EMID-700420

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 Sixth 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 "Sixth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon." This report reflects discussions in pre-submission meetings held with the New Mexico Environment Department on March 26 and April 18, 2018. In those meetings, the content of the report and the approach for inclusion of those results into this report were discussed and agreed upon.

If you have any questions, please contact Danny Katzman at (505) 309-1371 (danny.katzman@em-la.doe.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@em.doe.gov).

Sincerely,

Arturo Q. Duran
Compliance and Permitting Manager
Environmental Management
Los Alamos Field Office

Enclosures:

1. Two hard copies with electronic files – Sixth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon (EM2019-0133)

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

cc (letter with CD/DVD enclosure[s]):
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EM-LA-40AD-00432

April 2019
EM2019-0133

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

EM2019-0133

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

April 2019

Responsible program director:

Bruce Robinson		Program Director	Water Program	4/19/19
Printed Name	Signature	Title	Organization	Date

Responsible N3B representative:

Erich Evered		Program Manager	N3B Environmental Remediation Program	4/22/2019
Printed Name	Signature	Title	Organization	Date

Responsible DOE EM-LA representative:

Arturo Q. Duran		Compliance and Permitting Manager	Office of Quality and Regulatory Compliance	4/25/19
Printed Name	Signature	Title	Organization	Date

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Attachment 1 Data Associated with the “Sixth Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon” (on CD included with this document)

1.0 INTRODUCTION

This sixth 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 and fourth quarterly reports (N3B 2018, 700032; N3B 2018, 700108) provided an update of the geochemistry data from the two amendments tests. The fifth quarterly report provided updates on the geochemistry at R-42 and R-28, including data from extended purge events conducted in October and November 2018 (the "October 2018 purge"), and additional samples collected in December 2018 (N3B 2019, 700214).

This sixth quarterly report provides an evaluation of groundwater geochemistry from the first sampling event conducted in March 2019 as the beginning of a series of forthcoming biweekly events that employ time-series sampling during 1000-gal. purges at R-42 and R-28. The report also includes an updated analysis of hydraulic behavior at the two wells to explore insights into whether there have been reductions in aquifer permeability associated with the tests or chromium reduction. An analysis of the amount of chromium reduction to date at each of the two test wells is also presented.

An update on an ongoing evaluation of the geochemical condition at extraction well CrEX-3 is also included. The geochemistry at CrEX-3 appears to be showing effects related to one (or both) of the two amendments tests and has resulted in having to pause continuous pumping at CrEX-3 because the geochemistry of its water is causing plugging of influent bag filters at the treatment system.

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).

As described in section 5.0 of this report, it is recommended that the next status report be submitted at the end of December 2019.

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. Operational timelines and operational descriptions are also provided in Figure 2.1-1 (and in subsequent R-42 Figures 2.1-2 through 2.1-14). The approximate timeline for injection batches are plotted near the left-most of the vertical dashed timelines presented on each figure. Operational activities to the right of the amendment injection included the start of continuous pumping of R-42 in August 2017, and then the subsequent transition in September 2017 to pumping 5 days/wk (8 hr/day) from the well. This pumping was stopped in October 2017. Biweekly 50-gal. purges were initiated after a dilution tracer test was conducted in January 2018, as described in the second quarterly report (LANL 2018, 603031). Following the dilution tracer test, each sampling event involved an approximate 50-gal. purge and did not include injections or water circulation. From October 22 and until November 2, 2018, an extended semicontinuous purge and sampling event was conducted at approximately 3 gallons per minute (gpm) (2.9 gpm) for 170 hr during the period. This R-42 3-gpm purge and sampling event was conducted to obtain samples representing groundwater further into the aquifer than is likely achieved during the 50-gal. purges. Beginning on March 19, 2019, biweekly sampling began involving time-series sample collection across 1000-gal. purges. Samples were collected at approximately 50, 350, 700, and 1000 gal. The objective was to evaluate whether purging beyond 50-gal. would provide data more representative of the aquifer further from local-scale conditions that may persist near the well.

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 contractor Los Alamos National Security, LLC (LANS) to Newport News Nuclear BWXT-Los Alamos, LLC (N3B) beginning on April 30, 2018.

Figures 2.1-2 through 2.1-14 either show the full amendment period as in Figure 2.1-1, or the figures show a focused period that depicts only the more recent data from March 19, 2019, when the 1000-gal. purge event was conducted. This was the first event of a series of forthcoming 1000-gal. purges.

Figures 2.1-3 and 2.1-4 focus only upon a subset of the analytes (i.e., iron, manganese, and arsenic). Figures 2.1-5 and 2.1-6 focus on sodium and sulfate. Figures 2.1-7 and 2.1-8 show concentration trends for some of the other elements of interest, including arsenic and selenium over the full amendment period.

Figures 2.1-9 and 2-1.10 show concentration trends for selected anions. Figures 2.1-11 and 2.1-12 focuses on a subset of recent data for nitrate and nitrite only. Figures 2.1-13 and 2.1-14 focus on recent bromide data.

Cr(VI) concentrations (measured as total chromium) in R-42 decreased to below the New Mexico groundwater standard of 0.05 mg/L soon after the dithionite deployment and have remained well below this level. Since the beginning of 2018 and including the March 2019 purge, chromium concentrations have remained at levels below 0.01 mg/L (Figure 2.1-1), which suggests that the aquifer in the vicinity of R-42 maintains sufficiently reducing conditions to reduce and immobilize Cr(VI). The pH before, during, and following the October 2018 purge is approximately 7.0 standard units. This value remains significantly lower than pre-deployment values that were near 8.0. The persistence of these lower pH values is indicative of a continued influence from geochemical reactions following the dithionite deployment.

Concentrations of dissolved iron have persisted at elevated levels over the better part of the past year and at concentrations approximately a thousand times higher than the pre-amendment level (i.e., 10 mg/L versus 0.01 mg/L). There was a period in late 2017 when iron was lower, likely because of the use of a sampling circulation loop. The loop drew water from the well and up to the surface sampling point and then returned unsampled water back down into the well. In the process, atmospheric oxygen was likely introduced into the well water prompting iron oxidation and precipitation in the well bore and minimized iron concentrations in samples. Following a slow but steady decline in dissolved iron over the past year during which the 50-gal. purge sampling method was conducted, the extended purge conducted in October 2018 prompted an increase in the iron concentration from approximately 10 to 15 mg/L (Figures 2.1-3 and 2.1-4). The level has fallen further (to 8 mg/L) during the recent 1000-gal. purge samples, indicating a partial return towards pre-amendment conditions.

Manganese and arsenic trends are also shown in Figures 2.1-3 and 2.1-4. The trend for arsenic during the March 2019 purge correlates with that of iron, which fell. Manganese increased from 2.65 to 3.64 mg/L during the purge. Both manganese and arsenic exhibited elevated levels shortly after amendment injections. These levels have been slowly diminishing over the past year. Concentrations of both manganese and arsenic have remained well above pre-amendment levels, indicating persistent reducing conditions (i.e., the pre-amendment level is approximately 0.001 mg/L for both). Similar to iron, the manganese and arsenic levels suggest that the purge captured groundwater that exhibits reducing conditions.

Figures 2.1-5 and 2.1-6 present sodium and sulfate trends. The amendment, containing sodium dithionite and sodium sulfite (and to a lesser extent sodium bromide), was the origin of the elevated sodium. These chemicals also provided the sulfur that acted as the primary sulfur source that produced sulfate through oxidation reactions. Sulfate has been the most prominent anion measured in R-42 since the amendments. Sodium has helped to ionically balance sulfate (i.e., maintain charge balance) in samples following the time of the amendment. Sodium has most likely acted as an accompanying ion to sulfur species during the amendment test (i.e., accompanied sulfate and other more reduced sulfur species such as sulfite) and can be considered as a tracer to the sulfur species. Sulfate and sodium levels initially spiked upwards following amendment deployment and then subsequently trended downwards. At first, during post-amendment pumping, the sulfate and sodium levels fell rapidly, and then during later phases the levels decreased more slowly as they began approaching pre-amendment levels. During the March 2019 purge, sulfate persisted above the pre-amendment levels of approximately 80 mg/L. The sulfate level also increased from 175 to 237 mg/L over the course of the purge.

Before the October 2018 purge event, the diminished sulfate and sodium levels had fallen to levels approximately double their historical concentrations (from June 2016, before a local test that involved a sodium addition). The data from the October 2018 purge resulted in increased levels of both, possibly drawing concentrations of these now soluble species from downgradient (i.e., the migration area as shown in Figure 2.1-17). It is also possible that sodium and sulfate were present in low permeability zones near the well that the 50-gal. purges were accessing. Following peaking of levels during the October 2018 purge, sulfate and sodium levels began to decrease, suggesting that the pumping also began reaching further out towards the influence of aquifer regions where concentrations of both are lower. Like the previous purge, the March 2019 1000-gal. purge also drew in subsequently higher concentrations of both sodium and sulfate.

Figures 2.1-11 and 2.1-12 illustrate the long-term and recent trends for both nitrate and nitrite. The nitrate has been depressed below pre-deployment levels since the end of the post-amendment purges, indicating a continued reduced state in the R-42 samples from October 2017 to mid-October 2018. With the exception of a single outlying data point, nitrite was not detected during this period. As shown in

Figure 2.1-6, upon the start of the recent October 2018 purge, nitrite appeared while nitrate nearly disappeared. The nitrate-to-nitrite flip appears to represent a shift that was close to stoichiometric in regard to nitrogen. In the recent March 2019 purge samples, nitrate increased and nitrite decreased, potentially indicating a more oxidative environment. However, nitrate at low levels of 0.5 mg/L is still well below the pre-amendment level of approximately 20 mg/L of nitrate.

Figures 2.1-13 and 2.1-14 show long-term and recent trends for bromide. Bromide originated from the co-deployed amendment tracer (i.e., sodium bromide). The bromide was predominantly captured during the initial post-amendment months when continuous pumping was conducted. Bromide levels steadily trailed off until August 2018, when the concentration essentially reached pre-deployment levels of approximately 0.2 mg/L, indicating a return of ambient groundwater conditions with respect to conservative ions. Like sodium and other analytes previously described, bromide exhibited a modest increase in concentration during the October 2018 purge. The concentration held relatively stable in the sample following the purge. Although the increase in bromide was modest (from approximately 0.22 to 0.45 mg/L), the increase indicates that the October 2018 purge effectively reached further into the radius of influence (ROI) and possibly also into downgradient migration zones (see Figures 2.1-15 through 2.1-17 for an illustration of a conceptualized model of amendment study stages over time), or into low permeability zones adjacent to the well that the 50-gal. purges did not access. The concentration of bromide fell towards pre-amendment levels during the March 2019 purge.

Concentrations of other constituents (e.g., calcium, magnesium, potassium and chloride) remain close to pre-amendment levels.

The March 2019 1000-gal. purge suggests that ROI region(s) in the R-42 vicinity are still exhibiting reducing conditions. The dissolved oxygen and oxidation-reduction potential field measurements also remained low, indicative of reducing conditions. Breakthrough or near-breakthrough of ambient levels for species that are not susceptible to reducing ROI conditions is evident for calcium, magnesium, and chloride.

Concentrations of other elements or ions not shown in Figures 2.1-1 through 2.1-14 can be found in Attachment 1 (on CD included with this document).

2.2 Molasses at R-28

Overall, conditions are similar in the recent 1000-gal. purge, as were conditions at the end of the purge in October, and continue to show Cr(VI) reduction and precipitation.

Figure 2.2-1 shows an updated plot of the concentration trends of selected dissolved cations and metals, including chromium, measured in samples collected from R-28 as a function of time. Operational timelines or other operational descriptions are also provided in Figure 2.2-1 (and in subsequent R-28 Figures 2.2-2 through 2.2-14). The approximate timeline for injection batches are plotted near the left-most of the vertical dashed lines presented on each figure. The other vertical dashed lines shown to the right indicate subsequent dates when operational activities were conducted. Chronologically, following the amendment injection, these operational activities included the start of “no net pumping,” a 1000-gal. purge sample, and a transition to 50-gal. purge sampling. Finally, from October 22 and until November 2, 2018, an extended semicontinuous purge and sampling event was conducted at approximately 2.6 gpm (for 170 hr during the period). As Figure 2.2-1 shows, no purging/sampling occurred from April 19 to June 13, 2018. This gap in sampling is a result of the transition of environmental work from LANS to N3B. On March 19, 2019, a 1000-gal. purge was performed where four samples were taken at times that were spread throughout the purge with the goal to obtain samples representing groundwater further into the aquifer than is likely achieved during the 50-gal. purges.

Figures 2.2-3 and 2.2-4 focus on chromium, pH, and total organic carbon (TOC). Following the injection, chromium concentrations increased to greater than 1.5 mg/L, potentially associated with small-scale leaching of the stainless-steel well screen. Following the 1000-gal. purge in November 2017, chromium concentrations declined from approximately 0.15 mg/L following the purge to approximately 0.065 mg/L in April 2018. During this period, pH was low (less than 5.5, with two exceptions) likely because of the production of organic acids from fermentation. At these lower pH levels, organic acids concentrations are assumed to correlate with the concentration of TOC, which remained elevated, at approximately 1000 mg/L in April 2018. The data indicate that the persistence of Cr(III) produced from reduction of Cr(VI) in groundwater was caused by the increased solubility of Cr(III) minerals at the observed pH levels and potentially additional complexation by organic acids. The pH data was not collected from April through the October 2018 purge event. During this period, as TOC (and organic acids) declined, reaching a minimum of 102 mg/L on September 17, 2018, this decline is believed a probable factor that caused chromium concentrations to decrease to below 0.05 mg/L during mid-July 2018. The chromium concentration has remained below 0.05 mg/L since that time. During the October 2018 purge, chromium concentrations fell further and to the lowest levels yet observed (approximately 0.01 mg/L), while pH increased to above 5.5 indicating diminishing levels of organic acids. TOC concentration initially increased during the purge and then fell back towards pre-purge levels. The data indicated a different geochemical environment in the aquifer adjacent to R-28 compared with the area in the aquifer further into the ROI. The rise in observed pH and fall in chromium levels over the October 2019 purge suggested falling concentrations of organic acids that would solubilize chromium. The March 2019 1000-gal. purge continued with trends similar to the October 2018 purge where pH further increased and chromium further decreased. These chromium results indicate the longevity of the Cr(VI)-reducing conditions generated by the injected molasses.

Figures 2.2-5 and 2.2-6 focus on the iron and manganese data. Dissolved iron and manganese were initially generated after the molasses injection. Following a general decline over the subsequent test period, both iron and manganese levels have remained elevated throughout the test and recently remain at about three orders of magnitude higher than pre-amendment levels. Both iron and manganese levels were observed to rise, prompted by the beginning of the October 2018 extended purge followed by falling concentrations. These initial increases indicated that the pumping reached further out into the ROI. The concentrations decreased as a result of the March 2019 purge.

Figures 2.2-7 and 2.2-8 show concentration trends for some of the other elements of interest, including arsenic and selenium. Arsenic has demonstrated a slow and steady decline since February 2018. The purges may have accelerated the rate of decline in arsenic levels, which fell from 0.007 to 0.004 mg/L. With one exception at 0.014 mg/L in June 2018, selenium has remained undetected since March 2015. Although nickel levels fell overall throughout the period, the purge drew higher nickel levels temporarily. The recent samples following the purge exhibit the lowest nickel concentration values to date.

Figures 2.2-9 and 2.2-10 show concentration trends for selected anions. Chloride concentrations generally fell throughout the test period, starting from elevated concentrations above 1000 mg/L in the molasses amendment and approaching historical background levels in the most recent sample set. The October 2018 and March 2019 purges accelerated the rate of decline, indicating that the pumping pulled water from portions of the aquifer outside of the ROI.

Figures 2.2-11 and 2.2-12 illustrate bromide, sulfate, and TOC trends. Sodium bromide is the tracer that was introduced with molasses. Sulfate may come from either of two potential sources: (1) from the aquifer outside of the ROI that contains approximately 60 mg/L or (2) from the molasses amendment itself, which contained approximately 1000 mg/L of organic sulfur that may be converted to sulfate by microbes or oxidation. The TOC represents molasses and/or ethanol and metabolic reaction products from each, such as organic acids (as described previously in this section). The levels of all three (i.e., TOC, bromide, and sulfate) were elevated following the molasses deployment and ethanol chase. Both the bromide and sulfate levels decreased following the ethanol chase (and then rebounded to an extent), TOC levels rose slightly following the addition of the ethanol. TOC, bromide, and sulfate levels generally fell over the subsequent period as upgradient water flowed through the well and purges were conducted. Sulfate levels fell to below pre-amendment concentrations in July 2018, indicating action of sulfate-reducing bacteria in conjunction with a general washout of the amendment solution, which contained elevated levels of sulfate. Sulfate concentrations rose during the March 2019 1000-gal. purge and, while at 34 mg/L, are still lower than the pre-amendment level of 60 mg/L. The increase suggests the pumping of water that is influenced by lingering amendment with elevated sulfate or by water from outside of the sulfate-reducing zone. The bromide level has been falling since the October 2018 purge and through the March 2019 purge. This is indicative that the pumping has drawn out the majority of amendment solution that was still lingering in the vicinity of R-28 at the time of the October 2018 purge. TOC levels have held static since the end of the October 2018 purge. The levels, which are above 20 mg/L, are still well above the pre-amendment levels near 1 mg/L, indicating less microbial consumption and, more specifically, in conjunction with the pH data, indicating less fermentation.

Figures 2.2-13 and 2.2-14 illustrate the nitrate and nitrite trends during the test progression. Nitrate has been reduced below pre-deployment levels since deployment of the molasses and ethanol. Nitrite exhibited an initial spike following molasses deployment, followed by a depression subsequent to the ethanol chase. Following a partial rebound in September 2017, the nitrite has been generally decreasing. More recently, since about July 2017, both nitrite and nitrate have been decreasing more visibly, as shown in Figure 2.2-13. The levels of both nitrate and nitrite fell to nondetect during the October 2018 extended purge event and also remained nondetect after the last sample collected in December 2018. This may indicate that the nitrogen sources in the molasses were consumed by microbes and that any nitrogen contribution from the aquifer was also consumed, or that more electrons in the reducing water are going to denitrification versus fermentation and sulfate reduction compared with the condition of the near-well environment before purging. Concentrations of both held relatively steady and low since the October 2018 purge and through the March 2019 purge. Nitrate increased only slightly and nitrite had a subtle decreasing trend possibly indicating the return towards more oxidative conditions.

Concentrations of other constituents have held static since the October 2018 purge and through the March 2019 purge. Potassium is holding and still well above pre-amendment levels (Figure 2.2-1). Sodium and calcium stayed near pre-amendment levels.

Concentrations of other elements or ions not shown in the figures can be found in Attachment 1 (on CD included with this document).

3.0 ESTIMATES OF CHROMIUM AMOUNTS REDUCED IN R-42 AND R-28 PILOT AMENDMENT TESTS

Estimates of Cr(VI) reduced in the R-42 and R-28 pilot amendments tests are broken into two separate calculations for each well: (1) reduction resulting from drawing Cr(VI)-bearing groundwater into/through the treatment zone as a result of pumping the wells, and (2) reduction resulting from natural groundwater flow through the treatment zone during periods of no pumping. In both cases, it is assumed that the water moving into/through the treatment zone had an average Cr(VI) concentration equal to what was measured in the respective wells before the amendment additions (approximately 0.7 mg/L for R-42 and approximately 0.5 mg/L for R-28). It is also assumed that all the Cr(VI) in the water moving into/through the treatment zone was completely reduced. The latter assumption is justified by the observation that there has been little or no Cr(VI) detected in either well since the amendment additions, and it is also supported by the observation of persistent elevated concentrations of the reduced iron (Fe^{2+}) and manganese (Mn^{2+}) species in both wells, which are fundamentally incompatible with the presence of Cr(VI).

3.1 Contributions from Pumping at Both Wells

The calculation of the contribution from pumping for each well is straightforward, and it should have relatively little uncertainty. The cumulative pumped volumes from each well is multiplied by the respective pre-amendment Cr(VI) concentrations to arrive at:

- R-42: (110,000 gal.)(3.785 L/gal.)(0.0007 g Cr(VI)/L) = approximately 290 g Cr(VI)
- R-28: (30,000 gal.)(3.785 L/gal.)(0.0005 g Cr(VI)/L) = approximately 57 g Cr(VI)

The calculation of contributions from natural flow for each well is more complicated and far more uncertain. These contributions are the subject of the next two sections.

3.2 Contribution from Natural Flow at R-28

R-28 has not been pumped for most of the time since the molasses amendment injection, and the total volume pumped has been only approximately equal to the volume of molasses solution injected. Figure 3.2-1 shows the concentration histories of chloride ion (Cl^-) and bromide ion (Br^-) in R-28 since the molasses injection. Both anions are non-reactive, and both were distributed uniformly in the molasses amendment solution at concentrations that were significantly elevated over background concentrations (Cl^- from being a constituent of the molasses, and Br^- as an introduced tracer). The concentration histories of these two anions in R-28 after the amendment addition can be divided into roughly three periods: (1) a period where the concentrations were basically the same as in the injected amendment solution (about the first 70 days), (2) a period where concentrations were significantly lower but remained relatively steady (about the next 240 days), and (3) a period where concentrations dropped to close to background levels but remained slightly elevated over background (the next 240+ days, with this third period still continuing). The three periods are shown in Figure 3.2-1 (note that the transitions between periods are not abrupt, but rather gradually occur over weeks). The Cl^- and Br^- behaved somewhat differently in that the Cl^- concentrations during the second time period are relatively steady, whereas the Br^- concentrations show a slow, steady decline during this period. The reasons for this are unknown. We use the Cl^- concentrations for the analyses here, mainly because Br^- elutes from an ion chromatography column in the tail of the Cl^- chromatography peak, and measured Br^- concentrations can thus be somewhat affected by the chromatographic tailing behavior of Cl^-, particularly when Cl^- concentrations significantly exceed Br^- concentrations, as they do here. However, the Br^- concentrations would yield a similar result if the decline in Br^- during the second period were ignored and an average concentration were used.

The post-injection concentrations observed in R-28 reflect the drift of the amendment solution that was injected upgradient of the well back toward the well. The direction of drift is also the direction that Cr(VI)-bearing water is assumed to be moving into the treatment zone. It is assumed that approximately half the volume of amendment solution (15,500 gal.) was injected upgradient of the well, and the other half was injected downgradient and drifted away from the well (never to be seen again in R-28, and to have no effect on R-28 observations in the absence of sustained pumping at a relatively high rate, which never occurred). It is also assumed that the concentrations in R-28 reflect a flux-weighted contribution from the entire 15,500 gal. of amendment solution that was injected upgradient of R-28, even though only a small fraction of the upgradient injection should have ever actually flowed through R-28. The three periods of relatively steady but different Cl^- (and Br^-) concentrations are taken to reflect three different flux contributions. The transition from the first to the second period is taken to correspond to the period when the molasses solution was replaced by molasses-free inflowing water in the “flow zone” of highest flux, and the transition from the second to the third period is taken to correspond to when the molasses solution was replaced by inflowing water in the zone of second highest flux. The third flow zone is still presumably contributing amendment solution at a very low rate. The assumed situation is schematically depicted in Figure 3.2-2. The volumetric fractions of flow contributed from each of the three flow zones is calculated using the concentrations during the three periods as follows:

$$\boldsymbol{F_3 = \frac{C_3 - C_b}{C_1 - C_b}}$$ **Equation 1**

$$\boldsymbol{F_2 = \frac{C_2 - C_b}{C_1 - C_b} - F_3}$$ **Equation 2**

$$\boldsymbol{F_1 = 1 - F_2 - F_3}$$ **Equation 3**

where, F_x = fractional flow contribution from zone that stops contributing amendment solution after period x,

C_x = concentration during period x,

C_b = pre-amendment background concentration.

Using the chloride concentrations, and assuming C_1 - C_b = 950 mg/L, C_2 - C_b = 180 mg/L, and C_3 - C_b = 20 mg/L, F_1 = 0.811, F_2 = 0.168, and F_3 = 0.021. Furthermore, the fraction of amendment solution that was injected into each of the three zones can be estimated, which is not necessarily the same as the fractions given by F_1, F_2 and F_3, as follows:

$$\boldsymbol{MF_i = \frac{F_i T_i}{F_1 T_1 + F_2 T_2 + F_3 T_3}}$$ **Equation 4**

where, MF_x = mass or volume fraction injected into zone that stops contributing amendment solution after period x,

T_x = time at which period x ends.

