

Dear reviewer,

Thank you for your comments, the following are our responses. Comments are highlighted in boldface and our responses are in normal text.

(‘Equation’ refers to the equations in manuscript, while ‘Eq’ refers to the equations in this document.)

The paper has some interesting aspects. A fully coupled isotope transport model in the soil-plant-atmosphere continuum needs to be improved in the recent literature. Some approximations have been made to simulate isotope transport in soil using HYDRUS for example, but the results could be better. This is an intricate problem that must consider water content and movement influences water temperature, and both influence isotope transport and fractionation, and temperature may also affect water movement.

The paper claims to solve the transport equations simultaneously. I would like to see the numeric scheme that shows this back-forward process. And yet more information about it is needed. Unfortunately, numerical implementation has only one paragraph.

Thank you for your comments. Indeed, we did not introduce how to solve soil water, heat, and isotope transport equations simultaneously, and the solvers we used in detail. We will provide this information as appendix in the revised version of manuscript.

The transport equations of soil water, heat, and isotopes are:

$$\frac{\partial \theta}{\partial t} + \frac{\partial \theta_v}{\partial t} = -\frac{\partial q}{\partial z} - S \quad (1)$$

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = -\frac{\partial q_T}{\partial z} \quad (2)$$

$$\frac{\partial (C_{il}(\theta + a\theta_v))}{\partial t} = -\frac{\partial q_i}{\partial z} - C_{il}S \quad (3)$$

where θ and θ_v are the soil water content and equivalent liquid water content ($\text{m}^3 \text{m}^{-3}$), respectively; q is the water flux (m s^{-1}); S is the sink term (s^{-1}); C_{soil} is the soil heat capacity ($\text{J m}^{-3} \text{K}$); T is the temperature; λ_E is the latent heat of vaporization (J kg^{-1}); ρ is the water density (kg m^{-3}); q_T is the heat flux ($\text{J m}^{-2} \text{s}^{-1}$); C_{il} is the isotopic concentration of soil water (kg m^{-3}); α is the equilibrium fractionation coefficient (α^* in the manuscript); q_i is the isotopic flux ($\text{kg m}^{-2} \text{s}^{-1}$). Detailed description of Eq. (2) can be referred to Appendix A.

The equivalent liquid water content θ_v ($\text{m}^3_{\text{liquid water}} \text{m}^{-3}_{\text{soil}}$) can be expressed by pore space within soil $\theta_s - \theta$ ($\text{m}^3_{\text{air}} \text{m}^{-3}_{\text{soil}}$) and the saturated vapor concentration within soil air is expressed as Cv_{sat} ($\text{m}^3_{\text{liquid water}} \text{m}^{-3}_{\text{air}}$):

$$Cv_{sat} = \frac{m^3_{\text{liquid water}}}{m^3_{\text{air}}} = \frac{\frac{\text{mass}_{\text{liquid water}}}{\rho_{\text{liquid water}}}}{\frac{\text{mass}_{\text{air}}}{\rho_{\text{air}}}} = \frac{\frac{\text{mass}_{\text{vapor}}}{\rho_{\text{liquid water}}}}{\frac{\text{mass}_{\text{air}}}{\rho_{\text{air}}}} \quad (4)$$

where θ_s is the saturated soil water content ($\text{m}^3 \text{m}^{-3}$); $m^3_{\text{liquid water}}$ and m^3_{air} are the volume of liquid water (m^3) and air (m^3) within soil pore space; $\text{mass}_{\text{liquid water}}$ and mass_{air} are the mass of liquid water (kg) and mass of air (kg) in the soil pore space; $\rho_{\text{liquid water}}$ and ρ_{air} are the density of liquid water (kg m^{-3}) and air (kg m^{-3}), respectively; $\text{mass}_{\text{vapor}}$ is the mass of vapor (kg) within soil

pore space.

Then, the ideal gas law can be incorporated into Eq. (4):

$$Cv_{sat} = \frac{\frac{mass_{vapor}}{\rho_{liquid\ water}}}{\frac{mass_{air}}{\rho_{air}}} = \frac{\rho_{air}}{\rho_{liquid\ water}} \frac{P_{vapor_{sat}} M_{water}}{P_{air} M_{air}} \quad (5)$$

where $P_{vapor_{sat}}$ and P_{air} are the saturated vapor pressure (kpa) and air pressure (kpa), respectively; M_{water} and M_{air} are the mole weight of water ($kg\ mol^{-1}$) and air ($kg\ mol^{-1}$), respectively.

