Surface Soil Radionuclides and Inorganic Chemicals

Introduction

Results reported herein are from soil samples collected during 2001 from a grid of 16 locations surrounding the WIPP site (the Near Field grid) and a grid of 16 locations approximately 12 miles southeast of the WIPP (the Cactus Flats grid, Fig. 2). The 2001 soil samples were collected after the arrival of the first mixed waste shipments at WIPP. Thus, the data for the radioactive and hazardous waste constituents are results from the monitoring phase. Measurements were made by CEMRC on the 2001 surface soil samples for ^{234}U, ^{235}U, ^{238}U, ^{230}Th, ^{232}Th, ^{228}Th, ^{239,240}Pu, ^{137}Cs, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{228}Ac, ^{241}Am, and ^{40}K. The natural radionuclides ^{208}Tl, ^{212}Bi, ^{214}Pb and ^{212}Pb are measured after allowing for ingrowth to equilibrium and their concentrations do not represent natural levels in the environment. The activity of ^{214}Pb was used to estimate the original environmental concentration of ^{226}Ra. The activity of ^{208}Tl, ^{212}Bi and ^{212}Pb can be used to estimate activities of other members of the thorium series. Results are also presented for 43 non-radiological analytes measured using ICP-MS, AAS and IC.

One finding presented in the CEMRC 2000 Report was that there were significant differences in many analyte concentrations between the Near Field and Cactus Flats grids. In a subsequent publication differences in soil texture were identified as a likely cause for these observations (Kirchner et al., in press). The need for data on the vertical distribution of radionuclides in the soils was also identified in the CEMRC 2000 Report. In 2001 samples were taken from within the vertical soil profile to depths of 125 cm at four sampling locations.

Methods

The 16 sampling locations constituting each grid are distributed over approximately 16,580 hectares. In both 1998 and 1999 at each of the 32 locations (grid nodes), soil was collected from three randomly selected sites within a 50-m radius of the selected reference point. In 2000, one sample was collected at each of the 32 grid nodes. In 2001, two samples were collected at each of the 32 grid nodes. One of each pair of the 2001 samples was analyzed and the other was archived. Four additional field duplicates were collected at randomly selected reference points each year. Individual sampling sites were selected on the basis of relatively flat topography, minimum surface erosion and minimum surface disturbance by human or livestock activity. At each sampling site, approximately 20 g of soil were removed using a plastic trowel from near the center of each of two 25-cm x 25-cm areas and placed in a plastic bag for inorganic analyses. In addition, approximately 8 L of soil were collected from within the two sampling areas to a depth of approximately 2-cm for radionuclide analyses. Soil samples were excavated using a trowel and placed in plastic bags for transport and storage. Sampling equipment was cleaned between samples.

Initial preparation of the samples for radiological analyses consisted of passing the soil through a 2-mm sieve to remove rocks, roots and other materials. Samples were then dried at 105˚C for 12 hours and ground using a jar mill. Approximately 300-mL aliquots were used for gamma spectroscopy analysis. The samples for gamma analysis were sealed in a ~ 300-mL can and stored for at least 21 days to allow radon progeny to reach equilibrium with parent radionuclides.

Gamma spectroscopy analysis was conducted using high purity Ge (HPGe) detector systems for 2-3 days. A set of soil matrix standards was prepared using NIST traceable solutions and used to establish matrix-specific calibration and counting efficiencies.

A 15-g and a 2-g aliquot of soil were used for actinide analyses. The 15-g aliquot of soil was used for the analysis of Am and Pu. The aliquots were heated in a muffle furnace at 500 °C to combust organic material and spiked with a radioactive tracer to allow determination of the efficiency of extraction.

The aliquots then underwent dissolution with HNO_3, HF and HCl followed by digestion with perchloric acid to remove silica. The samples were then dissolved in dilute HNO_3 and boric acid.

U and Th were determined by sequential analysis using the 2-g aliquot of soil. The aliquots were spiked with radioactive tracers and then underwent NaOH fusion. The fused sample was dissolved in HCl and treated with HF and perchloric acid to remove silica.

Multiple precipitation, co-precipitation and ion-exchange and/or extraction chromatography procedures were then used to separate and purify the desired elements from each of the aliquots. The elements of interest from each were then precipitated with NdF_3, deposited onto filters, mounted and counted on an alpha spectroscopy system. A summary of QA/QC for radioanalyses is presented in Appendix L.

