



## **Revised Predictions of Uranium Concentrations along Lang Draw Bear Creek Uranium, Converse County, Wyoming**

In October 2011, Tetra Tech GEO prepared a report which described the development of one-dimensional transport models to predict uranium concentrations along Lang Draw and along the Northern Pathway downgradient of the tailings impoundment at the former Bear Creek Uranium facility. These models were developed using PHREEQC (Parkhurst and Appelo, 1999), a geochemical modeling code which simulates chemical reactions and one-dimensional transport along a uniform flow field. The model for Lang Draw matched observations in monitoring wells close to the tailings impoundment, but the simulated concentrations at two downgradient wells (MW-108 and MW-109) were significantly higher than observed. This current report describes additional calibration efforts to better match observed concentrations in these two wells, and presents predictions using this revised model.

In the development of the October 2011 model, the distribution of ferrihydrite (amorphous  $\text{Fe}(\text{OH})_3$  and similar solids) was simplified so that its concentration was uniform throughout the model, and it was set to a low concentration of 0.0001 moles of ferrihydrite per liter of water, based on the calibration of the model to the observed breakthrough of chloride (a conservative species) and of uranium in the upgradient wells. With this concentration, sorption of uranium to the sediments was minimal. The calibration process indicated that the sorption of uranium near the tailings impoundment was minor, and this ferrihydrite concentration provided good results. As a result of the uniform-distribution simplification, very limited sorption of uranium was simulated in the downgradient part of the flow path (i.e., near MW-108 and MW-109).

In a series of publications using the Bear Creek Uranium site as an example, Zhu (2003) and Zhu and others (2001, 2002) used ferrihydrite concentrations of ranging from 0.05 moles per liter to .4 moles per liter, based on reported measurements of total iron present in the Wasatch Formation (0.4 weight %) and calculations of the amount of ferrihydrite needed to account for the observed acidity in solid samples collected at the site (4 weight %), assuming that the ferrihydrite was the only source of acidity. Zhu and others did not calibrate their various models, but these values likely provide an upper estimate of the concentration of ferrihydrite present in the natural environment.

In the present recalibration of the Lang Draw model, the concentration of ferrihydrite was assumed to vary along the flow path. The conceptual model used, with respect to the distribution of ferrihydrite, is that during the period of time when low-pH tailings fluids were entering the N sand and the groundwater pumpback system was not yet implemented, iron oxide minerals would be dissolved from the N sand, and the iron would be transported

downgradient and re-precipitate in downgradient areas. Thus, the concentrations of ferrihydrite would be low near the tailings impoundment, and be higher downgradient. Further downgradient (beyond the zone of re-precipitation), ferrihydrite (or probably crystalline iron oxides) concentrations would be at the ambient concentrations. During this process of iron dissolution, transport, and precipitation, uranium would be transported, and co-precipitated with the iron.

This conceptual model was used to assign initial ferrihydrite concentrations in different parts of the flow path, and UCODE\_2005 (Poeter and others, 2008) was used to calibrate the model, refining the estimates of ferrihydrite concentrations, as well as developing an estimate of the groundwater flow velocity and the concentration of uranium in the influent water. The model was calibrated to observations of concentrations of uranium, sulfate, chloride, and pH, as before. The changes in the set-up of the model were primarily in the use of five different parameters for the concentrations of ferrihydrite, and increasing the ferrihydrite concentrations in the downgradient part of the flow path so that the modeling results were sensitive to those concentrations.

Table 1 provides the values of the ferrihydrite concentrations for the 2011 version of the model, and the updated parameters. These values were determined by UCODE through the non-linear regression process. Ferrihydrite concentrations in the upgradient parts of the model are similar to those determined in the 2011 version, but the concentrations in the downgradient parts have increased significantly from the very low values used previously.

Table 1. Concentrations (moles per liter) of ferrihydrite in the 2011 model and revised model.

<b>Distance (m)</b>	<b>Ferrihydrite 2011 Model</b>	<b>Ferrihydrite Revised Model</b>
0 - 220	0.0001	0.004055
220 - 476	0.0001	0.002931
476 - 648	0.0001	0.03121
648 - 840	0.0001	0.88876
840 - 968	0.0001	0.11637

The calibrated groundwater velocity was 35.8 m/yr, which is assumed to be uniform throughout the model. The initial upstream concentration of uranium was 1,650 pCi/L.

