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Title:

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STATISTICAL ANALYSES OF THE BACKGROUND DISTRIBUTION OF GROUNDWATER SOLUTES, LOS ALAMOS NATIONAL LABORATORY, NEW MEXICO

By

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INTRODUCTION

Background or baseline water chemistry data and information are required to distinguish between contaminated and non-contaminated waters for environmental investigations conducted at Los Alamos National Laboratory (referred to as the Laboratory). The term "background" refers to natural waters discharged by springs or penetrated by wells that have not been contaminated by LANL or other municipal or industrial activities, and that are representative of groundwater discharging from their respective aquifer material. These investigations are conducted as part of the Environmental Restoration (ER) Project, Groundwater Protection Program (GWPP), Laboratory Surveillance Program, the Hydrogeologic Workplan, and the Site-Wide Environmental Impact Statement (SWEIS).

This poster provides a comprehensive, validated database of inorganic, organic, stable isotope, and radionuclide analyses of up to 136 groundwater samples collected from 15 baseline springs and wells located in and around Los Alamos National Laboratory, New Mexico. The region considered in this investigation extends from the western edge of the Jemez Mountains eastward to the Rio Grande and from Frijoles Canyon northward to Garcia Canyon. Figure 1 shows the fifteen stations sampled for this investigation. The sampling stations and associated aquifer types are summarized in Table 1.

Site Selection Methodolgy

The choice of location and hydrogeochemical setting of the sampling sites was made by the authors using previously published knowledge of the Jemez Mountains-Pajarito Plateau region (Vuataz and Goff, 1986; Shevenell et al., 1987; Shevenell and Goff, 1995; Adams et al., 1995; Blake et al., 1995). We also discussed the locations of sampling sites with researchers at the New Mexico

Environment Department (NMED). From these deliberations, eleven springs and four wells were chosen and the sites are separated into three aquifer material types: alluvium, perched intermediate (depth) volcanic rocks (Bandelier Tuff, Tschicoma Formation, hydro (phreatic)-magmatic deposits, and Cerros del Rio basalt), and the regional aquifer (Puye Formation and Santa Fe Group sediments).

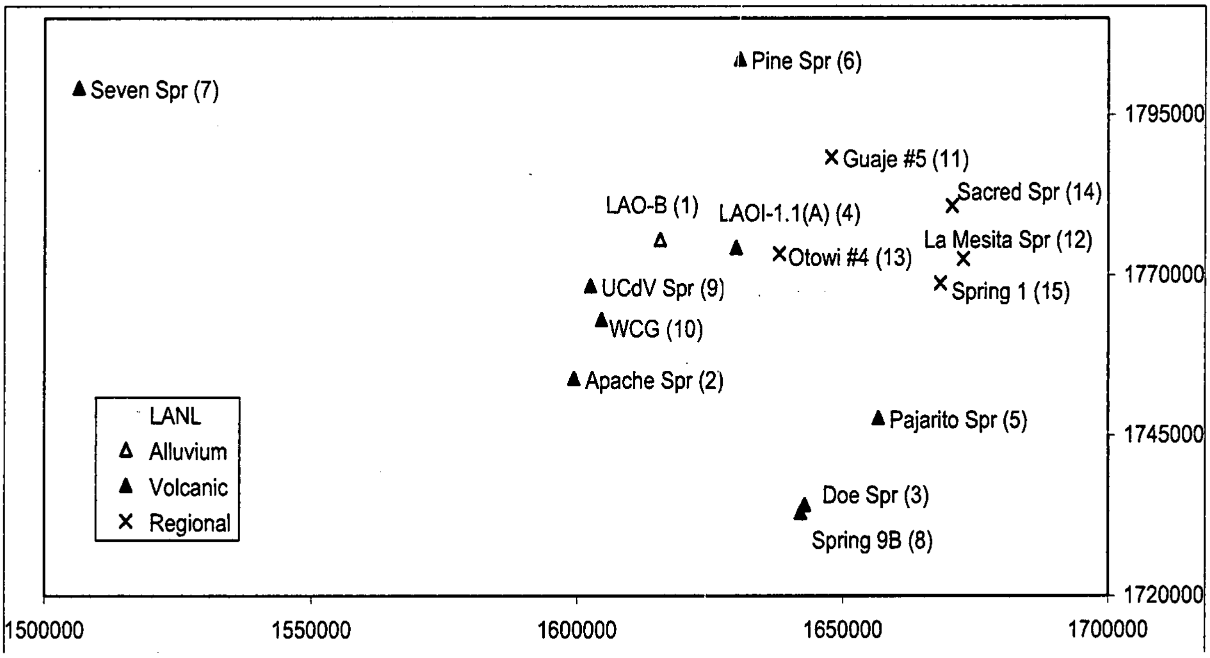

Figure 1. Map of sampling locations of LANL background springs and wells.

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Table 1. Geographic and Hydrogeological Information for LANL Background Springs and Wells.

Location	Abbreviated Location	Location Code	Aquifer type	Location Type	Easting (ft)	Northing (ft)	Source[a]	Elevation (ft)[b]	Location Notes
Apache Spring	Apache Spg	2	Volcanic rocks	Spring	1598966	1753454	GPS	8274	Lava of Tschicoma Formation
Doe Spring	Doe Spg	3	Volcanic rocks	Spring	1642350	1733760	GPS	5541	Cerros del Rio hydromagmatic tuffs
Guaje #5	Guaje #5	11	Regional aquifer	Well	1647260	1788038	Blake	6319	Santa Fe Group sediments
La Mesita Spring	La Mesita Spg	12	Regional aquifer	Spring	1672180	1772148	Trimble_GPS	5581	Santa Fe Group sediments
LAO-B	LAO-B	1	Alluvium	Well	1615149	1775170	FIMAD	7326	Volcanic-rich alluvium
LAOI-1.1(A)	LAOI-1.1(A)	4	Volcanic rocks	Well	1629427	1773925	FIMAD	6837	Bandelier Tuff
Otowi #4	Otowi #4	13	Regional aquifer	Well	1637546	1772968	Blake	6627	Santa Fe Group sediments
Pajarito Spring	Pajarito Spg	5	Volcanic rocks	Spring	1656224	1747274	Blake	5587	Landslide blocks in Cerros del Rio basalt and Totavi Lentil
Pine Spring	Pine Spg	6	Volcanic rocks	Spring	1630151	1803290	Blake	7238	Puye Formation and lavas of Keres Group
Sacred Spring	Sacred Spg	14	Regional aquifer	Spring	1670060	1780451	GPS	5650	Santa Fe Group sediments
Seven Springs	Seven Spg	7	Volcanic rocks	Spring	1505978	1798869	Blake	8143	Bandelier Tuff
Spring 1	Spring 1	15	Regional aquifer	Spring	1667883	1768364	GPS	5584	Landslide blocks in Cerros del Rio basalt, Santa Fe Group sediments, and Totavi Lentil
Spring 9B	Spring 9B	8	Volcanic rocks	Spring	1641613	1732525	GPS	5492	Cerros del Rio basalt and hydromagmatic deposits
Location	Abbreviated Location		Aquifer Type	Location Type	Easting (ft)	Northing (ft)	Source[a]	Elevation (ft)[b]	Location Notes
Upper Canyon de Valle Spring	UCdV Spg	9	Volcanic rocks	Spring	1601989	1767970	Trimble_GPS	8494	Upper Bandelier Tuff
Water Canyon Gallery	WCG	10	Volcanic rocks	Spring	1604088	1762656	GPS	8002	Upper Bandelier Tuff
Rio Grande	RG	na	River	River	na[d]	na	na	na	None

[a] Location sources were FIMAD, Blake report, and GPS instruments.
[b] Elevation from GPS instruments.
[c] n/a = not applicable.
[d] na = not available.

Objectives

The objectives of this background hydrogeochemical investigation include:

- Reviewing available background hydrogeochemical data collected at the Laboratory and surrounding areas prior to 1997;
- Collecting additional groundwater samples from background stations (springs and wells) for alluvial and perched intermediate groundwater and the regional aquifer; and
- Providing validated analytical results and statistical distributions for the different analytes occurring within alluvial and perched intermediate groundwater and the regional aquifer.

Field Methods, Analytes, and Analytical Methods

Groundwater samples were collected and analyzed for chemical constituents in 1997, 1998, 1999, and 2000 during six sampling events. Both filtered and non-filtered groundwater samples were collected for analyses of major solutes, trace elements, and radionuclides (excluding tritium). Non-filtered groundwater samples were collected for stable isotope (hydrogen, oxygen, and nitrogen) analyses. Table 2 provides a list of chemicals analyzed as part of this investigation.

Groundwater and drinking water standards based on State of New Mexico (New Mexico Water quality Control Commission) and USEPA are provided in Table 3. A list of analytes, analytical methods, and reporting limits provided by EES-6 and/or Paragon Analytics, Inc is provided in Table 4.

TABLE 2. Field parameters and analytes for LANL background Spring and Well Investigation

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Field Parameters
temperature, turbidity, specific conductance, pH, and dissolved oxygen.

Major Solutes and Total Suspended Solids
Ca, Mg, Na, K, HCO_3, Cl, SO_4, SiO_2, total dissolved solids (TDS), and total suspended solids (TSS).

Trace Elements and Dissolved Organic Carbon
Ag, Al, As, B*, Ba, Be, Br, Cd, Co, Cr, Cs*, Cu, F, Fe, Hg, I*, K, Li*, Mn, Mo*, NH_4, Ni, NO_2, NO_3, Pb, PO_4, Rb*, Sb, Se, Sn*, Sr*, Ti*, Tl, U, V, Zn, and dissolved organic carbon (DOC) fractionation analysis.

Radionuclides and Stable Isotopes
low-detection limit tritium, stable isotopes ($^{18}O/^{16}O$, $^{15}N/^{14}N$, D/H), and radionucludes (^{90}Sr, ^{234}U, ^{235}U, ^{238}U, ^{137}Cs, ^{241}Am, ^{238}Pu, and $^{239,240}Pu$, gross alpha, gross beta, and gross gamma).

B* and other specified analytes are included in the EES-6 analytical suite.

TABLE 3. USEPA Maximum Contaminant levels (MCLs) and NMED (WQCC) and Groundwater Standards and DOE Derived Concentration Guidelines (DCGs).

