

**Associate Directorate for Environmental Management**

P.O. Box 1663, MS M992
Los Alamos, New Mexico 87545
(505) 606-2337

**Environmental Management**

1900 Diamond Drive, MS M984
Los Alamos, New Mexico 87544
(505) 665-5658/FAX (505) 606-2132

Date: JUL 11 2017

Refer To: ADEM-17-0164

LAUR: 17-25406

Locates Action No.: n/a

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

**Subject: Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater
beneath Mortandad Canyon**

Dear Mr. Kieling:

Enclosed please find two hard copies with electronic files of the Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon. This work plan addresses one of several activities being conducted under Los Alamos National Laboratory's Work Plan for Chromium Plume-Center Characterization.

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,

Bruce Robinson, Program Director
Environmental Remediation Program
Los Alamos National Laboratory

Sincerely,

David S. Rhodes, Director
Office of Quality and Regulatory Compliance
Los Alamos Environmental Management
Field Office

BR/DR/SS:sm

Enclosures: Two hard copies with electronic files – Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon (EP2017-0091)

Cy: (w/enc.)
Cheryl Rodriguez, DOE-EM-LA
Stephani Swickley, ADEM ER Program

Cy: (w/electronic enc.)
Laurie King, EPA Region 6, Dallas, TX
Raymond Martinez, San Ildefonso Pueblo
Dino Chavarria, Santa Clara Pueblo
Steve Yanicak, NMED-DOE-OB, MS M894
Michelle Hunter, NMED GWQB
emla.docs@em.doe.gov
Public Reading Room (EPRR)
ADESH Records
PRS Database

Cy: (w/o enc./date-stamped letter emailed)
lasomailbox@nnsa.doe.gov
Peter Maggiore, DOE-NA-LA
Kimberly Davis Lebak, DOE-NA-LA
David Rhodes, DOE-EM-LA
Bruce Robinson, ADEM ER Program
Randy Erickson, ADEM
Danny Katzman, ADEM-PO
Jocelyn Buckley, ADESH-EPC-CP
Mike Saladen, ADESH-EPC-CP
John Bretzke, ADESH-EPC-DO
Michael Brandt, ADESH
William Mairson, PADOPS
Craig Leasure, PADOPS

LA-UR-17-25406
July 2017
EP2017-0091

Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon



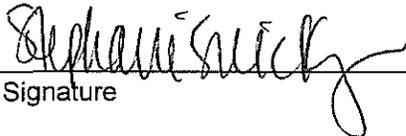
Prepared by the Associate Directorate for Environmental Management

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. The U.S. government has rights to use, reproduce, and distribute this document. The public may copy and use this document without charge, provided that this notice and any statement of authorship are reproduced on all copies.

Pilot-Scale Amendments Testing Work Plan for Chromium in Groundwater beneath Mortandad Canyon

July 2017

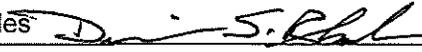
Responsible project manager:

Stephani Swickley		Project Manager	Environmental Remediation Program	7/6/17
Printed Name	Signature	Title	Organization	Date

Responsible LANS representative:

<i>for</i>	Randall Erickson		Associate Director	Associate Directorate for Environmental Management	7/6/2017
	Printed Name	Signature	Title	Organization	Date

Responsible DOE-EM-LA representative:

David S. Rhodes		Office Director	Quality and Regulatory Compliance	7-11-2017
Printed Name	Signature	Title	Organization	Date

CONTENTS

1.0 INTRODUCTION 1

 1.1 Objectives 1

 1.2 Conceptual Model 2

2.0 RATIONALE FOR SELECTION OF LOCATIONS FOR TESTING 3

3.0 TEST METHODOLOGY 5

 3.1 Sodium Dithionite at R-42 5

 3.1.1 Deployment 5

 3.1.2 Sampling 6

 3.2 Molasses at R-28 6

 3.2.1 Deployment 6

 3.2.1 Sampling 7

4.0 KEY MONITORING INDICATIONS 7

5.0 REPORTING 8

6.0 WASTE MANAGEMENT 9

7.0 REFERENCES AND MAP DATA SOURCES 9

 7.1 References 9

 7.2 Map Data Sources 10

Figures

Figure 1.0-1 Injection, extraction, and monitoring wells in the area of the chromium plume 11

Figure 1.0-2a Lithologic column for corehole 3 showing rock types for individual beds making up strata in the upper part of the regional aquifer 12

Figure 1.0-2b Lithologic column for corehole showing rock types for individual beds making up strata in the upper part of the regional aquifer 13

Figure 1.0-3 Results from duplicate column experiments passing untreated R-42 water through Miocene Pumiceous sediments treated with an excess of sodium dithionite 14

Figure 1.0-4 Breakthrough profiles of Cr(VI) and tritium (both expressed as C/Co) in a column filled with SCI-2 sediments and biostimulated with 3.4 g/L molasses, injected only while the tritium was injected 15

Figure 2.2-1 Trends for four constituents at monitoring well R-28 following injection of 30,000 gal. of potable water on September 29, 2016 16

Figure 3.2-1 Breakthrough curves for deuterium and sulfonate tracers in R-28 17

1.0 INTRODUCTION

This work plan presents the objectives and approach for implementing pilot-scale amendments testing for chromium (Cr) contamination beneath Mortandad Canyon at Los Alamos National Laboratory (LANL or the Laboratory). It addresses one of several activities conducted under the New Mexico Environment Department– (NMED-) approved “Work Plan for Chromium Plume-Center Characterization” (LANL 2015, 600615; NMED 2015, 600958). Other activities conducted as part of plume-center characterization include pumping to evaluate source removal at extraction well CrEX-3, tracer studies to evaluate hydraulic properties of the aquifer, and bench-scale biogeochemical and mineralogical characterization to design the pilot-scale test. Data from these studies will also help guide future large-scale treatment options. Figure 1.0-1 shows the project site. The proposed pilot-scale amendments testing is intended to scale up from the bench-scale experiments and to provide important information that may be applied to full-scale remedial options for the chromium plume to be presented in a future corrective measures evaluation report.

1.1 Objectives

The overarching objective of this work plan is to evaluate the feasibility of in situ treatability of hexavalent chromium [i.e., reduction of Cr(VI) to Cr(III)] in the deep and heterogeneous aquifer beneath Mortandad Canyon. In general, converting Cr(VI) to Cr(III) is straightforward under geochemically reducing conditions. The main challenges associated with full site-scale remediation tend to be related to aquifer characteristics, including large-scale heterogeneity, hydrostratigraphic complexity, mineralogy of aquifer materials, and naturally occurring groundwater chemistry.

In addition to testing whether lasting reducing environments conducive to Cr(VI) reduction can be established in situ within the aquifer with chemical amendments or bioamendments, other specific objectives of this field testing include determining (1) the reduction capacity induced by different amendments, (2) the volume of the treated zone relative to the volume of injected amendment solution, and (3) any potential adverse conditions that may occur within the aquifer as a result of the amendments. It is important to note that while the amendment solutions will displace the aquifer water as they are injected, the expectation is that both the chemical and biological amendments will react primarily with immobile phases/constituents in the aquifer (i.e., with the iron phases in the sediments in the case of dithionite) and with microbes attached to the sediments in the case of molasses, to establish geochemical conditions that are conducive to reducing Cr(VI) to Cr(III).

Reduction capacity is the mass of chromium that can be reduced from Cr(VI) to Cr(III) within the treatment zone as contaminated groundwater flows through the zone. For the dithionite, reduction capacity may be quite large from a single deployment as demonstrated by studies conducted at the U.S. Department of Energy’s Hanford Site where over 10 yr of effective reduction has been documented (DOE 2012, 602481). For biostimulation approaches, reduction capacity is regulated by the availability of nutrients to microbial populations that must be restimulated periodically to maintain reducing conditions. Typically, redeployments of nutrients are required every few months to every few years depending on the nature of the physical and chemical interactions of the amendment with the aquifer matrix, groundwater chemistry, and groundwater flow conditions (ESTCP 2010, 602491).

