

New Mexico Geological Society

Downloaded from: <http://nmgs.nmt.edu/publications/guidebooks/47>



Aqueous geochemistry of upper Los Alamos Canyon, Los Alamos, New Mexico

Patrick A. Longmire, Stephen Kung, Jeremy M. Boak, Andrew I. Adams, Florie Caporuscio, and Robert N. Gray, 1996, pp. 473-480

in:

Jemez Mountains Region, Goff, F.; Kues, B. S.; Rogers, M. A.; McFadden, L. S.; Gardner, J. N.; [eds.], New Mexico Geological Society 47th Annual Fall Field Conference Guidebook, 484 p.

This is one of many related papers that were included in the 1996 NMGS Fall Field Conference Guidebook.

Annual NMGS Fall Field Conference Guidebooks

Every fall since 1950, the New Mexico Geological Society (NMGS) has held an annual [Fall Field Conference](#) that explores some region of New Mexico (or surrounding states). Always well attended, these conferences provide a guidebook to participants. Besides detailed road logs, the guidebooks contain many well written, edited, and peer-reviewed geoscience papers. These books have set the national standard for geologic guidebooks and are an essential geologic reference for anyone working in or around New Mexico.

Free Downloads

NMGS has decided to make peer-reviewed papers from our Fall Field Conference guidebooks available for free download. Non-members will have access to guidebook papers two years after publication. Members have access to all papers. This is in keeping with our mission of promoting interest, research, and cooperation regarding geology in New Mexico. However, guidebook sales represent a significant proportion of our operating budget. Therefore, only *research papers* are available for download. *Road logs, mini-papers, maps, stratigraphic charts*, and other selected content are available only in the printed guidebooks.

Copyright Information

Publications of the New Mexico Geological Society, printed and electronic, are protected by the copyright laws of the United States. No material from the NMGS website, or printed and electronic publications, may be reprinted or redistributed without NMGS permission. Contact us for permission to reprint portions of any of our publications.

One printed copy of any materials from the NMGS website or our print and electronic publications may be made for individual use without our permission. Teachers and students may make unlimited copies for educational use. Any other use of these materials requires explicit permission.

This page is intentionally left blank to maintain order of facing pages.

AQUEOUS GEOCHEMISTRY OF UPPER LOS ALAMOS CANYON, LOS ALAMOS, NEW MEXICO

PATRICK A. LONGMIRE¹, STEPHEN KUNG¹, JEREMY M. BOAK¹, ANDREW I. ADAMS¹,
FLORIE CAPORUSCIO² and ROBERT N. GRAY³

¹Environmental Science and Waste Technology, MS J534, Los Alamos National Laboratory, Los Alamos, NM 87545;

²Advanced Sciences Incorporated, MS M327, 2237 Trinity Dr., Los Alamos, NM 87544; ³Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131

Abstract—Geochemical characterization of alluvial ground water within upper Los Alamos Canyon, Los Alamos, New Mexico is required for environmental investigations. Ground water is one of the primary pathways for migration of solutes, including ³H, ⁹⁰Sr, and other radionuclides. Alluvial ground water varies from a native Ca²⁺-Na⁺-HCO₃⁻ ionic composition to a Na⁺-Ca²⁺-Cl⁻-HCO₃⁻ ionic composition, with increasing chloride and sodium concentrations occurring downgradient of facility discharges. Rock-water interactions, including precipitation/dissolution reactions of silicates and silica glass, control major-ion chemistry for the silica-rich solutions. Hydrolysis of volcanic glass, enriched in silica, aluminum, and sodium, may result in the formation of amorphous Al(OH)₃, kaolinite, and smectite over long periods of time. Formation of these geochemically reactive phases provides active surface sites for cation exchange of ⁹⁰Sr²⁺ with other divalent metals. Results of geochemical modeling using the computer code MINTQA2 suggest that alluvial ground water is undersaturated with respect to SrCO₃ and SrSO₄ and precipitation of these two minerals is unlikely from a thermodynamic basis. Sorption coefficient (K_d) values for strontium measured on organic-rich Los Alamos Canyon soils and channel sediments range from 15.8 to 67.7 ml/g (mean value of 35.7 ml/g) and from 8.8 to 41.3 ml/g (mean value of 21.4 ml/g), respectively, suggesting that this cation is a nonconservative solute that is partially removed from solution through cation exchange. The isotope ⁹⁰Sr is considered to be the most important radionuclide for risk analysis because of its low maximum contaminant level (8 pCi/L) and widespread distribution in the alluvium in upper Los Alamos Canyon.

INTRODUCTION

Geochemical characterization of ground-water systems, including the alluvial ground water, within upper Los Alamos Canyon, Los Alamos, New Mexico is required as part of environmental investigations conducted under the Resource Conservation Recovery Act (RCRA) operating permit of Los Alamos National Laboratory (LANL) (EPA, 1990). Alluvial ground water in upper Los Alamos Canyon is not used as a source of water supply; however, the fate and transport of anthropogenic solutes is of primary interest. Upper Los Alamos Canyon is that portion of Los

Alamos Canyon west of the confluence with Pueblo Canyon at NM-4. DP Canyon is a secondary canyon connected to upper Los Alamos Canyon (Fig. 1) and is also included in this investigation. Los Alamos Canyon lies on the east flank of the Jemez volcanic field and the active west margin of the Española basin of the Rio Grande rift. Upper Los Alamos Canyon has a drainage area of 26.9 km² and a channel length of 19.8 km.

The ground-water pathway in upper Los Alamos Canyon is important because of the presence of saturated alluvium, which provides recharge to perched zones at intermediate depth in the Guaje Pumice bed at the

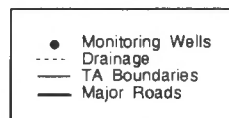
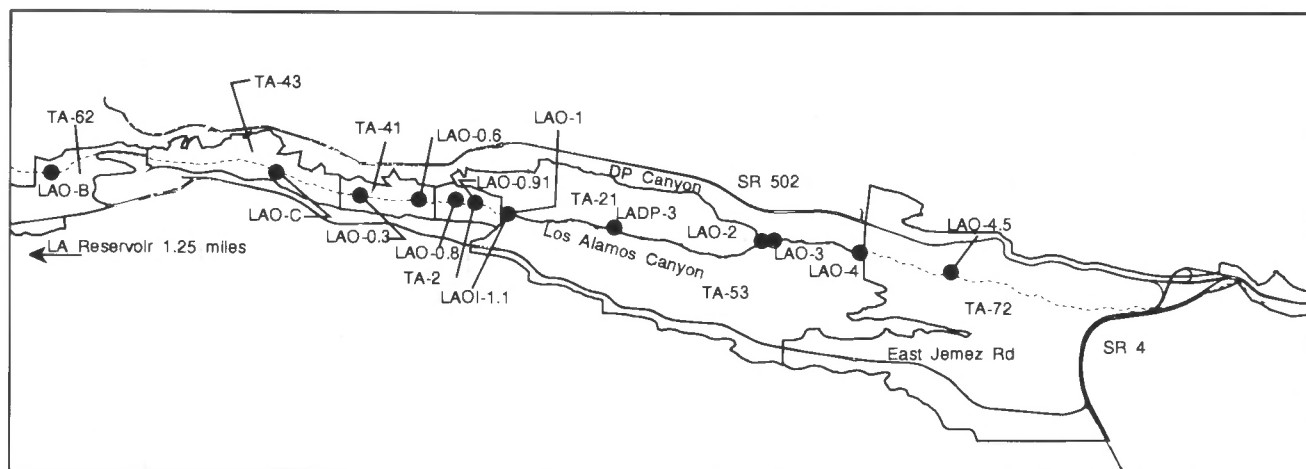


FIGURE 1. Ground-water sampling locations in Los Alamos Canyon.

base of the Otowi Member of the Bandelier Tuff and the Puye Formation, and possibly to deeper Santa Fe Group sediments (main aquifer). The hydrology and geochemistry of the alluvium is relevant for understanding the distribution and potential fate of contaminants in upper Los Alamos Canyon. Infiltration of surface water occurs under saturated- and unsaturated-flow conditions, given the presence of coarse-grained alluvial sediments and volume of ground water in storage in the alluvium. In addition to tritium (^3H) and ^{90}Sr , the presence of other solutes including chloride, chromium, nitrate, and uranium have been documented in the alluvial ground water within upper Los Alamos Canyon (LANL, 1995).

