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Application of a numerical model for simulating water flow, isotope transport, and heat transfer in the unsaturated zone

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Abstract

A controlled field experiment was conducted to provide data for a one-dimensional numerical model for simulating transient water flow, isotope transport, and heat transfer in the unsaturated zone (ODWISH). The experiment consisted of allowing water to evaporate from homogeneously packed sand columns and periodically sampling to observe changes in the distributions of moisture, temperature, and oxygen-18 enrichment. The peaks of the oxygen-18 distributions were used to determine the value of moisture content at liquid discontinuity, a parameter important for modeling water vapor flow. Modeling transient second-stage evaporation from soil necessitated implementing a retention relation $\Psi(\theta)$ that is applicable for dry soils, above the evaporation front, where vapor flow is dominant. A retention model for dry soils was developed, connected to the Van Genuchten model and the resulting two-segment retention relation was implemented in the numerical model. The connection point for the retention relation is the moisture content at liquid discontinuity, which was also used in the numerical model to locate the evaporation front. Simulations showed that the ODWISH model reproduces reasonably well the experimental distributions of moisture content, isotopic enrichment, and temperature, and that the model accounts for the major processes involved in water movement in the shallow unsaturated zone and the associated isotope transport. The most significant discrepancies between the simulations and the experimental data can probably be attributed to inadequencies of the available two-segment $\Psi(\theta)$ relationship over the wide range of pressure heads Ψ encountered during the experiment. The ODWISH model was employed to test the sensitivity of the isotope profile development to diurnal variations in temperature and humidity. The results indicated that daily, or even weekly, averages are adequate for predicting isotope profile development.

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Notation

g	acceleration of gravity (cm s^{-2})
h	relative humidity
h_a	relative humidity of atmospheric air
K	hydraulic conductivity (cm s^{-1})
n	porosity
R	ideal gas constant (cm^2 s^{-2} K^{-1})
t	time (s)
T	temperature of soil (°C)
z	depth below surface (cm)
δi	relative isotopic enrichment; $\delta_i = (R_i/R_{st}) - 1$
Δt	time increment in simulation (h)
Δz	depth increment in simulation (cm)
θ	volumetric water content in soil
θ_{wk}	volumetric water content at liquid discontinuity
λ	thermal conductivity of soil (cal cm^{-1} s^{-1} $°C^{-1}$)
τ^l, τ^v	tortuosity factor for liquid and vapor
Ψ	pressure head (cm)
ω_1	weight factor for time in the implicit finite difference equations of water and heat flow
ω_2	weight factor for time in the implicit finite difference equation of isotope transport

1. Introduction

Shurbaji and Phillips (1995) described a one-dimensional numerical model which simulates transient water flow, isotope transport, and heat transfer in saturated and unsaturated soils (ODWISH). This model combines the Philip and De Vries (1957) theory for simultaneous heat and moisture transfer in porous media with stable isotope transport theory. The numerical model supplements previous analytical solutions for evaporation from soils (e.g. Barnes and Allison, 1984; Walker et al., 1988; Barnes and Walker, 1989) by allowing the transient development of stable isotope profiles in soil water to be simulated under fluctuating surface boundary (humidity and temperature) conditions and for field conditions where evaporation and infiltration processes coexist. The three blocks of the ODWISH model, describing water flow, heat transfer, and isotope transport were tested separately by Shurbaji and Phillips (1995). A controlled field experiment was conducted to provide data that are needed for further evaluation of the model by comparison between model predictions and experimental observations. Application of the model required a retention relation $\Psi(\theta)$ that is suitable for very dry soils (where soil moisture is discontinuous) and wet soils (where the liquid film is continuous) and a reliable method for determining the value of moisture content at liquid discontinuity.

The moisture content at liquid discontinuity is an important parameter for calculating water vapor fluxes following the formulations of Philip and De Vries (1957), which are incorporated in the ODWISH model. However, although Philip and De Vries (1957) introduced the parameter, they did not describe how it should be

quantified. Gee (1966) determined the value of this parameter by examining plots of the moisture distribution in soil columns and took the moisture content where $|\partial\theta/\partial z|$ was maximum as the moisture content at liquid discontinuity. Given the uncertainties involved in the measurement of moisture content at low values, this method can be only approximate. In this study, a different approach is presented, using isotopic enrichment profiles instead of moisture distributions to determine the value of moisture content at liquid discontinuity.

The soil moisture retention relation $\Psi(\theta)$ is necessary for modeling water flow in the unsaturated zone. The Van Genuchten model (1980) is suitable for wet soils where liquid film is continuous, but is less appropriate for dry soils where the liquid film is discontinuous (Nimmo, 1991; Ross et al., 1991). A retention model that covers a wider range of moisture content is needed in this study, which investigates water movement in soils ranging from very dry (discontinuous liquid phase) above the evaporation front to relatively wet deeper in the soil profile. To cover the entire range of moisture content, a two-segment model, using $\Psi(\theta)$ equations based on the Kelvin and Van Genuchten relations, was developed and implemented in ODWISH. Rossi and Nimmo (1994) have also presented two-segment and three-segment models for describing soil water retention from saturation to oven dryness. These relations may be promising if implemented in a numerical model that simulates evaporation from soil based on the theory of Philip and De Vries (1957) such as ODWISH. Scanlon (1994) and Scanlon and Milly (1994) conducted a study on water and heat fluxes in desert soils using a finite element model (Milly, 1982), which does not include a retention relation for the top dry soil and thus is not capable of showing the progress of the evaporation front in the soil profile.

2. Methods

Collection and analysis of a comprehensive set of field data were needed to evaluate the utility of ODWISH under field conditions. The experimental depth distributions of moisture, temperature, and isotopic enrichment provide a basis for evaluating the performance of the numerical model in simulating the processes involved in water flow, heat transfer, and isotope transport.

2.1. Data requirements for the transient model

Experimental data required for the ODWISH model include the temporal distributions of temperature and relative humidity at the surface, and the initial depth distributions of temperature, moisture content, and isotopic enrichment. Data on the depth distributions of temperature, moisture content, and isotopic enrichment at the end of the simulation period are needed for comparison with the model simulations. A controlled field experiment was designed and conducted to study the development of isotope profiles under natural conditions and to provide the data base for evaluating the numerical model. The simulations in this study focus on the top 1 m, the depth most affected by daily variation in temperature and also the

zone of active evaporation and associated isotopic enrichment. Medium-dependent parameters required for the model application are porosity and moisture content at liquid discontinuity. The medium-dependent relations required are the soil moisture retention relation, the unsaturated hydraulic conductivity function, and the thermal conductivity relation.

