

## NUMERICAL MODELING OF STABLE ISOTOPE FRACTIONATION AND MULTIPHASE REACTIVE TRANSPORT OF WATER AND WATER VAPOR USING TOUGHREACT

M. Singleton, E. Sonnenthal, M. Conrad and D. DePaolo

Earth Sciences Division, Lawrence Berkeley National Laboratory  
University of California  
Berkeley, CA 94720, USA  
e-mail: [mjsingleton@lbl.gov](mailto:mjsingleton@lbl.gov)

### **ABSTRACT**

Variations in the ratios of stable isotopes (i.e.,  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/\text{H}$ ) in water and water vapor can yield important constraints on vadose zone hydrological processes such as infiltration, evapotranspiration, mixing and recharge. In order to quantitatively model the behavior of stable isotopes in simulations of unsaturated flow, we implemented the temperature-dependent equilibration of stable isotopic species between water and water vapor, and their differing diffusive transport properties into the thermodynamic database of the reactive transport code TOUGHREACT (Xu and Pruess, 2001). This allows for the development of physical models, which describe stable isotope fractionation in tandem with multiphase flow, heat transport, mineral-water-gas reactions, and the transport of any number of gaseous and aqueous species.

### **INTRODUCTION**

The transport of stable O and H isotopes in water within drying soil columns has been studied extensively (e.g. Barnes and Allison, 1983, 1984; Allison et al., 1994; Shurbaji et al., 1995; Mathieu and Bariac, 1996b, Melayah et al., 1996). However these models do not account for the effects of recharge during the wet seasons typical in semi-arid climates. Previous approaches to the problem of infiltration water include: a semi-empirical model (Barnes and Allison, 1988), a mixing scheme (Mathieu and Bariac, 1996a), and an analytical model to predict overall average pore water isotope compositions (DePaolo et al., *in review*).

In order to develop a general transport model for stable isotopes that considers drying and recharge in vadose zone soils, we make use of the thermodynamic framework of the TOUGHREACT transport code. These reactive transport models provide a quantitative method to link the observed isotopic profiles to soil properties, climate conditions,

and infiltration through the vadose zone at the Hanford Site, WA, USA.

### **Background: Stable isotope measurements**

As is traditional in stable isotope studies, the isotope compositions discussed here are measured relative to a well-defined standard material (Standard Mean Ocean Water, or SMOW, for water and vapor samples). Stable isotope compositions are defined in ‰ units, calculated as delta values from the isotopic ratio ( $R$ ), where:

$$\delta = \left[ \frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1 \right] \times 1000 \quad (1)$$

Based on this system, typical ocean waters have  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of 0. Meteoric precipitation over land varies as a function of temperature, latitude, and altitude, but generally has  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values that are less than zero due to the fractionation of lighter isotopes during the phase change from liquid to vapor. In his classic paper, Craig (1961) documented a linear relationship, known as the Global Meteoric Water Line, between the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of meteoric waters collected all over the world. However, in arid and semi-arid climates the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of shallow lakes and near-surface soil waters are often shifted off of the Meteoric Water Line. This observation can be explained by the strong mass dependence of diffusion processes, which fractionate stable isotopes during evaporation. These processes will be discussed in the following section that describes the TOUGHREACT stable isotope model.

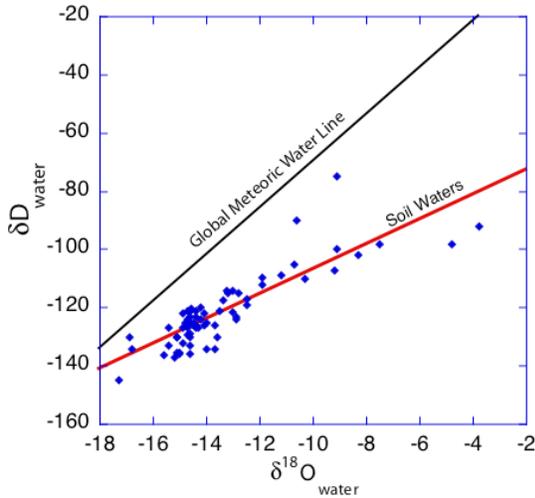


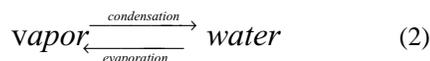
Figure 1. Hydrogen and oxygen isotope compositions of soil waters collected from the Hanford vadose zone.