USEPA (mg/L, MFL, or pCi/L)
Asbestos (7 MFL), As (0.05), Ba (2), Be (0.004), Cd (0.005), Cr (0.1), CN (0.2), F (4), Pb (0.05), tot. Hg (0.002), NO_3 (10), NO_3 (1), Se (0.05), Ag (0.1), Tl (0.002), U (0.02), Cl (250), Cu (1), Fe (0.3), Mn (0.05), SO_4 (250), TDS (500), Zn (5), pH (6.5-8.5), Al (0.05-0.2), B (0.75), Co (0.05), Mo (1), Ni (0.1), gross alpha (15 pCi/L), gross beta (4 millirems/yr), and $^{226\,\&\,228}$Ra (5 pCi/L)

NMWQCC (mg/L, pCi/L)
As (0.1), Ba (1), Cd (0.01), Cr (0.05), CN (0.2), F (1.6), Pb (0.05), Hg (0.002), NO_3 as N (10), Se (0.05), Ag (0.05), U (5), $^{226\,\&\,228}$Ra (30 pCi/L), Cl (250), Cu (1), Fe (1), Mn (0.2), SO_4 (600), TDS (10,000), Zn (10), pH (6-9), Al (5), B (0.75), Co (0.05), Mo (1), and Ni (0.2)

DOE DCG (pCI/L)
Tritium (80,000), ^{7}Be (40,000), ^{90}Sr (40), ^{234}U (20), ^{235}U (24), ^{238}U (24), ^{137}Cs (120), ^{241}Am (1.2), ^{238}Pu (1.6), ^{239}Pu (1.2), and ^{240}Pu (1.2)

Both filtered (NM Water Quality Control Commission regulations) and non-filtered groundwater (EPA) samples are collected for analyses of major anions, trace elements, and radionuclides (excluding tritium which is non-filtered only). MFL means million fibers/L longer than 10 micrometers.

Table 4. Reporting Limits Provided by EES-6 and Paragon Analytics, Inc.

Analyte	Analytical Method		Reporting Limit (ppm)	
	EES	Paragon	EES	Paragon
Ag	GFAA	ICP-AES	0.001	0.01
Al	ICP-AES	ICP-AES	0.02	0.2
Alkalinity	Titration	Titration	1	1
As	Hydride-AA	ICP-AES	0.0001	0.01
B	ICP-AES	ICP-AES	0.002	
Ba	ICP-AES	ICP-AES	0.002	0.1
Be	ICP-AES	ICP-AES	0.002	0.005
Br	IC	IC	0.01	0.01
Ca	ICP-AES	ICP-AES	0.02	1
Cd	GFAA	GFAA	0.001	0.005
Cl	IC	IC	0.01	0.01
ClO_3	IC	IC	0.02	Not analyzed
Co	GFAA	ICP-AES	0.002	0.01
$CO_3/HCO_3/OH$	Titration	Titration	0.5	0.5
Conductivity	Electrode	Electrode	0.5	0.5
Cr	GFAA	ICP-AES	0.002	0.01
Cs	GFAA	GFAA	0.002	Not analyzed
Cu	GFAA	GFAA	0.002	0.01
F	IC	IC	0.01	0.01
Fe	ICP-AES	ICP-AES	0.01	0.1
Hardness	Calculated	Calculated		Calculated
HCO_3	Titration	Titration	0.5	0.5
Hg	Cold Vapor AA	Cold Vapor AA	0.0002	0.0002
I	IC	IC	0.01	Not analyzed
K	AA	ICP-AES	0.01	1
Li	ICP-AES	ICP-AES	0.01	Not analyzed
Mg	ICP-AES	ICP-AES	0.01	1
Mn	ICP-AES	ICP-AES	0.002	0.01
Mo	GFAA	ICP-AES	0.002	0.01
Na	AA	ICP-AES	0.01	1
NH_4	Electrode	Electrode	0.02	0.5
Ni	GFAA	ICP-AES	0.002	0.02
NO_2	IC	IC	0.01	0.05
NO_3	IC	IC	0.01	0.05
OH	Titration	Titration	0.5	Not analyzed
Pb	GFAA	ICP-AES	0.002	0.003
pH	Electrode	Electrode	0.05	0.05
PO_4	IC	IC	0.02	0.05
Rb	GFAA	ICP-AES	0.002	Not analyzed
Sb	Hydride AA	ICP-AES	0.0001	0.02
Se	Hydride AA	ICP-AES	0.0001	0.005
Si	ICP-AES	ICP-AES	0.02	0.02
SO_4	IC	IC	0.02	0.02
S_2O_3	IC	IC	0.01	Not analyzed
Sn	GFAA	ICP-AES	0.005	0.02
Sr	ICP-AES	ICP-AES	0.002	0.02
Ti	ICP-AES	ICP-AES	0.002	0.002

Tl	GFAA	ICP-AES	0.002	0.01
TSS	Filtration 1L	Filtration 1L	0.1	Not analyzed
U	ICP-MS	LIKPA	Not analyzed	0.0002
V	ICP-AES	ICP-AES	0.002	0.01
Zn	ICP-AES	ICP-AES	0.01	0.02
TDS	Calculated	Calculated	Calculated	Calculated

AA - Atomic Absorption Spectroscopy
GFAA - Graphite Furnace AA
IC - Ion Chromatography
ICP-AES - Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS - Inductively Coupled Plasma Mass Spectroscopy
LIKPA – Laser Induced Kinetic Phosphorimetric Analysis

Statistical Evaluation

Several data preparation steps were conducted before statistical analyses could be performed on the LANL background water chemistry data.

Data were subject to a routine data validation.

Data were inspected for suspect values that are exceptionally high or low relative to the rest of the data.

Data qualifiers were reviewed and any R qualifiers (denoting rejected values) were noted, and R qualified data were not used in statistical analyses.

Non-detected sample results were noted. Non-detected sample results for inorganic and other analytes were typically reported as less than ("<") the instrument detection limit (IDL) for that chemical. Values that were reported as nondetected by the analytical laboratory were replaced by one-half of the detection limit value for statistical analyses (EPA 1992, 54947).

The statistical analysis of the available baseline data involves several exploratory data analysis (EDA) tools. These tools include:

Normal quantile plots: Normal quantile plots (also known as a normal quantile-quantile or q-q plot) are a particular type of quantile plot. The quantiles of the data set (y-axis) are plotted against the quantiles for a standard normal (x-axis).

Box plots: Box plots are used to show differences between two or more sample locations or other data groupings. The area enclosed by the box shows the concentration range containing the middle half of the data; that is, the lower box edge is at the 25th percentile, and the upper box edge is at the 75th percentile.

Regression analysis and Scatter plots: Regression analysis provides a measure of the association between pairs of variables. Linear regression analysis provides a measure of the degree of fit (coefficient of determination or r^2) and the slope/intercept of the least-squares linear model. A coefficient of determination of zero indicates no relationship between the two measurements. A coefficient of determination of 1 indicates a linear relationship between the measurements.

Scatter plot matrix: The scatter plot matrix is used to illustrate the relationship between more than two measurements.

Several examples of these types of plots are shown in Appendix A.

Statistical Results

Summary statistics for selected analytes (filtered and nonfiltered samples) the water chemistry baseline data are listed in Table 5[1]. Table 5 lists selected analytes from the contract analytical laboratories (EES-6, Paragon Analytics, Inc., General Engineering Laboratories, Huffman Laboratories, Western Michigan University, Geochron Laboratories, Coastal Science Laboratories, and the University of Miami).

[1] Table 5 provides a statistical summary of sample results before non-detects were replaced by one-half of the detection limit and rejected data were omitted.

Table 5. Statistical Summary of Selected Analytes (including field replicate samples and New Mexico Environment Department samples)

				Filtered Samples								
Group	Lab[a]	Analyte	Units	Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
metals	CL	Arsenic	µg/L	67	1.7E+00	2.5E+00	5.5E+00	2.7E+00	6.2E-01	23%	0	57
metals	CL	Barium	µg/L	67	3.5E+00	2.2E+01	1.1E+02	3.9E+01	3.4E+01	87%	0	2
metals	CL	Beryllium	µg/L	67	1.0E-02	2.0E-01	9.8E-01	2.3E-01	2.3E-01	104%	1	50
metals	CL	Iron	µg/L	67	7.3E+00	4.7E+01	4.6E+03	2.3E+02	7.6E+02	333%	0	51
metals	CL	Manganese	µg/L	67	5.0E-02	1.4E+00	2.5E+01	3.0E+00	5.2E+00	171%	5	27
metals	CL	Mercury	µg/L	67	1.0E-02	2.0E-02	4.0E-02	1.7E-02	6.4E-03	37%	10	53
metals	CL	Molybdenum	µg/L	13	2.9E+00	2.9E+00	4.9E+00	3.3E+00	7.6E-01	23%	0	11
metals	CL	Strontium	µg/L	15	4.6E+01	6.2E+01	4.7E+02	1.2E+02	1.4E+02	117%	0	2
metals	CL	Uranium by TUICPMS	µg/L	32	2.5E-02	3.2E-01	9.1E+00	1.0E+00	2.1E+00	210%	0	0
metals	CL	Uranium by TUKPA	µg/L	32	7.0E-02	3.5E-01	9.0E+00	1.1E+00	2.1E+00	192	0	2
metals	CL	Uranium	µg/L	49	2.5E-02	3.3E-01	9.1E+00	1.1E+00	2.1E+00	201%	0	0

Table 5. Statistical Summary of Selected Analytes (including field replicate samples and New Mexico Environment Department samples)

Group	Lab[a]	Analyte	Units	Filtered Samples								
				Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
metals	EES	Arsenic	µg/L	91	1.0E-01	7.0E-01	4.4E+00	1.1E+00	1.0E+00	90%	0	4
metals	EES	Barium	µg/L	91	4.0E+00	2.4E+01	1.3E+02	3.9E+01	3.3E+01	83%	0	0
metals	EES	Beryllium	µg/L	91	1.0E+00	2.0E+00	2.0E+00	1.8E+00	3.7E-01	20%	0	91
metals	EES	Iron	µg/L	91	6.5E+00	3.0E+01	1.9E+03	1.8E+02	3.7E+02	210%	0	30
metals	EES	Manganese	µg/L	91	1.0E+00	2.0E+00	5.7E+01	4.6E+00	7.2E+00	155%	0	46
metals	EES	Mercury	µg/L	91	1.0E-02	5.0E-02	2.4E-01	7.8E-02	5.4E-02	69%	1	69
metals	EES	Molybdenum	µg/L	90	1.0E+00	2.0E+00	4.0E+00	2.0E+00	5.7E-01	28%	0	68
anion	EES	NO_3 (N)	mg/L	90	2.3E-03	2.9E-01	2.2E+00	3.9E-01	5.0E-01	128%	0	8
metals	EES	Strontium	µg/L	91	4.2E+01	9.5E+01	1.0E+03	1.7E+02	2.0E+02	117%	0	0
metals	EES	Uranium by TUICPMS	µg/L	15	2.0E-01	4.0E-01	1.1E+01	1.3E+00	2.7E+00	210%	0	2