Assuming that T_1 = 70 days, T_2 = 310 days, and T_3 = 550 days (approximately the current time), MF_1 = 0.471, MF_2 = 0.433, and MF_3 = 0.096.

The flow contribution of each zone (in L/day) is calculated by apportioning the 15,500 gal. of amendment solution injected upgradient according to the mass fractions given by the MF_x values, and dividing by the times, T_x:

$$\boldsymbol{Flow_i = \frac{(15{,}500\ gal)\left(3.785\frac{L}{gal}\right)MF_i}{T_i}}$$ **Equation 5**

Using the values given above, $Flow_1$ = 395 L/day, $Flow_2$ = 82 L/day, and $Flow_3$ = 10 L/day, which yields a total flow of 487 L/day of water flowing into the treated zone through a cross-sectional area perpendicular to flow defined by the reach of the 15,500 gal. of amendment solution injected upgradient. It can be readily verified that the three individual zonal flows have fractional flows equal to the values of F_1, F_2,and F_3 given above. With this approach, the key assumption is that half the amendment solution is injected upgradient, and half is injected downgradient. The flow estimate will be directly proportional to the volume assumed to be injected upgradient. It is also assumed that the observations in R-28 are representative of the entire cross-sectional area of the treated zone perpendicular to flow. If the injected solution were distributed in a cross-sectional area that is two times greater than that of a base case, then it would be expected that the upgradient distance the amendment solution was injected to would be approximately half that of the base case to conserve volume. In this case, the linear flow velocities perpendicular to the cross-sectional area would need to be half the base case velocities to result in the same zonal arrival times at R-28, but the linear velocities would be distributed over twice the area, which would result in the same volumetric flow through the treated zone.

Using the total flux estimate of 487 L/day of inflowing water, and multiplying by a pre-amendment Cr(VI) concentration of 0.5 mg/L over a 550-day period, yields an estimate of 134 g of Cr(VI) reduced as a result of natural flow around R-28, to date. Given the additional estimate of 57 g reduced during pumping (above), the total estimate of Cr(VI) mass reduced in the vicinity of R-28 to date is 191 g. This estimate clearly has considerable uncertainty, especially for the contribution from natural flow, given the assumptions involved.

Alternatively, the volumetric flow rate can be estimated through the treated zone using the decline in Br^- concentrations in R-28 during the second of the three periods shown in Figure 3.2-1, assuming that the decline reflects the flushing of a well-mixed volume around R-28 equal to the amendment solution volume. The assumption of perfect mixing over approximately 31,000 gal. of pore volume of porous media is not precise, similar to the assumption that the concentration decline in R-28 accurately reflects a decline in average concentrations over a much larger volume. Also, the fact that the Cl- concentrations did not decline as the Br^- concentrations did during the second time period further complicates this approach. Figure 3.2-3 shows the results of a log-linear fit to the bromide concentration data during the second time period, and the resulting volumetric flow rate estimate, given by (-slope)*(31,000 gal.)(3.785 L/gal.), is equal to 1067 L/day, or about 2.2 times the estimate of 487 L/day provided above. If this value is used instead of the estimate of 487 L/day, the mass of Cr(VI) reduced as a result of natural flow would be 294 g instead of 134 g, increasing the total mass of Cr(VI) reduced to 350 g from approximately 190 g.

3.3 Contribution from Natural Flow at R-42

At R-42, an estimate of the natural volumetric flow rate through the treated zone is complicated by the fact that nearly 8 times the volume of the injected dithionite amendment solution was pumped from R-42 before natural flow conditions were established. This precludes any possibility of applying an estimation approach similar to that used for R-28 at R-42. However, similar to the situation at R-28, Br^- concentrations did decline rather steadily at R-42 for a time period spanning from just after a January 2018 attempt at a borehole dilution tracer test to just before an extended purge in October 2018 (Br^- was also introduced as a tracer with the amendment solution at R-42). Figure 3.3-1 shows the results of a log-linear fit to the Br^- concentration data during this time period, and the resulting volumetric flow rate estimate through the treatment zone is (-slope)*(10,000 gal.)(3.785 L/gal.) = 360 L/day. If the factor of 2.2 difference between this type of estimate and the more rigorous flow estimate at R-28 is assumed to apply at R-42, a more rigorous flow estimate at R-42 would be 163 L/day. These two flow estimates (360 L/day and 163 L/day) result in estimates of 126 and 57 g, respectively, for the mass of Cr(VI) reduced because of natural flow through the treatment zone at R-42. Although these mass estimates are considered more uncertain than the estimates for natural flow through the treatment zone at R-28, the fact that the estimated mass of Cr(VI) reduced as a result of pumping is much greater at R-42 (290 g versus 57 g at R-28) means that the greater uncertainty for natural flow at R-42 corresponds to a much smaller fraction of the total Cr(VI) mass reduction estimate at R-42 than at R-28. The estimates of total Cr(VI) mass reduced at R-42 are 416 g or 347 g, depending on which of the above estimates is used for the contribution from natural flow.

3.4 Estimates of Natural Flow Rates at R-42 and R-28 before Amendment Additions, and Corresponding Estimates of Permeability Reduction by Amendments

Estimates of natural flow rates through the treatment zones at R-42 and R-28 before amendment additions can be obtained by analyzing responses of tracers or conservative species in these two wells after injections conducted in 2016. In July 2016, 15,000 gal. of a 0.005 molar bicarbonate (HCO_3^-) and 0.005 molar carbonate (CO_3^{2-}) solution in potable water was injected into R-42. Figure 3.4-1 shows the increases in concentrations of conservative species as they moved back into the well, replacing the low-ionic-strength potable water. It took approximately 90 days for the groundwater to replace the potable water in R-42, and using the methods presented above, an estimate of the natural flow rate is given by (7,500 gal.)(3.785 L/gal.)/(90 days) = 315 L/day. This is slightly less than the flow rate of 360 L/day estimated from the decline in Br^- concentrations during the dithionite amendment test, but it is approximately twice the value of the 163 L/day estimate obtained by dividing the Br^- estimate by 2.2 (the factor accounting for the difference between the Br- estimate and the “more rigorous” flow estimate at R-28). This result is considered to provide justification for the correction factor of 2.2 because there was evidence that the natural flow velocity in the vicinity of R-42 decreased after the dithionite injection, as indicated by a decrease in specific capacity in the well after the injection and the fact that the specific capacity never fully recovered [see “Second Quarterly Report on Pilot-Scale Amendments Testing for Chromium in Groundwater Beneath Mortandad Canyon” (LANL 2018, 603031), April 2018]. Although the volume of water injected in 2016 was 15,000 gal. versus only 10,000 gal. of dithionite (plus chase) in August 2017, this difference in volumes is considered small enough that the analysis of the 2016 injection still provides a valid comparative estimate of the natural flow rate before the amendment test. Note that if 10,000 gal. had been injected in 2016, the time for groundwater to replace potable water would likely have been less than 90 days, so the smaller volume would have been at least partly offset by a shorter time used in the flow velocity calculation. If the post-amendment flow rate estimate of 163 L/day obtained by applying the factor of 2.2 is used, then it is possible that the permeability in the vicinity of R-42 was reduced by about a factor of 2 as a result of the amendment injection.

At R-28, 15,000 gal. of a tracer solution plus 15,000 gal. of chase water (both potable water) were injected on September 29, 2016. Figure 3.4-2 shows the concentrations of conservative species in R-28 after the injection, and it is apparent that groundwater replaced the potable water after approximately 60 days. Using the methods presented above, an estimate of the natural flow rate is given by (15,000 gal.)(3.785 L/gal.)/(60 days) = 946 L/day. There was no obvious multiple-plateau-concentration response, as was observed after the molasses addition at R-28 (Figure 3.2-1), so the assumption is that the entire 15,000 gal. injected upgradient of R-28 moved uniformly downgradient. Also, the tracers injected into R-28 in 2016 decreased to essentially negligible concentrations after about 60 days, which further supports the assumption that the injected water moved uniformly downgradient (Figure 3.4-3 provides a comparison of the tracer concentration history in 2016 and the Br- concentration history from September 2017 through April 2018). The flow-rate estimate of 946 L/day implies almost a factor of 2 decrease in permeability in the vicinity of R-28 after the amendment addition (using the more rigorous estimate of 487 L/day obtained for the post-amendment flow rate). Thus, the fractional permeability reduction at R-28 as a result of the molasses amendment addition is estimated to be almost the same as the fractional permeability reduction at R-42 (about a 50% reduction).

Tables 3.4-1 and 3.4-2 provide a summary of specific-capacity estimates for R-42 and R-28 over a period spanning deployment of amendments. The specific capacity estimates have clearly decreased over the time period following deployment; however, it is not possible to discern whether the decrease is related to conditions in the filter pack and/or well screen or whether it is because of conditions in the aquifer within the ROI. Recommendations are provided below to further address this question.

3.5 Comparison of Cr(VI) Reduced So Far at R-42 and R-28 with Lab-Estimated Reduction Capacities for the Two Amendments

The amounts of Cr(VI) estimated to be reduced per mole of amendment introduced at R-42 and R-28 can be compared with laboratory estimates of the reduction capacities for the two amendments. For dithionite, estimates of reduction capacity derived from laboratory column experiments ranged from 0.006 to 0.009 moles Cr(VI)/mole dithionite, and for molasses estimates obtained in a similar manner ranged from 0.005 to >0.011 moles Cr(VI)/mole molasses [see "Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization," Attachments 7 and 8 (LANL 2018, 602964)].

The best estimates of Cr(VI) reduction at R-28 and R-42 (from both pumping and natural flow) are approximately150 g at R-28 and approximately 350 g at R-42. These masses correspond to 2.9 and 6.6 moles of Cr(VI), respectively. Neither one of these values reflects a full reduction capacity because Cr(VI) is still being reduced at both locations. Approximately 2000 moles of dithionite were injected at R-42, and approximately 21,000 moles of molasses were injected at R-28 (assuming a molasses molecular weight of 180 g/mole). Thus, the moles of Cr(VI) estimated to be reduced so far per mole of dithionite at R-42 is 0.0033, and the moles of Cr(VI) estimated to be reduced per mole of molasses at R-28 is 0.00014. These values correspond to 35 to 55% of the laboratory-derived reduction capacity estimate for dithionite, and 1 to 3% of the laboratory-derived estimate for molasses. Thus, the reduction capacity of the dithionite amendment addition at R-42 is estimated to be as much as half consumed, and the reduction capacity of the molasses amendment addition is estimated to be only a few percent consumed.

3.6 Significant Figures of Results

Different numbers of significant figures were used when reporting the results of the various calculations in the analysis and write-up in section 3 of this report. Given the uncertainties associated with the assumptions behind the calculations, no more than two significant figures should be reported for any of the numbers, and in most cases, it is probably more appropriate to only report one significant figure. When a greater number of significant figures is presented, it is done to facilitate reproduction of the calculations, not to imply a greater precision or certainty to the numbers.

4.0 ANALYSIS OF POTENTIAL AMENDMENTS INFLUENCE AT CrEX-3

Observations in the treatment system, manifested as plugging of the treatment system influent bag filter and increasing pressures observed only at the CrEX-3 wellhead, suggest that factors associated with one or both of the amendments test may be responsible. Investigations are underway to characterize the condition at CrEX-3 and develop a conceptual model for the spatial scale of aquifer that may be favorably and unfavorably affected by an amendment deployment.

As described in the "Semiannual Progress Report on Chromium Plume Control Interim Measure Performance" (N3B 2019, 700356), pumping at CrEX-3 has been limited to periodic sampling since the middle of 2018 because continuous pumping causes plugging at the influent bag filter within 2 days. This condition began approximately 1 yr after deployment of amendments in R-42 and R-28 leading to speculation that the condition at CrEX-3 may be related. The influent bag filters have been observed to be covered with a reddish substance. Recent wellhead filter tests confirm that the reddish substance originates from CrEX-3. Initial microscope observations indicate that the reddish substance is amorphous. Slight increases in manganese and arsenic, as well as possible very low concentrations of 1,6-naphthalene disulfonate observed at CrEX-3 in the Fall of 2018, may indicate a connection between CrEX-3 and geochemical conditions associated with molasses testing at R-28.

As of this report, preliminary geochemical modeling has begun and sample material has been collected from filters placed at extraction wellheads. Analyses are currently being conducted on initial samples of solid fractions using standard analytical methods and scanning electron microscopy. Additional sampling and characterization strategies will be coordinated with NMED through the chromium technical team.

5.0 DISCUSSION AND RECOMMENDATIONS

Results to date illustrate that both dithionite and molasses can support Cr(VI) reduction in groundwater over long periods of time. Results from both the October 2018 purge and the first of the biweekly extended (1000-gal.) time-series purge events (March 2019) provided additional insights into conditions within the ROI at R-42 and R-28. The biweekly sampling will be conducted for at least several more rounds until a sufficient data set is available to further characterize the geochemical conditions around the wells.

As discussed above, the dithionite amendment test at R-42 still requires more time to determine Cr(VI) reduction capacity imparted to the aquifer in the ROI. Chromium has not yet begun to break through into R-42. Other indicators such as iron, manganese, and arsenic either continue to decrease towards pre-amendment levels or hold at steady levels since the October 2018 purge tests indicating that, although the reducing conditions near the well have been diminishing, they are still significant and are effectively reducing chromium.

The molasses amendment test at R-28 will similarly require more time for breakthrough to occur. As discussed above, significant reduction capacity is apparently still present in the ROI around R-28. Following the initial purges, reducing conditions in the aquifer have treated chromium below the pre-deployment level of 0.5 mg/L. Slightly elevated chromium (as dissolved Cr(III)) was linked to low pH conditions and did not become treated to the New Mexico groundwater standard level (0.05 mg/L) until mid-2018 when pH had rebounded up to approximately 5.5. Since that time and as the pH has further increased, the dissolved chromium continued to decrease and is recently at its lowest achieved levels of around 0.01 mg/L. The pH continues to increase but has not yet returned to pre-deployment levels. Iron and manganese levels and other indicators such as dissolved oxygen and oxidation-reduction potential indicate the persistence of reducing conditions amenable to reducing Cr(VI).

The results of the March 2019 purge indicate that favorably reducing and varying geochemical conditions remain present in the aquifer surrounding R-42 and R-28. The path forward is to continue conducting purges and sampling protocol that is expected to provide data that will facilitate further assessment of conditions in the aquifer and possibly help accelerate completion of the present study phase (Phase 1). The data from the extended purge continue to show concentrations of byproduct constituents (e.g., sulfate, iron, manganese) that do not allow direct land application of produced water without treatment. Therefore, continuous pumping for the Phase 1 test at R-42 and R-28 creates significant logistics challenges related to management of produced water since these waters are not compatible with the current ion-exchange treatment system. Further sampling will be conducted on a biweekly basis and continued as a time-series sampling over a purge volume of approximately 1000 gal. Samples will be collected at approximately 50 gal., 350 gal., 700 gal., and 1000 gal. At pumping rates of approximately 3 gpm and 2.6 gpm at R-42 and R-28, respectively, the sampling can be conducted within an 8-hr work day. Samples will be analyzed for metals, anions, and TOC. Field parameters will be collected for each sample in the time series.

In order to better determine whether decreases in specific capacity observed at each well is because of conditions in the well or filter pack or in the aquifer, each of the wells will be redeveloped using mechanical methods. Following redevelopment, dilution tracer tests will be conducted in a manner consistent with pre-amendment dilution tests to generate data that may provide insights into aquifer conditions associated with the amendments testing and resultant geochemical conditions.

As described in section 4.0, additional characterization of the geochemical condition at CrEX-3 will be conducted. Additional sampling and analysis, mining of existing data, and geochemical modeling will be conducted. Additional characterization tools such as x-ray diffraction and x-ray fluorescence may be used, as necessary. One goal is to characterize the condition at CrEX-3 to enable development of ways to bring the well back online or to determine when conditions at the well may naturally enable operation. An additional goal is to glean important information that is related to objectives that may be part of a phase 2 amendment study, which is to characterize the spatial extent beyond amendment deployment locations that effects of amendments test may manifest.

It is also recommended that because of the slow rate of change of geochemical conditions around R-42 and R-28, the next status report be submitted at the end of December 2019 instead of July 2019. Updates and ongoing evaluation of biweekly sampling, geochemical modeling, and evaluation of new data collected in support of characterization at CrEX-3 will be provided through frequent technical team meetings, and then documented in the report submitted in December 2019.

6.0 REFERENCES AND MAP DATA SOURCES

6.1 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), March 2018. "Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization," Los Alamos National Laboratory document LA-UR-18-21450, Los Alamos, New Mexico. (LANL 2018, 602964)

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)

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 2018, 700108)

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 2019, 700214)

N3B (Newport News Nuclear BWXT-Los Alamos, LLC), March 2019. “Semiannual Progress Report on Chromium Plume Control Interim Measure Performance,” Newport News Nuclear BWXT-Los Alamos, LLC, document EM2019-0059, Los Alamos, New Mexico. (N3B 2019, 700356)

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)

6.2 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.

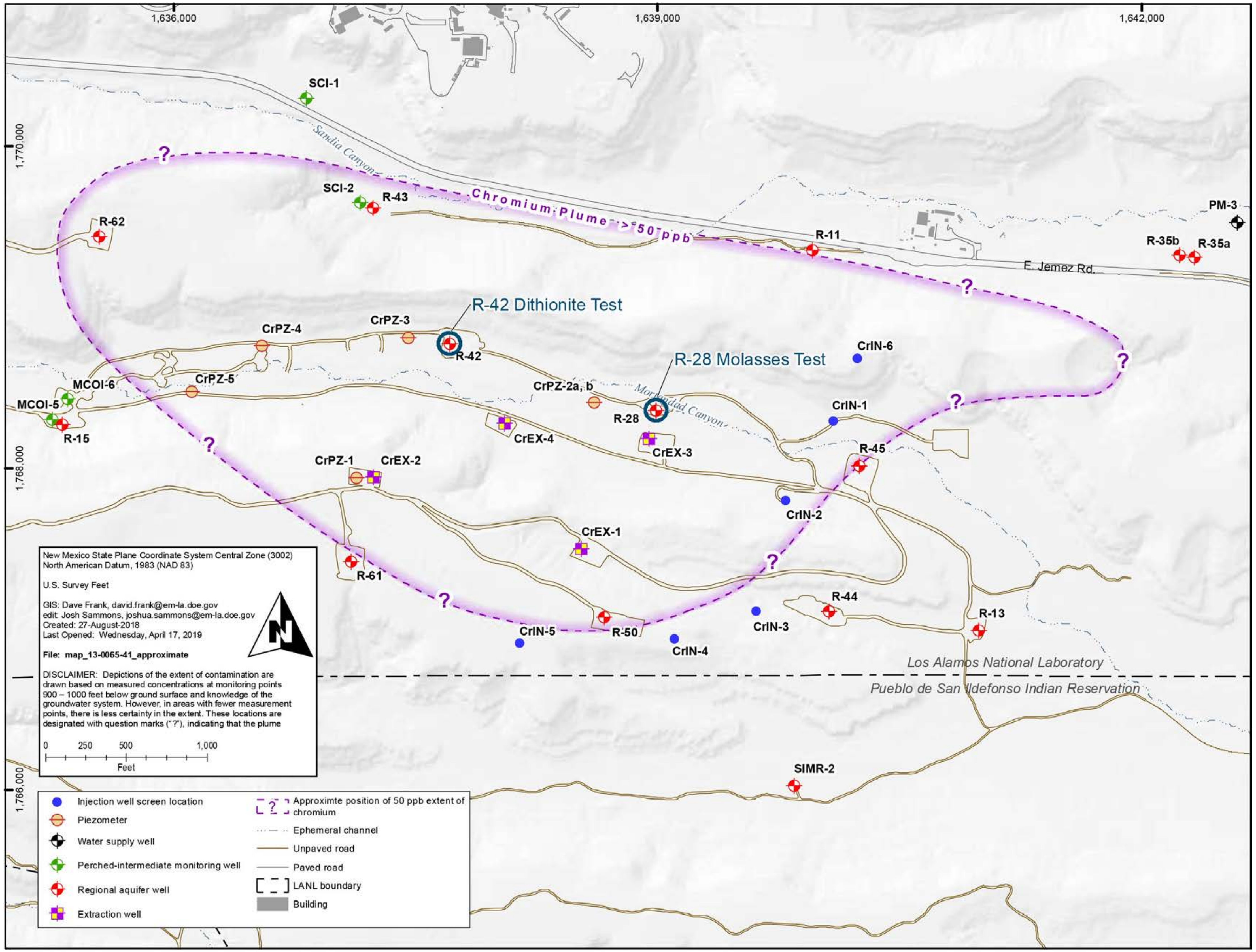
Chromium plume > 50 ppb; Los Alamos National Laboratory, ER-ES, As published; \\slip\gis\GIS\Projects\13-Projects\13-0065\shp\chromium_plume_2.shp; 2018.

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.



