



## ***Natural major and trace element background geochemistry of selected soil profiles, Los Alamos, New Mexico***

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# NATURAL MAJOR AND TRACE ELEMENT BACKGROUND GEOCHEMISTRY OF SELECTED SOIL PROFILES, LOS ALAMOS, NEW MEXICO

ERIC V. MCDONALD<sup>1</sup>, PATRICK A. LONGMIRE<sup>2</sup>, PAULA M. WATT<sup>3</sup>, RANDALL T. RYTI<sup>4</sup> and STEVEN L. RENEAU<sup>1</sup>

<sup>1</sup>Geology and Geochemistry Group, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545; <sup>2</sup>Environmental Science and Waste Technology Group, J534, Los Alamos National Laboratory, Los Alamos, NM 87545; <sup>3</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131; <sup>4</sup>Neptune and Co., Inc., 1505 15th St., Los Alamos, NM, 87544

**Abstract**—Background-elemental concentrations for 24 metals and nonmetals relevant to the Environmental Restoration Project at Los Alamos National Laboratory were determined for a variety of soils and geomorphic settings across the Pajarito Plateau. Approximately 175 soil samples were analyzed for background-elemental concentrations using HNO<sub>3</sub> (leachable element concentration) and HF (total element concentration) sample digestion techniques. Leachable background elemental concentrations in soils provide information for risk calculations relevant to the bioavailability of elements. Background-elemental concentrations in soils on the Pajarito Plateau generally vary with parent material, the degree of soil development, and other factors. Soil B horizons typically have higher concentrations of several trace elements, including As, Be, Th, and U, relative to soil A and C horizons. Higher concentrations of these trace elements in B horizons may be due to higher abundances of chemically active phases that enhance the adsorption of metals, such as ferric (oxy)hydroxides and clay minerals. Variations in soil-elemental concentrations may also be related to mineralogical variations in soil parent materials. Background-elemental soil data are used to determine possible contamination or to establish clean-up levels based on the calculation of a horizon-specific upper tolerance limit (UTL) for each element.

## INTRODUCTION

Determining environmental impacts to surface waters, groundwaters, soils, sediments, and bedrock at Los Alamos National Laboratory (LANL) from Laboratory activities over the past ca. 50 yrs requires knowledge of background-elemental chemistry of geological and hydrological media. Accurate determination of natural background levels forms the basis for the statistical analysis to support risk management decisions for the Environmental Restoration Project and are required as part of the Resource Conservation and Recovery Act (RCRA) corrective action process developed by the U.S. Environmental Protection Agency (EPA). Specifically, adequate information about background elemental chemistry is required to (1) develop sampling and remediation strategies at sites, (2) understand processes controlling contaminant transport, (3) distinguish between contaminated and non-contaminated media, and (4) establish cleanup levels for sites to be remediated. During the past four years, extensive analysis of soils have been conducted across LANL to determine the natural background levels of a variety of major and trace metals and nonmetals. Development of a defensible background elemental data set for soils at LANL, however, has been complicated because the geochemical characteristics of soils on the Pajarito Plateau vary widely, largely due to local variations in parent material, topography, soil age, surficial processes, climate, and vegetation.

The purpose of soil characterization studies presented here is to determine the nature and variability of background-elemental concentrations and soil parameters within different soil horizons for a variety of soil profiles at LANL. We summarize work presented in two extensive reports by Longmire et al. (in press a, b) including: (1) results of soil characterization studies conducted by Watt (1996) and McDonald (unpubl., 1993); (2) analytical methods used to determine background chemical (analyte) distributions in soils; (3) relations among background levels of trace elements, soil chemistry, and the degree of soil development (pedogenesis); and (4) statistical analysis of the background-elemental data set for soils.

## SAMPLING SITES AND METHODS

### Site characteristics and field methods

Twenty-one soil profiles distributed across the Pajarito Plateau were described in the field and sampled for chemical analyses (Fig. 1; Table 1). These localities allowed sampling of many of the varied soils and geomorphic settings that occur on the Pajarito Plateau, providing an evaluation of the variability in soil characteristics and chemistry within several of the soil series previously described by Nyhan et al. (1978). Most sampled soils were collected from mesa tops. Other geomorphic settings sampled included Holocene and Pleistocene alluvium and colluvium (Table 1).

TABLE 1. Summary of soil sample site locations and environmental settings.

Site #	Technical Area	General Location	Soil Classification	Vegetation	Topographic Setting	Surficial Material
Lower Los Alamos Canyon	TA-72	Los Alamos Canyon	Typic Ustipsamment	piñon-juniper	canyon bottom	Holocene alluvium
Upper Los Alamos Canyon	TA-72	Los Alamos Canyon	Cumelic Haploxeroll	fir	canyon bottom	Holocene colluvium
EG&G Gully	TA-73	Los Alamos	Udic Ustochrept	piñon-juniper	mesa-top gully	Holocene colluvium
Twomile Mesa	TA-69	Twomile Mesa	Typic Haplustalf	ponderosa pine	mesa top	Pleistocene alluvium
Water Tanks Trench	TA-16	West Jemez Road	Calcic Haploxeralf	ponderosa pine	base of western scarp	Holocene colluvium
Frijoles Mesa	TA-49	Frijoles Mesa	Typic Dystrandept	ponderosa pine	mesa top	El Cajete Pumice
Ancho Canyon Mesa	TA-39	State Highway 4	Calcic Haploxeralf	piñon-juniper	mesa top	pre-El Cajete soil
Fracture Fill	TA-46	Mesita del Buey	no soil	piñon-juniper	mesa top	pre-El Cajete soil
AC-1	TA-33	Ancho Canyon	Andic Dystrachrept	ponderosa pine	canyon bottom	Holocene alluvium
TA-16-WT-1	TA-16	West Jemez Road	Udic Paleustalf	ponderosa pine	base of western scarp	pre-El Cajete colluvium
TA-16-S-1	TA-16	West Jemez Road	Udic Paleustalf	ponderosa pine	alluvial fan	Pleistocene alluvium
TA-16-S-2	TA-16	West Jemez Road	Typic Haplustalf	ponderosa pine	base of western scarp	Holocene colluvium
TA-51	TA-51	Mesita del Buey	Lithic Ustochrept	piñon-juniper	mesa top	pre- and post El Cajete soils
TA-63-1	TA-63	Pajarito Road	Typic Haplustalf	grass	mesa top	pre- and post El Cajete soils
TA-63-2	TA-63	Pajarito Road	Typic Haplustalf	grass	mesa top	pre- and post El Cajete soils
TA-63-3	TA-63	Pajarito Road	Lithic Ustochrept	grass	mesa top	post El Cajete sediment
TA-63-4	TA-63	Pajarito Road	Udic Ustochrept	grass	mesa top	post El Cajete sediment
TA-67-67-E1	TA-67	Pajarito Mesa	Typic Haplustalf	piñon-juniper	mesa top	pre- and post El Cajete soils
TA-67-67-E3	TA-67	Pajarito Mesa	Typic Haplustalf	piñon-juniper	mesa top	pre- and post El Cajete soils
TA-67-67-W1	TA-67	Pajarito Mesa	Typic Haplustalf	piñon-juniper	mesa top	pre- and post El Cajete soils
TA-67-67-W5	TA-67	Pajarito Mesa	Typic Haplustalf	piñon-juniper	mesa top	pre- and post El Cajete soils