Chemical amendments typically do not travel far from the injection location within an aquifer because of their high reactivity with dissolved oxygen in the groundwater and iron associated with aquifer sediments. The distance a bioamendment may travel is a function of the rate at which the amendment is metabolized by native microbes (which is, in turn, a function of microbial concentrations plus physical and chemical conditions in the aquifer), its biodegradation rate, and groundwater velocity. For either chemical amendments or bioamendments, the effective radius of injection is a function of the proportion of porous

and permeable strata within the injection interval, the volume of injected fluid, and the mobility and reactivity of the amendment. Figure 1.0-2 illustrates the highly stratified nature of the aquifer in the vicinity of wells R-42 and R-28. The detailed stratigraphy shown in the figures was derived from sieve analysis of discrete beds identified from core material obtained from sonic drilling near R-42 (CH-3, now CrPZ-3) and R-28 (CH-2, now CrPZ-2) (Figure 1.0-1). Amendments are likely to preferentially enter the more highly porous and permeable units that constitute a relatively small fraction of the formation within the screened interval, assuming the “sandy-pebble” and “pebbly-sand” units are the preferential units. The expected radius of injection will therefore likely be much greater within more permeable units and result in “disc”-shaped areas of primary treatment that extend laterally much farther than in the less-permeable units. More laterally extensive treatment of high-permeability units is actually beneficial because these units are where the Cr(VI) should be migrating the fastest, so treatment of these units will have the greatest impact on plume migration. If Cr(VI) is present in the less-permeable units, it should back-diffuse into the treated high-permeability units and encounter the reducing conditions established within those zones, at least until the reduction capacity is depleted.

Potential adverse geochemical effects that result from use of these amendments in the aquifer, including potential adverse biofouling effects within a deployment location, will also be evaluated. Potential adverse effects include precipitation of pore-filling minerals and dissolution of naturally occurring constituents (e.g., arsenic) found in aquifer materials. The results of these tests will be used to parameterize and refine predictive models that can be used to design additional pilot amendments testing as well as potential full-scale remediation strategies.

1.2 Conceptual Model

The chromium plume in the regional aquifer beneath Mortandad Canyon exists in the hexavalent [Cr(VI)] form. A common remediation strategy for Cr(VI) in groundwater involves manipulating aquifer conditions with the goal of converting Cr(VI) to Cr(III) within the aquifer (in situ) (Evanko and Dzombak 1997, 102743; Fruchter et al. 2000, 602475; Hawley et al. 2005, 602490; Stanin 2005, 602489; Vermeul et al. 2006, 602478; Varadharajan et al. 2017, 602477). Cr(III) typically precipitates as hydroxide complexes that have a very low solubility and are incorporated into iron-rich phases or adsorb strongly to sediment surfaces, which effectively immobilizes the Cr because Cr(III) is not easily reoxidized to Cr(VI) under most geochemical conditions (Hawley et al. 2005, 602490; Stanin 2005, 602489; Varadharajan et al. 2017, 602477). The Laboratory has been conducting bench-scale column experiments using various amendments applied to aquifer sediments and groundwater from the Chromium Project site have shown that reduction of chromium in groundwater is easily achieved and persists for extended periods of time. Experiments with sodium dithionite were very effective at reducing ferric iron phases in aquifer sediments and imparting immobile reduced (ferrous) iron capacity to reduce Cr(VI) to Cr(III).

Figure 1.0-3 shows the results of duplicate column experiments in which Miocene Pumiceous sediments were treated with an excess of sodium dithionite and then packed into two columns. The batch pretreatment of sediments was done to provide an upper bound estimate of reduction capacity of the sediments. Experiments are currently underway to evaluate the reduction capacity of sediments treated by column injections of finite pulses of dithionite solution, similar to a field deployment. Groundwater from R-42 was flushed through the columns after an initial flush involving treated CrEX-3 water. The upper plot of this figure shows the flow rates and nitrate concentrations as a function of pore volumes of water eluted through the columns. Despite the sporadic breakthroughs of nitrate, no Cr(VI) eluted from either column. Although the intent was to run the columns until Cr(VI) breakthrough was observed, the columns began to clog before this occurred. The clogging was believed to be a consequence of the very long times that the columns were run, not any sort of unfavorable reactions occurring in them. Columns run for many months in the laboratory, as these had been, invariably tend to decrease in permeability because of sediment

redistribution and possibly biofilm growth, which is difficult to avoid over long times. After flow was stopped, sediment from the columns was sectioned into ~1-cm-long segments and leached with 2 molar nitric acid. The lower plot of Figure 1.0-3 shows the chromium profile in the acid-leached sediments from the two columns. The data show a very sharp chromium front that reached about two-thirds to four-fifths of the way through the columns. Based on this information, it can be surmised that the breakthrough of Cr(VI) would have occurred at around 200–240 pore volumes if the columns had continued to flow. These column-experiment results are not expected to correspond perfectly to field results, but they are a clear indication of the potential for significant and relatively long-term reduction imposed by dithionite. Key differences between the column experiment and field conditions are (1) the R-42 water used in the experiments was degassed and thus was probably lower in oxygen concentrations than in situ groundwater, (2) the column porosity was higher than formation porosity, and (3) the sediments were likely more efficiently reduced by dithionite in the batch treatment than can be expected in situ. However, taking into account all these factors, it is still estimated that dithionite-treated sediments may be capable of effectively reducing Cr(VI) from at least 100 pore volumes of water that pass through the sediments. Long-term chromium reduction in these experiments is believed to be caused by reaction of the reduced iron with aqueous Cr(VI) to generate Cr(III).

Bench-top testing using acetate and molasses as bioamendments has demonstrated that biosimulation can be easily achieved by the addition of nutrients to the aquifer sediments. Biostimulation of aquifer sediments using acetate and molasses rapidly established strong reducing conditions and complete removal of Cr(VI). The removal of Cr(VI) is attributed to direct reduction of Cr(VI) by microbes and indirect reduction by substrates, such as ferrous iron and sulfide compounds, resulting from microbial anaerobic respiration. Molasses was selected as the preferred biostimulant because laboratory experiments indicated molasses treatments are much more effective at inducing longer-lasting reducing conditions that are conducive to Cr(VI) reduction.

Figure 1.0-4 shows the results of a column experiment using a 3.4 g/L molasses treatment with Miocene Pumiceous sediments. The plot shows the breakthrough profile of Cr(VI) along with the breakthrough of tritium used as conservative tracer during the injection of the molasses pulse. The profile of pH over time is also shown. The data show that Cr(VI) was completely removed from the column effluents as soon as the molasses solution was injected. This effect is attributed to the reduction of Cr(VI) chemically by molasses and the rapid establishment of anaerobic reducing conditions conducive to Cr(III) precipitation. The pH dropped to about 5.5 during the molasses injection because the microbes transform the sugar compounds to organic acids that are further degraded to smaller organic substrates. The pH rebounded to neutral after molasses exited the column. The Cr(VI) reduction capacity measured under the experimental conditions was 15 pore volumes. Reinjection of molasses rapidly restored Cr(VI) reduction. The reduction capacity induced was very similar to the capacity induced during the initial treatment. This capacity might be larger or lower when biostimulation is induced in situ in the field. Induced reduction capacity will depend on the water chemistry, including the availability of oxygen, nitrate, and the presence of other redox active substrates. No clogging was observed in the column at any time during the experiment based on no observable reduction in the flow rate produced by the syringe pump feeding the column, which is sensitive to back pressure.

2.0 RATIONALE FOR SELECTION OF LOCATIONS FOR TESTING

A phased approach is proposed for the pilot testing. During phase one, two tests are proposed: a chemical amendment at R-42 and a biostimulant amendment at R-28. Information obtained from these tests will be used to select the amendment approach for a cross-hole test between CrPZ-1 and CrEX-2 (Figure 1.0-1). The cross-hole test location is expected to provide even better information on aquifer

characteristics and potential treatability than either of the single-well test locations. The goal is to optimize the study design based on information from the two test sites and apply it at the cross-hole location.

