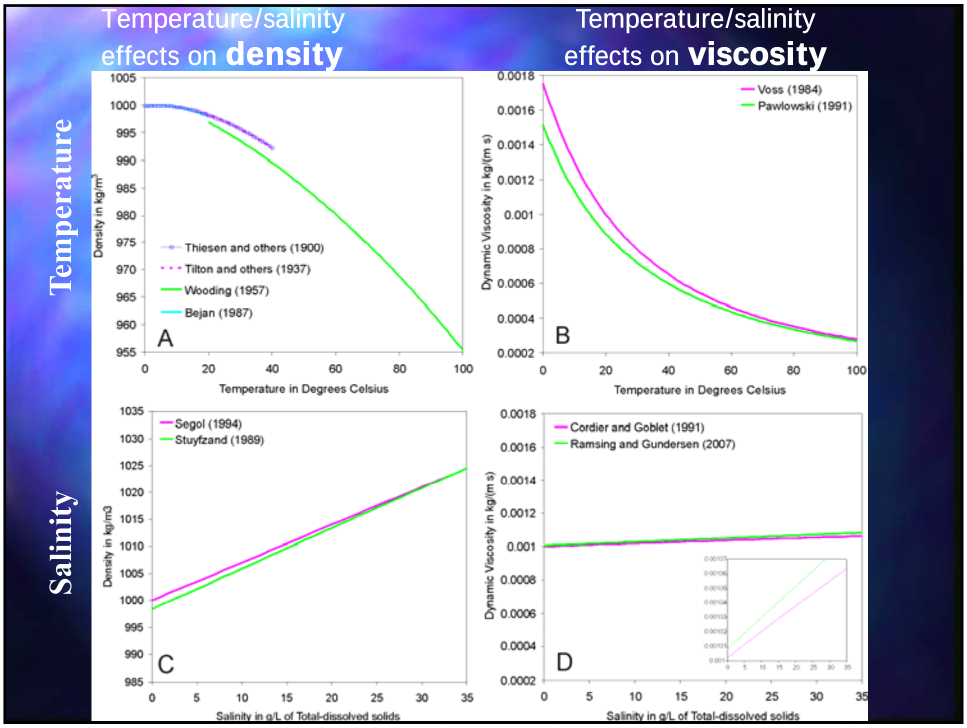
Presentation 5

Concepts and Equations of Solute and Heat Transport

Solute and Heat Transport

- Need to represent solute transport because density is a function of concentration, and concentration may change in response to flow field
- Density is also a function of temperature. As temperature increases, density decreases. Temperature may change in response to flow field



Solute Transport Processes

- Physical Transport of solute
  - Advection
  - Diffusion
  - Mechanical Dispersion
- Reactive Transport
  - Geochemical reactions
  - Biological reactions

Advection

- Transport of solute in flowing groundwater with average groundwater velocity
- In most cases, advection is primary process for solute transport

Advective Velocity and Mass Flux

Velocity of Advective Transport

advective velocity

$$v_i = \frac{q_i}{\theta}$$

interstitial velocity
pore water velocity
seepage velocity

q: specific discharge (Darcy flux; Darcy velocity)

$$q_i = \frac{Q}{A} = -K_i\left(\frac{\partial h_f}{\partial x_i} + \frac{\rho - \rho_f}{\rho_f}\frac{\partial z}{\partial x_i}\right)$$

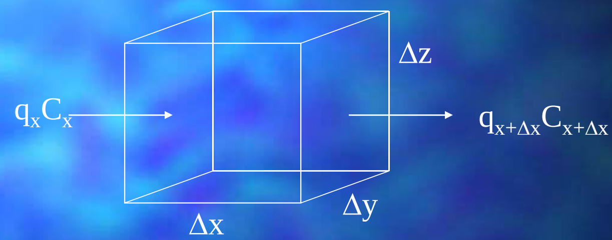
θ: “effective” porosity

Advective Mass Flux

$$\frac{mass}{area \cdot time} = qC$$

Mass per unit time per unit <u>bulk</u> area

Derivation of Equation for Advective Transport



ΔStorage= $\Delta C \cdot \theta / \Delta t$

In – Out = ΔStorage

1 Dimension

$$\frac{\Delta C}{\Delta t} = -\frac{q_x C_x - q_{x+\Delta x} C_{x+\Delta x}}{\theta \Delta x} = -\frac{\Delta(vC)}{\Delta x}$$