Soil sample aliquots of 0.1 g were analyzed for the inorganic analytes using the soil collected from near the center of the sampling areas. These samples were neither sieved nor ground to prevent potential contamination by metals. EPA Method 3052 (microwave digestion) was used to prepare samples for both the AA and ICP-MS. ICP-MS was used to analyze samples for Ag, Al, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Pr, Sb, Si, Sm, Sr, Th, Ti, Tl, U, V and Zn using EPA Method 200.8. Hg was determined with flow injection hydride ICP-MS using EPA Method 1631 for digestion. As and Se were determined on the AA using the EPA 7000 series methods. The lower detection limits for both of these systems are in the low parts per billion range (Appendix K). Soil samples were analyzed by IC for chloride, fluoride, nitrate, phosphate and sulfate using EPA Method 300.0. A summary of QA/QC methods for inorganic analyses is presented in Appendix K. The mean concentrations of these analytes reported herein for soils include only those values that are above detection levels. Thus, some estimates of the mean may be biased toward larger values.

Reported concentrations are blank-corrected. Negative concentrations of analytes can result when both the sample and the blank have concentrations above the MDL, and are hence regarded as detectable quantities, with the blank concentration exceeding the sample concentration. Thus negative values are invariably small and represent values very near the blank concentrations.

Quality Control

Reproducibility of the measurements for the non-radiological analytes was determined from comparing five sets of laboratory duplicates. Relative Percent Differences (RPDs) were computed for all pairs for which the measurements were greater than the Minimum Detectable Concentration (MDC). The RPD is calculated as

$$RPD = 2\frac{|c_1 - c_2|}{c_1 + c_2} \times 100\%$$

where c_i is the concentration of the i^{th} duplicate. The RPD is the difference divided by the mean of two values expressed as a percent.

Reproducibility of the measurements of radionuclides was determined by comparing measurements from four sets of laboratory duplicates. Relative Error Ratios (RERs) were computed for all measurements for which concentrations were greater than the MDC. RER is computed as

$$RER = \frac{|c_1 - c_2|}{\sqrt{s_1^2 + s_2^2}}$$

where c_i is the concentration of the i^{th} duplicate and s_i is the estimated standard deviation of the i^{th} concentration. The standard deviation incorporates counting uncertainty and uncertainties associated with other aspects of the instrument measurements. Relative error ratios are used in addition to RDPs when comparing duplicate samples of radionuclides because they take into account counting and other uncertainties that are associated with activity measurements. RERs were computed for ^{228}Ac, ^{241}Am, ^{212}Bi, ^{214}Bi, ^{137}Cs, ^{40}K, ^{212}Pb, ^{214}Pb, ^{239}Pu, ^{228}Th, ^{230}Th, ^{232}Th, ^{208}Tl, ^{234}U, ^{235}U, and ^{238}U.

Results and Discussion

Reproducibility of Measurements

The average RPDs for the non-radiological analytes ranged from 5% to 27% with the exception of those analytes which had measurements below the Practical Quantitation Limit (PQL) of 5 × MDL (Table K3). The maximum RPD values ranged from 9% to 41%. The average RPD value is appropriate for estimating the reproducibility on the average of several samples, whereas the maximum RPD is a conservative estimate of the uncertainty in reproducibility that could be observed on any single measurement. The RPDs reflect the uncertainty in estimated concentrations due to variability in analysis and heterogeneity in the samples. Heterogeneity in the non-radiological samples was probably high because of the relatively small aliquots analyzed and because the samples were not ground. All of the duplicate comparisons were considered acceptable as defined under the Quality Assurance/Quality Control criteria defined for soils (Appendix K), meeting either a criteria of an RPD < 35% or sample measurements < 5 × MDL (the Practical Quantitative Limit).

The measurements of radionuclides in laboratory duplicates were generally in good agreement. RPDs ranged between 1% and 37%. RPDs hold meaning only when the RERs are relatively low, i.e. when the differences do not fall within the range of analytical uncertainty. The maximum RER was 2.19 for the radionuclides measured by gamma analysis (Table L5). The maximum RER for gamma analyses was incorrectly reported as 0.21 in the CEMRC 2000 Report. The correct maximum RER value for 2000 soil samples was 2.5. The RERs for the actinides measured by alpha spectroscopy ranged between 0.80 for ^{241}Am to 1.68 for ^{228}Th. These RERs are comparable to the RERs for soil radionuclide measurements reported in the DOE/WIPP Site Environmental Report (2001, *Waste Isolation Pilot Plant 2000 Site Environmental Report*, DOE/WIPP-01-2225, hereafter DOE/WIPP SER). The duplicate soil analyses reported in the DOE/WIPP SER were limited to ^{234}U, ^{238}U, ^{40}K and ^{137}Cs because ^{238}Pu, and ^{239,240}Pu were not detected in any soil samples, and the 2 measurements of ^{241}Am that were above detection levels were less than twice their total propagated uncertainty values and hence judged to be absent in the samples. The maximum RER reported in the DOE/WIPP SER was 2.42.

