some leaching or corrosion process of the stainless-steel casing. Interestingly, nickel concentrations did not drop nearly as much as chromium during the purge. Also, the fact that neither chromium nor nickel concentrations dropped to background levels during the purge suggests that the leaching or corrosion process is relatively rapid (rapid enough to sustain measurable elevations over background despite a water residence time of only an hour or so in the casing/piping).

The fact that the rate of decrease in concentrations of all constituents appears to have stopped, or at least slowed significantly, after the purge relative to before the purge suggests that the purge may have increased the skin effect that was already in place before the purge. This result is somewhat troubling in that it suggests that additional purges may be necessary to obtain representative samples of groundwater chemistry just outside the R-28 wellbore. The apparent increased skin effect might be attributable to drawing some biomass or other debris into the well screen during the purge. Pressure transducer measurements during the purge have not yet been evaluated. A “push” rather than a purge (or some combination of the two) might be considered in the future to test the hypothesis of biofouling or other debris deposition in the well screen, which is quite speculative at this stage. Predictions for when Cr(VI) concentrations are expected to rebound in R-28 under pre-test natural flow conditions are pending.

To provide perspective on the expected drift travel time of the molasses plume in the vicinity of R-28, Figure 14 provides a comparison of the bromide concentrations in R-28 with the concentrations of a conservative naphthalene disulfonate (1,6-NDS) tracer injected into R-28 during a tracer test in 2016 in which approximately the same amount of water was injected as in the molasses test. Whereas the bromide was injected in 30,000 gal. of water and followed with a 1500-gal. chase, the tracer in 2016 was injected in 15,000 gal. of water and followed with a 15,000-gal. chase. It is apparent that the 30,000 gal. of water injected in 2016 had already effectively drifted out of R-28 by the time of the November 20, 2017, purge, although the purge did help to “reset” the bromide trend such that it moved closer to the 2016 test result. The bromide concentrations are now lingering much longer/higher than would have been predicted from the 2016 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 or ESHID. This information is also included in text citations. ERIDs were assigned by the Associate Directorate for Environmental Management's (ADEM's) Records Processing Facility (IDs through 599999), and ESHIDs are assigned by the Environment, Safety, and Health Directorate (IDs 600000 and above). IDs are used to locate documents in the Laboratory's Electronic Document Management System and in the Master Reference Set. The NMED Hazardous Waste Bureau and ADEM 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)

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)

4.1 Map Data Sources

Point features; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder 15-0059;\\slip\gis\GIS\Projects\14-Projects\14-0062\project_data_NEPA_plate.gdb;merge_all_well_features;2017

WQH Drainage_arc; Los Alamos National Laboratory, ENV Water Quality and Hydrology Group; 1:24,000 Scale Data; 03 June 2003.

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

Structures; Los Alamos National Laboratory, KSL 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, GIS projects folder; \\slip\gis\GIS\Projects\13-Projects\13-0065\project_data.gdb; chromium_perchlorate_plume; 2017

