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Chapter 2

SOIL PROFILE THORIUM AND URANIUM CONCENTRATION DISTRIBUTIONS IN SOUTHEASTERN MISSOURI SOILS

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ABSTRACT

Understanding of the pedogenic pathways associated with Thorium (Th) and Uranium (U) migrations and accumulations in soil is (i) important to understanding Th and U soil chemistry and (ii) important for discriminating between natural background and anthropogenic concentrations. Twenty five soil series, some with multiple pedons, were assessed (i) to determine the Th and U distributions in soil profiles and (ii) to infer pedogenic processes important to the Th and U soil profile distributions. Alfisols and Ultisols were selected because they reside on stable landscapes and possess argillic horizons (diagnostic soil horizons having illuviation accumulations of clay) and possessed forest vegetation prior to European settlement. The majority of pedons exhibiting argillic

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horizon expression (Alfisol, Ultisol, and some Mollisol) show Fe-oxyhydroxide maxima corresponding precisely with the argillic horizon. Pearson Correlation coefficients indicate consistently statistically significant correspondences involving iron-oxyhydroxides (Fe) with both Th and U for most of the selected soils. Pedons not showing relationships involving Fe with Th and U either possess a lithologic discontinuity (change in parent material inferring inherited concentration differences) or simply lack sufficient elemental variation to formulate significant correlations. Most soils have Th/U ratios between 3 and 4; however, the range in the Th/U ratios spans from 1.4 to 12.6, demonstrating parent material heterogeneity.

Keywords: Aqua-regia digestion, argillic horizon, cambic horizon, thorium, uranium

INTRODUCTION

Nuclear Chemistry of Thorium and Uranium

In 1828, J.J. Berzelius isolated thorium (Th) from the Norwegian ore “thorite”. In 1841 B. Peligot, using a reductive process, produced metallic uranium. Chadwick discovered the neutron in 1932, which eventually led to the understanding that neutron capture and subsequent β^- emission yielded an element with one additional proton. In 1940 E.M. McMillan and P.H. Abelson demonstrated that neutron capture converted $^{238}\text{U}_{92}$ to $^{239}\text{U}_{92}$; after which, β^- -emission yielded $^{239}\text{Np}_{93}$. G.T. Seaborg and E.M. McMillan (1951) shared the Nobel Prize for their discovery of numerous elements of the Actinide Series.

Thorium (Th) is the first element in the Actinide series having atomic number 90 and an electronic configuration of $[\text{Rn}] 6d^2 7s^2$. Uranium is the third element in the Actinide series having an atomic number of 92 and an electronic configuration of $[\text{Rn}] 5f^3 6d^1 7s^2$. The 5f orbitals are less effective in penetrating the inner core electrons than the 4f orbitals (Lanthanide series) and are, therefore, more energetically favored for bonding and may exhibit appreciable covalent character. The second element in the Actinide series is Protactinium, having two isotopes and an exceptionally trace crustal abundance. Thorium(IV) has an ionic radius of 95 pm, whereas uranium(IV) and uranium(VI) have ionic radii of 89 and 73 pm, respectively. The long lived isotope of thorium is $^{232}\text{Th}_{90}$ and the two long-lived isotopes of uranium are $^{235}\text{U}_{92}$ and $^{238}\text{U}_{92}$.

Thorium ($^{238}\text{Th}_{92}$) is a radioactive element, decaying to $^{228}\text{Ra}_{88}$ by α -emission, followed by β^- emission to yield $^{228}\text{Ac}_{89}$ and a second β^- emission to yield another isotope of thorium ($^{228}\text{Th}_{90}$). $^{228}\text{Th}_{90}$ decays by α -emission to yield $^{224}\text{Ra}_{88}$. The half-life of $^{232}\text{Th}_{90}$ decay to ^{228}Ra is long-lived (1.41×10^{10} years), whereas the half-lives of the other elements in the sequence are comparatively short (hours to several years). Uranium decay is an isotope function, with (i) $^{238}\text{U}_{92}$ decaying by α -emission to $^{234}\text{Th}_{90}$ (half life of 4.45×10^9 years) and by two successive β^- emissions to yield $^{230}\text{Th}_{90}$ and (ii) $^{235}\text{U}_{92}$ decaying by α -emission to yield $^{231}\text{Th}_{90}$ (half life of 7.04×10^8 years) and later in the decay sequence to yield $^{227}\text{Th}_{90}$.

Introduction to Soil Thorium and Uranium

The earth's crustal abundance of thorium is approximately 8.1 mg Th/kg, whereas uranium's crustal abundance is approximately 2.3 mg U/kg (Greenwood and Earnshaw, 1984). Rock types vary greatly in their thorium concentrations, with granites (16 mg Th/kg) and shales (12 mg Th/kg) having greater abundances than basalts (2.7 mg Th/kg) (Wanty and Nordstrom, 1995). Similarly, rock types vary greatly in their uranium concentrations, with granites (4.4 mg U/kg) and shales (3.8 mg U/kg) having greater abundances than basalts (0.8 mg U/kg) (Wanty and Nordstrom, 1995). Thus, neither element is particularly rare. In the case of thorium, geologic processes tend not to accumulate thorium in specific formations and thorium remains rather disperse. Thorium is largely associated with the mineral 'monazite', (lanthanum, other rare earth elements, Th-bearing phosphate). The high density and relative inertness of monazite to chemical weathering permits monazite accumulation in fluvial sediments or as monazite sands. Thorium is also associated with the mineral 'uranthorite' $[(\text{U,Th})\text{SiO}_4]$.

Common uranium bearing minerals include: uraninite $[\text{UO}_2]$, pitchblende $[\text{U}_3\text{O}_8]$, coffinite $[\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}]$, brannerite $[\text{UTi}_2\text{O}_6]$, davidite $[(\text{REE})(\text{Y,U})(\text{Ti,Fe}^{3+})_2\text{O}_{38}]$, and thucholite [Uranium-bearing pyrobitumen]. Uranium-bearing minerals that are less common include: autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \times 8-12 \text{ H}_2\text{O}]$, carnotite $[\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \times 1-3 \text{ H}_2\text{O}]$, selecite $[\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \times 10 \text{ H}_2\text{O}]$, torbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \times 12 \text{ H}_2\text{O}]$, tyuyamunite $[\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \times 5-8 \text{ H}_2\text{O}]$, uranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \times 8-10 \text{ H}_2\text{O}]$, uranophane $[\text{Ca}(\text{UO}_2)_2(\text{HSiO}_4)_2 \times 5 \text{ H}_2\text{O}]$, and zeunerite $[\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \times 8-10 \text{ H}_2\text{O}]$. Uranium(V) species and associated minerals

are comparatively rare because of disproportionation into U(IV) and U(VI) species (Greenwood and Earnshaw, 1984).

