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Date: APR 30 2013
Refer To: EP2013-0073

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

APR 2013

Subject: Submittal of the Interim Measures Work Plan for the Evaluation of Chromium Mass Removal

Dear Mr. Kieling:

Enclosed please find two hard copies with electronic files of the Interim Measures Work Plan for the Evaluation of Chromium Mass Removal.

This interim measures work plan (IMWP) was prepared in response to the requirements in a letter from the New Mexico Environment Department, dated January 25, 2013, directing Los Alamos National Laboratory to assess the potential for active long-term removal of chromium from the regional aquifer via pumping with a pilot extraction test well. The results of the assessment are presented in this IMWP.

If you have any questions, please contact John Bennett at (505) 606-1768 (jbennett@lanl.gov) or Cheryl Rodriguez at (505) 665-5330 (cheryl.rodriguez@nnsa.doe.gov).

Sincerely,

Daniel R Cox for JM

Jeff Mousseau, Associate Director
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Sincerely,

for PM

Peter Maggiore, Assistant Manager
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35819

JM/PM/DM/JB:vt

Enclosures: Two hard copies with electronic files – Interim Measures Work Plan for the Evaluation of Chromium Mass Removal (LA-UR-13-22534)

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LA-UR-13-22534
April 2013
EP2013-0073

Interim Measures Work Plan for the Evaluation of Chromium Mass Removal

Los Alamos
NATIONAL LABORATORY
EST. 1943

Prepared by the Environmental Programs Directorate

EP2013-0073

Interim Measures Work Plan for the Evaluation of Chromium Mass Removal

April 2013

Responsible project manager:

John Bennett		Project Manager	Environmental Programs	4/24/13
Printed Name	Signature	Title	Organization	Date

Responsible LANS representative:

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Figures

1.0 INTRODUCTION

This interim measures work plan (IMWP) describes proposed activities to address chromium contamination in groundwater beneath Los Alamos National Laboratory (LANL or the Laboratory). The Laboratory proposes to conduct interim measures in accordance with Section VII.B.1 of the March 1, 2005, Compliance Order on Consent (the Consent Order). The IMWP is being prepared in response to requirements in a letter from the New Mexico Environment Department (NMED), dated January 25, 2013 (NMED 2013, 521862), which directed that the IMWP assess the potential for active long-term removal of chromium from the regional aquifer via pumping with a pilot extraction test well. This IWMP describes the work that will be conducted to determine whether a pilot extraction well can achieve active long-term chromium removal from the regional aquifer; further, it describes additional work to support the overall approach to remediation of chromium contamination. The results of the first portion of the work conducted under this IMWP will be included in a supplemental IMWP (SIMWP) that will describe additional interim measures activities that may include the installation of a pilot pumping well to evaluate chromium mass removal from the regional aquifer. Additional details are discussed in section 2.3, and a proposed schedule is discussed in section 3.0.

Investigations related to chromium contamination are summarized in a number of reports, including the Investigation Report for Sandia Canyon (LANL 2009, 107453) and the Phase II Investigation Report for Sandia Canyon (LANL 2012, 228624). These investigations have identified the probable Cr(VI) source was cooling tower effluent released near the head of Sandia Canyon between 1956 and 1972. Chromium was transported down the canyon in surface-water flow. Chromium is present in the Sandia Canyon wetland and sediments; it is also present in the subsurface in the vadose zone (including in perched-intermediate groundwater) and in the regional aquifer beneath Sandia and Mortandad Canyons. Figure 1.0-1 illustrates the transport paths taken by chromium from the surface to the regional aquifer, an estimated initial source volume of Cr(VI), the estimated present-day distribution of both Cr(III) and Cr(VI) along the pathway, and the extent of the Cr(VI) plume (>50 ppb) within the regional aquifer beneath Sandia and Mortandad Canyons. Much of the initial Cr(VI) released has been reduced to less mobile and less toxic Cr(III) in wetland sediments and by iron Fe(II)-bearing minerals within sediment and rocks as water has encountered these media.

Figure 1.0-2 shows the extent of the Cr(VI) plume within the regional aquifer. Chromium(VI) concentrations are highest at regional wells R-28 and R-42. Chromium concentrations at these wells have varied by as much as 25% across multiple quarterly sampling rounds but overall are relatively stable over the period of record for these wells. At the distal portions of the plume, particularly at regional wells R-43 and R-50, recent groundwater data indicate increasing chromium concentrations over the last several sampling rounds. These wells do not have the same period of record as R-28 and R-42, and therefore, the longer-term trends are not known.

2.0 OBJECTIVES AND APPROACH

The activities proposed under this IMWP focus on evaluating the potential for mass removal within the regional aquifer beneath Mortandad Canyon and in perched-intermediate groundwater beneath Sandia Canyon. Wells selected for this evaluation are generally situated near the center of mass within the chromium plume. Activities are also proposed to further refine the understanding of the properties of the aquifer with respect to chromium distribution and attenuation. The data collected based on this IMWP will enable the locating and designing of a pilot pumping well, which is specifically designed to further evaluate the potential for source removal. These data will help to characterize the expected performance of long-term pumping for source removal and the natural processes within the subsurface flow medium that may affect chromium migration. The proposed activities described below will reduce several key uncertainties related to the potential role of subsurface hydrogeological and geochemical processes in the aquifer on the distribution, potential for mass removal, and long-term stability of chromium.

The objective of the first set of activities, hydraulic and tracer field tests, is to provide additional details of aquifer and contaminant-plume behavior under extended pumping periods using several existing monitoring wells as pumping and observation locations. The hydraulic and contaminant transient data derived from pumping these wells are expected to provide the information necessary to optimize the location and design of a pilot pumping well as part of the SIMWP to further evaluate the potential for chromium mass removal from the regional aquifer through a pump-and-treat system. Pumping at these wells will also result in some contaminant mass removal from the regional and perched-intermediate aquifers.

In situ geochemical studies (tracer push/pull tests) coupled with the pumping tests will provide information on the role of advection, dispersion, and diffusion on the contaminant distribution and behavior during pumping. The impact of some of these processes is expected to be affected by complex fine-scale stratigraphy in regional aquifer sediments (Figure 2.0-1) that may have highly heterogeneous hydrogeologic properties (Figure 2.0-1). Complex aquifer heterogeneity that includes zones of relatively low aquifer porosity and permeability could potentially manifest as a secondary source of contamination during pumping for source removal if contaminant concentrations and mass in the zone of more active groundwater flow are reduced. The aquifer heterogeneity is expected to play a major role in the distribution and speciation of chromium mass.

The water removed during these relatively short-term field tests will be treated at the surface and disposed of through land application, in compliance with a temporary discharge permit from the NMED Ground Water Quality Bureau. In support of potential longer-term pumping for source removal and as a larger-scale remedy, a study will be conducted to evaluate the feasibility of reinjection of large volumes of treated water, one of several options for large-scale water disposition. The study is described in detail in section 2.2.2.

An additional activity related to source control is concurrently being implemented under a separate work plan to address source control for the chromium project (LANL 2011, 207053). This activity involves constructing a grade-control structure (GCS) in the spring of 2013 in the Sandia Canyon wetland to ensure long-term physical and geochemical stability of contaminated sediments within the wetland. The design of the GCS will enable a substantial reduction in effluent volume necessary to sustain the wetland while also potentially reducing downcanyon flux of effluent through residual chromium inventory in the vadose zone to the regional aquifer.

