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Independent Review of Groundwater Remediation Strategy for Hexavalent Chromium and RDX Groundwater Plumes at Los Alamos National Laboratory

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Executive Summary

Site operations at the Los Alamos National Laboratory (LANL) resulted in the release of oxidized chromium, Cr(VI), into Sandia Canyon from cooling tower effluent from 1956 until 1972. The chromium traveled with the surface water approximately 3 miles downstream before migrating below ground surface. Chromium concentrations exceed 50 µg/L in the upper portion of the aquifer (Looney et al., 2012, LANL 2009).

Another LANL groundwater plume of concern is associated with RDX (Royal Demolition Explosive, 1,3,5-trinitro-1,3,5-triazine). Between 1951 and 1996, RDX was released to the mesa-top facilities' process water outfall, adjacent and underlying soils, and alluvial sediments, along with surface water in Cañon de Valle. Between 2000 and 2010, two remedial actions were deployed, removing much of the near-surface RDX, however, recharge due to precipitation has transported RDX into the perched-intermediate zone and into the regional aquifer (Robinson et al., 2020).

The report documents an independent technical review by scientists from the Department of Energy (DOE) Network of National Laboratories for Environmental Management and Stewardship (NNLEMS) to provide recommendations for potential near term actions to address and optimize remediation for both the Cr(VI) and RDX plumes. The proposed near-term remedial actions include design of pump and treat systems for Cr(VI) and monitoring and study for natural attenuation for RDX. The review assesses existing data, conceptual and numerical modeling, and it recommends a technical integration process to support identifying and implementing strategic, effective and efficient remedies. The DOE Environmental Management Los Alamos Field Office (EM-LA) and their cleanup contractor Newport News Nuclear-BWTX, LLC Los Alamos (N3B) provided the information required for the review. Interviews were also conducted with regulators to obtain the full spectrum of technical, regulatory and scientific perspectives.

The independent review team was impressed by the capabilities, experiences, innovativeness, and insightfulness of the technical representatives from both the regulator, the New Mexico Environment Department (NMED) and N3B. Incorporation of vadose zone flow pathways in the conceptual site model (CSM) and configuring the numerical modeling for the site was generally state-of-the-practice (or better). This could be considered state-of-the-art by addressing uncertainties related to spatial extent of hydraulic windows. The reviews from the regulators were thorough and often provided useful concepts for consideration and future study/resolution.

The overarching consensus recommendation of independent review team is that the LANL groundwater plumes should be addressed in context of the emerging "management of complex sites" paradigm.

A central theme of the technical review is a recommendation to consider/use strategies that have been developed to support remediation of complex groundwater plumes. These strategies provide a structure and opportunities for facilitating collaborative and positive interactions between DOE and its technical team with regulators and their technical experts. Importantly, as described below, the complex site paradigm has been inclusive in its development and broadly accepted, including key federal and state regulators at every step. The complex site paradigm is emerging as an important tool in addressing the nation's most significant environmental challenges; a number of guidance documents are available to support both the general approach and site-specific applications (e.g., ITRC, 2004 and 2017; NRC, 2013). Likewise, the U.S. EPA Superfund Task Force has recommended broadening the use of adaptive management for complex sites and is currently running select pilot studies (EPA, 2018).

A primary goal of the complex site paradigm is to explicitly recognize that it is difficult, or intractable, to generate advanced knowledge that is sufficient to provide a technically defensible basis for the final remediation decision, design and implementation. Instead, an adaptive management strategy encourages a focus on what can be done now with the information that is known, what can be done to stabilize the plume and mitigate risk, and what achievable interim objectives can be added as part of the adaptive management process that will allow success for all parties. Technologies can be optimally implemented in a manner that is targeted in space, time, and goal-oriented. Finally, implementation of the technologies can, and should, be performed in such a manner that the system response to each action provides actionable data to help resolve uncertainties and inform the next stage of remediation decisions and design.

The review team was provided a scope of work with a list of questions. Summary observations related to those questions are provided below, and a full list of questions can be found in Section 1.0.

General assessment of the conceptual and numerical modeling observations:

- The existing conceptual models and numerical model results provide reasonable and effective support for several types of near-term remedial action decisions, notably designing and projecting the plume behavior for Cr(VI) and RDX, risks to potential receptors over the next several decades and interim actions such as pump and treat.
- The current conceptual models do not provide the decision support eventually needed for longer-term remedial action objectives. Specifically, more focus is recommended on the remaining residual vadose zone contaminants, projecting the quantity, location and future release profiles of Cr(VI) and RDX into the groundwater, understanding large-scale matrix diffusion, characterizing mass flux from residual source zones in the groundwater, and quantifying attenuation processes and other biogeochemical dynamics.
- Once additional characterization information on the nature and extent of sources above the regional water table is available for the conceptual model, numerical modeling will be needed to robustly support a technical basis for design of remedies to manage and control sources.
- There are a number of uncertainties in the parameters of the regional groundwater model – for many of the traditional model parameter uncertainties, refinements would have a relatively small (incremental) impact on results so these would be a low-medium priority for the EM-LA team.
- Because of long transport distances, fracture flow and matrix diffusion, and the resulting patchy nature of active water flow and contaminants in the vadose zone, the vadose modeling has a relatively high uncertainty.

Assessment of data gaps:

There are a number of challenges and opportunities related to future characterization and site-specific geology and biogeochemistry, with a focus on potential remediation options to consider for the future portfolio of remediation and monitoring technologies. These deliberations were done in the context of our overarching recommendation for classifying LANL groundwater according to the complex site paradigm and presuming that a suite, or portfolio, of remedial actions will be needed to address these important and recalcitrant contaminant plumes. Further, the effort was informed by the substantial history of characterization, field testing, and the data and results from the interim pump and treat that was recently performed to control the Cr(VI) plume footprint, and measurements of the distribution of RDX in the nearfield vicinity of the release area. The existing data gaps do not impact the ability of the EM-LA team to design, build and operate a pump and treat system to meet appropriate objectives (e.g., to limit plume growth and mitigate key risks). The remaining data gaps could be managed and addressed during the deployment and operation of such an interim remediation and resolved in a phased manner according to the recommended adaptive site management paradigm.

- Data gaps in the regional aquifer related to geochemistry, hydrogeology and various environmental remediation technologies (Section 6.2) included: the nature, location and quantity of contamination in vadose zone and projection of future mass flux to the groundwater plume(s); projection of primary and secondary impacts of potential in situ reduction technologies; limited understanding of contaminant plume structure and depth of contaminant penetration; rates and role of natural attenuation; need for additional remediation technologies that would complement pump & treat (e.g., in situ treatment and control of surface discharges); and the influence of matrix diffusion on remediation timeframe. Data gaps associated with the vadose zone and perched intermediate zone aquifer (Section 6.3) included: challenges associated with the scale of the vadose and groundwater contamination in a heterogeneous system; effects of Cr(III) precipitate remobilization and colloidal transport in vadose sediments and rock; understanding of vadose sources and key hydrogeochemical controls; complex vadose fracture flow, and migration potential from the vadose zone to the intermediate perched water zone and into the underlying groundwater.
- The process used to designate locations and objectives for the next set of wells was generally reasonable and appropriate. Following installation, the resulting data would support the EM-LA team and regulators in identifying future objectives for monitoring, and the potential location and type of additional monitoring that would be most beneficial.
- Many of the identified data gaps would be most effectively addressed by implementing large scale remedial actions, complementary to pump and treat, such as in situ treatment and control of surface discharges, and then observing responses.
- For RDX, the review team agrees that the natural attenuation strategy is technically defensible and viable and recommends collecting and organizing data using multiple lines of evidence as described in relevant EPA guidance documents. If the multiple lines of evidence do not continue to support monitored natural attenuation (MNA), then the site should consider a contingency for reducing source mass flux to the regional groundwater using a targeted in situ vadose zone treatment.

<u>Provide an independent assessment on alternative remediation decision and implementation processes for subsurface Cr(VI) and RDX plumes observations:</u>

- The "interim" corrective action strategy is aligned with the recommended adaptive site management paradigm for complex sites.
- A full Corrective Measures Evaluation (CME) process could easily get bogged down in the long list of uncertainties and has the potential to lead to disputes that have no clear path for resolution.
- For both Cr(VI) and RDX, the behavior of vadose zone sources is important and will require additional study to support future decision-making and to estimate remediation time frame. However, this should not be viewed as an impediment to advancing near-term "interim" corrective actions.

In summary, below is a breakdown of both the short and long-term recommendations the review team has for EM-LA for consideration based on the observations above.

Short-Term Recommendations

- The review team urges the EM-LA team and regulators to collaborate as they finalize the plans for installing the next phase of borehole/wells. Given the logistics and costs of installing wells to this depth, the review team recommends that decisions on these and other future boreholes emphasize maximizing the value of each borehole for establishing vertical and lateral extent of the contaminant plume while balancing design and construction options to allow multiple uses (e.g., extraction and monitoring) and innovative sampling (e.g., integrated borehole flowmeter testing to provide vertical profiling capabilities).
- The review team supports the proposed accelerated "interim" corrective action process (i.e., developing a preferred remedy based on existing data with the annotation that the objectives need to be clear and a recognition that such a remedy may not achieve final remedial action objectives).
- The review team does not support the short-term need for a Full CME with a comprehensive evaluation process (> circa 2 years), since the current state of knowledge is insufficient to define the suite of actions that will be needed to achieve final remediation objectives.
- The review team recommends developing a consolidated modeling strategic plan as part of the adaptive site management paradigm. This plan should prioritize the phased plans for improving and advancing models so that they can meet the evolving needs of EM-LA. Some of the early actions include incorporating key processes into decision-making models to address the potential for continuing sources.

Medium-Term Recommendations

- The review team recommends documentation of the modeling using available consensus best-practice standards and guides for groundwater modeling. The most important recommendations for advancing regional groundwater modeling to support future stages of remediation include better projections of the location and intensity of source mass flux from the vadose zone and improved estimates of natural attenuation rates.

- The review team recommends considering key alternative conceptualizations and parameterizations as the CSM evolves due to new information and aquifer responses to interim remedial actions.
- The review team encourages staging of major well installation campaigns to allow a period of monitoring after new wells are installed to allow the new information to accrue and be incorporated into the CSM.
- The review team affirms the current process of using the vadose zone modeling as a semiquantitative tool to inform the boundary conditions for the groundwater model (state-of-practice). If a future reduction in the source mass flux is needed to achieve remediation goals, then additional vadose data and modeling capabilities may be required to inform remediation decisions.

Long-Term Recommendations

- Current numerical (constitutive) models could be supplemented in the future by looking for opportunities to implement strategies based on mass balance, mass flux and/or similar emergent or integrative system behaviors.
- The review team recommends implementation of phased remedies and actions to supplement the adaptive management strategy, including: (as needed) actions to address residual sources in the vadose zone and shallow groundwater, boundary conditions and driving forces (i.e., source mass flux and vadose moisture and groundwater movement), and enhanced/natural attenuation.

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Acronyms and Abbreviations

3D	Three-dimensional
ARARs	Applicable or Relevant and Appropriate Requirements
ASTM	American Society of Testing and Materials
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CME	Corrective Measures Evaluation
Cr	Chromium
Cr(VI)	Hexavalent Chromium
CRM	Chromium Regional Model
CSM	Conceptual Site Model
DOE	Department of Energy
EM	Environmental Management
EM-LA	Environmental Management Los Alamos Field Office
EPA	Environmental Protection Agency
ERT	Electrical Resistivity Tomography
FEHM	Finite Element Heat and Mass Transfer Code
HMX	High Melting Explosive
ITRC	Interstate Technology and Regulatory Council
LA	Los Alamos
LANL	Los Alamos National Laboratory
LM	Legacy Management
MADS	Model Analysis and Decision Support
MC	Monte Carlo
MCLs	Maximum Contaminant Levels
MLS	Multilevel Sampler
MNA	Monitored Natural Attenuation
N3B	Newport News Nuclear-BWXT, LLC Los Alamos
NMED	New Mexico Environment Department
NNLEMS	Network of National Laboratories for Environmental Management and Stewardship
NRC	National Research Council
ORP	Oxidation Reduction Potential
P&D	Pipe and Disk
POC	Point of Contact
QA	Quality Assurance
RDX	Royal Demolition Explosive
RA	RDX Regional Aquifer Model
RVZM	RDX Vadose Zone Model
SMEs	Subject Matter Experts
SRS	Savannah River Site
TNT	Trinitrotoluene
USGS	United States Geological Survey
VZ	Vadose Zone
VZM	Vadose Zone Model

1. Introduction

The Department of Energy (DOE) Environmental Management Los Alamos Field Office (EM-LA) is entering an important phase of decision-making and potential technology deployment to address key subsurface and groundwater contamination challenges – notably the hexavalent chromium (Cr(VI)) and Royal Demolition Explosive (RDX) groundwater plumes associated with historical releases at the Los Alamos National Laboratory (LANL). The EM-LA strategies and decisions are informed by many years of field hydro-bio-geo-chemical characterization, laboratory studies, field and pilot tests, and conceptual/numerical modeling, as well as consideration of regulatory requirements and stakeholders' acceptance. To support the upcoming environmental management decisions, EM-LA engaged the DOE Network of National Laboratories for Environmental Management and Stewardship (NNLEMS), a consortium of DOE national laboratories, to provide technical experts to perform an independent review of the LANL Groundwater Strategy. The NNLEMS was charted by the DOE Offices of Environmental Management (EM) and Legacy Management (LM) to provide access to the robust EM-LM capabilities and recognized expertise in the national laboratories.

The overarching objectives of the review are to provide recommendations to support near-term EM-LA decisions for the Cr(VI) plume and for the RDX plume. The proposed near-term remedial actions include design of pump and treat systems for Cr(VI) and monitoring studies for natural attenuation for RDX. For Cr(VI), the review will focus on the readiness for expanding and deploying the next phase of remediation to reduce potential risks and impacts. For both chromium and RDX the review will assess the supporting data, the conceptual and numerical modeling, and the EM-LA technical integration process that supports identifying and implementing strategic, effective and efficient remedies. Appendix A provides summary and key background information on chromium and RDX in the groundwater and vadose zone beneath LANL (excerpted from the scope of work provided by EM-LA). Preliminary questions listed below were developed for the review by EM-LA and, subsequently, refined and finalized as part of the kick-off activities for the Groundwater Remediation Strategy Review.

<u>Questions Focusing on the Hexavalent Chromium Plume:</u>

1. Is the existing data set from the chromium (Cr) groundwater plume sufficiently robust to support selection and design of remedial alternatives? Is the current data sufficient to understand both vertical migration of Cr within the regional aquifer and any potential impact to water supply wells?
2. Are there data gaps that necessitate additional study before selection of the presumptive pump-treat- and reinject remedy as an accelerated cleanup action? (As distinguished from potential data gaps that can be investigated while remediation is underway).
3. Are the Cr numerical models sufficiently robust to support evaluation of cleanup alternatives and remediation designs?
4. Are there traditional or emerging technologies (in addition to pump/treat/inject and in situ reduction) that have not yet been identified and that should be considered as possibilities to accelerate Cr remediation in the regional aquifer?
5. Is it necessary to attempt to control any Cr discharge that may be ongoing from the vadose zone to the regional aquifer? If so, what measures are available to achieve this?

Questions Focusing on the RDX Plume:

1. Is the RDX site (surface, perched-intermediate and regional aquifer) sufficiently well characterized to support a decision of long-term monitoring (as opposed to active remediation)?
2. Are the numerical models of RDX sufficiently robust to support this conclusion?
3. Does the vadose zone model reasonably account for RDX discharge to the regional aquifer from the overlying perched-intermediate zone?
4. In addition to the two surface corrective measures that have already been implemented to remove RDX as a source of recontamination, are there any measures that are necessary, as well as technically and financially feasible, to control vadose zone RDX discharge to the regional aquifer?

The team includes six scientists/engineers, points of contact (POC) for regulatory support, and a technical editor. The participants were selected from the DOE's national laboratories that are participating in the NNLEMS. The participants are recognized state-of-science and state-of-practice experts in the areas of subsurface modeling, remediation system selection, planning, deployment, and regulatory and stakeholder topics. EM-LA and their cleanup contractor, Newport News Nuclear-BWTX, LLC Los Alamos (N3B), provided the information required for the review. Interviews were conducted with regulators (NMED) to obtain the full spectrum of technical, regulatory and scientific perspectives.

2. Primary Background and Target Problem

The purpose of the technical team is to provide an independent assessment on a range of topics, including: the maturity and adequacy of conceptual and numerical models, the logic and defensibility of proposed strategies, and the appropriateness of the time frame for initiating the next phase(s) of remediation. The team also assessed and categorized the urgency of data gaps, affirmed current strategies and approaches where appropriate, and identified alternative or supplemental strategies where these might reduce uncertainty, improve performance, reduce costs, or provide improved robustness/sustainability.

3. Assessment Topics for Addressing Key Issues

The following issues are addressed in the report:

General assessment of the conceptual and numerical modeling, including:

- Assessing the adequacy of modeling to provide a technical basis for environmental management decisions such as initiating the next phase(s) of groundwater remedial action or determining if future risks associated with RDX are low.
- Structuring of the models to include alternative conceptualizations and parameterization of processes to support EM decision-making.
- Using mass balance, mass flux and risk concepts to separately explore (compare and contrast) the future natural and mitigation scenarios for chromium and RDX.
- Evaluating the nature and potential significance of model uncertainties.

Assessment of data gaps, including:

- Identifying data gaps and designation into two categories: a) those that may need to be addressed before initiating further remedial action(s), and b) those that can be managed and addressed during the deployment and operation of the next stages of (interim) remediation.
- Reviewing previous work that identified data gaps needed to advance remediation (e.g., resulting in current plans to install two additional wells) and the proposed time frame for installation, sampling and obtaining representative data.
- Identifying data gaps that would be beneficially addressed by introducing significant stressors to the subsurface (e.g., implementing remedial actions and observing responses).
- Identifying data gaps that are constitutive (i.e., uncertainties in individual parameters) and those that represent emergent properties (e.g., source mass flux and water balance). Assessing the potential to beneficially advance environmental decisions through emphasis of emergent behaviors to overcome the inherent-intractable uncertainties associated with a complex system of this scale (e.g., heterogenous vadose zone over 300 m thick).

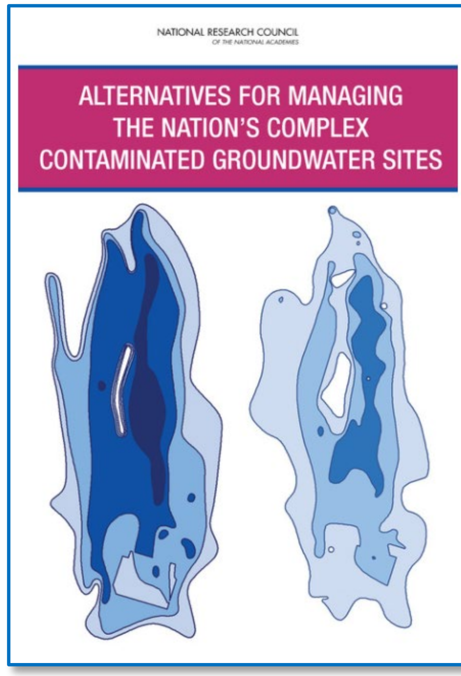
<u>Provide an independent perspective on alternative remediation decision and implementation processes for subsurface Cr(VI) and RDX plumes, specifically:</u>

- For Cr(VI) – weigh the relative benefits and risks of the Full Corrective Measures Evaluation (CME) with a comprehensive evaluation process (> circa 2 years) versus an accelerated “interim” corrective action process (i.e., developing a presumptive (preferred) remedy based on existing data and filling in critical data gaps but using an accelerated planning and deployment strategy).
- For RDX – assess potential risks of the no further action strategy.
- For both Cr(VI) and RDX– assess significance and projected behavior of vadose zone sources on future groundwater contamination and on remediation time frame.

4. Central Theme and Primary Recommendation

A key overarching framework for all of the detailed technical recommendations in this review is the need to alter the remedial paradigm from that of standard remediation processes toward a new classification of the LANL groundwater plumes as a complex site. This strategy and classification provides the structure and new opportunities for facilitating collaborative and positive interactions between DOE and its technical team with regulators and their technical team. Importantly, as described below, the complex site paradigm is broadly accepted and has been inclusive in its development process, including key federal and state regulators at every step. The complex site paradigm is emerging as an important tool in addressing the nation’s most significant environmental challenges; several guidance documents are available to support both the general approach and site-specific applications (e.g., ITRC, 2004 and 2017; NRC, 2013). Likewise, the U.S. EPA Superfund Task Force has recommended broadening the use of adaptive management for complex sites and is currently running select AM pilots (EPA, 2018). **The consensus recommendation of the independent review team is that the LANL groundwater plumes should be addressed in context of the "management of complex sites" paradigm.**

4.1. Framework for Complex Site Remediation



The traditional regulatory implementation paradigm presumes that a reasonable technology (or technologies) can be identified to achieve remedial objectives. In this scenario, the default strategy is a basic "**study → select → design →build → monitor"** linear process. While the traditional paradigm includes a contingency process, the general presumption is that a period of study can support a reasonable and appropriate technology decision that will achieve the final remedial action objectives. For example, under the Resource Conservation and Recovery Act (RCRA), there is a corrective measures study, followed by corrective measures selection based on a set of screening criteria. Unfortunately, complex sites are poorly suited to the traditional linear process; the significant uncertainty inherent in environmental cleanup at complex sites has necessitated more flexible-iterative approaches. Over the past two decades, remediation of complex sites has achieved progress and success by focusing on developing and achieving interim goals (steps toward final remedial objectives) and using the information obtained during each step to resolve uncertainties and to improve and refine the technology decision for later stages of the remediation.

