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Thorium and Uranium Soil Profile Concentrations in Mississippi River Floodplains in Southeastern Missouri

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Abstract

In southeastern Missouri, the abundances of thorium and uranium were determined for two soil series in floodplains of the Mississippi River. The soils were Entisols and Inceptisols receiving annual flood inundation with alluvium accumulation. Aqua regia digestion provided thorium concentrations ranging from 4.4 to 10.3 mg·kg^{-1} across all soil horizons from all pedons. Similarly, aqua regia digestion provided uranium concentrations ranging from 0.4 to 1.1 mg·kg^{-1}. The silty clay Inceptisol pedons manifested greater uranium concentrations than the sandy loam to silt loam Entisols. A Na-acetate leach was performed to estimate salt-displaceable thorium and uranium to ascertain relative availability for plant uptake and mobility. Thorium concentrations ranged from 18 to 66 µg·kg^{-1}, whereas uranium concentrations ranged from 20 to 279 µg·kg^{-1}. The aqua regia digestion concentrations and the pollution index values collectively suggest that these soils have not been environmentally impacted. Uranyl leaching or uranyl loss during river transport may have reduced the uranium concentrations.

Keywords

Thorium, Uranium, Alluvium, Heavy Metals, Actinides

1. Introduction

1.1. Thorium and Uranium General Chemistry

Uranium (atomic number 92) has oxidation states +2, +4, +5 and +6, whereas thorium (atomic number 90) has oxidation states +2, +3, and +4. The thorium ground state electronic configuration is [Rn]6d^{2}7s^2, whereas the uranium ground state electronic configuration is $[\mathrm{Rn}]5f^3 6d^1 7s^2$. Uranium will decay to thorium along multiple pathways. The Uranium-238 decay chain has sequential main decays: 1) $^{238}\mathrm{U} \rightarrow {}^{234}\mathrm{Th}$ with α (He) emission, 2) $^{234}\mathrm{Th} \rightarrow {}^{234}\mathrm{Pa}$ with β emission, 3) $^{234}\mathrm{Pa} \rightarrow {}^{234}\mathrm{U}$ with β emission, 4) $^{234}\mathrm{U} \rightarrow {}^{230}\mathrm{Th}$ with α emission. The longest half-life is 4.5×10^9 years for $^{238}\mathrm{U} \rightarrow {}^{234}\mathrm{Th}$. The thorium-232 decay chain features: 1) $^{232}\mathrm{Th} \rightarrow {}^{228}\mathrm{Ra}$ with α emission, 2) $^{228}\mathrm{Ra} \rightarrow {}^{228}\mathrm{Ac}$ with β emission, 3) $^{228}\mathrm{Ac} \rightarrow {}^{228}\mathrm{Th}$ with β emission. The longest half-life is 1.4×10^{10} years for $^{232}\mathrm{Th} \rightarrow {}^{228}\mathrm{Ra}$ (Lee, 1991; Aide, 2017).

Brown and Ekberg (2016) reviewed thorium hydrolysis with equilibrium K values, where sequentially produced thorium species include $\mathrm{ThOH^{3+}}$, $\mathrm{Th(OH)_2^{2+}}$, $\mathrm{Th(OH)_3^{+}}$ and $\mathrm{Th(OH)_4}$. Polynuclear thorium species are largely produced at greater than 1 millimolar thorium activities, and the species include $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_2(OH)_3^{5+}}$, $\mathrm{Th_4(OH)_8^{8+}}$, $\mathrm{Th_4(OH)_{12}^{4+}}$, $\mathrm{Th_6(OH)_{15}^{9+}}$, $\mathrm{Th_6(OH)_{14}^{10+}}$. Noncrystalline $\mathrm{ThO_2}$ is represented as: $\mathrm{ThO_2 + H^+ = Th^{4+} + 2H_2O}$ with $\log K = 8.8 \pm 1$ at infinite dilution and T = 298 K. Uranyl hydrolysis species include simple $\mathrm{(UO_2)_3(OH)_n^{2-n}}$ ($n = 1$ to 4) or polynuclear complexes $\mathrm{(UO_2)_m(OH)_n^{2m-n}}$ ($m =$ 2 to 4; $n = 1$ to 7) (Kalintsev et al., 2024). At 10^{-5} molar $\mathrm{UO_2^{2+}}$ the uranyl ion is the dominant species at pH values more acidic than pH = 5.2, whereas $\mathrm{(UO_2)_3(OH)_5^{+}}$ is the more dominant species in more alkaline pH levels (Baes & Mesmer, 1976).