2.1 Hydraulic and Tracer Tests

A series of field tests will be performed to address the objectives discussed above and will include long-term hydraulic and tracer tests. During the tests, four regional monitoring wells (R-42, R-28, R-43 screen 1, and R-62) and one perched-intermediate monitoring well (SCI-2) will be pumped for extended periods. The field-testing operations and procedures will be similar at each well, the details of which are discussed below. For all tests, before groundwater pumping is initiated, a set of tracers will be introduced into the aquifer to perform dilution and “push-and-pull” tracer tests. The data collected during the hydraulic and tracer tests will be interpreted using different analytical and numerical techniques (integrated open-source computational framework for Model Analysis & Decision Support [MADS], http://mads.lanl.gov; multiwell variable-rate pumping-test analysis tool [WELLS], http://wells.lanl.gov; Istok et al. 2002, 240568; Shook et al. 2004, 240124; Schroth and Istok 2006, 240126; Huang et al. 2010, 240125). The interpretation will provide estimates of spatial variability in the aquifer hydrogeological and geochemical properties. Special attention will be placed on characterizing (1) the spatial distribution, including shape and size, of the high-permeability zone observed at R-28; (2) the spatial distribution of the chromium contaminant plume; and (3) the location and properties of potential contaminant reservoirs (e.g., pore spaces, mineralogical/ geochemical facies) in the aquifer. The analyses of the field tests will evaluate the potential for active removal of chromium contaminant mass from the aquifer via pumping of contaminated groundwater.

Each field test will start with a dilution test in which a dilution tracer is dissolved in groundwater and passively introduced into the aquifer through the well screen. The dilution tracers will be applied to estimate ambient groundwater flow velocities by measuring the decline of tracer concentrations in the well over time, which directly results from ambient flow through the well (Drost et al. 1968, 240121). The dilution tracer will passively migrate from the well for up to 5 d before the push-and-pull tracer test begins.

The push-and-pull tracer tests will follow the dilution tests and include four stages in sequence, with well-specific durations for these stages: (1) introducing two tracers into the aquifer through the well screen; (2) pushing the tracers out of the well with additional groundwater, (3) waiting for a period for migration (advection, dispersion, diffusion) of the tracers into the aquifer materials by ambient groundwater flow and diffusion processes to allow sufficient contact time and still allow reasonable recovery of the tracers, and (4) pumping for a period for “pulling” the tracers back out of the aquifer. The duration and applied groundwater volumes in stages 1 and 2 are contingent upon local hydrogeologic conditions at each well and will be informed by data from the dilution tracer test. Information about the groundwater velocity obtained during the dilution tests may be applied to constrain the duration of the waiting period in stage 3 as well. The duration of the waiting period in stage 3 also depends on well-specific hydrogeological conditions and the pumping rate during the last stage 4. The last “pulling” stage will occur simultaneously with the pumping test phase planned for each well.

During the last stage field analyses will be conducted of water-borne redox-indicating species using field Hach kits. The species analyzed could include nitrate, nitrite, ammonia, total chromium, Cr(VI), total iron, Fe(II), total manganese, and sulfide. Measurement of these species at different times during the pumping period will provide qualitative indications of redox conditions in the aquifer based on the presence or absence of redox-sensitive species. Some of these species are sensitive to changes in oxidation state that may occur during sampling, sample handling, and the time before analysis, so Hach kit analyses will be conducted in the field to minimize these concerns. The presence of redox-sensitive species will provide insights into whether conditions conducive to chromium reduction exist. In general, if no reduced species are detected, it will not be definitively concluded that there is no potential for chromium reduction (because of the potential for oxidation of such species during sampling); however, if reduced species are detected (even in the presence of dissolved oxygen or other oxidized species), it will be taken as an indication that conditions exist in the aquifer conducive to the formation of these reduced species. The potential for chromium reduction can then be evaluated based on known information about the relative ease of reduction of the detected species and Cr(VI). Experience indicates that the kinetics of reduction of the redox-sensitive species are generally slow enough that they can be detected in on-site Hach kit analyses of groundwater samples that also contain significant amounts of oxygen. Field measurements of pH, specific conductance, dissolved oxygen, and oxidation-reduction potential (ORP or Eh) will also be conducted using a multiparameter sonde to complement the measurements of redox-indicating species.

The pumped groundwater will be sampled at varying frequencies throughout the pumping period in each well and analyzed for all injected tracers. Initial sampling frequencies will be approximately hourly and adjusted as necessary based on fast-turnaround analytical results. The normalized tracer concentration (concentration divided by injection mass) versus time transients (breakthrough curves) of the push-and-pull tracers will provide information about groundwater flow and solute transport processes in the aquifer (Reimus et al. 2006, 240120; SNL 2007, 240122). The interpretation of breakthrough curves will help characterize advective groundwater flow and diffusive mass transfer between higher permeability and lower permeability zones in the aquifer, as indicated in Figure 2.0-1. The two push-and-pull tracers (a halide and a fluorinated benzoate) are both monovalent anions, but the halide, a much smaller ion, has a diffusion coefficient about 3 times larger than the fluorinated benzoate (Reimus et al. 2007, 240128). Thus, the halide will diffuse farther out of high-permeability zones into lower permeability zones than the benzoate during the injection and waiting periods of the tests. If mass transfer rates between high- and low-permeability zones are large enough, this difference will result in a somewhat lower and later peak concentration and a longer/higher tail concentration for the halide than the benzoate during the pumping period. These differences in breakthrough curves will allow estimates of diffusive mass transfer rates in the aquifer. If no differences in breakthrough curves are observed, then an upper limit on the mass transfer rate(s) can still be estimated. Using two tracers with different diffusion coefficients also allows more defensible estimates of ambient advective flow velocities to be obtained from the push-pull test (by providing information to allow the effects of diffusion to be “backed out” of the calculations, if necessary, which will complement the flow velocity estimated from the dilution tracer test). A depiction of the diffusion processes affecting tracer transport in the aquifer and the expected normalized tracer breakthrough curves are shown in Figure 2.1-1.

The magnitude of the separation of the tracer breakthrough curves will reflect the magnitude of the diffusive mass transfer rate(s) between the high- and low-permeability zones in the aquifer. If no separation is observed in the tracer breakthrough curves, then it can be concluded that the mass transfer rates were likely slower than the duration between introduction of the tracer and initiation of pumping, and therefore, it will only be possible to place an upper bound on the rate. Diffusive mass transfer between the high- and low-permeability zones represents an important attenuation process for chromium transport in the aquifer, as diffusion out of rapidly-flowing water into more slow-flowing or near-stagnant water will significantly increase chromium travel times. It will also potentially allow chromium to contact adsorbing or reducing surfaces that it would not otherwise contact. Furthermore, separation of tracer breakthrough curves will provide information on the potential importance of chromium mass that may be present in less permeable strata within the regional aquifer. This information can provide significant insights into expected operational performance of pump and treat systems.

The pumping tests at each well will be performed at a constant rate, with the rate and duration optimized for each well. The pumping rate at each well will differ as constrained by the hydrogeological conditions at the well. The pumping test duration will be optimized by two sets of data monitored during the pumping tests: (1) pumping drawdowns observed in the pumping and observation wells and (2) geochemical transients in the pumped groundwater. The constraints for the tests are that (1) drawdowns in the pumping wells do not exceed predefined maximum levels, (2) drawdowns in the nearby monitoring wells are sufficient to characterize aquifer heterogeneity, and (3) transients in key geochemical constituents, such as chromium, nitrate, sulfate, perchlorate, and tritium, are well characterized.

Drawdowns at the pumping well are constrained by the submergence of the pumped screen. The pumping will be performed at constant rates that are expected to cause drawdown, but care will be taken to maintain water levels above the well screen to avoid damage to the wells. The drawdowns at the pumping and monitoring wells will be influenced by various hydrogeologic factors. Some of these factors will slow down the pace of groundwater decline; these factors include “delayed yield” from the vadose zone or from low-permeability zones, lateral-recharge boundaries, high-permeability zones, aquifer “leakage,” vertical flow from hydrostratigraphic units next to the pumped strata, and/or three-dimensional flow effects. In addition, no-flow boundaries or low-permeability zones may increase the rate of groundwater decline. Most of these factors have been observed during past pumping tests conducted in the regional aquifer within the chromium plume area. A conceptual representation of the observed and expected drawdown transients during the pumping test conducted at R-28 in 2012 is shown in Figure 2.1-2. The late-time drawdown transients (past the 10-d duration of the 2012 test [LANL 2012, 228624]) are not known; they will depend on the hydrogeological conditions in the aquifer, and important information about the aquifer properties can be gleaned from understanding these conditions.