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

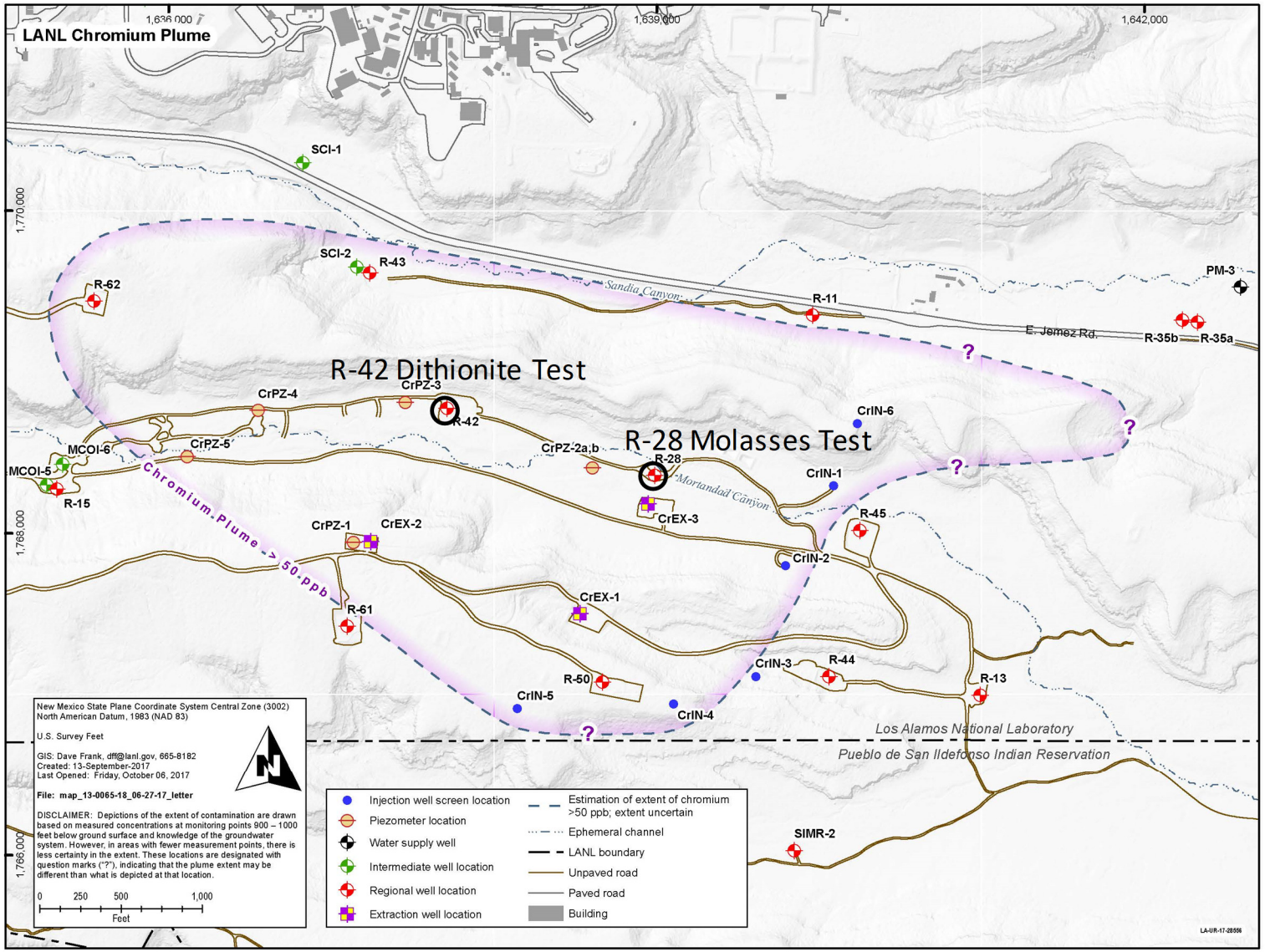


Figure 1 **Map of the Cr(VI) plume showing locations of R-42 dithionite test and R-28 molasses test**

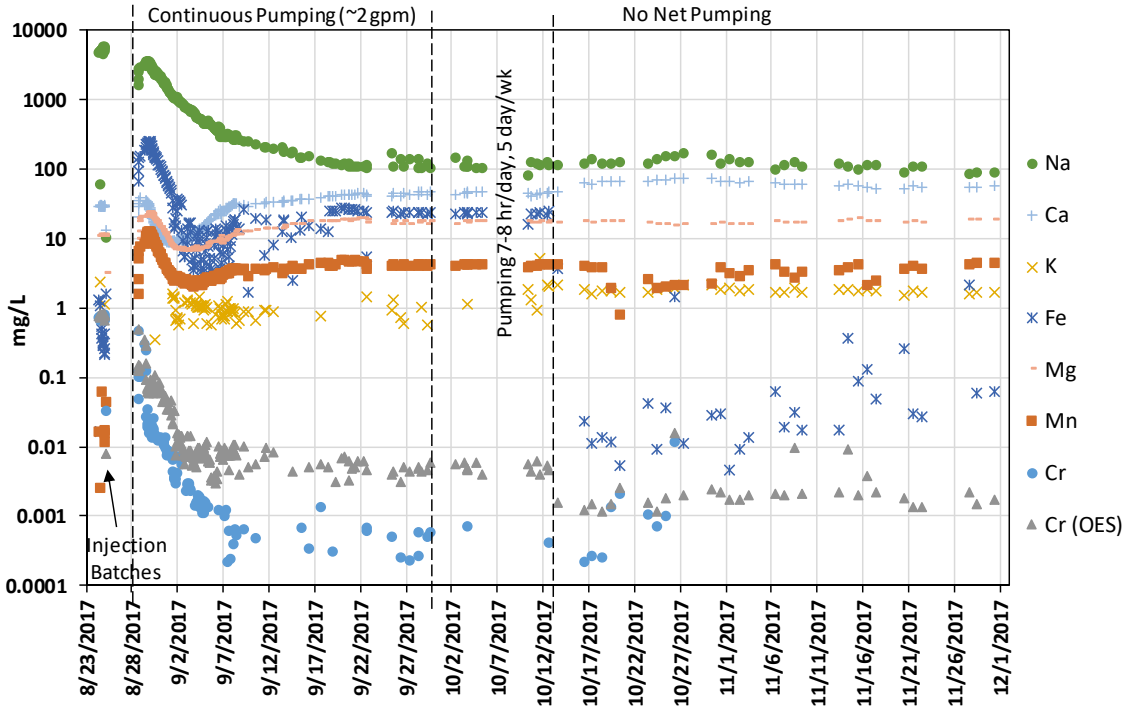


Figure 2 **Concentrations of selected cations and metals in R-42 dithionite test as a function of time. The more reliable analytical results for chromium (inductively coupled plasma mass spectrometry [ICP-MS]) are lagging, so chromium results from ICP optical emission spectrometry (ICP-OES) are also shown.**