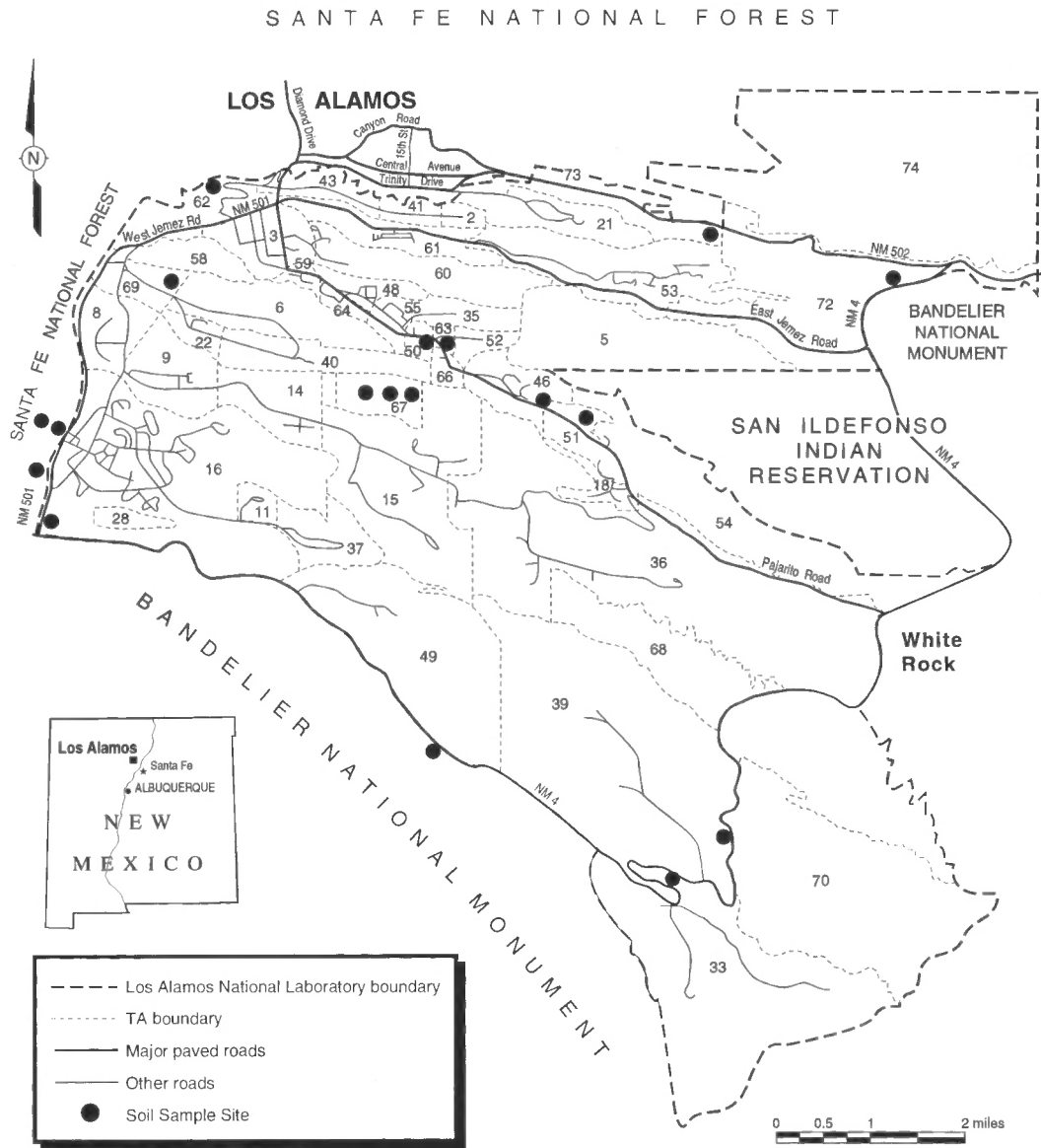


FIGURE 1. Map of Los Alamos National Laboratory showing distribution of background soil sample sites (solid circles). Several sites shown on map represent more than one sampled soil profile. Numbers within Technical Area (TA) boundaries are TA number.

Elevation of studied soils ranges from 1900 to 2400 m. Annual precipitation averages about 34 to 48 cm and daily air temperature averages about 9.6 to 8.8°C, with precipitation increasing and temperature decreasing east to west across the plateau (Bowen, 1992). Vegetation ranges from piñon-juniper woodland in the drier, eastern part of the Laboratory to ponderosa pine forests in the wetter, western part (Table 1). The parent materials for the soils include weathered and eroded Bandelier Tuff, alluvium partially derived from the Bandelier Tuff and/or Tschicoma Formation dacite, wind-blown sediment, and the ca. 50-60 ka El Cajete pumice (ages from Reneau et al., 1996).

Soils were described using standard terminology and techniques (Soil Conservation Survey, 1981). Soils were sampled vertically by genetic horizon with a single, representative bulk sample of approximately one kilogram (kg) collected for each horizon. Unweathered Bandelier Tuff and clay-size material lining vertical fractures in the tuff were also collected at a few sites. Depths of individual soil horizons sampled varied among soils but all soils were continuously sampled from the surface to the base of the profile (depths varied from 25 to 394 cm).

#### Sample preparation and analytical methods

Soil samples were passed through a 2.0 mm (20 mesh) sieve to remove pebbles and roots. Soil samples were either air-dried or dried in a

forced-air circulation oven at 105°C for 24 hrs. All samples were split into two representative fractions, with one fraction for soil characterization and the other for trace element chemistry. All equipment used in sample preparation was cleaned between each sample. Physical and chemical properties, consisting of texture, cation exchange capacity (CEC), extractable ferric (oxy)hydroxides, and pH, were determined for all soil horizons using standard laboratory soil characterization procedures (American Society of Agronomy, 1986).

