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Letter Report: Stable Hydrogen and Oxygen Isotope Analysis of B- Complex Groundwater Samples

March 2018

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1.0 Executive Summary

Plutonium production operations at the U.S. Department of Energy Hanford Site has led to contamination of groundwater with high levels of contaminants, such as uranium, technetium-99, and nitrate. The B-Complex located in the 200 East Area of the Central Plateau represents a complex environmental problem due to contamination from waste released directly to cribs and trenches, as well as a waste storage tank overfill event. In addition, a perched water aquifer is present beneath this area and represents an ongoing concern for groundwater contamination. In an effort to understand possible sources of groundwater contamination, deuterium (^2H) and 18-oxygen (^{18}O) analysis of two groundwater samples from the B Complex area was performed. Isotopic data were collected to assess possible sources of groundwater contamination. Results from the analyses indicated that the groundwater has similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios to regional precipitation and Columbia River water. Groundwater samples are depleted (results are more negative) in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope ratios, when compared to perched water samples analyzed approximately one year earlier. The groundwater isotope ratios were also compared to sediment pore water samples from boreholes drilled at nearby liquid waste sites. Results from all three sample sets (i.e., groundwater, perched water, and pore water) will be used to update the conceptual site model for the B Complex area.

2.0 Background

Plutonium production operations that occurred at the U.S. Department of Energy Hanford Site produced waste streams containing contaminants such as nitrate, technetium-99 (Tc-99) and uranium (U) that were discharged to waste sites and B, BX, and BY tank farms in the B Complex area. As a result of the 241-BX-102 tank overfill event that released liquid waste to the subsurface and the waste site discharges to cribs, trenches and tile fields, the vadose zone and groundwater beneath the B-Complex have become contaminated. Fine-grained zones made up of Cold Creek Unit sediments have caused the formation of a perched water aquifer approximately 4.6 meters above the B-Complex water table. The perched-water, which is high in contaminants such as U, represents a future source of groundwater contamination.

The study described in this report analyzed $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in two groundwater samples. One groundwater sample was from monitoring well 299-E33-38, which is adjacent to the 216-B-47 Crib within the 216-BY Cribs, and one was from monitoring well 299-E33-345 which is near the 216-B-7A&B Cribs to the north of the 241-B Tank Farm.

3.0 Approach and Methods

Two B-Complex groundwater samples were taken in August 2017 from wells 299-E33-345 (B3BJW8) and 299-E33-38 (B3BJW7). Locations of the wells used for sampling are shown in Figure 1. Samples were received and stored at $-20\text{ }^\circ\text{C}$ until analyses were performed.

Measurement of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ content of water samples was performed using a Los Gatos Research water analyzer spectroscopy-based isotope measurement platform. Samples were filtered ($0.45\text{ }\mu\text{m}$

syringe filter) and dispensed into glass autosampler vials. Each sample was analyzed on two separate days. Triplicate analyses on multiple sample replicates were used for the samples which resulted in a