Davis et al. (2004) observed pH dependent uranium (VI) adsorption onto aquifer sediments. Empirical surface complexation models describe the variation in U(VI) retardation with respect to pH; however, more sophisticated models may over-estimate or under-estimate uranium (VI) adsorption. Bao et al. (2021) phosphoric acid altered phyllosilicate mineral surfaces resulting greater uranium adsorption. Bachmaf and Merkel (2011) performed batch experiments to study uranium sorption on selected clay minerals as a function of pH (4 - 9) and ionic strength. Kaolinite, with a greater abundance of aluminol sites, exhibited greater uranium sorption than montmorillonite. At neutral to high pH levels, Catalano and Brown (2005) proposed that uranium adsorption onto montmorillonite occurred because of strong, inner-sphere complexation reactions. Carbonate significantly reduced adsorption; however, iron on the clay edges supported uranyl retention.

Recent interest involves investigating microbial activities to limit uranium aquifer mobility. Wufuer et al. (2025) reviewed literature concerning uranium's microbial interactions, emphasizing uranium-transforming taxa (*Geobacter sulfurreducens*, *Shewanella oneidensis*, and *Desulfovibrio desulfuricans*) in addition to resilient fungi and algae. Microbial detoxification strategies included enzymatic reduction, biosorption, bioaccumulation, and biomineralization. Renshaw et al. (2005) reported that *Geobacter sulfurreducens* reduced the highly mobile $\mathrm{UO_2^{2+}}$ to $\mathrm{UO_2^{+}}$ after which $\mathrm{UO_2^{+}}$ undergoes disproportionation to $\mathrm{UO_2^{2+}}$ and $\mathrm{UO_2}$. Thus, a more immobile uranium species is synthesized. Williams et al. (2013) noted that organic electron donors stimulate microbial $\mathrm{UO_2^{2+}}$ reduction to less soluble $\mathrm{UO_2}$, which is an emerging strategy for immobilizing uranium. They further noted that the long-term stability of immobilized U(IV) must be investigated.

1.2. Thorium and Uranium Soil Concentrations

For the United States, non-impacted surface soil uranium concentration typically range from 0.3 to 10.7 mg·kg^{-1}, with a mean of 3.7 mg·kg^{-1}. For the United States, the soil surface thorium concentrations range from 2.2 to 21.0 mg·kg^{-1}, with a mean of 7.6 mg·kg^{-1} (Kabata-Pendias, 2011). In a previous southeast Missouri study involving soils that were not inundated by the Mississippi River, the mean whole soil uranium concentrations ranged from 0.58 to 2.80 mg·kg^{-1} (Aide et al., 2014). In a study of heavy metal bearing soil in New Orleans, Louisiana, Nyachoti et al. (2023) noted that the uranium soil concentrations in riverbank soils ranged from 0.59 to 2.53 mg·kg^{-1}, with a mean of 1.76 mg·kg^{-1}. Megumi and Mamuro (1977) proposed that the frequently observed greater thorium concentrations compared to uranium are likely attributed to the greater leaching tendency of uranyl ions. In an East Africa study, Mwalongo et al. (2023) reported that rock phosphate uranium concentrations ranged from 10.7 to 632 mg·kg^{-1}, whereas phosphate fertilizer uranium concentrations ranged from 108 to 281 mg·kg^{-1}. Thus, phosphate fertilization may incrementally add uranium to the soil environment. Harmsen and de Haan (1980) noted that soil organic matter and selected organic acids may increase the solubility of thorium and uranium. In the Mediterranean region, Guillén et al. (2026) observed anthropogenic and naturally occurring radionuclide and soil organic matter complexes. Both uranium and thorium complexation reactions primarily involved humic acids.

The purpose of this study is to document thorium and uranium concentrations in selected Mississippi River floodplain soils. A secondary purpose is to determine if the total and salt-exchangeable soil thorium and uranium concentrations reflect differences between the soil series.

2. Materials and Methods

2.1. Study Area

The study area is located on floodplains along the Mississippi River in Cape Girardeau County, Missouri. The climate is continental humid. The average summer temperatures are 25˚C to 26˚C and the typical annual precipitation is 1.14 to 1.27 m (Festervand, 1981). The soils used in this investigation were selected from the Caruthersville and Commerce soil series, because these two soils are widely occurring and offer very contrasting soil textures to assess the influence of phyllosilicate adsorption.