Concentrations of trace elements were analyzed using two sample digestion methods: total element concentrations extracted from the complete digestion of soil material using concentrated hydrofluoric acid (HF); and partial element concentrations extracted from partial digestion of soil material using concentrated nitric acid (HNO<sub>3</sub>) at pH 1 (EPA Method 3050A; EPA, 1986). The latter method is used for estimating the bioavailability of elements, information required for performing risk analyses, by approximating the partial dissolution of soil particles, consisting of coatings including clay minerals, ferric (oxy)hydroxides, and calcium carbonate, that might occur in a low pH environment inside the human gastrointestinal system (LANL unpubl.; EPA, 1986). In all instances, element concentrations from partial digestion techniques are less than the total-element concentrations. Trace element chemistry was determined using EPA-SW846 analytical methods (Table 2), described in detail in

TABLE 2. Summary of analytical techniques used in background soil characterization at Los Alamos National Laboratory.

Element	Technique	Element	Technique	Element	Technique
Al	ICPES	Cu	ICPES	SO <sub>4</sub>	IC
As	ETVAA	Fe	ICPES	Ta	ICPMS
Ba	ICPES	K	ICPES	Tl	ICPMS
Be	ICPES	Mg	ICPES	Th	ICPMS
Ca	ICPES	Mn	ICPES	U	ICPMS
Cd	ICPES	Na	ICPES	V	ICPES
Cl	IC	Ni	ICPES	Zn	ICPES
Co	ICPES	Pb	ICPES		
Cr	ICPES	Sb	ICPES		

IC: ion chromatography

ICPES: inductively coupled plasma emission spectroscopy

ICPMS: inductively coupled plasma mass spectrometry

ETVAA: electrothermal vapor atomic absorption spectroscopy

EPA (1986), Gautier and Gladney (1986), and Gladney et al. (1980, 1981). The elements As, Ba, Be, Cr, Hg, Pb, Mn, Sb, Th and U are of primary concern to LANL because numerous potential release sites (PRSSs) and solid waste management units (SWMUs) at the Laboratory may contain elevated concentrations of these elements. Other elements and compounds of secondary importance include Al, Ca, Cd, Cl, Co, Cs, Cu, Fe, K, Mg, Na, Se, Sr, SO<sub>4</sub><sup>2-</sup>, Ta, Ti, Tl, V, Zn and Zr. Radioactive isotopes were not analyzed in this investigation. Quality assurance was provided by concurrent analysis of different National Institute of Standards and Technology (NIST), EPA, and United States Geological Survey (USGS) reference materials described by Gladney et al. (1981). Quality control samples, including duplicates and spiked samples, were analyzed at frequencies specified by the EPA (1986). The lowest detection limits for specific elements and species using ICPES, ICPMS, IC and ETVAA were 0.08 (Be), 0.12 (Ta), 12 (sulfate) and 0.3 (As) ppm, respectively. Precision values for all elements except As were  $\pm 10\%$  and  $\pm 20\%$ , respectively. Precision values of the other were  $\pm 10\%$ .

## CHARACTERIZATION OF BACKGROUND SOILS

### Soil stratigraphy

An important characteristic of many of the soils across the Laboratory is the complex soil stratigraphy that has resulted from one or more soil profiles that are superimposed upon pre-existing (i.e., older) profiles. Complex soil profiles consist of a surface soil that may partially overlap an underlying and now buried soil. The occurrence of buried soils across the Laboratory is particularly relevant to spatial variability of background geochemistry and to the transport and fate of numerous contaminants found at LANL. First, B horizons of these buried soils typically have the strongest degree of horizon development, including the highest concentrations of Fe oxides and clay-sized material. As a result, the close proximity of these buried soil B horizons to the soil surface will directly influence the fate and transport of any surface and subsurface contaminants. Second, where these horizons have been re-exposed at the surface due to recent erosion or excavations, the degree of B horizon development may strongly influence local background geochemistry because the highest concentration of several important trace elements, such as As, Be and U, are usually associated with well-developed, buried soil B horizons (discussed below).

### Soil chemistry

The presence of geochemically reactive phases within the soil environment, including clay minerals, carbonate minerals, and ferric (oxy)hydroxides, are particularly relevant to natural variations in background levels of trace elements as well as the transport and fate of numerous inorganic and organic contaminants found at the Laboratory. Significant variation in the amount of clay-sized material (less than 2 micrometers) occurs among sampled soils. Clay-size material ranges from 0.7 wt% (AC-1) within a C horizon to 63 wt% (Twomile Mesa) within a Bt horizon. Significant variation in the amount of clay-size material can also occur vertically within a single profile. Measurable calcium carbonate content of the soils is variable, ranging from 0.3 wt% (TA-63-2) in a Btk horizon to 100 wt% (Twomile Mesa) in a Bkm horizon; however, most soil horizons have no measurable calcium carbonate. Cation ex-

change capacity (CEC) in the sampled soils ranges from 2.7 meq/100g-soil (AC-1) in an A horizon to 43 meq/100g-soil (TA-51) in an A horizon, which reflects the different types and amounts of clay minerals and variations in organic matter content in these soils. Soil pH ranges from 5.0 (TA-16-S-2) in an A horizon to 7.7 (TA-67-W5) in a C horizon. Overall, sampled B horizons generally have the highest CEC, largely due to a higher clay mineral content. Oxalate-extractable Fe (reported as mean wt% Fe<sub>2</sub>O<sub>3</sub>) ranges from 0.04 wt% (Ancho Canyon Mesa) in a Bt horizon to 1.69 wt% (upper Los Alamos Canyon) in a Bw horizon. Dithionite-extractable Fe (reported as mean wt% Fe<sub>2</sub>O<sub>3</sub>) ranges from 0.26 wt% (AC-1) in a C horizon to 1.26 wt% (TA-67-E1) in a Bt horizon. Generally, higher percentages of dithionite-extractable ferric (oxy)hydroxides occur in well-developed soil profiles containing one or more B horizons than ferric (oxy)hydroxides extracted from the less developed soils. In general, weakly developed soil Bw horizons have higher quantities of amorphous forms of ferric (oxy)hydroxides relative to more developed soil Bt horizons (Birkeland, 1984). With time and increased degrees of soil formation, amorphous and poorly crystalline forms of ferric hydroxides are transformed into more developed crystalline forms (Schwertmann and Taylor, 1989).

## BACKGROUND GEOCHEMISTRY

### Trace element abundance

Mean-element concentrations were evaluated in this study based on variations in concentrations among three master soil horizons (A, B and C horizons, Fig. 2). Transitional horizons were grouped according to the dominant master horizon (e.g., BA horizons were grouped with all B horizons). Most samples were collected from B horizons (n=132), with a smaller number of samples collected from the A (n=25) and C horizons (n=24). Sampling of soil B horizons was emphasized in this study because the B horizons appear to have the greatest degree of spatial variability.