Comparison to Other Studies

The concentrations of the inorganic analytes (Figs. 20 and 21) and radionuclides (Figs. 22 and 23) are generally consistent between years. As was noted previously (CEMRC 2000 and Kirchner et al. In Press), there are notable differences between the mean concentrations of many of the analytes between the Near Field and Cactus Flats grids. The higher concentrations of many metals and radionuclides on the Cactus Flats grid as compared to the Near Field grid is probably due to a higher proportion of fine soil particles in the Cactus Flats samples (Tables 10 and 11).

The activity concentrations of ^{137}Cs, ^{234}U, ^{235}U, ^{238}U, and ^{40}K in CEMRC 2001 samples fell within the ranges reported in the DOE/WIPP SER (*op. cit.*). It should be noted, however, that the mean concentrations of ^{234}U, ^{235}U, and ^{238}U reported for 2001 are significantly higher ($p < 0.05$) than the mean values reported for 1998 and 2000 (Figs. 22 and 23). The 2001 mean values for the uranium isotopes showed an increase of 18% or more over the means from previous years. It was suspected that this increase resulted from the change in the sample preparation methodology for actinide analyses even though both methods were expected to result in complete dissolution of the samples. To evaluate this hypothesis 10 samples from 2000 were reanalyzed using the new methodology. Each of the new measurements exceeded the corresponding measurement made in 2000. The average RPDs between the 2000 and 2001 measurements for ^{234}U, ^{235}U and ^{238}U were 17%, 28% and 19%, respectively. Thus, the change in methodology does appear to be the cause of the increase.

The maximum ^{239,240}Pu concentration (0.40 mBq g^{-1}) was within the range reported by Kenney et al. (1995, *Radionuclide Baseline in Soil Near Project Gnome and the Waste*

Isolation Pilot Plant, EEG-58) at the WIPP (0-0.74 mBq g^{-1}) and was lower than background concentrations found at Hueston Woods and Urbana, Ohio (0.7-1.0 mBq g^{-1}) (Alberts et al., 1980, *J. Environ. Qual.* 9, 592) and at a series of 15 locations between Ft. Collins and Colorado Springs, Colorado (0.6-1.7 mBq g^{-1}) (Hodge et al., 1996, *Chemosphere* 32, 2067).

Tables presenting soil data summarized herein are available on the CEMRC web site at http://www.cemrc.org.

Table 10. Summary Statistics for Inorganic Analytes in Soil Samples Collected in 2001

