Simulation of 1-D solute transport with equilibrium controlled non-linear sorption

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OUTLINE OF THE TALK

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- Need for study
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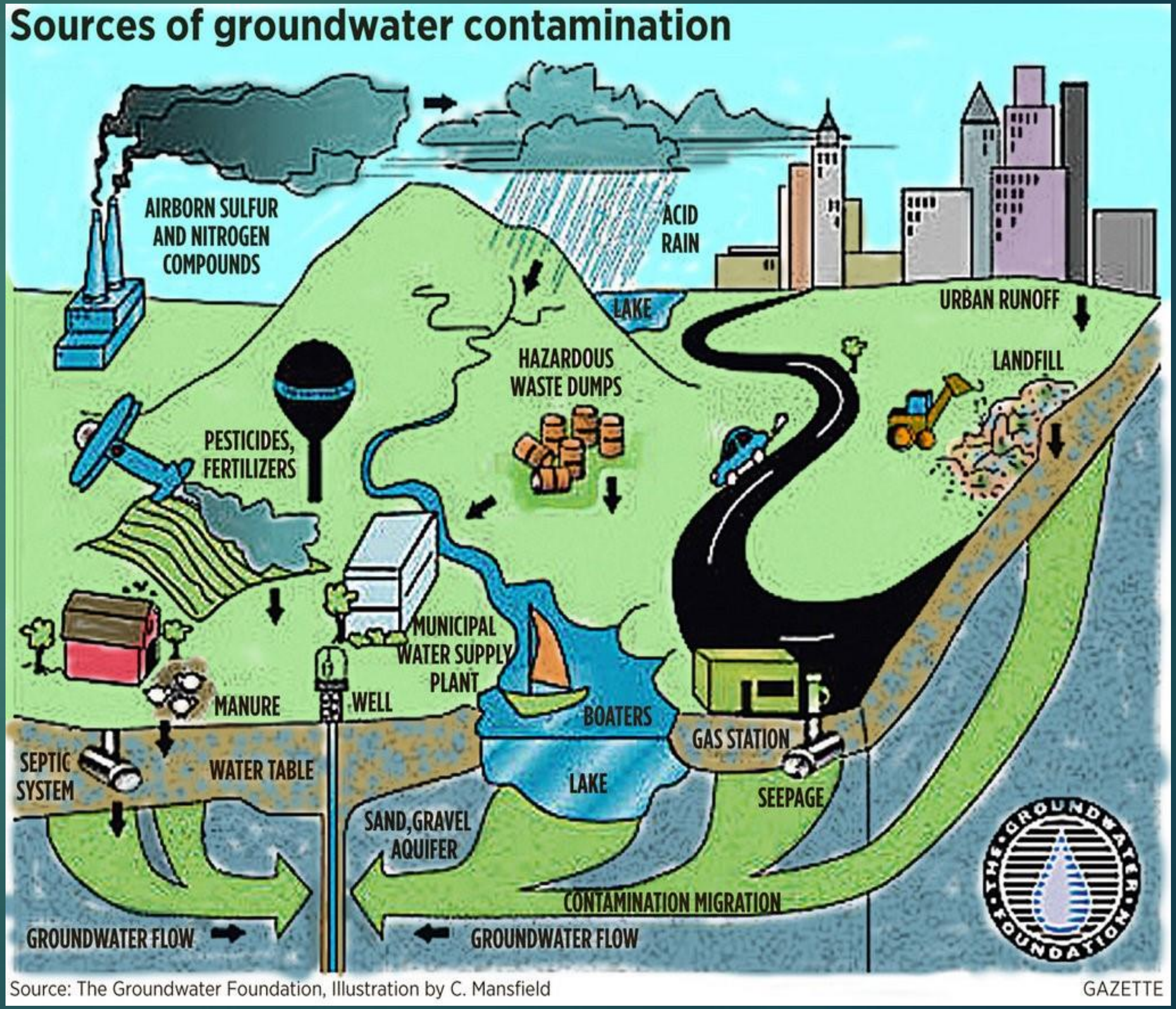
1. INTRODUCTION

