Dear reviewer,

We were so lucky to receive such a detailed and high-quality review from you. This is one of the best review comments we received in the last two years in my academic career, and it will substantially improve the quality of manuscript.

As such, we are happy to provide our responses below to each of your comments. Comments are highlighted in boldface and our responses are in normal text.
('Eq' refers to the equations in manuscript, while 'Equation' refers to the equations in this document.)

We believe our objective is to exhibit the robustness and accuracy of MOIST, rather than have new insights into existing experiments. While our validations are not exhaustive, we have compared MOIST with two revised versions of HYDRUS-1D, which were published by Stumpp et al. (2012) and Zhou et al. (2021), respectively. Figure 11 in the manuscript showed that the results obtained from MOSIT were comparable to those obtained using two versions of revised HYDRUS-1D, and the statistical information presented in Table 6 indicated that MOIST slightly outperforms than them under certain conditions. However, we acknowledge that more validations are necessary in the future.

Regarding to the sensitivity analysis on the choice of kinetic fractionation factor formulations, we have included this in Appendix A of this document and plan to put it in the discussion section of the revised manuscript.

0/ It would be useful to provide a list of notations with the units.

Thank you for your comments. We will provide a list of notations with the units as appendix in the revised manuscript.

1/L39: do you really address this problem with the MOIST model?

In the study of Haverd and Cuntz (2010), the heat flux was calculated as the sum of sensible and latent heat (Eq. A.24 from Haverd and Cuntz (2010)), without considering the variation of heat capacity of the liquid and vapor phases. We implemented these variations in our heat transport equation. However, this consideration was not originally addressed in our work; rather, we just highlighted a limitation in the heat transport equation used by Haverd and Cuntz (2010).

2/ L57: I do not consider that a Matlab program is something fully accessible as paying for an expensive Matlab licence is necessary to use the developments

Thank you for your comments. MATLAB is one of widely used computer programming environment. We chose MATLAB because the good performance of the ode solvers, as described in Appendix B. Once well-tested, we will consider migrating MOIST to an open-source language, such as Python, so that the program is available both in MATLAB and Python.

3/ Eq. (4) Dv is not defined

Thank you for your comments. We will define Dv in the revised manuscript.

4/ Eq. (5) looks strange

Thank you for pointing out a typo in the manuscript (our program used the correct equation). The Eq. (5) should be:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = \frac{\partial}{\partial z}\left(k_H\frac{\partial T}{\partial z}\right) - C_w q_l\frac{\partial T}{\partial z} - C_{vh}\frac{\partial q_v T}{\partial z} - \rho\,\lambda_E\frac{\partial q_v}{\partial z} \tag{1}$$

5/ Eq (10) in Braud et al. (2005) (their Equation (9) has an additional term). Why do you neglect it (as in Haverd and Cuntz, 2010)?

Thank you for your comments. We did not neglect the additional term. As shown below, the Cv term in Equation (2) includes the additional term in Braud et a. (2005). Considered the vapor movement within soil is dominated by the Fick's law:

$$q_v = -D_v\,\frac{\partial c_v}{\partial z} \tag{2}$$

Similarly, the isotope movement in vapor phase within soil can be written as:

$$q_{iv} = -D_{iv}\frac{\partial c_{iv}}{\partial z} \tag{3}$$

However, Equation. (3) can be further written as:

$$q_{iv} = -D_{iv}\frac{\partial c_{iv}}{\partial z} = -D_{iv}\frac{\partial(c_v\,\alpha\,c_{il})}{\partial z} = -D_{iv}\alpha\,c_{il}\frac{\partial c_v}{\partial z} - D_{iv}c_v\left(\alpha\frac{\partial c_{il}}{\partial z} + c_{il}\frac{\partial\alpha}{\partial z}\right) \tag{4}$$

Then, by incorporating $\frac{D_{iv}}{D_v} = \alpha_{diff}$ and Equation. (2):

$$q_{iv} = -\alpha_{diff}\alpha\,c_{il}q_v - D_{iv}c_v\left(\alpha\frac{\partial c_{il}}{\partial z} + c_{il}\frac{\partial\alpha}{\partial z}\right) \tag{5}$$

Therefore, the isotope movement in vapor phase consists of a convection term ($-\alpha_{diff}\alpha\,c_{il}q_v$) and a diffusion term ($-D_{iv}c_v\,\alpha\frac{\partial c_{il}}{\partial z}$), as shown in the Braud et al. (2005).