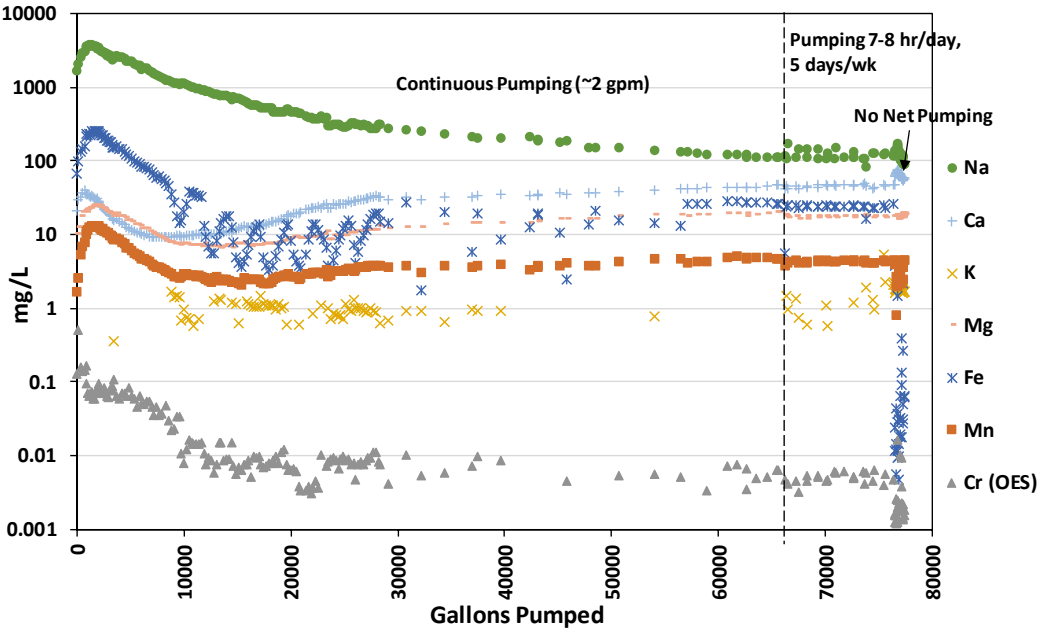


Figure 3 **Data of Figure 2 plotted as a function of gallons pumped from R-42. Chromium data from ICP-MS (blue dots in Figure 2) are omitted. Zero gallons pumped corresponds to 8/28/17 in Figure 2, and earlier data points from Figure 2 are not shown because these corresponded to injection batches that were not pumped from the well.**

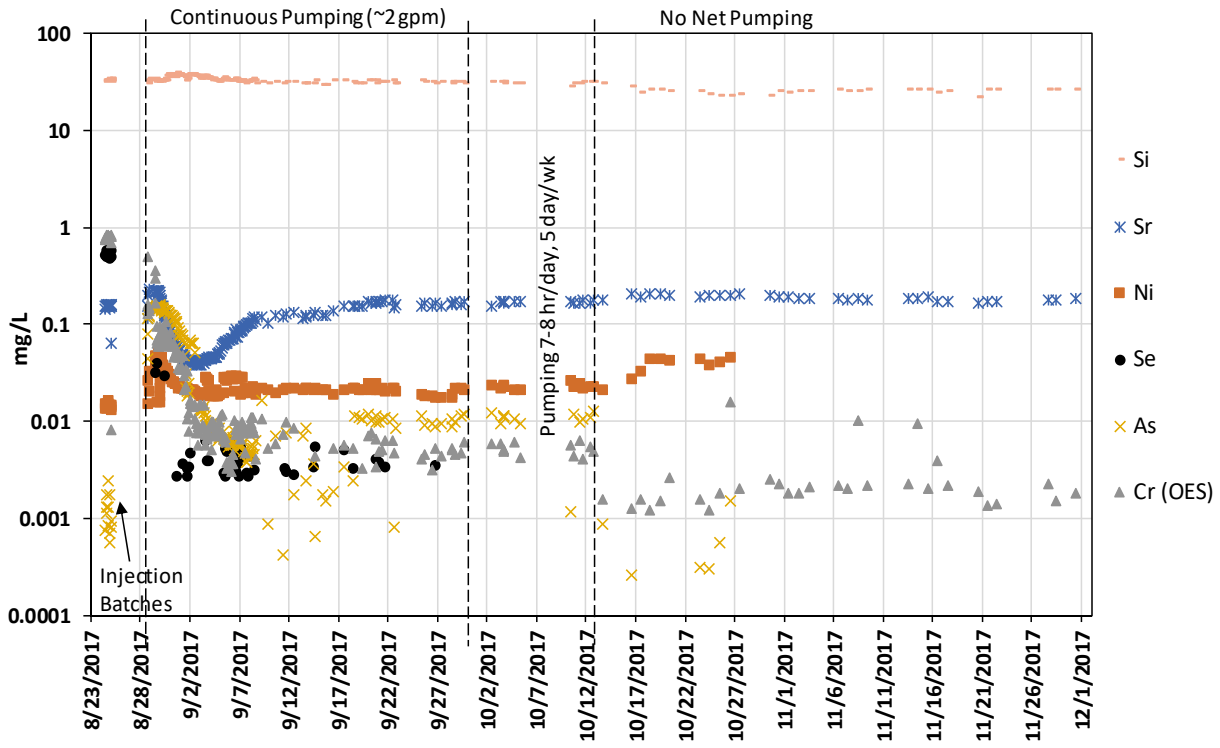


Figure 4 **Concentrations of selected constituents during R-42 dithionite test as a function of time**