Soil horizon sampling for two soil pedons for each soil series occurred at soil depths of 0 - 15, 15 - 30, 30 - 45, 45 - 60, 60 - 90, and 90 - 120 cm. Sampling locations are for the Caruthersville pedons are Lat: 37.1623 and Lon: −89.4432 and for the Commerce pedons are Lat: 37.3160 and Lon: −89.5127.

2.2. Experimental Protocols

All soil horizons were previously analyzed to provide routine soil chemical characterization (Aide & Aide, 2025). An aqua regia digestion was employed to estimate near total thorium and uranium abundances. Homogenized samples (0.75 g) were equilibrated with 0.01 liters of aqua-regia 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 emission-mass spectrometry. A Na-acetate leach protocol was performed to estimate salt-exchangeable thorium and uranium concentrations and is understood to be an operational fraction to estimate salt-displaceable species, hence provide mobility and plant uptake likelihoods. For the Na-acetate leach, a 0.75 g soil sample passing a 60-mesh sieve was leached with a sodium acetate matrix at 30˚C for one hour. The samples were analyzed using inductively coupled plasma emission-mass spectrometry. The detection limit for the Na-Acetate leach was 1 $\mu g \cdot kg^{-1}$ for both thorium and uranium, both well below the actual reported concentrations.

For both the aqua regia digestions and the Na-Acetate leach, two reference samples and duplicate sampling were included for quality assurance. The solutions are analyzed using inductively coupled plasma emission-mass spectrometry. Both chemical extraction protocols were performed by Activation Laboratories (Ancaster, Ontario). Simple soil statistics included mean, standard deviation, and linear regression analysis using Excel.

2.3. Soils Employed in the Study Area

The Commerce soil series (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) are deep, somewhat poorly-drained soils formed in loamy to fine-textured alluvium with a horizon sequence of A-Bw. The Caruthersville soil series (Coarse-silty, mixed, superactive, calcareous, thermic Typic Udifluvents) are deep, moderately well-drained soils formed in coarse-textured to loamy alluvium having a horizon sequence of A-C horizons. All sampled pedons reside on floodplains receiving annual Mississippi River inundation.

Situated on a modern floodplain that does not receive Mississippi River inundation, but drains into the Mississippi River, the Kaintuck soil series was sampled to provide thorium and uranium aqua regia digestion and Na-Acetate concentrations for comparison with the annually flooded Mississippi River floodplain soils. The Kaintuck series (Coarse-loamy, siliceous, superactive, nonacid, mesic Typic Udifluvents) consists of very deep, well-drained soils that have ochric epipedons and an A and C horizon sequence. The aqua regia digestion of the Kaintuck soil series for thorium ranged from 2 to 2.3 $mg \cdot kg^{-1}$ (mean of 2.1 $mg \cdot kg^{-1}$) and uranium ranged from 0.6 to 0.8 $mg \cdot kg^{-1}$ (mean of 0.7 $mg \cdot kg^{-1}$).

3. Results and Discussion

3.1. The Aqua Regia Digestion Values for the Caruthersville and Commerce Soil Series

Routine soil characterization has been previously reported (Aide & Aide, 2025); however, for brevity the dominant soil properties are listed below. For the soil horizons of the Caruthersville pedons, the pH range is 7.7 to 8.1, the soil organic matter content range is 0.4% to 1.6%, the soil textures range from sandy loam to silt loam, and the cation exchange capacity range is 13.5 to 23.3 cmol·kg^{-1}. For the soil horizons of the Commerce pedons, the pH range is 7.6 to 7.9, the soil organic matter content range is 2.2% to 3.4%, the soil textures are generally silty clay, and the cation exchange capacity range is 23.6 to 40.4 cmol·kg^{-1}.

The mean thorium aqua regia digestion concentration is 5.39 mg·kg^{-1} for the Caruthersville soil series and 5.95 mg·kg^{-1} for the Commerce soil series (**Table 1**). The aqua regia digestion thorium concentrations for the Caruthersville pedons range from 4.4 to 10.3 mg·kg^{-1} with only minor differences between the two pedons. Similarly, aqua regia digestion thorium concentrations for Commerce pedons range from 5.0 to 6.7 mg·kg^{-1} with only minor differences between the two pedons. The mean uranium aqua regia digestion concentration is 0.57 mg·kg^{-1} for the Caruthersville soil series and 0.96 mg·kg^{-1} for the Commerce soil series. The aqua regia digestion uranium concentrations for Caruthersville pedons range from 0.4 to 0.7 mg·kg^{-1} with only minor differences between the two pedons. The aqua regia digestion uranium concentrations for Commerce pedons range from 0.8 to 1.1 mg·kg^{-1}, with only minor difference between the two pedons.

