

Establishing a Geochemical Heterogeneity Model for a Contaminated Vadose Zone – Aquifer System

Chris Murray*, John M. Zachara, Jim P. McKinley, Yi-Ju Bott, and Dean Moore
Pacific Northwest National Laboratory, Richland, WA 99354



Background

The Hanford IFRC is performing two experiment types to quantify and understand the behavior of U(VI) in the coupled vadose zone-groundwater-river system.

- 1) Natural gradient tracer experiments where site waters with different U(VI) concentration and composition are injected into the site to investigate in-situ adsorption/desorption rate and extent.
- 2) Comprehensive monitoring experiments where groundwater U(VI) concentrations and composition are monitored with depth over short time scales to: i) quantify U(VI) recharge to the aquifer from water table rise and fall events, ii) evaluate mixing between different hydraulic conductivity visits, and iii) determine U fluxes in and out of the IFRC site.

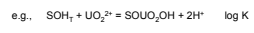
Motivation

Because of the complexity of the linked groundwater-river system, reactive transport models that integrate hydrologic and geochemical properties and processes over the 3-D spatial domain of the IFRC site are needed to interpret the field experiments.

Heterogeneity models result from the geostatistical analysis of site and sediment characterization data. The geochemical heterogeneity model (GHM) describes the distribution of chemical parameters/properties necessary to calculate the aqueous concentration of U(VI) given variable water composition, time scale, and spatial location. The model is under development and is not complete. It is closely linked with the development of conceptual models for U(VI) reaction and kinetics (Kent and Haggerty).

Approach

The GHM is based on a surface complexation model SCM of U(VI) adsorption/desorption (Kent and Haggerty).



1000H bicarbonate extractable U(VI) (total adsorbed U) and K_d were measured on the < 2 mm size fraction that hosts almost all contaminant U(VI).

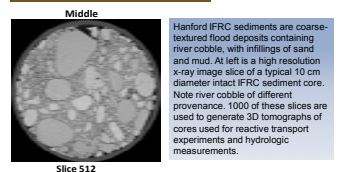
Note that $K_d = \frac{\text{adsorbed U (mol/kg)}}{\text{total aqueous U (mol/L)}} = \frac{\log K (\text{UO}_2^{2+}) (\text{SOH}_2)/(\text{H}^+)^2}{[\text{U}_{\text{aq}}]}$

- 1) Determined primarily by pH, HCO_3^- , and Ca^{2+} . Computed by thermodynamic code.
- 2) Proportional to surface area, e.g., $[\text{SOH}_2] = 3.84 \mu\text{mol sites/m}^2$

K_d can be used as an objective function to estimate log K given $[\text{SOH}_2]$, or $[\text{SOH}_2]$ given log K.

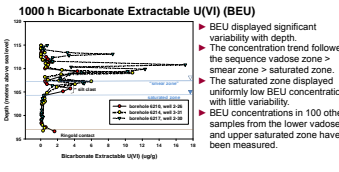
The characterization properties bicarbonate extractable U(VI), K_d , and surface area on the < 2 mm fraction, and mass % of the < 2 mm fraction become the initial parameters for the GHM.

Characterization Results

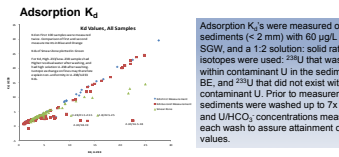


Hanford IFRC sediments are coarse-textured flood deposits containing river cobbles, with fillings of sand and mud. At left is a high resolution x-ray image slice of a typical 10 cm diameter intact IFRC sediment core. Note river cobble of different provenance. 1000 of these slices are used to generate 3D tomographs of cores used for reactive transport experiments and hydrologic measurements.