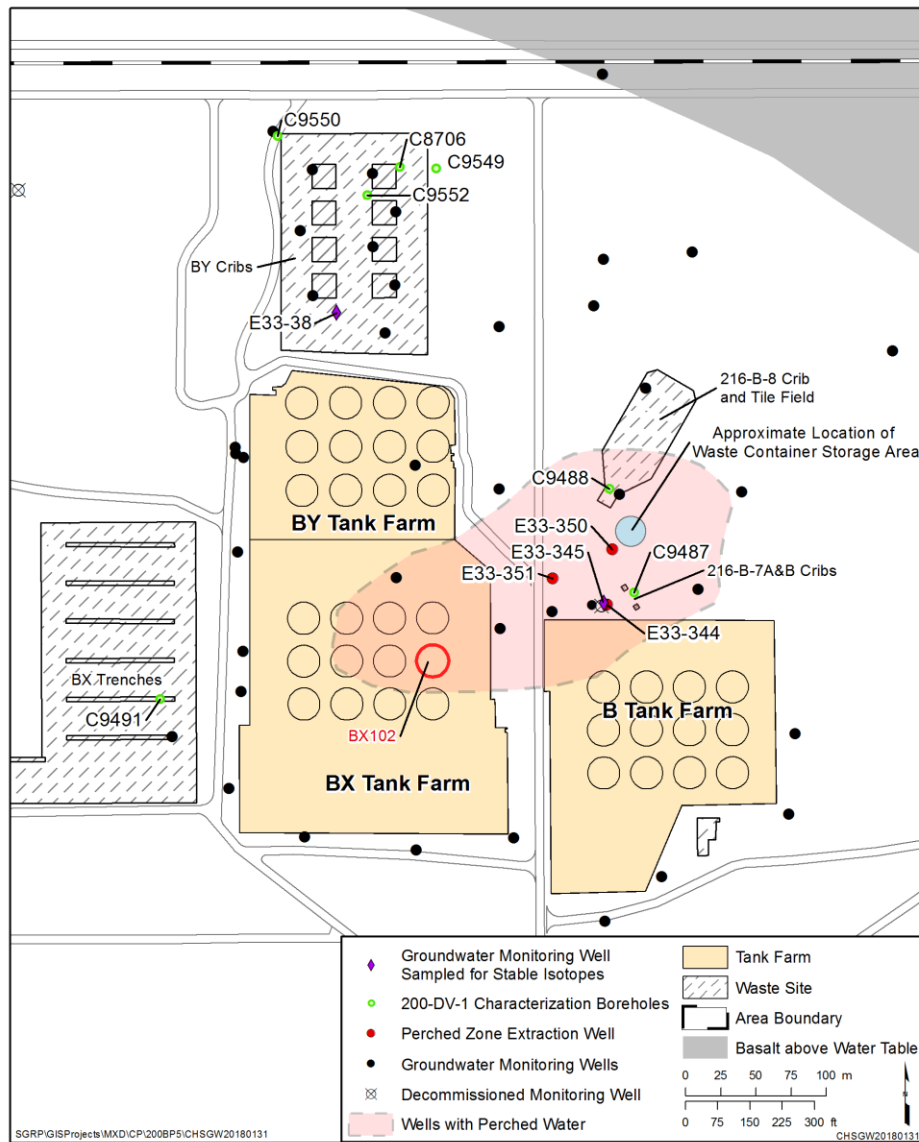


Figure 1. Schematic of B-BX-BY Tank Farms, showing well locations for groundwater sampling.

total of 18 replicates per sample. The instrument was calibrated using in-house standards, for which values were confirmed during this project using Vienna Standard Mean Ocean Water ($\delta^2\text{H} = 0\text{‰}$ and $\delta^{18}\text{O} = 0\text{‰}$) and Standard Light Antarctic Precipitation 2 ($\delta^2\text{H} = -427.5\text{‰}$ and $\delta^{18}\text{O} = -55.50\text{‰}$).

4.0 Results

Isotopic analysis for oxygen and hydrogen are developed and applied for multiple purposes (Prudic et al. 1997). For instance, the stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) can be used to assist with tracking of underground contaminant plumes or linking a source to a measured water sample. Isotopic data were collected to assess possible water sources for the groundwater. Isotopic ratios for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are reported in delta (δ) notation, defined as

$$\delta = \left(\frac{R_{sa}}{R_{std}} - 1 \right) \times 1000$$

where R is the ratio of the abundance of the heavy to light isotope (i.e., $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$), *sa* denotes the sample, and *std* indicates the standard (McKinney et al. 1950). Delta values are reported in per mil (‰), with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values relative to Vienna Standard Mean Ocean Water ($\delta^2\text{H} = 0\text{‰}$, $\delta^{18}\text{O} = 0\text{‰}$).

Isotopic analysis results for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the groundwater samples are shown in Table 2. Comparison of the groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results to the global meteoric water line (Craig 1961), and an assembled regional meteoric water line (Graham 1983) show fairly good agreement between the samples and the local meteoric water line (Figure 2). Groundwater samples were taken from two locations approximately 300 meters apart, one below the 216-BY Cribs (B3BJW7) and the other below the 216-B-7A&B Cribs (B3BJW8), which is also below the B-Complex perched water aquifer. Isotope results for groundwater samples also fall within the range of isotope data for Columbia River water samples (Figure 2). Groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results for the two samples are nearly identical. The low $\delta^{18}\text{O}$ values for the groundwater samples from the B-Complex also fall within ranges for other isotopically-depleted Columbia River Basalt Aquifer groundwaters (Brown et al. 2010).