This paper describes the aqueous geochemistry of ground water within the alluvium and Guaje Pumice bed within upper Los Alamos Canyon and it also addresses important geochemical processes that control the fate and transport of ^{90}Sr within the alluvium. The isotope ^{90}Sr , which has a half life of 29.1 yrs and decays to ^{90}Y by emission of a β particle, is produced and processed at Los Alamos National Laboratory (LANL) and was a radiological constituent of previous discharges at Technical Area (TA)-2, TA-21, and other facilities adjacent to upper Los Alamos Canyon.

MATERIALS AND METHODS

Monitoring wells were installed to collect ground-water samples and to evaluate local flow conditions within the alluvium and the Guaje Pumice bed, using hollow-stem auger and air rotary techniques without drilling fluids. Monitoring wells constructed of PVC were installed by the Water Quality and Hydrology Group (ESH-18) (1966 and 1990), by the Environmental Systems and Waste Characterization Group (CST-7) and Laboratory contractors (1994). The screen lengths in the monitoring wells are variable and the top of the screens were generally set at the water table, although the saturated thickness of the alluvium fluctuates seasonally.

Ground-water samples for inorganic solutes were collected either using downhole dedicated positive displacement pumps (bladder pump) or disposal bailers. The monitoring wells were purged by pumping a minimum of three well volumes before sampling. Temperature and specific conductance were determined from an aliquot collected during sampling. Since 1994, ground-water samples collected for analysis of dissolved inorganic solutes were pressure-filtered through a $0.45\ \mu\text{m}$ Gelman filter and acidified with ultrapure HCl , HNO_3 , and H_2SO_4 , depending on sample analysis, to a pH of < 2.0 . All ground-water samples collected in the field were stored at 4°C until analyzed. Alkalinity was determined in the field immediately after collection using standard techniques.

Ground-water samples were analyzed using a variety of laboratory techniques specified in EPA-SW 846 (EPA, 1986). Sulfate, F, Br, PO_4^{3-} , NO_2^- , NO_3^- , and Cl were determined by ion chromatography (IC). Analyses of Ca, Mg, Na, K, Fe, Sr, Al, SiO_2 , Mn, Fe, Ba, and trace elements were by graphite furnace atomic absorption (GFAA), cold vapor atomic absorption (CVAA), inductively-coupled plasma emission spectroscopy (ICPES), and inductively-coupled plasma mass spectrometry (ICPMS) at LANL laboratories (EES-1 and CST-9) following EPA-SW846 protocols (EPA, 1986). Radionuclide activity in ground water was determined by liquid scintillation counting (^3H), electrolytic enrichment (low-level ^3H), and gas proportional counting (^{90}Sr) at CST-9 group laboratories and LANL contract laboratories (Rust Geotech, Grand Junction, Colorado; University of Miami, Miami, Florida). Sample duplicates, laboratory blanks, and field blanks were collected and analyzed according to EPA procedures. The precision limits for major ions and trace elements were generally $\pm 10\%$.

Batch sorption/desorption experiments were conducted, using ^{85}Sr as a surrogate for ^{90}Sr , on soils and channel sediments collected in TA-2, TA-41 and TA-72. The isotope ^{85}Sr has a short half life (65 days) and it emits a strong gamma ray at 514 KeV that can be measured by gamma spectrometry. For each experiment, two grams of air-dried soil or sediment were placed in a clean centrifuge tube and 20 ml of solution containing 2 to 23×10^{-13} M strontium were added. The sealed centrifuge tube was placed on a shaker for at least 72 hours. All stock solutions were adjusted to pH 6.8 ± 0.1 by adding NaOH or HCl solutions. For all of the solutions, 0.01 M KCl was used as a background electrolyte to provide a constant ionic strength. Measurements were performed at the counting room at CST-7 using a sodium iodide and/or germanium detec-

tor. Details of the adsorption/desorption experiments were provided by Kung (1995).

Calculations of solute speciation, PCO_2 , and solid phase saturation indices were made using the computer code MINTEQA2 (Allison et al., 1991), with single ion activity coefficients calculated using the Davies equation. MINTEQA2 quantifies possible rock-water and water-atmosphere reactions, but, modeling results should be interpreted with caution and are limited by the scope of our understanding of hydrologic flow conditions (saturated and unsaturated), possible reaction mechanisms, and kinetic constraints in a disequilibrium-dominated system.

AQUEOUS CHEMISTRY

This section presents a summary of the aqueous chemistry of ground water within the alluvium and the Bandelier Tuff (Guaje Pumice bed). Water-quality data consisting of major ions, trace elements, radionuclides, organic compounds, and stable isotope ratios have been collected at the Laboratory since 1945, primarily on unfiltered ground-water samples. The U.S. Geological Survey monitored the effects of releases of radioactive effluents and conducted geohydrological studies in the Los Alamos area for the Atomic Energy Commission (AEC) from 1949 through 1969. Results of these studies are available in a series of reports and publications that were summarized by Bennett (1990) and discussed in detail in EPG (1990, 1992-1995). Starting in 1970, the Laboratory initiated a formal environmental monitoring program, which is required by DOE Order 5400.1 (DOE, 1988), and continues under the direction of the Laboratory's ESH Division. Since 1971, surveillance and monitoring data have been published annually by the Laboratory in a formal report.

Aqueous chemistry of native ground water

In upper Los Alamos Canyon, the quality of ground water in both the alluvium and Guaje Pumice bed is monitored by 15 and two observation wells, respectively (Fig. 1); the construction of most of the wells is described by Purtymun (1995). Ten of these wells were installed as early as 1966 as part of the Laboratory's surveillance program; the other seven were installed at TA-2, TA-21, TA-41 and TA-62 in 1993 and 1994 for the Environmental Restoration (ER) Project.

Alluvial ground water generally is oxidizing based on both measurable dissolved oxygen concentrations greater than 3 mg/L and the presence of Fe_2O_3 and $\text{Fe}(\text{OH})_3$ in aquifer material derived from the Bandelier Tuff (Broxton et al., 1995a). Dissolved organic carbon (DOC), however, occurs in the 1 to 5 mgC/L range, in the form of low-molecular weight organic acids produced by the decomposition of forest litter. These hydrophilic and hydrophobic organic acids may contribute to the localized reducing conditions in the alluvium, although oxidizing conditions prevail in alluvial ground water. The anions of organic acids are complexing agents capable of binding with dissolved metals (Stumm and Morgan, 1996; Stevenson, 1994). The ability to form metal-organic complexes potentially influences the fate and transport of metals and radionuclides (Stevenson, 1994).

