

Background

Uranium from nuclear industrial activities has a wide range of $^{235}U/^{238}U$ and $^{236}U/^{238}U$ due to variable combinations of isotopic separation producing enriched fuels with high ²³⁵U/²³⁸U and residual depleted U with low ²³⁵U/²³⁸U, and nuclear transformations altering $^{235}U/^{238}U$ as well as producing ^{236}U during the operation of uranium-fueled nuclear reactors. In contrast, natural background uranium has essentially constant $^{235}U/^{238}U$ (to within $\pm 0.7\%$ (Stirling et al., 2007; Weyer et al., 2008), virtually zero ²³⁶U/²³⁸U, but variable ²³⁴U/²³⁸U due to alpha recoil effects (Osmond and Cowart, 1992). These contrasts in isotopic composition between natural and processed uranium, as well as the wide isotopic compositional range of processed uranium, provide the means to trace contaminant uranium in the environment and delineate the sources and history of contamination (Christensen et al. 2004, 2007). In the 300 Area U fuel rods for Hanford's nuclear reactors were manufactured, along with research and development of chemical processes and testing of materials in several small research nuclear reactors. Uranium bearing waste from these various processes was disposed to a number of different seepage ponds and trenches in the 300 Area, ultimately resulting in a persistent groundwater U plume. U isotopic analyses of Columbia River samples trace 300 Area U 350 km down river and provide contraints on U discharge rates from the 300 Area to the Coumbia River (Christensen et al. 2010, in prep). Here we discuss our U isotopic studies (supported by previous ERSP funding, and currently by 300 Area IFRC ERSP funding) of the groundwater of the 300 Area, with a particular focus on the IFRC experimental well array, and of vadose zone and aquifer sediment samples both from beneath the process ponds and within the IFRC array. These data not only provide insights into the sources and temporal dynamics of the U plume, but also aid in the planning of experiments within the IFRC array (e.g. identification of wells with similar and contrasting U isotopic compositions to the IFRC array). Planned experiments will involve adsorption/desorption of U within the IFRC experimental array that will be monitored in part through U isotopic analysis of groundwater samples from the array.

300 Area Groundwater Uranium Isotopic Variation

To map the spatial and temporal U isotopic variation of the 300 Area groundwater plume, we have analyzed a series of groundwater samples (Fig. 1). Presented in Fig. 2 are U isotopic data for samples covering 2003 to 2009. Significant variation is observed that mirrors that for the Process Pond sediment leachates, though in detail the two arrays cross each other at a low angle (Fig. 4) suggesting a second processed enriched U source composition. No consistent relationship is seen between ground water U concentration and isotopic composition, consistent with variable release of U from contaminated sediments with a range of U isotopic composition.



Figure 1. Map of the 300 Area showing locations of sampled groundwater wells. seeps and of vadose zone pits beneath the North and South Process Ponds, and the site of IFRC well plot. Also shown are contours of U groundwater concentration for Dec. 2003-Summer 2004. (after Hartman et al. 2005)



Figure 2. Plot of 236U/238U vs. 235U/238U for 300 Area groundwater samples for 2004-2009. Numbers by data points give well number, concentration (ppb), and sample date. Samples for well 1-17A show significant change between July 2005 and September 2005. An earlier sample (blue) of 1-17A from August 2003 is nearly identical to the July 2005 sample. Samples from wells 2-1, 2-2, 4-7 and 1-21A also show significant isotopic changes over 3-4 yrs, though higher frequency changes have yet to be investigated by sampling.

INTEGRATED FIELD RESEARCH CHALLENGE SITE

Hanford 300 Area

Uranium Isotope Systematics in the 300 Area U Plume and the IFRC Plot: **Progress Towards a Site U Isotopic Model** John N. Christensen¹, James P. McKinley², Mark E. Conrad¹, Deborah Stoliker³, Donald J. DePaolo¹ and John M. Zachara²

300 Area & IFRC Sub-pond Sediments Uranium Isotope Stratigraphy

To investigate vadose zone sources of U in the 300 Area, sediment samples from four pits from beneath the former process ponds (locations in Fig. 1), and samples from borings produced from IFRC well construction (Fig. 5) and the drilling of 2-5 (C5708) were analyzed for U isotopic composition. Bicarbonate extractions were performed on the "Pit" samples and 2-5 samples, while extractions with both bicarbonate and model groundwater solutions were conducted on the boring samples from IFRC wells. The extracted U was quantified and measured for isotopic composition (Figs. 3 & 4).