$\Delta x \rightarrow 0:$

$$\frac{\partial C}{\partial t} = -\frac{\partial (vC)}{\partial x}$$

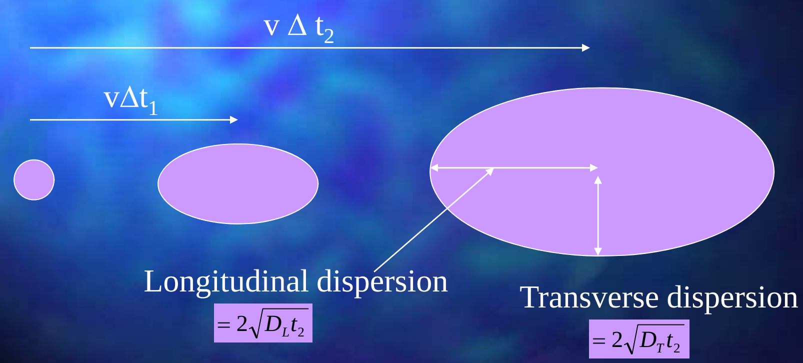
Equation for Advective Transport

3 Dimensions

$$\frac{\partial C}{\partial t} = -\frac{\partial (v_x C)}{\partial x} - \frac{\partial (v_y C)}{\partial y} - \frac{\partial (v_z C)}{\partial z}$$

Dispersion

Spreading of a solute over a greater area than would be predicted solely from average groundwater velocity

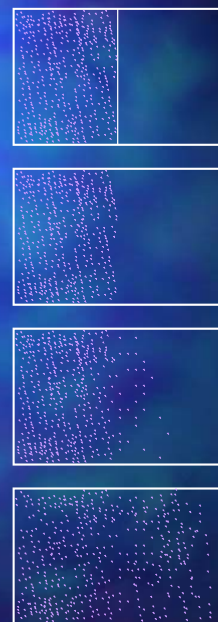


Hydrodynamic Dispersion

- Molecular Diffusion
- Mechanical Dispersion

Molecular Diffusion

- Spread of solute caused by concentration gradients



(A) Container with saline water and distilled water separated by a glass plate

(B) Ionic distribution after removal of glass plate

(C) Ionic distribution at time t1 after removal of plate

(D) Final ionic distribution

Fick's Law of Diffusion

$$F = -D^* \frac{\partial C}{\partial l}$$

F: diffusion mass flux
D^*: effective diffusion coefficient [L^2/T]

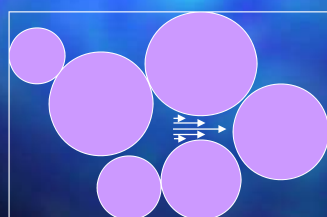
$$D^* = D_0 \tau$$

D_0: molecular diffusion coefficient in open water
τ: is the tortuosity, defined as the length of a sample divided by the length of a flow path through a sample ($\tau < 1$)

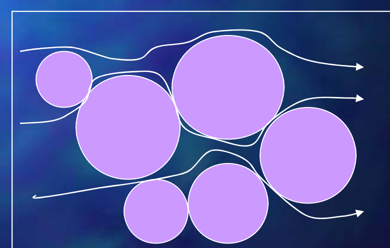
Mechanical Dispersion

- Spreading of solute as a result of differences in actual velocity and average velocity

Pore Scale



Macro Scale



Representation of Mechanical Dispersion in Transport Model

- By detailed (complete) description of hydraulic conductivity field
- By analogy to Fick's second law of diffusion, i.e., mass flux (F) due to dispersion is proportional to concentration gradients

$$F = -D_{ij} \frac{\partial C}{\partial x_i}$$

Dispersion Coefficients for 1-D Flow in X direction

$$D_{xx} = \alpha_L v + D^*$$

$$D_{yy} = \alpha_T v + D^*$$

Dispersion Coefficients

$$D_{xx} = \alpha_L \frac{v_x^2}{v} + \alpha_{TH} \frac{v_y^2}{v} + \alpha_{TV} \frac{v_z^2}{v} + D^*$$