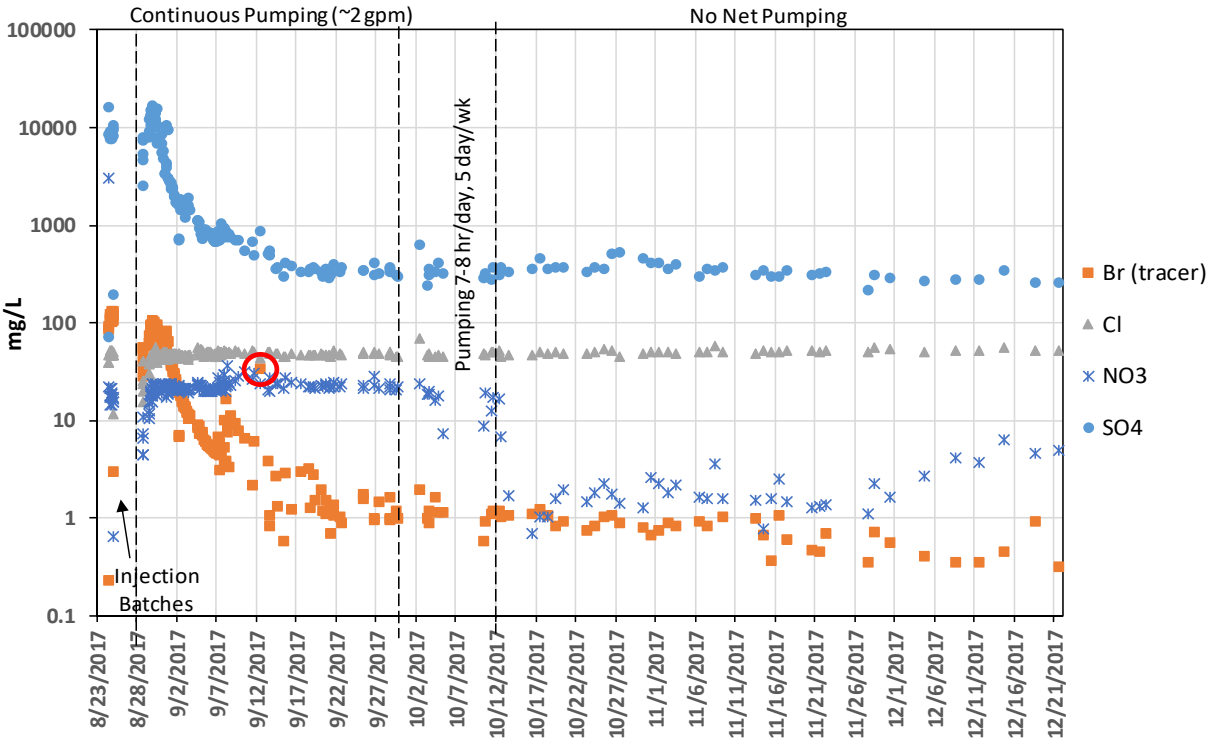


Figure 5 **Concentrations of anions in R-42 dithionite test as a function of time. Circled bromide point causes a significant discontinuity in bromide recovery curve (Figure 7), but it was verified by two repeat analyses.**

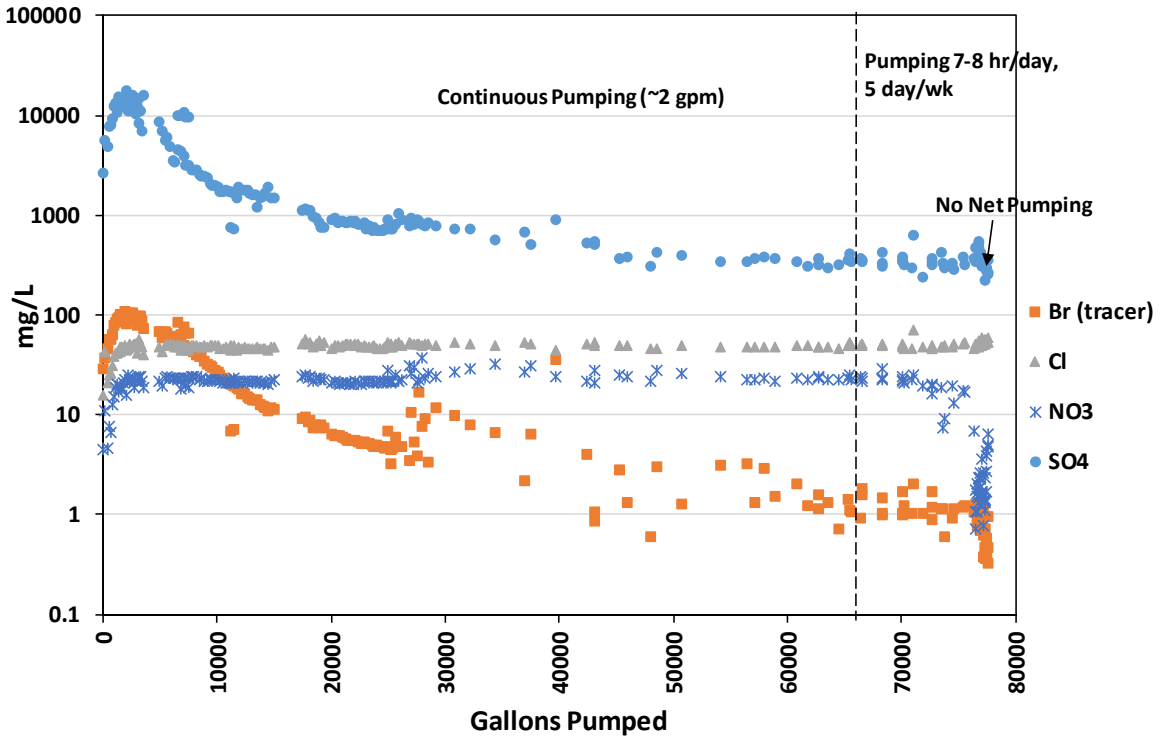


Figure 6 **Data of Figure 5 plotted as a function of gallons pumped from R-42. Zero gallons pumped corresponds to 8/28/17 in Figure 5, and earlier data points from Figure 5 are not shown because these corresponded to injection batches that were not pumped from the well.**