Eq. (5) can be further simplified by applying the ideal gas law again on P_{air} :

$$Cv_{sat} = \frac{\rho_{air}}{\rho_{liquid\ water}} \frac{P_{vapor_{sat}} M_{water}}{P_{air} M_{air}} = \frac{\rho_{air}}{\rho_{liquid\ water}} \frac{P_{vapor_{sat}} M_{water}}{\rho_{air} \frac{R}{T} M_{air}} \quad (6)$$

where R is the ideal gas constant ($J\ mol^{-1}\ K^{-1}$). Similarly, the unsaturated vapor concentration in soil pore space in terms of equivalent liquid water content, Cv , is given by:

$$Cv = \frac{\rho_{air}}{\rho_{liquid\ water}} \frac{P_{vapor_{sat}} M_{water}}{P_{air} M_{air}} = \frac{\rho_{air}}{\rho_{liquid\ water}} \frac{P_{vapor} M_{water}}{\rho_{air} \frac{R}{T} M_{air}} \quad (7)$$

Saturated vapor pressure, $P_{vapor_{sat}}$, can be calculated by Tetens formula (Ham, 2015). Then, Cv_{sat} is written as:

$$Cv_{sat} = \frac{0.61078 e^{\frac{17.269T}{T+237.29}} M_{water}}{\rho_{liquid\ water} RT} \quad (8)$$

Considering the influence of variation of both soil water content and temperature on the relative humidity, h_r is given by (Philip, 1957):

$$h_r = e^{\frac{M_w h_g}{RT}} \quad (9)$$

Besides, according to the definition of h_r :

$$h_r = \frac{P_{vapor}}{P_{vapor_{sat}}} \quad (10)$$

which can be rewritten by combining Eqs. (6) and (7):

$$h_r = \frac{Cv}{Cv_{sat}} \quad (11)$$

Therefore, the equivalent water content of the volumetric water vapor content, θ_v , can be written as:

$$\theta_v = (\theta_s - \theta) Cv_{sat} h_r \quad (12)$$

Introducing Eq. (12) to Eqs. (1) - (3):

$$\frac{\partial \theta}{\partial t} + \frac{\partial((\theta_s - \theta) Cv_{sat} h_r)}{\partial t} = -\frac{\partial q}{\partial z} - S \quad (13)$$

$$\frac{C_{soil} \partial T}{\partial t} + \frac{\rho \lambda_E \partial((\theta_s - \theta) Cv_{sat} h_r)}{\partial t} = -\frac{\partial q_T}{\partial z} \quad (14)$$

$$\frac{\partial(C_{ii}(\theta + a Cv_{sat} h_r (\theta_s - \theta)))}{\partial t} = -\frac{\partial q_i}{\partial z} - C_{ii} S \quad (15)$$

Note that the head-based Richards' equation is used in our model, $\frac{\partial h}{\partial t}$, $\frac{\partial T}{\partial t}$, and $\frac{\partial C_{il}}{\partial t}$ are isolated to solve Eq. (13), (14), and (15) for h , T , and C_{il} at each time step simultaneously. Since $C_{v_{sat}}$ is the function of T (Eq. (8)), h_r is the function of h and T (Eq. (9)), and α is the function of T (Equation. (18)), the analytical expressions of $\frac{\partial h}{\partial t}$, $\frac{\partial T}{\partial t}$, and $\frac{\partial C_{il}}{\partial t}$ can be written as:

$$\frac{\partial h}{\partial t} = \frac{1}{A} \left(-\frac{\partial q_T}{\partial z} - B \frac{\left(\frac{A}{C} \left(\frac{\partial q}{\partial z} + S \right) + \frac{\partial q_T}{\partial z} \right)}{\frac{D}{C^{A-B}}} \right) \quad (16)$$

$$\frac{\partial T}{\partial t} = \frac{\frac{A}{C} \left(\frac{\partial q}{\partial z} + S \right) + \frac{\partial q_T}{\partial z}}{\frac{D}{C^{A-B}}} \quad (17)$$

$$\frac{\partial C_{il}}{\partial t} = \frac{F}{E} \quad (18)$$

with coefficients A to E:

$$A = \rho \lambda_E \left((\theta_s - \theta) C_{v_{sat}} \frac{\partial h_r}{\partial h} - C_{v_{sat}} h_r \frac{\partial \theta}{\partial h} \right) \quad (19)$$

$$B = C_{soil} + \rho \lambda_E \left((\theta_s - \theta) C_{v_{sat}} \frac{\partial h_r}{\partial T} + (\theta_s - \theta) h_r \frac{\partial C_{v_{sat}}}{\partial T} \right) \quad (20)$$