Soil Chemistry of Thorium

Thorium hydrolysis, with emphasis on the normal soil pH environment ranges of pH 3 to pH 8, has been reviewed (Baes and Mesmer, 1976; Hichung, 1989; Langmuir, 1997). The predominant monomer Th-OH species include: Th^{4+} , $\text{Th}(\text{OH})^{3+}$, $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, and $\text{Th}(\text{OH})_4$. Polymeric Th-OH species include: $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_2(\text{OH})_3^{5+}$, and $\text{Th}_2(\text{OH})_4^{4+}$, $\text{Th}_4(\text{OH})_8^{8+}$, $\text{Th}_6(\text{OH})_{15}^{9+}$, and $\text{Th}_6(\text{OH})_{14}^{10+}$. The more important thorium hydrolysis reactions are:



The log K hydrolysis values for $\text{Th}_4(\text{OH})_8^{8+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$ are $\log K_{4,8} = -21.1$ and $\log K_{6,15} = -36.76$, respectively. The speciation of the important thorium species as a function of pH is illustrated in Figure 1.

The solubility of ThO_2 may be estimated from thermochemical data as:



Thorium readily forms complexes with fluoride (ThF_2^{2+} and ThF_3^+ in strongly acidic media), phosphate ($\text{ThH}_2\text{PO}_4^{3+}$ near pH 1 and $\text{Th}(\text{HPO}_4)_2$ with optimum speciation at pH 4.6 and $\text{Th}(\text{HPO}_4)_3^{2-}$ with optimum speciation at pH 6), and sulfate (ThSO_4^{2+} and $\text{Th}(\text{SO}_4)_2$ at pH 1) (Langmuir and Herman, 1980). Thorium also forms strong coordinate bonds with oxalate, citric acid and ethylenediaminetetraacetic acid (Langmuir and Herman, 1980). Sulfate, fluoride, phosphate and the organic ligands were shown to increase the solubility of Thorianite (ThO_2) (Langmuir and Herman, 1980). ThO_2 and

noncrystalline $\text{Th}(\text{OH})_4$ have been proposed as the solid phases most likely to limit Th solubility, with an expected range of 10^{-10} to 4×10^{-4} mole/liter in low-Eh ground waters and 10^{-10} to 10^{-7} mole/liter in high-Eh ground waters (Langmuir, 1997).

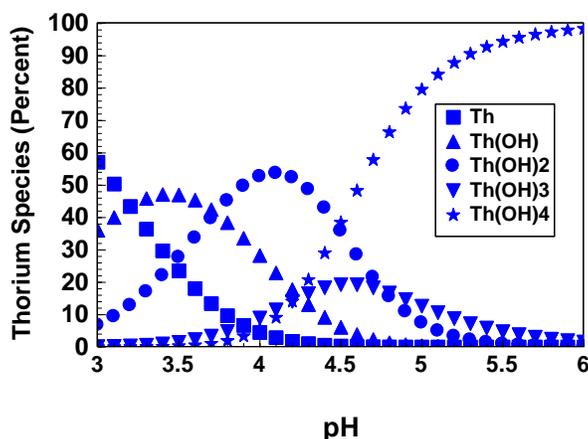
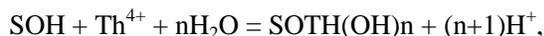


Figure 1. The distribution of important Th species as a function of pH.

The adsorption of Th onto substrates has garnered recent attention. Riese (1982) assumed the adsorption of Th was according to:

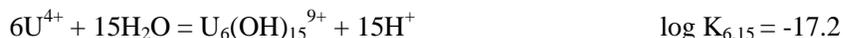
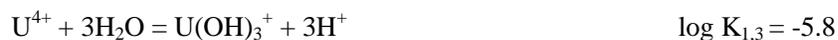


where SOH was the site-bonding hydroxyl and n has values of 1, 2, 3, and 4. Riese observed that adsorption on quartz ($\alpha\text{-SiO}_2$) with Na_2SO_4 as a supporting electrolyte (ionic strength = 0.01 mole/liter) was optimized from pH 3 to pH 4. Sulfate complexes limited thorium adsorption.

Soil Chemistry of Uranium

Hydrolysis of U(IV) is presented as (Baes and Mesmer, 1976):





The solubility of U(IV) may be estimated from thermochemical data, with the assumption that UO_2 is the crystalline phase, as:



or



Hydrolysis of U(VI) is presented as (Baes and Mesmer, 1976):



In low ionic strength media, the U(VI) polymers are not as thermodynamically favored, with the exception of $(UO_2)_3(OH)_5^+$.

The solubility of U(VI) may be estimated from thermochemical data, with the assumption that $UO_2(OH)_2$ is the crystalline phase (Baes and Mesmer, 1976) as:



The reduction of U(VI) to U(IV) may be presented as (Baes and Mesmer, 1976):



Using MinteqA2 software (Allison et al., 1991), U(VI) speciation may be estimated from thermochemical data for pH intervals from pH 4 to pH 8. Setting the total U(VI) concentration at 10^{-8} mole/liter, the $p\text{CO}_2$ pressure at 0 and again at 0.02 bar were the primary model inputs. Establishing a constant ionic strength with 0.01 mole NaNO_3 /liter, activity coefficients were estimated using the Davis equation. In the CO_2 closed system, UO_2^{2+} is the dominant species in very acidic media, whereas $\text{UO}_2(\text{OH})^+$ predominates from pH 6 to pH 8 (Table 1). The ion pair UO_2NO_3^+ is an important secondary species, particularly in acidic media. In the CO_2 open system, UO_2^{2+} is the dominant species in very acidic media; however, the UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are increasingly dominant U(VI) species upon transition from acidic media to neutral and then alkaline media. Importantly, the uranyl carbonate complexes are stable at Eh conditions that would promote U(VI) reduction in CO_2 closed systems. This MinteqA2 simulation of dilute U(VI) speciation corresponds closely with the analytical data and its MinteqA2 simulation as presented by Langmuir (1997) and also the data analysis from Waite et al. (1994).

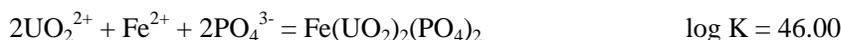
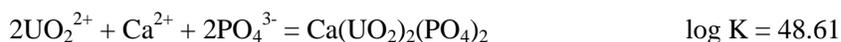
Table 1. Estimated uranium(VI) speciation (percent) using MinteqA2 with and without carbon dioxide spanning a pH interval from pH 4 to pH 8

CO ₂ at 0.0 bar					
U(VI) species	4	5	6	7	8
UO_2^{2+}	97.8	90.4	50.8	5.5	trace
$\text{UO}_2(\text{OH})^+$	trace	8.4	47.2	51.3	14.0
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	trace	trace	trace	trace	1.1
UO_2NO_3^+	2.2	1.2	trace	trace	trace
$(\text{UO}_2)_3(\text{OH})_5^+$	trace	trace	trace	42.0	85.7
CO ₂ at 0.02 bar					
U(VI) species	4	5	6	7	8
UO_2^{2+}	96.7	43.9	trace	trace	trace
$\text{UO}_2(\text{OH})^+$	trace	4.1	trace	trace	trace
UO_2NO_3^+	1.3	trace	trace	trace	trace
UO_2CO_3	1.1	51.3	84.2	4.5	trace
$\text{UO}_2(\text{CO}_3)_2^{2-}$	trace	trace	14.1	78.9	2.6
$\text{UO}_2(\text{CO}_3)_3^{4-}$	trace	trace	trace	16.6	97.4