2.1 Sodium Dithionite at R-42

The R-42 location is selected for the sodium dithionite deployment because it has the highest Cr(VI) concentrations observed in the plume (currently around 700 µg/L), and therefore it offers the opportunity to evaluate Cr(VI) reduction capacity more quickly than at other locations. Additionally, hydraulic responses to pumping from nearby extraction wells CrEX-1 and CrEX-3 indicate that the R-42 location is somewhat hydrologically isolated from nearby pumping and injection activities that will occur in 2017. This relative hydraulic isolation means the movement of water in R-42 as a result of pumping at the extraction wells (CrEX-1, CrEX-2, and CrEX-3) should be minimal, and the planned continuous pumping at R-42 will thus dominate the local groundwater gradient. Furthermore, push-pull and dilution tracer tests conducted in 2014 indicated that groundwater flow velocities at R-42 are relatively slow (on the order of 0.1 m/d), which favors a push-pull test because it makes the test results less dependent on the natural flow velocity in the aquifer, allowing more straightforward, less uncertain test interpretations. The low natural flow velocity also makes it much easier to recover injected fluids for evaluation of any adverse geochemical effects of the dithionite treatment, and it further helps minimize the volume of water that will contain elevated concentrations of any problem constituents. In the 2014 push-pull test, it was demonstrated that >90% of the introduced tracer was recovered from R-42 after an 11-d drift period (the time after tracer injection and before pumping), so any adverse effects (e.g., generation of a transient elevated sulfate pulse or other undesirable reaction products) should be captured through pumping after the planned 2-d drift period (see below).

2.2 Molasses at R-28

The R-28 location is selected for the molasses bioamendment because it also has relatively high Cr(VI) concentrations (currently around 480 µg/L), and it has a very high natural groundwater flow velocity (estimated to be approximately 1 m/d), which makes the location amenable to a “push-drift” test in which R-28 is only passively sampled after the injection of the molasses. The test design for the R-28 location is greatly aided by the results of passive monitoring that was conducted after a tracer injection in R-28 in 2016. That tracer deployment used a total volume of approximately 15,000 gal. of tracer solution plus 15,000 gal. of chase solution (potable water was used for both), which is approximately the total volume being proposed for the molasses injection (~31,000 gal.). Figure 2.2-1 shows the responses of major anions and Cr(VI), respectively, in R-28 as a function of time after the 2016 tracer injection under what should be essentially the same flow and pumping conditions as in the pilot molasses test (CrEX-3 was pumping during the first 6 wk of the 2016 tracer test). Having this information makes it possible to know when Cr(VI) levels should return to pre-test concentrations if the water injected into R-28 contained no molasses. Therefore, the effects of the molasses treatment on Cr(VI) breakthrough can be inferred from the difference in the observed behavior of Cr(VI) relative to that of Figure 2.2-1. Furthermore, the breakthrough of the bromide tracer (planned for pilot tests at both R-28 and R-42) will help to identify any differences in hydrologic conditions relative to the 2016 tracer test, which will be important for test interpretation. The previous tracer test also provides information on how long the molasses solution is expected to remain upgradient of R-28 to provide biostimulation of the aquifer. By design, the test will interrogate only processes occurring upgradient of R-28 because processes occurring downgradient or at oblique angles to the gradient can be interrogated only by drawing water into the well by pumping.

3.0 TEST METHODOLOGY

3.1 Sodium Dithionite at R-42

3.1.1 Deployment

A push-pull approach will be used at well R-42. The test will involve injecting an estimated 9000 gal. of a sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) solution containing approximately ~ 0.05 mol/L (300 kg) dithionite in untreated R-42 water buffered to approximately pH 7.0 using 250 kg of sodium sulfite (Na_2SO_3). Laboratory tests have shown that keeping the pH buffered to neutral or alkaline conditions stabilizes the dithionite, and the sulfite also serves as an additional form of reduced sulfur to help to establish reducing conditions. Buffering with a sodium bicarbonate/carbonate mixture also stabilizes dithionite, but sodium sulfite is preferred as a buffer because it will maintain low alkalinity in the dithionite solution and thus avoid calcite precipitation in the groundwater, which is naturally saturated with respect to calcite. Five kilograms of sodium bromide (NaBr) will be added to the injection solution to introduce bromide to serve as a conservative tracer. Monitoring the bromide and breakdown products of the dithionite will provide a basis for estimating the volume of aquifer that the dithionite affected relative to the volume seen by the tracer during the deployment. A preinjection sample will be collected to characterize the groundwater chemistry at the well immediately before dithionite is deployed in the well.

The sodium dithionite solution will be deployed in the well as rapidly as possible with the goal of not exceeding a 100-ft water level rise in the well. Previous tracer injection rates in R-42 were approximately 15 gallons per minute (gpm) with a 10–12 ft water-level rise in the well. The pump will be removed and the dithionite solution will be deployed via nonmetallic tremie that will terminate below the water level in the well but above the screened interval. This configuration will ensure that the dithionite solution is minimally exposed to air, thus minimizing the potential for degradation before it enters the aquifer. Because the dithionite solution will be slightly denser than water, the tremie configuration will also allow the dithionite solution to sink into the well screen and naturally find preferential hydrostratigraphic pathways. After the sodium dithionite solution is injected, approximately 1000–1500 gal. of potable water (without dithionite or bromide tracer) will be introduced to R-42 as “chase” water to flush the dithionite solution out of the well and filter pack. Potable water will be used for the chase water because it has no Cr(VI) other than naturally occurring concentrations.

The injected solution will be allowed to sit in the aquifer for 2 d before continuous pumping at R-42 begins. The continuous pumping rate is yet to be determined but is expected to be between 3 and 8 gpm, depending on the pump used. Continuous, extended pumping will occur to facilitate breakthrough of chromium and related redox sensitive constituents (e.g., nitrate). Because water generated from continuous pumping will need to be dispositioned via land application, continuous pumping will not be conducted for the period when land application under the Laboratory’s Discharge Permit (DP-1793) is not allowed because of frozen ground conditions, nominally between December and approximately the end of March. At 3 gpm, the lowest expected pumping rate, the equivalent of 1 injection volume (approximately 10,000 gal.) of dithionite solution plus chase water will be extracted from the well approximately every 2.3 d. During the first several days of pumping, elevated concentrations of both sodium and sulfate are expected because these are the two primary breakdown products of sodium dithionite. Additionally, elevated concentrations of sulfite can be expected as well as elevated concentrations of iron and manganese that will be liberated as reduced species from aquifer sediments. Naturally occurring arsenic may be also liberated. Reduced iron, manganese, or arsenic will reoxidize when they encounter the naturally high dissolved oxygen content (6–7 mg/L) in groundwater outside the treated zone. The pulse of sodium and sulfate generated through breakdown of the dithionite will be largely removed during the continuous pumping at R-42 during the first 2 wk of continuous pumping.

3.1.2 Sampling Program

Samples will be collected during the pumping phase to analyze for the bromide tracer, iron, manganese, Cr(VI), nitrate, sulfate, pH, alkalinity, and various trace metals such as arsenic, selenium, and uranium. Although these are the species of greatest interest, the analyses will be conducted for a full suite of cations and anions. Upon initiation of pumping at R-42, sampling will be conducted at least twice daily for the first 2 wk. Field parameters will also be collected and measured through a flow-through cell. The frequency of sampling may then be adjusted according to the results of the initial 2 wk of data and in consultation with the New Mexico Environment Department (NMED). On-site field instrumentation will be used to attempt to measure reduced sulfur species, including dithionite, in real time. Real-time field data may also be collected periodically using HACH kits for iron, manganese, sulfide, and sulfate to guide the sampling program. The concentration histories of these species relative to the bromide tracer will provide key information on the aquifer volume that was effectively treated by the dithionite injection. Note that many samples will also be collected of batches of injection solution and analyzed for dithionite and bromide, as well as major ions.

Hydraulic testing will be conducted in R-42 after breakthrough occurs to characterize potential changes in hydraulic conditions within the treatment zone.

3.2 Molasses at R-28

3.2.1 Deployment

A push-drift test is planned for the molasses deployment at R-28. Before the molasses is injected, the existing pump in R-28 will be pulled and the well will be redeveloped to remove any biofilm present in the lower portion of the screen. Biofilm has historically been observed in video logs run in R-28. Redevelopment will involve swabbing, surging, bailing, and pumping to remove as much of the existing biofilm as possible. The pump will then be removed to allow injection of molasses via a tremie set downhole below the water level in the well and above the screen. As with the dithionite, the tremie configuration will allow the molasses solution to sink into the well screen and naturally find preferential hydrostratigraphic pathways. A preinjection sample will be collected to characterize the groundwater chemistry at the well immediately before molasses is deployed in the well.