New Mexico State Plane Coordinate System Central Zone (3002)
North American Datum, 1983 (NAD 83)

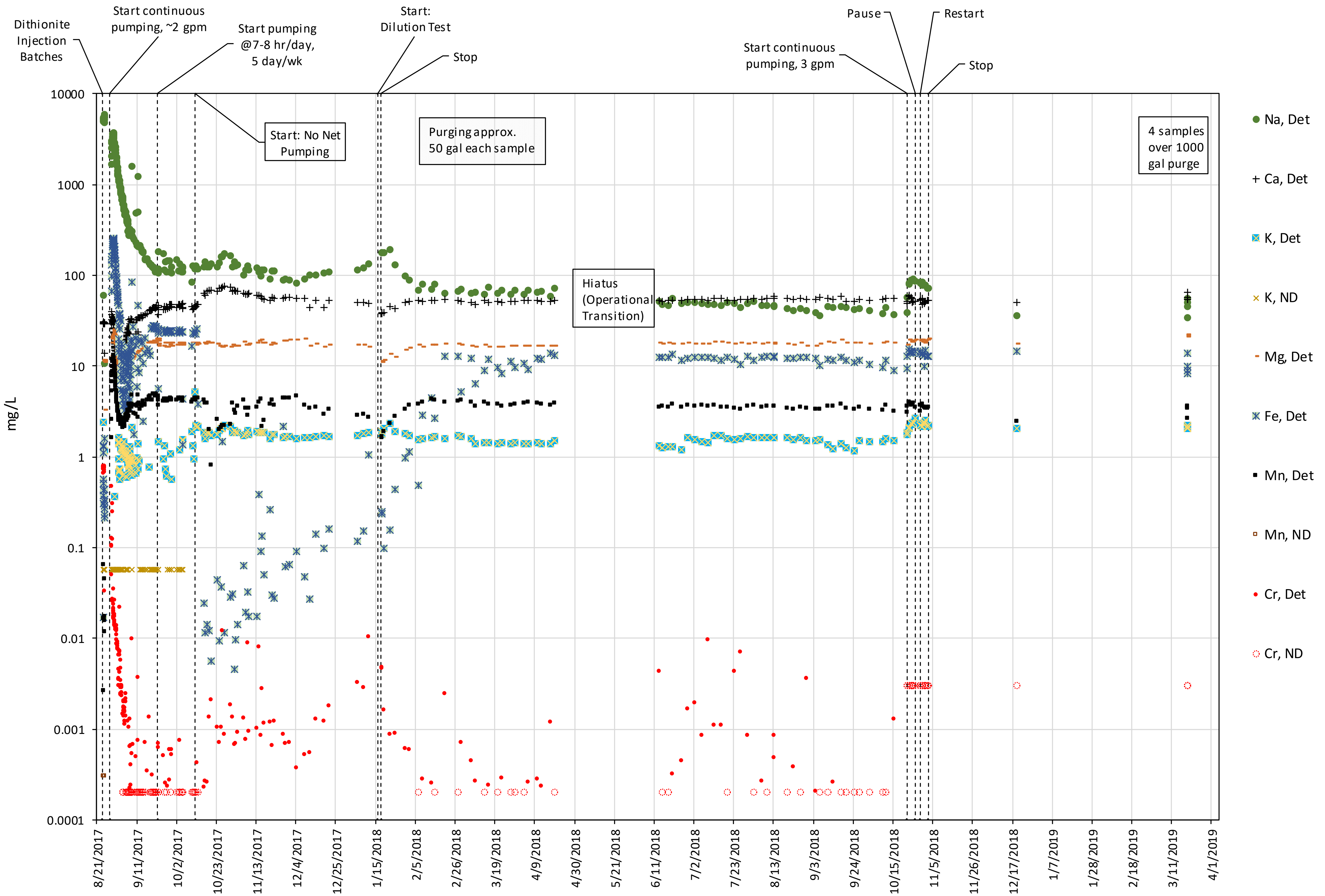
U.S. Survey Feet

GIS: Dave Frank, david.frank@em-la.doe.gov
edit: Josh Sammons, joshua.sammons@em-la.doe.gov
Created: 27-August-2018
Last Opened: Wednesday, April 17, 2019

File: map_13-0065-41_approximate

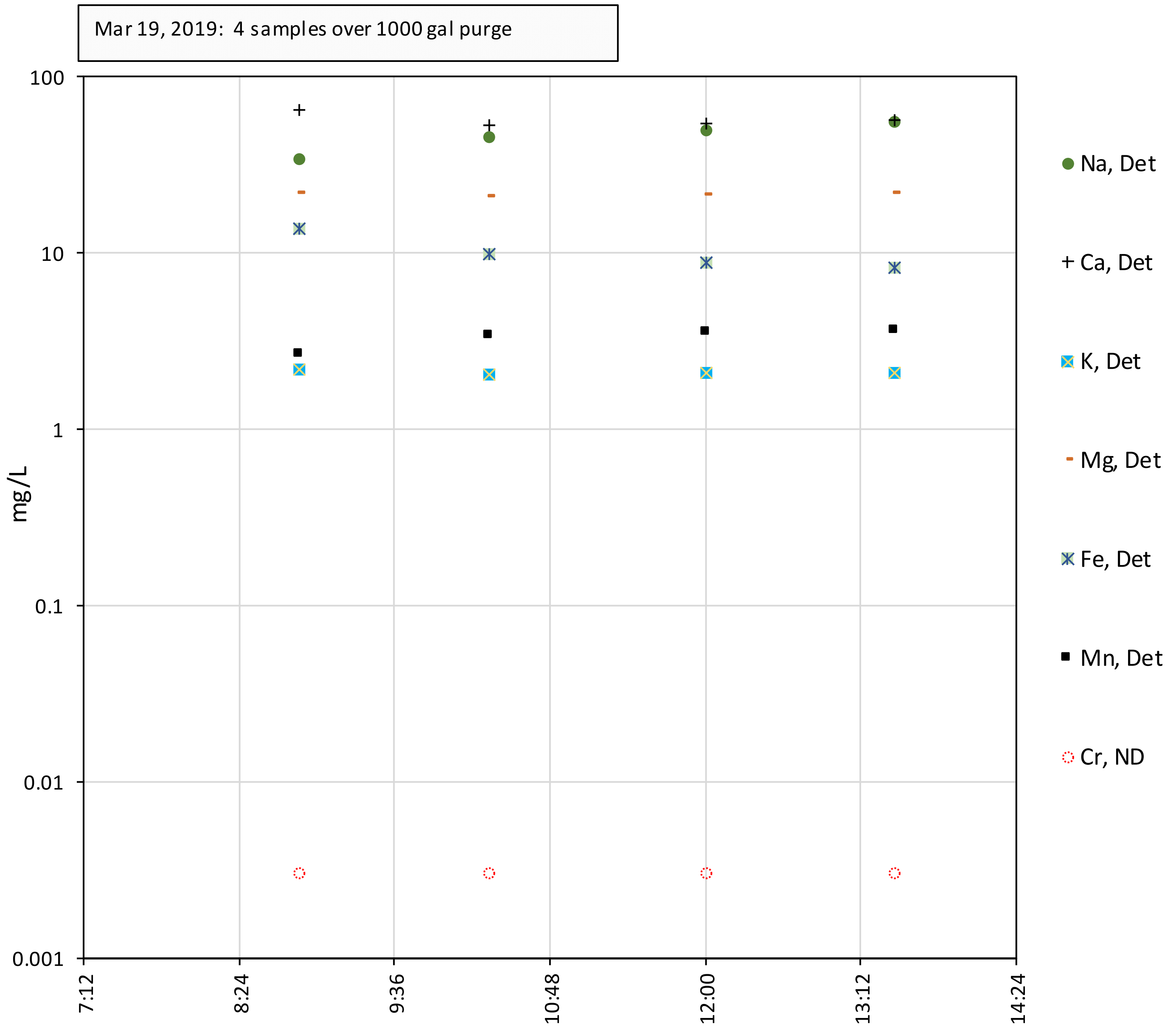
DISCLAIMER: Depictions of the extent of contamination are drawn based on measured concentrations at monitoring points 900 – 1000 feet below ground surface and knowledge of the groundwater system. However, in areas with fewer measurement points, there is less certainty in the extent. These locations are designated with question marks ("?"), indicating that the plume

Figure 1.0-1 Map showing estimated 50 ppb extent of the Cr(VI) plume and monitoring wells (including R-42 and R-28), piezometers, and Interim Measure infrastructure wells



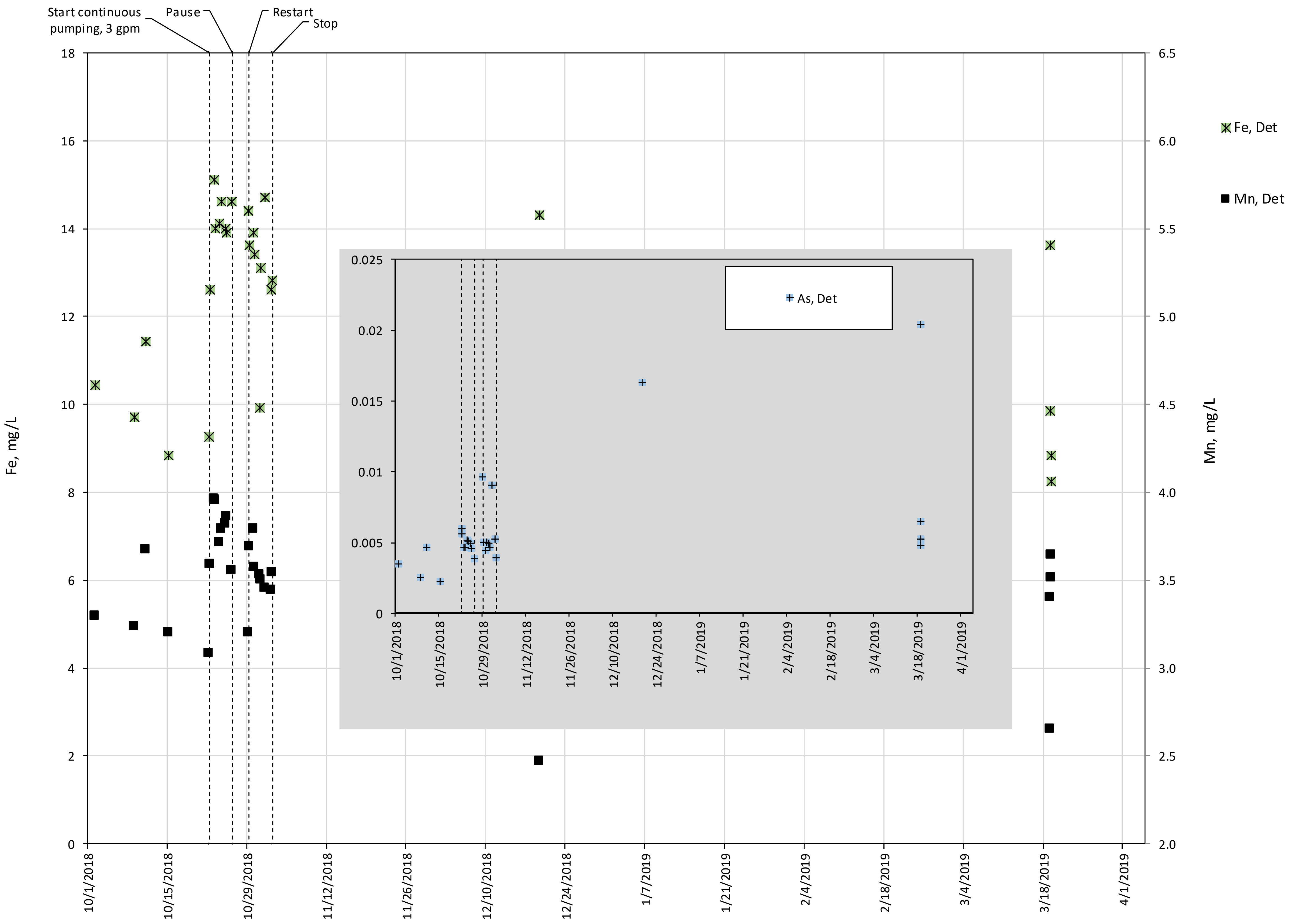
Notes: The pre-test concentrations were approximately as follows: Na = 50–60 (16), Ca = 30 (55), K = 2, Mg = 12 (15), Fe = 0.01 (0.1), Mn = 0.001, Cr = 0.7. Values indicate levels immediately preceding 2017's amendment. Also, if different, historic values are included in parentheses. Values are in mg/L. All results are from filtered samples. Acronyms: Det = Detected, ND = Not Detected.

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



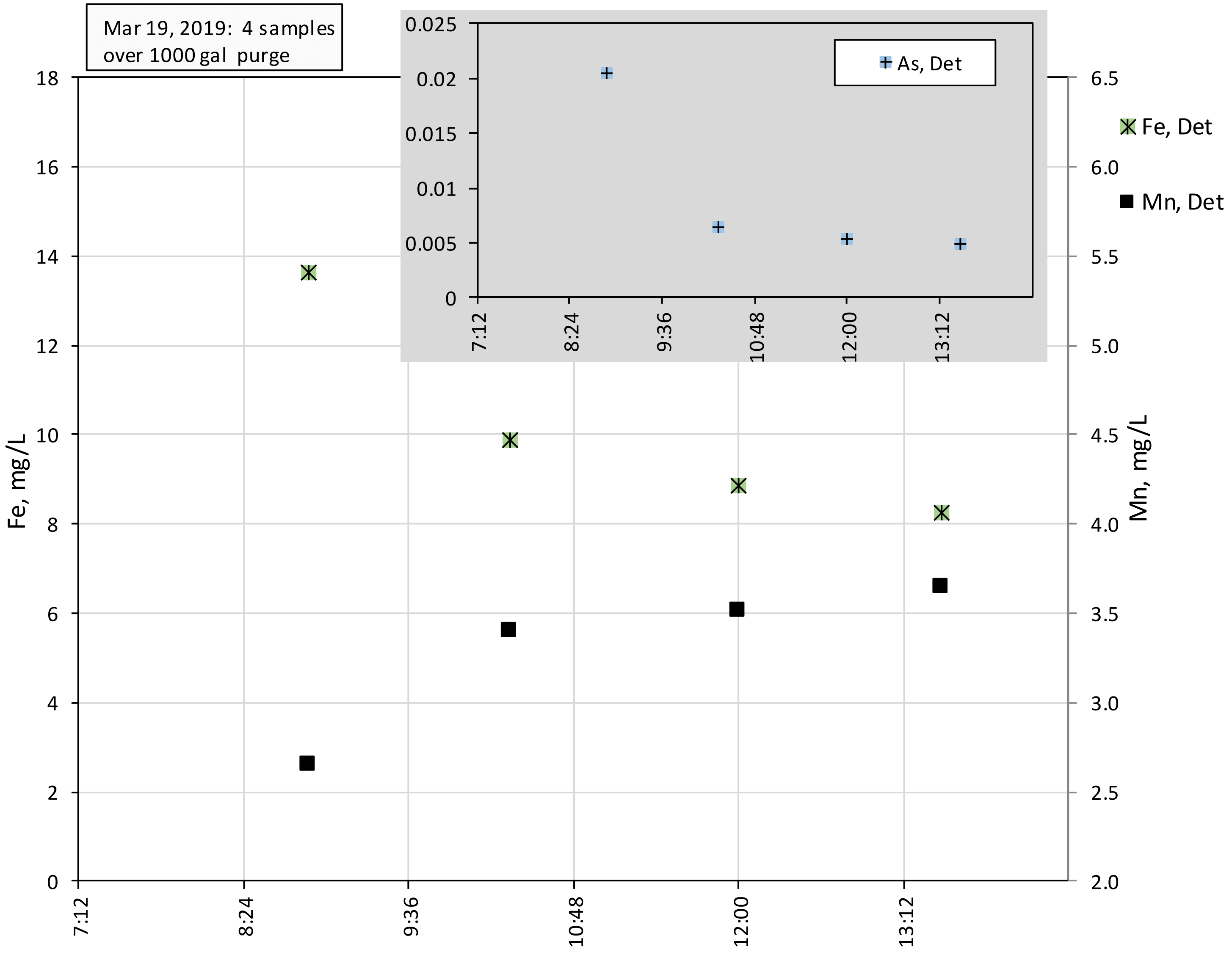
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected, ND = Not Detected.

Figure 2.1-2 **Time-series plot showing concentrations of constituents from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019**



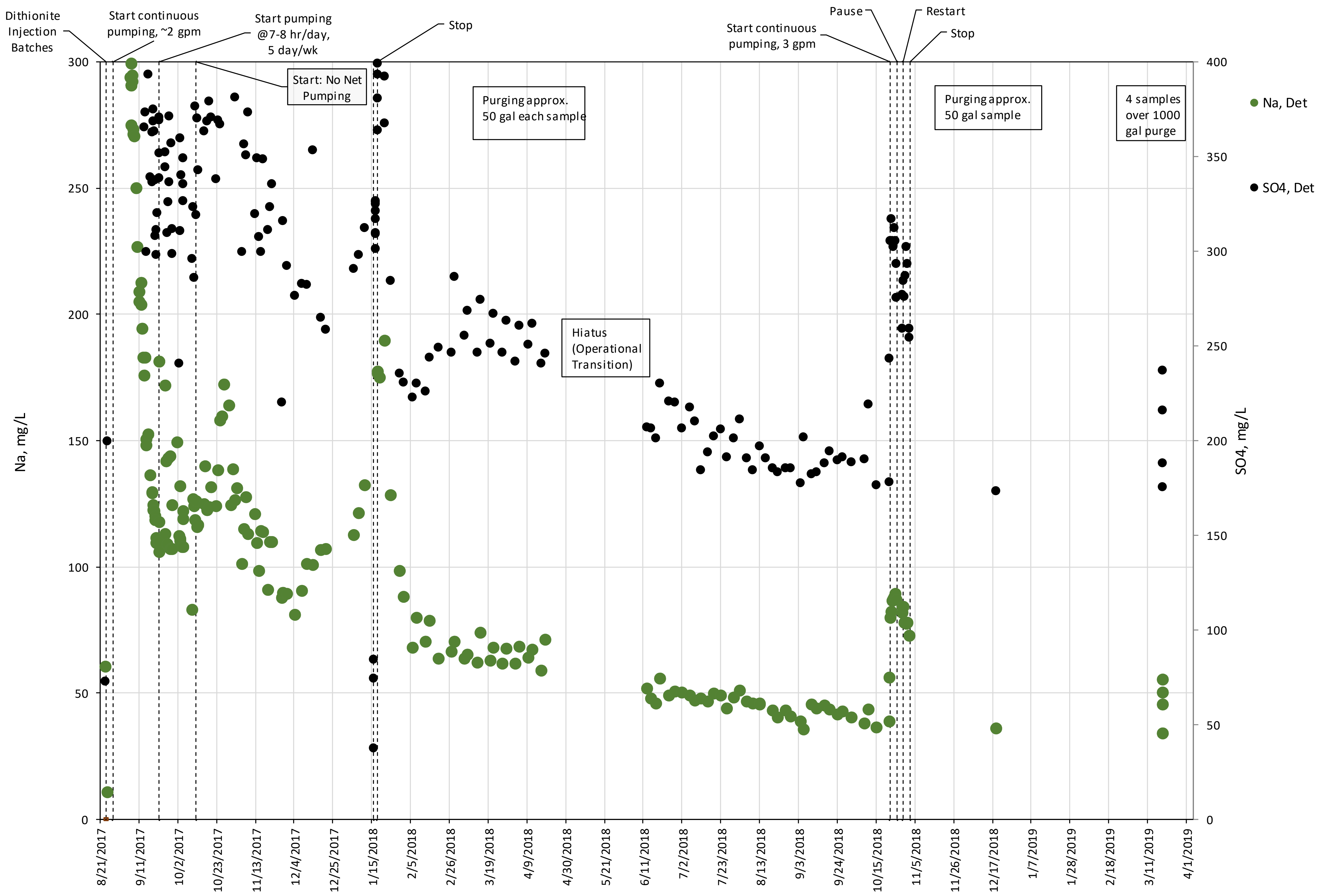
Notes: All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.1-3 **Concentrations of iron, manganese, and arsenic in R-42 dithionite test as a function of time**



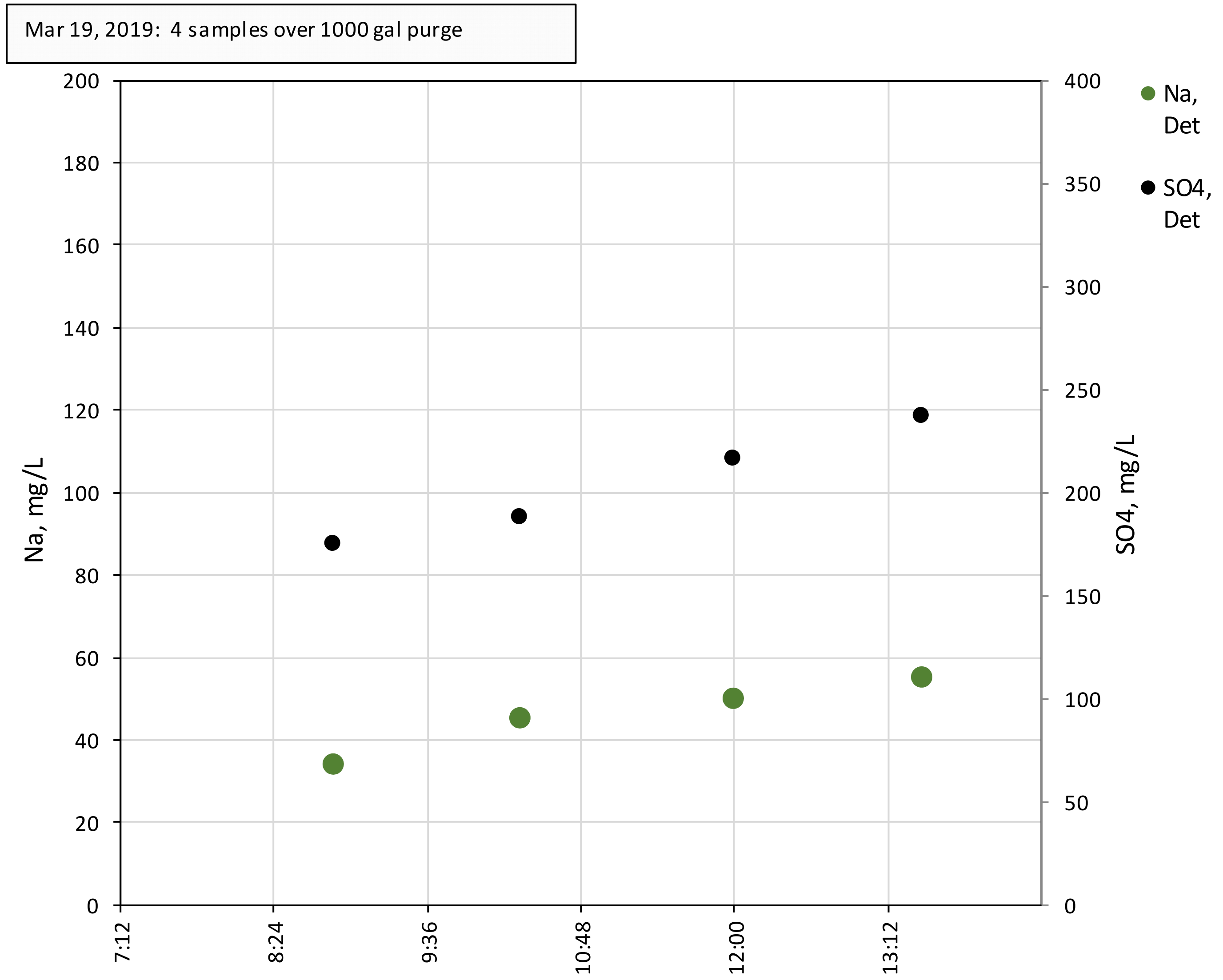
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.1-4 **Time-series plot showing concentrations of iron, manganese, and arsenic from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019**



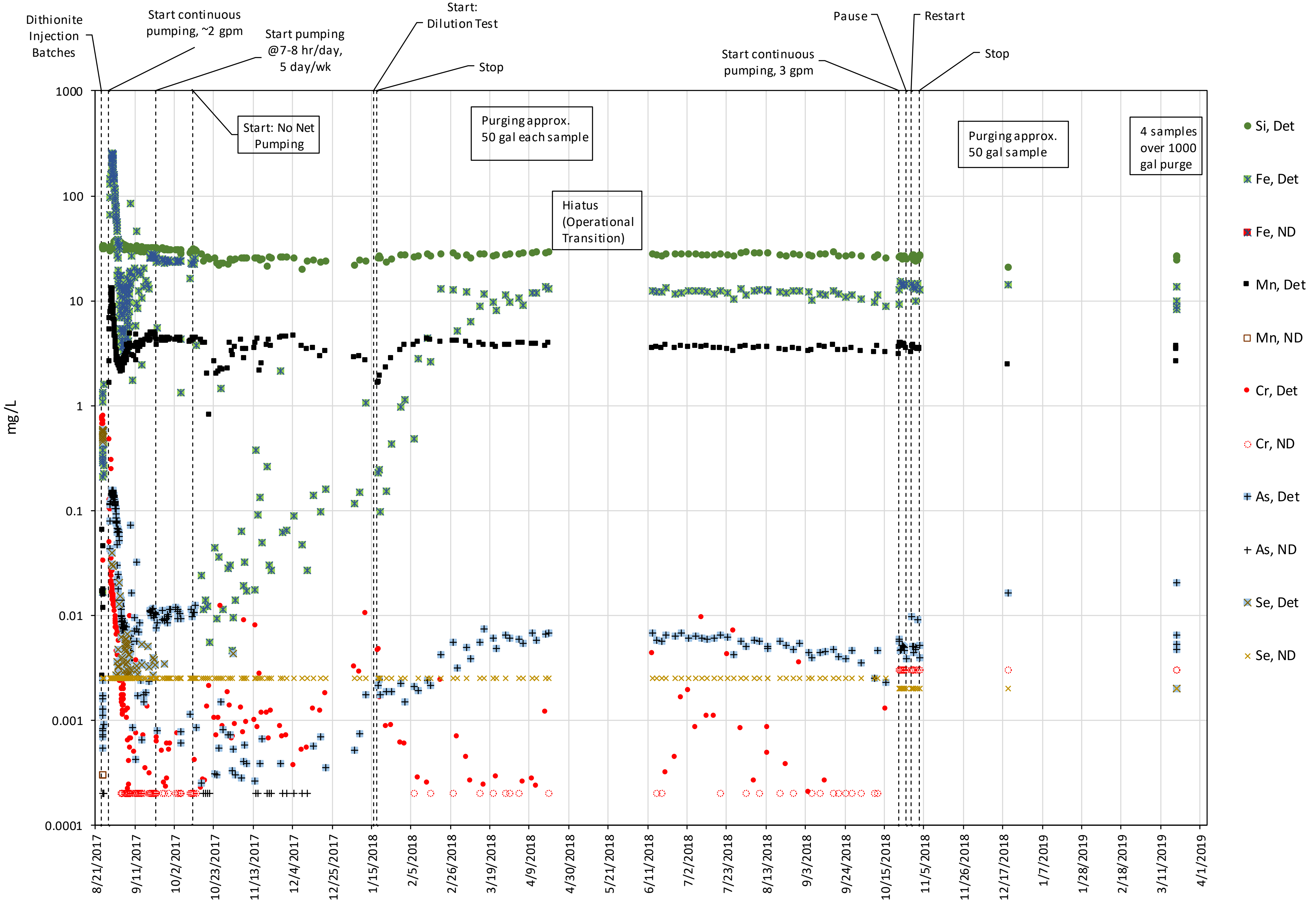
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: Na = 50–60 (16); SO4 = 80.
All results are from filtered samples. Acronyms: Det = Detected