Typically, the pH range of minimal solubility of the U(VI) minerals is also the pH range for optimal adsorption of U(VI). In general, U(IV) complexes are

less soluble and less mobile than U(VI) complexes (Phillips et al., 2006). Hsi and Langmuir (1985) investigated the adsorption of U(VI) onto noncrystalline $\text{Fe}(\text{OH})_3$ and goethite ($\alpha\text{-FeOOH}$) in 0.1 mole NaNO_3 /liter suspensions as a function of total carbonate and pH. Hsi and Langmuir documented that the optimum adsorption pH was near pH 6.3 to 6.5 for noncrystalline $\text{Fe}(\text{OH})_3$ and U(VI)-carbonate complexes reduce U(VI) adsorption in alkaline media. For goethite suspensions the pH of maximum U(VI) adsorption shifted from pH 5.7 to pH 8.0 as the total carbonate concentration decreased. Waite et al. (1994) investigated U(VI) adsorption onto hydrous ferric oxides and documented that the maximum U(VI) adsorption spanned the range from pH 5 to pH 9, with increased carbonate concentrations limiting the U(VI) adsorption in the pH interval from pH 8 to pH 9. In general, U(VI) adsorption into Fe-oxyhydroxides is greater than phyllosilicate minerals. At Eh values less than 0.2 volts, U(VI) reduction to uraninite (UO_2) is favored. Stewart et al. (2007) observed that U(VI) reduction is inhibited in the presence of ferrihydrite.

Precipitation reactions involving U(VI) include (Chen and Yiacoumi, 2002):



Great interest exists to better understand Th and U transport in natural systems, e.g. soil profiles, sediments and aquifers (Aide et al., 2011; Bidoglio et al., 1989; Hamby et al., 2002; Varinlioglu and Kose, 2005; Johnson et al., 2004). Johnson et al. (2004) investigated Nevada soil sites having been impacted by depleted uranium. Uranium retention is based primarily on soil type, soil binding site concentrations, the presence of phyllosilicates and their associated Fe-oxyhydroxides, the contaminant concentration, the presence of competing ions, and the pH and Eh dependent contaminant speciation. The observed that distribution coefficients, K_d = concentration of the sorbed contaminant/the contaminant in the aqueous phase) increased with soil pH 7 to pH 11. The presence of U-silicate mineral aggregates limited vertical vadose

zone transport. Roh et al. (2000) investigated two U impacted sites at Oak Ridge, TN. Sequential leaching demonstrated that soil U was substantially associated with carbonates (45%) and Fe-oxyhydroxides (40%).

Thorium and Uranium Pathways in the Soil Environment

Plant uptake of Th and U has been investigated in pristine and impacted regions to (i) infer the extent of plant uptake and (ii) determine the likelihood that plant materials may be employed to remove Th and U from the soil environment (Ebbs et al., 1998; Raju and Raju, 2000; Shahander and Hossner, 2002; Morton et al., 2002; Shtangeeva and Ayrault, 2004; Kumar et al., 2008). Harvest removal is the withdrawal of Th- and U-bearing plant material from the soil environment, whereas residues (litter) are plant materials placed at the soil surface by mechanical harvesting or natural forest/grassland accumulation (Figure 2). In India, Kumar et al. (2008) compared Th and U uptake in plant materials with respect to total soil abundances, observing that U, relative to Th, was preferentially accumulated by plant materials. Morton et al. (2002) observed the uptake of Th and U in Blueberries (*Vaccinium pallidum* Aiton) grown in Spodosols. They documented mean blueberry Th concentrations in the leaf (1.59×10^{-1} mg Th/kg) and stem (9.1×10^{-2} mg Th/kg) was substantially greater than the corresponding U concentrations (8.65×10^{-3} mg U/kg for leaf tissues and 7.95×10^{-3} mg U/kg for stem tissues). Shtangeeva and Ayrault (2004) investigated Th uptake in wheat (*Triticum vulgare* var 'Horst') in soil not considered Th or U contaminated and observed that wheat seedlings accumulated 0.1 mg Th/kg in the leaves and 0.71 mg Th/kg root systems. They speculated that microbial activity and exuded organic acids in the rhizosphere may have promoted Th plant uptake.

Residue decomposition generally results in the return of inorganic Th and U to the soil environment. Soil organic matter (humus) is a highly reactive semi-stable product of the microbially-directed soil decomposition of plant and animal tissues. Soil organic matter contains variable concentrations of aromatic and aliphatic carboxyl, alcohol and amine groups whose resultant charge density is pH dependent (Norvell, 1991). At a pH of 7, soil organic matter has a negative charge density, which retains cations, including Th and U (Chopping and Shambhag, 1981). Organic complexes of Th and U may be replaced by other cations, especially divalent and trivalent cations, buffering the soil solution (Essington, 2004).

Phyllosilicates (clay minerals) typically manifest a net negative charge density because of isomorphous substitution and unsatisfied edge charges. These negative charges provide charge capacity to electrostatically retain cations, including U and Th (Moon et al., 2006). Additionally, Mn- and Fe-oxyhydroxides are variable charges surfaces that acquire a positive charge density when the pH is more acid than the mineral's point of zero net charge density (Sato et al., 1997; Chen and Yiacoumi, 2002;). Thus Th and U, along with its hydroxyl-monomers and hydroxyl-polymers, participate in adsorption reactions at the colloidal interfaces of the phyllosilicates and Mn- and Fe-oxyhydroxides (Barnett et al., 2000 and 2002; Cygan, 2002; Davis et al., 2002; Honeyman and Ranville, 2002; McKinley et al., 1995; Runde, 2002; Runde et al., 2002; Turner et al., 1996). Wind and water erosion of clays and other colloids may be an important source of U and Th transport (Bednar et al., 2004).

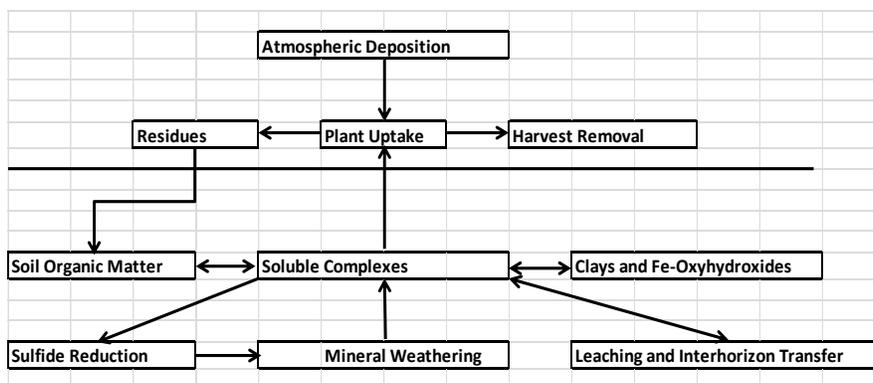


Figure 2. Illustration of the various U and Th pathways in the soil environment.