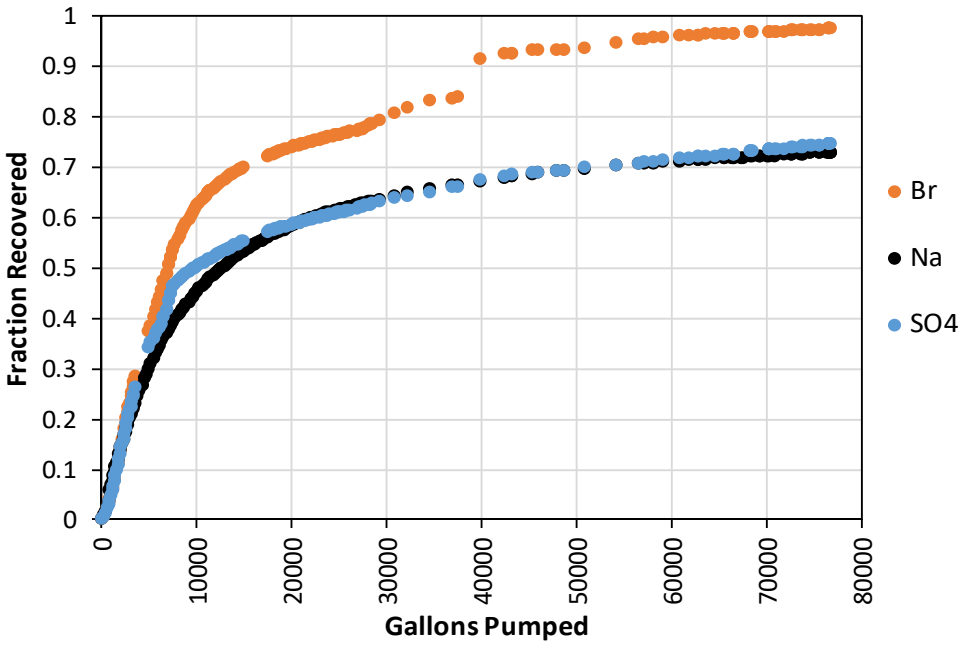


Figure 7 **Fractional recoveries of bromide, sodium, and sulfate as a function of volume pumped from R-42. Sulfate recovery is based on assuming 2 M of sulfate generated for every mole of dithionite injected, and 1 M of sulfate for every mole of sulfite injected.**

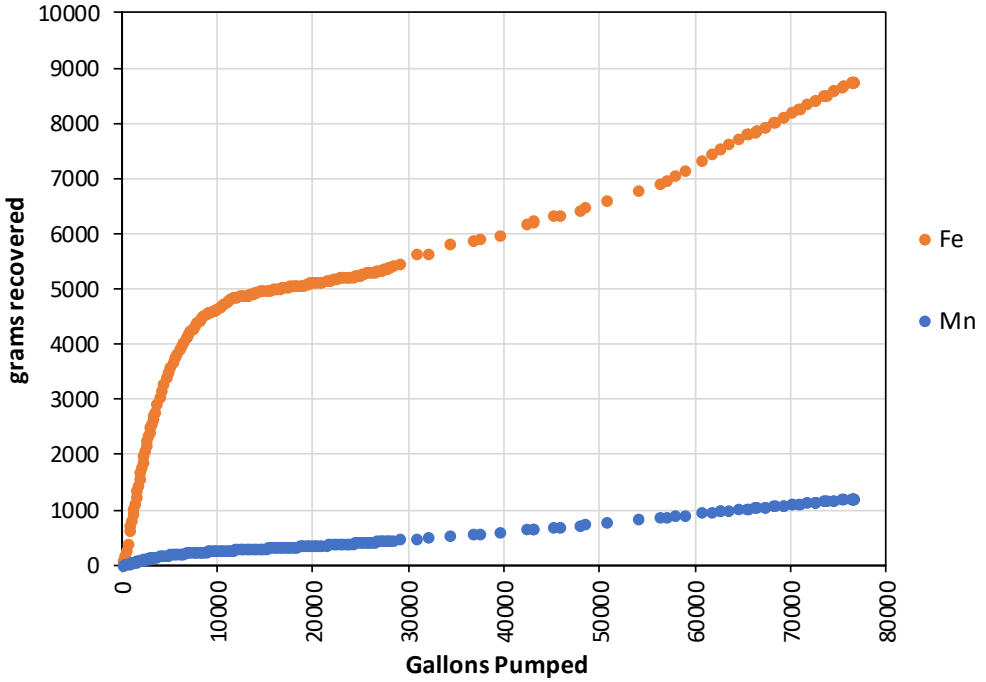


Figure 8 **Recoveries of iron and manganese in R-42 dithionite test as a function of volume pumped**

