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Date: February 14, 2001
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FEB 2001 RECEIVED

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SUBJECT: GROUNDWATER ANNUAL STATUS SUMMARY REPORT FOR FISCAL YEAR 2000

HSWA LANL G/m/HWP

Dear Mr. Young:

Enclosed for your information and comment is the draft version of the *Groundwater Annual Status Summary Report for Fiscal Year 2000.* We plan to incorporate comments in the final version of this report, which will be completed in time for the annual review meeting in March.

I look forward to receiving yours and other Bureau's comments by February 26. Please call me (505) 665-4681 if you have any questions.

Sincerely,

Charles L. Nylander

Charles L. Nylander
Water Quality and Hydrology Group

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GROUNDWATER ANNUAL STATUS REPORT
for
FISCAL YEAR 2000

Los Alamos National Laboratory
February 9, 2001

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1.0 INTRODUCTION

This is the fourth Annual Report intended to provide the Department of Energy (DOE), the New Mexico Environment Department (NMED), and other interested stakeholders with a status of the groundwater protection and management activities performed during fiscal year 2000. This report describes how the data collected over the past year has been integrated to revise the Los Alamos National Laboratory's (LANL's or Laboratory's) conceptual model of the hydrogeologic setting and to resolve the decisions that form the basis of the Hydrogeologic Workplan. It also provides a projection of activities for fiscal year 2001.

This document is intended as an addendum to the Hydrogeologic Workplan. This document is specifically written as a summary-level report and relies on information incorporated by reference.

1.1 Background

The need to prepare this Annual Report comes from commitments made in the Groundwater Protection Management Program Plan (GWPMPP) (LANL, 1996) and the Hydrogeologic Workplan (LANL, 1998). The Laboratory has had groundwater programs in place since 1945. The early programs were focused on the need to develop reliable water supplies. Groundwater quality has been monitored through the environmental surveillance program using existing test wells, water supply wells, and springs. Since the early 1990s, there has been an increased emphasis on understanding the hydrogeologic environment in order to more effectively protect and manage the groundwater resource.

The GWPMPP (approved by DOE in 1996) provides for submittal of an annual groundwater status report to DOE summarizing the status of groundwater protection activities listed in the GWPMPP. The GWPMPP was prepared in response to the DOE requirement to conduct operations in an environmentally safe manner. DOE Order 5400.1: "General Environmental Protection Program" establishes environmental protection requirements, authorities, and responsibilities for all DOE facilities (DOE 1990). The goal of this order is to ensure that operations at DOE facilities comply with all applicable environmental laws and regulations, executive orders, and departmental policies.

The Hydrogeologic Workplan (approved by NMED in 1998) commits the Laboratory to prepare an annual report to summarize the activities of the previous fiscal year and to make recommendations for the current fiscal year activities. The Hydrogeologic Workplan was prepared in response to the NMED request to prepare a hydrogeologic work plan to address the requirements of the Resource Conservation and Recovery Act (RCRA) and the Hazardous and Solid Waste Amendments of 1984 (HSWA) as detailed in the regulations and in the Laboratory's RCRA/HSWA permit. The Hydrogeologic Workplan is the implementing document for the GWPMPP and the Laboratory's institutional commitment to complete a hydrogeologic characterization program. It describes the data collection and analysis activities that will characterize the hydrogeologic setting of the Laboratory as part of the Pajarito Plateau within the regional context of the Española Basin. The need for characterization of the hydrogeologic setting beyond that already established by studies over the past 50 years has been recognized as a critical step in developing an effective monitoring program and in managing the groundwater resource.

This Annual Report serves as the annual status report for both the GWPMPP and the Hydrogeologic Workplan. Further, this Annual Report serves as the update mechanism for the scope and schedule in the Hydrogeologic Workplan. Specifically, the Hydrogeologic Workplan will not be revised; however, changes to the scope and schedule outlined in the plan will be discussed with NMED in quarterly meetings and at the annual meeting. Those changes for which there is concurrence by all parties will be documented in this Annual Report.

1.2 FY00 Accomplishments Summary

This section is intended to provide a concise list of FY00 groundwater activity accomplishments. More detailed descriptions of these activities are contained in the referenced sections.

- Drilled and constructed four wells (R-19, R-9i, CDV-15, and R-31); completed four wells (R-15, R-25, R-9, R-12); started drilling R-22 (Section 4.1)
- Conducted two rounds of quarterly sampling (R-9, R-9i, R-12, R-15) (Section 4.1)
- Completed Well Completion Reports for R-9, R-9i, R-12, R-15, R-19 (Section 4.1)
- Produced the FY99 Groundwater Protection Program Annual Status Report, published as a LANL Status Report (LA-13710-SR) (Section 4.2.1)
- GIT participated in ESH Division Review and the presentation was rated as "outstanding" and received Los Alamos Achievement Award.
- Developed a stochastic approach to modeling variations in hydraulic conductivity within the Puye Formation for the regional aquifer model (Section 4.2.2)
- Evaluated pump test simulations for possible O-1/R-5 cross-hole testing in support of R-5 siting decision (Section 4.2.2)
- Analyzed site-wide hydraulic conductivity trends using hydraulic conductivity data, water levels, and inverse modeling (Section 4.2.2)
- Updated Los Alamos Canyon model, including predicting potential impacts of the Cerro Grande fire (Section 4.3.2)
- Hosted a field trip of characterization activities for the National Groundwater Association.
- External Advisory Group produced two reports and Groundwater Integration Team (GIT) responded with two action plans (Section 2.2)
- Underwent a Management Assessment for compliance with ER Project QA Plan
- Database runoff flow and chemistry modules available to public at: http://www.esh.lanl.gov/~esh18/teams/GCFire/index.html (Section 5.0)
- Incorporated DP Monitoring Well Project into ER Project "Project Planning and Control System" (PP&CS) (Section)
- Produced monthly joint DP/ER status reports
- Held GIT bi-weekly meetings, three quarterly meetings and the Annual Meeting (Section 2.1)
- Successfully awarded a task order for ER Project Groundwater Investigation Focus Area field support and drilling
- Underwent an audit for compliance with Laboratory Implementation Requirements (LIRs) by the Project Management Division
- Prepared data reports on the mechanical testing of hydrologic properties on samples from R-9, R-12, R-25 (Section 4.1.2)
- Produced an expanded Hydrogeologic Atlas (Section 4.2.1)
- Implemented well head protection after Cerro Grande fire (Section 2.1.4)
- Developed a proposal for monitoring at Los Alamos Canyon low-head weir

1.3 Annual Report Organization

This report is organized to present the programmatic and technical activities that have been accomplished during the year. The programmatic activities are described in Section 2. The data that have been collected and analyzed during the past four years have resulted in a major revision to the Hydrogeologic Conceptual Model. The resulting FY00 Hydrogeologic Conceptual Model revisions are presented in Section 3.

Both the GWPMPP and the Hydrogeologic Workplan describe data collection and interpretation activities. These activities consist of both non-field and field activities. Data collection activities are primarily field activities and include some that are regional in scale (e.g. sample all springs) and some that are specific to particular geographic areas, particularly the sites of regional aquifer wells. Data interpretation involves primarily non-field activities, which includes tasks such as historical data compilation and computer modeling. The status of the data collection and interpretation activities is described in Section 4 of this report. A major component of the hydrogeologic characterization is management of the data. Section 5 describes the data management activities in FY00. Section 6 summarizes the progress made toward resolving the decisions described in the Hydrogeologic Workplan by integrating the data collected in FY00. Section 7 contains a summary of activities proposed for FY01.

2.0 PROGRAMMATIC ACTIVITIES

Programmatic activities are those functions that are required to manage the technical, cost, and schedule aspects of the program and to communicate the status and results of the program to stakeholders. The technical aspects of the program are governed by the Groundwater Integration Team (GIT), an interdisciplinary Laboratory group that provides guidance and oversight to the program. The GIT meets on a bi-weekly basis to consider the status of the data collection and data interpretation activities.

The GIT holds three quarterly meetings and one annual meeting per fiscal year. The purpose of these meetings is to communicate the status of the program activities with stakeholders and provide an opportunity to receive feedback and input from the stakeholders on the progress and plans for the program. The issues discussed and decisions made in the quarterly and annual meetings become addenda to the Hydrogeologic Workplan. Section 2.1 summarizes those meetings and the resulting decisions.

The technical aspects of the program have also been reviewed by the External Advisory Group (EAG), which has provided peer review of the program. A summary of the EAG semi-annual reports and the action plans developed to respond to those reports are described in Section 2.2.

2.1 Summary of FY00 Meetings

Four meetings were held to discuss the groundwater characterization activities that occurred in FY00. The participants of the meetings were Laboratory staff involved in the activities, DOE representatives, and NMED representatives from the bureaus of Hazardous Materials (HMB), Groundwater Quality, and DOE Oversight. Other interested stakeholders that attended the meetings were representatives from San Ildefonso Pueblo, Santa Clara Pueblo, Los Alamos County, New Mexico Attorney General, Northern New Mexico Citizens Advisory Board, and Concerned Citizens for Nuclear Safety. A summary of each meeting and the points of agreement are provided in the following sections.

2.1.1 October 13-15, 1999 Quarterly Meeting

The notes from the October 13-15, 1999 Quarterly Meeting were issued by memorandum from Charles Nylander of the Laboratory's Water Quality and Hydrology Group (ESH-18) on November

24, 1999. The topics in the first day of the meeting were a review of the performance of the hydrogeologic characterization program and updates on the modeling activities for the vadose zone and regional aquifer and the geochemical conceptual model. The second day of the quarterly meeting included status reports from the Information Management, Well Construction, Hydrology, Modeling, and Geochemistry subcommittees. The second day also included presentations on the Data Quality Objectives re-iteration effort and lessons learned from R-25.

The significant issues discussed were:

- Well construction schedule for FY00 is to complete R-25 and R-31, drill and complete R-5, R-7, R-19, R-27, and a well in TA-15.
- Making data from the Hydrogeologic Characterization Program available through the internet will be a priority in the coming year.
- There was a commitment to distribute Field Implementation Plans for the regional aquifer wells to the four Accord pueblos, NMED, and EAG for review before drilling activities begin.
- The draft data release policy that was proposed should be finalized with input from the stakeholders.
- NMED voiced a concern about communication and LANL agreed to resume sending out weekly drilling reports.
- NMED also continued to express concern regarding the timing of installing wells in the perched zones and installing intermediate wells to define the extent of plumes discovered while drilling regional aquifer wells. LANL committed to discuss the proposed response to contamination process with NMED.
- NMED committed to review minutes from quarterly and annual meetings and respond with a letter acknowledging the issues and action items identified.
- LANL and NMED agreed to form a policy group to define the "end state" of the Hydrogeologic Characterization Program.

2.1.2 January 27, 2000 Quarterly Meeting

The January 27, 2000 Quarterly Meeting is documented in notes issued in a memorandum from Charles Nylander of the Laboratory's Water Quality and Hydrology Group (ESH-18) on February 16, 2000. The agenda included presentations on modeling, information management, well construction, geochemistry, and hydrology from the Groundwater Integration Team subcommittees. There were special presentations on response to contamination pilot test, well prioritization, plans for existing test wells, and management of produced water.

The major agreements and action items reached in the meeting were:

- The FY00 drilling schedule was revised as follows: complete R-12, R-31, R-19, CDV-15-3, and R-9 intermediate well; and begin drilling R-7 and R-5.
- The Groundwater Annual Status Report for Fiscal Year 1999 will be mailed out to everyone on the mailing list prior to the March Annual Meeting.
- Evaluation of existing test wells to determine if they should be plugged and abandoned will be added to the scope of FY01 activities.
- LANL and NMED agreed to reach consensus on well prioritization prior to the March Annual Meeting.
- NMED urged LANL to develop a Standard Operating Procedure for management of water produced during drilling, completion, and hydrologic testing activities.

2.1.3 March 29-31, 2000 Annual Meeting

The notes from the March 29-31, 2000 Annual Meeting were distributed as a memorandum from Charles Nylander, ESH-18, dated August 14, 2000. The agenda for the meeting included status reports from the GIT subcommittees: well construction, modeling, hydrology, geochemistry, and information management. There was discussion of the following management issues: anticipated scope and schedule for the remainder of FY00, process for data distribution, recent groundwater findings, plugging and abandonment, quality assurance, and sampling. There were technical presentations on stratigraphy at R-31, geology and hydrology of the regional aquifer, stable isotopes and anions as vadose zone tracers, approaches to under standing recharge to the regional aquifer, refinements to understanding of vadose zone from injection test data, and the ER Project approach to risk assessment.

Major agreements reached in the meeting were:

- Replace R-1 with R-24 in the proposed drilling schedule for FY01. With this change, the FY01 drilling schedule is to drill and complete R-5, R-8, R-22, R-24, and R-27.
- Develop modeling and information management work plans with more detailed scope than what is in the Hydrogeologic Workplan.
- Ensure the Hydrogeologic Characterization activities are conducted in compliance with a Quality Assurance Plan.
- In response to LANL's concern regarding the constraints on well development imposed by short filter pack lengths, the NMED committed to reviewing the Hazardous and Solid Waste Amendments (HSWA) permit for technical details regarding length of filter pack for monitoring wells.
- In response to concerns raised by stakeholders, LANL committed to tailoring the technical level of discussions to stakeholder interests by including information such as references to standards, distance from receptors, mobility of contaminants, potential treatment technologies.
- The managers from LANL, NMED, and DOE agreed to draft a final Hydrogeologic Workplan goal statement.

2.1.4 June 22, 2000 Quarterly Meeting

The notes from the June 22, 2000 Quarterly Meeting were distributed as a memorandum from Charles Nylander, ESH-18, dated December 18, 2000. The agenda for the meeting included status reports from the GIT subcommittees: well construction, modeling, hydrology, geochemistry, and information management. There was discussion of the following management issues: program status after the Cerro Grande fire, damage assessment and well head protection, and an update on information management and modeling workplan revision. There was a technical presentation on the affect of drilling additives on water chemistry.

Major agreements reached at the meeting were:

- Safety precautions after the Cerro Grande fire prohibit activities in the canyons during the rainy season. Therefore, R-7 in Los Alamos Canyon will be replaced by R-22 on the mesa near Area G in the FY00 schedule, if funding is available after the fire rehabilitation has been completed. Also, due to less funding from DP, drilling of R-5 will be postponed until FY01.

- FY01 schedule is to complete R-22; drill and complete R-7, MCOBT-1, MCOBT-2, CDV-R37-2, R-27, R-5, and R-24; and begin drilling R-8.
- The Hydrogeologic Workplan section on information management and modeling will be revised instead of creating two additional workplans. A draft of the Hydrogeologic Workplan Section 3 is expected to be complete by June 30 for discussion with NMED.
- There was agreement that due to the combined effects, Torquease and EZ mud will no longer be used together. However, the data collected from well R-19 shows that the additives break down sufficiently with well development and can be used to facilitate drilling when necessary.
- NMED expressed concern that funding to drill R-22 may not be available. LANL committed to bring the NMED concerns to LANL management.
- LANL and NMED committed to discussing the possibility of combining R-27 and R-28. Access concerns would require moving R-27 close enough to R-28 that drilling a single well might be most appropriate.

2.2 External Advisory Group Activities

The GIT formed an External Advisory Group (EAG) to provide an independent review of the GIT's implementation of the Laboratory's Hydrogeologic Workplan. The EAG consists of six members with diverse technical and professional backgrounds to provide a broad technical and managerial review of the Laboratory's Hydrogeologic Workplan activities and methods.

The EAG consists of the following members:

- Robert Charles, Ph.D.—Dr. Charles has a doctorate in Geology with a specialty in geochemistry. He also has a Master of Arts degree in Organizational Management, and has more than 25 years of experience in his disciplinary areas. Dr. Charles served as Chair of the EAG.
- Jack Powers, P.E.—Mr. Powers is a drilling consultant with more than 45 years of worldwide professional drilling experience.
- Robert Powell, M.S.—Mr. Powell has a Master of Science degree in Environmental Science and 25 years of experience and 33 groundwater-related publications. Mr. Powell has expertise in the area of low-flow groundwater sampling.
- Elizabeth Anderson, Ph.D.—Dr. Anderson has a doctorate degree in inorganic chemistry and more than 20 years of experience in health and environmental science. Dr. Anderson is a nationally renowned expert on risk assessment and established the major national risk assessment programs at the Environmental Protection Agency.
- David Schafer, M.S.—Mr. Schafer has 25 years of experience focused on computer modeling using numerical models, analytic element models, and proprietary analytical models that he has developed.
- Charles McLane, Ph.D. - Dr. McLane, the founder of McLane Environmental, has over 20 years of experience in hydrogeology, environmental investigation and remediation, and exposure and risk assessment.

The EAG met in conjunction with the October 13-15, 1999 Quarterly Meeting and the March 29-31, 2000 Annual Meeting for semi-annual reviews of activities proposed under the Hydrogeologic Workplan. The EAG provides a report of findings and observations based on the semi-annual reviews. And in response to the EAG report, the GIT develops an action plan that specifies how the recommendations of the EAG will be incorporated into the program. In FY00, the following reports were completed:

- Semi-Annual Report to the Groundwater Integration Team (GIT) of the Los Alamos National Laboratory by the External Advisory Group (December 23, 1999)
- Los Alamos National Laboratory Groundwater Integration Team Action Plan for the External Evaluation Group December 1999 Recommendations (March 2000)
- Semi-Annual Report to the Groundwater Integration Team (GIT) of the Los Alamos National Laboratory by the External Advisory Group (June 26, 2000)
- Los Alamos National Laboratory Groundwater Integration Team Action Plan for the External Evaluation Group March 2000 Recommendations (September 20, 2000)

At each EAG semi-annual review, there were sessions for stakeholders to discuss concerns about the program. The stakeholders appreciated these sessions, and the EAG has committed to holding similar sessions in conjunction with each semi-annual review.

3.0 FY00 HYDROGEOLOGIC CONCEPTUAL MODEL

The FY00 Hydrogeologic Conceptual Model constitutes a concise description of the current understanding of the Pajarito Plateau hydrogeologic setting. In previous Groundwater Annual Status Reports, the hydrogeologic conceptual model has been shown with additions and deletions highlighted in the text and the rationale for those changes described beneath each element. For this report, the hydrogeologic conceptual model was completely revised to improve clarity and remove redundant elements. To improve readability, the changes from the previous version are not shown. The synthesis of data collected during the fiscal year that have previously been a feature of this section are now included in Section 7, Status of Program with Respect to Resolving Decisions.

Section 3.1 describes the elements of the hydrogeologic conceptual model relating to the mesas. Section 3.2 describes the elements related to alluvial groundwater. Section 3.3 addresses the elements related to perched intermediate groundwater, and Section 3.4 addresses the elements relating to the regional aquifer. Section 3.5 describes elements of the geochemical conceptual model.

3.1 Mesas

- Within drier mesas (generally in the eastern portion of the Laboratory), water occurs in the Bandelier Tuff under unsaturated conditions. Relatively little water (~1 mm/yr) moves downward beneath the mesa tops under natural conditions, due to low rainfall, high evaporation, and efficient water use by vegetation. Atmospheric evaporation extends within mesas, drying out the mesa interior and decreasing downward flow. Moisture content of the tuff varies with recharge rate and with texture of the lithologic units.
- For wet mesas (generally along the western portion of the Laboratory), water occurs in the Bandelier Tuff primarily under unsaturated conditions. Groundwater also occurs as transient zones of saturation and in perennial saturated ribbons of limited spatial extent, which feed springs on the mesa sides. The saturated zones are localized by fractures and by permeability changes related to lithologic variations within the Bandelier Tuff. Higher rainfall and increased welding and jointing of the tuff lead to greater recharge rates for wet mesas than observed in drier mesas.
- In addition to spring discharge at mesa sides, saturated and unsaturated flow through mesas result in recharge to the underlying intermediate perched zones or the regional aquifer.
- Mesa top recharge under disturbed surface conditions is higher than under natural conditions. Increased recharge occurs when the soil is compacted, vegetation is disturbed,

or more water is added to the hydrologic system by features such as pavement, lagoons, or effluent disposal.

- Fractures within mesas could provide preferential pathways for contaminants, especially in regions of high infiltration and in rocks of low matrix permeability. Fracture flow is less likely to occur when the rock matrix is porous and permeable, because water is drawn out of the fractures. Contaminants in vapor form readily migrate through mesas.
- Water quality within mesas reflects the initial composition of rainwater, chemical interaction with the surrounding rocks, evaporative concentration of solutes, and effluent discharges at the mesa surface.

3.2 Alluvial Groundwater

- Infiltration of surface water flow (caused by effluent discharges, spring discharge, or stormwater runoff) maintains shallow groundwater in the alluvium of some canyons. Alluvial groundwater is unconfined and is perched on underlying Bandelier Tuff, Cerros del Rio basalts, or Puye Formation. Evapotranspiration and infiltration into the underlying rocks deplete alluvial groundwater as it moves down the canyons. Alluvial groundwater is a source of recharge to underlying intermediate perched zones and to the regional aquifer, usually by unsaturated flow.
- Dry canyons have little surface water flow. In these canyons groundwater may occur seasonally in the alluvium. Dry canyons are generally those that head in the eastern portion of the Pajarito Plateau.
- In wet canyon bottoms, infiltration of surface water maintains shallow groundwater in the alluvium. Wet canyons generally have large surface water flow, head in the Jemez Mountains, or receive effluent discharges. Groundwater levels are typically highest in the late spring due to snowmelt runoff and in mid-to-late summer due to thunderstorms. Groundwater levels and extent of saturation decrease during the winter and early summer when runoff is at a minimum.
- Recharge from alluvial groundwater by unsaturated flow accounts for important volumes of recharge and relatively rapid rates of groundwater flow (reaching the regional aquifer in decades or less). In some cases recharge might occur by saturated flow. Faults, fractures, joints, surge beds, and higher permeability geologic units that underlie saturated alluvium (such as the Guaje Pumice Bed, Cerro Toledo Interval, Cerros del Rio basalts, and Puye Formation) could provide pathways for downward movement of water and contaminants.
- Water quality of the alluvial groundwater reflects the composition of storm runoff, snowmelt, and effluent discharges where present. In canyons affected by effluents, the alluvial groundwater and sediments contain the majority of adsorbing contaminants (such as plutonium). Mobile solutes (such as tritium, high explosive compounds, and anions) migrate with moving groundwater and are present in recharge.

3.3 Intermediate Perched Groundwater

- Intermediate perched zones occur beneath major canyons; particularly wet canyons that receive effluent discharges, have large surface water flow, or head in the Jemez Mountains. These intermediate perched zones occur in the Guaje Pumice Bed at the base of the Bandelier Tuff, the underlying Cerros del Rio basalts, and the Puye Formation. The location of intermediate perched zones is determined by presence of sufficient recharge, permeability variations of the rocks (reflecting lithologic variations), and geologic structure. Intermediate perched zones may be confined or unconfined. Discharge from these intermediate perched zones occurs at springs or results in recharge to the underlying regional aquifer.

- Intermediate perched zones beneath canyons do not generally extend laterally beneath the mesas. Lateral movement of intermediate perched groundwater may occur if the dip of the perching horizon and the canyon orientation do not coincide.
- In the western portion of the Laboratory, groundwater occurs as a large (300 ft-thick) intermediate perched zone within the lower Bandelier Tuff and the Puye Formation, approximately 700 ft below the mesa top. Most recharge for this zone originates as underflow of groundwater from the Jemez Mountains, with some contribution from recharge through mesas and canyon bottoms. Discharge from the intermediate perched zone results in recharge to the underlying regional aquifer.
- Water quality within intermediate perched zones reflects that of the recharge water including effluent discharges and native groundwater. Flow within intermediate perched zones could transport contaminants some distance away from their surface source.

3.4 Regional Aquifer

- The regional aquifer beneath the Pajarito Plateau occurs in rocks of the Puye Formation, the Cerros del Rio basalts, the Tschicoma Formation, and the Santa Fe Group. The hydraulic conductivity of aquifer rocks is heterogeneous and averages approximately 140 m/yr. The aquifer is unconfined in the west and confined or partially confined in some locations near the Rio Grande.
- At the western edge of the plateau the water table is located approximately 300 to 400 m below ground surface. The hydraulic gradient in the western portion of the aquifer is generally downwards. The flow of groundwater is east/southeast, towards the Rio Grande. The hydraulic gradient in the eastern portion of the aquifer near the Rio Grande is generally upwards. Groundwater velocities vary spatially with a typical value of 10m/yr. Local deviations in flow direction occur due to lithologic heterogeneities and water supply pumping.
- The Rio Grande is the main discharge area for the regional aquifer. The largest component of recharge occurs as underflow of groundwater from the Sierra de los Valles, to the west of the Pajarito Plateau. Recharge also occurs by leakage from mesas, from alluvial groundwater in canyon bottoms on the Pajarito Plateau, and from intermediate perched groundwater. Local recharge on the Pajarito Plateau is important because it provides pathways for contaminants that originate from effluent discharges.
- The radiocarbon ages of water from deep wells beneath the Pajarito Plateau range from about one to six thousand years, although activities of tritium indicate that a portion of the water is less than 50 years old. The chemistry of groundwater in many wells near the Rio Grande (high total dissolved solids, high concentrations of naturally occurring elements such as arsenic, boron, uranium, and fluoride, and depleted stable isotope values) is different from that beneath the Pajarito Plateau and from the eastern Española Basin. This suggests that old water (about 30 thousand years) discharges near the river. Water flowing east/southeast from beneath the Pajarito Plateau mixes with this older water as it approaches the Rio Grande.

3.5 Geochemical Conceptual Model

The following eleven elements reflect the current understanding of the geochemistry of groundwater and are represented in the FY00 geochemistry conceptual model.

A. Due to geochemical processes, the natural composition of groundwater can vary within the alluvium, perched intermediate zones, and the regional aquifer.

B. Residence times of groundwater and chemical solutes (mass of water or solute/flux of water or solute) increase with depth and from west to east across the Pajarito Plateau. Accordingly, increasing concentrations of major ions and trace elements are observed along the flow paths.

C. Reactive minerals and solid phases approach equilibrium with groundwater when the residence time exceeds the reaction half time (amount of time required for 50 % of reactant A to form product B assuming there is no B initially present). These reactive constituents, consisting of $CaCO_3$, Ca-smectite, kaolinite, sodium feldspar, amorphous SiO_2, MnO_2, and $Fe(OH)_3$, may control groundwater composition for the major ions and selected trace elements including aluminium, iron, and manganese.

D. Alluvial aquifer materials provide the largest reservoir for effluent discharged constituents such as strontium-90, cesium-137, plutonium-238, plutonium-239,240, and americium-241 due to the constituents nature to readily adsorb onto clay- and silt-sized material.

E. In general, adsorption of radionuclides and inorganic species decrease at circum -neutral pH conditions as follows: cesium-137 (highest sorption) = americium-241 > strontium-90 > uranium > nitrate = sulfate = chloride = perchlorate = TNT = RDX = tritium (lowest sorption). Adsorption capacities of sediments and aquifer material may change over time due to changes in solution speciation and mineralogy.

F. Activities of adsorbing radionuclides and inorganic species generally decrease downgradient along the groundwater flow path.

G. Non- and semi-sorbing constituents can migrate from alluvial groundwater to perched intermediate zones and to the regional water table.

H. Adsorption processes dominate over mineral precipitation for removing metal and radionuclide constituents from groundwater. However, in isolated cases where effluent discharges have changed alluvial groundwater alkalinity or pH, elements such as strontium and barium may precipitate as $SrCO_3$, $BaCO_3$, $BaCO_3$, and precipitate as $(Sr\text{-}Ba)SO_4$ in alluvial groundwater.

I. Transport of constituents in groundwater occurs as both dissolved solutes and as colloids. Colloids may include natural material (silica, organic matter, calcium carbonate, clay minerals, and ferric hydroxide) and possibly solid phases associated with Laboratory discharges.

J. A component of groundwater within perched intermediate zones and to the regional water table is less than 59 years old, based on measurable tritium activities considerably above the comsogenic baseline of 1 pCi/L.

K. Increasing concentrations of dissolved organic carbon, carbonate alkalinity, calcium, potassium, iron, manganese, and other solutes occur in alluvial groundwater since the Cerro Grande fire. Oxidation and reduction reactions and carbonate complexation with metals influence aqueous speciation of redox-sensitive solutes.

4.0 FY00 DATA COLLECTION, INTERPRETATION, AND MANAGEMENT

In FY00, the new geologic, hydrologic, and geochemical data were collected from boreholes and newly completed wells of the Monitoring Wells Installation Project (MWIP) and from existing wells and surface water sampling conducted through the Environmental Surveillance Program. Other data comes from on-going geologic and hydrologic studies conducted through programs and projects such as the Seismic Hazards Program and the ER Project. This section describes the data collection efforts and provides interpretation of those data. It is intended to be a summary level description. Detailed descriptions are available in documents cited within the text. Section 4.1 presents the geologic data collection and interpretation, including geophysical data. Section 4.2 summarizes the hydrologic data collection and interpretation. Section 4.3 describes

geochemical data collection and interpretation. Section 4.4 is a report of the well construction and development improvements that were put in place in FY00.

The majority of new data comes from the drilling, sampling, and logging of new boreholes. The following is a synopsis of the history of drilling, sampling, logging and well completion activities through FY00. Figure 4.0-1 shows the locations and status of regional aquifer wells that were proposed as part of the Hydrogeologic Workplan (LANL, 1998) as well as "nature and extent" wells completed in response to findings during regional aquifer well drilling. Figure 4.0-2 shows the locations and status of the proposed alluvial wells.

- *Well R-9:* This well was completed in Los Alamos Canyon in October 1999 at a total depth of 771 ft with one 65-ft screen at the regional water table. Geophysical logging of the cased hole, screen development, and pump installation were completed in early FY00. The "Characterization Well R-9 Completion Report" (LA-UR-XXXX) was published in late FY00. Figure 4.0-3 provides well construction, stratigraphic, and hydrologic information for completed well R-9.
- *Well R-12:* This well was completed in Sandia Canyon in January 2000 at a depth of 86 ft with 3 screens, two in the upper perched zone and one at the regional water table. In FY00, geophysical logging and hydrologic testing were conducted and the Westbay Multiport Sampling system was installed. The "Characterization Well R-12 Completion Report" (LA-UR-3785) was published in late FY00. Figure 4.0-4 provides well construction, stratigraphic, and hydrologic information for completed well R-12.
- *Well R-15:* R-15 was completed in Mortandad Canyon in September 1999 at a depth of 1107 ft with one 60-ft screen at the regional water table. Screen development and pump installation were completed in early FY00. The "Characterization Well R-15 Completion Report" (LA-UR-4139) was published in late FY00. Figure 4.0-5 provides well construction, stratigraphic, and hydrologic information for completed well R-15.
- *Well R-25:* R-25 was completed at TA-16 on the mesa above Cañon de Valle in September 2000 to a depth of 1942 ft with nine screens, two in the upper perched zone and seven in the regional aquifer. Screen repairs, screen development, geophysical logging and Westbay Multiport Sampling system installation were completed in FY00. The completion report for Well R-25 will be published in FY01. Figure 4.0-6 provides well construction, stratigraphic, and hydrologic information for completed well R-25.
- *Well R-31:* R-31 was completed at TA-39 in the north fork of Ancho Canyon in April 2000 with five screens, two in the perched zone and three in the regional aquifer. Screen development, geophysical logging and Westbay Multiport Sampling system installation were completed in FY00. The completion report for Well R-31 will be published in FY01. Figure 4.0-7 provides borehole construction, stratigraphic, and hydrologic information for completed well R-31.
- *Well R-19:* R-19 was completed near TA-36 on the mesa above Threemile and Potrillo canyons to a depth of 1902 ft with seven screens, two in the perched zone and five in the regional aquifer. Screen development and installation of Westbay Multiport Sampling system were completed in FY00. The "Characterization Well R-19 Completion Report" (LA-UR-4085) was published in late FY00. Figure 4.0-8 provides borehole construction, stratigraphic, and hydrologic information for completed well R-19.
- *Well R-9i:* R-9i was completed in March, 2000 near the eastern boundary in Los Alamos Canyon to a depth of 322 ft with two screens in the upper saturated zones identified during the drilling of Well R-9. Screen development and installation of Westbay Multiport Sampling system were completed in April, 2000. The "Characterization Well R-9i Completion Report" (LA-UR-XXXX) was published late FY00. Figure 4.0-9 provides borehole construction, stratigraphic, and hydrologic information for well R-9i.

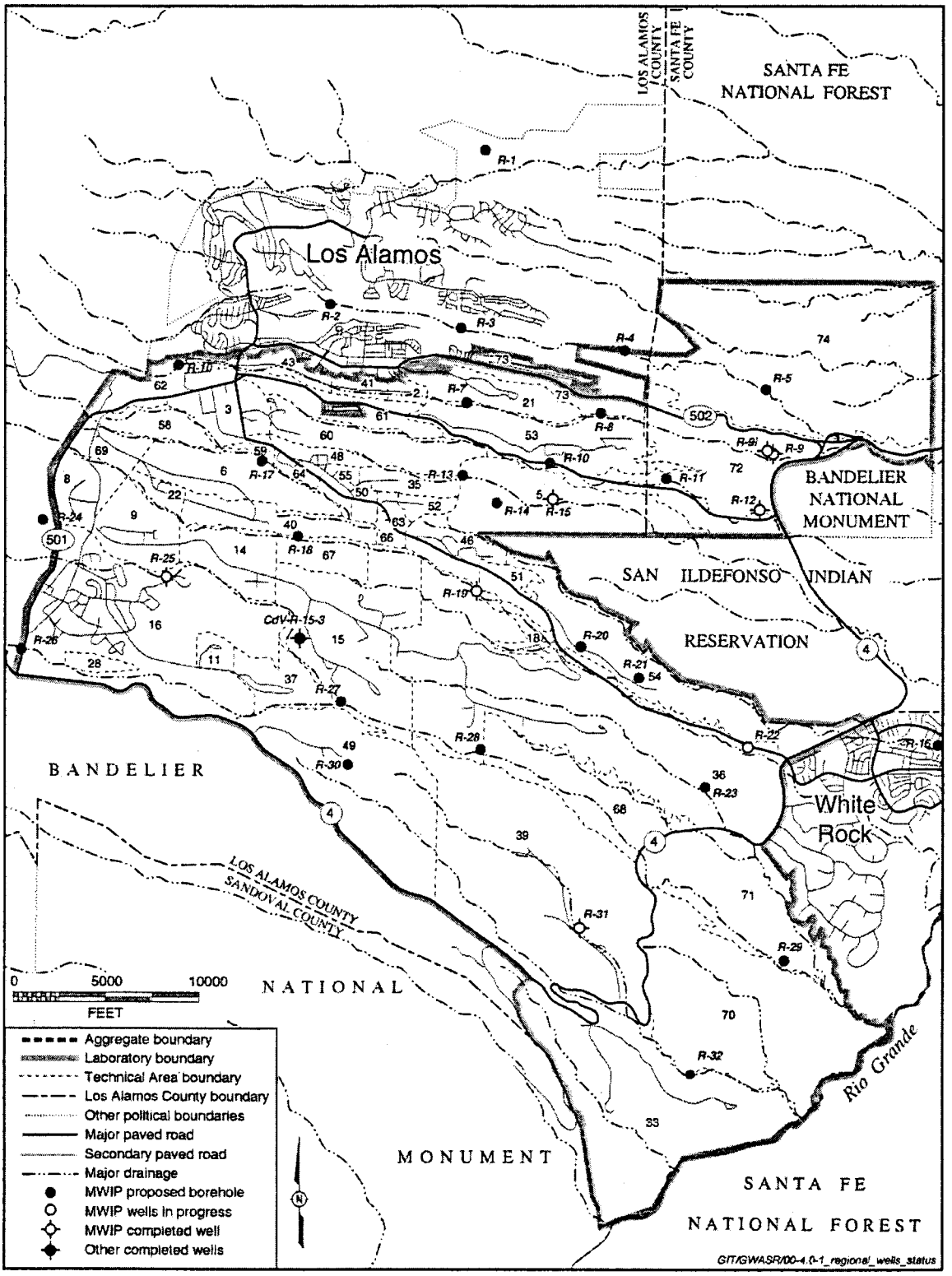

Figure 4.0-1. Completed, in progress, and proposed MWIP regional aquifer wells as of the end of FY00.