The shape and size of the zone of pumping influence (the area around the pumping well within which pumping drawdowns occur) during the pumping tests at each well depend on the local aquifer conditions. The pumping influence zone will be characterized by observing the drawdowns in nearby monitoring wells, including R-1, R-11, R-13, R-15, R-28, R-33, R-34, R-35a, R-35b, R-36, R-42, R-43, R-44, R-45, R-50, R-61, and R-62. It should be noted that some of these will be pumping wells at different stages of the field study. The drawdowns from all the monitoring wells are expected to be relatively small, and their interpretation will require post-processing of the collected data to remove barometric, tidal, and water-supply pumping effects. The goal is to ensure measured drawdown transients caused by pumping at the monitoring wells in the study area are sufficient to characterize the aquifer properties (e.g., heterogeneity, anisotropy, and boundary effects).

During the pumping tests, water samples will be collected regularly for geochemical analyses. Transients in key geochemical constituents such as chromium, nitrate, sulfate, and perchlorate will be characterized and closely monitored. These samples will be collected and submitted for analysis on a weekly basis. Samples will be also collected daily and archived for possible analysis if the results of weekly samples indicate changes that should be explored with more frequent sample analysis. Tritium will be monitored at a biweekly frequency. Selected samples will also be analyzed for chromium isotopes and analyzed on a monthly basis. Transients in chromium isotopes will provide information on aquifer heterogeneity with respect to Cr(VI) reduction potential. Transients in concentrations and other field parameters (e.g., pH and temperature) are expected to provide important information about the hydrogeological and geochemical conditions at the site. Depending on the local aquifer conditions near the pumped wells, different geochemical and hydrological conditions might remain steady, increase, or decrease (more complex transients are plausible as well). Steady conditions will indicate a well-mixed plume within the primary porosity within the capture zone. Increasing or decreasing values of key indicator constituents will suggest that pumping is pulling water from more- or less-contaminated portions (vertically or laterally) of the aquifer, respectively. The shape of the transient curves for the different geochemical indicators will be indicative of the processes that cause the observed fluctuations: linear trends will indicate water mixing and exponential trends may suggest more complicated hydraulic or geochemical processes such as diffusion from tighter pore spaces or adsorption. During the 10-d R-28 pumping test in 2012, the chromium concentrations declined at a steady linear pace without reaching an equilibrium level (LANL 2012, 228624).

The analyses will utilize existing models and computational tools (MADS; WELLS; Istok et al. 2002, 240568; Shook et al. 2004, 240124; Schroth and Istok 2006, 240126; Huang et al. 2010, 240125).

2.1.1 R-42 and R-28 Field Tests

Field tests at regional monitoring wells R-42 and R-28 will be conducted consecutively, starting with R-42. Estimated pumping durations to achieve drawdown sufficient to be detectable in surrounding wells is approximately 100 d at R-42 and 70 d at R-28. Figure 2.1-3 illustrates the zones of influence expected to be observed during the R-42 and R-28 pump tests. If the pumping-test durations needed to observe drawdown at surrounding wells are shorter than expected at the two pumping wells, both wells may be pumped simultaneously for a period allowable under the discharge permit. For each well, the sequence will be to first run the dilution test and then the coupled push-and-pull tracer and pumping tests.

The dilution test in R-42 will use disodium 1,5-naphthalene disulfonate (NDS) with a mass less than 200 g as a tracer. The tracer will be dissolved in approximately one circulation loop volume of aquifer groundwater pumped from R-42 and poured back into the borehole (the water in the injection borehole will be circulated to the surface and returned to the aquifer for some period of time during the dilution test to keep the borehole well mixed, and the volume injected will be the estimated volume of the borehole/screen between the injection point and the pump intake plus the volume of the tubing running to the surface and back). The push-and-pull tracer test in R-42 will use sodium 2,6-difluorobenzoate (DFBA) (less than 5 kg) and sodium iodide (NaI) (less than 5 kg) as tracers. Both tracers will be mixed together in 1500 gal. of aquifer groundwater pumped from R-42. The water will be poured back into the borehole at a rate that does not create a substantial increase in the regional water-levels, and the tracer solution will be "chased" with at least 4000 gal. of groundwater pumped from R-42. It is expected that the tracer introduction will take less than 24 h. After a waiting period of an estimated 20 to 30 d, the pumping test will be started and will provide a pull back of the tracer from the aquifer. It should be noted that the exact chase volume and waiting period will be determined after analyzing the results of the dilution tracer test, which will indicate how rapidly water is flowing through the injection interval. The flow rate through the injection interval will dictate how much chase volume can be injected and how long the tracer solution can be allowed to "drift" with the ambient flow in the aquifer and still recover most of the tracer during pumping. The goal is to maximize the volume and representativeness of the aquifer that is interrogated while ensuring that good recovery of the tracers is obtained. The pumping rate at R-42 is expected to be approximately 8 gallons per minute (gpm) and continue for up to 100 d; the pumping rate and duration may be adjusted during the test to maximize the information content of the collected data.

The R-28 field test will be very similar to the procedure outlined for R-42 above and will use the same dilution and push-and-pull tracers. The only differences will be that (1) the push-and-pull tracers will be chased with up to 10,000 gal. of groundwater pumped from R-28, and (2) the pumping rate will be approximately 28 gpm. The pumping-test duration at R-28 will be up to 70 d.

A schematic representation of capture zone and tracer impact zone during R-28 field test is presented in Figure 2.1-4. The capture and tracer zone estimates assume groundwater flow in uniform and isotropic aquifer. The capture zone presented in the figure assumes a quasi-steady-state flow regime, which is expected to be achieved within about 10 d after the pumping has been commenced. The time-dependent (transient) capture zones representing the volume of water pumped during the R-28 pumping test will define the portion of the aquifer from which the pumped water is extracted. Existing tools and models will be applied for evaluation the transient capture zones and the actual zones of influence for each pumping well during the proposed field tests (Vesselinov et al. 2006, 098324; Vesselinov and Robinson 2006, 240123; LANL 2012, 228624).

2.1.2 R-43, Screen 1, and R-62 Field Tests

Regional monitoring wells R-43 and R-62 are located to the west of (generally upgradient of) R-42 (Figure 1.0-2). The two wells will be subject of field tests similar to the ones proposed for R-42 and R-28 above and the same dilution and push-and-pull tracers will be used. The field tests will be conducted consecutively starting with R-43, screen 1, with pumping durations up to 45 d. The primary goals of the R-43, screen 1, and R-62 field tests are to perform tracer-test analyses and to observe transients in the geochemical constituencies during the pumping. These data will provide important information on groundwater flow and transport properties. A secondary goal of these field tests is to collect pumping drawdown data. Hydraulic responses in all the nearby monitoring wells are not expected within 45 d of pumping of R-62 and R-43. However, hydraulic cross-communication between R-62 and R-43 and some of the very closely placed monitoring wells may be observed.

Wells R-42 and R-28 are located in the central portion of the chromium plume where the highest contaminant concentrations are detected. R-43, screen 1, and R-62 are located at the northwestern and western edges of the plume, respectively. Their testing will be critical to characterize (1) the location and properties of the contaminant source, (2) the spatial extent of the plume, and (3) the impact of mixing contaminated and clean aquifer water. Since the contaminant concentrations in this area are lower than in the R-42/R-28 area, the field tests will provide better information about the potential impact of naturally occurring geochemical processes in the aquifer on chromium contaminant concentrations (e.g., retardation, attenuation, etc.) because these processes may already be depleted in the R-42/R-28 area, but not in the R-43/R-62 area.