Table 5. Statistical Summary of Selected Analytes (including field replicate samples and New Mexico Environment Department samples)

Group	Lab[a]	Analyte	Units	Filtered Samples								
				Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
rad-iso	CL	Americium-241	pCi/L	53	-4.7E-03	2.0E-02	2.4E-01	2.9E-02	4.2E-02	141%	0	45
rad-gross	CL	Gross Alpha Radiation	pCi/L	35	-7.8E-01	2.0E-01	7.2E+00	8.5E-01	1.9E+00	217%	0	6
rad-gross	CL	Gross Beta Radiation	pCi/L	35	1.8E-01	2.1E+00	5.9E+00	2.3E+00	1.5E+00	65%	0	14
rad-gross	CL	Gross Gamma Radiation	pCi/L	33	1.2E+02	2.0E+02	3.2E+02	2.1E+02	6.0E+01	29%	0	6
rad-iso	CL	Plutonium-238	pCi/L	53	-4.1E-02	1.0E-02	1.1E-01	1.4E-02	2.3E-02	163%	0	49
rad-iso	CL	Plutonium-239	pCi/L	53	-1.1E-02	9.0E-03	1.3E-01	1.3E-02	2.1E-02	165%	0	48
rad-iso	CL	Uranium-234	pCi/L	53	1.0E-02	2.4E-01	7.8E+00	7.8E-01	1.5E+00	187%	0	6
rad-iso	CL	Uranium-235	pCi/L	53	-4.9E-03	1.6E-02	2.6E-01	3.0E-02	4.8E-02	160%	0	40
rad-iso	CL	Uranium-238	pCi/L	53	-5.0E-03	1.3E-01	4.7E+00	4.4E-01	8.9E-01	205%	0	7
rad-iso	CL	Strontium-90	pCi/L	53	-3.0E-01	2.0E-02	5.5E-01	4.8E-02	1.7E-01	365%	0	53
rad-iso	CL	Tritium (University of Miami)	pCi/L	30	1.3E-01	1.6E+00	7.1E+01	1.9E-01	2.5E+01	134%	0	0
rad-gscan	CL	Cesium-137	pCi/L	53	-2.5E+00	-1.7E-01	2.2E+00	-2.3E-01	9.8E-01	-428%	0	53

Table 5. Statistical Summary of Selected Analytes (including field replicate samples and New Mexico Environment Department samples)

Group	Lab[a]	Analyte	Units	Non Filtered Samples								
				Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
metals	CL	Arsenic	µg/L	28	1.9E+00	2.6E+00	6.7E+00	3.0E+00	1.0E+00	33%	0	18
metals	CL	Barium	µg/L	28	3.6E+00	2.8E+01	1.1E+02	4.2E+01	3.2E+01	76%	0	0
metals	CL	Beryllium	µg/L	28	2.0E-01	3.0E-01	1.2E+00	4.0E-01	2.5E-01	62%	0	28
metals	CL	Iron	µg/L	28	2.7E+01	1.4E+02	6.7E+03	5.0E+02	1.2E+03	249%	0	16
metals	CL	Manganese	µg/L	28	5.0E-02	2.6E+00	3.1E+01	6.1E+00	8.1E+00	132%	3	6
metals	CL	Mercury	µg/L	28	2.0E-02	2.0E-02	5.0E-02	2.2E-02	6.1E-03	28%	10	16
metals	CL	Molybdenum	µg/L	10	2.9E+00	2.9E+00	4.9E+00	3.4E+00	8.1E-01	24%	0	8
metals	CL	Strontium	µg/L	12	4.8E+01	6.5E+01	4.6E+02	1.0E+02	1.2E+02	113%	0	0
metals	CL	Uranium	µg/L	15	7.0E-02	5.5E-01	8.6E+00	1.2E+00	2.2E+00	179%	0	0

Group	Lab[a]	Analyte	Units	Non Filtered Samples								
				Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
metals	EES	Arsenic	µg/L	61	1.0E-01	1.1E+00	4.4E+00	1.3E+00	1.1E+00	84%	0	4
metals	EES	Barium	µg/L	61	4.0E+00	2.7E+01	1.3E+02	4.3E+01	3.4E+01	81%	0	0
metals	EES	Beryllium	µg/L	61	1.0E+00	2.0E+00	2.0E+00	2.0E+00	1.3E-01	6%	0	61
metals	EES	Iron	µg/L	61	9.4E+00	2.3E+02	7.7E+03	6.5E+02	1.2E+03	184%	0	5
metals	EES	Manganese	µg/L	61	1.0E+00	4.0E+00	1.4E+02	1.1E+01	2.1E+01	194%	0	24
metals	EES	Mercury	µg/L	61	1.0E-02	2.0E-02	1.3E-01	3.6E-02	3.2E-02	89%	0	32
metals	EES	Molybdenum	µg/L	61	1.0E+00	2.0E+00	1.3E+01	2.5E+00	1.8E+00	70%	0	39
metals	EES	Strontium	µg/L	61	4.9E+01	9.3E+01	1.1E+03	1.7E+02	2.1E+02	119%	0	0
anion	EES	Nitrate (N)	mg/L	61	2.3E-03	2.3E-01	2.2E+00	3.6E-01	4.8E-01	134%	0	11

Table 5. Statistical Summary of Selected Analytes (including field replicate samples and New Mexico Environment Department samples)

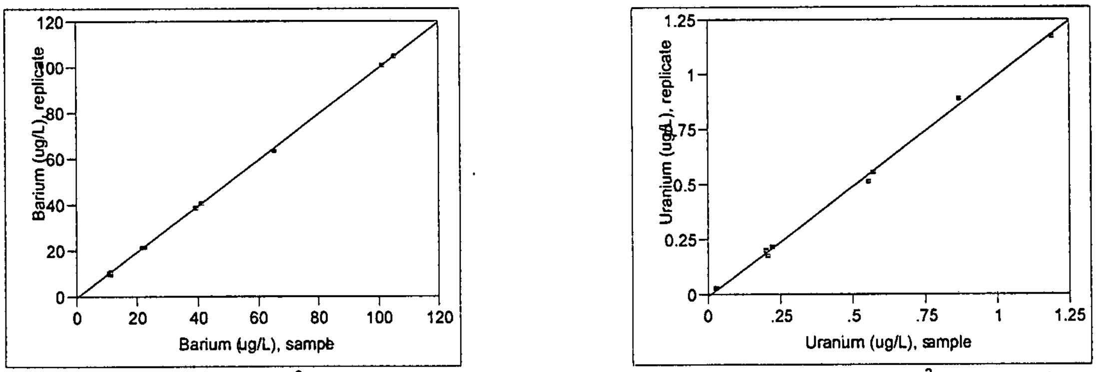
				Non Filtered								
Group	Lab[a]	Analyte	Units	Count	Minimum	Median	Maximum	Average	St. Dev.	CV	Rejected Values	Non-Detects
rad-iso	CL	Americium-241	pCi/L	43	-3.0E-03	2.4E-02	1.9E-01	3.5E-02	4.2E-02	121%	0	35
rad-gross	CL	Gross Alpha Radiation	pCi/L	28	-5.0E-01	6.0E-01	6.8E+00	9.2E-01	1.5E+00	160%	0	9
rad-gross	CL	Gross Beta Radiation	pCi/L	28	-3.2E-01	2.3E+00	7.5E+00	2.7E+00	2.1E+00	77%	0	6
rad-gross	CL	Gross Gamma Radiation	pCi/L	27	1.0E+02	2.1E+02	4.0E+02	2.2E+02	7.7E+01	34%	0	5
rad-iso	CL	Plutonium-238	pCi/L	43	-1.3E-02	7.0E-03	5.7E-02	1.2E-02	1.7E-02	144%	0	41
rad-iso	CL	Plutonium-239,240	pCi/L	43	-1.1E-02	6.8E-03	4.8E-02	8.6E-03	1.1E-02	133%	0	42
rad-iso	CL	Uranium-234	pCi/L	43	2.0E-02	3.4E-01	8.0E+00	7.9E-01	1.5E+00	189%	0	5
rad-iso	CL	Uranium-235	pCi/L	43	-2.0E-03	2.2E-02	3.3E-01	3.7E-02	5.8E-02	158%	0	25
rad-iso	CL	Uranium-238	pCi/L	43	1.0E-02	2.5E-01	5.0E+00	4.5E-01	9.4E-01	208%	0	5
rad-iso	CL	Strontium-90	pCi/L	43	-7.6E-01	0.0E+00	4.0E-01	-4.5E-03	2.1E-01	-4633%	0	43
rad-iso	CL	Tritium University of Miami	pCi/L	80	-2.6E-01	2.3E+00	6.8E+01	1.7E+01	2.3E+01	133%	0	0
rad-gscan	CL	Cesium-137	pCi/L	43	-2.7E+00	-1.3E-01	2.1E+00	-2.2E-01	1.3E+00	-605%	0	43

[a] CL = contract laboratory (Paragon Analytics, Inc., General Engineering Laboratories, Huffman Laboratories, Western Michigan University, Geochron Laboratories, Coastal Science Laboratories, and the University of Miami), EES = Earth and Environmental Science Division.

[b] n/a = not applicable.

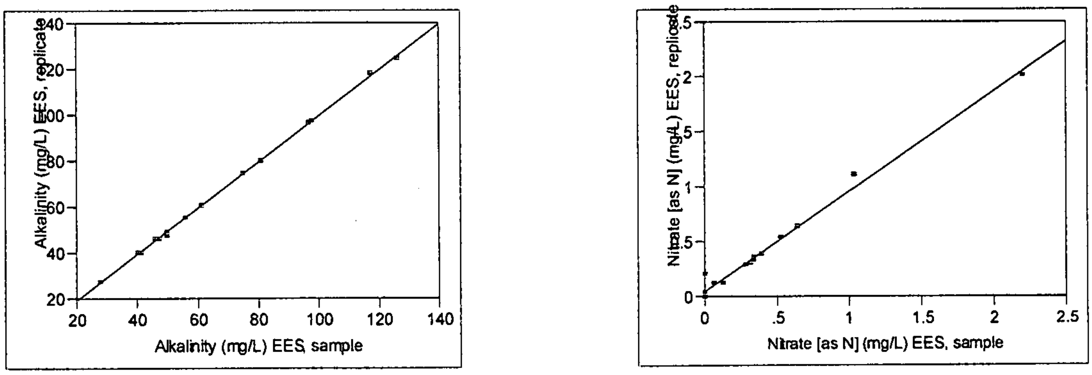
Evaluation of Field Replicate Samples

As a quality assessment measure for the investigation, field replicate samples were collected and submitted for analysis to contract analytical laboratories or the EES-6 analytical laboratory. Results for selected analytes are shown in Figure 2. Field replicate samples provide a measure of the variability within a sampling event (sample collection and preparation) and analytical laboratory measurement variability. The scatter plots in Figure 2 illustrate that field replicate sample results are identical or nearly identical to the original sample result for most of these analytes.