$$D_{yy} = \alpha_{TH} \frac{v_x^2}{v} + \alpha_L \frac{v_y^2}{v} + \alpha_{TV} \frac{v_z^2}{v} + D^*$$

$$D_{zz} = \alpha_{TV} \frac{v_x^2}{v} + \alpha_{TV} \frac{v_y^2}{v} + \alpha_L \frac{v_z^2}{v} + D^*$$

$$D_{xy} = D_{yx} = \frac{(\alpha_L - \alpha_{TH}) v_x v_y}{v}$$

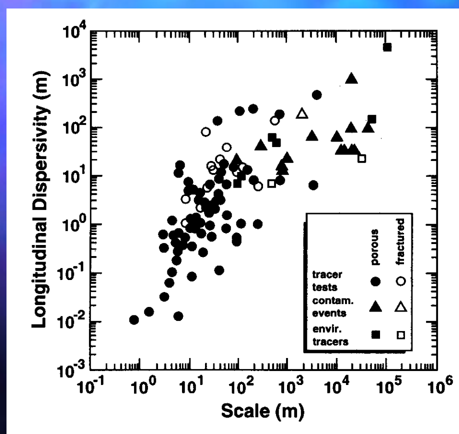
$$D_{xz} = D_{zx} = \frac{(\alpha_L - \alpha_{TV}) v_x v_z}{v}$$

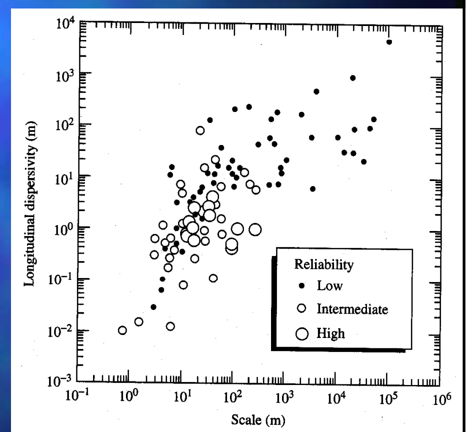
$$D_{yz} = D_{zy} = \frac{(\alpha_L - \alpha_{TV}) v_y v_z}{v}$$

α_L = longitudinal dispersivity
α_{TH} = horizontal transverse dispersivity
α_{TV} = vertical transverse dispersivity
D* = molecular diffusion coefficent

Originally from Burnett and Frind (1987), and currently used in MT3DMS

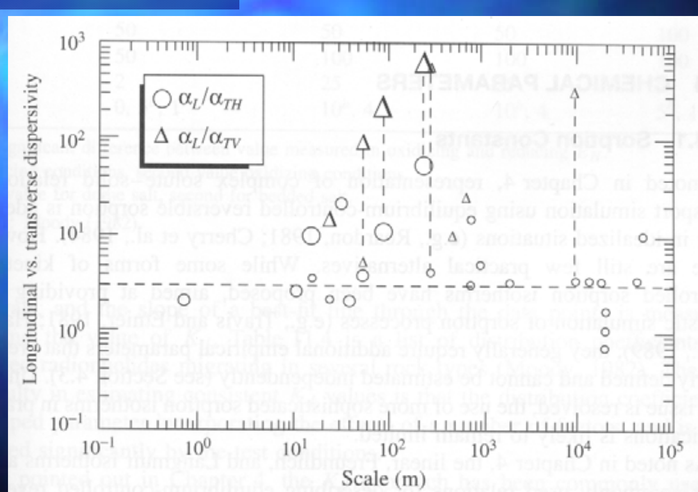
Values of Longitudinal Dispersivity





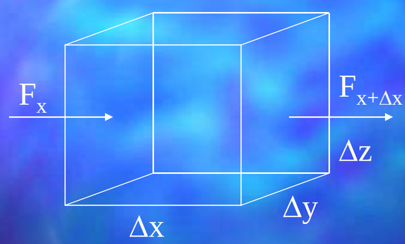
Source: Gelhar et al. (1992)

Dispersivity Ratios



Source: Gelhar et al. (1992)

Derivation of Equation for Dispersive Transport



Inflow=$F_x\theta$
Outflow=$F_{x+\Delta x}\theta$
ΔStorage= $\Delta C\cdot\theta/\ \Delta t$
In – Out = ΔStorage