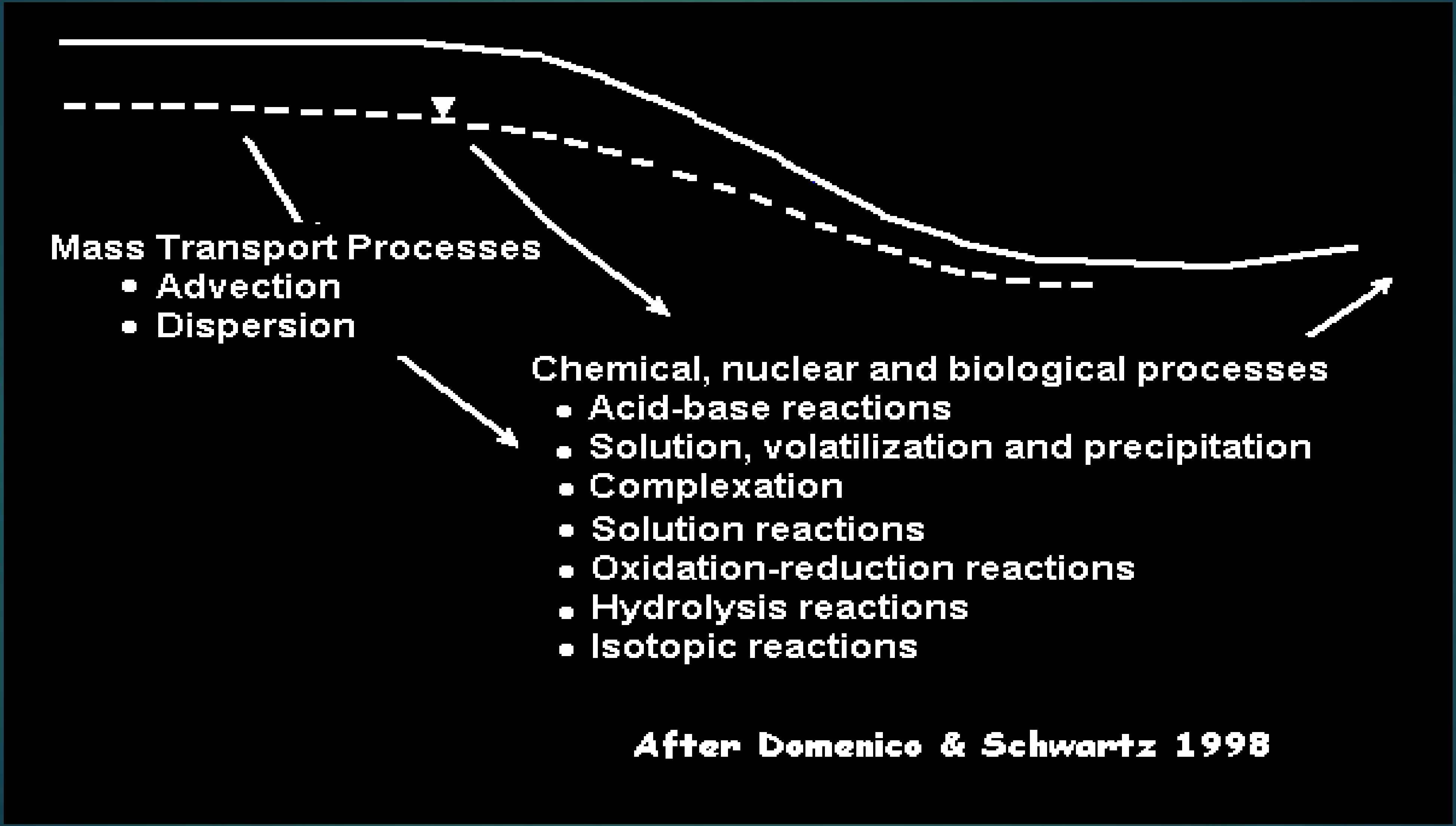
- **Groundwater pollution** (also called **groundwater contamination**) occurs when pollutants are released to the ground and make their way down into groundwater.
- This type of water pollution can also occur naturally due to the presence of a minor and unwanted constituent, contaminant or impurity in the groundwater, in which case it is more likely referred to as contamination rather than pollution.
- A Simulation is the imitation of the operation of real-world process by use of models representing the key characteristics and behavior of the selected system or process. Computer programs are used to perform a simulation.