For each well, the field test sequence will be to first run the dilution test and then the coupled push-and-pull tracer and pumping tests. The design of the R-43, screen 1, and R-62 field tests will be very similar to the procedures outlined for R-42 above. The only differences will be that (1) the push-and-pull tracers will be chased with up to 3000 gal. of groundwater, (2) the pumping rate will be approximately 5 to 8 gpm, and (3) the pumping-test duration will be up to 30 d.

2.1.3 SCI-2 Field Test

Intermediate monitoring well SCI-2 is screened in a perched-intermediate zone of saturation within the vadose zone beneath Sandia Canyon. The Cr(VI) concentrations in the intermediate groundwater (~500 ppb) are less than the maximum concentrations detected in the regional aquifer (~1000 ppb). Therefore, the contamination in this zone is not the primary source for the contamination in the regional aquifer. However, because of its location, it is expected that the zone is along a contaminant flow path (past or current) through the vadose zone. A field test similar to the one planned for R-43, screen 1, and R-62 will be conducted at SCI-2. The field test sequence will be to first run the dilution test and then the coupled push-and-pull tracer and pumping tests, again using the same dilution and push-and-pull tracers. The only differences will be that (1) the push-and-pull tracers will be chased with up to 1000 gal. of groundwater, (2) the pumping rate will be approximately 2 to 3 gpm, and (3) the pumping-test duration will be up to 30 d. The pumping duration may be constrained by the yield of the perched-intermediate zone. The pumping test and the subsequent recovery will provide important information about the spatial extent, groundwater volume, and recharge capacity of this zone. The chromium concentrations and other geochemical transients in SCI-2 groundwater detected during the pumping and recovery will provide information about the contaminant transport properties of the vadose zone. The tracer tests will provide information about groundwater velocity and advective, dispersive, and diffusive properties of the rocks in this perched-intermediate zone.

2.2 Geochemical Characterization

Geochemical characterization work will be implemented as part of this IMWP under two separate studies.

The first study includes quantifying chemical speciation of chromium and iron on samples collected from within the chromium contamination area and comparing them with samples collected from outside the chromium contamination area (i.e., background samples). These data will indicate whether Cr(VI) reduction within the chromium-contaminated zone has occurred.

The second study will evaluate geochemical interactions that could occur with the injection of treated water. Water removed during the field tests proposed under this IMWP will be treated by ion exchange and disposed of by land application, as governed by the temporary discharge permit for the field tests. However, if large-scale pumping with a pilot well is recommended in the SIMWP, other water disposition methods, including injection, will be considered to dispose of the larger volumes of treated water. Therefore, another activity will be to characterize interactions between reinjected treated water and aquifer materials to determine the viability and operational requirements of injection.

Based on the results of these two studies and the field tests, the SIMWP may propose additional geochemical characterization if necessary. Additional studies may include laboratory batch and column experiments to evaluate chromium attenuation mechanisms in aquifer sediments.

2.2.1 Chemical Speciation of Chromium and Iron

Information on the speciation of contaminant chromium is considered necessary for addressing the long-term fate and transport of chromium in groundwater beneath the Laboratory. Chemical speciation of chromium is a key parameter for understanding the geochemical processes of chromium present in the subsurface and assessing the long-term stability and attenuation potential of vadose-zone and aquifer materials. Cr(III) has extremely low mobility under typical groundwater conditions found beneath the Laboratory. In the 2009 Sandia Canyon investigation report (LANL 2009, 107453), a synchrotron based X-ray absorption near-edge structure (XANES) method was used to evaluate the attenuation capacity of vadose zone and regional aquifer materials for Cr(VI). That study exposed noncontaminated rock samples to Cr(VI)-bearing water in a laboratory setting to determine their attenuation potential. The findings showed that reduction of Cr(VI) to Cr(III) does occur naturally in the environment in the presence of ferrous iron-bearing minerals.

The focus of the proposed activities under this IMWP is to determine chemical speciation of chromium in field samples from within the chromium-contaminated zone to determine the nature of attenuation that has resulted from the presence of contaminant chromium in the regional aquifer and perched-intermediate zones. In addition, the study will incorporate the site conditions (mineralogy, chemistry) to accurately determine speciation and distribution of chromium and other coassociated elements, particularly iron, on rock and grain surfaces that have been exposed to Cr(VI) along the flow path.

The results from the 2009 Sandia Canyon investigation report (LANL 2009, 107453) and other studies suggest that divalent Fe(II) is the prime inorganic constituent to reduce Cr(VI) in a natural system. Thus, a combination of synchrotron-based techniques such as XANES, micro–x-ray fluorescence (μ-XRF) element maps and x-ray absorption fine structure (XAFS) will be used to quantify both Cr(III)/Cr(VI) and Fe(II)/Fe(III) ratios and to identify the correlation between chromium and iron at a given location in the sample. The results of this study will serve to (1) directly observe chromium speciation on materials from the contaminated area and check the correlation with primarily iron-bearing minerals to understand their effect on chromium reduction, and to (2) provide necessary knowledge to guide potential additional geochemical characterization activities to address chromium contamination in groundwater beneath the Laboratory.

Two to four representative archived core/cuttings samples from within the contaminated area (e.g., potentially from R-28, R-42, MCOI-6, and SCI-2) and two to four representative archived core/cuttings samples from noncontaminated areas (e.g., from MCOI-10 and LAOI-7) will be characterized using XRD, XRF, and scanning electron microscopy (SEM). Sample results showing the highest chromium content will be selected for XANES, μ-XRF, and XAFS measurements to ensure that the concentrations of chromium and iron are above the detection limits of these techniques. The results from the noncontaminated samples will be compared with the results those from contaminated samples, particularly for iron.

XANES, μ-XRF, and XAFS measurements will be conducted at the Stanford Synchrotron Radiation Lightsource (SSRL). Two types of measurements will be conducted. One is to determine the oxidation state of chromium and iron of the field samples with an effort to quantify the ratios of Cr(III)/Cr(VI) and Fe(II)/Fe(III). Another will focus on μ-XRF element maps and XAFS analysis to determine chemical coordination and distribution of chromium and other coassociated elements, particularly iron, on rock and particle surfaces from contaminated portions of the subsurface. These data will be used to guide further geochemical characterization, if necessary, planned for the SIMWP, as described in section 2.3.

2.2.2 Geochemical Characterization for Injection of Treated Water into the Aquifer

The purpose of this proposed activity is to evaluate potential interactions between injected treated water and aquifer materials. Water/rock interactions are essential geochemical processes that regulate the groundwater chemistry in aquifer systems. Injection of large amounts of treated water into the regional aquifer could alter groundwater chemistry and cause the formation of precipitates within the screened interval of an injection well or within the surrounding pore space. Injection might also liberate naturally occurring constituents (e.g., arsenic) or otherwise stable contaminants. To understand potential issues that could arise from injection of treated water into the regional aquifer, combined laboratory static bench tests accompanied by geochemical modeling will be conducted.

Batch studies will be performed with representative core and cuttings samples from the predominant lithologic units found below the water table beneath Sandia and Mortandad Canyons (the Puye Formation and Miocene pumiceous unit). Treated groundwater generated during the field tests will be used in the experiments to represent injection water. Solid samples will be brought in contact with the treated groundwater at various conditions to ensure that potential variations in fluid composition, mineral heterogeneity and exposure degree (the ratio between liquid and solid, for example, liquid/solid ratio and time) are considered. Geochemical and transport modeling will be used to simulate physicochemical interactions in the reinjection water/rock system to assess long-term groundwater chemistry in the regional aquifer. Post-characterization (XRD, XRF, SEM) will be performed on representative solid samples to look for precipitates and changes in mineralogy. Fluid composition before and after the batch test will be analyzed using a combination of wet chemical methods (e.g., inductively coupled plasma, high-performance liquid chromatography, titration).