$$C = (1 - C_{v_{sat}} h_r) \frac{\partial \theta}{\partial h} + (\theta_s - \theta) C_{v_{sat}} \frac{\partial h_r}{\partial h} \quad (21)$$

$$D = (\theta_s - \theta) C_{v_{sat}} \frac{\partial h_r}{\partial T} + (\theta_s - \theta) h_r \frac{\partial C_{v_{sat}}}{\partial T} \quad (22)$$

$$E = \theta + \alpha C_{v_{sat}} h_r (\theta_s - \theta) \quad (23)$$

$$F = -\frac{\partial q_i}{\partial z} - C_{il} S - C_{il} \frac{\partial \theta}{\partial h} \frac{\partial h}{\partial t} -$$

$$C_{il} \theta_s \left(C_{v_{sat}} h_r \frac{\partial \alpha}{\partial T} \frac{\partial T}{\partial t} + \alpha h_r \frac{\partial C_{v_{sat}}}{\partial T} \frac{\partial T}{\partial t} + \alpha C_{v_{sat}} \left(\frac{\partial h_r}{\partial h} \frac{\partial h}{\partial t} + \frac{\partial h_r}{\partial T} \frac{\partial T}{\partial t} \right) \right) + C_{il} \left(C_{v_{sat}} h_r \theta \frac{\partial \alpha}{\partial T} \frac{\partial T}{\partial t} + \alpha h_r \theta \frac{\partial C_{v_{sat}}}{\partial T} \frac{\partial T}{\partial t} + \alpha C_{v_{sat}} h_r \frac{\partial \theta}{\partial h} \frac{\partial h}{\partial t} \right) \quad (24)$$

Eqs. (13), (14), and (15) were transformed into a system of coupled ordinary differential equations by Eqs. (16)-(24). This system is solved by MATLAB solvers (ode113/ode23tb) simultaneously.

The derivative vector $\left(\frac{\partial h}{\partial t}, \frac{\partial T}{\partial t}, \text{ and } \frac{\partial C_{il}}{\partial t} \right)$, having a length of the number of spatial discretization multiplied by three.

To construct the derivative vector, values from Eq. (17) were calculated firstly because they were also used in Eq. (16). Eq. (17) shows that temporal variation of temperature was influenced by q , q_T , θ , and other parameters from coefficients A - D . Reversely, T influences h_r and $C_{v_{sat}}$ (Eqs. (19)-(22)) and further affect the water transport within soil (Eq. (16)).

Eq. (16) showed that temporal variation of h was closely related to T because $\frac{\left(\frac{A}{C} \left(\frac{\partial q}{\partial z} + S \right) + \frac{\partial q_T}{\partial z} \right)}{\frac{D}{C^{A-B}}}$ from

Eq. (16) is $\frac{\partial T}{\partial t}$ (Eq. (17)). Besides, soil heat properties, such as soil heat capacity and latent heat of

vaporization (included in coefficients A and B), were also involved in soil water (vapor) movement.

Eq. (24) shows that isotope transport was influenced by all the parameters coupled. Specifically, water transport (Eq. (16)) affects isotopic fluxes since isotopes were treated as solutes, while heat transport (Eq. (17)) had an influence on equilibrium fractionation coefficients and further on the isotopic concentration in soil water. Both water and heat transport affected h_r and $C_{v_{sat}}$ in soil. Therefore, values for derivative vector construction from Eq. (18) were calculated based on Eqs. (16), (17), (23), and (24).

Finally, the derivative vector, along with the initial conditions and the time span were passed to the solvers. The solver then computed the solution of this system over the specified time span numerically. Numerical schemes of solvers are described below.

Numerical scheme of ode113

The ode113 solver uses an adaptive, variable-order, variable-step-size (VOVS) method. This is implemented with a variable order Adams-Bashforth-Moulton (ABM) method (ode113, 2023), which is a combination of an explicit types of the Adams-Bashforth (AB) and an implicit type of Adams-Moulton (AM) methods. Specifically, the AB method is used to estimate the solution at the new time step by taking multiple previous time steps into account, while the AM method is used to make corrections.

The ode113 can select automatically between the 1st and 13th order approximation (the highest order used appears to be 12) during the computation based on the estimation errors. This is helpful for minimizing the estimated errors and for achieving high efficiency in time. Moreover, the time step size is adjusted according to the estimation error. In this way, ode113 can handle a wide range of ODE problems with high accuracy and efficiency.

Therefore, ode113 can do a good job when the transport media is relatively uniform. However, ode113 is susceptible to numerical oscillation when hydraulic conductivities between layers differed greatly because of the adopted explicit scheme.

