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United States Department of the Interior

U.S. GEOLOGICAL SURVEY
Water Resources Division
1400 Independence Road, MS-100
Rolla, Missouri 65401

July 14, 1999

Mr. Dan Wall
U.S. Environmental Protection Agency
Superfund Branch
726 Minnesota Avenue
Kansas City, Kansas 66101

Dear Dan:

This letter summarizes results of the USGS (U.S. Geological Survey) analysis of a radioactive soil sample (soil 153) from the SLAPS (St. Louis Airport Site), and my observations on the UMR (University of Missouri-Rolla) leaching study conducted using four soil samples collected from the SLAPS. At your request, the UMR leaching study was performed under contract to the USGS. Soil sample 153 was collected on December17, 1997 by DOE (U.S. Department of Energy) contractors from an excavation in the western part of the site. Geochemical analyses and interpretation of the solid-phase association of U (uranium), Th (thorium), and Ra (radium) in soil sample 153 was made with the help of Bob Zielinski, USGS Denver, Colorado. Bob is an expert on U, Th, and Ra geochemistry.

BACKGROUND

During the fall of 1996, the U.S. Environmental Protection Agency (EPA) Region VII requested the USGS to participate in a STWG (SLAPS technical working group). Other participants include representatives from the DOE, DOE contractors, the MDNR (Missouri Department of Natural Resources), UMR, the City of St. Louis, and St. Louis County. The original mission of the STWG was to review historic hydrogeologic and water-quality data from the site to help the EPA identify data gaps that needed to be addressed before rendering a final ROD (record of decision) for the SLAPS. The purpose of the USGS involvement was to provide the EPA with an impartial technical resource regarding ground-water flow and radionuclide geochemistry. The USGS has participated in numerous meetings, provided reviews of hydrogeologic and water-quality data, conducted limited investigations of ground- and surface-water interactions along Coldwater Creek and water and sediment quality of Coldwater Creek, and installed and maintained a continuous recording stream-gaging station immediately downstream from the SLAPS. These limited investigations were done at the recommendation of the STWG and conducted in cooperation with the EPA.

During 1997, the USACE (U.S. Army Corps of Engineers) assumed responsibility for all FUSRAP (Formerly used sites remedial action program) sites from the DOE. The USACE conducted an EE/CA (engineering evaluation/cost assessment) at the SLAPS in 1998 (U.S. Army Corps of Engineers, 1998a). The EE/CA included a proposal to remove the radioactively contaminated materials at the SLAPS for permanent disposal at a secure facility in the western United States. In that proposal, subsurface materials exceeding 15 pCi/g (picocuries per gram) activity of Ra, 15 pCi/g of Th, and 50 pCi/g of U would be removed. Hereinafter, these activities are referred to as 15:15:50 (U.S. Army Corps of Engineers, 1998a). The activity levels are the sums for the individual isotopes for each element. Because the soil cleanup levels were based on future land use and human exposure scenarios and not on ground-water protection, the STWG wanted to know if the proposed 15:15:50 activity levels were protective of ground-water resources at the site. The UMR leaching study was developed to provide preliminary information to address this question.

SITE DESCRIPTION

The SLAPS is a 22 acre site north of Lambert-St. Louis International Airport (fig. 1). Between 1946 and 1966, the site was used to store uranium and thorium-bearing residues resulting from U-ore processing at the former AEC (U.S. Atomic Energy Commission) St. Louis downtown processing plant. The residues consisted of barium sulfate cake and raffinate (liquid waste) residues, among others. During 1966 and 1967, the residues were sold and removed from the SLAPS (Bechtel National Inc., 1994). Part of the sold residues were transported to a site just north of the SLAPS, referred to as the HISS (Hazelwood Interim Storage Facility), where some of the residues currently (1999) remain. After the residues were removed from the SLAPS, structures at the site were demolished and the site was graded and covered with 1 to 3 ft (feet)of clean fill to achieve surface radioactivity levels acceptable at that time (U.S. Army Corps of Engineers, 1998a).

The SLAPS is underlain by a variable thickness (55 to 90 ft) of unconsolidated deposits consisting of fill, locss, glacial till, and lake sediments (U.S. Army Corps of Engineers, 1998b). These deposits have been separated into fill, loess, unit 3 (subdivided into subunits 3T, 3M, and 3B), and unit 4 (fig. 2). Unit 3 is a sequence of glaciolacustrine silty clays and clays. Subunit 3M is highly plastic clay that is locally varved (Bechtel National, Inc., 1994). Unit 4 ranges from clayey gravel to gravelly clay with sands and sandy gravel. Pennsylvanian shale and siltstone underlie the unconsolidated deposits in the eastern part of the site and Mississippian-age limestone underlies the rest of the site and areas to the north. According to the MDNR, the Mississippian limestones in the vicinity of the SLAPS have been used for domestic and commercial water supplies.

A monitoring well network has been installed at the SLAPS and vicinity (fig. 3). Results of historic water-level measurements by the DOE indicate depths to ground water generally are less than 20 ft. The DOE proposed that two ground-water flow systems occur within the unconsolidated deposits at the site—a shallow aquifer and deep aquifer. The shallow and deep unconsolidated aquifers are separated by an aquitard consisting primarily of the 3M subunit. The separation of the unconsolidated deposits into two aquifers was based mainly on differences in measured hydraulic heads between wells completed above or below the 3M subunit and the observation that water levels in several shallow wells appeared to respond to precipitation, whereas water levels in several deep wells did not respond (Bechtel National Inc., 1994). According to the USACE, in areas where the 3M subunit is present, an upward gradient exists between deep and shallow wells. This occurs across most of the SLAPS and the ballfields area to the north (fig. 4). However, the 3M subunit is not present in the extreme eastern and southern parts of the SLAPS and USACE data indicate that gradients appear to be downward in these areas (fig. 4).

PROBLEM

Data collected during 1997 indicate that shallow ground water above the 3-M subunit has been contaminated by various constituents including U. During a reconnaissance of Coldwater Creek in 1997, the USGS discovered a small (estimated discharge less than 0.005 ft^3/s [cubic feet per second]) seep near the SLAPS. A water sample from the seep contained large concentrations of NO_3 (nitrate as nitrogen; 62 mg/L [milligrams per liter]), Sr [strontium; 650 ug/L (micrograms per liter)], and U (2,000 ug/L). Although a considerable amount of data exists regarding concentrations of radioactive constituents in SLAPS soils, little is known about the solid-phase association of the radionuclides. The solid-phase association of the radionuclides can greatly affect how easily they may be mobilized. Based on the detection of radionuclide contamination in shallow ground water at the site, the STWG expressed concern that radionuclides may be leached from residual materials (below the proposed 15:15:50 activity level) left behind after cleanup of the site. Because of downward gradients in the eastern part of the site, this area has the highest potential for radionuclides leached from residual materials to be transported into the underlying bedrock aquifer.

PURPOSE AND APPROACH

To determine if residual materials have the potential to leach appreciable amounts of radionuclides, the STWG suggested a limited scope leaching study be performed. This proposed study, albeit limited, would to provide data needed to assess the large term impacts of residual materials on ground-water quality at the SLAPS. The USACE agreed to provide field equipment and support personnel for the collection of subsurface soil samples from the site and the USGS agreed to contract to a local University to conduct the actual leaching experiments. The USGS, in conjunction with the USACE and MDNR, developed a generalized sampling plan and scope for the leaching experiments. The bid for the leaching study was awarded to UMR in the late spring of 1998. Part of the investigation involved an initial characterization of a single contaminated soil from the west part of the site by the USGS. Upon completion of the initial characterization by the USGS, the UMR leaching studies commenced.

The specific objectives of the leaching study were to:

1. provide information on the soil-phase association of radionuclides in soils at the SLAPS and
2. determine the quantity of radionuclides (primarily Ra, Th, and U) that can be readily leached from contaminated soils containing concentrations of Ra, Th, and U below the EE/CA activity level of 15:15:50.

The purpose of this letter is to provide of summary of the USGS characterization effort (objective 1) and my observations of the results of the UMR leaching studies (objective 2),

DESCRIPTION AND RESULTS OF OBJECTIVE 1

Soil sample 153 was collected from the western part of the SLAPS near Coldwater Creek (fig. 5) during an interim removal action of radioactively contaminated materials. The sample was collected prior to the establishment of the USACE 15:15:50 activity level for subsurface soils and was intentionally collected from an area of elevated radioactivity.

A summary of the analyses performed on the soil sample is given in figure 6. A scan of the bulk sample [940 g (grams total weight)] indicated a total dose equivalent of 130 to 160 uR/hr (microrems per hour). The sample was air dried and divided into two size fractions using a 10 mesh, 2.0 mm (millimeter) pore-size sieve (splits 1 and 2, fig. 6). A split of the minus 10 mesh fraction was archived and the remaining minus 10 mesh fraction was divided into three additional size fractions (split 3, 0.297 to 2.0 mm; split 4, 0.125 to 0.297 mm; and split 5, less than 0.125 mm). A "heavy mineral separation" was done on split 4 (0.125 to 0.297-mm fraction) to further separate this fraction by particle density (fig. 6). This separation was achieved by mixing the solids with bromoform [specific gravity of 2.89 g/cm^3 (grams per cubic centimeter)] to concentrate the denser grains. The heavy mineral fraction was further separated into magnetic (C1), semi-magnetic (C2), and non-magnetic (C3) fractions (splits 6, 7, and 8, fig. 6). The magnetic fraction typically contains magnetic particles and minerals such as magnetite, and ferrous metals. The semi-magnetic fraction typically contains slightly magnetic particles and minerals such as limonite and Fe (iron) oxides, and the non-magnetic fraction contains non-magnetic particles and minerals such as zircon.