$Ba\ [rep.] = -0.3 + 1.00{*}Ba,\ r^2 > 0.99,\ n = 11$

$U\ [rep.] = -0.01 + 1.00{*}U,\ r^2 > 0.99,\ n = 8$



$Alk.\ [rep.] = -0.6 + 1.00{*}Alk.,\ r^2 > 0.99,\ n = 15$

$NO_3^-\ [rep.] = 0.06 + 0.91{*}NO_3^-,\ r^2 = 0.99,\ n = 15$

Figure 2. Comparison of field replicate samples (plus symbols are non-filtered samples and squares are filtered samples)

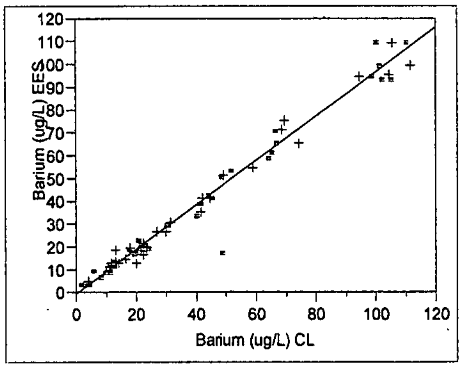
Comparison of Results by Analytical Laboratory and Method

Sample results from the contract analytical laboratories were compared to the EES-6 analytical laboratory as another quality assurance measure for the investigation. In addition, the laboratories used different analytical methods for some analytes (uranium, tritium, and trace metals).

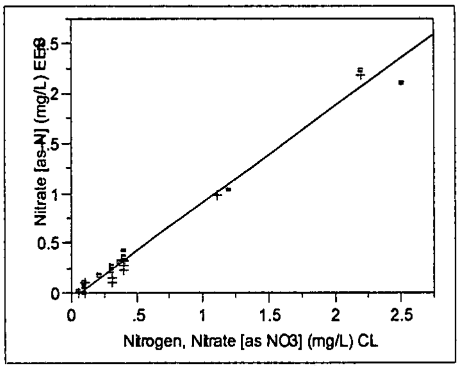
Contract and EES-6 analytical laboratory sample results for selected inorganic chemicals are shown in Figure 3. The sample results for these analytes from the EES-6 analytical laboratory are comparable to the values reported by the contract analytical laboratories (Figure 3). Results for barium and nitrate are basically identical between the EES-6 and contract analytical laboratories as illustrated by the scatter plots for these analytes (Figure 3).

The EES-6 analytical laboratory sample results for bicarbonate and total dissolved solids are greater than the comparable contract analytical laboratory sample results (slope is greater than 1.0 for these analytes, see Figure 3).

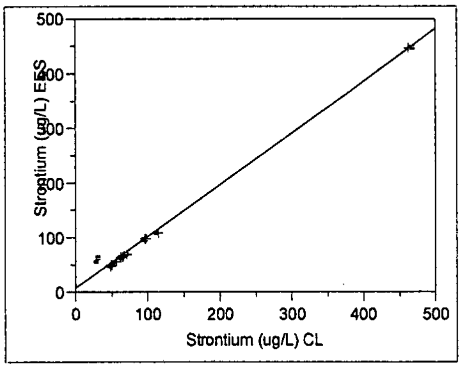
Two methods were used to determine uranium concentrations including ICP-MS and KPA. These methods were used for 27 samples, and the concentrations reported for ICP-MS and KPA agree reasonably well except for two samples.



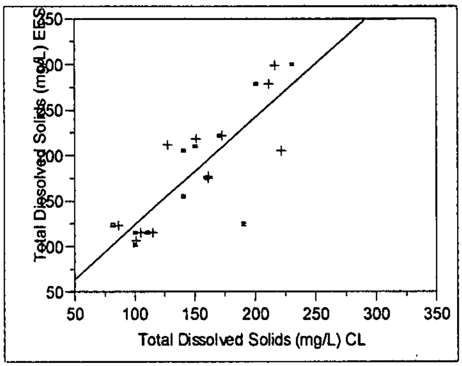
Ba EES = -0.2 + 0.97*Ba, r^2 = 0.97, n = 70



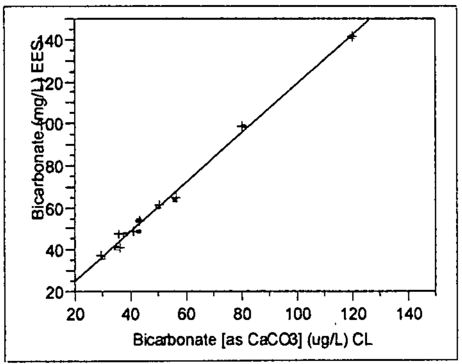
NO_3^- EES = -0.06 + 0.96*NO_3^-, r^2 = 0.98, n = 31



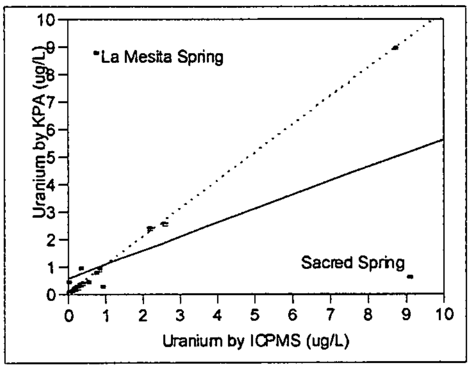
Sr EES = 8.8 + 0.94*Sr, r^2 = 0.99, n = 24



TDS EES = 5.7 + 1.18 TDS, r^2 = 0.69, n = 24



HCO_3^- EES = 2.2 + 1.17 HCO_3^-, r^2 > 0.99, n = 18



U by KPA = 0.61 + 0.51*U by ICP-MS, r^2 = 0.26,n = 27

U by KPA = 0.04 + 1.02*U by ICP-MS, r^2 = 0.99, 25*

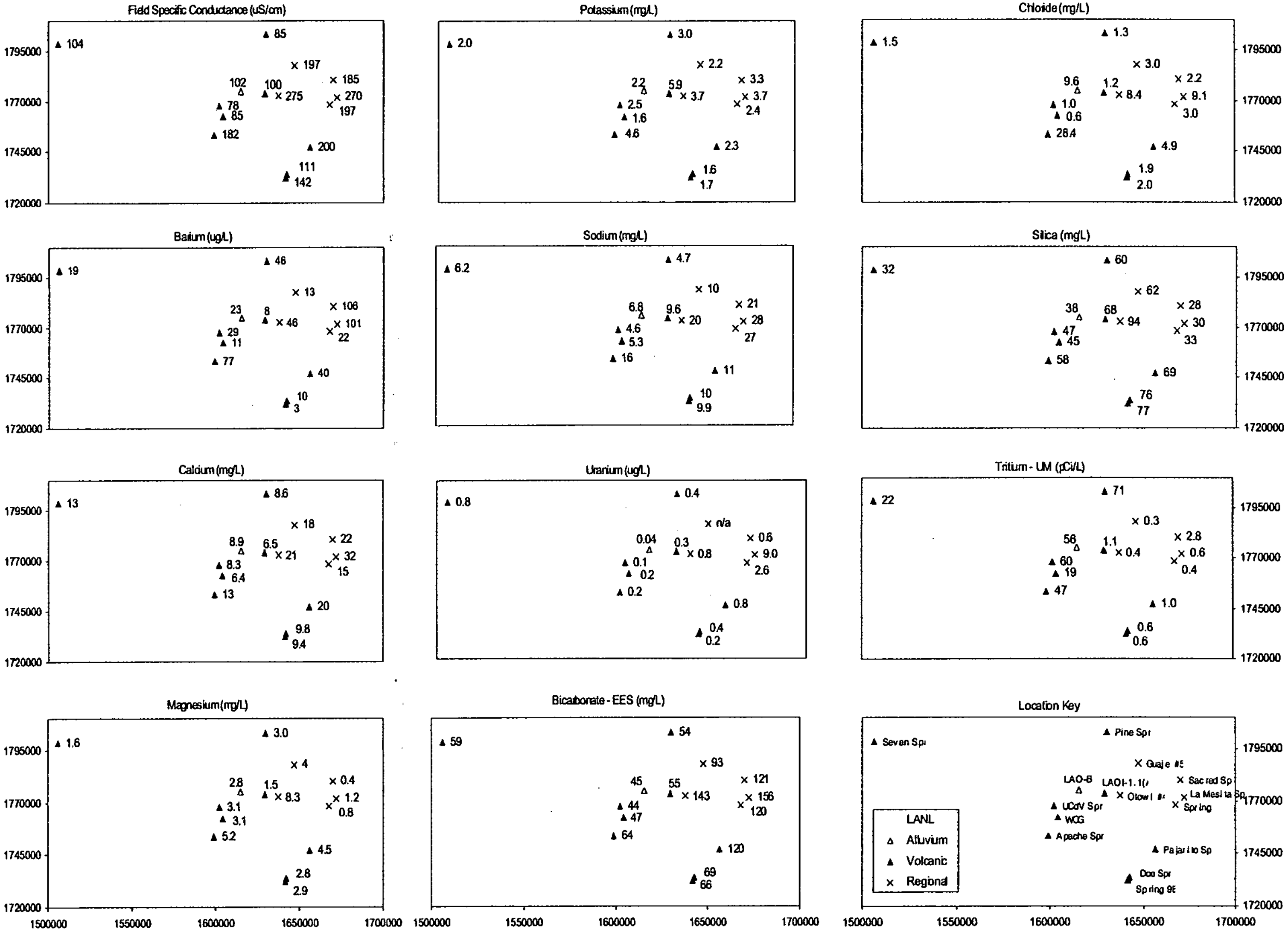
* without two outliers

Figure 3. Comparison of water chemistry results for analytical laboratories and methods (plus symbols are non-filtered samples and squares are filtered samples)

Spatial Trends in Water Chemistry Results

Spatial trends for average, filtered or dissolved concentrations of selected analytes are shown in Figure 4. The average tritium concentrations for sampling stations located near recharge boundaries (Water Canyon Gallery, Apache Spring, Upper Canyon de Valle, and Pine Spring) in the Sierra de los Valles are greater than from springs that discharge to the Rio Grande. In general, concentrations of other analytes (TDS and bicarbonate) follow an opposite pattern where higher concentrations (increasing residence times) are reported for locations with low tritium (smaller amounts of recent recharge). Some sample locations are spaced closely together, and the pair of locations most closely spaced (Doe Spring and Spring 9B) tend to have similar average concentrations for the analytes illustrated on Figure 4.