2.3 Supplemental Interim Measures Work Plan

At the completion of the activities discussed in sections 2.1 and 2.2, the SIMWP will be prepared, summarizing the results of the hydraulic and tracer field tests at R-42 and R-28 and the characterization of reinjection water. The SIMWP will also include recommendations regarding the installation of a pilot pumping well to further evaluate the potential for chromium mass removal from the regional aquifer. If a pilot pumping well is recommended, the SIMWP will also recommend the location, design, and operational conditions for the pumping well as an important component of integrated remedial activities for chromium contamination. The SIMWP will include recommendations for the disposition of the considerable quantities of treated water likely to be generated from the additional pumping actions, incorporating the results of the characterization study of reinjection water geochemistry. The SIMWP may also propose additional geochemical characterization, if necessary, depending on the results of the field tests and of the chromium and iron speciation work.

3.0 SCHEDULE

The proposed start date for the hydraulic and tracer tests is June 2013, with the R-42 and R-28 tests conducted during calendar year 2013. The temporary discharge permits that govern disposition of treated water require that land application cease when the ground is too frozen to allow for infiltration of sprayed water. Therefore, it is anticipated that the pumping tests and associated land application of water from R-42 and R-28 will cease sometime in mid- to late November 2013. Geochemical characterization activities will be performed through approximately February 2014. The SIMWP will be submitted to NMED by March 31, 2014, and will include a schedule for any additional work that is proposed. Since analytical results and hydraulic data will be generated at a high frequency during all aspects of this work, it is recommended that frequent discussions are held with NMED to facilitate real-time interpretation of the results.

Pumping and tracer tests at SCI-2, R-43-1, and R-62 will begin in early spring 2014 and are expected to be complete by mid-summer 2014. The Laboratory recommends that the integrated results of this IWMP and the SIWMP be included as content in a corrective measures evaluation (CME) report. The CME report would recommend all aspects of the final remedial approach for the chromium contamination.

4.0 REFERENCES

The following list includes all documents cited in this plan. Parenthetical information following each reference provides the author(s), publication date, and ER ID. This information is also included in text citations. ER IDs are assigned by the Environmental Programs Directorate's Records Processing Facility (RPF) and are used to locate the document at the RPF and, where applicable, in the master reference set.

Copies of the master reference set are maintained at the NMED Hazardous Waste Bureau and the Directorate. The set was developed to ensure that the administrative authority has all material needed to review this document, and it is updated with every document submitted to the administrative authority. Documents previously submitted to the administrative authority are not included.

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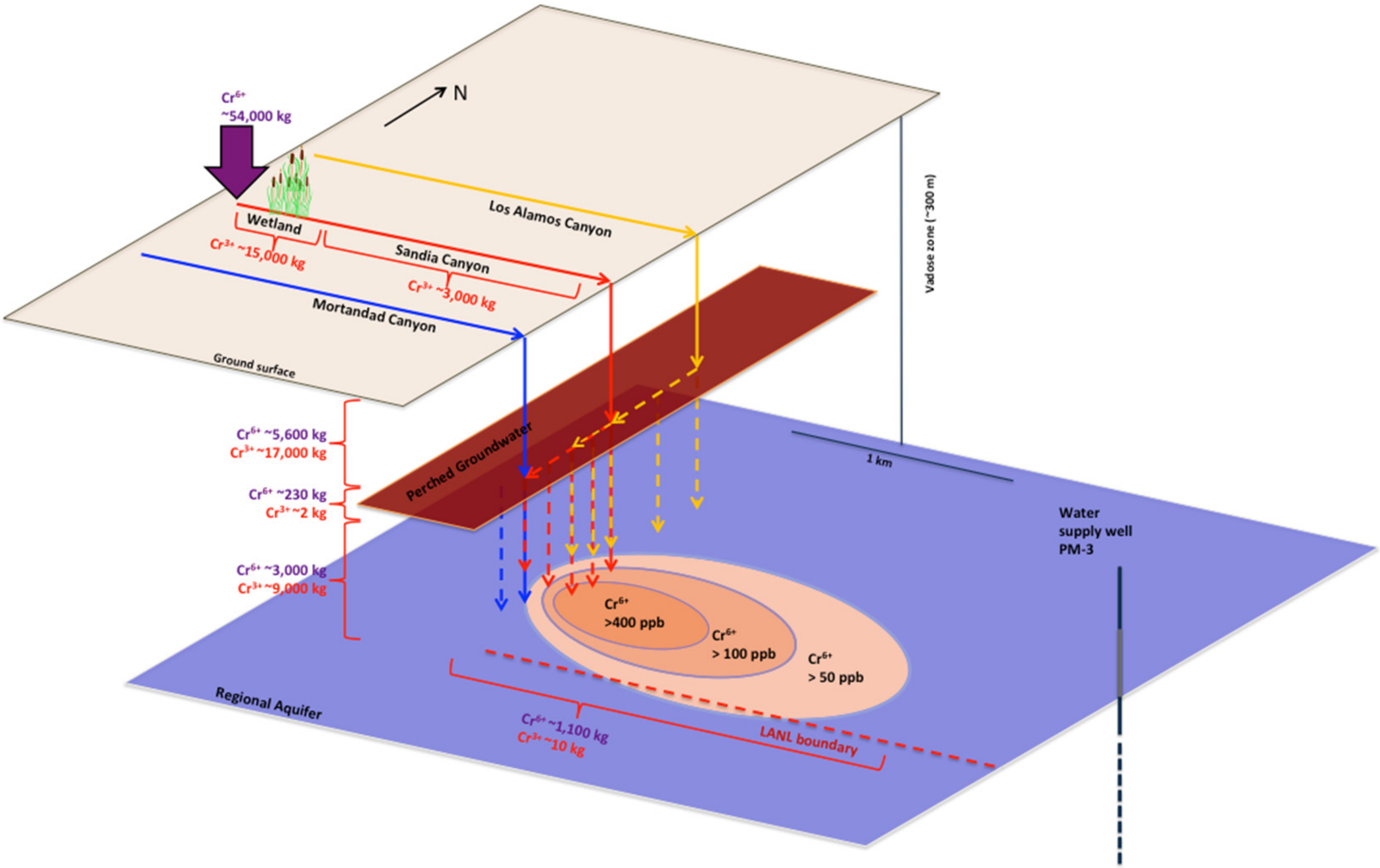


Figure 1.0-1 Conceptual three-dimensional representation of surface-water and groundwater flow paths that influence chromium migration