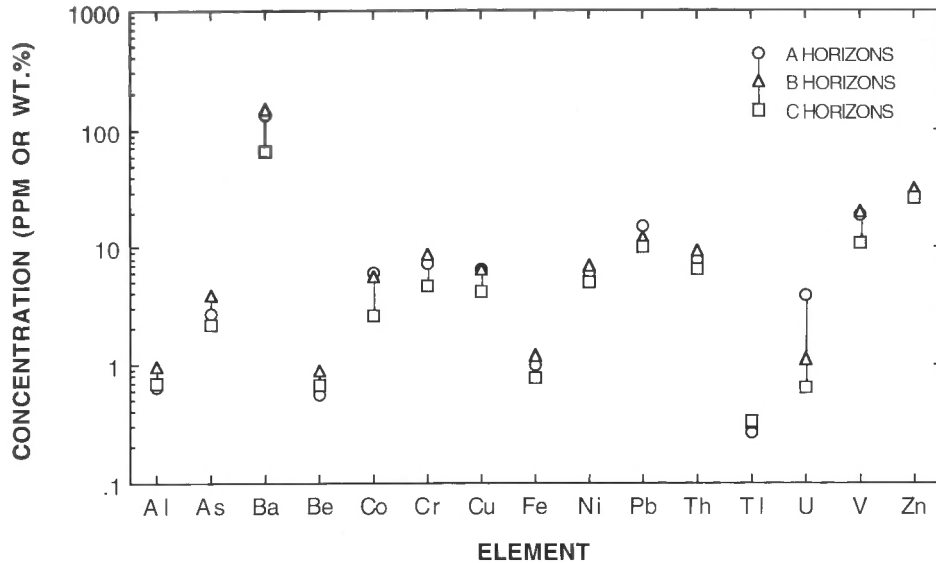
Mean element concentrations resulting from HNO<sub>3</sub> digestion of soil samples vary widely (Fig. 2), primarily reflecting variation among soil parent materials and redistribution of elements from soil-forming processes. Ranges in element distributions in the A, B and C horizons generally exceed a factor of ten for most of the elements (Fig. 2). Soil B horizons generally contain higher concentrations of Al, As, Ba, Be, Cr, Fe, Ni, Tl, Th and V than do A and C horizons. The A horizons sampled during this investigation contain higher concentrations of Co, Pb, and U relative to the B and C horizons, and the C horizons have higher concentrations of Tl relative to the A and B horizons.

### Element redistribution within soil horizons

Element redistribution or leaching within the different soil horizons is evaluated by comparing analytical results from HNO<sub>3</sub> digestion to those obtained from HF digestion (Fig. 3). Large differences in concentrations between the total element and HNO<sub>3</sub>-digested samples suggest that most of the element is chemically fixed within primary silicate minerals with minimal redistribution of the element into secondary surface coatings. By contrast, small differences in element concentrations between HNO<sub>3</sub>-digested samples and total-element analyses suggest that other elements have been largely mobilized and concentrated on surfaces and/or coprecipitated with acid-soluble phases including ferric (oxy)hydroxides, calcium carbonate, solid organic matter, and clay minerals such as smectite and kaolinite.

Aluminum shows the highest mean digestion ratios (5.8-7.6) of all the elements (Fig. 3) suggesting that Al is mainly concentrated within primary silicate phases that are only partially digested by HNO<sub>3</sub> at pH 1. Some Al is associated with smectite and kaolinite (Watt, 1996) and these two clay minerals are partially digested using HNO<sub>3</sub> (Lindsay, 1979), which probably provides the lower ratio of 5.8 in B horizons. Many trace and major elements, including Al, Ba, Th, and U, are structurally incorporated within silicate and oxide lattices associated with volcanic glass within the Bandelier Tuff (Broxton et al., 1995). Lower mean digestion ratios (between 2.4 and 5.8) are observed for As, Ba, Be, Cr, Tl, U and V, suggesting that these elements occur in both primary silicate and oxide minerals and in secondary soil phases. Several trace elements, including

FIGURE 2. Nitric acid ( $\text{HNO}_3$ ) digestible element concentrations in A, B and C horizons of background soils, Los Alamos, New Mexico. Concentrations of aluminum and iron are in units of weight percent; other elements are in units of ppm.



As and Be, show an increase in soils containing well-developed B horizons (discussed below). The lowest mean digestion ratios ( $< 2$ ) are observed for Co, Cu, Fe, Ni, Pb, Th and Zn, suggesting that these elements largely occur within secondary soil phases.

Smaller digestion ratios are observed for Al, As, Be, Ba, Fe, Cr and Th within the B horizons than in the A and C horizons (Fig. 3). This suggests that these elements may have been redistributed within the B horizons and concentrated within secondary soil phases. Other elements, including Pb, U and Zn, have lower digestion ratios within the A horizons relative to the B and C horizons, whereas Cu, Ni and Tl have lower digestion ratios within the C horizons. Uranium has the greatest range of mean digestion ratios (2.0-5.7), illustrating the presence of anthropogenic U (discussed below) within secondary soil phases of A horizons for some mesa top soils (sites TA-63 and TA-67, Table 1). Iron and V are generally distributed uniformly among A, B and C horizons. The HF/ $\text{HNO}_3$  digestion ratio for Fe is approximately 1.6 for the different soil horizons. Iron occurs in different primary silicate and oxide minerals (clay minerals, ferric (oxy)hydroxide,  $\text{Fe}_3\text{O}_4$ , and Fe-bearing silicates) digested by HF and in secondary soil phases (clay minerals, ferric (oxy)hydroxide) digested by  $\text{HNO}_3$ .

#### GEOCHEMISTRY OF IRON AND SELECTED TRACE ELEMENTS

Selected trace elements, including As, Be, Fe, Th and U, can systematically vary as a function of soil age, soil and parent material mineralogy, the amount and composition of eolian dust and other forms of aerosols, the degree of chemical weathering, and pore water chemistry. Because the distribution of As, Be, Fe, Th and U illustrate the spatial variability of natural background levels and because these elements are important with respect to determining potential release sites of contaminants, the distribution of these elements within LANL soils is discussed in more detail below. More detailed discussions of the geochemical characteristics of these trace elements were provided by Longmire et al. (in press, a,b).