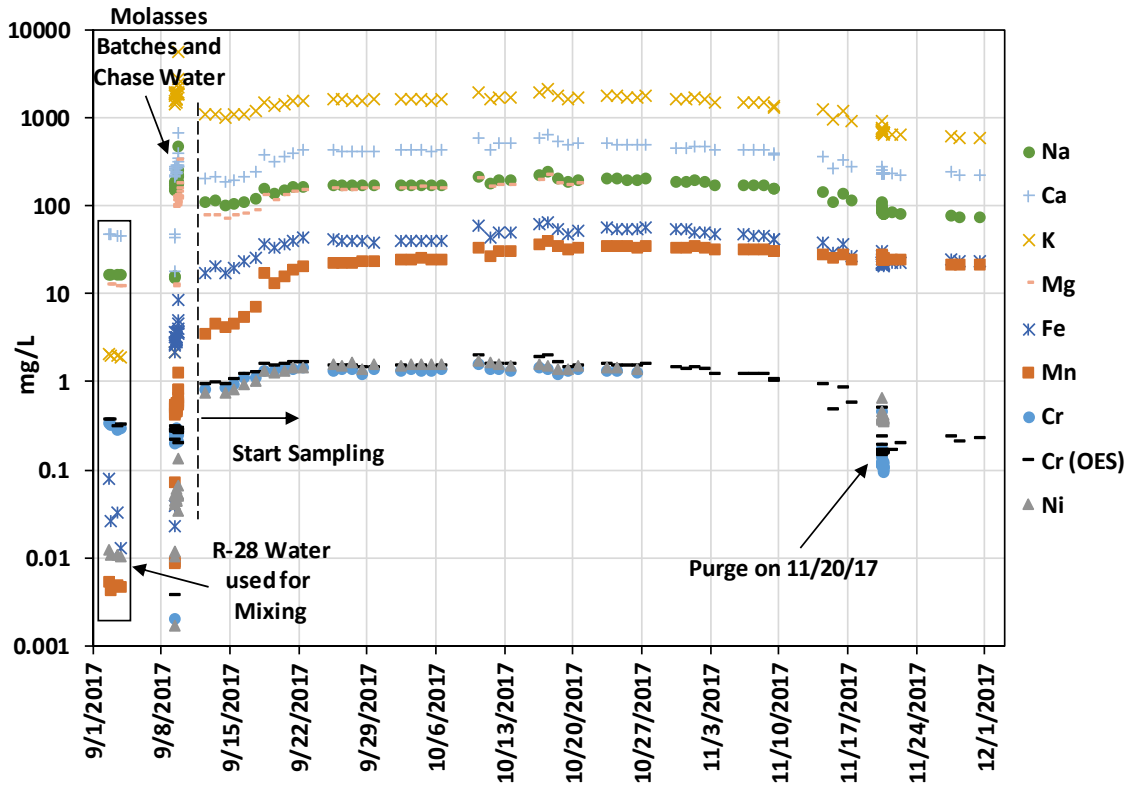


Figure 9 **Concentrations of selected cations and metals in R-28 molasses test as a function of time. The more reliable analytical results for chromium (ICP-MS) are lagging, so chromium results from ICP-OES are also shown.**

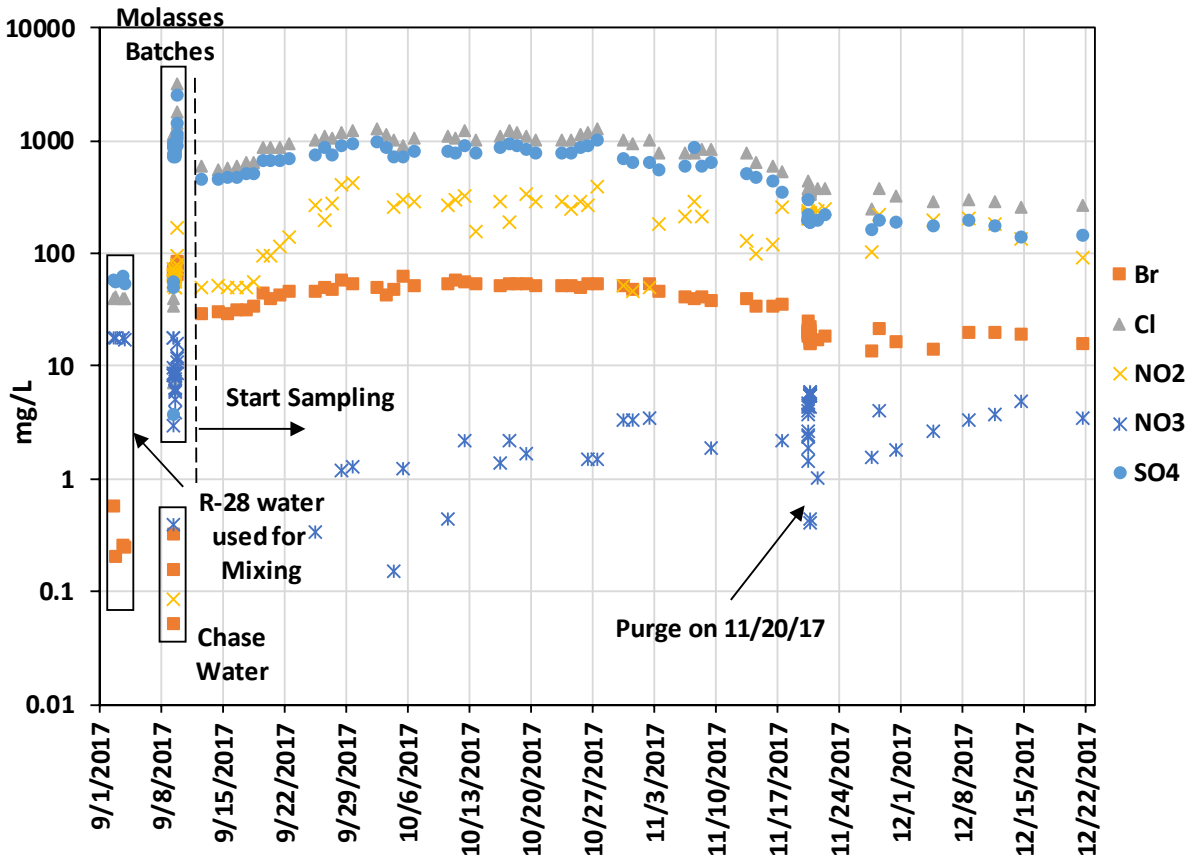


Figure 10 **Concentrations of anions in R-28 molasses test as a function of time**