Analyte		Near Field			Cactus Flats		
	Unit	[a]N	[b]Mean	Range	N	Mean	Range
Ag	mg kg^{-1}	21	8.8E-03	4.8E-03 - 1.2E-02	20	1.3E-02	7.0E-03 - 3.1E-02
Al	mg kg^{-1}	21	3.7E+03	2.3E+03 - 5.6E+03	19	3.7E+03	2.2E+03 - 6.9E+03
As	mg kg^{-1}	21	2.5E+00	1.8E+00 - 4.3E+00	20	3.2E+00	9.5E-01 - 5.6E+00
Ba	mg kg^{-1}	21	2.6E+01	1.6E+01 - 4.3E+01	19	3.0E+01	1.6E+01 - 5.9E+01
Be	mg kg^{-1}	21	1.5E-01	1.0E-01 - 2.1E-01	20	2.0E-01	1.1E-01 - 3.2E-01
Ca	mg kg^{-1}	21	7.0E+02	4.0E+02 - 2.3E+03	20	7.3E+02	4.0E+02 - 2.1E+03
Cd	mg kg^{-1}	20	3.9E-02	2.6E-02 - 6.0E-02	20	5.4E-02	2.4E-02 - 9.5E-02
Ce	mg kg^{-1}	21	7.7E+00	5.1E+00 - 1.2E+01	20	8.0E+00	4.9E+00 - 1.3E+01
Chloride	mg kg^{-1}	21	6.1E-01	8.4E-02 - 1.8E+00	20	6.9E-01	1.2E-01 - 5.2E+00
Co	mg kg^{-1}	21	9.1E-01	6.2E-01 - 1.2E+00	20	1.1E+00	6.9E-01 - 1.8E+00
Cr	mg kg^{-1}	21	4.9E+00	3.7E+00 - 6.3E+00	20	6.2E+00	3.9E+00 - 8.6E+00
Cu	mg kg^{-1}	21	2.0E+00	1.3E+00 - 2.7E+00	20	2.6E+00	1.7E+00 - 3.8E+00
Dy	mg kg^{-1}	21	3.0E-01	2.2E-01 - 4.1E-01	20	3.7E-01	2.4E-01 - 5.6E-01
Er	mg kg^{-1}	21	1.4E-01	1.0E-01 - 1.9E-01	20	1.8E-01	1.2E-01 - 2.8E-01
Eu	mg kg^{-1}	21	1.0E-01	6.9E-02 - 1.4E-01	20	1.2E-01	7.6E-02 - 1.7E-01
Fe	mg kg^{-1}	21	3.8E+03	2.7E+03 - 5.0E+03	19	4.3E+03	3.1E+03 - 6.1E+03
Fluoride	mg kg^{-1}	18	2.2E-01	3.0E-02 - 4.0E-01	14	4.4E-01	2.8E-01 - 6.1E-01
Gd	mg kg^{-1}	21	5.6E-01	3.9E-01 - 7.4E-01	20	6.8E-01	4.4E-01 - 9.9E-01
Hg	mg kg^{-1}	11	3.7E-03	2.3E-03 - 6.3E-03	20	5.0E-03	2.6E-03 - 1.3E-02
K	mg kg^{-1}	21	9.9E+02	7.1E+02 - 1.4E+03	20	1.1E+03	5.9E+02 - 2.0E+03
La	mg kg^{-1}	21	3.9E+00	2.8E+00 - 5.2E+00	20	4.5E+00	2.9E+00 - 6.7E+00
Li	mg kg^{-1}	21	3.1E+00	2.4E+00 - 4.2E+00	20	3.6E+00	2.2E+00 - 6.1E+00
Mg	mg kg^{-1}	21	5.8E+02	3.7E+02 - 8.9E+02	19	6.2E+02	3.8E+02 - 1.3E+03
Mn	mg kg^{-1}	21	4.9E+01	3.5E+01 - 6.4E+01	19	6.0E+01	4.1E+01 - 9.3E+01
Mo	mg kg^{-1}	21	1.1E-01	7.4E-02 - 1.7E-01	20	1.7E-01	1.0E-01 - 2.8E-01
Na	mg kg^{-1}	21	1.7E+01	1.1E+01 - 2.8E+01	20	1.7E+01	1.0E+01 - 3.8E+01
Ni	mg kg^{-1}	21	2.9E+00	2.0E+00 - 4.5E+00	20	1.1E+00	-3.7E+00 - 4.2E+00
Nitrate	mg kg^{-1}	12	8.8E+00	1.9E+00 - 4.1E+01	20	7.3E+00	2.5E+00 - 2.4E+01
Pb	mg kg^{-1}	21	2.9E+00	2.1E+00 - 4.2E+00	20	3.8E+00	2.7E+00 - 5.0E+00
Phosphate	mg kg^{-1}	2	4.6E+00	4.6E+00 - 4.6E+00	13	6.1E+00	3.0E+00 - 1.3E+01
Sb	mg kg^{-1}	21	7.4E-02	4.4E-02 - 1.4E-01	20	1.1E-01	5.8E-02 - 1.6E-01
Sc	mg kg^{-1}	21	7.1E-01	5.1E-01 - 9.9E-01	20	8.3E-01	5.0E-01 - 1.3E+00
Si	mg kg^{-1}	21	6.3E+02	9.0E+01 - 1.1E+03	20	1.9E+02	-9.2E+01 - 1.2E+03
Sm	mg kg^{-1}	21	6.1E-01	4.3E-01 - 8.3E-01	20	7.0E-01	4.7E-01 - 1.0E+00
Sr	mg kg^{-1}	21	4.5E+00	3.2E+00 - 6.5E+00	20	5.1E+00	3.3E+00 - 8.4E+00
Sulfate	mg kg^{-1}	2	2.8E+00	2.7E+00 - 2.9E+00	13	2.9E+00	1.6E+00 - 3.8E+00

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Table 10. Summary Statistics for Inorganic Analytes in Soil Samples Collected in 2001 (Cont.)

Analyte		Near Field			Cactus Flats		
	Unit	[a]N	[b]Mean	Range	N	Mean	Range
Th	mg kg^{-1}	21	1.3E+00	8.3E-01 - 3.1E+00	20	1.4E+00	9.8E-01 - 2.1E+00
Ti	mg kg^{-1}	21	7.6E+01	3.5E+01 - 1.1E+02	19	6.3E+01	4.2E+01 - 1.1E+02
Tl	mg kg^{-1}	21	3.7E-02	2.3E-02 - 5.5E-02	20	5.1E-02	3.1E-02 - 7.8E-02
U	mg kg^{-1}	21	1.1E-01	7.4E-02 - 2.2E-01	20	1.2E-01	8.1E-02 - 1.8E-01
V	mg kg^{-1}	21	8.5E+00	3.9E+00 - 1.7E+01	20	6.2E+00	4.0E+00 - 1.6E+01
Zn	mg kg^{-1}	15	1.3E+01	1.1E+01 - 1.6E+01	20	1.4E+01	1.1E+01 - 2.1E+01