Figure 3. Plot of 236U/238U of sediment sample leachates vs. sampling depth. Plotted are results for NPP1. NPP2, SPP1, SPP2 (Fig. 1) and for samples from borings from wells 2-26, 2-30, 2-31 and 2-5 in the IFRC plot (Fig. 5). There's little U isotopic difference between the bicarbonate and model groundwater leachates (not shown). Significant U isotopic local spatial heterogeneity (vertical & horizon (al) is represented by the sampled IFRC sediments, nearly spanning that of the ments during operation of the ponds, but also potentially spread laterally (& vertically) due to historic floods prior to dam control of the Columbia.



Figure 4. Plot of 236U/238U vs. 235U/238U comparing sediment leachates (Fig 3) to 300 Area groundwater samples (from Fig. 2, now shown). In general both arrays reflect variable mixing between a processed enriched U and depleted U (with perhaps natural U fuel). This mixing for the most part likely occurred as a part of the disposal history of the process ponds and trenches, rather than mainly controlled by mixing the within the plume.

²³⁶U/²³⁸U for Samples Collected on 9/2/08 of 100 200 200 ²⁰⁴ Aprox.gw flow 9/2/09 Figure 5 Deep microbiological characterization well • ERT and core (i.e., characterization) Primary gw injection well + ERT and characterizati Iulti-level groundwater monitoring well clusters Spring 2009 Passive U Mobilization Experimen Well 3-30 — Bailed Samples Pumped Samples



0 4/17/09 4/27/09 5/7/09 5/17/09 5/27/09 6/6/09 6/16/09 6/26/09 Sampling Date Figure 7. Time series comparing U concentrations of groundwater taken (bailed = blue diamond, pumped = red squares) from 3-30 during the passive mobilization experiment The water table depth is show (blue squares) for comparison. Sharp rises in U concentration are associated with rises of the water table into the lower vadose ("smear") zone. Subsequent U excursions require greater rises in water table elevation. (See poster by J. McKinley et



- * Large U isotopic differences are evident between sediments from different process ponds and at the scale of the IFRC plot, along with U isotopic variations with depth. (Figs. 3 & 4) * Groundwater U and sediment leachate U isotopic compositions fall along similar, roughly parallel, arrays indicating mixtures involving both processed enriched U fuels and depleted U (and possibly
- processed natural U), likely developed during the history of disposal to the process ponds and trenches (Fig. 4). Sediment U isotopic variation has some spatial correlation with the observed U isotopic variation in the 300 Area groundwater U plume (Figs. 4 & 11), and at the scale of the IFRC plot as shown by the Spr. 2009 passive U mobilization experiment and IFRC well samples from 9/2/08 (Figs. 5, 6 & 8).
- * the isotopic composition of the added U that produced the observed U concentration excursions in 3-30 can be mapped to the U isotopic stratigraphy of borings from nearby 3-31 implicating the local "smear" zone as the source (Fig. 8 & 9).
- * There is a time lag of about a day between rises in the water table and the release of U from the 3-31 "smear" zone sediment to 3-30 groundwater (Figs. 7 & 10). Once the water table is at a new high, the influence of 3-31 sediment on 3-30 groundwater wanes also after about a day (Figs. 7 & 10).

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IFRC Plot Groundwater Uranium Isotopic Variation: A Snapshot on 9/2/08



samples collected over an 8 hour period on 9/2/08. Approximate groundwater flow was toward the river at <4 (?) m/day. Black contours are for aroundwater 236U/238UDashed lines represent the boundaries of the former SPP complex. Small insets show depth profiles of 236U/238U for the three borings for wells 2-26, 2-30, 3-31 that are compared and shown in greater detail in Figs. 2 and 4. Well 3-31 is within a ormer subpond, well 2-26 is in between two sub-ponds, while 2-30 and 2-5 are withir the main pond footprint. The local effect of sediment hosted U at 2-30 on groundwa ter can be seen in the contours of 236U/238U. The effect of local sediment U is also revealed in the passive U mobilization experiment described below (Figs. 7-10).