Chemical analysis of the various fractions was done using ICP-AES (inductively coupled argon plasma-atomic emission spectrometry) and INAA (instrumental neutron activation). Split 7 contained insufficient sample size (less than 1g) for analyses by either ICP-AES or INAA. Analysis of radioisotopes was done by low energy gamma-ray spectrometry on all fractions containing sufficient amounts of material (about 50 g). An initial semi-quantitative chemical analysis was performed on all splits using ES (emission spectrometry). Polished grain mounts of the heavy-mineral fractions (splits 6, 7, and 8) were used for fission-track radiography. Fission-track radiography is specific for U. In this process, the mount of sample grains is overlain with a thin sheet of mica and the assembly placed in a nuclear reactor where fission of the ^{235}U is induced. Fission fragments of the ^{235}U pass through the mica causing damage observed as visible tracks. The density of the tracks is proportional to the concentration of ^{235}U in the underlying sample grains.

Soil sample 153 was coarse grained with 53 percent of the sample being larger than sand-size (0.063 to 2.0 mm) material (table 1). Chemical and radiometric analyses of various fractions (U and Th by INAA and Ra by low energy gamma-ray spectrometry) indicated that the soil sample contained larger than background concentrations of U [240 ppm (parts per million) and ^{226}Ra (1,400 pCi/g), and at or near background concentrations of Th (8.5 ppm, table 1). Concentrations of Th and U in Missouri soils average about 9.6 ppm and 4 ppm, respectively (Tidball, 1984). Because of their small U contents, background activities of ^{226}Ra, a daughter product of ^{238}U, in Missouri soils also are small and in the order of 1 pCi/g. There is a marked radioactive disequilibrium in the sample with ^{226}Ra activities greatly exceeding those of its parent in all measured fractions (table 1). This disequilibrium is consistent with the preferential extraction of U from the ore.

Although the heavy mineral fractions (splits 6, 7, and 8) comprised less than 2 percent by weight of the total sample, they contained the largest concentrations of U (1,070 to 1,290 ppm) and other trace elements, such as Sb (antimony), As (arsenic), Cr (chromium), Co (cobalt), and Fe (figs. 7a-c). Concentrations of U and most trace elements increased as Fe concentrations increased in the various sample splits (figs. 7d-e). Correlation coefficients between Sb, As, Cr, Co, U, Zn (zinc), and Fe ranged from 0.972 to 0.999 (table 2). Iron-rich minerals, especially Fe oxides, are common sinks for trace elements and the strong positive correlation coefficients between these elements and Fe in table 2 suggests they are associated with Fe-rich phases, probably Fe oxides. This hypothesis is consistent with photographic and fission-track analyses of individual grains from the heavy magnetic and semi-magnetic fractions (splits 6 and 7). The largest density of fission tracks, indicative of ^{235}U, are associated with reddish Fe-oxide coatings on angular grains, many of which appear to be fragments of ferrous metal (fig. 8).

Unlike U and most other trace elements that are enriched in the heavy minerals, Th is depleted in the heavy mineral fractions (fig. 9a). Concentrations of Th are strongly negatively correlated with Fe and U (-0.995 and -0.967) and most other trace elements, indicating that Th is probably is not associated with Fe-rich phases (table 2). The strong negative correlation between Th and U is graphically illustrated in figure 9b. Concentrations of Th are positively correlated with K (potassium, 0.985), and Rb (rubidium, 0.989; table 2). Like Th, concentrations of K and Rb are smaller in the heavy mineral fractions (splits 6 and 8) indicating they are preferentially concentrated in less dense mineral phases (table 1). Potassium and Rb commonly are associated with clay minerals, micas, and orthoclase feldspar—all of which have densities less than bromoform. The small (less than 10 ppm) Th concentrations in the various splits precludes substantial contamination with Th-enriched minerals. The positive correlations between Th, K, and Rb suggest that the most likely host for Th is clay minerals; however, this cannot be proven with the available data. Allthough Th concentrations in the sample are background, the data suggest that 230^{Th} is enriched in the sample.

Concentrations of ^{226}Ra are positively correlated (0.971) with Ba (barium, table 2). Radium exhibits no strong correlation with any other trace elements or major cations, suggesting it primarily is associated with a Ba-rich phase. The isolated positive correlation between ^{226}Ra and Ba is consistent with the known disposal at the SLAPS of barite ($BaSO_4$) wastes that contained Ra. Barite is a dense (specific gravity of 4.5 g/cm^3), non-magnetic mineral that should be concentrated in the non-magnetic heavy mineral fraction (split 8). Unfortunately, because of the limited sample size, this fraction could not be analyzed for ^{226}Ra by gamma-ray spectrometry. In splits analyzed by gamma-ray spectrometry, the ^{210}Pb daughter (lead-210; half-life of 22.6 years) is nearly in radioactive equilibrium with the ^{226}Ra parent (fig. 10), indicating that the proposed barite host of the excess ^{226}Ra in soil sample 153 is in the order of 50 to 100 years. The isotope ^{214}Pb is a short lived daughter (half-life of 3 minutes) of ^{226}Ra that reaches radioactive equilibrium with the parent ^{226}Ra very quickly. The similar activities of ^{226}Ra and ^{214}Pb in the various splits serve as a validation of the measured ^{226}Ra activities (fig. 10). To confirm the presence of barite, additional analysis using XRD (X-ray diffraction) or SEM (scanning electron microscope) could be done on the remaining sample from split 8.

The apparent age of the hypothesized radiobarite is based on the assumptions that (1) barite is the major host of ^{226}Ra in the soil, and (2) all ^{210}Pb is produced in situ by the decay of ^{226}Ra originally incorporated into the radiobarite precipitates. The estimated age of the proposed radiobarite host (50 to 100 years) is slightly older than the probable maximum age of 55 years for process wastes placed at the SLAPS. One possible explanation for this could be the presence of some unprocessed solid mill tailings at the SLAPS. If the SLAPS soils and wastes contain some unprocessed solid mill tailings, additional ^{226}Ra and ^{210}Pb could be present. Mill tailings generally approximate radioactive equilibrium between ^{226}Ra and ^{210}Pb because they retain most of ^{226}Ra and ^{210}Pb present in the original ore. Radium in the tailings resides in barite; however, ^{210}Pb may reside in barite and other detrital materials in the tailings. Any ^{210}Pb contributed by detrital materials in mill tailings (or unprocessed ore) in the SLAPS soil sample 153 will cause the calculated age for the hypothesized radiobarite to be too old. The presence of substantial ^{230}Th (unsupported by U) in SLAPS soils would suggest contamination by mill tailings.

In summary, analyses of SLAPS soil sample 153 indicates that the sample contained elevated concentrations of U, ^{226}Ra, ^{210}Pb, and background concentrations of Th. There is an obvious radioactive disequilibrium in the sample manifested by a large excess ^{226}Ra activity compared to its parent ^{238}U. This disequilibrium is consistent with the processes of U extraction and Ra concentration that occurred at the St. Louis downtown processing plant from which the wastes originated. Radium was concentrated in barite-rich wastes (radiobarite) that were disposed at the SLAPS. Excluding any source from ^{230}Th, the source of the excess ^{226}Ra in the sample is probably between 25 and 75 years old, based on the fact that the ^{210}Pb daughter is nearly in radioactive equilibrium with ^{226}Ra parent. Given that the sample appears to have some ^{230}Th, the age of the excess 226Ra, is probably younger and no more than about 50 years old. Concentrations of U are positively correlated with Fe and other trace elements. These correlations, and evidence from fission-track radiography, indicate that the U is preferentially concentrated in Fe-oxides. Most of the Fe oxides are anthropogenic in origin and appear to be partially oxidized, angular, magnetic to semi-magnetic, fragments of ferrous metal. Thorium is positively correlated with K and Rb, and tends to be concentrated in the less dense fraction of the sample indicating that it is associated with clay minerals, orthoclase, or micas.

DESCRIPTION AND RESULTS OF OBJECTIVE 2.

Batch leaching studies were conducted under a variety of conditions (aerobic, anaerobic) using four soil samples from the SLAPS and deionized water as the leaching agent. The resulting solutions were analyzed for radionuclides and trace elements by several techniques. Detailed results of the leaching study are presented in a comprehensive document prepared by Dr. Mark Fitch, Department of Civil Engineering, UMR (Fitch, 1999). Although Dr. Fitch has discussed the study results in detail, the following are some of my general observations of the results, and how they compare and contrast with objective 1 results and previous USGS studies on uranium transport at the Weldon Spring site about 15 miles southwest of the SLAPS.

At the request of the USGS, an additional replicate for each of the four soil treatments was run during the 30-day aerobic leaching experiments. The leached soils and solutions (filtrate passed through a 0.45 micrometer filter) from these four replicate samples were transferred to the USGS laboratory in Denver, Colorado, for analysis. The leached soils, and a split sample from the archive of each original soil, were analyzed for U concentrations by INAA. The solutions were analyzed by ICP-MS (inductively coupled argon plasma-mass spectrometry). for dissolved trace elements, including U. Results of the USGS analyses are listed in tables 3 and 4.