Figure 2.1-5 Concentrations of sodium and sulfate in R-42 dithionite test as a function of time



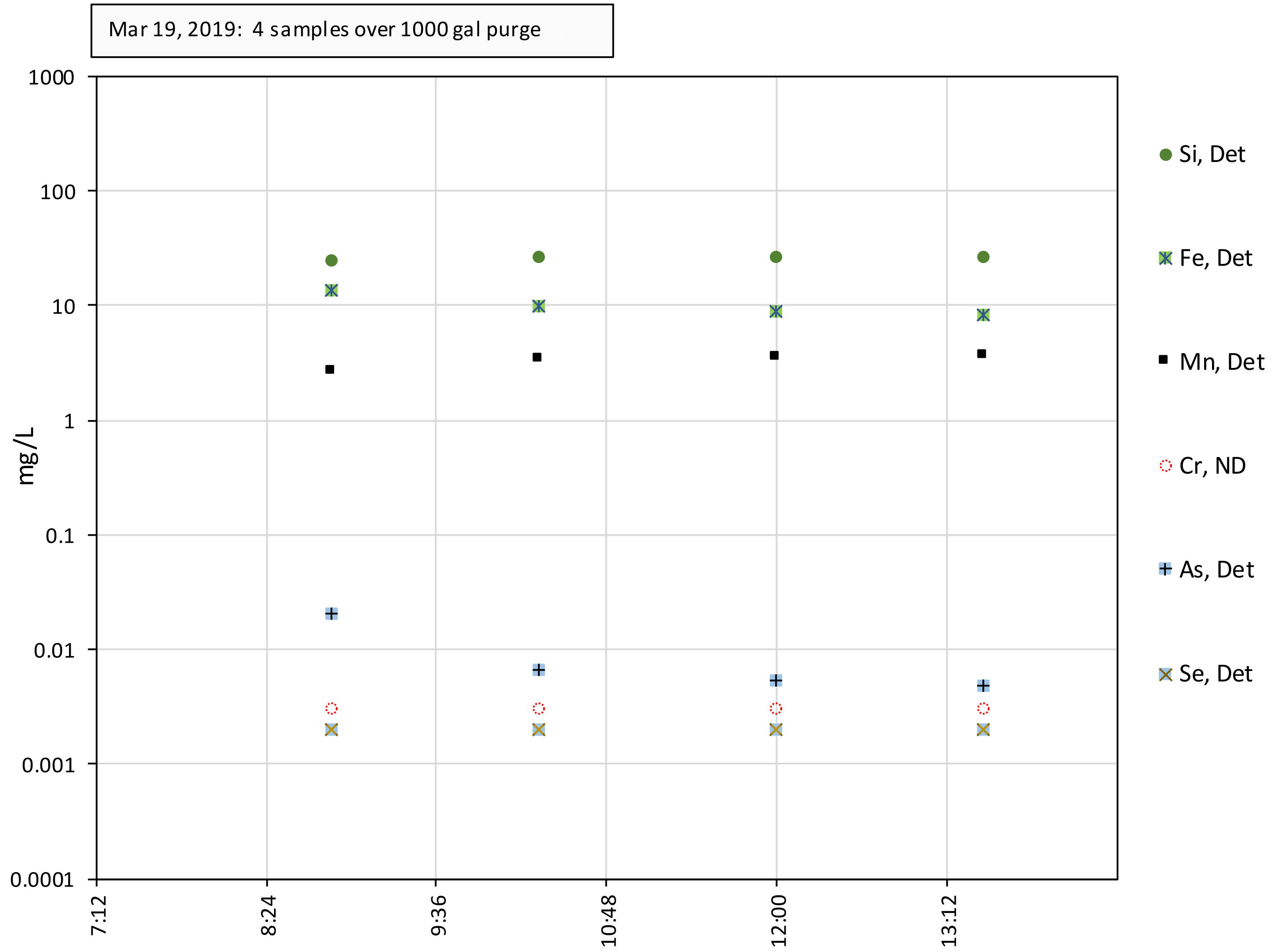
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.1-6 **Time-series plot showing concentrations of sodium and sulfate from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019**



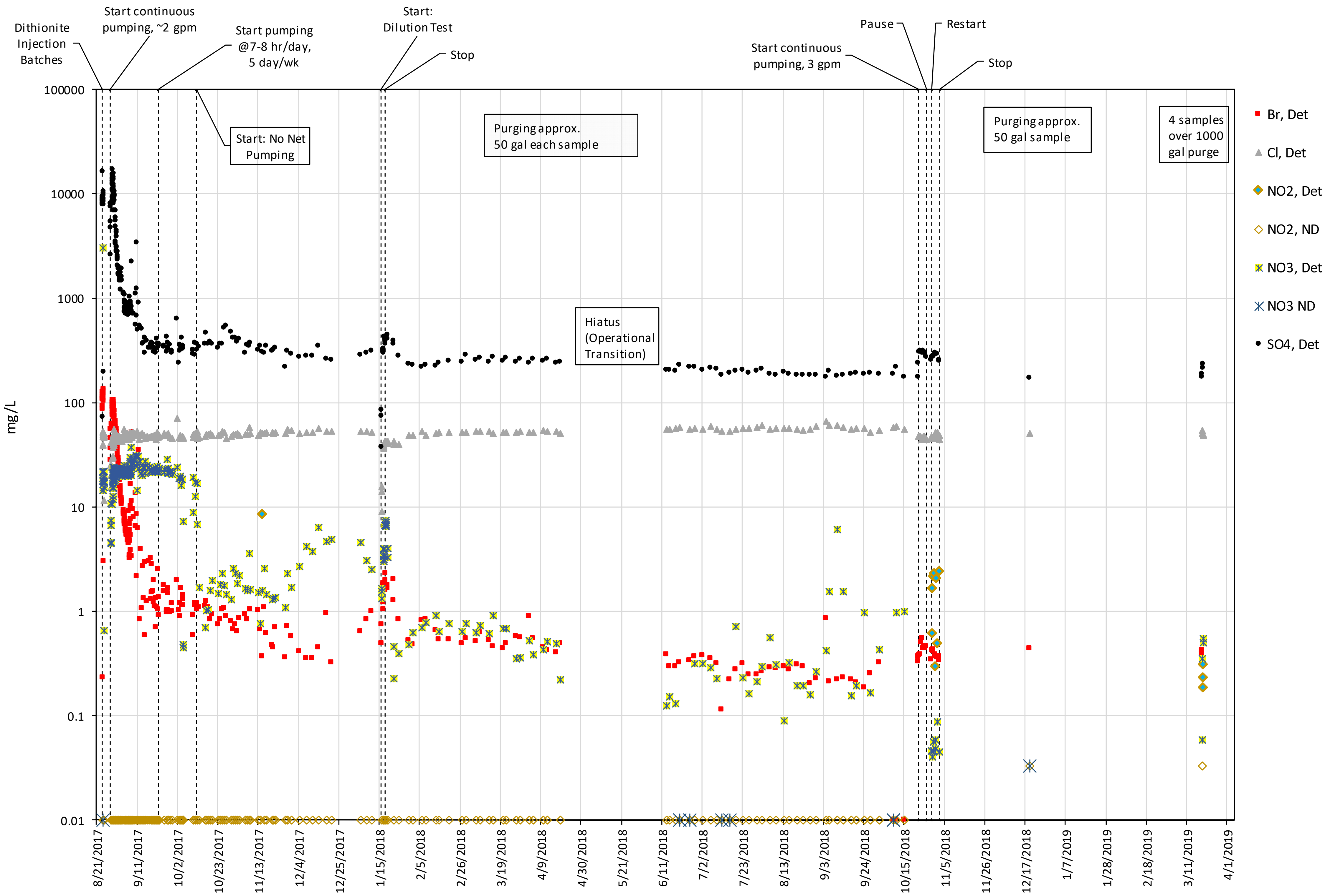
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: Si = 35, Fe = 0.01 (0.1), Mn = 0.001, Se = 0.002 (<0.005), As = 0.001 (0.002), Cr~0.7 (~1.0).
All results are from filtered samples. The detection limit for chromium changed in October 2018 with the change in contract from EES to GEL laboratory. Acronyms: Det = Detected, ND = Not Detected

Figure 2.1-7 Concentrations of selected constituents during R-42 dithionite test as a function of time



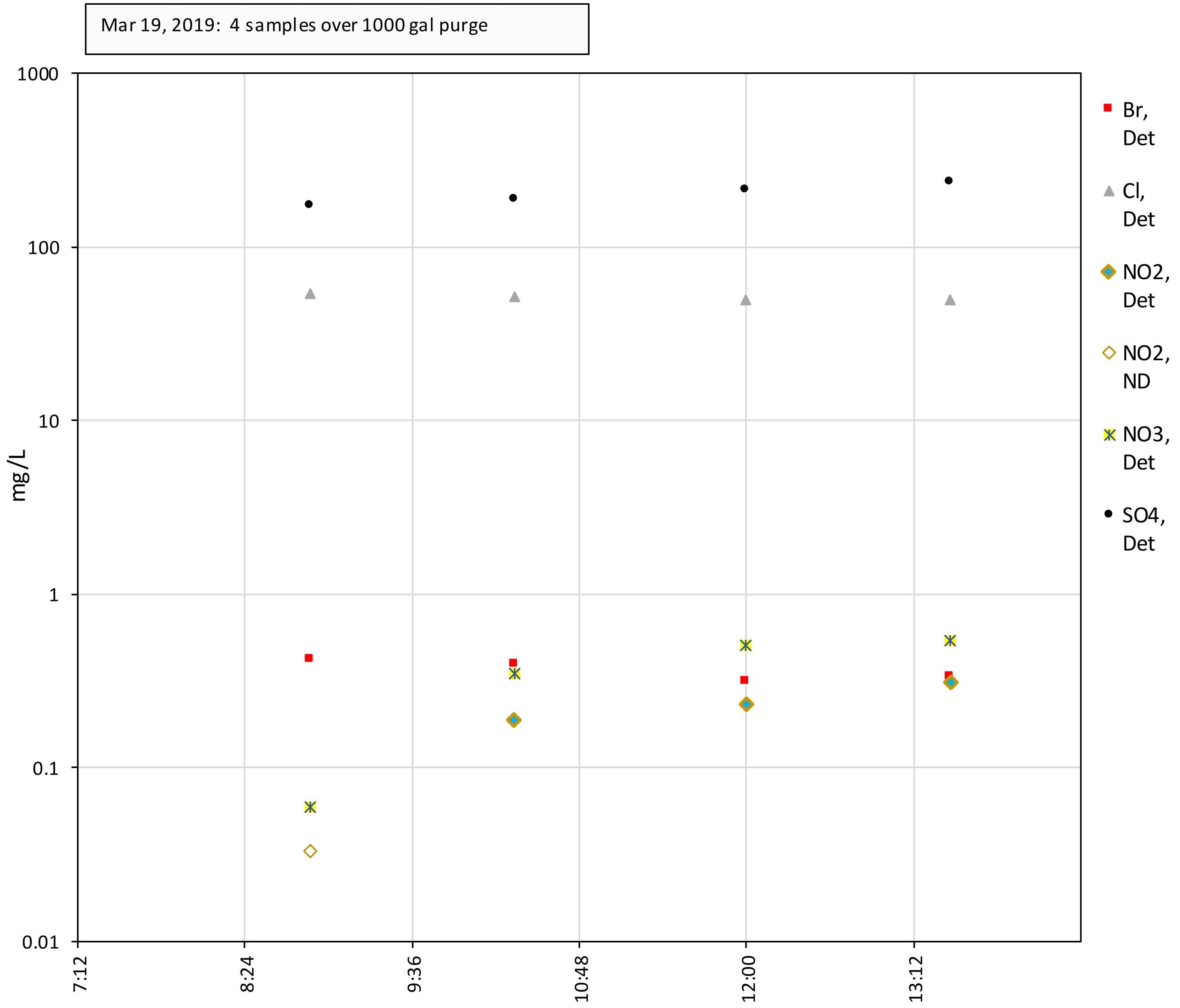
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.1-8 **Time-series plot showing concentrations of select constituents from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019**



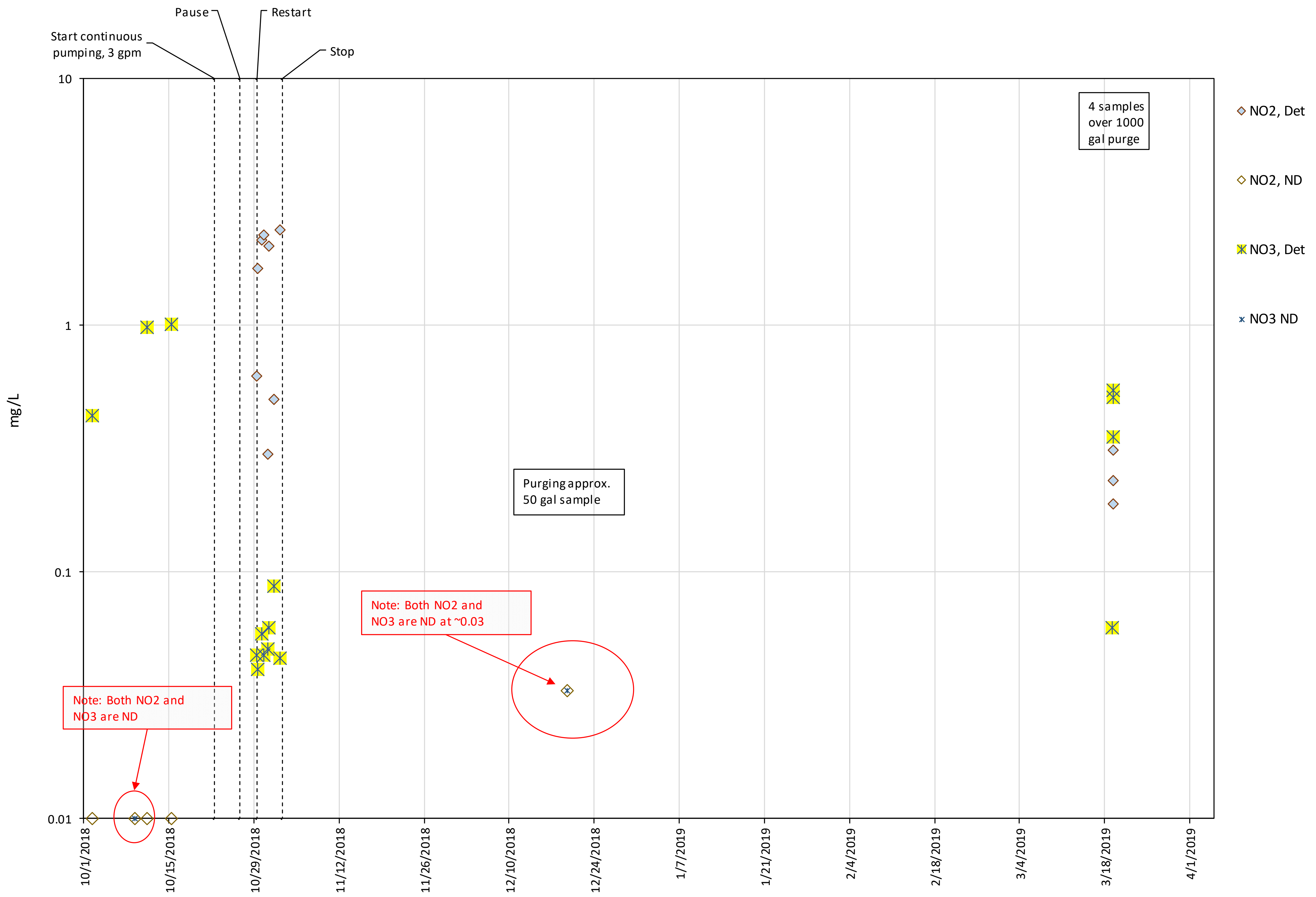
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: Br ~0.2 Cl = 50-60 (45), NO2 <0.2, NO3 = 20 (25), SO4 = 80.
Acronyms: Det = Detected, ND = Not Detected

Figure 2.1-9 Concentrations of select anions in R-42 dithionite test as a function of time



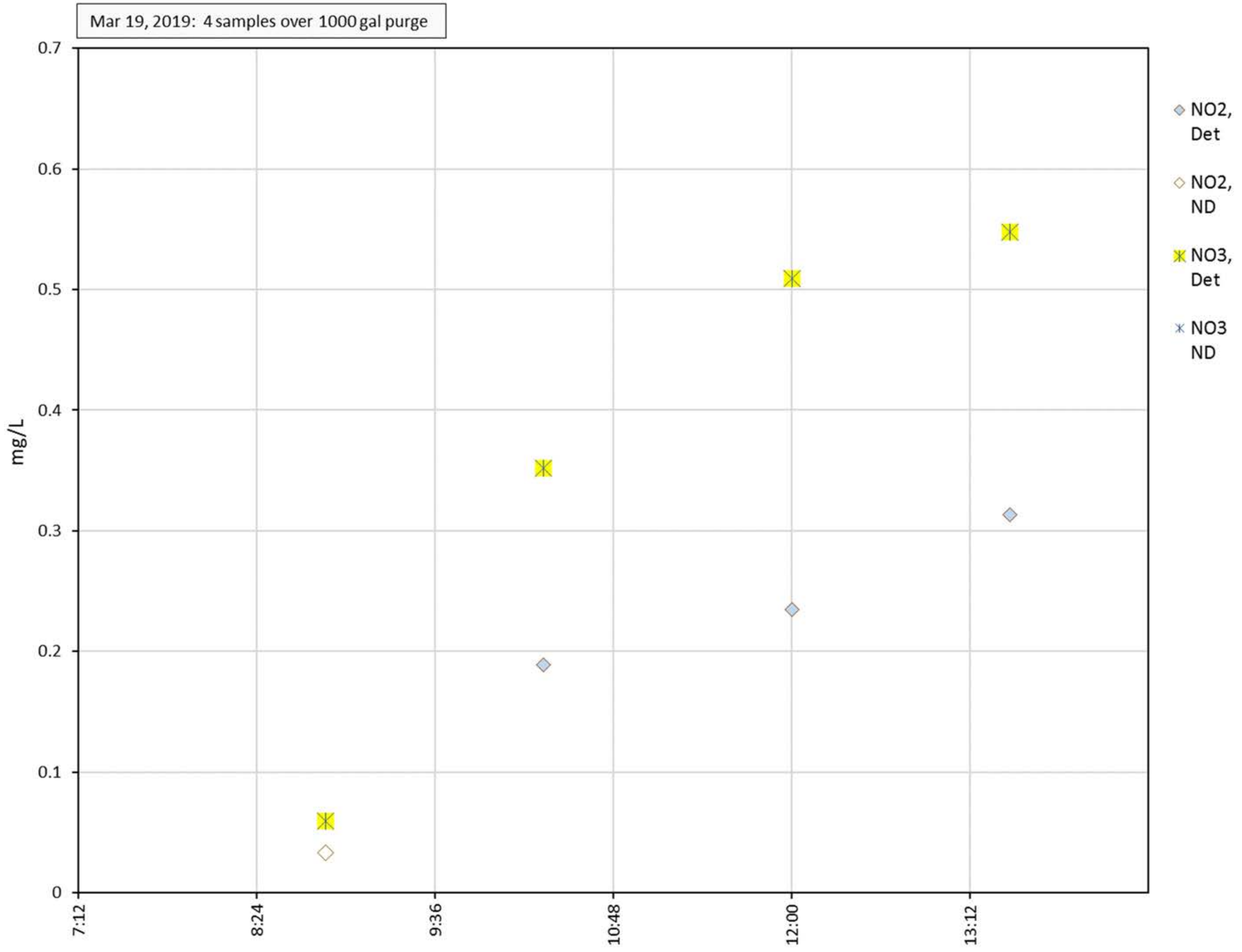
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. Acronyms: Det = Detected.

Figure 2.1-10 **Time-series plot showing concentrations of select anions from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019**



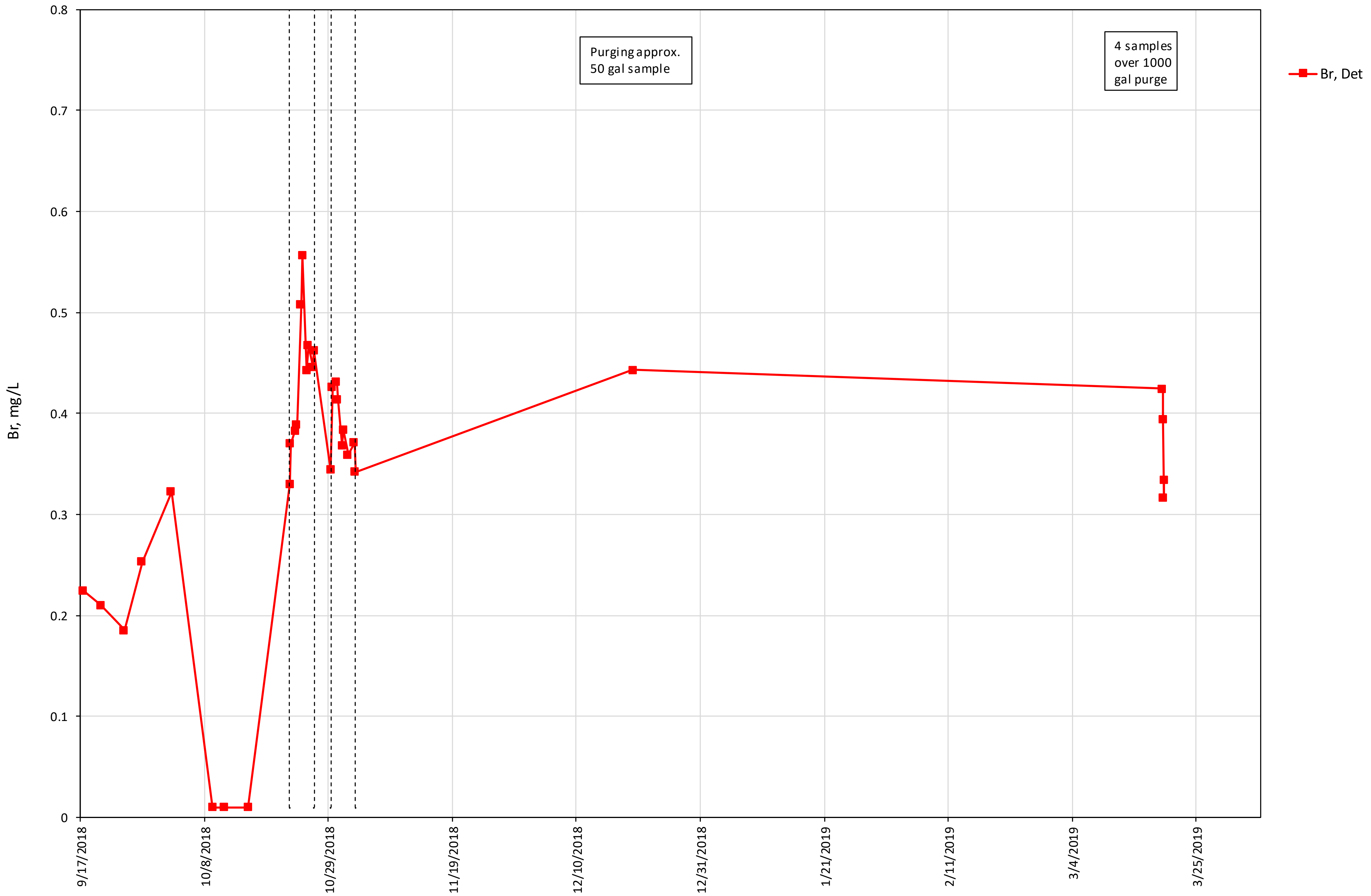
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: NO_2 <0.2, NO_3 = 20 (25).
Acronyms: Det = Detected, ND = Not Detected.