#### As, Be and Fe distributions

Bivariate plots of Fe versus As and Fe versus Be for A, B and C soil horizons extracted using  $\text{HNO}_3$  digestion suggests a strong correlation between increases in  $\text{HNO}_3$ -digestible Fe and increased abundances of  $\text{HNO}_3$ -digestible As and Be (Figs. 4, 5). Concentration of  $\text{HNO}_3$ -digestible As and Be are also generally higher in B horizons than in C or A horizons. Furthermore, concentration of As and Be generally increases

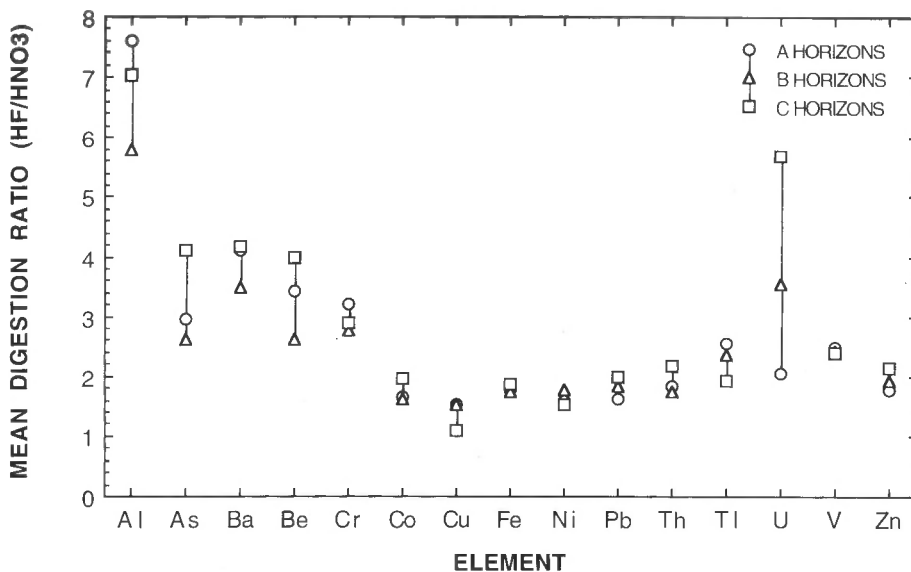


FIGURE 3. Element versus mean element digestion ratios (HF/ $\text{HNO}_3$ ) in A, B and C horizons of background soils, Los Alamos, New Mexico.

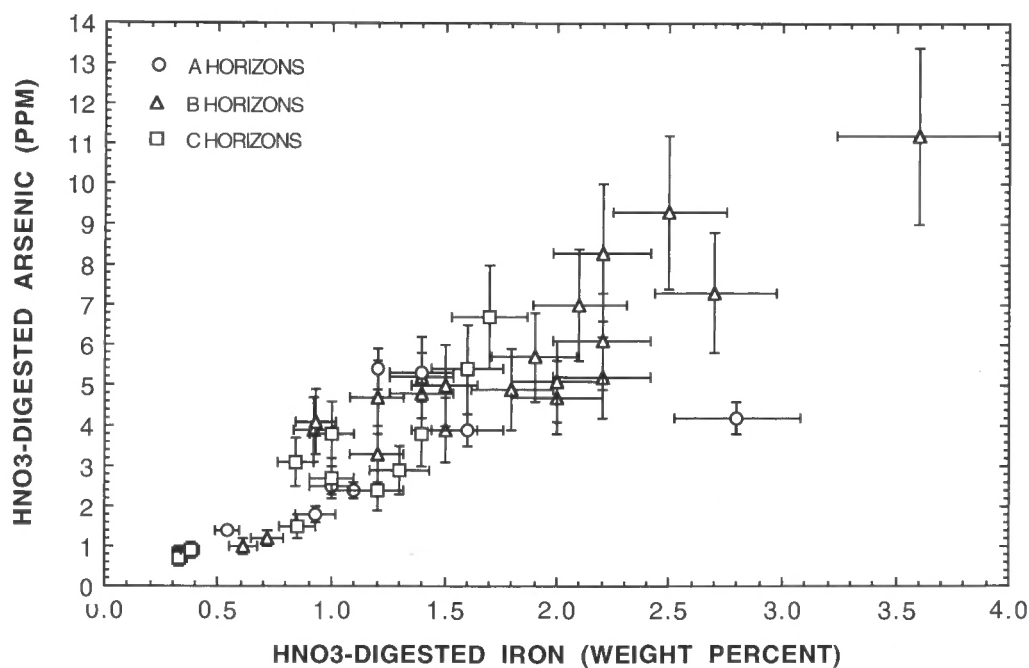


FIGURE 4. Nitric acid ( $\text{HNO}_3$ ) digestion of Fe concentration versus  $\text{HNO}_3$  digestible As concentration in background soils, Los Alamos, New Mexico. Error bars represent  $\pm$  one standard deviation.

with the relative strength of the B horizon, with higher concentrations in well-developed Bt horizons relative to the more weakly-developed Bw horizons. These two relations suggest that enrichment of As and Be in soils on the Pajarito Plateau correlates with increasing soil development, specifically the formation of B horizons containing ferric (oxy)hydroxides and clay minerals. Many studies have shown that the abundance of ferric (oxy)hydroxides and clay minerals increase as B horizon development increases (Birkeland, 1984). These geochemically reactive minerals usually have high surface areas and are characterized by a net-negative surface charge that enhances the adsorption of cationic trace elements in soil environments (Sposito, 1984, 1989). In addition to As and Be, other trace elements, including Cr, Mn and Ni, correlate well with  $\text{HNO}_3$ -digestible Fe in the soil profiles (Longmire et al., in press a, b).

Several studies indicate that adsorption of As and Be may be enhanced from ferric (oxy)hydroxides and clay minerals. Under environmental pH conditions (5-8.5) encountered in most soils at LANL, dissolved As is predicted to occur as neutral species or oxyanions in +3 ( $\text{H}_3\text{AsO}_3^0$ ,  $\text{H}_2\text{AsO}_3^-$ ) or +5 ( $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ) valence states depending on the oxidation-reduction potential (Eh) of the pore water. Studies of As adsorption onto adsorbent surfaces show that uptake is controlled to a large degree by the content of extractable Fe- and Al-hydrous oxides occurring as amorphous or cryptocrystalline phases (Livesey and Huang, 1981). Arsenic adsorption is also largely controlled by the surface area of the adsorbent (Sposito, 1984), and experimental studies have shown that amorphous  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  have high sorptive capacities for As (Holm et al., 1979; Leckie et al., 1980). Beryllium forms hydroxy complexes ( $\text{BeOH}^+$ ,  $\text{Be}(\text{OH})_2^0$ , and