After 30 days, solutions in contact with each of the four soil samples had near neutral pH (7.36 to 8.02) and small to moderate concentrations of HCO_3 (24 to 95 mg/L, table 3). The pH of deionized water typically is about 5.5 (water in equilibrium with atmospheric carbon dioxide (CO_2) indicating that the soils slightly buffered the solutions. The U concentrations in solutions equilibrated with soils 1 and 3 (2.5 and 1.2 ug/L) were at background for ground water in the area and consistent with background concentrations of U in ground water at the Weldon Spring site (Schumacher, 1993). The U concentration was slightly elevated in the soil 2 solution (13 ug/L) and large in the soil 4 solution (653 ug/L, table 3). The U concentration in the soil 4 solution was re-analyzed and verified. Although large, the concentration of U in solution 4 represents the removal of only about 8 percent of the U initially present in soil 4 (table 4). Increased concentrations of Mo (molybdenum) were detected in solutions 1 and 2 (121 and 116 ug/L) and solutions 2 and 3 contained increased Se (selenium) concentrations (143 and 232 ug/L). The increased Mo and Se concentrations are not unusual considering that these elements commonly are enriched in U ores. However the large Al (aluminum) concentration (2,550 ug/L) in the soil 1 solution (table 3) is unusual. This concentration greatly exceeds the water solubility of Al (less than about 2 ug/L) at the measured solution pH and indicates incomplete separation of solids. poor removal of colloidal Al during filtration, or contamination during the experiment or filtration of samples.

Solutions in contact with soils that had larger U concentrations, such as soil 4 (81 ppm), also had larger concentrations of U (fig. 11). Concentrations of HCO_3 also increased with U concentrations in the solutions (fig. 11). Fission-track radiography and chemical analyses of the SLAPS soil sample 153indicate that U (and other trace elements) are associated with Fe oxides. This association is consistent with published studies on trace element sorption by Fe oxides. However, in oxidized solutions, U is present as the uranyl (UO_2^{2-}) ion, which forms strong aqueous complexes with carbonate. The formation of these aqueous U-carbonate complexes decreases the sorption of U onto Fe oxides and increases its solubility (Ames and others, 1983). Because concentrations of U and HCO_3 appear to increase together, it is probable that the amount of U leached from the various soils is a complex function of U concentration in the soil (probably sorbed into Fe oxides) and solution bicarbonate concentration.

A particular deficiency in using Kd values to describe the sorption of solutes is the dependence of the Kd values on solution parameters, such as pH and concentrations of competing and complexing ions. The variation in the Kd values that UMR calculated for U [120 to 11,700 mL/g (milliliters per gram)] is, in part, caused by the inability of the simple Kd model to describe the sorption and desorption of U. Schumacher and Stollenwerk (1991) concluded that the sorption of U by soils could not be simulated by the Kd model, but could be simulated using a diffuse-layer surface-complexation approach. To test if a similar approach was applicable to data from the SLAPS leaching experiments, a simulation of U leaching from Fe oxide as a function of solution bicarbonate was done using the geochemical code PHREEQC (Parkhurst, 1985). The simulation was conducted in several steps as follows:

1. a solution of uranium nitrate was equilibrated with calcite (approximate the effect of competing divalent cation sorption onto the Fe oxides),
2. the resulting solution from step 1 was equilibrated with Fe oxides allowing U and Ca (calcium) to sorb (create an Fe oxide that was enriched in U), and
3. the Fe oxide from step 2 was then equilibrated with deionized water that had dissolved various amounts of calcie (this step simulated the effect of leaching U-rich Fe oxide as was done in the UMR leaching studies).

The increase in solution HCO_3 concentrations was assumed to be caused by the dissolution of small amounts of calcite in the soils; therefore, calcite dissolution was used in step 3 as the source of bicarbonate. The thermodynamic data used in the simulations were identical to that used by Schumacher and Stollenwerk (1991).

The simulations were performed with solution U concentrations in step 1 from 1 to 23 ppm and HCO_3 concentrations in step 3 from 0 to 95 mg/L. The initial U concentrations in the Fe oxide in step 2 were 1,150 and 23,000 ppm or about 50 and 1,100 ppm in the whole soil. Curves representing the simulated U and HCO_3 concentrations, and the measured values from the experiments are shown in figure 12. In the simulations, less than 5 percent of the U initially sorbed onto the Fe oxide was removed by the deionized water at HCO_3 concentrations up to 95 mg/L. The simulated curves illustrate the effect of HCO_3 concentration on desorption of U from Fe oxides, with the quantity of U leached proportional to the solution bicarbonate concentration. Generally, the measured values plot within the range of the simulated values; however, the trend of the measured values does not exactly follow that of the simulated curves. An exact fit to the measured data was not expected because the simulations greatly oversimplified the system by ignoring other sources of U, such as mineral phases or desorption from other mineral surfaces, and additional competing ions, etc. Results of the simulations are consistent with the hypothesis that most U in the soils is probably associated with Fe oxides and, depending on the solution HCO_3 concentration, small amounts of U (a few percent by weight) can be leached from the soil.

Results of ground-water monitoring at the SLAPS indicate that water in the shallow unconsolidated aquifer generally is aerobic and alkaline (U.S. Army Corps of Engineers, 1998b). The detection of larger than background U concentrations in several shallow monitoring wells at the SLAPS and a seep along the western part of the site is consistent with the results of the UMR leaching studies and geochemical simulations. Results from the leaching studies indicate that under aerobic conditions, U can be leached from contaminated soils by solutions containing small to moderate concentrations (25 to 100 mg/L) of bicarbonate. Thermodynamic data indicate that under aerobic conditions and near neutral pH values, the solubility of U in solutions containing more than 100 mg/L of HCO_3 is in excess of 1,000 ug/L. However, under the Fe-reducing or sulfate-reducing conditions that exist throughout much of the deep unconsolidated aquifer, the solubility of U will be controlled by reduced U mineral phases and be less than a few micrograms per liter.

The Kd values calculated for U and other constituents in the UMR study were not calculated in the traditional manner and should be used with caution. Typically, Kd values for inorganic solutes are calculated by measuring the quantity of the solute removed from a solution. However, in the SLAPS leaching studies, the Kd values were calculated by measuring the quantity of solute leached from the solid phase. In calculating Kd values by leaching the solutes from the solid phase, the assumption is made that the process is readily reversible, which may not be correct. For example, precipitation of a mineral phase typically occurs much more rapidly than dissolution of the same phase; thus, the Kd model may not be applicable. Typically, the sorption of inorganic solutes onto a solid phase occurs more rapidly than the release of the solute from the solid phase, and Kd values calculated from each process (sorption and desorption) may be significantly different. If U and other radionuclides in the SLAPS soils are present in mineral phases, then the slow dissolution of these phases may result in larger solution concentrations than the Kd values calculated from the experiments would predict. In addition, the poor mass balance closures, the low activities of the solutions, and short counting times for the gamma-ray spectrometry performed at the UMR (6 hours), result in many concentrations reported near the limits of detection where measurement error can be large.

In summary, results of the UMR leaching experiments are consistent with the results of a detailed geochemical analysis of the SLAPS soil sample 153. The five soil samples collected and analyzed during the combined UMR-USGS investigations contained background concentrations of Th but elevated U concentrations. The USGS soil sample (SLAPS soil sample 153) was intentionally collected from an area of elevated radioactivity and also contained ^{226}Ra activities substantially larger than background. None of the four soil samples leached by UMR had elevated ^{226}Ra concentrations. Uranium in the soil samples examined appears to be associated with Fe oxides, whereas Ra appears to be associated with barite. No specific Th-enriched phases were identified, and no measurable Th or ^{226}Ra were leached from the soils. This observation is consistent with the extremely small solubilities of Ra and Th, and the small quantities of these elements in the soils. However, the experiments indicate that significant amounts of U (in excess of 600 ug/L) may be leached from the soils depending on the concentration and solid-phase association of U in the soil and the solution HCO_3 concentration. Although consistent with published literature and previous geochemical investigations of U migration at the Weldon Spring site, the current experiments were based on an extremely limited data set and should be verified before any final conclusions are made regarding the potential for residual materials at the SLAPS to contaminate ground water.

I appreciated the opportunity to work with the EPA and USACE on this project. Because the geochemistry of radionuclides is complex and difficult to understand, I think it would be beneficial to ask Bob Zielinski and Steve Sutley (USGS, Denver Colorado), to attend the next STWG meeting. Please contact me at (573)-308-678 if you have any questions.

Sincerely;

John G. Schumacher
Hydrologist

Cc: Greg Hempen, Project Manager, U.S. Army Corps of Enginners, St. Louis District
Larry Erickson, Remedial Project Manager, Missouri Department of Natural Resouces