6/ Eq. (12) there are several options in the literature for the specification of nD. Why do you chose this formulation?

Thank you for your comments. We chose nD equation from Melayah et al. (1996) because it describes the isotopic fractionation, which is caused by diffusion, in both wet and dry soil. In addition, the sensitivity analysis (Appendix A) showed that the MOIST is not sensitive to the choice of formulations when considering kinetic fractionation. Moreover, Braud et al. (2005) have stated that there are no objective criteria for selecting one formulation over others. Nevertheless, in the future, we can easily update this formulation in the MOIST source code with a more reasonable one, if needed.

7/ Eq. (24) and (25) (even if taken from Haverd and Cuntz, 2010) are strange as they are already provided in a discretized form, contrarily to the other equations. Same comment for Eq. (27)

Thank you for your comments. We presented the continuous form in a discretized form (Eq. (24), (25), and (27)) were written in a discretized form because they arethey are only used in the top half layer for upper boundary solutions. However, they should be in the continuous form. We will fix this problem we will add the continuous form in the revised manuscript.

8/ section 2.1.4: the formulation of the boundary conditions for the various equations is very important for getting correct results. The authors put much effort in fully coupling the equations in the soil but put much less attention in the formulation of the boundary conditions. The choices made would require more justifications even if they seem to be similar to Haverd and Cuntz (2010).
More generally, it seems that the authors have recoded the Haverd and Cuntz (2010) model without considering the litter. It would be relevant to say it if it the truth.

We utilized the equations of energy, water, and isotope mass conservation at the air-soil interface proposed by Haverd and Cuntz (2010) but did not consider the litter layer at the current stage of our work. MOIST is based on cell-centered numerical method, which requires us to consider the water content, temperature and isotopic compositions at soil-air interface and the fluxes within the top layer. This means that the fluxes from the center of the topsoil layer to the soil-air interface are balanced by the fluxes from soil-air interface to the atmosphere. The upper boundary calculation method from Haverd and Cuntz (2010) met our requirements, so we recoded the upper boundary from 'Soil-Litter-Isotope' model (Haverd and Cuntz, 2010). We will make this clearer in the revised manuscript.

162. Should be Eq. (24) and (25)?
Sorry for the typo. They should be Eq. (24) and (25). We will address this in the revised manuscript.

9/ L191: should be Eq. (19)?
Thanks. It should be Eq. (19). We will correct it in the revised manuscript.

10/ the description of the numerical implementation is too short. What are the variables that you are computing? I would be curious to see the three discretized coupled equations in order to see where is the benefit of having them fully coupled. In other words, on which system of equations do you implement the Matlab solver (in the equations presently given in the paper, there are more than three unknown sets of variables).

Thank you for your comments. We added detailed descriptions about the numerical implementation in Appendix B.

11/ L194: when you use the soil water pressure as variable, it is continuous at the interface between layers with different hydraulic properties, which limits the problem you mention here.

We agree. Our intention was to state that when physical properties are different between soil layers, the hydraulic conductivity can vary drastically at the layer interface, leading to potential oscillation problems. We will provide a more accurate statement in the revised manuscript.

11/ L220. The reference with the DOI of the dataset should appear in the reference list, not only in the text. This is a reference like a standard paper and it should be cited as such.

Thank you for your comments. We will cite the dataset correctly in the revised manuscript.

12/ Eq. (34) and (35): did you checked the MOIST model behavior using the Van Genuchten (1980) model for the retention curve and the Brooks and Corey (1964) model for the hydraulic conductivity as done in Braud et al. (2005)?

Thank you for your comments. We will add this information (like Table 2 in Braud et al., 2005 and Fig 3 in Zhou et al., 2021) in the revised manuscript.

13/Figure 5, 6, 7: You could zoom on the 0-0.5 cm layer and avoid the 0 y-axis at the very top of the figure to get more legible figures. Furthermore, the Test case 3 is almost invisible (at least on a printed version).

Thank you for your comments. We will update these figures in the revised manuscript.

14/Section 3.2: graphical comparison is fine, but I would like to see a comparison between the simulated peak concentration and slope of the oxygen 18 – deuterium relationships (see Braud et al., 2005, Tables 3 and 5). This would provide a more robust evaluation of the model performance.