2.2. Controlled field experiment

Sevilleta dune sand (taken from the Sevilleta National Wildlife Refuge 20 km north of Socorro, New Mexico) was the porous medium used in this experiment. Eight PVC columns, each 105 mm in diameter and 2.0 m in length, were packed with air-dry sand. The sand was added in lifts of approximately 50 mm and compacted by tapping the base of the column after each addition. Each column had about 100 mm of gravel at the base to allow free drainage of water. The average dry bulk density of the sand in the columns was 1.550 g cm^{-3}. Temperature probes were installed in one of the columns at depths of 2.0, 4.0, 10.0, 22.2, 27.7, 42.2, 82.0, and 148.0 cm below the soil surface. About 2.5 pore volumes of tap water, having an isotopic composition of $\delta^2H = -97.7‰$, $\delta^{18}O = -11.6‰$ vs. Standard Mean Ocean Water (SMOW), were run through each of the columns; then the columns were covered and allowed to drain for 24 h. The columns were then all sealed at the bottom and weighed. All subsequent isotopic measurements were referenced to the initial tap water rather than SMOW. The calculated values for the isotopic composition of atmospheric water vapor were $\delta^2H = -82.2‰$ and $\delta^{18}O = -15.1‰$ vs. tap water. These values were calculated from the minimum soil water isotopic composition at the surface and the fractionation factor at 25°C (see Table 1, Shurbaji and Phillips, 1995).

In the field, a drilling rig was used to auger eight holes to host the experimental columns. The columns were lowered into the holes until the sand surface in the columns was level with the soil surface outside the columns. Soil was added in each hole to insure that contact was made between the PVC pipe and the native soil. A probe which measures both temperature and relative humidity was placed on the ground surface to establish the top boundary condition for the transient model. The temperature probes buried in the soil at various depths were connected to a Campbell (Logan, UT) CR7 data logger programmed to take automatic readings every 3 h. Fig. 1 shows the observed relative humidity and temperature at the soil surface.

A wooden structure carrying an inclined cover of 1.5 m height, made of a translucent fiberglass screen, served to keep the soil columns free from any input water (e.g. rain) unaccounted for in the simulation runs. The columns were allowed to evaporate during a total period of 108 days. The columns were pulled from the ground using a fork lift. Columns were removed from the ground at time intervals of 1, 10, 49, 69, and 89 days after the emplacement. The last two columns were flooded with runoff water from a heavy rainfall event and thus were excluded from the analysis. One column was removed in each sampling period. After each column was removed, samples of soil for water content and isotopic analysis were collected by first sectioning the PVC tube into four pieces and then extruding and collecting

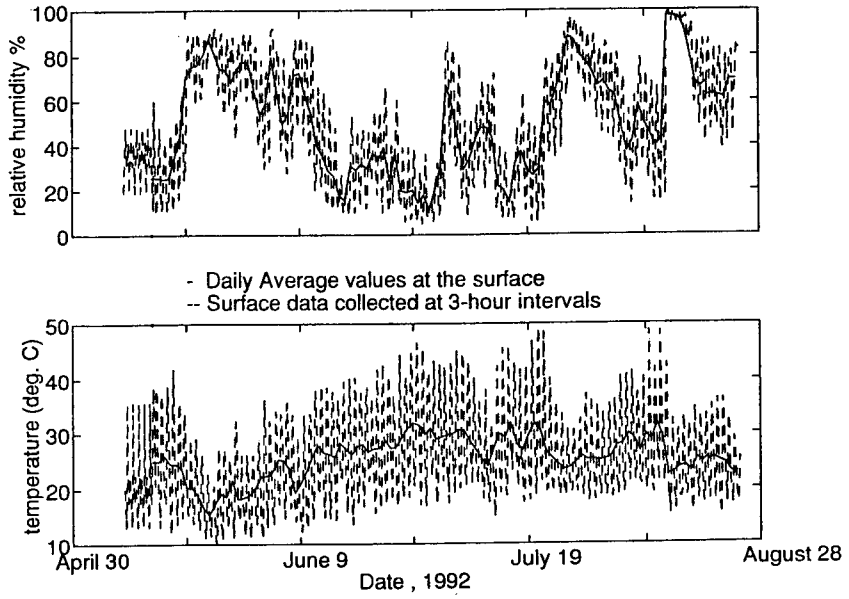

Fig. 1. Observed relative humidity and temperature at the soil surface (controlled field experiment).

samples from the PVC tube pieces at 20 mm intervals near the surface (where rapid change in the isotopic and moisture profiles was expected) and at 180 mm intervals deeper in the columns, where little change was expected. Soil samples were stored in airtight jars. Approximately half of each sample was used for soil water extraction for determination of the moisture content and the isotopic composition.

2.3. Laboratory procedures

Porosity, dry bulk density, and saturated hydraulic conductivity were measured using standard techniques (Black, 1965). The average values of these parameters were 0.351, 1.554 g cm^{-3}, and 0.013 cm s^{-1}, respectively. The particle size distribution was obtained using sieve analysis (Fig. 2). The soil is fairly homogeneous, clean, coarse sand. The thermal conductivity relation $\lambda(\theta)$ was adapted from Knowlton (1989) for dune sand from the same area (see Fig. 3). He measured the thermal conductivity for the soil using a cylindrical source thermal conductivity probe following the procedure of De Vries and Peck (1958).

Water was extracted from the soil for stable-isotope measurement using a vacuum distillation method (described below). Moisture content was determined from weight loss of soil during distillation. The oxygen-18 isotopic composition ($\delta^{18}O$) of soil water was measured using the CO_2–H_2O equilibration method on 0.5 ml of the distillate, following the procedure outlined by Roether (1970) and Socki et al. (1992). To determine the deuterium isotopic composition (δ^2H) of the water, a zinc reduction technique was employed to generate hydrogen gas from the water sample

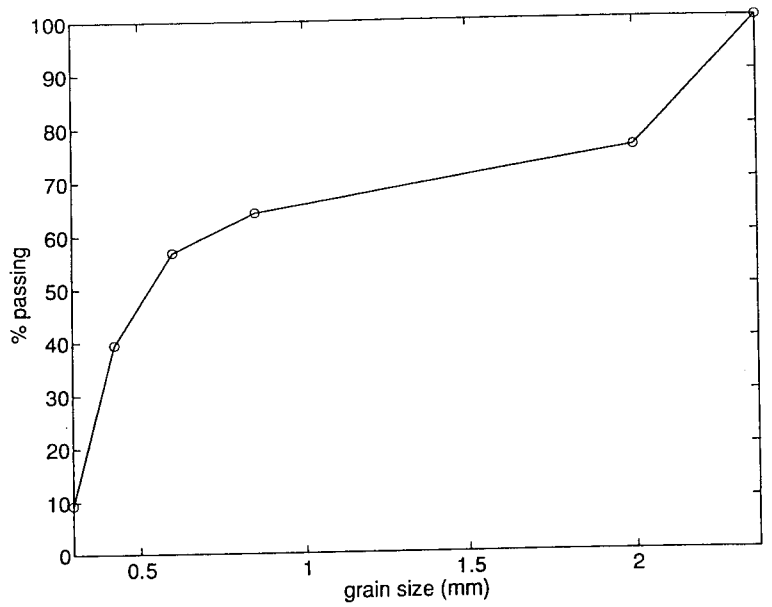

Fig. 2. Size distribution of soil grains.