1D and v is aligned with x axis

$$\frac{\Delta C}{\Delta t} = -\frac{F_x - F_{x+\Delta x}}{\Delta x} = -\frac{\Delta F}{\Delta x}$$

$$\frac{\partial C}{\partial t} = -\frac{\partial F}{\partial x}$$

$$F = -D\frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

Advection-Dispersion Equation

- Assumptions
  - v and D are spatially uniform
  - v is aligned with x axis
  - no sinks/sources

$$\frac{\partial C}{\partial t} = \underbrace{-v_x\frac{\partial C}{\partial x}}_{\text{ADV}} + \underbrace{D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} + D_z\frac{\partial^2 C}{\partial z^2}}_{\text{DSP}}$$

Governing Equation for Solute Transport

$$\frac{\partial C}{\partial t} = \overbrace{-\nabla \cdot (\vec{v} C)}^{\text{ADV}} + \overbrace{\nabla \cdot (D \cdot \nabla C)}^{\text{DSP}} \overbrace{- \frac{q_s}{\theta} C_s}^{\text{SSM}} + \overbrace{\sum_{k=1}^{N} R_k}^{\text{RCT}}$$

Or, as in MT3DMS

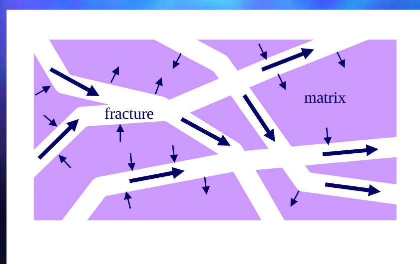
$$\left(1 + \frac{\rho_b K_d^k}{\theta}\right) \frac{\partial (\theta C^k)}{\partial t} = \overbrace{\nabla \cdot \left[\theta \left(D_m^k + \boldsymbol{\alpha} \frac{\mathbf{q}}{\theta}\right) \cdot \nabla C^k\right]}^{\text{DSP}} \overbrace{- \nabla \cdot (\mathbf{q} C^k)}^{\text{ADV}} \overbrace{- q'_s C_s^k}^{\text{SSM}} + \overbrace{\sum R_n}^{\text{RCT}}$$

Validity of the Advection-Dispersion Model

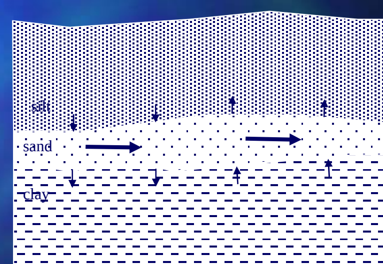
- Dispersion should only be used to account for solute spreading caused by small-scale, randomly distributed heterogeneities in the hydraulic conductivity field. Larger K trends should be explicitly delineated and included in the flow model.

Alternative to Advection-Dispersion Model

- Dual-domain (dual-porosity) mass transfer



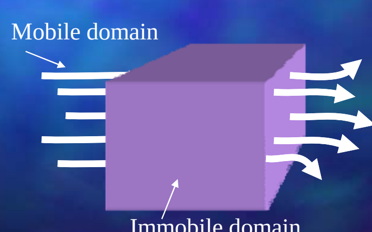
1. Fractured flow system



2. Heterogeneous porous media

Dual-Domain Mass Transfer Approach

- Aquifer is conceptualized as consisting of two distinctive and overlapping domains:
  - a mobile (or fast) domain where transport is mainly by advection, and
  - an immobile (or slow) domain where transport is mostly by diffusion
- Interaction between the two domains is characterized by kinetic mass transfer



Dual Domain Equations

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = -\nabla \cdot (\vec{v} C_m) + \nabla \cdot (D \cdot \nabla C_m) - \frac{q_s}{\theta} C_s$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \beta (C_m - C_{im})$$

θ_m = porosity of mobile domain
θ_m = porosity of the immobile domain
$\theta = \theta_m + \theta_{im}$ = total porosity
β= first-order mass transfer rate between the mobile and immobile domains

Single-Species Chemical Reactions

- Sorption
  - Mass transfer (or partitioning) process between the contaminants dissolved in groundwater (solution phase) and the contaminants sorbed on porous media (solid phase) including absorption (incorporation into the interior of a solid); adsorption (attraction to a surface); and ion exchange
- First-order rate reactions
  - Radioactive decay
  - Biodegradation
  - Hydrolysis

