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Multiphase reactive transport modeling of stable isotope fractionation of infiltrating unsaturated zone pore water and vapor using TOUGHREACT.

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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. These models are used to illustrate the evolution of stable isotope profiles in semi-arid regions where recharge during wet seasons disturbs the drying profile traditionally associated with vadose zone pore waters. During drainage from the surface, evaporation causes a shift to higher $\delta^{18}\text{O}$ and δD values, which is preserved in the deeper pore waters. For an equivalent net infiltration rate, this shift from the input water isotopic composition increases with increasing grain size. The shift toward isotopically heavier waters also increases for lower net infiltration rates.

INTRODUCTION

The fraction of rainfall that percolates deep into the vadose zone in arid regions is difficult to predict, but important for understanding groundwater recharge and contaminant transport. For example, at the Hanford Site in south-central Washington State, USA, where a large amount of radionuclide contamination is present in the vadose zone above the water table, it is critical to know the net water infiltration flux, as this determines how rapidly radionuclides or other contaminants will reach groundwater. The vadose zone hydrological processes that control net infiltration (or percolation) rate also generate variations in the ratios of stable isotopes (i.e., $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) in water and water vapor.

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, 1996a, Melayah et al., 1996). However these models do not account for disturbances due to recharge during the wet seasons typical in semi-arid climates. Previous approaches to the problem of recharge water include: a semi-empirical model (Barnes and Allison, 1988), a mixing scheme (Mathieu and Bariac, 1996b), and an analytical model to predict overall average pore water isotope compositions (DePaolo et al., *in review*).

We use the thermodynamic framework of the TOUGHREACT transport code to develop a general transport model for stable isotopes that considers drying and recharge in vadose zone soils, and compare these model profiles to measurements from the Hanford Site, WA, USA. Reactive transport models of stable isotope transport provide a quantitative method to link the observed isotopic profiles to soil properties, climate conditions, and percolation through the vadose zone.

Background: Stable isotope measurements

As is traditional in stable isotope studies, the isotopic compositions discussed here are measured relative to a well-defined standard material (Standard Mean Ocean Water, or SMOW). 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 δD and $\delta^{18}\text{O}$ values near 0 ‰. Meteoric precipitation over land varies as a function of temperature, latitude, and altitude, but generally has δD and $\delta^{18}\text{O}$ values that are shifted to values less than zero due to the fractionation of lighter isotopes into the vapor phase during the change from liquid to vapor. Craig (1961) documented a linear relationship, known as the Global Meteoric Water Line (GMWL), between the δD and $\delta^{18}\text{O}$ values of meteoric waters collected all over the world. However, in arid and semi-arid climates the δD and $\delta^{18}\text{O}$ values of shallow lakes and near-surface soil waters are often shifted off of the GMWL (Figure 1). This observation can be explained by the strong mass dependence of diffusion processes, which fractionate stable isotopes during evaporation. These processes will be discussed the section below that describes the TOUGHREACT stable isotope model.

The Hanford Site

TOUGHREACT isotope transport models are used to interpret the stable isotope compositions of vadose zone pore water samples from the Hanford Site. 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 seasonal shifts in average temperature and humidity, from approximately 70% at 1 °C in the winter to 40% at 23 °C in the summer (Hoitink et al., 2002).

Winter rain and snow generally accounts for more than two-thirds of the annual precipitation at Hanford, and has $\delta^{18}\text{O}$ values that range from -19 to -16 ‰ and δD values that range from -142 to -120 ‰ (Graham, 1983; and data in report BWI-DP-061). The $\delta^{18}\text{O}$ and δD values of summer precipitation are typically higher, and plot to the right of the GMWL. It is these summer precipitation samples that impart a lower slope (~ 5.8) to the Local Meteoric Water Line (LMWL; Figure 1). It is not clear whether the lower slope of the LMWL reflects evaporation that occurred during precipitation events, or indicates that evaporation took place in the open-top collection devices described in Graham (1983) prior to sample collection.

Two 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 ‰ and an average δD of -146 ‰. Although the isotope composition of atmospheric humidity may change in response to regional weather patterns, the August samples represent reasonable values for the summer months, when evaporation is most effective.

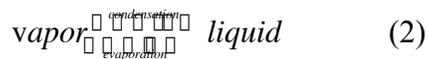
Hanford vadose zone samples

An ongoing collaborative effort between LBNL's Center for Isotope Geochemistry and researchers at Pacific Northwest National Laboratory (PNNL) has resulted in more than 100 stable isotope 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 LMWL (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‰ and δD values up to -75‰ . 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‰ , representing a shift of about $+2.5\text{‰}$ from precipitation and local groundwater (DePaolo et al., *in review*).

RESULTS AND DISCUSSION**Stable isotopes in TOUGHREACT**

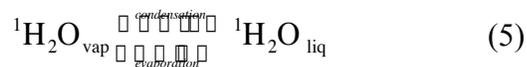
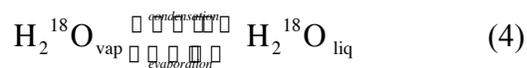
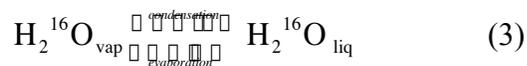
Any approach to predicting stable isotope profiles in drying soils must consider the complex interaction of multiple processes (drainage, temperature effects on flow and isotope fractionation, diffusive transport, etc.). Developing tractable analytical equations for these processes requires simplification, which leads to analytical methods that are not easily adapted to field conditions. 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). For these reasons, 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 of simulating stable isotope transport. Rather than accounting for isotopes as non-reactive tracers, TOUGHREACT isotope models treat the water isotope species as reactive constituents within a multiphase transport model. TOUGHREACT couples the hydraulic transport capabilities of TOUGH2 (Pruess, 1991; Pruess et al., 1999) with reactive transport based on thermodynamic principles of chemical equilibrium and kinetics (Xu and Pruess, 2001). The general equilibrium reaction considered here is the phase change of water:



The temperature-dependent equilibrium constant for this reaction is calculated based on the International Formulation Committee steam table equations (Pruess et al., 1999).

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:



Both the steam table based vapor-liquid equilibrium and isotopic equilibrium are maintained by using the following temperature-dependent equilibrium values in the TOUGHREACT thermodynamic database:

$$\log K' = \log \frac{[liquid]}{[vapor]} \quad (7)$$

$$\log K^* = \log \left[\frac{[liquid]}{[vapor]} \right]_{eq} \quad (8)$$

Where K' is the equilibrium dissociation constant for the more abundant, lighter isotopomer of water ($^1\text{H}_2\text{ }^{16}\text{O}$), as defined by the steam table vapor pressure. The equilibrium constant for the much less abundant, heavier isotopic species (K^*) are then determined using the appropriate isotopic fractionation factor (α_{eq}). The temperature-dependent equilibrium fractionation factor (α_{eq}) for hydrogen and oxygen isotopes of water during liquid-vapor exchange are calculated based on the experimentally determined values 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. We follow the assumption that all isotopomers of water have the same molecular diameter, and thus the fractionation of stable isotopes by diffusion is a function of their respective masses ($\text{H}_2\text{ }^{18}\text{O} > \text{HDO} > \text{H}_2\text{O}$).

Using TOUGHREACT, the diffusion coefficients for gas species are calculated assuming ideal gas behavior as a function of temperature, pressure, molecular weight, and molecular diameter, according to Lasaga (1998), as follows:

$$D = \frac{RT}{3\sqrt{2}PN_A d_m^2} \sqrt{\frac{8RT}{M}} \quad (9)$$

where D is the diffusion coefficient (m^2/s), R is the gas constant ($8.31451 \text{ m}^2 \text{ kg s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$), T is temperature in Kelvin units, P is the gas pressure ($\text{kg m}^{-1} \text{ s}^{-2}$), N_A is Avogadro's number ($6.0221367 \times 10^{23} \text{ mol}^{-1}$), d_m is the molecular diameter (m), and M is the molecular weight (kg/mol).

