

Sorption and Decay

Equilibrium-Controlled Linear or Non-linear Sorption

- Sorption refers to the mass transfer process between the contaminants dissolved in groundwater (aqueous phase) and the contaminants sorbed on the porous medium (solid phase).
- Assume equilibrium conditions exist between the aqueous-phase and solid-phase concentrations and that the sorption reaction is fast enough relative to groundwater velocity so that it can be treated as instantaneous.
- The functional relationship between the dissolved and sorbed concentrations under a constant temperature is referred to as the sorption isotherm.
- Implemented in model through the use of a retardation factor.

Linear isotherm:

$$\bar{C} = K_d C \quad (2.13)$$

where K_d is the distribution coefficient, L^3M^{-1} . The retardation factor is thus given by,

$$R = 1 + \frac{\rho_b}{\theta} \frac{\partial \bar{C}}{\partial C} = 1 + \frac{\rho_b}{\theta} K_d \quad (2.14)$$

The Freundlich isotherm is a non-linear isotherm which can be expressed in the following form:

$$\bar{C} = K_f C^a \quad (2.15)$$

where

K_f is the Freundlich constant, $(L^3M^{-1})^a$;

a is the Freundlich exponent, dimensionless.

Both K_f and a are empirical coefficients. When the exponent a is equal to unity, the Freundlich isotherm is equivalent to the linear isotherm. The retardation factor for the Freundlich isotherm is defined accordingly as:

$$R = 1 + \frac{\rho_b}{\theta} \frac{\partial \bar{C}}{\partial C} = 1 + \frac{\rho_b}{\theta} a K_f C^{a-1} \quad (2.16)$$

Another non-linear sorption isotherm is the Langmuir isotherm, which is described by the equation:

$$\bar{C} = \frac{K_l \bar{S} C}{1 + K_l C} \quad (2.17)$$

where

K_l is the Langmuir constant, $L^3 M^{-1}$;

\bar{S} is the total concentration of sorption sites available, MM^{-1} .

The retardation factor defined for the Langmuir isotherm is then,

$$R = 1 + \frac{\rho_b}{\theta} \frac{\partial \bar{C}}{\partial C} = 1 + \frac{\rho_b}{\theta} \left[\frac{K_l \bar{S}}{(1 + K_l C)^2} \right] \quad (2.18)$$

Nonequilibrium Sorption

- When the local equilibrium assumption is not valid, it is assumed that the sorption process can be represented through a first-order reversible kinetic reaction as follows,

$$\rho_b \frac{\partial \bar{C}}{\partial t} = \beta \left(C - \frac{\bar{C}}{K_d} \right)$$

- where β is the first-order mass transfer rate between the dissolved and sorbed phases, T^{-1} ; and K_d is the distribution coefficient for the sorbed phase
- Equation needs to be solved simultaneously with the transport governing equation to obtain solutions of solute transport affected by non-equilibrium sorption.

Radioactive Decay or Biodegradation

- The first-order irreversible rate reaction term included in the governing equation:

$$-(\lambda_1 \theta C + \lambda_2 \rho_b \bar{C})$$

- representing the mass loss of both the dissolved phase C and the sorbed phase \bar{C} .
- The rate constant is usually given in terms of the half-life:

$$\lambda = (\ln 2) / t_{1/2}$$

- where $t_{1/2}$ is the half-life of radioactive or biodegradable materials, i.e., the time required for the concentration to decrease to one-half of the original value.

Chemical Reaction Package

Sorption:

Linear isotherm

Kinetic rate reaction:

First-order irreversible kinetic reaction

Variable input: ☒ Layer by layer ☐ Cell by cell

☐ Specify IC of sorbed phase

Layer: 1

Bulk density: 25200.0 (kg/m³)

Edit...

Immobile porosity: 0.0

Edit...

Species	(Units)	Pest
IC sorbed phase		0.0
1st sorption const.	(m ³ /kg)	4.0e-006
2nd sorption const.		0.0
Rate const. (dissolved)	(1/d)	0.0000274
Rate const. (sorbed)	(1/d)	0.0000274

Reset

Help...

OK

Cancel

Chemical Reaction Package

Sorption:

Freundlich isotherm

Kinetic rate reaction:

Zero-order reaction (decay or production)

Variable input: ☒ Layer by layer ☐ Cell by cell

☐ Specify IC of sorbed phase

Layer: 1

Bulk density: 25200.0 (kg/m³)

Edit...

Immobile porosity: 0.0

Edit...

Species	(Units)	Pest
IC sorbed phase		0.0
1st sorption const.	(m ³ /d)	4.0e-006
2nd sorption const.		4.0e-006
Rate const. (dissolved)	(mg/l) * (1/d)	0.0000274
Rate const. (sorbed)	(1/d)	0.0000274

Reset

Help...

OK

Cancel