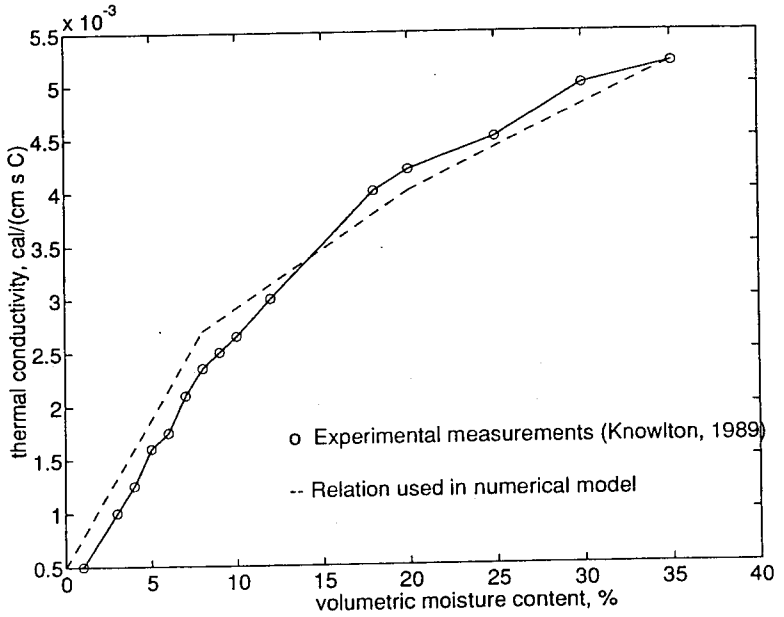

Fig. 3. Thermal conductivity as a function of moisture content for Sevilleta sand.

(Coleman et al., 1982; Kendall and Coplen, 1985). All isotopic measurements were performed on a Finnegan-MAT (San Jose, CA) Delta E mass spectrometer.

2.4. Vacuum distillation method

The apparatus consisted of a short glass tube connected at each end to a glass flask. These flasks will be referred to as the boiling flask and the capture flask. The glass tube was connected to a vacuum pump through a valve. The soil sample was placed in the boiling flask, then quickly connected to the glass tube and capture flask assembly, which was flooded with dry nitrogen gas. A liquid nitrogen bath was then placed around the boiling flask for 10 min to freeze out the soil moisture. This was done to minimize water loss when the system of flasks and tube were subsequently evacuated to remove atmospheric air. After evacuation of the system to 100 mtorr, the valve to the vacuum pump was closed and the liquid nitrogen bath transferred to the capture flask. A heating element was placed under the flask containing the soil sample and the sample was kept at 100–120°C for a period ranging from 100 to 250 min, based qualitatively on the water content and soil texture of the sample. The end-point of the distillation was determined by using a heat gun on the tube and boiling flask, to vaporize any condensed water and move it into the capture flask. When no further condensation at the top of the boiling flask was observed, the sample was heated for an additional 20 min (as a precaution) and then the system was flooded with dry nitrogen gas. The capture vessel was then weighed (to determine soil moisture content) and the water transferred to a storage bottle. Additional details on the laboratory procedure have been given by Knowlton (1989).

The soil water distillation must proceed very nearly to completion or the isotopic composition of the distillate will be lighter than that of the soil water. The distillation procedure should closely approximate a theoretical Rayleigh distillation process. The Rayleigh equation was used to calculate that, to obtain distillate compositions within 0.1 $\delta^{18}O$ and 1.0 $\delta^{2}H$ of the soil water, 99.75% of the soil water must be captured. Systematic errors owing to incomplete extraction during vacuum distillation of soil water have been experimentally demonstrated by Woods (1990), Ingraham and Shadel (1992), and Walker et al. (1994). A series of experiments was therefore conducted to test the accuracy and precision of the vacuum distillation method described above. All of these experiments were conducted using the same Sevilleta sand that was used to pack the soil columns. First, systematic experiments were set up to determine the minimum heating and freezing times necessary to obtain unbiased soil water analyses. The results of these experiments are summarized in the experimental procedure above, but they are probably useful only for soil types similar to the sand tested. Details have been given by Knowlton (1989).

A second experiment employing numerous replicate samples was set up to assess the accuracy of the analytical procedure, its precision, and the sources of variability. In this experiment, four splits of a single soil sample were oven-dried and then wetted to 11.5% volumetric water content with distilled water having a composition of $-11.92 \pm 0.13‰$ $\delta^{18}O$ and $-96.6 \pm 0.7‰$ $\delta^{2}H$. Each split was separately distilled and the distillate divided into six aliquots. Three of the aliquots were reduced to

Table 1
Standard deviation estimates for hierarchical analysis of sources of variability in soil water analysis

Source	$\delta^{18}O$	$\delta^{2}H$
Distillation	0.130	0.97
Gas preparation	0.070	0.74
Mass spectrometry	0.022	0.14
Total	0.15	1.20

hydrogen gas by the zinc method for ^{2}H analysis and three were equilibrated with CO_2 for ^{18}O analysis. Each gas sample was then analyzed three times on the mass spectrometer, for a total of 36 ^{18}O and 36 ^{2}H analysis. The resulting data were evaluated by means of standard hierarchical statistics analysis (Snedecor and Cochran, 1973). The results are shown in Table 1; data are given by Knowlton (1989). Total standard deviations were calculated as the square root of the sum of the variances from the distillation, the gas preparation, and the mass spectrometer. The sample means and single standard deviations are $-11.93 \pm 0.15‰$ $\delta^{18}O$ and $-98.4 \pm 1.2‰$ $\delta^{2}H$. The means compare favorably with the distilled water used to wet the soil samples, and the standard deviations indicate adequate reproducibility for the purposes of this study. For ^{18}O, the hierarchical analysis indicates that irreproducibility in the distillation contributes about 75% of the total variance, the CO_2 equilibration contributes 22%, and the remaining 3% is attributed to the mass spectrometer. For ^{2}H the hierarchical analysis shows that 62% of the much larger total variance can be attributed to the distillation, 36% to the hydrogen gas reduction, and 2% to the mass spectrometer.