Figure 2.1-11 Concentrations of nitrate and nitrite in R-42 dithionite test as a function of time



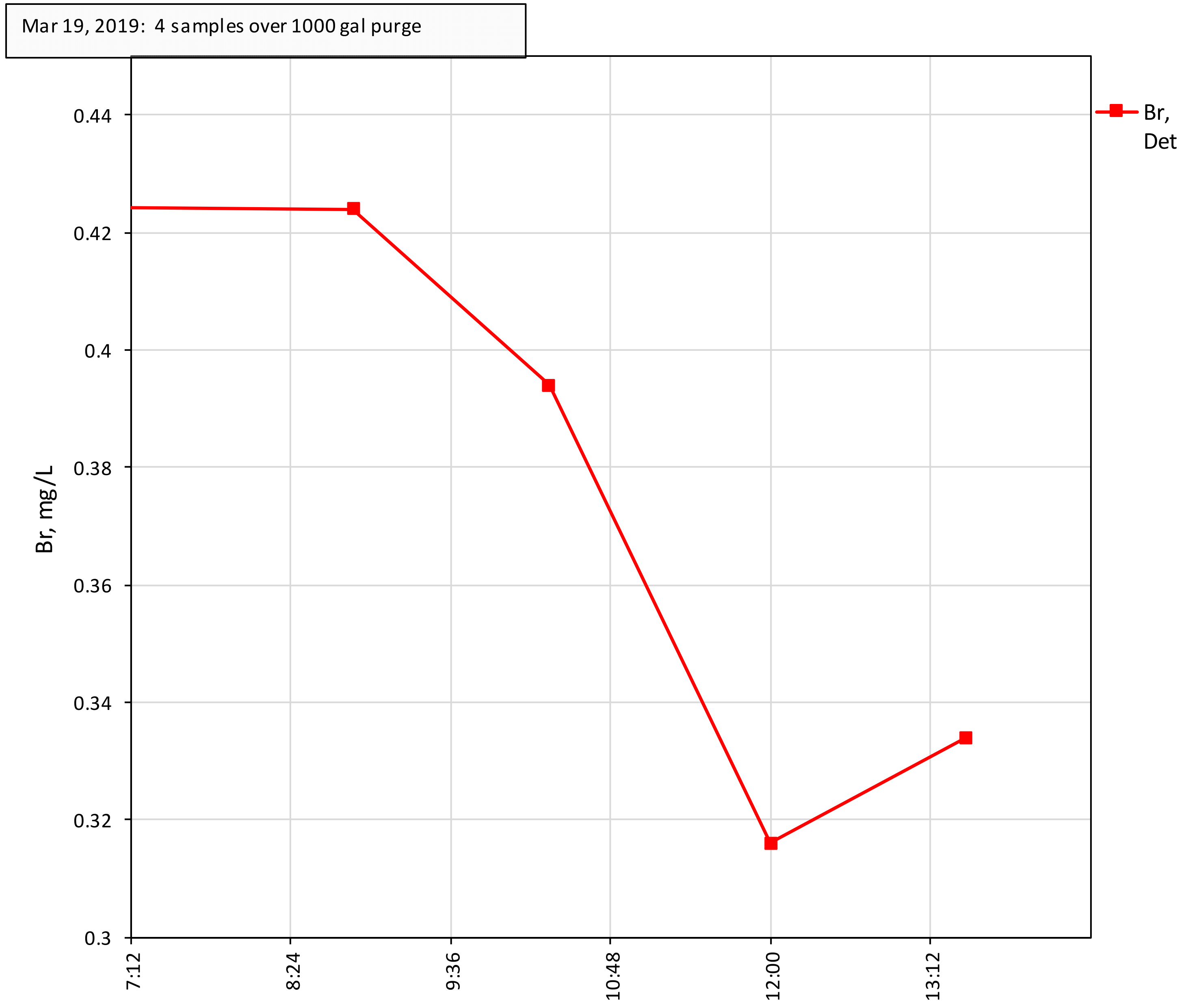
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. Acronyms: Det = Detected, ND = Not Detected.

Figure 2.1-12 Time-series plot showing concentrations of nitrate and nitrite from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019



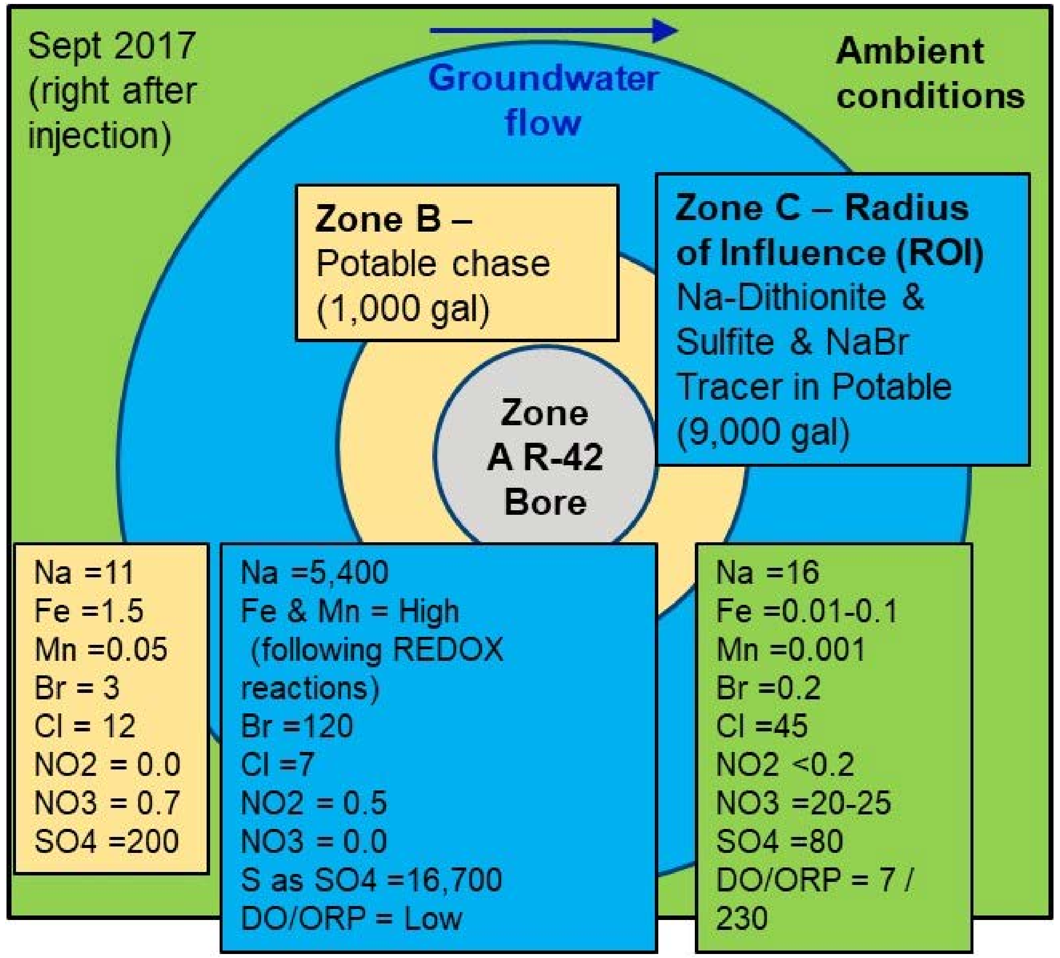
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: Br ~0.2. Acronyms: Det = Detected.

Figure 2.1-13 Concentration of bromide in R-42 dithionite test as a function of time



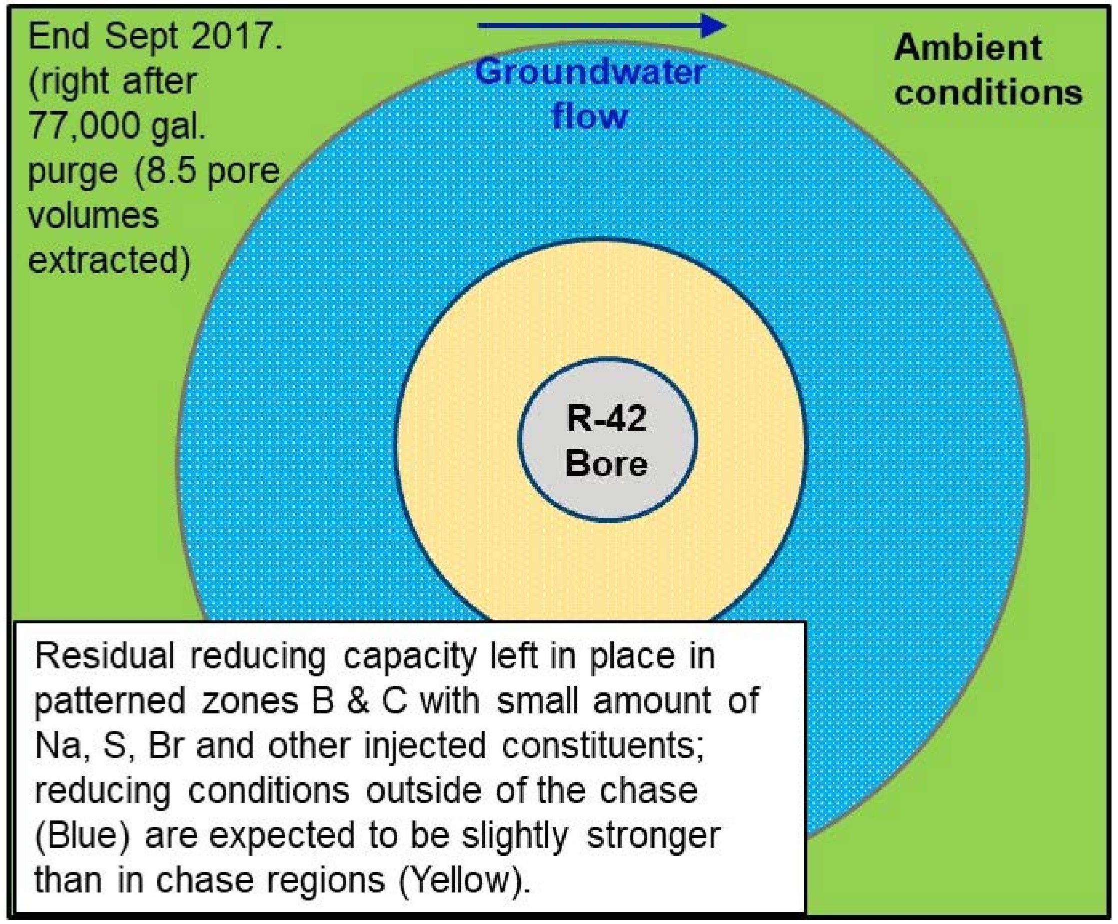
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. Acronyms: Det = Detected.

Figure 2.1-14 Time-series plot showing concentrations of bromide from the approximately 1000-gal. purge conducted at R-42 on March 19, 2019



Note: Element and compound levels as mg/L.

Figure 2.1-15 Progressive snapshots of the conceptual R-42 plan view model: September 2017 (right after injection)



Residual reducing capacity left in place in patterned zones B & C with small amount of Na, S, Br and other injected constituents; reducing conditions outside of the chase (Blue) are expected to be slightly stronger than in chase regions (Yellow).

Figure 2.1-16 Progressive snapshots of the conceptual R-42 plan view model: End September 2017 (right after 77,000-gal. purge)

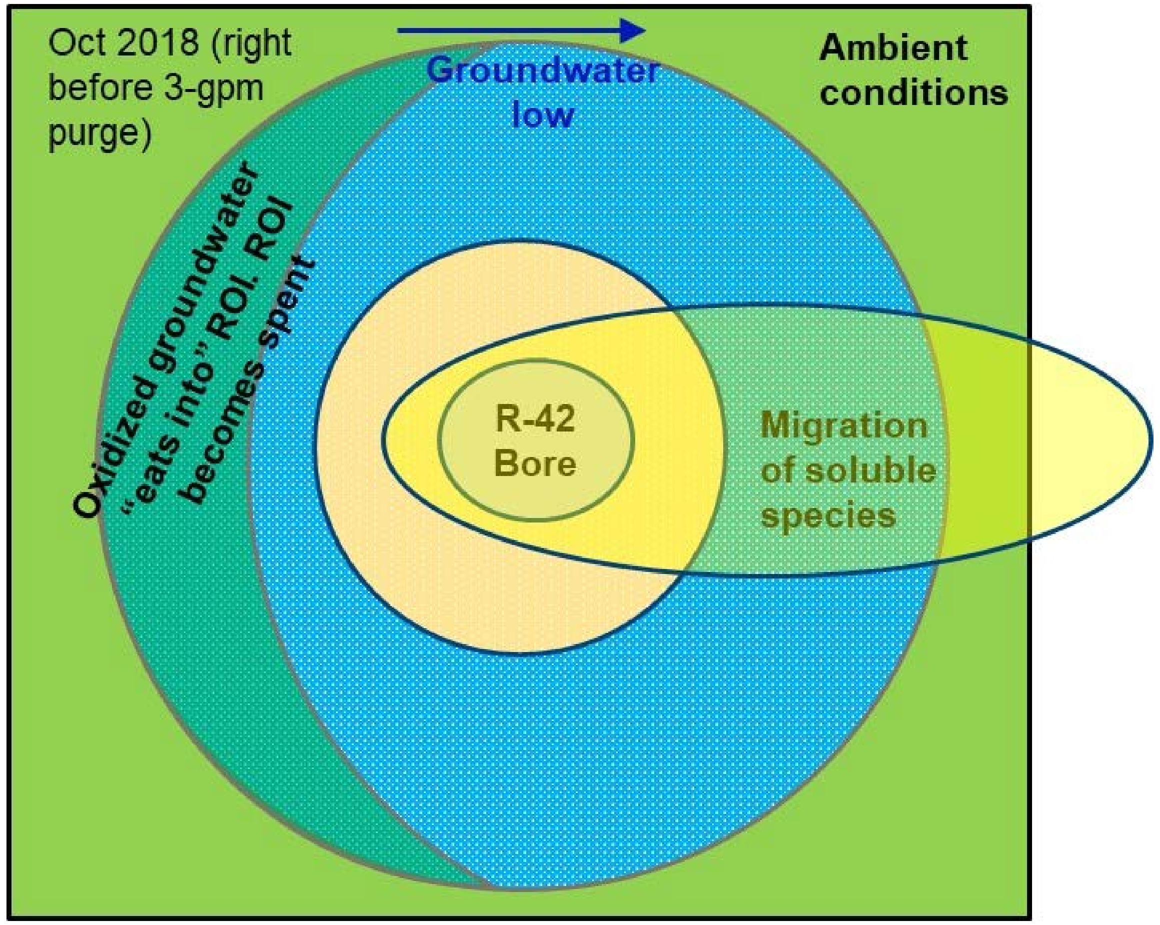
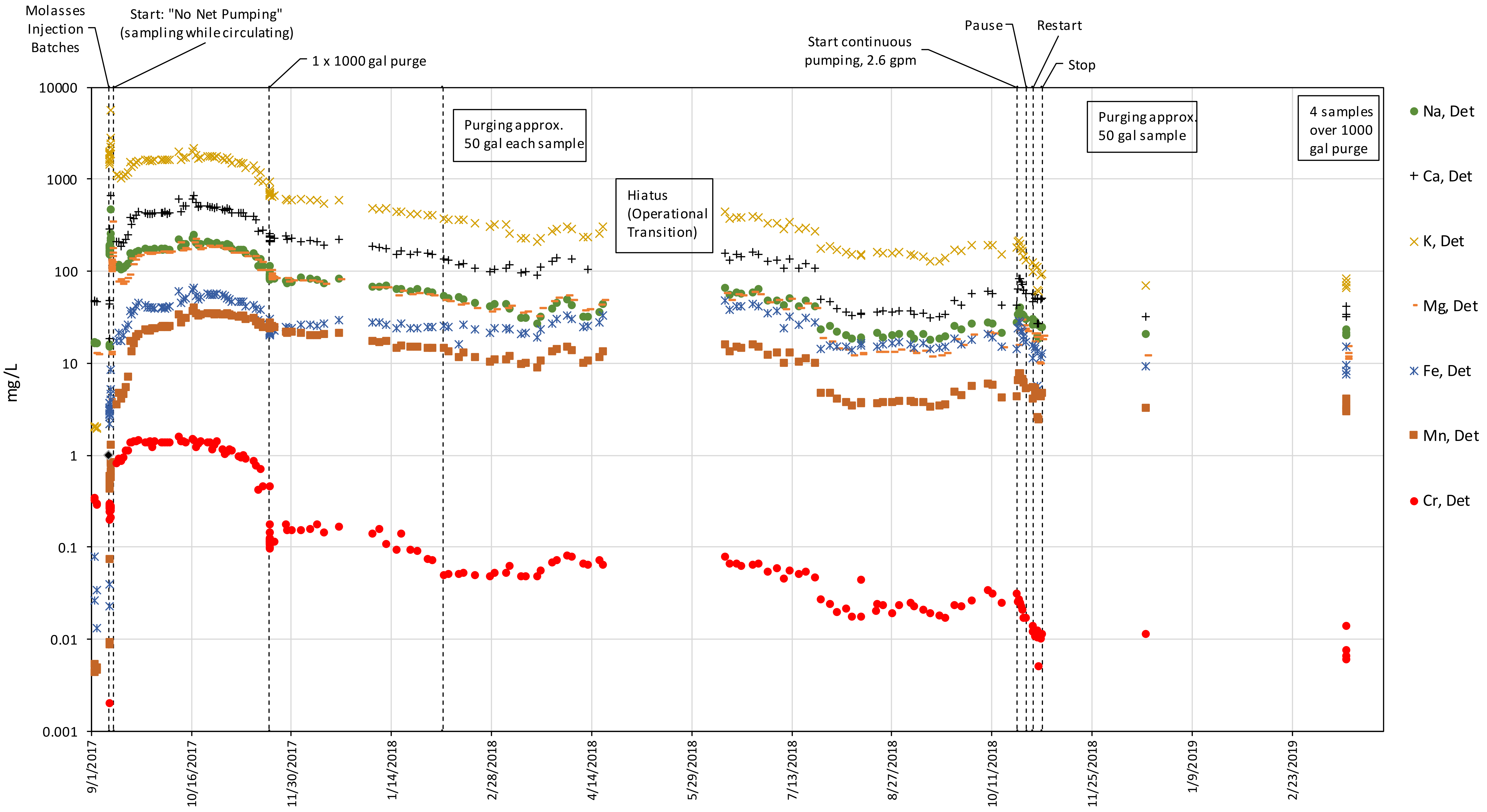
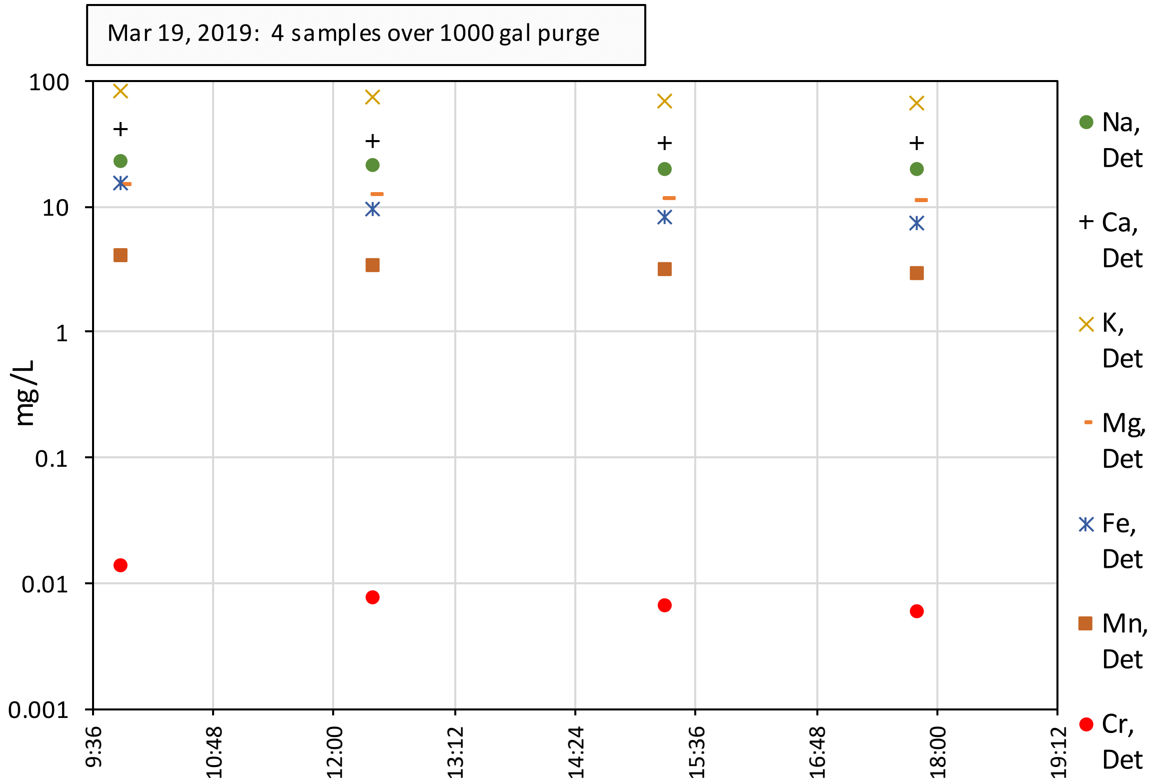


Figure 2.1-17 Progressive snapshots of the conceptual R-42 plan view model: October 2018 (right before October 2018 purge)



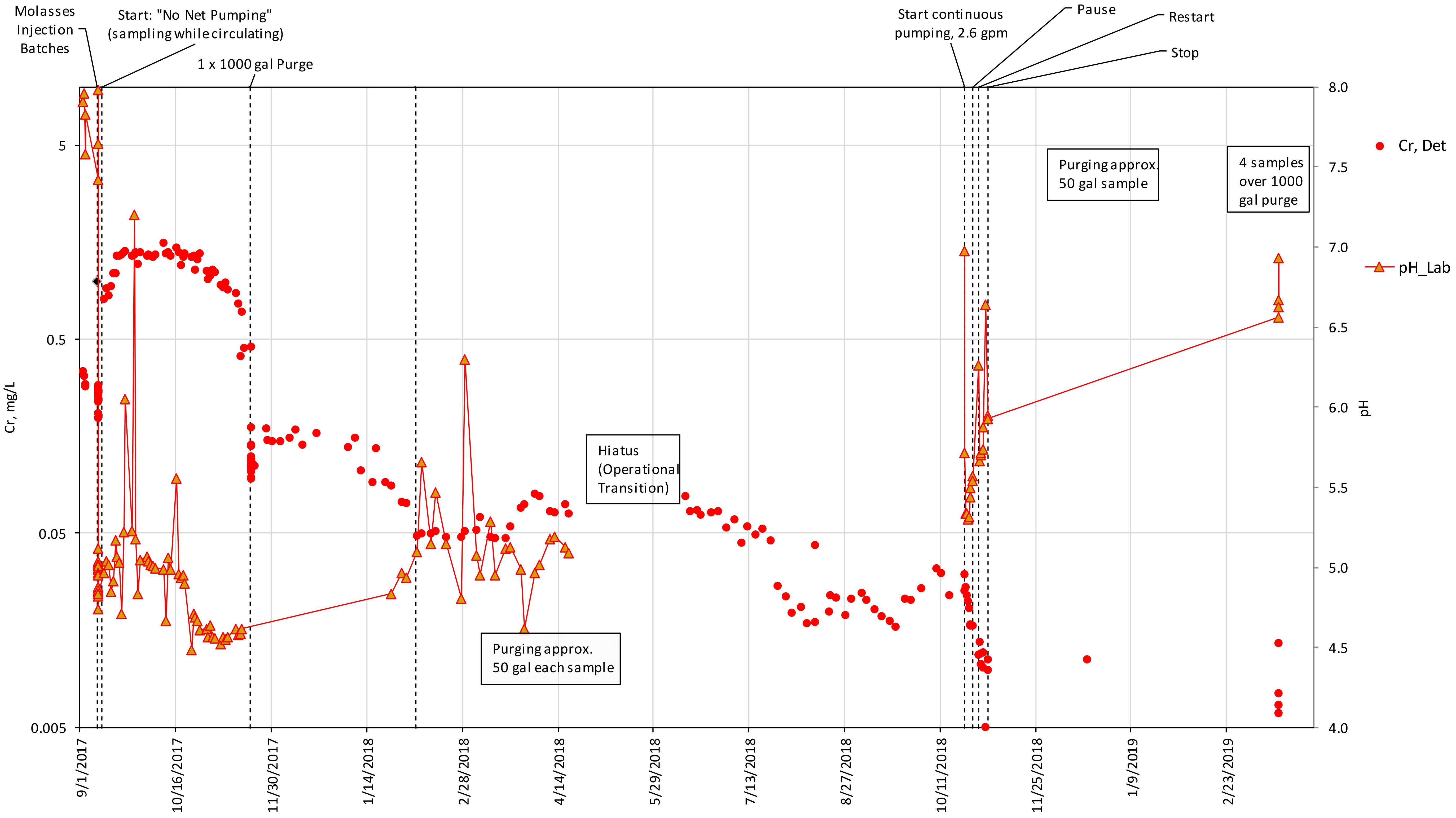
Notes: The pre-test concentrations were approximately as follows. Values are shown in mg/L: Na = 16; Ca = 47, K = 2, Mg = 12, Fe = 0.01–0.025, Mn = 0.001–0.005, Cr = 0.5. All results are from filtered samples. Acronyms: Det = Detected, ND = Not Detected.