## RESULTS AND DISCUSSION

### Stable isotopes in TOUGHREACT

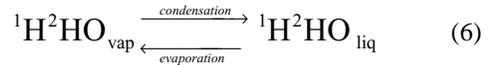
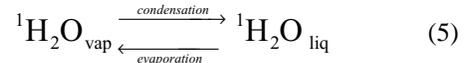
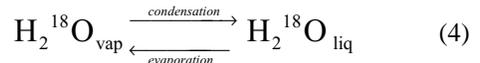
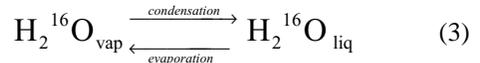
Any approach to predicting stable isotope profiles in drying soils must consider the complex interaction of multiple processes (drainage, temperature effects on flow and isotope fractionation, diffusive transport, etc.). Developing tractable mathematical equations for these processes requires simplification, which leads to analytical methods that are not easily adapted to field conditions. Likewise, previous numerical models have relied on simplifications such as neglecting the temperature dependence of isotope fractionation or using non-dimensional parameters to define flow regimes (vapor-dominated vs. liquid-dominated). Furthermore, the existing models are not readily applicable to developed transport model meshes and hydraulic parameters, making it difficult to link observed isotope compositions with hydrological processes.

The approach described here differs markedly from previous methods to simulate isotope transport. Rather than accounting for isotopes as non-reactive tracers, TOUGHREACT isotope models treat the water isotope species as reactive constituents within the transport model. TOUGHREACT couples the hydraulic transport capabilities of TOUGH2 (Pruess, 1991) with reactive transport based on thermodynamic principles of chemical equilibrium and kinetics (Xu and Pruess, 2001). The general equilibrium reaction considered here is:



The temperature-dependent equilibrium constant for this reaction is calculated based on the well-known steam table equations (International Formulation Committee, 1967).

Similarly, isotope exchange reactions can be described by equilibrium constants, defined in the standard thermodynamic form as the quotient of the activities of the products and reactants (Criss, 1999). The isotope exchange reactions relevant to liquid-vapor fractionation are:



The temperature-dependent equilibrium constants for hydrogen and oxygen isotopes of water during liquid-vapor exchange are calculated based on the experimentally determined fractionation factors of Horita and Wesolowski (1994), which are valid from the freezing point to the critical temperature of water.

In addition to phase changes, the presence of a strong isotopic and concentration gradient (i.e. low humidity in the atmospheric boundary layer), fractionates water isotopes by diffusion as a result of their differing molecular masses and molecular diameters. Temperature gradients have a complex effect on the diffusion and isotopic exchange of stable isotopes, but to simplify the interpretation of model results, these effects will be addressed in a future study. We follow the common assumption that all isotopomers of water have the same molecular diameter. Therefore, the fractionation of stable isotopes by diffusion is a function of their respective masses ( $\text{H}_2^{18}\text{O} > \text{HDO} > \text{H}_2\text{O}$ )

By implementing the differing diffusive transport properties and isotope equilibration of water isotopomers into the thermodynamic database of TOUGHREACT, it is possible to consider stable isotope transport in any geologic context that can be described by a TOUGH2-based hydraulic model. The only requirement is that the stable isotope compositions relevant to the system have been established by sample measurements.