Thank you for your comments. We will add this information in Section 3.2 in the revised manuscript.

15/ the demonstration from Eq. (43) to (47) would require more details to be fully understandable.

Thank you for your comments. Eq. (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, Eq. (41) and (42) were used as an example for understanding the error difference between segregated and coupled method.

The example in the manuscript:

$$\frac{\partial \theta}{\partial t} = \frac{\partial q}{\partial z} \tag{6}$$

$$\frac{\partial (c\theta)}{\partial t} = 2\frac{\partial (qc)}{\partial z} \tag{7}$$

Equation (7) can be rewritten by chains rule:

$$c\frac{\partial\theta}{\partial t}+\theta\frac{\partial c}{\partial t}=2\left(q\frac{\partial c}{\partial z}+c\frac{\partial q}{\partial z}\right)\tag{8}$$

If segregated method is used to solve these two equations for θ and c, they should be written discrete form in both spatial and temporal (explicit is the simplest to understand):

$$\frac{\theta_z^{t+1}-\theta_z^t}{\Delta t}=\frac{q_{z+1}^t-q_z^t}{\Delta z}\tag{9}$$

However, $\frac{\partial\theta}{\partial t}$ is not equal to $\frac{\theta_z^{t+1}-\theta_z^t}{\Delta t}$ within a small time step and this is true between $\frac{\partial q}{\partial z}$ and $\frac{q_{z+1}^t-q_z^t}{\Delta z}$ within a small spatial step. Therefore, error terms should be introduced to balance Equation (9), which are Err1 and Err2 in Eq. (43). Then θ can be solved in Equation (9) and further used to solve c in Equation (8).

In the coupled method, Equation (8) can be rewritten by combining Equation (6):

$$\theta\frac{\partial(c)}{\partial t}=2\left(q\frac{\partial(c)}{\partial z}+c\frac{\partial(q)}{\partial z}\right)-c\frac{\partial(q)}{\partial z}\tag{10}$$

Rewritten Equation (10) in discrete form can obtain Eq. (47) in the manuscript. Compared to segregated method, the coupled method can potentially reduce numerical errors by analytically inserting Equation (6) into Equation (10). Therefore, the coupled method should be more accurate than segregated method on solving a set of partial differential equations.

16/ Figure 12 is not cited in the paper. Furthermore, if the purpose of the figure were to demonstrate that the coarser vertical spatial resolution provides results as accurate as in Figure 5, it would be more informative to show the difference between both simulations. Visually, it seems that the peak is simulated deeper in Figure 12 than in Figure 5, which would not be very satisfactory as the peak is located at the evaporation front.

We forgot to cite Fig 12 at the end of line 554.

Regarding to the discrepancy in peak locations between Fig 12 and Fig 5, this is because when the coarse spatial step is used, some surface information could be lost. For example, in Fig 12, the soil water profile is also different from that in Fig 5 because we cannot capture the drying layer when the spatial step is larger than its thickness. This also explains why the peak locations in the isotope profiles are deeper in Figure 12, as the layer thickness is 0.1 m, which is larger than the location of the peak (around 0.05 m). Therefore, with larger spatial discretization, more surface information may be lost. However, MOIST still reflects the correct trend even under with coarse spatial discretization.

17/ L588-593: this paragraph is not supported by the results. Other reasons than solving or not the fully coupled equations could explain discrepancies between the models, one of them being the specification of the boundary conditions or the specification of the kinetic fractionation factor, that may be different in the different models.

Agreed. Indeed, there are many reasons could be related to the discrepancies between the model

because MOIST and HYDRUS have many differences. The upper boundary will play an important role, especially the water, heat, and isotopic fluxes vary constantly under field simulations. We will this in the revised manuscript.

18/ L595-610: the question of the numerical method (cell-centered versus vertex-centered) is strange here as the method used in the MOIST model has not been presented before.

Thank you for your comments. We will include the cell-centered method in method section.

Appendix A

According to Braud et al. (2005), we conducted the sensitive analysis on various formulations of the kinetic fractionation factor (α_k) to calculate upper boundary conditions of isotope transport under non-saturated and non-isothermal conditions. These conditions are chosen because they are closer to reality than saturated and isothermal conditions.

The formulations used in five cases are described below.