A third experiment was conducted to verify that the column emplacement, recovery, and sampling procedures did not unduly bias the resulting isotopic measurements. One of the soil columns, packed and processed in the same manner as all of the rest, was left in the ground for 24 h, then recovered, sampled, processed by distillation in the usual manner, and analyzed on the mass spectrometer. The results

Table 2
Moisture content and isotopic enrichment of water distilled from a soil column that was sampled 24 h after the emplacement: water used to wet the soil had $\delta^{18}O = -11.6‰$ and $\delta^{2}H = -97.7‰$, vs. Standard Mean Ocean Water (SMOW)

Depth (cm)		Moisture content (%)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
From	To			
2	4	4.62	−6.71	−70.1
4	6	4.63	−7.23	−73.6
8	10	5.96	−12.2	−93.5
24	28	6.44	−12.1	−94.6
45	50	6.71	−12.3	−90.2
65	70	6.72	−12.0	−90.7
95	100	7.00	−12.5	−97.7

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are given in Table 2. The top two samples, above 6 cm depth, have obviously already been enriched by evaporation. The means and standard deviations of the five samples below this depth are $-93.35 \pm 3.1‰$ δ^2H and $-12.21 \pm 0.17‰$ $\delta^{18}O$. These results show biases of +4.4 and −0.6‰ in δ^2H and $\delta^{18}O$ relative to the tap water used to wet the columns, which are small compared with the evaporative enrichments of approximately +40‰ ^2H and +15‰ ^{18}O that were observed later in the experiment. The standard deviation of the $\delta^{18}O$ analysis from the controlled field experiment is nearly the same as from the laboratory experiment, but the standard deviation of the ^2H field analysis is about twice that of the laboratory experiment. Only the ^{18}O results were numerically modeled.

The results of this testing indicate that the vacuum distillation method developed by Knowlton (1989) yields soil water isotopic analysis with accuracy and precision that compare favorably with the results of the methods evaluated by Ingraham and Shadel (1992) and Walker et al. (1994). The results compare well with those from the most widely employed method, azeotropic distillation using organic liquids. This vacuum distillation technique has the advantages that it does not require toxic and flammable organic liquids and that the distilled soil water can easily be weighed to evaluate the completeness of the distillation or determine the soil water content. It also avoids the drift in mass spectrometer readings that has sometimes been observed in samples from azeotropic distillations, which is apparently due to incomplete elimination of the organic phase from the water sample. It has the limitations that the distillation time is significantly longer than for azeotropic distillation (100–250 min compared with 30 min), that the high temperature of the distillation will probably extract water from gypsum and other hydrated phases, and that it has not been tested for fine-grained soils.

2.5. Moisture content at liquid discontinuity

In this study, the experimental soil is fairly homogeneous and thus should have a unique value for moisture content at liquid discontinuity θ_{wk}, which is a characteristic property of porous media (Philip and De Vries, 1957; Gee, 1966). Above the evaporation front (and for moisture content lower than θ_{wk}), soil water may be visualized as liquid islands linked by a vapor continuum (Philip and De Vries, 1957). Because of the large isotope fractionation accompanying evaporation, the evaporation front is clearly defined in the stable isotope profiles (Barnes and Allison, 1983). Barnes and Allison (1983) indicated that above the isotope peak, vapor flow is dominant and the liquid phase is discontinuous; below the isotope peak moisture content is higher, the liquid phase is continuous, and liquid water flow is dominant. The model of Barnes and Allison (1983) implicitly assumes that the isotope peak (the evaporation front) corresponds to the value of moisture content at liquid discontinuity. In this study, our approach for estimating the value of θ_{wk} is based on plots of isotopic enrichment against moisture content for columns subject to evaporation. Fig. 4 shows the oxygen-18 enrichment vs. moisture content for all experimental soil columns regardless of duration of evaporation. The maximum enrichment always occurs at the same value of moisture content, 2.6%, which is assumed to be the moisture content at

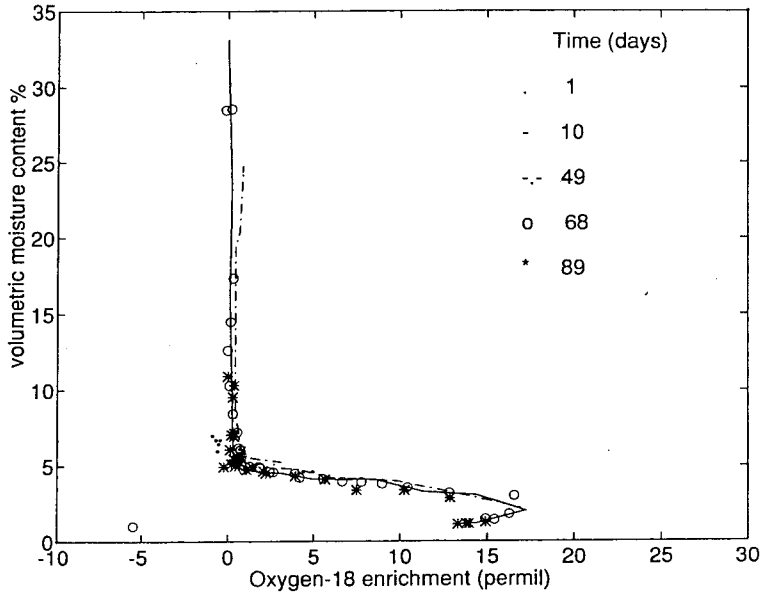

Fig. 4. Oxygen-18 enrichment as a function of moisture content for all experimental soil columns.

liquid discontinuity θ_{wk}. For very dry soils where the isotope peak is broad, the zone of combined vapor and liquid flow is very short (about 2 cm) and the moisture content change is very small (Shurbaji and Phillips, 1995), and for all practical purposes the value of moisture corresponding to the isotope maximum can be assumed to equal the moisture content at liquid discontinuity.

2.6. Retention relation and hydraulic conductivity function

The measured retention relation $\Psi(\theta)$ for the soil (Fig. 5(a)) was determined using the filter paper method of Fawcett and Collis-George (1967). For the same Sevilleta soil, McCord (1989) used a hanging column apparatus to measure the hysteretic retention relation. Based on seven cores, he presented the hanging column data shown in Fig. 5(a) for the average drying retention relation. The hanging column data set and the filter paper data set show very similar trends but the hanging column matric heads are systematically slightly more negative than the filter paper heads. The difference between these two data sets may be attributed to two factors. First, in the filter paper method, a disturbed soil sample was used, whereas, for the hanging column apparatus, a non-disturbed sample was used. Second, McCord averaged data from seven cores, whereas one set of data (from the homogenized soil used for packing the columns) was used for the filter paper method. The moisture content of importance in this study, where the soil profile is drying, is generally lower than the moisture range measured by the hanging column apparatus. For the field simulations, the filter paper data was used to parameterize the $\Psi(\theta)$ relationship because it

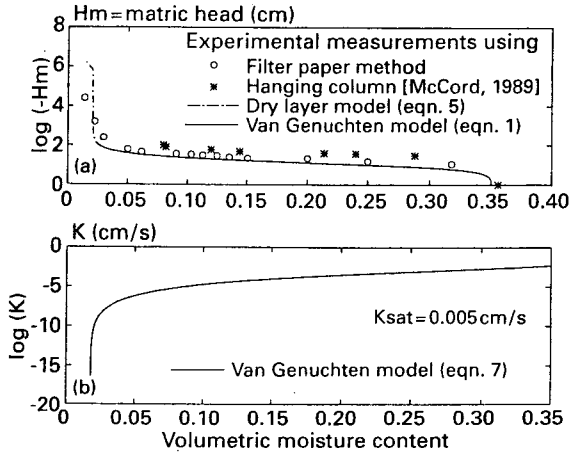

Fig. 5. (a) Matric head data and modeled relations as a function of moisture content; (b) modeled hydraulic conductivity as a function of moisture content.

provides data over a wider range of moisture contents and is suitable for very dry soils. The retention relation used in the ODWISH model consists of two segments joined at the value of moisture content at liquid discontinuity θ_{wk}.