Table 1. Aqua regia digests Thorium and Uranium concentration for the Caruthersville and Commerce soil series.

Horizon	Thorium (mg/kg)		Uranium (mg/kg)	
Caruthersville	Pedon #1	Pedon #2	Pedon #1	Pedon #2
A	5.8	5.3	0.7	0.7
C1	5.3	4.4	0.6	0.5
C2	5.3	5.0	0.5	0.5
C3	4.7	10.3	0.6	0.7
C4	4.6	4.6	0.5	0.5
C5	4.8	4.6	0.6	0.4
Mean	5.39		0.57	
Commerce	Pedon #1	Pedon #2	Pedon #1	Pedon #2
A	5.6	5.9	0.9	1.0
Bw1	6.1	5.9	1.0	1.0
Bw2	6.1	6.7	0.9	1.0
Bw3	5.9	6.3	0.9	1.1
Bw4	6.0	5.0	1.0	0.8
Mean	5.95		0.96	

The thorium and uranium concentration values are like those reported for United States soils by Kabata-Pendias (2011). The uranium concentration values are like those of the Louisiana Mississippi River riverbank soils as reported by

Nyachoti et al. (2023). None of the thorium or uranium concentration values appear to be an environmental threat.

In general, the pedons of the Commerce series show slightly greater thorium and moderately greater uranium concentrations (**Figure 1**). Regression analysis demonstrates a linear relationship involving the uranium concentration (mg·kg^{-1}) and the cation exchange capacity (CEC with units of cmol·kg^{-1}). The regression equation is:

Uranium = 0.022 (CEC) + 0.25 with $r^2 = 0.73$.

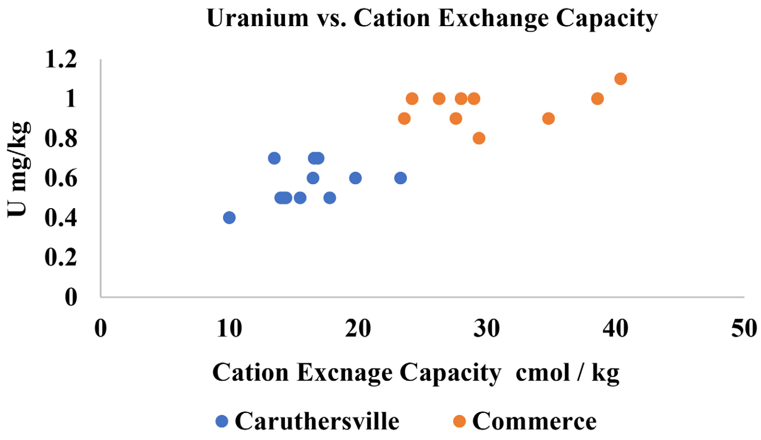

Figure 1. Relationship of uranium (mg·kg^{-1}) to cation exchange capacity (cmol·kg^{-1}) for the Caruthersville and Commerce pedons.

Considering cation exchange capacity as a proxy for clay content, then there exists a strong relationship between uranium and clay content. Thorium did not manifest any linear relationship to cation exchange capacity.

3.2. The Na-Acetate Leach Concentration Values for the Caruthersville and Commerce Soil Series

The Na-Acetate leach thorium concentrations for Caruthersville pedons range from 18 to 66 µg·kg^{-1} (mean of 34.5 µg·kg^{-1}) with pedon #1 having slightly greater thorium contents (**Table 2**). The Caruthersville corresponding Na-leach uranium concentrations range from 20 to 111 µg·kg^{-1} (mean of 66.4 µg·kg^{-1}) with only incidental differences between the two pedons. For the Commerce series, the Na-Acetate leach thorium concentrations range from 19 to 28 µg·kg^{-1} (mean of 22.1 µg·kg^{-1}) and the uranium concentrations range from 176 to 279 µg·kg^{-1} (mean of 226 µg·kg^{-1}).