Equilibrium-Controlled Sorption

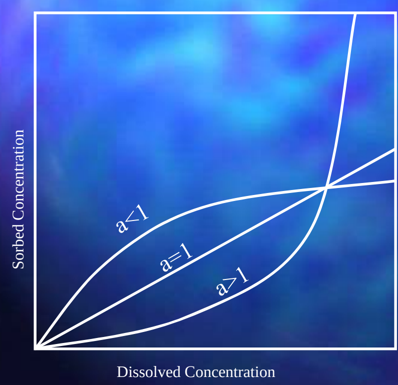
- Key assumptions
  - LEA (local equilibrium assumption)—mass transfer (partitioning) process is instantaneous
  - Reversible—total mass is not changed
- Retardation concept
  - Advancing contaminant plume appears “retarded” because dissolved contaminants are sorbed on to porous materials, leaving less solute for transport
  - Retreating contaminant plume appears “retarded” because sorbed contaminants are de-sorbed into the dissolved phase, leaving more solute behind

Sorption Isotherms

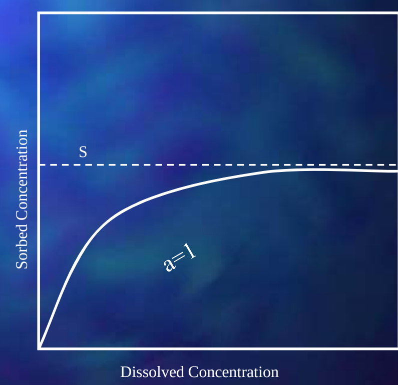
- Linear sorption $\bar{C} = K_d C$
- Freundlich sorption $\bar{C} = K_f C^a$
- Langmuir sorption $\bar{C} = \dfrac{K_l \bar{S} C}{1 + K_l C}$
- Nonequilibrium sorption $\rho_b \dfrac{\partial \bar{C}}{\partial t} = \beta \left(C - \dfrac{\bar{C}}{K_d} \right)$

Freundlich and Langmuir Isotherms

Freundlich isotherm. A linear isotherm is a special case for which the exponent, a, is equal to 1.



A Langmuir isotherm where S is the maximum sorption capacity



Method for Including Sorption into Transport Model

- Retardation Coefficient

$$R\frac{\partial C}{\partial t} = ADV + DSP$$

1st-Order Irreversible Rate Reactions

Rate coefficient for dissolved species

$$R\frac{\partial C}{\partial t} = ADV + DSP - \left(\lambda_1 C + \lambda_2 \frac{\rho_b}{\theta}\overline{C}\right)$$

Rate coefficient for sorbed species

relation between rate coefficient [T^{-1}] and half life [T]

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

Zero-Order Reactions

Rate coefficient for dissolved species

$$R\frac{\partial C}{\partial t} = ADV + DSP - \left(\lambda_1 \theta + \lambda_2 \rho_b\right)$$

Rate coefficient for sorbed species

γ_1 [$ML^{-3}T^{-1}$] and γ_2 [$MM^{-1}T^{-1}$] are the zeroth-order rate coefficients for the dissolved and sorbed phase. Positive rate coefficients indicate decay; negative values indicate growth.

Heat/Energy

- Stored
- Conducted
- Dispersed
- Convected
- Produced/Lost
- Key parameters
  - Thermal conductivity (k_T)
  - Specific heat capacity (c_P)

Heat Capacity

- Heat is stored in the fluid *and solid*
- Heat capacity of the fluid and solid represented as: c_{Pfluid} & c_{Psolid}
- Energy stored in fluid: $\theta c_{Pfluid} \rho T$
- Energy stored in the solid: $(1-\theta) c_{Psolid} \rho_s T$

Heat/Energy Transport

- Fourier's law for heat transport:

$$q_T = -k_T \frac{\partial T}{\partial x}$$

- Heat is conducted through fluid *and solid*
- Thermal conductivity of the fluid and solid represented as: k_{Tfluid} & k_{Tsolid}
- Bulk thermal conductivity:

$$k_{Tbulk} = \theta k_{Tfluid} + (1-\theta) k_{Tsolid}$$

Heat Flux

- Dispersive heat flux: $\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\rho c_{Pfluid} D \frac{\partial T}{\partial x} \right)$
- Convective heat flux: $\frac{\partial T}{\partial t} = -\frac{\partial \left(v \rho c_{Pfluid} T \right)}{\partial x}$
- Produced/Lost (reaction): $\theta \rho \gamma_{fluid} + (1-\theta) \rho_s \gamma_{solid}$