Gas transport takes place through advection and diffusion, with the diffusive fluxes for gases following Fick's Law. The diffusive flux (F_D) is therefore expressed as follows:

$$F_D = D \nabla S_g \tau (\nabla S_g C) \quad (10)$$

where τ is the porosity, S_g is the gas saturation, τ is the tortuosity, and C is the gas species concentration. To account for heterogeneity in porosity and gas saturation, the product τS_g outside of the gradient operator (∇) is calculated at grid block interfaces using harmonic weighting.

Temperature gradients have a complex effect on the diffusion and isotopic exchange of stable isotopes, since both the isotopic fractionation factors and transport are temperature dependent. TOUGHREACT is capable of simulating the effects of temperature gradients on heat and fluid transport, while maintaining temperature dependent changes in chemical and isotopic equilibrium. However, to focus on the effects of recharge in semi-arid climates, and simplify the interpretation of these results, the effects of temperature gradients and transient temperature profiles will be addressed in a future study. The use of isothermal models presented here will provide a reasonable approximation to field conditions at Hanford in the wet winter months, when measurements of soil temperature (Hoitink et al., 2002) show the least variation with depth.

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 in 1, 2, or 3 dimensions. The only requirement is that the stable isotope compositions relevant to the system have been established by sample measurements.

We consider models of stable isotope transport in a range of sediment types, increasing in grain size from clayey silt, to silty sand, to medium sand. The dependence of capillary pressure and effective conductivity on moisture content for these unsaturated sediments is based on the equations of van Genuchten (1980). Parameters for these sediments (Table 1) are based on the range of values reported for sediments at the Hanford Site (Kincaid et al., 1998; Zhang et al. 2002).

TOUGHREACT model results:

A 7.5m deep profile through unsaturated sediments is simulated as a vertically oriented, 1-dimensional series of 98 equal volume grid blocks, bounded on the top and bottom by inactive blocks. The top inactive block provides the atmospheric boundary condition, and the bottom inactive block provides an infinite reservoir for draining fluids.

Drying soil

TOUGHREACT simulations of stable isotope transport were carried out using three hypothetical soil types with no input from infiltration to facilitate qualitative comparisons with data and model results from previous studies of drying soil columns (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, 1996b, Melayah et al., 1996). Specifically, a vapor-dominated zone at the top reaches a peak ($\delta^{18}\text{O}_{\text{MAX}}$) at the evaporation front, followed by decreasing $\delta^{18}\text{O}$ with depth.

The vapor-dominated zone occurs above the evaporation front, and consists of sediments that have very low moisture content (Barnes and Allison 1983; Shurbaji et al. 1995). The vapor-dominated zone is a transition between atmospheric gas with low humidity and pore vapor at the evaporation front. This transition takes place across gradients in concentration and isotopic composition, from atmospheric humidity to 100% humidity at the evaporation front, and from the isotopic composition of atmospheric vapor to pore vapor in isotopic equilibrium with pore water.

As demonstrated in Figure 3, the depth and thickness of the high $\delta^{18}\text{O}$ zone is related to soil properties, which determine the transport and distribution of water and water vapor in the column. However, 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).

Analytical solution for $\delta^{18}\text{O}_{\text{MAX}}$

The dependence of $\delta^{18}\text{O}_{\text{MAX}}$ on humidity and temperature can be calculated without the use of numerical solutions, and makes a useful comparison with the results of TOUGHREACT numerical simulations. For an initially water-saturated soil, the soil-atmosphere interface represents the boundary between a reservoir of liquid water at depth in the soil and an infinite reservoir of water vapor (the atmosphere). In a column of initially water-saturated soil, the $^{18}\text{O}/^{16}\text{O}$ or D/H ratio at the evaporation front reaches a steady state value (R_{sat}^s) (Zimmerman et al. 1967; Barnes and Allison, 1983), which depends on the humidity (h), the isotopic ratios of the atmospheric vapor (R_a) and the soil water well below the evaporation front (R_{res}), the kinetic evaporation fractionation factor at zero humidity ($\alpha_{\text{evap}}^{h=0}$), and the temperature dependent equilibrium fractionation factor (α_{eq}):

$$R_{sat}^s = \alpha_{evap}^{h=0} (1 - h) R_{res} + \alpha_{eq} h R_a \quad (11)$$

For an unsaturated soil, the soil-atmosphere interface represents the boundary between liquid water *and* water vapor in the soil, and an infinite reservoir of water vapor (the atmosphere). Both liquid and vapor phase transport are active below the evaporation front in unsaturated soils that are not in contact with a water table, and the kinetic fractionation factor is dependent on the atmospheric humidity. Both diffusion theory (Ehhalt and Knott, 1965) and kinetic theory (Criss, 1999) have been used to derive the equation for the kinetic isotopic fractionation factor during evaporation into a humid atmosphere (α_{evap}) as:

$$\alpha_{evap} = \frac{\alpha_{evap}^{h=0} (1 - h)}{1 - \alpha_{eq} h \frac{R_a}{R_{sat}^s}} \quad (12)$$

Equation 11 is then recast to obtain the steady-state isotope ratio of pore water at the evaporation front in a column of unsaturated soil:

$$R_{unsat}^s = \alpha_{evap} (1 - h) R_{res} + \alpha_{eq} h R_a \quad (13)$$

Measurements of evaporating water-drop stable isotope compositions in a dry N₂ atmosphere (Stewart, 1975) are used here for the kinetic fractionation of ¹⁸O and ¹⁶O at zero humidity, ($\alpha_{evap}^{h=0}$, 1.027 at 20° C). The predicted values of $\delta^{18}\text{O}_{MAX}$ (from R_{unsat}^s) that would be obtained at different humidities in drying soil columns with no input water are shown in Figure 4, based on conditions at the Hanford Site ($\delta^{18}\text{O}_a = -21\text{‰}$, $\delta^{18}\text{O}_{res} = -16.5\text{‰}$).

In a humid atmosphere, $\delta^{18}\text{O}_{MAX}$ has a curvilinear relation to humidity (Figure 4). It is also interesting to note that $\delta^{18}\text{O}_{MAX}$ would vary with temperature because of its dependence on

the equilibrium fractionation factor (α_{eq}). This temperature dependence is enhanced with higher humidity, as the equilibration with atmospheric vapor plays a more significant role.

Simulations of a drying soil column using TOUGHREACT can be used to evaluate the maximum soil water $\delta^{18}\text{O}$ or δD value at any humidity. TOUGHREACT solves the diffusion, equilibration, and multiphase transport equations directly, and does not rely on predetermined kinetic fractionation factors. Nevertheless, this direct approach results in predictions of $\delta^{18}\text{O}_{max}$ that closely match the magnitude and curvilinear behavior predicted by equation 13 (Figure 4).

It is useful to note that the isotopic ratio of near-surface soil waters can be increased or decreased without any loss to evaporation, when in contact with an atmosphere of 100% humidity, but with an atmospheric vapor that is out of equilibrium with the soil water. In this case, the soil column will have a profile that reflects this shift in soil water isotopic composition toward equilibrium with the atmosphere near the surface. In the case of 100% relative humidity there will not be a vapor-dominated zone at the top of the column, since there is no vapor concentration gradient between the atmosphere and the soil.

Net 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, net infiltration (i.e. deep percolation or recharge) ranges from 0.1 to 200 mm per year at the Hanford site (Gee et al, 1992), and has a significant effect on stable isotope profiles in the Hanford vadose zone.

Net infiltration was implemented in TOUGHREACT simulations as water input to the uppermost soil grid block and specifying constant or time-dependent water input rates.

Infiltrating waters are input at the same temperature as the model soil grid blocks, and have an

isotopic composition similar to winter precipitation and groundwaters at Hanford ($\delta^{18}\text{O} = -16.5\text{‰}$ and $\delta\text{D} = -135\text{‰}$). The initial soil water isotopic compositions for all of the models described here were set equal to the input water, but become shifted to higher values as evaporation and infiltration commence. The time required for all of the initial water to be flushed from the profile ranges from about 4 years for medium sand to over 20 years for clayey silt.