According to the National Research Council (NRC, 2013), "*limitations of currently available remedial technologies … make achievement of MCLs throughout the aquifer unlikely at most complex groundwater sites in a time frame of 50-100 years*." The Interstate Technology and Regulatory Council (ITRC, 2004) further notes that "*technical and nontechnical challenges can impede remediation and may prevent a site from achieving federal- and state-mandated regulatory cleanup goals within a reasonable time frame…. At some sites, complex site-specific conditions make it difficult to fully remediate environmental contamination using proven remediation approaches*." The ITRC guidance lays out a recommended process for remediation management at complex sites, termed "**adaptive site management**." Adaptive site management is useful for sites with significant uncertainty. This approach allows for advancing the remediation despite uncertainties, by using an iterative process that includes periodic evaluations, by updating and refining the conceptual site model over time, setting and tracking interim objectives, and implementing new technologies supporting ultimate objectives.

4.2. Definition of Complex Site – Application to LANL Groundwater

Figure 1 is a simplified composite sketch depicting the scale and some of the flow patterns and features of the vadose zone contamination and groundwater Cr(VI) plume beneath LANL. This figure was modified and expanded from the earlier, 2013, independent technical review (Looney et al., 2012). Figure 1 depicts complex and intermingled infiltration pathways for the various canyons (water sources). Each major pathway is shown using arrows where the red arrows show the interpreted path of Sandia Canyon Cr(VI) contamination to the regional aquifer. Solid arrows represent pathways for which there are data supporting the presence of the pathway, although additional quantification and confirmation of these pathways is needed. Dashed arrows indicate potential pathways that are anticipated to be present and may impact the overall hydrologic system dynamics. All arrows represent pathways for either water or contaminant that could be modified via a remedial action.

A. Sandia Canyon Waste discharge and wetland
B. Sandia Canyon upper infiltration zone
C. Sandia Mortandad Canyon perched water lateral transport at Puye-Basalt
D. Lower infiltration zone and contaminant discharge to groundwater
E. Los Alamos Canyon discharges
F. Perched water lateral transport and mixing with Sandia discharge
G. Mortandad Canyon discharges
H. Mortandad Canyon groundwater plume and mixing with Sandia Cr(VI) plume
I. Regional aquifer Cr(VI) plume

J. Other potential infiltration paths to groundwater

Figure 1 is a composite that shows the multiple canyon drainages (with varying Cr(VI) levels – blue, yellow and red), depicts vadose zone complexities in the form of an isometric flow diagram, and identifies approximate scale of the vadose zone (100s of meters) and scale of the plume in the groundwater (1000s of meters). Note that this figure does not depict geochemistry, knowledge gaps on timing and locations of sources, or some of the related factors that further complicate environmental management. The RDX plume shares many of the challenges of the chromium plume with a relatively higher fraction of the residual mass held up in the vadose zone and a significantly smaller groundwater plume footprint.

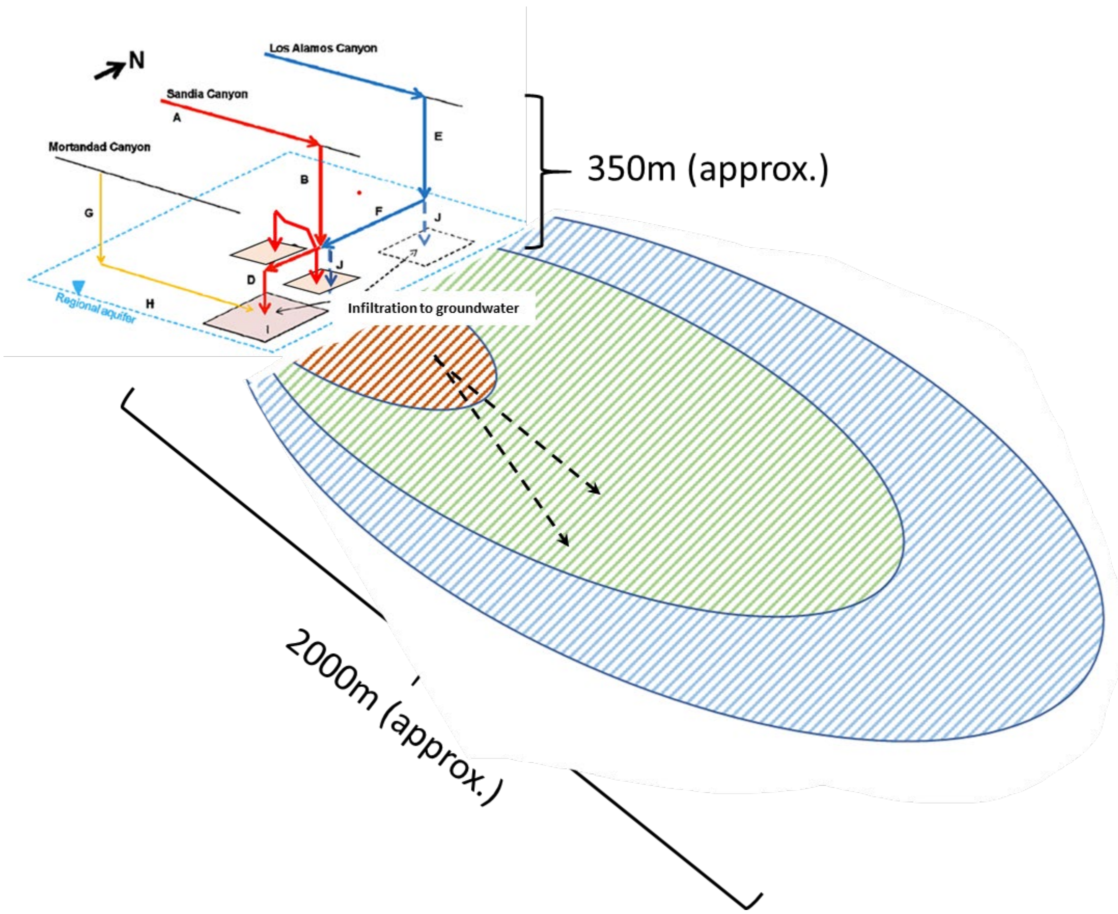


Figure 1. Simplified sketch depicting key complexities and scale for the subsurface chromium (VI) plume beneath LANL (corrected and expanded from Looney et al., 2012).

Recent documents describing management of complex sites provide information on identifying such sites and determining if a site could benefit from applying the complex site framework. Specifically, the guidance documents define a number of factors, including geologic conditions, hydrogeologic conditions, geochemical conditions, contaminant related factors, scale, site remedial objectives, expected changes over time, overlapping responsibilities, institutional controls, land use, funding, and regulators/stakeholder concerns. Within each category, the guidance documents provide specific examples of the types of conditions that would result in determining if a site could/should be considered a complex site. Further, the documents indicate that if a site is considered positive for one or more of the categories, it is a candidate for management as a complex site benefitting from the adaptive iterative approach.

Figure 2 provides a graphical summary of the specific tabulated factors defining complex sites (as developed by NRC and ITRC). As shown in Figure 2, the groundwater plumes beneath LANL satisfy over half of the categories with particularly significant contributions from: a) geologic conditions (e.g., heterogeneity, preferential flow paths, faults, fractured rock, and presence of low permeability media), b) hydrogeologic conditions (e.g., deep groundwater), and c) large scale site. Note that all aspects of the site do not need to be complicated for a site to be classified as a complex site. The New Mexico Environment Department (NMED) regulators/scientists noted that modeling the behavior of the plume below the water table was not particularly complex. However, in follow-on discussion, they and others also noted that the scale, locations, and potential for future source terms to the groundwater were uncertain. Specifically, the location where contaminants enter the groundwater, location of contaminant held up in the vadose zone, the concentrations of the contaminants, their geochemical forms, and potential movement of Cr in groundwater in depth-discrete zones are ambiguous. It is these diverse unknowns, data gaps, and uncertainties that inform our classification of the LANL groundwater plumes. In the final analysis, the definition of a complex site is best determined based on several factors, the presence of significant (and difficult to resolve) uncertainties, criteria satisfied in the table from the guidance documents, and, most importantly, sites that would benefit from iterative and adaptive site management – such as sites where there are technical disagreements that are stifling the advancement of remediation.

The independent review team consensus is that the LANL subsurface plumes, both Chromium(VI) and RDX should be classified as "complex sites."

Technical Challenges	Examples
Geologic conditions ☑	• Geologic heterogeneity/preferential flow paths ☑ • Faults ☑ • Fractured bedrock ☑ • Karst geology • Low-permeability media ☑
Hydrogeologic conditions ☑	• Extreme or variable groundwater velocities ☑ • Fluctuating groundwater levels • Deep groundwater contamination ☑ • Surface water and groundwater interactions and impacted sediment
Geochemical conditions	• Extreme geochemistry (such as unusually high or low pH or alkalinity, elevated electron acceptors, extreme redox conditions) • Extreme groundwater temperatures
Contaminant-related conditions ☑	• Light or dense nonaqueous phase liquids (LNAPL or DNAPL) • Recalcitrant contaminants ☑ • High contaminant concentrations or multiple contaminants ☑ • Emerging contaminants
Large-scale site ☑	• Location and extent of contamination ☑ • Number, type and proximity of receptors • Depth of contamination ☑ • Extensive or comingled plumes ☑ ☑

Nontechnical Challenges	Examples
Site objectives ☑	• Societal expectations and social acceptability ☑ • Changing site objectives • Adopting site objectives that differ from promulgated screening levels or closure criteria (such as MCLs)
Managing changes that may occur over long time frames ☑	• Phased remediation ☑ • Future use • Site management • Multiple responsible parties • Staff turnover/Loss of institutional knowledge • Litigation
Overlapping regulatory responsibilities	• Federal and state cooperation • Changing laws and regulation • Financial responsibility • Orphan sites • Contaminants without regulatory criteria or guidance (such as emerging contaminants)
ICs	• Tracking and managing ICs • IC enforcement • Long-term management of institutional controls
Changes in land use ☑	• Changing land use or water use • Multiple owners • Site access ☑
Funding	• Lack of funding (state, federal, or private industry) • Politics that alter funding/program priorities • Unwilling or unknown RPs

In addition to the nontechnical challenges listed, accounting for stakeholder perspectives is a significant challenge at some sites. ☑

Figure 2. Annotated listing of factors that define "Complex Sites." Items relevant to LANL groundwater were checked based on consensus determination of independent review team.

4.3. Common Collateral Impacts of the Traditional Paradigm when Applied to Complex Sites

There are a number of adverse collateral effects that often result from applying the traditional linear "deterministic" management strategy versus a preplanned adaptive iterative management strategy. Importantly, the traditional strategy presumes that the process will result in a technology, or a portfolio of technologies, that will achieve the final remedial action objectives. For the site owner, this can provide a sense of certainty -- "…if I do follow this remedial plan, at the end I will be done…"; however, if the remediation underperforms and contingencies are needed, this initial perceived certainty can lead to assessments of failure, resistance to taking further action, and a desire to jump directly to technically impractical solutions. For the regulator and stakeholder, the paradigm that the selected technology (or technology portfolio) needs to have a high potential to successfully achieve final remedial objectives can lead to intractable requests for data and analysis and/or requirements to grossly overdesign remediation systems leading to higher costs and inefficiencies (e.g., using a source treatment for a dissolved plume or assuming that pump and treat will effectively remediate a source zone). Finally, the traditional paradigm encourages a focus on filling in data gaps and resolving uncertainties prior to taking action; thus, the attention of both site staff and regulators is on what is not known, and less focus is put on what is known. While the traditional approach does provide a pathway for responding to contingencies, for example through ongoing-periodic "5 year" reviews, the composite collateral impacts of the traditional deterministic approach can lead to conflicts and disputes between parties making progress on remediation at complex sites difficult.

4.4. Principal Benefits of Adaptive Management Paradigm

Managing complex sites relies on an iterative-adaptive paradigm that explicitly recognizes that it is difficult, or intractable, to generate advance knowledge that is sufficient to provide a technically defensible basis for the final remediation decision, design, and implementation. The adaptive management strategy encourages a focus on what can be done now with the information that is known, what can be done now to stabilize the contamination, and what achievable interim objective can be set that will allow success for all parties. Technologies can be optimally implemented in a manner that is targeted in space, time, and goal. Finally, implementation of the technologies can, and should, be done in such a manner that the system response to each action provides meaningful data to help resolve uncertainties and inform the next stage of remediation decisions and design.

A key to the adaptive management strategy is that the stages of the remediation need to be planned to play out for timeframes that provide stability and certainty for the site owner, that provide data over representative time scales for the particular site (often 5 to 10 years), and that allow time for additional data collection and follow-on technology decision evaluation and regulatory approvals. As described, the adaptive process requires a trust and collaboration among all parties. The optimal collaboration requires the various parties to recognize the perspectives and risks of those across the table. For example, in this scenario, site owners are proceeding without the certainty of the total future scope and need, or regulators may need to provide space for nonstandard or innovative approaches. Ultimately, all parties are taking risks with the caveat that one or more actions could underperform. The potential benefits of the collaboration are significant with the potential to facilitate steady progress toward remedial objectives.

4.5. Adaptive Management Paradigm and Technical Impracticability

Significant data gaps and uncertainties will always be present at complex sites, even after a long period of characterization and modeling. The intractability of resolving all data gaps could be posited as a basis for technical impracticability. We urge that technical impracticability be considered a classification of last resort and be contemplated after reasonable iterative-adaptive management activities have been performed. Notably, technical impracticability does not mean that the site owner can stop remediation activities and expenditures. Instead, it implies that the owner must continue to take action to protect receptors for an indefinite period of time. Thus, a traditional adaptive management paradigm as described in more detail below will put in place the infrastructure for providing protection of receptors, will put the protections in place in a timely manner, and will provide the data that could potentially lead to a remediation portfolio that will meet remedial objectives and eliminate the need for a determination of technical impracticability. Adaptive management supports a primary shared goal to clean up and restore the groundwater system to the extent practicable but is also the most appropriate path to a technically based collaborative determination of technical impracticability.

4.6. Typical Adaptive Management Phases and Actions

The phases and actions in the adaptive management paradigm are defined by clear-limited objectives. For example, a pump and treat system is often put in place to control or limit the spread of the plume. The system is designed to meet that objective and there is no attempt to fully remediate residual sources or fully remediate the plume to remedial objectives. The limited design objectives avoid overdesigning the pump and treat in an inefficient attempt to achieve goals that this system will not be able to meet (and a potential future assessment that the pump and treat was a failure). In the adaptive management paradigm, the pump and treat can be efficiently designed to meet an achievable objective, can be implemented quickly even with typical data gaps, can provide information to resolve data gaps, and can reduce the sense of urgency while allowing future tests of technology in or near the residual source areas. The pumping can also provide some mass removal and help resolve where vadose sources (windows) are entering the groundwater. At other DOE sites, the protections provided by an initial pump and treat system in an adaptive management paradigm encouraged testing of thermal and in situ redox treatment technologies that would otherwise have been difficult to test because of the potential to spread contamination. The stages of an adaptive management paradigm are often focused on spatial zones in the subsurface but can also be focused on particular geochemical species or conditions, interfaces, flux boundaries, and/or areas for enhanced attenuation or passive/active interception.

Figure 3 exemplifies the spatial framework and some of the associated factors that inform adaptive management. This figure was originally developed in the early 1990s to communicate the approaches DOE was using to manage complex groundwater remediation at the Savannah River Site (SRS). Efficient and effective environmental cleanup requires matching the character of remediation and stabilization methods to the nature of the target zone of contamination, as the nature of the target zone evolves through the life of the remedial project. Figure 3 shows the different areas of a generalized contaminant plume, i.e., the disturbed zone, the impact zone, and the transitional zone, and describes the general characteristics of each zone. Thus, physical and chemical methods (e.g., trapping, immobilization, destruction, or isolation) that directly address the source contaminants are often appropriate for the disturbed zone during the remedial process. A variety of methods that include both active treatments (e.g., pump and treat or active bioremediation) and enhanced attenuation technologies (e.g., geochemical manipulation or reactive barriers) are often suitable for the primary contamination zone or impact zone. Various strategies based on natural attenuation processes may be applicable to the primary contamination zone and these passive methods are well suited to the transition or baseline portions of the plume. This spatial conceptual framework, based on matching technology attributes to site-specific conditions and needs, has proven to be effective in supporting environmental management decisions. Key factors in selecting rational and optimal remedies are captured in existing regulatory decision guidelines and include ability to implement, expected performance, uncertainties/risks, and costs for actions as they apply to the various target zones. In addition to the traditional factors, emphasis is increasingly placed on sustainability and metrics for evaluating remedial actions and balancing benefits against the associated environmental burdens and collateral damages.

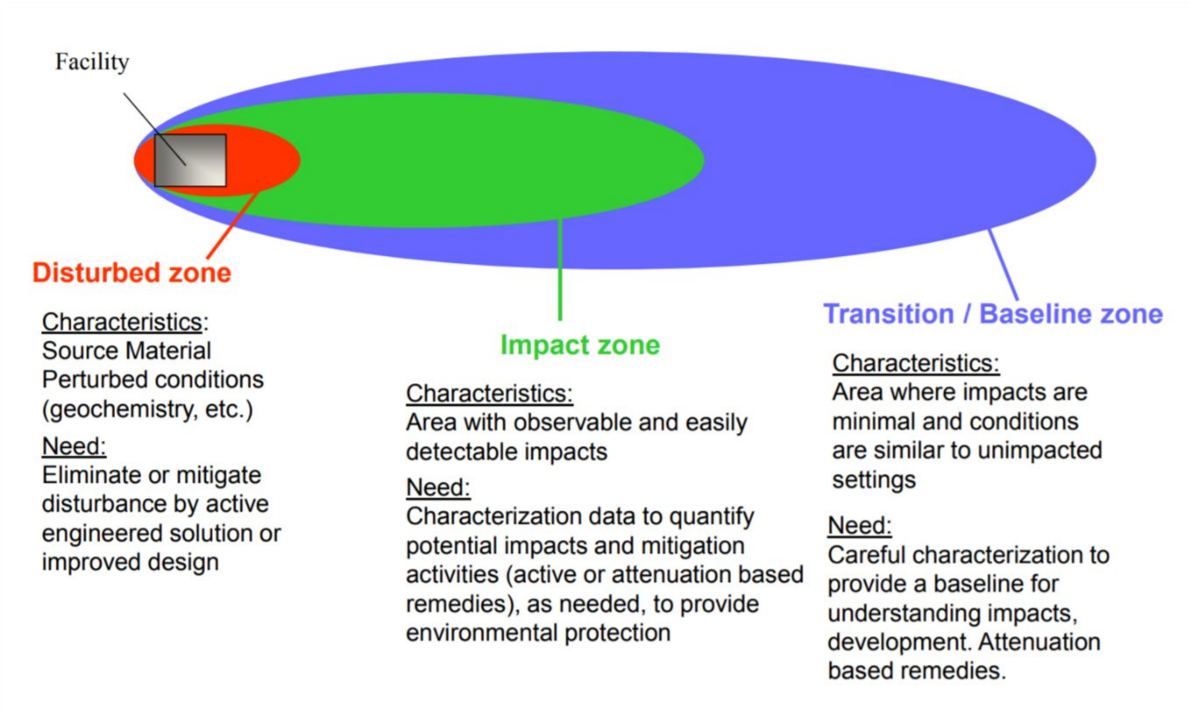


Figure 3. Simplified conceptualization of an example spatial framework at a contaminated groundwater site. At LANL, the >300m thick vadose zone would be added above the red oval and the complex geometry of the transport pathway emphasized.

For the LANL groundwater plumes, future targets for adaptive management remedial actions, following limited pump and treat if implemented, could include the vadose zone (modifying transport pathways, driving forces, and/or treating areas of accumulation), residual source zones near/in the groundwater, and natural/enhanced attenuation.

4.7. LANL-Specific Adaptive Site Management Recommendations

The independent review team was impressed by the capabilities, experiences, innovativeness, and insightfulness of the technical representatives from both the regulators (NMED) and DOE support contractor. As described in the later sections of the report, the work at the site was generally state-of-practice (or better) and in many cases was state-of-art. The reviews from the regulators were thorough and often provided useful concepts for consideration and future study/resolution. Given the quality and quantity of work by all parties, the independent technical team is confident in a long-term synergistic and positive relationship. We believe that disputes could be minimized based on emerging guidelines for iterative-adaptive management of complex sites. We encourage consideration of the referenced guidance documents and possibly setting up a collaborative team, including all parties, to consider and plan the strategic transition.

5. Modeling

5.1. Modeling Approaches

Multiple conceptual models have been generated to represent key elements of groundwater flow and contaminant transport of chromium and RDX at LANL. These include representations of the vadose zone and the regional aquifer in chromium and RDX contamination areas. Below is a short description of each numerical model. Full descriptions may be found in EP2018-0026 (LANL's *Compendium of Technical Reports Conducted Under the Work Plan for Chromium Plume Center Characterization*) and EM2020-0135 (LANL's *Fate and Transport Modeling and Risk Assessment Report for RDX Contamination in Deep Groundwater*).