[a] N = number of samples > MDC
[b] Mean = arithmetic mean

Table 11. Summary Statistics for Radionuclides in Soil Samples Collected in 2001

Analyte		Near Field			Cactus Flats		
	Unit	[a]N	[b]Mean	Range	N	Mean	Range
^{228}Ac	mBq g^{-1}	20	9.2E+00	6.3E+00 - 1.4E+01	20	1.1E+01	8.9E+00 - 1.6E+01
^{241}Am	mBq g^{-1}	18	4.4E-02	1.3E-02 - 1.0E-01	19	4.8E-02	3.0E-02 - 1.0E-01
^{212}Bi	mBq g^{-1}	20	8.9E+00	6.1E+00 - 1.4E+01	20	1.1E+01	7.8E+00 - 1.7E+01
^{214}Bi	mBq g^{-1}	20	8.3E+00	5.9E+00 - 1.2E+01	20	9.7E+00	7.6E+00 - 1.3E+01
^{137}Cs	mBq g^{-1}	20	4.0E+00	3.0E-01 - 8.8E+00	20	5.0E+00	2.6E+00 - 9.6E+00
^{40}K	mBq g^{-1}	20	2.2E+02	1.7E+02 - 3.2E+02	20	2.1E+02	1.7E+02 - 3.0E+02
^{212}Pb	mBq g^{-1}	20	8.6E+00	6.3E+00 - 1.3E+01	20	1.1E+01	8.1E+00 - 1.5E+01
^{214}Pb	mBq g^{-1}	20	8.8E+00	6.5E+00 - 1.3E+01	20	1.0E+01	8.2E+00 - 1.4E+01
^{239}Pu	mBq g^{-1}	17	1.4E-01	5.4E-02 - 3.1E-01	20	1.8E-01	8.8E-02 - 4.0E-01
[c] ^{226}Ra	mBq g^{-1}	20	8.8E+00	6.5E+00 - 1.3E+01	20	1.0E+01	8.2E+00 - 1.4E+01
^{228}Th	mBq g^{-1}	18	9.0E+00	6.8E+00 - 1.3E+01	20	1.1E+01	8.6E+00 - 1.6E+01
^{230}Th	mBq g^{-1}	18	1.0E+01	7.3E+00 - 1.4E+01	20	1.2E+01	9.2E+00 - 1.6E+01
^{232}Th	mBq g^{-1}	18	8.7E+00	6.4E+00 - 1.2E+01	20	1.1E+01	8.4E+00 - 1.5E+01
^{208}Tl	mBq g^{-1}	20	2.7E+00	1.9E+00 - 4.1E+00	20	3.3E+00	2.5E+00 - 4.8E+00
^{234}U	mBq g^{-1}	18	9.1E+00	6.5E+00 - 1.3E+01	20	1.0E+01	8.4E+00 - 1.3E+01
^{235}U	mBq g^{-1}	18	5.4E-01	3.3E-01 - 7.6E-01	20	6.3E-01	4.1E-01 - 8.6E-01
^{238}U	mBq g^{-1}	18	9.2E+00	6.8E+00 - 1.3E+01	20	1.1E+01	8.0E+00 - 1.3E+01

[a] N = number of samples > MDC
[b] Mean = arithmetic mean
[c] Based on ^{214}Pb at equilibrium