Figure 4. Spatial trends for selected analytes for LANL background springs and wells.



Evaluation of Key Analytes

A brief narrative is provided below for field parameters and several selected analytes.

Field Measurements: Temperature, turbidity, specific conductance, and pH were measured for nearly all sampling events at each location. Temperature increases with depth in a geothermal gradient from the alluvial station, to the volcanic stations, and are greatest in the regional sampling locations. Specific conductance also varies with rock type. The pH of these waters tends toward being slightly alkaline and the pH is most variable for the volcanic rocks.

Arsenic: This inorganic was detected in about 15% of the contract laboratory samples. There are no outliers and most of the detected sample results appear to be from the regional aquifer.

Barium: This inorganic was detected in about 97% of the contract laboratory samples. There are no outliers and no significant differences by rock type, water chemistry, or tritium concentration groups. Concentrations are typically consistent by sample location. Sample results are multimodal (perhaps bimodal) suggesting there are two or more underlying statistical populations.

Iron: This inorganic was detected in about 24% of the contract laboratory samples. The iron sample results for Pine Spring were outliers and are roughly 10-100 times larger than sample results for other locations. The sample results for most locations are variable. Iron data probably are derived from a mixture distribution that suggest multiple statistical populations.

Perchlorate -Incorporate new LANL and NMED Results

Uranium: This inorganic was detected in 100% of the contract laboratory samples. Uranium concentrations are much greater in selected regional aquifer locations (La Mesita Spring and Spring 1), and the concentration distribution is multimodal due to low variability within locations and large differences between some locations.

Nitrate: This water quality parameter was detected in about 91% of the EES laboratory samples. Concentrations of nitrate varied by location but did not vary significantly by rock type or location groups. Nitrate concentrations are multimodal (perhaps bimodal).

Total dissolved solids: This water quality parameter was calculated for the groundwater samples. Total dissolved solids increase from the alluvial location to volcanic rock locations, and is greatest for the regional locations. The overall TDS distribution is multimodal due to this variation between rock types.

Gross Alpha Radiation: This radioactivity measure was detected in about 83% of the contract laboratory samples. La Mesita Spring has greater gross alpha activity than other locations. The higher gross alpha activity is the result of natural uranium and its decay products.

Americium-241: This radionuclide was detected in about 15% of the contract laboratory samples. Nearly all of the detected sample results for this radionuclide came from a single sampling event in 1997, which raises questions regarding possible analytical laboratory problems with these values.

Plutonium-283 and plutonium-239: These two radionuclides were detected in about 8 to 9% of the contract laboratory samples. The high frequency of non-detected sample results makes it difficult to draw conclusions from statistical analyses.

Strontium-90: This radionuclide was not detected in the contract laboratory samples. Thus, the statistical plots are only presenting instrument noise and not measured strontium-90 concentrations.

Tritium: Tritium varies by location and exhibits a decreasing trend from the alluvial location to the volcanic rock location to the regional aquifer locations.

Comparison with Cerro Grande Fire Sampling

The Cerro Grande fire burned several major watersheds west of and within the Laboratory during May 2000. These include Guaje Canyon, Pueblo Canyon, Los Alamos Canyon, Sandia Canyon, Mortandad Canyon, Pajarito Canyon, and Cañon de Valle. Several background springs discharging within the Sierra de los Valles, including Apache Spring, upper Cañon de Valle Spring, and Pine Spring, were not impacted from the fire based on sampling results conducted since May 2000. Water Canyon Gallery also was not impacted by the fire based on sampling results. Alluvial well LAO-B was not damaged by the Cerro Grande fire, however, west of the well, upper Los Alamos Canyon was severely burned and both surface water and alluvial groundwater was impacted.

Increasing concentrations of dissolved and total major ions, most notably calcium, potassium, and bicarbonate, iron, manganese, strontium, natural uranium, TOC, and DOC were observed in surface water and alluvial groundwater for a period of time. Sampling of storm water runoff (Gallaher et al., 2002), springs, and alluvial groundwater from 2001 to 2004, by LANL and the NMED, has shown that most analytes are approaching pre-fire concentrations.

Summary

Hydrogeochemical investigations of background, non-Laboratory influenced or contaminated groundwater are mandated by several institutional programs, RFI work plans, and permits. To satisfy these requirements, we conducted a comprehensive field, chemical, radiochemical, isotopic, and statistical investigation of 15 background waters within the Pajarito Plateau – Jemez Mountains region from 1997 to 2000. The sites for this background hydrogeochemical investigation were chosen to provide data for groundwater occurring in shallow alluvium (one site), relatively shallow volcanic and volcaniclastic rocks (nine sites), and the regional aquifer (five sites). Groundwater samples collected at the 15 sites or stations have similar geohydrology and geochemical characteristics to those within LANL.

Recommendations

As a result of this study, we suggest the following recommendations for future work related to background groundwater:

1. The detailed lithology, the criteria for stratigraphic divisions and the nomenclature of sedimentary units beneath the Pajarito Plateau remains poorly described and highly confused (i.e., compare the highly contrasting stratigraphy of Purtymun, 1995 to that of Goff et al., 2002). Because units such as the Puye Formation, Totavi Lentil, and various sub-units within the Santa Fe Group host or partially host the regional aquifer and five background sites, these geologic deficiencies and inconsistencies should be resolved.

2. The LANL conceptual hydrologic model should continually be revised to conform to the updated and/or current geologic framework and hydrogeochemical model.

3. Because so much has been invested in acquiring the data and data analyses described herein, LANL should continue to sample and analyze the waters from these sites (perhaps on a yearly basis) to provide a long-term data set. This data set could be used to reference possible changes in water quality, and chemical and isotopic compositions for the 15 background sites. Current methods of data validation, data screening, interlaboratory comparisons, and statistical evaluations should be continued or improved, as needed.

4. Reliable information on baseline concentrations of major ions, trace ions, metals, stable isotopes, and radionuclides is needed for the regional aquifer wells being drilled and sampled. Statistically relevant prediction limits may require greater sample location coverage and longer time series than are currently available. One of the longer-term goals may be to develop a data set with comparable groupings at other DOE sites. The feasibility of this long-term

objective will ultimately be tied to the degree of spatial variation in water chemistry.

5. Impacts of the Cerro Grande fire on the hydrogeochemistry of four background sample sites are apparently negligible. Nonetheless, these sites discharge groundwater from relatively shallow volcanic and volcaniclastic (perched) aquifers that ring the western, hydraulically upgradient areas of LANL. Continued sampling and analysis of waters from these sites on a yearly basis is highly recommended.

Acknowledgements

We wish to thank Jennifer Koefed (University of New Mexico) and Andrew Adams (Los Alamos National Laboratory) for field assistance during the project. Anthony Garcia (EES-6) provided many of the figures. We also thank Charlie Nylander (Program Manager, LANL), Allyn Pratt (LANL), and Bruce Robinson (LANL) for institutional support. The Environmental Restoration Program and the Groundwater Protection Program of Los Alamos National Laboratory funded this project.

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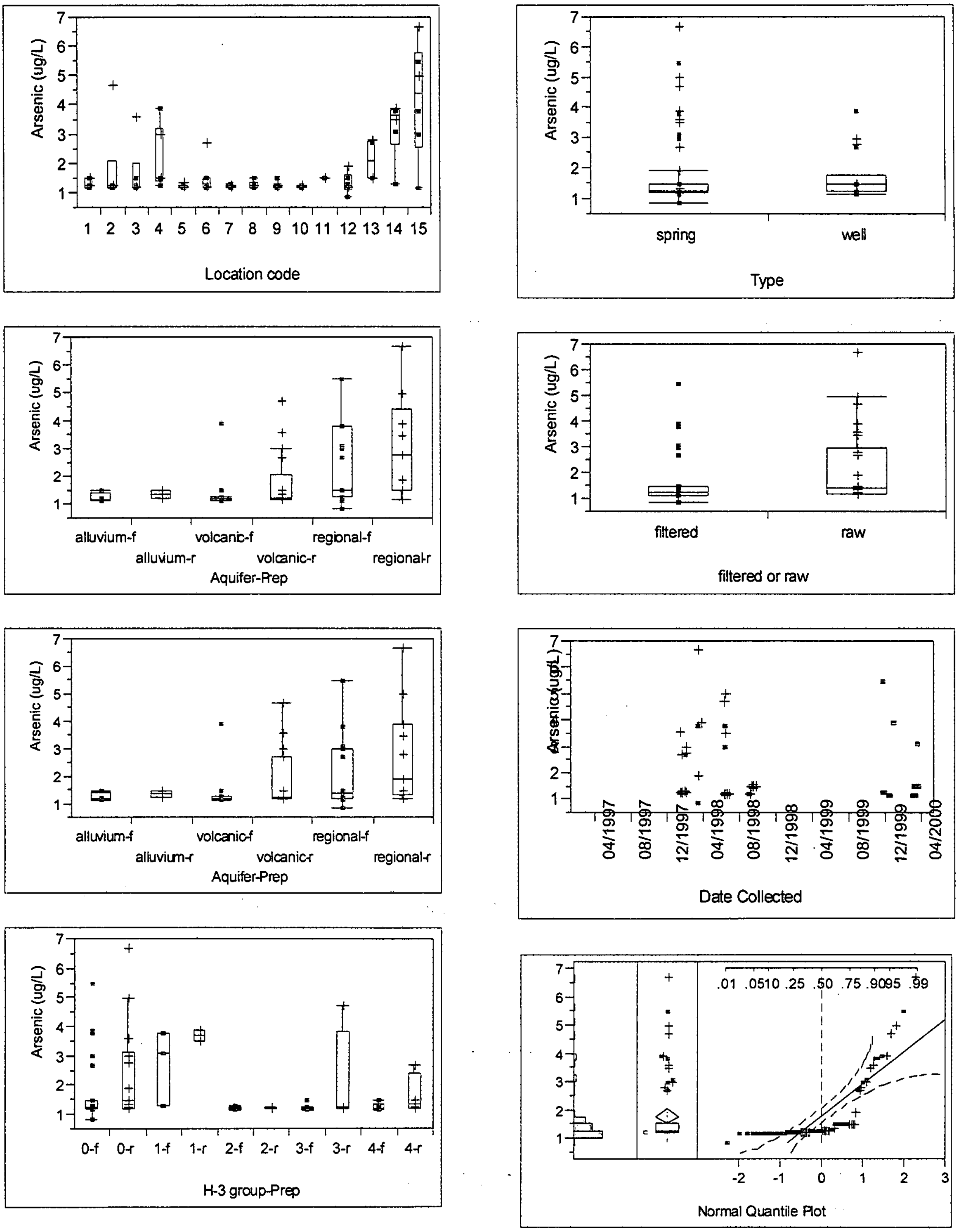

Figure A-1. Arsenic Plots [note "+" are non-filtered samples and squares are filtered samples].