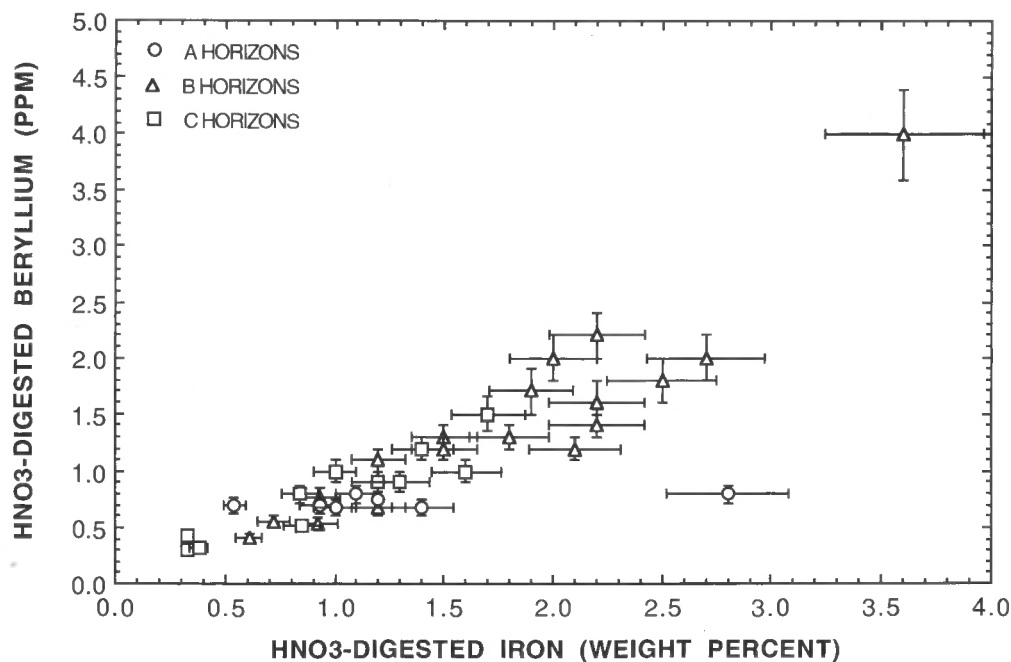


FIGURE 5. Nitric acid ( $\text{HNO}_3$ ) digestion of Fe concentration versus  $\text{HNO}_3$  digestible Be concentration in background soils, Los Alamos, New Mexico. Error bars represent  $\pm$  one standard deviation.

Be(OH)<sub>3</sub>) above pH 6 (Rai and Zachara, 1984). Very little data are available on adsorption and precipitation/dissolution reactions of Be at low temperatures. Available thermochemical data suggest that β-Be(OH)<sub>2</sub> is moderately insoluble and this phase precipitates rapidly from solution (Rai and Zachara, 1984). There is some evidence that Be adsorption onto soil surfaces (iron oxides and clay minerals) is pH dependent. Column experiments (Alesii et al., 1980; Korte et al., 1976) also indicate that Be was more strongly attenuated in soil environments than were Zn, Cd, Ni and Hg. Korte et al. (1976) suggested that calcareous soils high in clay minerals appear to be effective in Be retention. Although systematic relations between HNO<sub>3</sub>-digestible Fe and HNO<sub>3</sub>-digestible As and Be suggest that secondary minerals in soils on the Pajarito Plateau may enhance the retention of As and Be within soil B horizons, additional studies are required to evaluate possible mechanisms of adsorption.

#### Th and U distributions

Thorium and uranium are important actinide elements that occur naturally in the Bandelier Tuff and in soils forming on the Pajarito Plateau. These elements may also occur above background concentrations in soils resulting from LANL activities. An understanding of background elemental distributions of Th and U provides constraints on the distribution, fate, and transport of anthropogenic actinide elements.

Total Th and U concentrations in soil samples collected from the B and C horizons generally fall within the distribution for the Tshirege Member of the Bandelier Tuff, where tuff mapping unit 1 has the highest concentrations of Th and U, followed by mapping units 2 and 3 (Broxton, et al., 1995; Longmire et al., in press, b). Several soil samples collected from A and transitional B horizons at mesa top sites (TA-63 and TA-67, Table 1) however, contain elevated concentrations of U, which may represent aerosol dispersion of anthropogenic U from nearby firing sites used for testing and development of high explosives and weapons (Fig. 6). Anthropogenic U may occur in several oxidation states over time, including 0, IV and VI. Anthropogenic U(VI) minerals are more stable under atmospheric conditions than are U metal and U(IV) minerals. Uranium metal will oxidize to U(IV) and U(VI) minerals and these alteration minerals are observed at LANL (Watt, 1996). Mineralogical studies conducted on depleted U (<sup>238</sup>U) samples collected from a nearby firing test site show that schoepite (UO<sub>3</sub>·2H<sub>2</sub>O) is the dominant U(VI) mineral forming from the oxidation of U metal (Watt, 1996). Schoepite may also be an alteration (oxidation) product of anthropogenic U metal, accounting for the elevated concentrations of U observed in studied mesa top soils.

#### STATISTICAL ANALYSIS OF LANL BACKGROUND SOIL DATA

Comparisons of LANL site data to background data are needed as part of the RCRA corrective action process developed by the EPA (EPA, 1989, 1992). Application of background soil data for determining possible contamination or to establish clean-up levels is based on the calculation of a horizon-specific upper tolerance limit (UTL) for each element (Table 3). The UTL is equal to the mean plus the standard deviation of the measured concentration for each element multiplied by k-factors (one-sided normal tolerance factors), using the 95<sup>th</sup> percentile at 95% confidence. For elements that are normally distributed without any data transformation and the elements that are normally distributed after a square root transformation, UTLs were calculated using the following equation:

$$UTL_{0.95,0.95} = \text{mean} + \text{standard deviation} * k_{0.95,0.95}$$

The k-factor is dependent on the number of background samples, with k-factor values increasing as sample size decreases (Gilbert, 1987; EPA, 1989). The UTLs for log-normally distributed elements are estimated by a simulation process (Longmire et al., in press b) The calculated UTL results were screened to ensure that the estimated UTLs were not artificially inflated due to a small sample size. Site data greater than the UTL-calculated threshold value are considered to exceed the normal maximum background concentration for a particular element.