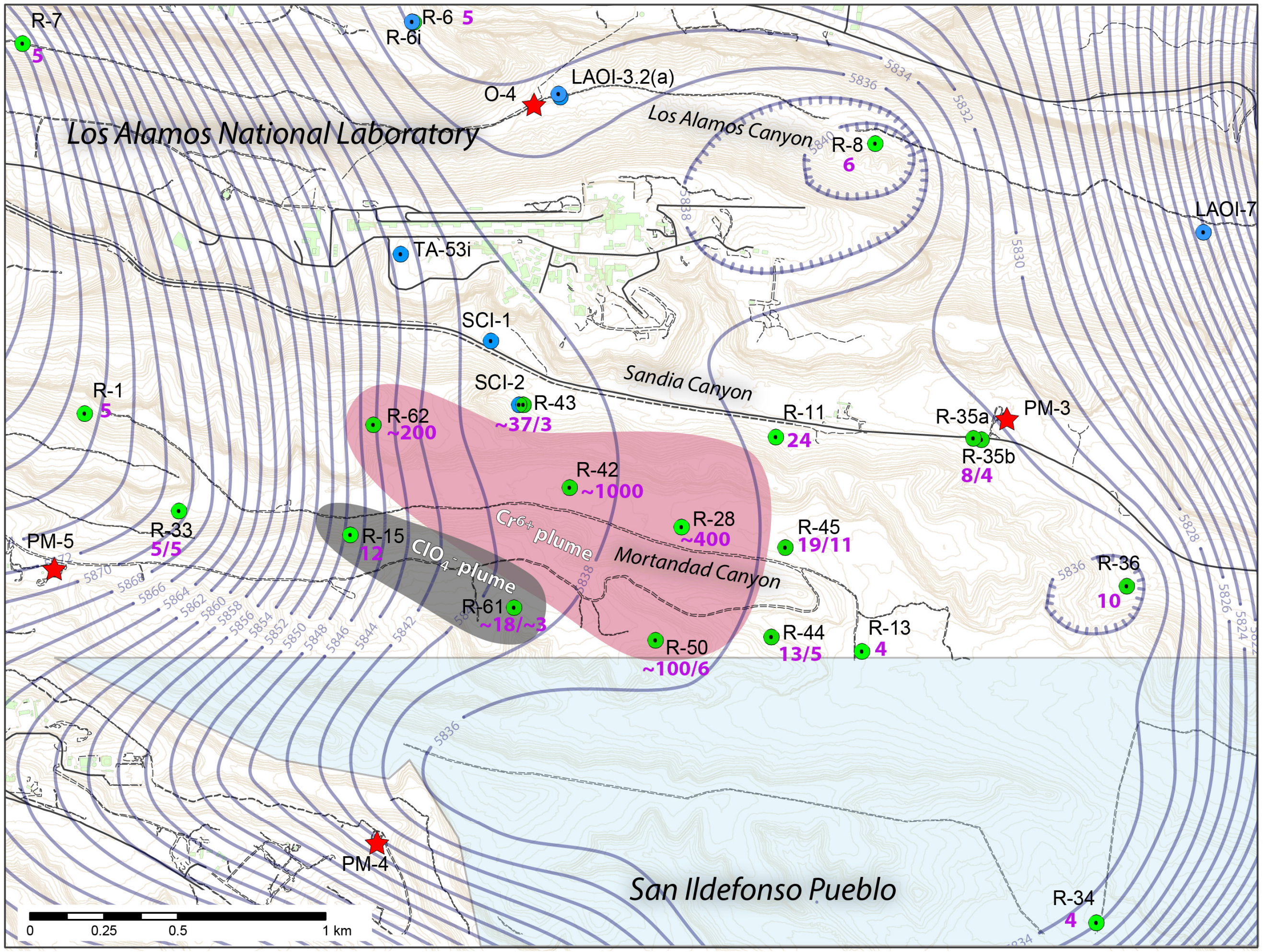
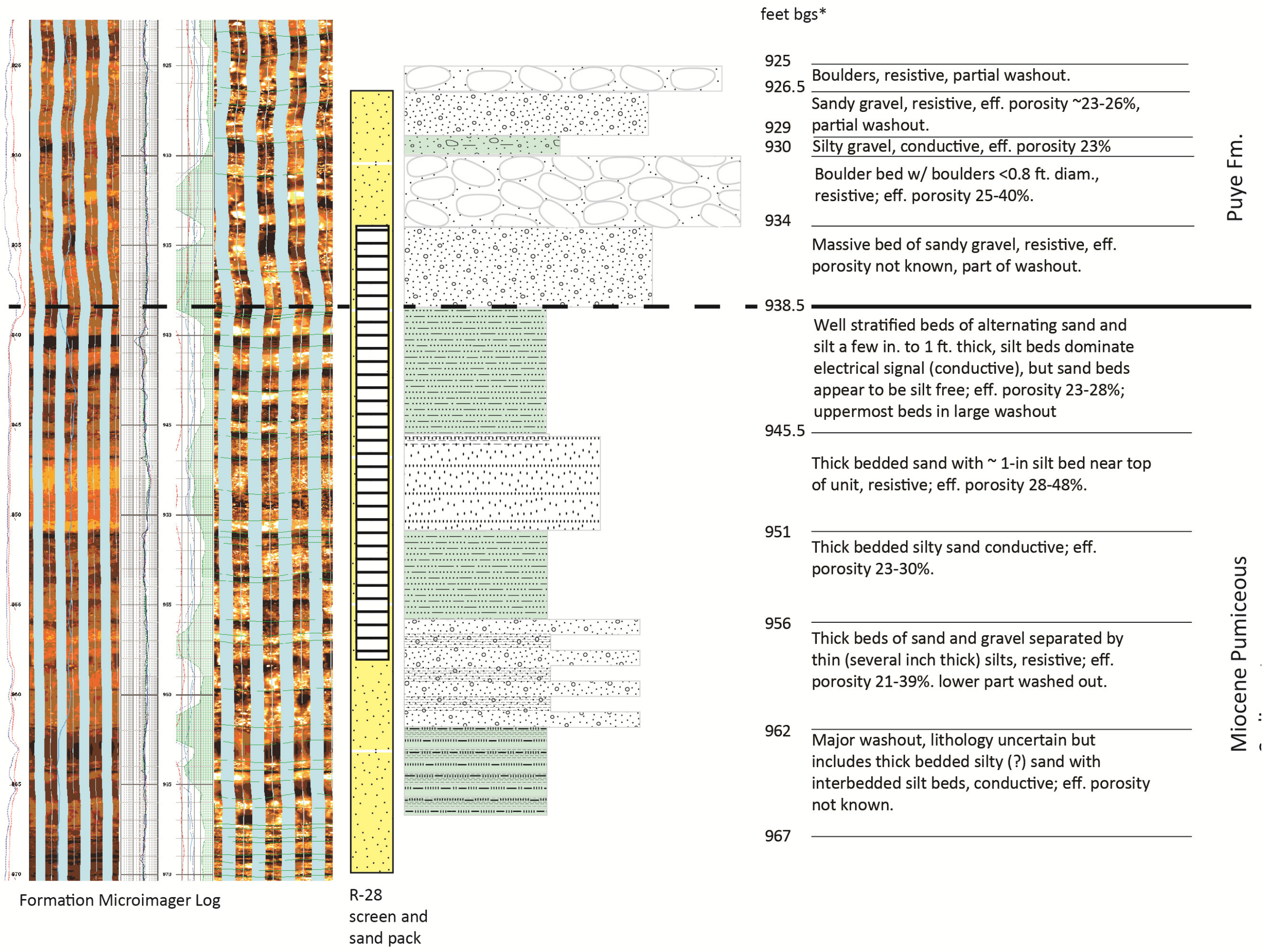


Figure 1.0-2 Plan view of the Cr(VI) plume (>50 ppb contour shown in pink) in the regional aquifer with nearby regional monitoring wells (green circles), perched-intermediate monitoring wells (blue circles), and water-supply wells (red stars). Contour lines (2-ft intervals) represent the regional water table elevations. The approximate area of perchlorate contamination greater than approximately 2 ppb in the regional aquifer is shown in grey. Numbers beneath the well names refer to the approximate chromium concentrations. Two numbers represent concentrations for upper and lower screens.



925 – 926.5 Boulders, resistive, partial washout.

926.5 – 929 Sandy gravel, resistive, eff. porosity ~23-26%, partial washout.

929 – 930 Silty gravel, conductive, eff. porosity 23%

930 – 934 Boulder bed w/ boulders <0.8 ft. diam., resistive; eff. porosity 25-40%.

934 – 938.5 Massive bed of sandy gravel, resistive, eff. porosity not known, part of washout.

938.5 – 945.5 Well stratified beds of alternating sand and silt a few in. to 1 ft. thick, silt beds dominate electrical signal (conductive), but sand beds appear to be silt free; eff. porosity 23-28%; uppermost beds in large washout

945.5 – 951 Thick bedded sand with ~ 1-in silt bed near top of unit, resistive; eff. porosity 28-48%.

951 – 956 Thick bedded silty sand conductive; eff. porosity 23-30%.

956 – 962 Thick beds of sand and gravel separated by thin (several inch thick) silts, resistive; eff. porosity 21-39%. lower part washed out.

962 – 967 Major washout, lithology uncertain but includes thick bedded silty (?) sand with interbedded silt beds, conductive; eff. porosity not known.

Sediment facies within the screened interval for R-28. Green shaded units are electrically conductive, non-shaded units are electrically resistive.