Native ground water in the alluvium has a $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-$ ionic composition with an average total dissolved solids (TDS) concentration less than 120 mg/L (LANL, 1995). Observation well LAO-B serves as a background well for upper Los Alamos Canyon and is located near the western boundary of the Laboratory (Fig. 1). The concentration of chloride measured at LAO-B is approximately 7 mg/L (Fig. 2), which is similar to chloride concentrations measured at the Los Alamos Reservoir (LANL, 1995). Activities of ^3H measured at LAO-B are less than 65 pCi/L, which is within the range of rainfall and snowmelt (Adams et al., 1995) and background springs (Blake et al., 1995). Observation well LAO-C, located west of TA-41, serves as a background well for TA-2 and TA-41. Ground water from LAO-C contains higher concentrations of major ions than ground water from LAO-B.

Native ground water in the Guaje Pumice bed also has a $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-$ ionic composition with an average TDS concentration less than 200 mg/L (Table 1) (LANL, 1995). Concentrations of calcium and bicarbonate are higher in the Guaje Pumice bed relative to LAO-B. Observation well LAO-I-1.1 serves as a provisional background well for the Guaje Pumice bed and is located at the eastern end of TA-2 (Fig. 1). The

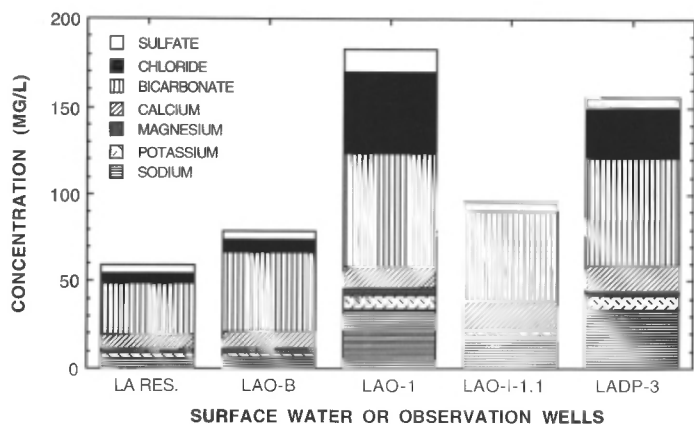


FIGURE 2. Water-quality data for Los Alamos reservoir, the alluvium, and the Guaje Pumice bed, upper Los Alamos Canyon, Los Alamos, New Mexico.

concentration of chloride measured at LAO-I-1.1 is less than 2 mg/L (Fig. 2; Table 1), which is lower than chloride concentrations measured in the alluvium (LANL, 1995). Concentrations of trace metals are less than 0.1 mg/L. Activities of ³H measured at LAO-I-1.1 are less than 3 pCi/L, which suggests that the Guaje Pumice bed is recharged by meteoric water west of TA-2, possibly within the Pajarito fault system and Rendija Mountain fault zone.

Anthropogenic sources impacting ground water quality

Ground water collected from LAO-1 has a Ca²⁺-Na⁺-Cl-HCO₃⁻ ionic composition (Fig. 2) and TDS contents ranging between 165 and 280 mg/L from 1984 to 1990 (Fig. 3). The influence of road salt and other sources of sodium and chloride on alluvial ground-water compositions can be seen by comparing the compositions of water from LAO-B (upgradient from any such sources) and from LAO-1. In general, concentrations of sodium and chloride increase along the ground-water flow path in the alluvium, contributing to the increase in TDS content (Fig. 3). A sharp decrease in TDS, however, occurs between observation wells LAO-3 and LAO-4 (Fig. 3). Observation well LAO-4 is completed in the alluvium and weathered Bandelier Tuff (Purtymun, 1995). Geochemical modeling using the computer code MINTEQA2 (Allison et al., 1991) suggests that the change is not due to precipitation of any saturated mineral phases. Therefore, the decrease may be the result of mixing alluvial ground water, characterized by a higher TDS content (LAO-3), with ground water from the Bandelier Tuff (Otowi Member or Guaje Pumice bed) with a lower TDS content, for example LADP-3 and LAOI(A)-1.1.

Ground-water samples collected from LADP-3 east of TA-2, which is completed in the Guaje Pumice bed, are characterized by mixed-ion composition where Na⁺, Ca²⁺, HCO₃⁻, and Cl⁻ are the dominant species. The TDS concentration in this ground water ranges from 182 to 229 mg/L (Table 1). Ground water sampled from LADP-3 is enriched in chloride

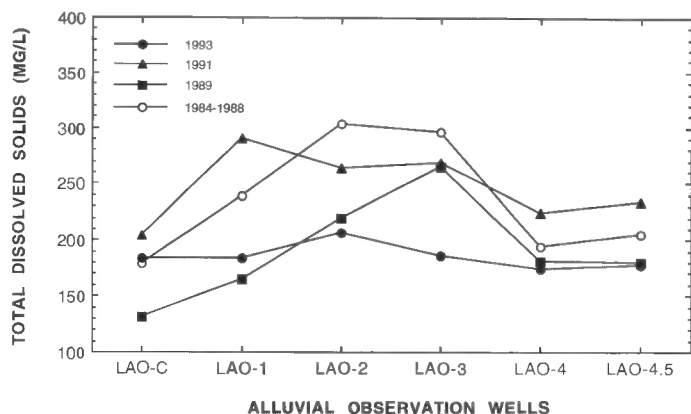


FIGURE 3. Total dissolved solids content in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

TABLE 1. Summary of selected analysis on filtered ground-water samples, Guaje Pumice bed, intermediate perched zone, upper Los Alamos Canyon, Los Alamos, New Mexico.

Well	LADP-3 Date 04/26/95	LADP-3 Date 12/16/94	LADP-3 Date 12/01/93	LAOI-1.1 Date 05/17/95	LAOI-1.1 Date 02/16/95	LAOI-1.1 Date 11/17/94
Analysis ^a						
Al	0.05	0.03	0.21	0.51	6.40	0.31
B	0.03	0.025	0.04	<0.010	0.010	0.014
Ba	0.03	0.02	0.02	0.02	0.02	<0.01
Ca	10.2	7.76	11.7	6.37	4.03	1.63
Cl	35.1	21.7	46.8	1.01	1.04	1.49
Cr	0.007	0.005	0.003	0.001	0.002	0.001
F	0.18	0.12	0.38	0.14	0.13	0.18
Fe	<0.01	<0.01	0.13	0.19	0.76	0.11
HCO ₃	56.8	60.1	65.0	60.4	56.3	51.0
K	7.56	6.33	8.70	5.46	6.04	3.62
Mg	3.06	2.44	4.08	1.19	1.01	0.37
Mn	0.03	0.03	0.44	0.03	0.07	0.06
Na	25.2	22.9	33.8	13.4	14.5	18.6
NH ₄	0.22	0.09	0.32	0.05	0.05	0.39
NO ₃	1.10	0.73	1.21	1.32	<0.02	0.96
pH ^b	7.44	6.87	6.62	7.32	7.29	7.05
SiO ₂	59.7	54.1	42.8	67.8	95.9	64.4
SO ₄	5.93	4.78	12.8	1.88	2.23	4.18
Sr	0.08	0.06	0.13	0.05	0.04	0.02
Zn	0.04	0.67	0.16	0.05	0.06	0.13
TDS ^c	205	182	229	160	189	148
³ H ^d	1472	1849	5974	2.01	2.30	0.77

a. All analyses are in mg/L, except where noted.
 b. Standard units.
 c. TDS is total dissolved solids.
 d. Tritium activity is in pCi/L.

and sodium relative to LAO-B and, except for chloride and sodium, is chemically similar to alluvial ground water collected from monitor well LAO-1 (Fig. 2). This similarity in major-ion compositions suggests that alluvial ground water is recharging the Guaje Pumice bed. In addition, ³H was detected in samples from LADP-3 at activities of approximately 6000 pCi/L in 1993 (Table 1; Broxton et al., 1995b), confirming an alluvial ground water component within the Guaje Pumice bed. Activities of ³H have decreased in samples collected from LADP-3 since 1993 (Table 1).