SOURCES OF CONTAMINATION

- IRRIGATION
- LANDFILLS
- UNDERGROUND STORAGE TANKS
- SEPTIC TANKS
- INDUSTRIES
- OIL SPILLS
- URBAN RUNOFF
- ETC



PROCESS OF CONTAMINATION TRANSPORT



sorption

- It refers to the mass transfer between the contaminant dissolved in GW (aqueous phase) and the contamination sorbed on the porous medium (solid phase).
- Three types of equilibrium controlled sorption isotherms (linear, Freundlich and Langmuir) are considered in MT3DMS transport model.

2. Need for Study

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To understand the need of current study we have different aspects to look for some of which are mentioned below

- Contamination of groundwater has the potential to damage human health, the environment, and socioeconomic growth. Several research have revealed, that high amounts of Metals, fluoride, nitrate, and tenacious organic contaminants are threat to human being.(Wu, Zhang and Zhou, 2020).
- Land and forest quality is also compromised by GW pollution. Also polluted GW can cause soil pollution and land degradation. In many agricultural areas & flat terrain, high groundwater salinity influences soil salinization.
- To achieve the sustainable economic growth globally there should be a balance between natural resources and their requirement & demand.

3. Objectives of the Study

- To do a comprehensive study about fate of contaminant and its transport.

- To study the behavior of contaminant transport incorporating with equilibrium controlled nonlinear sorption (Freundlich isotherm sorption) and to gain the knowledge about how sorption affects the transport of contaminant with subsurface water.

4.Methodology

Advance Solute Transport Numerical Models

The advanced solute transport models, also known as extended solute transport models or fully coupled (hybrid) models, are applied to solve complex problems, either one- or multidimensional, that often involve multiple chemical species, diverse transport processes, material heterogeneity, complex boundary conditions, and time-varying stresses.

Examples- MT3D, MT3DMS, GMS , HYDRUS and Processing Modflow etc.

MT3DMS

- The abbreviation for MT3DMS is "The modular three-dimensional multispecies Transport model" It was developed by Chunmiao Zheng in 1990. It was a USEPA financed development and after development the USEPA made it public.

- MT3DMS can be used to simulate various physical and chemical changes undergoing solute transport process also there is independency to selection of different boundary conditions. The basic chemical package for this software can simulate for single contaminant but for multi species and additional package named RT3D is given separately. The basic chemical reaction package named RCT is capable of solving single species with conditions like equilibrium-controlled or rate-limited or non-linear sorption and 1st order kinetic reactions.

Mathematical background of MT3DMS

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Governing equations for solute transport.

Since for sorption generally local equilibrium is assumed, the governing equation for the transport model of solute is given as:

$$R\theta \frac{\partial \bar{C}}{\partial C} = \frac{\partial}{\partial x_i} \left\{ \theta Dij \frac{\partial C}{\partial x_j} \right\} - \frac{\partial}{\partial x_i} (\theta \nu_i C) + q_s Cs - q_s' C - \lambda_1 \theta C - \lambda_2 \rho_b \bar{C}$$

Darcy's law relates transport and flow equations.

$$v_i = \frac{q_i}{\theta} = -\frac{k_i}{\theta} \frac{\partial h}{\partial x_i}$$