Table 2. Groundwater samples analyzed for deuterium ($\delta^2\text{H}$) and 18-oxygen ($\delta^{18}\text{O}$) content.

| Sample ID | Well ID | $\delta^{18}\text{O}$ (‰) | | $\delta^2\text{H}$ (‰) | | N |
|-----------|-------------|---------------------------|----------------|------------------------|----------------|----|
| | | Ave. (‰) | Stan. Dev. (‰) | Ave. (‰) | Stan. Dev. (‰) | |
| B3BJW7 | 299-E33-38 | -17.03 | 0.25 | -132.8 | 1.4 | 18 |
| B3BJW8 | 299-E33-345 | -17.00 | 0.31 | -132.5 | 2.0 | 18 |

For comparison, isotope data for perched water samples and sediment pore water samples are also shown in Figure 2. The perched water samples were collected from wells 299-E33-344, 299-E33-350, and 299-E33-351 (Figure 1) (PNNL-26341). These data show that the groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios are depleted when compared to the perched water samples.

The sediment pore water samples were collected from 200-DV-1 Operable Unit (OU) borehole C9487 near the 216-B-7A&B Cribs, borehole C9552 at the 216-BY Cribs, and borehole C9488 at the 216-B-8 Crib and Tile Field (Figure 1). Isotope values for the groundwater sample taken near the 216-B-7A&B Cribs are in between isotope values for pore water from two of the sediment samples from borehole C9487 taken during the 200-DV-1 OU sampling effort (Szecsoy et al. 2017). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios for the C9487 sediment pore water samples are consistent with the local meteoric water line. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios

for pore water from the 227.2-227.7 ft. bgs sample interval was slightly enriched compared to the groundwater, while the pore water from the 232.0-233.0 ft. bgs sample interval was depleted relative to the isotope ratios for the groundwater. Likewise, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios for the C9488 sediment pore water sample, which was taken from the 216-B-8 Crib and Tile Field, were enriched compared to the groundwater, but depleted compared to perched water samples. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios for vadose zone sediment pore water samples from the C9552 borehole, which is the closest 200-DV-1 OU sample taken in the 216-BY Cribs, were shifted to the right of the local meteoric water line in the isotope plots, likely indicating more extensive evaporation history (Szecsody et al. 2017). As a result, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios for vadose zone sediment pore water samples from the C9552 borehole could not be correlated to the groundwater $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from well 299-E33-38. Borehole C9552 is approximately 100 meters northeast of well 299-E33-38. Proximity of 200-DV-1 OU borehole locations to the groundwater sampling wells are shown on Figure 1.