Numerical schemes of ode23tb

Ode23tb is a solver specifically designed for solving ODEs with highly oscillatory solutions (ode23tb, 2023), such as those arising from heterogeneity in hydraulic conductivities between soil layers. The 'tb' stands for that the solver combines a trapezoidal rule (sometimes referred as the second-order AM method (Adams methods, 2023)) with a 2nd order backward differentiation formula (BDF). Because of this, ode23tb is an efficient and accurate solver for stiff ODE systems, making it less susceptible to numerical instability.

Like ode113, ode23tb can adjust the step size automatically based on the estimated error and the oscillatory behavior of the solution. However, ode23tb is an implicit solver, making it more computationally expensive than other solvers. But because it adopts the trapezoidal BDF method, it is more efficient and accurate than other types of implicit methods, such as the fully implicit Euler method or the backward Euler method (Time integration, 2023). Therefore, ode23tb may work

better than ode113 when the soil physical properties are greatly differed between layers.

Another question is, how do equations 41 and 42 take isotope fractionation from temperature variation into account?

Thank you for your comments. Equation (41) and (42) in the manuscript are ‘thought’ experiment. They were used to illustrate the error difference between segregated and coupled methods. The segregated method may introduce more errors than coupled method because more errors could be accumulated as compared to the coupled method. The coupled method, however, can reduce the error accumulation by solving a set of equations simultaneously. In our manuscript, Equation (41) and (42) were used as an example for understanding the error difference between segregated and coupled method.

Appendix A:

The heat transport equation within soil is written as:

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = \frac{\partial}{\partial z} \left(k_H \frac{\partial T}{\partial z} \right) - C_w q_l \frac{\partial T}{\partial z} - C_{vh} \frac{\partial q_v T}{\partial z} - \rho \lambda_E \frac{\partial q_v}{\partial z} \quad (A1)$$

Eq. (A1) can be rewritten by the chains rule:

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = \frac{\partial}{\partial z} \left(k_H \frac{\partial T}{\partial z} \right) - C_w q_l \frac{\partial T}{\partial z} - C_{vh} q_v \frac{\partial T}{\partial z} - C_{vh} T \frac{\partial q_v}{\partial z} - \rho \lambda_E \frac{\partial q_v}{\partial z} \quad (A2)$$

Then:

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = \frac{\partial}{\partial z} \left(k_H \frac{\partial T}{\partial z} \right) - (C_w q_l + C_{vh} q_v) \frac{\partial T}{\partial z} - (C_{vh} T + \rho \lambda_E) \frac{\partial q_v}{\partial z} \quad (A3)$$

where $C_w q_l + C_{vh} q_v$ and $C_{vh} T + \rho \lambda_E$ can be treated as constants within each layer, and Eq. (A3) is written as:

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = - \frac{\partial}{\partial z} \left(-k_H \frac{\partial T}{\partial z} + Constant_1 T + Constant_2 q_v \right) \quad (A4)$$

where $Constant_1 = C_w q_l + C_{vh} q_v$ and $Constant_2 = C_{vh} T + \rho \lambda_E$.

Assuming $q_T = -k_H \frac{\partial T}{\partial z} + Constant_1 T + Constant_2 q_v$, then:

$$C_{soil} \frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = - \frac{\partial q_T}{\partial z} \quad (A5)$$

Eq. (A5) is the same as Eq. (2).

Reference

Time integration:

https://space.mit.edu/RADIO/CST_online/mergedProjects/DES/theory/time_integration.htm, last access: 28 February 2023.

Ham, J. M.: Useful equations and tables in micrometeorology, *Micrometeorology in Agricultural Systems*, 533–560, <https://doi.org/10.2134/agronmonogr47.c23>, 2015.

ode23tb: <https://www.mathworks.com/help/matlab/ref/ode23tb.html>, last access: 28 February 2023.

ode113: <https://www.mathworks.com/help/matlab/ref/ode113.html>, last access: 28 February 2023.

Philip, J. R.: Evaporation, and moisture and heat fields in the soil, *Journal of Meteorology*, 14, 354–366, [https://doi.org/https://doi.org/10.1175/1520-0469\(1957\)014<0354:EAMAHF>2.0.CO;2](https://doi.org/https://doi.org/10.1175/1520-0469(1957)014<0354:EAMAHF>2.0.CO;2), 1959.

Adams methods:

https://web.mit.edu/10.001/Web/Course_Notes/Differential_Equations_Notes/node6.html, last access: 28 February 2023.