Approximately 48,000 lb of a 20% molasses solution will be mixed into approximately 25,000 gal. of untreated R-28 water, and the resulting approximately 30,000 gal. of diluted molasses solution will be injected into R-28. The injection solution is expected to be approximately 38.4 g/L molasses. Ten kilograms of NaBr will also be added to the injection solution, with the bromide serving as a conservative tracer. The intent is to complete the entire injection in 1 d, which should be feasible because of the high flow capacity of this well. During the 2016 tracer injection, 30,000 gal. of water was injected in a single 8-h shift, an average of over 60 gpm.

Molasses injection will be followed immediately by approximately 1000–1500 gal. of potable chase water mixed with approximately 150 gal. of 95% denatured ethanol to briefly sterilize the well and surrounding filter pack and aquifer. The ethanol solution will rapidly drift out of the filter pack, and microbial growth will eventually be stimulated in the well as molasses and native microbes drift back in, but the ethanol treatment should suppress rapid growth of residual biofilms that are not removed by the well redevelopment procedure described above. The ethanol is not expected to play a significant role in observable biogeochemical changes because it will rapidly drift downgradient of R-28, and most of its biostimulation effects will therefore not be observable. Potable water will be used for the chase water because it has no Cr(VI) other than naturally occurring concentrations. The pump will be reinstalled immediately after the molasses and chase-water injection and set low in the sump and pumped to remove

any molasses solution that may have settled into the sump. The pump will then be raised to a position approximately mid-screen and set up for frequent sampling at the well-head using a circulation loop.

3.2.1 Sampling Program

R-28 will be monitored for bromide tracer, iron, manganese, Cr(VI), nitrate, sulfate, pH, alkalinity, and various trace metals such as arsenic, selenium, and uranium (same as with the dithionite test) with the addition of total organic carbon. The microbial density in groundwater will be also be monitored, although it will be used only qualitatively because the majority of the biomass growth is expected to remain fixed on sediments. Sampling will begin immediately following reinstallation of the sampling pump and circulation system. Sampling will be conducted twice daily for at least the first 2 wk. Field parameters will also be collected and measured through a flow-through cell. The frequency of sampling may then be adjusted according to the results of the initial 2 wk of sampling and in consultation with NMED. The volume water in the circulation loop will be removed before each sample is collected. Note that many samples will also be collected of batches of injection solution and analyzed for molasses (via total organic carbon) and bromide as well as major ions.

The concentration histories of these species relative to the bromide tracer will provide key information on the aquifer volume that was effectively treated by the molasses injection. The circulation loop will not be run continuously because this will raise the temperature in the well and potentially induce biofouling as the molasses solution (organic carbon) drifts back through the well under natural flow conditions (with some flow also presumably induced by the pumping of CrEX-3 nearby). Based on the results of the 2016 tracer test, the portion of 30,000-gal. solution that is pushed upgradient can be expected to pass through R-28 wellbore by natural flow within about 2 mo, with the concentrations of either molasses or its reaction products (or both) remaining high for about 1 mo and then steadily declining for the next month until background levels are reached (Figure 3.2-1). Depending on what is observed during the passive monitoring of R-28, a decision may be made to conduct continuous pumping to induce breakthrough of Cr(VI) into the well.

Hydraulic testing will be conducted in R-42 after breakthrough occurs to characterize potential changes in hydraulic conditions within the treatment zone.

4.0 KEY MONITORING INDICATIONS

Monitoring at both R-42 and R-28 will mainly address the Cr(VI) reduction capacity induced by the treatments and the generation of byproducts that could have potential adverse effects (including biofouling at R-28). Based on laboratory experiments, it is expected that the reduction capacity induced by the dithionite treatment at R-42 could approach or exceed 100 pore volumes, which would mean that as much as 1,000,000 gal. may have to be pumped from R-42 before significant Cr(VI) breakthrough occurs (i.e., 100 times the amendment volume of 10,000 gal.). At a pumping rate of 3 gpm, it would take about 230 d for Cr(VI) breakthrough, and at 8 gpm, it would take about 86 d. However, these estimates are considered to be upper limits for reduction capacity because the sediments in laboratory experiments were likely much more efficiently reduced by dithionite than they will be in the aquifer. Also, non-ideal flow effects from differences in vertical flow distribution within the well during dithionite injection relative to flow distribution during pumping (for instance, from density-driven flow of the concentrated dithionite solution) could result in earlier breakthrough of Cr(VI). The return concentrations of the bromide tracer will help to evaluate the effectiveness of the dithionite treatment if this occurs (the bromide response can be used to account for the effects of non-ideal flow). Also, slower than anticipated kinetic effects could potentially result in earlier than expected breakthrough of Cr(VI) [i.e., Cr(VI) could move through the treated zone too quickly to be entirely reduced]. Potential kinetic effects can be evaluated by interrupting the pumping of

R-42 to increase residence times in the treatment zone or possibly by changing (lowering) the R-42 pumping rate. The effective volume of aquifer treated by the dithionite relative to the total volume of dithionite solution injected will be estimated by comparing the responses of the bromide tracer with key dithionite reaction byproducts, including dissolved iron and manganese, as well as various sulfur species that are reaction products of dithionite consumption. It is anticipated that the vast majority of groundwater with elevated total dissolved solids (TDS) and byproduct concentrations will be pumped from R-42 within approximately the first 30,000 gal. of pumping. In column experiments, the high-TDS water transports effectively conservatively, and significantly elevated concentrations of byproducts do not linger more than a few pore volumes.

At R-28, monitoring will include measurements of total organic carbon concentrations (as an indication of molasses concentrations) in addition to measurements of Cr(VI), nitrate, dissolved iron and manganese, and sulfate/sulfide. These measurements will provide information on the bioconsumption rate of the molasses and the establishment of reducing geochemical conditions that should be conducive to Cr(VI) reduction. It is not anticipated that any geochemical signature of the amendment deployment will be observed at CrEX-3 because the tracers injected into R-28 in 2016 were not detected in CrEX-3 during the 6 wk that CrEX-3 pumped after the tracer deployment. Based on the results of laboratory experiments, it is expected that Cr(VI) will not appear in the passively monitored R-28 for at least 1 yr, although as in the case of the dithionite deployment at R-42, the largest uncertainty associated with this prediction is how uniformly the molasses is distributed hydrologically during the deployment (with the main concern being density-driven flow effects).

As at R-42, the response of the bromide tracer will help separate out any effects of non-ideal flow during the deployment. A delayed disappearance of the bromide tracer relative to the observed disappearance of tracers after the 2016 tracer injection may indicate biofouling of the aquifer and well. Such a delay would suggest that flow rates through the aquifer in the vicinity of R-28 have decreased relative to that observed during the 2016 tracer test. If the appearance of Cr(VI) takes more than a year, pumping of R-28 may be considered. The treated aquifer volume is expected to be essentially equal to the 30,000-gal. injection volume of the bioamendment solution divided by effective porosity because laboratory data suggest molasses transports almost conservatively and its bioconsumption is delayed by a few days, so it should go where the bromide tracer goes during the deployment. Monitoring of the bromide tracer, molasses, and various biogeochemical reaction products will verify this expectation.

At both R-42 and R-28, once initial breakthrough of Cr(VI) occurs, selected samples may be analyzed for chromium isotopes ($^{53}\text{Cr}/^{52}\text{Cr}$) to determine if Cr(VI) is being partially reduced as it moves through the treatment zone as indicated by enrichment in the heavier chromium isotope relative to well-established ratios for the regional aquifer elsewhere in the chromium plume.

5.0 REPORTING

A quarterly summary report is proposed for the pilot-scale testing. Reports would include monitoring data from each location and interpretation of the results collected over the period of record before each report. The goal is to deploy each of the amendments described in this work plan by September 15, 2017. The first report will be submitted to NMED by January 30, 2018, and quarterly, thereafter. A recommendation to terminate summary reports would be included in a summary report at a time that chromium breakthrough defined by approximately 50% of the chromium concentration at each well before introduction of the amendment. Additional considerations regarding the disposition of pumped water will need to be addressed when contaminant concentrations greater than land-application limits (e.g., 45 $\mu\text{g}/\text{L}$ for chromium) are produced at the wellhead. The cross-hole test between CrPZ-1 and CrEX-2 using a

preferred amendment and a refined deployment plan will be proposed when sufficient information is available to support a work plan for the cross-hole amendments test.