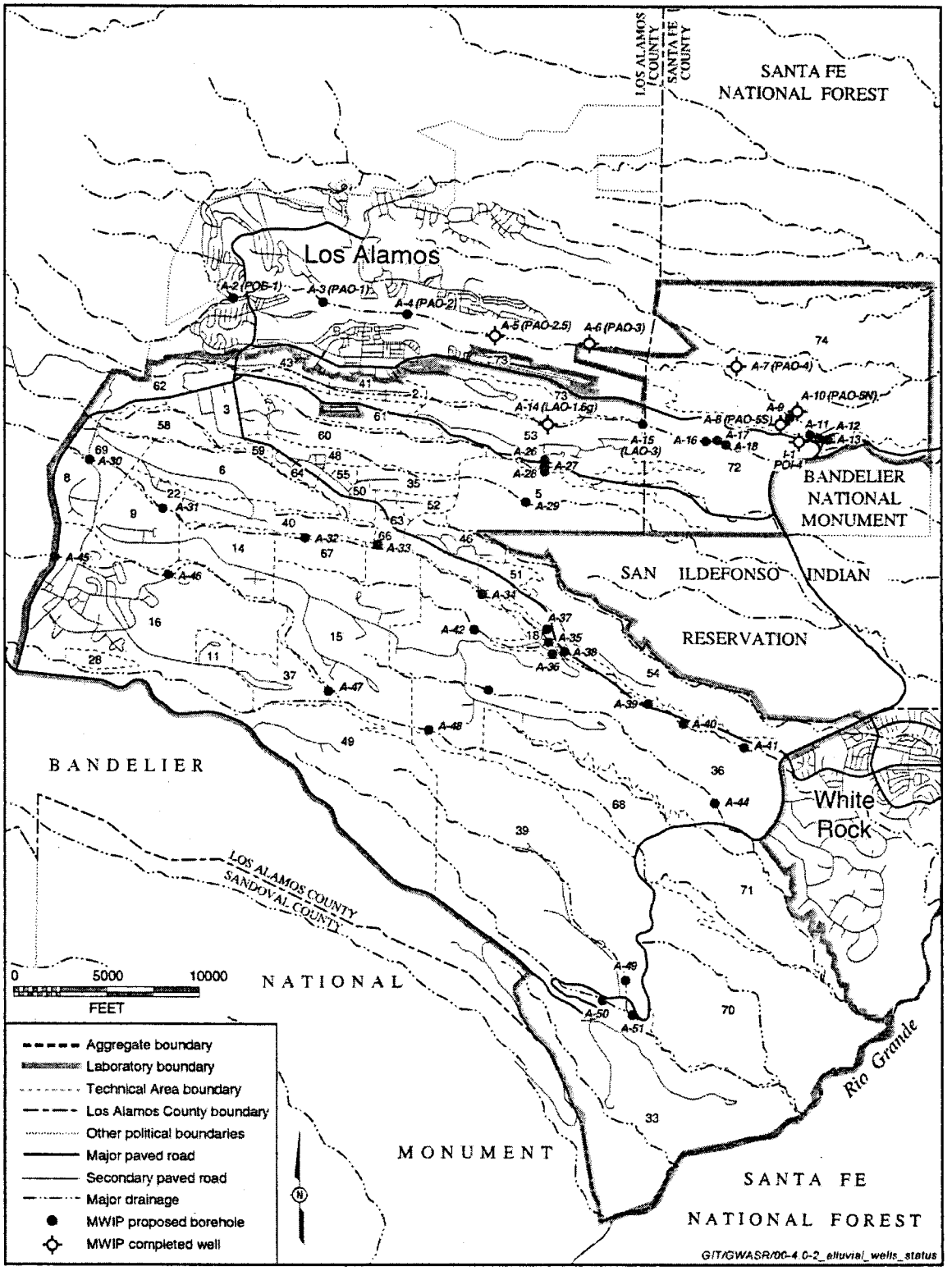

Figure 4.0-2. Completed and proposed MWIP alluvial wells as of the end of FY00.

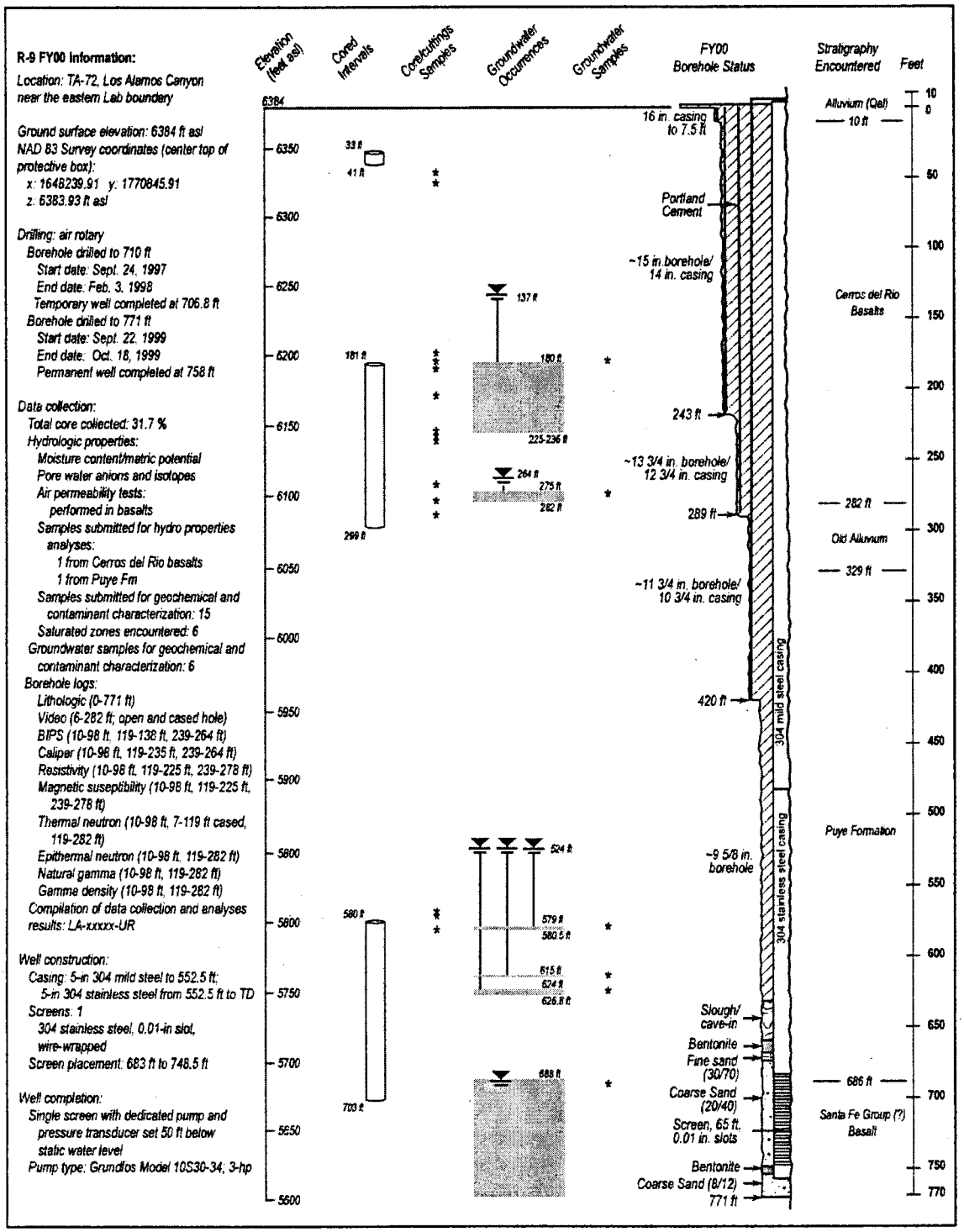

Figure 4.0-3. Construction, stratigraphic, and hydrologic information for completed well R-9.

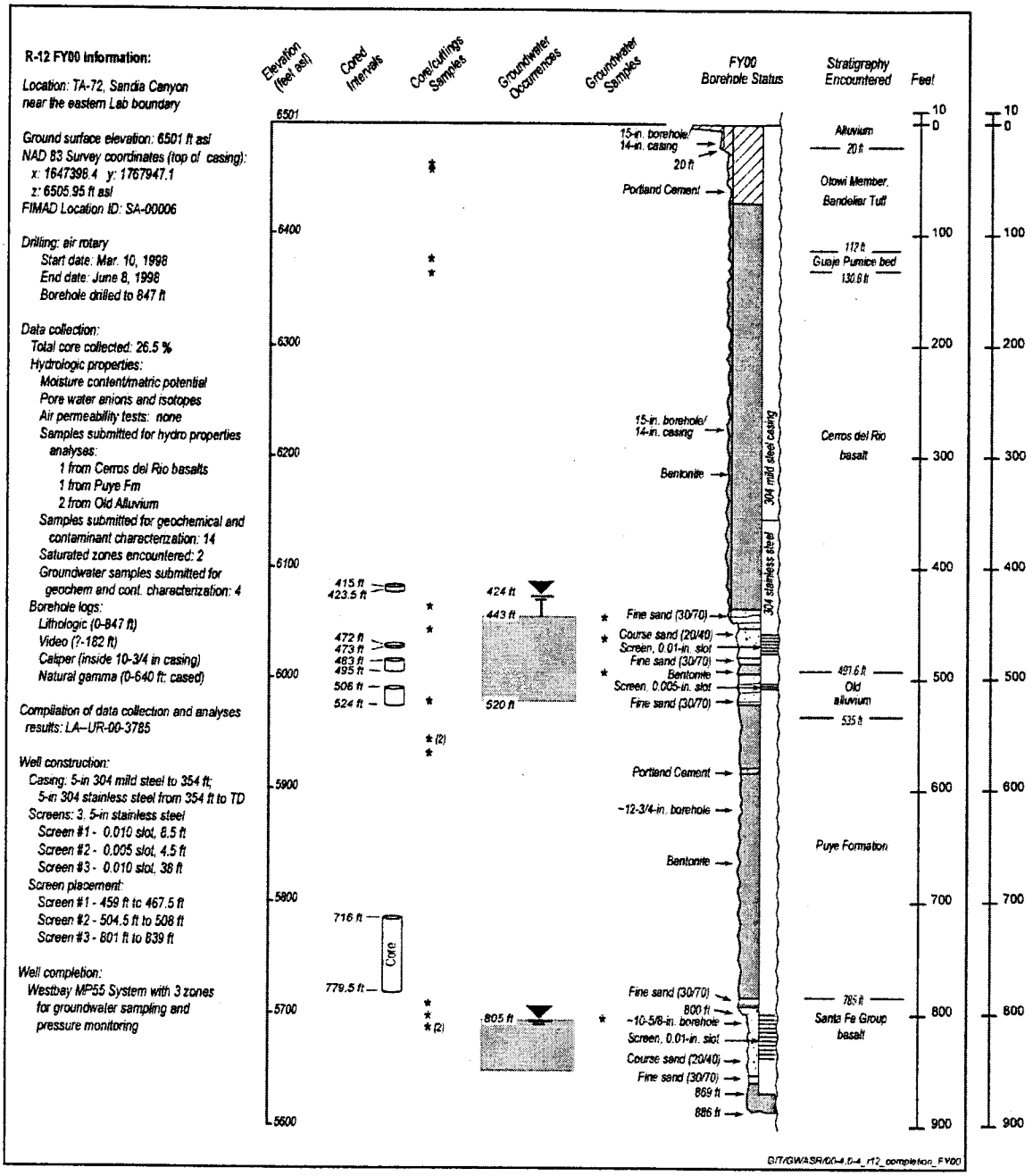

Figure 4.0-4. Construction, stratigraphic, and hydrologic information for completed well R-12.

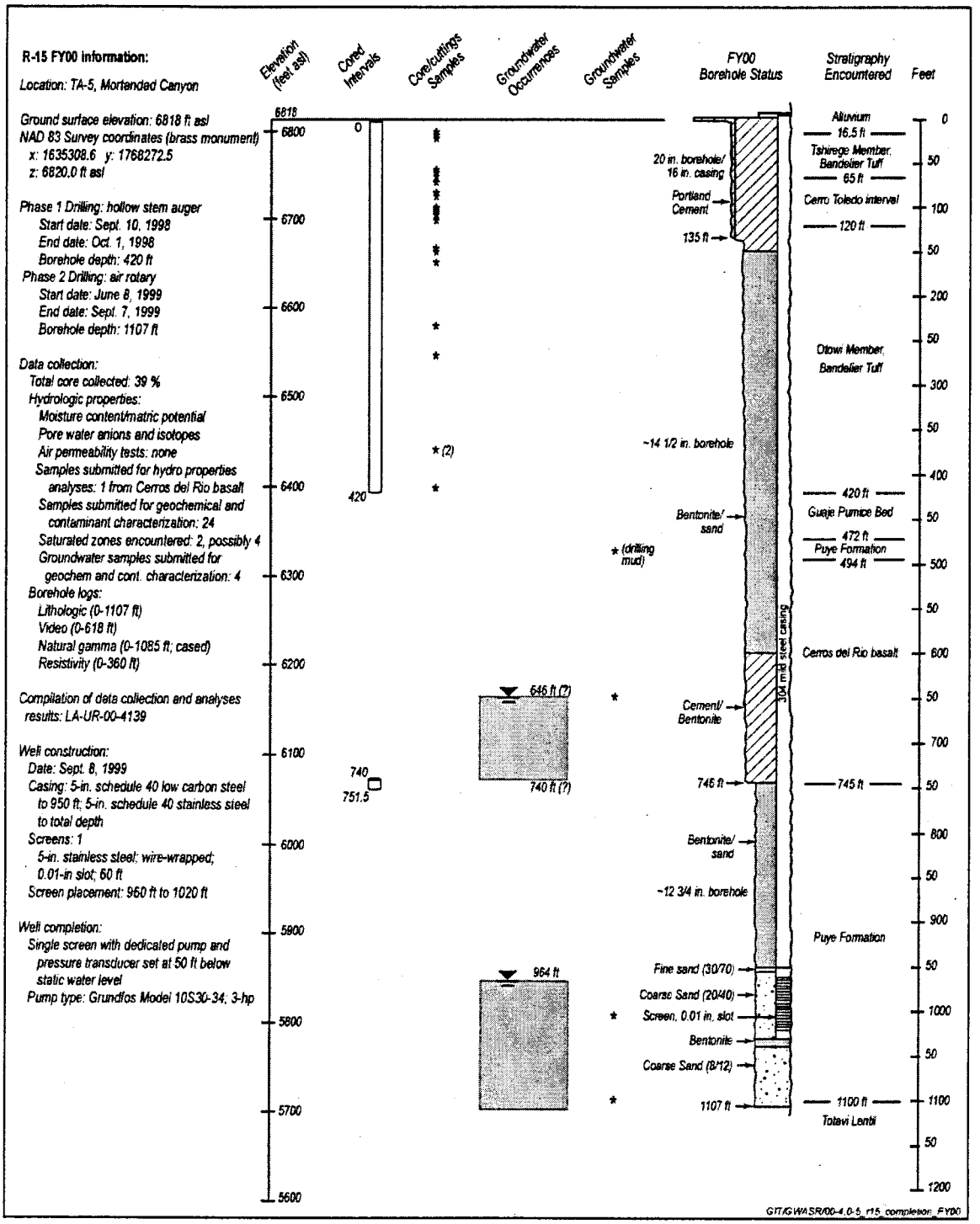

Figure 4.0-5 Construction, stratigraphic, and hydrologic information for completed well R-15.

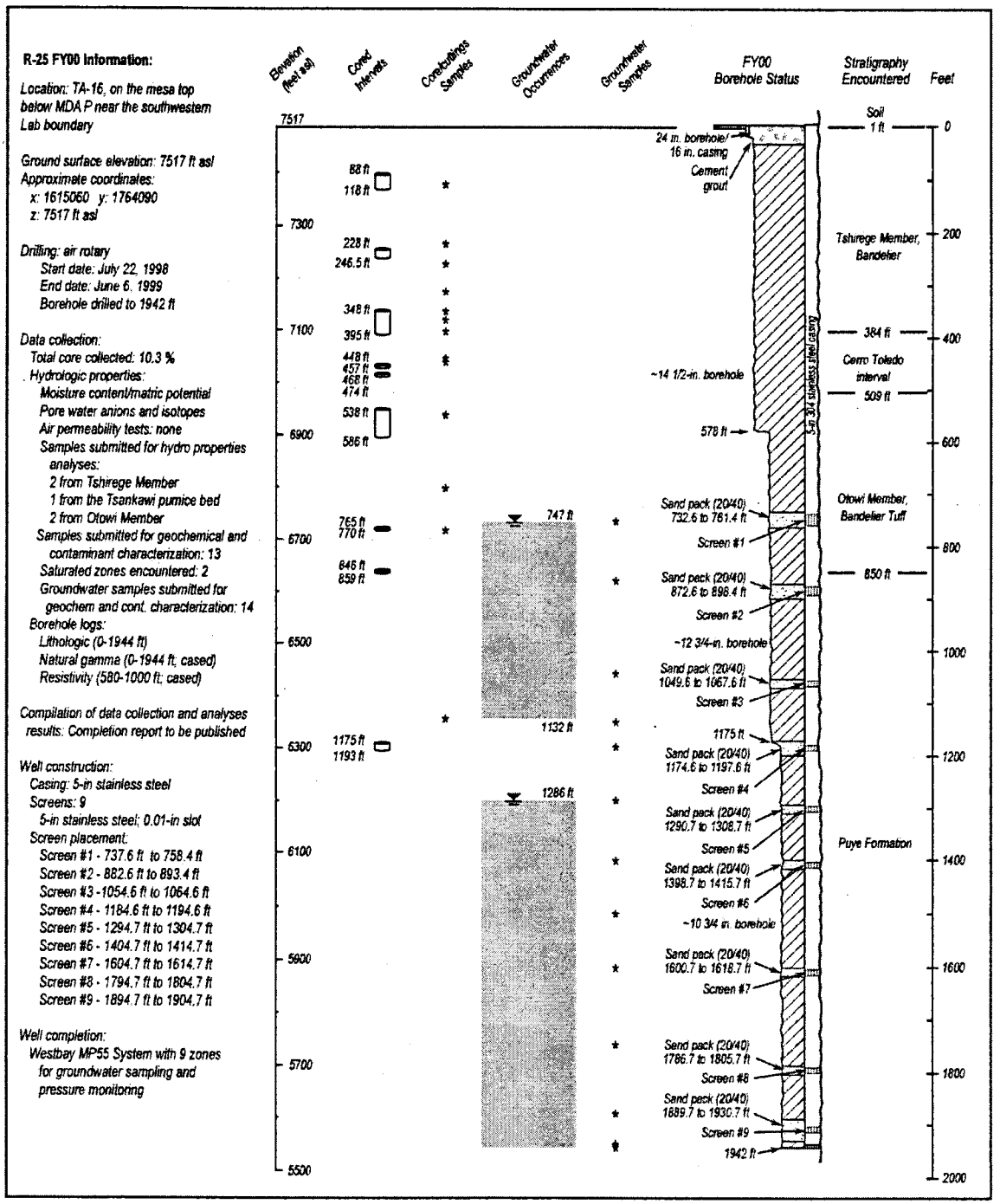

Figure 4.0-6 Construction, stratigraphic, and hydrogeologic information for completed well R-25.

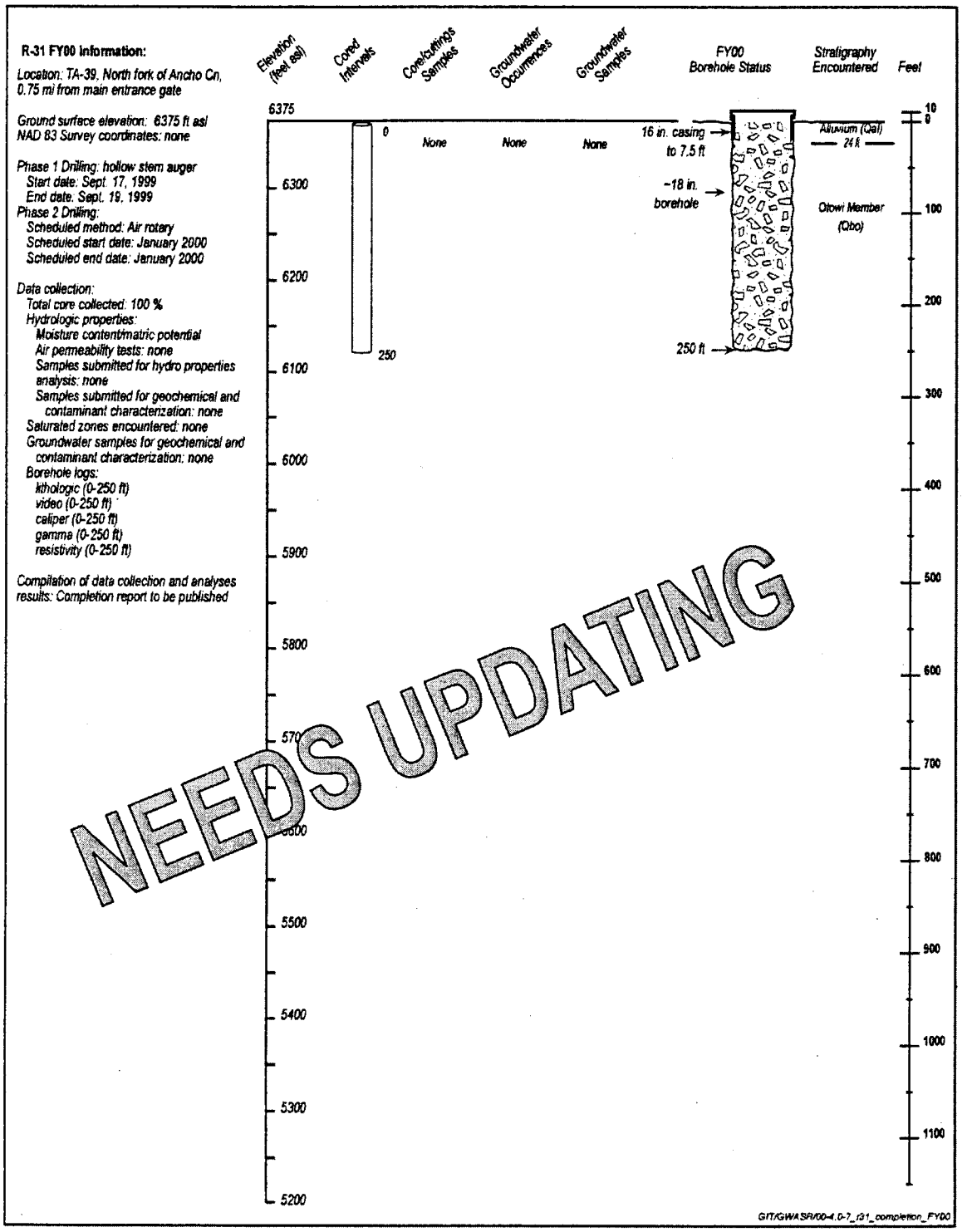

Figure 4.0-7 Construction, stratigraphic, and hydrogeologic information for completed well R-31.

Figure 4.0-8 Construction, stratigraphic, and hydrologic information for completed well R-19.

Figure 4.0-9 **Construction, stratigraphic, and hydrologic information for completed well R-9i.**

- *Well CdV-R-15-3:* Well CdV-R-15-3 was completed at TA-15 on the mesa above Cañon de Valle in June 2000 with six screens, three in the upper perched zone and three in the regional aquifer. Screen development and geophysical logging were conducted in August 2000 and the Westbay Multiport Samping system was installed in September 2000. The "Progress Report for Plume-Chasing and Characterization Well Cañon de Valle R-15-3 (CdV-R-15-3)" (LA-UR-00-4527) was published in late FY00. Figure 4.0-10 provides borehole construction, stratigraphic, and hydrologic information for well CdV-R-15-3.
- *Well R-22:* Borehole R-22 was drilled on Mesita del Buey east of TA-54 MDA G to a depth of 978 ft by the end of FY00. The borehole was drilled to total depth and the well completed in December 2000. Figure 4.0-11 provides borehole construction, stratigraphic, and hydrologic information for well R-22 as of the end of FY00.

4.1 Geologic Data Collection and Interpretation

4.1.1 Geologic Data Collection

New geologic samples and information were obtained in FY00 from drill holes completed during the year: R-9i, R-19, R-31, and CdV-R-15-3. In addition to data obtained from active drill holes, the analysis of data required for preparation of Completion Reports for drill holes R-9, R-12, and R-15 provided new insights into the LANL site geology **(add References for R-9, R-12, and R-15 completion reports).**

4.1.1.1 Petrology

New petrologic data were collected by analysis of cuttings from drill holes R-9i, R-19, R-31, and CdV-R-15-3. Although core was only obtained from the Bandelier Tuff section at R-31 and R-19, the cuttings collected by reverse circulation from all of the drill holes provide reliable petrologic information with good stratigraphic control. Petrologic and geochemical analysis of several size fractions of cuttings from R-19 was conducted to evaluate the degree of mixing of cuttings during drilling. Results of this analysis indicate that segregation of different size fractions does not result in significant geochemical fractionation, at least down to fragment sizes as small as 1 mm. The most complete petrologic data sets created during the year were from R-19 and R-15, although partial data became available for CdV-R-15-3 as the year drew to a close. Samples from R-31 will not be processed and analyzed until next year. Samples from R-9i will not be analyzed beyond the visual analysis of cuttings because detailed analyses are already available from adjacent drill hole R-9.

4.1.1.2 Stratigraphy

New stratigraphic information was obtained from examination of cuttings, borehole video analysis, and geophysical logging of drill holes R-9i, R-19, R-31, and CdV-R-15-3. The geophysical logs are described in Section 4.1.3. The combined analysis of borehole videos, cuttings, and geophysical logs provides abundant, well-constrained data on stratigraphic relations at the site. Comparison of predicted stratigraphy with the as-drilled stratigraphy has proved to be a useful test of the 3D Site Geologic Model, illustrating problems with the model and providing guidance on actions needed to correct and improve the model.

4.1.1.3 Fracture Characteristics

New information on fractures is somewhat limited by the lack of new core samples, but fracture assessment based on borehole videos played an important role in locating screened intervals in drill hole R-31. Fracture density with little evidence of clay filling in the Cerros del Rio basalts at 666-676 ft depth, as seen in the borehole videos at R-31, was a factor in determining the

Figure 4.0-10 Construction, stratigraphic, and hydrologic information for borehole CdV-R-15-3 as of end of fiscal year 2000

Figure 4.0-11 Construction, stratigraphic, and hydrologic information for borehole R-22 as of end of fiscal year 2000

placement of screen #3 in this borehole. Future sampling and monitoring will provide hydrologic information from this fractured basalt unit.

4.1.2 Geological Interpretation

4.1.2.1 Tshirege Member, Bandelier Tuff

Coring of Bandelier Tuff was accomplished at R-31 in FY99 and at R-19 in FY00. Core was not collected at CdV-R-15-3 because the suite of borehole logs now collected by Schlumberger provides continuous in-situ data that supplant much of the spot information obtained from core (see section 4.1.3). At R-19, geophysical logs indicate a steady rise in the abundance of bound water, particularly in capillary water from top to bottom in the lowest unit (Qbt 1) of the Tshirege Member. This increase in water content, most notably in capillary water, reflects the increasing matrix porosity, with depth, of Qbt 1. The values of capillary water content are comparable to those in the Otowi Member, and reflect the high matrix porosity typical of vitric nonwelded tuff. At CdV-R-15-3 there are similar saturation effects in Qbt 1 with additional evidence of increases in saturation at the transition from vapor-phase alteration to glass (the Qbt 1v to Qbt 1g transition), and in the Tsankawi Pumice Bed at the base of the Tshirege Member.

4.1.2.2 Cerro Toledo Interval

The Cerro Toledo interval was thicker than anticipated in drill holes R-19 and CdV-R-15-3. At R-19 the thickness is 266 ft, far greater than the predicted 60 ft. Similarly, at CdV-R-15-3, the as-drilled thickness was 220 ft, greater than the predicted thickness of 95 ft. Revisions to the 3-D Geologic Model are needed in view of the unexpected magnitude of Cerro Toledo deposition in this part of the LANL site. The correspondingly less-than-expected thickness of the underlying Otowi Member indicates that erosion thinned the Otowi Member and the Cerro Toledo sediments accumulated in the thinned area. Further drilling in the central, southern, and southwestern parts of the LANL site should provide the information necessary to revise the geometry of the erosional and depositional relations between the Cerro Toledo and the Otowi Member.

The Cerro Toledo interval at R-19 and CdV-R-15-3 consists of detritus from volcanic centers to the west as well as reworked material from the Otowi Member. The most detailed information on the Cerro Toledo was obtained from R-19. In R-19 the coarsest sediments are present in the upper approximately 10 ft of the sequence and in the lower approximately 125 ft. Grain-size analysis of representative cuttings indicates considerable variability in sediment size, ranging from layers with >98 weight percent (wt %) of clasts >2 mm to fine sands with >55 wt % clasts of <1 mm (based on cuttings returns). Despite variability in clast sizes and clast lithologies, the deposits of the Cerro Toledo interval in R-19 and in CdV-R-15-3 show little variability in properties measured by borehole logging. Caliper-measured borehole dimensions, gamma signals, capillary and bound water, and neutron measures of water residence environment are all strikingly homogeneous. This homogeneity contrasts with the highly heterogeneous nature of all of these properties within the deeper Puye sediments.

There is a modest rise in capillary water content within the lower 25 ft of Cerro Toledo sediments in both R-19 and CdV-R-15-3. This rise is likely associated with a small increase in porosity. The most significant differences between the Cerro Toledo sediments and the bounding tuffs are a lower gamma signal (attributable principally to lower U and Th content) and much lower abundances of capillary water (less available porosity).

4.1.2.3 Otowi Member and Guaje Pumice Bed

Borehole logs for the Otowi Member in both R-19 and CdV-R-15-3 indicate density and porosity properties comparable to unit Qbt 1g of the Tshirege Member, which is also a vitric nonwelded tuff. In both drill holes the Guaje Pumice Bed is an interval with considerably larger pore structure and greater water content than the overlying ash flows.

4.1.2.4 Basalts

In FY99, basalts of the Cerros del Rio volcanic field from drill holes R-9 and R-12 were found to consist of similar series of tholeiitic lavas overlying alkalic lavas. This sequence has since been found in drill hole R-15, indicating that this flow series extends across a distance of at least 2.5 miles beneath Los Alamos, Sandia, and Mortandad Canyons. Drilling of drill hole R-9I, adjacent to R-9 in Los Alamos Canyon provided more information on the hydrogeologic properties of this widespread lava series. The alkalic lavas contain two perched horizons in R-9/R-9i, one perched horizon in R-12, and one perched horizon in R-15. These lavas produce very fine (about 1-5 mm) and angular drill cuttings, in contrast to the tholeiitic lavas that produce larger (cm-scale) and more rounded cuttings. The fragmentation properties of the alkalic lavas suggest pervasive microfractures.

The alkalic to tholeiitic Cerros del Rio lava series, including basal tephra and basaltic sediments, is 280 ft thick at R-9/9i, 359 ft thick at R-12, and 255 ft thick at R-15. These thicknesses are close to or slightly thicker than predicted by the 3D Geologic Model existing at the time of drilling. A somewhat greater thickness (390 ft) was predicted for Cerros del Rio lavas in R-31, approximately 6 miles to the south, where again the actual thickness drilled (425 ft) was slightly thicker than predicted. Although petrologic data are not yet available for the Cerros del Rio lavas at R-31, gamma logs and borehole videos indicate at least six flows of varied composition. These flows overlie a thick sequence of axial river gravels, indicating a Rio Grande paleochannel about three miles west of the present Rio Grande channel. A perched horizon may occur above one of the interflow sedimentary layers at R-31, but if a perched horizon is present, the thickness and yield are considerably less than to the north at R-9/9i, R-12, and R-15.

Drill holes R-19 and CdV-R-15-3 encountered Cerros del Rio basalt at depths close to those anticipated from the 3D Geologic Model, but the flow series were thinner than anticipated (155 ft vs. 400 ft in R-19; 49 ft vs. 63 ft in CdV-R-15-3). In CdV-R-15-3, a possible occurrence of perched water at the top of the Cerros del Rio lavas led to placement of a screen (screen #3) at that horizon in the constructed well.

The occurrence of tholeiitic lava overlying an alkalic lava in the Cerros del Rio basalts of R-19 is superficially similar to the tholeiitic-over-alkalic flow series documented in drill holes to the northeast (R-15, R-12, R-9 and R-9i). However, there are several differences that distinguish the lavas at R-19. The tholeiites in the other drill holes have higher SiO2 and higher K2O/P2O5 ratios than the tholeiitic lavas at R-19. The lower silica content and K2O/P2O5 in the upper lavas at R-19 make it less likely that these lavas are derived from the underlying alkalic lavas. In contrast, the lavas to the northeast probably evolved in a single magma chamber by olivine fractionation and increased crustal assimilation. The differences at R-19 also make it unlikely that the same Cerros del Rio lava flows found beneath the mid-reaches of Los Alamos, Sandia, and Mortandad Canyons extend as far to the southwest as Three Mile Canyon and R-19. To the southeast, the complexity of the lava series at R-31 shows that many more flows are present at this site; whether any of these flows can be correlated with flows to the northwest or north is not yet determined.