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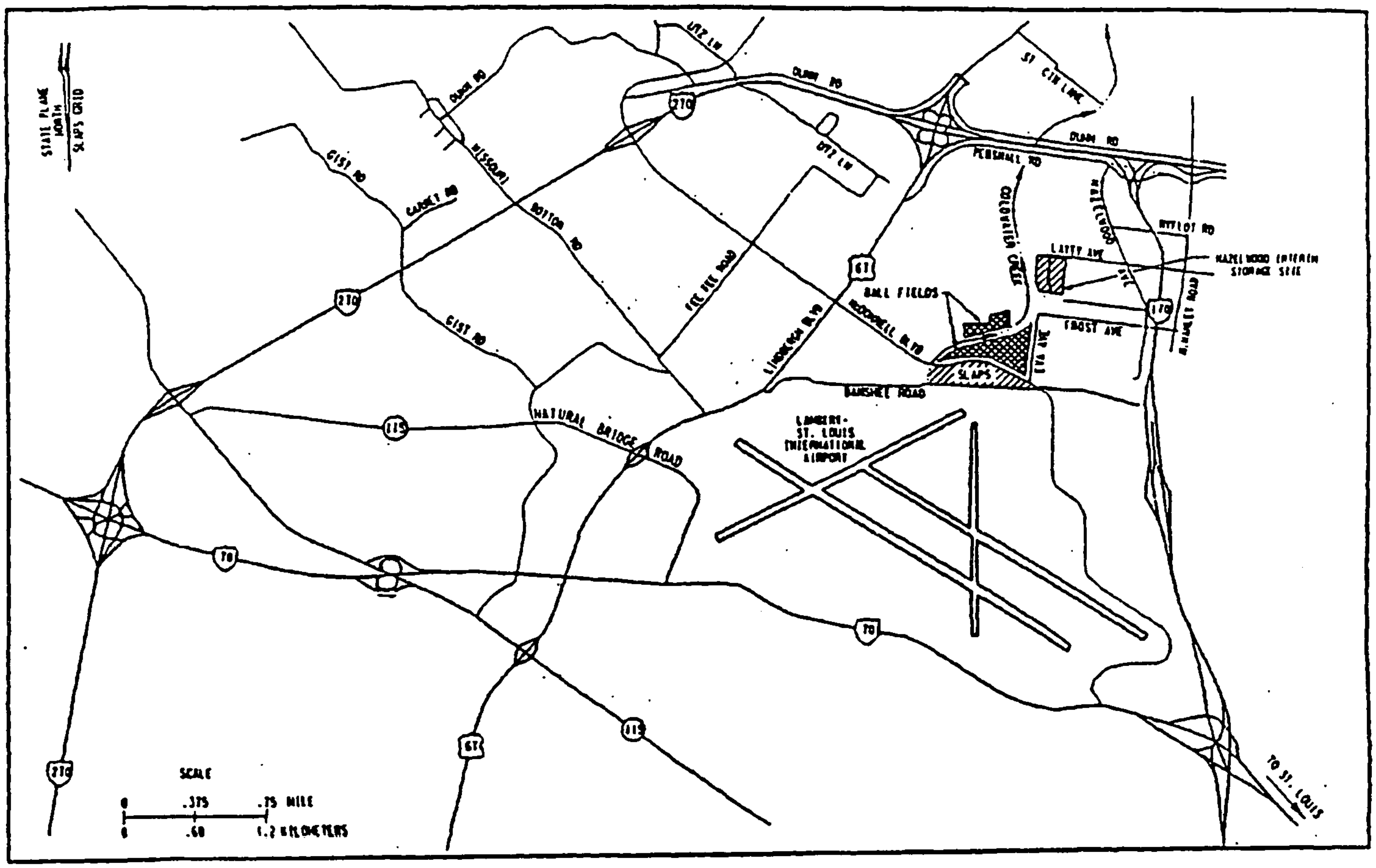

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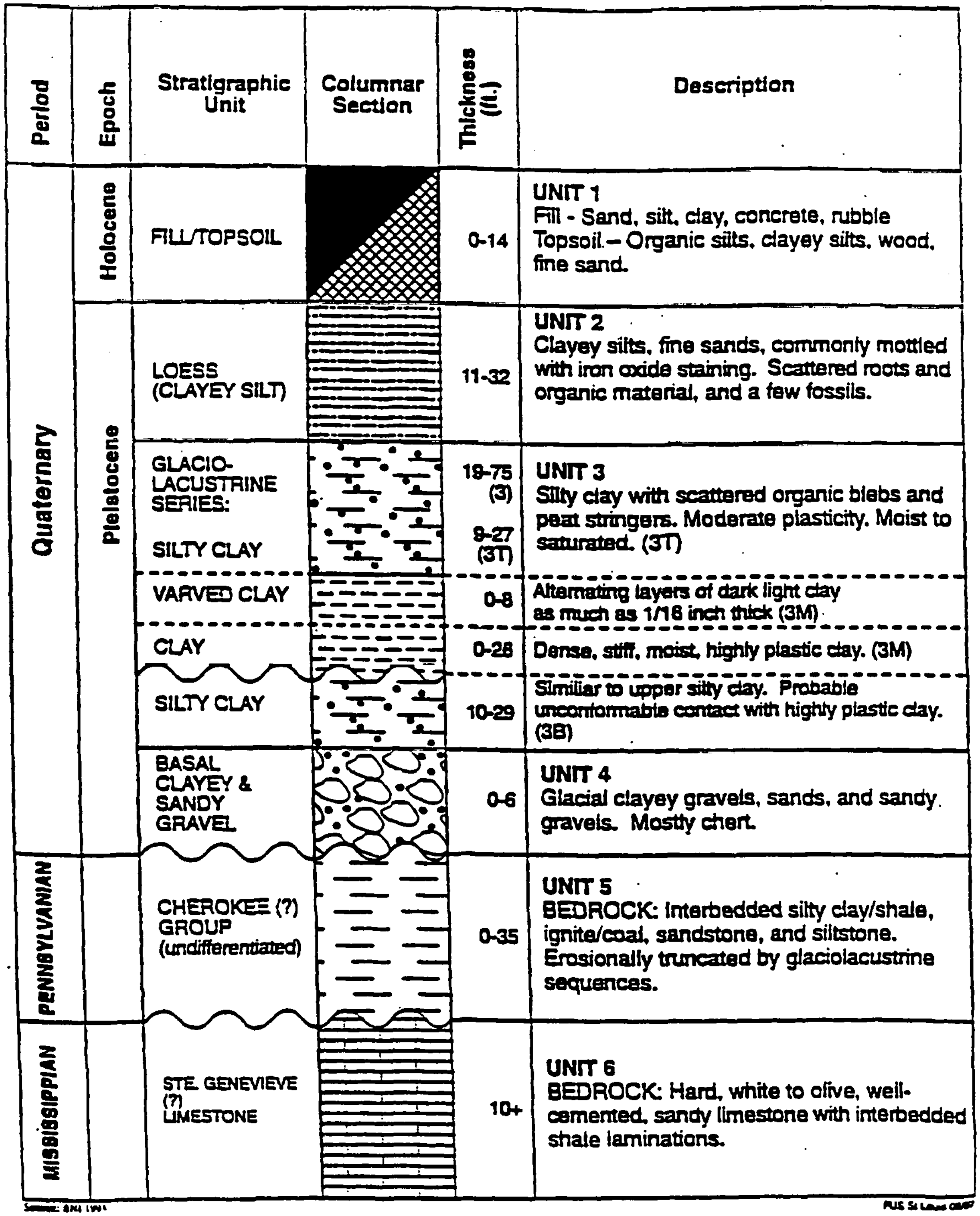
Figure 1. Location of SLAPS and the ballfields (source: Bechtel National, Inc., 1994)



Period	Epoch	Stratigraphic Unit	Columnar Section	Thickness (ft.)	Description
Quaternary	Holocene	FILL/TOPSOIL		0-14	**UNIT 1** Fill - Sand, silt, clay, concrete, rubble Topsoil – Organic silts, clayey silts, wood, fine sand.
	Pleistocene	LOESS (CLAYEY SILT)		11-32	**UNIT 2** Clayey silts, fine sands, commonly mottled with iron oxide staining. Scattered roots and organic material, and a few fossils.
		GLACIO-LACUSTRINE SERIES: SILTY CLAY		19-75 (3) 9-27 (3T)	**UNIT 3** Silty clay with scattered organic blebs and peat stringers. Moderate plasticity. Moist to saturated. (3T)
		VARVED CLAY		0-8	Alternating layers of dark light clay as much as 1/16 inch thick (3M)
		CLAY		0-28	Dense, stiff, moist, highly plastic clay. (3M)
		SILTY CLAY		10-29	Similiar to upper silty clay. Probable unconformable contact with highly plastic clay. (3B)
		BASAL CLAYEY & SANDY GRAVEL		0-6	**UNIT 4** Glacial clayey gravels, sands, and sandy gravels. Mostly chert.
PENNSYLVANIAN		CHEROKEE (?) GROUP (undifferentiated)		0-35	**UNIT 5** BEDROCK: Interbedded silty clay/shale, ignite/coal, sandstone, and siltstone. Erosionally truncated by glaciolacustrine sequences.
MISSISSIPPIAN		STE. GENEVIEVE (?) LIMESTONE		10+	**UNIT 6** BEDROCK: Hard, white to olive, well-cemented, sandy limestone with interbedded shale laminations.

Figure 2. Site stratigraphy at SLAPS (source: Bechtel National, Inc., 1994).