6.0 WASTE MANAGEMENT

All investigation-derived waste (IDW) generated during the pilot-scale amendments testing will be managed in accordance with EP-DIR-SOP-10021, "Characterization and Management of Environmental Programs Waste." This procedure incorporates the requirements of all applicable U.S. Environmental Protection Agency and NMED regulations, U.S. Department of Energy orders, and Laboratory implementation requirements, policies, and/or procedures. IDW will also be managed in accordance with the approved waste characterization strategy form for well rehabilitation.

7.0 REFERENCES AND MAP DATA SOURCES

7.1 References

The following reference list includes documents cited in this plan. 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.

DOE (U.S. Department of Energy), March 2012. "Hanford Site Third CERCLA Five-Year Review Report," DOE/RL-2011-56, Rev. 1, Richland, Washington. (DOE 2012, 602481)

ESTCP (Environmental Security Technology Certification Program), February 2010. "Final Report Loading Rates and Impacts of Substrate Delivery for Enhanced Anaerobic Bioremediation," U.S. Department of Defense Environmental Security Technology Certification Program, Project No. ER-0627, Arlington, Virginia. (ESTCP 2010, 602491)

Evanko, C.R., and D.A. Dzombak, October 1997. "Remediation of Metals-Contaminated Soils and Groundwater," Technology Evaluation Report TE-97-01, document prepared for Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvania. (Evanko and Dzombak 1997, 102743)

Fruchter, J.S., C.R. Cole, M.D. Williams, V.R. Vermeul, J.E. Amonette, J.E. Szecsody, J.D. Istok, and M.D. Humphrey, "Creation of a Subsurface Permeable Treatment Zone for Aqueous Chromate Contamination Using In-situ Redox Manipulation," *Groundwater Monitoring and Remediation*, Vol. 20, No. 2, pp. 66-77. (Fruchter et al. 2000, 602475)

Hawley, E.L., R.A. Deeb, M.C. Kavanaugh, and J.A. Jacobs, 2005. "Treatment Technologies for Chromium(VI)," Chapter 8 from *Chromium(VI) Handbook*, CRC Press, Inc., Boca Raton, Florida. (Hawley, et al. 2005, 602490)

LANL (Los Alamos National Laboratory), July 2015. "Work Plan for Chromium Plume Center Characterization," Los Alamos National Laboratory document LA-UR-15-24861, Los Alamos, New Mexico. (LANL 2015, 600615)

NMED (New Mexico Environment Department), October 15, 2015. "Approval with Modifications, Work Plan for Chromium Plume Center Characterization," New Mexico Environment Department letter to D. Hintze (DOE-NA-LA) and M. Brandt (LANL) from J.E. Kieling (NMED-HWB), Santa Fe, New Mexico. (NMED 2015, 600958)

Stanin, F.T., 2005. "The Transport and Fate of Chromium(VI) in the Environment," Chapter 5 from *Chromium(VI) Handbook*, CRC Press, Inc., Boca Raton, Florida. (Stanin 2005, 602489)

Varadharajan, C., H.R. Beller, M. Bill, E.L. Brodie, M.E. Conrad, R. Han, C. Irwin, J.T. Larsen, H.-C. Lim, S. Molins, C.I. Steefel, A. van Hise, L. Yang, and P.S. Nico, April 2017. "Reoxidation of Chromium(III) Products Formed under Different Biogeochemical Regimes," *Environmental Science & Technology*, Vol. 51, pp. 4918-4927. (Varadharajan et al. 2017, 602477)

Vermeul, V.R., J.E. Szecsody, M.J. Truex, C.A. Burns, D.C. Girvin, J.L. Phillips, B.J. Devary, A.E. Fischer, and S.-M.W. Li, October 1994. "Treatability Study of In Situ Technologies for Remediation of Hexavalent Chromium in Groundwater at the Puchack Well Field Superfund Site, New Jersey," Pacific Northwest Laboratory Report PNL-16194, Richland, Washington. (Vermeul et al. 2006, 602478)

7.2 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

Drainage channel; Los Alamos National Laboratory, ER-ES, As published, GIS projects folder; \\slip\gis\GIS\Projects\11-Projects\11-0108\gdb\gdb_11-0108_generic.mdb; drainage; 2017

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

Paved Parking; Los Alamos National Laboratory, KSL Site Support Services, Planning, Locating and Mapping Section; 12 August 2002; as published 29 November 2010

Unpaved road; 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_road; 2017

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

LANL Areas Used and Occupied; Los Alamos National Laboratory, Site Planning & Project Initiation Group, Infrastructure Planning Office; 19 September 2007; as published 13 August 2010

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

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

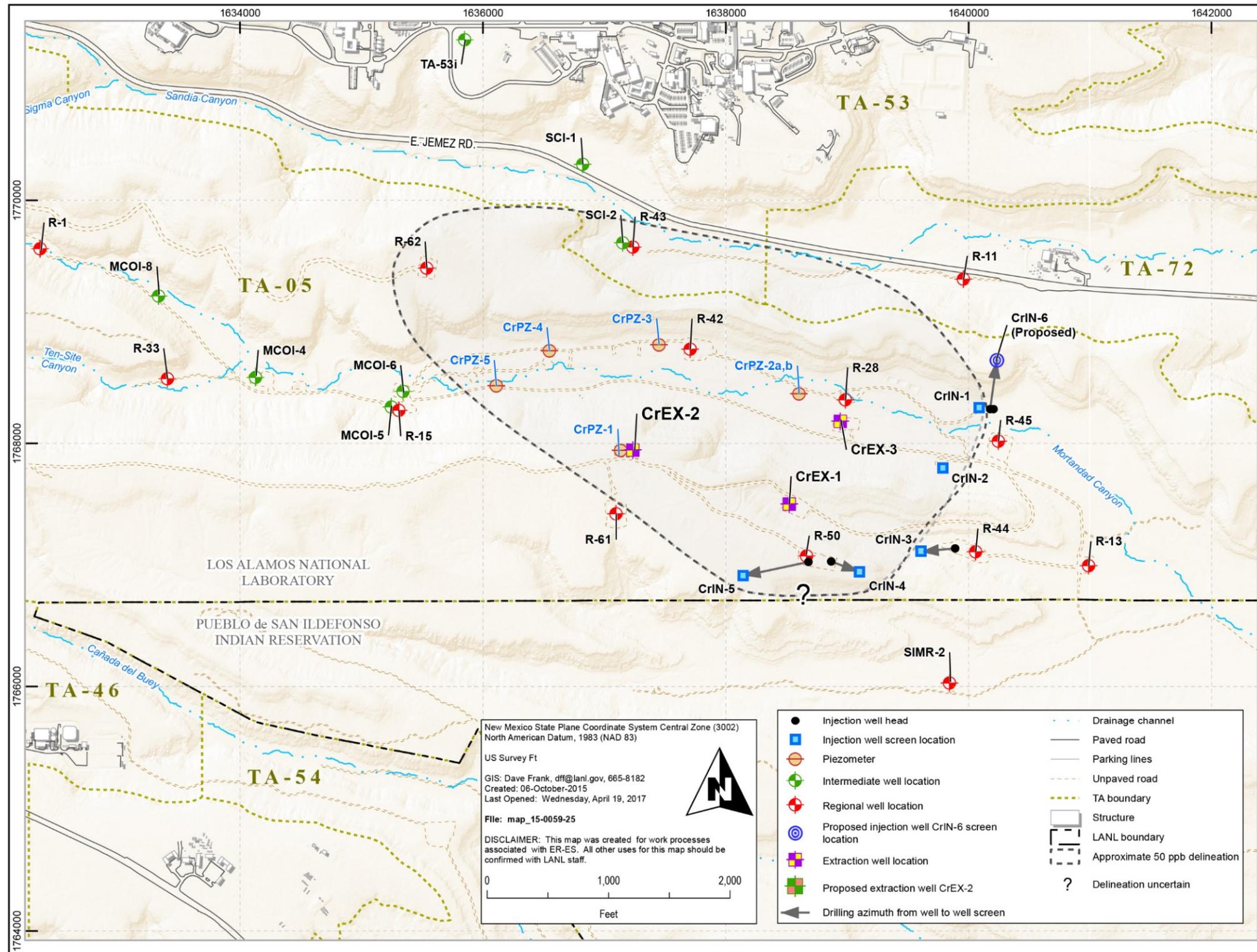


Figure 1.0-1 Injection, extraction, and monitoring wells in the area of the chromium plume