In comparing the as-drilled depths and thicknesses of the Cerros del Rio lavas with those predicted from the 3D Geologic Model, it is evident that the predictions of depth to flow tops have been relatively accurate in the central part of the LANL site (within 1 ft at CdV-R-15-3, 3 ft at R-19, and 25 ft at R-15). The basal depths of these lavas, however, have differed from predicted values by as much as 115 ft at R-15 and 348 ft at R-19. The greater reliability of upper-contact elevations and contrasting lack of constancy in basal contact elevations indicates infilling of irregular terrain to form a relatively continuous basaltic mesa beneath this part of the LANL site. At R-31, in the southeastern part of LANL, the thickness of Cerros del Rio lavas was very close to that predicted, but the lavas were 210 ft deeper than expected. Terrain effects, particularly in the

locations and trends of paleocanyons, contribute some uncertainty in prediction of elevation and thickness of the Cerros del Rio lavas.

Older Miocene lavas were encountered in R-9. Although such lavas were predicted to occur in R-15, they were not found. The lavas of greatest hydrogeologic importance are those of the Cerros del Rio volcanic field, which commonly contain perched horizons and host significant portions of the water table in the eastern part of the site.

Figure 4.1.2.-1 is a west-to-east cross section incorporating data from earlier drill holes, drill holes completed this fiscal year (R-19, CdV-R-15-3), and one drill hole that was completed after the end of the fiscal year (R-22). This figure illustrates the importance of both the Puye Formation and the Cerros del Rio lavas in hosting the top of the region aquifer. Section 4.1.2.6 summarizes new information obtained this year on units of hydrogeologic importance.

4.1.2.5 Puye Formation

Drilling completed during FY00 provided more information on the extent of the Puye Formation, but also provided samples that require a reassessment of how the Puye Formation is defined and its hydrogeologic significance. In drill holes R-19, CdV-R-15-3, and R-31 the 3D Geologic Model current at the time of drilling predicted that the depths drilled would encounter and penetrate axial river gravels at the base of the Puye formation and enter sediments of the Santa Fe Group. Only R-31 encountered axial gravels, and none of these drill holes penetrated to the Santa Fe Group. Both R-19 and CdV-R-15-3 passed from previously well-known Puye fanglomerate deposits into mixed fanglomerate and silicic pumiceous units at depths near those where Santa Fe Group sediments were predicted. All of the fanglomerate-pumiceous deposits appear to be derived from volcanic highlands to the west, northwest, or southwest; no evidence of plutonic sources to the east (characteristic of the Santa Fe Group) was found. For the purposes of this report, the deeper sediments with predominantly silicic pumiceous sources are included within the discussion of the Puye Formation. However, further work is needed to determine whether these deposits should be considered part of the Puye Formation, assigned to a different stratigraphic series (e.g., the Cochiti Formation), or defined as a new unit.

4.1.2.5.1 The Puye Fanglomerates

Grain-size analysis of Puye cuttings from R-19 indicates great variability in clast-size distributions. Coarse fanglomerates produce cuttings with 84 wt % of clasts >4 mm in size and <1 wt % are of the sand component (<2 mm clasts). More typical fanglomerates in the Puye at R-19 produce about 40 wt % clasts >4 mm and 20-50 wt % sand particles of <2 mm. Some horizons consist almost entirely of sand-sized detritus. Petrographic analysis shows that most of the clastic materials in the 2-4 mm size range are derived from intermediate-composition volcanic rocks, dacites and rhyodacites typical of the Tschicoma Formation. However, a sample of fanglomerate at R-19 above the zone of more pumiceous sediments (Section 4.1.2.5.2) contains clasts of well-cemented sandstone and coarse quartz grains.

Chemical data were collected for size fractions of the Puye fanglomerates at R-19 to test for homogeneity and representative character of the cuttings. Analyses of the 2-4 mm, 1-2 mm, and <1 mm size fractions were completed for samples from 900-905 ft depth (upper fanglomerate) and from 1170-1175 ft, 1205-1210 ft, and 1410-1415 ft (lower fanglomerate). Three defining constituents (SiO_2, Fe_2O_3, and Sr) and one ratio (Sr/Rb) are plotted against depth in Figure 4.1.2-2. The data indicate coherence between the upper and lower fanglomerates, with systematic increase in SiO_2 and decrease in Fe_2O_3 and Sr with depth. Gamma logs at R-19 indicate a relatively abrupt transition to higher K plus Th content at about 1360-ft depth within the lower fanglomerate. The K_2O values for the 2-4 mm and 1-2 mm size fractions of the sample at 1410-1415 ft depth are higher than those in the samples above 1360 ft. The principle cause of the higher gamma signal may be in Th content, which was not determined by XRF analysis.

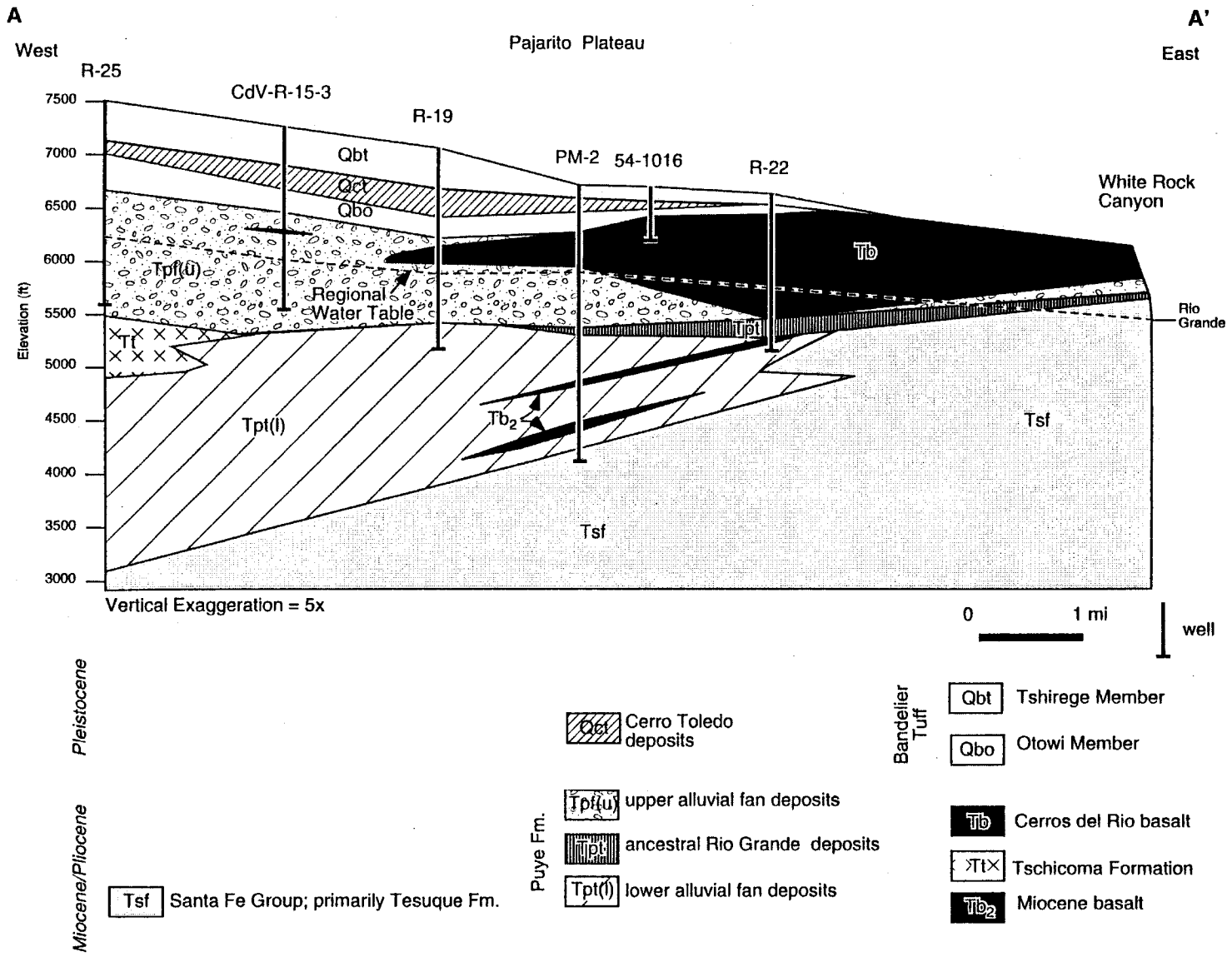

Figure 4.1.2-1 East-west cross section showing stratigraphic relations of geologic units making up the Pajarito Plateau.

Differences between the 2-4 mm, 1-2 mm, and <1 mm size fractions at each horizon in the fanglomerates are minimal, a strong indication that selective disaggregation or borehole segregation of finer fragments is not a concern with the drilling methods currently used. In terms of source detritus, the similarity between all three size fractions also indicates a single or well-mixed source for all deposits within the fanglomerates without significant contributions from other sources in the finer detritus. This contrasts markedly with the situation in the Cerro Toledo deposits, where admixture of coarse Tschicoma detritus and finer Otowi detritus leads to significant chemical differences between the 2-4 mm and <1 mm size fractions (Figure 4.1.2-2).

Quantitative XRD data from 2-4 mm size fractions of other representative samples from the Puye fanglomerates shows that some clay alteration occurs, but is limited to approximately 1-2% smectite. Appreciable amounts of glass (13-14%) remain in all of the fanglomerate samples of the upper Puye, evidence of limited alteration. Clays were separated from fanglomerate samples at 1205-1210 ft depth and 1380-1385 ft depth in R-19. These clays are poorly-ordered illite-smectites with about 4-6% kaolinite, common to most alteration typical of the Puye Formation. The significant amounts of remnant glass attest to the very incomplete alteration of these sedimentary deposits.

4.1.2.5.2 Pumiceous Deposits (Lower Puye?)

Below the upper Puye fanglomerates in both R-19 and CdV-R-15-3, sediments are distinctly more siliceous and pumice rich. At R-19 the pumiceous sediments are generally finer-grained than the upper fanglomerates; drill cuttings contain <25 wt % clasts of >4 mm and >60 wt % sands of <2 mm. An exception to this occurs above screen #7 at R-19, where >4 mm clasts comprise >80 wt % of the deposit at 1830-1835 ft depth. The typical pumiceous sediments of this interval contain variable clast admixtures of mostly aphyric to poorly porphyritic pumice plus intermediate volcanic rocks, with rare fragments of lavas with andesitic to basaltic composition.

The pumiceous deposits have geochemical indicators of predominantly rhyolitic sources, unlike the intermediate-composition Tschicoma sources that characterize the overlying Puye fanglomerates. The differences between the Puye fanglomerates and the underlying pumiceous deposits are clearly seen in a plot of Sr versus Rb content that defines a distinctive high Sr, low Rb field for the upper fanglomerates and a low Sr, high Rb field for the lower pumiceous sediments (Figure 4.1.2-3). Also shown in Figure 4.1.2-3 is the very distinctive low-Rb, low-Sr field for the <1 mm size fraction from the Cerro Toledo deposits, contrasted with the Tschicoma-like compositions for the 2-4 mm size fractions in the Cerro Toledo.

Mineralogic data from the pumiceous sediments at R-19 shows that, as in the overlying fanglomerates, some clay alteration occurs but is limited to about 1-2% smectite. Greater amounts of glass occur in the pumiceous deposits than in the fanglomerates (26-78% versus 13-14%). The almost complete preservation of all glass to maximum borehole depth at R-19 is evidence of very limited alteration. As in the fanglomerates, the clays are poorly-ordered illite-smectites with approximately 1% kaolinite.

Intercalated within the pumiceous sediments at R-19 are relatively homogeneous pumice beds. The pumices in these deposits are poorly porphyritic, with <1% quartz, sanidine, and albite phenocrysts. The pumices range from average sizes of 2-4 mm to deposits in which 87 wt % of the pumices is >4 mm in size, and many are cm-size. Chemical analyses show that the <1 mm size fractions in the pumice beds are considerably more mafic than the coarser (2-4 mm) pumice-dominated size fraction. The finer fraction has lower SiO_2 and higher Fe_2O_3, MgO, V, Cr, Sr, and Ba. The differences in SiO_2, Fe_2O_3, Sr, and Sr/Rb in the two size fractions indicate a fine-sand source with different origins than the pumices that comprise the bulk of the deposit (Figure 4.1.2-2). In terms of potential water-rock interactions, the higher surface area and higher Fe content of the finer fraction may dictate interactions with contaminants that are very different from those that would occur if the coarser pumices alone comprised the deposit. The pumices in all

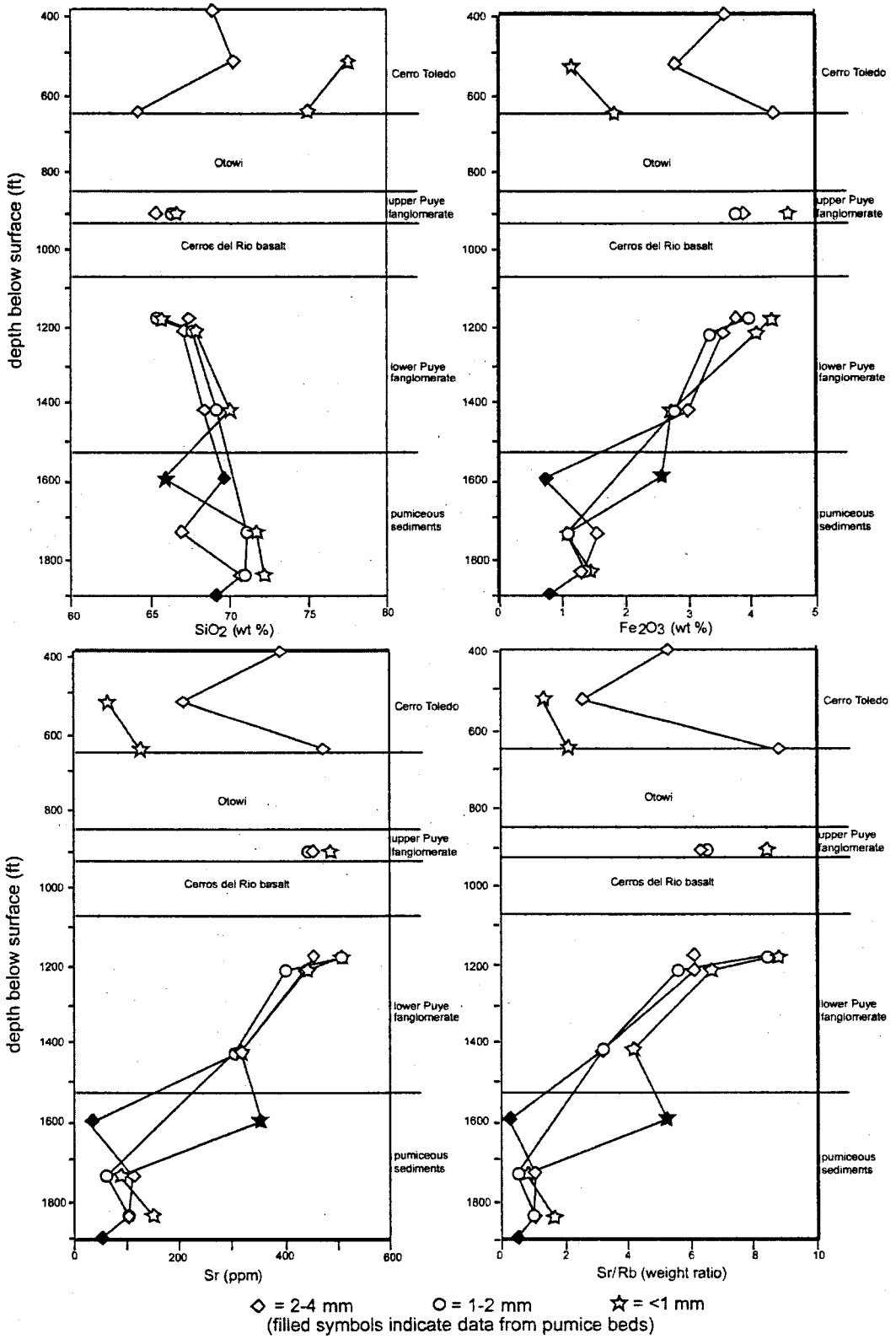

Figure 4.1.2-2 Silica, iron, strontium and strontium/rubidium ratios with depth and size fractions in basalts and sediments in R-19.

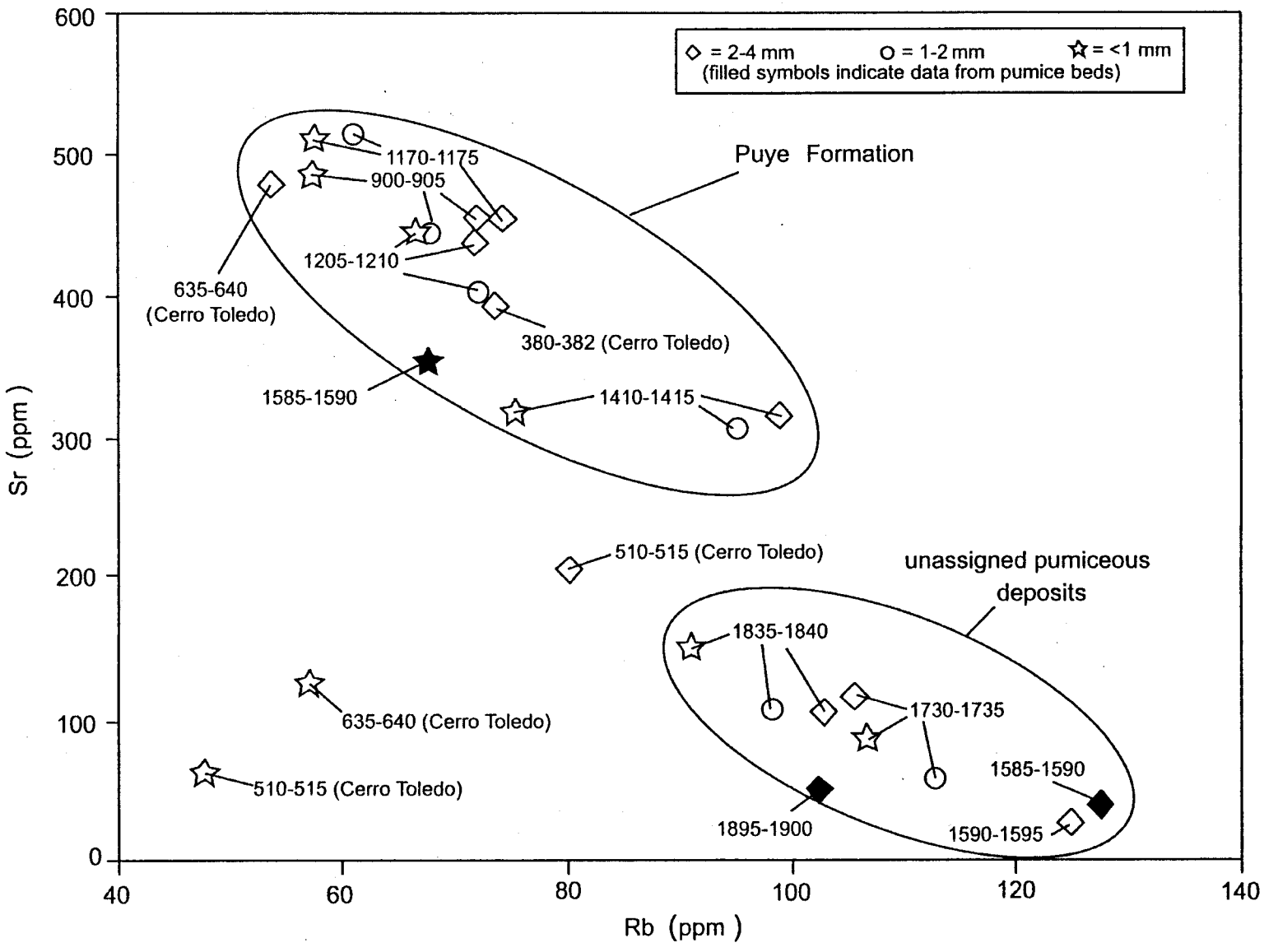

Figure 4.1.2-3 Strontium versus rubidium systematics in pumiceous deposits as seen in boreholes R-19 and CdV-R-15-3.

beds are slightly rounded and slightly to moderately clay-coated, indicating minor amounts of reworking. None of the pumice beds appear to be undisturbed primary falls. However, the preservation of original glass is extensive. Screen #5 at R-19 is located within the pumice bed at 1581-1595 ft depth and is thus situated to sample waters from an exceptionally glass-rich horizon with Fe-rich fines.

4.1.2.5.3 Alteration in the Puye

The Puye deposits are highly variable in clast size distributions, matrix sorting, and pore-size distributions. As noted above, the current drilling program provides evidence of a relatively constant transition from less silicic to more silicic and increasingly pumiceous source lithologies with depth. Superimposed on these variations is evidence of local zones of extensive clay alteration.

Clay alteration is considered extensive in samples where virtually all glass has altered to clay. Known occurrences of extensive clay alteration within the Puye are so far confirmed for samples from R-9 and R-12, in parts of Los Alamos and Sandia Canyons at the eastern part of the LANL site. Cuttings from the earlier well O-1 suggest that such alteration may also occur in Pueblo Canyon north of R-9, but clay was used in drilling that hole and the evidence of past alteration is yet to be verified by more careful studies of the available samples. The extensive clay alteration in R-9 and R-12 occurs about 100-200 ft above the present water table and continues through the Puye sediments to the deepest unit sampled (Miocene basalts) in which the current water table was encountered.

Data from R-15, R-19, and CdV-R-15-3 show that extensive alteration of the Puye Formation to clay is absent in these drill holes, both above the water table and to depths of at least 725 ft below the water table in R-19 and 475 ft in CdV-R-15-3. The relationships between glass and clay abundances in Puye sediments in two of the essentially unaltered drill holes (R-19, R-15) and in two of the extensively altered drill holes (R-12, R-9) are summarized in Figure 4.1.2-4. The cause of alteration and the areal extent of alteration are not yet known, although the preservation of saturated and largely unaltered glass in the central to southwestern parts of LANL indicate that saturation at ambient conditions does not lead to extensive clay alteration.

4.1.2.6 Hydrogeologic Interpretations

Alluvium, Bandelier Tuff, lavas of the Cerros del Rio volcanic field, and some portions of the upper Puye Formation all play roles in hosting perched water at LANL. The combined information from borehole geophysics and sample analyses indicates that vadose-zone saturation arises in intervals of enhanced porosity, either matrix porosity as in the Guaje Pumice Bed or fracture porosity as in the Cerros del Rio lavas. However, in addition to available porosity, perched horizons require a barrier to downward flow. Available data suggests that transitions to zones with less porosity can impede downward flow and produce saturation, but the most extensive perched horizons develop above zones of extensive clay alteration. The high-permeability perched horizon in basalt at R-9/9i (see Section 4.2) is an example of such a perched zone. Chemical data from the clays that underlie this perched zone indicate that the hydrogeologic impact of sealing clays affects transport as well as flow. Perched water from this interval at R-9 contains anomalously high U content; analysis of clay-rich basaltic tephra of the perching horizon also shows an anomalously high U content and a high U/Th ratio (Figure 4.1.2-5). The high U/Th ratio in the clay-rich tephra is unusual and provides further evidence that the additional U is likely to be anthropogenic. The anomalously high U content of the clay also indicates that clays play an active role in accumulation of contaminants.

Clays underlying LANL can play a significant role in hydrogeologic properties, but not all clay zones are involved. For instance, the zone of extensive clay alteration in the lower Puye Formation at R-12 is not presently associated with any perched water, although the same zone of alteration at R-9 supports three thin perched horizons with a common head near the top of the

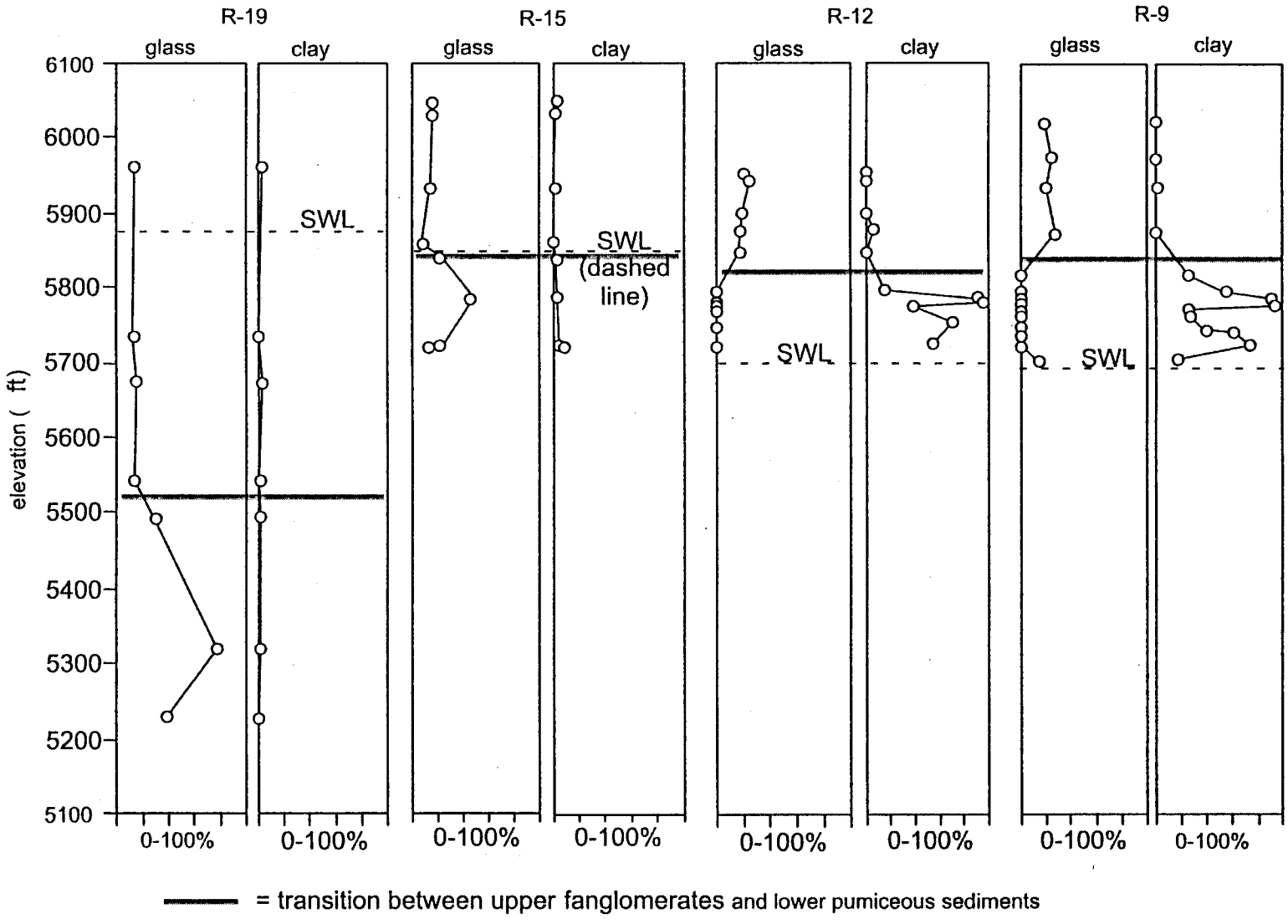

Figure 4.1.2-4. Glass and clay distributions in the Puye Formation.

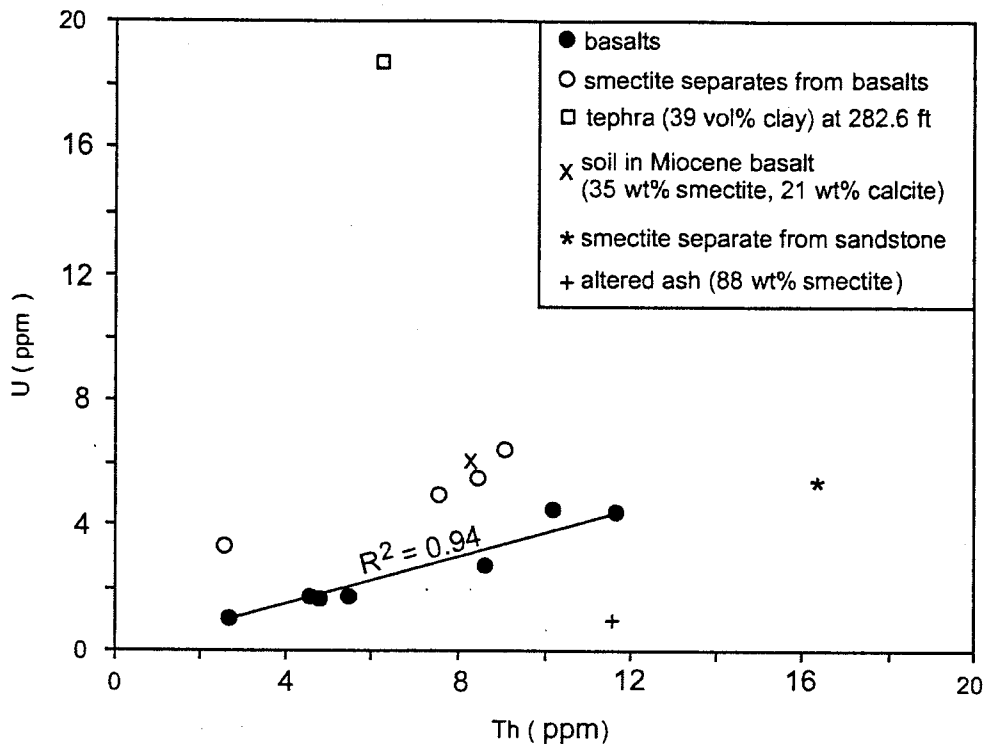

Figure 4.1.2-5 Uranium versus thorium systematics at R-9 for basalts and samples from soil, sandstone, and altered ash.

alteration. Future drilling will help to define the limits of perching horizons in both areal extent and in relation to the distributions of clays or other barriers.

Data obtained through future drilling, and through analyses of water composition at selected horizons, can help to define aquifer connections in geochemically differing tuffs, lavas, and sediments. The absence of Santa Fe Group sediments at depths within the range of likely contaminant transport simplifies the treatment of sedimentary units in such an analysis, but the presence or absence of extensive clay alteration in the Puye is an important hydrogeologic factor that needs to be modeled realistically.

4.1.3 Geophysical Testing

The use of geophysical logs has steadily increased as drilling methods and requirements for site characterization have evolved during the implementation of the Hydrogeologic Workplan. In FY00, more geophysical log data was collected than ever before. The increased use of geophysics results, in part, from drilling techniques that allow more access to long stretches of open borehole, maximizing the number and types of tools that can be run. Additionally, the transition from air-assisted casing-advance drilling to fluid-assisted open bore-hole drilling has led to the use of more geophysical logging in order that perched groundwater zones can be identified and included as part of multi-screen well designs. Screen placements for all wells rely on integration of geophysical logs, video logs, and lithologic information from drill cuttings.

Table 4.1-1 describes the major geophysical logs collected as part of borehole characterization efforts during FY00. This table summarizes the type of parameters measured, the purpose of the log, information about whether the log can be used in cased holes, and information about vertical resolution and depth of investigation. Table 4.1-2 is a summary of the geophysical logs for each

R-well installed to date. Digital data from these logs is currently stored in staging tables in preparation for their upload into the Water Quality Database. For interested users, paper copies of these logs and copies of borehole video logs are stored in files at the Field Support Facility and at two locations in the LANL Pueblo Complex (Records Processing Center and Groundwater Focus Area). Geophysical logs run and processed by Schlumberger and SDI are combined in single displays called montages; paper copies and electronic files of montages are stored at the LANL Pueblo Complex.

Table 4.1-1 Summary of Principal Geophysical Logs Run during FY-00

Geophysical Tool	Parameter Measured	Vertical Resolution	Depth of Investigation	Used in Casing	Log Purpose
Gamma Ray Scintillator (GR)	Gross gamma activity of formation	10 in	10 in	Yes	Yields gross gamma activity for stratigraphic correlation, clay estimation, correlate depth shifts between logging runs.
Hostile Environment Natural Gamma Sonde (HNGS Spectral Gamma)	^{40}K, U series, Th series activities of formation	20 in	9.5 in	Yes	Yields K, U, Th concentrations for stratigraphic correlation, clay estimation.
Geochemical Tool (ECS)	Concentrations of Si, Ca, Al, Fe, Ti, Gd, S, Cl, and H	20 in	7 in	Yes	Yields concentrations of rock-forming elements for estimation of mineralogy and lithology, good for stratigraphic correlation and estimation of clay contents.
LithoDensity Tool (LDT; Gamma-Gamma Density log)	Measures formation electron density	6 to 11 in	2 to 2.5 in	Yes	Yields estimates of bulk density and porosity; photoelectric absorption yields estimate of average formation atomic number for estimation of lithology.
Combinable Magnetic Resonance (CMR)	Nuclear magnetic resonance measurements of H protons	9 or 21 in	0.5 to 1.5 in		Yields estimates of pore volume and pore size, bound and free moisture, and hydraulic conductivity (where saturated). In unsaturated zone, yields estimates of moisture content and lithology.
Array Induction Tool	Formation resistivity	1, 2, or 4 ft	10, 20, 30, 60, and 90 in		Measures drilling fluid invasion into borehole wall and provides information on permeability and lithology.
Epithermal Neutron Tool (CNT-G and APT tools)	Measure of H in formation	18 in CNT-G 3 in APT	9 in CNT-G 3 in APT		Yields estimates of moisture in unsaturated zone, porosity in saturated zone; can be used to identify clays.
Formation Microimager (FMI)	High resolution resitivity imaging	0.2 in	0.5 in	No	Provides lithologic and structural information.
Borehole Video	Imaging of borehole walls	n/a	n/a	No	Provides lithologic and structural information
Borehole Deviation (Gyro and GPIT)	Maps path of borehole	n/a	n/a	Gyro Yes GPIT No	Provides information borehole deviation and information for making depth corrections to borehole depths
Multi-Finger Caliper	Borehole shape	0.2 in	n/a	No	Maps borehole rugosity; indicates wash outs; provides lithologic information; contributes to interpretation of other logs.