The wet portion of the retention relation ($\theta_{wk} \leqslant \theta \leqslant n$) is prescribed by the Van Genuchten model (Van Genuchten, 1980)

$$\psi(\theta) = -\frac{1}{\alpha_2}[(S_{e2})^{-\frac{1}{\gamma}} - 1]^{\frac{1}{\beta_2}} \tag{1}$$

where S_{e2} and γ are given by the relations

$$S_{e2} = \frac{\theta - \theta_{r2}}{n - \theta_{r2}} \tag{2}$$

$$\gamma = 1 - \frac{1}{\beta_2} \tag{3}$$

where θ is the moisture content, n is the porosity, and θ_{r2}, β_2 and α_2 are Van Genuchten fitting parameters. The portion of the retention relation for moisture content lower than the moisture content at liquid discontinuity ($\theta_{r1} \leqslant \theta \leqslant \theta_{wk}$) should be parameterized in a way that reflects the fact that this portion applies to the dry layer above the evaporation front where vapor diffusion to the atmosphere controls the matric potential. The Kelvin relation (Edlefsen and Anderson, 1943, p. 145) provided the basis for the vapor flow formulations (Philip and De Vries, 1957) which were incorporated in the ODWISH model. The Kelvin relation is given by

$$\psi = \frac{RT}{g}\ln(h) \tag{4}$$

In this dry layer, or vapor flow zone, the relative humidity varies linearly from a value

close to unity at the evaporation front, h_{wk}, to the relative humidity value of the atmospheric air at the soil surface. A mathematical form analogous to Eq. (4) should be suitable for this zone. The form of the retention relation used for this portion was given by

$$\psi(\theta) = \beta_1 \ln[\alpha_1 + S_{e1}(h_{wk} - \alpha_1)] \tag{5}$$

in which the value of β_1 should be close to $\{RT/g\}$ and the value of α_1 should be close to the minimum atmospheric relative humidity in the study area or smaller. The value of h_{wk} is calculated by inverting Eq. (4) using $\Psi(\theta_{wk})$ for Ψ. $\Psi(\theta_{wk})$ is calculated from the Van Genuchten model, Eq. (1). In Eq. (5), S_{e1} is given by

$$S_{e1} = \frac{\theta - \theta_{r1}}{\theta_{wk} - \theta_{r1}} \tag{6}$$

where the value of θ_{r1} is chosen to be close to the minimum moisture content observed at the soil surface under dry conditions. In the equations above, the following should be observed: $\theta_{r1} \leqslant \theta_{r2} \leqslant \theta_{wk} \leqslant n$. The hydraulic conductivity function is given by (Van Genuchten, 1980)

$$K = 0 \qquad \theta < \theta_{wk}$$

$$K = K_s S_{e2}^{1/2}[1 - (1 - S_{e2}^{1/\gamma})^{\gamma}]^2 \qquad \theta > \theta_{wk} \tag{7}$$

where K_s is the saturated hydraulic conductivity. The experimental data were used to specify $\theta_{r1} = 0.013$, $\theta_{wk} = 0.026$, $n = 0.351$, and $\alpha_1 = 0.2$. The Van Genuchten equation parameters were fitted to match the retention data. Fig. 5 shows the experimental retention data, the two-segment retention relation given by the model presented above, and the unsaturated hydraulic conductivity. Values used to generate these relations were $\theta_{r2} = 0.021$, $\alpha_2 = 0.09$, $\beta_2 = 2.85$, and $K_s = 0.005$ cms^{-1}. These values were used in all of the model simulations.

3. Results and discussion

3.1. Sensitivity of parameters and relations

The relations and parameters which describe the soil under study are $\Psi(\theta)$, $K(\theta)$, $\lambda(\theta)$, n, τ^{v}, τ^{l}, and θ_{wk}. The transient water flow equation is most sensitive to the characteristic retention relation $\Psi(\theta)$ and hydraulic conductivity function $K(\theta)$. The heat transfer equation is sensitive to the thermal conductivity relation $\lambda(\theta)$. The isotope equation is sensitive to the temperature distribution (which depends on the thermal conductivity relation and temperature at the soil surface), to the atmospheric relative humidity, and to the retention relation and hydraulic conductivity function for wet profiles, and is almost not sensitive for very dry soils. None of the three governing equations in the ODWISH model (describing water flow, heat transfer, and isotope transport) is sensitive to porosity or tortuosity.

It is a common practice to adjust one or more of these relations and parameters,

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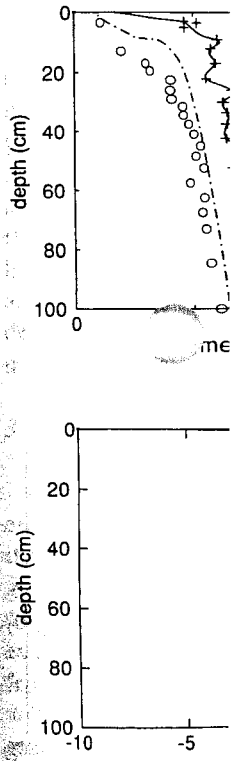

Fig. 6. Run 1: comparisc
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within their uncertainty limits, during calibration simulation runs until a good match is achieved between model predictions and observations. Other simulation runs may be used to justify the earlier choice of parameters. The value of θ_{wk} and the retention relation (given by Eq. (5)) for the dry layer (above the evaporation front) were obtained from the experimental data and will be left fixed in the simulations.