### Model applications

TOUGHREACT isotope transport models are used to explain the stable isotope compositions of vadose zone pore water samples from the Hanford Site in

south-central Washington state, USA. During the Cold War, plutonium for nuclear weapons was produced and separated from other reactor products at the Hanford Site, which led to the contamination of the vadose zone and local groundwater from spills and leaks of radioactive materials. Long-term remediation efforts will require a detailed understanding of fluid flux through the vadose zone under various climatic conditions to predict how contamination will impact the Columbia River and other regional water resources.

### ***Hanford climate***

Like many semi-arid localities, local precipitation at Hanford exhibits strong seasonal fluctuations from averages around 2.6 cm/month during the winter months to 0.7 cm/month during the dryer summer months (Gee et al., 1992; Hoitink et al., 2002). The precipitation variations are accompanied by similar shifts in average temperature and humidity, from approximately 70% at 1 C in the winter to 40% at 22 C in the summer (Hoitink et al., 2002).

Samples of near-surface atmospheric vapor collected in August 2002, at the Hanford VZ300N site have an average  $\delta^{18}\text{O}$  value of  $-21\text{‰}$  and an average  $\delta\text{D}$  of  $-146\text{‰}$ . Although the isotope composition of atmospheric humidity may change in response to regional weather patterns, the August samples represent likely values for the summer months, when evaporation is most effective.

### ***Hanford vadose zone samples***

An ongoing collaborative effort between LBNL's Center for Isotope Geochemistry and researchers at Pacific Northwest National Lab, has resulted in more than 100 stable isotopic measurements of pore waters from sediment core samples collected at Hanford. The locations of these cores include both homogenous sediments and layered sedimentary sequences from vegetated and non-vegetated sites. Evaporation and isotopic equilibration with atmospheric water vapor has shifted unsaturated zone pore waters at Hanford off of the local meteoric water line (Figure 1). Pore waters in the upper 2m are most strongly affected (Figure 2), and have  $\delta^{18}\text{O}$  values up to  $-3.8\text{‰}$  and  $\delta\text{D}$  values up to  $-75\text{‰}$ . The isotopic compositions of deeper pore waters vary with grain size and moisture content, but generally have average  $\delta^{18}\text{O}$  values around  $-14.5\text{‰}$ , which represents a shift of about  $+2.5\text{‰}$  from precipitation and local groundwater (DePaolo et al., *in review*).

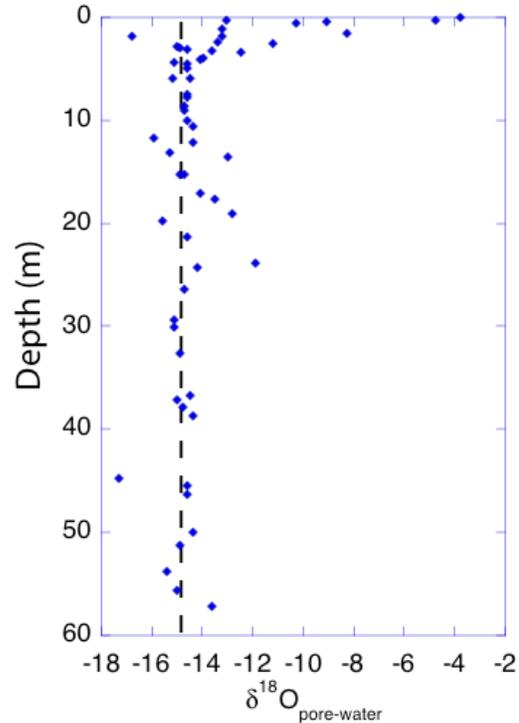


Figure 2. Soil water  $\delta^{18}\text{O}$  values with depth in the Hanford vadose zone. Below the evaporation zone, soil waters  $\delta^{18}\text{O}$  values are shifted 2.5 ‰ (dashed line) higher than local precipitation ( $-16.5\text{‰}$ )

### **TOUGHREACT model results:**

#### ***Drying soil***

To facilitate qualitative comparisons with data and model results from previous studies of drying soil columns, TOUGHREACT simulations of stable isotope transport were carried out using three hypothetical soil types with no input from infiltration (Figure 3). The general features shown in Figure 3 are consistent with data from soil waters collected throughout the world, and described using analytical models (Barnes and Allison, 1983, 1984; Allison et al., 1994) and numerical methods (Shurbaji et al., 1995; Mathieu and Bariac, 1996a, Melayah et al., 1996). Namely, a vapor-dominated zone at the top reaches a peak ( $\delta^{18}\text{O}_{\text{MAX}}$ ), followed by decreasing  $\delta^{18}\text{O}$  with depth.