Constant infiltration

Infiltration from rainwater, for the sake of simplicity, will first be considered here as a constant flux of water at the surface, equal to the average annual net infiltration rate. This constant flux model (Figure 5) predicts the average isotopic shift in vadose zone pore waters due to evaporation at the surface imparted on draining water. A constant input rate of 50 mm/yr results in average pore water $\delta^{18}\text{O}$ values that are higher than the input water ($\delta^{18}\text{O} = -16.5\text{‰}$), and depend on soil properties as predicted by the analytical model of DePaolo et al. (*in review*). Smaller grain size increases the liquid saturation in the sediments during infiltration, which in turn limits the amount of vapor loss near the surface. As a result, the smallest grain soil, clayey silt, has the highest volumetric water content (32%) and the smallest shift toward higher $\delta^{18}\text{O}$ values at depth (+0.9 ‰). With increasing grain size in the silty sand and medium sand, the fraction of water retained in pore space under constant drainage decreases (7.8% and 3.8% respectively), and the $\delta^{18}\text{O}$ values are shifted higher (+2.5‰ and +3.9‰).

Periodic infiltration

Under a constant infiltration flux, the lack of dry periods prevents the formation of high $\delta^{18}\text{O}$ and δD “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 (50 mm/yr) comes during 0.3 yr wet periods that are followed 0.7 year dry periods (zero recharge).

Changes in moisture content during periodic infiltration

Changes in moisture content caused by wet and dry seasons are reflected in measurements of capillary pressure (P_{cap}) in the VZ300N lysimeter (Sisson et al., 2002), a large (3 m wide x 8 m deep) caisson filled with sand from the Hanford formation and allowed to undergo natural recharge and drainage at the Hanford Site since 1978 (Gee, 1987). The lysimeter is instrumented with advanced tensiometers to measure P_{cap} (Sisson et al, 2002), and drainage is continuously monitored from a tipping cup at the bottom. The average drainage rate measured in the lysimeter over the past several years is 55 ± 10 mm/yr (Sisson et al, 2002). Capillary pressure reaches a maximum shortly after the wet season, as the accumulated water percolates downward, increasing moisture content. The time lags between capillary pressure maximums (less negative values) recorded by successively deeper tensiometers give an estimate of the downward velocity of the wet season pulse (approximately 3m/yr in 2002 and 7m/yr in 2003). Following the post-wet season increase in P_{cap} , drainage and evaporation gradually cause decreased (lower) capillary pressures until the wet season of the following year.

Model calculations of P_{cap} for silty sand during simulated wet and dry seasons reasonably match the observed annual variations in capillary pressures recorded by the 0.9 and 1.5 m deep

tensiometers in the lysimeter (Figure 6). In the silty sand periodic infiltration model, P_{cap} increases to -43 mbar at 1.5m following the wet season, which is simulated by input of water in the top block of soil. Following this increase, the P_{cap} gradually decreases during the following dry season to a minimum of -84 mbar. Model results do not show the degree of damping with depth observed in the deeper tensiometers (Sisson et al., 2002) where the amplitude of P_{cap} minimums narrow to approximately -20 mbar at 2.1 m depth.

Stable isotope profiles during wet/dry seasons

During the wet season, isotopically light input water ($\delta^{18}O = -16.5 \text{ ‰}$) infiltrates below the surface (Figure 7A), resulting in $\delta^{18}O$ values that decrease toward the precipitation value. Below this minimum, $\delta^{18}O$ values increase slightly, where water from the previous dry season has mixed with infiltration water and percolated downward. During the dry season, a high $\delta^{18}O$ zone of evaporation is developed in the top 1m of the profile (Figure 7B).

Model results for silty-sand predict that a second set of these evaporation and preserved rain compositions may be present from 1-2 m depth, where water from the previous rain event infiltrated deeper than the evaporation front. Below about 2.5 m depth, the pore water $\delta^{18}O$ reach a steady-state value that is higher than the initial $\delta^{18}O$ value of the infiltrating water. Unsaturated zone dune sand isotope profiles with a subsurface isotopic minimum at 1-2 m depth similar to these model predictions have been documented by Barnes and Allison (1988, their Figures 12a and b), and were attributed to the infiltration of isotopically light precipitation. In addition, model results from a time step shortly after an infiltration pulse may be compared with samples from an ongoing study, taken from the VZ300N lysimeter in March 18, 2003, shortly after the end of the wet season (Figure 8). Although this model is not calibrated specifically to the field experiment, the silty sand parameters (Table 1) are similar to parameters determined by

inverse models of the lysimeter (Zhang et al., 2003), making a reasonable comparison for considering drainage rates under analogous conditions.

Model predictions (dashed) for a water input rate (q) equivalent to 50 mm/yr indicate a profile similar to the $\delta^{18}\text{O}$ data from samples collected in March 2003. In the model profile, infiltration leads to a minimum $\delta^{18}\text{O}$ peak (-15.6‰) at 0.6 m depth. Below the minimum, $\delta^{18}\text{O}$ increases to a maximum of -13.6‰ at 1.5 m where mixing of evaporated waters and infiltration waters has taken place. The $\delta^{18}\text{O}$ of deep soil waters is predicted to be -14.0‰, slightly higher than the $\delta^{18}\text{O}$ values in deep samples collected in vadose zone cores from the Hanford Site (Figure 2).

Various drainage rates can be considered in order to predict the effects of changing environments on the $\delta^{18}\text{O}$ profile. For example, if the climate became wetter, or the surface was revegetated by a fire, net infiltration may be expected to increase. A periodic infiltration model with a factor of three increase in water input (150 mm during the wet season) predicts a distinct isotopic profile that does not resemble the profile from March 2003 (Figure 8). With increased infiltration rate, the low $\delta^{18}\text{O}$ pulse travels deeper into the profile, causing a broad low $\delta^{18}\text{O}$ zone in the top 3 m ($\delta^{18}\text{O} = -16.2\text{‰}$). The deep maximum in $\delta^{18}\text{O}$ (-14.8‰) that consists of a mixture of old evaporated water and lower $\delta^{18}\text{O}$ infiltrating water occurs around 3.6 m depth. Deep soil waters in this higher infiltration rate model are shifted only 0.7‰ higher than the $\delta^{18}\text{O}$ value of input water.

A factor of three decrease in the net infiltration rate may be considered to predict the isotopic record of consecutive dry years or increased water uptake by plants. Decreasing the annual wet season input of water in the model to 16.7 mm/year results in a more $\delta^{18}\text{O}$ -shifted profile, with a small minimum $\delta^{18}\text{O}$ of -12.5‰ at 0.3m (Figure 8). Below this low, $\delta^{18}\text{O}$

increases to -9.5% at 0.9m, where input waters have mixed with evaporated water and percolated downwards. In this low infiltration rate model, the $\delta^{18}\text{O}$ value of deep soil waters is shifted $+8.1\%$ higher than the input water, and significantly higher than observed deep vadose zone values at Hanford.

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.

TOUGHREACT simulations with isotope fractionation provide new insights into the behavior of water isotopes in unsaturated zone pore waters in semi-arid climates. This study uses TOUGHREACT multiphase transport models to consider disturbances to stable isotope profiles through the vadose zone that result from water input during wet seasons in semi-arid climates. In semi-arid climates, alternating wet and dry seasons lead to annual fluctuations in moisture content, capillary pressure, and stable isotope compositions in the vadose zone. The effective depths of evaporation and wetting events are primarily controlled by soil properties and infiltration rate. Repeated annual cycles of wet and dry seasons in a semi-arid climate lead to a consistent shift in the isotopic composition of deep vadose zone pore waters, which is inversely proportional to the amount of infiltration.