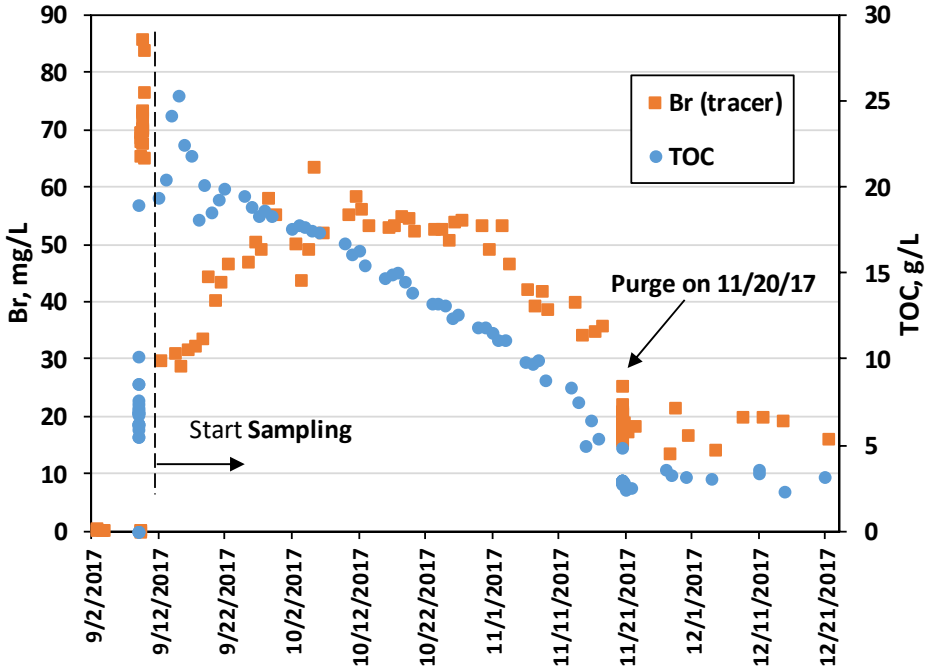


Figure 11 **Concentrations of bromide and TOC in R-28 molasses test. Note that unlike other plots, concentration scales are not logarithmic.**

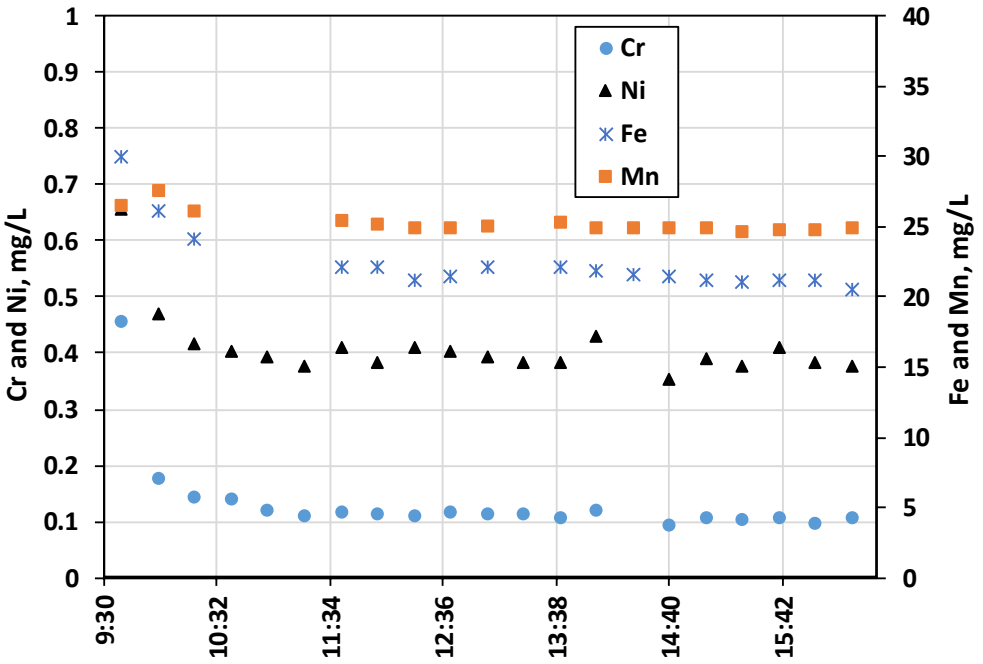


Figure 12 **Concentrations of selected metals during the R-28 purge on 11/20/17**