*bgs = Below ground surface.

Figure 2.0-1 Detailed stratigraphy within the screened interval in regional well R-28

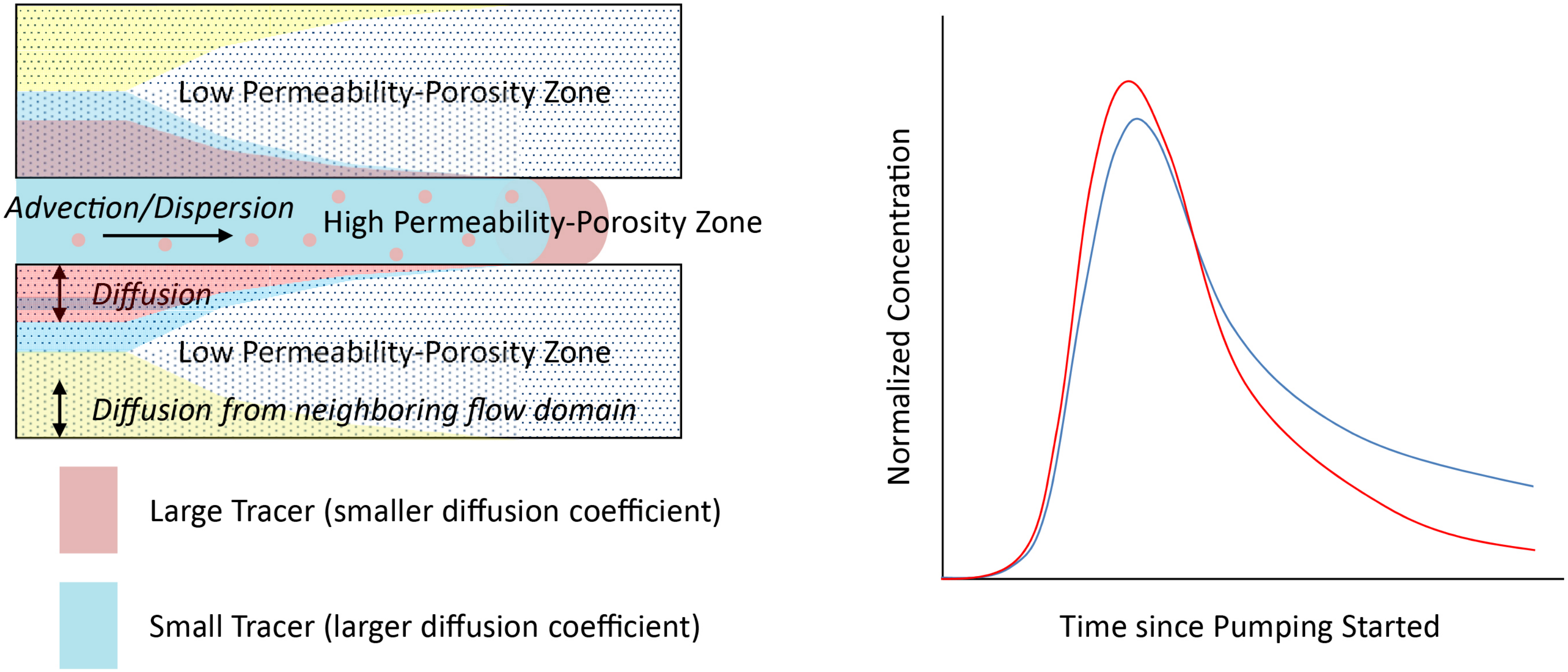


Figure 2.1-1 **Schematic of tracer transport and resulting breakthrough curves for two different size tracer molecules transporting through heterogeneous strata with varying permeability-porosity**

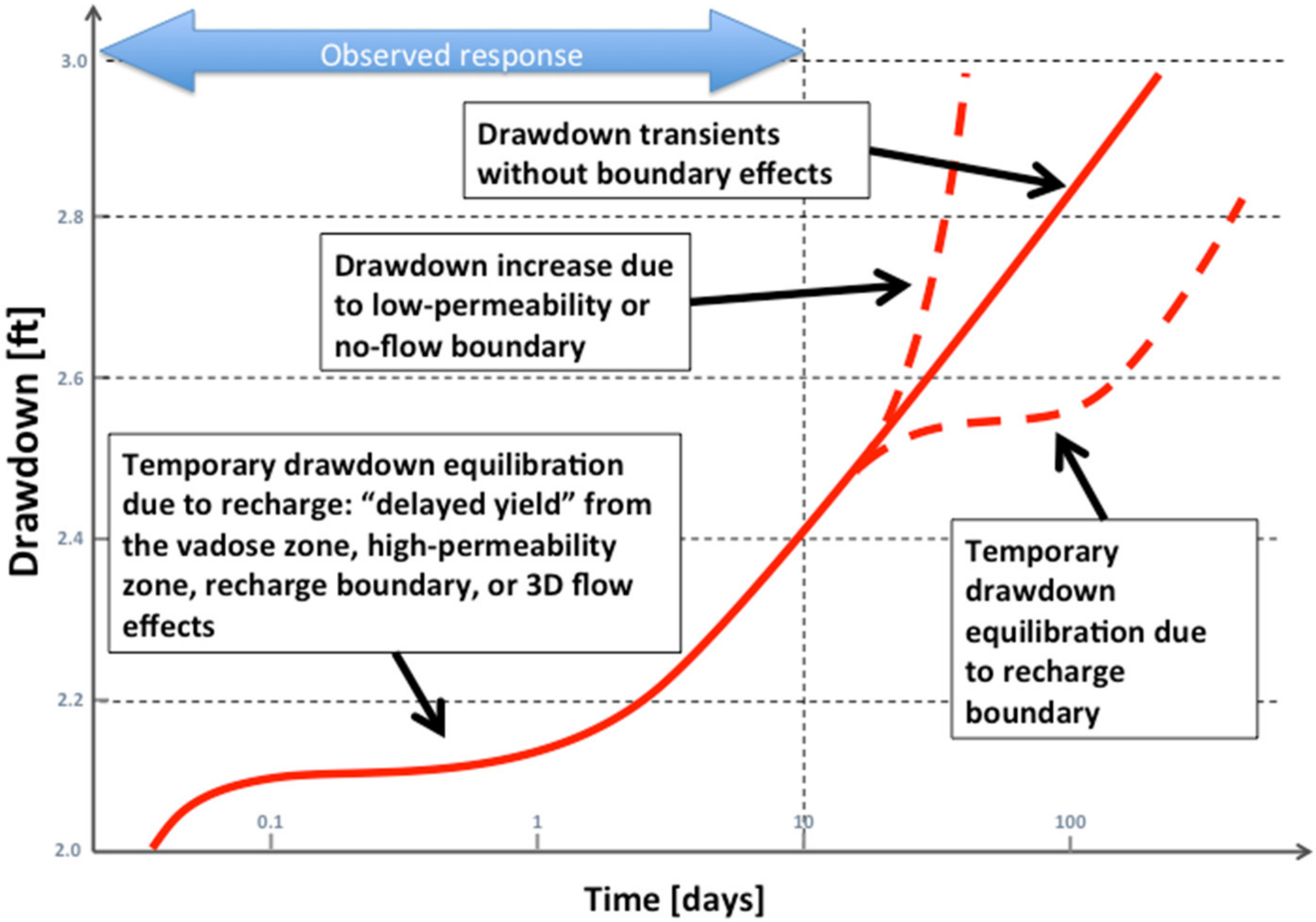


Figure 2.1-2 Observed (first 10 d) and hypothetical (after 10 d of pumping) drawdown versus time curves during pumping at R-28 (similar behavior may be observed at R-42)