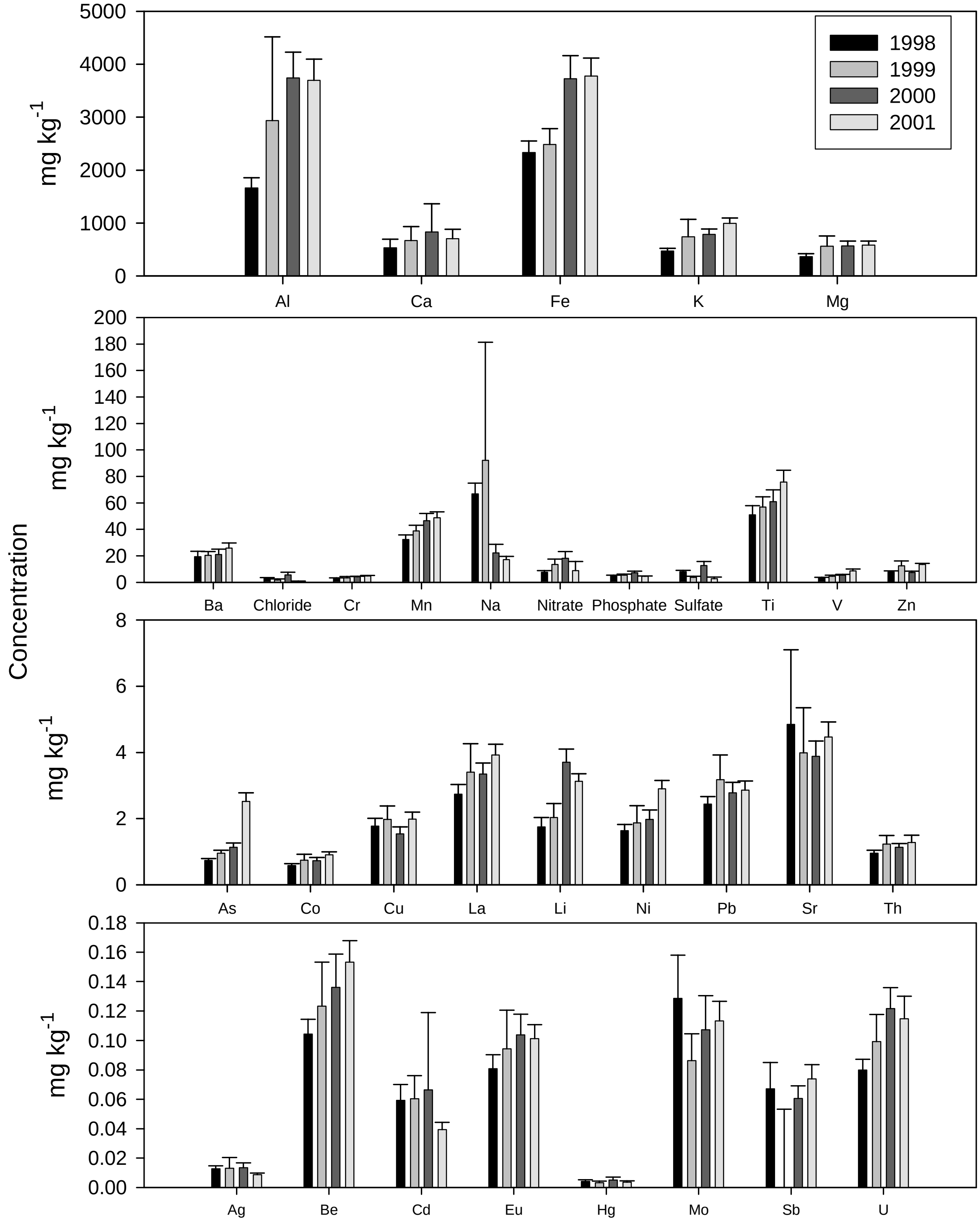

Figure 20. Mean Concentrations of Inorganic Analytes in Soil Samples from Near Field Grid Collected during 1998 – 2001

Error bars show upper 95% confidence intervals for concentrations.