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



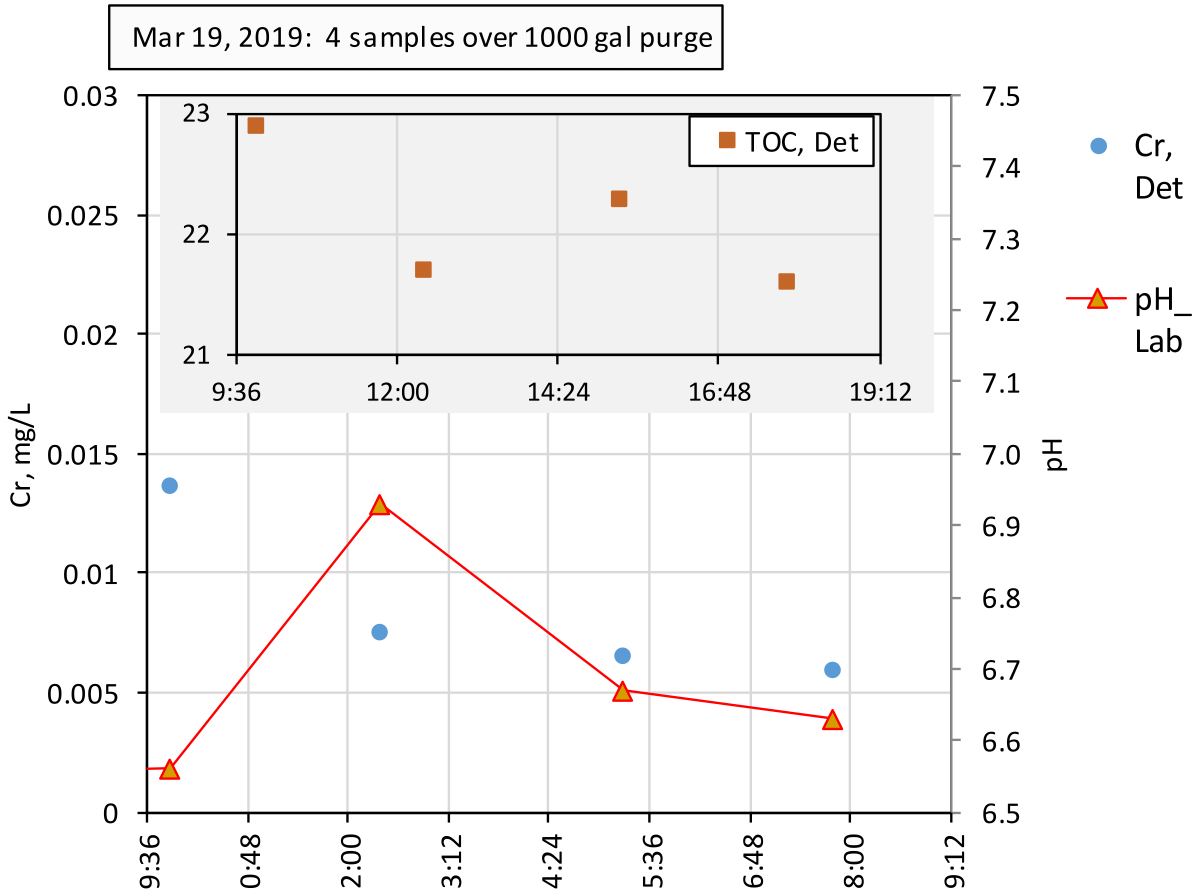
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.2-2 **Time-series plot showing concentrations of select cations from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019**



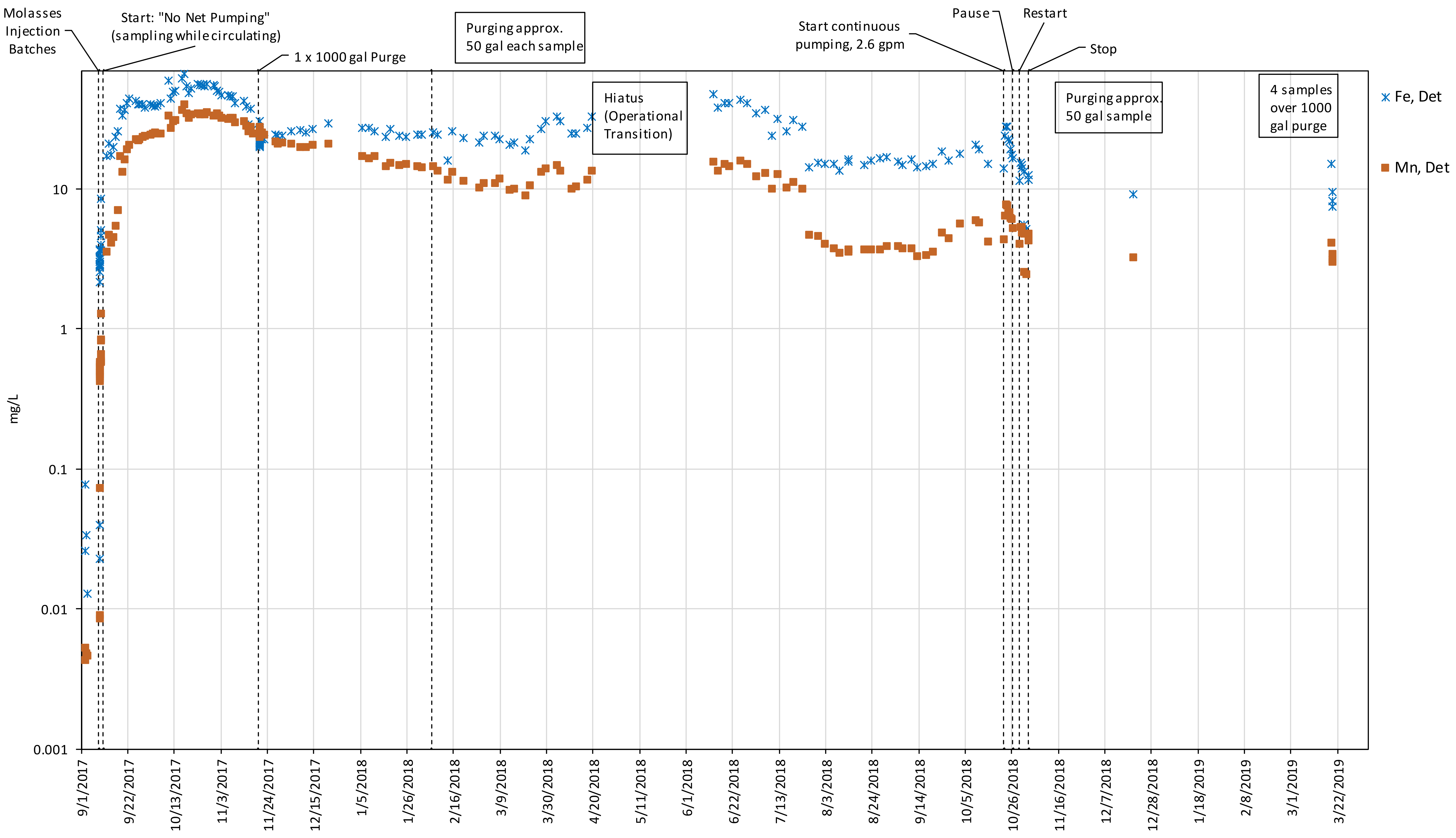
Notes: The pre-test concentrations were approximately as follows. Values both immediately preceding 2017's amendment injection and also, if different, values for (2014/2015) are shown in mg/L: Cr = 0.5. pH = 7.8. All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.2-3 Concentrations of selected chromium, pH, and TOC in R-28 molasses test as a function of time



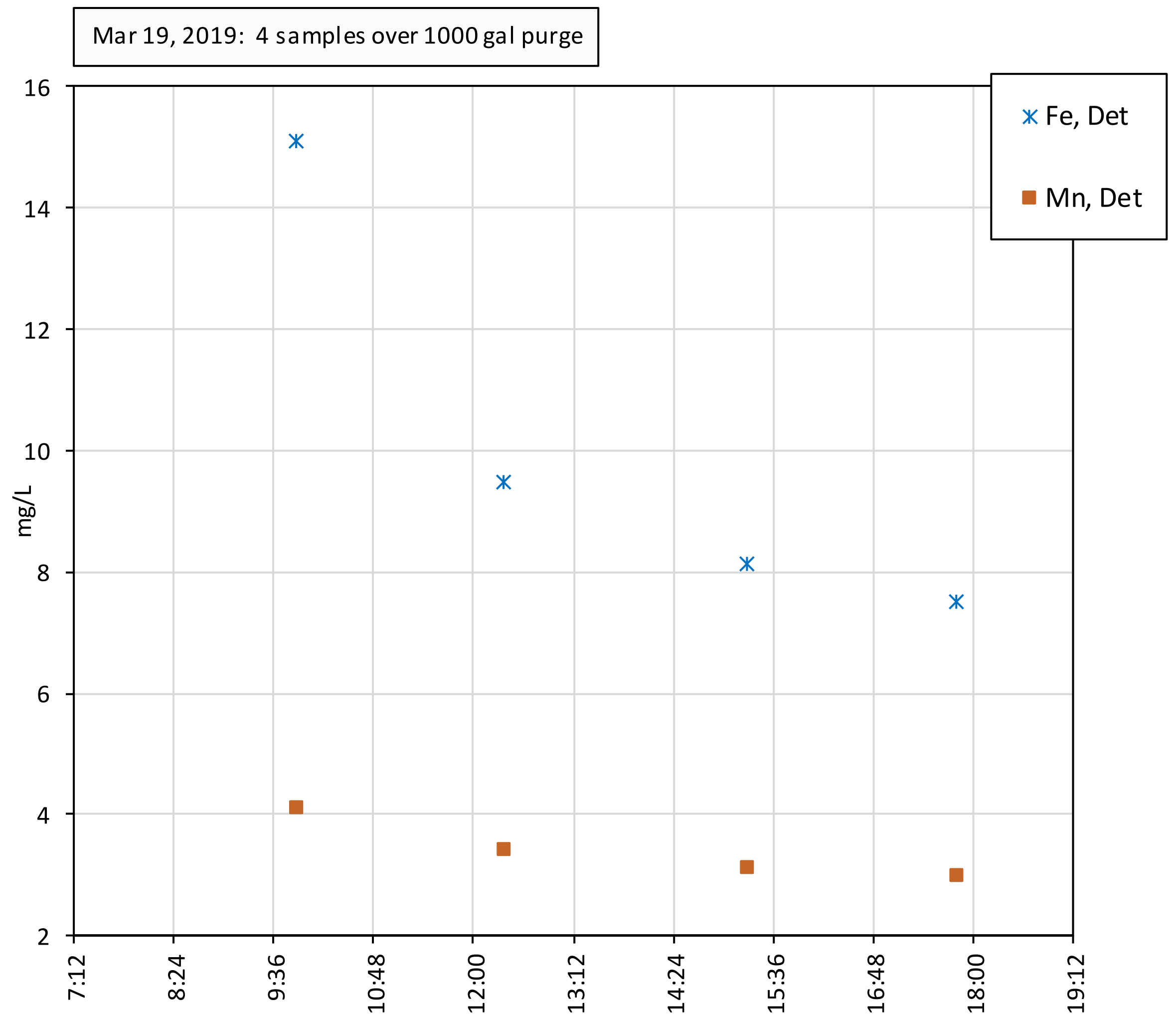
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. Chromium results are from filtered samples. Acronyms: Det = Detected.

Figure 2.2-4 **Time-series plot showing pH and chromium concentrations from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019**



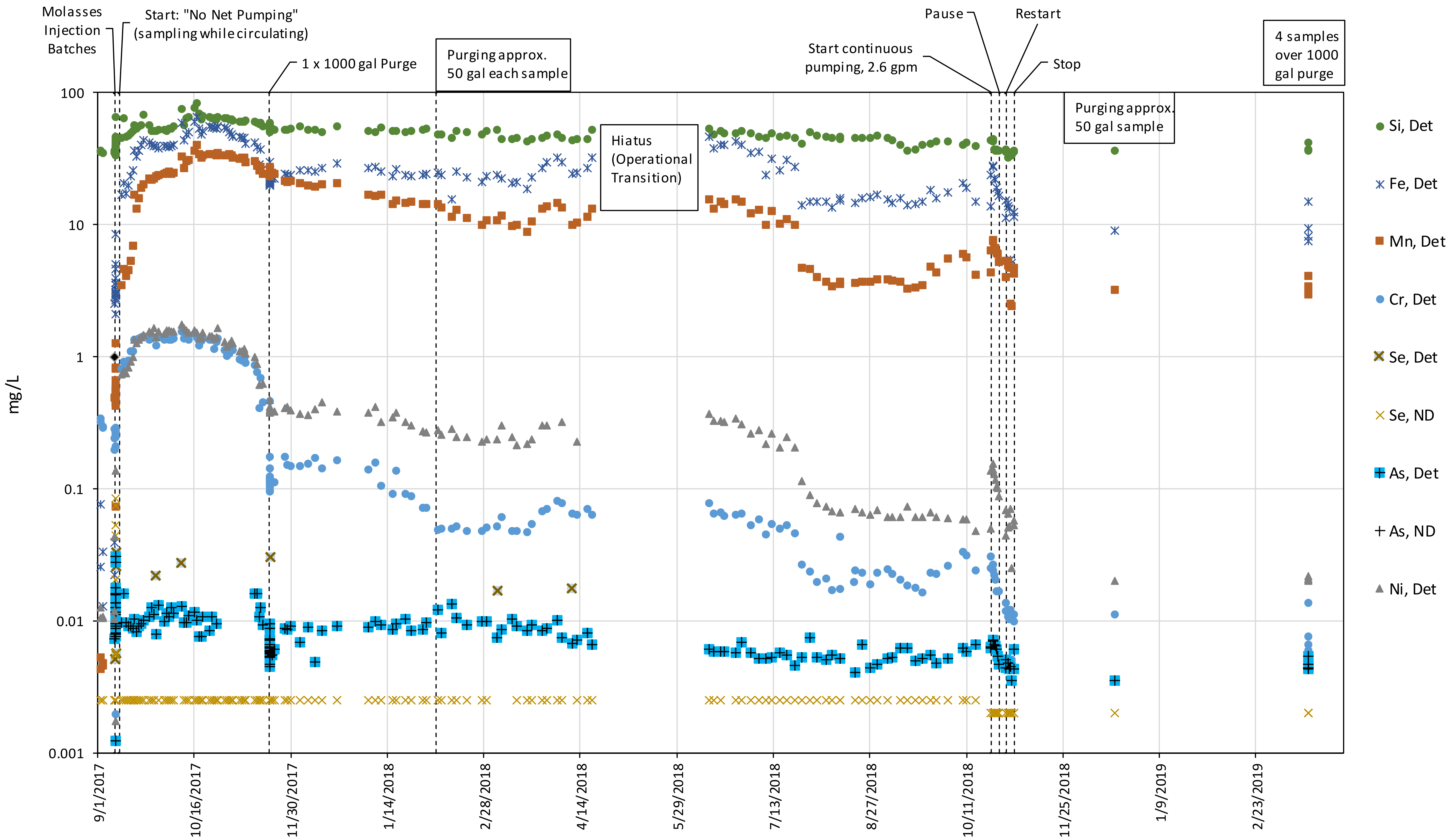
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. The pre-test concentrations were approximately as follows. Values are shown in mg/L: Fe = 0.01–0.025 and Mn = 0.001–0.005.All results are from filtered samples. Acronyms: Det = Detected.

Figure 2.2-5 Concentrations of iron and manganese in R-28 molasses test as a function of time



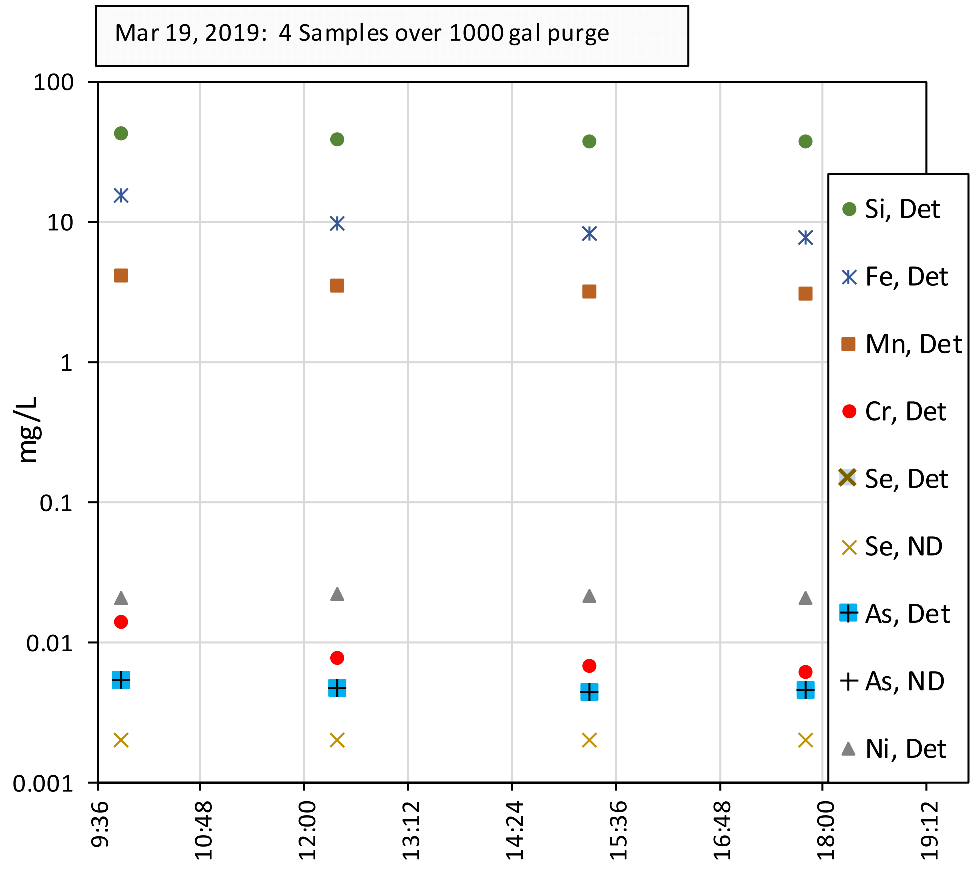
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples.
Acronyms: Det = Detected.

Figure 2.2-6 **Time-series plot showing concentrations of iron and manganese from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019**



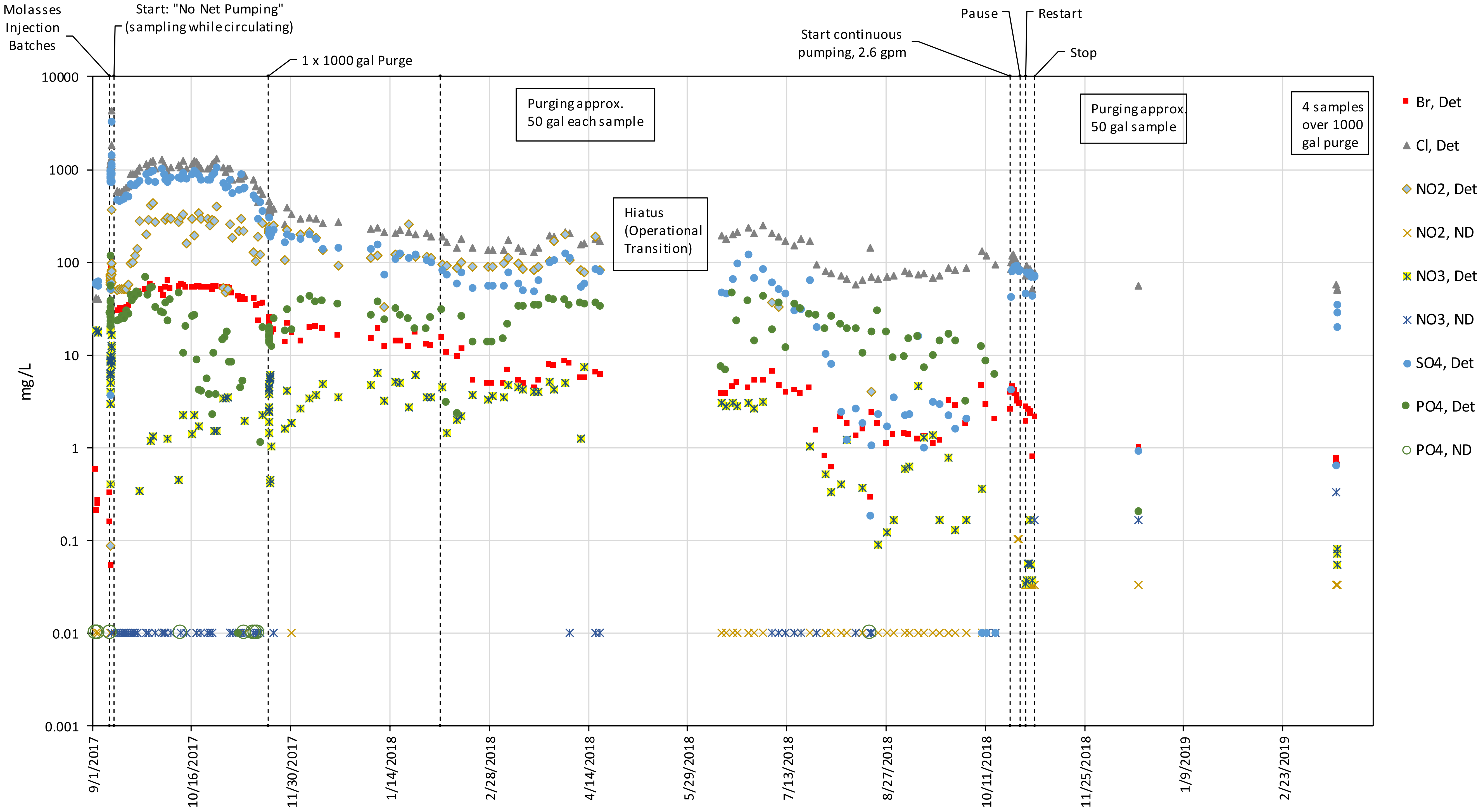
Notes: The pre-test concentrations were approximately as follows. Values are shown in mg/L: Si = 35, Fe = 0.01–0.025, Mn = 0.001–0.005, Cr = 0.5, Se = ND–0.01, As = 0.0005, Ni = 0.01–0.04. All results are from filtered samples. Acronyms: Det = Detected, ND = Not Detected.