5.1.1. The Chromium Regional Model (CRM) was developed with the objectives of providing spatial and temporal predictions of Cr concentrations in the regional aquifer and their uncertainties, understanding the locations and fluxes associated with hydraulic windows (see Figure 1), and evaluating the aquifer monitoring well network (Jordan et al., 2021). The top of the model is defined by the regional-aquifer water table, and the hydrogeologic parameters are assigned through inversions of field data. The model is calibrated to reproduce:

a. Water levels measured from monitoring wells in the regional aquifer
b. Transients in the hydraulic drawdowns in the regional aquifer caused by water-supply pumping and project-related pumping activities
c. Chromium concentration transients observed in regional aquifer monitoring wells.

5.1.2. A three dimensional, coupled vadose-zone/saturated zone model of the chromium contamination area (LANL 2008). The major goals of these model analyses are to:

a. Simulate groundwater flow and contaminant transport behavior at the site.

b. Predict the fate of contaminants in the vadose zone, including impacts on the regional aquifer concentrations of proposed/potential remedial actions.
c. Analyze the system behavior under different future natural and mitigation scenarios.

Various types of model analyses (model inversions and calibrations, sensitivity analyses, uncertainty analyses, etc.) have been carried out using the open-source code MADS (Model Analysis & Decision Support). Forward model runs including flow and transport modeling are accomplished using the Finite Element Heat and Mass Transfer Code (FEHM).

5.1.3. The RDX Regional-aquifer Model (RA) was developed as the primary decision support tool for analysis of downgradient RDX concentrations (Foster et al. 2020). The RA was informed by the conceptual site model and calibrated using site RDX concentration data, hydraulic head measurements, RDX concentration trends, water level gradients, and spatial homogeneity of saturated hydraulic conductivity. The model has been calibrated using data through December 2019. Model inputs were described with informative prior distributions. Where data was scarce, other lines of evidence were used to inform the distributions, including the multiphase RDX Vadose Zone Model (RVZM) and Pipe & Disk (P&D) analytical screening tool, which was used to identify the source zone locations in the aquifer. The RA was integrated into the decision support tool and risk assessment, which included extensive uncertainty quantification and ensemble simulations.

5.1.4. The RDX Vadose Zone Model (RVZM) is considered as another line of evidence in bounding parameter distributions/ranges, particularly where few data or literature knowledge previously exist. In particular, the RVZM is used to estimate travel times and pathways of RDX from its infiltration below the surficial alluvial aquifer to the top of the regional aquifer water table and to help formulate distributions of RDX concentration and recharge fluxes to the RA.

The main modeling efforts are focused on refining the two regional models (CRM and RA) through updated calibrations and heterogeneous parameter estimation. It is reasonable to focus the modeling and uncertainty quantification activities on the regional aquifer since the compliance points are in the regional aquifer – however the projected spatial and temporal source mass flux of both Cr and RDX are currently uncertain. While characterization of the area associated with the initial release of RDX has been performed, there are insufficient data in the perched water and vadose zones to support parameterization of a full three-dimensional (3D) unsaturated flow and transport model. Further, simulating the vadose zone flow and transport (particularly including perched aquifer tables) is difficult and time consuming; these various factors generally support the strategy of decoupling the vadose and saturated zone modeling. Such decoupling of the vadose-zone model and saturated-zone model has been commonly used, for example, in the assessments of the Yucca Mountain and the Hanford Central Plateau. The current approach – assigning the uncertainty in the source zone transport and input to the vadose zone – seems a reasonable path forward and good usage of resources/efforts. Overall, the numerical conceptualizations are considered to meet State of the Practice criteria in that the approaches taken to build, calibrate, and employ these models are current and generally accepted as good practice within the Environmental Management Field.

5.2. Model Sufficiency

In addition to the modeling approaches, the sufficiency of the current models and modeled results to provide robust decision support was evaluated. This evaluation considered the ability of the current models to be used to answer the range of expected future remediation questions (e.g., can increases or decreases in infiltration through accumulated vadose zone sources be represented? Can models account for source zone isolation, stabilization, destruction, etc. ?) As part of this exercise, comments from NMED on the most recent semiannual progress report on chromium plume control performance were considered (NMED, 2021).

5.2.1. Current Modeling Objectives and Interim Goals

Current models are appropriate and sufficiently robust to support initiating the proposed next phase(s) of remedial action – pump and treat for Cr(IV) and monitoring of natural attenuation for RDX. These models should be applied to develop achievable "interim" objectives for each proposed remedial action, to optimize the designs for those limited-stated objectives, and to identify criteria and potential contingency actions. During the next stages of modeling, we recommend focusing on improved communications of interpretations and modeled results rather than making major changes in the numerical models themselves. A key area of emphasis, identified by both NMED and this review team, is developing explicit capture zone descriptions and plume projections for any proposed pump and treat option.

The field data (water levels, potentiometric surfaces, and concentration maps) being used for calibration appear to be appropriate to support the numerical modeling of the groundwater. However, continued focus on producing the highest quality data is recommended. For example, consider developing specific documented guidelines on the timing of data collection, focusing on near-synoptic water level data (e.g., quarterly sampling during stable periods of time with limited pumping) and more intensive synoptic data collection when significant actions such as well pumping are initiated.

5.2.2. Longer-Term Modeling Objectives and Site Goals

Currently, the modeled results do not provide a firm quantitative basis to support the entire portfolio of environmental management decisions needed to achieve final remedial action objectives. Specifically, the current conceptual model does not provide sufficient information to confidently support the understanding of the remaining residual vadose zone contaminants and projecting the quantity, location, and future release profiles of Cr(VI) and RDX into the groundwater (e.g., predicting releases, flushing and back diffusion of Cr from the vadose zone tuff into fractures, and subsequent migration to groundwater). Thus, the models do not robustly support a technical basis for design of remedies to manage and control the future source mass flux. Importantly, the existing models and model results provide reasonable and effective support for several types of near-term remedial action decisions – notably design of pump and treat systems for Cr(VI), supporting a period of monitoring and study for natural attenuation of RDX, and projecting the plume growth and risks to potential receptors over the next several decades. Thus, as described below, refinement of the modeling over time will be needed over the longer term.

The capabilities (strengths and weaknesses) of existing models exemplify the importance of our recommended "complex site" classification for LANL groundwater plumes. Such a classification would recognize the intractability of a fully comprehensive model, would encourage collecting targeted-supplemental data, and would provide a pathway for the model to evolve over time to provide key capabilities.

5.3. Integrated Modeling Recommendation

While the EM-LA team has generated reasonable and technically defensible models, these models are currently insufficient to support efforts to achieve final long term remedial action objectives. The review team has developed a number of integrating and specific recommendations for consideration. In general, the modeling process would benefit from an overarching structure and plan. This would reduce the temptation to address individual topics on an ad hoc basis while simultaneously avoiding the intractability of addressing all the outstanding issues at the same time (i.e., attempting to fix everything at once).

Consistent with the adaptive site management framework, the central modeling recommendation of the independent review team is to focus on developing a clear, organized, prioritized, and sequenced plan for modeling Cr(VI) and RDX. Consistent with the complex site paradigm, this consolidated modeling strategic plan would recognize the challenges and intractability of attempting to develop a perfect model (i.e., a model that prioritizes high *accuracy* in addressing the many legitimate questions that can be raised), focusing instead on advancing the current high-quality models in a planned, organized, and strategic fashion. Where possible, the consolidated modeling strategic plan should look for technically based opportunities built on data and theory to simulate the observed emergent behaviors of the complex system, rather than relying solely on the discretized deterministic traditional constitutive approach. This system response modeling is best informed by data collection during the implementation of future large-scale testing and phases of remediation, which are the basis for adaptive management for complex sites.

We recommend close cooperation among the technical teams from EM-LA and NMED in developing the consolidated modeling strategic plan. We recommend organizing the consolidated modeling strategic plan into broad objective-based categories such as the subsection headings in the narrative below. We recommend developing the plan by identifying objectives rather than the precise details of all actions that are needed/planned (an attempt to develop the precise details is unlikely to succeed and would be burdened by the same intractability dynamics as the current discussion). The final document should outline the categories of planned activities, the objectives of each of the planned activities, the prioritization and sequencing of the activities, and the requirements and success metrics for each category of activities. We recommend developing the consolidated modeling strategic plan as a key next step and propose a target time frame of approximately six months with an appropriate follow-on period for regulatory concurrence and finalization.

5.4. Opportunities for Modeling Enhancements

This evaluation procedure resulted in a number of recommended opportunities for modeling enhancements in both the model construction and results communication. In general, implementation of these recommendations would result in incremental model improvements; thus, while these might be beneficial, we have assigned them a moderate to moderately low priority. In conjunction with the included recommendations to improve the site conceptual models, we recommend consideration of the following specific actions to improve the robustness of numerical models:

5.4.1. Estimation of Hydraulic Conductivity

There were extensive efforts to estimate the hydrological parameters and their uncertainty in the RA. For RDX, distribution of hydraulic conductivity was developed while considering the scale dependency of hydraulic conductivity on factors such as core soil texture data (small-scale), single-well pump tests (intermediate-scale), and inverse modeling of the flow and transport model. For Cr(VI), the hydrological model was calibrated based on the pilot point method (Jordan et al., 2021). The pilot point (or anchor) methods were developed in the 2010s and have been extensively used in the industry and academia. This method enables hydrological model calibration including the spatial heterogeneity of the hydraulic conductivity field.

Interim calibration results for Cr(VI) presented in Jordan et al. (2021) were used to demonstrate workflow. However, their calibration results (Figure 4) do not adequately capture the breakthrough even though the data points are within the uncertainty bounds. The arrival time is different, and the shape of the breakthrough is not matched. We recognize that matching concentrations is quite difficult (Chen et al., 2020). Still, we have concerns that all the breakthrough curves (from the Monte Carlo (MC) simulations) vary only in magnitude but not in the arrival times.

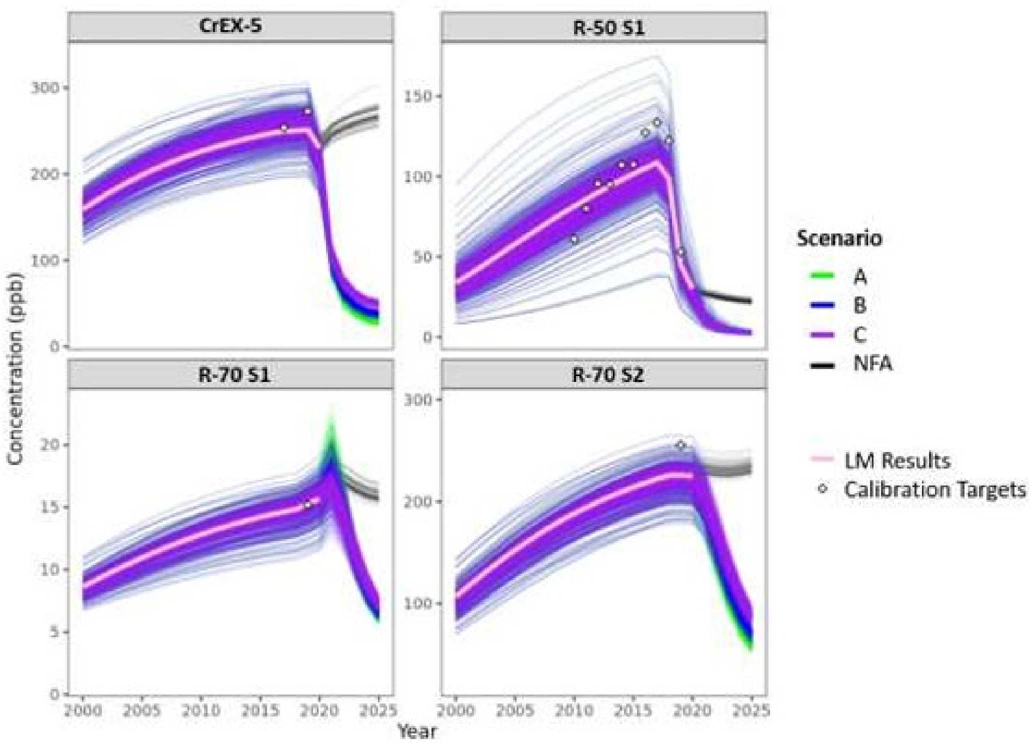


Figure 4. Figure 7 from Jordan et al., 2021. "Probabilistic Groundwater Modeling of the Chromium Plume at Los Alamos National Laboratory – 21165". Original caption: Forward modeling results for the focus wells, using the MCMC posterior parameter sets from the uncertainty analysis. The LM (classical

calibration) result is also shown through the time period with history-matching (i.e., concentration calibration targets through 2019).

Recommendations from the independent technical review team include:

- Changing the objective functions during the calibrations to moment-based metrics, so that the characteristic metrics (such as magnitude/arrival of breakthrough curves) are represented (Harvey et al., 1995; Nowak et al., 2006; Murakami et al., 2010),
- Checking whether the source zone area or dispersivity is not overestimated (Figure 7 in Jordan et al., 2021 suggests that the actual breakthrough is sharper),
- Considering the development of guided approaches that incorporate semiquantitative knowledge of geologic structures and depositional processes to maximize the fidelity of the hydraulic conductivity field to real-world conditions and to support improved future simulation of structurally controlled preferential flow and macro-scale matrix diffusion.

Similarly, the topic of a potential deep high-permeability (preferential) pathway has been raised by NMED. This specific pathway is somewhat speculative, and significant additional verification data are needed to determine the presence and significance of such a pathway. The independent review does not support including this specific feature in the baseline model at this juncture, but a set of sensitivity runs may be appropriate. The nature and parameterization of such a scoping model and sensitivity runs could be collaboratively developed by the LANL modeling team and the NMED subject matter experts (SMEs). In a general sense, preferential pathways and heterogeneity are known to exist in all hydrogeological systems and the various models are important tools for exploring alternative CSMs.

5.4.2. Estimation of Dispersivity and Matrix Diffusion Impacts

The probability distribution of the dispersivity for the RA was developed based on extensive literature review; however, site data were not used. An extensive review of the dispersivity and its scale and direction dependency were discussed in the report. However, it is not clear why the other site datasets were used since Gelhar et al (1992) was based in a completely different site with a different geology type. The dispersivity is also dependent on the integral scale of the spatial heterogeneity of hydraulic conductivity (Rubin, 2003).

We recommend considering the tracer test inversion approach to estimate the dispersivity (Nowak and Cirpka, 2006) and to help assess potential impacts of macro-scale matrix diffusion. Additional modeling of the attenuation resulting from matrix diffusion may be useful and appropriate (see Farhat et al., 2022 for example).

5.4.3. Sorption Coefficient

There were extensive efforts to estimate the sorption and Kd values in the RA based on the literature review and sorption experiments using the cores and groundwater from the site. In the ensemble simulations, one Kd value was sampled in each simulation and assigned to the whole aquifer.

RDX's sorption depends on matrix mineralogy, pH, organic carbon content, and other factors. Redox conditions can also influence the apparent sorption, as reducing conditions can result in RDX degradation. Alkaline hydrolysis of RDX can occur under highly alkaline (pH > 10) conditions. Although the regional aquifer is generally in one formation (the Puye Formation), Kd can vary in space if the geochemical conditions vary. While this is not a high priority, a scoping evaluation of the potential worth of including a spatial-conditional heterogeneity in Kd in groundwater models – the review team recommends implementing spatial-conditional heterogeneity in Kd only if the scoping evaluation indicates a potential to significantly impact model results.

5.4.4. Source Zone Treatment

Although the RVZM was used for general travel time estimation, the results were not directly coupled because "the RVZM has a limited extent that does not include (key vadose zone complexities and the resultant) location(s) where the highest RDX has been measured in the regional aquifer." It is not clear why. The source zone is important, and "hydraulic windows" are among regulator concerns for both Cr(VI) and RDX. Additional vadose zone model (VZM) development is needed to support future long term environmental management decisions.

As mentioned in the previous section, a primary focus on the regional aquifer appears to be appropriate at this time. However, the presence of preferential flow paths in the vadose zone are likely and in the groundwater are speculated. Preferential flow paths have been highlighted by regulators as topics of concern. As depicted in Figure 1, complex-circuitous preferential flow paths in the vadose zone have been linked to "hydraulic windows" where contaminants enter the deep regional aquifer. These entry windows are important because they determine the source term in the RRM. The precise location, scale, and magnitude of the current and future source mass flux to the regional aquifer is uncertain. We support the EM-LA team strategy of incorporating a putative set of preferential vadose zone (VZ) paths in current models because this provides an improved estimate of localized entry concentrations and a generalized scale. Ignoring the preferential pathways would directly lead to simulated breakthrough curves that are broader than the actual breakthrough. We believe that incorporation of preferential VZ flow pathways in the conceptual site model (CSM) and in configuring the numerical modeling is a commendable state of practice activity with the following caveat: the current implementation of the location and spatial extent of the hydraulic windows is uncertain and will need to be improved in the future to support the development of a complete environmental management remediation portfolio. In this important topic, the independent review team recommends moving the work from state-of-practice toward state-of-art. The refinement can be initially extended using historical plume data, responses to the recent interim pump and treat, targeted characterization, and responses to future large scale remediation activities such as pump and treat, in situ source mass flux controls, and boundary condition modifications.

We encourage the EM-LA team to evaluate the current VZ models to avoid potential misfit biased towards dilution due to: (1) the actual source zone to the regional groundwater model (infiltration window) is smaller, leading to potential higher local concentration, (2) there is a more pronounced preferential flow in the regional aquifer, and/or (3) the grid size is numerically contributing to dispersivity.

Future improvement of the VZM is important to consider, particularly on the characterization side because a significant fraction of RDX mass remains in the vadose zone for RDX and a significant residual mass likely remains for chromium. The extent of perched zones is important because they modulate the source mass flux to the regional aquifer. In addition, the potential infiltration window or fast flow paths needs to be identified adequately, because they determine the near-field plume characteristics in the regional aquifer model. The challenge of VZ depth and difficulty of access to the regional aquifer results in data and well network limitations, increasing the need to maximize the benefits and strategic value of other types of recommended characterization activities such as permeability estimation (Broxton et al., 2021). Geophysical methods for the vadose zone (such as electromagnetic surveys and seismic methods) should be explored to help identify or confirm preferential flow paths and the location and spatial extent of hydraulic windows.

In addition, we encourage the EM-LA team to do numerical simulations of several reasonably-bounded extreme scenarios (e.g., localized sources with high concentrations). These simulations would demonstrate the safety margin that exists in their conceptual model.

5.4.5. Boundary Conditions

The EM-LA team has significant historical data and justification for the boundary conditions used in the model for the regional aquifer model, including information on infiltration (precipitation, evapotranspiration, surface water discharges and flow, topography, groundwater pumping, etc.). The information is generally sufficient for supporting many of the next environmental management decisions. We recommend considering gathering supplemental data (see below) and augmenting the boundary conditions in key areas to support some of the future environmental management decisions that may be needed. Notably, we recommend developing a more granular understanding of the drivers and location of surface infiltration (particularly along the length of the channels that received original major Cr(VI) discharges). We also recommend gathering confirmatory information on the significant amount of recharge from the toe of the upgradient hills/mountains because this water is important in the model results, influencing (diluting) the concentrations of RDX. The LANL modeling team presented reasonably compelling information suggesting that dynamic changes in offsite pumping should not be strongly influencing modeling results for the Cr(VI) plume. However, it would be a good practice to examine this topic further (as a moderate to moderately-low priority) because some of the offsite pumping wells may correspond to potential exposure/risk.

5.4.6. Capture Zone Mapping

To strengthen site interpretations and enhance the utility of results for actionable decision support, we recommend the modeling team supplements current documentation of results with capture zone and flood zone interpretations by hydrogeologic mapping on top of water table maps and particle tracking for comparison. Document impacts to the capture zone of injection/extraction numerical experiments and cite results of these and any other sensitivity studies in interpretations of behavior of the current system or future proposed systems.

5.4.7. Water Table Mapping

Similarly, we recommend the team produce additional water table maps. Compare kriged results to simpler three-point estimations, produce maps of the changes in water table elevations on a quarterly basis, and quantify impacts of variable observed water levels in terms of uncertainty. If disparities are uncovered, consider both advanced interpolation options (for instance directional kriging) as well as identification of critical locations of data gaps.

5.4.8. Explicit Adherence to Standards

Because of the level of complexity and scrutiny at this site, we recommend explicitly mapping the steps taken in building, interpreting, and presenting results from site models to workflows described in federal and international groundwater modeling standard; see numerous relevant references from the American Society of Testing and Materials (ASTM), EPA, and United States Geological Survey (USGS).

5.5. Recommended Additional Documentation and/or QA Tools

The general assessment of the independent review team supported the general high quality and current status/approaches in the vadose zone and groundwater models. Normal quality checks, validation and verification efforts were described by the team and appear to be reasonable. However, a notable deficiency is that the documentation and QA for the work is not currently organized and maintained according to the latest ASTM guides and standards. We recommend that the modeling team implement actions within the Consolidated Modeling Strategic Plan to implement these industry standard guidelines for organizing and maintaining model information and traceability. A current listing of relevant ASTM guidelines and standards is provided in the table below.