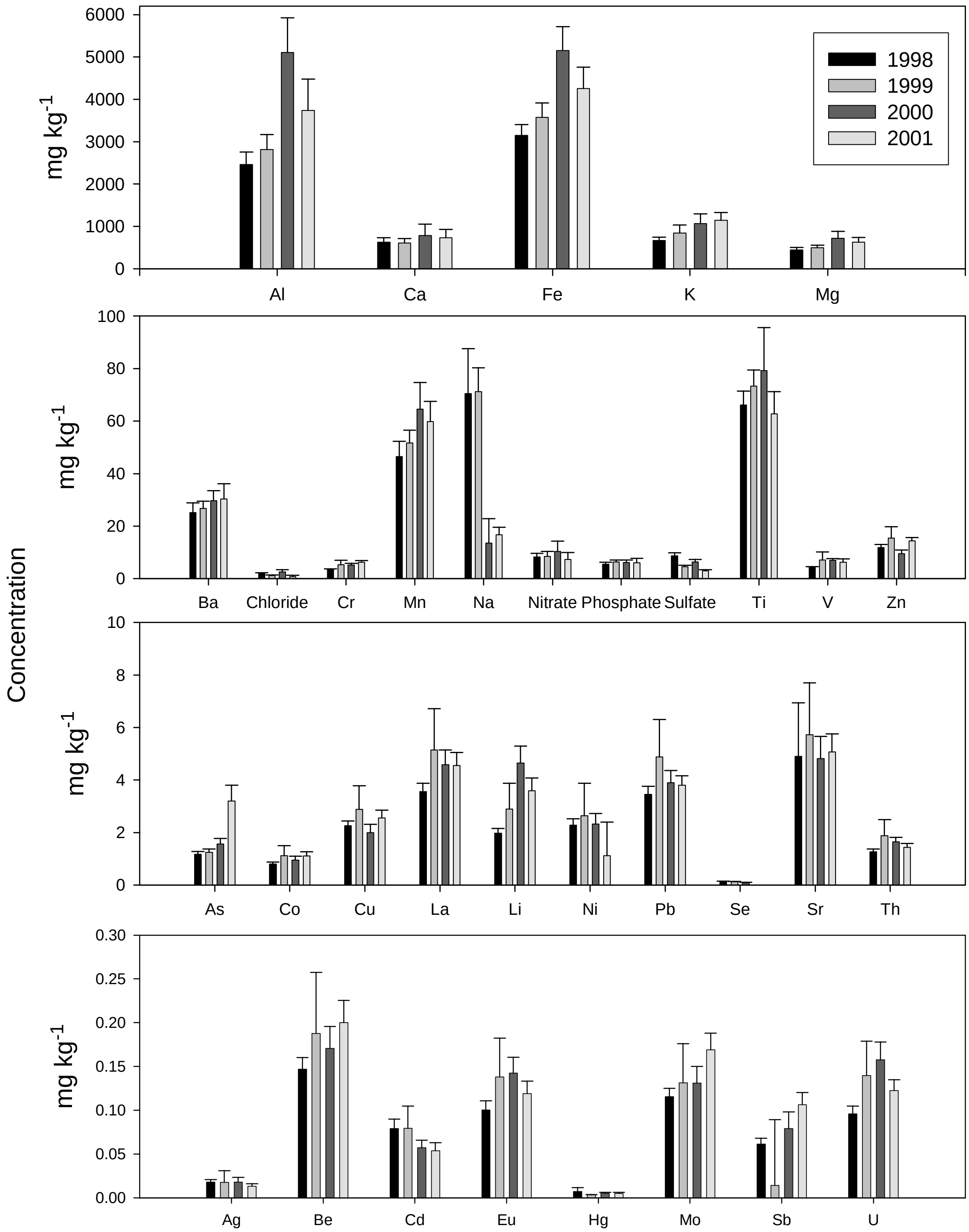

Figure 21. Mean Concentrations of Inorganic Analytes in Soil Samples from Cactus Flats Grid Collected during 1998 - 2001

Error bars show upper 95% confidence intervals for concentrations.

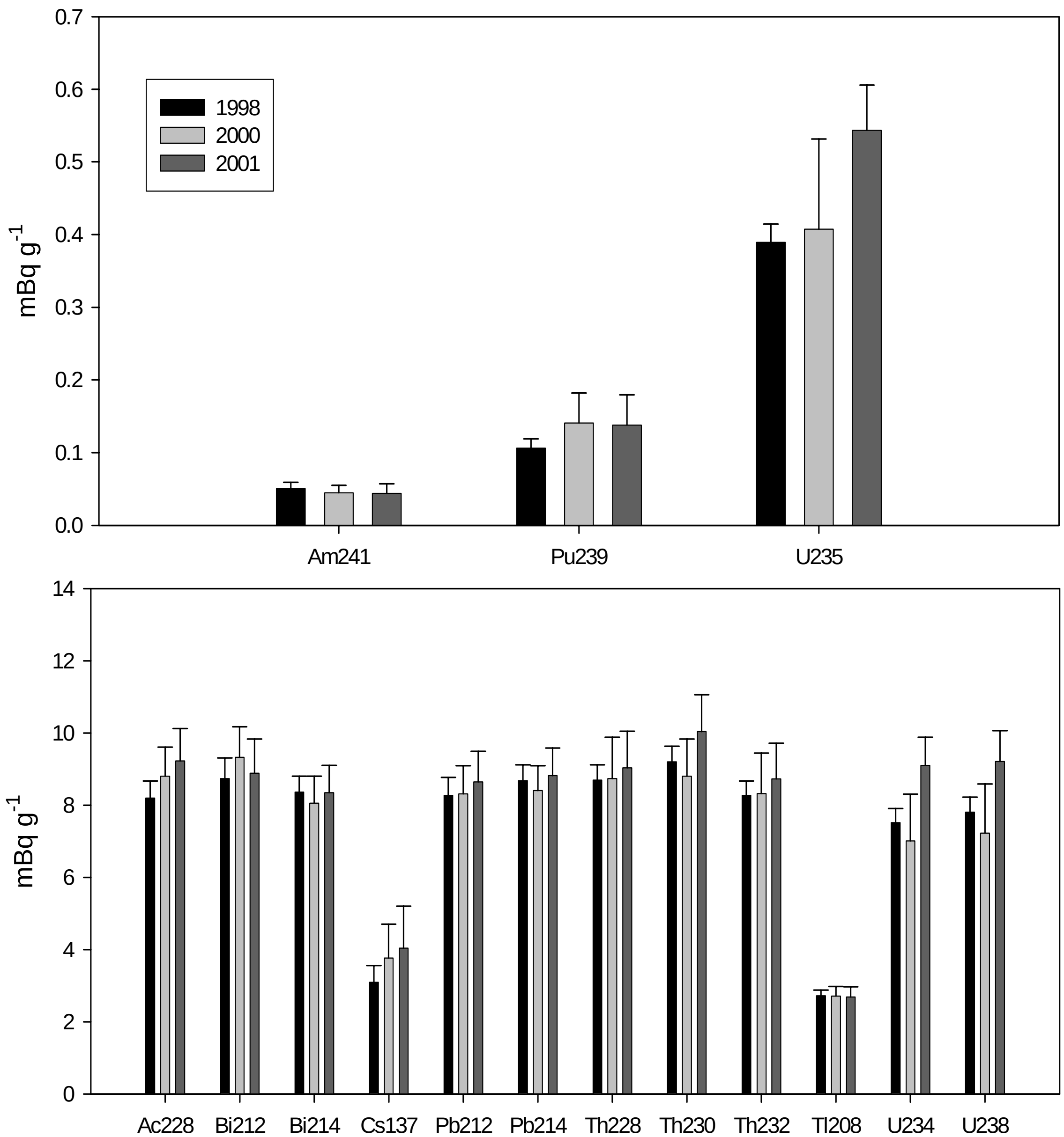

Figure 22. Mean Concentrations of Radionuclides in Soil Samples from Near Field Grid Collected during 1998 – 2001