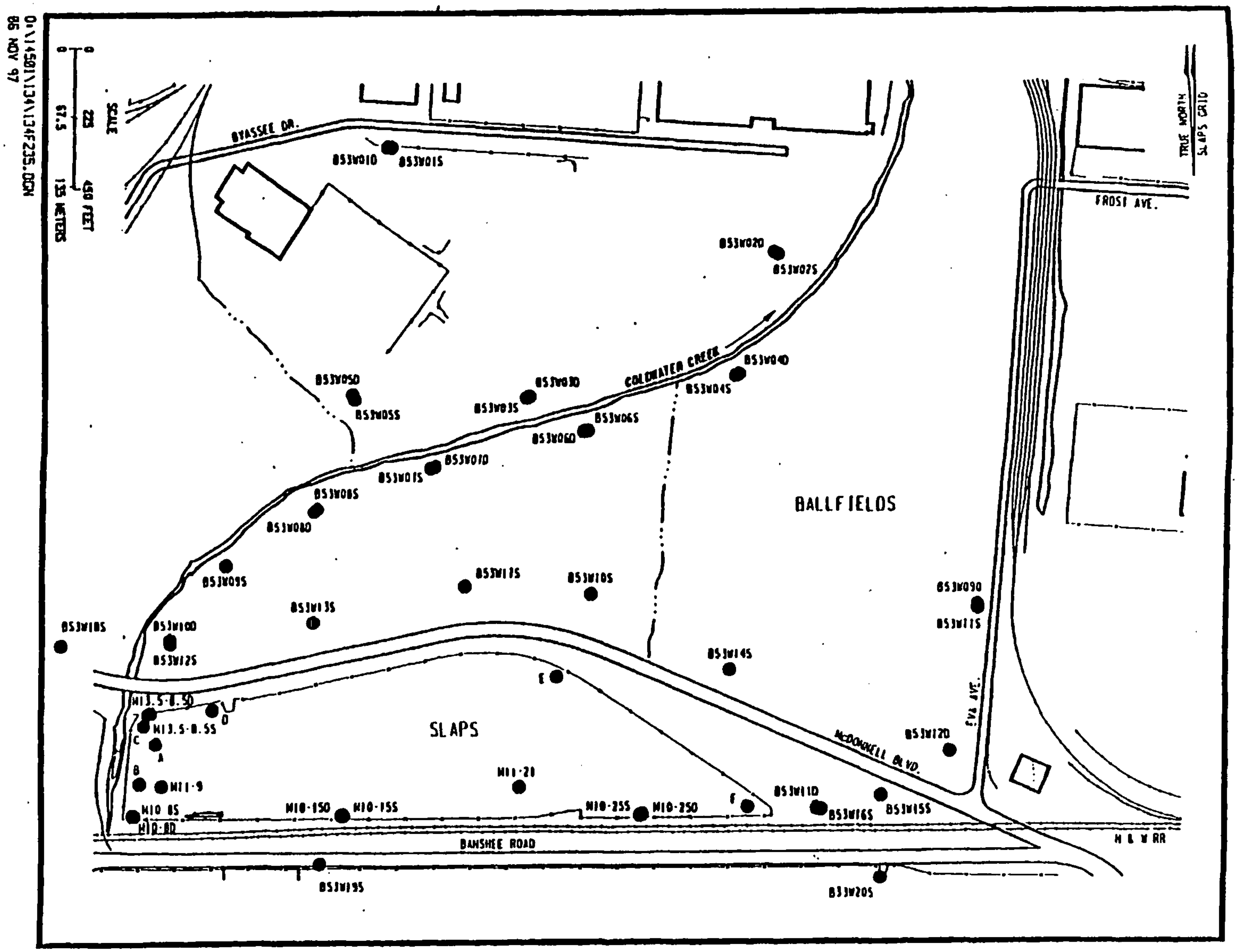


Figure 3. Monitoring well locations at SLAPS (source: Bechtel National, Inc., 1994).

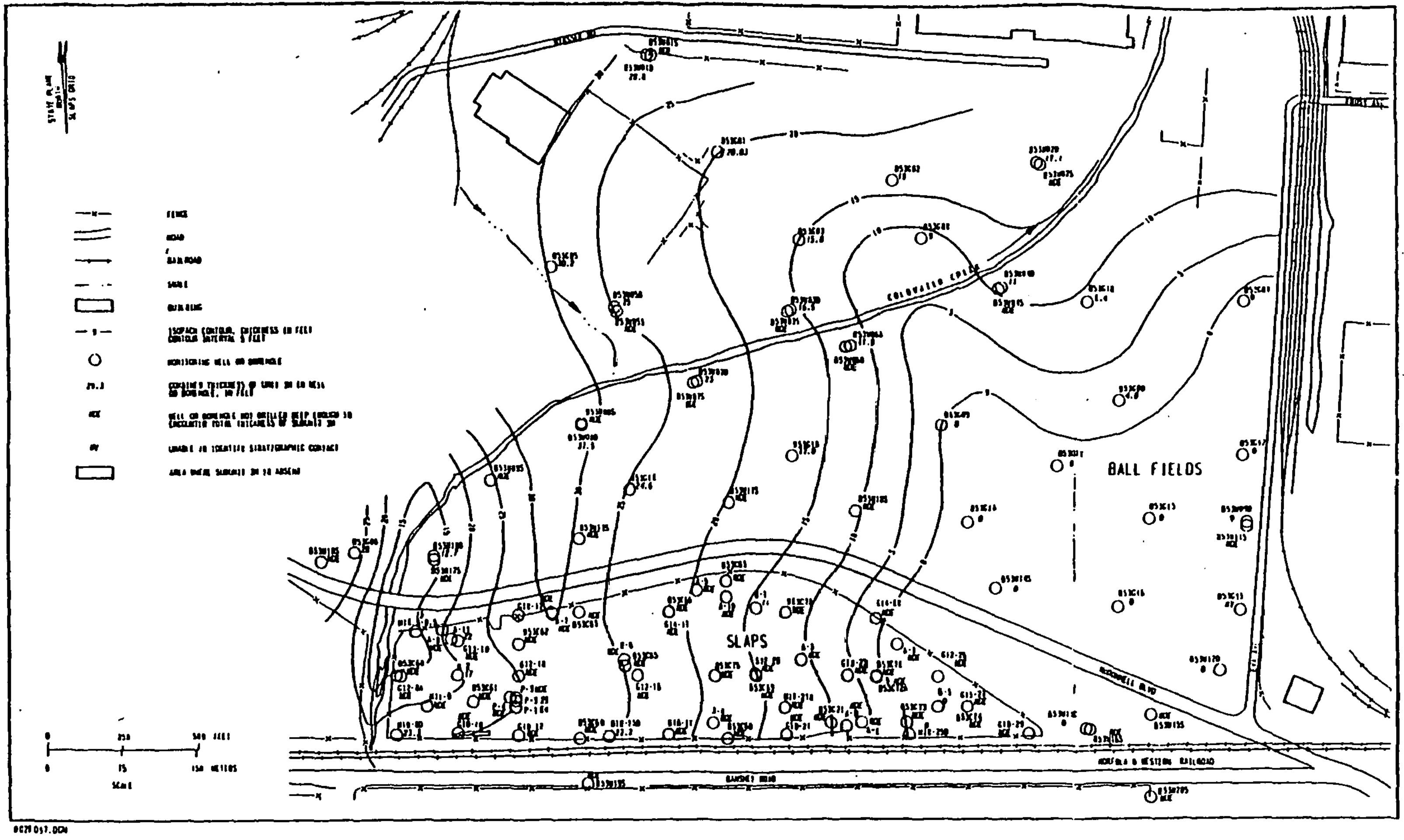


Figure 4. Isopach map of subunit 3M (source: Bechtel National, Inc., 1994).