Solution Technique

- MT3DMS applies FDM , TVD(The ultimate scheme)and Mixed approaches counter the errors and to improve the efficiency of model and to improve the accuracy of the solution results.
- At nodal concentration a third order polynomial interpolation is used by the ultimate scheme to determine the concentration at the interface.
- Now for a FDM grid with similar spacing with a coordinate system originated at point j with velocity ‘v’ (left to right). At time level n+1 on point j concentration caused by advection only can be given as;

$$\boldsymbol{C_j^{n+1}} = \boldsymbol{C(0, \Delta t)} = \boldsymbol{C(-v\Delta t, 0)}$$; Δt = time step for transport

Chemical reaction package (RCT)

- Since our study is based on Freundlich sorption isotherm which is a non-linear isotherm empirical model/equation is described as:

$$\bar{c} = K_f c^a$$

Here, K_f = Freundlich constant/Adsorption capacity, $(L^3M^{-1})^a$

a = Freundlich exponent/ adsorption intensity, dimensionless.

The chemical reaction package is named as RCT package and for selecting the type of isotherm the value of their coefficient the instruction is given in MT3DMS manual. Kf=SP1 and a=SP2

p2.rct - Notepad

File Edit Format View Help

```
         2          0          2          0
         0  1.587E+0                              RHOB
         0   1.40E-0                              SP1
         0        .8                              SP2
```

Major steps taken for Simulation

1. Data processing

- Transport model creation
- Input files generation
- Run the simulation

2. Data visualization

- Export The Output observation files to excel
- BTCs plotting and trend analysis.

Transport model Formation

For this study the same problem is taken as illustrated in (Grove and Stollenwerk, 1984) considering the Freundlich isotherm.

Model parameters were taken as;

Grid-space(ΔX) = 0.160 cm, Dispersity(a_L) = 1.0 cm, GW seepage-velocity(v)= 0.1 cm/s, Porosity(θ) = 0.37,

Bulk density(ρb) =1.587 g/cm3, Source concentration (Co) = 0.05 mg/l, Pulse Input time (t_o)= 160 seconds.

Initial and Boundary conditions for our model is provided as;

- $C(x,0) = 0$
- $-\theta D\left(\frac{\partial C}{\partial x}\right) + qC\,\Big|(x=0) = \begin{cases} fo & 0 < t < to \\ 0 & t > to \end{cases}$
- $\frac{\partial C}{\partial x}(\infty, t) = 0 \qquad t > 0$

RCT input file

For the current study we need to generate input file for chemical reaction package (.RCT file) every single time with a different value of K_f and a, for this the generated input .RCT file is modified each time before a new simulation is being run

```
p2.rct - Notepad
File   Edit   Format   View   Help
         2          0            2          0
         0    1.587E+0                                  RHOB
         0      .30E-0    Kf                            SP1
         0          .7                                  SP2
                       a
//Freundlich: use the following input
         2          0            2          0
         0    1.587E+0                                  RHOB
         0      .30E-0                                  SP1
         0          .7                                  SP2
```

For the it mainly in three sets of values to analyze the behavior of BTCs of contaminant at 8 cm distance from the input source point keeping all other parameters identical to the original problem.