Error bars show upper 95% confidence intervals for concentrations.

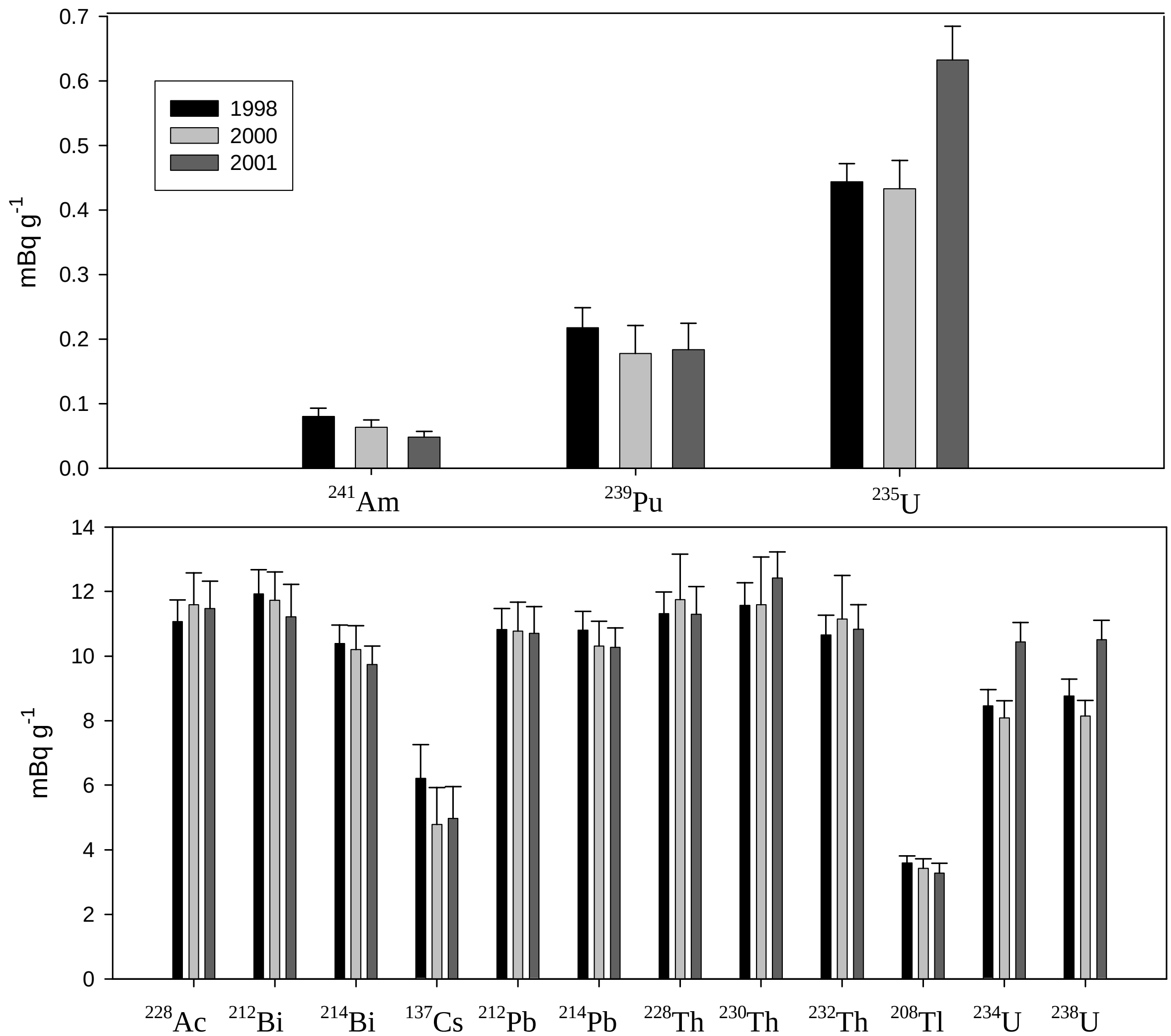

Figure 23. Mean Concentrations of Radionuclides in Soil Samples from Cactus Flats Grid Collected during 1998 – 2001

Error bars show upper 95% confidence intervals for concentrations.