The objective of this research was to determine the soil profile distributions of thorium and uranium to infer the soil processes responsible for their accumulation in diagnostic soil horizons. All soils are considered pristine, that is, they have not been impacted by U and Th because of human activities.

MATERIALS AND METHODS

Soil profiles were selected to represent many soil series having an appreciable areal extent across southeastern Missouri and which also provided a broad array of soil series having alluvial and loess parent materials (Table 1

and Table 2). The studied soil orders include: Alfisols, Ultisols, Mollisols, Entisols, Inceptisols and Vertisols. Several of the soils (Caneyville, Frenchmill, Hildebrecht, Irondale, Kilarney, and Knobtop series) are located near ancestral Pb-mine sites, whose Pb-ore was known to have secondary concentrations of Zn and Cd (Aide et al., 2008, Aide 2009, Aide and Braden, 2009).

All soils were classified and sampled in excavated pits using USDA-NRCS protocols (Soil Survey Division Staff, 1993). Routine laboratory analysis include mechanical analysis, cation exchange capacity, pH, exchangeable cations, total acidity, Bray-1 phosphorus, 2M KCl sulfate extraction, and organic matter by loss on ignition using routine methods (Carter, 1985).

The soil characterization data was used primarily to verify that the pedons actually represented the soil series and to assess if these soil properties show relevant relationships with the Th and U soil profile distributions.

The Selected Soils of the Study Area

Table 2 displays the classification and drainage of soils in the study area, whereas Table 3 displays the parent materials and the existing vegetation/usage. The pedons range from excessive well-drained to very poorly-drained. The Alfisols, Ultisols and Mollisols have A (ochric, umbric or mollic) - E - Bt (argillic or natric) - C or R horizon sequences. The Entisols and Inceptisols possess Ap (ochric) - Bw (cambic) - C horizon sequences. The Vertisols possess Ap - Bsg horizon sequences. Soil textures range from loamy sand to clay.

Summers are hot and humid with a mean July temperature of 26°C and winter temperatures are mild with a mean January temperature of 2°C. The mean annual precipitation of 1.19 m is seasonally distributed, with greater rainfall in spring. Vegetation is either a mixed hardwood forest or land that has been cleared of vegetation, land-graded and employed in row-crop agriculture. The study area is remote from any thorium or U industrial or mining areas and is considered a relatively pristine soil resource in terms of Th and U.

Table 2. Classification and drainage class of soils

Soil Series	Classification	Drainage Class
Alred	Loamy-skeletal over clayey, siliceous, semiactive, mesic Typic Paleudalfs	well drained
Amagon	Fine-silty, mixed, active, thermic Typic Endoaqualfs	poorly drained
Broseley	Loamy, mixed, superactive, thermic Arenic Hapludalfs	somewhat excessively drained
Calhoun	Fine-silty, mixed, active, thermic Typic Glossaqualfs	poorly drained
Caneyville	Fine, mixed, active, mesic Typic Hapludalfs	well drained
Clana	Mixed, thermic Aquic Udipsamments	moderately well drained
Commerce	Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts	somewhat poorly drained
Crowley	Fine, smectitic, thermic Typic Albaqualfs	somewhat poorly drained
Dubbs	Fine-silty, mixed, active, thermic Typic Hapludalfs	well drained
Foley	Fine-silty, mixed, active, thermic Albic Glossic Natraqualfs	poorly drained
Frenchmill	Loamy-skeletal, mixed, active, mesic Typic Paleudults	well drained
Heldebrecht	Fine-silty, mixed, active, mesic, Oxyaquic Fragiudalfs	moderately well drained
Irondale	Loamy-skeletal, mixed, active, mesic Typic Hapludults	well drained
Killarney	Loamy-skeletal, mixed, active, mesic Typic Fragiudults	moderately well drained
Knobtop	Fine-silty, mixed, active, mesic Aquic Hapludults	moderately well drained
Lilbourn	Coarse-loamy, mixed, superactive, nonacid, thermic Aeric Fluvaquents	somewhat poorly drained
Malden	Mixed, thermic Typic Udipsamments	excessively drained
Menfro	Fine-silty, mixed, superactive, mesic Typic Hapludalfs	well drained
Portageville	Fine, smectitic, calcareous, thermic Vertic Endoaquolls	poorly drained
Reelfoot	Fine-silty, mixed, superactive, thermic Aquic Argiudolls	somewhat poorly drained
Rueter	Loamy, mixed, superactive, mesic, shallow Vitritorrandic Haploxerolls	well drained
Sharkey	Very-fine, smectitic, thermic Chromic Epiaquerts	poorly drained
Taumsauk	Loamy-skeletal, mixed, active, mesic Lithic Hapludults	somewhat excessively drained
Tiptonville	Fine-silty, mixed, superactive, thermic Oxyaquic Argiudolls	moderately well drained
Wilbur	Coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts	moderately well drained

Laboratory Protocols

An aqua regia digestion was employed to obtain a near total estimation of elemental abundance associated with all but the most recalcitrant soil chemical environments (Aide and Fasnacht, 2010). Aqua-regia digestion does not appreciably degrade quartz, albite, orthoclase, anatase, barite, monazite, sphene, chromite, ilmenite, rutile and cassiterite; however, anorthite and phyllosilicates are partially digested. Homogenized samples (0.75g) were equilibrated with 0.01 liter of aqua-regia (3 mole nitric acid: 1 mole hydrochloric acid) in a 35°C incubator for 24 hours. Samples were shaken, centrifuged and filtered (0.45 µm), with a known aliquot volume analyzed using inductively coupled plasma – mass spectrometry (ICP-MS). The aqua regia digestion procedure was performed by Activation Laboratories (Toronto, Canada). In this procedure, selected samples were duplicated and known reference materials were employed to guarantee analytical accuracy. The detection limit for Fe was 0.01 percent, the detection limit for Th was 0.1 mg/kg and the U detection limit was 0.1 mg/kg.

A hot water extraction was performed to recover only the most labile or potentially labile fractions. A hot water extraction involved equilibrating 0.5 g samples in 0.02 L distilled-deionized water at 80°C for one hour followed by 0.45µm filtering and elemental determination using ICP-MS. For the water extraction, selected samples were duplicated and reference materials were employed to guarantee analytical precision. The detection limits for Th and U were 0.1 µg/kg-soil.

Some soil pedons were grouped for statistical analysis because they represent the same soil series and were located in close proximity. Regression analysis and Pearson correlations were performed using Microsoft Excel. To test the null hypothesis that the linear regression slope (β_1) is zero, the variance of the error about the slope was estimated to create confidence intervals ($\alpha = 0.05$) were developed (Johnson and Kuby, 2004). Paired T-tests were used to establish correlation confidence.

RESULTS AND DISCUSSION

Relationship Involving Iron, Thorium and Uranium and Soil Profile Depth

The thorium and uranium soil profile distributions for 25 soil series show a range in distribution trends.