Table 4.1-2 Geophysical Logs Collected in Existing R-Wells

Well Name	Log Date	Contractor	Top (ft)	Bottom (ft)	Service
CDV-R15-3	27-Apr-00	MK/PMC	0	1680	Video
	27-Apr-00	MK/PMC	484	1670	Gamma
	28-Apr-00	Schlumberger	41.5	1680.5	Hole Deviation
	28-Apr-00	Schlumberger	33	1682	Electrical Log
	28-Apr-00	Schlumberger	76	1680	HNGS Spectral Gamma
	28-Apr-00	Schlumberger	132	1668	Porosity
	29-Apr-00	Schlumberger	982	1677.5	Spinner/Temperature
	01-May-00	MK/PMC	0	1680	Video
	10-Aug-00	WGII/PMC, LANL	0	1673	Video
	11-Aug-00	WGII/PMC, LANL	0	1660	Gamma
R-9	11-Feb-00	Schlumberger	122	747	Porosity
	11-Feb-00	Schlumberger	27	760	Multi-finger Caliper
	11-Feb-00	SDI	0	750	Hole Deviation
	11-Feb-00	Schlumberger	71	732	HNGS Spectral Gamma
R-9i	18-Mar-00	Schlumberger	41	280	Porosity
	18-Mar-00	Schlumberger	41	280	HNGS Spectral Gamma
	18-Mar-00	Schlumberger	20	305	Multi-finger Caliper
R-12	08-Feb-00	Schlumberger	46	741	Multi-finger Caliper
	08-Feb-00	Schlumberger	0	869	HNGS Spectral Gamma
	08-Feb-00	SDI	0	860	Hole Deviation
	08-Feb-00	Schlumberger	115	720	Porosity
R-15	11-Feb-00	Schlumberger	20	1027	Multi-finger Caliper
	11-Feb-00	Schlumberger	104	1017	Porosity
	11-Feb-00	Schlumberger	62	1003	HNGS Spectral Gamma
	11-Feb-00	SDI	0	1020	Hole Deviation
R-19	13-Mar-00	SAIC	0	1903	Video
	13-Mar-00	LANL	0	1903	Video
	13-Mar-00	SAIC	0	1903	Gamma
	13-Mar-00	SAIC	0	1903	Video
	13-Mar-00	LANL	0	1903	Video
	16-Mar-00	Schlumberger	130	1868	Porosity
	16-Mar-00	Schlumberger	204	1886	Electrical Log
	16-Mar-00	Schlumberger	0	1077	Hole Deviation
	16-Mar-00	Schlumberger	0	1886	Density Log
	16-Mar-00	Schlumberger	1170	1882	Formation Micro Imager
	16-Mar-00	Schlumberger	230	1876	Porosity/Permeability
	16-Mar-00	Schlumberger	0	1886	HNGS Spectral Gamma
	03-Apr-00	SAIC	0	1902	Gamma
	03-Apr-00	SAIC	0	1766	Gamma

Well Name	Log Date	Contractor	Top (ft)	Bottom (ft)	Service
R-22	12-Oct-00	MK	0	1475	Gamma
	13-Oct-00	Schlumberger	50	1453	HNGS Spectral Gamma
	13-Oct-00	Schlumberger	50	1474	Porosity
	13-Oct-00	Schlumberger	50	1477	Density Log
	25-Oct-00	MK	0	1473	Gamma
	27-Oct-00	MK	0	1459	Gamma
	03-Nov-00	MK			Video
	07-Nov-00	MK	0	1465	Video
	13-Nov-00	MK	0	1472	Video
	20-Nov-00	MK	0	1470	Gamma
	20-Nov-00	MK	0	1472	Video
R-25	21-Apr-99	Schlumberger	22	1876	Gamma Spectroscopy
	21-Apr-99	Schlumberger	1216	1885	Ultrasonic Imager
	21-Apr-99	Schlumberger	1216	1891	Porosity
	21-Apr-99	Schlumberger	1216	1892	Cement Bond Log
	21-Apr-99	Schlumberger	789	1880	Multi-finger Caliper
	10-Feb-00	Schlumberger	128	1838	HNGS Spectral Gamma
	10-Feb-00	Schlumberger	30	1846	Multi-finger Caliper
	10-Feb-00	SDI	0	1840	Hole Deviation
	10-Feb-00	Schlumberger	134	1844	Porosity
R-31	24-Jan-00	SAIC	0	787	Caliper
	25-Jan-00	SAIC	0	787	Video
	25-Jan-00	SAIC	0	787	Gamma
	25-Jan-00	SAIC	0	787	Gamma
	25-Jan-00	SAIC	0	787	Video
	09-Feb-00	SDI	10	1050	Hole Deviation
	09-Feb-00	Schlumberger	120	1080	Porosity
	09-Feb-00	Schlumberger	0	1096	HNGS Spectral Gamma
	09-Feb-00	Schlumberger	0	1096	Porosity
	09-Feb-00	Schlumberger	0	1096	HNGS Spectral Gamma
	10-Feb-00	SAIC	0	1103	Gamma
	10-Feb-00	Schlumberger	35	1074	Multi-finger Caliper
	06-Mar-00	SAIC	0	1077	Gamma
	17-Mar-00	Schlumberger	70	1063	HNGS Spectral Gamma
	17-Mar-00	Schlumberger	35	1074	Multi-finger Caliper
	17-Mar-00	Schlumberger	100	1070	ETTD
	17-Mar-00	Schlumberger	80	1063	Porosity
	30-Mar-00	SAIC	0	1077	Video

4.2 FY00 Hydrologic Data Collection and Interpretation

4.2.1 Hydrologic Data Collection

Several kinds of data for characterizing hydrologic systems at LANL were collected in FY00. These include observations on the occurrence and movement of water in both unsaturated and

saturated conditions. Hydrologic testing was conducted to estimate hydraulic properties of the saturated and perching zones. This section describes the collection of hydrologic data from boreholes and wells installed in FY00.

Also in FY00, the preliminary hydrogeologic atlas, prepared in FY99, was expanded from 25 to 45 sheets. The additional sheets include a geologic map, subsurface maps for six geologic/ hydrogeologic units not covered in the preliminary version, and a selection of cross sections. The expanded atlas also presents several other new kinds of data: outcrops and subsurface extent of units, available hydraulic-conductivity values, and occurrences of intermediate-depth perched water in wells. FY00 is the last year that entire sets of the atlas will be distributed. The 3-D geologic model upon which the atlas is based is updated annually. The latest version of any sheet in the atlas can be obtained upon request from FIMAD, using the plot ID or number.

4.2.1.1 Data Collection in Unsaturated Zones

In FY00, hydrologic data for unsaturated zones were derived mainly from samples previously submitted for lab analysis and from two modeling studies. Eight samples of core collected from the unsaturated zones in R-9 and R-12 were submitted in FY99 to a commercial laboratory for testing of a full range of hydraulic properties. In FY00, results were compiled and presented in a LANL data report (Stone, 2000).

For FY00, hydrologic data collection activities increased over FY99 in the Cañon de Valle alluvial aquifer and SWSC, Burning Ground and Martin springs. The alluvial holes in Cañon de Valle and the springs were instrumented with automated pressure transducers, temperature, and conductivity probes. In addition, three alluvial holes were installed in Martin canyon (only one hole was saturated when drilled). Periodic measurements of surface flow in Cañon de Valle provided data on flow changes throughout the year.

4.2.1.2 Data Collection in Saturated Zones

In FY00, hydrologic data for saturated zones were obtained from core samples previously submitted for laboratory testing and observations on groundwater occurrence and field testing in wells R-9i, R-19, CdV-R-15-3 and R-22. Three samples of core collected from the saturated zones in R-9, R-12 and R-25 were submitted in FY99 to a commercial laboratory for analysis of saturated hydraulic conductivity. In FY00, results were compiled and presented in a LANL data report (Stone, 2000).

Hydraulic properties of saturated materials were determined mainly by straddle packer/injection testing. Preliminary results are shown in Table 4.2-1 and are tabulated in the well completion reports for R-9i, R-19, R-31, and CDV-R-15-3. Analysis of the data from the testing is ongoing and will be presented in separate reports.

Well R-9i was installed to permit monitoring of two zones of perched water in the Cerros del Rio basalt that were encountered, but cased off, during installation of well R-9. Drilling was stopped periodically to facilitate the detection of first occurrence of saturation. Water levels behaved essentially the same as when these perched zones were penetrated in R-9. Straddle-packer/injection slug tests and a pumping test were performed. This hydrologic testing indicated that the lower perched zone was very tight whereas the upper zone was quite permeable.

R-15 was completed in Mortandad Canyon in FY99. During drilling, an injection test was conducted in the borehole in the Cerros del Rio basalt and was reported in the Ground Water Annual Status Report for FY99. In FY00 a pumping test was conducted in the single screen installed in the regional aquifer in R-15. Analysis of the test data gave an estimate transmissivity of 94.96 ft^2/day and an estimate of storativity of 0.01242 for the regional aquifer at this location.

Table 4.2.1-1 Summary of Hydrologic Testing in FY00

Well	Saturated Zone	Screen	Geologic Unit	Hydraulic Conductivity ft/d)	Type of Test
R-9i	Upper perched	1	Cerros del Rio Basalt	37.07	injection and pumping
R-9l	Lower perched	2	Cerros del Rio Basalt	0.78	injection and pumping
R-15	Regional	1	Puye Formation	see text in Section 4.2.1.2	pumping
R-19	Regional	4	Puye Formation	17.5	injection
	Regional	5	Puye Formation	19.6	injection
R-31	Perched	1	Cerros del Rio Basalt	1.07	injection
	Regional	2	Cerros del Rio Basalt	0.42	injection
	Regional	3	Cerros del Rio Basalt	3.62	injection
	Regional	4	Puye Formation	0.009	injection
	Regional	5	Puye Formation	0.007	injection
CDV-R-15-3	Regional	4	Puye Formation	0.25	injection
	Regional	5	Puye Formation	0.10	injection

At R-19, no perched water was identified. The use of drilling fluid made water-level measurements with electric probe nearly impossible, so it was difficult to recognize perched water prior to well construction and development. The first water encountered was in the Cerros del Rio basalt, and it is believed to represent the regional aquifer. Two screened intervals were tested by the straddle-packer/injection method. Analysis of hydrologic-test data is not yet complete.

Similarly, measurement of water level in this well prior to development at CdV-R-15-3 was hampered by the presence of drilling fluid in the rods. Straddle packer/injection tests were planned for evaluating hydraulic conductivity of the materials behind screens 3, 5, and 6. Screen 3 is located in a potential zone of perched water and the other two are in the regional zone of saturation. Such testing is not appropriate for screen 4 as it straddles the regional water table. The interval at screen 3 did not contain enough water to warrant testing. Data were successfully obtained from screens 5 and 6. Analysis of hydrologic-test data is not yet complete.

No perched water was detected in R-22, which is located on the mesa north of Pajarito Canyon. The apparent lack of perched saturation is noteworthy. Materials behind the four screens below the regional water table were tested by the straddle-packer/injection method. Analysis of hydrologic-test data is not yet complete.

4.2.2 Hydrologic Data Interpretation

Hydrologic data is interpreted in order to quantify the processes that control the flow of water through the geohydrologic system. Modeling is the primary tool used to interpret the hydrologic data collected in FY00. This section describes the modeling in the unsaturated and saturated zones.

4.2.2.1 Unsaturated Zone Data Interpretation

Interpretative work in the unsaturated zone has been focused in three areas. Flow and transport modeling in Los Alamos Canyon was refined with the updated geologic model and incorporation of geochemical conditions. The second area of vadose zone work was modeling flow of water through the Bandelier tuff using data from large-scale injection tests conducted in the 1960's.

Unsaturated zone interpretation was also focused in TA-16, where water quality sampling of alluvial water and springs confirmed the conceptual model of climatic controls on flow through the unsaturated zone in this portion of the Laboratory.

4.2.2.1.1 Flow and Transport in Los Alamos Canyon

A flow and transport model for Los Alamos Canyon was developed in previous years. In FY00 the flow model was updated with a new version of the geologic model that included a more accurate representation of the basalt units. Using this updated flow model, the issue of transport of tritium and other contaminants from the surface to the water table of the regional aquifer was examined. The model domain extends from middle Los Alamos Canyon to approximately the eastern boundary of the Laboratory (Figure 4.2.2-1), and encompasses Los Alamos and DP canyons at locations where historic releases of contaminants, including tritium, have occurred. Using hydrostratigraphic, hydrolologic, and field data including water budget studies, a base case model was established that is consistent with the available information and provides a basis for examining the migration of tritium to the regional aquifer. Measured tritium concentration-time histories in water sampled in alluvial wells provides the source term for transport modeling. In this model, tritium is assumed to be a nonsorbing, liquid-borne solute that decays with the appropriate half-life. The tritium source term in this model is focused in Los Alamos and DP canyons and, due to changes in Laboratory operations, has declined steadily from the maximum releases in the early 1970's to today.

The model suggests that transport of tritium and other contaminants is most rapid in the eastern portion of the model, where the uppermost rock units below the alluvium are basalts or a thin layer of the Puye Formation overlaying the basalts. In this portion of the domain, fracture flow is likely to occur, resulting in more rapid travel times than in middle Los Alamos Canyon, which has a significant thickness of Bandelier tuff. Travel times through the Bandelier tuff and Puye Formation (to the regional aquifer) are predicted to be approximately 50 years, versus the likelihood of transport to the water table in 10 years or less through the basalt units and the Puye Formation. As a result, the total mass flux of tritium reaching the water table is predicted to be dominated by transport from middle to lower Los Alamos Canyon through the basalts and Puye Formation (Figure 4.2.2-2).

Wells such as Otowi-1 are susceptible to contamination in this portion of the Laboratory because of the hydrogeology and the lack of sorption of tritium. Although with present data the models cannot be calibrated to predict precise future concentrations of tritium in the aquifer or in a water supply well, the model results (Figure 4.2.2-2) suggest that the rate of tritium arrival at the water table (where it may then be brought to the surface in a water supply well) may be at or near its peak. Continued monitoring is required to establish a trend in tritium concentration. In the absence of a continued high-concentration source at the surface, it is very unlikely that concentrations will climb to values even approaching regulatory limits because of the lack of additional releases, dilution in groundwater and at the pumping wells, and radioactive decay. Long-term monitoring is needed to confirm this conclusion and to establish the time frame over which these concentration changes will occur. Current modeling suggests that several decades of regular monitoring will be necessary to definitively establish long-term trends.

Recent alluvial groundwater data and analysis of the water budget information for Los Alamos Canyon has resulted in somewhat revised estimates of infiltration rate along the canyon bottom. By including streambed infiltration in the surface and alluvial aquifer model, this analysis concluded that previous model predictions of infiltration rate into the deep vadose zone probably underestimated the infiltration rate in some portions of the canyon and overestimated it in others. Of course, higher infiltration rates result in more rapid travel times through the vadose zone. The deep vadose zone flow and transport model for Los Alamos Canyon includes a variety of different infiltration scenarios to capture the uncertainty in this critical parameter. Therefore, the current estimates are still within the range of values assumed in the modeling analyses.

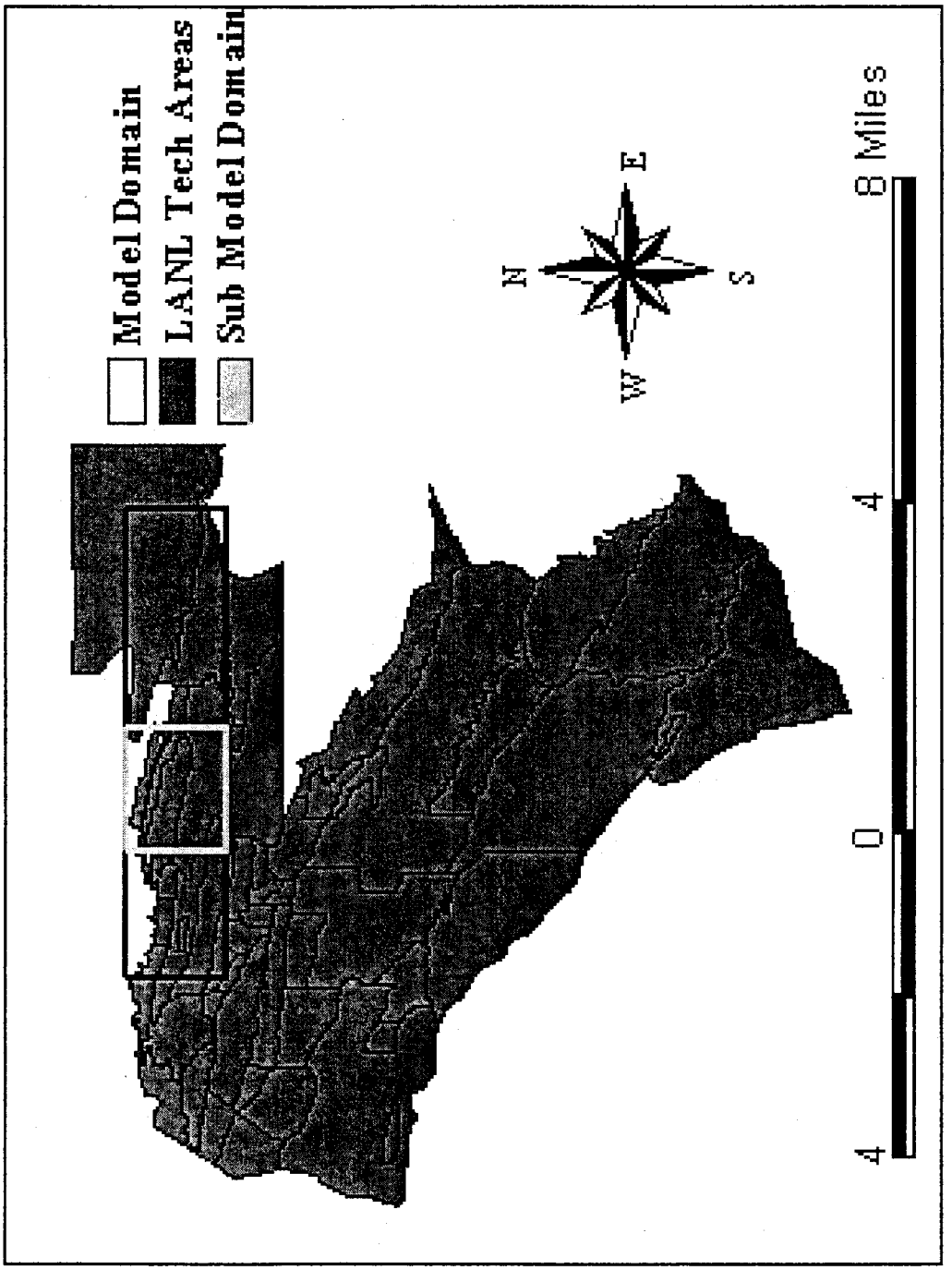

Figure 4.2.2-1 Location and dimensions of the model domain for the Los Alamos Canyon flow and transport model. The black outline is the full model, and the gray outline is a sub-model region for which detailed calculations were carried out.

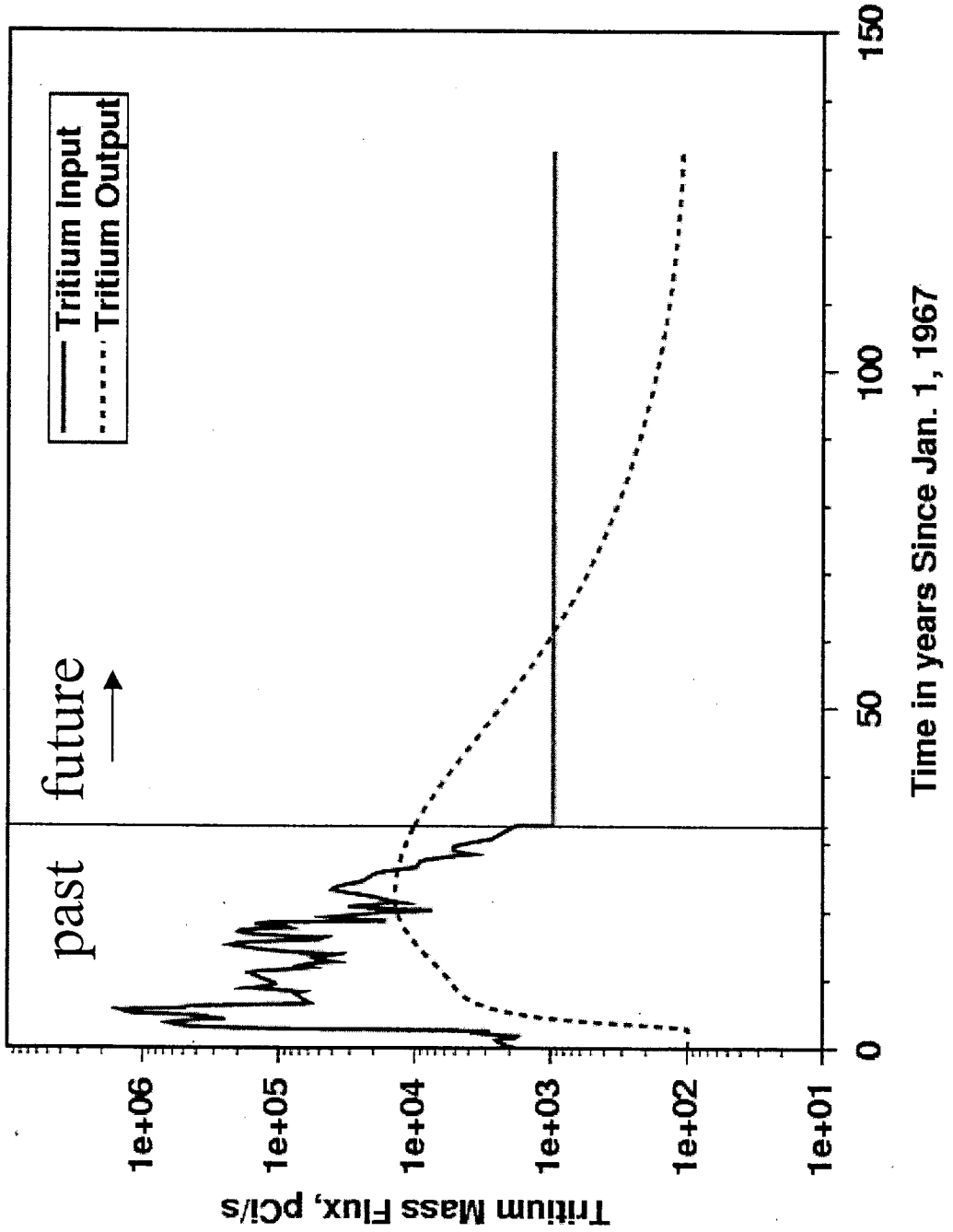

Figure 4.2.2-2 Tritium mass flux versus time, past and future model predictions. The solid curve represents the input tritium mass flux within the model domain; the dashed curve is a prediction of the mass flux reaching the regional aquifer.

4.2.2.1.2 TA-50 Injection Test Study

In the 1960's, Los Alamos National Laboratory and the U.S. Geological Survey conducted a series of tests to explore the possible use of injection wells for water disposal. The original intent of these studies was to determine if shallow injection wells drilled into the unsaturated zone on the Pajarito Plateau could be used to safely dispose of liquid effluent from Laboratory operations. The method was never used at Los Alamos, and current regulations, along with the Laboratory's desire to be responsible stewards of the environment, preclude this concept from ever being implemented. Nevertheless, data collected from these injection tests, which used uncontaminated water, can be used to understand the hydrologic processes controlling the movement of moisture in the unsaturated Bandelier tuff.

Information collected from two test areas is available for interpretation. A report by Purtymun et al. (1989) summarizes the goals of these tests to be:

- To investigate the rates of injection and the operating conditions under which the tuffs would accept water; and
- To monitor the movement of moisture from the injection well to the surrounding tuff.

Detailed descriptions of the testing methodology, layout, and measurement techniques are presented in Purtymun et al. (1989). In the current study, we interpreted and modeled the test results for the experiment called "Test 1 at Site 2" in Purtymun et al. (1989), a test consisting of an injection period of 89 days.

The model assumed a hydrologic mechanism that considered only matrix flow. The agreement between the numerical model and the data was quite acceptable, both qualitatively and quantitatively. The migration of moisture injected in an open interval of the wellbore exhibited flow that was controlled by both gravity and capillary forces. Flow was preferentially downward, as would be expected under conditions of relatively high flow rate. Lateral and upward migration also occurred due to the capillary driving forces in this unsaturated rock. The effects of an abrupt transition in hydrologic properties at the interface between two sub-units were also observed in both the data and the numerical model. In addition to this qualitative agreement, the model provided an adequate match to data on the rates of migration of the water plume in the vertical (upward and downward) and lateral directions. This agreement was achieved using hydrologic properties derived from laboratory measurements performed on samples collected from boreholes on the Pajarito Plateau, though not from the site of the injection test itself. This result may imply that if the conceptual model is correct, then the exact values of the hydrologic properties is not critical as long as the parameters are derived from the same hydrologic unit.

The representativeness of the experimental results requires discussion, given that the data are for a point-source injection from a wellbore, rather than natural infiltration. In determining whether preferential flow through fractures is occurring, the downward flux of water is a key factor, along with the hydrologic properties of the rock. To estimate the equivalent infiltration rate during the test, the fluid injection rate is divided by the cross sectional area of the water plume at a particular time. Applying this method at day 55 of injection, an estimated flux of about 2.7×10^4 mm/y is obtained. This rate is much higher than the average infiltration rates estimated for the Pajarito Plateau, even in canyons. Values this large probably occur only locally in areas of ponding or underneath locations with streamflow. The implication of this calculation is that if matrix-dominated flow is observed at the high effective infiltration rates of this injection test, then it is even more likely to be the case under natural and disturbed conditions on the Plateau.

With respect to the hydrologic conditions encountered in locations where dissolved contaminants are an issue, the consequence of matrix-dominated flow is to decrease travel velocities beyond what would be the case if preferential channeling through fractures were to occur. For example, for an infiltration rate of 1 mm/y, typical of a mesa location, and a water content of 0.1, downward

velocities will be on the order of 0.01 m/y. Under these conditions, a non-sorbing contaminant front would take 10,000 years to percolate through 100 m of unsaturated Bandelier Tuff.

A similar calculation for a wet-canyon scenario (500 mm/y, water content of 0.25) yields a transport velocity of 2 m/yr, or a travel time of 50 yr to traverse 100 meters of Bandelier Tuff. Corresponding estimates, if the hydrology were controlled by fractures, would be to reduce the water contents to 10^{-3} or lower to account for the small fraction of the total rock volume that is taken up by the fracture void space. Travel times to traverse the same 100 meters of Bandelier Tuff would be 100 years for the mesas and 0.2 yr for the wet canyons. In addition, if water containing contaminants percolates through the rock matrix, it is likely to be in intimate contact with the rock surfaces. Therefore, for contaminants that sorb to the rock, matrix-dominated flow increases the likelihood of retardation. This process can also occur during fracture flow, but sorption is not as effective because the contaminant must first diffuse to the fracture surface and into the rock matrix in order to sorb. As a result, even sorbing contaminants are probably relatively mobile under fracture flow conditions.

Qualitatively, the existing information on groundwater contaminant migration from Laboratory facilities agrees with this assessment of the role of the Bandelier Tuff in the unsaturated zone. There is evidence that some nonsorbing contaminants such as tritium have traveled significant depths through the unsaturated zone, even to the regional aquifer (Rogers, 1998) during the 50+ years of Laboratory operation. This is probably a consequence of releases into canyons, and transport at high percolation rates through either the Bandelier Tuff or other rocks, depending on the local geology. However, most known contaminant releases have not traveled that far, and still reside in the unsaturated zone. Releases on mesas, with low infiltration rates, or sorption of contaminants such as strontium and uranium onto the Bandelier Tuff, are the probable explanation.

In addition to providing a context for assessing the risk of Laboratory-derived groundwater contamination, the results also provide direction for future unsaturated zone characterization activities. At present, there appears to be no need to embark on a costly and time-consuming effort to characterize the fracture systems in the Bandelier Tuff for the purpose of predicting water percolation and contaminant transport. Note that this conclusion refers only to liquid movement through the Bandelier Tuff up to unit 3 of the Tshirege member. It does not apply to other rock types of interest, such as the uppermost sub-units of the Tshirege member at TA-16 or the basalt units. Additionally, this conclusion does not imply that other types of fracture studies are not important and useful site characterization activities.

Another implication of the results is that contaminants released on mesas or in canyons with significant thicknesses of Bandelier tuff should be able to be approximately mapped using a series of relatively shallow, vertical boreholes to determine the vertical extent of transport. Contaminant fronts that are mapped in this way would provide information on field scale infiltration rates and sorption characteristics that could be applied to calibrate models of flow and transport. They would also provide confirmation of the results of the injection test study, especially with respect to contaminant transport. Thus, although the conclusions of this modeling effort do not apply to all contaminants at all Laboratory sites, the observations and accompanying modeling provide an important perspective on flow and transport through the unsaturated zone under the Pajarito Plateau.

4.2.2.1.3 TA-16 Vadose Zone Interpretation

Recent drought conditions are reflected in water quantity and temperature in the TA-16 area. Results of alluvial aquifer and spring sampling in the TA-16 area indicate a strong drought effect where water levels and spring flows decreased. In addition, the extent of surface flow down Cañon de Valle was reduced dramatically. Preliminary analysis of spring temperature data suggests that the drought has affected the spring water temperature response. Burning Ground spring in particular, shows a significant reduction in temperature variability. In addition, the

differences in temperature response between the springs have apparently changed. Prior to the drought, Martin spring had a more constant and, on the average, warmer temperature than either SWSC or Burning Ground springs. Since the drought, Burning Ground has had the warmest and most constant temperature. It appears that during the drought, Burning Ground spring has been more isolated from fast-path recharge that caused more temperature variation prior to the drought.

Spectral analyses of springflow time series data were conducted in order to understand flow dynamics. The spectral results show that the springflow has two dominant patterns: a series of low-frequency modes that follow the seasonal and longer-term climate conditions, and a large number of higher frequency modes which display a characteristic spectrum related to local, short-term weather conditions at the site. These results support the TA-16/wet mesa conceptual model that describes a larger, longer residence time flow system and smaller, faster, intermittent flowpaths that superimpose recharge on the larger flow system.

4.2.2.2 Saturated Zone Data Interpretation

Data collected in the saturated zone has been incorporated into the regional aquifer model to facilitate data interpretation. The regional aquifer modeling activities integrated the new geologic and hydrologic data collected in R-wells into the regional model in order to:

- Provide support to well siting decisions
- Formally integrate geochemical tracers (^{3}H, ^{14}C, $\delta^{18}O$, Cl) into the process of model development and validation
- Begin development of a facies-based approach to modeling heterogeneity within the Puye Formation

The process of integrating new geologic and hydrologic data into the flow model was dominated by issues raised by changes in the site-wide geologic model (Carey et al., 1999) pertaining to Santa Fe Group rocks. New water level data and pump test results from R-wells were also incorporated into the model parameterization and calibration process. Estimating permeability variations within the regional aquifer, using a combination of data summary and analysis and inverse modeling techniques, was a major focus of FY00 activities. The inverse modeling methods, including model calibration and sensitivity analysis, also provided detailed information about the sensitivity of model results to parameter uncertainty.

There were several important results from this work pertaining to hydraulic conductivity of the Santa Fe Group rocks. First, inverse modeling demonstrated that large-scale permeability of the Santa Fe Group rocks appears to be lower than that which has been inferred from numerous pump tests in older wells on the Pajarito Plateau. The most likely reasons for this are that the older tests:

1) Were conducted under non-ideal pump test conditions, such as lack of monitoring wells and very short time-scales,
2) Encountered aquifer heterogeneity that could not be accounted for quantitatively in pump test interpretation, and
3) Scaling effects.

Of these possible reasons, scaling effects are probably the most important. For example, north-south trending faults in Santa Fe Group Rocks associated with basin rifting may reduce effective permeability at the site-scale relative to estimates derived from hydraulic testing at individual wells.

Second, both data analysis and inverse flow modeling independently demonstrated that the conceptual model of heterogeneity within the Santa Fe Group (two large-scale facies, the "Los Alamos aquifer" and "lower Santa Fe Group") is not consistent with existing hydrologic data (water levels and permeability estimates). At this time, it is unclear whether such large-scale features exist at all. Alternative conceptual models, such as much smaller-scale heterogeneity, that can be best captured by stochastic modeling approaches are being evaluated. Since none of the wells installed in FY00 penetrated the Santa Fe Group, there may not be opportunities to better characterize hydrofacies within these rocks until later in the characterization program.

To provide modeling support to siting of R-5 as a monitoring well for hydraulic testing purposes, a pump test at O-1 was simulated to predict levels of drawdown under a variety of scenarios. The primary goal of these simulations was to provide estimates of between-well distances that would be favorable for the conjunctive use of R-5 and O-1 for data collection. We estimated that the maximum between-well distance for adequate response in R-5 was approximately 400m, although closer distances would be preferable. An important ancillary benefit of this work was the development of general methodologies for using FEHM to study hydraulics during a pump test, assuming a non-uniform hydraulic conductivity field. This capability allows us to map heterogeneous aquifer properties, distributed according to known or hypothesized hydrostratigraphic zonations, onto a numerical mesh appropriate for pump test analysis. The methods developed for this particular application (pumping at O-1) can be easily applied to pump test design and/or interpretation at other sites in the future.

Simulations at the basin-scale were run to calculate transport of groundwater tracers (^{3}H, ^{14}C, $\delta^{18}O$, Cl). All of these simulations were designed to estimate steady-state concentrations of tracers in groundwaters, and so should reflect "background" concentrations in the aquifer assuming no impact of human activities. For each of these tracers, simulated and measured concentrations in wells were compared. One goal of this comparison was to provide an independent assessment of the validity of the model, particularly regarding recharge assumptions. The results provided substantial model validation in that the predicted concentrations were qualitatively consistent with measurements, particularly in those wells in the vicinity of LANL. Both Cl and $\delta^{18}O$ simulations provided independent validation of the large-scale recharge rates that are applied in the regional model and were estimated using hydrologic data and inverse modeling approaches alone.

The simulations also highlighted aspects of the model that should be improved. For example, the model underestimated ^{14}C ages in waters near the Rio Grande, indicating that model resolution and/or parameterization is lacking in the region beneath the river. Also, the model did not capture small-scale variations in $\delta^{18}O$ within the LANL site. To do so will require small-scale refinement of the recharge model. Further modeling of both $\delta^{18}O$ and ^{3}H will be very useful in this refinement process.

Progress in developing a facies-based model for the Puye Formation was difficult due to the Cerro Grande fire, since access to Puye outcrops in canyons was very limited and staff members with field expertise regarding the Puye were redirected to fire-related efforts. Completed activities include compilation of a comprehensive literature review, conduct of reconnaissance field trips, and provision of initial, bounding estimates for facies geometries. Due to the limited nature of the initial data set, a Gaussian approach (Gomez-Hernandez, 1991), rather than a facies-based approach, was used to simulate stochastic hydraulic conductivity fields. As the data set improves, a facies-based method of simulating stochastic hydraulic conductivity fields will be used. The initial Gaussian-based simulated stochastic hydraulic conductivity fields were used to provide ranges of travel times from TA-16 to the PM well field. These ranges were much better constrained than the initial simulations, which were based on a deterministic model of the Puye (Keating et al. 1999). The "most likely" travel times predicted by the model were in the range of two to three hundred years.