Broxton et al. (1995b) presented a volumetric-mixing curve of Cl⁻ for the Guaje Pumice bed (LADP-3) and alluvial ground water (LAO-1). Chloride is a conservative species that migrates at the same rate of ground-water flow, and concentration decreases of chloride are primarily due to hydrodynamic dispersion and mixing. Sodium may undergo cation exchange and its concentrations may decrease along the ground-water flow path due to this process. End members for this mixing curve include a Cl⁻ concentration of 1.0 mg/L (10^{-4.55} M) for noncontaminated ground water in the Guaje Pumice bed (LAOI(A)-1.1) and an average Cl⁻ concentration (64.5 mg/L, 10^{-2.74} M) in ground-water samples collected from LAO-1 over 25 yrs (1966-1991). Alluvial monitoring well LAO-1 is located hydrologically upgradient of LADP-3 and is considered to represent alluvial ground water infiltrating to the Guaje Pumice bed east of TA-2. Chloride concentrations in LADP-3 were 46.8 mg/L (10^{-2.88} M) in December 1993 (Table 1). Results of calculations by Broxton et al. (1995b) suggest that as much as 73% of the ground water in the Guaje Pumice bed at LADP-3 is derived from alluvial ground water (Broxton et al., 1995b). Chloride concentrations have decreased since December 1993, suggesting that the volumetric mixing between alluvial and Guaje Pumice bed ground waters is decreasing. For example, this mixing ratio decreases to 34% calculated from the December 1994 analytical data (Table 1).

Distributions of radionuclides and trace elements in alluvial ground water

This section presents a discussion of selected trace elements and radionuclides in alluvial ground water in upper Los Alamos Canyon. Downgradient from TA-41 and TA-2, the measured concentrations (as activities) of ³H and ⁹⁰Sr, the concentrations of major cations and anions, and some trace metals (chromium and uranium) in alluvial ground water generally are above the natural background or regional fallout levels observed at Los Alamos Reservoir (LANL, 1995). Reference to state and federal maximum contaminant levels (MCLs) and to the Department of

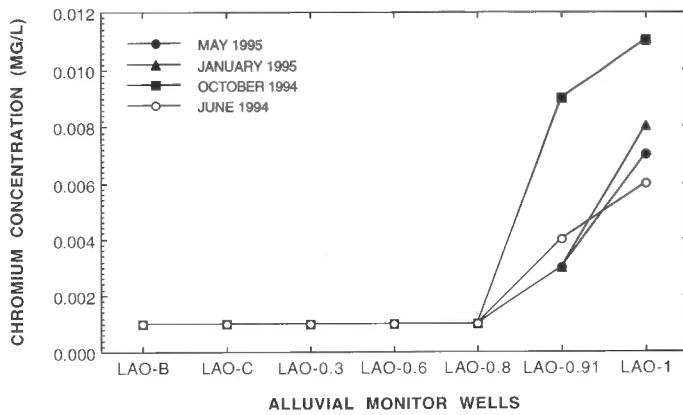


FIGURE 4. Chromium concentrations in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

Energy (DOE) calculated derived concentration guides (DCGs) for ground water are only for comparison purposes because alluvial ground water is not used as a source of water supply in upper Los Alamos Canyon.

Concentrations of chromium at LAO-1 increase by a factor of 12 (0.012 mg/L) above background samples collected from other monitoring wells west of TA-2 (Fig. 4). Potassium dichromate ($K_2Cr_2O_7$) was used prior the mid 1970s as an anti-corrosive agent for the cooling water at TA-2, which is located upgradient from LAO-0.91 and LAO-1 (LANL, 1995). Under moderately oxidizing conditions and nearly neutral pH values that prevail in the alluvium and the Bandelier Tuff in upper Los Alamos Canyon, chromium is predicted to be stable as $CrOH^{2+}$, $Cr(OH)_2^+$, and possibly CrO_4^{2-} based on thermochemical data provided by Rai and Zachara (1984) and Brookins (1988). Being only slightly charged, these species would not be strongly adsorbed onto mineral surfaces within the alluvium. The lack of strong adsorption could account for the elevated concentrations of chromium observed in ground water at LAO-0.91 and LAO-1. Chromium concentrations in LADP-3 are elevated above those measured in LAO1-1.1 (Table 1), suggesting that chromium is not significantly adsorbed onto mineral surfaces within the Bandelier Tuff. The MCL for total chromium is 0.1 mg/L, and no analytical results of ground-water samples collected in upper Los Alamos Canyon exceed this standard.

The highest activities of ^{90}Sr in alluvial ground water (Fig. 5) occur in samples collected from monitoring wells LAO-1, LAO-2 and LAO-3, which imply that TA-2 and TA-21 are contaminant sources for ^{90}Sr . Higher activities of ^{90}Sr were observed in the middle to late 1970s and early 1980s (LANL, 1981); activities of this radionuclide decreased slightly in the early 1990s compared with earlier values (LANL, 1995). Downgradient of TA-2, ^{90}Sr activities have been elevated above background in alluvial ground water for the past several decades (LANL, 1995). Most recent sample analyses show that activities of ^{90}Sr are generally decreasing with time, and activities of this radionuclide in alluvial ground water presently range from 2 to 50 pCi/L. The DCG (drinking water) and MCL for ^{90}Sr is 8 pCi/L. Maximum activities of this radionuclide shift down-gradient to the east over time, illustrating migration of this contaminant plume.

Tritium, in the form of tritiated water (HTO) is a mobile species in ground water and is expected to migrate at the same rate as ground water in the alluvium and other saturated zones. Tritium has a half-life of 12.43 yrs. Its residence time in the alluvium is expected to be less than that of ^{90}Sr , which is adsorbed and, therefore, retarded in migration rate relative to that of water, including tritiated water. Tritium activities have been above background (relative to those in observation wells LAO-B and LAO-C) in all wells downgradient from TA-41 and TA-2 since 1966 when the monitoring wells were installed (Bennett, 1990; EPG, 1990; EPG, 1992-1995; Fig. 6). Releases of tritium resulted from a leak in the cooling water system delay line at the Omega West Reactor at TA-2 (discussed in detail in EPG, 1995). Tritium activities fluctuate in observation wells farther downgradient (LAO-2, LAO-3, LAO-4, LAO-4.5, LAO-5, and LAO-6) (Fig. 6). Facilities at TA-21 have discharged tritium into Los Alamos Canyon via DP Canyon, probably the result of a leaking tritiated water tank at the tritium facility (LANL, 1981). During the mid-1960s, tritium activities were greater than 200,000 pCi/L in ground-water samples collected from observation well LAO-2 (in DP Canyon). Tritium activities in all observation wells have decreased since the 1960s (Fig. 6).