Stable isotope profiles provide a dynamic record of evaporation and infiltration in the unsaturated zone. For the range of infiltration rates measured at the Hanford Site (0.1-200 mm/yr), stable isotope profiles are affected by surface conditions on annual to decadal time

scales, and therefore can provide a record of recent events such as dumped or spilled waste water, soil removal, and devegetation by brush fires. Numerical simulations of transport and isotope fractionation using TOUGHREACT provide a method to quantitatively interpret the relation of stable isotope depth profiles to net infiltration rate.

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REFERENCES

- Allison, G. B., G. W. Gee, and S. W. Tyler, Vadose-zone techniques for estimating groundwater recharge in arid and semiarid regions, *Soil Sci. Soc. Am. J.*, 58, 6-14, 1994.
- Barnes, C. J., and G. B. Allison, The distribution of deuterium and oxygen 18 in dry soils, 1, Theory, *J. Hydrol.*, 60, 141-156, 1983.
- Barnes, C. J., and G. B. Allison, The distribution of deuterium and oxygen 18 in dry soils, 3, Theory for non-isothermal water movement, *J. Hydrol.*, 74, 119-135, 1984.
- Barnes, C. J., and G. B. Allison, Water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen, *J. Hydrol.*, 100, 143-176, 1988.
- Craig, H., Isotopic variations in meteoric waters. *Science*, 133, 1702-1703, 1961.
- Criss, R.E., *Principles of Stable Isotope Distribution*. Oxford University Press, New York, 246 p., 1999.

DePaolo, D.J, Conrad, M.E., Maher, K., and Gee, G.W., Oxygen and hydrogen isotopes in pore fluids from a 70m-thick vadose zone soil section at Hanford, Washington: Implications for recharge and horizontal fluid movement, *Vadose Zone Journal*, in review.

Ehhalt, D. and Knott, K., Kinetische isotopentrennung bei der verdampfung von wasser, *Tellus*, 17, 389-397, 1965.

Gee, G.W. 1987. Recharge at the Hanford Site: Status Report. PNL- 6403. Pacific Northwest Laboratory, Richland, WA.

Gee, G.W., Fayer M.J., Rockhold, M.L., and Campbell, M.D. Variations in recharge at the Hanford Site, *Northwest Science*, 66, 237-250, 1992.

Graham, D.L., Stable isotopic composition of precipitation from the Rattlesnake Hills Area of South-Central Washington State, Rockwell Hanford Operations, RHO-BW-ST-44 P, 1983.

Hoitink, D. J., Ramsdell, J. V. Burk, . K. W., Shaw, W. J., Hanford Site Climatological Data Summary 2001 With Historical Data PNNL-13859, 2002.

Horita, J. and Wesolowski, D.J., Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature, *Geochim. Cosmochim. Acta*, 58 (16), 3425-3437, 1994.

Kincaid CT, MP Bergeron, CR Cole, MD Freshley, NL Hassig, VG Johnson, DI Kaplan, RJ Serne, GP Streile, DL Streng, PD Thorne, LW Vail, GA Whyatt, and SK Wurstner. 1998. Composite Analysis for Low-Level Waste Disposal in the 200 Area Plateau of the Hanford Site. PNNL-11800, Pacific Northwest National Laboratory, Richland, Washington.

Lasaga, A.C., Kinetic Theory in the Earth Sciences, Princeton, New Jersey, Princeton University Press, 1998.

Mathieu, R., and T. Bariac, 1996, An isotopic study (^2H and ^{18}O) of water movements in clayey soils under a semiarid climate, *Water Resour. Res.*:32 (4), 779-789, 1996a.

Mathieu, R., and T. Bariac, A numerical model for the simulation of stable isotopes profiles in drying soils, *J. Geophys. Res.*:101, 12,685-12,696, 1996b.

Melayah, A, L. Bruckler, and T. Bariac, Modeling the transport of water stable isotopes in unsaturated soils under natural conditions, 2. Theory, *Water Resour. Res.*, 32, 2047-2045, 1996.

Pruess, K., TOUGH2, a general-purpose numerical simulator for multiphase fluid and heat flow, Report LBL-29400, Lawrence Berkeley Laboratory, Berkeley, CA, May 1991.

Pruess, K., C. Oldenburg and G. Moridis. TOUGH2 User's Guide, Version 2.0, Lawrence Berkeley National Laboratory Report LBNL-43134, Berkeley, CA, November 1999.

Shurbaji, A. M., F. M. Phillips, A. R. Campbell, and R. G. Knowlton, Application of a numerical model for simulating water flow, isotope transport, and heat transport in the unsaturated zone, *J. Hydrol.*, 171, 143-163, 1995.

Sisson, J.B., Gee, G.W, Hubble, J.M., Bratton, W.L., Ritter, J.C., Ward, A.L., and Caldwell, T.G., Advances in tensiometry for long-term monitoring of soil water pressures, *Vadose Zone Journal*, 1, 310-315, 2002.

Stewart, M.K. Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops: applications to atmospheric processes and evaporation of lakes, *J. Geophys. Res.*, 80, 1133-1146, 1975.

van Genuchten, M.T. A closed-form equation for predicting the hydraulic conductivity of unsaturated flow, *Soil Sci. Soc. Am.*, 44, 892-898, 1980.

- Xu, T. and Pruess, K., Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1. methodology, *Am. J. Sci.*, 301, 34-59, 2001.
- Zhang, Z.F., Ward, A.L., and Gee, G.W., Estimating field-scale hydraulic parameters of heterogeneous soils using a combination of parameter scaling and inverse methods, PNNL-14109, Pacific Northwest National Laboratory, 2002.
- Zhang, Z. F., A. L. Ward, and G. W. Gee. Estimating soil hydraulic parameters of a field drainage experiment using inverse techniques. *Vadose Zone J.*, 2, 201-211, 2003.
- Zimmerman, U., Ehhalt, D., Munnich, K.O., Soil water movement and evapotranspiration: changes in the isotopic composition of the water, In *Proceedings of the Symposium on Isotopes in Hydrology* (Vienna, 1966). International Atomic Energy Agency, Vienna, 567-584, 1967.

Figure Captions

Figure 1. Hydrogen and oxygen isotope compositions of soil waters collected from the Hanford vadose zone. The value of average precipitation used for model input waters is shown as a grey box. Pore water stable isotope data from DePaolo et al (*in review*) and unpublished data from ongoing studies are shown as blue diamonds. Also shown are the Global Meteoric Water Line (GMWL) of Craig (1961) and the Hanford Local Meteoric Water Line (LMWL), based on data from Graham (1983) and report BWI-DP-061.

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 ‰). Pore water stable isotope data from DePaolo et al (*in review*) and unpublished data from ongoing studies are shown as blue diamonds.

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 ‰), the model soils were subjected to 20 years of drying in an atmosphere with $h=40\%$ and $\delta^{18}\text{O}_a = -21$ ‰.

Figure 4. Values for $\delta^{18}\text{O}_{\text{max}}$ determined at different values of humidity ($\delta^{18}\text{O}_a = -21$ ‰) using analytical solutions for saturated (Eq. 11) and unsaturated (Eq. 13) sediment columns, and results from numerical simulations using TOUGHREACT.

Figure 5. Model steady-state $\delta^{18}\text{O}$ values calculated for the soils in Figure 3 ($h=40\%$ and $\delta^{18}\text{O}_a = -21\text{‰}$), but with a constant infiltration of 5 cm/yr of water with a $\delta^{18}\text{O}$ value of -16.5‰ .

Figure 6. Capillary pressures respond to the annual cycle of wet and dry seasons in the VZ300N lysimeter at Hanford (solid lines), and in TOUGHREACT models with periodic water input (dashed lines). Data from Sisson et al. (2002) and <http://vadose.pnl.gov>.

Figure 7. A sequence of 0.1 yr time steps (1-4, and 9) from the periodic infiltration model illustrates disturbances to the isotopic profile during the wet season (A) and effects of infiltration and evaporation during the dry season (B) for a hypothetical silty-sand soil.