Table 1: Relevant American Society for Testing and Materials (ASTM) Standards

ASTM Number	Title	Year
ASTM D5979-96	Standard Guide for Conceptualization and Characterization of Groundwater Systems	2014
ASTM D5447-17	Standard Guide for Application of a Numerical Groundwater Flow Model to a Site-Specific Problem	2017
ASTM D5490-93 (e1)	Standard Guide for Comparing Groundwater Flow Model Simulations to Site-Specific Information	2014
ASTM D5609-16	Standard Guide for Defining Boundary Conditions in Groundwater Flow Modeling	2016
ASTM D5610-94	Standard Guide for Defining Initial Conditions in Groundwater Flow Modeling	2014
ASTM D5981/D5981M-18	Standard Guide for Calibrating a Groundwater Flow Model Application	2018

ASTM D5611-94	Standard Guide for Conducting a Sensitivity Analysis for a Groundwater Flow Model Application	2016
ASTM D5718-13	Standard Guide for Documenting a Groundwater Flow Model Application	2013
ASTM D653-14	Standard Terminology Relating to Soil, Rock, and Contained Fluids	2014

6. Potential Methods for Data Gap Closure

6.1. Integrated Characterization, Geology, Biogeochemistry, and Remediation Recommendations

There are a number of challenges and opportunities related to future characterization and site-specific geology and biogeochemistry, with a focus on potential remediation options to consider for the future portfolio. These deliberations were done in the context of our overarching recommendation for classifying LANL groundwater according to the complex site paradigm and presuming that a suite, or portfolio, of remedial actions will be needed to address these important and recalcitrant contaminant plumes. Further, the effort was informed by the substantial history of characterization, field testing, and the data and results from the interim pump and treat that was recently performed to control the Cr(VI) plume footprint, and measurements of the distribution of RDX in the nearfield vicinity of the release area.

Recent field testing demonstrated that targeted pumping, treatment, and injection can be effective in limiting the expansion of contaminant plumes in the groundwater beneath LANL. Thus, the review team generally supports an EM-LA next-step strategy to implement an additional phase of pump and treat for Cr(VI). However, based on experience at complex sites, pump and treat alone is unlikely to achieve remedial objectives in a “reasonable” time frame (e.g., 30 to 100 years). A strategy that includes additional targeted pump and treat for Cr(IV) should be designed to meet clear and achievable objectives and would likely need to be integrated into a more comprehensive strategy, including activities that provide source mass flux control and enhanced/monitored attenuation. Similarly, there are reasonable data suggesting substantive attenuation of RDX in the vadose zone, but this information does not currently meet all of the guidelines for documenting monitored natural attenuation as described by EPA; we recommend steps to augment the information. We encourage organizing evidence of attenuation for both Cr(VI) and RDX using the lines of evidence outlined in EPA guidance documents. Toward this end, a mass-balance based conceptual site model is recommended as an important programmatic element. While there are significant data gaps and uncertainties related to mass balance at this site, this process would assist in prioritizing data needs/interpretation and would dovetail with the modeling recommendations described above. A mass-balance-based approach would support targeted and optimized technology deployments, a combined remedy paradigm including plume management and source mass flux controls, and appropriate future transitions to enhanced or monitored natural attenuation.

Regulators expressed concern about current conceptual models and how these are presented and used in developing and supporting decisions. For example, the nature and projection of mass flux into the groundwater over time has been treated inconsistently (“declining significantly” based on data in

PowerPoint presentations but assumed constant in models) – interpretations for such a key factor significantly impact the potential combination of technologies/actions needed to meet phased adaptive site management objectives. We encourage developing decisions and actions based on the best current conceptual models, even in cases where significant uncertainties persist. However, significant and important uncertainties and the associated hypotheses should be clearly identified, be assessed by sensitivity analysis, and be subject to contingency mitigation.

Significant and commendable progress has been made in understanding, modeling, and planning for mitigation of contaminants in LANL groundwater. Some of the observations and recommendations from a previous independent review (Looney et al., 2012) remain relevant and we urge revisiting those as a component of developing the path forward (notably recommendations related to incorporation of large-scale attenuation processes and use of geochemical trends and fingerprinting). The independent team provides more specific thoughts, topical observations, and recommendations below.

The review team supports and recognizes the several decades of general high-level technical work by the EM-LA team and the high-level-focused technical review being provided by NMED. These wide-ranging past and present technical efforts have been reasonably comprehensive. Thus, the bulk of the recommendations being made by the technical team build on the past work, focus on strategic programmatic adjustments, and consider the real-world challenges of understanding and remediating contaminants in a complex geology with a significant depth to groundwater. In this scenario, practical considerations become important, such as the cost of well installation, infrastructure needed to collect samples from depth, geologic heterogeneity, and geochemical representativeness of samples.

Consistent with the recommended adaptive site management paradigm, our review urges the EM-LA team and NMED regulators to develop a sequenced and coordinated phased strategy that balances multiple and competing objectives, maximizes the value of future characterization and monitoring investments, and allows sufficient time for each phase to provide actionable information. The entire sequence of recommended phases might include five categories: 1) plume control and risk mitigation, 2) vadose zone source mass flux characterization, 3) source mass flux control (in the groundwater), 4) vadose zone and boundary condition controls, and 5) documentation of attenuation processes. We recommend that the information be developed in a stepwise responsive manner over 20 to 30 years with time allowed for data to be gathered and interpreted in each phase. Each major phase or action should be run for a sufficient time period to allow the system to respond sufficiently to elucidate key information, and those data should be used to inform and adjust future actions.

6.2. Regional Aquifer

6.2.1. Data gaps in regional aquifer current remediation implementation and testing (i.e., groundwater pump and treat, abiotic/biotic reduction testing) and preliminary recommendations

Conceptual models and predictions for the regional groundwater are more straightforward and well developed compared to the vadose zone. However, for the regional groundwater there are several data gaps in the topic areas of geochemistry, hydrogeology, and environmental remediation technology.

a. Potential for development of an RDX plume in the regional aquifer. This topic has been investigated (EM2019-0235) and the results provide a viable conceptualization of key aspects of the geochemical and hydrologic controlling factors. The historical data document localized detections of elevated RDX in the regional aquifer that are related to infiltration zones near Cañon de Valle. The data suggest that migration of the detected RDX in the regional groundwater is limited and the elevated RDX measurements are approximately 3 miles from the nearest water supply well. RDX concentration in one well is increasing, so localized remediation may eventually have to be considered.

b. Future role of RDX held up in the vadose zone. According to the EM2019-0235 report, there is only a small inventory of RDX in regional groundwater (35 to 415 Kg or 4 to 14% of the projected releases). The LANL data suggest that the bulk of the RDX remains in the vadose zone and is likely accumulated in patchy and discontinuous zones and lenses throughout the vadose zone. In our assessment, the significance of these zones is that they serve as residual source zones that will release RDX over time and contribute to the source mass flux into the regional groundwater. The review team does not believe that the vadose zone presence of perched or pore water above maximum contaminant levels (MCLs) or similar applicable standards (applicable or relevant and appropriate requirements (ARARs)) poses any risk. Because of the low risk, namely limited presence in the regional groundwater, the review team supports a provisional MNA strategy. This would involve focusing on developing metrics for RDX mass balance and quantifying source mass flux to the regional groundwater and all of the various water fluxes. We urge the EM-LA team to incorporate this information into the site models and develop uncertainties and data that would trigger contingencies. If a contingency is triggered, additional data collection (e.g., more detailed delineation of vadose zone RDX profiles to better define the location of residual RDX accumulation) and formulation of alternatives for targeted remediation to bring the source mass flux down to an acceptable level is recommended.

c. Primary and secondary impacts of potential in situ reduction technologies The EM-LA team recently completed field pilot tests of in situ abiotic and biotic reduction technologies for Cr(VI). The technologies created reduced zones in a single pilot well by injection of abiotic (i.e., Na-dithionite injection) or biotic (electron donor, i.e., molasses) amendments. These technologies resulted in elevated iron and manganese concentrations in the treatment zone and nearfield groundwater, similar to previous lab and field scale experiments of in situ reduction. Elevated Fe and Mn were observed in previous DOE efforts at Hanford, WA; Vancouver, WA; and Ft Lewis, WA (for Na-dithionite injections). At the Hanford 100-D site, aqueous arsenic (as arsenite) was also elevated in the reduced zone. However, downgradient monitoring wells show that iron, manganese, and arsenic decrease significantly outside the immediate reduced zone, even though downgradient water was at levels that were considered anoxic (i.e., dissolved oxygen was also removed by the reduced zone). The use of Na-dithionite in porous media aquifers creates a reduced zone of adsorbed ferrous iron, iron sulfide, and siderite precipitates, which were identified by iron extractions of the reduced sediment. The specific distribution of these different ferrous iron phases varied with the site hydrogeology. At the Hanford site, the reductive capacity was primarily adsorbed ferrous iron, whereas at the Ft Lewis site, the reductive capacity was primarily iron sulfides. Because multiple ferrous iron phases were present at these sites, as the reduced zone is slowly oxidized by inflow of contaminants and dissolved oxygen, the different ferrous iron phases oxidize at different rates (i.e., adsorbed ferrous iron first, then iron sulfides, then some siderite oxidizes). Therefore, both the reducing potential and redox capacity change over time. Past LANL studies examined RDX degradation under abiotic and biotic reducing conditions at laboratory scale. Applying this to the regional aquifer would be particularly challenging because of the low concentrations and patchy nature of the measured RDX. A potential future target would be perched zones or residual accumulation areas for RDX in the deep vadose zone (to control the source mass flux). This "enhanced attenuation" scenario could provide a contingency if MNA is not sufficient. If targeted remediation of RDX were to be considered, RDX abiotic degradation by alkaline hydrolysis might be more easily managed at field scale (i.e., injection of NaOH to maintain pH > 10, Heilmann et al., 1996). It should be noted that aqueous hydrolysis is a source area treatment (i.e., OH^--laden water reacting directly with aqueous RDX). For in situ remediation of Cr(VI) and RDX, collateral impacts (both beneficial and adverse) need to be considered. As described above, actively changing redox conditions, pH, or other "master" variables can significantly impact concentrations of non-target constituents, result in formation clogging, alter subsurface biology, and affect nearfield monitoring data. In some cases, the collateral impacts are negative, such as clogging and release of contaminants from the formation, while in other cases the impacts can be positive such as formation of reduced iron minerals that can provide future natural attenuation capacity.

d. <u>Additional depth discrete data are needed to better understand the structure of the contaminant plumes</u>. Some depth discrete information about contaminant distribution can be obtained from samples (and pore water extracted from vadose zone cores) collected during drilling. Because fluids are used during drilling, there is potential for dilution. However, a wide range of tracers (aqueous, organic, gas phase) have been used during drilling to systematically quantify and correct for drilling effects on contaminant concentrations (Kloppmann et al., 2001; Friese et al., 2017, McKinley and Colwell, 1996), and microbial contamination (Kallmeyer et al., 2007). For example, the use of a perfluorocarbon tracer in drilling mud showed only 1% drilling fluid contamination in split spoon cores taken ahead of the drill bit (i.e., core samples contained 14 ng/g compared to 1500 ng/g in the mud, McKinley and Colwell, 1996) because fluids tend to travel laterally at the drill bit rather than vertically downward due to formation anisotropy. In addition, well development reintroduces subsurface conditions in sediments next to the well that were altered by drilling. Geochemical indicators (i.e., specific conductivity, pH, Eh, O_2, CO_2) can also be used during well development to monitor the rate of return to formation conditions.

e. Depth of contaminant penetration in the regional groundwater. Contaminant migration deep in the regional aquifer is highly uncertain. Although the source of the contamination is the vadose zone, there appears to be indication that, in some locations, higher contaminant concentrations are deeper within the regional aquifer. Therefore, depth-discrete contaminant concentrations are needed that cover the shallow to deeper regions of the regional aquifer. This includes deep samples that show background contaminant concentrations. Because well drilling at these depths is expensive, one idea is to obtain depth discrete information from a single borehole with a design that includes separate smaller diameter wells with short screens, various multiple screen designs with packer systems and the like. These are challenging to implement at the depths needed for LANL groundwater but may be appropriate for key locations.

6.2.2. Potential technologies to complement pump and treat and accelerate chromium remediation.

a. Use of in situ treatment technologies (biogeochemical manipulations) in the regional aquifer for remediation. The single-well demonstration tests of the abiotic and biotic technologies were successful, providing useful and important data. In general, these tests confirmed that the widespread use of in situ reduction technology to control the entire chromate plume at this site is not practical due to the depth and dispersed size of the plume and the potential for adverse collateral impacts of applying a source treatment technology to a dilute plume. The independent review team urges consideration of in situ remediation technologies to treat smaller area hot spots (residual and secondary source areas) in the regional aquifer in combination with technologies such as hydraulic control (i.e., pump and treat) for remediation of the dispersed chromate plume. This strategy requires developing additional information on the size and location of the hot spots to support remediation design so that the benefits and risks of deployment are properly balanced.

b. Multiple surface discharges that have infiltrated to groundwater. Controls (manipulation) of surface discharges to modify infiltration and similar boundary conditions in an arid climate regime can provide significant benefits. Looney et al. (2012) noted that the potential value of such activities to support remediation in Western arid climates are amplified (compared to Eastern-humid climates) because the total quantity of water moving in the arid systems is relatively low and small changes in boundary conditions can result in large changes in hydrologic driving forces and water/mass balance. Of the current surface water discharges, only one (or a few) contain, or contained, elevated Cr(VI). Surface discharges can also influence Cr movement based on geochemical factors -- elevated ionic strength can decrease the already low chromate adsorption.

   All discharged water has the potential to influence the downward movement of any residual Cr(VI) present in the vadose zone that it contacts along its complex flow path to the regional groundwater. Thus, one can envision a scenario where surface discharges could be modified to reduce infiltration over key reaches (i.e., areas where the infiltrating water would mobilize Cr(VI)) to reduce and control source mass flux to the regional aquifer), but with the downside of extending the time frame of the release. Alternatively, infiltration can be focused to areas where the water would contact and maximize flushing of Cr(VI) to the regional groundwater, but with the downside of potentially increasing nearfield concentrations in the next few decades. This is a clear example of a topic where incorporation of a sustainable and relatively inexpensive technology class into the overall remediation portfolio might provide benefits to LANL environmental decision-making, but the remaining uncertainties preclude determining the best design and how the technology would fit within the overall remediation portfolio. According to the adaptive site management strategy, studies related to the potential impacts of manipulating surface discharges would be included in the longer-term plan while allowing clearly beneficial short-term activities to proceed.

In general, when evaluating the migration of Cr and RDX, the potential influence of all surface discharges, localized infiltration, and similar boundary conditions should be considered in combination with knowledge of preferential vadose zone flow pathways and zones of perched water accumulation (i.e., interfaces). The information should inform mass balance modeling and support development of the portfolio of remedies for these groundwater plumes at the complex site.

6.2.3. Natural attenuation (e.g., reduced minerals) impacts on chromate plume extent and behavior.

Monitored natural attenuation is an environmental management strategy that relies on a variety of attenuation processes to transform or immobilize contaminants. MNA is appropriate at sites where contamination poses relatively low risks, the plume(s) are stable or shrinking, and the natural attenuation processes are projected to achieve remedial objectives in a reasonable time frame compared to more active methods. The conceptual model of natural attenuation as a mass balance between the loading (mass flux from residual contamination in the subsurface) and attenuation of contaminants in the plume is a powerful framework for understanding, documenting, and managing MNA. For Cr(VI) in the regional groundwater, natural attenuation alone does not appear to be sufficient to limit plume migration based on the historical record. However, as discussed below, there is ample evidence in the literature for the occurrence of measurable attenuation of Cr(VI) and similar contaminants in bulk oxic aquifer systems (i.e., the attenuation rates are not 0). Thus, the review team recommends a focused study of attenuation rates using experiments designed to measure low attenuation rates that would be applicable to the distal lower concentration portions of the plume. This is a medium priority because understanding attenuation is not critical to near term actions (such as pump and treat) but is central to developing a reasonable protective end state while supporting performance models and informing contingency decisions.

MNA remedies recognize dilution and dispersion as attenuation processes and allow for these to contribute to an MNA remedy; however, recent EPA guidance developed to support CERCLA (EPA 1998, 2008a,b,c, 2010 and 2015) does not support MNA remedies based solely on dilution and dispersion. The guidelines typically require multiple lines of evidence (tiers) that focus on contaminant trends and statistics in the plume/wells (see Looney et al., 2012), demonstrate biogeochemical conditions that support one or more recognized attenuation processes (e.g., the presence of reduced or mixed iron minerals, redox disequilibria), and studies of attenuation rates from site specific or relevant site data. Notably, there are a number of supporting references that document attenuation of Cr(VI) in groundwater and in fractured rock systems (see for example Palmer and Puls, 1994; Zhao et al., 2017; Chapman et al., 2021; Ceballos et al., 2019; and EPA 2008b; EPA, 2009). A number of these references were co-authored by regulators and individuals who developed the EPA MNA guidance for inorganic contaminants.

To fully meet regulatory guidelines and protocols, the EM-LA team should structure their study of natural attenuation to conform to the relevant guidance documents, specifically:

- Evaluate contaminant specific attenuation of inorganic contaminants considering the most recent (EPA 2008a, 2008&b, 2010 and 2015) guidance documents related to metals, radionuclides, inorganic anions and presence of mineral phases that contribute to attenuation (see EPA 2009).
    - Clear and organized data.
    - Evaluate using the tiered lines of evidence.
    - Documentation of site-specific attenuation mechanisms that reduce the quantity, toxicity, and/or mobility of chromium.
    - Explicitly account for the source mass flux and the various mechanisms of chromium attenuation/mobilization (mass balance).
    - For the identified attenuation process, provide data related to attenuation rates and capacity/sustainability.
- Review and examine whether the current monitoring well network is adequate to meet MNA objectives; if the MNA remedy is functioning properly, provide sufficient information on the lateral and vertical extent of the plume.
- Provide an assessment of the robustness of the MNA remedy and examine contingencies as needed.

Natural oxic aquifers at other DOE sites have been shown to have some natural reductive capacity due to dissolution of minerals that result in aqueous Fe^{2+} and/or Mn^{2+}. For example, oxic Hanford formation sediments from the vadose zone in an anaerobic environment resulted in a small amount of redox reactive ferrous iron that could slowly reduce pertechnetate (Szecsody et al., 2014). The oxic, unconfined aquifer at Hanford also has a low, but measurable reductive capacity that is able to slowly reduce carbon tetrachloride and chloroform, which impacts monitored natural attenuation (Amonette et al., 2012).

The potential to evaluate whether certain wells are undergoing transitions in oxidation-reduction conditions (prior to establishment of steady-state conditions) may be evaluated through calculating the extent of redox disequilibrium in the system (Bethke, 2008; Bethke et al., 2020; Gardiner, 2021; GWB Online Academy, 2020; Lindberg and Runnels, 1984). Redox disequilibrium calculations help to identify whether the system is transitioning between dominant redox couples (e.g., Fe^{3+}/Fe^{2+}, SO_4^{2-}/S^{2-}, NO_3^-/NO_2^-, NO_3^-/NH_4^+, O_2/H_2O, etc.). These calculations can help identify whether the system is at steady state or in flux. At groundwater temperatures, many redox reactions will not reach equilibrium due to kinetic constraints. Lindberg and Runnells (1984) compiled more than 600 analyses of 30 groundwater wells that included a minimum of two measures of oxidation state and calculated redox couple species distributions for each sample. Next, they calculated E_h/pE values for the different redox couples using the Nernst equation. Comparison of these values showed that redox couples in a sample are generally in a state of disequilibrium with each other. GWB Online Academy (2020) describes how redox disequilibrium can be accounted for in geochemical models, such as The Geochemist's Workbench® (Bethke et al., 2020), by disabling one or more redox coupling reactions. All coupled redox reactions reflect the Master E_h for the system, while disabled redox couples behave independently based on their Nernstian E_h. Identifying whether there is a redox transition, and which redox couples are controlling the transition, can help to identify controls on Cr geochemistry (i.e., local chemical changes and Cr release due to an influx of new fluids from other zones, or new transport of Cr to the well zone). Coupling the redox disequilibrium analysis with the source attribution analysis for Cr may assist in identifying the potential and extent of natural attenuation that occurs in the regional aquifer.

For some redox couples, such as iron, it is difficult to accurately evaluate the equilibrium with just aqueous samples as some ferrous or ferric precipitates have some degree of solubility which influence the system's redox state. In shallow aquifers, different redox-sensitive probe compounds have been injected then withdrawn to evaluate redox conditions (Fan et al., 2015).

6.2.4. Influence of chromate diffusion on achieving remedial targets.

Heterogeneous sites can present a challenge to achieving remedial targets for groundwater contamination. Matrix diffusion, also known as back diffusion, is a process that can have both negative and positive impacts. Matrix diffusion can increase remedial time frames and limit groundwater clean-up performance of pump and treat systems due to the need for contaminants to diffuse into the preferential flow zones for collection (negative). Matrix diffusion can also reduce the spread of a contaminant plume and contribute to natural attenuation (positive). Remediation of highly heterogeneous systems such as the vadose zone and regional aquifer at LANL are complicated by the challenges associated with characterizing the flow system, the potential for small aperture fractures that restrict flow, dead end fractures that become contaminant sinks, and primary porosity that allows diffusion into the rock matrix. All of these factors are influenced by the geology of the site. Recognition of the uncertainty in a fractured aquifer site CSM is important. Adaptive site management approaches can be well suited for these sites. Further, extensive and well-designed pilot testing can be an important part of the feedback loop in remedy selection. Fractured bedrock aquifers with dead-end fractures together with primary porosity can be subject to diffusion and back-diffusion processes. This will extend the time needed to remediate the site. Pump and Treat may be combined with newer, more innovative technologies either sequentially or concurrently to better achieve remedial goals. Pump and Treat can be an effective interim action at fractured rock sites, allowing protection of downgradient receptors while characterization to support other remedies is carried out.