Figure 2.2-7 Concentrations of selected constituents during R-28 molasses test as a function of time



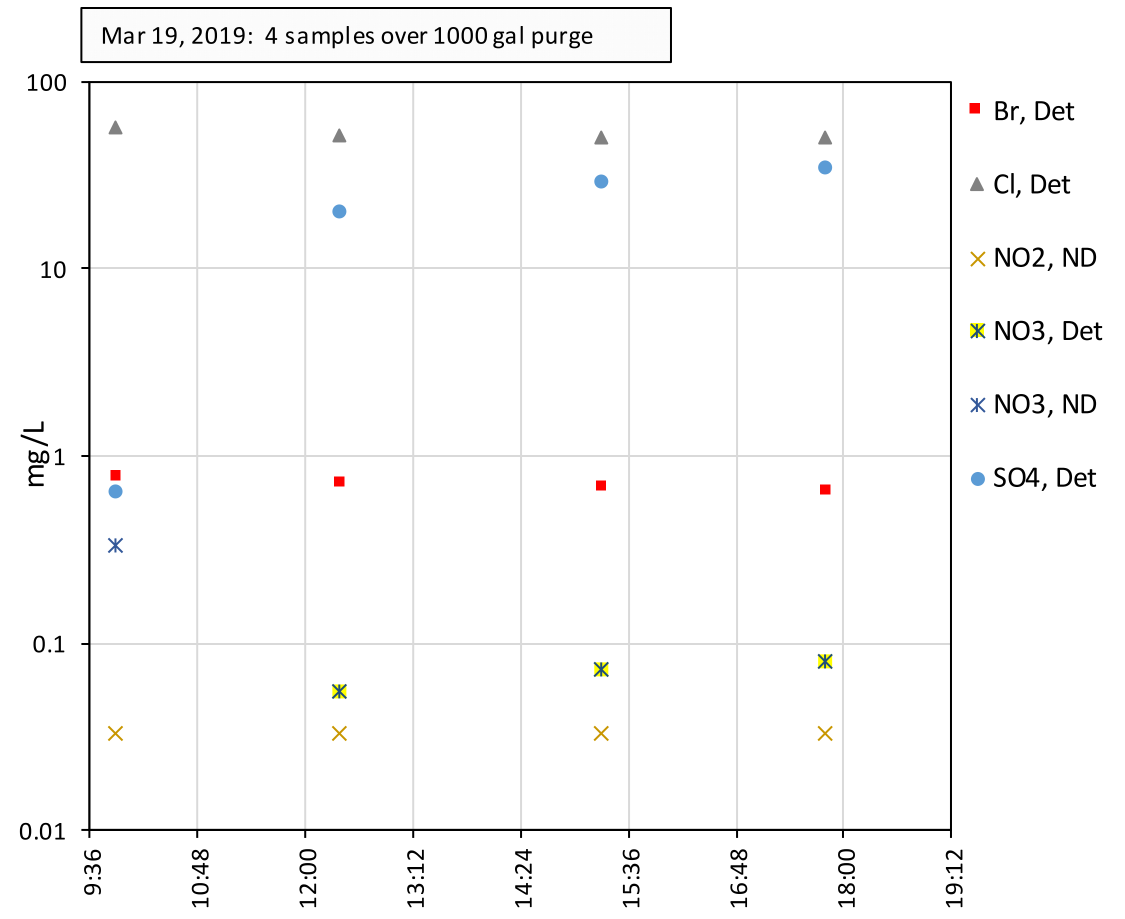
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples.
Acronyms: Det = Detected, ND = Not Detected.

Figure 2.2-8 **Time-series plot showing concentrations of select cations from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019**



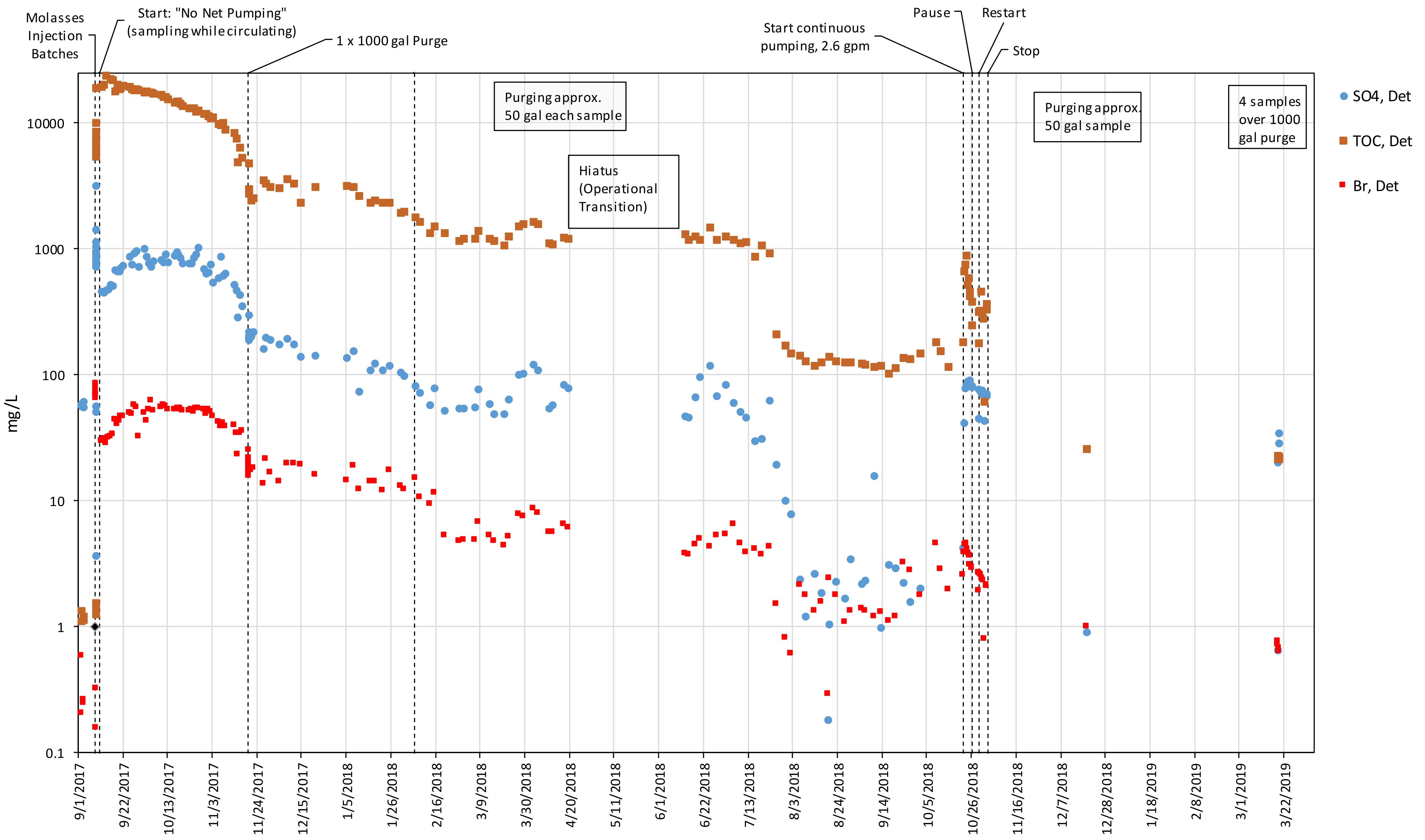
Notes: The pre-test concentrations were approximately as follows. Values are shown in mg/L: Br = 0.2, Cl = 45, NO2 <0.01, NO3 = 19, SO4 = 60, PO4 <0.01. Acronyms: Det = Detected, ND = Not Detected, Flt = Filtered Sample.

Figure 2.2-9 Concentrations of anions in R-28 molasses test as a function of time



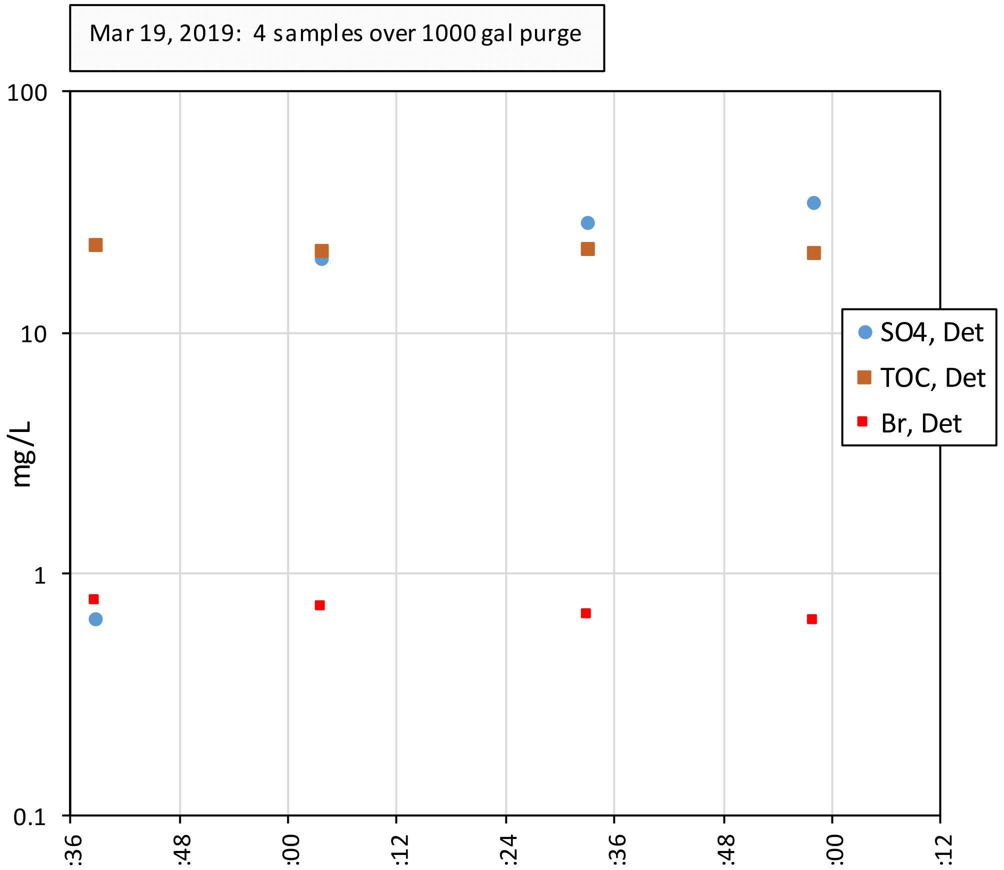
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples
Acronyms: Det = Detected, ND = Not Detected.

Figure 2.2-10 Time-series plot showing concentrations of select anions from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019



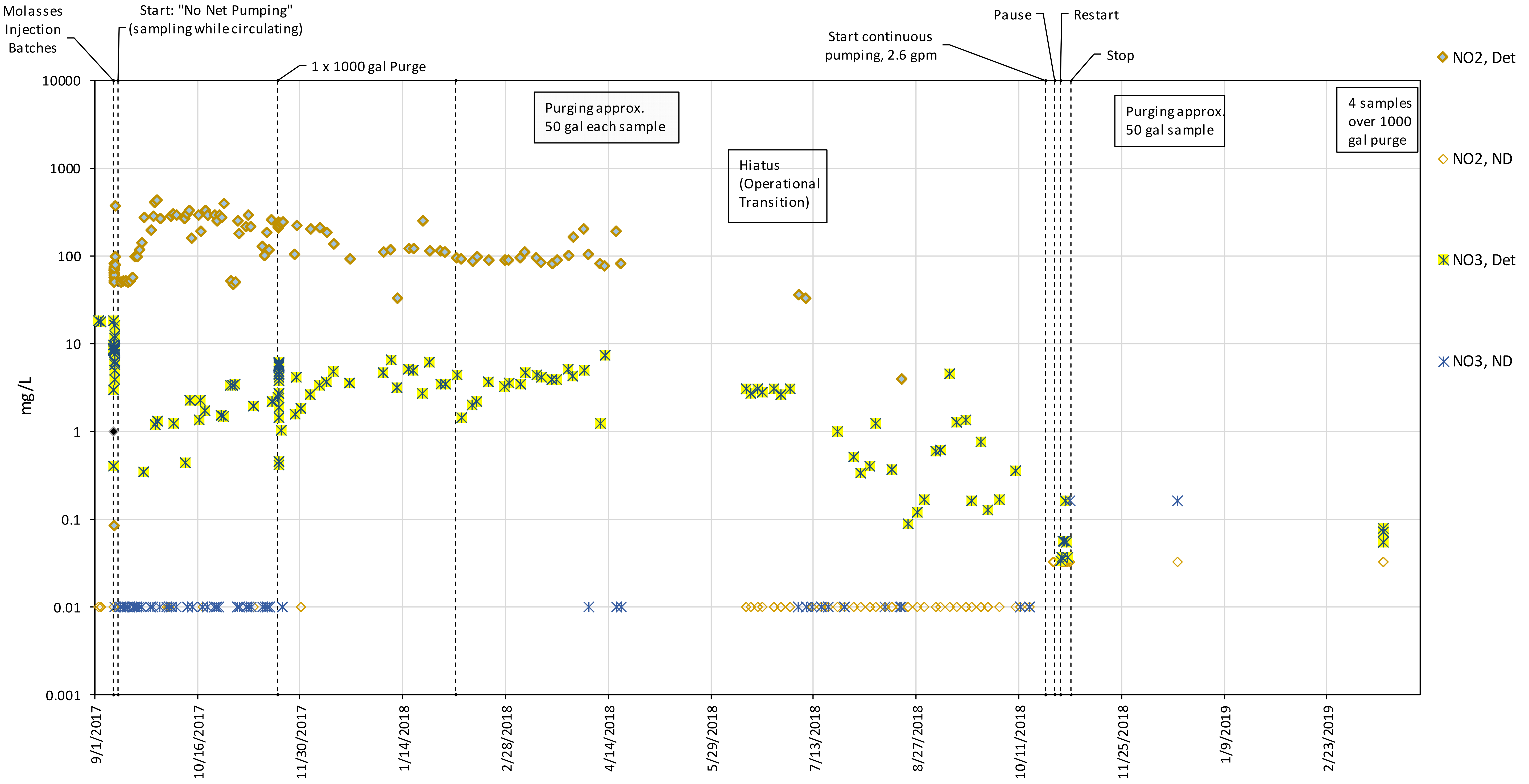
Notes: The pre-test concentrations were approximately as follows. Values are shown in mg/L Br = 0.2, SO4 = 60, TOC = 1. Acronyms: Det = Detected.

Figure 2.2-11 Concentrations of bromide, sulfate, and TOC in R-28 molasses test as a function of time



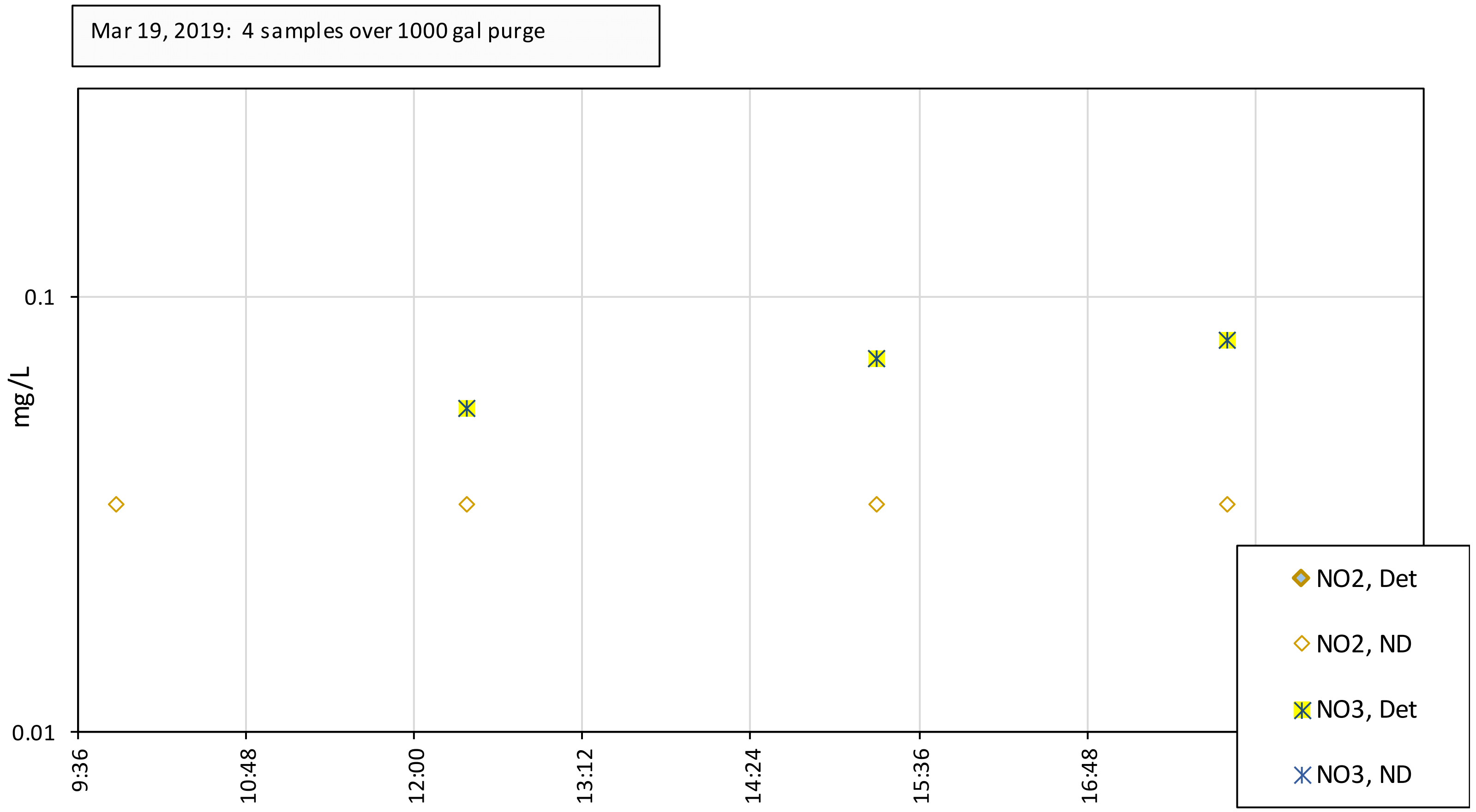
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples
Acronyms: Det = Detected.

Figure 2.2-12 Time-series plot showing concentrations of sulfate, bromide, and TOC from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019



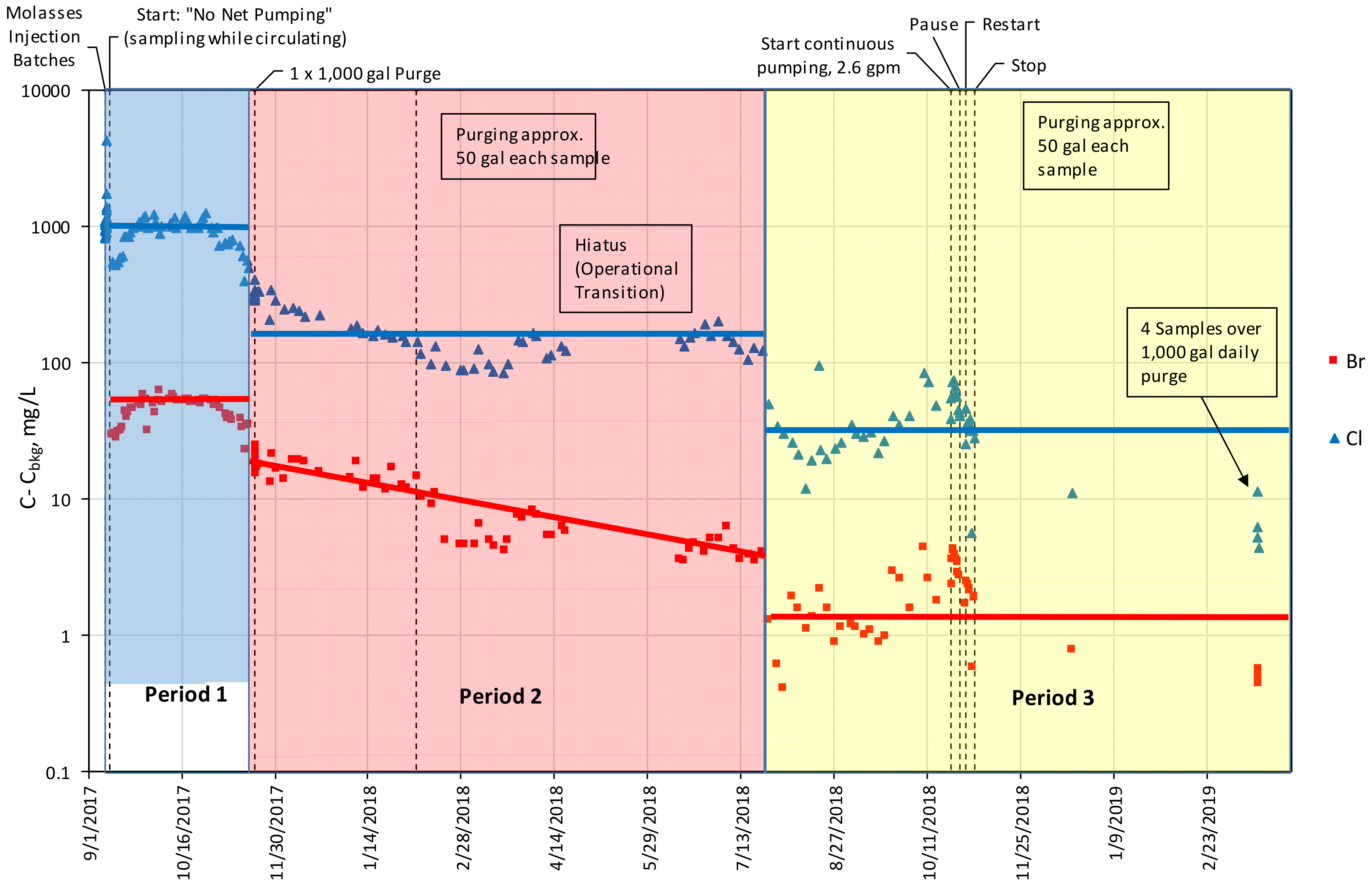
Notes: The pre-test concentrations were approximately as follows. Values are shown in mg/L: NO2 <0.01, NO3 = 19.
Acronyms: Det = Detected, ND = Not Detected.

Figure 2.2-13 Concentrations of nitrate and nitrite in R-28 molasses test as a function of time



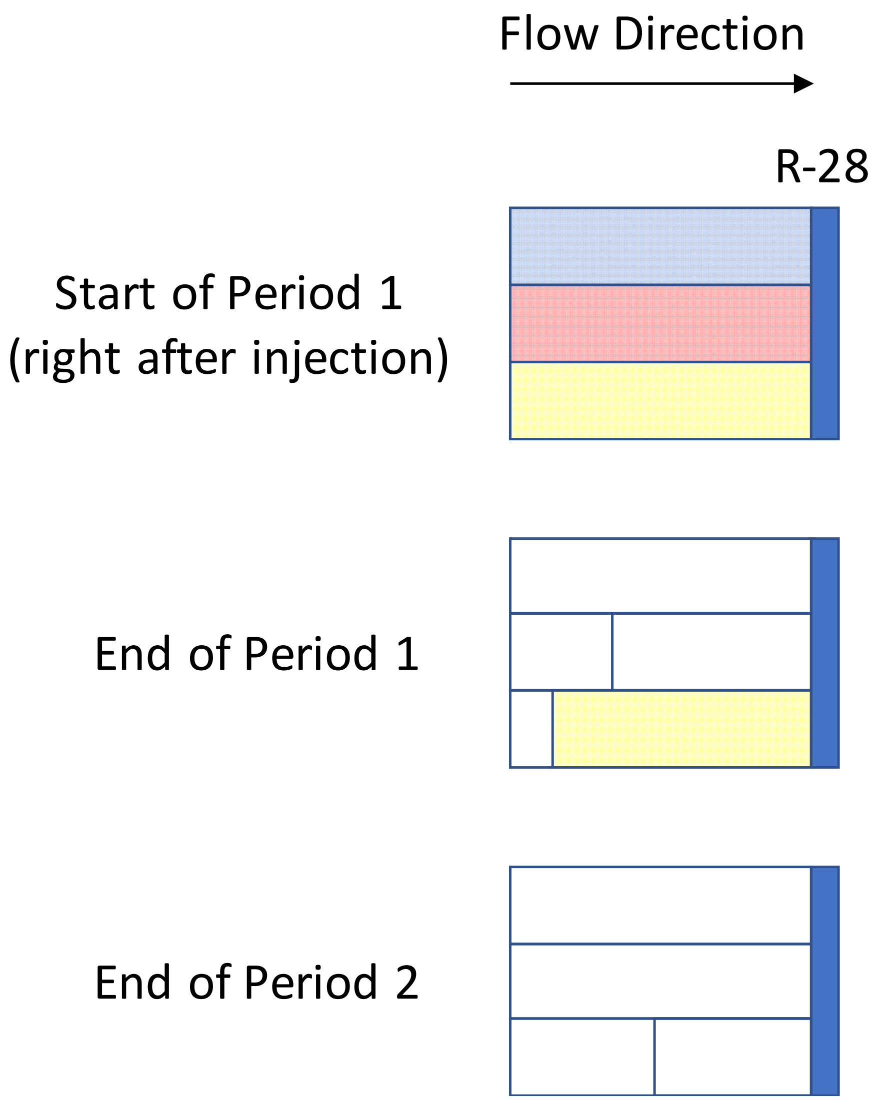
Notes: Four samples taken through purge at approximately 50, 350, 700, and 1000 gal. All results are from filtered samples. Acronyms: Det = Detected, ND = Not Detect.