Concentrations of uranium are generally within the microgram per liter ($\mu g/L$) range within alluvial ground water; however, concentrations of this solute that are elevated above a baseline in observation wells LAO-B and LAO-C occur in ground water collected from observation wells LAO-2 and LAO-3 (Fig. 7). Elevated concentrations of uranium have been documented in surface water samples collected in DP Canyon (LANL, 1981). These concentrations may account for the distribution of uranium concentrations observed in alluvial ground water east of the DP

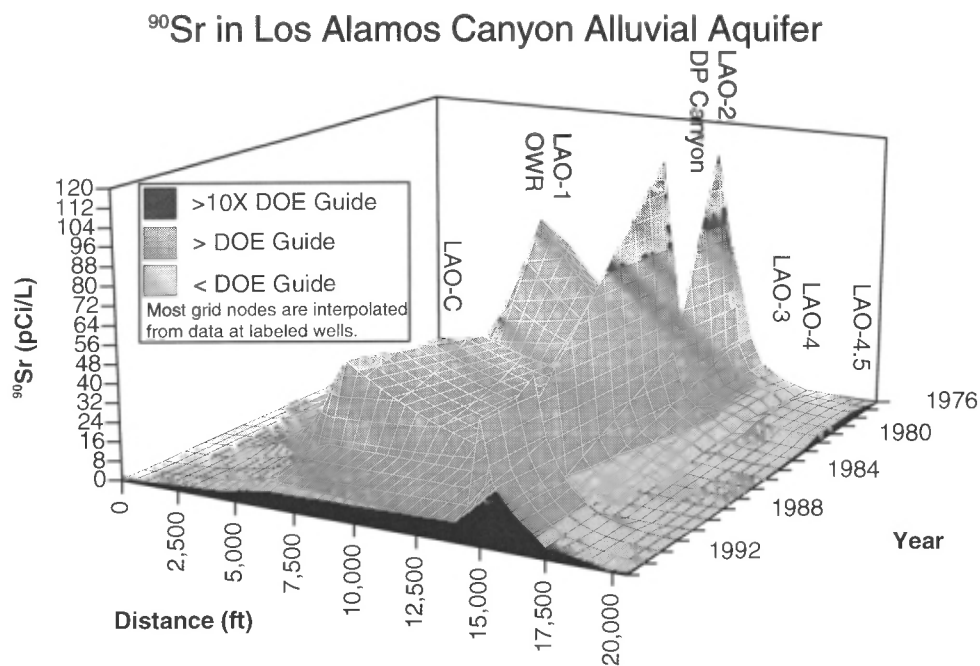


FIGURE 5. Distribution of ^{90}Sr activities in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

Tritium in Los Alamos Canyon Alluvial Aquifer

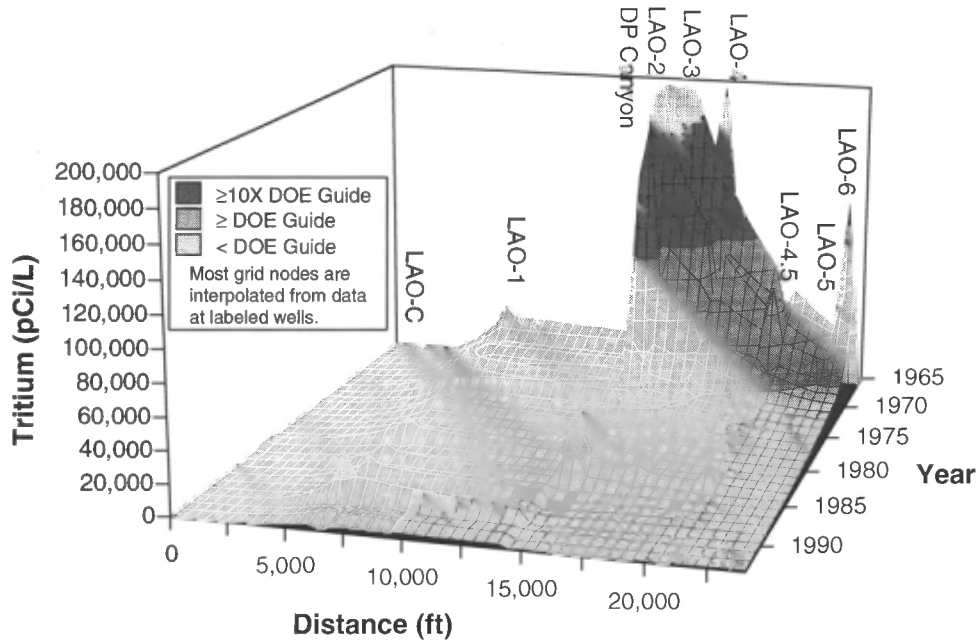


FIGURE 6. Distribution of ³H activities in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

Canyon and Los Alamos Canyon confluence, because surface water is directly connected to alluvial ground water. Concentrations of uranium in alluvial ground water are significantly below the EPA MCL of 20 µg/L and the state of New Mexico standard of 5 mg/L.

Although the ground-water flow rate is substantial (274 m/yr, Gallaher, 1995), it is clear that a complete flushing of ⁹⁰Sr, chromium, uranium and other solutes within the alluvium in upper Los Alamos Canyon has not occurred. These data suggest that contaminants remain in the sediments and alluvial ground water in upper Los Alamos Canyon. Trends in the data also suggest that residual releases may occur from the source inventories at TA-2, TA-21, and TA-41 (LANL, 1995).

GEOCHEMICAL EQUILIBRIUM MODELING

Solid-solution phase calculations were performed with the computer code MINTQA2 (Allison et al., 1991) using analytical results obtained from filtered (less than 0.45 µm) alluvial ground-water samples collected in 1994. The purpose of the calculations was to assess the importance of precipitation reactions and to determine speciated forms of natural and anthropogenic solutes. The saturation index (SI) is a measure of the degree of undersaturation or oversaturation of a solid phase in water [SI = log₁₀ {activity product/ solubility product}; at equilibrium SI = 0 ± 0.5].

Alluvial ground water is calculated to be in equilibrium with both silica glass and silica precipitate but oversaturated with respect to cristobalite (Fig. 8). Thermodynamic (solubility) data contained in MINTQA2 show that silica glass has a slightly lower solubility (10^{-3.02} M) than silica precipitate (10^{-2.71} M) and the glass is less reactive than the amorphous precipitate. Volcanic glass is abundant in the Bandelier Tuff (Broxton et al. 1995a), and is an important source of detritus in the alluvium. Amorphous silica glass and silica precipitate could be important adsorbents for radionuclides (such as ⁹⁰Sr) in alluvial ground water because of their net negative surface charge above pH 2 (Stumm and Morgan, 1996) and their larger surface areas relative to crystalline silicates. Calculations also show that alluvial ground water is oversaturated with respect to sanidine and other silicates (biotite and hornblende) observed in the Bandelier Tuff (not shown in Fig. 8). These calculations imply that most high-temperature silicates that formed in the Bandelier Tuff during magma genesis and subsequent deposition are not in equilibrium with alluvial ground water, because the SI values are greater than 0.5. Alluvial ground water approaches equilibrium with respect to amorphous Al(OH)₃ along the ground-water flow path at several monitoring wells (Fig. 8). This phase is thermodynamically predicted to precipitate from solution during the

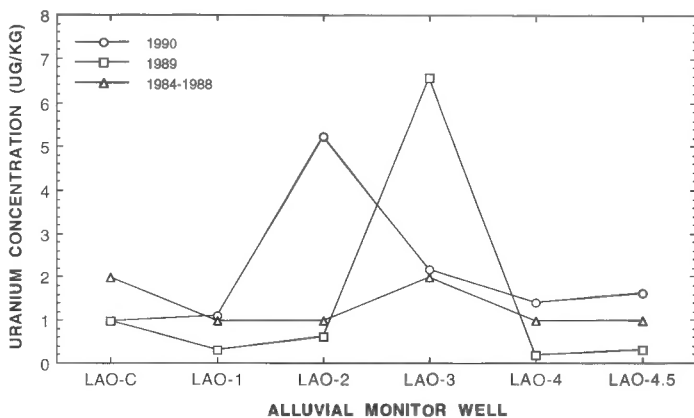


FIGURE 7. Uranium concentrations in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