To resolve small-scale features in the Puye Formation, the resolution of our numerical mesh had to be increased beyond practical limits, given the scale of the basin model. Therefore, a sub-model of the basin model was developed that focused on the Pajarito Plateau and improved the vertical resolution in the mesh. The disadvantage of this approach is that lateral model boundaries can no longer be assumed to be no-flow, actual fluxes are uncertain, and transport calculations may be sensitive to this uncertainty. To mitigate these disadvantages, the basin model was used to calculate "best estimate" fluxes to the submodel boundaries and to calculate uncertainty limits for these estimates.

4.3 Geochemical Data Collection and Interpretation

Geochemical data collection activities in FY00 included data collected from newly installed boreholes and wells as well as groundwater sampling of supply wells, test wells, springs, and alluvial wells. All hydrochemical data collected from boreholes and pre-developed monitoring wells are screening data. These data are useful for geochemical interpretation and decision making during well completion. Hydrochemical data appropriate for regulatory decisions will be collected from R wells when they are completed and properly developed as monitoring wells.

Data collection activities included:

- Collection of core and cuttings for geochemical-contaminant analyses during drilling of boreholes R-31, R-19, R-15, and CDV-15-3
- Collection of groundwater samples both during drilling and from newly completed wells to evaluate natural solute (inorganic-radionuclide) and contaminant distributions in perched zones and in the regional aquifer
- Collection of groundwater samples from alluvial wells and springs in Cañon de Valle to evaluate water and contaminant balance and estimate residence times and mixing of groundwater and surface water
- Collection of water quality samples from test wells and supply wells on and adjacent to the Pajarito Plateau as part of the annual environmental surveillance and compliance monitoring activities
- Performance of geochemical modeling using MINTEQA2 and PHREEQC2.2 to quantify aqueous speciation, mineral equilibrium, and adsorption reactions using groundwater and mineralogical samples collected from the completed wells and boreholes

4.3.1 Geochemical Data Collection

4.3.1.1 Borehole R-31

Groundwater samples were collected from borehole R-31 from two perched zones (525 and 625 ft) on January 22 and 23, 2000 and from the regional aquifer (1087 ft) on February 7, 2000. The samples were analyzed for high explosive (HE) compounds and degradation products. Drilling fluids were used at R-31 and chemical characterization of groundwater was limited to potential contaminants of concern including HE compounds. No HE compounds and/or degradation products were observed at R-31 during drilling.

4.3.1.2 Borehole R-19

Groundwater samples were collected during drilling at borehole R-19 from two perched zones (738 and 832.8 ft) on February 24 and 29, 2000 and from the regional aquifer (1157

and 1860 ft) on March 3 and 12, 2000. The samples were analyzed for high explosive (HE) compounds and degradation products; stable isotopes of hydrogen, nitrogen, and oxygen; total organic carbons (TOC); anions; and metals. Drilling fluids were used at R-19 and chemical characterization of groundwater was mainly limited to potential contaminants including HE compounds. HE compounds and degradation products were estimated (J values for validated data) at low concentrations in the groundwater sample collected from 833 ft. These include: HMX (0.11μg/L, J value); nitrobenzene (0.36 μg/L, J value); 2-amino-4,6-dinitrotoluene (0.36 μg/L, J value); and 2,6-dinitrotoluene (0.34 μg/L, J value). In the groundwater sample collected from 1157 ft, 2-amino-4,6-dinitrotoluene was detected (J value) at a concentration of 0.19 μg/L. The other groundwater samples collected from borehole R-19 did not contain HE compounds and/or degradation products.

4.3.1.3 Borehole R-15

Distributions of tritium and perchlorate were measured in core, cuttings, and groundwater samples collected from borehole R-15 (Longmire et al., 2000) (Figure 4.3.1-1). Tritium was measured at an activity of 3,770 pCi/L within a perched zone (646 ft) encountered in the Cerros del Rio basalt at R-15. Concentrations of perchlorate within the same zone were 12 ppb. Tritium and perchlorate are mobile species that have been discharged to Mortandad Canyon and both constituents occur in alluvial groundwater. Concentrations of perchlorate in the Bandelier Tuff reached 400 ppb and correlated very well with nitrate in the vadose zone. Concentrations of perchlorate reached 1,662 ppb within a buried soil at the base of saturation within the basalt (Figure 4.3.1-1). Perchlorate was not detected in the regional aquifer during drilling of R-15, and activities of tritium were less than 3 pCi/L (Longmire et al., 2000). The Laboratory annually analyzes for tritium, perchlorate, and other constituents during sampling of alluvial groundwater in Mortandad Canyon. Perchlorate and other constituents are included in the quarterly sampling at R-15.

4.3.1.4 Borehole CDV-15-3

Six ground water samples were collected from borehole CDV-15-3 from two perched zones (622 and 1137 ft) and from the regional aquifer (1250, 1497, 1620, and 1650 ft) (Hickmott, 2000). The samples were analyzed for HE compounds and degradation products, nitrogen isotopes, screening analytes, and TOC. The two perched groundwater samples were collected on March 23 and 30, 2000. Groundwater samples from the regional aquifer, with increasing depth, were collected on April 4, April 24, July 31, and August 3, 2000. Drilling fluids were used at CDV-15-3 and chemical characterization of groundwater was limited to potential contaminants including HE compounds.

HE degradation products, including 4-amino-2,6-dinitrotoluene (0.11 μg/L, j-qualified) and 2,6-dinitrotoluene (0.49 μg/L), were observed near detection limit (0.25 μg/L) in only one out of six samples at CDV-15-3 during drilling. This filtered sample was collected from the upper perched zone at 622 ft (Hickmott, 2000). HE compounds and degradation products were not detected in non-filtered samples collected at CDV-15-3. HE compounds and degradation products and other constituents will be included as part of the analytical suite for quarterly sampling at CDV-15-3.

4.3.1.5 Cañon de Valle Alluvial Wells and Springs

Intensive geochemical and contaminant data collection in the Cañon de Valle alluvial aquifer, SWSC, Burning Ground, and Martin springs occurred in FY00. Quarterly grab sampling and monthly flow integrated sampling were completed for major cations and anions and HE. Springs were sampled every other day for bromide and stable isotopes ($\delta^{18}O$ and δD). Precipitation was sampled on an event basis for $\delta^{18}O$ and δD.

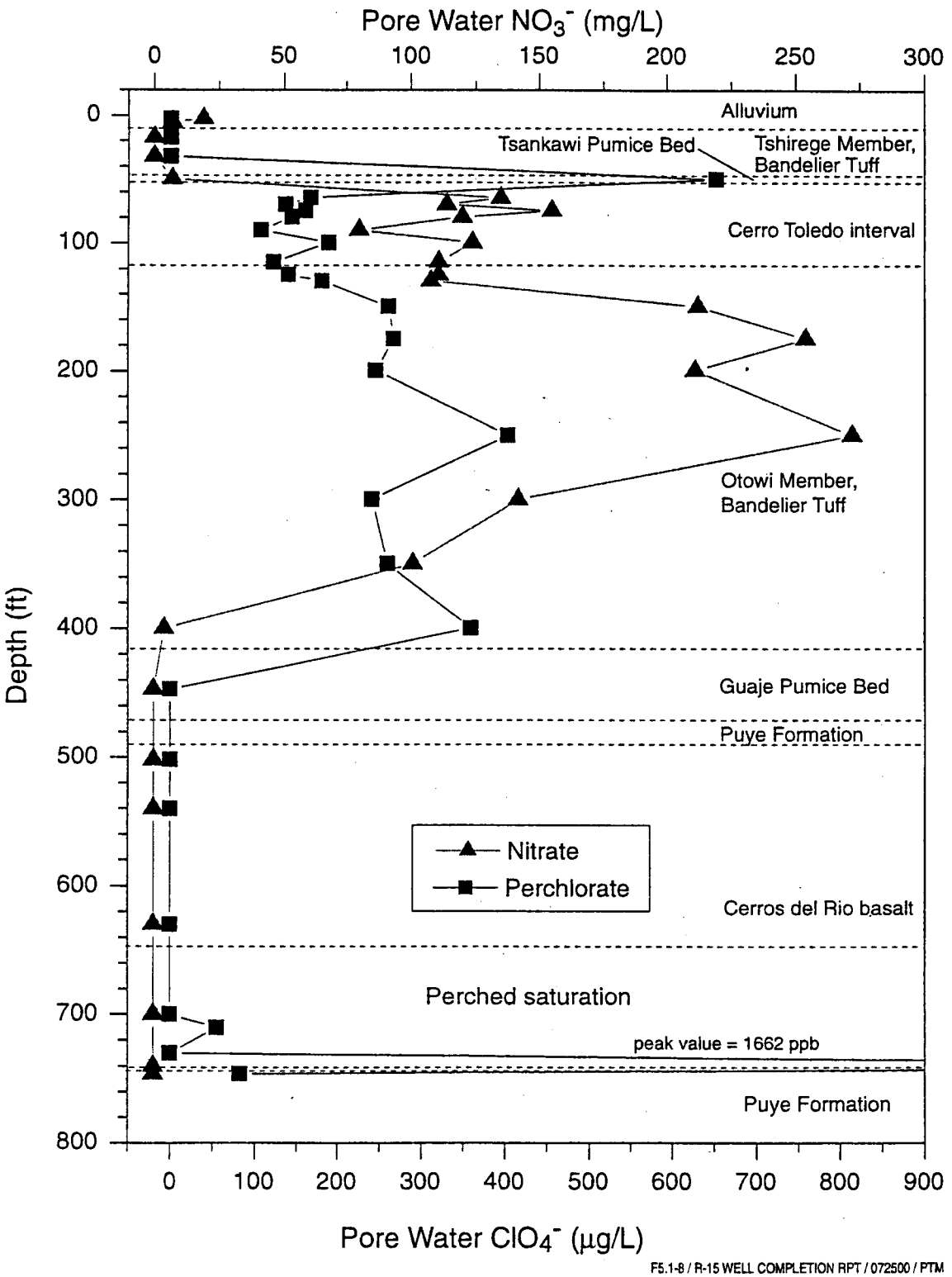

Figure 4.3.1-1 Pore water nitrate and perchlorate concentrations for borehole R-15.

4.3.1.6 Quarterly Groundwater Sampling During FY00

Quarterly groundwater sampling was initiated during FY00 at R-9, R-9I, R-12, R-15, and R-19. Each characterization well was developed and aquifer performance testing was conducted prior to groundwater sampling. Groundwater samples were analyzed for inorganic, organic, and radiological constituents as described below. Analytical results are being validated by the Environmental Restoration (ER) Project and shall be released following electronic data validation.

4.3.1.6.1 Quarterly Groundwater Sampling at R-9

Quarterly groundwater sampling took place at R-9 on February 28 and September 29, 2000. Potential contaminants of concern at R-9 include tritium, strontium-90, uranium and plutonium isotopes, and americium-241. Characterization well R-9 contains a 15-ft single screen at the top of the regional aquifer (688.6-704 ft). The characterization well is in upper Los Alamos Canyon west of New Mexico State Road 4. Field parameters including pH, temperature, specific conductance, and turbidity were measured at R-9 before and during sample collection. Groundwater samples were analyzed for radionuclides (tritium, strontium-90, gamma spectroscopy, uranium and plutonium isotopes, and americium-241), RCRA metals, anions, stable isotopes of hydrogen, nitrogen, and oxygen, volatile and semi-volatile organic compounds, and TOC. Humic acid fractionation was not measured at R-9 due to funding constraints.

4.3.1.6.2 Quarterly Groundwater Sampling at R-9I

Quarterly groundwater sampling was initiated at R-9I on September 14 and 15, 2000. Characterization well R-9I contains two 10-ft screens (189-199 ft and 270-280 ft) within the Cerros del Rio basalt and is equipped with Westbay Instruments sampling equipment. Potential contaminants of concern at R-9I include tritium, strontium-90, uranium and plutonium isotopes, and americium-241. The characterization well is in upper Los Alamos Canyon west of New Mexico State Road 4 near R-9. Field parameters including pH, temperature, specific conductance, and turbidity were measured at R-9I before and during sample collection. Groundwater samples were analyzed for radionuclides (tritium, strontium-90, gamma spectroscopy, uranium and plutonium isotopes, and americium-241), RCRA metals, anions, stable isotopes of hydrogen, nitrogen, and oxygen, volatile and semi-volatile organic compounds, humic acid fractionation, and TOC.

4.3.1.6.3 Quarterly Groundwater Sampling at R-12

Quarterly groundwater sampling was initiated at R-12 on September 18-20, 2000. Characterization well R-12 contains three screens, two within the Cerros del Rio basalt (459-467.5 ft and 504.5-508 ft) and one at the top of the regional aquifer (801-8839 ft), and is equipped with Westbay Instruments sampling equipment. Potential contaminants of concern at R-12 include tritium, strontium-90, nitrate, uranium and plutonium isotopes, and americium-241. The characterization well is in upper Sandia Canyon west of New Mexico State Road 4. Field parameters including pH, temperature, specific conductance, and turbidity were measured at R-12 during sample collection. Groundwater samples were analyzed for radionuclides (tritium, strontium-90, gamma spectroscopy, uranium and plutonium isotopes, and americium-241), RCRA metals, anions, stable isotopes of hydrogen, nitrogen, and oxygen, volatile and semi-volatile organic compounds, and TOC. Humic acid fractionation was not measured at R-12 due to funding constraints.

4.3.1.6.4 Quarterly Groundwater Sampling at R-15

Quarterly groundwater sampling was initiated at R-15 on February 24, 2000. Characterization well R-15 contains a single 60-ft screen at the top of the regional aquifer

(958.6-1020.3 ft), and the well is in upper Mortandad Canyon. Potential contaminants of concern at R-15 include perchlorate, tritium, strontium-90, nitrate, uranium and plutonium isotopes, and americium-241. Field parameters including pH, temperature, specific conductance, and turbidity were measured at R-15 before and during sample collection. Groundwater samples were analyzed for radionuclides (tritium, strontium-90, gamma spectroscopy, uranium and plutonium isotopes, and americium-241), RCRA metals, anions, stable isotopes of hydrogen, nitrogen, and oxygen, volatile and semi-volatile organic compounds, and TOC.

4.3.1.7 Sampling of Water Supply Wells in FY00

In 2000, the Laboratory sampled water supply wells for four contaminants of concern: strontium-90, tritium, high explosives, and perchlorate. The frequency of monitoring varies from annual to monthly depending on the contaminant and sampling location. The wells are part of the Los Alamos water-supply system and are leased and operated by the County of Los Alamos.

At the Annual Meeting in March 2000, there was a presentation regarding Environmental Surveillance Program strontium-90 data for 1999 that raised concerns about the quality of analytical data. The following discussion provides background on this issue.

The Laboratory's Water Quality and Hydrology Group collects annual environmental surveillance samples for runoff, surface water, sediments, and groundwater. The 1999 data set for strontium-90 from these media had analytical problems; therefore, the decision was made by the Laboratory and DOE not to use the strontium-90 data set.

The Laboratory's Analytical Chemistry Sciences Group developed a new strontium-90 method using a chelating filter (disk) in an attempt to lower detection limits, improve cost effectiveness, and minimize solvent use. The group started evaluating and testing the strontium-90 procedure in 1995. They ran National Institute of Standards and Technology, Environmental Measurements Laboratory, and open quality control samples during their data development and validation. They presented the procedure and data for peer review at the Bioassay, Environmental, and Analytical Radiochemistry conference in October 1996. This method was used for most strontium-90 analysis from 1997 to 1999.

Because of concern about possible presence of strontium-90 in water samples from the regional aquifer, the Analytical Chemistry Sciences Group was requested in 1999 to establish lower detection limits for the analytical method. This was accomplished by increasing the sample size and the count time.

Once 1999 analytical results became available, it was determined that numerous analytical values for strontium-90 were questionable. A Corrective Action Request was submitted to the Analytical Chemistry Sciences Group, which included an initial list of seven samples suspected of being in error. After several iterations, this list was expanded to 28 samples. Our concerns regarding possible analytical problems were based on:

- Comparison of analytical results to previous sample values
- Comparison of analytical results to split sample analytical results from the NMED DOE Oversight Bureau
- Lack of gross beta measurements supporting strontium-90 values for these samples and lack of strontium-90 in reanalysis of the samples
- Knowledge that strontium-90 was detected in our quality control blanks (which could have been contaminated during preparation or analysis)
- Unfavorable analytical results for our quality control spiked samples

The Analytical Chemistry Sciences Group responded with a draft Corrective Action Report dated August 10, 2000. The Corrective Action Report noted that the analytical method employs selective extraction resins. A change in the formulation of the resin used in the filter disks may have resulted in strontium-90 false positives because radon was present in samples. This change in the resin occurred after the initial method validation for the strontium-90 separation procedure.

In preparing for the annual report "Environmental Surveillance at Los Alamos during 1999" in August 2000, there was lack of confidence in the strontium-90 results for 1999 runoff, surface water, groundwater, and sediment samples. For this reason the Laboratory and DOE concluded that the strontium-90 data set for 1999 would not be used. For reference, the report Environmental Surveillance at Los Alamos during 1999 is available on the web at http://lib-www.lanl.gov/pubs/la-13775.htm. This referenced report contains a listing of the 1999 strontium-90 data along with NMED DOE Oversight Bureau data collected at the same stations and a description of our quality control samples.

In an effort to improve the quality, timeliness, independence, and costs of analytical data, the Laboratory's Environmental Surveillance Program committed in early 2000 to the use of outside analytical laboratories to analyze most of the environmental surveillance samples.

4.3.1.7.1 Analysis for Strontium-90 in Samples from Water Supply Wells

All Los Alamos water supply wells were sampled quarterly for strontium-90 in 2000; this sampling will continue in 2001. Table 4.3.1-1 compiles the quarterly strontium-90 results received to date for 2000. In 2000 strontium-90 was initially detected in Otowi-1, G-3A, and PM-1. Otowi-1 is located in lower Pueblo Canyon several miles east-northeast of the Laboratory's main technical area. Although Otowi-1 was constructed in 1990, it did not become operational until 1997. Major water production from the well began in the spring of 2000. G-3A is in Guaje Canyon, on Forest Service land north of Los Alamos.

The detection for Otowi-1 occurred in a laboratory duplicate analysis; the original analysis did not yield a detection. Reanalysis of the original samples and subsequent sampling at both wells has not confirmed either of the detections of strontium-90.

Table 4.3.1-1 Water Supply Well Sampling, CY2000 Sr-90 Results (pCi/L)

Location	Note	Sample Date	Result	1-Sigma Uncertainty	MDA	3-Sigma Detect? *	Analytical Lab
G-1A		03/07/00	0.02	0.04	0.13	ND	Paragon
G-1A		08/14/00	0.02	0.045	0.15	ND	Paragon
G-2A		03/07/00	0.03	0.04	0.13	ND	Paragon
G-2A	lab dup	03/07/00	0.03	0.04	0.13	ND	Paragon
G-2A		06/20/00	0.05	0.04	0.13	ND	Paragon
G-2A		08/14/00	-0.04	0.045	0.15	ND	Paragon
G-3A		03/07/00	0.01	0.035	0.12	ND	Paragon
G-3A		06/20/00	0.17	0.045	0.13	Detect	Paragon
G-3A	rerun	06/20/00	0.00	0.03	0.10	ND	Paragon
G-3A		08/03/00	0.01	0.04	0.14	ND	Paragon
G-3A		08/03/00	0.0683	0.163	0.558	ND	GEL
G-3A		08/14/00	0.02	0.045	0.15	ND	Paragon
G-4A		03/07/00	0.01	0.04	0.13	ND	Paragon
G-4A		06/20/00	0.00	0.04	0.13	ND	Paragon
G-4A		08/14/00	-0.05	0.045	0.15	ND	Paragon
O-1		06/20/00	0.06	0.05	0.16	ND	Paragon

Table 4.3.1-1 Water Supply Well Sampling, CY2000 Sr-90 Results (pCi/L)

Location	Note	Sample Date	Result	1-Sigma Uncertainty	MDA	3-Sigma Detect? *	Analytical Lab
O-1	rerun	06/20/00	0.01	0.035	0.11	ND	Paragon
O-1	lab dup	06/20/00	0.19	0.05	0.15	Detect	Paragon
O-1		08/03/00	0.06	0.04	0.13	ND	Paragon
O-1		08/03/00	0.0296	0.2125	0.744	ND	GEL
O-1	dup	08/03/00	-0.09	0.05	0.17	ND	Paragon
O-1	dup	08/03/00	-0.101	0.193	0.682	ND	GEL
O-1		08/14/00	-0.01	0.05	0.16	ND	Paragon
O-1	lab dup	08/14/00	0.00	0.045	0.16	ND	Paragon
O-1	dup	08/14/00	0.01	0.045	0.15	ND	Paragon
O-4		06/20/00	0.07	0.05	0.16	ND	Paragon
O-4	lab dup	06/20/00	0.14	0.045	0.15	ND	Paragon
O-4		08/14/00	0.05	0.045	0.15	ND	Paragon
PM-1		02/14/00	0.01	0.03	0.10	ND	Paragon
PM-1		06/20/00	0.04	0.045	0.15	ND	Paragon
PM-1		08/14/00	-0.04	0.045	0.16	ND	Paragon
PM-2		02/14/00	0.00	0.035	0.11	ND	Paragon
PM-2		06/20/00	0.13	0.05	0.16	ND	Paragon
PM-2		08/14/00	0.03	0.045	0.16	ND	Paragon
PM-3		06/20/00	0.10	0.04	0.13	ND	Paragon
PM-3	rerun	06/20/00	0.01	0.035	0.13	ND	Paragon
PM-3		08/14/00	0.05	0.05	0.16	ND	Paragon
PM-4		06/20/00	0.09	0.04	0.12	ND	Paragon
PM-4	rerun	06/20/00	0.05	0.03	0.10	ND	Paragon
PM-4		08/03/00	-0.11	0.05	0.16	ND	Paragon
PM-4		08/03/00	0.224	0.201	0.68	ND	GEL
PM-4		08/14/00	-0.02	0.045	0.15	ND	Paragon
PM-5		02/14/00	0.03	0.035	0.12	ND	Paragon
PM-5		06/20/00	0.06	0.04	0.13	ND	Paragon
PM-5		08/14/00	-0.02	0.045	0.16	ND	Paragon
PM-5	lab dup	08/14/00	0.10	0.055	0.17	ND	Paragon

*Note: detection defined as analytical result ≥ 3 × one sigma uncertainty and ≥ method detection limit (MDA)

A sample collected from water supply well PM-1 on March 9, 1999 by NMED's DOE Oversight Bureau resulted in an apparent detection of strontium-90. In contrast, a split sample collected by LANL on March 9, 1999 yielded no detection of strontium-90, with a detection limit below the analytical result for NMED's sample. PM-1 is located in Sandia Canyon at the eastern Laboratory boundary and is not downstream of any known Laboratory sources of strontium-90. The EPA MCL for strontium-90 is 8 pCi/L.

In early August 1999, LANL learned that strontium-90 was apparently detected in the March 9, 1999 NMED sample from water supply well PM-1. LANL immediately submitted for analysis a larger volume sample previously collected from PM-1 on June 8, 1999, so that a better detection limit could be obtained. The larger volume sample did not show detection of strontium-90.

Table 4.3.1-2 compiles strontium-90 data collected for water supply well PM-1 by LANL and NMED's DOE Oversight Bureau. The LANL data show significant decreases in our analytical detection limit for strontium-90 since 1998. LANL collected two samples (on June 8 and December 13, 1999) after the March 9, 1999 date of the apparent detection of strontium-90 by NMED. LANL has sampled the well on a quarterly schedule in 2000 and this will continue during

Table 4.3.1-2 Strontium-90 Data for Water Supply Well PM-1

LANL AND NMED STRONTIUM-90 VALUES PRIOR TO 1999

Station	Date	Value	1 Sigma Uncertainty	MDA	Detection?*	Data Source
PM-1	07/12/76	-1.10	0.80	3.00	ND	LANL
PM-1	02/28/80	0.10	0.30	3.00	ND	LANL
PM-1	12/02/94	0.30	0.80	3.00	ND	LANL
PM-1	06/12/95	4.60	10.80	3.00	ND	LANL
PM-1	04/25/96	0.20	0.90	3.00	ND	LANL
PM-1	06/25/97	<0.60		0.60	ND	NMED
PM-1	06/25/97	-0.90	1.80	3.00	ND	LANL
PM-1	06/08/98	0.33	0.78	3.00	ND	LANL

LANL AND NMED STRONTIUM-90 VALUES FOR 1999

Station	Date	Value	1 Sigma Uncertainty	MDA	Detection?*	Data Source
PM-1	3/9/99	0.31	0.25	0.77	ND	LANL
PM-1	3/9/99	1.14	0.115	0.15	Detect	NMED
PM-1	6/8/99	0.10	0.05	0.10	ND	LANL
PM-1	12/13/99	-0.75	0.22	0.44	ND	LANL

LANL strontium-90 values for 2000

Location	Date	Result	1 Sigma Uncertainty	MDA	Detection?*	Data Source
PM-1	2/14/00	0.01	0.03	0.10	ND	LANL
PM-1	6/20/00	0.04	0.045	0.15	ND	LANL
PM-1	8/14/00	-0.04	0.045	0.16	ND	LANL

*Note: detection defined as analytical result ≥ 3 × one sigma uncertainty and ≥ method detection limit (MDA)

2001. Of the 15 measurements tabulated, only one (March 9, 1999 NMED DOE Oversight Bureau sample) is an analytical detection of strontium-90.

In summary, the PM-1 strontium-90 data, taken over a 25-year period, do not make a case for presence of strontium-90 in this well. For any single measurement, an error may result due to problems such as contamination during collection; sample mix-ups; and analytical laboratory problems such as recording errors, analysis inaccuracy, or difficulties with analytical media or instruments. Therefore, regular monitoring is required to assemble the body of data needed to determine the presence of a particular analyte.

4.3.1.7.2 Analysis for Perchlorate in Samples from Water Supply Wells

Water supply wells are sampled on a semi-annual basis and none have shown perchlorate in samples Table 4.3.1-3. However, perchlorate was detected in samples collected during 2000 from the Otowi-1 water-supply well at concentrations of 1.9 to 3.5 ppb. Following the initial discovery, Otowi-1 has been sampled monthly for perchlorate.

Table 4.3.1-3 Results of Perchlorate (ppb) Analysis in LANL Water Supply Wells

Sample Date	Analytical Laboratory	PM-1	PM-2	PM-3	PM-4	PM-5	O-1	O-4	G-1A	G-2A	G-3A	G-4A	G-5A
2/14/00	Babcock	<4	<4	OS	OS	<4	OS	OS					OS
2/14/00	EES-1	<2	<2	OS	OS	<2	OS	OS					OS
3/7/00	Babcock			OS	OS		OS	OS	<4	<4	<4	<4	OS
3/7/00	EES-1			OS	OS		OS	OS	<2	<2	<2	<2	OS
6/21/00	Babcock			<1	<1		3.5J	<1					
6/21/00	EES-1			<2	<2		2	<2					
6/29/00	Babcock			<1	<1		3.3J						
6/29/00	EES-1						2						
7/6/00	Babcock						3.5J						
7/6/00	Babcock						2J						
7/6/00	EES-1						1.7						
7/6/00	EES-1						2.0						
8/3/00	Babcock				<1		2J				<1		
8/3/00	Babcock						2.3J						
8/14/00	Babcock						2.4J						
8/14/00	Babcock						<1						
9/12/00	Babcock						2.4J						
9/12/00	Babcock						1.9J						
10/10/00	Babcock						<1						

Notes:

OS - the well was out-of-service on that date.

J - the sample result is estimated because it is below the analytical laboratory's Reporting Limit of 4 ppb, but above the laboratory's Minimum Detection Limit of 1 ppb.

Analytical Laboratories - E.S. Babcock & Sons (Babcock) has a Reporting Limit of 4 ppb and a Minimum Detection Limit of 1 ppb. Los Alamos National Laboratory's EES-1 analytical laboratory has a Minimum Detection Limit of 1 ppb.

Perchlorate is a non-radioactive chemical compound that contains a chlorine atom bound to four oxygen atoms. Perchlorate is used in a variety of industrial processes. At the Laboratory, perchlorate is a byproduct of the perchloric acid used in nuclear chemistry research.

The chemical was first detected in Otowi-1 in late June 2000 during regular sampling as part of the Laboratory's water-quality assurance activities. Follow up sampling confirmed its presence. Perchlorate has not been found in any other water supply wells.

Test results from independent analytical laboratories corroborated the Laboratory's in-house analytical results: perchlorate concentrations in the Otowi-1 well ranged from 2 to 3.5 ppb in four separate samples taken between June 21 and July 6.

The EPA has not established a drinking water standard for perchlorate. The State of California, which has perchlorate contamination in drinking water supplies in some areas, has established a perchlorate water-supply action level for concentrations greater than 18 ppb. The State of New Mexico has not established an action level or regulatory standards for perchlorate.

4.3.1.7.3 Analysis for Tritium in Samples from Water Supply Wells

Tritium was found in Otowi-1 in a June 21, 2000 sample at a concentration of 38.3 +/- 1.3 pCi/L. This concentration is 500 times lower than the federal drinking water standard, but is above background concentrations that can be found in groundwater around the Laboratory. Otowi-1 is now sampled monthly for tritium.

Federal drinking water standards state that water is safe to drink if it contains tritium in concentrations lower than 20,000 pCi/L. Concentrations of tritium in the regional aquifer in other parts of the Laboratory can be found ranging between one and three pCi/L; tritium concentrations in Northern New Mexico surface water and rainwater range from 30 to 40 pCi/L.

In January 2000, hydrologists with the NMED reported that samples taken in June 1999 from the Otowi-1 supply well contained tritium in concentrations of 39.9 pCi/L.

Tritium also has been seen in the deep aquifer of a test well several hundred yards downstream from the Otowi-1 supply well. The concentration of tritium in Test Well-1 was 360 pCi/L in 1993. The test well just penetrates the top of the regional aquifer about 600 feet beneath the canyon floor. In contrast, the area within the aquifer from which Otowi-1 draws its water begins at just about 1000 ft below the canyon floor (and about 400 ft lower than the top of the aquifer and Test Well-1) and continues down an additional 1460 ft.

4.3.1.7.4 Analysis for High Explosives in Samples from Water Supply Wells

In 1998, drilling of characterization well R-25 at TA-16 in the southwest portion of the Laboratory revealed the presence of HE constituents at concentrations above the EPA Health Advisory guidance values for drinking water. As a result, the Laboratory has tested all nearby water supply wells for these compounds. None of the analytical laboratories detected any HE compounds or their degradation products in any of the water samples from any of the supply wells sampled.

All water supply wells are sampled annually for HE compounds. The three wells nearest to TA-16 (PM-2, PM-4, and PM-5) are sampled quarterly. The schedule of results received to date for 2000 is shown in Table 4.3.1-4.

Table 4.3.1-4: Results of Analysis for High Explosives (ppb) in Samples from Water Supply Wells

Sample Date	PM-1	PM-2	PM-3	PM-4	PM-5	O-1	O-4	G-1A	G-2A	G-3A	G-4A	G-5A
2/14/00		ND		OS	ND							
6/20/00	ND	ND			ND			OS	ND	ND	ND	OS
6/21/00			ND	ND		ND	ND					
8/14/00		ND		ND	ND							

ND - the target analyte was not detected above the analytical laboratory's Minimum Detection Level (MDL)
OS - the well was out-of-service on that date.

4.3.2 Geochemical Data Interpretation

In FY00 interpretation of geochemical data included the following:

- Geochemical and transport modeling of strontium and uranium to address the questions of ^{90}Sr and uranium distributions, the chemical forms of ^{90}Sr and uranium in groundwater, and transport of ^{90}Sr and uranium movement in groundwater
- Geochemistry and contaminant chemistry in TA-16 to further refine the TA-16 conceptual model and to verify the effectiveness of the remedial actions at the 260 outfall
- Environmental tracer simulations for the regional aquifer in the Española Basin

4.3.2.1 Geochemical and Transport Modeling of Strontium and Uranium

The groundwater pathway is one of the primary mechanisms for migration of solutes, including tritium, ^{90}Sr, uranium, and other metals in upper Los Alamos Canyon. Surface water infiltration

creates a saturated zone in the alluvium of this canyon within the Laboratory boundaries, which is longitudinally and seasonally varying in extent.

Uranium has been found in surface sediment, surface water, and alluvial and perched groundwater in upper Los Alamos Canyon. It is necessary to understand how this uranium will move through the environment. Geochemistry and transport models are discussed below. This information is used to guide future data collection efforts.

Geochemical and transport modeling of strontium (including natural strontium and strontium-90) and uranium in upper Los Alamos Canyon was completed in FY00. The computer programs MINTEQA2 (Allison et al., 1991) and PHREEQC2.2 (Parkhurst and Appelo, 1999) were used during this investigation. MINTEQA2 (combination of the computer programs MINeql (MINEQL) and waTEQuilibrium (WATEQ4)) was developed by Pacific Northwest National Laboratory for the EPA in 1985 and revised in 1999. PHREEQE (PH-REdox-EQuilibrium-Equations) was developed by the US Geological Survey in 1980 (Parkhurst et al., 1980) and has been significantly revised (PHREEQC) in 1995 (Parkhurst, 1995) and 1999 (PHREEQC2.2) (Parkhurst and Appelo, 1999). PHREEQC and PHREEQC2.2 are computer programs written in the C programming language that are designed to perform a wide variety of aqueous geochemical calculations. The model simulations were performed to evaluate aqueous speciation, mineral equilibrium, and adsorption reactions that influence the fate and transport of strontium and uranium in alluvial groundwater and perched groundwater within the Cerros del Rio basalt.

Geochemical modeling is conducted to help interpret observed trends in groundwater chemical data, and it is also useful in predicting future solute concentrations. Geochemical modeling is a viable tool for understanding and quantifying water-rock interactions occurring on a molecular scale (for example, adsorption and precipitation processes) as well as on watershed and regional flow scales. Evaluation and implementation of active and passive remediation (monitored natural attenuation) options are excellent applications of geochemical modeling. Geochemical modeling simulations should be coupled with hydrogeologic data to obtain the most relevant and meaningful results.

4.3.2.1.1 Geochemical Modeling of Strontium-90

Downgradient of TA-2, activities of ^{90}Sr have been elevated above background in alluvial groundwater for the past several decades (Figures 4.3.2-1 and 4.3.2-2). Analyses of most recent samples show activities of ^{90}Sr in alluvial groundwater range from 0.4 to 33.9 pCi/L (ESG, 1999) and are generally decreasing with time. Maximum activities of this radionuclide shift down-gradient to the east, illustrating migration of this contaminant plume. To date, ^{90}Sr has not been detected in perched zones within the Cerros del Rio basalt at R-9 or R-9I due to its ability to undergo cation exchange with solid organic carbon and specific adsorption onto hydrous ferric oxides.