Case 1:

$$\alpha_k = \frac{D_v}{D_{iv}} \tag{A1}$$

Case 2:

$$\alpha_k = \left(\frac{D_v}{D_{iv}}\right)^{nk} \tag{A2}$$

where *nk* is calculated by:

$$nk = \frac{(\theta_{surface} - \theta_r)0.5 + (\theta_s - \theta_{surface})}{\theta_s - \theta_r} \tag{A3}$$

where $\theta_{surface}$ is the soil water conent at soil surface (m³ m⁻³); θ_r is residual soil water content (m³ m⁻³); θ_s is the saturated soil water content (m³ m⁻³).

Case 3:

$$\alpha_k = 1 \tag{A4}$$

Case 4:

$$\alpha_k = 1 + n_k\left(\frac{D_v}{D_{vi}} - 1\right)\frac{r_{am}}{r_a} \tag{A5}$$

where r_a is the sum of r_{am} and r_{aT}; r_{am} and r_{aT} are turbulent and molecular resistances to the water vapor transport. r_{am} can be calculated by (Brutsaert, 1982):

$$if \ \frac{u^* Z_{om}}{v} \leq 1$$

$$r_{am} = 13.6\left(\frac{v}{D_v}\right)^{\frac{2}{3}} \tag{A6}$$

$$if \ \frac{u^* Z_{om}}{v} \geq 1$$

$$r_{am} = 7.3\left(\frac{u^* Z_{om}}{v}\right)^{\frac{1}{4}}\left(\frac{v}{D_v}\right)^{\frac{1}{2}} \tag{A7}$$

where u^* is the friction velocity, which is 0 in this case because the wind speed is 0 m s⁻¹; Z_{om} is the roughness length for momentum (m), v is the air kinematic viscosity (m² s⁻¹).

Case 5:

$$\alpha_k = 1 \tag{A8}$$

$$n_D \neq 1 \tag{A9}$$

where n_D is calculated by:

$$n_D = 0.67 + 0.33exp(1 - \frac{\theta_{surface}}{\theta_r})$$ (A10)

Table A1 was formatted as Table 6 from Braud et al. (2005) and our results were found to be similar. However, calculated maximum δ^2H values were slightly smaller than those reported by Braud et al, (2005). This difference may be attributed to the discrepancies in the model structure, upper boundary calculation, and the numerical schemes used.

Table A1 demonstrated that the variations of indexes among the 5 cases are small. As mentioned above, α_k is not equal to one in cases 1, 2, and 4, while it is equal to one in cases 3 and 5. Thus, cases 1, 2, and 4 can be grouped together as group 1, while cases 3 and 5 can be grouped together as group 2. The differences of inner group are much smaller than inter group. This suggests that MOIST is not sensitive to the formulations used to calculate the kinetic fractionation coefficient, but rather to the consideration of kinetic fractionation itself. If kinetic fractionation is not considered (α_k is 1), the maximum δ values of isotope species will be underestimated, as observed in cases 3 and 5, because the isotope enrichment at soil surface will not occur. The kinetic fractionation cannot be ignored in reality. Therefore, MOIST should perform consistently across available formulations used to calculate the kinetic fractionation coefficient.

Table A1. Comparison of formulations used to calculate kinetic fractionation coefficient under non-saturated and non-isothermal conditions.

	Case1	Case 2	Case 3	Case 4	Case 5
Calculated max δ^2H (‰)	39.65	39.51	36.06	38.39	36.90
Calculated max $\delta^{18}O$ (‰)	20.84	20.69	17.12	19.47	18.05
Depth of maximum (m)	0.02	0.02	0.02	0.02	0.02
Calculated liquid HDO/$H_2^{18}O$ slope	1.93	1.93	2.13	2.00	2.07
Calculated vapor HDO/$H_2^{18}O$ slope	3.51	3.47	2.87	3.64	3.00

Appendix B.

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

$$\frac{\partial \theta}{\partial t} + \frac{\partial \theta_v}{\partial t} = -\frac{\partial q}{\partial z} - S \qquad (B1)$$

$$C_{soil}\frac{\partial T}{\partial t} + \rho \lambda_E \frac{\partial \theta_v}{\partial t} = -\frac{\partial q_T}{\partial z} \qquad (B2)$$

$$\frac{\partial(C_{il}(\theta+\alpha\theta_v))}{\partial t} = -\frac{\partial q_i}{\partial z} - C_{il}S \qquad (B3)$$

where θ and θ_v are the soil water content and equivalent liquid water content (m^3 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 (J m^{-3} 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 (J m^{-2} 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 (kg m^{-2} s^{-1}). Explanation of Equation. (B2) can be referred to Appendix C.