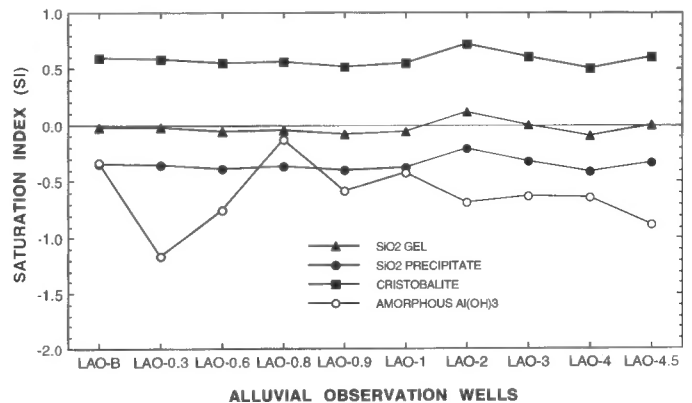
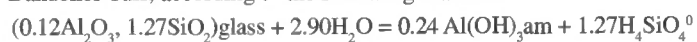


FIGURE 8. Saturation indices (SI = log₁₀ activity product/solubility product) for alumina and silica phases in alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico. The computer code MINTQA2 (Allison et al., 1991) was used for the calculations.

hydrolysis of aluminum-rich volcanic glass, with a composition of 12 wt.% Al_2O_3 and 76 wt.% SiO_2 (Broxton, unpubl. data) present in the Bandelier Tuff, according to the following reaction:



The adsorptive characteristics of amorphous $\text{Al}(\text{OH})_3$, which include its pH at point of zero charge ($\text{pH}_{\text{pzc}} = 5.0$; Stumm and Morgan, 1996) and its large surface area, should enhance removal of cationic solutes under near-neutral pH conditions. At pH values > 5 , amorphous $\text{Al}(\text{OH})_3$ has negative surface charge sites available for cation exchange. In addition, continued hydrolysis of the glass and amorphous $\text{Al}(\text{OH})_3$ may enhance the precipitation of kaolinite and smectite, which are found as minor constituents in glass-rich portions of the Bandelier Tuff (Broxton et al., 1995a; LANL, 1995).

Calculations using MINTEQA2 suggest that total dissolved strontium, consisting mainly of nonradiogenic strontium with very small concentrations of ^{90}Sr (50 pCi/L is equivalent to $10^{-14.4}$ M strontium), in alluvial ground water is stable as Sr^{2+} (Fig. 9). The aqueous complex SrCO_3^0 is stable above a pH value of 9.6 based on MINTEQA2 results and is not present in significant concentrations at the lower pH values characteristic of the alluvial aquifer. This neutral complex does not adsorb onto mineral surfaces above their pH_{pzc} , which are characterized by a net negative surface charge, as strongly as Sr^{2+} (Stumm and Morgan, 1996).

Alluvial ground water is predicted to be undersaturated with respect to solid strontium sulfate and carbonate phases (Fig. 9) and precipitation of these two minerals is unlikely. Alluvial ground water approaches equilibrium with barite (BaSO_4) along the ground-water flow path. Barite is relatively insoluble ($K_{\text{sp}} = 10^{-9.98}$ M, Allison et al., 1991) requiring less than 0.05 and 10 ppm of dissolved barium and sulfate, respectively, to reach mineral saturation. Coprecipitation of strontium with barium, as $\text{Ba}_{1-x}\text{Sr}_x\text{SO}_4$, however, is thermodynamically possible at low temperatures based on both model simulations using MINTEQA2 and experimental results reported by Felmy et al. (1993). Barite and celestite (SrSO_4) have the same crystal structure and show complete solid solution at low temperatures, and synthesized materials commonly have variable Ba-Sr mole fractions (Felmy et al., 1993). Future work in this area will have applications to remediating soil and ground water at industrial sites contaminated by barium and strontium, where coprecipitation of these metals is a viable remediation option.

Results of geochemical modeling infer that rather than precipitating as a stoichiometrically pure phase, Sr^{2+} probably undergoes cation exchange reactions with different adsorbents including solid organic matter, amorphous solids, and clay minerals. Strontium effectively competes for exchange sites with other divalent and monovalent cations such as Ca^{2+} and Mg^{2+} , Na^+ , and K^+ . In addition to cation exchange, radioactive decay and hydrodynamic dispersion and mixing partially account for the decreased activity of ^{90}Sr observed along the ground-water flow path in the alluvium in upper Los Alamos Canyon.

To examine the geochemistry of uranium, MINTEQA2 (Allison et al. 1991) was used to determine stable dissolved species of this solute. Cal-

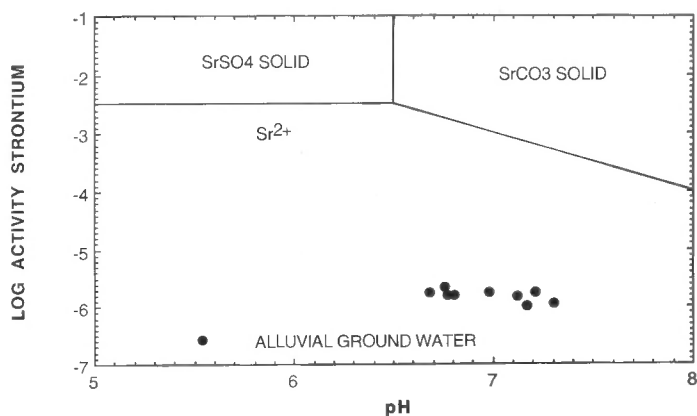


FIGURE 9. Activity versus pH diagram for the $\text{Sr-SO}_4\text{-HCO}_3\text{-H}_2\text{O}$ system at 25°C for alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico.

culations suggest that uranium [U(VI)] is stable mainly as $\text{UO}_2(\text{CO}_3)_2^{2-}$ with small percentages of UO_2CO_3^0 between pH values of 6.8 and 7.3 (Fig. 10). These two U(VI) species have been shown experimentally to adsorb only partially onto mineral surfaces (such as kaolinite, smectite, hydrous iron oxides, silica glass, and solid organic matter) at nearly neutral and higher pH values in the presence of CO_2 gas (Hsi and Langmuir 1985; Waite et al. 1994). Smectite, maghemite, and hematite occur in small amounts (less than 2 wt.%) throughout the Bandelier Tuff (Broxton et al., 1995a) and alluvium. Smectites with a large surface area (600-800 m^2/g ; Stumm and Morgan, 1996) are highly selective for adsorbing cationic radionuclides (Brookins, 1984). Ferric oxyhydroxide and magnetite and its alteration products such as hematite, especially within the vapor phase portion of the Bandelier Tuff, have an affinity for uranium species through surface complexation (Hsi and Langmuir 1985; Ho and Miller 1986; Waite et al., 1994). Since only partial adsorption of this species to mineral surfaces is expected, varying uranium concentrations are observed in alluvial ground water (Fig. 7).

SORPTION EXPERIMENTS

Batch sorption experiments for strontium were conducted on 20 soil samples and 16 channel sediment samples collected in TA-2, TA-21, and TA-41, upper Los Alamos Canyon (Kung, 1995). Desorption experiments were conducted after the sorption experiments were completed. Sorption coefficients (K_d) for strontium ranged from 15.8 to 67.7 ml/g, with a mean value of 35.7 ml/g, for the soils and from 8.8 to 41.3 ml/g, with a mean value of 21.4 ml/g, for the channel sediments (Kung, 1995). The K_d is the mass of adsorbate (grams of strontium) per mass of adsorbent (grams of soil or channel sediment) per equilibrium concentration of adsorbate (grams/milliliter). Strontium adsorption (cation exchange) onto Los Alamos Canyon soils and channel sediments was found to be strongly dependent on solid organic matter (Fig. 11) and less dependent on clay-sized material for all soil and channel sediment samples. Solid organic matter occurs as surface coatings on soil and sediment particles, which hinders the availability and reactivity of additional exchange sites on clay minerals. The K_d values for strontium, measured on a poorly-developed soil and channel sediments exposed near NM-4 containing small amounts of solid organic matter (< 1 wt%), range from zero to 10 ml/g (Fig. 11) (Kung, unpubl. data). This decrease in strontium sorption capacity of the organic poor-soils and sediments near NM-4 suggests that the mobility of strontium will be enhanced in the eastern portion of upper Los Alamos Canyon. Because the K_d values for strontium vary for the soils and sediments, different K_d values should be used rather than one single value in transport calculations for alluvial ground water.