Because chloride is unretarded, its breakthrough at different wells is the best indicator of the groundwater velocity. Figure 1 shows the match between simulated and observed chloride concentrations. As discussed in Tetra Tech (2011), MW-9 is completed in a deeper, less permeable, interval than the other monitoring wells, and the one-dimensional model was

unable to match observations from this well. The chloride concentrations for the other wells match the observations well, except at MW-109. The model simulates either faster breakthrough at MW-109 than observed, or the observed concentrations have been decreased by a mechanism such as dilution which is not incorporated into the model. Dilution could be caused by several different mechanisms, such as recharge of surface flow near the well and lateral and/or vertical convergence of groundwater flow toward Lang Draw. In spite of the apparent mismatch of the concentrations or the time of breakthrough in MW-109, the velocity simulated in the model (35.8 m/yr) is a good estimate of the groundwater flow velocity.

Figure 2 shows the simulated and observed values of pH. The model matches the average values of pH reasonably well, but the simulated values do not cover the entire range of the measurements. The pH is controlled by acidity of the incoming water, dissolution and precipitation of calcite, location of the pH front at the beginning of the simulation, dissolution and precipitation of ferrihydrite, degassing of CO<sub>2</sub>, and as well as other less important reactions. With all these variables that affect the pH, it was difficult to match the range or the rate of movement of the pH front. For MW-12 and MW-14, the model simulates a faster rate of movement of the pH front than was observed. However, for MW-108, the observed pH front moved faster than simulated. The general trends are simulated, but the timing of the passage of the pH front is either too short or too long by a few years, depending on location.

The sulfate results (Figure 3) indicate that the simulated sulfate concentrations tend to be higher than observed, with the passage of a sulfate peak down the flow path. The data do not show clearly discernible peaks at the monitoring wells. These results suggest that the sulfate concentration in the assumed input water source (MW-86) (9,040 mg/L) was too high. The average sulfate concentration near the tailings impoundment may have been lower than measured in MW-86.

The simulated and observed concentrations of uranium are shown in Figure 4. At MW-12, the simulated peak concentration is slightly less than observed, and the simulated peak is slightly later than observed. The simulated chloride peak was in approximately January 2001, and the simulated uranium peak was in approximately August 2004. This difference is the result of the simulated sorption of uranium on ferrihydrite. The simulated peak for MW-14 is also slightly later than observed, but the peak concentration matches well. At MW-108, the observed concentrations are slightly greater than simulated. Additionally, the observed values have been trending downward, while the simulated values are trending upward. In 2008, the simulated values begin to increase more rapidly than previously, but this change has not been observed in the measured values. MW-108 is in the middle of the model zone which had the highest concentrations of ferrihydrite, based on the calibration by UCODE. While the model predicts that uranium concentrations will increase with a reduction in pH, the observations indicate that

a decline in pH has already occurred, without an increase in uranium concentrations. A likely cause is that as ferrihydrite “ages” through time, it crystallizes to other minerals and becomes less soluble (more stable) (Das and others, 2011; Majzlan and others 2004; Zhu and others, 2012). Thus, when small decreases in pH occur, the transformed ferrihydrite does not dissolve and release sorbed uranium.

At MW-109, the model matches the observed concentrations remarkably well. Because of the downgradient location of this well, the data do not yet indicate an increase in concentrations resulting from movement from the impoundment area.

Figure 5 shows the predicted concentrations of uranium to 2084. MW-12 and MW-9 show a double peak, caused by dissolution of ferrihydrite and release of uranium as the pH front moves through these locations. The model predicts a peak in uranium concentration passing through MW-108 in approximately 2015. This is caused by a decrease in pH upgradient of MW-108, releasing uranium sorbed to ferrihydrite. This part of the model has the highest ferrihydrite concentration, and thus is a reservoir for sorbed uranium. As noted above, the model shows increasing dissolved uranium concentrations while the observations show decreases over the same period. The simulated release of uranium upgradient of MW-108 causes uranium concentrations to increase in MW-108 and MW-109. The modeled transport of the peak through MW-109 is delayed because of the high concentration of ferrihydrite in the model. The difference in the trends of uranium concentrations in the observations and simulations suggest that the simulations may be conservative (predict higher concentrations than will occur).