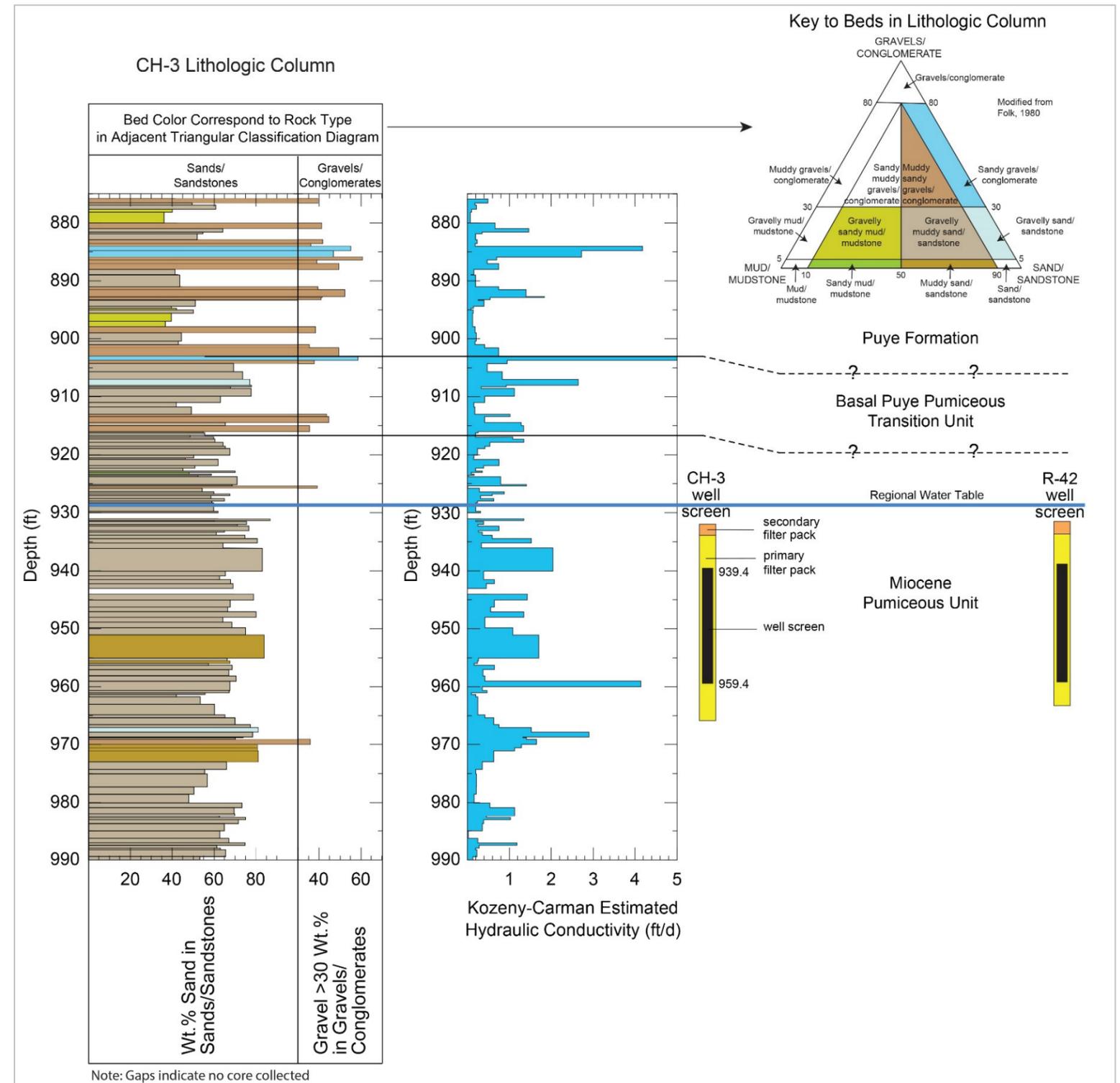


Figure 1.0-2a Lithologic column for corehole 3 (CH-3) showing rock types for individual beds making up strata in the upper part of the regional aquifer. The relative position of the R-42 well screen is included for reference.

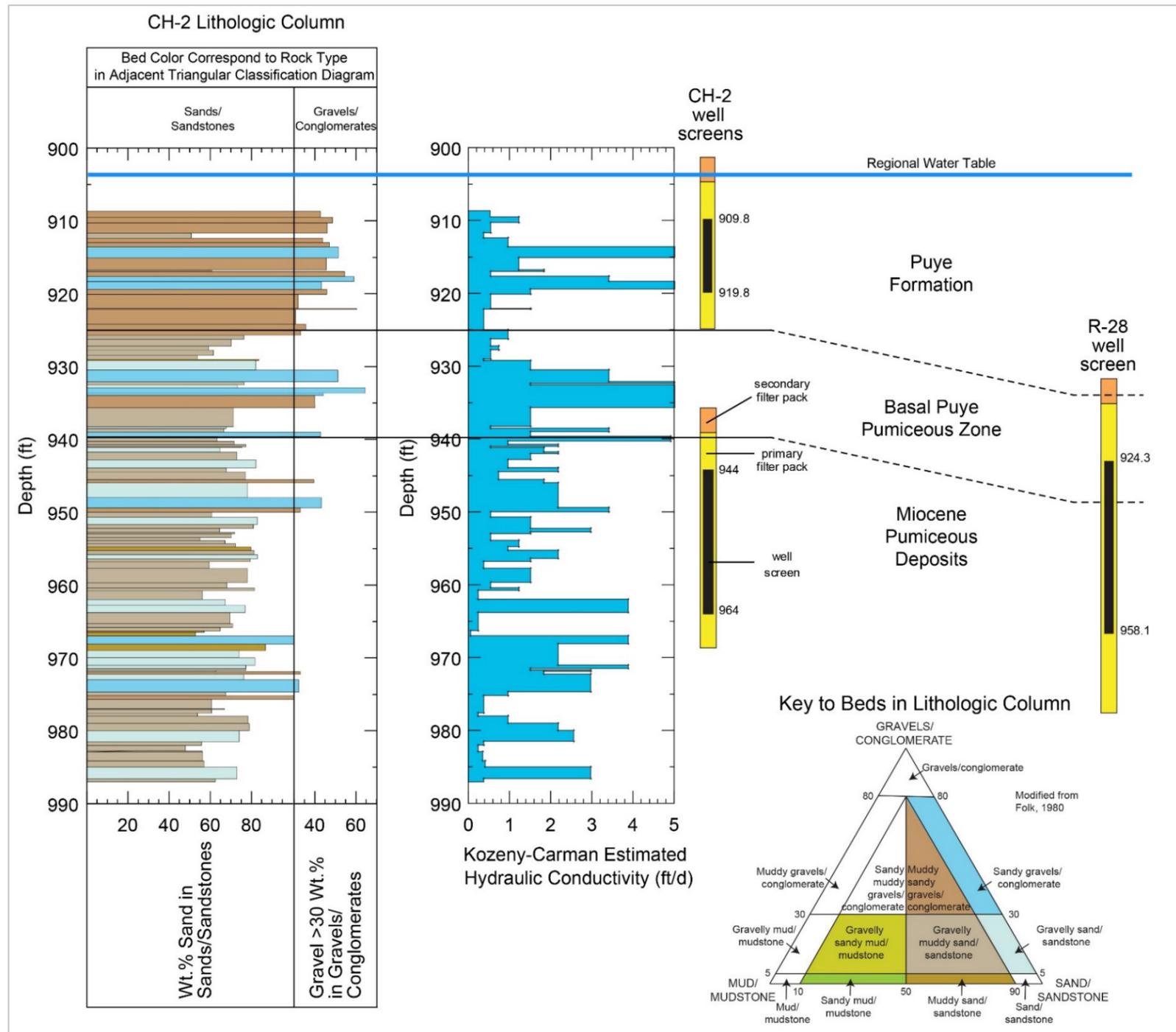


Figure 1.0-2b Lithologic column for corehole 2 (CH-2) showing rock types for individual beds making up strata in the upper part of the regional aquifer. The relative position of the R-28 well screen is included for reference.