As demonstrated in Figure 3, the value for  $\delta^{18}\text{O}_{\text{MAX}}$  in the soil column is controlled by the concentration (i.e. humidity) and isotopic composition of atmospheric vapor ( $h=40\%$  and  $\delta^{18}\text{O}=-21\text{‰}$  for all three soils). However the variation in  $\delta^{18}\text{O}$  with depth is related to soil properties, which determine the transport and distribution of water and water vapor in the column.

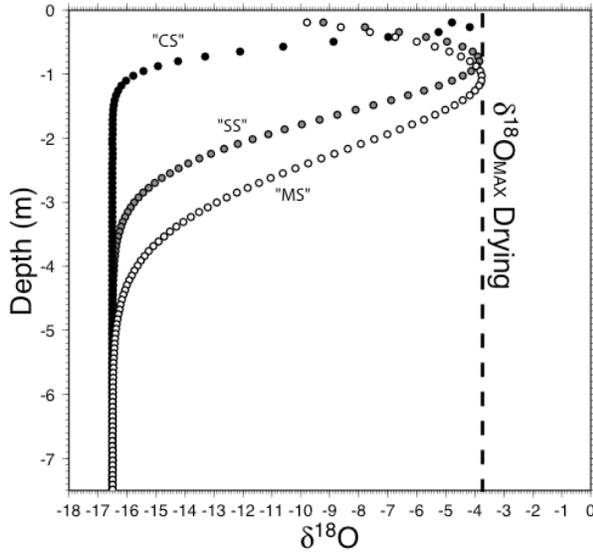


Figure 3. TOUGHREACT stable isotope model results for three hypothetical soil types: clayey-sand (“CS”), silty-sand (“SS”), and medium sand (“MS”). Starting from an initial pore water  $\delta^{18}\text{O}$  value similar to precipitation at Hanford ( $-16.5\text{‰}$ ), the model soils were subjected to 20 years of drying in an atmosphere with  $h=40\%$  and  $\delta^{18}\text{O}_{\text{vap}}=-21\text{‰}$ .

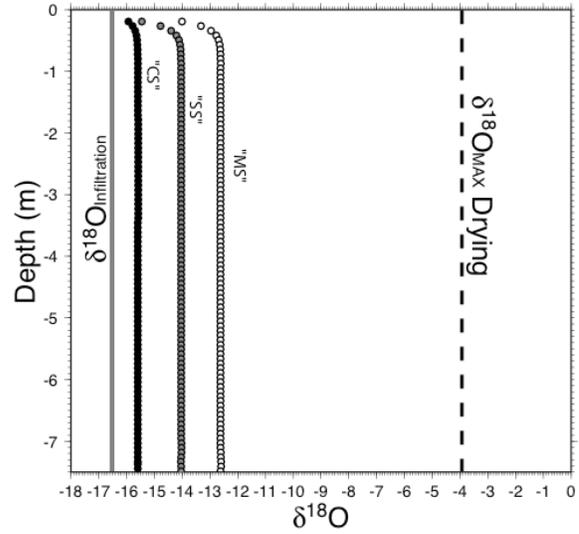


Figure 4. Model steady-state  $\delta^{18}\text{O}$  values calculated for the atmosphere and soils discussed in Figure 3, but with a constant infiltration of 5 cm/yr of water with a  $\delta^{18}\text{O}$  value of  $-16.5\text{‰}$ .