Calculated UTLs are generally similar among A, B and C horizons for most trace elements and metals, although, as discussed above, factors such as the degree of pedogenesis and soil parent material appear to control the concentration of certain key elements in soils. One reason for the similarity among UTLs may be that background elemental data is simply lumped together according to soil master horizons rather than combining background data according to dominant soil properties or processes (i.e., clay illuviation) that may control or influence the distribution of key elements. For example, Bt horizons that mainly obtain the highest levels of chemically reactive phases are combined with Bw horizons as well as BC and BA transitional horizons that largely contain lower levels of chemically active phases. In other words, some Bw, BC and BA horizons are chemically more similar to A or C horizons than to Bt horizons. Although using UTLs based on master horizons may provide an initially workable estimate of LANL-wide background, given the large spatial variability of soils across LANL, development of UTLs based on a subdivision of soil samples according to dominant or important soil constituents (i.e. organic matter, clay content, ferric

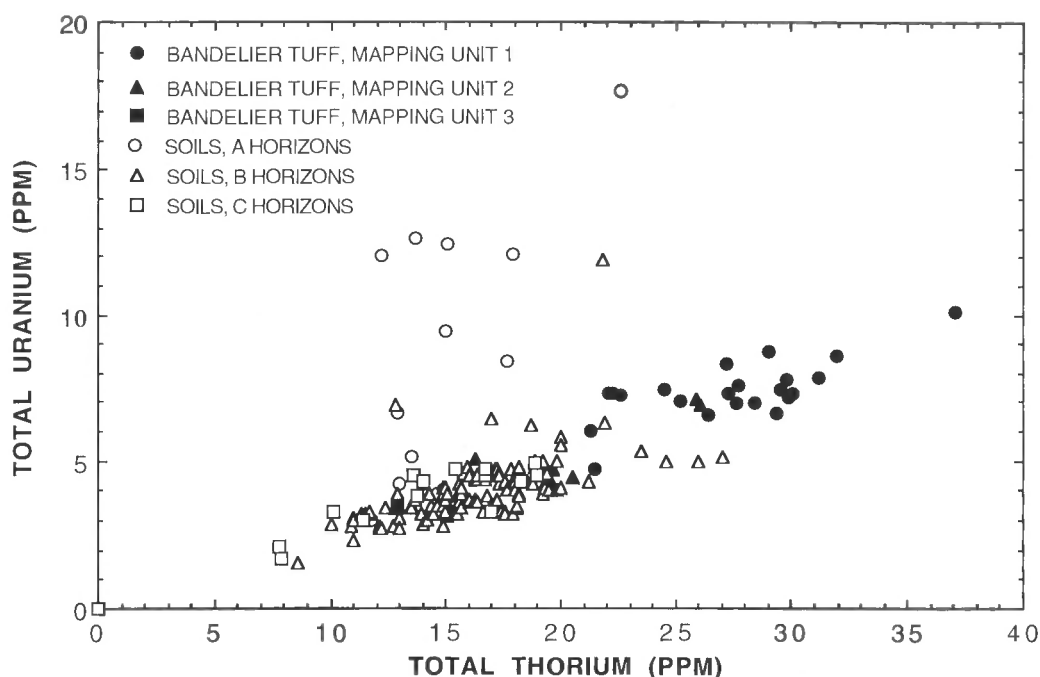


FIGURE 6. Total (HF digestible) Th concentration versus total U concentration in Bandelier Tuff and background soils, Los Alamos, New Mexico.



TABLE 3. Summary of proposed background soil upper tolerance limits (UTLs) for Los Alamos National Laboratory. UTLs are based on HNO<sub>3</sub>-digestible element concentrations.

Element	Soil Master Horizon			All Data
	A	B	C	
Aluminum	26600	43600	38700 *	38700
Antimony	0.5	1	ND	1
Arsenic	6.99	8.12	6.58	7.82
Barium	263	321	286	315
Beryllium	1.41	1.91	1.95 *	1.95
Cadmium	1.4	2.7	ND	2.7
Calcium	4030	6480	5930	6120
Chlorine	25	78.2	170	75.9
Chromium	19.3 *	19	17	19.3
Cobalt	31	14.8	41.2	19.2
Copper	30.7 *	29.2	22.2	30.7
Iron	18100	21800	18500	21300
Lead	28.4	22.3	21.9	23.3
Magnesium	3460	4480	4610 *	4610
Manganese	1000	673	463	714
Mercury	ND	0.1	0.1	0.1
Nickel	12.2	16	13.3	15.2
Potassium-TOTAL	33200	33400	41800	35000
Potassium	3070	3420	3410 *	3410
Selenium	0.7	1.3	1.7	1.7
Sodium	602	798	2680	915
Sulfate	42.7	249	712	317
Tantalum	ND	ND	ND	ND
Thallium	0.4	1	0.6	1
Thorium	13.3	15	12.3	14.6
Thorium-TOTAL	20.5	22.7	25.3	22.6
Uranium	1.87 *	1.72	1.36	1.87
Uranium-TOTAL	5.1	5.34	6.58	5.45
Vanadium	42.8	42	32	41.9
Zinc	47.1	51.5	50.8 *	50.8

\* Values were trimmed to the all data UTL to eliminate inflated UTLs.  
ND = Not detected.

(oxy)hydroxides may provide a better and more accurate estimate of elemental background concentrations at LANL. An additional reason for similar UTLs among A, B and C horizons is that UTLs for the A and C horizons may be inflated due to the smaller sample size for these horizons (n = 25, 24), and in turn, a higher k-factor value, relative to the number of B horizon samples (n = 132). Further, the UTL data set presented here is largely based on soils found on mesa tops and Pleistocene colluvial deposits. Poorly developed soils common to alluvium along canyon bottoms or colluvium along steep-sided canyon walls, which have been undersampled in this study relative to older, well-developed soils, may have statistically different elemental background concentrations.

### SUMMARY

Background-elemental concentrations were determined for a variety of soils and geomorphic settings across LANL. Approximately 175 background soil samples were analyzed for 24 metals and nonmetals relevant to the Environmental Restoration Project at LANL. HNO<sub>3</sub> and HF sample digestion techniques were used prior to chemical analyses. Leachable (HNO<sub>3</sub> digestion) elemental concentrations in background soils provide information relevant to the bioavailability of elements for risk calculations.

Background-elemental concentrations extracted from HNO<sub>3</sub> digestion of soils on the Pajarito Plateau generally vary with parent material, the degree of soil development, and other factors. Well-developed soils typically have higher concentrations of several trace elements, including As, Be, Th and U, than weakly developed soils. Higher concentrations of trace elements in B horizons may be due to higher concentrations of geochemically reactive phases that enhance the adsorption of metals, such as ferric (oxy)hydroxides and clay minerals, in B horizons relative to A and C horizons. Variations in soil-elemental concentrations may also be related in part to climate, topography, and to the parent materials, which include alluvial fan deposits, sheet wash material, colluvium, wind-blown sediment, El Cajete pumice, and the Bandelier Tuff.

Several soils downwind of LANL firing sites used in explosives testing contain anomalous concentrations of uranium within A horizons, suggesting that these horizons have received wind-blown U derived from these firing sites. Samples that included probable anthropogenic U are

not included in the background-elemental data set for the Laboratory. The B and C horizons are less affected by the anthropogenic U and these horizons generally have uranium concentrations similar to other background soil horizons.