Figure 8. Stable isotope profiles at the beginning of the dry season for pulsed infiltration models using 16.7, 50, and 150 mm/year net infiltration rates of winter precipitation (input water $\delta^{18}\text{O}$ of -16.5‰). Model results are compared with data collected as part of an ongoing study of the VZ300N lysimeter in March 2003, shortly after the wet season. The lysimeter has a measured drainage rate of 55 ± 10 mm/yr (Sisson et al., 2002).

Table 1. Parameters for calculating unsaturated hydraulic conductivities and capillary pressures in TOUGHREACT models using the equations of van Genuchten (1980).

Material	$\theta_{\text{saturated}}$ (v/v)	θ_{residual} (v/v)	α (mm^{-1})	n	$K_{\text{saturated}}$ (m/s)
Medium sand	0.33	0.03	0.040	3.6	5×10^{-4}
Silty sand	0.35	0.05	0.010	2.4	5×10^{-5}
Clayey silt	0.38	0.07	0.002	1.2	5×10^{-7}

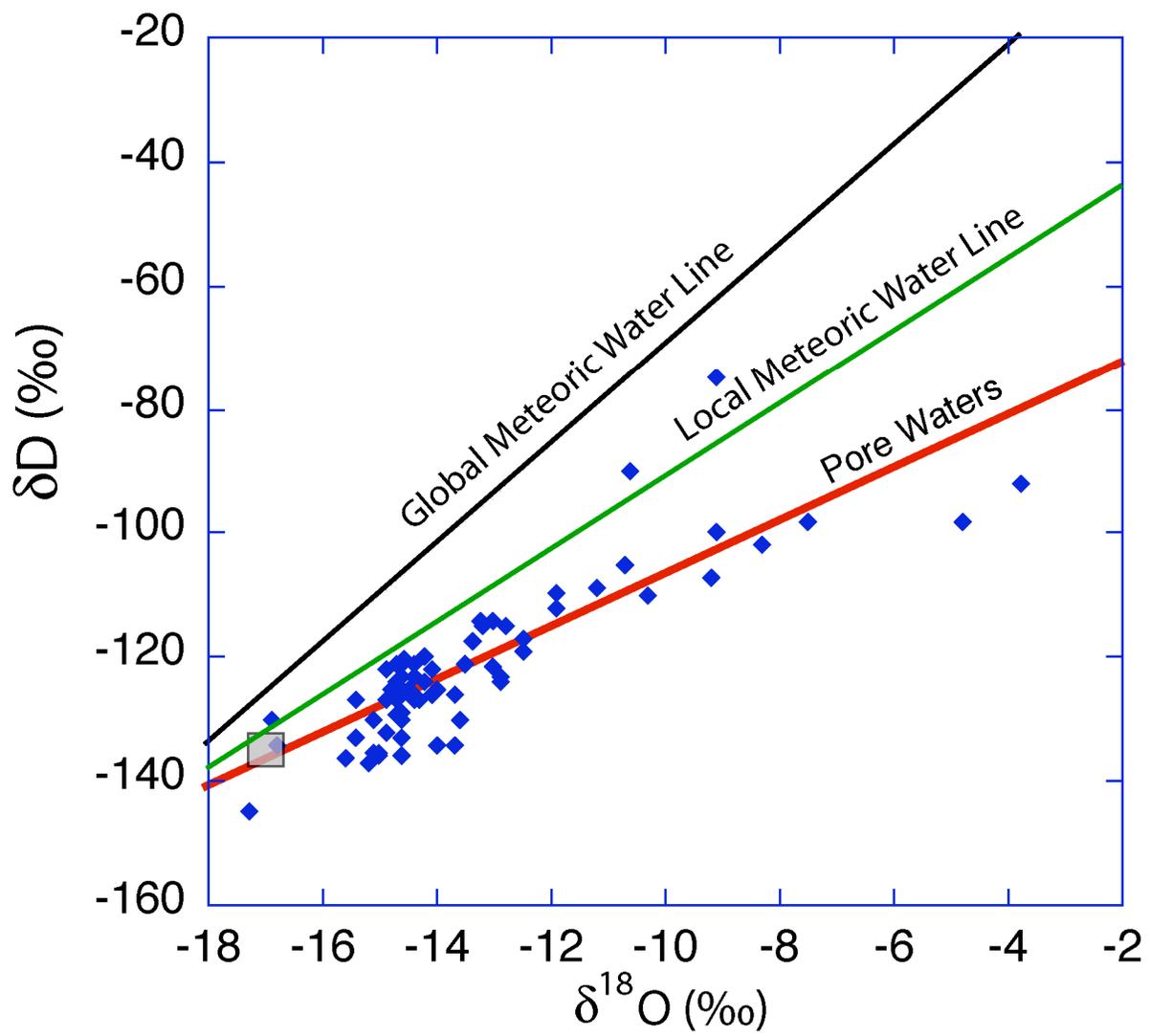


Figure 1

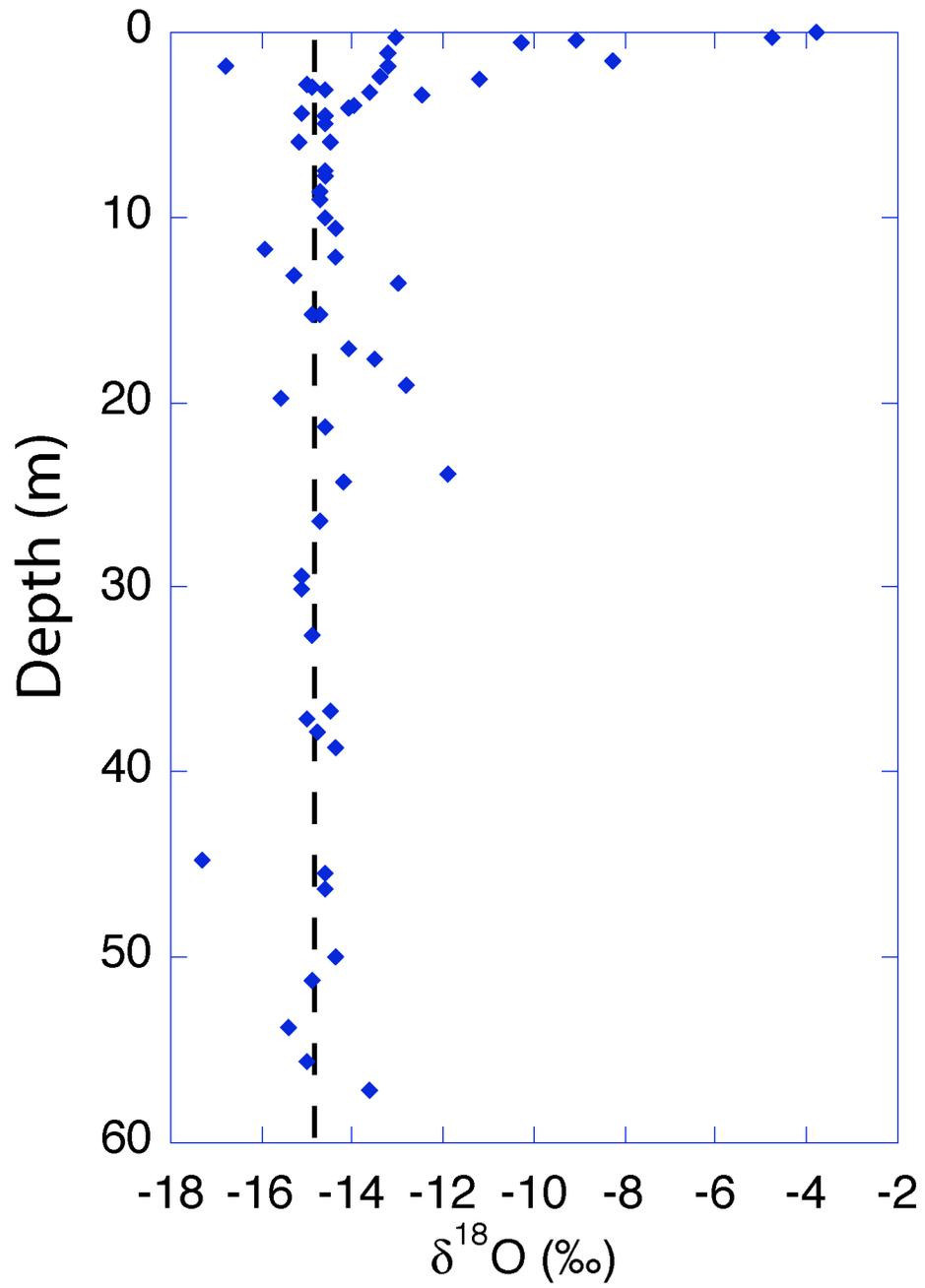


Figure 2