Approximately 30% of the sorbed strontium was desorbed from the channel sediment samples (Kung, 1995). This suggests that semireversible cation exchange is the preferred adsorption process, rather than specific adsorption (surface complexation) involving iron oxyhydroxides and other adsorbents. Cation exchange involving strontium can be represented by

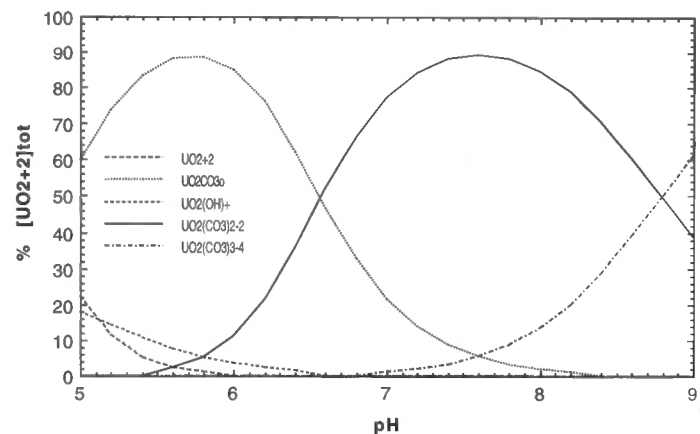


FIGURE 10. Uranyl in LAO-B, alluvial ground water, upper Los Alamos Canyon, Los Alamos, New Mexico. Log molality uranium = -8.4 and log molality HCO_3^- = -3.1 at 9.2°C .

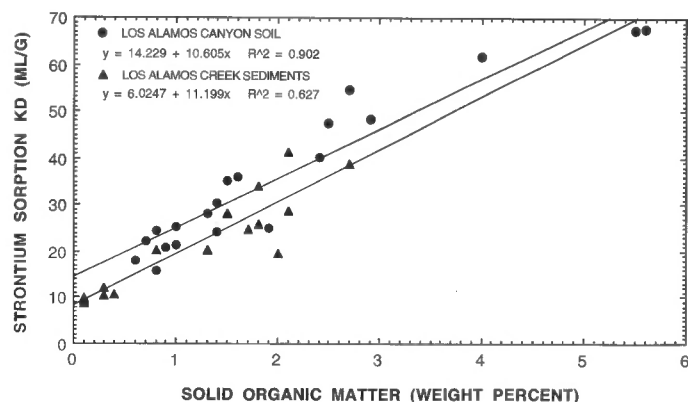


FIGURE 11. Correlation between strontium sorption coefficients (K_d) and percentage of solid organic matter for soils and channel sediments, upper Los Alamos Canyon, Los Alamos, New Mexico (Kung, 1995).

a reaction with solid organic matter consisting of aromatic-carboxylic-phenolic functional groups (Fig. 12). Complexation of metals, including strontium, with solid organic matter occurs at a large number of different reactive sites with binding affinities ranging from weak forces of attraction (water bridge) to formation of highly stable coordinate linkages such as a chelate (ring) structure (Stevenson, 1994). Results of the sorption experiments show that soils containing higher amounts of solid organic matter will remove strontium from solution to a greater extent than organic-poor channel sediments. Sorption coefficients for strontium in the alluvium are expected to be lower than those of the soils, because of lesser amounts of solid organic matter.

An average retardation factor (R_f) for strontium in the alluvium can be approximated using the average K_d value for channel sediments by the following equation:

$$R_f = \frac{1+pK_d}{n} = 1 + \frac{(1.42\text{g/cm}^3)(21.4\text{ml/g})}{0.30} = 102.3$$

where p is the bulk density (Rogers and Gallaher, 1995) and n is the effective porosity (Gallaher, 1995). Using an average ground water flow velocity of 274 m/yr for the alluvium (Gallaher, 1995), strontium is predicted to migrate at an average rate of 2.7 m/yr. At this rate, in the 53 yrs since 1943, when the first reactor was constructed at TA-2, strontium discharged at that time should have migrated 143 m. This distance is smaller compared to the widespread distributions of ^{90}Sr observed in the alluvium in upper Los Alamos Canyon (see Fig. 5). Several possibilities account for this discrepancy in strontium mobility between field observations and experimental results. Aqueous solutions containing ^{90}Sr were discharged to Los Alamos creek and DP creek, which contain small amounts of solid organic matter. These channel sediments are characterized by small K_d and R_f values for strontium enabling a faster migration of this radionuclide in active drainage channels. Through surface-water transport, suspended sediments containing adsorbed ^{90}Sr are carried along the drainage channels, creating a line source for strontium distributions in upper Los Alamos Canyon. In addition, colloidal transport of ^{90}Sr may increase the distribution of this radionuclide in alluvial ground water.

CONCLUSIONS

The ground-water pathway is one of the primary mechanisms for migration of solutes including ^3H , ^{90}Sr , and metals in upper Los Alamos Canyon. Surface water infiltration creates a saturated zone in the allu-

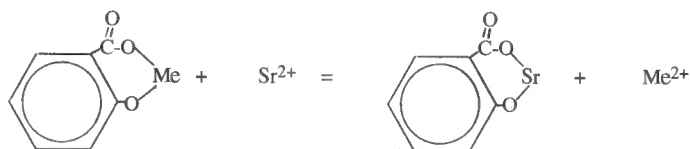


FIGURE 12. Reaction involving strontium with solid organic material consisting of aromatic-carboxylic-phenolic functional groups. Me represents a divalent metal such as Ca^{2+} or Mg^{2+} .

vium of this canyon within the Laboratory boundaries, which is longitudinally and seasonally varying in extent. Alluvial ground water varies from a native $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ ionic composition to a $\text{Na}^+\text{-Ca}^{2+}\text{-Cl}^-\text{-HCO}_3^-$ ionic composition, with increasing chloride and sodium concentrations occurring down-gradient of facility discharges.

Down-gradient of TA-2, activities of ^{90}Sr and ^3H have been elevated above background in alluvial ground water for the past several decades. Analyses of most recent samples show that activities of ^{90}Sr in alluvial ground water range from 2 to 50 pCi/L and are generally decreasing with time. Maximum activities of this radionuclide shift down-gradient to the east over time, illustrating migration of this contaminant plume.

Results of calculations using MINTEQA2 suggests that strontium is stable as Sr^{2+} in alluvial ground water, which is undersaturated with respect to solid strontium sulfate and carbonate phases. Thus Sr^{2+} , rather than precipitating as a stoichiometrically pure phase, probably undergoes cation exchange reactions with solid organic matter and other amorphous and crystalline phases. This process partially removes ^{90}Sr from solution. Sorption coefficients (K_d) for strontium, measured on Los Alamos Canyon soils and channel sediments, range from 15.8 to 67.7 ml/g, with a mean value of 35.7 ml/g, for the soils and from 8.8 to 41.3 ml/g, with a mean value of 21.4 ml/g, for the channel sediments. Strontium exchange was found to be strongly dependent on solid organic matter and less dependent on clay-sized material for all soil and channel sediment samples. Because the K_d values for strontium vary for the soils and sediments, different K_d values should be used rather than one single value in transport calculations for alluvial ground water. Additional sources of ^{90}Sr occur in DP Canyon, which increases the distribution of this radionuclide within active drainage channels. Colloidal transport and surface water transport probably are important factors that contribute to the ^{90}Sr distributions observed in upper Los Alamos Canyon.