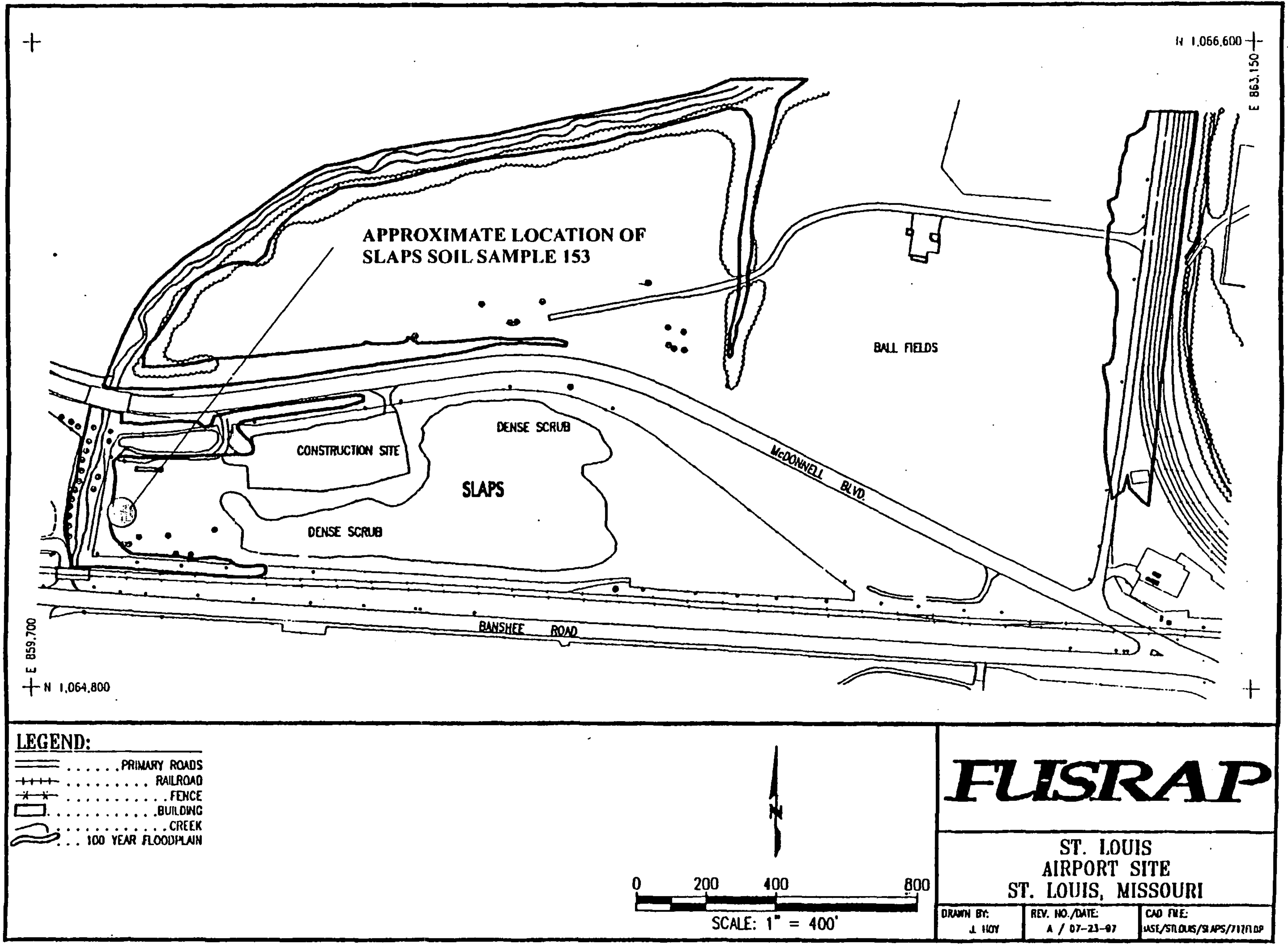
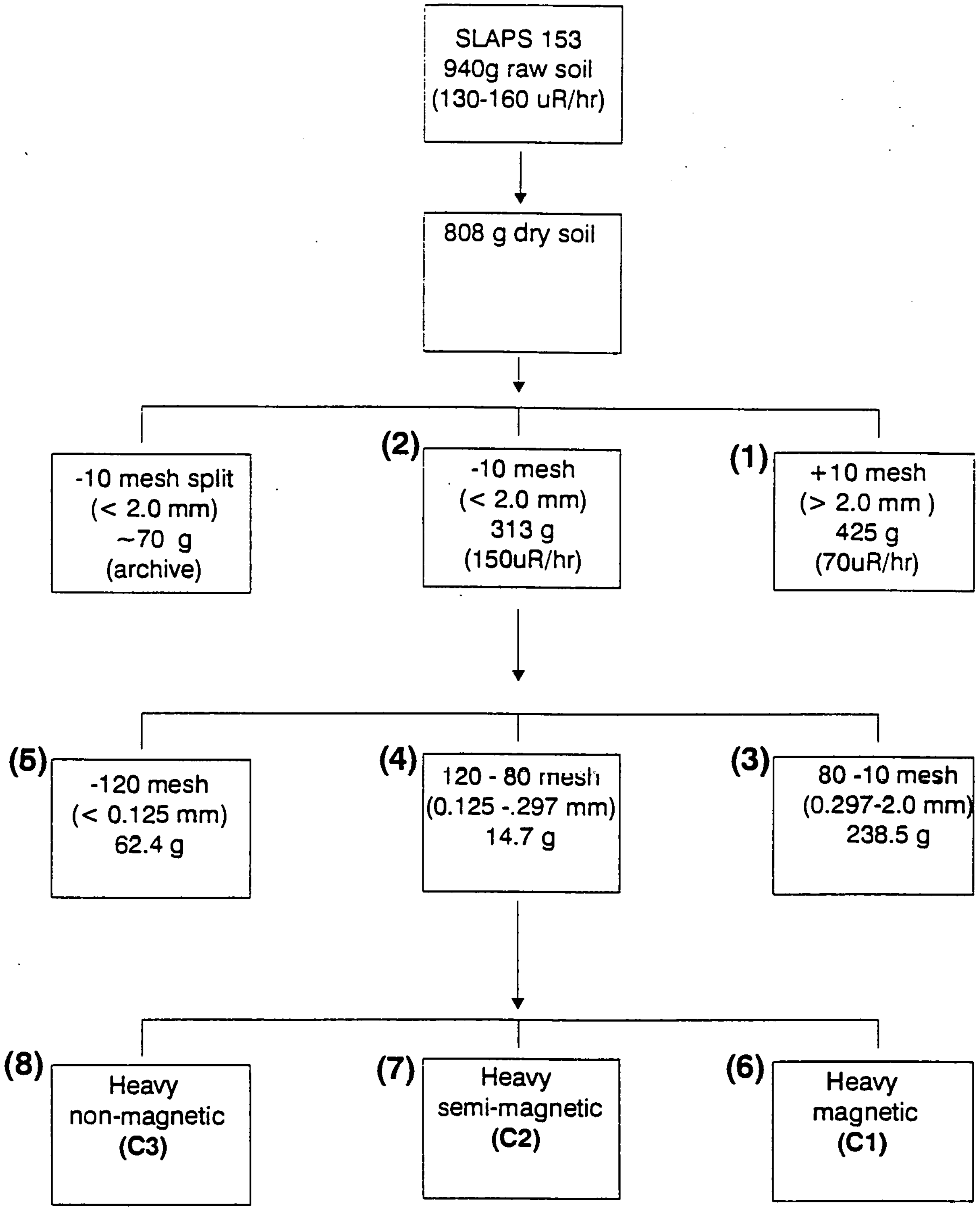


Figure 5. Approximate location of SLAPS soil sample 153 collected by U.S. Army Corps of Engineers contractors (source: Bechtel National, Inc., 1994).



SUMMARY OF ANALYSES PERFORMED

ANALYSIS	TARGET	SPLITS
Gamma-ray spectrometry	(226Ra, 228Ra, 210Pb)	1,2,3, 5
Emission spectrometry	(Elemental chemistry)	1,2,3,4,5,6,7,8
Mineralogy (X-Ray diffraction)	(general mineralogy)	4, 6 7,8
Fission track radiographs	(U distribution within grains)	4, 6,7,8
Instrumental neutron activation (INAA)	(U, Th concentrations)	1,2,3, 5, ,8

Figure 6. Summary of sample preparation and analyses performed on SLAPS soil sample 153.

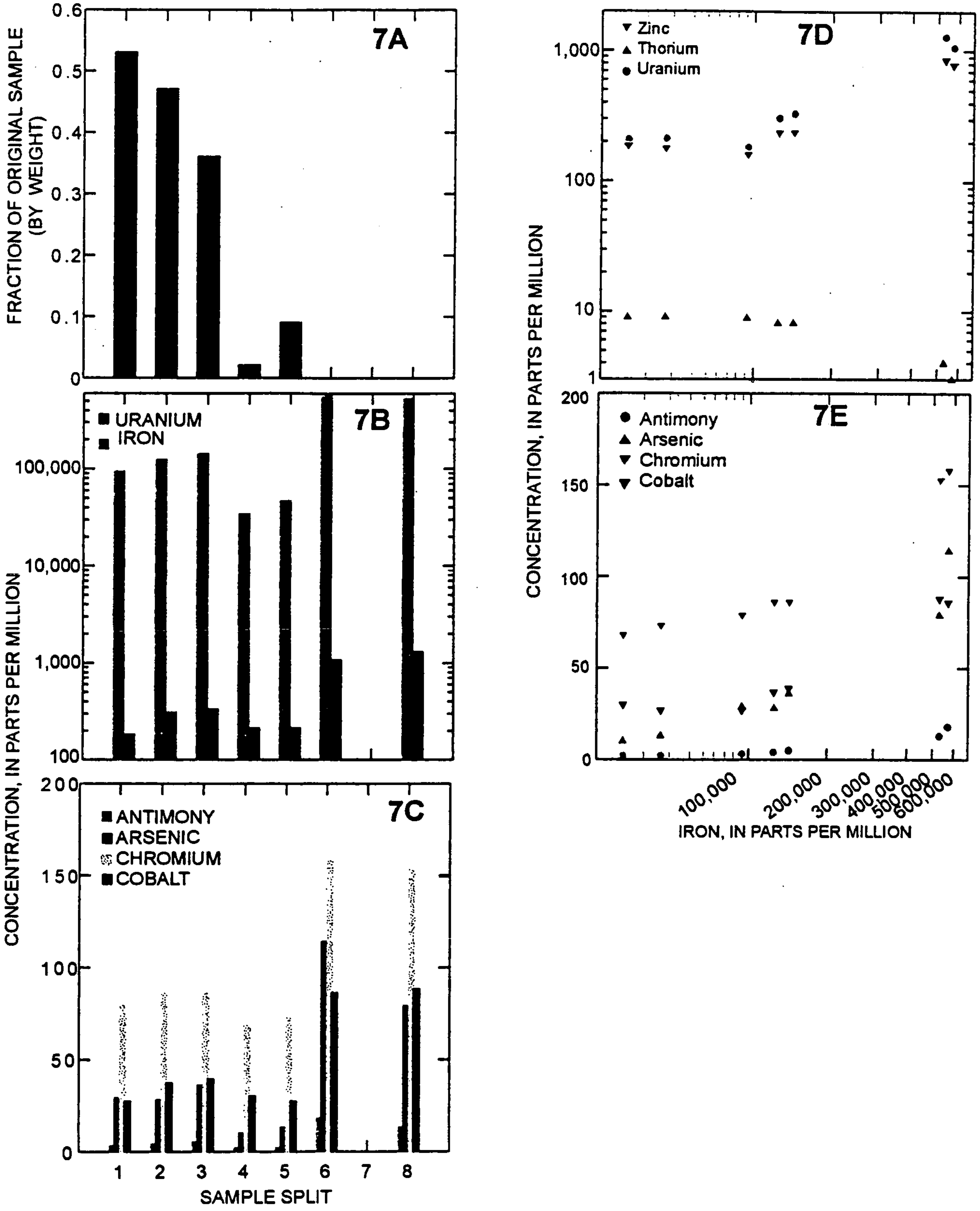
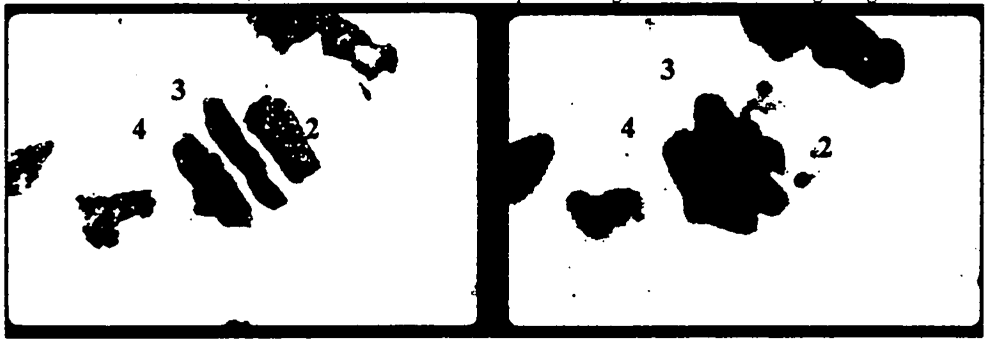


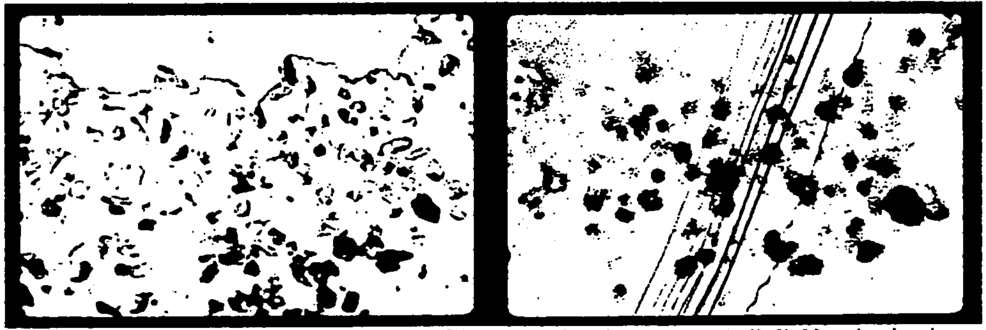
Figure 7. Fraction of total sample in each split and concentrations of uranium, iron, and other selected trace elements in sample splits from SLAPS soil sample 153 (7a, 7b, 7c). Correlation between iron, and uranium, and thorium, and other selected trace elements in sample splits from SLAPS soil sample 153 (7d, 7e).