- ▶ Total U analyses of sieve fractions indicated that sorbed U resides in the < 2 mm fraction that represents 5-40% of the sediment mass (20% on average).
- ▶ Geochemical characterization measurements have been performed on the < 2 mm fraction only.
- ▶ Reactive transport model calculations will initially be performed using < 2 mm properties, parameters, and correlations with the > 2 mm materials behaving as a diluent.
- ▶ The initial step in upscale/mixing movement from < 2 mm, to field-textured sediments.

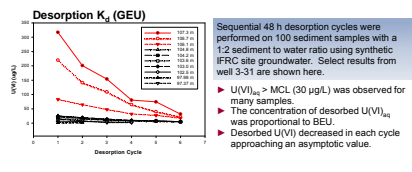


- ▶ BEU displayed significant variability with depth.
- ▶ The concentration trend followed the sequence vadose zone > smear zone > saturated zone.
- ▶ The saturated zone displayed uniformly low BEU concentrations with little variability.
- ▶ BEU concentrations in 100 other samples from the lower vadose and upper saturated zone have been measured.



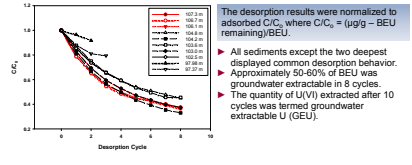
Adsorption K_d 's were measured on 1000 h BE-sediments (< 2 mm) with 60 $\mu\text{g/L}$ U(VI)T, IFRC-SGW, and a 1:2 solution: solid ratio. Two isotopes were used: ^{235}U that was present within contaminant U in the sediments prior to BE, and ^{238}U that did not exist within contaminant U. Prior to measurement, the sediments were washed up to 7x with SGW and UHCO_3 concentrations measured after each wash to assure attainment of acceptable values.

- ▶ K_d 's on the first 100 sample set were measured twice to assess reproducibility (red and blue), which was within acceptable bounds.
- ▶ K_d 's ^{238}U and K_d 's ^{235}U displayed close to 1:1 correlation for most samples, as expected if residual contaminant U(VI) did not influence measurements.
- ▶ K_d 's $^{238}\text{U} < K_d$'s ^{235}U for two subsets of samples that contained high residual contaminant U(VI) after BE.
- ▶ K_d 's ^{238}U represented the most artifact free measurement, ranging from 0.8 to 28 L/kg.
- ▶ Adsorption $K_d < \text{Desorption } K_d$ for comparable samples.

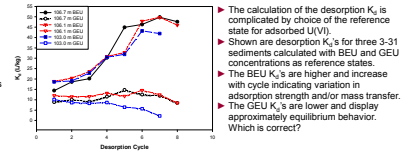


Sequential 48 h desorption cycles were performed on 100 sediment samples with a 1:2 sediment to water ratio using synthetic IFRC site groundwater. Select results from well 3-31 are shown here.

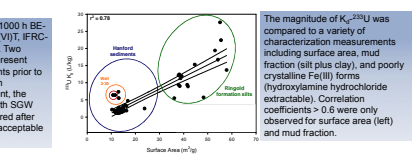
- ▶ $\text{U(VI)}_{\text{aq}} > \text{MCL}$ (30 $\mu\text{g/L}$) was observed for many samples.
- ▶ The concentration of desorbed U(VI)_{aq} was proportional to BEU.
- ▶ Desorbed U(VI) decreased in each cycle approaching an asymptotic value.



- ▶ All sediments except the two deepest displayed common desorption behavior.
- ▶ Approximately 50-60% of BEU was groundwater extractable in 8 cycles.
- ▶ The quantity of U(VI) extracted after 10 cycles was termed groundwater extractable U (GEU).