The degree of attenuation along the chromate flow path, maximum plume depth and Cr(VI) mass distribution and obtaining evidence for diffusion into the rock matrix are important considerations at complex sites. As discussed above, back diffusion could extend the time needed for site remediation. However, chromate reduction reactions can occur concurrently with forward matrix diffusion and immobilization of Cr. Such processes, if occurring at the LANL site, would enhance attenuation due to matrix diffusion and concomitant reduction, thus decreasing the potential for matrix diffusion.

6.2.5. Assessment/development of an optimized and minimized well monitoring network.

LANL has used various tools through the years to optimize their monitoring well network. The technical review team affirms this approach. Note that the sparse well network and the cost to install additional wells is a challenge for such tools. In general, the typical well spacing in the regional aquifer for the Cr(VI) plume (with a centerline distance of several km) may be sufficient because the regional groundwater system is fairly well behaved and the current models are able to reasonably match most of the observed water levels, contaminant concentrations, and responses to stresses such as pump tests and pump and treat system operation. Thus, we recommend that future well locations for the regional aquifer should focus on providing information to address specific targeted objectives (e.g., lateral or vertical extent of contamination, or the location of vadose zone source flux windows). The complex and patchy flow in the vadose zone is more challenging in terms of characterization and monitoring locations. There is virtually no limit to the number and spacing of wells/boreholes required to provide a comprehensive understanding of the location and behavior of vadose zone water and Cr(VI).

The review team affirms the strategy of the following:

- Decoupling the vadose zone and regional groundwater models,
- Emphasizing a mass flux approach for the regional groundwater,
- Estimating the location, scale, and intensity of vadose zone source mass flux based on groundwater data models and responses to stresses, and
- Using borehole and surface geophysics, gas monitoring, and other tools to collect indirect or inferred data in holes that are located near putative transport pathways.

The RDX surface source and vadose transport pathway has a smaller footprint – in this scenario, additional strategically placed vadose zone monitoring locations/boreholes are recommended if an attenuation mass balance cannot be adequately documented with other types of data.

As a supplement to the optimization tools already applied, a hydraulic head and gradient monitoring network design and optimization methodology could be considered for the EM-LA team as a tool to help inform discussions between the EM-LA team and regulators. This approach uses three different and largely independent approaches to monitoring network design that enables location optimization for additional monitoring wells and identification of wells in the current monitoring network that could be removed with minimal effect on meeting current and future monitoring objectives. The three different sets of results are then combined into a final data set indicating potential areas for the installation of new monitoring wells. Additionally, the approach can enable the identification of wells in the existing network that could be removed with minimal effect on the ability of the monitoring network to predict heads at unmonitored locations and to detect changes in the hydraulic gradient.

6.2.6. Potential approaches to characterize physical heterogeneities and contaminant migration pathways

There are a number of available technologies and innovations to support better understanding/characterization of important physical heterogeneities (e.g., permeability change with depth and location), Cr(VI) migration pathways, RDX accumulation zones, and the like). The following are a few examples. Several of these are discussed in more detail in Appendix B.

a. Integrated Borehole Flowmeter Test for Depth-Discrete Hydraulic Conductivity and Geochemical Measurements in Long Screened Wells at LANL. Long-screened wells enable collection of average regional groundwater, although also dilute contaminant concentrations if traveling in discrete depth zones within the regional aquifer. Monitoring wells with short screens can be placed in those discrete depth zones if there is sufficient knowledge of the depth interval. Borehole flow meter and passive multi-level sampler data can be used to identify depths of high flow and/or high contaminant concentrations, so are useful to design short-screened monitoring well depths, even if the consent order doesn't allow for this type of data.

   An integrated borehole flowmeter and Cr sampling test will measure vertical profiles (i.e., depth discrete) of relative hydraulic conductivity, Cr, and indicator geochemical parameters (pH, Eh, cations/anions, chemical tracers, etc.) in the regional aquifer. The information will provide evidence to support/reject heterogeneities (and estimated hydraulic conductivity) identified from depth discrete core grain size analysis. Electronic borehole flow meter data is at a larger scale in the surrounding aquifer (i.e., feet to tens of feet) than borehole hydraulic conductivity estimates, as the hydraulic conductivity is measured from water (and contaminant) flow into the screened interval. This data can be compared with permeability estimates from five core holes that have indicated that the pumiceous subunit of the Puye Formation (Tpf(p)) is a zone of highest conductivity in the screened interval from 275-meter to 300-meter depth, and the conclusion that 90% of the groundwater flux should place in 55 to 62% of the aquifer (Broxton et al., 2021). The technology will reduce uncertainties associated with flow of chromate through the regional aquifer.

b. Passive Multi-Level Sampler for Depth-Discrete Geochemical Sampling in Long Screened Wells at LANL. A passive multi-level sampler can measure vertical profiles (i.e., depth discrete) of chromate and indicator geochemical parameters (pH, Eh, cations/anions, chemical tracers, etc.) in a well with a long-screened interval in the regional aquifer. The information can provide evidence to support/reject hypotheses of zones of high hydraulic conductivity and interconnections with other areas. This field scale data from this passive sampler is near a well, so should correlate well with permeability estimates from five core holes that has indicated that the pumiceous subunit of the Puye Formation (Tpf(p)) is a zone of highest conductivity (Broxton et al., 2021). This data is at a smaller scale than permeability and chromate concentration data from an electronic borehole flow meter (feet to tens of feet near a well) and a push/pull test (depending on volumes used). The technology will reduce uncertainties associated with depth zones in that chromate flows through the regional aquifer in a well with a long-screened interval without resorting to multiple wells screened at specific depths.

6.2.7. Review of data from previous in situ treatment pilot studies

a. Estimating the approximate redox potential of the abiotic and biotic reduced zones from existing data. Nitrate requires greater reducing conditions than chromate. For well R-42 (dithionite reduced zone), chromate was reduced from 1 to 0.001 mg/L (1000x), and nitrate was reduced from 100 to 1 mg/L (100x). For well R-28, chromate was reduced from 2 to 0.007 mg/L (285x), nitrate was reduced from 20 to 0.1 mg/L (200x). The data may indicate that the dithionite reduced zone has a lower redox potential. Nitrate is more readily reduced in the biotic reduced zone. In addition, chromate and nitrate were slowly reduced in R-28, which is consistent with a slowly developing reduced zone, in contrast to a rapidly created reduced zone with dithionite.

b. Estimating the approximate size of the abiotic and biotic reduced zones from existing data. At dates where 50-, 350-, 700-, and 1000-gallon purge volumes were used for R-42 and R-28, the change in chromate, nitrate, Fe, and Mn concentrations for the different purge volumes can show a relative size of the reduced zone. For example, for well R-42 (dithionite), nitrate increased from 0.05 to 0.9 mg/L (i.e., pulling in water from outside the reduced zone with higher nitrate concentration). In contrast, for well R-28 (bioreduced zone), the nitrate concentration increased only slightly from 0.06 to 0.08 mg/L (assuming the later points correspond to higher purge volumes at the same date). This data may indicate that the bioreduced zone is larger than the dithionite-reduced zone. In the 2021 Waste Management Symposium paper on stratigraphy (Broxton et al., 2021), the saturated hydraulic conductivity was calculated from the grain size distributions of many samples of the cores. Assuming the stratigraphy is the same near the well as in the core from the well, this data could be used in simulations of injection of 50 to 1000 gallons to estimate the size of the zone the purge water is pumped from (and the depth range).

c. In general, the pilot studies highlighted some of potential benefits and challenges of in situ redox manipulation. Some of the primary benefits include reductions in contaminant concentrations that are particularly impactful in areas of residual sources and in areas where source mass flux and inputs from the vadose zone are significant. Some of the challenges include logistics and costs of access through the deep vadose zone, limited spatial coverage from each injection well, and nearfield biogeochemical collateral impacts. Based on the lessons learned, the review team believes that there may be the potential for future use of in situ redox remediation, but that these technologies would need to be targeted to limited areas to address known source zones and areas of mass flux and not used to address large dilute or dispersed plumes.

6.3. Vadose Zone and Perched-Intermediate Zone Aquifer

6.3.1. Remediation of Cr discharge from the vadose zone to the regional aquifer

The vadose zone beneath LANL is a more challenging environment for contaminant remediation due to shallow alluvium in places and mainly fractured rock vadose zone (~1,000 ft thick) and fractured rock regional aquifer. If there was significant Cr(VI) in the vadose zone, it would potentially migrate to the regional aquifer and be a continued long-term source. To evaluate the potential risk for impact to groundwater, the Cr mass, located within the vadose zone, current and future (if changing) water flux through the vadose zone are needed. If the potential risk of long-term Cr migration through the vadose zone to groundwater would potentially have sufficient impact on Cr groundwater concentrations, then vadose zone remediation could be evaluated. Changes in the surface water flux into the vadose zone can be evaluated (i.e., either minimizing infiltration or flushing to groundwater assuming water is captured in a pump and treat system). In situ gas-phase remediation of chromium can also be considered for the vadose zone with the following caveats. Previous gas phase reduction technologies have been used at different sites that are made up of porous media (Thornton and Amonette, 1999), and application to a fracture flow system would likely be challenging and possibly ineffective.

If there were significant chromate hot-spots identified in the vadose zone, which would potentially migrate to the regional aquifer, gas phase abiotic or biotic reduction could be considered. One gas phase technology (H_2S gas) has been demonstrated in a shallow porous media field site (White Sands, NM) for chromate. This could be used below the basalt and has the potential to advect into fractures well (as opposed to a liquid phase reductant). The use of H_2S for reduction of pertechnetate has been demonstrated at the laboratory scale (Szecsody et al., 2014), but is unlikely to be used at field scale at the DOE Hanford site due to hazards associated with field scale H_2S use. Bioreduction of chromate under vadose zone conditions has been demonstrated in sediments at higher water content (Oliver et al., 2003), as well as gas phase reduction of other metals (Chung et al., 2006: Hol et al., 2010). Reduction of chromate using gas phase amendments has also been demonstrated at the laboratory scale at higher water content (Bagwell et al., 2020).

6.3.2. Characterization of the potential of Cr(III) precipitate oxidation/remobilization or colloidal transport in shallow sediments

Significant chromium mass as $Cr(III)(OH)_3$ or mixed $(Fe, Cr)(OH)_3$ precipitates exist in the shallow wetlands alluvial sediments, and are generally immobile, as Cr(III) precipitates do not reoxidize under most natural reducing or oxidizing conditions. In some cases, Cr(III) precipitates have been reported to be oxidized by MnO_2 (Steinpress, 2005; Butler et al., 2015, details in Appendix A). In addition, Cr(III) precipitates have also been reported to migrate short distances on inorganic colloids (Zhou et al., 2019). Although Cr(III) oxidation by Mn oxides may be insignificant or Cr(III) precipitate movement with colloids may mobilize only short distances, these processes should be investigated to minimize risk of source area Cr movement over the long term.

6.3.3. Understanding the RDX source (surface, perched zone) and key transport and geochemical controls – does data support strategy for long-term monitoring?

RDX contamination near surface, in the vadose zone, and in the perched-intermediate aquifer has been extensively investigated, but there may be increased infiltration after the 2011 Las Conchas fire that may promote increased infiltration of RDX deeper into the vadose zone. Subsurface contamination resulted primarily from sumps and drains from Building 260 in area TA-16, which drained millions of gallons per year from 1951 to 1996. The near surface contamination has been remediated primarily by removing 1500 cubic yards of RDX-contaminated materials and the use of a shallow permeable reactive barrier. The remaining RDX inventory is in the perched-intermediate aquifer (263-1478 Kg, 30-51%), vadose zone (545 to 940 Kg, 32 to 62%), with lesser amounts in regional groundwater (35 to 415 Kg, 4 to 14%) and springs (35 to 56Kg, 2 to 4%), based on an updated survey in 2017 (EM2019-0235). RDX concentrations in the perched intermediate aquifer are stable or decreasing. Because the original source of RDX infiltration has been removed (i.e., discharges from Building 260), natural infiltration of precipitation should be significantly less. However, the 2011 Las Conchas fire burned significant vegetation, so may result in increased infiltration into the vadose zone.

6.3.4. Electrical Resistivity Tomography (ERT) survey in vadose zone in Cañon de Valle to compare to previous ERT survey

While the previous survey was used to show zones of higher electrical conductivity (i.e., fracture flow zones), an additional survey at this time may indicate any change in fracture flow (i.e., elevated infiltration due to the 2011 Las Conchas fire). It should be noted that the previous ERT survey had some limitations due to buried pipelines. There have been more recent advances in ERT inverse modeling to remove the effects of buried high conductivity structures.

6.3.5. RDX migration

If RDX appears to be migrating downward in the vadose zone resulting in increasing concentration in the perched-intermediate aquifer (at ~600-700 ft depth), vadose zone remediation in selected locations (if identified) could be considered to minimize downward migration into the regional aquifer. Technologies to degrade RDX include abiotic or biotic reduction (previously investigated at LANL at the laboratory scale, and Na-dithionite tested at the Pantex, TX perched aquifer), oxidation using permanganate (previously tested at the Pantex, TX perched aquifer at ~250 ft depth), alkaline hydrolysis, and thermal treatment. These technologies have been used in shallow porous media aquifers, where conditions are more easily controlled than a deep fracture flow vadose zone. Any addition of water with reductive or alkaline amendments may also drive RDX and co-contaminants deeper. Creating alkaline conditions in vadose zone sediments has been previously investigated at the laboratory scale in multiple studies (Szecsody et al., 2011, Emerson et al., 2018) and has been considered at field scale for uranium remediation. In those studies, a 5% ammonia gas injection (with 95% N2) resulted in 3.1 mol/L (pH 11.8) pore water. The alkaline pore water slowly dissolved some minerals (montmorillonite, illite, muscovite) and as the pH neutralized, other aluminosilicates formed, incorporating uranium. Although transport properties of ammonia gas have been extensively studied at the laboratory scale in experiments to 30 ft length and modeled at field scale, the efficiency of injecting ammonia gas into a porous tuff to create alkaline conditions in the pore water has not been studied, nor has the subsequent reactivity with RDX been studied. RDX may be degraded in the alkaline pore water, but over time, the alkaline pore water will be neutralized by reactions with minerals in the rock matrix, so experiments are needed to evaluate the relative rates of RDX alkaline hydrolysis and pH neutralization.

7. Conclusions

Based on the independent review, the independent review team formulated the following observations, overarching recommendation, and topical responses to the scope questions:

The team was impressed by the capabilities, experiences, innovativeness, and insightfulness of the technical representatives from both the regulators (NMED) and DOE support contractor. As described in the later sections of the report, the work at the site was generally state-of-practice (or better) and in some cases was state-of-art. The reviews from the regulators were thorough and often provided useful concepts for consideration and future study/resolution.

A consensus recommendation of the independent review team is that the LANL groundwater plumes should be addressed in the context of the "management of complex sites" paradigm using an iterative-adaptive site management strategy that has been described in several guidance documents over the past decade. The complex site paradigm explicitly recognizes that it is difficult, or intractable, to generate advance knowledge that is sufficient to provide a technically defensible basis for the final remediation decision, design, and implementation. The adaptive management strategy encourages a focus on what can be done now with the information that is known, what can be done to stabilize the plume and mitigate risk, and what achievable interim objectives can be set that will allow success for all parties. Technologies can be optimally implemented in a manner that is targeted in space, time, and goal. Finally, implementation of the technologies can, and should, be done in such a manner that the system response to each action provides actionable data to help reduce uncertainties and inform the next stage of remediation decisions and design.

<u>General assessment of the conceptual and numerical modeling observations:</u>

- The existing conceptual models and numerical model results provide reasonable and effective support for several types of near-term remedial action decisions, notably designing and projecting the plume behavior for Cr(VI) and RDX and risks to potential receptors over the next several decades.
- The current conceptual models and data gaps do not provide the decision support eventually needed for longer-term remedial action objectives, specifically, the remaining residual vadose zone contaminants and projecting the quantity, location, and future release profiles of Cr(VI) and RDX into the groundwater. These need to be addressed within the framework of the recommended adaptive site management paradigm.
- Once additional characterization information on the nature and extent of sources above the regional water table is available for the conceptual model, numerical modeling will be needed to robustly support a technical basis for design of remedies to manage and control sources.
- There are a number of uncertainties in the parameters of the regional groundwater model – for many of the traditional model parameter uncertainties, refinements would have a relatively small (incremental) impact on results so these would be a low-medium priority for the EM-LA team.
- The vadose zone transport modeling has a relatively high uncertainty because of long transport distances, fracture flow and matrix diffusion, and the resulting patchy nature of active water flow and contaminants in the vadose zone.

<u>Assessment of data gaps:</u>

- There are a number of challenges and opportunities related to future characterization and site-specific geology and biogeochemistry, with a focus on potential remediation options to consider for the future portfolio of remediation and monitoring technologies. These deliberations were done in the context of our overarching recommendation for classifying LANL groundwater according to the complex site paradigm and presuming that a suite, or portfolio, of remedial actions will be needed to address these important and recalcitrant contaminant plumes. Further, the effort was informed by the substantial history of characterization, field testing, and the data and results from the interim pump and treat that was recently performed to control the Cr(VI) plume footprint, and measurements of the distribution of RDX in the nearfield vicinity of the release area. The existing data gaps do not impact the ability of the EM-LA team to design, build and operate a pump and treat system to meet appropriate objectives (e.g., to limit plume growth and mitigate key risks). The remaining data gaps could be managed and addressed during the deployment and operation of such an interim remediation.

  - Data gaps in the regional aquifer relate to geochemistry, hydrogeology and various environmental remediation technologies (Section 6.2):
    - Role of RDX in vadose zone and potential for future development of RDX plume,
    - Primary and secondary impacts of in situ reduction technologies,
    - Lack of understanding of contaminant plume structure,
    - Depth of contaminant penetration into regional aquifer,
    - Remedial technologies complementary to pump and treat; include, in situ treatment, and control of surface discharges,
    - Impacts of natural attenuation on chromate plume,
    - Influence of chromate diffusion on achieving remedial targets,
    - Assessment and development of optimized and minimized well monitoring network,
    - Lack of characterization of physical heterogeneities that would affect contaminant migration, and,
    - Using data from previous in situ pilot studies.
  - Data gaps associated with the vadose zone and perched intermediate zone aquifer (Section 6.3):
    - Effects of Cr(III) precipitate remobilization and colloidal transport in shallow sediments,
    - Complete understanding of RDX sources and key hydrogeochemical controls,
    - Changes in fracture flow characteristics, and,
    - Migration potential of RDX from vadose zone to intermediate perched water aquifer.
- The process used to designate locations and objectives for the next set of wells was reasonable and appropriate.
- The new data would support the EM-LA team and future objectives for monitoring (if needed), and if/where additional monitoring might be most beneficial.
- Many of the identified data gaps would be most effectively addressed by implementing large scale remedial actions, complementary to pump and treat, such as in situ treatment and control of surface discharges, and then observing responses.

<u>Provide an independent assessment on alternative remediation decision and implementation processes for subsurface Cr(VI) and RDX plumes observations:</u>

- The "interim" corrective action strategy is aligned with the recommended adaptive site management paradigm for complex sites.
- A full Corrective Measures Evaluation (CME) process could easily get bogged down in the long list of uncertainties and has the potential to lead to disputes and technical issues that have no clear path for near-term resolution.
- For RDX, the review team agrees that the natural attenuation strategy is technically defensible and viable and recommends collecting and organizing data using multiple lines of evidence as described in relevant USEPA guidance documents. If the multiple lines of evidence do not continue to support MNA, then the site should consider a contingency for reducing source mass flux to the regional groundwater using a targeted in situ vadose zone treatment.
- For both Cr(VI) and RDX, the projected behavior of vadose zone sources on future groundwater contamination is important and will require additional study to support future decision-making and to estimate remediation time frame. However, this should not be viewed as an impediment to advancing near-term Interim corrective actions.

In summary, the review recommends addressing the two LANL groundwater plumes as complex sites and to apply an adaptive site management strategy. Below is a breakdown of key associated short-, medium- and long-term recommendations. Short term recommendations would focus on the next 2 to 5 years, medium term from 3 to 10 years, and long-term > 10 years.

Short-Term Recommendations

- The review team urges the EM-LA team and regulators to collaborate to finalize the plans and to take steps to maximize the value of each borehole for establishing vertical and lateral extent of contaminant plume given the logistics and costs of installing wells to this depth.
- The review team does not support the need for a Full CME with a comprehensive evaluation process (> circa 2 years), since the current state of knowledge is insufficient to define the suite of actions that will be needed to achieve final remediation objectives.
- The review team supports the proposed accelerated "interim" corrective action process (i.e., developing a presumptive (preferred) remedy based on existing data with the annotation that the objectives need to be clear and a recognition that such a remedy will not achieve final remedial action objectives).
- The review team recommends developing a consolidated modeling strategic plan as part of the adaptive site management paradigm. This plan should prioritize the phased plans for improving and advancing models so that they can meet the evolving needs of EM-LA. Some of the early actions include incorporating key processes into decision-making models to address the potential for continuing sources.