### Infiltration

The examples of drying soil columns discussed in the previous section are useful for understanding the effects of evaporation that predominate during dry months. However, infiltration ranges from 0.1 to 200 mm at the Hanford site (Gee et al, 1992), and has a significant effect on stable isotope profiles in the Hanford vadose zone.

### Constant infiltration

In simple terms, infiltration can be considered as a constant flux of water at the surface, equal to the average annual infiltration rate. This constant flux model (Figure 4) should predict the average isotopic shift in vadose zone pore waters due to evaporation at the surface. An infiltration rate of 5 cm/yr results in average pore water  $\delta^{18}\text{O}$  values that are higher than the precipitation waters ( $\delta^{18}\text{O} = -16.5\text{‰}$ ), and depends on soil properties as predicted by the analytical model of DePaolo et al. (*in review*).

### Periodic infiltration

Under a constant infiltration flux, the lack of dry periods prevents the formation of high  $\delta^{18}\text{O}$  and  $\delta\text{D}$  “bulges” commonly observed in arid and semi-arid soil cores. As a more realistic alternative, pulses of infiltration are used to approximate the wet and dry seasons at Hanford so that all of the recharge (5 cm/yr) comes during 0.3 yr wet periods that are followed 0.7 year dry periods. For a “silty sand” similar to the Hanford Formation sands, these alternating wet and dry seasons result in an undulating pattern of pore water  $\delta^{18}\text{O}$  values in the top 2m, and provide a possible explanation for the patterns of  $\delta^{18}\text{O}$  values observed at the from samples collected in the Hanford vadose zone (Figure 5).

With pulsed infiltration, there is a zone of evaporation at the top during the dry season, but below that the  $\delta^{18}\text{O}$  and values decrease toward the precipitation value where water from the previous rain event infiltrated deeper than the evaporation front. Model results predict that a second set of these evaporation and preserved rain compositions may be present from 1-2 m depth. Below about 2.5 m depth the  $\delta^{18}\text{O}$  values reach a steady-state value similar to constant infiltration conditions.

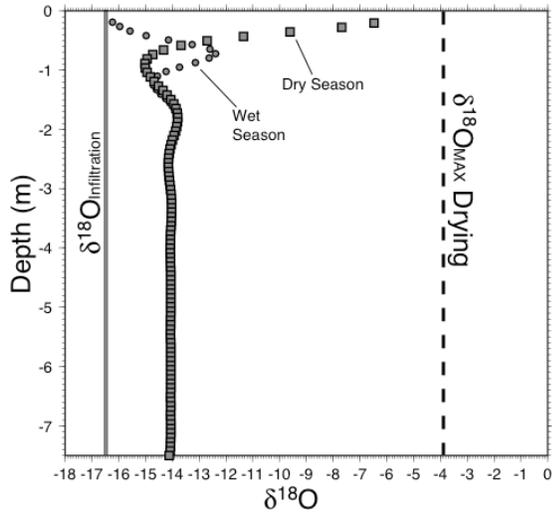


Figure 5. Model results for pulses of infiltration, used to simulate the effects of wet (dots) and dry (boxes) seasons on the  $\delta^{18}\text{O}$  profile of a hypothetical silty-sand soil.

## CONCLUSIONS

The reactive transport capabilities of TOUGHREACT are applied to a new model of stable isotope transport in unsaturated soils. One-dimensional model results of pore water  $\delta^{18}\text{O}$  values compare well with depth profiles observed at Hanford and with published data from arid localities. These models provide a method to quantitatively link the observed isotopic profiles to soil properties, climate conditions, and infiltration through the vadose zone.

Work is in progress to use TOUGHREACT stable isotope models to: (1) consider the effects of recharge in conjunction with temperature gradients have on stable isotope transport in unsaturated soil columns, (2) make use of stable isotope measurements from the Drift Scale Heater Test at Yucca Mountain to provide constraints on vapor diffusion through the matrix and fractures in a boiling, fractured-rock system (3) predict soil gas isotope compositions for use in detection of buried radioactive and mixed waste.

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