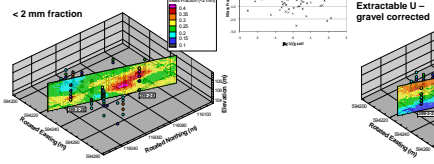
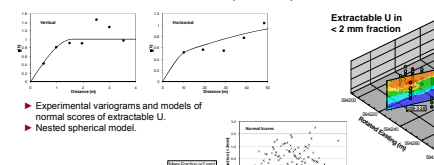
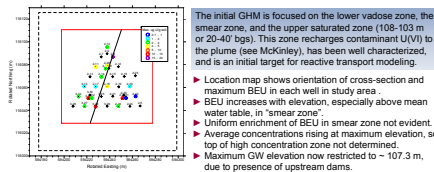


- ▶ The calculation of the desorption K_d is complicated by choice of the reference state for adsorbed U(VI).
- ▶ Shown are desorption K_d 's for three 3-31 sediments calculated with BEU and GEU concentrations as reference states.
- ▶ The BEU K_d 's are higher and increase with cycle indicating variation in adsorption strength and/or mass transfer.
- ▶ The GEU K_d 's are lower and display approximately equilibrium behavior. Which is correct?



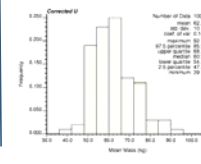
- ▶ IFRC site sediments originate from both the Hanford and Ringold formation.
- ▶ The Ringold is fine-grained with higher surface area and significant phyllosilicate content.
- ▶ The phyllosilicate fine-fraction in the Hanford is believed to originate from Ringold formation reworking.
- ▶ There is considerable unexplained variability in Ringold formation K_d .
- ▶ Variability in the Hanford formation K_d may be explained by facies variations.

Spatial Distribution of Extractable U

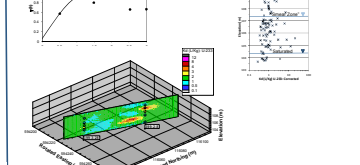
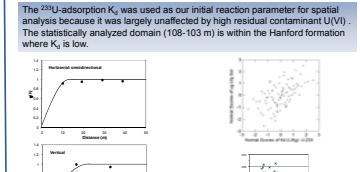


- ▶ Sequential Gaussian simulation used to generate 100 realizations of extractable U in < 2 mm fraction, and of fraction < 2 mm. Cross-sections show E-type estimates, average of 100 realizations.
- ▶ Realizations generated independently, no correlation found in scatter plot of extractable U and mass fraction < 2 mm.
- ▶ Grid resolution: 1 m horizontal, 0.1 m vertical, total of ~410K nodes in 3-D grid volume
- ▶ Gravel correction assumes coarse fraction is inert.
- ▶ Extractable U distribution cuts across grain size variations. Distribution of extractable U is variable in upper "smear zone".

Mass of Extractable U



Spatial Distribution of K_d 's ^{238}U



- ▶ Experimental variogram and model for K_d 's ^{238}U similar to extractable U.
- ▶ No correlation of K_d 's ^{238}U and mass fraction < 2 mm.
- ▶ Weak but significant correlation of normal score transforms of K_d 's ^{238}U and extractable U ($r = 0.55$), but no trend seen with elevation.
- ▶ Sequential Gaussian simulations of K_d 's ^{238}U were generated independently of extractable U and mass fraction < 2 mm.
- ▶ K_d hot spots observed that show no property correlation.

Conclusions

- ▶ K_d and surface area measurements have been difficult and repeated multiple times.
- ▶ 1000 h BEU displays weak correlation with K_d , and decreased through the smear zone.
- ▶ Residual U(VI) after 1000 h BE still reactive.
- ▶ K_d 's ^{238}U (V) correlates with S and mud fraction.
- ▶ The adsorption K_d is relatively uniform at low value and exhibits hot spots.
- ▶ Accessible inventory of adsorbed U(VI) in the greater smear zone is ~ 62 kg.

Future Research

- ▶ More surface area measurements and their geostatistical distribution.
- ▶ Causes for unexplained variations in K_d , e.g., controlling property.
- ▶ Reconciling differences in adsorption and desorption K_d .
- ▶ Spatial distributions of mass transfer parameters or their surrogates (by correlation).
- ▶ Inclusion of GHM's into reactive transport calculations.
- ▶ Comparison of GHM – informed interpretations to field experiment results.