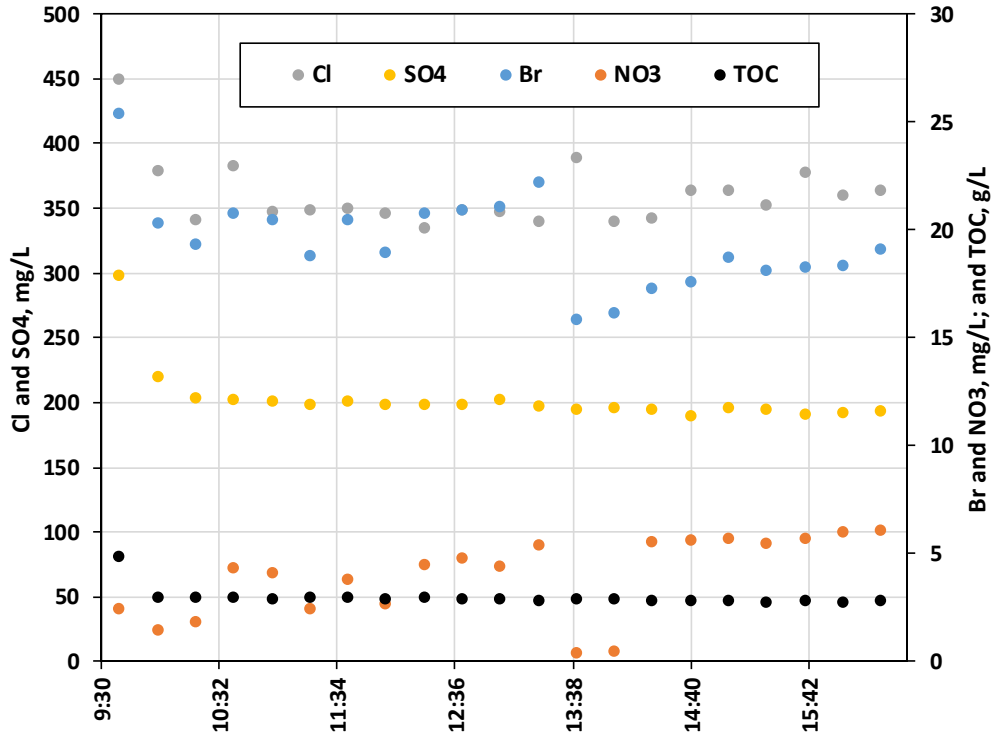


Figure 13 **Concentrations of anions and TOC during R-28 purge on 11/20/17**

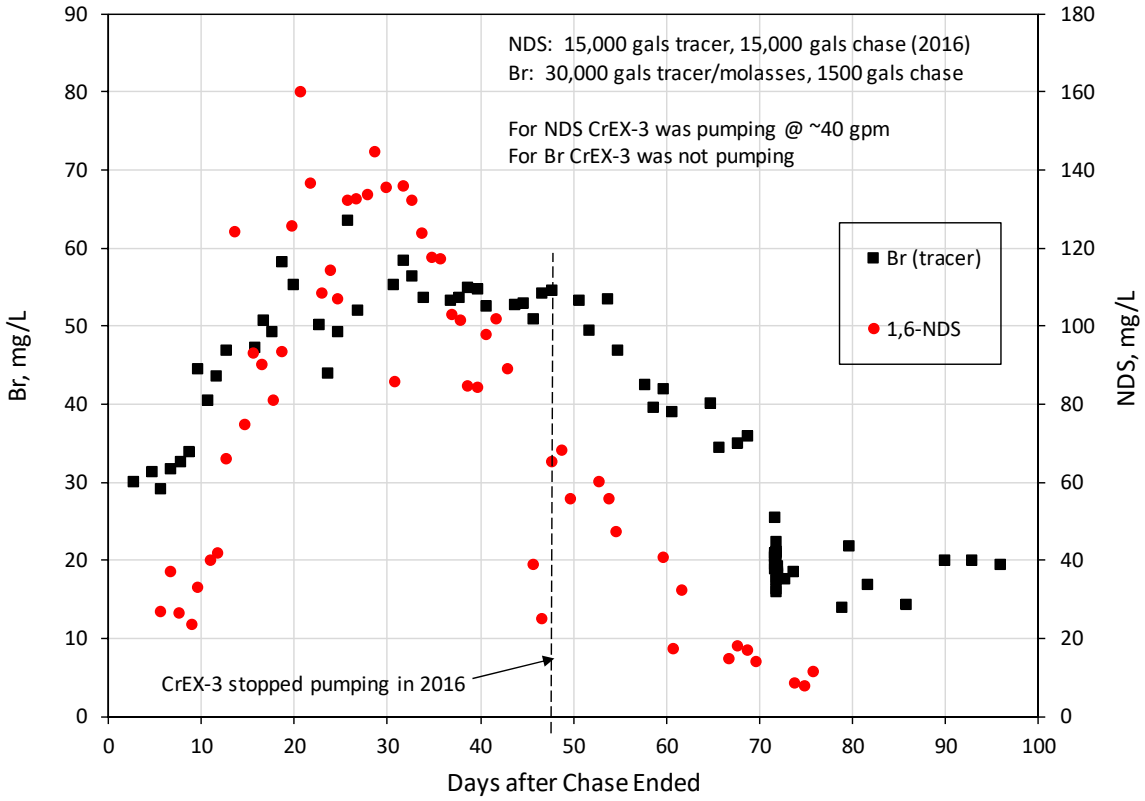


Figure 14 **Comparison of responses of bromide in 2017 molasses test and 1,6-NDS in 2016 tracer test in R-28. Both tracers were passively sampled after injection into R-28. Details of the injections are provided at the top of the plot. Well CrEX-3 was not pumped during the 2017 molasses test.**