Figure 6. Plot of 236U/238U vs. 235U/238U comparing groundwater samples from the IFRC plot (collected 9/2/08) to groundwater samples to other nearby wells (see also Figs. 2 & 8). Inset shows expanded detail for the IFRC well samples and their well

IFRC Spring 2009 Passive U Mobilization Experiment



Figure 8. Plot of 236U/238U vs. 235U/238U for samples from 3-30 collected between 4/23/09 and 6/13/09 during the passive U mobilization experiment All samples, with the notable exception of the sample taken 5/18/09, fall along mixing lines between a deep ("smear" zone) vadose zone source characterized by bicarbonate leachates from 3-31 and "background" groundwater U. The sample from 5/18 was affected by a different vadose zone source, and represents U imported from the east of 3-30. All 2s errors are smaller than the data symbols.



Figure 9. (A)Uranium mixing diagram plotting the inverse of U groundwater concentration vs. 235U/238U. The data indicate mixing between relatively low and high 235U/238U end-members. with the low 235U/238U end-member associated with high U concentration. (B) The calculated percentage of 3-31 sediment U (represented by bicarbonate leachates) in the 3-30 groundwater J samples plotted against 1/[U] (ppb-1). The data indicate that the "background" groundwater U concentration increased from 40 ppb to 63 ppb with time (between 4/23/09 and 6/13/09).



Figure 10. Time series of water table depth compared to the calculated percentage of the 3-31 sediment U end-member represented in the groundwater U at 3-30. Water depths are plotted only for those dates for which the U isotopic composition data is available.

Observations

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Mapping Groundwater U Isotopic Variation



Figure 11. (A) Version of Fig. 2 highlic ing groups of groundwater samples isotopic composition that are the mapped onto (B), modified from Fig. 1.

Influence of Mixing on 300 Area Groundwater Uranium



Figure 14. Plots of 235U/238U (in A) and 236U/238U (in B) vs. 1/[U] illustrating possible mixing relationships in the 300 Area groundwater U plume. No one mixing line covers all samples, but a fan of mixing lines appear to have a common endmember with a 235U/238U of ~0.0079 and 236U/238U of ~150. The other endmembers v between different sectors of the 300 Area depending on local U contributions from contaminated sedimen

Conclusions

+ Bicarbonate and model groundwater leachates of IFRC sediment samples have similar isotopic compositions, but reveal significant U isotopic variability both horizontally and vertically, including within the "smear" zone.

 \star \star At the spatial scale of the IFRC well plot, resolvable, systematic differences in groundwater U isotopic compositions were found for samples collected on a single day(9/2/08). These differences may be attributable to local U isotopic heterogeneity hosted in the IFRC sediments. The 2009 passive experiment revealed that water table rises into the "smear" nobilized U with distinct isotopic compositions that can be mapped back to the local sediment within the "smear" zone

+ Different vadose/"smear" zone reservoirs of U contamination in the 300 Area (and at the scale of the IFRC plot) have different U isotopic signatures, providing both the means to match sediment source to groundwater U contamination, but also provides a probe of contamination history and of the hosts of labile U.

* Significant spatial (and temporal) variation is observed in the U isotopic composition of 300 Area groundwater allowing the tracking of water masses independent of U concentration, and the constraining of the location along the shore of the locus of Columbia River contamination.

Future Research

The Building time-series of isotopic analyses from selected 300 Area and IFRC wells (packed off and shallow wells) during passive groundwater rise (spring 2010). This will allow further isotopic fingerprinting of "smear" zone sources, characterization of timescales for mobilization, and tracking of the resulting U through the well array.

+ Development of more detailed U isotopic stratigraphy for IFRC sediments across the array, particularly through the vadose "smear" zone.

Additional U (& Sr) isotopic analyses of serial (varying contact time and with increasing reagent aggressiveness) leaching experiments on IFRC sediment samples, size fractions and mineral separates.

+ U and Sr isotopic analysis of IFRC groundwater samples collected during/post injection of groundwater with similar 236U/238U but lower [U] (Desorption Injection Experiment) and higher [U] (Adsorption Injection).

The U and Sr isotopic analysis of IFRC groundwater samples collected during/post injection of groundwater with much higher 236U/238U but diluted to similar [U] (U exchange experiment).

See also posters by J. McKinley et al. (The deep vadoze zone as a source of uranium to the unconfined aquifer at the Hanford Site IFRC), J. Zachara et al. (Multi-Scale Mass Transfer Processes Controlling Natural Attenuation......)

and V.R. Vermeul et al. (River Induced Wellbore Flow Dynamics in Hanford IFRC Monitoring Wells: Evidence, Implications, and Mitigation)

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