Medium-Term Recommendations

- The review team recommends documenting the modeling using available consensus best-practice standards and guides for groundwater modeling. The most important recommendations for advancing regional groundwater modeling to support future stages of remediation include better projections of the location and intensity of source mass flux from the vadose zone and improved estimates of natural attenuation rates.

- The review team recommends considering key alternative conceptualizations and parameterizations as the CSM evolves due to new information and aquifer responses to interim remedial actions.
- The review team encourages staging of major well installation campaigns to allow a period of monitoring after new wells are installed to allow the new information to accrue.
- The review team affirmed the current process of using the vadose zone modeling as a semiquantitative tool to inform the boundary conditions for the groundwater model (state-of-practice). If a future reduction in the source mass flux is needed to achieve remediation goals, then additional vadose modeling capabilities may be required to inform technology decisions.

Long-Term Recommendations

- Current numerical (constitutive) models could be supplemented in the future by looking for opportunities to implement strategies based on mass balance, mass flux, and/or similar emergent or integrative system behaviors.
- The review team recommends implementation of phased remedies and actions to supplement the adaptive management strategy, including: (as needed) actions to address residual sources in the vadose zone and shallow groundwater, boundary conditions and driving forces (i.e., source mass flux and vadose moisture and groundwater movement), and enhanced/natural attenuation.

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Appendix A – Synopsis of Key Information Related to LANL Groundwater Plumes (excerpted from EM-LA Scope of Work)

A-1. Hexavalent Chromium (Cr) Groundwater Plume Background

An estimated 26,000 to 105,000 kg of chromium (Cr) were released into Sandia Canyon from surface water outfalls during Los Alamos National Laboratory (LANL) site operations from 1956 until 1972. While a portion of the chromium was converted to stable trivalent Cr in a large wetland located downgradient of the major outfall, chromate or hexavalent chromium has also infiltrated vertically through the approximately 1,000 ft thick alluvial vadose zone deposits to the regional aquifer. The chromium plume in the regional aquifer has a current footprint of approximately half a square mile where concentrations exceed the New Mexico groundwater standard of 50 µg/L in an interval approximately 50 ft thick in the upper portion of the aquifer. Measurements in some of the monitoring wells that define lateral and distal plume boundaries have shown increasing chromium concentrations over the past years indicating potential expansion of the plume. In one regional groundwater monitoring well, chromium was detected at higher concentrations in deeper zones. Portions of the plume also contain nitrate and tritium at concentrations below standards and perchlorate locally above the New Mexico groundwater standard.

The chromium plume is one major focus of the Department of Energy Environmental Management Los Alamos Field Office (EM-LA) groundwater program, the 2016 Compliance Order on Consent (Consent Order) between EM-LA and the New Mexico Environment Department (NMED), and stakeholders. Current efforts are concentrated on implementing an interim measure (IM) for mitigation of the chromium plume impact to ensure that contamination does not adversely impact receptors or the environment surrounding LANL.

Work performed over the past decade and a half has yielded long-term groundwater monitoring data, laboratory and field experimental results, a general conceptualization of flow in the vadose zone and upper portion of the regional aquifer, and numeric models for Cr fate and transport from the vadose zone to the upper regional aquifer.

Specifically, laboratory and field projects have been executed for:

1. Investigation of the feasibility of chromium source removal from the center of the plume (~400-1,000 µg/L).
2. Characterization of the distribution of chromium and related biogeochemical species and conditions in the aqueous and solid phases within the vadose zone and in the regional aquifer.
3. Characterization of key attributes of the aquifer, including heterogeneity and dual porosity, principally for the purpose of evaluating potential in situ remedial strategies.
4. Study of the geochemical conditions around injection wells in support of the interim measure.
5. Evaluation of various approaches or engineered solutions that may be viable as remediation strategies for the Cr plume.
6. Characterization of the infiltration beneath the shallow alluvial groundwater in Sandia Canyon.

7. Evaluation of potential source areas for the Cr plume using machine learning data analyses of geochemical data.
8. Injection studies and tracer tests.
9. Monitored natural attenuation study, laboratory bio-treatability and chemical treatability studies, and field pilot treatability tests.

The ongoing field activities and groundwater modeling studies are focused on control of the chromium plume at the LANL boundary, and evaluations of the IM performance to optimize pump-treat-inject operational strategies with the end goal being identification of plume remediation alternatives. Of particular importance to EM-LA and stakeholders now are reviewing all of the available data and study results and preparing a Corrective Measures Evaluation (CME) Report that evaluates potential remedial alternatives and recommends a remedy being protective of human health and the environment in compliance with the Consent Order requirements. EM-LA is also entertaining the option under the Consent Order of an accelerated corrective action to move straight into remedy installation and implementation. EM-LA would request that the independent review examine data gathered to date through the pilot and field tests, as well as interim measure performance, to see if moving forward with remedy is supported or if gaps exist that need to be addressed prior to remedy implementation.

A-2. Royal Demolition Explosives (RDX) Groundwater Plume Background

Cañon de Valle is a steep sided canyon that runs from west to east across the Pajarito Plateau in the southwestern portion of LANL. Cañon de Valle has intermittent flows of water, primarily during the spring snow melt and during late summer monsoonal events. From 1951 until 1996, these flows were supplemented with process water flowing into Cañon de Valle from high explosives machining performed in TA-16.

Starting in 1951 and continuing to the present, RDX has been machined at Building 260 near the northern boundary of TA-16. This structure is located a short distance south of the south rim of Cañon de Valle. During machining, water is sprayed on the RDX to cool it and remove the machined particles of RDX. From 1951 until 1996 the process water from the machining was directed into a trough which led to a small pond north of the building. In this pond the larger particles of entrained RDX settled to the bottom. From this settling pond the water flowed down the canyon wall and into the bottom of the canyon, carrying with it both small particles and dissolved phase RDX. During the later years of its operation, this was an EPA permitted outfall. Starting in 1996, the pond and outfall ceased operation. Since that time, the process water has been captured in sumps adjacent to Building 260. This waste stream is currently managed by pumping the sumps and treating the water at the TA-16 high explosives wastewater treatment plant.

Due to the change in the handling of the process water in 1996, no additional RDX has being introduced into the Cañon de Valle hydrogeological system for the last 24 years. In addition, two remedial actions (in 1999 and 2010) excavated and disposed of material containing RDX from places where it had been detected in surface and near surface locations. As a result, no new RDX is being released to contaminate groundwater.

During the 45-year period that the process water was released into Cañon de Valle, a certain portion of it soaked into the ground and began infiltrating downward. This water carried dissolved phase RDX molecules with it. The infiltrating water encountered the top of the perched-intermediate groundwater zone located approximately 600 feet below ground surface and began mixing as it infiltrated further. Eventually, a portion of this perched-intermediate groundwater infiltrated into the top of the regional aquifer. This is located approximately 1,000 feet below ground surface. Laterally, the portions of both the perched-intermediate zone and the regional aquifer impacted by RDX are limited to relatively small areas. The NMED tap water screening level for RDX is 9.66 µg/L. The highest concentration of dissolved phase RDX in the perched-intermediate zone in the last year was 160 µg/L, though in most places where it is detected the concentrations range from 1 to 60 µg/L. The highest concentration of dissolved phase RDX reported in groundwater samples from the underlying regional aquifer in the last year was 18.3 µg/L.

Characterization activities have been conducted to develop the hydrogeologic conceptual model at TA16. These activities included:

1. Investigating the nature of the contaminant source.
2. Installing perched-intermediate and regional groundwater monitoring wells.
3. Performing groundwater monitoring to delineate the nature and extent of contamination.
4. Conducting single- and multi-well aquifer tests and cross-hole tracer tests to characterize hydraulics of the perched-intermediate and the regional aquifer.
5. Developing the conceptual model including the hydrogeology, infiltration, and recharge factors controlling the attenuation of RDX.
6. Evaluating potential technologies for remediation of RDX.
7. Developing groundwater flow and transport models to evaluate contaminant fate and transport and potential corrective actions.

The ongoing activities include fate and transport modeling and risk assessment for RDX contamination in deep groundwater. The overall conclusions of the risk assessment are (1) there is no current or reasonably foreseeable future unacceptable risk to human health associated with RDX contamination in the regional aquifer and (2) based on land use controls restricting potable groundwater wells, there is no current, potential, or reasonably foreseeable future unacceptable risk to human health from drinking groundwater from the perched-intermediate groundwater. EM-LA recommends to NMED long-term groundwater monitoring to monitor the plume and ensure protection of human health in accordance with the Consent Order.

Appendix B - Recommended Technologies and Associated Strategies

Short narratives that provide additional detail on some of the technology recommendations.

The review team also recommends that the EM-LA team review the report of a previous National Laboratory groundwater review (Looney et al., 2012), *Independent Technical Review of the Interim Measure Alternatives Analysis for Chromium Contamination in Groundwater at Los Alamos National Laboratory, New Mexico, SRNL-STI-2012-0060*. This report provides additional detailed evaluation and recommendations.

B-1. Passive Multi-Level Sampler for Depth-Discrete Geochemical Sampling in Long Screened Wells

Summary Information

Objective and Potential for Risk Reduction: A passive multi-level sampler can measure vertical profiles (i.e., depth discrete) of chromate and indicator geochemical parameters (pH, ORP, cations/anions, chemical tracers, etc.) in a well with a long-screened interval the regional aquifer. The information can provide evidence to support/reject hypotheses of zones of high hydraulic conductivity and interconnections with other areas. This field scale data from this passive sampler is near well, so should correlate well with permeability estimates from five core holes that have indicated that the pumiceous subunit of the Puye Formation (Tpf(p)) is a zone of highest conductivity (Broxton et al., 2021). This data is at a smaller scale than permeability and chromate concentration data from an electronic borehole flow meter (feet to 10s of feet near a well) and a push/pull test (depending on volumes used). The technology will reduce uncertainties associated with depth zones in that chromate flows through the regional aquifer in a well with a long-screened interval without resorting to multiple wells screened at specific depths.

Focus Area(s): Identify depth zones of chromate transport

Description: A new or existing well is needed that is screened over a long interval(s) in the regional aquifer. Passive multi-level sampling surveys have been previously shown to be effective for measuring depth-discrete geochemical and microbial patterns (Baldwin et al., 2008, Lasagna et al., 2016, McMillan et al., 2018). A detailed description of the multilevel sampler (MLS) is described in Baldwin and others (2008). The improved information increases confidence in source/plume evaluations to help answer key conceptual site model (CSM) questions needed to address risks. This information can also inform model configuration and increase confidence in model predictions needed to address risks.

The MLS system is a passive sampler system of small vials filled with deionized water that are placed at different depths in a well for several weeks. Vertical water movement in the well bore is minimized by rubber seals between sample vials and appears to function well given the depth-discrete data that is obtained. In an example from the Hanford 100-D area, a diagram of the MLS system is shown in Figure 5 (left), an image of installation into a well in Figure 5 (center), and the resulting vertical profiles of dissolved oxygen and chromate in one well (Figure 5 right). In this unconfined aquifer, a reduced sediment barrier was created with sodium dithionite, and the vertical profile showed the 100-110 ft depth is most reducing, 90 to 100 ft depth is sub-oxic, and 85 to 90 ft is highly oxic (due to the fluctuating water table). Aqueous chromate is at the highest concentration at the shallowest depth, which has little to no reductive capacity, is present at a lower concentration in the 90 to 100 ft depth where the sediment has some reductive capacity and is fully reduced in the 100 to 110 ft depth where the sediment has significant reductive capacity. The conclusions of that study, which included depth-discrete profiles from 8 wells was that portions of the reduced sediment barrier were prematurely oxidized by: a) seasonal fluctuating water table (i.e., top few feet of the unconfined aquifer), and b) high permeability zones at specific depths. High permeability zones that contained low reductive capacity was not fully characterized by these MLS surveys but required additional depth-discrete hydraulic characterization using an electronic borehole flow meter.

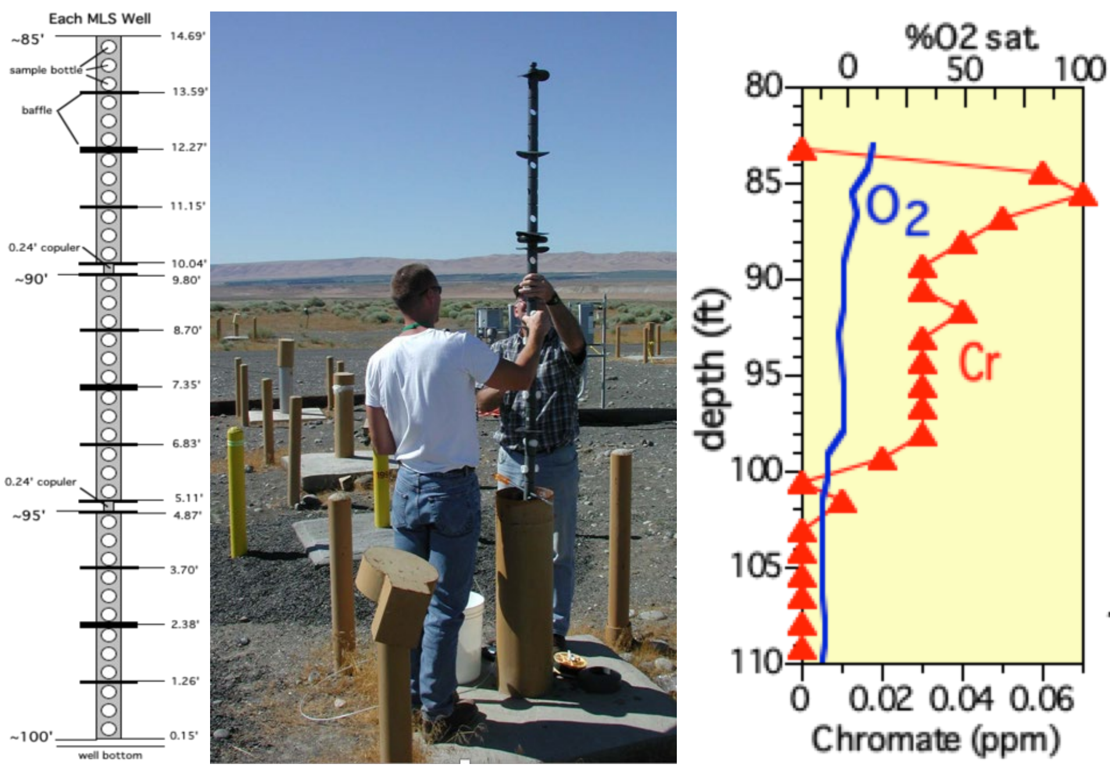

Figure 5. Multilevel sampler system (MLS) installation in a well to collect depth-discrete samples in wells with a long-screened interval (left and center), and chromate and dissolved oxygen results (right) from a well at the Hanford 100-D area that was geochemical.

Development Status: Passive multi-level sampling is mature and there are several options for equipment to conduct the testing.

LANL Site-Specific Advantages/Disadvantages:

Advantages include:

- Generates actionable data using an existing or new well
- If a new well is drilled, fresh sediment core samples (which could be collected in such a way as to preserve the redox state) can be analyzed in parallel
- Simple and relatively inexpensive to deploy and interpret if existing well can be used
- Vertical profiling of concentrations can help interpret source configuration for nearfield applications
- Does not require extraction of contaminated water
- Relatively simple technology
- Helps interpretation of other well sampling and testing efforts.
- Is applied in a single well

Disadvantages include:

- Information obtained is local to the interrogated well
- Well construction can impact test results - the rubber seal between sample vials needs to work properly, and if the sand pack is a higher permeability than the surrounding aquifer, there can be vertical migration within the sand pack even if the rubber seal between sample vials within the well works well
- There may be some alteration of water samples at LANL due to the time it takes to pull the MLS sample string from 1000 ft depth

Technology Inter-Relationships: This passive multi-level sample can be coupled with electronic borehole flowmeter to provide an overall interpretation useful for updating site hydrogeologic information. This type of testing supports design and interpretation of other well sampling and evaluation techniques. This technology could also be correlated with depth-discrete passive sampling in well(s).

B-2. Integrated Borehole Flowmeter Test for Depth-Discrete Hydraulic Conductivity and Geochemical Measurements in Long Screened Wells at LANL

Summary Information

Objective and Potential for Risk Reduction: An integrated borehole flowmeter and Cr sampling test will measure vertical profiles (i.e., depth discrete) of relative hydraulic conductivity, Cr, and indicator geochemical parameters (pH, ORP, cations/anions, chemical tracers, etc.) in the regional aquifer. The information will provide evidence to support/reject heterogeneities (and estimated hydraulic conductivity) identified from depth discrete core grain size analysis. Electronic borehole flow meter data is at a larger scale in the surrounding aquifer (i.e., feet to 10s of feet) than borehole hydraulic conductivity estimates, as the hydraulic conductivity is measured from water (and contaminant) flow into the screened interval. This data can be compared with permeability estimates from five core holes that has indicated that the pumiceous subunit of the Puye Formation (Tpf(p)) is a zone of highest conductivity in the screened interval from 275-meter to 300-meter depth, and the conclusion that 90% of the groundwater flux should reside in 55 to 62% of the aquifer (Broxton et al., 2021). The technology will reduce uncertainties associated with flow of chromate through the regional aquifer.

Focus Area(s): Identify zones of high hydraulic conductivity and correlation with chromate transport

Description: A new or existing well is needed that is screened over a long interval(s) in the regional aquifer. Electromagnetic borehole flowmeter (EBF) surveys are effective for measuring the vertical GW-flow distribution in wells under ambient (static) and dynamic (e.g., pumping-induced) test conditions. For the dynamic test, the data provide direct measurements of GW inflow along the saturated well screen during a constant rate of pumping (e.g., with pump placed near the top of the well screen). The various measured inflow rates vs. depth are directly related to the vertical profile of hydraulic conductivity outside the well screen within the surrounding aquifer formation (Figures 6 and 7). The test can be augmented by collection of a water sample at each position of the flowmeter. The concentration and flow data can be interpreted together to algebraically estimate concentration profiles for any measured GW constituent (conceptually shown in Figure 7). A detailed description of EBF instrumentation and application of surveys for site characterization is presented by Flach et al. (2000a/b, 2002), Spane and Newcomer (2008), Molz et al. (1994), and Young et al. (1998). The improved information increases confidence in source/plume evaluations to help answer key CSM questions needed to address risks. This information can also inform model configuration and increase confidence in model predictions needed to address risks.

Vertical concentration profile and hydraulic properties can be used to interpret source flux and plume conditions and how vertical heterogeneity is affecting overall contaminant behavior. Example data from the DOE Hanford site shows the raw pumping data is shown in Figure 8a, and the relative hydraulic conductivity shown in Figure 8b. For this borehole, about 85% of the flow occurs in the 89 to 92 and 94 to 95-foot intervals of the 22 ft screen length. Contaminants can also be measured in the partially screened intervals during the EBF data. A comparison of electronic borehole flow meter relative hydraulic conductivity to chromate data collected with a passive sampler (Figure 8) shows a general correlation where chromate is moving more rapidly (and at a higher concentration) in high conductivity zones at the 95- to 98-foot depth.

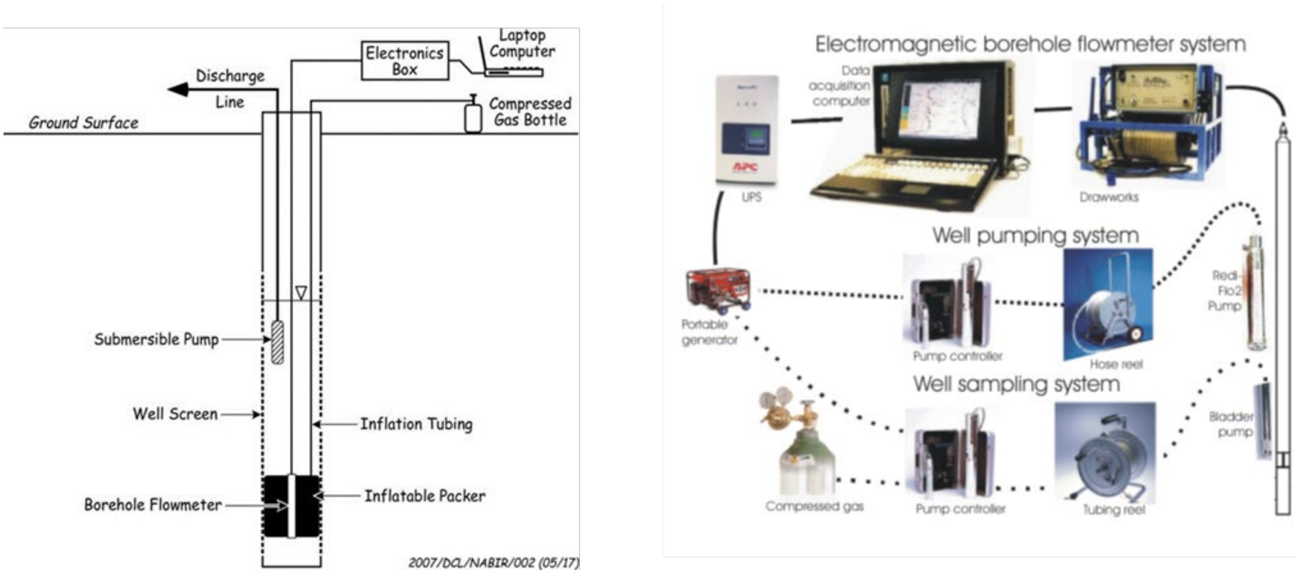

Figure 6. Example Test Configuration. Basic system on the left - the borehole flowmeter is moved up through the well during the test to evaluate different intervals; equipment for integrated tests including concentration profiling is shown on the right.