Results of calculations using MINTEQA2 suggest that strontium is stable as Sr^{2+} in alluvial groundwater, and groundwater is undersaturated with respect to solid strontium sulfate and carbonate phases (Longmire et al., 1996a). Rather than precipitating as a stoichiometrically pure phase, Sr^{2+} probably undergoes cation exchange with solid organic matter and other amorphous and crystalline phases. This process partially removes ^{90}Sr from solution.

Sorption coefficient (Kd) values for strontium measured on Los Alamos Canyon soils range from 15.8 to 67.7 ml/g, with a mean value of 35.7 ml/g. In channel sediments from the Kd ranges from 8.8 to 41.3 ml/g with a mean value of 21.4 ml/g (Longmire et al., 1996a). This suggests that $^{90}Sr^{2+}$ is a non-conservative solute that is partially removed from solution through cation exchange and possibly through surface complexation (chemical binding of metals onto specific adsorption sites present on solid surfaces) onto hydrous ferric oxide (HFO). Distribution coefficients for strontium measured on the Bandelier Tuff range from 12.3 to 34.8 ml/g, depending on the amount of clay minerals present. The values were lower than those measured on surficial material due to smaller

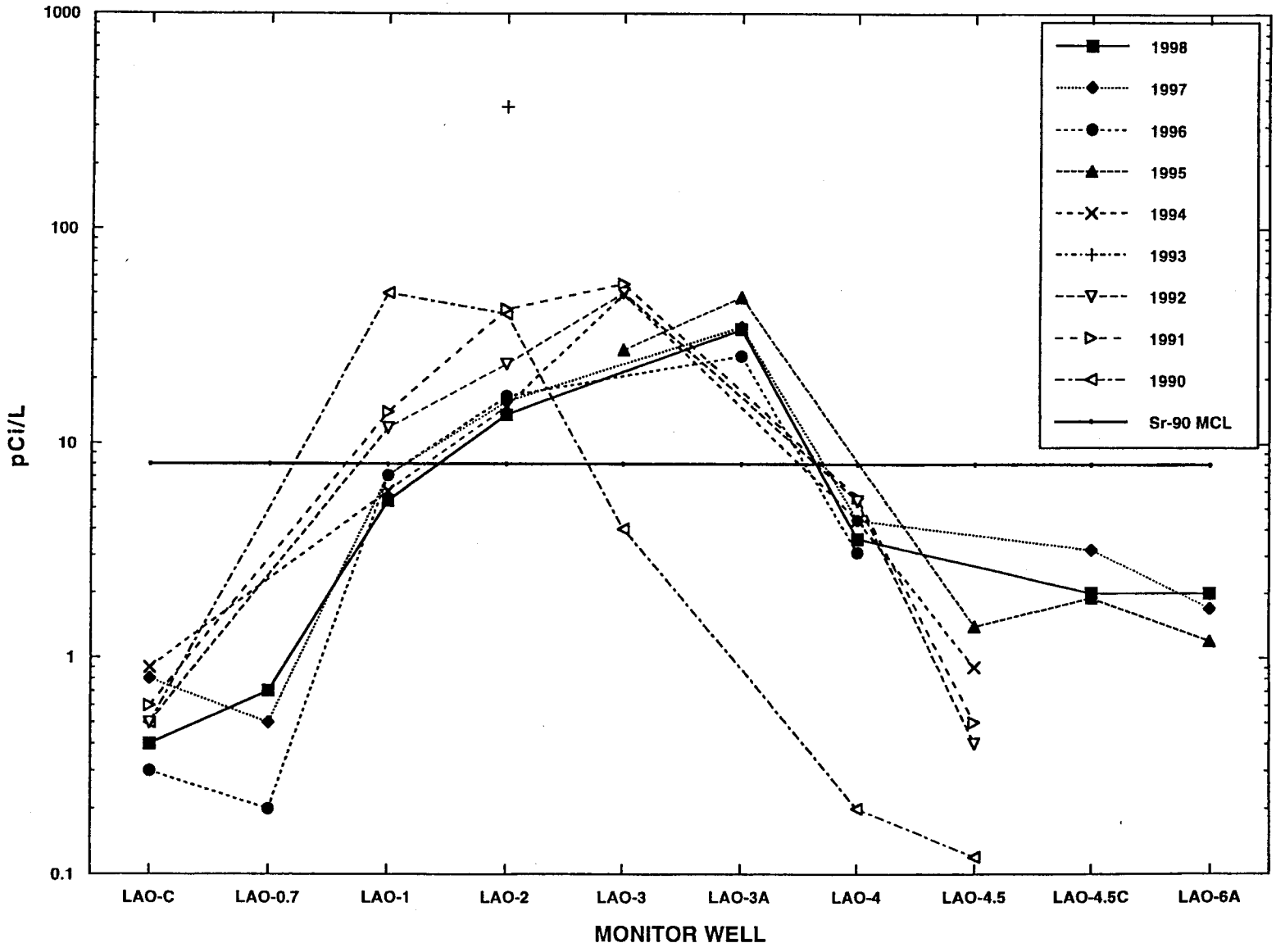

Figure 4.3.2-1 Distribution of strontium-90 in upper Los Alamos Canyon, 1990-1998 (source of data: ESH-18).

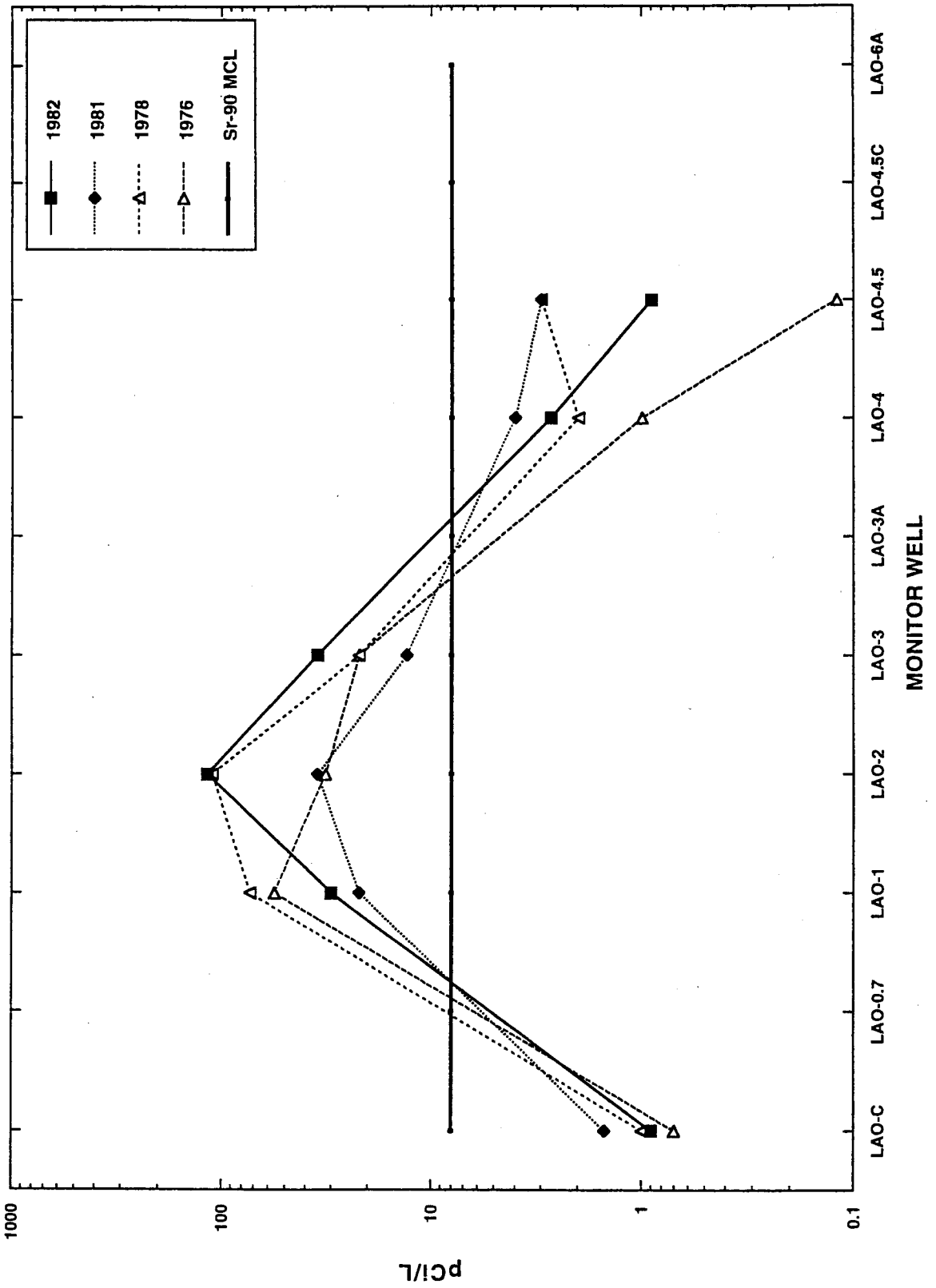

Figure 4.3.2-2 Distribution of strontium-90 in upper Los Alamos Canyon, 1976-1982 (source of data: ESH-18).

amounts of solid organic carbon. Because the Kd values for strontium vary for the soils and sediments, different Kd values, rather than one single value, should be used in transport calculations for alluvial groundwater.

HFO has been investigated over the past several decades for its adsorption capacity for a wide range of inorganic and organic adsorbates, including uranium and other actinides (Dzombak and Morel, 1990; Langmuir, 1997; Hsi and Langmuir, 1985, Longmire et al., 1996b; Stumm and Morgan, 1996; Waite et al., 1994). The diffuse layer model (DLM) considers solution speciation and aqueous ion activities. The DLM is more rigorous than the Kd model because it includes sorbent (solid material) properties (surface area and concentration), sorbate (solute) concentration, and groundwater composition (pH and solute concentration). The DLM model uses the electric double-layer (EDL) theory that assumes that the positive or negative surface charge of a sorbent, in this case HFO, in contact with solution generates an electrostatic potential that declines rapidly away from the adsorbent surface (Langmuir, 1997). The potential is the same at the zero (adsorbent surface) and d (solution) planes.

HFO and hematite (Fe_2O_3) are stable under oxidizing conditions characteristic of alluvial and perched groundwater zones in upper Los Alamos Canyon and provide active sorption sites for uranium and possibly ^{90}Sr. Smectite, kaolinite, and solid organic matter provide additional active surface sites for cation exchange of $^{90}Sr^{2+}$ with other divalent metals.

Results of adsorption modeling using the DLM with HFO contained in MINTEQA2 suggest that strontium, as Sr^{2+}, is partially removed from solution with increasing pH (Figure 4.3.2-3). For this simulation, pH values vary from 6.35 to 7.85 in model input, which are typical for alluvial groundwater in upper Los Alamos Canyon. Analytical results of filtered groundwater samples collected from LAO-0.91 were used as input for this simulation. LAO-0.91 is immediately south of the former leach field (SWMU 2-009) within TA-2 and contains ^{90}Sr, ^{137}Cs, and other fission products below the alluvial water table. The concentration of HFO is assumed to be 1.46 g/L for this simulation. Total dissolved strontium (0.14 ppm) was used as input for the adsorption simulation, which includes activity of ^{90}Sr. In 1994, the activity of ^{90}Sr at LAOR-1, immediately north of LAO-0.91, was 20.8 pCi/L (ESG, 1995), which is equivalent to$1.7 \times 10^{-14.5}$ M (1.5×10^{-10} mg/L) strontium.

The adsorption edge plot for non-radiogenic strontium shown in Figure 4.3.2-3 parallels the increasing number of negative charged surface sites on HFO. Approximately 62% (0.09 ppm) of the strontium is removed from solution in the absence of competing ions such as Ca^{2+}. Calcium effectively competes with strontium for adsorption sites resulting in decreasing adsorption of strontium (17%, 0.02 ppm adsorbed). This competing ion effect increases with increasing pH.

Distribution coefficients for strontium, based on the DLM, were calculated using MINTEQA2 as a function of pH (Figure 4.3.2-4). A calculated Kd is then determined from model output by the following expression (Langmuir, 1997):

$$Kd(ml/g) = \frac{(\text{moles adsorbed/kg } H_2O\ (m))(10^{03}\ mg/g)}{(\text{moles dissolved/kg } H_2O\ (m))\ (\text{conc. of adsorbent } (mg/ml))}$$

Between pH values of 6.35 and 7.85, calculated Kd values for strontium range from 2.3 to 1056 ml/g in the absence of Ca^{2+}, whereas the maximum Kd value decreases to 61 ml/g in the presence of Ca^{2+} (19.3 mg/L). These calculated Kd values suggest that strontium, including $^{90}Sr^{2+}$, strongly adsorbs onto HFO in the absence of calcium using the DLM, and the values are much higher than those measured on soil and channel sediments described above. The calculated Kd values for strontium, however, are consistent with the experimental results when Ca^{2+} is present as a competing adsorbate. Measured Kd values provide a more conservative estimate on the adsorption of $^{90}Sr^{2+}$, and these values are recommended for input to transport calculations.

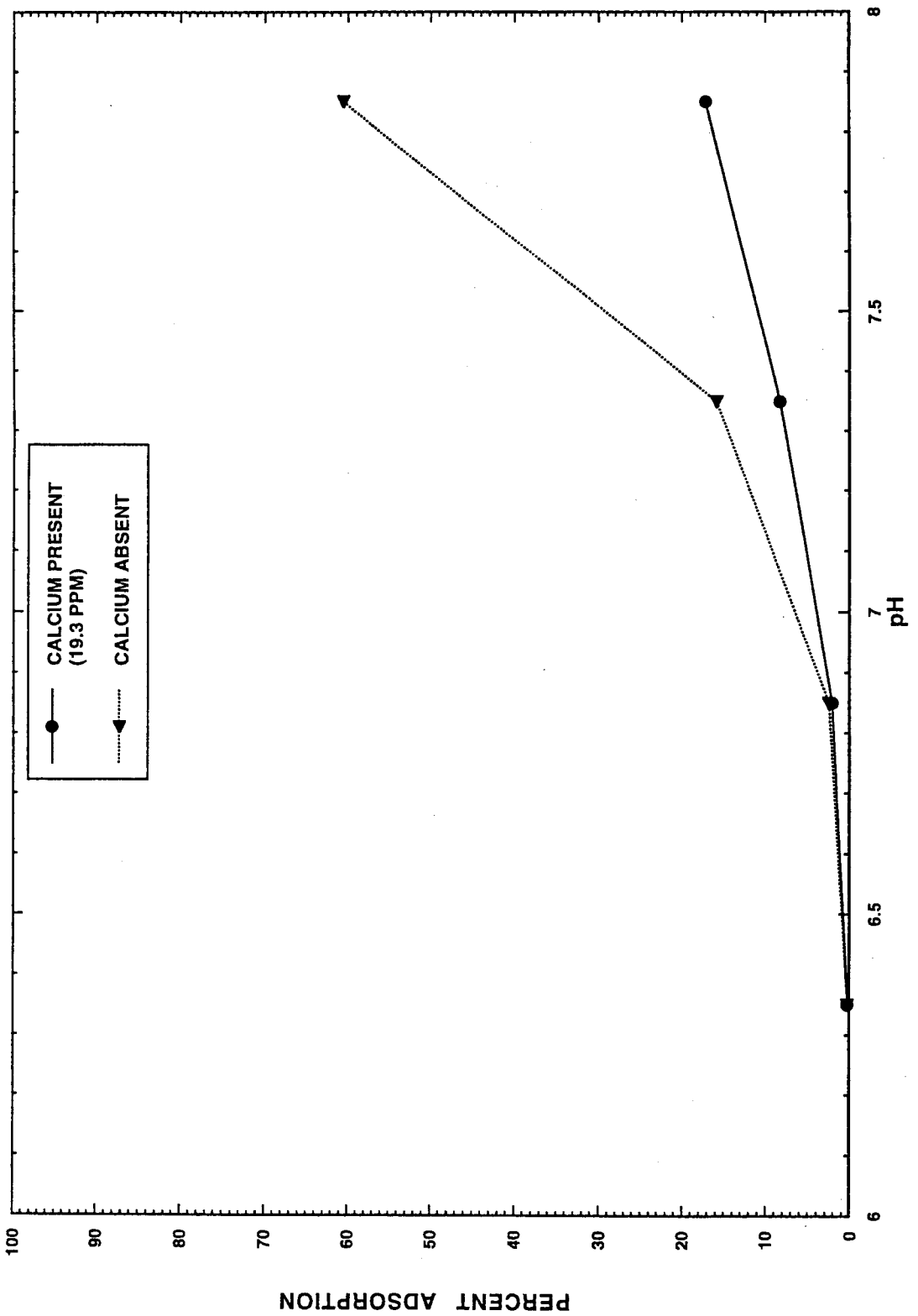

Figure 4.3.2-3 Percent of adsorption of strontium onto hydrous ferric oxide (1.46 g/L) in the presence and absence of calcium at LAO-0.91 calculated by MINTEQA2 (total dissolved strontium = 0.14 ppm, 25C).

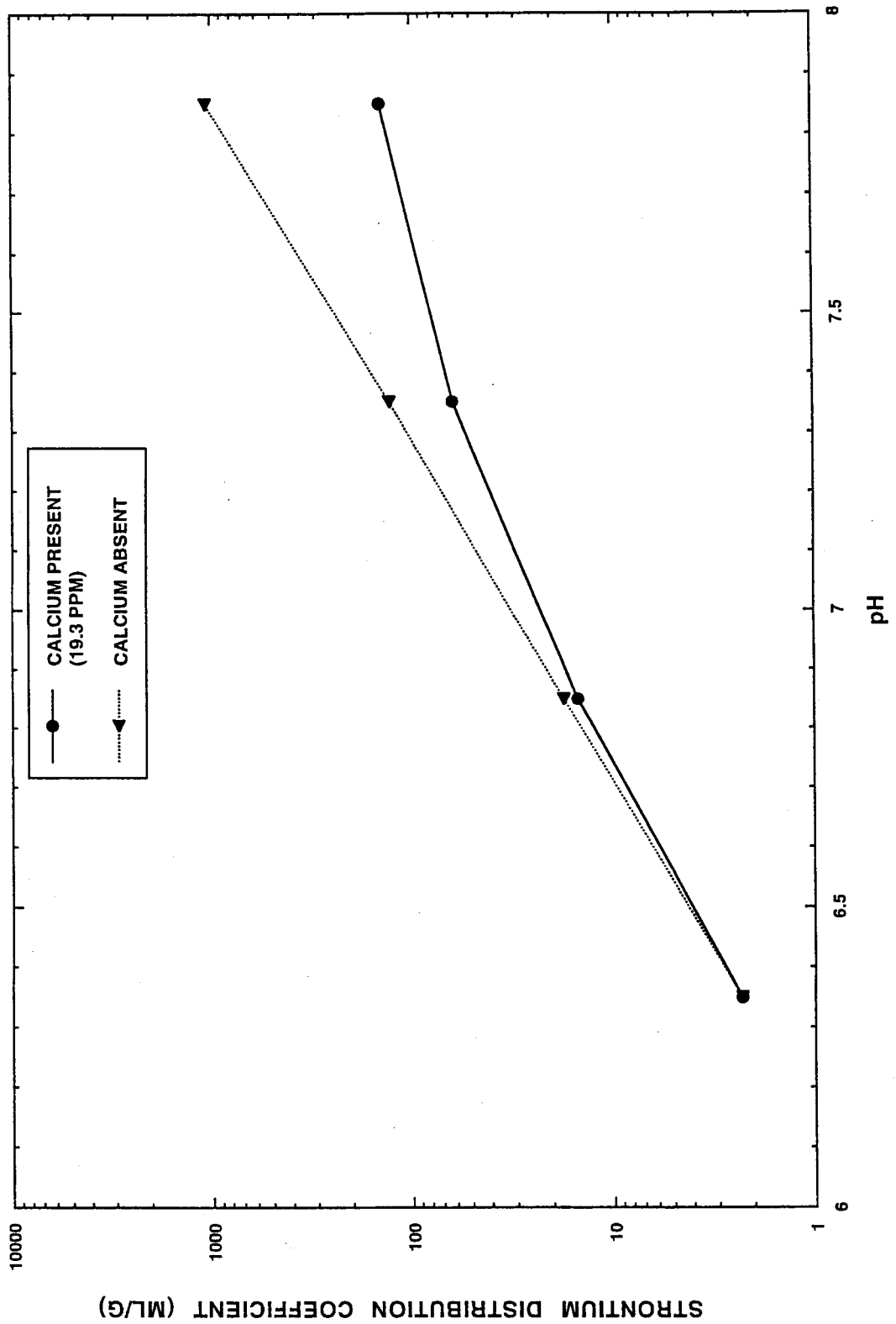

Figure 4.3.2-4 Calculated distribution coefficients for strontium adsorption onto hydrous ferric oxide (1.46 g/L) (MINTEQA2) in the presence and absence of calcium at LAO-091 (total dissolved strontium = 0.14 ppm, 25 C).

4.3.2.1.2 Geochemical Modeling of Uranium

Downgradient of TA-2, concentrations of uranium have been elevated above background in alluvial groundwater for the past several decades (ESG reports). Recently, within alluvial groundwater and surface water, uranium concentrations are typically less than 20 µg/L, the maximum contaminant level (MCL) for this constituent. Under oxidizing conditions typical of alluvial and perched groundwater within upper Los Alamos Canyon, dissolved and adsorbed uranium are stable in the +6 oxidation state. Dissolved uranium (VI) species stable as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_4)_3^{4-}$ are semisorbing under circum-neutral pH conditions (Langmuir, 1997).

Alluvial groundwater is predicted to be undersaturated with respect to uranium (VI) phases including schoepite ($UO_2(OH)_2$), uranophane ($Ca(UO_2)2(SiO_3OH)_2$, autunite ($Ca(UO_2)_2(PO_4)_2$) , rutherfordine (UO_2CO_3), haiweeite ($Ca(UO_2)_2(Si_2O_5)3.5H_2O$), weeksite ($Na_2(UO_2)_2(Si_2O_5)3.4H_2O$), and soddyite ($(UO_2)_2SiO_4.2H_2O$). Adsorption processes are inferred to dominate for partially removing uranium from solution in alluvial groundwater.

Elevated concentrations of dissolved uranium (48.4 µg/L) were observed in the lower perched zone (275 ft-depth) within the Cerros del Rio basalt during drilling of R-9 (Broxton et al., 2000). This borehole groundwater is characterized by a sodium-bicarbonate composition and has a pH of 8.8, conducive to the formation of uranyl carbonato complexes.

The lower perched zone at R-9 (275 ft) has a pH value of 8.8 and is characterized by a sodium (4.35 mM, 100 mg/L) and bicarbonate (1.73 mM, 105 mg/L) ionic composition (Broxton et al., 2000). This groundwater is considered to be relatively oxidizing based on presence of HFO, nitrate, sulfate, uranium (VI) and absence of reducing agents (electron donors) such as hydrogen sulfide, DOC, and methane. Total uranium concentrations (suspended and dissolved fractions) are 112 µg/L (112 ppb) in this perched zone (Broxton et al., 2000). Dissolved uranium concentrations are 48.4 µg/L, whereas concentrations of suspended (adsorbed) uranium are 63.6 ppb. Under oxidizing conditions, uranyl forms strong (soluble) complexes with bicarbonate and carbonate under alkaline pH conditions (Langmuir, 1997).

For the lower perched zone in R-9, a calculated Kd for uranium is given by:

$$Kd = 0.0636\ (mg/kg)/0.0484\ (mg/L) = 1.31\ L/kg \text{ or } 1.31\ ml/g.$$

This low Kd value implies that dissolved uranium (mainly as the uranyl tricarbonato complex) is mobile under alkaline and oxidizing conditions characteristic of the lower perched zone at R-9. The Kd value is consistent with the elevated dissolved uranium measured in the lower perched zone and with experimental results of uranium adsorption onto the Bandelier Tuff reported by Longmire et al. (1996b).

Fracture flow dominates within the Cerros del Rio basalt, providing conduits for recharge to the upper and lower perched zones. Results of the adsorption modeling simulation, using the DLM, suggest that in the lower perched zone 57.5 % of uranyl (64 ppb sorbed uranium) is bound as a surface complex, $\equiv SO2UO_2^+$, where ≡SO2 represents a weak sorption surface site (number 2) on HFO. Dissolved (non sorbed) uranium is predicted to occur both as $UO_2(CO_3)_2^{2-}$ at 5.1% (7 µg/L) and as $UO_2(CO_3)_3^{4-}$ at 36.6% (41 µg/L). The model simulation predicts 48 µg/L of dissolved uranium at a pH value of 9.0. This is in excellent agreement with the measured dissolved uranium (48.4 µg/L) at a pH of 8.8.

Uranyl complexation with bicarbonate and carbonate in the lower perched zone of R-9 decreases the amount of adsorption by 41.7 %, which results in uranium concentrations exceeding the proposed EPA MCL of 20 µg/L. The same computation was performed with PHREEQC2.2, which produced a very similar result, illustrating compatibility between the two computer codes and model verification.

Adsorption of UO_2^{2+} (as Hfo_wOUO_2^{1+}) onto HFO under varying pH conditions (4.0-9.5) is shown in Figure 4.3.2-5. Concentrations of uranyl and HFO are 0.054 ppm and 1.46 g/L, respectively, which are representative of conditions in the lower perched zone of R-9. Increasing adsorption of UO_2^{2+} occurs between pH 4.0 and 5.5 in which the complex UO_2F^+ is predicted to dominate in solution. Maximum adsorption of UO_2^{2+} onto weak sites (Hfo_wOUO_2^{1+}) is predicted to occur between pH 5.5 and 6.0 corresponding to minimum concentrations of poorly sorbing and soluble uranyl dicarbonato and uranyl tricarbonato complexes. At a pH of 8.8 characteristic of the lower perched zone at R-9, Hfo_wOUO_2^{1+} decreases in concentration as the uranyl tricarbonato complex dominates.

A calculated Kd for uranium, based on surface complexation (DLM), concentration of HFO (1.46 mg/ml, based on nitric acid digestion of a non-filtered water sample), and molalities of adsorbed and dissolved uranium, for this zone at pH9.0 is given by the following expression:

$$Kd_{sc} = \frac{(2.71 \times 10^{-07}\ m)(10^{03}\ mg/g)}{(2.00 \times 10^{-07}\ m)(1.46\ mg/ml)} = 928\ ml/g$$

This value is much higher than the Kd calculated from suspended and dissolved uranium fractions (1.3 ml/g) discussed above. This calculation possibly invokes colloidal transport of uranium with HFO as the adsorbent because uranium should not be mobile at such a high Kd value. Further investigation of colloid transport is warranted at the Laboratory based on water quality data, specifically radiochemical results (^{90}Sr, ^{241}Am, ^{238}Pu, and $^{239,240}Pu$) for non-filtered samples, reported by the ER Project and ESH Division.

Figure 4.3.2-6 shows calculated Kd values for uranium based on the DLM under varying pH conditions (4.0-9.5). A maximum value (48,230 ml/g) is reached at a pH of 6.0, which corresponds to minimum concentration of uranyl dicarbonato and tricarbonato complexes. At higher pH values, Kd values decrease as a consequence of the stability of these soluble complexes.

4.3.2.1.3 Reactive Transport Modeling of Uranium

One dimensional (D) transport of uranium (VI) at R-9 was simulated using PHREEQC2.2 (Parkhurst and Appelo, 1999), which included surface complexation reactions involving uranium under open PCO_2 conditions ($10^{-3.76}$ bar). The advective-dispersive transport capabilities of PHREEQC2.2, based on an explicit finite difference algorithm, are derived from a formulation of one D, advective-dispersive transport presented by Appelo and Postma (1993). A single cell or a series of cells, each of which has the same pore volume, represents the one-D column. Length(s) of cell(s) are defined and a time step provides the time necessary for a pore volume to migrate through each cell. The length of the cell divided by the time step determines the velocity of water in each cell. For these simulations, a column consisting of one cell is modeled and 20 pore volumes of filling solution, consisting of DP Canyon surface water-alluvial groundwater, are moved through the column. The length of the column is 84 m, which represents the thickness of the Cerros del Rio basalt above the lower perched zone at R-9.

The time step was determined by the length of column (84 m), rate of recharge (m/yr), and assumed fracture porosity (unitless) using the following expression to estimate the time step:

$$\text{time step (sec)} = ((\text{length (m)}/\text{recharge rate (m/yr)})(\text{porosity})(3.16 \times 10^{7}\ \text{sec/yr})$$

$$\text{time step (sec)} = ((84\ \text{m})/(0.2\ \text{m/yr}))(0.01)(3.16 \times 10^{7}\ \text{sec/yr})$$

$$\text{time step (sec)} = 1.33 \times 10^{08}$$

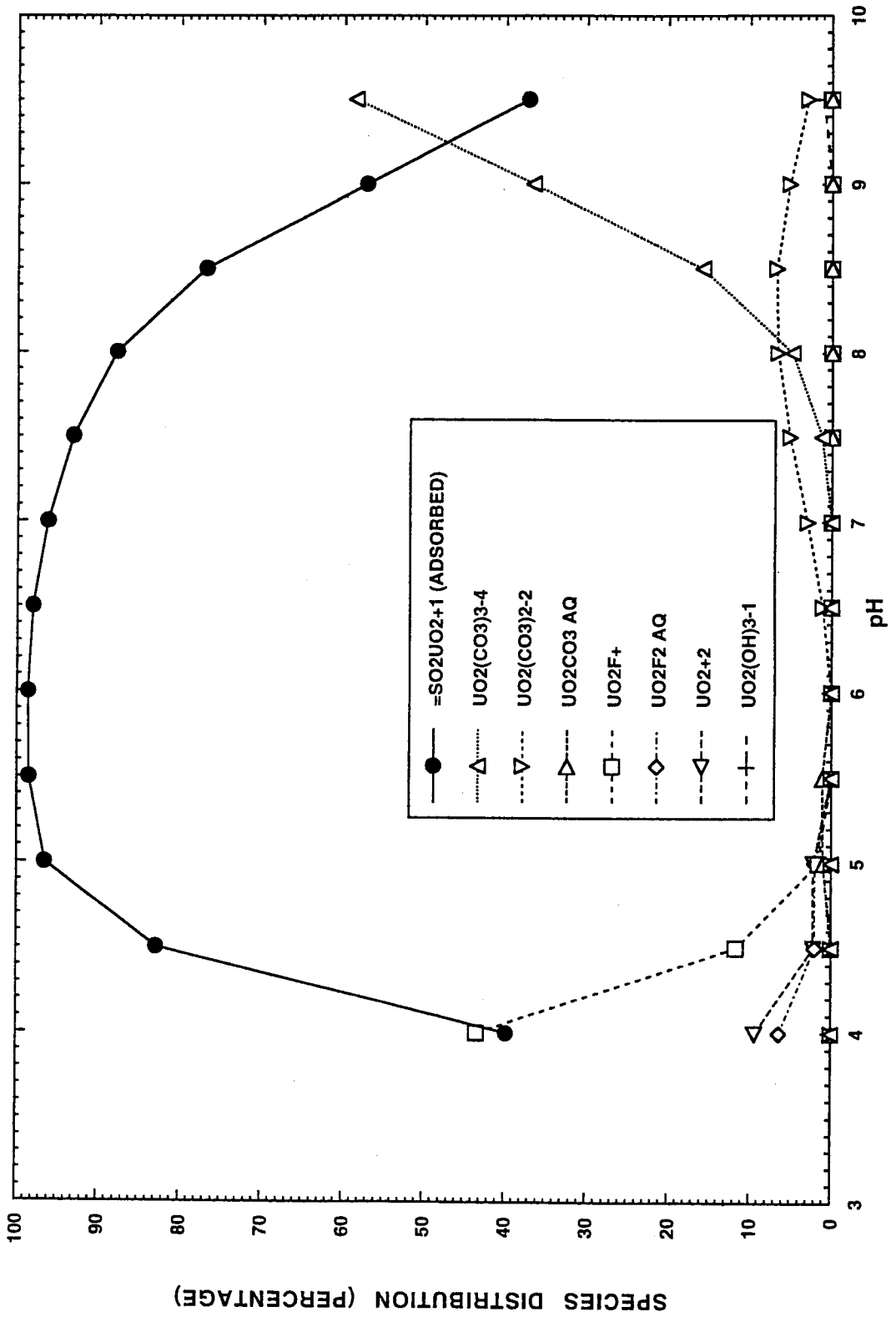

Figure 4.3.2-5 Calculated distributions of adsorbed and dissolved uranyl species for R-9 (275 ft zone) (hydrous ferric oxide = 1.46 grams per liter and total dissolved uranyl = 0.054 ppm, 25 C).