The revised model matches uranium concentrations in MW-108 and MW-109 better than the 2011 model, but does not appear to fully incorporate the geochemical behavior of the system. Being a one-dimensional model, it does not incorporate the effects of transverse dispersion or the effects of converging flow indicated by the water-level data. Further, it does not include the effects of aging of ferrihydrite. Monitoring data from MW-108 indicate that a decrease in pH has already occurred without causing an increase in uranium concentrations. Thus, the model is likely predicting higher future concentrations in MW-109 than will occur.

### References

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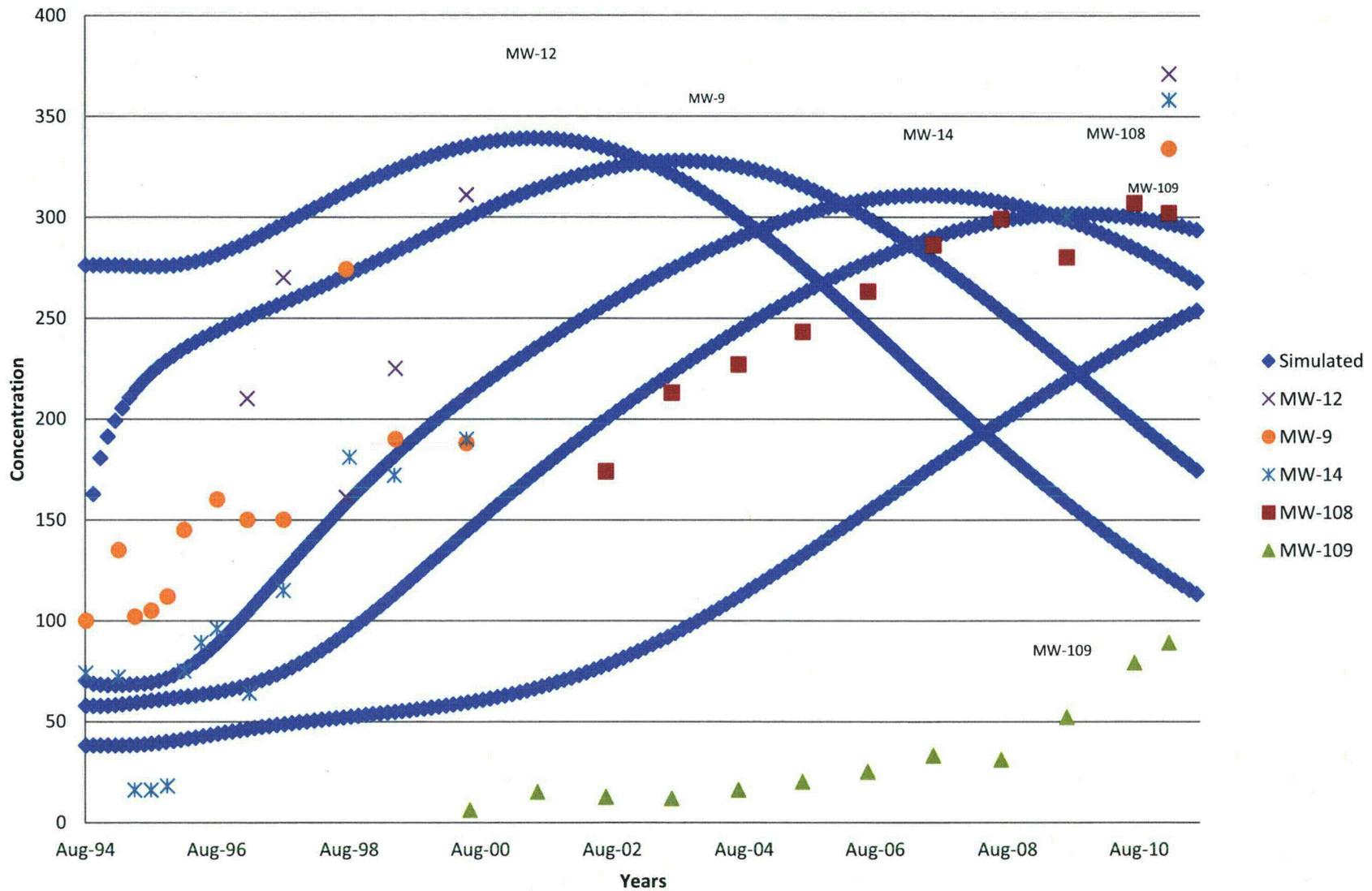
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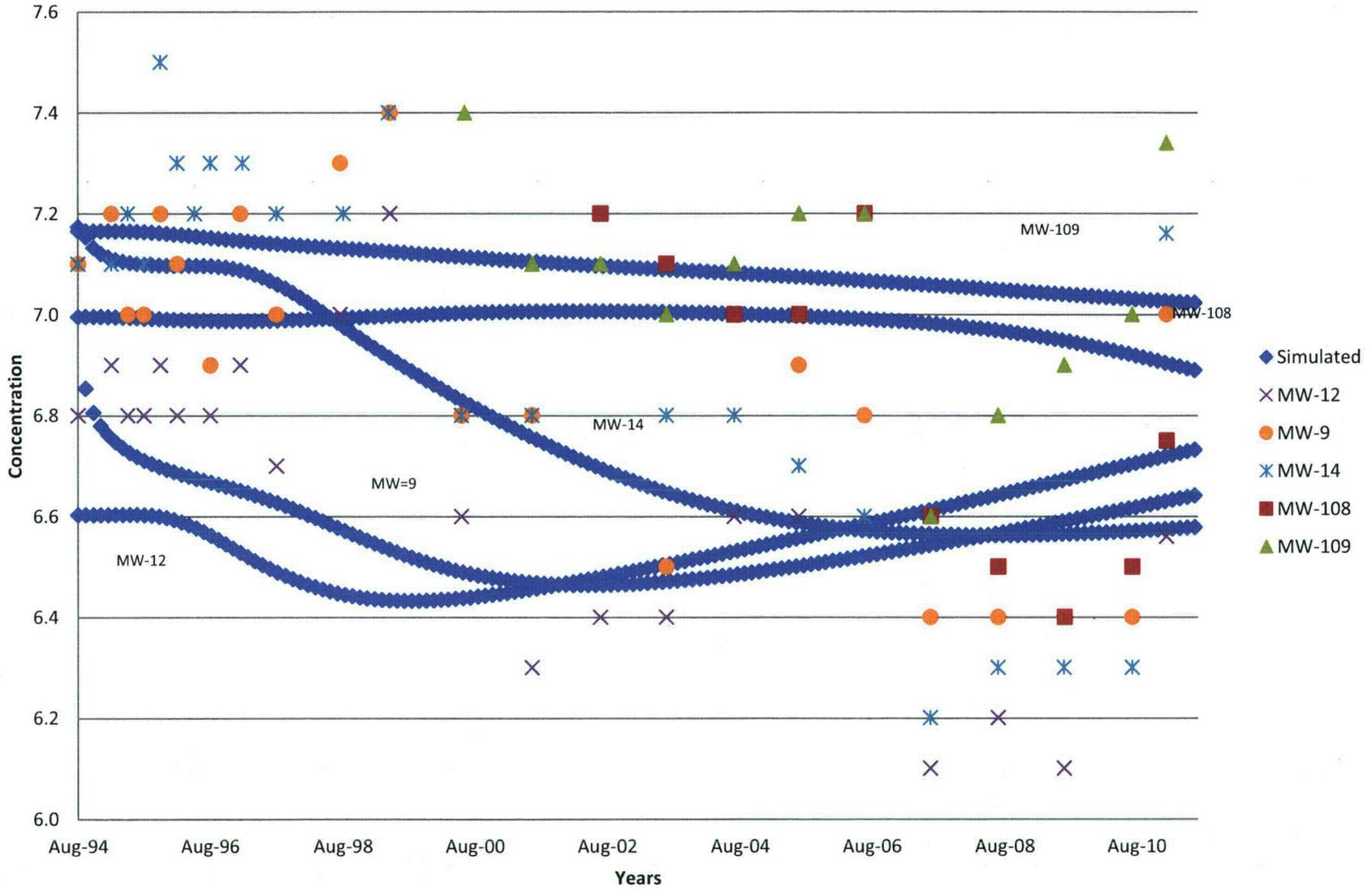
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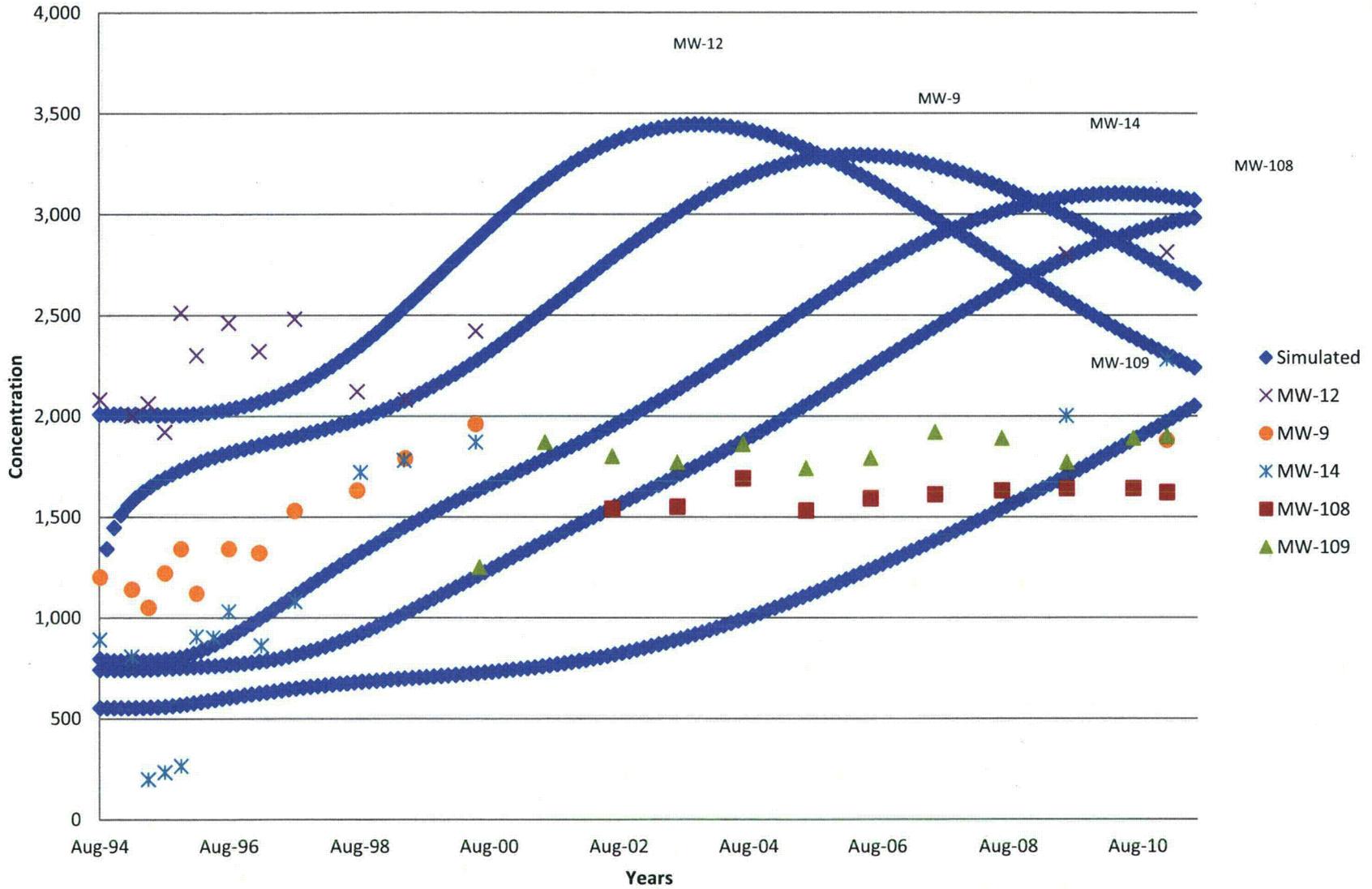
**Figure 1. Comparison of observed and simulated concentrations of chloride (mg/L) along Lang Draw**