A. Photograph (left) of grains from the magnetic fraction of the heavy mineral concentrate (split 6) and corresponding radiograph (right) showing tracks resulting from ^{235}U fission (black areas). Note that most grains in the photograph are angular, dark, probably metallic, and are coated with reddish iron oxides, such as grain 1. The dark, non-oxidized part of grain 1 is clear on the radiograph image (right) indicating this area contains little or no U, whereas the reddish oxidized part of the grain is black indicating a large concentration of ^{235}U.



B. Photograph (left) of grains from the semi-magnetic fraction of the heavy mineral concentrate (split 7). Note the three rectangular grain in the center of the photograph. The dark and reflective grain (2) is barely visible on the radiograph indicting a small ^{235}U content, whereas the two reddish partially oxidized grains to the left (grains 3 and 4) are black indicating a large ^{235}U content.

C. Photograph (left) of grains from the semi-magnetic fraction of the heavy mineral concentrate (split). Note the dark, unoxidized "ribbon" in the center grain 5 is clear on the radiograph indicating a small ^{235}U concentration compared to the oxidized exterior of the grain, which is black.



D. Photograph (left) of grains from the non-magnetic fraction of the heavy mineral concentrate (split 8). Note the abundance of clear grains in the photograph that contain small ^{235}U concentrations as indicated by the low density of fission tracks on the radiograph.

Figure 8. Photographs and radiographs of selected grains from the heavy mineral grains from splits 6, 7, and 8.

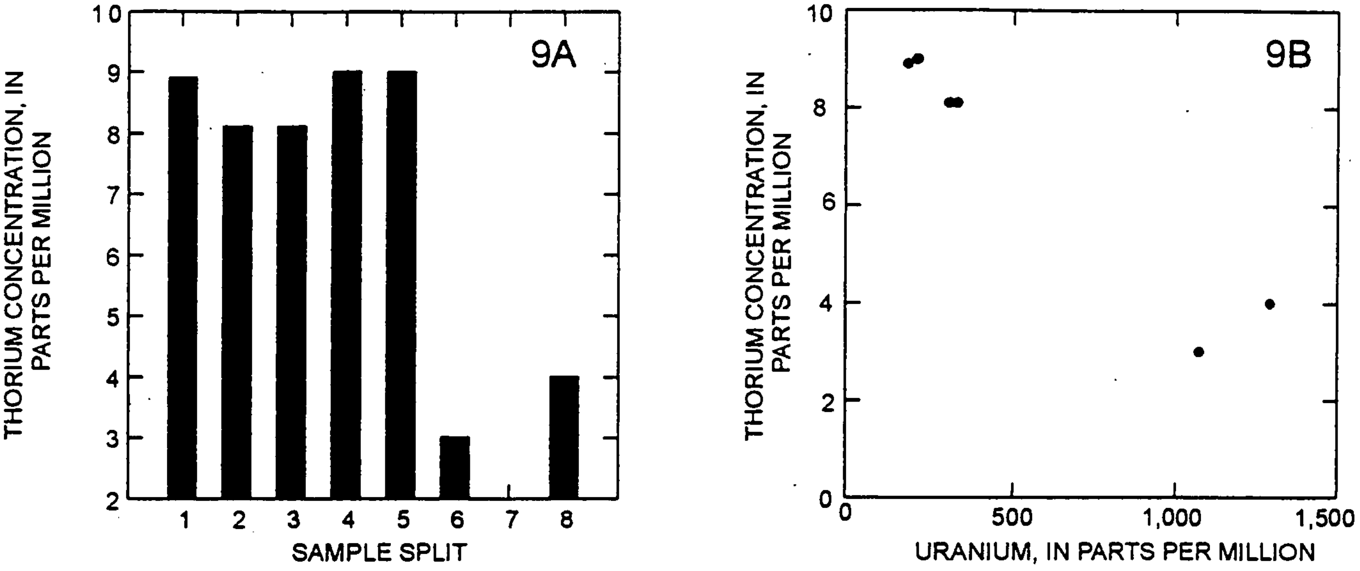


Figure 9. Plot of thorium concentrations in various splits from SLAPS soil 153 and relation of uranium to thorium concentrations.

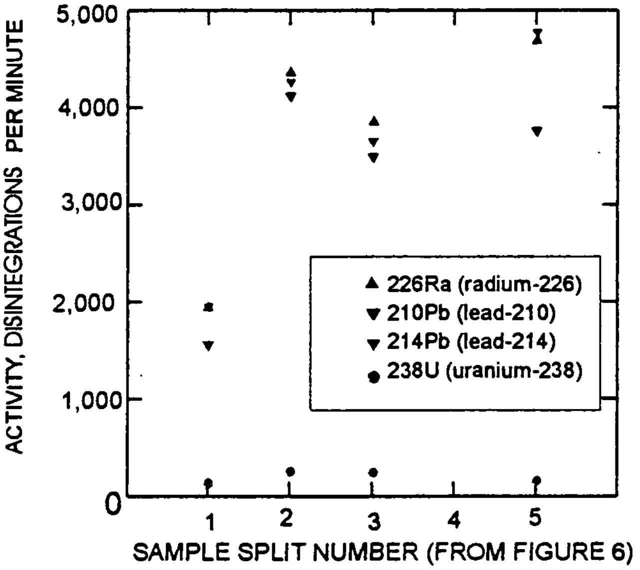


Figure 10. Activity of selected radioisotopes in various sample splits from SLAPS soil 153.

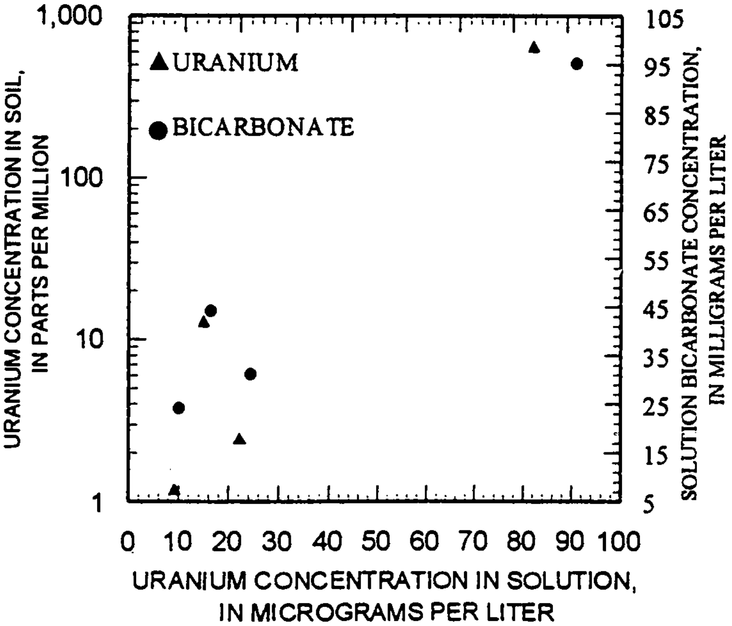


Figure 11. Relation between uranium concentration in soil and solution bicarbonate and uranium concentrations in the UMR leaching experiments.