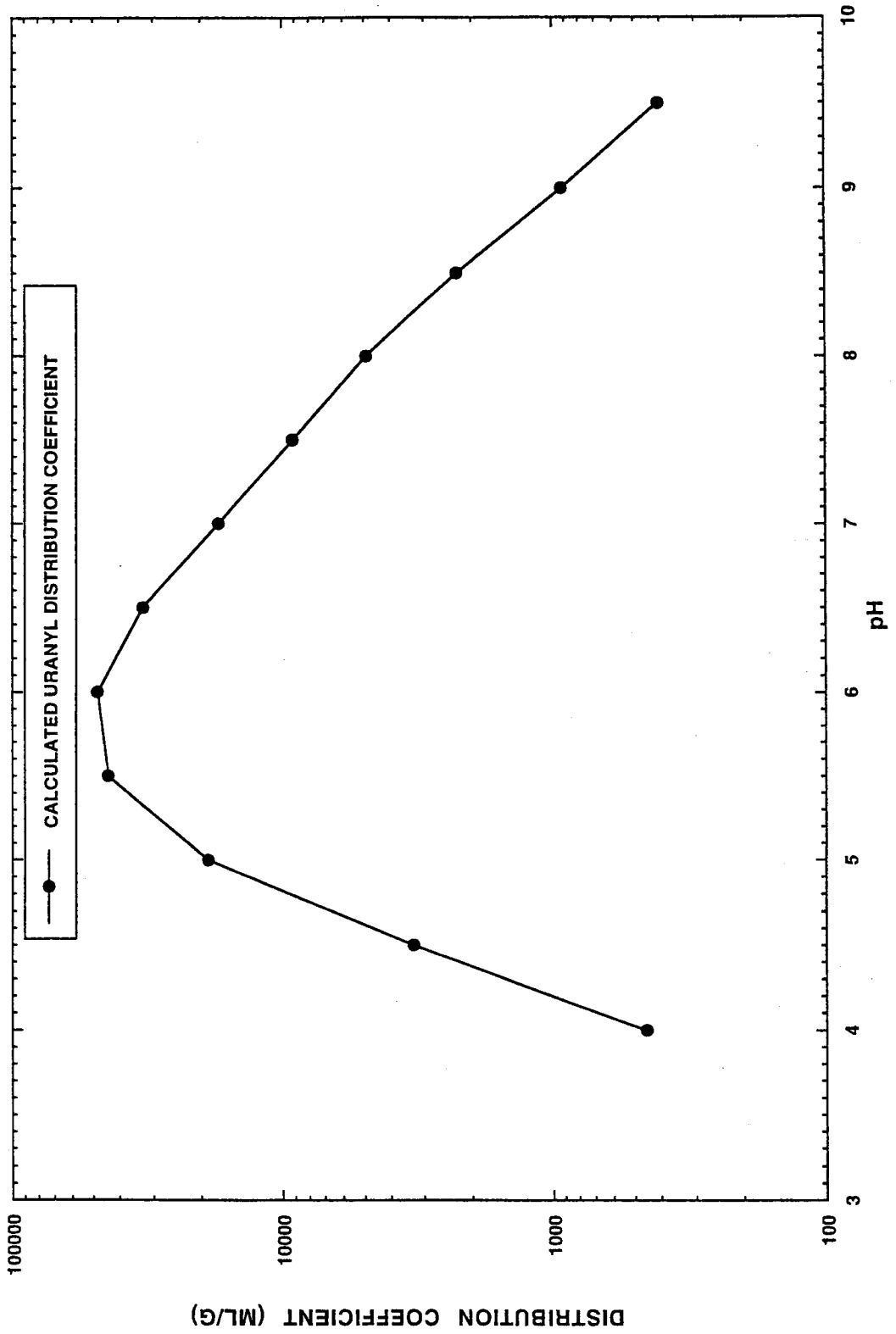

Figure 4.3.2-6 Calculated distribution coefficients for uranyl adsorption onto hydrous ferric oxide (1.46 g/L) in the presence of calcium (2.91 ppm) at borehole R-9 (275 ft zone) (total dissolved uranyl = 0.054 ppm, 25 C).

Modeling parameters used in the one-D transport simulations are provided in Table 4.3.2-1.

Table 4.3.2-1 Model Input Parameters for One Dimensional Transport Simulations for R-9

Simulation No.	1	2	3
Recharge (m/yr)	0.2	0.2	0.2
Pore Volumes	20	20	20
Column Length (m)	84	84	84
Fracture Porosity	0.01	0.01	0.01
Time Step (sec)	1.33e08	1.33e08	1.33e08
Velocity (m/sec)	6.41e-07	6.41e-07	8.41e-07
Total Time (yr)	84.0	84.0	84.0
Dispersivity (m^2/sec)	0.1	0	0.1
Boundary Condition	flux (Cauchy)	not applicable	Constant (Dirichlet)
pe	4.0	4.0	4.0

Rates of recharge in upper Los Alamos Canyon vary from 0.2 to 0.4 m/yr (Gray, 1997). A recharge rate of 0.2 m/yr was selected for the model simulations, which provides a longer time step to account for adsorption. Fracture flow dominates in the Cerros del Rio basalt, based on examination of basalt outcrops and visual descriptions of core collected at R-9 (Broxton et al., 2000). An estimated fracture porosity of 0.01 was used in the simulations. Longitudinal dispersion and advection were included in the model simulations, and an estimate of the former parameter is 0.1 m^2/sec. Flux boundary conditions were selected to include longitudinal dispersivity for simulation 1:

$$C(x_{end}, t) = C_0 + \frac{D_L}{v}\frac{\partial C(x_{end}, t)}{\partial x}$$

Where,

$C(x_{end}, t)$ is concentration of the solute in the bottom of the column as a function of time (molal/sec),
C_0 is initial concentration (molal),
D_L is longitudinal (hydrodynamic) dispersion coefficient (m^2/sec),
v is pore water velocity (m/sec), and
x is distance (m).

This boundary condition is appropriate for laboratory columns with inlet tubing much smaller than the column cross section. This expression may apply to field situations where fracture apertures are much smaller than the matrix cross section.

Groundwater chemistry of Spring 9B was used as a proxy of native groundwater within the lower perched zone at R-9 prior to recent recharge (60 years) from the alluvial aquifer containing Laboratory effluents (Table 4.3.2-2). This spring discharges from the Cerros del Rio basalt and represents the native groundwater chemistry available for the basalt. Uranium concentrations from the spring are less than 1 µg/L and the spring has tritium activities less than 1pCi/L, suggesting that the groundwater is older than 60 years. Concentration of major anions including chloride, nitrate, and sulfate, is less than 3 mg/L at Spring 9B. The pe ($-\log_{10}$activity of electron) of the solution is set at a default value of 4.0, which is consistent with the overall oxidizing conditions of the perched groundwater.

Monitoring well LAO-2 within DP Canyon contains native alluvial groundwater that is recharged by surface water containing Laboratory effluents such as ^{90}Sr and uranium. Analytical results for LAO-2 are provided in Table 4.3.2-2. Previous sampling records for DP Canyon surface water are incomplete; therefore, analytical results for recent sampling of LAO-2 (filtered) are used as a proxy for surface water infiltrating the Cerros del Rio basalt at R-9. This aqueous solution is used as influent (filling solution) for the column simulations. The average concentration of uranium in DP Canyon surface water (DPS-1) is 82.7 μg/L from 1969 through 1997, and this value is used as input for the simulations.

Table 4.3.2-2 Quality of Screening Groundwater Samples Collected at Spring 9B and Alluvial Monitor Well LAO-2[1]

Location	Spring 9B	LAO-2
Geologic Unit	CR basalt[2]	Alluvium
Sample Treatment	Filtered	Filtered
Date Sampled	01/07/00	06/07/94
Al	0.003 ± 0.001	0.14 ± 0.02
Ca	9.82 ± 0.02	20.3 ± 0.5
Cl	1.95	58.3
CO_3	0	0
F	0.44	0.76
Fe	0.02 ± 0.01	0.02 ± 0.01
HCO_3	66.0	77.5
K	1.50 ± 0.03	7.90 ± 0.02
Mg	2.83 ± 0.02	4.69 ± 0.12
Mn	<0.001	<0.01
Na	10.3 ± 0.1	37.6 ± 0.2
NH_4	<0.02	0.09
NO_3 (as NO_3)	0.99	0.18
PO_4	<0.02	0.28
pH (standard unit)	8.54	6.98
SiO_2	76.8	52.2
Sr	0.047	0.16
SO_4	1.95	13.0
U	0.00056	0.083
TDS	172.8	274.8
Conductance(μS/cm) (μS/cm)	145	364
Balance (%)	+1.05	+0.47

1. Units in ppm except as noted.
2. Cerros del Rio basalt.

A sensitivity analysis was performed by using different uranium concentrations for LAO-2 (10, 20, 30, 40, and 60 μg/L) to evaluate the amount of uranium within the infilling solution (influent) required to simulate observed uranium concentrations in the lower perched zone of R-9 (Table 4.3.2-3). Uranium concentrations less than 83 μg/L were insufficient to reproduce both suspended (adsorbed) and dissolved uranium concentrations observed in borehole R-9. Adsorbed uranium was overestimated while dissolved uranium was underestimated for the consecutive passing of each pore volume. The pe ($-\log_{10}$activity of electron) of the solution is set at a default value of 4.0, which is consistent with the overall oxidizing conditions of the surface water/alluvial groundwater, prior to the fire.

Table 4.3.2-3 Variation of Model Input Parameters, including Initial, Dissolved, and Adsorbed Uranium Concentrations, for One Dimensional Transport Simulations for R-9

Initial Uranium (μg/L)	10	20	30	40	60
Pore Volume 1 (M)	2.62e-08	5.24e-08	7.86e-08	1.05e-07	1.57e-07
Pore Volume 5 (M)	2.33e-08	4.67e-08	7.00e-07	9.34e-08	1.40e-07
Pore Volume 10 (M)	3.09e-08	6.18e-08	9.28e-08	1.24e-07	1.85e-07
Pore Volume 15 (M)	3.65e-08	7.31e-08	1.10e-07	1.46e-07	2.19e-07
Pore Volume 20 (M)	3.95e-08	7.89e-08	1,18e-07	1.58e-07	2.37e-07
Adsorbed Uranium (M)					
Pore Volume 1	1.58e-08	3.17e-08	4.75e-08	6.34e-08	9.50e-08
Pore Volume 5	9.39e-08	1.88e-07	2.82e-07	3.76e-07	5.64e-07
Pore Volume 10	1.64e-07	3.29e-07	4.93e-07	6.58e-07	9.86e-07
Pore Volume 15	2.01e-07	4.03e-07	6.04e-07	8.06e-07	1.21e-06
Pore Volume 20	2.19e-07	4.37e-07	6.56e-07	8.75e-07	1.31e-06

Surface complexation using the DLM was incorporated in the model simulations to quantify adsorption of UO_2^{2+} onto HFO at a measured concentration of 1.46 g/L. The reactive phase HFO occurs as coatings on fracture fill material within the Cerros del Rio basalt at R-9. Thermodynamic data (Log K association) for surface complexation of UO_2^{2+}, based on the DLM, for strong sites (Log K_1^{int} = 5.2) (Hfo_sOHUO_2^{2+}) and weak sites (Log K_2^{int} = 2.8) (Hfo_wOUO_2^{1+}) were reported by Langmuir (1997). Weak adsorption sites (0.003 mol active site HFO/L) present on HFO are more abundant than the strong sites (8.2e-05 mol active site HFO/L). Adsorption of UO_2^{2+} onto the strong sites is predicted to occur at much lower molalities than the weak sites and are not listed in this report. Total uranium concentrations, consisting of suspended (adsorbed) and dissolved fractions, are calculated during the passing of each pore volume of the filling solution (LAO-2).

Figure 4.3.2-7 shows the number of pore volumes versus calculated uranium concentrations with model constraints for simulation number 1 provided in Table 4.3.2-1. The zero pore volume represents the initial solution within the simulated column containing 0.56 μg/L (ppb) dissolved uranium at a pH value of 8.90. The amount of uranium predicted to adsorb onto the weak surface sites (Hfo_wOUO_2^{1+}) is 0.011 ppb. Dissolved uranium concentrations are predicted to increase to 51.6 ppb when the first pore volume of infilling solution (LAO-2) reacts with the initial solution and partial adsorption of UO_2^{2+} onto HFO takes place. At this pore volume, 28.4 ppb uranium are predicted to adsorb onto HFO at a pH of 8.60. Within the second pore volume, dissolved uranium concentrations are predicted to slightly decrease to 45.8 ppb, and 60 ppb uranium are predicted to adsorb onto HFO at a calculated pH of 8.55. These results most closely match measured concentrations of dissolved and suspended uranium within the lower perched zone at R-9, which are 48.4 μg/L and 63.6 ppb, respectively.

Continued passing of infilling solution results in slightly decreasing concentrations of dissolved uranium (pore volumes 3 and 4) followed by an increase in solute concentrations for the remaining pore volumes (Figure 4.3.2-7). Concentrations of adsorbed uranium are predicted to increase with each successive passing of infilling solution. Results of this model simulation suggest that within the second time step of 2.62 x 10^8 seconds (8.3 years), uranium predominately in the form of $UO_2(CO_3)_3^{4-}$ has migrated 84 m under fracture flow conditions to approximate uranium concentrations currently observed at R-9.

Figure 4.3.2-8 shows the number of pore volumes versus calculated uranium concentrations for advective flow (no dispersion). The first pore volume represents the mixed solution (initial and infilling) in the simulated column containing 70.0 μg/L (ppb) dissolved uranium at a pH value of 8.67. The amount of uranium predicted to adsorb onto the weak surface sites (Hfo_wOUO_2^{1+}) is

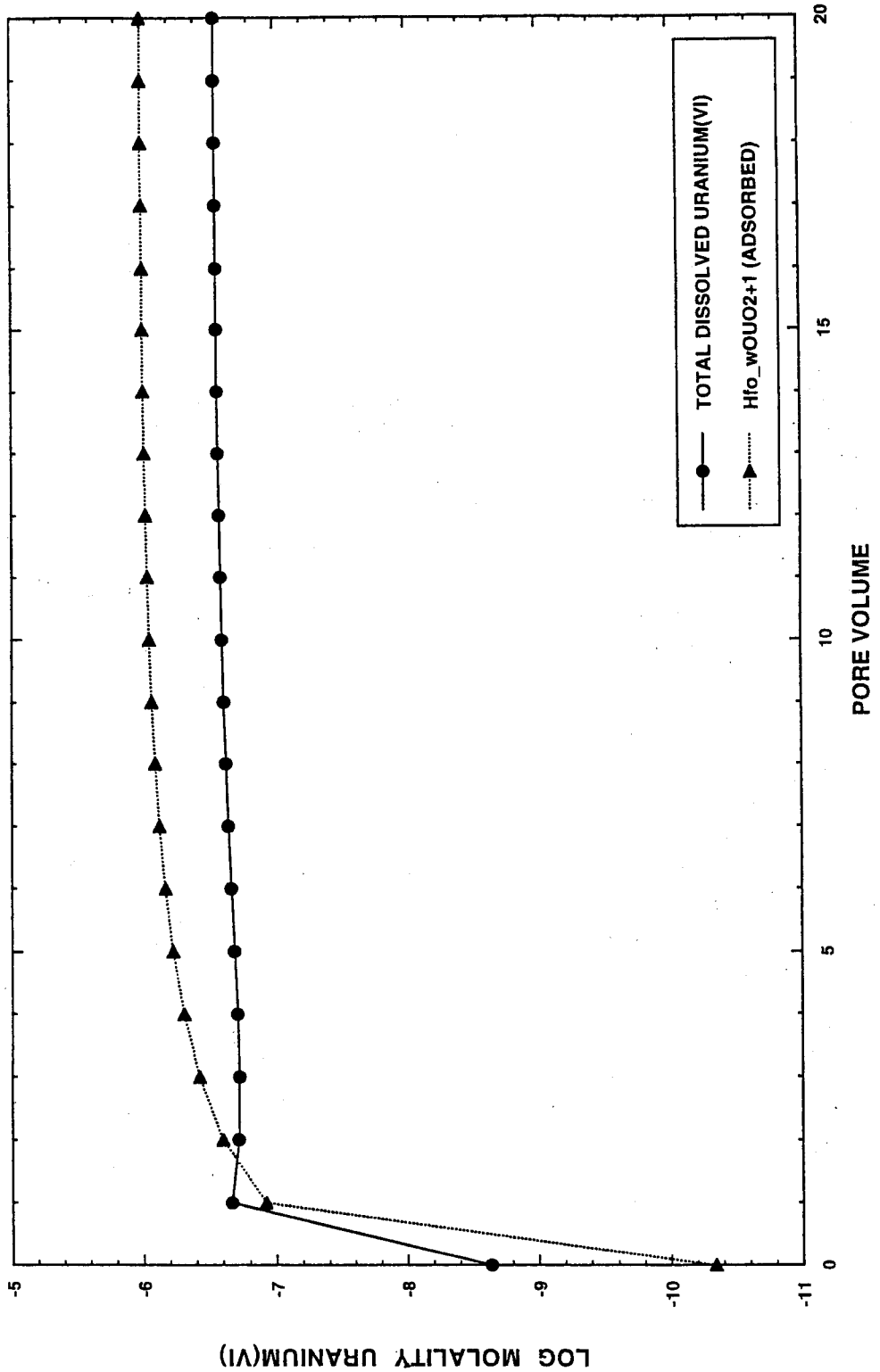

Figure 4.3.2-7 Results of transport modeling using PHREEQC2.2 to simulate adsorption of the uranyl cation onto hydrous ferric oxide (Hfo) (1.46 g/L). (Dispersivity = 0.10 m2/sec, time step = 1.33e08 seconds, recharge rate = 0.2 m/yr, and fracture porosity is estimated at 0.01).

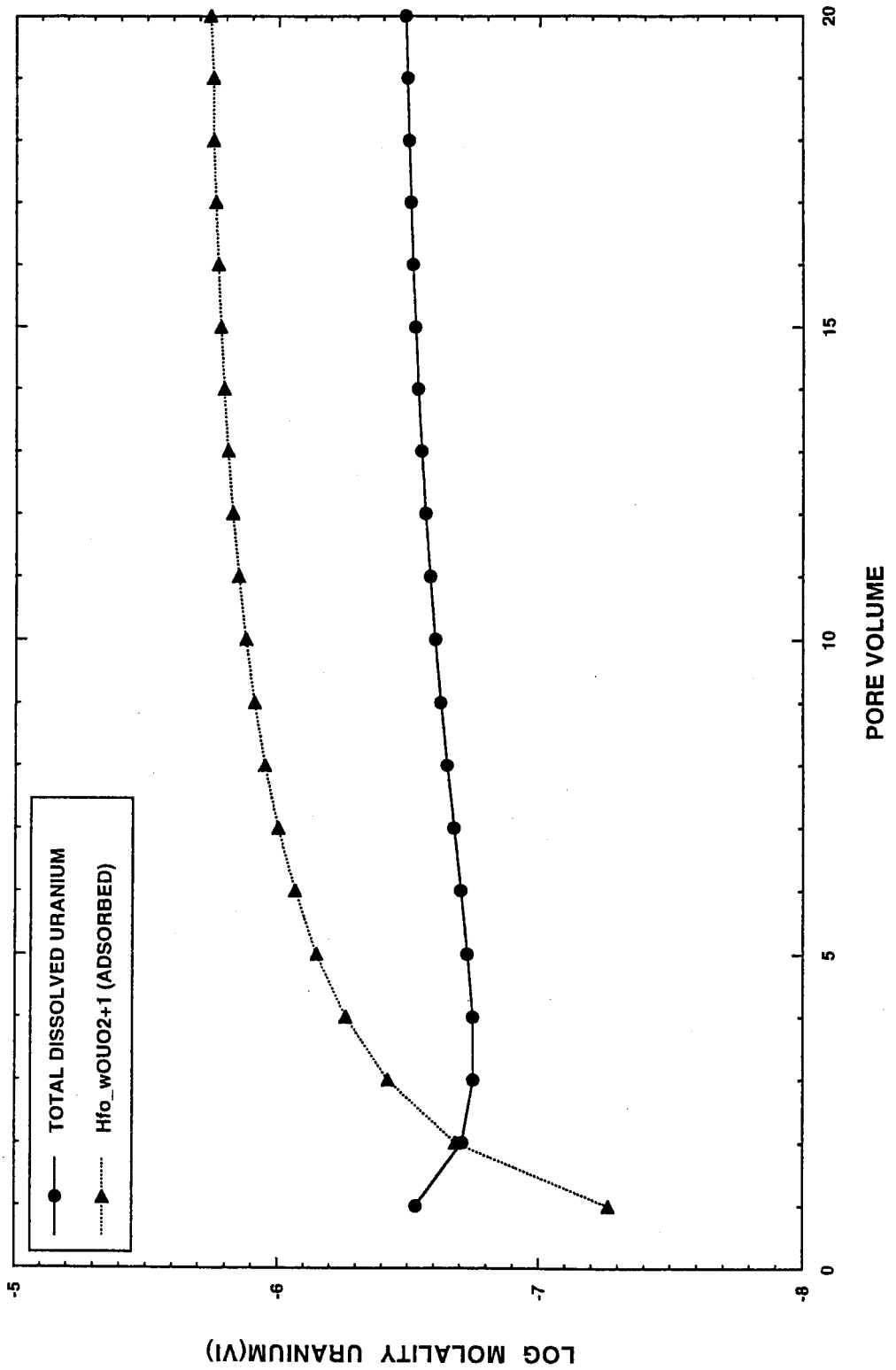

Figure 4.3.2-8 Results of advective transport modeling using PHREEQC2.2 to simulate adsorption of the uranyl cation onto hydrous ferric oxide (Hfo) (1.46 g/L). (Time step = 1.33e08 seconds, recharge rate = 0.2 m/yr, and fracture porosity is estimated at 0.01).

13 ppb. Dissolved uranium concentrations are predicted to decrease to 46.6 ppb when the second pore volume of infilling solution (LAO-2) reacts with the initial solution and continued adsorption of UO_2^{2+} onto HFO takes place. At this pore volume, 49.4 ppb uranium is predicted to adsorb onto HFO at a calculated pH of 8.55. Within the third pore volume, dissolved uranium concentrations are predicted to further decrease to 42.4 ppb, and 90.0 ppb uranium is predicted to adsorb onto HFO at a calculated pH value of 8.51. These results do not closely match measured concentrations of dissolved and suspended uranium in the lower perched zone at R-9.

Continued passing of infilling solution results in increasing concentrations of dissolved uranium (pore volumes 4 through 20) followed by an increase in solute concentrations for the remaining pore volumes (Figure 4.3.2-8). The amount of adsorbed uranium is predicted to increase with each successive passing of infilling solution. Model simulations that include dispersion produce a better match between observed and calculated concentrations of dissolved and suspended uranium.

Figure 4.3.2-9 shows the number of pore volumes versus calculated uranium concentrations with model constraints for simulation number 3. This simulation uses the constant (Dirichlet) boundary condition represented by the following expression:

$$C(x_{end}, t) = C_0.$$

The zero pore volume represents the initial solution within the simulated column containing 0.56 μg/L (ppb) dissolved uranium at a pH value of 8.90. The amount of uranium predicted to adsorb onto the weak surface sites ($Hfo_wOUO_2^{1+}$) is 0.011 ppb. Dissolved uranium concentrations are predicted to increase to 51.7 ppb when the first pore volume of infilling solution (LAO-2) reacts with the initial solution and partial adsorption of UO_2^{2+} onto HFO takes place. At this pore volume, 31.3 ppb uranium is predicted to adsorb onto HFO at a calculated pH of 8.59. Within the second pore volume, dissolved uranium concentrations are predicted to slightly decrease to 44.4 ppb and 69.9 ppb uranium is predicted to adsorb onto HFO at a calculated pH value of 8.53. These results reasonably match measured concentrations of dissolved and suspended uranium in the lower perched zone at R-9, which are 48.4 and 63.6 ppb, respectively.

Continued passing of infilling solution results in slightly decreasing concentrations of dissolved uranium (pore volumes 3 and 4) followed by an increase in solute concentrations for the remaining pore volumes (Figure 4.3.2-9). Concentrations of adsorbed uranium are predicted to increase with each successive passing of infilling solution. Results of this model simulation suggest that within the second time step of 2.62×10^8 seconds (8.3 years), uranium predominately in the form of $UO_2(CO_3)_3^{4-}$ has migrated 84 m under fracture flow conditions to simulate uranium concentrations currently observed at R-9.

4.3.2.1.4 Summary and Conclusions from Geochemical and Transport Modeling of Strontium and Uranium

Strontium and uranium geochemical and transport modeling is summarized below.

1. Dissolved uranyl (UO_2^{2+}) in natural and contaminated systems significantly adsorbs onto hydrous ferric oxide (HFO) between pH values 5-8.

2. Dissolved uranium (VI) species, in the form of uranyl carbonato complexes ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) does not completely adsorb onto HFO. Increasing alkalinity decreases uranium adsorption under alkaline pH (7.5 and higher) conditions typical of basalt perched zones.

3. Dissolved calcium (Ca^{2+}) strongly competes for sorption sites, which decreases uranyl adsorption onto HFO. This effect is more likely to occur within alluvial groundwater than in sodium-rich perched groundwater within the Cerros del Rio basalt.

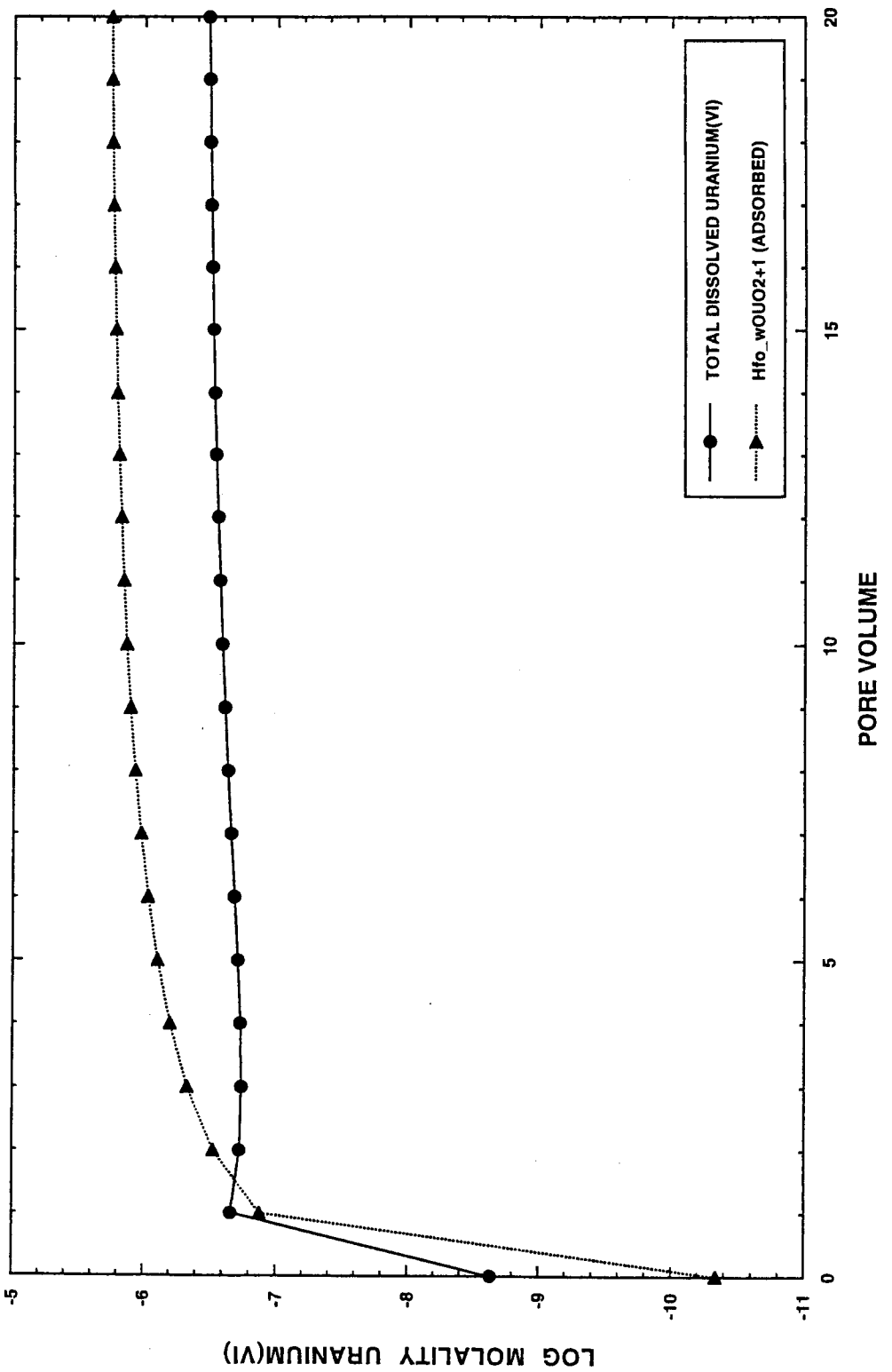

Figure 4.3.2-9 Results of transport modeling using PHREEQC2.2 to simulate adsorption of the uranyl cation onto hydrous ferric oxide (Hfo) (1.46 g/L). (Dispersivity = 0.1 m2/sec, time step = 1.33e08 seconds, recharge rate = 0.2 m/yr, and fracture porosity estimated at 0.01).

4. Results of modeling simulations suggest that uranyl sorption onto HFO may form colloids, which do not adsorb and move more readily than non-colloidal uranium, especially in fractured tuff and basalt.

5. The amount of adsorption of uranium onto HFO (and other adsorbents) is an important component of transport modeling.

Recommendations for additional modeling include:

1. Additional characterization of HFO is recommended to further validate adsorption modeling using MINTEQA2 and PHREEQC2.2.

2. Additional characterization of groundwater is required because, since the Cerro Grande fire, the aqueous chemistry has changed significantly. Increasing concentrations of calcium, potassium, bicarbonate, manganese, iron, uranium, dissolved organic carbon, and other solutes are observed in surface water and alluvial groundwater.

3. Additional modeling will help quantify geochemical processes occurring in alluvial groundwater that recharges perched groundwater in upper Los Alamos Canyon.

4. Further characterization of colloids is warranted to better explain the transport of sorbing chemicals including strontium, uranium, plutonium, and americium in the subsurface.

4.3.2.2 TA-16 Geochemistry and Contaminant Chemistry

Removal of contaminated material at the 260 outfall, MDA P, and from MDA R eliminated a substantial part of the high explosives and barium inventories at TA-16. These source removal activities should have a positive effect on the contaminant signatures of the Cañon de Valle hydrologic system in the future.

Bromide tracer was not detected above background levels in the springs. This result is not surprising considering the drought conditions. Because the 260 interim measure activities may have removed much of the bromide source, there may not be any further detections of the tracer in the springs.

Additional data analysis has been done on barium in the spring waters. There is a systematic bias in barium concentrations where most of the unfiltered samples have larger concentrations than filtered samples. This result suggests that while most of the barium is probably dissolved, a percentage of the barium inventory is probably colloidal. Geochemical modeling results using PHREEQC suggest that barite ($BaSO_4$) colloids could be present in the spring waters. It is also possible that barium is adsorbed on iron oxy-hydroxides or aluminosilicate mineral colloids that also typically have higher unfiltered versus filtered concentrations. In addition, the PHREEQC results suggest that several iron and aluminum phases are supersaturated in the spring waters. The potential transport effects of barium colloids on the deeper subsurface system is currently being investigated.

Along with the reductions in spring flows and lack of bromide tracer, the stable isotope data show substantial drought effects where the previously observed temporal variability in isotopic compositions was significantly reduced. This result is similar to the temperature response in the springs and is attributed to the lack of input from short and/or fast path recharge to the spring systems. The lack of fast input apparently prevented transfer of storm-to-storm or seasonal variability in isotopic composition to the springs. Thus, the spring flow that was observed during the drought is probably related to the larger, longer residence time flow system described in the spectral analysis discussion in the TA-16 hydrology section (Section 4.2.2.1.3).

The stable isotope data support the wet mesa and TA-16 conceptual model in an additional way. The collection of spring data over an annual time cycle, and the drought effect permits us to bound the isotopic composition of the main recharge pathway to the springs. From these data, the recharge model of Vuataz and Goff (1986) can be used to estimate the maximum elevation of recharge for the springs. The lowest measured isotopic value of the spring waters (-11.3 ‰) gives the highest elevation estimate from the model. The resulting elevation of 7878 ft suggests that the maximum elevation recharge area occurs just west of Highway 501 and the Pajarito fault. Thus, the flow lengths of the main recharge pathway(s) to the springs appear to be less than two km long. Other isotopic values measured from the spring samples give lower elevations. The elevation estimates are consistent with the TA-16 conceptual model that suggests recharge could be occurring in the vicinity of the Pajarito fault zone as well as the TA-16 mesa.

4.3.2.3 Environmental Tracer Simulations for Española Basin

The calibrated model of groundwater flow in the Española Basin was used to simulate the steady-state transport of several naturally occurring environmental tracers, including ^{14}C, $\delta^{18}O$, Cl^-, and ^{3}H. The simulation results were compared with measurements of these environmental tracers in groundwater in the basin to help evaluate the groundwater model and indicate what modifications to the model, if any, might be necessary. The simulations of tracer transport also helped to illustrate aspects of the groundwater model that were not previously obvious from analyses of the flow simulations and the measured hydraulic data alone. These aspects of the groundwater model pertained to the location of groundwater source areas, groundwater flow rates and directions, possible geologic controls on groundwater movement, and groundwater mixing behavior near the regional discharge areas.

4.3.2.3.1 Simulations with Carbon-14 Tracer

The ^{14}C transport simulations were used to calculate the ages of groundwater in the model, which could be compared to the groundwater ages estimated from ^{14}C measurements. The simulation results indicated that, as expected, young groundwater is present at shallow depths beneath the recharge areas in the mountains, and groundwater becomes progressively older as its moves toward the discharge areas and at depth. The groundwater model predicts that some of the oldest groundwater in the basin occurs beneath the Pajarito Plateau. The Pajarito Fault Zone impedes eastward groundwater movement from high elevation areas west of the Plateau, and the recharge model used in the transport simulations predicts that recharge is significant only along the western margin of the Plateau. Because of these factors, most of the groundwater discharge to the Rio Grande east of the Laboratory originates from the eastern part of the Española Basin. The simulation results indicate that groundwater ages increase rapidly with depth beneath the Plateau and eastward toward the Rio Grande. These trends in groundwater age are in qualitative agreement with the corrected groundwater ages calculated from the measured groundwater ^{14}C data. A detailed comparison between simulated groundwater ages and ages estimated from the ^{14}C data indicated fair agreement at several wells on the Pajarito Plateau, but simulated ages were too young compared to ages estimated from the ^{14}C data at several wells near the Rio Grande. Although the groundwater model predicts the presence of very old groundwater at depth beneath the Rio Grande, this simulated old water becomes mixed with younger, shallow water as it rises toward the river. The groundwater model also predicts that because basalt flows Tb1 and Tb2 have a high permeability and low porosity, these basalt layers will provide a conduit for the rapid movement of water beneath the Pajarito Plateau.

4.3.2.3.2 Simulations with Delta Oxygen 18 Tracer

Because the $\delta^{18}O$ of recharge is strongly negatively correlated with elevation in the model, the simulations of $\delta^{18}O$ transport provide an especially useful method for tracking the movement and subsequent mixing of recharge in the groundwater model. These simulations indicate that although the Pajarito Fault Zone slows the eastward movement of groundwater from areas west of the fault zone, much of the old groundwater deep beneath the Pajarito Plateau in the LANL

area originates from the upper part of the Sierra de los Valle west of the fault zone. The simulations predict that the $\delta^{18}O$ of groundwater becomes lighter with increasing depth beneath the Plateau, but that the lightest $\delta^{18}O$ is found in groundwater east of the Rio Grande because of the high elevation of the recharge areas in the Sangre de Cristo Mountains. The model predicts an abrupt transition in the $\delta^{18}O$ of groundwater beneath the Rio Grande where the groundwater recharged in the eastern and western parts of the basin converges. A comparison between the simulated and measured $\delta^{18}O$ values at wells on the Pajarito Plateau indicates that both the simulated and measured values are within a range of −12 to −10 per mil. This indicates that the recharge model may be reasonably approximating the actual recharge elevations of groundwater beneath the Plateau. However, the measured variability in $\delta^{18}O$ within this range is not reproduced by the model simulations. An analysis in the trends of the differences in the simulated and measured $\delta^{18}O$ suggests that, in general, a relatively larger proportion of isotopically heavy, low-elevation recharge at wells in the northern part of LANL and a relatively larger amount of isotopically light, high-elevation recharge at wells in the southern part of LANL in the model would improve the comparison. Whether adjustments should be made to the recharge model, to the permeabilities of the hydrogeologic units in the model, or both, has not yet been determined.