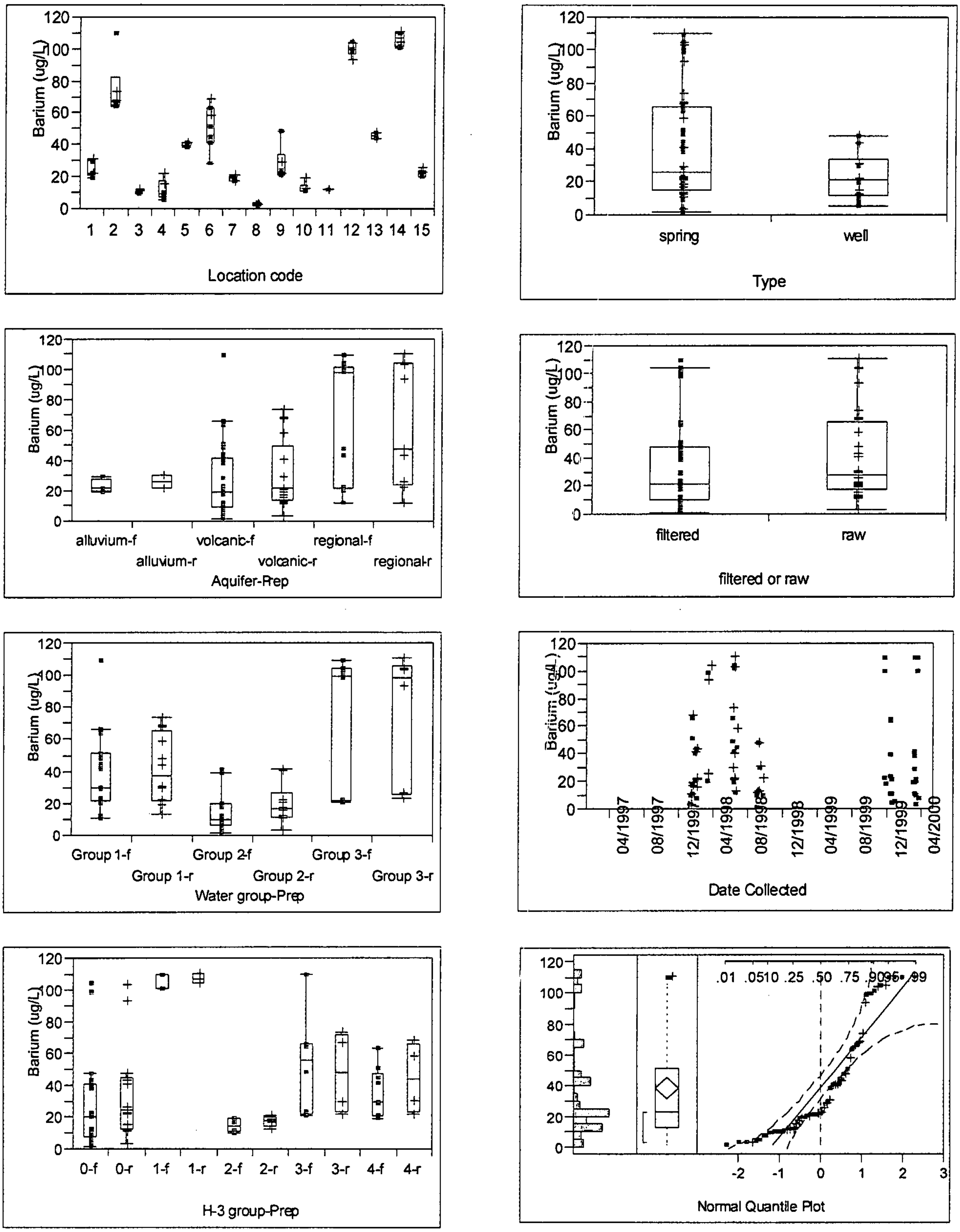

Figure A-2. Barium Plots [note "+" are non-filtered samples and squares are filtered samples].

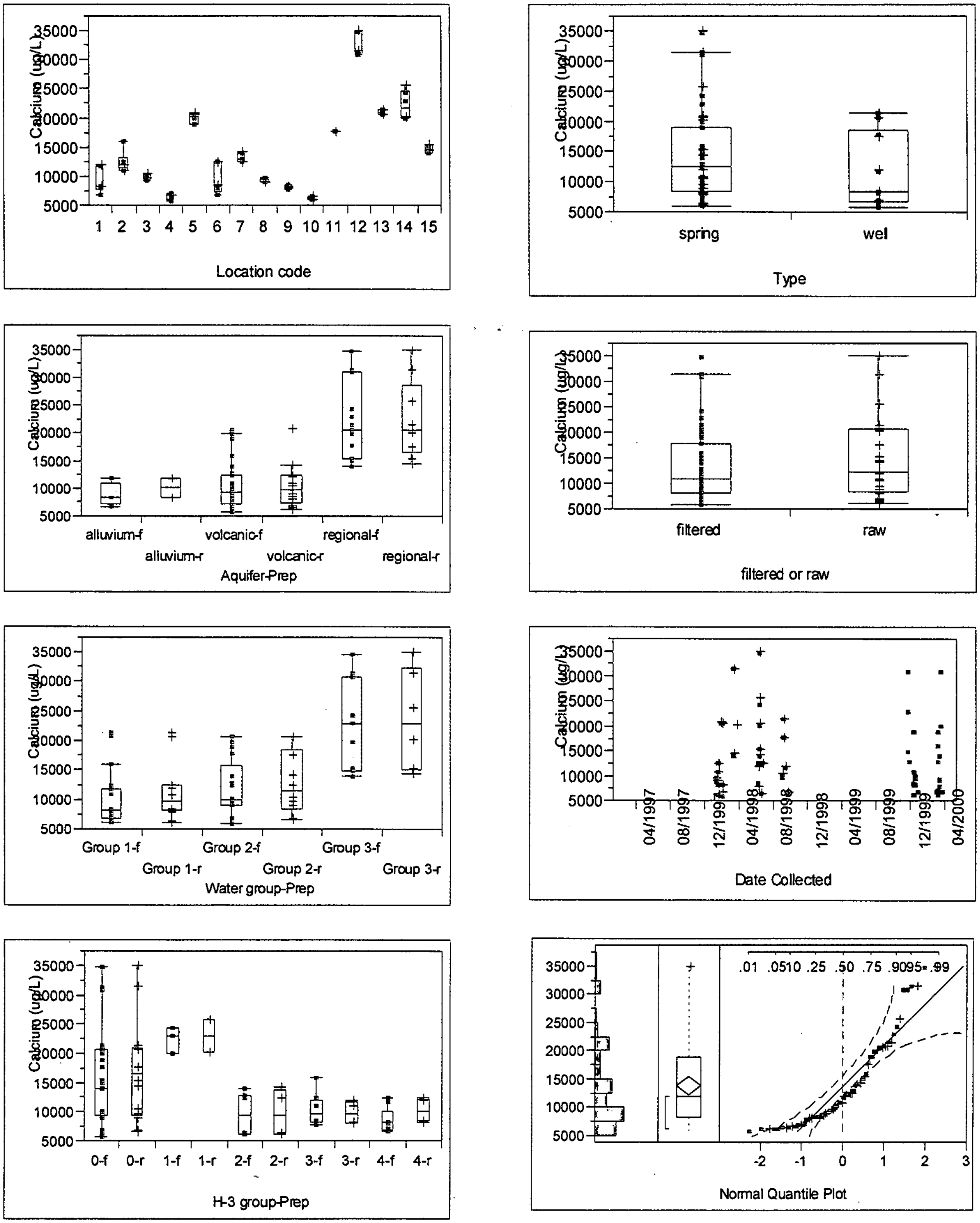

Figure A-3. Calcium Plots [note "+" are non-filtered samples and squares are filtered samples].