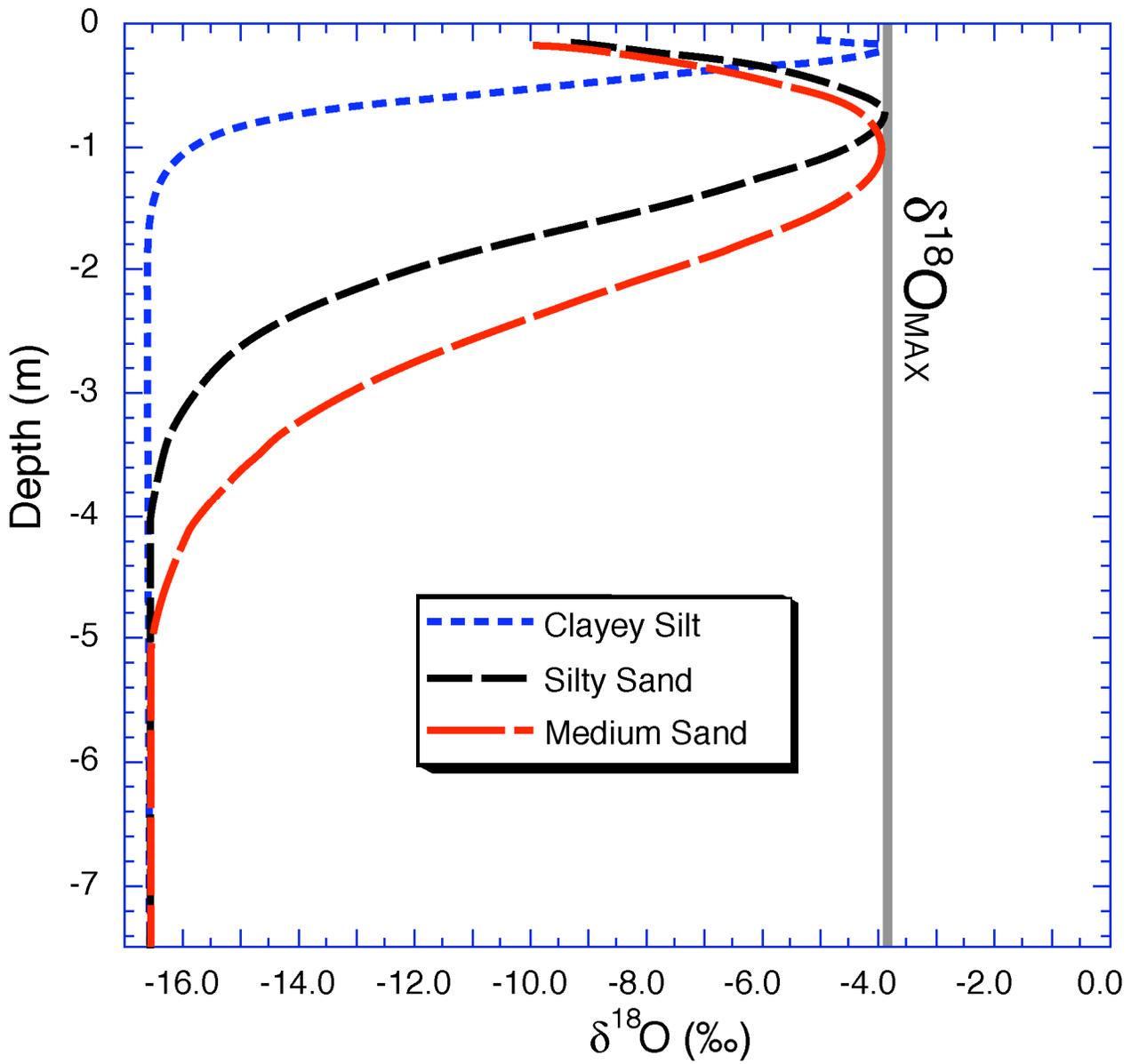


Figure 3

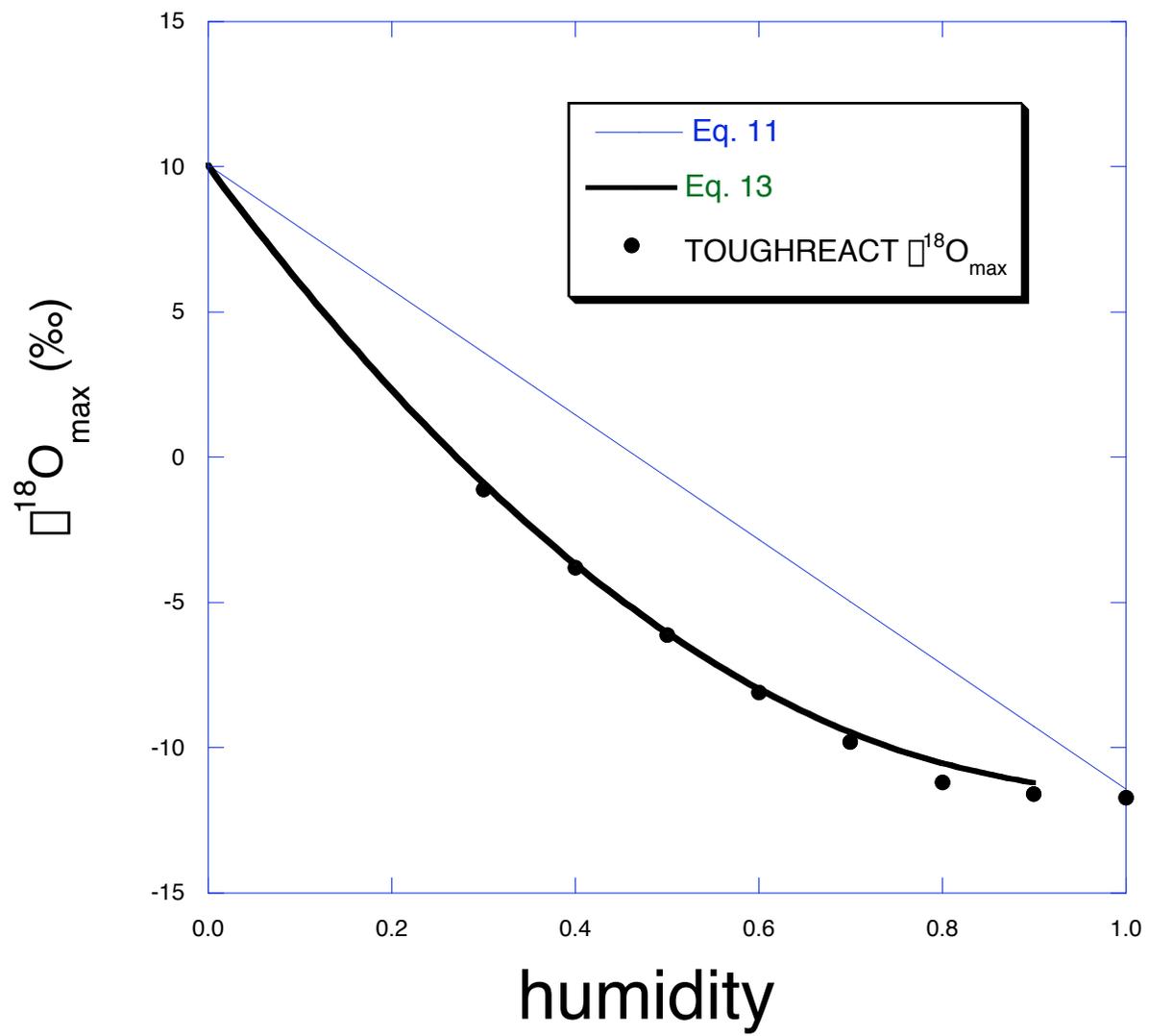


Figure 4

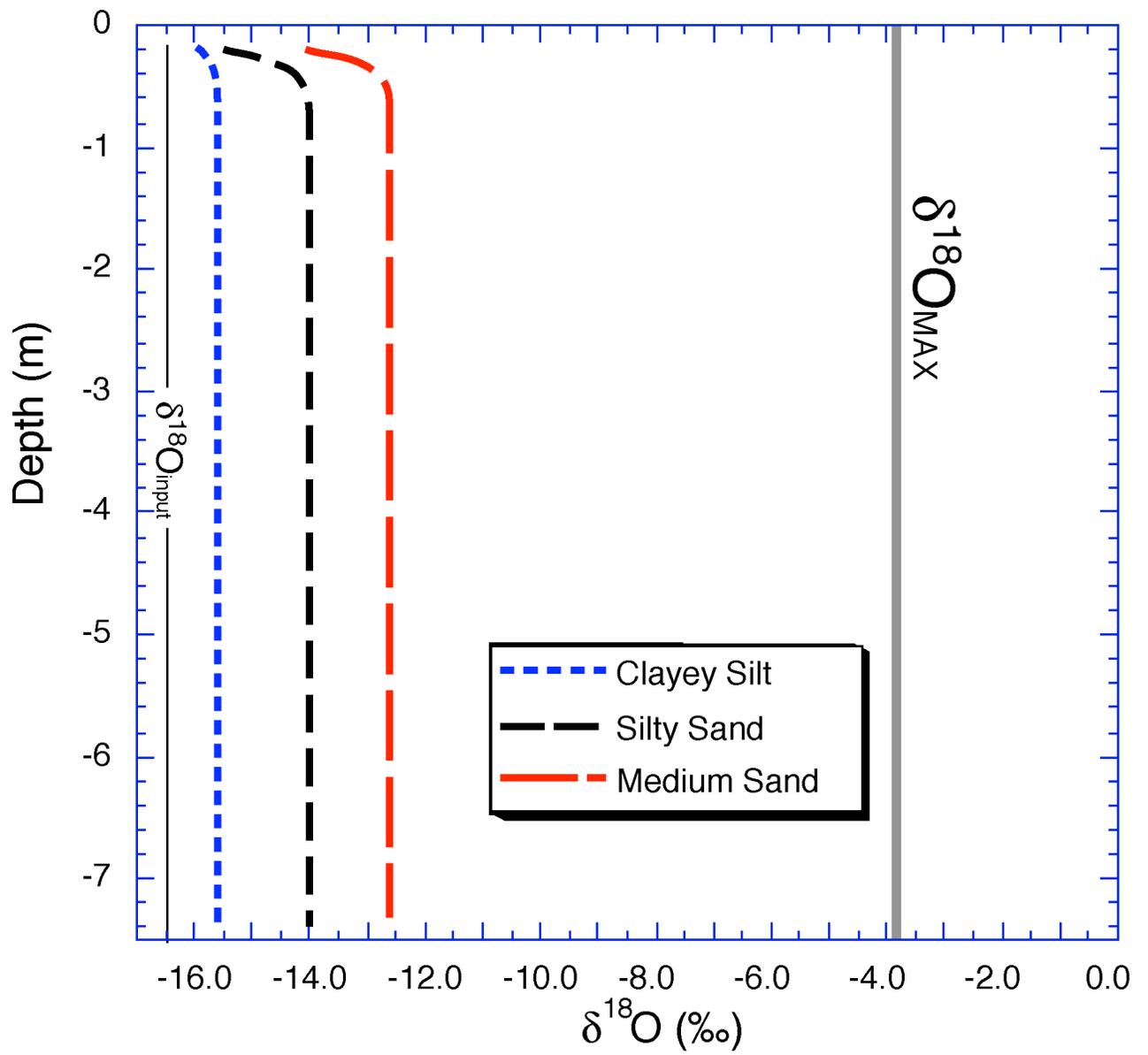


Figure 5

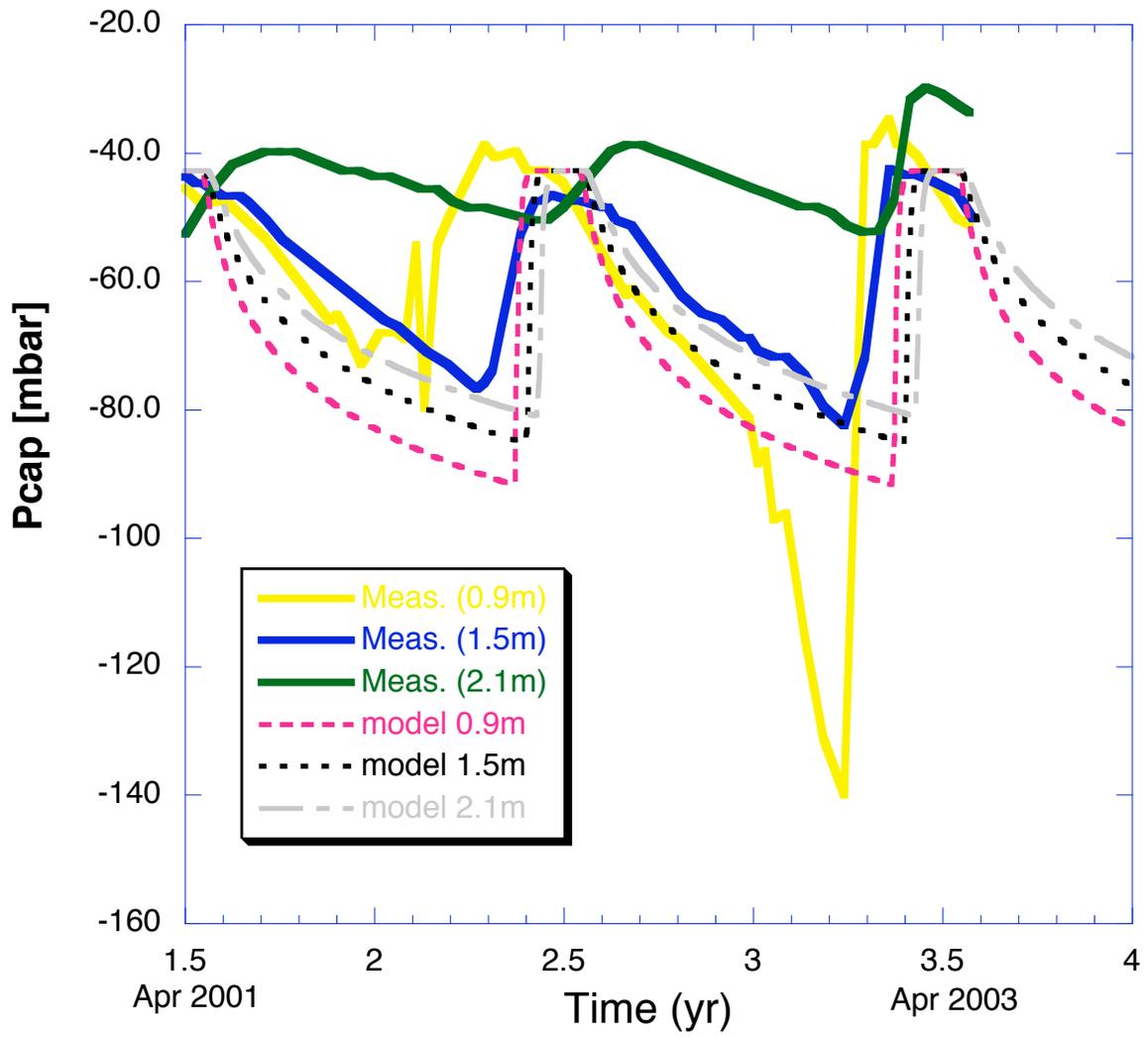


Figure 6

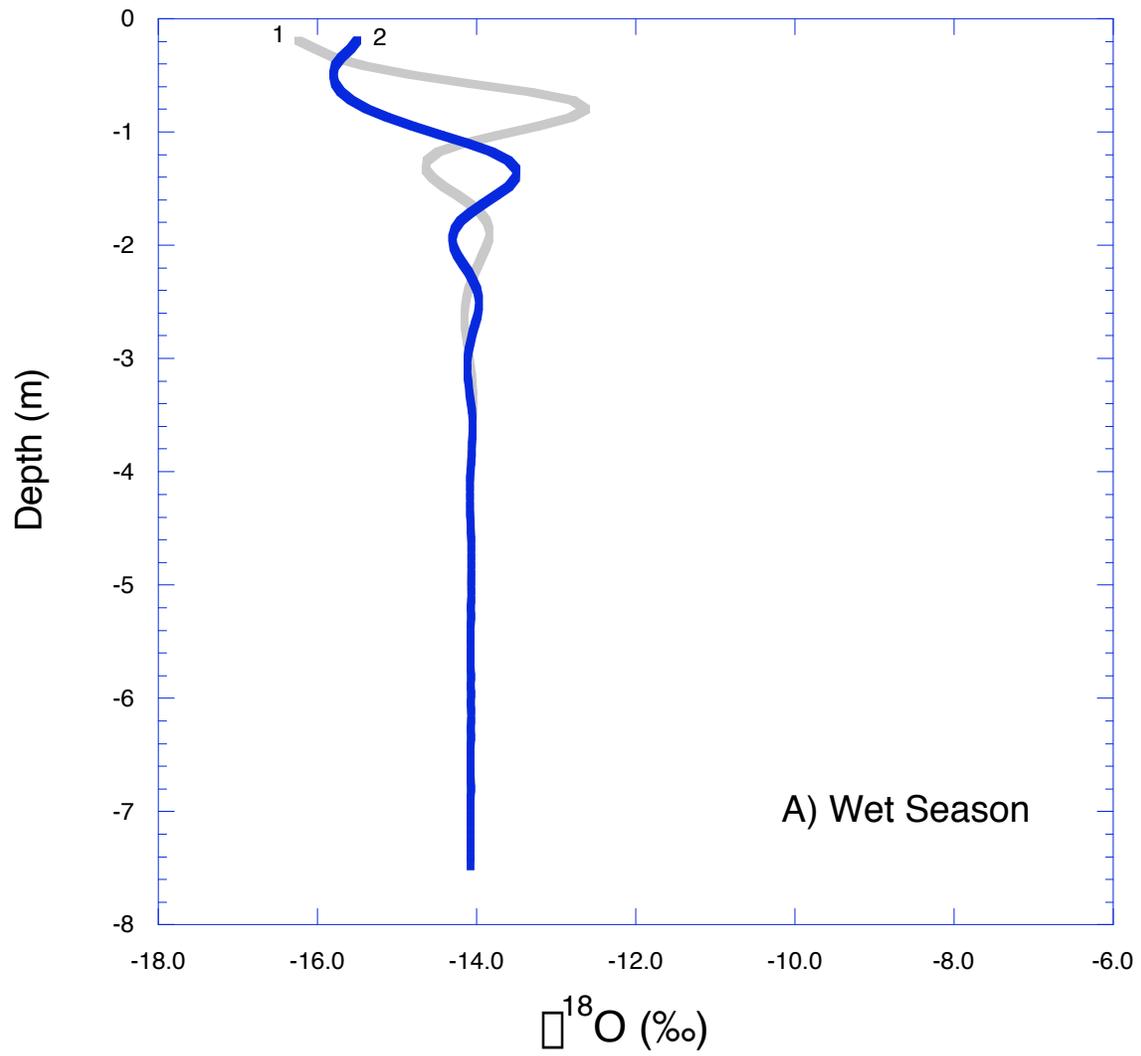


Figure 7A

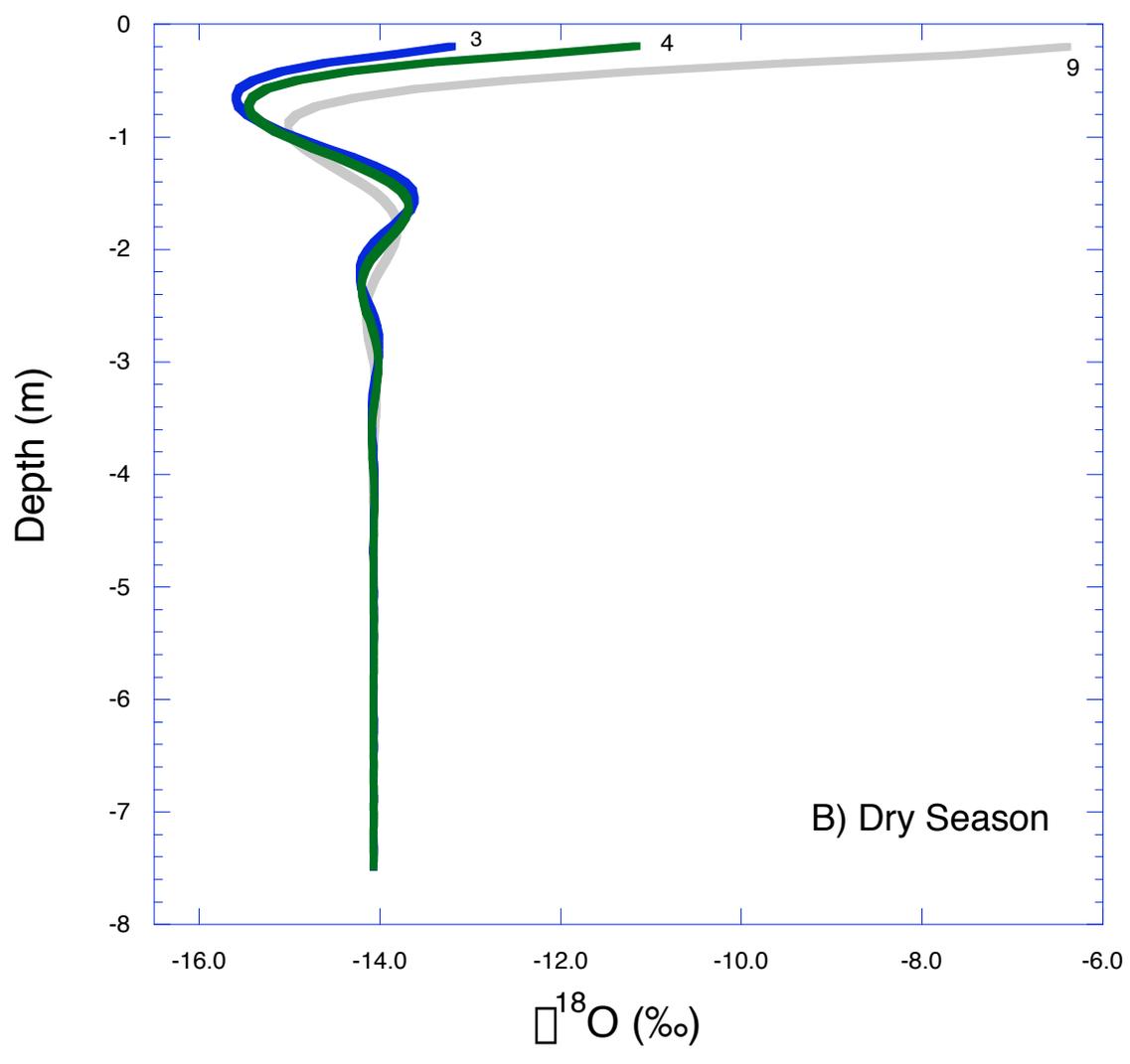


Figure 7B