**Figure 2. Comparison of observed and simulated concentrations of pH along Lang Draw**



**Figure 3. Comparison of observed and simulated concentrations of sulfate (mg/L) along Lang Draw**



**Figure 4. Comparison of observed and simulated concentrations of Uranium (pCi/L) along Lang Draw**

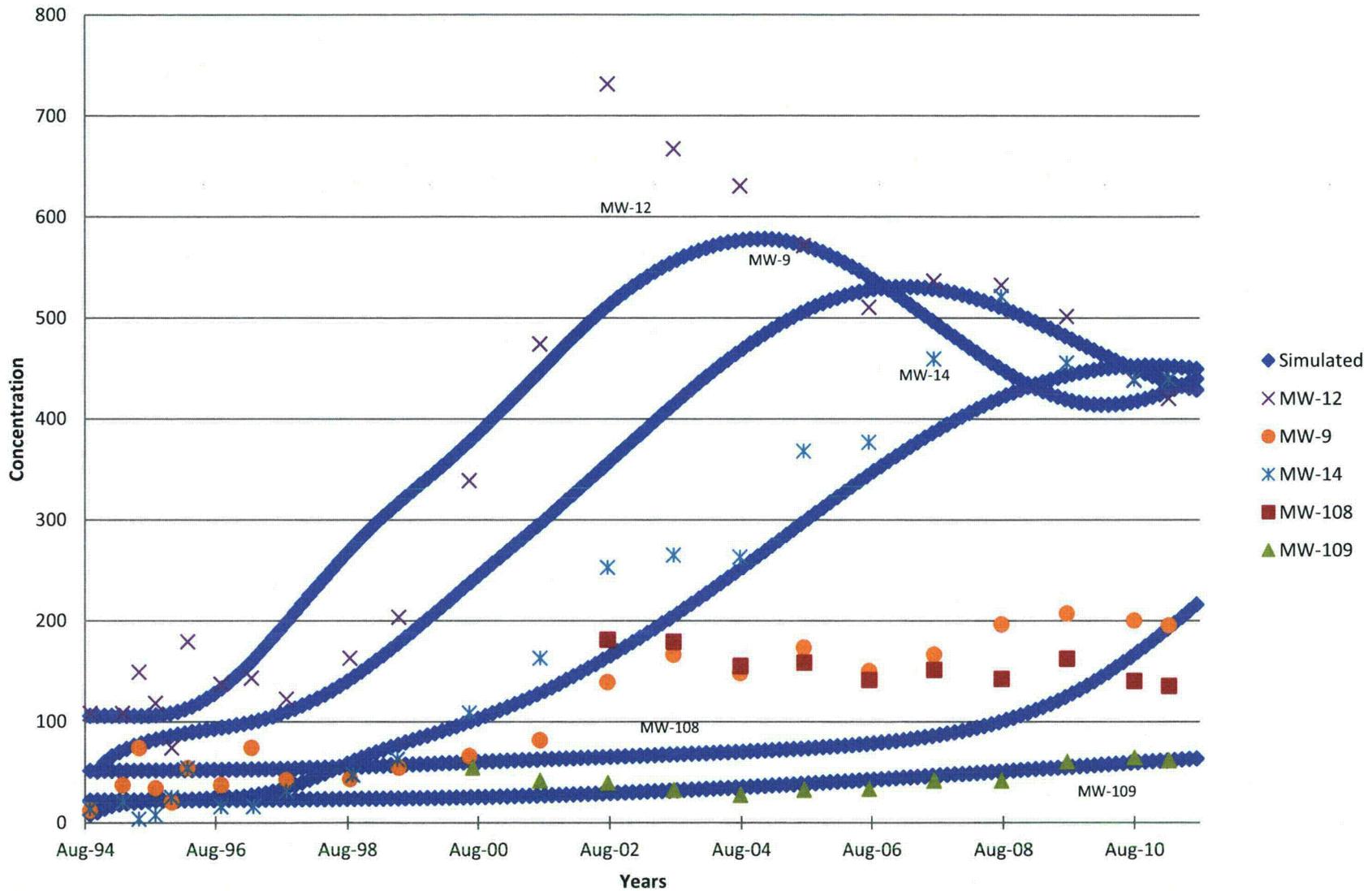


Figure 5. Predicted concentrations of Uranium (pCi/L) along Lang Draw