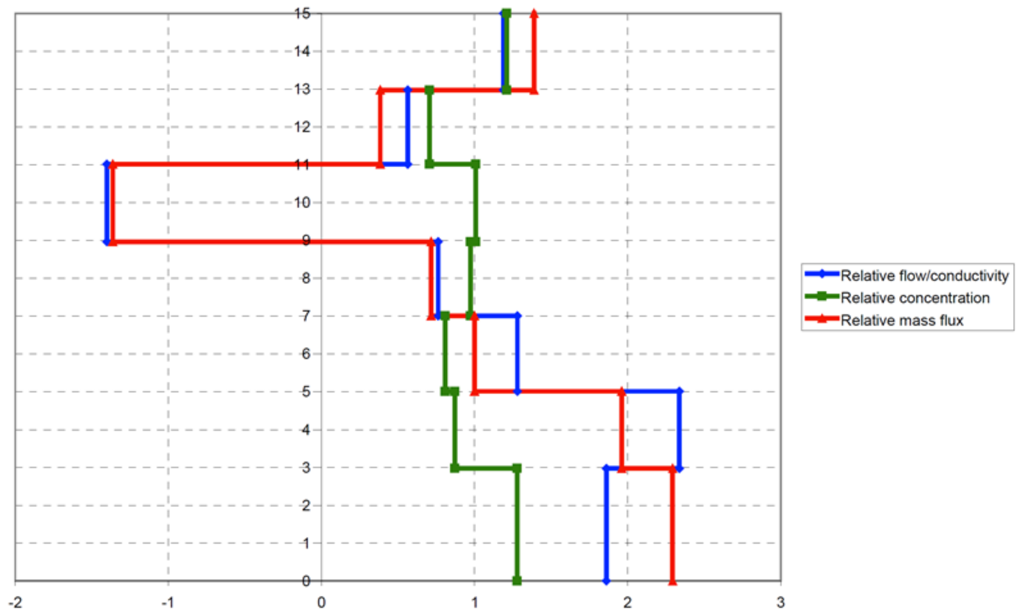

Figure 7. Example vertical profile data from a borehole flowmeter test combined with vertical profiling of well chemistry.

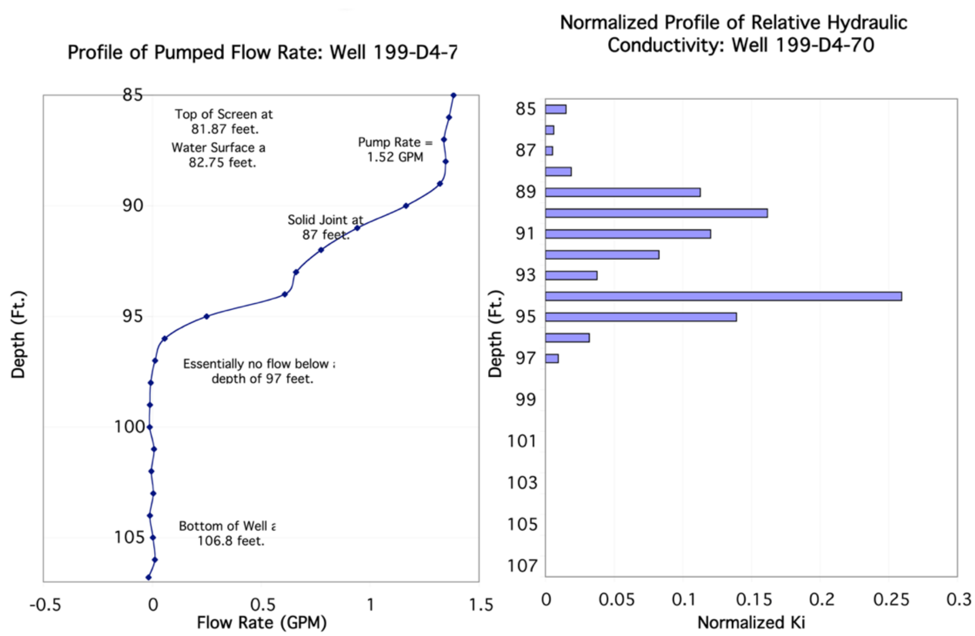

Figure 8. Electronic borehole flow meter data for a single well: a) raw pumping versus depth, and b) relative hydraulic conductivity versus depth.

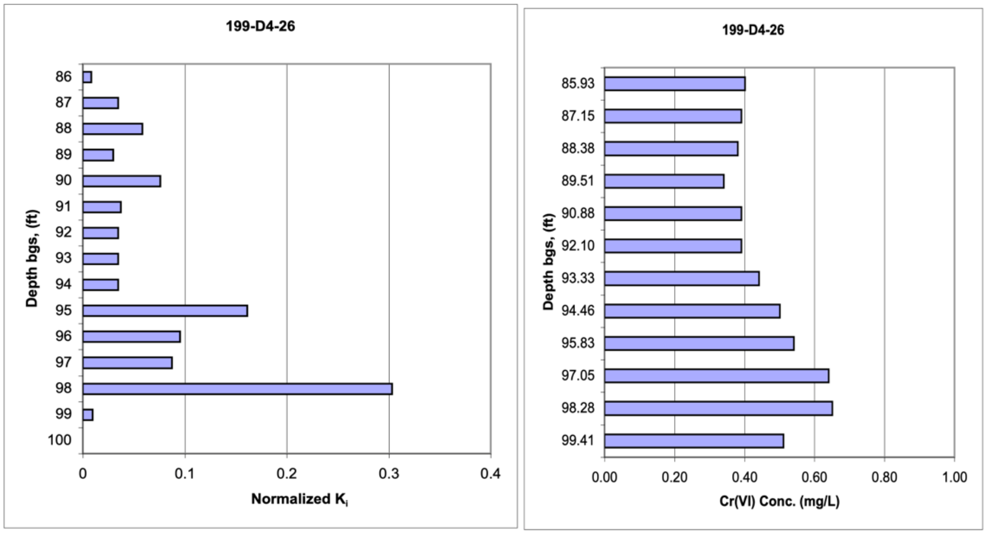

Figure 9. Relative hydraulic conductivity for Hanford borehole D4-26 (a) and depth-discrete chromate concentrations in a 15-ft screened interval.

Development Status: Borehole flowmeter testing is mature and there are several options for equipment to conduct the testing.

LANL Site-Specific Advantages/Disadvantages:

Advantages include:

- Generates actionable data using an existing or new well
- If a new well is drilled, fresh sediment core samples (which could be collected in such a way as to preserve the redox state) can be analyzed in parallel
- Simple and relatively inexpensive to deploy and interpret if existing well can be used
- Can provide estimates of subsurface hydrologic properties
- With vertical profiling of concentrations can help interpret source configuration for nearfield applications
- Helps interpretation of other well sampling and testing efforts
- Is applied in a single well

Disadvantages include:

- Information obtained is local to the interrogated well
- Well construction can impact test results and hinder evaluation of aquifer information – may not have wells in appropriate locations or with long-enough screens
- Custom equipment will be needed to sample cost-effectively from required depths with required pumping heads

- Requires extraction of contaminated water, though at volumes that are similar to volumes for standard well sampling (e.g., likely able to handle volumes based on existing purge water practices)
- Somewhat specialized analysis but multiple resources are available to facilitate testing and analysis (NL contacts: Brian Looney, SRNL; Rob Mackley, PNNL)

Technology Inter-Relationships: Borehole flowmeter should be coupled with hydraulic head monitoring or other types of hydrogeologic monitoring to provide an overall interpretation useful for updating site hydrogeologic information. This type of testing supports design and interpretation of other well sampling and evaluation techniques. This technology could also be correlated with depth-discrete passive sampling in well(s).

B-3. Remediation of RDX by Alkaline Hydrolysis in the Regional Aquifer with Aqueous Amendments and Vadose Zone using Gas Phase Amendments, if needed

Summary Information

Objective and Potential for Risk Reduction: RDX in the subsurface has been extensively investigated (EM2019-0235) and although there are RDX hots spots in the regional aquifer that are related to localized higher infiltration areas near Cañon de Valle, the conclusion was reached that these RDX hot spots are not migrating and are 3 miles from the nearest water supply well. The near surface contamination has been remediated primarily by removing 1500 cubic yards of RDX-contaminated materials and the use of a shallow permeable reactive barrier. The remaining RDX inventory is in the perched-intermediate aquifer (263 to1478 Kg, 30-51%), vadose zone (545 to 940 Kg, 32 to 62%), with lesser amounts in regional groundwater (35 to 415 Kg, 4 to 14%) and springs (35 to 56%, 2 to 4%), based on an updated survey in 2017 (EM2019-0235). The RDX concentration in one well is increasing, so localized hot spot remediation in groundwater may eventually have to be reconsidered. Because the original source of RDX infiltration has been removed (i.e., discharges from building 260), natural infiltration of precipitation should be significantly less. However, the 2011 Las Conchas fire burned significant vegetation, so may result in increased infiltration into the vadose zone. Therefore, methods to remediate RDX in the subsurface vadose zone, perched-intermediate aquifer, and regional groundwater need to be investigated. RDX degradation under abiotic and biotic reducing conditions have been investigated at the laboratory scale using subsurface media, which would be difficult to control at field scale given the depth of the regional aquifer and even more challenging in the perched intermediate aquifer and vadose zone due to water addition causing additional downward migration. If hot spot remediation were to be considered, RDX abiotic degradation by alkaline hydrolysis might be more easily managed at field scale in the regional aquifer (i.e., injection of NaOH to maintain pH > 10, Heilmann et al., 1996) or by NH_3 gas injection in the vadose zone and perched-intermediate aquifer without water addition (Szecsody et al., 2011). It should be noted that aqueous hydrolysis is a source area treatment (i.e., OH^--laden water reacting directly with aqueous RDX) and not a permeable reactive barrier treatment.

Focus Area(s): RDX remediation of hot spots by alkaline hydrolysis in the vadose zone, perched-intermediate aquifer, and regional aquifer.

Description: Alkaline hydrolysis of aqueous RDX, high melting explosive (HMX), trinitrotoluene (TNT), and other energetics is well established at the laboratory scale (Heilmann et al., 1996, Balakrishnan et al., 2003, Hwang et al., 2006) and at field scale (Davis et al., 2007). Aqueous energetics are degraded by alkaline hydrolysis using a number of different bases (i.e., direct source area treatment), and in situ application (i.e., permeable reactive barrier) is generally accomplished using lime (Martin et al., 2013, Petery et al., 2021). Most in situ permeable reactive barrier applications involve trenching and lime addition or source area treatment by injection of alkaline solutions. For application to the Los Alamos regional aquifer, source area treatment with alkaline water addition would be possible requiring no additional development. Injection of particulate lime into the fractured regional aquifer would create a permeable reactive barrier, but some development would be needed. Pressurized injections of lime has been done at shallower depths (Thompson and Robnett, 1976) and, in some cases 10s of feet in depth (Glendinning et al., 2015).

In the vadose zone, alkaline conditions can be created by ammonia gas injection (Szecsody et al., 2011, Zhong et al., 2015, Emerson et al., 2018) in laboratory experiments and was nearly implemented at field scale for uranium remediation. In those studies, a 5% ammonia gas injection (with 95% N_2) resulted in 3.1 mol/L (pH 11.8) pore water because most of the ammonia mass partitions into pore water. The advantage of using NH_3 gas for the vadose zone and perched intermediate aquifer is there is no water addition, so no increased mobilization of RDX or other co-contaminants.

The alkaline pore water slowly dissolved some minerals (montmorillonite, illite, muscovite) and as the pH neutralized, other aluminosilicates formed, incorporating uranium. Although transport properties of ammonia gas have been extensively studied at the laboratory scale in experiments to 30 ft length and modeled at field scale, the efficiency of injecting ammonia gas into a porous tuff to create alkaline conditions in the pore water has not been studied, nor has the subsequent reactivity with RDX been studied. RDX may be degraded in the alkaline pore water, but over time, the alkaline pore water will be neutralized by reactions with minerals in the rock matrix, so experiments are needed to evaluate the relative rates of RDX alkaline hydrolysis and pH neutralization.

<u>Development Status</u>: For the regional aquifer application, the use of source area treatment of RDX by alkaline water addition is well established and not depth limited. Lime injection into the subsurface has only been conducted at shallower (< 100 ft) depths at field scale. For the vadose zone and perched-intermediate application, the use of ammonia gas to create alkaline pore water has not been conducted at field scale, but the technology to inject ammonia gas is not depth limited. However, the relative rate of RDX degradation by NH_3-laden pore water to reactions of the alkaline pore water with mineral phases has not been investigated.

<u>Technology Inter-Relationships</u>: Different amendments can be used to abiotically or biotically degrade RDX and other energetics including a) reducing conditions, b) highly oxidizing conditions (i.e., permanganate), c) alkaline hydrolysis, and d) thermal treatment. Abiotic reducing conditions with Na-dithionite and oxidation using permanganate have been tested at field scale under the Pantex, Tx facility in a perched aquifer at 250 ft depth. While there are more options in the regional aquifer (i.e., different amendments can be injected as aqueous solutions), there are fewer options in the vadose zone and perched-intermediate aquifer without water addition. Ammonia gas can create alkaline conditions in vadose zone pore water, but the efficiency to degrade RDX under these conditions has not been evaluated.

B-4. Quantify Vadose Zone Cr Mass, Potential for Long-Term Impact on Groundwater, and Evaluate Gas Phase Remediation Strategy, if needed

Summary Information

Objective and Potential for Risk Reduction: The Los Alamos site with some shallow alluvium in places and mainly fractured rock vadose zone (~1000 ft thick) and fractured rock regional aquifer is a more challenging environment for contaminant remediation. If there was significant chromate in the vadose zone, it could potentially migrate to the regional aquifer and be a continued long-term source. To evaluate the potential risk for impact to groundwater, the Cr mass, location within the vadose zone, and current and future (if changing) water flux through the vadose zone is needed. If the risk potential of long-term Cr migration through the vadose zone to groundwater may have sufficient impact on Cr groundwater concentrations, then vadose zone remediation could be evaluated. Change in the surface water flux into the vadose zone can be evaluated (i.e., either minimizing infiltration or flushing to groundwater assuming water is captured in a pump and treat system). In situ gas-phase remediation of chromium can also be evaluated for the Los Alamos fracture flow vadose zone. Previous gas phase reduction technologies have been used at different sites that are porous media (Thornton and Amonette, 1999), and application to a fracture flow system would likely be challenging and possibly ineffective.

Focus Area(s): Identify potential of migration of shallow Cr(III) precipitates in the shallow subsurface.

Description: If there was significant chromate in the vadose zone, which would potentially migrate to the regional aquifer, gas phase abiotic or biotic reduction could be considered. One gas phase technology (H_2S gas) has been demonstrated in a shallow porous media field site (White Sands, NM) for chromate. This could be used below the basalt and has the potential to advect into fractures as well (as opposed to a liquid phase reductant). The use of H_2S for reduction of pertechnetate has been demonstrated at the laboratory scale (Szecsody et al., 2014), but is unlikely to be used at field scale at the DOE Hanford site due to hazards associated with field scale H_2S use. Bioreduction of chromate under vadose zone conditions has been demonstrated in sediments at higher water content (Oliver et al., 2003), as well as gas phase reduction of other metals (Chung et al., 2006, Hol et al., 2010). Reduction of chromate, nitrate, and cyanide using gas phase amendments (pentane, butyrate, butyl acetate) has also been demonstrated at the laboratory scale at higher water content (Bagwell et al., 2020).

Chromate can be biotically reduced to Cr^{III} and precipitates (Chai et al., 2009, Viamajala et al., 2007) or abiotically reduced by aqueous ferrous iron (He and Traina, 2004), adsorbed ferrous iron (Szecsody et al., 2004, Cheng et al., 2009) or structural Fe^{II} in clay (Jardine et al., 1999) forming $(Cr, Fe)(OH)_3$ precipitates that have a lower solubility than $Cr^{III}(OH)_3$ (Eary and Rai 1988; Loyaux-Lawniczak et al. 2001).

Development Status: A few cases of MnO_2 oxidation of Cr(III) precipitates have been reported, although under most subsurface geochemical conditions, Cr(III) precipitates remain immobile. Cr(III) precipitate (and other metal precipitates) movement on inorganic colloids have been studied in a few cases.

Technology Inter-Relationships: A proposed paper study of these processes under the specific LANL geochemical conditions will quantify the risk of potential migration of Cr into the deep subsurface. If the results show there is little potential of migration of Cr(III) precipitates, then existing groundwater models do not need to include additional source area terms. Alternatively, if results show there is limited, but slow migration of Cr(III) precipitates either by oxidation or colloidal transport, then, depending on the time scale of migration, this information may or may not need to be included in existing groundwater models. Cr(VI) and Cr(III) acidic (Szecsody et al., 2019) or alkaline extractions without and with an oxidant (Zhao et al., 2017) can be used to characterize which precipitates are Cr(VI) and Cr(III).

B-5. Characterization of the Potential Cr(III) Precipitate Oxidation/Remobilization or Colloidal Transport in Shallow Sediments

Summary Information

Objective and Potential for Risk Reduction: Significant chromium mass as Cr(III)$(OH)_3$ or mixed (Fe, Cr)$(OH)_3$ precipitates exist in the shallow wetland alluvial sediments, and are generally immobile, as Cr(III) precipitates do not reoxidize under most natural reducing or oxic conditions. In some cases, Cr(III) precipitates have been reported to be oxidized by MnO_2. In addition, Cr(III) precipitates have also been reported to migrate short distances on inorganic colloids. Although Cr(III) oxidation by Mn oxides may be insignificant or Cr(III) precipitate movement with colloids may mobilize only short distances, these processes should be investigated to minimize risk of source area Cr movement over the long term.

Focus Area(s): Identify potential of migration of shallow Cr(III) precipitates in the shallow subsurface.

Description: Chromate can be biotically reduced to Cr^{III} and precipitates (Chai et al., 2009, Viamajala et al., 2007). In addition, it can be abiotically reduced by aqueous ferrous iron (He and Traina, 2004), adsorbed ferrous iron (Jacobs and Testa, 2005, Szecsody et al., 2004, Cheng et al., 2009) or structural Fe^{II} in clay (Jardine et al., 1999, Loyaux et al., 2001), or organic matter (Anderson et al., 1994, Tian et al., 2010). The subsequent formation of (Cr, Fe)$(OH)_3$ precipitates have a lower solubility than $Cr^{III}(OH)_3$ (Eary and Rai 1988; Loyaux-Lawniczak et al. 2000; Wilkin et al., 2005), and are difficult to oxidize under most natural conditions, although oxidation can occur with MnO_2 (Steinpress, 2005; Butler et al., 2015). In addition, although unlikely, Cr(III) precipitates could also move on colloids such as Fe oxide particulates as previously reported in loess (Zhou et al., 2019) and for Cs (Flury et al., 2002). This is likely to move very short distances (feet), and over field realistic time scales, colloids aggregate (Czigany et al., 2005). However, cases referenced are in porous media, and it is unclear how colloidal transport might differ in fracture flow systems, although have been studied at Yucca Mountain to a limited extent (Baek and Pitt, 1996) and in other fracture flow systems (Vesper et al., 2001).

Development Status: A few cases of MnO_2 oxidation of Cr(III) precipitates have been reported, although under most subsurface geochemical conditions, Cr(III) precipitates remain immobile. Cr(III) precipitate (and other metal precipitates) movement on inorganic colloids have been studied in a few cases.

Technology Inter-Relationships: A proposed paper study of these processes under the specific LANL geochemical conditions will quantify the risk of potential migration of Cr into the deep subsurface. If the results show there is little potential of migration of Cr(III) precipitates, then existing groundwater models do not need to include additional source area terms. Alternatively, if results show there is limited, but slow migration of Cr(III) precipitates either by oxidation or colloidal transport, then, depending on the time scale of migration, this information may or may not need to be included in existing groundwater models.

B-6. Matrix Diffusion as a Natural Attenuation Mechanism

Summary Information

Past and emerging scientific literature demonstrates that matrix diffusion plays a role in attenuating the expansion of groundwater plumes at many sites. For example, parametric modeling applied to a heterogeneous geologic site with a constant source and no degradation in the plume, documented that matrix diffusion alone can significantly reduce plume lengths (based on a target regulatory standard) at appropriate sites, down to 20% of the baseline length compared to no matrix diffusion (Farhat et al., 2022). In general, this modeling indicated that, over time, matrix diffusion results in lower concentrations throughout the plume and smaller plume footprints. Importantly, the impacts of matrix diffusion are functionally and mathematically equivalent to recognized natural attenuation mechanisms such as sorption. Like sorption, matrix diffusion reduces the peak dissolved concentration in groundwater in the plume but has the collateral impact of increasing total remediation timeframe by extending "plume tailing." Matrix diffusion is particularly important in highly heterogeneous interbedded and fractured systems such as the LANL vadose zone and groundwater where the active flow occurs in a relatively small portion of the subsurface volume. A consensus recommendation for the EM-LA team and regulators is to assess the potential role of matrix diffusion in attenuating chromium and RDX, incorporate this as a recognized mechanism in monitored natural attenuation (MNA) calculations at this site, and also account for the collateral (negative) impacts of matrix diffusion by incorporation of the extended plume tailing into projections of remediation timeframe as necessary.