Table 3. Parent materials and vegetation class

Soil Series	Parent Materials	Vegetation
Alred	loess over cherty limestone residuum	mixed deciduous forest
Amagon	fine-silty alluvium	mixed deciduous forest
Broseley	sandy alluvium	row crop
Calhoun	fine-silty alluvium	mixed deciduous forest
Caneyville	loess	mixed deciduous forest
Clana	coarse-textured terrace (alluvium)	irrigated row crop
Commerce	loamy alluvial sediments	row crop
Crowley	fine-silty alluvium	irrigated row crop
Dubbs	silt over loamy sand alluvium	row crop
Foley	silty terrace material high in sodium	irrigated row crop
Frenchmill	fine-silty colluvium of acid igneous rocks	mixed deciduous forest
Heldebrecht	loess over dolomite residuum	mixed deciduous forest
Irondale	loess over rhyolite residuum and colluvium	mixed deciduous forest
Killarney	slope alluvium mixed with loess and slope alluvium	mixed deciduous forest
Knobtop	loess over rhyolite	mixed deciduous forest
Lilbourn	coarse-textured terrace (alluvium)	irrigated row crop
Malden	coarse-textured terrace (alluvium)	irrigated row crop
Menfro	loess	mixed deciduous forest
Portageville	fine-textured alluvium	irrigated row crop
Reelfoot	silty alluvium	row crop
Rueter	loess over cherty limestone residuum	mixed deciduous forest
Sharkey	fine textured alluvium	irrigated row crop
Taumsauk	colluvium or residuum weathered from rhyolite	mixed deciduous forest
Tiptonville	silty-textured alluvium	irrigated row crop
Wilbur	silty-textured alluvium	irrigated row crop

Table 4. Whole soil Mean Iron, Thorium, and Uranium concentrations (mg/kg-soil)

Soil Series	-----Iron-----		-----Thorium-----		-----Uranium-----	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Alred	24,430	12,600	9.20	5.82	0.66	0.20
Amagon	16,042	5,490	3.51	0.82	1.28	0.26
Broseley	10,530	3,940	2.30	1.33	0.63	0.13
Calhoun	17,380	7,660	3.91	1.82	1.08	0.17
Caneyville	22,150	7,340	5.39	2.76	1.01	0.39
Clana	12,030	3,320	2.41	1.28	0.84	0.21
Commerce	18,190	3,940	5.82	0.42	1.31	0.24
Crowley	25,190	9,520	7.62	1.78	1.98	0.93
Dubbs	15,690	4,420	4.16	1.63	1.00	0.12
Foley	28,210	4,120	8.17	1.27	1.69	0.23
Frenchmill	20,740	6,480	5.51	0.75	1.36	0.36
Hildebrecht	14,680	5,920	6.69	3.82	1.15	0.38
Irondale	21,580	5,470	6.77	2.78	1.30	0.30
Killarney	13,000	1,920	3.02	0.71	0.92	0.19
Knobtop	22,180	6,100	4.30	1.29	1.42	0.36
Lilbourn	13,090	1,350	2.71	1.02	0.88	0.17
Malden	10,590	1,190	2.42	0.50	0.73	0.11
Menfro	18,270	6,850	5.73	2.78	1.12	0.30
Portageville	37,360	2,710	10.33	0.73	2.66	0.13
Reelfoot	18,910	3,900	5.53	1.61	1.03	0.05
Rueter	16,700	6,660	5.74	2.71	0.58	0.13
Sharkey	30,330	6,940	8.58	1.90	2.80	1.30
Taumsauk	26,640	6,270	7.72	1.97	1.36	0.30
Tiptonville	15,450	6,230	4.23	1.97	1.05	0.10
Wilbur	17,720	2,730	4.16	1.08	1.00	0.16

All "pooled" pedons were adjacent, sharing a similar soil classification and having identical land use.

Table 3 displays the Fe, Th and U mean and standard deviation among the soil series selected for this study. The mean whole soil Th concentrations range from 2.3 to 10.3 mg Th/kg, whereas the mean whole soil U concentrations range from 0.58 to 2.80 mg U/kg. The mean whole soil Fe concentrations range from 10,530 to 37,360 mg Fe/kg. Coarse-textured soils (Broseley, Clana, Lilbourn and Malden) had the smallest concentrations of Th and U, with the exception that the loamy-textured Rueter pedon had a mean thorium concentration greater than mean thorium concentration of all of the sampled pedons and also exhibited the smallest mean U concentration of the study area.

Thorium correlations with Fe (Table 5) demonstrate appreciable correspondence for most of the sampled pedons. Four pedons did not have significant correlations involving Th with Fe (Commerce, Killarney, Portageville and Wilbur) with all four of those pedons having correspondingly small Fe standard deviations, suggesting that the lack of Fe variation contributed to the lack of Fe-Th correlation.

Sampled soils (pedons) having argillic horizons displayed greater Fe, Th and U concentrations in the argillic horizons than the overlying eluvial horizons. An example is the Th concentrations in the argillic horizons of the Menfro pedons (Figure 3).

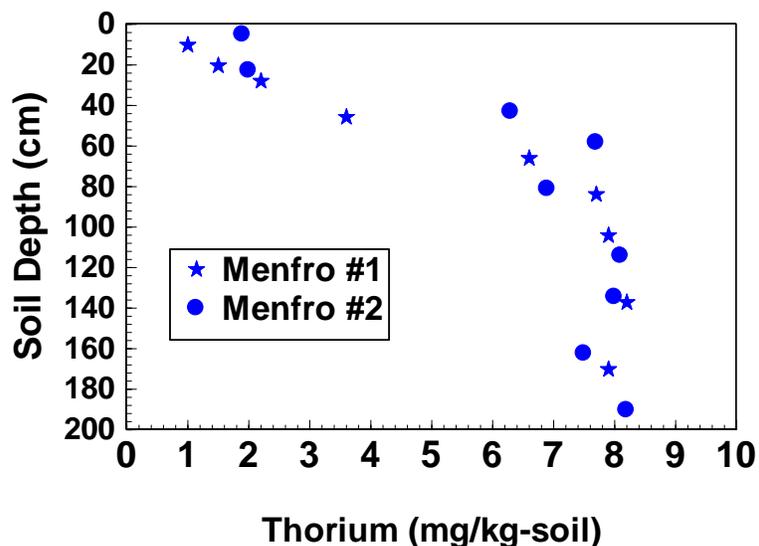


Figure 3. The distribution of thorium by soil depth in the Menfro pedons.