Figure 2.2-14 Time-series plot showing concentrations of select cations from the approximately 1000-gal. purge conducted at R-28 on March 19, 2019. Recent Period – Concentrations of nitrate and nitrite in R-28 molasses test as a function of time



Note: The amendment test is divided into three periods (shaded regions) of different approximately-steady concentrations of Cl^- in R-28 (concentrations roughly indicated by horizontal lines).

Figure 3.2-1 Background-corrected Cl^- and Br^- concentrations in R-28 during the molasses amendment test



Notes: Colors of amendment solution in "flow zones" correspond to color-shading of the time periods in Figure 3.2-1. The thicknesses of the "flow zones" are not intended to reflect actual thicknesses and are used only for illustration purposes. Likewise, the transitions between amendment solution and groundwater are depicted as being more abrupt than is likely occurring.

Figure 3.2-2 Schematic depiction of side view of upgradient distribution of molasses solution at R-28 at the start of the amendment test, at the end of period 1 (see Figure 3.2-1), and at the end of period 2 (see Figure 3.2-1).

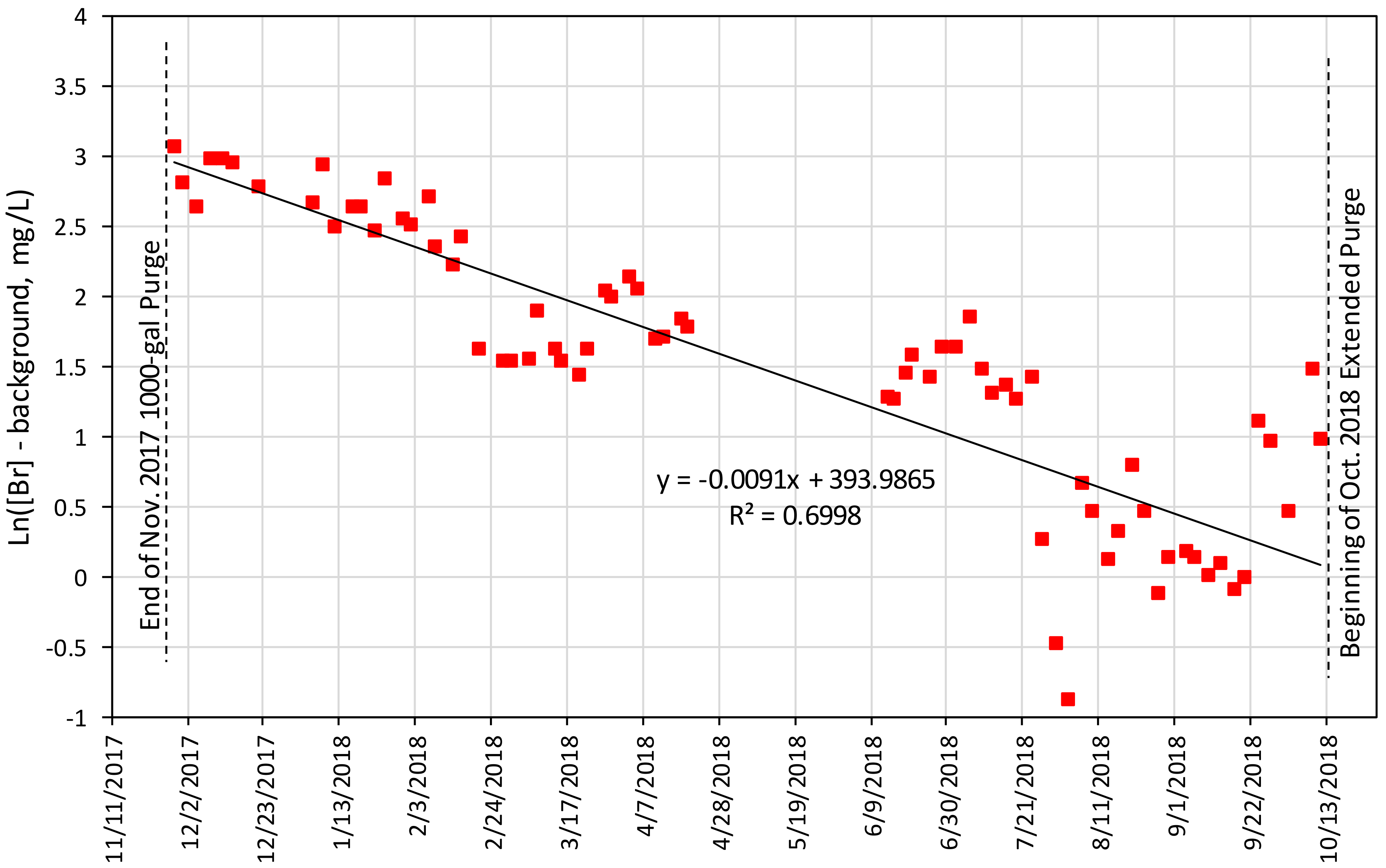
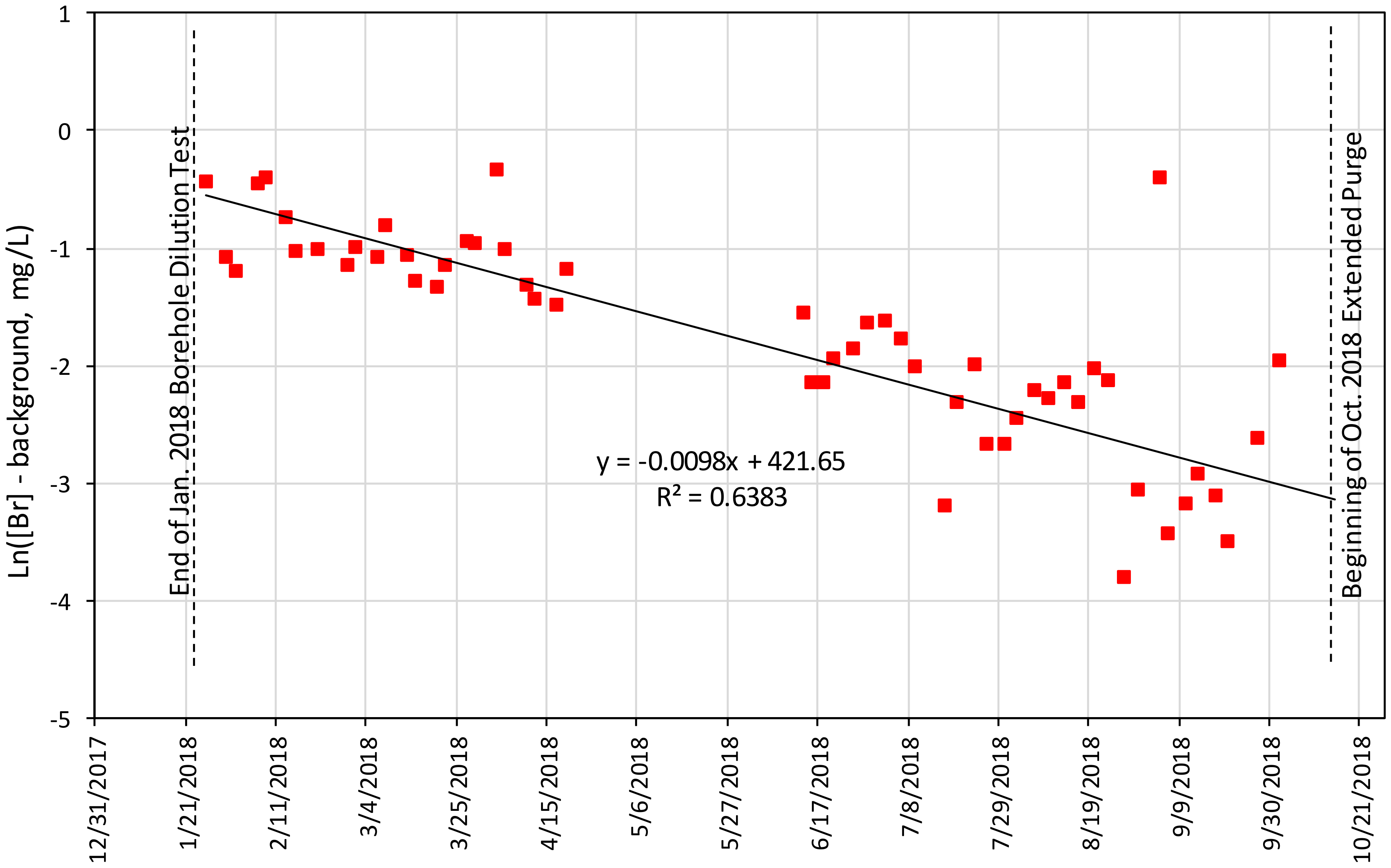
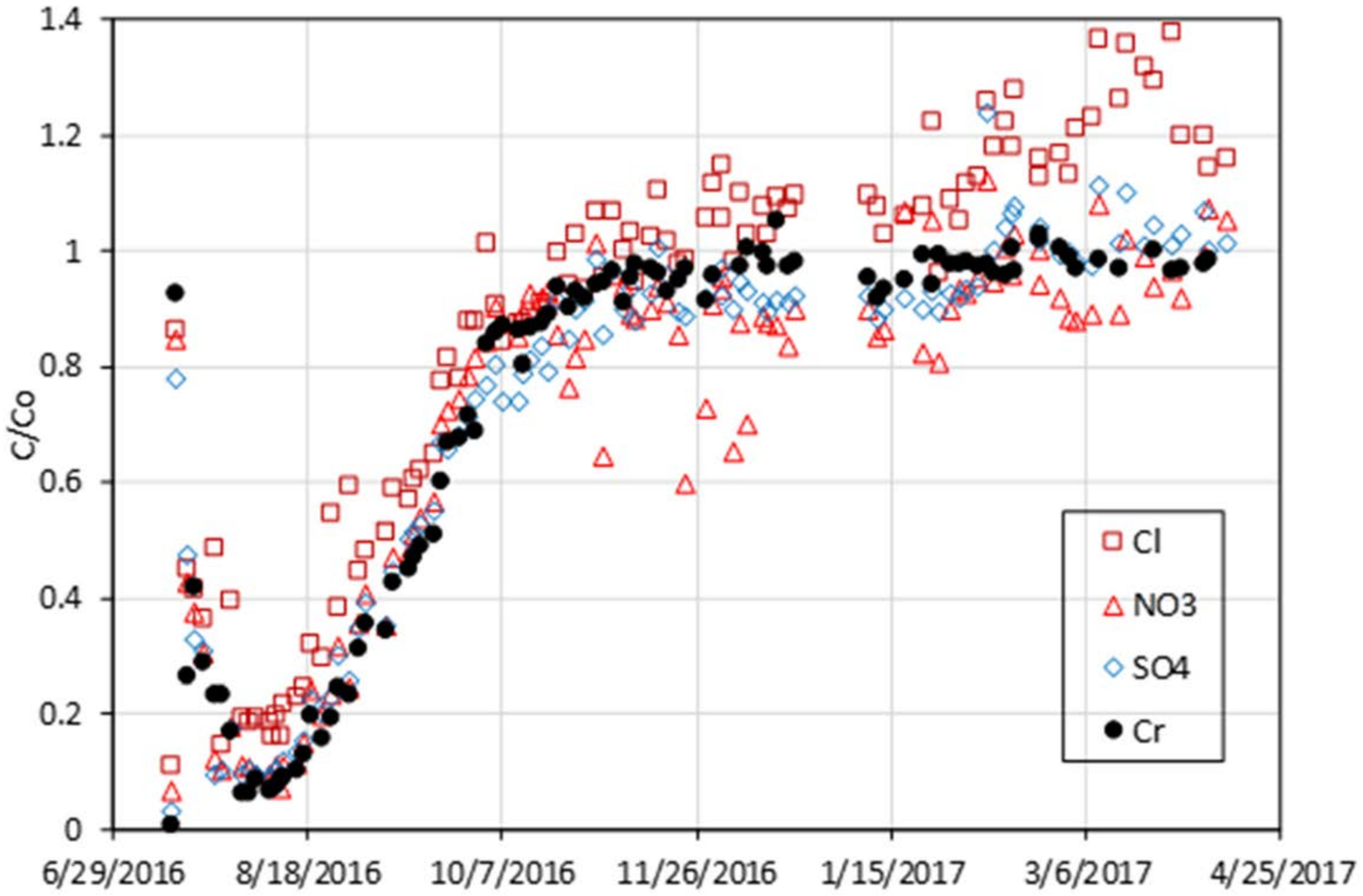


Figure 3.2-3 Log-linear fit to decline in background-subtracted Br^- concentrations during period 2 (and extending slightly into period 3) at R-28



Note: The slope obtained for R-42 is much more sensitive to the assumed background concentration of Br^- than at R-28 (Figure 3.2-3) because the Br^- concentrations are much closer to background at R-42.

Figure 3.3-1 Log-linear fit to decline in background-subtracted Br^- concentrations in R-42 between the end of the January 2018 borehole dilution tracer test and the beginning of the October 2018 extended purge



Note: Initial high concentrations are taken to reflect non-ideal mixing and flow distribution in the well during the injection.

Figure 3.4-1 **Increases in concentrations of conservative species as they moved back into R-42, after injection of 15,000 gal. of a 0.005 M HCO_3^-/0.005 M $CO_3^=$ solution mixed in potable water in July 2016**

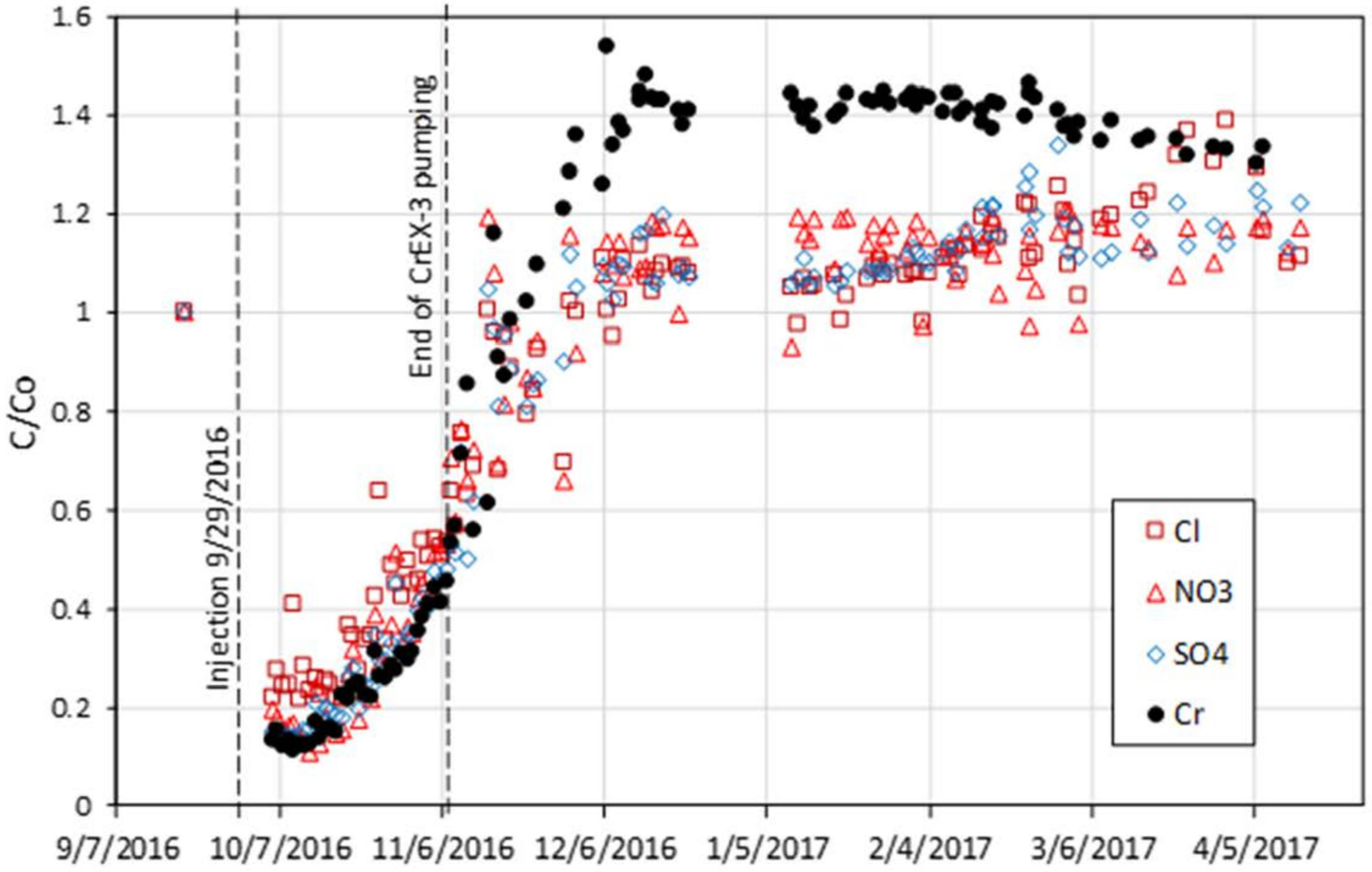
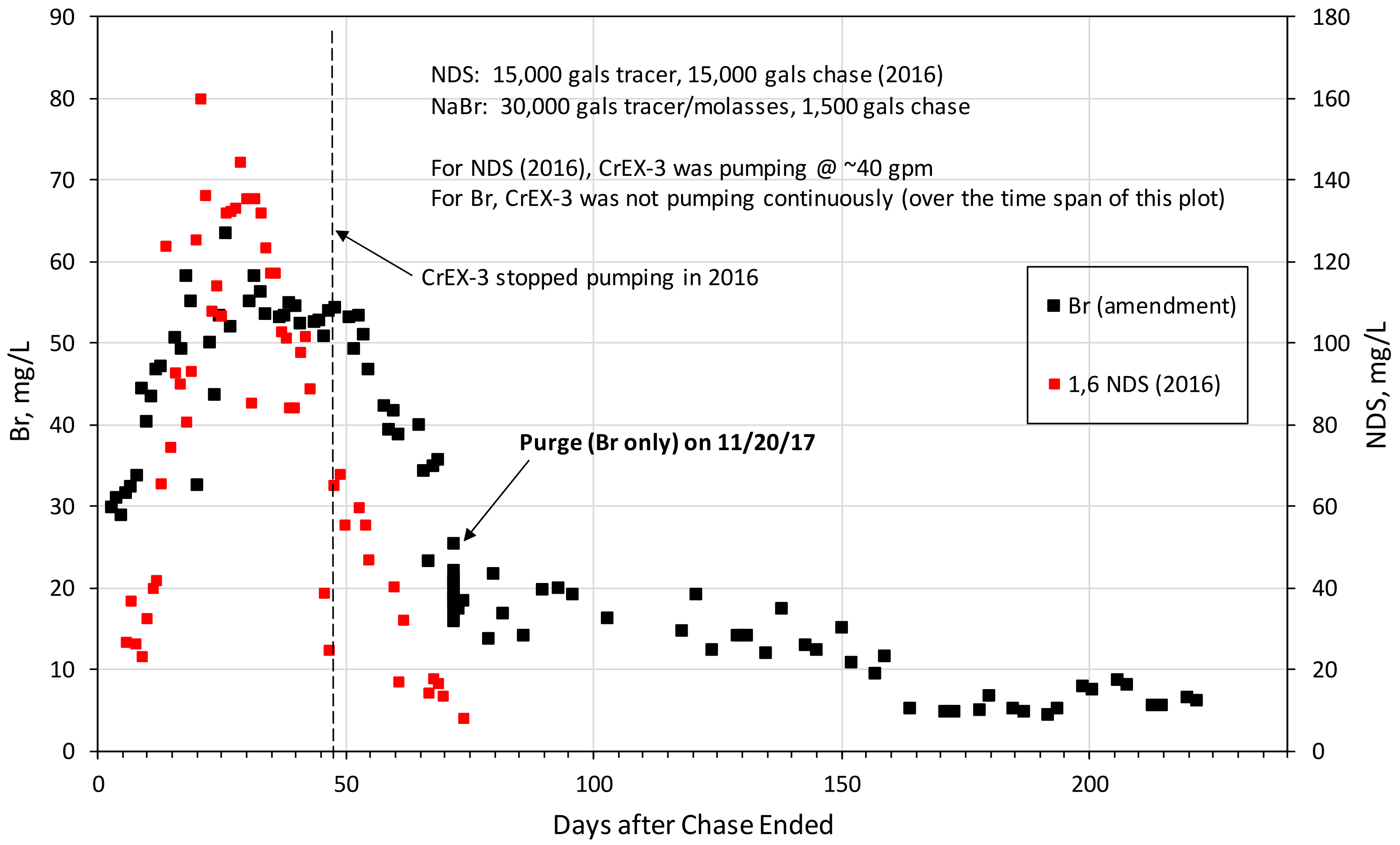


Figure 3.4-2 **Increases in concentrations of conservative species as they moved back into R-28, after injection of 15,000 gal. of tracer solution plus 15,000 gal. of chase water (both potable water) in September 2016**



Notes: Both tests involved approximately the same volume of water injected into R-28 (~30,000 gal.), although only the first 15,000 gal. of injected water in 2016 contained 1,6-NDS, whereas almost the entire ~30,000 gal. of water in 2017 contained Br$^-$.

Figure 3.4-3 Concentrations in R-28 of 1,6-NDS concentrations in 2016 and Br$^-$ from September 2017 through April 2018 (both plotted with time zero corresponding to the end of chase water injections)

Table 3.4-1
R-42 Specific Capacity Estimates

Event	Period	Pumping Rate (gpm)	Average Drawdown (ft)	Specific Capacity (gpm/ft)
Test-1	2009-11-14 to 2009-11-15	5.5	7.0	0.8
Pre-1	2013-06-17 to 2013-07-07	7.1	2.6	2.7
Pre-2	2013-07-11 to 2013-08-21	7.1	7.4	1.0
Pre-3	2014-04-21 to 2014-04-29	7.5	7.4	1.0
Post-1	2018-10-22 to 2018-10-26	2.9	5.4	0.5
Post-2	2018-10-29 to 2018-10-30	2.9	6.6	0.4

Table 3.4-2
R-28 Specific Capacity Estimates

Event	Period	Pumping Rate (gpm)	Average Drawdown (ft)	Specific Capacity (gpm/ft)
Test-1	2004-02-05 to 2004-02-06	9.45	0.8	11.8
Test-2	2004-03-07 to 2004-03-08	12.9	1.0	13.3
Pre-1	2013-09-07 to 2013-11-22	28.7	2.5	11.6
Pre-2	2014-05-30	26.5	2.1	12.6
Pre-3	2014-05-31 to 2014-06-03	26.5	2.2	12.1
Post-1	2018-10-22 to 2018-10-26	2.6	1.1	2.4
Post-2	2018-10-29 to 2018-10-30	2.6	0.7	3.8
Post-3	2018-11-01 to 2018-11-02	2.6	0.7	3.9

Attachment 1

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