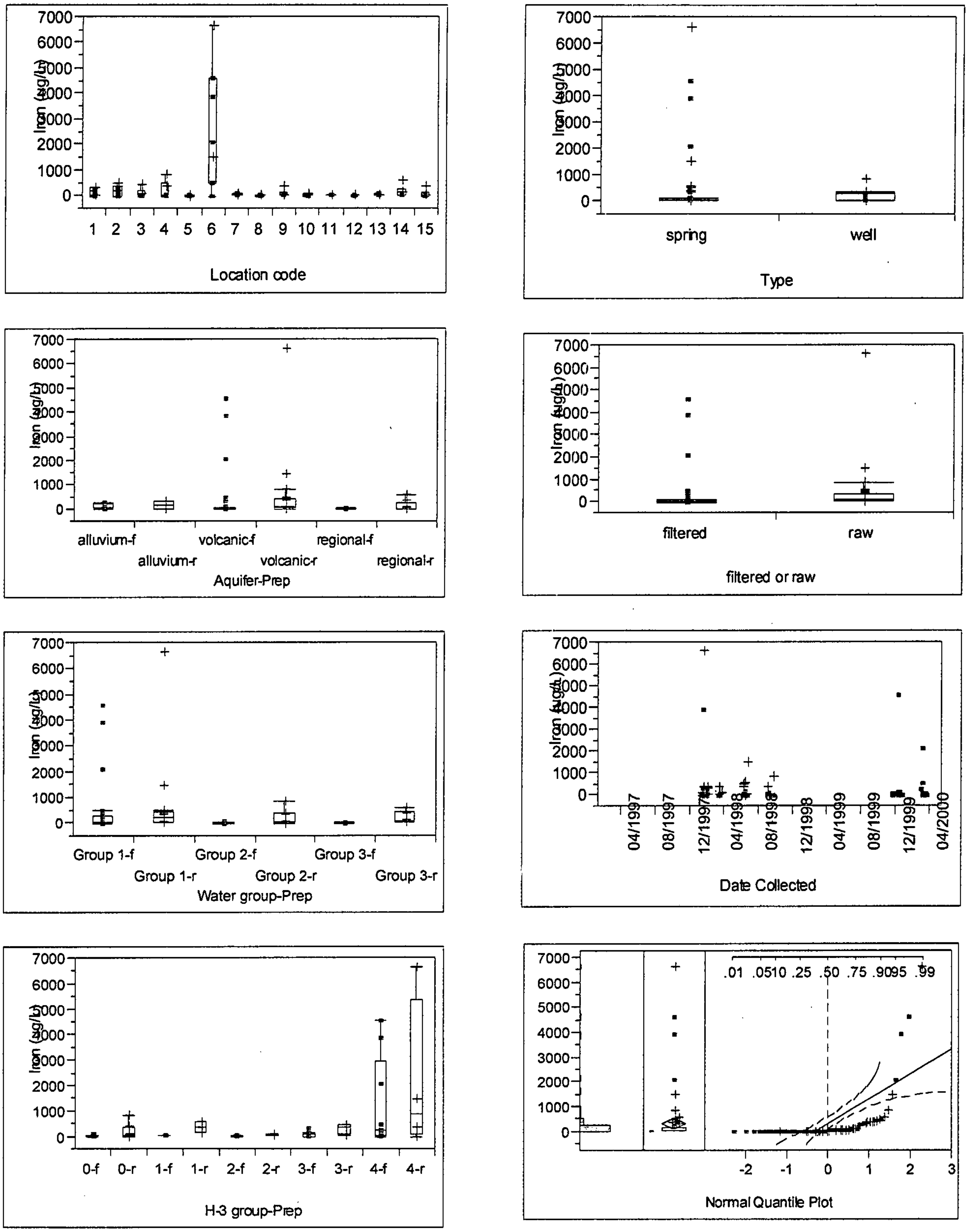

Figure A-4. Iron Plots [note "+" are non-filtered samples and squares are filtered samples].

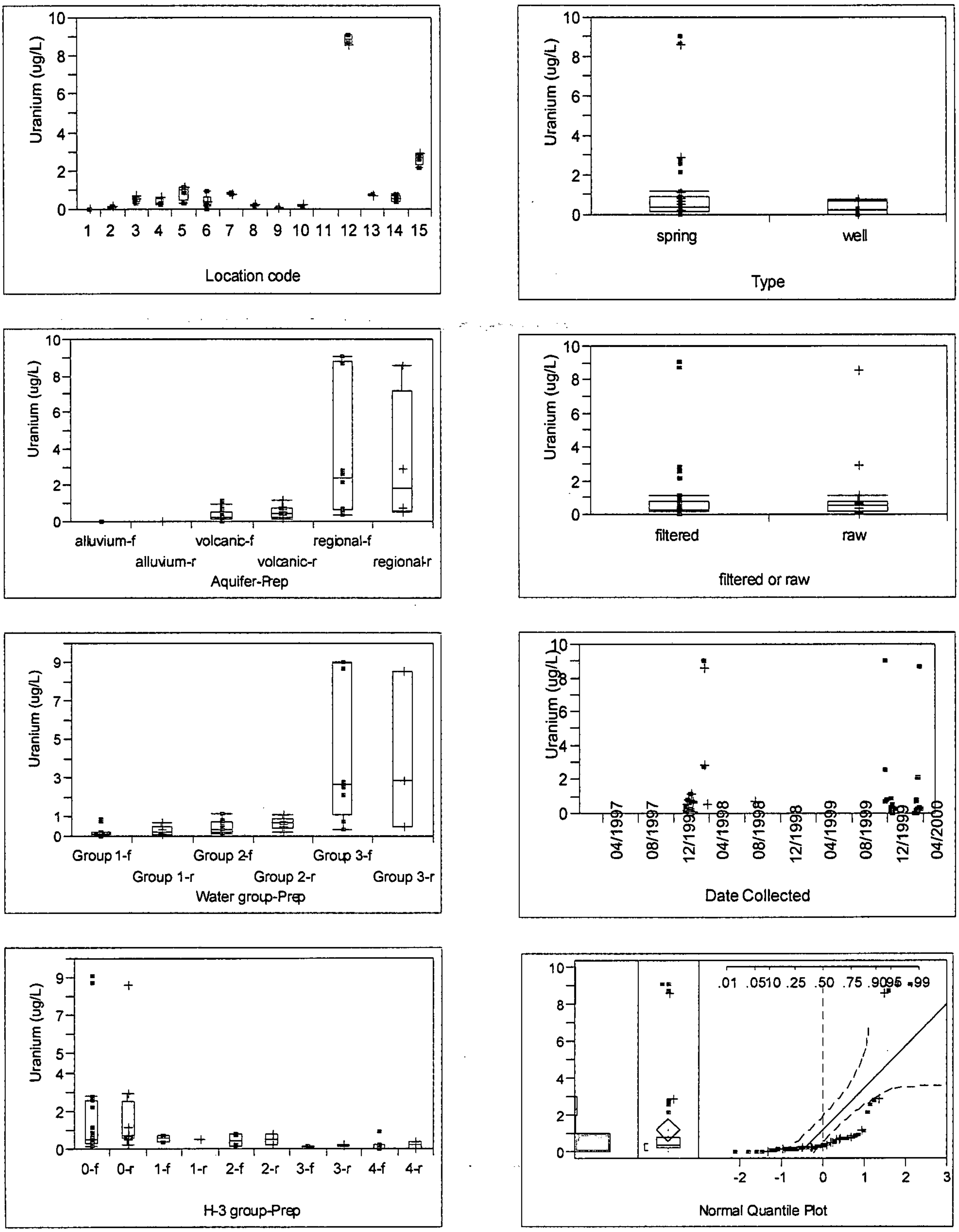

Figure A-5. Uranium Plots [note "+" are non-filtered samples and squares are filtered samples].

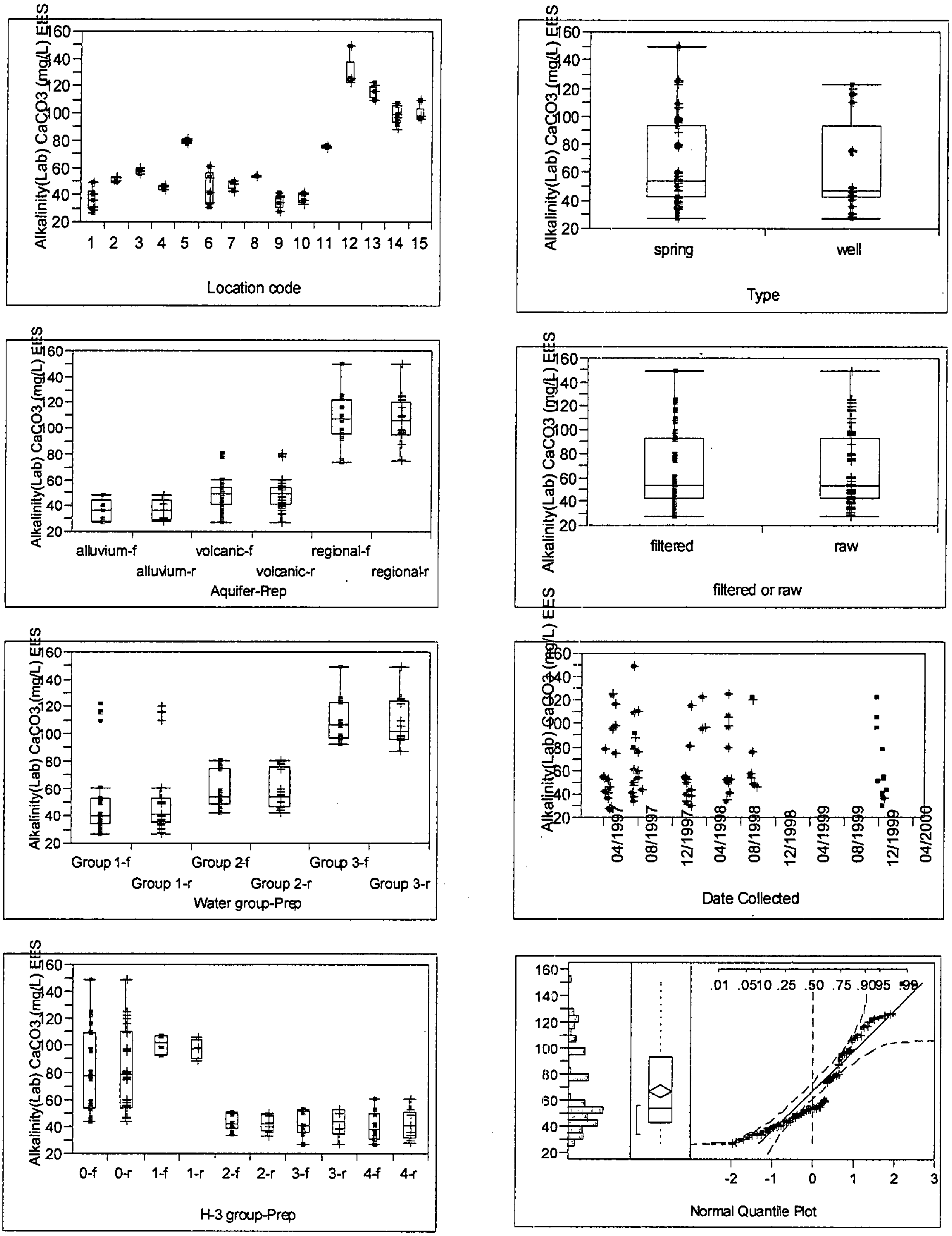

Figure A-6. Alkalinity Plots [note "+" are non-filtered samples and squares are filtered samples].