Table 5. Statistical evaluation of iron, thorium, and uranium concentrations in selected soil profiles

Soil Series	----- Th / U -----		-----Correlation (r)-----	
	Mean	Standard Deviation	Th-U	Th-Fe
Alred	12.6	6.1	0.96	0.98
Amagon	2.7	0.6	0.73	0.88
Broseley	3.5	1.4	0.84	0.91
Calhoun	3.6	1.3	0.75	0.35
Caneyville	5.1	1.0	0.96	0.84
Clana	2.8	0.9	0.85	0.95
Commerce	4.6	0.9	-----	-----
Crowley	4.0	1.0	0.64	0.81
Dubbs	4.1	1.5	-----	0.96
Foley	4.8	0.4	0.88	0.87
Frenchmill	3.8	0.3	0.95	0.89
Hildebrecht	5.8	1.5	0.81	0.99
Irondale	5.0	1.7	0.93	0.96
Killarney	3.9	1.8	-----	-----
Knobtop	3.0	0.3	0.98	0.94
Lilbourn	3.3	1.3	-----	0.40
Malden	3.4	0.7	0.37	0.69
Menfro	4.8	1.6	0.96	0.98
Portageville	3.9	0.4	-----	-----
Reelfoot	5.4	1.6	-----	0.97
Rueter	9.4	2.8	0.99	0.98
Sharkey	3.4	1.2	0.35	0.54
Taumsauk	1.4	0.4	0.97	0.97
Tiptonville	4.1	2.0	-----	0.71
Wilbur	4.3	1.5	-----	-----

All listed values are significantly valid at least to $\alpha = 0.05$.

The Crowley pedon was separated into its sand, silt and clay separates because the sand separate exhibited nodules of Fe- and Mn- oxyhydroxides. The sand and clay separates possess greater Fe, Th and U concentrations than the silt separate and corresponding whole soil (Figures 4 and 5). The clay, silt and to some extent the sand separate maintained reasonably consistent Th/Fe and U/Fe ratios, inferring that pedogenic processes responsible for accumulation of Th and U among the separates did not dramatically exhibit any positive or negative preference for Th with respect to U. The Foley pedons similarly exhibited pedogenic Fe- and Mn-bearing nodules in the sand separate. The sand separate demonstrated greater Fe, Th and U in the sand separates (Figures 6 and 7). The pooled Frenchmill, Irondale, Killarney and Knobtop were pooled because they formed in residuum of rhyolite. The clay separates were isolated from selected soil horizons to determine their Fe, Th and U contents. Figures 8 and 9 demonstrate that the clay separate typically shows greater Fe, Th and U concentrations and that little Th or U preference in its association with Fe is observed between the whole soil and the clay separate.

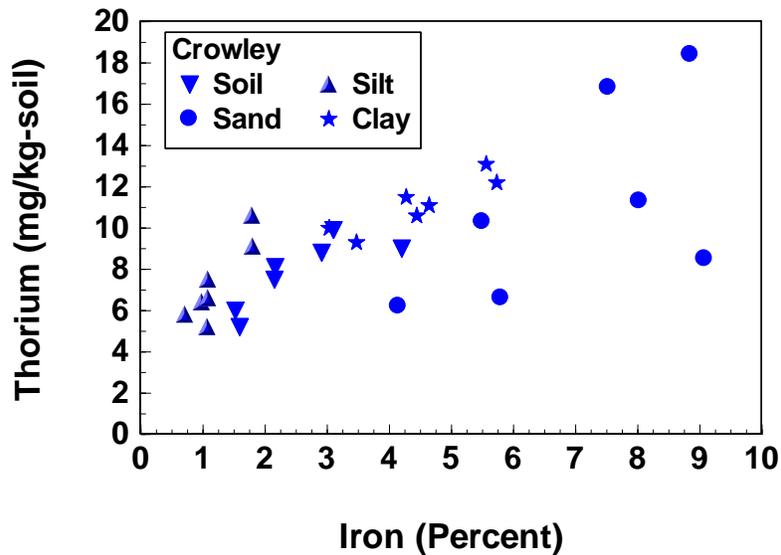


Figure 4. The thorium concentrations as a function of the corresponding Fe concentrations for the Crowley pedon.

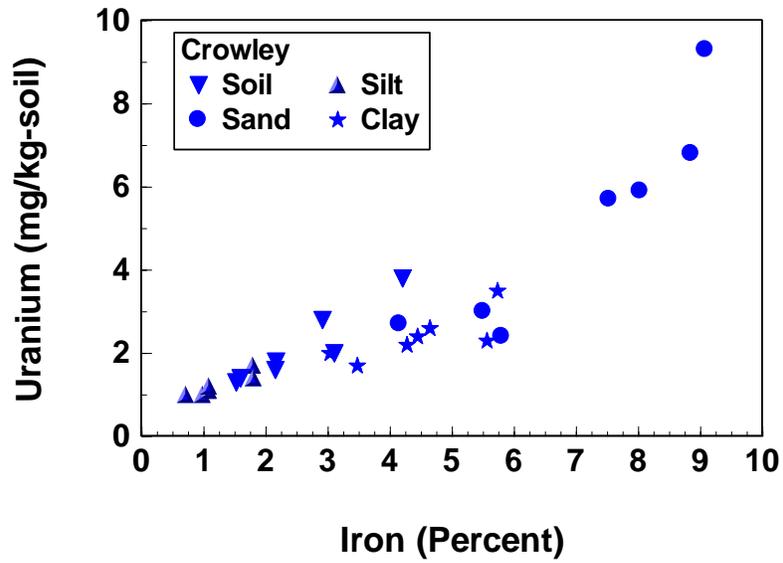


Figure 5. The uranium concentrations as a function of the corresponding Fe concentrations for the Crowley pedon.

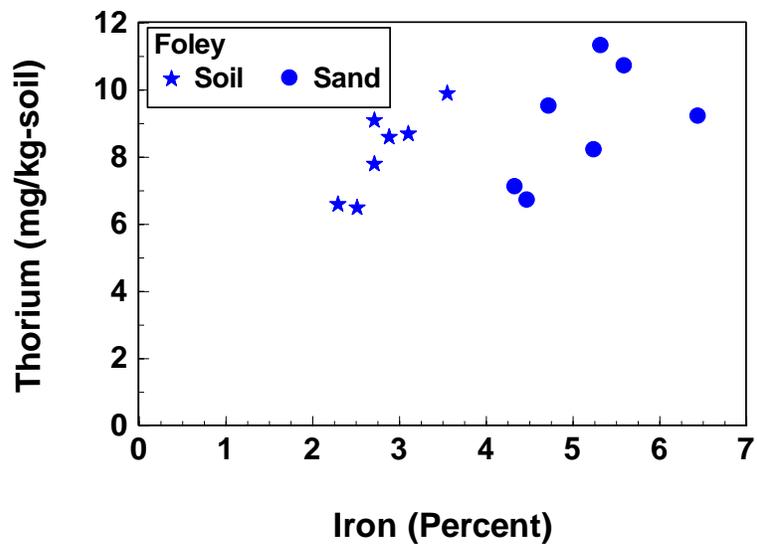


Figure 6. The thorium concentrations as a function of the corresponding Fe concentrations for the Foley pedon.