Table 2. Na-Acetate thorium and uranium concentration for the Caruthersville and commerce soil series.

Horizon	Thorium (µg/kg)		Uranium (µg/kg)	
Caruthersville	Pedon #1	Pedon #2	Pedon #1	Pedon #2
A	18	30	65	111

Continued

C1	26	27	100	67
C2	23	22	47	56
C3	54	24	97	45
C4	59	34	70	46
C5	66	32	73	20
Mean	34.5		66.4	
Commerce	Pedon #1	Pedon #2	Pedon #1	Pedon #2
A	28	23	197	236
Bw1	21	21	252	257
Bw2	24	23	208	225
Bw3	21	21	215	279
Bw4	19	20	227	166
Mean	22.1		226.2	

For both thorium and uranium, the ratio of the Na-Acetate leach concentrations to the aqua regia digestion concentrations are indicators of the salt-exchangeable percentage of the element, hence, the percentage availability of the element. The mean thorium ratios of the individual soil horizons for the Caruthersville pedons are 0.69% (standard deviation of 0.38%), whereas the mean thorium ratios of the individual soil horizons for the Commerce pedons is 0.37% (standard deviation of 0.05%). The mean uranium ratios of the individual soil horizons for the Caruthersville pedons are 11.56% (standard deviation of 3.82%), whereas the mean uranium ratios of the individual soil horizons for the Commerce pedons is 23.5% (standard deviation of 1.6%). Thus, the Commerce soil series has approximately twice the Na-Acetate leach ratio than the Caruthersville series.

The significance of the thorium and uranium Na-Acetate leach ratios involves estimating the amount of salt-displaceable thorium and uranium relative to the total element concentration. In our extractions, thorium salt-displaceable recovery was slightly greater for the Caruthersville pedons than the Commerce pedons. The corresponding uranium salt-displaceable recovery was significantly greater for the Commerce pedons than the Caruthersville pedons. Most importantly, uranium recoveries were much greater than the thorium recoveries, regardless of soil series.

3.3. Metal Pollution Index Values

The PI pollution index for aqua regia digestion concentrations (PI) is described as:

PI = [Mean Metal Concentration]/[Mean Geochemical Background Concentration].

The calculated PI values may be interpreted as: 1) PI < 1 is absent, 2) 1 < PI < 2 is low, 3) 2 < PI < 3 is moderate, 4) 3 < PI < 5 is strong, 5) PI > 5 is very strong (Kowalska et al., 2018; Gong et al., 2008). In this study, the geochemical background concentrations for thorium and uranium were from the Kaintuck soil series. The thorium pollution index for the Caruthersville and Commerce soil series was 2.56 and 2.83, indicating moderate thorium accumulations. The uranium pollution index for the Caruthersville and Commerce soil series was 0.81 and 1.37, indicating absent and low uranium accumulations, respectively.

In a previous southeast Missouri study involving soils that were not inundated by the Mississippi River, the mean whole soil thorium concentrations ranged from 2.3 to 10.3 mg·kg^{-1} and the uranium concentrations ranged from 0.58 to 2.80 mg·kg^{-1} (Aide et al., 2014). There was a strong tendency for increased uranium concentrations as the clay content increased. In this present study, the Kaintuck mean thorium concentration was 2.1 mg·kg^{-1}, a value lower than the range of thorium values in the Aide et al. (2014) study, thus the Kaintuck soil appears to be an acceptable geochemical baseline for uranium assessment and another soil may be more suitable for thorium. Given that the Caruthersville and Commerce aqua regia digestion values are representative of non-impacted soils and also considering that the utilized small geochemical background thorium concentration from the Kaintuck soil series raised the pollution index, the thorium PI levels more little indicate a little thorium accumulation. The thorium and uranium concentrations are not considered an environmental threat.

4. Summary and Future Research Needs

Thorium and uranium aqua regia digestion concentrations suggest that the floodplain soils of the Mississippi River across southeastern Missouri are not the result of human activities. Salt-displaceable uranium was significantly greater for the silty clay Inceptisols than the sandy-loam to silt loam Entisols. The phyllosilicate abundance is most assuredly involved in the greater uranium concentrations.

Future research activities need to investigate uranium plant uptake of naturally occurring vegetation to estimate if the salt-displaceable extraction is a reliable indicator of bioavailability. Additionally, further investigations involving episodic oxidation-reduction of floodplain sediments influencing uranium mobility are warranted.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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