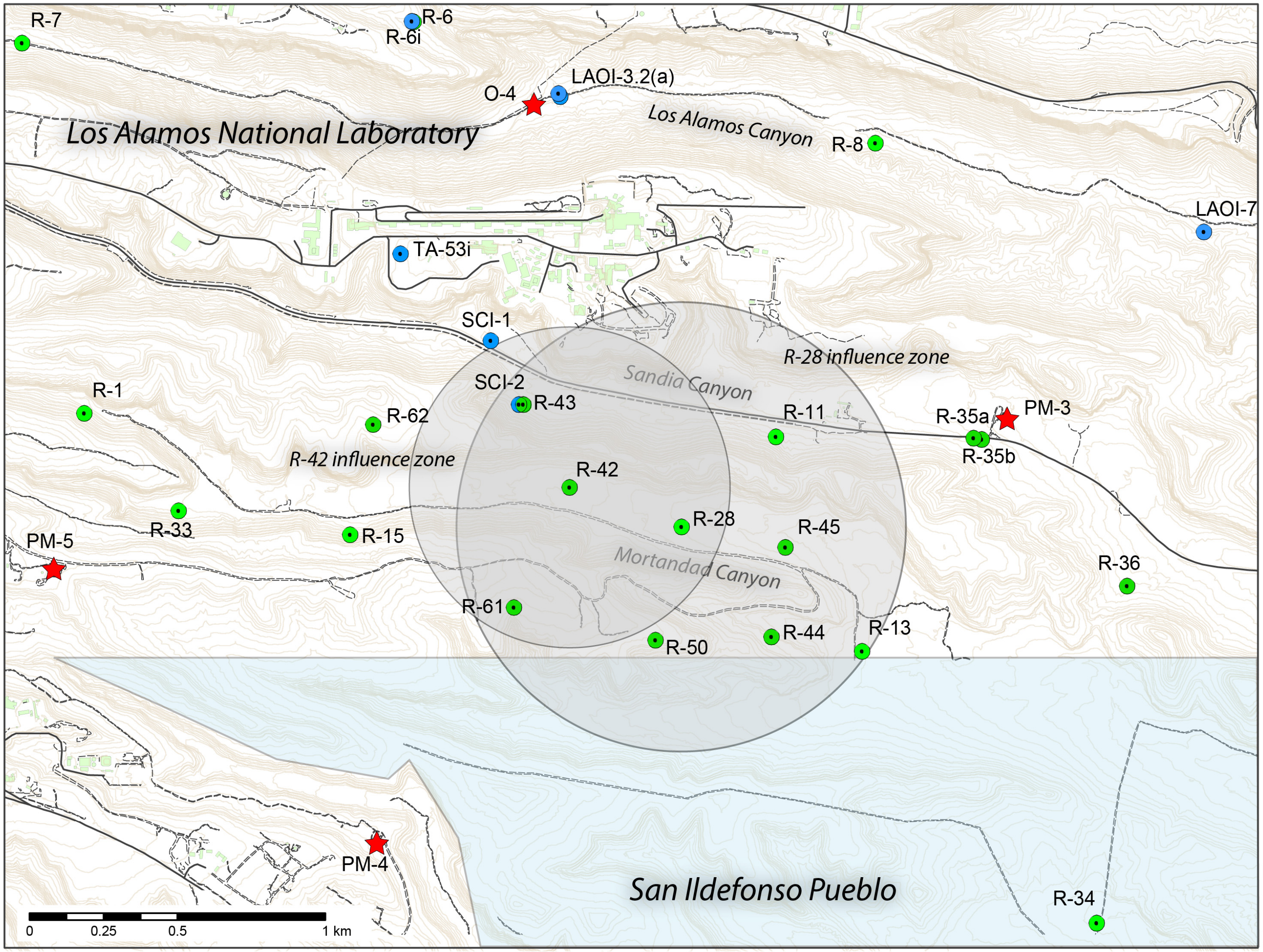


Figure 2.1-3 Expected zones of influence of R-42 and R-28 pumping test

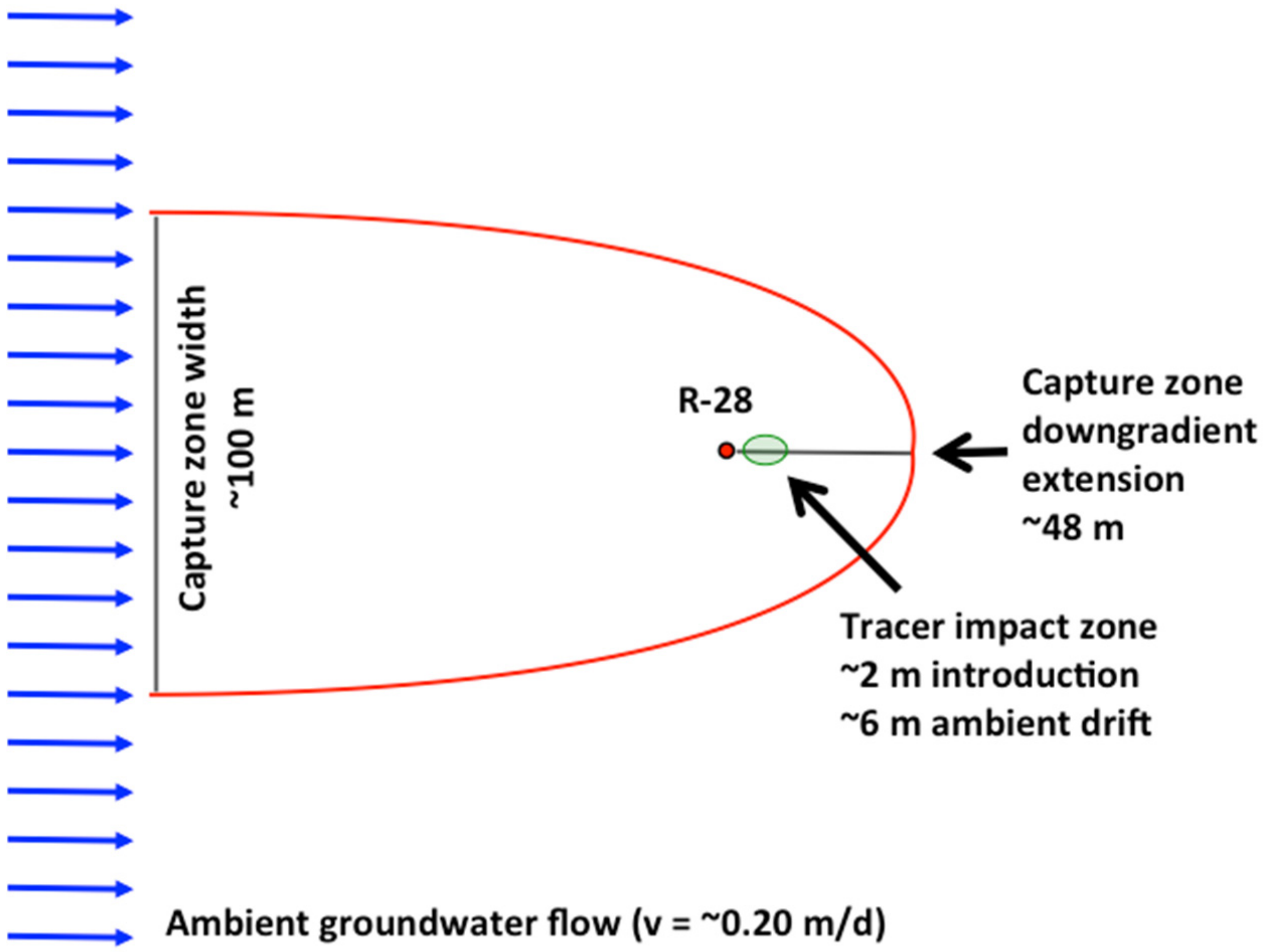


Figure 2.1-4 **Schematic representation of capture zone and tracer-impact zone during R-28 field test. The capture and tracer zone estimates assume steady-state groundwater flow in uniform and isotropic aquifer. The capture zone estimate assumes a quasi-steady-state flow regime, which is expected to be achieved within about 10 d after the pumping has commenced.**