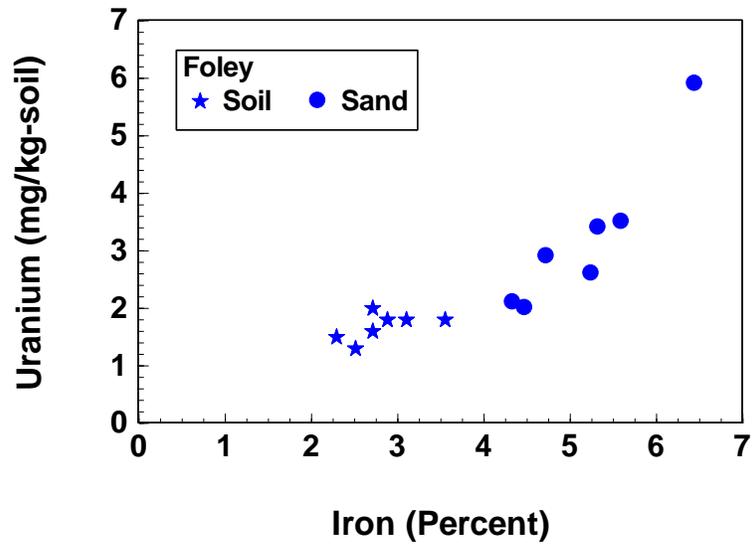


Figure 7. The uranium concentrations as a function of the corresponding Fe concentrations for the Foley pedon.

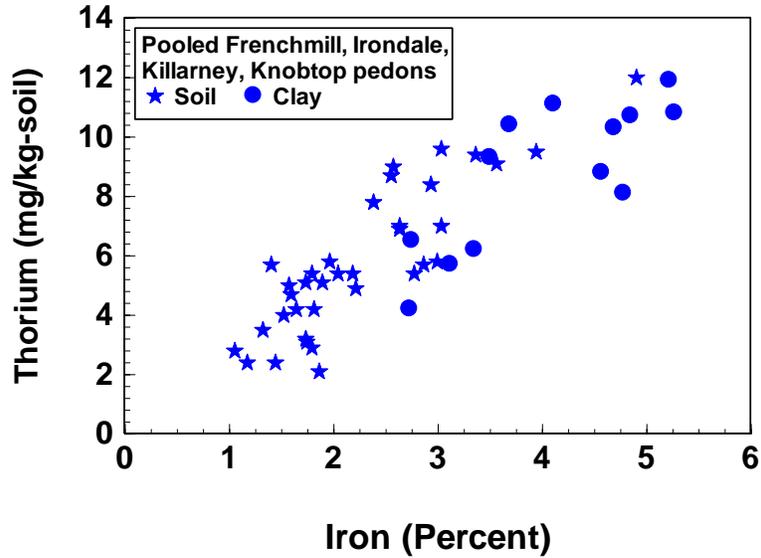


Figure 8. The thorium concentrations as a function of the corresponding Fe concentrations for the pooled Frenchmill, Irondale, Killarney and Knobtop pedons.

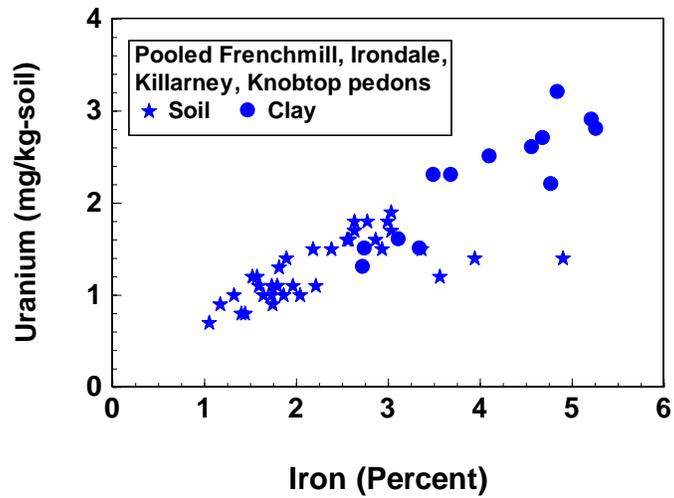


Figure 9. The uranium concentrations as a function of the corresponding Fe concentrations for the pooled Frenchmill, Irondale, Killarney and Knobtop pedons.

The Menfro pedons are developed entirely in deep loess. Thorium and Uranium are closely associated with Fe, with the argillic horizons having greater Fe expression than the eluvial horizons (Figures 10, 11).

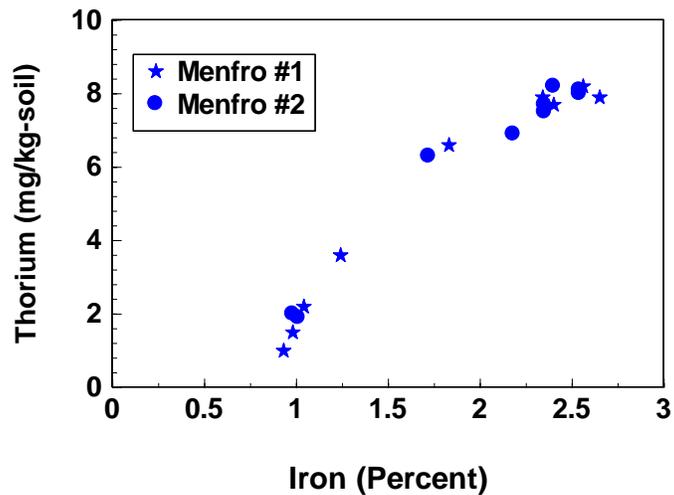


Figure 10. The thorium concentrations as a function of the corresponding Fe concentrations for the Menfro pedons.

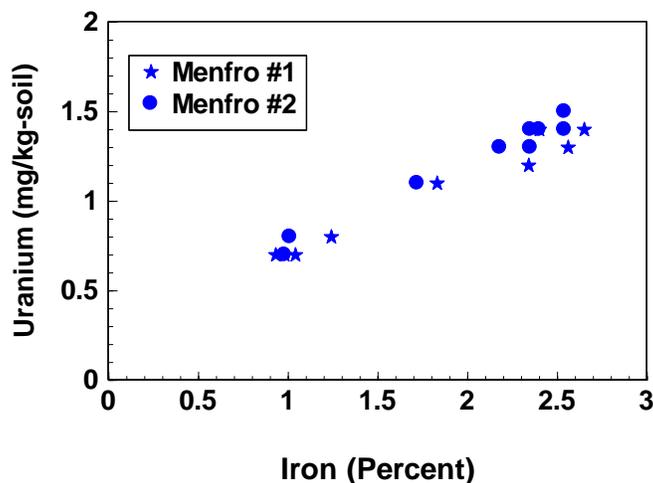


Figure 11. The uranium concentrations as a function of the corresponding Fe concentrations for the Menfro pedons.

Water Extracts Involving Zinc and Cadmium

Water extractions of selected soil horizons represents metal recovery of the most immediately plant available fraction within the soil environment. Water extractable Th and U were assessed for the Amagon, Calhoun, Sharkey, Caneyville, Wilbur Clana, Malden, and Lilbourn pedons. As expected, the relationship between the Th and U aqua regia digestion values and their corresponding Th and U water extraction values has no correlation. In general, the mean U water extraction values are greater than the mean Th water extraction values (Figures 12 and 13). The Amagon pedons had the greatest mean Th water extraction concentrations, whereas the Calhoun pedon had the greatest mean U water extraction concentrations ($9 \mu\text{g Th/kg}$ for the Amagon pedons and $16 \mu\text{g U/kg}$ for the Calhoun pedon). Conversely, the Caneyville and Wilbur pedons exhibited the smallest Th and U water extraction recoveries.