Description:

Although destructive (or transformative) processes that decrease the quantity, toxicity, and/or mobility of contaminants are the most beneficial and preferred mechanisms to support MNA in controlling groundwater plumes, non-destructive processes, such as immobilization via sorption are also recognized as viable MNA processes (EPA 2007). The potential role of matrix diffusion in MNA was recently recognized by the National Academies of Sciences, Engineering, and Medicine (2020):

"Matrix diffusion can be considered a natural attenuation process, because it attenuates the rate at which contaminants migrate in the forward direction, and it attenuates the contaminant discharge into the mobile fluid in the reverse direction…"

The potential impact of matrix diffusion has been quantitatively documented in the scientific literature. For example, early studies by Sudicky (1985), demonstrated the impact of matrix diffusion in a simple lab study of a high permeability sand layer sandwiched between two silt units (Figure 10). Comparison of the theoretical breakthrough curve to the attenuated breakthrough curve showed that the time to reach 35% of the source concentration increased from 9 days to 38 days (i.e., the plume was slowed by 75%). While this experiment used sand and silt, similar matrix diffusion impacts would be expected for a heterogeneous fractured system. Sudicky's early studies, later research, and emerging attenuation focused modeling (Farhat et al., preprint) support incorporation of matrix diffusion as an attenuation mechanism that is analogous to sorption.

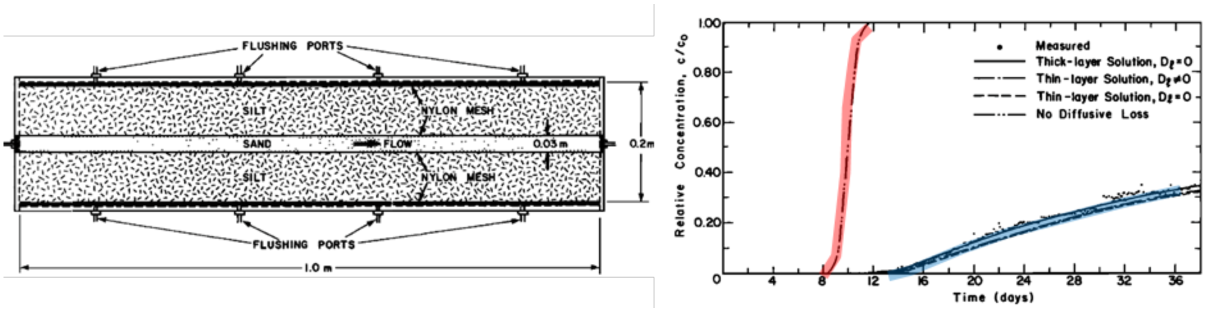

Figure 10. Attenuation impacts of matrix diffusion demonstrated in simple layered laboratory study (graphic adapted from Sudicky (1985)

Development Status: This is a straightforward concept that has significant documentation in the literature. Contaminant diffusion in and out of low permeability (low-k) zones in the subsurface is recognized as an important groundwater fate and transport process (e.g., Fetter 1999, National Research Council 2005 and 2013; Sale et al. 2013; Hadley and Newell 2014). Geologic heterogeneity and attendant matrix diffusion is one of the most prevalent hydrogeologic conditions found at hazardous waste sites (National Research Council 2005). Therefore, the presence of this heterogeneity should be considered a default assumption when working at groundwater cleanup sites (Payne et al. 2006). The literature demonstrates that matrix diffusion can provide significant attenuation of peak concentrations and plume growth, particularly for highly heterogeneous systems and similar settings in which most of the flow occurs in preferential flow zones or fractures. However, to date, matrix diffusion has not been recognized as an attenuation mechanism in EPA guidance documents. Additional modeling and documentation (see below) may be needed to incorporate matrix diffusion into the attenuation paradigm at LANL.

Site-Specific Advantages/Disadvantages: Incorporating matrix diffusion as a recognized attenuation mechanisms at LANL may be appropriate based on the complex highly heterogeneous geologic conditions. Advantages of this advancement would be a more complete conceptual model of attenuation processes impacting the plume, potential improvement in the understanding of historical and projected plume concentration profiles, and an improved basis for managing attenuation contributions to plume management strategies and to inform future contingency actions.

Technology Concepts for Consideration:

Inclusion of matrix diffusion as a mechanism contributing to attenuation at LANL requires additional documentation in the form of models or calculations and measurements in core material. Three potential approaches are identified and described in the next step/implementation details: 1) scoping models, 2) contaminant profiling in core material, and 3) site models that incorporate matrix diffusion or dual domain models:

1) Scoping models – Perform simple (e.g., 1D single fracture) modeling to document the potential magnitude/contribution of matrix diffusion to attenuating contaminants in the geology representative of the LANL vadose zone and groundwater. A properly scaled case with some bounding cases would provide information to the EM-LA team and regulators and support

improved technically-based future management. Note that this work could also be coordinated with sitewide modeling and potentially with some mass balance scoping modeling (e.g., REMChlor-MD).

2) Contaminant profiling in core material –These tests could be performed on existing (archived) core material or on new core material collected during upcoming drilling activities and would include penetration profiling of contaminants in the vicinity of any fractures identified in cores from contaminated areas. The penetration of contaminants into, and resulting concentration profile in the matrix, combined with site history, has the potential to provide actionable information on the extent and significance of matrix diffusion at this site. This semiquantitative information could be used in refining the site conceptual model and in improving the understanding of past and projected dynamic concentration trends throughout the plume.
3) Perform LANL sitewide models that incorporate matrix diffusion (or dual domain models) – perform more complete sitewide modeling using codes designed for fractured systems and that incorporate matrix diffusion explicitly or by mathematical methods such as dual domain. Note that this technology/approach represents a significant effort and could be implemented as needed during future years to support long term management goals.

B-7. Potential for Natural Attenuation and Chromium Input from Non-Contaminant Sources at Los Alamos National Laboratory, New Mexico

Prepared by the National Lab Network for Environmental Management and Stewardship, August 2021

- Outline of quantitative method for evaluating extent of natural attenuation in groundwater systems that could be applied towards the LANL site.
- Natural attenuation of Cr(VI) due to naturally-occurring Fe(II)-substituted minerals is possible in the regional aquifer and may explain the near steady-state of Cr_{total}/SO_4^{2-} at some of the monitoring wells.
- Upwelling of Cr(VI)-rich fluids along the regional fault system could be an additional deep source of Cr to the Regional Aquifer, independent of the anthropogenic source associated with prior activities at LANL.

Quantitative Method for Evaluating Extent of Cr*(VI) Natural Attenuation in Aquifers*

Potential naturally-occurring reductants for Cr(VI) to promote reduction to Cr(III) and precipitation of Cr(III) hydroxide include: humic substances (humic and fulvic acid), aqueous Fe(II), pyrite, magnetite, and ilmenite, and Fe(II)-containing chlorite (Zhao et al., 2017). Diffusion of Cr(VI)-rich groundwater from fractures and fast flow pathways, into bedrock matrix, can result in Cr(V) to Cr(III) reduction due to the extensive porosity within matrix that may contain naturally-occurring reductants. A peer-reviewed approach by Zhao et al. 2017 may be applied to aquifer solids associated with Cr(VI) plumes near the LANL site. The approach can be applied to quantify Cr(III) concentrations in aquifer rock matrices, which would provide information on the potential extent of natural attenuation that occurs.

The approach presented in Zhao et al., 2017, describes core selection at appropriate regions across a Cr(VI) groundwater plume, and application of both a hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) extractions to obtain total Cr, and Cr(VI), where the difference represents labile Cr(III) that can be attributed to natural attenuation in the aquifer matrix. The proposed analysis provides a unique dataset relative to direct sampling via conventional wells or multilevel monitoring systems, which provide results for fluid in the primary flow pathways/fractures and are not suitable for evaluating labile Cr(III) in the aquifer matrix.

Potential next steps for Cr(VI) at the LANL site:

- Identify appropriate samples for quantifying natural attenuation in the system – this likely would require new cores from strategic zones (an approach for core selection using the Discrete Fracture Network approach was noted in the Zhao et al., 2017 paper)
- Perform the H_2O_2 and NaOH extractions, and complementary analyses, presented in the Zhao et al., 2017, paper, to quantify labile Cr(III) in the samples
- Use results to define aquifer zones where natural attenuation is expected to occur, and to identify where enhanced attenuation may be achieved with additional remediation techniques, to constrain the Cr(VI) plume

Application of Well Geochemical Data to Evaluate Attenuation vs. Fluid Mixing in the Regional Aquifer

Due to the application of sulfuric acid during the zinc dianodic anticorrosion treatment that served as the primary source for the Cr(VI) plume, Cr and sulfate disposal history at the LANL site are linked (Looney et al., 2012). Because of this, evaluating the Cr_{total}/SO_4^{2-} can act as a proxy for identifying mixing versus geochemical reactions (adsorption, co-precipitation, redox reactions) that occur in the Regional Aquifer, as SO_4^{2-} may be applied as an approximately conservative tracer (Looney et al., 2012).

Based on an analysis of pre-2012 data, average ratios for the monitoring wells demonstrate a decrease in Cr_{total}/SO_4^{2-} moving away from the center of the plume; similar trends were observed for Cr_{total}/Cl^- ratios (Figure 11; Looney et al., 2012). This could result from Cr(VI) sorption; however this should not be a significant process at pH values near 8 (Looney et al., 2012). Cr(VI) reduction appears to have some impact on the extent of the plume, however prior evaluation of the LANL site recommended additional quantification of the rate and attenuation capacity of the Regional Aquifer (Looney et al., 2012).

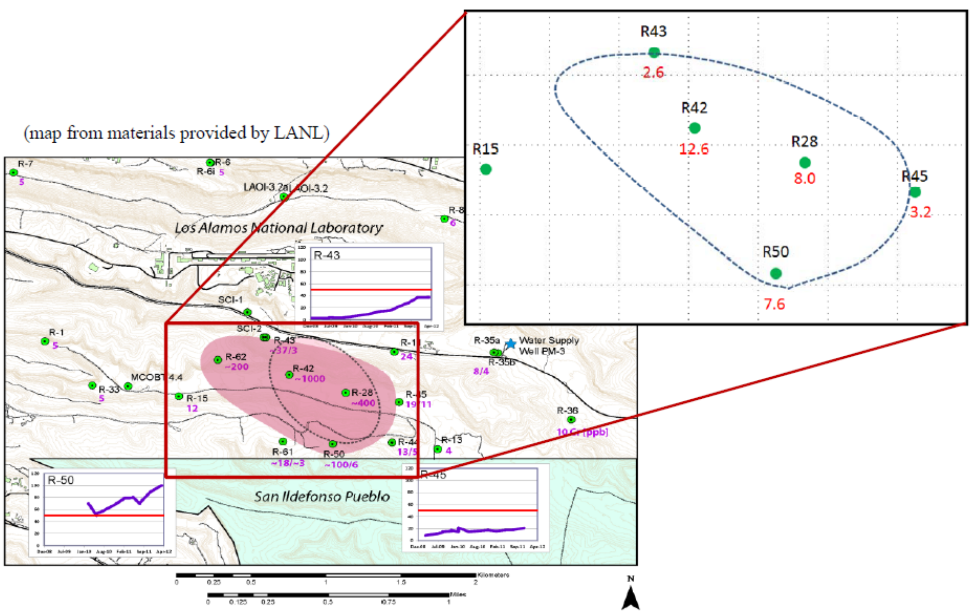

Figure 11. Map of Regional Aquifer monitoring wells, including an inset showing the Cr_{total}/SO42- ratios for a subset of the wells. Lower ratios near the edge of the area suggest a process in the reservoir that removes Cr from solution at the edges of the plume (from Looney et al., 2012).

As part of the 2021 NLNEMS effort, analysis of Cr_{total}/SO_4^{2-} data from 2013 through 2016 (Attachment 5 in LANL, 2018) showed that some of the monitoring wells remained near a steady state, while others showed a more dynamic change (Table B-1).

Table B-2: Percentage change in Cr_{total} /SO_4^{2-} ratio from prior year values. The base year value used for the calculation is 2013 unless otherwise indicated. Orange highlight indicates that the well has increased in aqueous Cr_{total}, and green highlight indicates minimal increase (≤1.0%) or decrease in aqueous Cr_{total}.

Well	2014	2015	2016
R-1	-3.1	13.0	47.2
R-11	-0.6	-5.5	-5.7
R-13	-15.5	-22.4	-18.9
R-14 S1[1]		3.7	11.1
R-15	-18.6	-8.6	-4.6
R-28	-10.5	-2.5	1.0
R-35a	33.1	19.0	46.1
R-35b	6.1	23.9	29.5
R-36	26.9	12.7	22.6
R-42	-10.1	-12.3	-15.5
R-43 S1	39.7	96.4	117.3
R-43 S2	80.9	62.5	111.5
R-44 S1	-1.1	-4.6	0.7
R-45 S1	1.6	17.1	30.6
R-45 S2	21.9	34.7	39.1
R-50 S1	-0.5	7.2	10.6
R-62	14.8	-8.2	4.9
R-67[2]			-38.0
SIMR-2[2]			-54.8

[1]Base year is 2014.
[2]Base year is 2015.

Wells highlighted in green may be good candidates for evaluating the extent of natural attenuation that may occur through mineral redox reactions (R-11, R-13, R-15, R-28, R-42, R-44 S1). Wells highlighted in orange may be good candidates for evaluating the influence of different groundwater types (impacted by anthropogenic and natural sources) on contributing elevated Cr(VI) to the system relative to sulfate (R-1, R-14, R-35, R-36, R-43, R-45, R-50, R-62). Well R-67 and SIMR-2 are considered background wells (LANL, 2018).

Natural Attenuation of Contaminants in Systems with Elevated O_2,aq

Prior analysis of the potential for Cr(VI) to be controlled via natural attenuation by redox-reactive minerals characterized a high reduction and attenuation potential in the surface wetland, moderate attenuation potential in the vadose zone and perched water pathway, and moderate to low attenuation potential in the regional aquifer (Looney et al., 2012). For example, iron carbonate (siderite) and Fe(II)-bearing phyllosilicate clays, which are identified as having reductive capacity towards certain contaminants (e.g., He et al., 2009), are potentially present in the Regional Aquifer (LANL, 2018) and may control Cr(VI) mobility in certain zones (e.g., Looney et al., 2012). Cr(VI) reduction in the presence hematite, due to small amounts of FeO present within the hematite, has been reported, along with Cr(VI) reduction by iron-containing silicates (Eary and Rai, 1989; cited in Palmer and Puls, 1996). Reduction of Cr(VI) by Fe(II)-bearing minerals has been observed in the presence of dissolved oxygen in laboratory experiments and field-scale transport experiments (Ilton et al., 1997; Kent et al., 1994; both cited in Ford et al., 2008). The laboratory-scale natural attenuation studies performed previously (LANL, 2018) may not be of sufficient temporal length to quantify the reaction kinetics of Cr(VI) reduction by Fe(II)-bearing minerals, which can be on the order of years. This points towards the need for additional investigation to quantify potential Cr(VI) reduction rates in the Regional Aquifer, even if the reaction kinetics are extremely slow or isolated in certain regions (e.g., wells identified in Table B-1 above).

Identifying Anthropogenic and Naturally-Occurring Source Terms of Cr

Application of machine learning towards the monitoring data collected from wells used to monitor the Cr plume revealed multiple distinct compositions of groundwater that contribute to the different wells (Table 2; LANL, 2018; Attachment 5). An increased understanding of these potential groundwater types that are mixing with background Regional Groundwater, and their sources (e.g., from the LANL-associated Cr source, or from another anthropogenic and/or natural source) would help in understanding contributions of Cr and controls on its mobility in the regional aquifer. Research on high-total dissolved solids in fluids associated with the Roberts Fault near Chimayo, NM, showed ~30 ppb Cr_{total} in fluids associated with intermittent CO_2 upwelling from depth (Keating et al., 2010), indicating that naturally occurring sources of elevated Cr are present in fluids sourced from the regional fault system.

B-8. Technology/Strategy: Redox Disequilibrium and Mixing Curves - Uranium

Summary Information

Objective and Potential for Risk Reduction: Evaluate redox disequilibrium and groundwater (GW) mixing curves as approaches to help identify driving forces for Cr(VI) transformations and speciation controls in the bedrock aquifers beneath LANL. Assess if the emergent plume is influenced by fluctuations in in pH/ORP and the spatially variable chemical conditions. New and existing monitoring well data could be used to support these analyses. The information may provide an additional line of evidence to support/reject the potential hypotheses relating to Cr(VI) geochemistry in the regional aquifer.

Description:

Redox Disequilibrium. Calculate the state of redox disequilibrium for wells in the regional aquifer to identify dominant redox couples (e.g., Fe^{3+}/Fe^{2+}, SO_4^{2-}/S^{2-}, NO_3^-/NO_2^-, NO_3^-/NH_4^+, O_2/H_2O, etc.) over space and time. The calculations can help to identify whether the system is at steady state or in flux. At GW temperatures, many redox reactions will not reach equilibrium due to kinetic constraints. Lindberg and Runnells (1984) compiled more than 600 analyses of 30 GW streams that included a minimum of two measures of oxidation state and calculated redox couple species distributions for each sample (see Figure 12). Next, they calculated E_h/pE values for the different redox couples using the Nernst equation. Figure 12 confirms that redox couples in a sample are generally in a state of disequilibrium with each other. GWB Online Academy (2020) describes how redox disequilibrium can be accounted for in geochemical models, such as The Geochemist's Workbench® (Bethke et al., 2020), by disabling one or more redox coupling reactions. All coupled redox reactions reflect the Master E_h for the system, while disabled redox couples behave independently based on their Nernstian E_h (see Figure 13). Identifying whether there is a redox transition, and which redox couples are controlling the transition, can help to identify controls on Cr(VI) geochemistry. Further, coupling the redox disequilibrium analysis with the mixing curve calculations can provide further information to support assessment of potential attenuation.

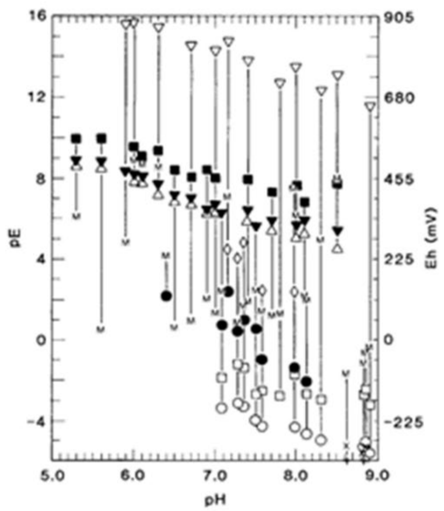

Fig. 1. Comparison of measured and computed Eh values in 30 ground waters as a function of pH. Symbols and couples are summarized in Table 1. Points connected by a vertical line are derived from a single water sample.

Table 1. Redox couples and plotting symbols used in the construction of Fig. 1

◇	Fe^{3+}/Fe^{2+}
▽	O_2/H_2O
○	HS^-/SO_4^{2-}
□	HS^-/S(rhombic)
■	NO_2^-/NO_3^-
▼	NH_4^+/NO_3^-
△	NH_4^+/NO_2^-
+	CH_4/HCO_3^-
x	NH_4^+/N_2
●	$Fe^{2+}/Fe(OH)_3(s)$
M	Field-measured Eh value

Lindberg and Runnells, 1984, Science, 225, 925–927.

Figure 12. Comparison of measured vs. computed E_h values in 30 ground waters as a function of pH (Lindberg and Runnells, 1984).

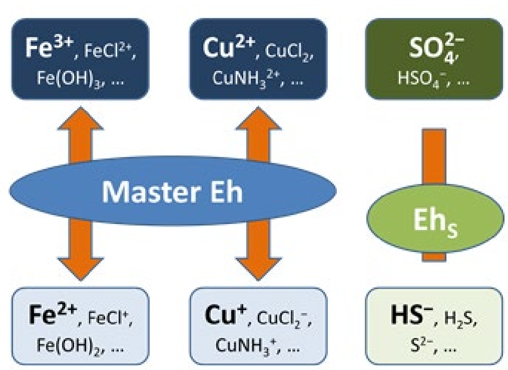

Figure 13. Schematic showing coupled and uncoupled redox reactions in a geochemical model (GWB Online Academy, 2020).

<u>Development Status</u>: The analysis approach is well developed. Existing chemical and isotope data may be reevaluated to identify any new insights. If new GW data must be collected, then a more focused effort would be required.

LANL Site-Specific Advantages/Disadvantages:

Advantages include:

- Provides actionable interpretations using existing data
- Simple and relatively inexpensive to implement and interpret
- Provides opportunity to confirm changes in the general nature of Cr(VI) attenuation using inexpensive cation/anion sample analyses (for newly collected GW samples) and geochemical calculations

Disadvantages include:

- Additional well samples and analytes would require time/financial investment

Technology Inter-Relationships: Results of analysis will be stronger if coupled with other existing data analysis tools such as review existing sediment and GW data, isotopes and chemical tracers as proxies of geochemical trends, and abandoned borehole/well investigation.