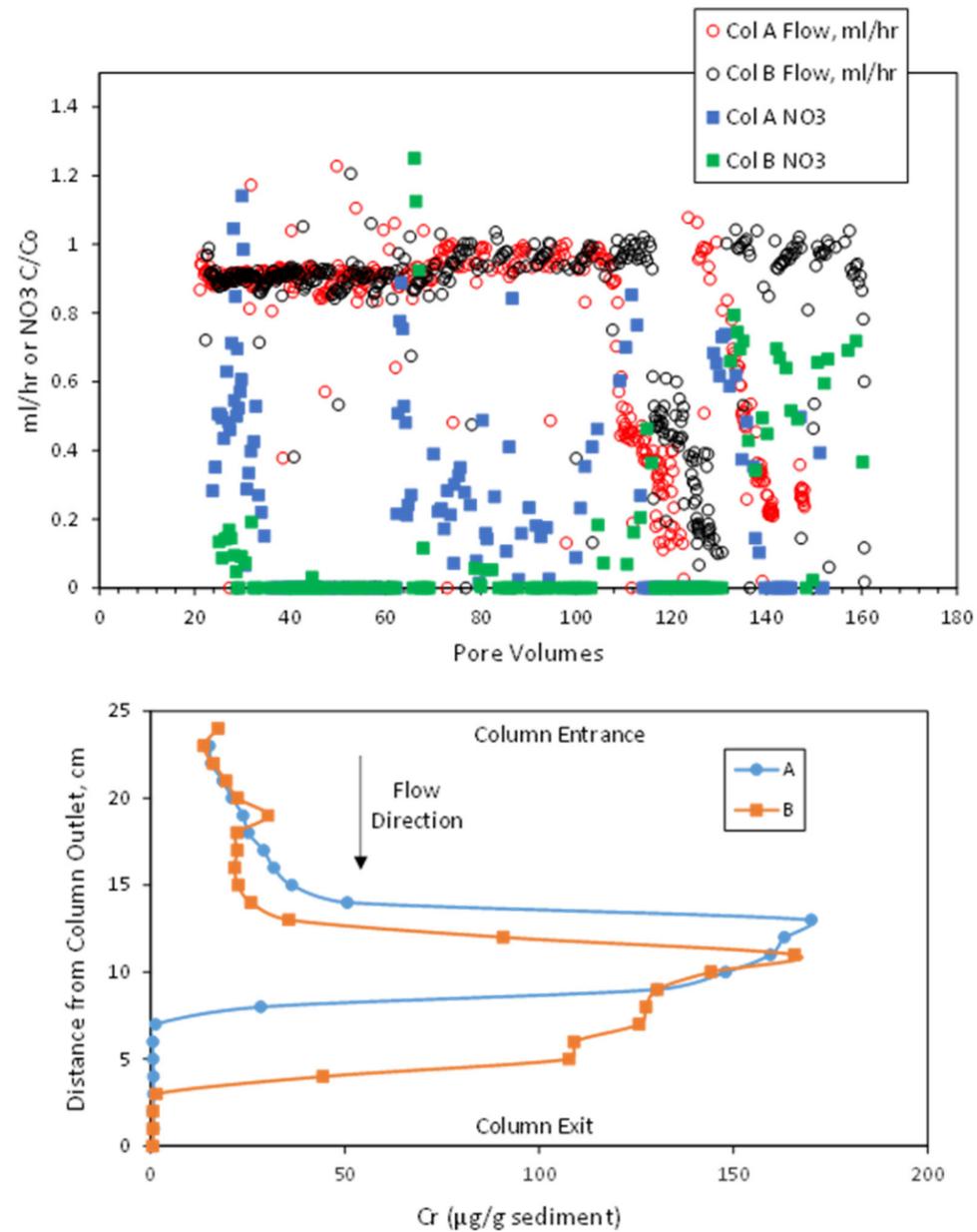


Figure 1.0-3 Results from duplicate column experiments passing untreated R-42 water through Miocene Pumiceous sediments treated with an excess of sodium dithionite. Upper plot shows flow rates and normalized concentrations (C/C_0 , where C is measured concentration and C_0 is injected concentration) of nitrate as a function of pore volumes eluted through each column. Cr(VI) never appeared above detection limits in the outlet flow from either column. Column pore volumes were approximately 17 and 18 mL respectively, resulting in mean residence times of 18–20 h at the average flow rates of 0.9–0.95 mL/h, and the porosity of both columns was about 0.59. Note the sporadic appearance and disappearance of NO_3^- , which possibly reflects different levels of oxygen in each batch of water injected. However, lower flow rates also seem to result in generally lower nitrate concentrations, which may indicate a rate-limited nitrate-reduction process. The lower plot shows the profile of chromium concentrations in the sediments of one of the columns. The chromium mass calculated to be in the column at the end of the experiment was greater than 80% of the estimated mass injected, which is probably within the error of the measurements. It may also indicate that a fraction of the reduced chromium was not leached by the 2 molar nitric acid. Some sediment mass was lost during sediment recovery from the columns, so an incomplete mass recovery was expected.

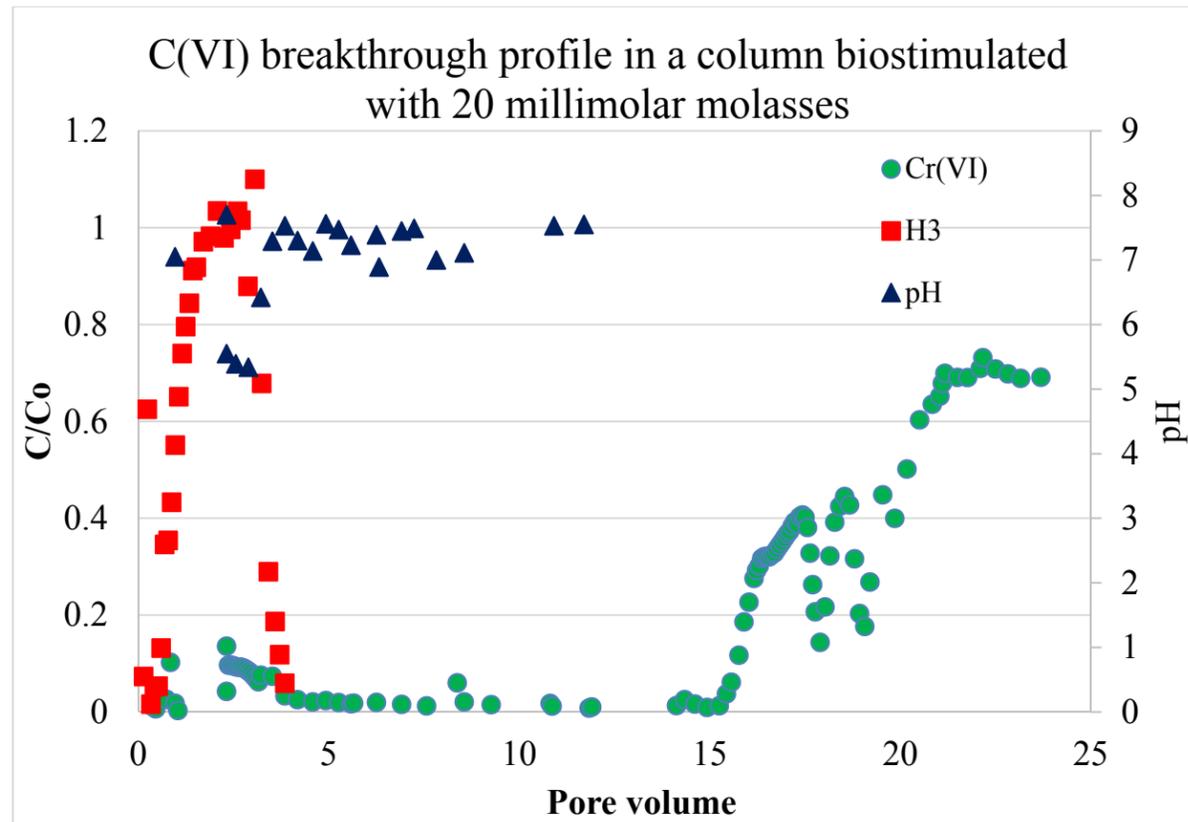


Figure 1.0-4 Breakthrough profiles of Cr(VI) and tritium (both expressed as C/C₀) in a column filled with SCI-2 sediments and biostimulated with 3.4 g/L molasses, injected only while the tritium was injected (about 2.3 pore volumes). Untreated R-42 water containing 950 µg/L at pH of 7.5 was continually injected through the column at an average flow rate of 1.8 mL/h. The pore volume of the column was 82.4 mL, resulting in a mean column residence time of about 47 h. The pH dropped to about 5.5 at the end of the molasses pulse but rebounded to 7.5 very rapidly. Nitrate was also reduced during the initial 15 pore volumes. The tritium pulse shown in red squares represents the breakthrough of a conservative tracer, and later experiments showed that it also approximates the breakthrough behavior of molasses. Total organic carbon concentrations (a proxy for molasses) were not measured in this experiment because of the presence of tritium in the samples.