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

$$Cv_{sat} = \frac{m^3_{liquid\,water}}{m^3_{air}} = \frac{\frac{mass_{liquid\,water}}{\rho_{liquid\,water}}}{\frac{mass_{air}}{\rho_{air}}} = \frac{\frac{mass_{vapor}}{\rho_{liquid\,water}}}{\frac{mass_{air}}{\rho_{air}}} \qquad (B4)$$

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

Then, the ideal gas law can be incorporated into Equation. B4:

$$Cv_{sat} = \frac{\frac{mass_{vapor}}{\rho_{liquid\,water}}}{\frac{mass_{air}}{\rho_{air}}} = \frac{\rho_{air}}{\rho_{liquid\,water}}\frac{P_{vapor_{sat}}M_{water}}{P_{air}M_{air}} \qquad (B5)$$

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.

Equation. A5 can be further simplified by applying the ideal gas law again on P_{air}:

$$Cv_{sat} = \frac{\rho_{air}}{\rho_{liquid\,water}}\frac{P_{vapor_{sat}}M_{water}}{P_{air}M_{air}} = \frac{\rho_{air}}{\rho_{liquid\,water}}\frac{P_{vapor_{sat}}M_{water}}{\rho_{air}\frac{R}{M_{air}}T M_{air}} \qquad (B6)$$

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:

$$Cv = \frac{\rho_{air}}{\rho_{liquid\,water}}\frac{P_{vapor_{sat}}M_{water}}{P_{air}M_{air}} = \frac{\rho_{air}}{\rho_{liquid\,water}}\frac{P_{vapor}M_{water}}{\rho_{air}\frac{R}{M_{air}}T M_{air}} \qquad (B7)$$

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

is written as:

$$Cv_{sat} = \frac{0.61078 e^{\frac{17.269T}{T+237.29}} M_{water}}{\rho_{liquid\ water} RT}$$ (B8)

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

$$h_r = e^{\frac{M_w h g}{RT}}$$ (B9)

Besides, according to the definition of h_r:

$$h_r = \frac{P_{vapor}}{P_{vapor_{sat}}}$$ (B10)

which can be rewritten by combining Equations. B6 and B7:

$$h_r = \frac{Cv}{Cv_{sat}}$$ (B11)

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

$$\theta_v = (\theta_s - \theta) Cv_{sat} h_r$$ (B12)

Introducing Equation.B11 to Equations. B1 - B3:

$$\frac{\partial \theta}{\partial t} + \frac{\partial \left((\theta_s - \theta)\ Cv_{sat} h_r \right)}{\partial t} = -\frac{\partial q}{\partial z} - S$$ (B13)

$$\frac{C_{soil} \partial T}{\partial t} + \frac{\rho \lambda_E \partial \left((\theta_s - \theta) Cv_{sat} h_r \right)}{\partial t} = -\frac{\partial q_T}{\partial z}$$ (B14)

$$\frac{\partial \left(C_{il} \left(\theta + \alpha Cv_{sat} h_r (\theta_s - \theta) \right) \right)}{\partial t} = -\frac{\partial q_i}{\partial z} - C_{il} S$$ (B15)

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 Equation. B13, B14, and B15 for h, T, and C_{il} at each time step simultaneously. Since Cv_{sat} is the function of T (Equation. B8), h_r is the function of h and T (Equation. B9), and α is the function of T, 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:

$$\frac{\partial h}{\partial t} = \frac{1}{A} \left(-\frac{\partial q_T}{\partial z} - B \frac{\left(\frac{-A}{C} \left(\frac{\partial q}{\partial z} + S \right) + \frac{\partial q_T}{\partial z} \right)}{\frac{D}{C} A - B} \right)$$ (B16)

$$\frac{\partial T}{\partial t} = \frac{\frac{-A}{C} \left(\frac{\partial q}{\partial z} + S \right) + \frac{\partial q_T}{\partial z}}{\frac{D}{C} A - B}$$ (B17)

$$\frac{\partial C_{il}}{\partial t} = \frac{F}{E}$$ (B18)

with coefficients A to E:

$$A = \rho \lambda_E \left((\theta_s - \theta)\ Cv_{sat} \frac{\partial h_r}{\partial h} - Cv_{sat} h_r \frac{\partial \theta}{\partial h} \right)$$ (B19)

$$B = C_{soil} + \rho \lambda_E \left((\theta_s - \theta) Cv_{sat} \frac{\partial h_r}{\partial T} + (\theta_s - \theta) h_r \frac{\partial Cv_{sat}}{\partial T} \right)$$ (B20)

$$C=(1-Cv_{sat}h_r)\frac{\partial\theta}{\partial h}+(\theta_s-\theta)Cv_{sat}\frac{\partial h_r}{\partial h} \tag{B21}$$

$$D=(\theta_s-\theta)Cv_{sat}\frac{\partial h_r}{\partial T}+(\theta_s-\theta)\,h_r\frac{\partial Cv_{sat}}{\partial T} \tag{B22}$$

$$E=\theta+\alpha Cv_{sat}\,h_r\,(\theta_s-\theta) \tag{B23}$$

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

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

$$\left.\frac{\partial Cv_{sat}}{\partial T}\frac{\partial T}{\partial t}+\alpha Cv_{sat}\theta\left(\frac{\partial h_r}{\partial h}\frac{\partial h}{\partial t}+\frac{\partial h_r}{\partial T}\frac{\partial T}{\partial t}\right)+\alpha Cv_{sat}h_r\frac{\partial\theta}{\partial h}\frac{\partial h}{\partial t}\right) \tag{B24}$$

Equations. B13, B14, and B15 were transformed into a system of coupled ordinary differential equations by Equations. B16-B24. This system is solved by MATLAB solvers (ode113/ode23tb) simultaneously. The derivative vector ($\frac{\partial h}{\partial t}$, $\frac{\partial T}{\partial t}$, and $\frac{\partial C_{il}}{\partial t}$), having a length of the number of spatial discretization multiplied by three.

To construct the derivative vector, values from Equation. B17 were calculated firstly because they were also used in Equation. B16. Equation. B17 showed 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 Cv_{sat} (Equations. B19-B22) and further affect the water transport within soil (Equation. B16).

Equation. B16 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 Equation. B16 is $\frac{\partial T}{\partial t}$ (Equation. B17). 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.

Equation. B24 shows that isotope transport was influenced by all the parameters coupled. Specifically, water transport (Equation. B16) affects isotopic fluxes since isotopes were treated as solutes, while heat transport (Equation. B17) 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 Cv_{sat} in soil. Therefore, values for derivative vector construction from Equation. B17 were calculated based on Equations. B16, B17, B23, and B24.

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.

Appendix C.

The heat transport equation within soil is written as:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = \frac{\partial}{\partial z}\left(k_H\frac{\partial T}{\partial z}\right) - C_w q_l\frac{\partial T}{\partial z} - C_{vh}\frac{\partial q_v T}{\partial z} - \rho\lambda_E\frac{\partial q_v}{\partial z} \tag{C1}$$

Equation. (C1) can be rewritten by the chains rule:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = \frac{\partial}{\partial z}\left(k_H\frac{\partial T}{\partial z}\right) - C_w q_l\frac{\partial T}{\partial z} - C_{vh}q_v\frac{\partial T}{\partial z} - C_{vh}T\frac{\partial q_v}{\partial z} - \rho\lambda_E\frac{\partial q_v}{\partial z} \tag{C2}$$

Then:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = \frac{\partial}{\partial z}\left(k_H\frac{\partial T}{\partial z}\right) - (C_w q_l + C_{vh}q_v)\frac{\partial T}{\partial z} - (C_{vh}T + \rho\lambda_E)\frac{\partial q_v}{\partial z} \tag{C3}$$

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 Equation. (C3) is rewritten as:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = -\frac{\partial}{\partial z}\left(-k_H\frac{\partial T}{\partial z} + Constant_1 T + Constant_2 q_v\right) \tag{C4}$$

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

Assuming $q_T = -k_H\frac{\partial T}{\partial z} + Constant_1 T + Constant_2 q_v$, Equation (C4) can be further simplified:

$$C_{soil}\frac{\partial T}{\partial t} + \rho\lambda_E\frac{\partial\theta_v}{\partial t} = -\frac{\partial q_T}{\partial z} \tag{C5}$$

Equation. (C5) is the same as Equation. (B2).

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