4.3.2.3.3 Simulations with Chloride Tracer

The simulations of Cl^- transport use the chloride mass-balance equation to estimate the concentration of Cl^- in the recharge. The current model of recharge estimates that above a ground-surface elevation of about 7100 ft, recharge is a constant fraction of precipitation. As a result, the simulated Cl^- concentration of most groundwater recharge in the Española Basin is about 5 to 6 mg/L using the current recharge model. The small amount of recharge with somewhat higher Cl^- concentrations estimated to be present at elevations where recharge becomes very small is easily diluted in the model by the much larger volume of high elevation recharge with a Cl^- concentration of 5 to 6 mg/L. Because of the uniformity of groundwater Cl^- concentrations in the model, Cl^- is not a particularly useful groundwater tracer for the combination of recharge parameters currently used to distribute recharge in the groundwater model. However, the $\delta^{18}O$ versus Cl^- relation predicted for recharge using the current recharge parameters is in good agreement with $\delta^{18}O$ and Cl^- data for most spring and well samples west of the Rio Grande. This may be more consistent with $\delta^{18}O$ and Cl^- data from wells east of the Rio Grande than is first apparent if one accepts the hypothesis of Anderholm (1994). The hypothesis states that many of the high Cl^- concentration in groundwater east of the Rio Grande are the result of septic tank effluent and other human effects.

4.3.2.3.4 Simulations with Tritium Tracer

Tritium transport simulations done thus far have examined only the steady-state distribution of tritium in groundwater that would be expected for the natural tritium-production rates in the atmosphere that occurred prior to nuclear weapons development and testing. Development of source terms for the tritium concentration of recharge that reflect the effects of atmospheric nuclear weapons tests and local Laboratory activities are underway. This will allow a more detailed evaluation of the significance of groundwater tritium measurements near LANL for groundwater model development.

4.4 Well Completion Improvements

Significant improvement was made in the number of wells drilled and completed in FY00. This improvement can be attributed to addition of fluids during drilling, changes in the process of drilling and completing wells, and establishment of standard protocols for well development.

4.4.1 Fluids used During Drilling

The drilling fluids used at R-19, R-31, and CDV-15-3 to enhance drilling performance were EZ-MUD and TORKease. Drilling fluids were not used at R-9 and R-12.

EZ-MUD is a viscosifier and borehole stabilizer that improves borehole stability. It consists of a long-chain polymer containing many functional groups made up of polyacrylamide/polyacrylate (PHPA) copolymer and hydrocarbon molecules. Some molecules tentatively identified in EZ-MUD include undecane ($C_{11}H_{24}$), 2,6-dimethyl-undecane ($C_{13}H_{28}$), 2-methyl-decane ($C_{11}H_{24}$), tridecane ($C_{13}H_{28}$), and tetradecane ($C_{14}H_{30}$). EZ-MUD eventually dissociates to smaller organic compounds containing carbon, hydrogen, nitrogen, and oxygen.

EZ-MUD has a negative charge density of 30% (0.3 mol per mol of polymer), which enhances the polymer's ability to adsorb cations. It is strongly hydrophobic (high molecular weight organic polymer), which lends the ability to adsorb organic compounds including RDX, HMX, and TNT.

EZ-MUD is a reducing agent (electron donor), which affects the solubility of redox-sensitive solids including ferric and manganese (oxy)hydroxides. It can potentially affect the speciation (form) of redox-sensitive solutes including iron, manganese, and nitrogen. EZ-MUD has a low aqueous solubility under near-neutral pH conditions. Nitric acid and sulfuric acid, applied at a pH of one, and sodium hypochlorite (bleach), which is an oxidizing agent or electron acceptor, can be used to break down EZ-MUD.

TORKease reduces frictional sticking of the drillstring encountered in low-permeable material. It consists of an emulsion of complex potassium stearates and has a specific gravity of 0.95 g/cm^3. When mixed with low ionic strength water typical of the regional aquifer, the TORKease solution has a pH range of 9.3 to 9.5.

To evaluate the potential effects of these fluids on groundwater quality characterization data and information were collected on the drilling fluids used to drill R-19. Borehole R-19 was drilled with fluids consisting of regional aquifer water, EZ-MUD, and TORKease to enhance drilling rates. One to two cups of EZ-MUD per thousand gallons of water were used at R-19 during drilling operations. EZ-MUD can be broken down by adding 5% sodium hypochlorite (bleach) to water injected into a well during development. This procedure was not followed at R-19 due to potential impacts of sodium hypochlorite on groundwater quality. When mixed with water, at a concentration of 1-quart EZ-MUD per 100 gallons water, the EZ-MUD solution is characterized by a pH of 8.5. Very small amounts of TORKease were used at R-19 according to the drillers' records.

Following a method provided by Baroid, titration tests were performed to determine the concentration of EZ-MUD remaining in R-19 during well development. Groundwater samples collected from screens three through seven were tested for EZ-MUD at the beginning of each day and during initial and final pumping. Groundwater samples were collected from June 20 through 24, 2000. Groundwater samples collected from R-19 showed small concentrations of EZ-MUD ranging between 0.017 and 0.063 parts per thousand, suggesting most of the residual EZ-MUD has been removed from the well.

Analysis of Total Organic Carbon (TOC) in water samples is used to determine the amount of EZ-MUD left in the borehole. Elevated TOC is consistent with the presence of residual EZ-MUD. Concentrations of TOC should decrease as EZ-MUD continues to dissociate, eventually approaching natural TOC concentrations. In R-19, concentrations of TOC ranged between 1.4 and 36.5 mg C/L, suggesting that residual EZ-MUD is present. During well development, concentrations of TOC generally decrease over time with some increases occurring periodically. Tests were not performed to quantify the potential amounts of TORKease remaining in the R-19

borehole. During quarterly sampling at the R wells, TOC will be measured to determine the presence of residual drilling fluids.

The following recommendations are made for application and removal of EZ-MUD from boreholes and characterization wells based on information and data collected on the physical and chemical properties of EZ-MUD and on field experience.

- Record the amount of EZ-MUD used during drilling, including the date and depth(s) with which it is applied.
- Remove EZ-MUD from boreholes and characterization wells prior to Westbay Instrument installation by vigorously developing each well following the protocols described in Section 4.4.3.
- Measure pH, turbidity, and TOC and perform polymer titration to evaluate dissolution (breakdown) of EZ-MUD polymer.
- Do not use EZ-MUD and TORKease together in boreholes where chemical and hydrologic data and information are collected. TORKease coats the EZMUD so that the EZ-MUD becomes more resistant to physical and chemical breakdown.

4.4.2 Well Construction Improvements

FY2000 was a banner year for the drilling program. All the wells that had been started in earlier years and all the scheduled wells for the current calendar year were completed. This success is due to:

- Use of multiple rigs to reduce well idle-time prior to completion by
  - spudding the hole and setting surface casing with a Central Mine Equipment (CME) - 750 hollow stem auger rig (and sometimes having that crew prepare a jack-cellar for the DR-24)
  - use of two Foremost DR-24 drilling rigs to drill the boreholes and set the casing
  - conducting well hydraulic-testing and development (and sometimes Westbay installation) with a workover/coring rig known as a Universal Drill Rig (UDR)
  - installation of most Westbay Systems with LANL's Smeal Rig
- At times working two 12-hr. shifts per day, seven days a week, reducing downtime (shutdown/startup time) between shifts and thereby reducing problems with sticking casing, borehole circulation, and borehole stability
- Drilling open borehole when hydrogeologic conditions permit, resulting in faster drilling rates than are possible by casing advance
- Use of geophysical logging and borehole video with logging of cuttings in lieu of coring to eliminate the time taken to trip in or out with the core barrel
- Use of less water and drilling fluid additives to minimize possible borehole contamination by introduced materials
- Use of the Field Support Facility (FSF) to fabricate mud/cementing trailers, dual-packer well-testing assemblies, and conveyor systems for cutting removal resulting in reduced drill rig and crew costs
- Use of a sprinkler system to disperse well development and circulation fluids shown not to be contaminated, reducing the potential for drilling shutdowns due to lack of storage/holding capacity

- Acquisition of third-party security-badged escorts for drilling crews to minimize the potential for lost work time due to delays in gaining access to secure areas
- Combining Site Specific Health and Safety Plans (SHASPs) for drill sites within a technical area, reducing review time and expediting work
- Performance of on-site training of drilling and field crews in OSHA HAZWOPER, first aid/CPR, and drill rig safety, resulting in less time away from drilling
- Large-volume purchase of advance casing and well construction materials, eliminating delays resulting from "waiting on materials" in order to complete construction of the wells
- Relaxation of the need to isolate all perched zones penetrated by the borehole by changing the focus to sequestering zones with contaminants for casing advance methods and quick-drilling open hole for those zones without contamination

4.4.3 Well Development Improvements

Wells must be methodically developed after construction to ensure that the water sampled from the wells is representative of the water in the formation. Development is the process of forcing water into and out of the saturated formations through the well screen in order to:

- Remove fines or drilling fluid from behind the screen
- Create a stable zone of filtration between the screen and the formation
- Increase hydraulic conductivity near the well

Well development is done using various combinations of four methods at LANL:

- Jetting - water is flowed into the screen by gravity
- Bailing - water is mechanically lifted out of the well so that water from the formation enters the well through the screen
- Airlifting - water is blown from the well by air pressure so that water from the formation enters the well through the screen
- Pumping - water is removed from the well with a submersible pump and water from the formation flows into the well

The well development process was improved in FY00 by developing and implementing standard well development protocols, careful planning, and oversight. A two or three stage protocol specifying the sequence and combination of development methods is formulated for each well. There are advantages and limitations of each development method (Table 4.4.3-1) that must be considered in developing the well-specific protocol.

In general, the well development protocols have a preliminary development stage that involves wire-brushing all screens then bailing opposite each screened interval. A second stage may be required if the water is very turbid. This stage involves some combination of the methods. Method selection is largely dependent on the amount of screen-specific development required. The third stage, final development, involves pumping opposite each screened interval.

Field parameters (pH, specific conductance, temperature, and turbidity) are checked once at the outset of bailing each screened interval to obtain a pre-development value, and also at regular intervals throughout pumping. Once turbidity at a given screen is <5 NTU, the pump is turned off. After a brief interval, the pump is turned back on and field parameters rechecked to see if they are still acceptable. This process is repeated three times. Development is halted when turbidity is <5 NTU, or cannot be improved during four episodes of pumping.

Table 4.4.3-1: Relative Advantages and Limitations of Well Development Methods

Method	Advantages	Limitations
Jetting	water flows into the formation	Water that is introduced must be removed
	Screen specific	Can not measure field parameters because water is not removed
		Low pressure
		No surging
Bailing	Measure field parameters in water removed from well	Not screen-specific
	Creates limited surging action	
Airlifting	Can measure field parameters	Not screen-specific
	Can surge	
Pumping	Can measure field parameters	Not screen-specific
	Can pulse	

5.0 FY00 INFORMATION MANAGEMENT

The majority of FY99 information management efforts were focused on project analysis, planning, requirements specification, and design. However, toward the end of FY99, intense system development efforts began. In FY00, the Water Quality Database (WQDB) team made significant progress in system development. Version 1.0 of the system was nearly complete at the end of the fiscal year. This first release of the system will be delivered to end users inside and outside of the Laboratory in early December 2000.

5.1 Hardware & Infrastructure

Server hardware was configured behind and outside of the Laboratory firewall (Figure 5.1-1). This configuration allows users internal and external to the Laboratory to access the WQDB. The data available outside the firewall is a subset of that which is available behind the firewall. The data stewards control release of data. At this time, data outside the firewall is updated manually. Updates are performed as the data stewards release new data. The WQDB team is currently working to automate this process. The automated updates will be performed nightly.

5.2 System Security

In addition to the Laboratory firewall security, the WQDB applications are designed to control who can access the system and the level of access that each user has. Some users have read-only access to the database. Others can read, enter, and edit data. Data entry and edit is further controlled by the assignment of data stewards and data steward proxies. Every piece of data in the WQDB is assigned a data steward. Only the data steward can perform updates or a user designated as a proxy for that data steward.

5.3 Software

A collection of web-based forms was developed for users to perform data entry and edit. These forms are used to maintain over a dozen lookup tables, station information, and basic sample information. Software was also developed to load electronic data deliverables from analytical laboratories into the WQDB.

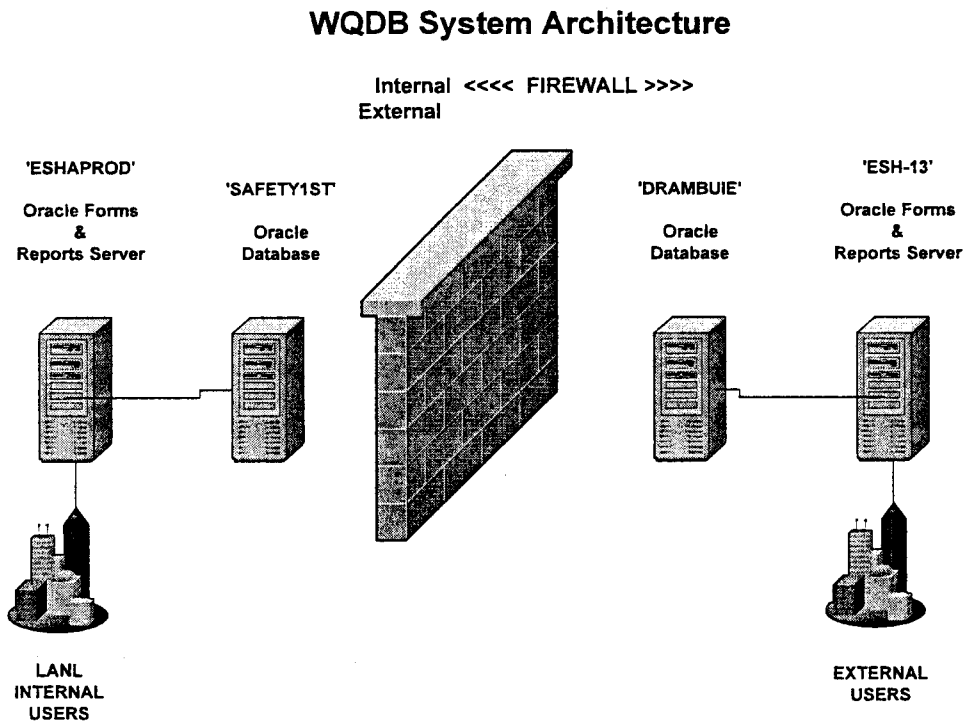

Figure 5.1-1 Water Quality Database System Architecture

5.4 Data Import

Data for location, sample, and analytical chemistry results were loaded into the WQDB. The system currently stores information for over 350 stations, over 400 samples taken during calendar year 2000, and over 10,000 chemistry results related to those samples. Due to the Cerro Grande fire, the majority of the data loaded into the WQDB by the end of FY00 was storm water data. Groundwater data loads began at the close of FY00.

5.5 Legacy Data Migration

Toward the end of FY00 a significant effort was started to migrate over five years of ESH-18 sample and chemistry data from the current Microsoft Access database repository to the WQDB. This includes storm water, surface water, groundwater, and sediment data. The data migration effort requires significant mapping of data from old values to new ones, and must be conducted carefully to maintain data integrity. This effort is ongoing and should be completed in January or February 2000.

5.6 Reports

A collection of web-based reports was developed at the end of FY00. The reports will be placed into production in early December 2000. These reports allow users to review chemistry data, station data, and standardized values that are maintained in the system lookup tables. Many of the reports feature input parameters that allow the user to tailor the content of the reports to their own needs. Users can also choose from three report output formats - HTML, PDF, or Microsoft Excel. The Microsoft Excel format is especially useful for retrieving data from the WQDB to serve as an input to another software package.

6.0 FY01 PLANNED ACTIVITIES

IN PROGRESS

7.0 STATUS WITH RESPECT TO HYDROGEOLOGIC WORKPLAN DECISIONS

The goal of the Hydrogeologic Characterization Program, as described in the Hydrogeologic Workplan, is to characterize the hydrogeologic setting beneath the Pajarito Plateau. The degree of characterization must be adequate to design a groundwater monitoring network that will reliably detect contamination from Los Alamos National Laboratory. The critical elements for designing a monitoring network are the hydrogeologic characteristics (e.g. saturated zones, flow direction, flow velocity) and delineation of groundwater contamination. The groundwater protection decision flow diagram developed for the Hydrogeologic Workplan summarizes the decisions that must be resolved to characterize the hydrogeologic setting. The decisions were formulated to guide data collection and ensure that the resulting data are adequate to provide the critical elements of monitoring network design.

These decisions apply to each aggregate individually defined in the Hydrogeologic Workplan. Resolution of these decisions for all aggregates will signal the successful completion of the hydrogeologic characterization program. This section of the Groundwater Annual Status Report for FY00 summarizes the progress made toward resolving decisions in aggregates where work was accomplished in FY00. In aggregates where no hydrogeologic characterization work was conducted in FY00, no additional progress can be reported. These aggregates are only briefly described in this section. Figure 7.0-1 provides a graphic summary of the progress toward resolution of the decisions in the Hydrogeologic Workplan.

7.1 Decision 1

Decision 1 concerns whether there are any sources of contamination present. If there are no contaminant sources sufficient to cause contamination, monitoring of that area is unnecessary. This decision was largely resolved at the start of the development of the Hydrogeologic Workplan because most of the aggregates are groupings of Potential Release Sites or operational sites where contaminants are likely to be present (LANL, 1998a). The one aggregate where sources of contaminants are not present is Aggregate 8 (Guaje, Bayo, Rendija, and Barrancas canyons). These areas were not used for Laboratory activities or, in the case of Bayo Canyon, a clean up had s been completed. Decision 1 is considered adequately resolved for all of the aggregates (Figure 7.0-1).

7.2 Decision 2

The second decision is intended to determine whether contaminants are present in sediments or alluvial groundwater that could migrate to deeper saturated zones. If contaminants are present, then further data collection is needed to understand the type and extent of contamination that could potentially impact deeper groundwater. If contaminants are not present, no further data collection is necessary because there is no source to migrate to groundwater. In order to resolve this decision, data to answer questions regarding the presence of alluvial water, concentration of contaminants in the water and sediments, and the standards that apply to the water or sediment must be collected.

The presence of contaminants in alluvial water in most of the aggregates was known from environmental surveillance data available at the time the Hydrogeologic Workplan was developed (LANL, 1998a). However, the extent of contamination in alluvial water and contaminant concentrations in sediment remain to be delineated as the ER Project canyons investigation progresses. For example, Aggregate 7, Mortandad Canyon, is the receiving canyon for the Los Alamos National Laboratory Radioactive Wastewater Treatment Facility. Prior to the development of the Hydrogeologic Workplan, extensive work on the extent and quality of alluvial groundwater had been completed and the presence of contaminants in alluvial water was known. The extent of contaminants within the sediments in Mortandad Canyon will be determined by geomorphic mapping and sampling by the Environmental Restoration (ER) Project.

Decision	Aggregate 1: Los Alamos/ Pueblo	Aggregate 2: Canada del Buey/ Pajarito	Aggregate 3: TA-49	Aggregate 4: Ancho/ Indio/ Chaquehul	Aggregate 5: Cañon del Valle	Aggregate 6: Water/ Potrillo/ Fence	Aggregate 7: Mortandad	Aggregate 8: Guaje/ Bayo/ Rendija
Are there sources of sufficient magnitude to cause contamination of groundwater?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Are the alluvial sediments and uppermost subsurface water at contaminant concentrations > regulatory risk limit or risk level?	Yes				Yes			
Is the intermediate perched groundwater at contaminant concentrations > regulatory limit or risk level?	Yes				Yes			
Is the regional aquifer as affected by the canyon systems by contaminant concentrations > regulatory limit or risk limit?								
What are the pathways for exposure to contaminants from alluvial sediments and uppermost subsurface water?					Yes			
Are there sufficient source terms to cause contamination if moved along the pathways in 1000 years?								No

- Decision resolved based on work done in FY00
- Decision not resolved, but some information from work done in FY00
- Decision resolved based on work prior to FY00
- Decision not resolved, but some information from work done prior to FY00
- No information to resolve decision

Figure 7.0-1 Summary of Decision Progress.

Within Aggregate 1 (Los Alamos, Pueblo, and Sandia canyons) the ER Project has made significant progress in defining the extent of contaminants in the sediments and alluvial water (LANL, 1998b, 1998c, 1998d, 1999). In FY00, work in Aggregate 1 focused on Acid and Pueblo canyons. In Acid Canyon two phases of sampling were conducted to better define the concentrations and inventory of plutonium-239, 240, cesium-137, strontium-90, mercury, zinc, polycyclic aromatic hydrocarbons (PAHs), DDT, and PCBs. Townsite runoff is likely the source of PAHs, zinc, and DDT in Acid Canyon (LANL, 2000a, 2000b, 2000c). In Pueblo Canyon, sampling was conducted in the reach that includes the Los Alamos County wastewater treatment plant to determine the relative contribution of inorganic and organic contaminants from the wastewater treatment plant, Acid Canyon, and runoff from the townsite.

Significant work has been accomplished in defining the extent of contamination in alluvial water and sediments in Aggregate 5 (Cañon de Valle). The principal constituents of concern in this aggregate are high explosives (HE), particularly RDX, TNT, and HMX; and inorganics, particularly barium. To date, 382 Potential Release Sites have been proposed for no further action based on human health concerns, although continued evaluation of ecological risk and risk to surface waters are ongoing at most of these sites. Twenty-eight sites have been cleaned up voluntarily. The voluntary remediations include HE sumps and drainlines at the 90s Line (320 cubic yards of soil removed), drainlines at Building 27 and V-Site (120 cubic yards of soil removed), and debris at Material Disposal Area (MDA) M (5460 cubic yards of soil removed). The most highly contaminated site within Aggregate 5 is the outfall from HE machining building 260. Soils, surface waters, and groundwaters are all contaminated with HE and barium at high levels and with many other constituents at low levels, due to discharge from the TA-16-260 outfall. HE levels range up to >20 wt % in the most highly contaminated soils directly downstream from the outfall. Barium is at levels greater than 10,000 ppm for 600 ft downgradient from the outfall. Surface waters, nearby springs (SWSC spring, Burning Ground spring, and Martin spring), and sediments in Cañon de Valle are contaminated with parts-per-billion levels of HE and above background levels of barium. The Building 260 outfall area is currently undergoing the first corrective measures study/corrective measures implementation (CMS/CMI) at LANL. An interim measure soil removal of about 2000 cubic yards was conducted in FY00.

Figure 7.0-1 reflects that Decision 2 is only partially resolved in most aggregates and is adequately resolved only in aggregates 1 and 5.

7.3 Decision 3

Decision 3 is intended to determine if contaminants are present in intermediate perched zones of saturation. If contaminants are not present, then the intermediate perched saturated zones are not sources of contaminants to deeper saturated zones. In order to resolve this decision, data must be collected to answer questions regarding the presence of intermediate perched water, concentration of contaminants in the water, and the standards that apply to the water. At the time the Hydrogeologic Workplan was developed, perched intermediate zones had been definitely identified only in Aggregate 1 (Los Alamos, Pueblo, and Sandia canyons) and were suspected (based on spring flow) in Aggregates 4 (Ancho Canyon), 5 (Cañon de Valle), and 6 (Water Canyon) (LANL, 1998a).

At the time the Hydrogeologic Workplan was developed, perched zones had been identified by test wells and intermediate depth wells in Los Alamos, Pueblo, and Sandia canyons (LANL, 1998a). Since the development of the Hydrogeologic Workplan, three wells have been drilled in Aggregate 1 (Los Alamos, Pueblo, and Sandia canyons). As described in Groundwater Annual Status Report for FY98, there are at least two intermediate perched zones below Los Alamos Canyon (R-9 and R-9i) and one below Sandia Canyon (R-12), all of which occur in the Cerros del Rio basalt (Nylander et al, 1999). The relationship between basalts and groundwater occurrence that was first observed in Aggregate 1 has been confirmed at all of the wells installed in the eastern portion of the Laboratory (R-15, R-22, R-31). Based on borehole samples, contaminants

detected in these Aggregate 1 perched zones include tritium, nitrate, uranium, chloride, and ammonium (Nylander et al, 1998), although only uranium in the lower perched zone at R-9 is above a proposed regulatory standard. Decision 3 has been adequately resolved for Aggregate 1.

In Aggregate 5, Cañon de Valle, the presence and quality of intermediate perched water were investigated in FY98 with the drilling of R-25 and in FY00 with the drilling and installation of CdV-15-3. At R-25 an upper zone of saturation was encountered from depths of 747 ft to 1132 ft in the lower part of the Otowi member of the Bandelier Tuff and the upper part of the Puye Formation (Nylander et al, 1999). HE compounds and associated degradation products were detected in water collected from the borehole. RDX and TNT are the contaminants of greatest concern because they are present in concentrations exceeding the EPA health advisory limits for drinking water (Nylander et al, 2000). In FY00 well CdV-15-3 was drilled as part of a program to determine the extent of HE contamination in groundwater. The water in the borehole of CdV-15-3 was sampled and analyzed. HE degradation products were observed near detection limit (0.25 µg/L) in only one out of six samples. This filtered sample was collected from the upper perched zone at 622 ft (Hickmott, 2000). High explosive compounds and degradation products were not detected in non-filtered samples collected at CDV-15-3. Decision 3, the presence of contaminants above a regulatory level, has been resolved for Aggregate 5.

In Mortandad Canyon, Aggregate 7, well R-15 was installed in FY99. An intermediate perched saturated zone was encountered in the Cerros del Rio basalts between the depths of 646 ft and 740 ft (Nylander et al, 2000). The major ion chemistry of the water collected from the R-15 borehole is similar to that of the TA-50 radioactive wastewater treatment plant discharge water. Sulfate, fluoride, and tritium are solutes associated with the discharge and were present in the perched groundwater (Nylander et al, 2000). None of the contaminants were above regulatory standards. The presence of contaminants above regulatory thresholds in perched intermediate groundwater has only been partially resolved in Aggregate 7. Two intermediate wells and two regional wells are planned to fully resolve this decision.

Decision 3 is adequately resolved in Aggregates 1 and 5 and partially resolved in Aggregate 7. No further data were collected on perched zones in Aggregates 2, 3, 4, or 8 in FY00. Figure 6-1 reflects that Decision 3 remains unresolved in these areas.

7.4 Decision 4

The intent of decision 4 is to determine if the regional aquifer has contaminant concentrations greater than a regulatory limit or risk threshold. To resolve this decision, data must be collected to determine the presence and concentration of contaminants. At the time the Hydrogeologic Workplan was developed, the presence of contaminants in the regional aquifer was known in Aggregate 1 (Los Alamos, Pueblo, and Sandia canyons) and Aggregate 7 (Mortandad Canyon), and suspected in Aggregate 4 (Ancho, Indio, and Chaquehui canyons) (LANL, 1998a).

In Los Alamos, Pueblo, and Sandia canyons (Aggregate 1), analysis of samples from Test Wells 1, 2, 3, and 4 contained tritium, strontium-90, and nitrate, although only the nitrate was above a regulatory standard (LANL, 1998a). Samples of borehole water from R-9 and R-12 found tritium activity in the groundwater of the regional aquifer from 14.4 to 46.9 pCi/L. These tritium activities are far below the regulatory standard (20,000 pCi/L), but indicate that the regional aquifer contains a component of surface water that is less than 50 years old (Nylander et al, 1999). In FY00, sampling of the water supply wells found tritium in Otowi-1 (Los Alamos Canyon) at 33 pCi/L, perchlorate at 1-3 µg/L, and no confirmed detection of strontium-90 (Section 4.3.1.7). These findings are consistent with the water quality analysis at R-9 and R-12. The presence of contaminants in the regional aquifer has been observed, although to above regulatory standards. However, eight more regional aquifer wells closer to historic sources, are proposed in Aggregate 1 to fully resolve Decision 4.

Borehole water samples from the regional aquifer in Well R-25 (Aggregate 5) contained HE and degradation products (Nylander et al, 1999), although it was unclear whether those samples had been contaminated by perched water in the borehole. Samples of regional aquifer water from the borehole at Well CdV-15-3 had no detectable HE or degradation products (Section 4.3.1.4). Quarterly sampling at both R-25 and CdV-15-3 will be necessary to resolve decision 4 for Aggregate 5.

Borehole water samples from the regional aquifer in Well R-15 (Aggregate 7) contained no contaminants and the tritium activity was less than 3 pCi/L (Section 4.3.1.3), indicating the water is greater than 50 years old and thus no component of meteoric water. Two regional aquifer wells are proposed for Mortandad Canyon to confirm the absence of contaminants in the regional aquifer in Aggregate 7.

Decision 4 is partially resolved in Aggregates 1, 5 and 7. No data on regional aquifer water quality is available for Aggregates 2, 3, 4, 6, and 8. Decision 4 is unresolved for these aggregates (Figure 7.0-1).

7.5 Decision 5

Decision 5 addresses the potential for contaminants to impact groundwater in the future. The previous four decisions are intended to determine if there is existing contamination that would require monitoring. The intent of Decision 5 is to determine whether pathways exist from the surface to the regional aquifer, indicating that there is the potential for contamination to impact groundwater in the future and that monitoring is warranted. Resolution of this decision requires data to answer six questions on recharge, hydraulic properties, retardation factors, and the role of fractures and faults (LANL, 1998a). The majority of the planned data collection in the Hydrogeologic Workplan is intended to answer these questions and resolve this decision.

At the time the Hydrogeologic Workplan was developed, only Aggregate 1 (Los Alamos, Pueblo, and Sandia canyons), where contaminants had been detected in the regional aquifer, was known to have viable contaminant transport pathways, although those pathways were undefined. Since that time, the understanding of pathways has been greatly enhanced in Aggregates 1 and 5 through data collection and interpretation with modeling tools as described in previous Groundwater Annual Status Reports (Nylander et al, 1999 and 2000) and in Sections 4.2.2 and 4.3.2 of this report.

In Aggregate 1, refined modeling of flow and transport in the vadose zone beneath Los Alamos Canyon suggests that the timeframe for transport contaminants to the regional aquifer varies with location in the canyon. In the upper canyon, where the underlying bedrock is the Bandelier Tuff and Puye Formation, the transport time for tritium and other contaminants is on the order of 50 years or so. The rate of flow of water and contaminants through the Bandelier Tuff is most influenced by low infiltration rates and matrix flow through these units. However, the travel time is much shorter, on the order of 10 years in the middle and lower portion of Los Alamos Canyon, which is underlain by basalt or a thin layer of Puye Formation over basalt. Flow and contaminant transport in this portion of the canyon is influenced by higher infiltration rates and flow in fractures rather than through the matrix that occurs in the basalts (Section 4.2.2.1.1). Additionally, geochemical modeling suggests that colloidal transport of uranium with hydrous ferric oxides as the adsorbent is occurring in Los Alamos Canyon (Section 4.3.2.1.3). For Aggregate 1, decision 5 is partially resolved in terms of defining what the transport pathways are. It is expected to be fully resolved with continued data collection and interpretation with hydrologic and geochemical modeling tools.

In Aggregate 5, Cañon de Valle, an enhanced understanding of the contaminant transport pathways has been developed based on vadose zone and regional aquifer modeling. In the vadose zone, a conceptual model was hypothesized and continues to be confirmed by data collected from springs, shallow boreholes, and well R-25 (Nylander et al, 1999, 2000). In the

vadose zone lateral flow is an important process in the transport of contaminants from the surface to intermediate perched saturated zones. Chloride mass balance studies indicate downward infiltration rates on the order of a few millimeters per year. This is too slow to account for HE and degradation compounds at the depths they have been observed (Nylander et al, 2000). There are thin perennial saturated ribbons in the mesa that feed three springs, controlled by permeability variations in the Bandelier Tuff and by fractures. Tracer studies at TA-16 indicate relatively direct connections of effluent sources with pathways to the springs (Nylander et al, 1999). In FY00, spectral analyses of springflow time series results support the conceptual model that describes a larger, longer residence time flow system, and smaller, faster, intermittent flowpaths that superimpose recharge on the larger flow system (Section 4.2.2.1.3).

Transport of contaminants in the regional aquifer from Aggregate 5 was examined using the regional aquifer model to predict travel times of HE from R-25 to the nearest water supply wells. In the model simulations, nearly all the HE introduced to the regional aquifer water table was predicted to be captured by PM-4, the nearest water supply well. Predicted travel times to PM-4 range from 80 to 1500 years. Qualitative information about aquifer properties suggest most likely travel times are in the high end of the range (Nylander et al, 2000). The absence of HE and degradation compounds in well CdV-15-3 (Section 4.3.1.4), which is located approximately half-way between R-25 and PM-4, supports the longer time frame prediction. In Aggregate 5, decision 5 is adequately resolved with sufficient understanding of the hydrogeology to support monitoring system design for the aggregate. Continued data collection is planned to complete the corrective action process.

Decision 5 is fully resolved for Aggregate 5 and partially resolved for Aggregate 1. Data collected from R-31 and R-15 will be used to begin resolving decision 5 in Aggregates 6 and 7. Through FY00, no data for resolving this decision has been collected in Aggregates 2, 3, 4, or 8 (Figure 7.0-1).

7.6 Decision 6

While decision 5 addresses the potential for contamination in the future, decision 6 is intended to define a time frame for "future". The decision attempts to resolve whether sources are present that would cause contamination in 1000 years. Resolution of this decision is likely to depend on a coupled systems model that links sources, pathways, and time. At the time the Hydrogeologic Workplan was developed, only Aggregate 8 (Bayo, Guaje, Rendija, and Barrancas canyons) was considered to have such limited potential sources that this decision could be considered resolved. For all the remaining aggregates, coupled systems modeling is planned (Revision of Section 3 of LANL, 1998a).

7.7 Summary

Figure 7.0-1 summarizes the degree to which data have been collected to resolve the six decisions described in the Hydrogeologic Workplan (LANL, 1998a).

Briefly the status with respect to decisions is:

- Decision 1 is considered adequately resolved for all of the aggregates.
- Decision 2 is only partially resolved in most aggregates and is adequately resolved in Aggregates 1 and 5.
- Decision 3 is adequately resolved in Aggregates 1 and 5, partially resolved in Aggregate 7; and unresolved in the remaining aggregates.
- Decision 5 is fully resolved for Aggregate 5; partially resolved for Aggregate 1; and unresolved in Aggregates 2, 3, 4, 6, 7, or 8.

- Decision 6 is considered fully resolved only in Aggregate 8 and unresolved in the remaining aggregates.

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