3.2. Comparison of simulations and field data

Two simulation runs were used for comparison with the controlled field experiment. The first run (referred to as Run 1) was for the 9 day period following the first day of the experiment. The second run (Run 2) was for the period between 49 and 69 days after the start of the field experiment. A gravity drainage (zero matric head gradient) boundary condition was used for the water flow equation at the bottom of the solution domain (1 m). This boundary condition is appropriate for the soil columns and is reasonable for field conditions. The values used in these simulations for depth increment Δz, time increment Δt, weight factor for time in the implicit finite

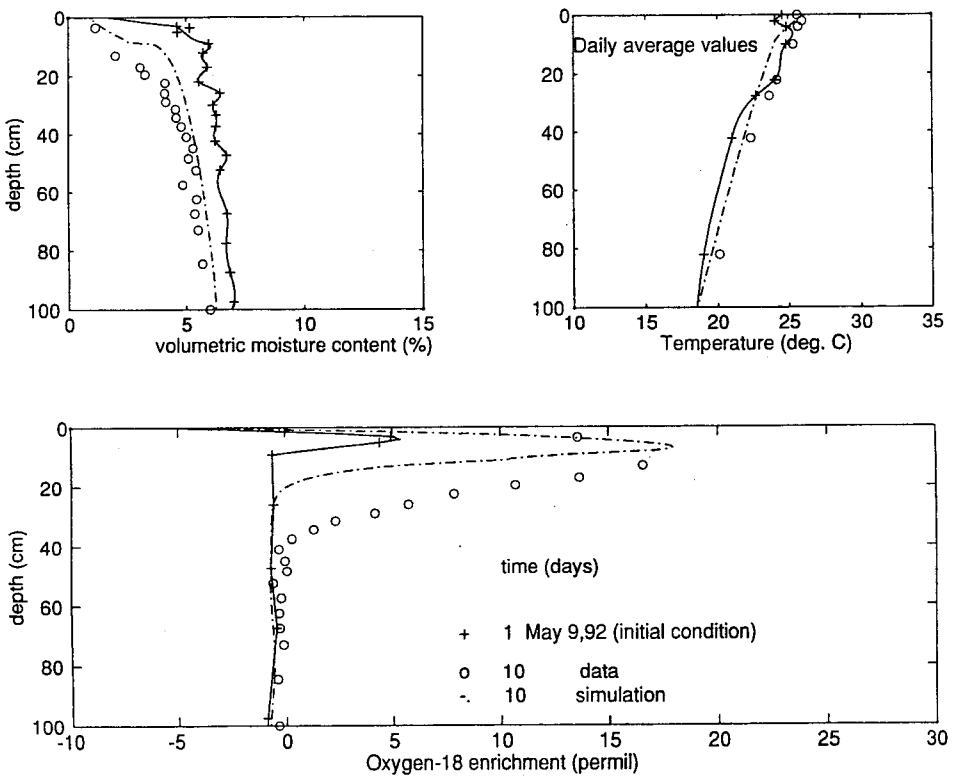

Fig. 6. Run 1: comparison between model simulations and experimental observations of moisture content, temperature, and oxygen-18 enrichment as a function of depth, after 10 days of evaporation.

difference equations of water and heat flow ω_1, and weight factor for time in the implicit finite difference equation of isotope transport ω_2 were 0.5 cm, 1 h, 0.7, and 0.7, respectively. The reader may refer to Shurbaji and Phillips (1995) for information about the numerical scheme used in ODWISH. For rigorous testing of the model performance in the field, it is important to extend the comparison between the observed profiles and the model predictions to include comparison of the cumulative fluxes of water, stable isotopes and heat with those calculated from the observed profiles. Also, it is important to obtain a good prediction of the detailed shape of the moisture and temperature distributions before any conclusions can be drawn about the isotope profile fit.

For low moisture contents the isotope profile development lost sensitivity for the changes in moisture content, and adjustment of the $\lambda(\theta)$ relationship was necessary to match the simulations to the observed oxygen-18 enrichment. The model output is sensitive to this relationship. The $\lambda(\theta)$ used in the model is compared with the field-measured $\lambda(\theta)$ from Knowlton (1989) in Fig. 3. The difference between the $\lambda(\theta)$ data and the adjusted relation may be because the field data were measured on undisturbed soil whereas the soil in the columns was repacked. Although the simulation in Run 1

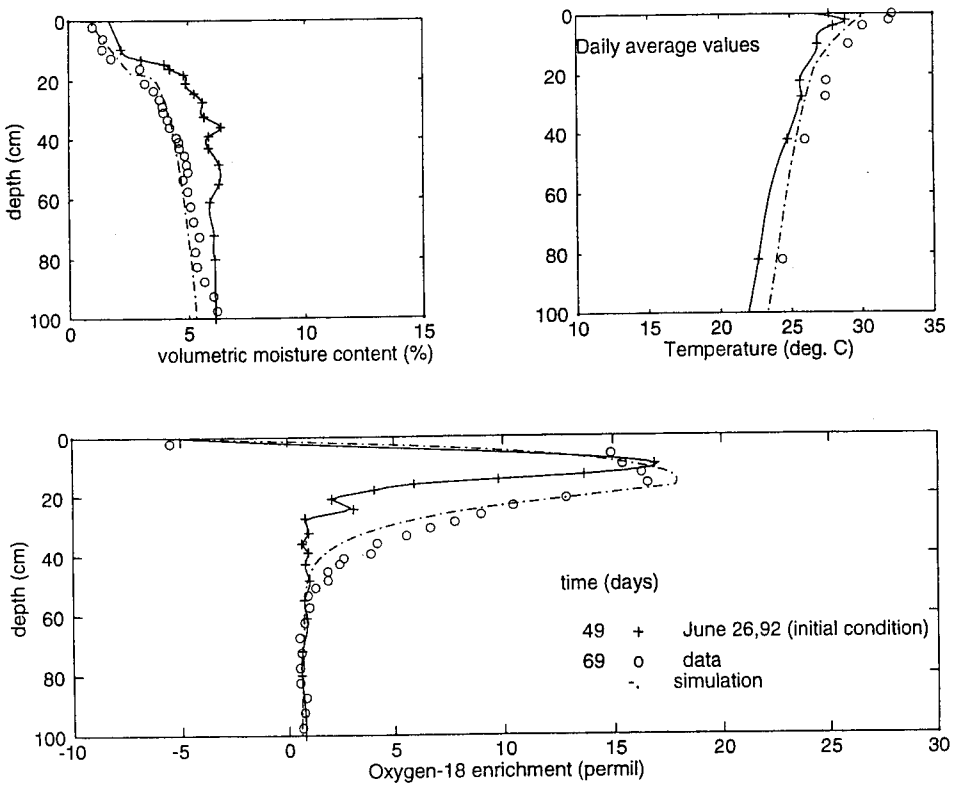

Fig. 7. Run 2: comparison between model simulations and experimental observations of moisture content, temperature, and oxygen-18 enrichment as a function of depth, after 69 days of evaporation.

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3.3. Development

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reproduces well the general magnitude of the oxygen-18 enrichment, it yields a somewhat shallower and thinner bulge of enrichment (Fig. 6). Comparison of the simulated and measured moisture content distributions in Fig. 6 shows that this discrepancy can be attributed to the shallower and more abrupt evaporation front calculated by the model. This, in turn, is due to the steep slope of the matric potential with moisture content in the vicinity of the moisture content at liquid discontinuity, as compared with the filter paper data (Fig. 5). The two-segment relation used in the model is not smooth in the vicinity of the evaporation front because the moisture content at liquid discontinuity (which is used to locate the evaporation front) was used in the retention relation as the connection point between the Kelvin (dry-layer) and Van Genuchten equations and differentiability at this connection point is not insured. We expect that implementation of a retention relation having a smoother curve at the value of moisture content at liquid discontinuity would produce smoother moisture distributions. By looking into this simulation run alone, the adjustment of $\lambda(\theta)$ may not be considered final, and may need to be reevaluated after fixing the discrepancies in the moisture distribution.