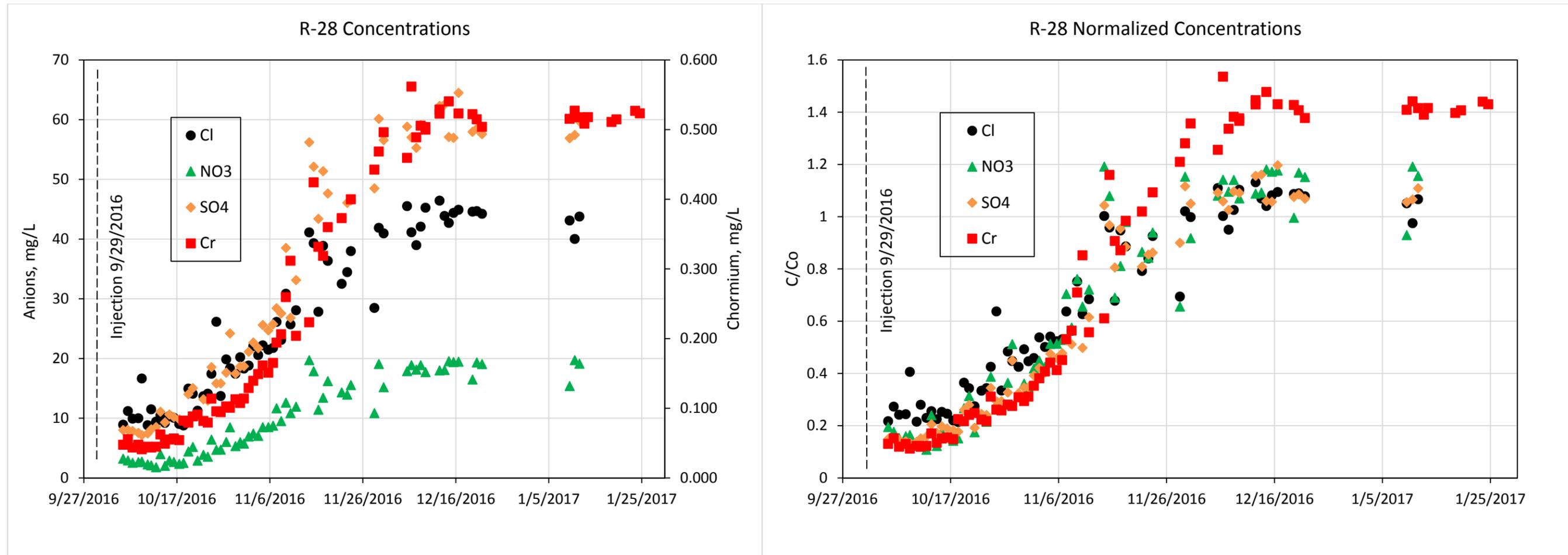


Figure 2.2-1 Trends for four constituents at monitoring well R-28 following injection of 30,000 gal. of potable water on September 29, 2016 (T = 0). Left panel shows the trends in concentrations; right panel shows the trends normalized to the concentrations present in the well before injection of potable water. Concentrations of chromium increased to levels above the T = 0 concentrations as tracer and chase water drifted away from the well. Increases over the T = 0 concentrations shown as C/Co values greater than 1 may be from pumping at nearby CrEX-3 or CrEX-1.

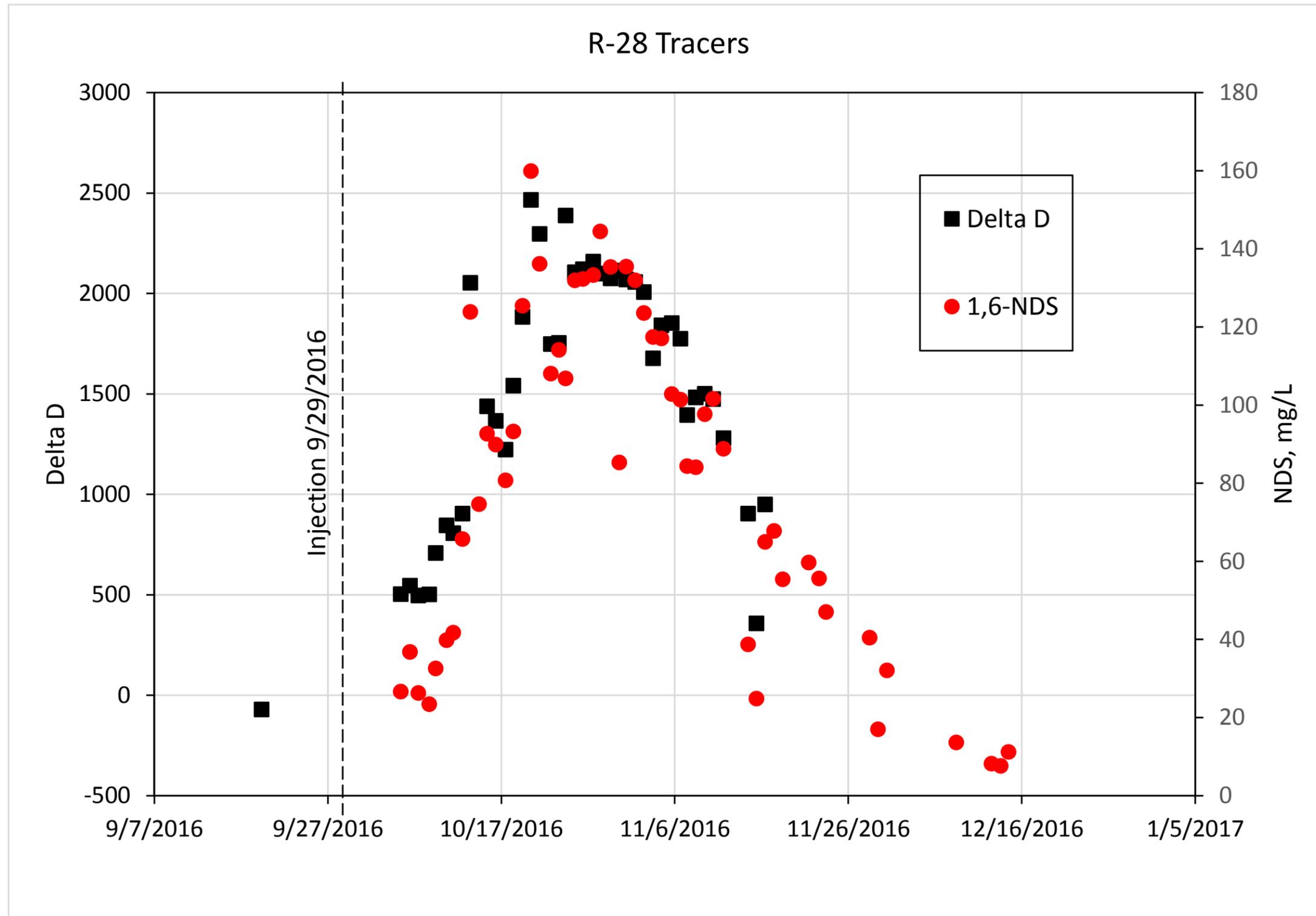


Figure 3.2-1 Breakthrough curves for deuterium and sulfonate tracers in R-28. Molasses concentrations would be expected to remain high during the time the tracer concentrations were increasing and then to decline at approximately the same time and rate as the decline in tracer concentrations.