Heat/Energy Transport (conserve Energy/Mass)

$$\frac{\partial}{\partial t}\Big(\overbrace{\left[\theta\rho c_{Pfluid} + (1-\theta)\rho_s c_{Psolid}\right]}^{\text{Stored}} T\Big) =$$

$$\nabla\cdot\Big(\overbrace{\left\{\left[\theta k_{Tfluid} + (1-\theta) k_{Tsolid}\right]\mathbf{I} + \theta\rho c_{Pfluid} D_{ij}\right\}}^{\text{Conducted and Dispersed}}\nabla T\Big)$$

$$-\nabla\cdot\overbrace{\left(\theta\rho c_{Pfluid} v_i T\right)}^{\text{Convected}} + \overbrace{q_s \rho c_{Pfluid} T_s}^{\text{Sink/Source}} +$$

$$\overbrace{\theta\rho\gamma_{fluid} + (1-\theta)\rho_s\gamma_{solid}}^{\text{RCT(produced/lost)}}$$

Factor out ρc_{Pfluid} for minimal change in density

$$\frac{\partial(\theta T)}{\partial t}\left(1+\frac{(1-\theta)\rho_s c_{Psolid}}{\theta\rho c_{Pfluid}}\right) = \nabla\cdot\left[\theta\left(\frac{k_{Tbulk}}{\theta\rho c_{Pfluid}} + D_{ij}\right)\cdot\nabla T\right]$$

$$-\nabla\cdot(\theta v_i T) + q_s T_s + \frac{\theta\gamma_{fluid}}{c_{Pfluid}} + \frac{(1-\theta)\rho_s\gamma_{solid}}{\rho c_{Pfluid}}$$

...and remember $v_i = \frac{q_i}{\theta}$ $\quad D_{ij} = \alpha\, v$

Production and decay are distributed sources/sinks

$$\mathrm{q}_s'\mathrm{T}_s' = \frac{\theta\gamma_{fluid}}{c_{Pfluid}} + \frac{(1-\theta)\gamma_{solid}}{c_{Pfluid}}\,\frac{\rho_s}{\rho}$$

Equation simplified to...

$$\frac{\partial(\theta T)}{\partial t}\left(1+\frac{(1-\theta)\rho_s c_{Psolid}}{\theta\rho c_{Pfluid}}\right)=\nabla\cdot\left[\theta\left(\frac{k_{Tbulk}}{\theta\rho c_{Pfluid}}+\boldsymbol{\alpha}\frac{\mathbf{q}}{\theta}\right)\cdot\nabla T\right]-\nabla\cdot(\mathbf{q}T)+q'_s T'_s$$

- Substitute: $\rho_b=\rho_s(1-\theta)$
- And substitute the Thermal Distribution Factor:

$$K_{d\_temp}=\frac{c_{Psolid}}{\rho c_{Pfluid}}$$

- And substitute the Molecular Diffusion Coefficient:

$$D_{m\_temp}=\frac{k_{Tbulk}}{\theta\rho c_{Pfluid}}$$

Heat transport...

$$\left(1+\frac{\rho_b K_{d\_temp}}{\theta}\right)\frac{\partial(\theta T)}{\partial t}=\nabla\cdot\left[\theta\left(D_{m\_temp}+\boldsymbol{\alpha}\frac{\mathbf{q}}{\theta}\right)\cdot\nabla T\right]-\nabla\cdot(\mathbf{q}T)+q'_s T'_s$$

Solute transport...

$$\left(1+\frac{\rho_b K_d^k}{\theta}\right)\frac{\partial(\theta C^k)}{\partial t}=\nabla\cdot\left[\theta\left(D_m^k+\boldsymbol{\alpha}\frac{\mathbf{q}}{\theta}\right)\cdot\nabla C^k\right]-\nabla\cdot(\mathbf{q}C^k)-q'_s C_s^k$$