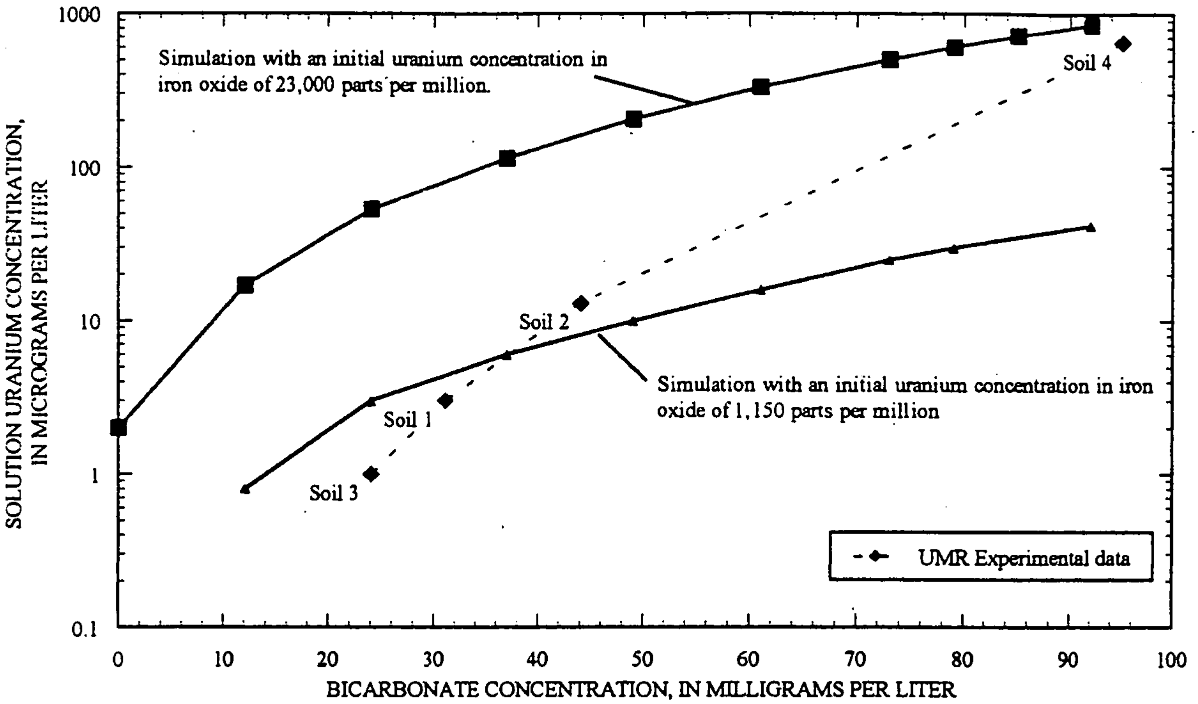


Figure 12. Effect of bicarbonate concentration on simulated uranium concentrations in solutions in contact with a soil sample containing 1.9 weight percent iron oxide. Iron oxide assumed to have 600 square meters of surface area per gram with a concentration of 0.01 moles exchangable surface sites. Simulations performed using PHREEQC (Parkhurst, 1985). Uranium concentrations from the UMR 30-day leaching experiments with SLAPS soils also shown.

Table 1. Results of instrumental neutron-activation analysis and inductively-coupled argon plasma (ICP) analysis of various splits of SLAPS soil sample 153.

[--, no data; ppm, parts per million; INAA, instrumental neutron activation; dpm/g, disintegrations per minute per gram; gamma, gamma-ray spectrometry; pCi/g, picocuries per gram; ICP, inductively-coupled argon plasma; <, less than; ES, emission spectrometry;]

		Sample split (fig. 6)							
Constituent	Method	1	2	3	4	5	6	7	8
Percent of total sample	Weight	53	47	36	2	9	--	--	--
Uranium, ppm	INAA	184	348	335	--	218	--	--	--
^{238}U, dpm/g	gamma	135	255	245	--	160	--	--	--
^{226}Ra, dpm/g[1]	gamma	1,940	4,360	3,850	--	4,685	--	--	--
^{214}Pb, dpm/g	gamma	1,950	4,265	3,650	--	4,775	--	--	--
^{210}Pb, dpm/g	gamma	1,555	4,120	3,495	--	3,765	--	--	--
^{226}Ra, pCi/g	gamma	874	1,964	1,734	--	2,110	--	--	--
Calcium, ppm	ICP	16,300	38,700	51,600	15,900	20,400	34,700	--	29,000
Sodium, ppm	ICP	8,440	7,050	6,790	9,350	8,990	492	--	515
Potassium, ppm	ICP	14,300	14,600	12,600	14,900	14,800	2,530	--	3,220
Antimony, ppm	ICP	3	4	5	2	2	18	--	13
Arsenic, ppm	ICP	29	28	36	10	13	114	--	79
Barium, ppm	ICP	780	1,010	1,010	1,110	1,130	1,100	--	1,600
Cerium, ppm	ICP	73	81	68	94	111	<40	--	105
Cesium, ppm	ICP	2	2	2	2	2	1	--	1
Chromium, ppm	ICP	79	86	86	68	73	158	--	153
Colbalt, ppm	ICP	27	37	39	30	27	86	--	88
Iron, ppm	ICP	93,900	124,000	142,000	33,800	46,700	568,000	--	528,000
Gold, ppm	ICP	86	198	105	118	1,360	1,500	--	1,730
Lanthanum, ppm	ICP	47.6	64	54	71	85	46	--	122
Lead[2], ppm	ES	1	1	150	300	150	300	700	200
Manganese[2], ppm	ES	500	700	500	700	500	1,000	1,000	300
Nickel, ppm	ICP	67	94	96	41	62	220	--	290
Rubidum, ppm	ICP	63	60	58	63	62	13	--	5
Strontium, ppm	ICP	134	143	142	173	186	142	--	59
Thorium[3], ppm	ICP	8.9	8.1	8.1	9	9	3	--	4
Uranium[4], ppm	ICP	182	306	331	209	212	1,070	--	1,290
Zinc, ppm	ICP	159	236	237	186	177	787	--	850
Zirconium, ppm	ICP	200	200	200	200	300	50	70	2,000

[1] Radium-226 activity in whole sample (1,400 pCi/g) calculated by normalizing activities in splits 1 and 2 (0.53 x 1,940 dpm + 0.47 x 4,360 dpm) and dividing this value by 2.22 dpm per picocurie.

[2] Semi-quantitative concentrations determined by emission spectrometry.

[3] Thorium concentration in whole sample (8.5 ppm) calculated by normalizing concentrations in splits 1 and 2 (0.53 x 8.9 ppm + 0.47 x 8.1 ppm).

[4] Uranium concentration in whole sample (240 ppm) calculated by normalizing concentrations in splits 1 and 2 (0.53 x 182 ppm + 0.47 x 306 ppm).

Table 2. Pearson Correlation Matrix of selected trace elements in various fraction of SLAPS soil sample 153.

[Shading indicates correlation is significant at the 0.10 level. Yellow indicates positive correlations. Blue indicates negative correlations.]

	Iron	Manganese	Antimony	Arsenic	Barium	Cesium	Chromium	Cobalt	Potassium	Radium[1]	Rubidium	Thorium	Uranium	Zinc
Iron	1													
Manganese	0.184	1												
Antimony	.983	0.345	1											
Arsenic	.972	.349	0.994	1										
Barium	.598	-.360	.487	0.407	1									
Cesium	-.953	-.172	-.931	-.891	-0.737	1								
Chromium	.999	.174	.979	.968	.608	-0.954	1							
Cobalt	.991	.148	.965	.941	.684	-.969	0.991	1						
Potassium	-.989	.805	-.987	-.959	-.885	-.335	-.984	-.986	1					
Radium[1]	-.128	.353	-.009	-.429	.971	.586	-.013	.350	0.12	1				
Rubidium	-.986	.765	-.978	-.937	-.891	-.419	-.985	-.990	.992	-0.435	1			
Thorium	-.995	-.261	-.991	-.976	-.589	.960	-.995	-.990	.985	-.296	0.989	1		
Uranium	.977	.032	.928	.900	.752	-.969	.979	.991	-.990	.495	-.998	-0.967	1	
Zinc	.986	.110	.951	.925	.715	-.980	.988	.996	-.988	.531	-.998	-.982	0.997	1

[1] ^{226}Ra (radium-226).

Table 3. Concentrations of alkalinity and selected trace elements in solutions equilibrated with soils from the SLAPS site.

[mg/L, milligrams per liter; ug/L, micrograms per liter; <, less than; --, no data; highlight indicates concentrations substantially above expected values]

Constituent	Soil 1, 30 day 07/21/98 0900	Soil 2, 30 day 07/21/98 0905	Soil 3, 30 day 07/21/98 0910	Soil 4, 30 day 08/19/98 0900
Bicarbonate[1], mg/L	31	44	24	95
pH (final)	8.02	7.93	7.36	7.62
Aluminum, ug/L	2,550	19	13	53
Arsenic, ug/L	<1	1	<1	2
Barium, ug/L	34	33	55	66
Beryllium, ug/L	<1	<1	<1	<1
Boron, ug/L	49	38	45	--
Cadmium, ug/L	<1	<1	<1	<1
Chromium, ug/L	2	2	1	3
Cobalt, ug/L	2	<1	<1	<1
Copper, ug/L	6	2	2	5
Lead, ug/L	1	<1	<1	<1
Manganese, ug/L	6	<1	<1	<1
Molybdenum, ug/L	121	116	39	37
Nickel, ug/L	11	1	1	2
Selenium, ug/L	12	143	232	3
Silver, ug/L	<1	<1	<1	<1
Uranium, ug/L	2.5	13	1.2	653
Zinc, ug/L	13	6.6	13	6

[1] Calculated from measured alkalinity values provided by the University of Missouri-Rolla.

Table 4. Summary of initial and final uranium concentrations in soil and water at the conclusion of the 30 day leaching experiments.

[ug/g, microgram per gram; ug/L, microgram per liter; ug, microgram; U, uranium; <, less than]

	Soil Uranium Concentration (ug/g)				Solution Uranium Concentration (ug/L)			
Soil	Before leaching[1] (ug/g)	After 30 day leaching (ug/g)	Pecent initial uranium lost	Total mass of uranium in soil before leaching (ug)	Before leaching (ug/L)	After 30 day leaching (ug/L)	Mass of uranium recovered in leachate (ug)	Percent of initial soil U recovered in solution
Soil 1	22	29.8	-35	440	<1	2.5	0.5	0.11
Soil 2	14.8	13.9	6	296	<1	13	2.6	0.88
Soil 3	9	9.3	-3	180	<1	1.2	0.24	0.13
Soil 4	81.8	77.4	5	1,636	<1	653	130.6	7.98

[1] Analyses were perfomed on a sub-sample from an archive and not the actual soil sample added to the bottle prior to leaching, and may not be representative of uranium concentrations in the soil actually leached.

Data Entry/Cross-Reference Form

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☐ Further Information Required

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Secondary Document Typ: Sampling/Analysis Data and

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Author's Company: USGS

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