

Savannah River Ecology Laboratory UNIVERSITY OF GEORGIA



Technical support for Monitored Natural Attenuation of a uranium and mercury contaminated wetland along the Savannah River, USA

Daniel I. Kaplan

Argonne National Laboratory – Kenneth Kemner, Edward O'Loughlin, Maxim I. Boyanov SREL/UGA – Peng Lin

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TNX Area, Savannah River Site, SC





TNX Area

- Former pilot scale nuclear facility (1958 1980).
- ➢ Released contaminants into unlined seepage basins:
- Cl, Cr, Hg, NO_3^- , Pu, Th, U, and Cl-hydrocarbons.
- Contaminants migrated to nearby wetland.
- Hg in surface sediments ranged 0.02 (background) to 12 mg/kg
- U ranged from 1 (background) to 1200 mg/kg
- Remediation source term removal, phosphate soil amendments, Monitored Natural Attenuation.





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Objective

Objective:

Characterize Hg and U sorption to TNX wetland sediments.



Intention:

- To providing a conceptual geochemical model for use in risk assessment calculations and
- To provide guidance for the selection of an appropriate in situ remediation strategy.

Approach:

- Using contaminated sediment, measure the proportion of Hg and U that might desorb from the sediment under natural wetland conditions.
- Conduct thermodynamic calculations
- X-ray Absorption Spectroscopy: U L_{III} edge XANES & EXAFS

In-situ desorption K_d values

Adsorption distribution coefficient, K_d, and Retardation Factor, R_f

$$K_{d} = \frac{C_{sediment}}{C_{aqueous}} = \left(\frac{C_{initial} - C_{eq}}{C_{eq}}\right) \times \left(\frac{Mass_{soil}}{Vol_{aq}}\right)$$

Retardation Factor = $\frac{FlowRate_{water}}{FlowRate_{contaminant}} \propto (1 + K_d)$

In-situ desorption distribution coefficient – measured with contaminated sediment from the study site

in situ $K_d = \frac{C_{Acid} + C_{OM} + C_{AmFeOxide}}{C_{Saturated Paste}}$

Kinetics: Adsorption occurs more quickly than desorption because the latter must break surface bonds (surface activation energies).

Fewer assumptions about: soil/contaminant aging, contaminant speciation

Desorption is the rate limiting step. As such, it's the parameter that best reflects contaminant migration through porous media.

Mercury Sequential Extraction



Sequential Extraction Procedure

Sequence	Extractant: Chemical composition	Targeted contaminant fraction	Contact time (days)	Solid:liquid (g/g)
1	Saturated paste extract: Uncontaminated TNX surface water	Pore water	7	~1:0.19
2	Dilute acid extract: Dilute acetic acid [0.44 M CH3COOH+0.1 M Ca(NO3)2]	Exchangeable	1	1:30
3	Oxidizing agent: sodium pyrophosphate [0.1 M (Na4P ₂ O ₇)]	Bound to organic fraction	1	1:30
4	Total digestion: Aqua regia +48% HF	Structural/precipitated/ Fe oxide	0.125	1:30

Sequential Extraction Results

		Solid phase Hg (%)		
Sediment	Aqueous phase Hg (µg/L)	Exchangeable	Organic	Structural/ Precipitated/ Fe Oxide
Background	<10	0	0	100
A-5	<10	0	8	92
B-3	<10	0	0	100
C-5	<10	0	4	96
D-28	<10	0	0	100



Intro | Study Site | Objective | Hg | U | Conclusions

Mercury (Ad)sorption & Desorption K_d

Adsorption

Mercury K_d Values and Filtration Ratios				-200 -
K _d (mL/g)	K_d average \pm standard deviation (mL/g)	Filtration ratio ^a (unitless)	Filtration ratio average ± standard deviation (unitless)	$-400 - \frac{1}{2}$
5,582 4,704 5,725	5,337 ±553	1.03 0.94 0.98	0.98 ± 0.05	Filtration ratio=



in situ desorption
$$K_d = \left(\frac{\text{Hg}_{\text{exch}} + \text{Hg}_{\text{ox}} + \text{Hg}_{\text{total digest}}}{\text{Hg}_{\text{saturated paste}}}\right)$$

In-situ K_d (mL/g) A-5 Sediment >6820 B-3 Sediment >630 C-5 Sediment >9450 D-28 Sediment >9200

6 pH



1000

800

600

400

200

0

Eh (mV)

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0₂ H₂O

H₂O H₂ 8

 $Hg_{< 0.45 \ \mu m}$

Hgunfiltered

10

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Mercury vs. soil size fractions

Sediment	Hg concentration (µg/g)			
	Whole	<2 µm	<0.5 µm	
Background	0.02	0.17	0.30	
A-5	6.82	1.69	0.98	
B-3	0.64	0.85	0.75	
C-5	9.45	6.76	5.75	
D-28	9.20	0.40	0.44	



Hg (and Th and U, data not shown) was not consistently enriched in fine grains.

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Sequential Extraction & *in situ* desorption K_d values (L/kg)

In-situ desorption K_d values (L/kg)

	102	103	Sediment 104	105	106
²³² Th	_c	1803	115	2255	_
²³⁵ U	_	-	193	_	_
²³⁸ U	1237	1297	170	6493	2110

- Th and U associated with exchangeable OM & amorphous Feoxide fraction.
- Bound strongly to sediments.

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Sequential Extraction (% of Th or U)

Sediment	Fraction	²³² Th	²³⁸ U
Incontaminated	Acid extractable	0	0
	Organic Fraction	61	9
	Amorph. Fe-oxide	39	0
	Cryst. Fe-oxide	0	0
	Structural	0	91
102	Acid extractable	1	26
	Organic fraction	84	57
	Amorph. Fe-oxide	10	4
	Cryst. Fe-oxide	5	2
	Structural	0	11
103	Acid extractable	1	36
	Organic fraction	65	37
	Amorph. Fe-oxide	15	6
	Cryst. Fe-oxide	7	3
	Structural	12	17
104	Acid extractable	0	25
	Organic fraction	78	57
	Amorph. Fe-oxide	6	3
	Cryst. Fe-oxide	7	2
	Structural	9	14
105	Acid extractable	1	26
	Organic fraction	88	56
	Amorph. Fe-oxide	7	5
	Cryst. Fe-oxide	4	2
	Structural	0	12
106	Acid extractable	0	44
	Organic fraction	91	41
	Amorph. Fe-oxide	7	3
	Cryst. Fe-oxide	2	1
	Structural	0	11

Oxidized-to-reduced sediments with depth (from nearby wetland – Tims Branch)



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Sediment U - Conclusions from cores



- Accumulation of U in the top 5-10 cm
- In drier or near-surface environments the predominant valence state is U^{VI}.
- Conversely, in saturated sediments that are not directly exposed to air the predominant valence state is stabilized as U^{IV}
- Important implications on modeling
 U transport & risk in the environment

Blue line = Total U Red histogram= U(IV) Grey histogram = U(VI)



Conclusions



- > Hg is very strongly bound to sediment, likely (co)precipitated in Fe, not S.
- U is very strongly bound to sediments as U(VI) near surface where most U resides and as U(IV) in deep saturated depths. U(VI) bound as dispersed hydrated ions to Fe-oxides (~40%) and OM (~60%).
- Given the ecologically sensitive nature of the wetland and the fact that the Hg is strongly bound to the sediment, it was concluded that a monitored natural attenuation approach for site remediation may be appropriate.