Fig. 7 compares the field and simulated data for Run 2. Exactly the same model parameter values were used as in Run 1. In this case, the match between the measured and calculated distributions of moisture, temperature, and oxygen-18 enrichment is very good. As the evaporation front deepens, and the humidity gradient between the evaporation front and the surface becomes less steep, the influence of the abrupt $d\Psi/d\theta$ produced by the Kelvin relation close to θ_{wk} evidently lessens, and a more gradual and realistic evaporation front is simulated. These comparisons indicate that the model simulates the main processes involved in evaporation from soils and the associated isotopic enrichment. However, they also illustrate that the particulars of the evolution of stable isotope profiles in evaporating soil water are sensitive to the hydraulic and thermal relations governing the evaporation process and that additional effort is warranted to develop and test formulations that more realistically describe the retention relation over the entire range from saturation to near-zero moisture contents.

3.3. Development of depth distributions

Fig. 8 illustrates the development of the depth distributions of moisture, oxygen-18 enrichment, and water vapor flux. The initial distribution was the same as for Run 1, that of the column sampled 1 day after evaporation started. The distributions are given for 3 days later and 10 days after the start of the experiment. At the drying front (evaporation front) water is enriched in the heavy isotopes as a result of water evaporation and the resulting isotopic fractionation. As time goes on, the drying front progresses deeper in the soil profile, and the evaporation rate decreases.

The average temperature gradient was 8°C m $^{-1}$ in the top 1 m. This temperature gradient causes part of the evaporated water to move downward in the vapor phase below the evaporation front. However, the value of the downward vapor flux in the zone below the evaporation front is much smaller than the upward water vapor flux in the dry layer above the evaporation front. The downward water vapor flux decreases

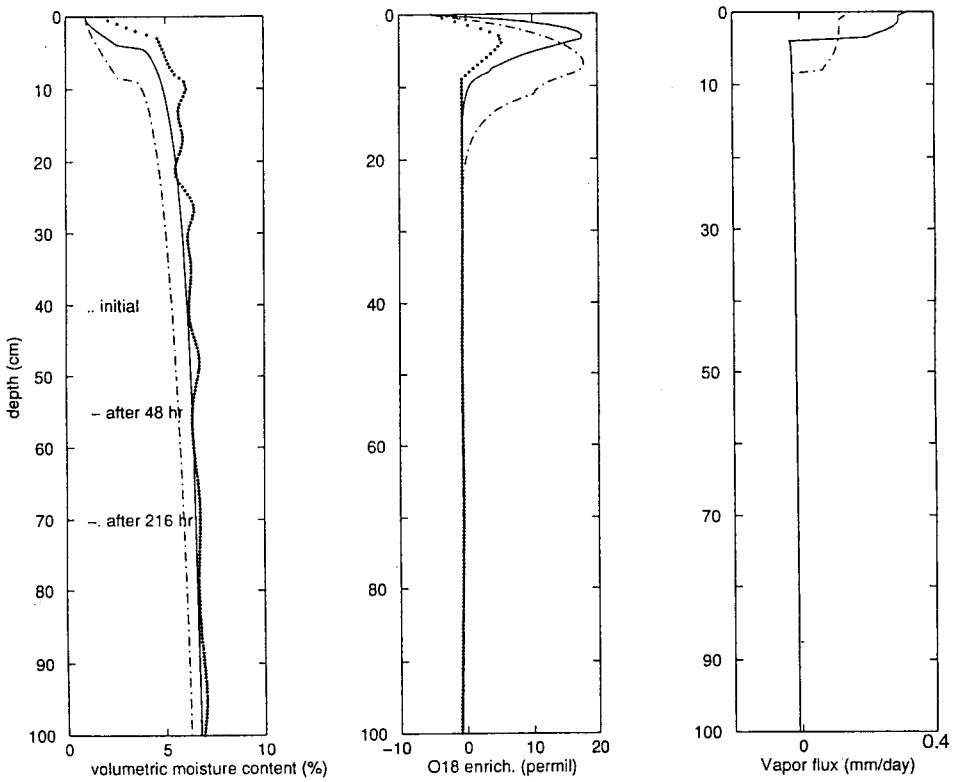

Fig. 8. Development of moisture content, oxygen-18 enrichment, and vapor flux distributions for Run 1.

with depth, which means that part of this water is condensed on the soil. This downward water vapor movement, and the consequent condensation, is not sufficient to change the curvature of the isotope profile.

3.4. *Effect of diurnal fluctuations in temperature and humidity*

Diurnal variations cause profound fluctuations in the upper boundary conditions for the model. For example, the near-surface temperature gradient reverses twice every 24 h. These fluctuations could potentially have significant effects on the development of the stable-isotope profiles. Barnes and Allison (1984) observed that the main effect of changing temperature on isotope profiles is on the height of the isotope peak, whereas other characteristics of the isotope profile are insensitive, and also that the establishment of the isotope profile takes several days or longer. Thus they concluded that the shape of the isotope profiles is not affected by diurnal fluctuations of humidity and temperature at the surface but by the average values. However, the effects of surface fluctuations on isotope profiles cannot be investigated by the commonly employed quasi-steady-state solutions. Using the ODWISH model,

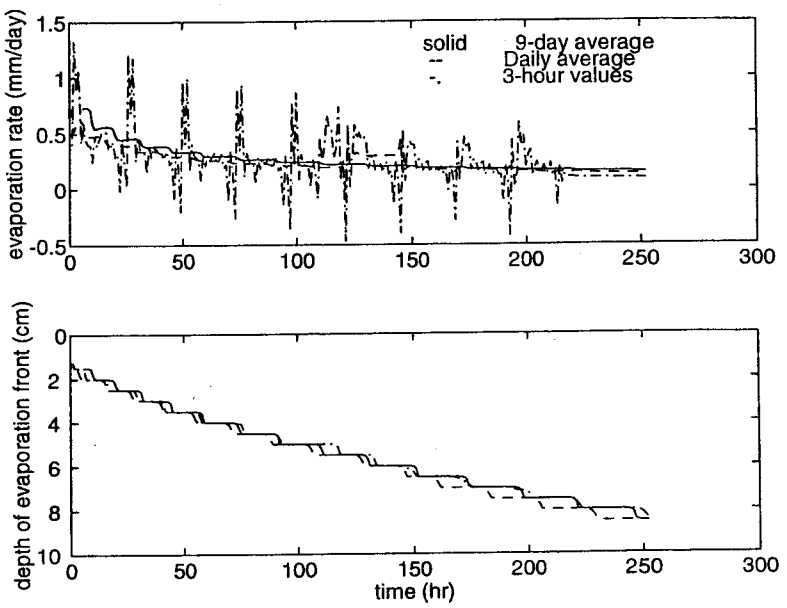

Fig. 9. History of evaporation rate and depth of evaporation front using three averaging periods for T and h.