Application of background soil data for determining possible contamination or to establish clean-up levels is based on the calculation of a horizon-specific UTL for each element. Site data greater than the UTL-calculated threshold value are considered to exceed the normal maximum background concentration for a particular element. UTLs for all elements were calculated for the A, B and C soil horizons; the greatest number of samples were collected from the B horizons. Calculated UTLs are generally similar among A, B and C master horizons, although several systematic trends indicate an enrichment of several trace metals within B horizons relative to A and C horizons. Reasons for similar UTL values may be (1) combined B horizon data is from a wide range of B horizons, ranging from weakly to strongly developed B horizons, (2) small sample size for A and C horizons resulting in higher UTLs relative to B horizons, and (3) predominance of sampling of well developed soils relative to weakly developed soils. Additional background samples collected from A horizons would enhance the data set because few samples (< 30) have been collected from these horizons. A horizons are particularly important because these surface horizons may be contaminated from nearby potential contaminant release sites.

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### REFERENCES

- Alesii, B. A., Fuller, W. H. and Bozle, M. V., 1980, Effect of leachate flow-rate in metal migration through soil: *Journal of Environmental Quality*, v. 9, p. 115-126.
- American Society of Agronomy, 1986, *Methods of soil analysis, Part 1. Physical and mineralogical methods*, No. 9, Part 1: Madison, American Society of Agronomy, 1188 p.
- Birkeland, P. W., 1984, *Soils and geomorphology*: New York, Oxford University Press, 372 p.
- Bowen, B. M., 1992, *Los Alamos climatology summary including latest normals from 1961-1990*: Los Alamos, Los Alamos National Laboratory Report LA-12232-MS, 254 p.
- Broxton, D. E., Heiken, G., Chipera, S. J., and Byers, F. M., Jr., 1995, *Stratigraphy, petrography, and mineralogy of Bandelier Tuff and Cerro Toledo deposits*: Los Alamos National Laboratory, Report LA-12934-MS, p. 93-109.
- EPA (U.S. Environmental Protection Agency), 1986, *Test methods for evaluating solid waste. Volume 1A; in Laboratory manual physical/chemical methods*: Washington, D.C., Office of Solid Waste, Waste Management Division, U.S. Environmental Protection Agency.
- EPA (U.S. Environmental Protection Agency), 1989, *Statistical analysis of groundwater monitoring data at RCRA facilities*: Washington, D.C., Interim final guidance, Office of Solid Waste, Waste Management Division, U.S. Environmental Protection Agency.
- EPA (U.S. Environmental Protection Agency), 1992, *Guidance for data usability in risk assessment (Part A)*: Washington DC, Office of Emergency Remedial Response, U.S. Environmental Protection Agency.
- Gautier, M. A. and Gladney, E. S., 1986, *Health and environmental data management, and quality assurance*: Los Alamos National Laboratory, Report LA-10300-M, Vols. I and II.
- Gilbert, R. O., 1987, *Statistical methods for environmental pollution monitoring*: New York, Von Nostrand Reinhold Company Inc., 320 p.
- Gladney, E. S., Curtis, D. B., Perrin, D. R., Owens, J. W. and Goode, W. E., 1980, *Nuclear techniques for the chemical analysis of environmental materials*: Los Alamos National Laboratory, Report LA-8192-MS.
- Gladney, E. S., Owens, J. W., Gunderson, T. C. and Goode, W. E., 1981, *Quality assurance for environmental analytical chemistry: 1976-1979*: Los Alamos National Laboratory, Report LA-8730-MS.

- Holm, T. R., Anderson, M. A., Iverson, D. G. and Stanforth, R. S., 1979, Heterogeneous interactions of arsenic in aquatic systems: *in* Jenne, E.A. ed., Chemical modeling of aqueous systems: American Chemical Society Symposium no. 93, p. 711-736.
- Hsi, C. K. 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.
- Korte, N. E., Skopp, J., Fuller, W. H., Nieble, E. E. and Alesii, B. A., 1976, Trace element movement in soils: influence of soil physical and chemical properties: *Soil Science*, v. 122, p. 350-359.
- Leckie, J. O., Benjamin, M. M., Hayes, K., Kaufman, G. and Altman, S., 1980, Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide: Electric Power Research Institute, RP-910.
- Lindsay, W. L., 1979, Chemical equilibria in soils: New York, Wiley-Interscience, 449 p.
- Livesey, N. T. and Huang, P. M., 1981, Adsorption of arsenate by soil and its relation to chemical properties and anions: *Soil Science*, v. 131, p. 88-94.
- Longmire, P. A., Reneau, S. L., Watt, P. M., McFadden, L. D., Gardner, J. N., Duffy, C. J. and Rytí, R. T. (in press, a), Natural background geochemistry, geomorphology, and pedogenesis of selected soil profiles and Bandelier Tuff, Los Alamos, New Mexico, 1995: Los Alamos National Laboratory, Report LA-12913-MS.
- Longmire, P. A., McDonald, E. V., Rytí, R. T., Reneau, S. L. and Watt, P. M. (in press, b), Natural background geochemistry and statistical analysis of selected soil profiles, Los Alamos, New Mexico: *in* Natural background geochemistry and statistical analysis of selected soil profiles, sediments, and Bandelier Tuff, Los Alamos, New Mexico: Los Alamos National Laboratory, Report LA-95-3468-UR.
- Nyhan, J. W., Hacker, L. W., Calhoun, T. E. and Young, D. L., 1978, Soil Survey of Los Alamos County, New Mexico: Los Alamos Scientific Laboratory Informal Report LA-6779-MS, 102 p.
- Rai, D. and Zachara, J. M., 1984, Chemical attenuation rates, coefficients, and constants in leachate migration, Vol. 1, a critical review: Electric Power Research Institute, EA-3356.
- Reneau, S. L., Gardner, J. N. and Forman, S. L., 1996, New evidence for the age of the youngest eruptions in the Valles caldera, New Mexico: *Geology*, v. 24, p. 7-10.
- Schwertmann, U. and Taylor, R. M., 1989, Iron oxides: *in* Dixon, J. B. and Weed, S. B., eds., Minerals in soil environments: Soil Science of America Book Series, no. 1, Madison, p. 379-438.
- Soil Conservation Survey, 1981, Examination and description of soils in the field; *in* Soil survey manual (USDA-ARS): Washington, D.C, U.S. Government Printing Office.
- Sposito, G., 1984, The surface chemistry of soils: New York, Oxford University Press, 234 p.
- Sposito, G., 1989, The chemistry of soils: New York, Oxford University Press, 277 p.
- Watt, P. M., 1996, Landscape evolution and soil genesis on the Pajarito Plateau and the impact of soil chemical and physical properties on contaminant uranium migration, Los Alamos National Laboratory, New Mexico [Ph.D. Dissertation]: Albuquerque, University of New Mexico.