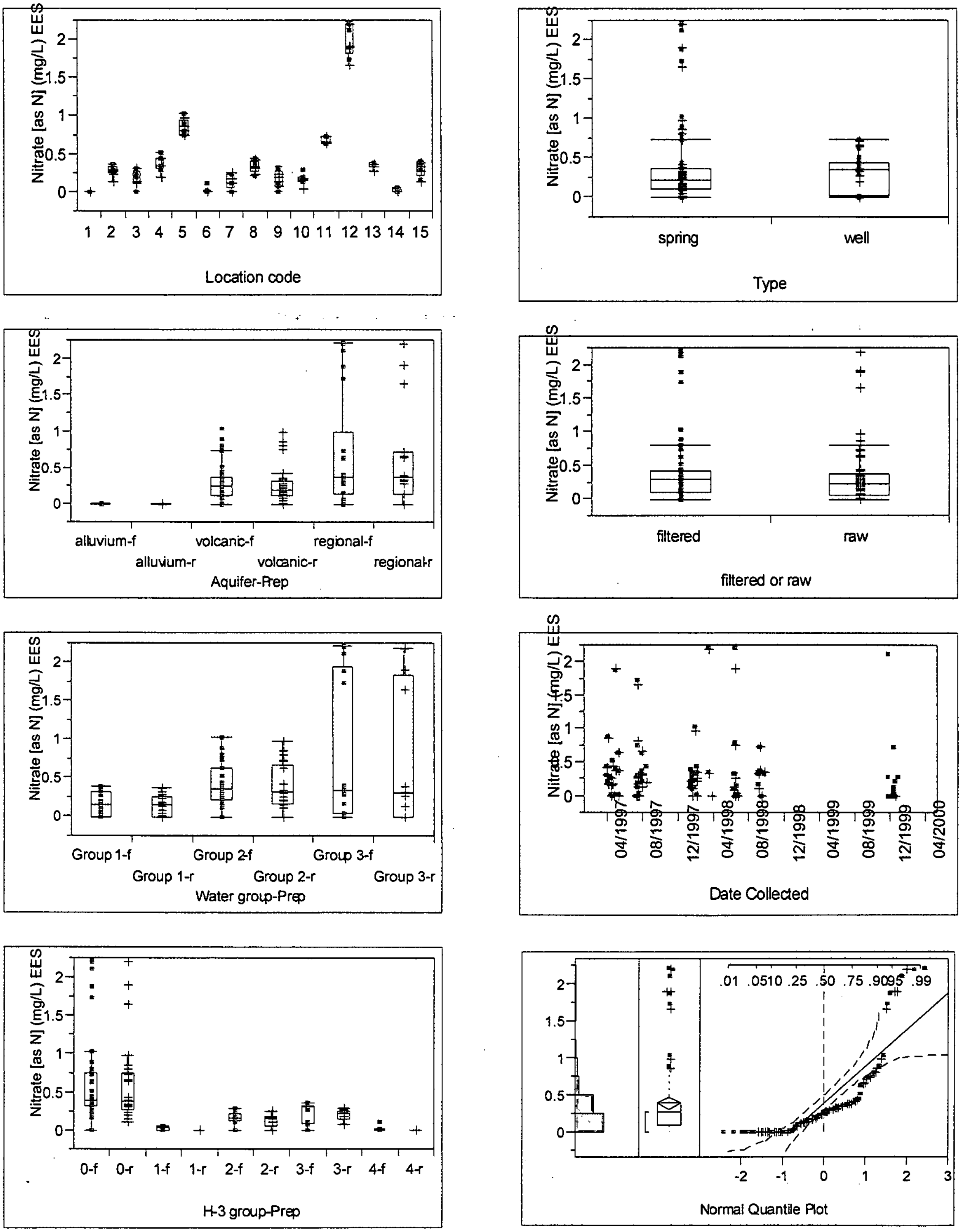

Figure A-7. Nitrate [N] Plots [note "+" are non-filtered samples and squares are filtered samples].

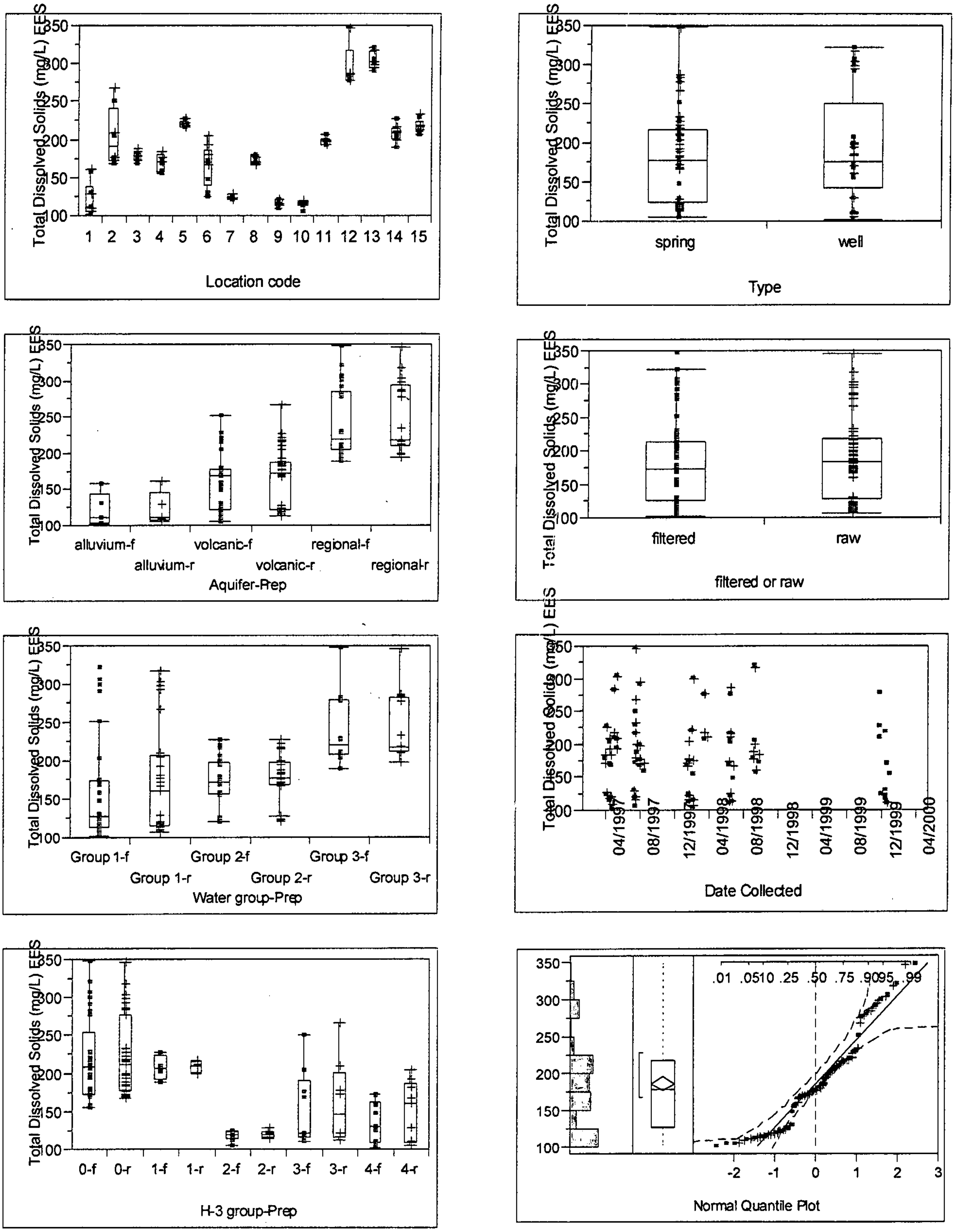

Figure A-8. TDS Plots [note "+" are non-filtered samples and squares are filtered samples].

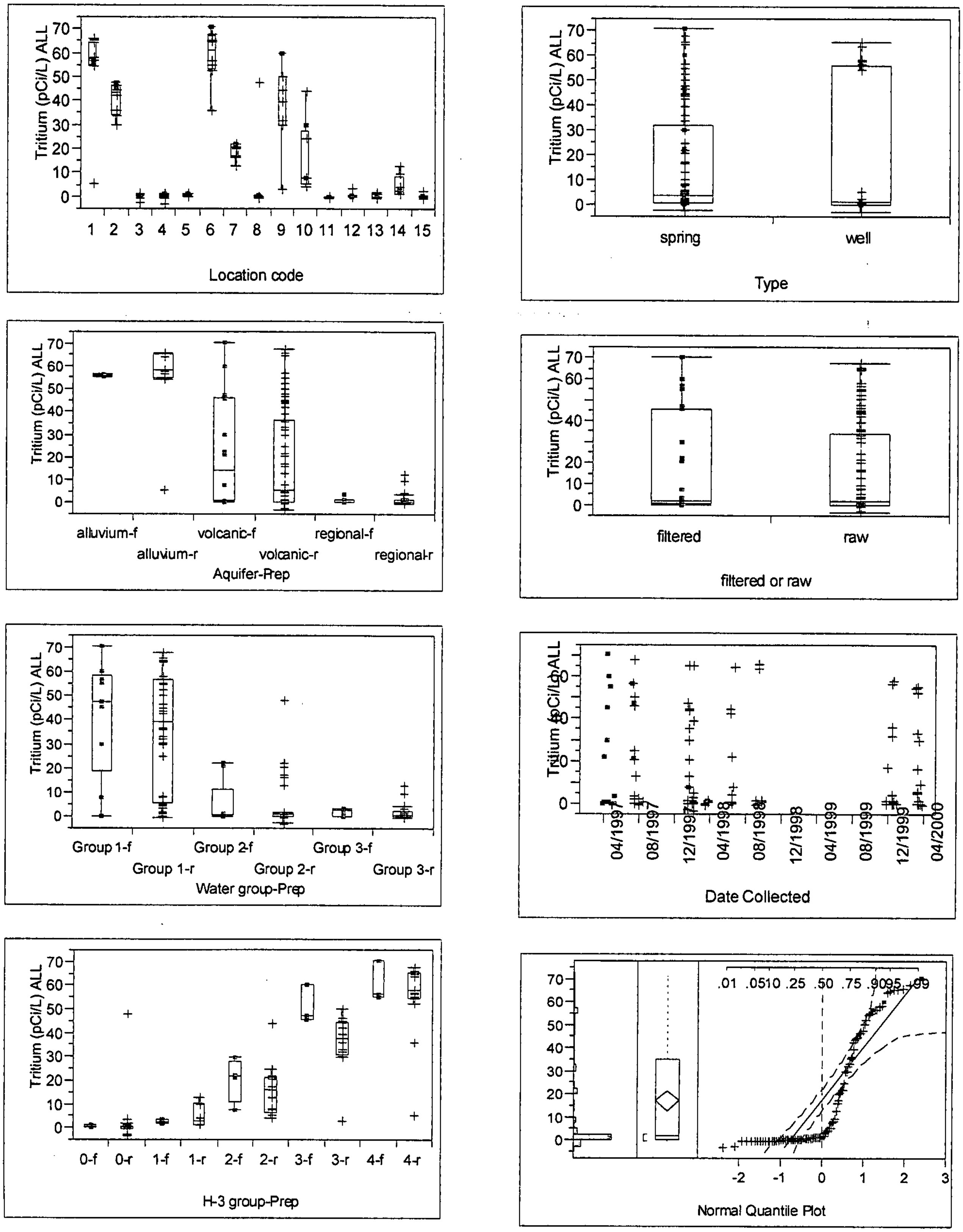

Figure A-9. Tritium ALL [combined analytical laboratory data] Plots [note "+" are non-filtered samples and squares are filtered samples].