a series of simulations therefore was conducted to assess the extent to which averaging of surface conditions affected the final stable-isotope distribution.The temporal average study was based on simulation Run 1. Fig. 9 shows the history of the evaporation rate and depth of the evaporation front during the 9 day period. Three data levels were considered for comparison. In the first case, the average temperature and humidity during the entire 9 day simulation period was used in the simulation. In the second case, the record of average daily temperature and relative humidity was used. In the third case, the eight daily measurements of temperature and humidity were used. The graph of evaporation rate using the entire data set shows that there was a short period during the night where the relative humidity was high and the temperature gradient reversed, resulting in downward movement of water vapor from the surface. The magnitude of the downward vapor flux is not large and the duration is short, thus the progress of the evaporation front depth is little affected by the fluctuations. Fig. 10 shows the effect of the three data averaging periods on the moisture content and isotope enrichment distributions. There is little difference between the simulations using the daily average surface condition and the daily fluctuating condition. The distributions resulting from the 9 day average boundary condition are only moderately different from those where average daily values were used. Thus, data on the average daily temperature and relative humidity at the soil surface should normally be adequate to model water flow and isotope transport in the shallow unsaturated zone. The moisture content distribution is almost completely insensitive to the daily fluctuations in the surface humidity and temperature.

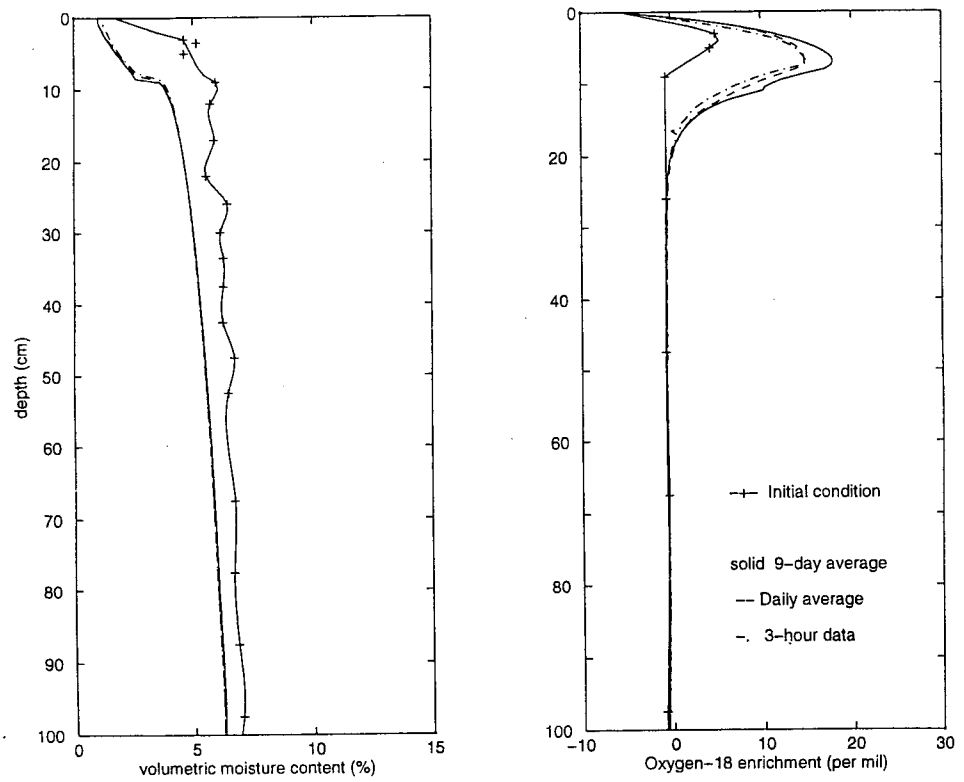

Fig. 10. Comparison between model predictions of moisture content and oxygen-18 enrichment after 9 days of evaporation for the three averaging periods.

Obtaining high-resolution humidity and temperature data is often difficult and apparently adds little to the accuracy of moisture or isotope distribution simulations. The isotope profile and moisture distribution develop over a relatively long time period and the daily fluctuations are quickly averaged out. Even weekly average values of temperature and humidity might be reasonable for simulation of long continuous drying periods.

4. Conclusions

A controlled field experiment was conducted to study second-stage evaporation in soils using oxygen-18 isotope profiles and their relation to moisture and temperature distributions. The data necessarily provide a basis for evaluating the ODWISH isotope transport model by comparing model predictions with field observations. Application of the model required a retention relation that is applicable over the entire range from very dry soils (where the soil moisture film is discontinuous) to wet soils (where the liquid film is continuous). A reliable method for determining the

value of moisture content at liquid discontinuity is also needed for the application of ODWISH, which calculates water vapor flow following the Philip and De Vries theory (1957).

Experimental observations showed that, for a given soil and regardless of the evaporation period, the maximum isotope enrichment occurs at a unique value of moisture content. This value was used as an estimate of the moisture content at liquid discontinuity, which is used also within the ODWISH model to locate the evaporation front in the soil profile. Measured isotope profile peaks in soils undergoing evaporation could be used to determine the value of this parameter, which is difficult to determine accurately using other physical methods. A dry-layer model was developed and connected to the Van Genuchten model for describing the retention relation. The dry-layer model was derived based on analogy with the Kelvin relation, which is applicable to dry soils and is the basis for the vapor flow formulations.

Based on two simulations for different evaporation periods, the model reasonably reproduces the experimentally observed depth distributions of moisture content, temperature and isotopic enrichment. These comparisons, together with the model testing in Shurbaji and Phillips (1995), indicate that the hydrologic–isotopic model satisfactorily simulates the processes involved in transient water movement in the shallow unsaturated zone and the associated isotope transport and fractionation processes, but also shows some discrepancy between the predicted and measured moisture distributions in the vicinity of the evaporation front. This is attributed to lack of smoothness in the two-segment retention relation at the connection of the two segments. A smoother transition between the two segments, possibly by including a third segment, should result in smoother moisture distributions and thus more realistic isotopic simulations. The three-segment relation of Rossi and Nimmo (1994) may offer a solution to this problem. We recommend testing this relation by implementing it in a numerical model that is capable of simulating moisture and heat transfer in the topsoil (e.g. Milly, 1982; Shurbaji and Phillips, 1995). The study also indicated that the development of the isotope profiles is sensitive to the thermal and hydraulic characteristics of the soil. This sensitivity could potentially be used to infer these properties in field studies. Based on comparison between simulations using different temporal averaging periods for humidity and temperature data at the soil surface, it was found that isotope profiles can be adequately reproduced using daily average values of humidity and temperature at the surface.

Acknowledgments

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