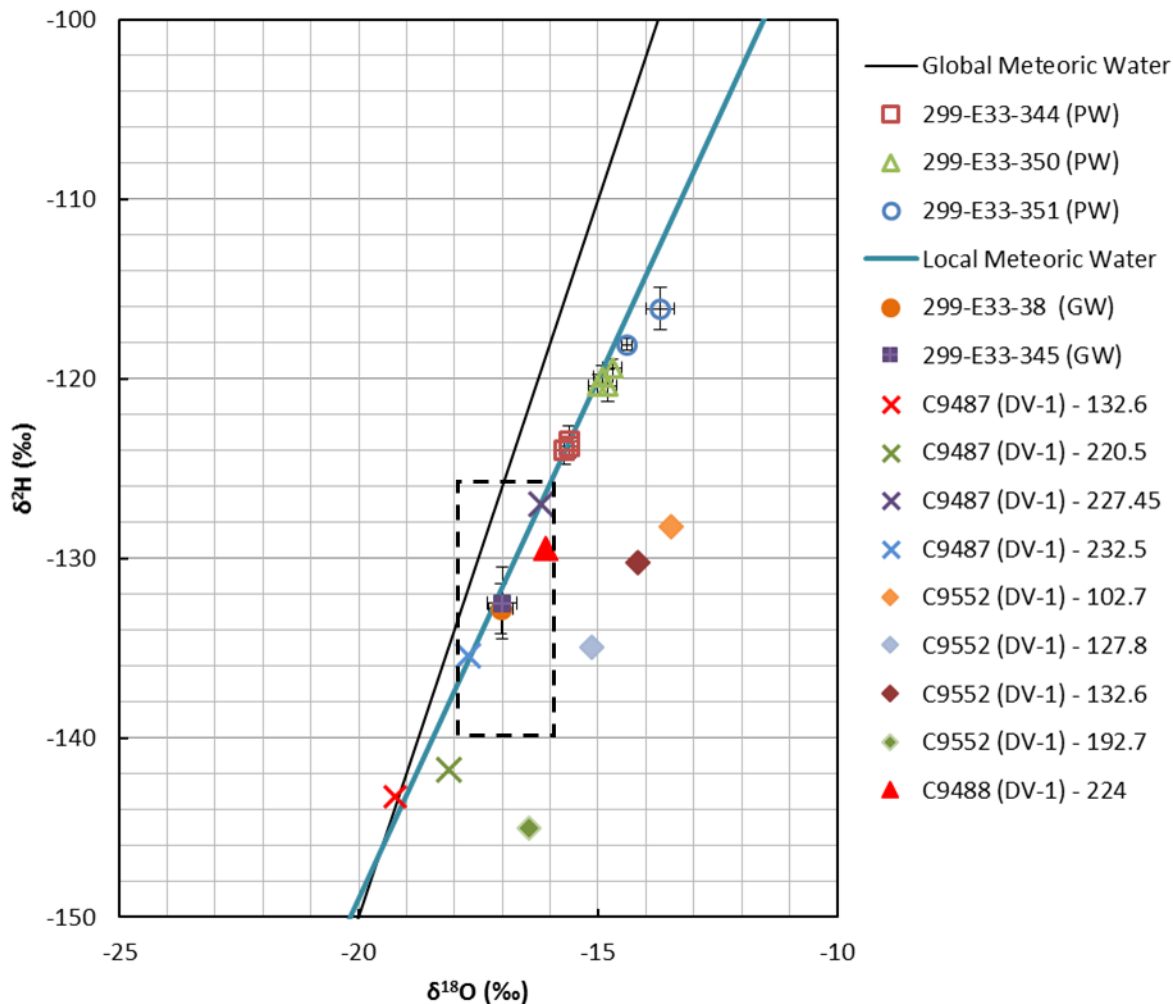


Figure 2. Isotope data for groundwater and perched water sample analyses. Trend lines for isotope values for global and local meteoric water are included for comparison. Error bars correlate to the standard deviation between replicate analyses. Dashed box shows area comprising measured values of isotopes ratios for Columbia River surface water at this location (Spane and Webber 1995).

5.0 Conclusions

Two groundwater samples from the B Complex area were analyzed to determine the stable $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope ratios in the samples. Isotopic data were collected to assess possible sources of groundwater contamination. Results from the analyses indicate that the groundwater has similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios to regional precipitation and Columbia River water. When compared to perched water samples analyzed approximately one year earlier, the groundwater samples are depleted (results are more negative) in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope ratios. The groundwater isotope ratios were also compared to sediment pore water samples from boreholes drilled at nearby liquid waste sites. The results from the groundwater samples, perched water samples, and pore water samples will be used to update the conceptual site model for the B Complex area.

6.0 References

- Brown, K. B., J. C. McIntosh, V. R. Baker and D. Gosch (2010). "Isotopically-depleted late Pleistocene groundwater in Columbia River Basalt aquifers: Evidence for recharge of glacial Lake Missoula floodwaters?" *Geophysical Research Letters* **37**(21).
- Craig, Harmon (1961) Isotopic variations in meteoric waters. *Science*, **133**, 1702-1703.
- DePaolo, D.J., M.E. Conrad, K. Maher, G.W. Gee (2004) Evaporation effects on oxygen and hydrogen isotopes in deep vadose zone pore fluids at Hanford, Washington. *Vadose Zone Journal*, **3**, 220-232.
- Graham, D.L. (1983) Stable isotopic composition of precipitation from the Rattlesnake Hills area of south-central Washington State. RHO-BW-ST-44 P. Rockwell Hanford Operations, Richland, WA.
- Lee et al. 2017 PNNL-26341
- McKinney, C.R., J.M. McCrea, S. Epstein, H.A. Allen, and H.C. Urey (1950) Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. *Reviews of Scientific Instruments*, **21**, 724-730.
- Prudic D, D Stonestrom, and R Streigl. 1997. Tritium, Deuterium, and Oxygen-18 in Water Collected from Unsaturated Sediments near a Low-Level Radioactive-Waste Burial Site South of Beatty, Nevada. Water Resources Investigations Report 97-4062, U.S. Geological Survey, Reston, Virginia.
- Szecsody et al. 2017 PNNL-26266
- Spane FA Jr. and WD Webber. 1995. Hydrochemistry and Hydrogeologic Conditions within the Hanford Site Upper Basalt Confined Aquifer System. PNL-10817, Pacific Northwest National Laboratory, Richland, Washington.



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