ACKNOWLEDGMENTS

This work was funded by the U.S. Department of Energy through the Los Alamos National Laboratory Environmental Restoration Project. We thank Bruce Gallaher for providing hydrological data and information; Cyndi Kruger of Golder and Associates for implementing the field investigations at TA-2 and TA-41; Jenny Harris of ERM for providing analytical data on soils, sediments, surface water and ground water; Jennifer Murphy of CST-7 for preparation of figures; and Allyn Pratt for funding the field work and providing administrative support. Earlier drafts of this paper were greatly improved through thoughtful critiques provided by Dr. Wesley Bradford, Mr. David Broxton, Mr. Bruce Gallaher, and Dr. Everett Springer. Special thanks are given to David Broxton for his technical guidance and support in geology throughout this phase of the RFI investigation.

REFERENCES

- Adams, A. I., Goff, F. and Counce, D., 1995, Chemical and isotopic variations of precipitation in the Los Alamos region, New Mexico: Los Alamos National Laboratory, Report LA-12895-MS.
- Allison, J. D., Brown, D. S. and Novo-Gradac, K. J., 1991, MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual, EPA/600/3-91/021, Office of Research and Development, Athens, Georgia.
- Bennett, K. D., 1990, Annotated bibliography of geologic, hydrogeologic, and environmental studies relevant to solid waste management units at Los Alamos National Laboratory: Los Alamos National Laboratory, Report LA-UR-90-3216.
- Blake, W. D., Goff, F., Adams, A. I. and Counce, D., 1995, Environmental geochemistry for surface and subsurface waters in the Pajarito Plateau and outlying areas, New Mexico: Los Alamos National Laboratory, Report LA-12912-MS.
- Brookins, D. G., 1984, Geochemical aspects of radioactive waste disposal: Springer-Verlag, New York, 347 p.
- Brookins, D. G., 1988, Eh-pH diagrams for geochemistry: Springer-Verlag, New York, New York, 176 p.
- Broxton, D. E., Heiken, G. H., Chipera, S. J. and Byers, F. M. Jr., 1995a, Stratigraphy, petrography, and mineralogy of Bandelier Tuff and Cerro Toledo deposits: Earth Science Investigation for Environmental Restoration—Los Alamos National Laboratory technical area 21: Los Alamos National Laboratory, Report LA-12934-MS, p. 33–63.
- Broxton, D. E., P. A. Longmire, P. A., Eller, P. G. and Flores, D., 1995b, Preliminary drilling results for boreholes LADP-3 and LADP-4: Earth science investigation for environmental restoration—Los Alamos National Laboratory Tech-

- nical Area 21: Los Alamos National Laboratory, Report LA-12934-MS, p. 93–109.
- DOE (US Department of Energy), 1988, General environmental protection program, DOE Order 5400.1, Washington, DC.
- EPA (US Environmental Protection Agency), 1990, RCRA permit no. NM0890010515, EPA Region VI, issued to Los Alamos National Laboratory, Los Alamos, New Mexico, effective May 23, 1990: EPA Region VI, Hazardous Waste Management Division, Dallas, Texas.
- EPA (US Environmental Protection Agency), 1986, Test methods for evaluating solid waste, volumes IA and IB: Laboratory manual, physical/chemical methods, SW-846, revision 0, third edition: EPA, Washington, DC.
- EPG (Environmental Protection Group), 1990, Environmental surveillance at Los Alamos during 1989: Los Alamos National Laboratory, Report LA-12000-ENV.
- EPG (Environmental Protection Group), 1992, Environmental surveillance at Los Alamos during 1990: Los Alamos National Laboratory, Report LA-12271-MS.
- EPG (Environmental Protection Group), 1993, Environmental surveillance at Los Alamos during 1991: Los Alamos National Laboratory, Report LA-12572-ENV.
- EPG (Environmental Protection Group), 1994, Environmental surveillance at Los Alamos during 1992: Los Alamos National Laboratory, Report LA-12764-ENV.
- EPG (Environmental Protection Group), 1995, Environmental surveillance at Los Alamos during 1993: Los Alamos National Laboratory, Report LA-12973-ENV.
- Felmy, A. D., Rai, D., and Moore D. A., 1993, The solubility of $(\text{Ba},\text{Sr})\text{SO}_4$ precipitates: thermodynamic equilibrium and reaction path analysis: *Geochimica et Cosmochimica Acta*, v. 57, pp. 4345–4363.
- Gallaher, B., 1995, Groundwater velocities in Los Alamos Canyon, Los Alamos: National Laboratory Memorandum ESH-18/WQ&H-95-409 to ESH-18 Reading File from Bruce Gallaher (ESH-18), Los Alamos, New Mexico.
- Ho, C. H. and Miller, N. H., 1986, Adsorption of uranyl species from bicarbonate solution onto hematite particles: *Journal of Colloid and Interface Science*, v. 110, p. 165–171.
- Hsi, C. D. and Langmuir, D., 1985, Adsorption of uranyl onto ferric oxyhydroxides: application of the surface complexation site-binding model: *Geochimica et Cosmochimica Acta*, v. 49, p. 1931–1941.
- Kung, S., 1995, Sorption and desorption of cesium and strontium on TA-2 and TA-41 soils: progress report to field unit 4: Environmental Restoration Project, Los Alamos National Laboratory, 164 p.
- LANL (Los Alamos National Laboratory), 1981, Formerly utilized MED/AEC sites remedial action program, radiological survey of the site of a former radioactive liquid waste treatment plant (TA-45) and the effluent receiving areas of Acid, Pueblo and Los Alamos Canyons, Los Alamos, New Mexico: Los Alamos National Laboratory, Report LA-8890-ENV (DOE/EV-0005/30).
- LANL (Los Alamos National Laboratory), 1995, RFI Work Plan for Los Alamos Canyon and Pueblo Canyon: Los Alamos National Laboratory, Report LA-UR-92-3825.
- Purtymun, W. D., 1995, Geologic and hydrologic records of observation wells, test holes, test wells, supply wells, springs, and surface water stations in the Los Alamos Area: Los Alamos National Laboratory, Report LA-12883-MS.
- Rai, D. and Zachara, J. M., 1984, Chemical attenuation rates, coefficients, and constants in leachate migration, volume 1: a critical review: Electric Power Research Institute Report EPRI EA-3356, prepared by Battelle, Pacific Northwest Laboratories.
- Rogers, D. B. and Gallaher, B. M., 1995, Unsaturated hydraulic characteristics of the Bandelier Tuff: Los Alamos National Laboratory, Report LA-12968-M5.
- Stevenson, F. J., 1994, Humus chemistry: genesis, composition, and reaction; second edition: Wiley and Sons, New York, NY, 496 p.
- Stumm, W. and Morgan, J. J., 1996, Aquatic chemistry, third edition: Wiley and Sons, New York, 1022 p.
- Waite, T. D., Davis, J. A., Payne, T. E., Waychunas, G. A. and Xu, N., 1994, Uranium (VI) adsorption to ferrihydrite: application of a surface complexation model: *Geochimica et Cosmochimica Acta*, v. 58, pp. 5465–5478.