In general, the eluvial horizons demonstrated greater U and Th water extraction values (Figure 14 and 15), inferring that organic complexes of Th and U are important fractions for augmenting Th and U in the water fraction.

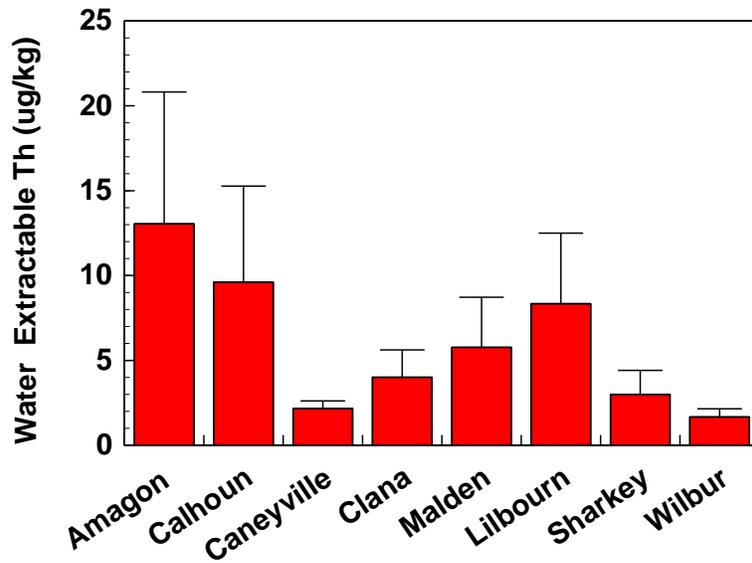


Figure 12. Mean water extractable thorium for selected soils. Error bars are standard deviations.

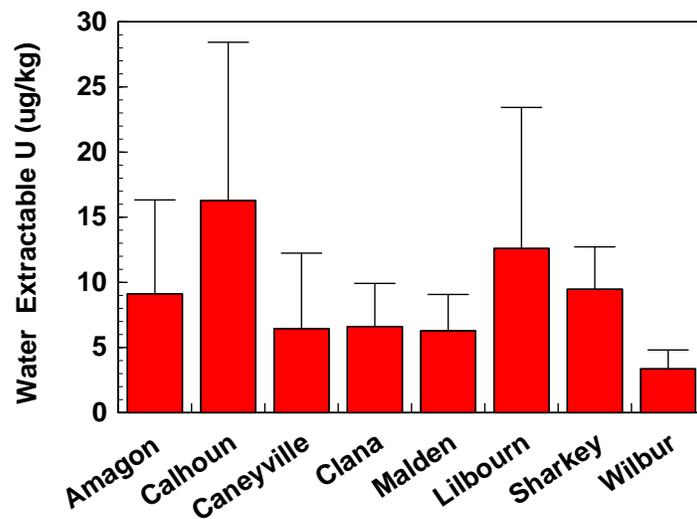


Figure 13. Mean water extractable uranium for selected soils. Error bars are standard deviations.

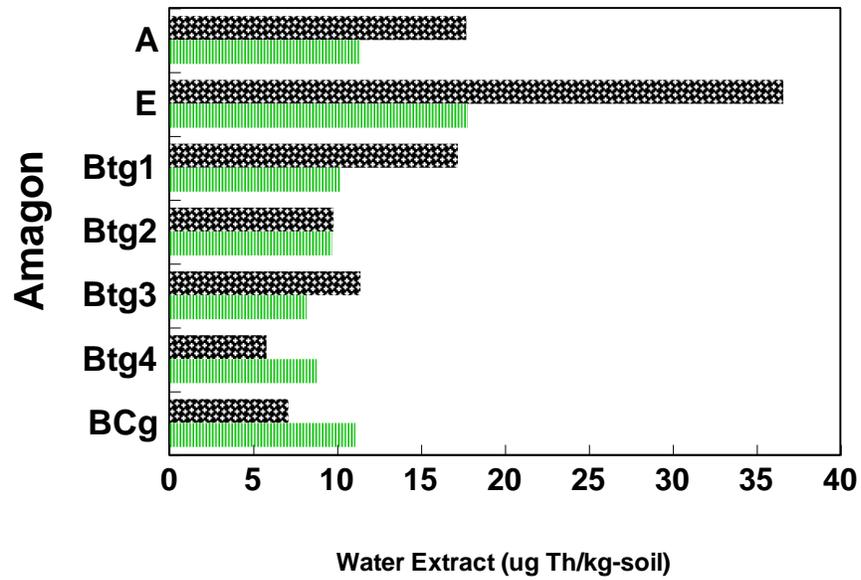


Figure 14. Water extractable thorium for horizons of two pedons of the Amagon series.

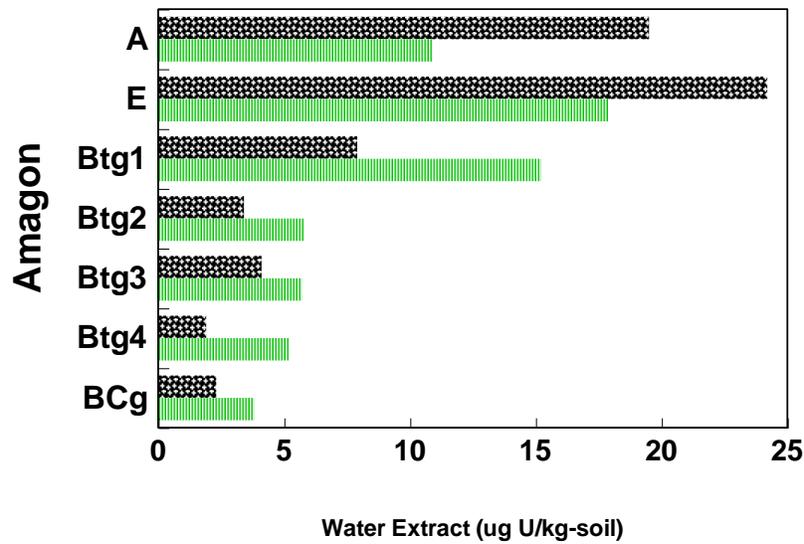


Figure 15. Water extractable uranium for horizons of two pedons of the Amagon series.

THORIUM AND URANIUM SOIL PROFILE

Distributions and Soil Morphology

The soil profile Th and U concentration distributions fall generally into two soil categories based on the presence of diagnostic soil horizons: the argillic soil horizon and the cambic soil horizon. The presence of Fe-oxyhydroxides associated with phyllosilicates provides greater site-bonding for Th and U. The presence of argillic horizons on stable landscapes will likely correlate with Th and U soil profile maxima given the abundance of binding sites. The clay eluviation-illuviation process likely provides interhorizon transport of Th and U. The soil organic matter component is not a dominant Th and U fraction; however, organic complexation of Th and U may promote plant uptake given the relative bonding strength of Fe-oxyhydroxides and the inertness of U and Th co-precipitation with the Fe-oxyhydroxide fraction.

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