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

ERIC V. MCDONALD[1], PATRICK A. LONGMIRE[2], PAULA M. WATT[1], RANDALL T. RYTI[3] and STEVEN L. RENEAU[4]

[1]Geology and Geochemistry Group, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 [2]Environmental Science and Waste Technology Group, J534, Los Alamos National Laboratory, Los Alamos, NM 87545 [3]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131 [4]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_3 (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 Ustopsamment	piñon-juniper	canyon bottom	Holocene alluvium
Upper Los Alamos Canyon	TA-72	Los Alamos Canyon	Cumulic 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 Dystrochrept	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

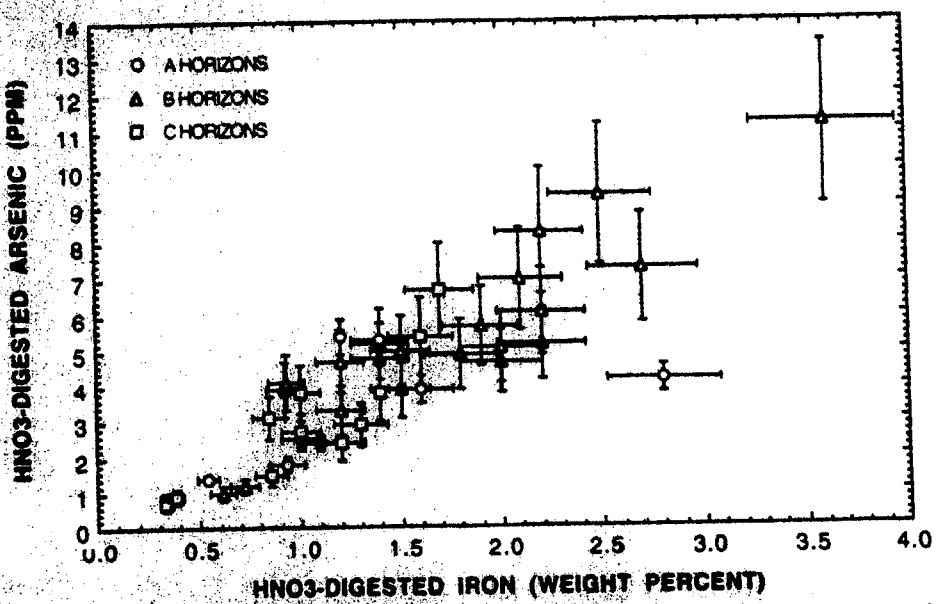

FIGURE 4. Nitric acid (HNO_3) digestion of Fe concentration versus HNO_3 digestable As concentration in background soils, Los Alamos, New Mexico. Error bars represent ± one standard deviation.

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 HNO_3-digestable 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 ($H_3AsO_3^0$, $H_2AsO_3^-$) or +5 ($H_2AsO_4^-$, $HAsO_4^{2-}$) 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 Fe(OH)$_3$ and Al(OH)$_3$ have high sorptive capacities for As (Holm et al., 1979; Leckie et al., 1980). Beryllium forms hydroxy complexes ($BeOH^+$, $Be(OH)_2^0$, and

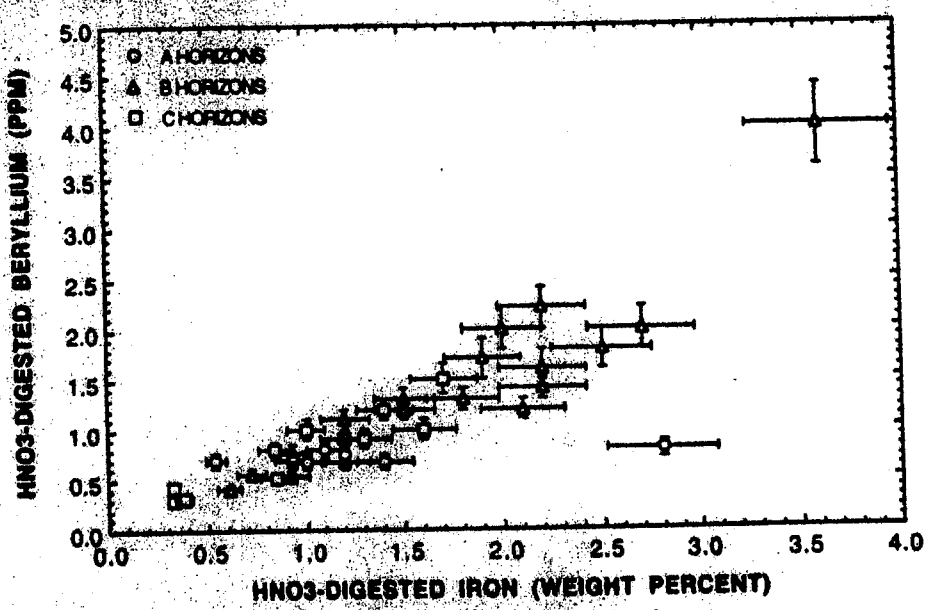

FIGURE 5. Nitric acid (HNO_3) digestion of Fe concentration versus HNO_3 digestable Be concentration in background soils, Los Alamos, New Mexico. Error bars represent ± one standard deviation.

TABLE 1. Summary of proposed background soil upper tolerance limits (UTLs) for Los Alamos National Laboratory. UTLs are based on HNO_3-digestable element concentrations.

Element	Soil Master Horizon			All Data
	A	B	C	
Aluminum	28600	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
Phosphorus	3070	3420	3410 *	3410
Selenium	0.7	1.3	1.7	1.7
Sodium	602	798	2680	915
Sulfur	42.7	249	712	317
Tungsten	ND	ND	ND	ND
Thallium	0.4	1	0.8	1
Thorium	13.3	15	12.3	14.6
Titanium-TOTAL	20.5	22.7	25.3	22.6
Uranium	1.87 *	1.72	1.36	1.87
Uranium-TOTAL	5.1	6.34	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_3 and HF sample digestion techniques were used prior to chemical analyses. Leachable (HNO_3 digestion) elemental concentrations in background soils provide information relevant to the bioavailability of elements for risk calculations.

Background-elemental concentrations extracted from HNO_3 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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