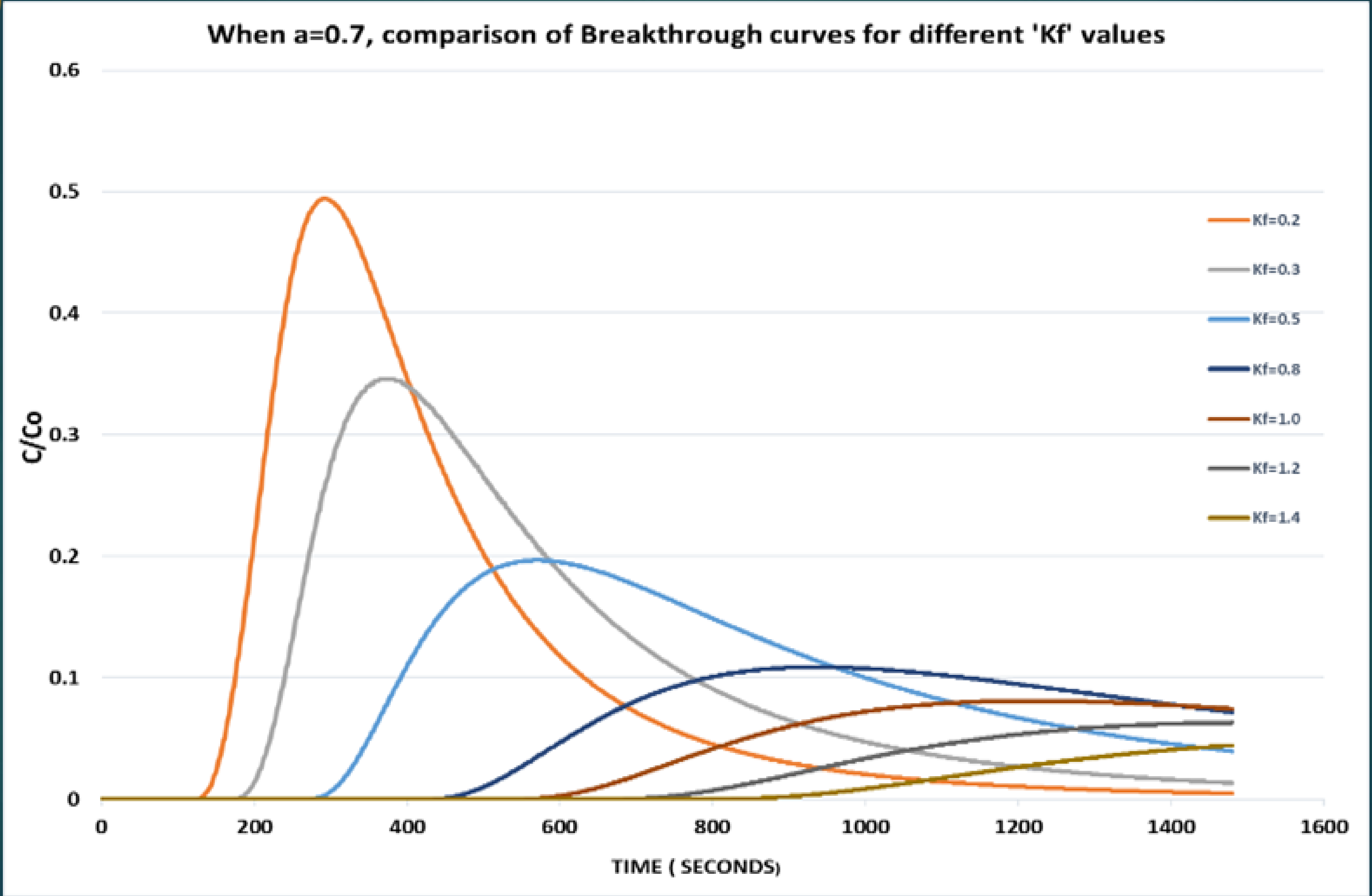
- SET-1   SP1= K_f = varies between 0.2 to 1.4 and SP2=a=0.7,
- SET-2   SP1= K_f= varies between 0.2 to 1.4 and SP2=a=0.6,
- SET-3   SP1= K_f= varies between 0.2 to 1.4 and SP2=a=0.8.

5. RESULTS

- For this study all the breakthrough curves are plotted at a distance of 8 cm from the initial source point of the concentration for a concentration pulse input for t_0=160 seconds and the initial concentration C_o=0.05 mg/l and the total time for simulation is taken as 1500 seconds.

- Here C/Co shows the relative aqueous phase concentration at that point with respect to initial concentration and time unit of simulation is taken in seconds.

- In this section we will do a trend analysis for the breakthrough curves for different 3 sets of K_f and a by varying the values of these parameters.


When a=0.7, comparison of Breakthrough curves for different 'Kf' values
C/Co
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
1400
1600
TIME (SECONDS)
Kf=0.2
Kf=0.3
Kf=0.5
Kf=0.8
Kf=1.0
Kf=1.2
Kf=1.4

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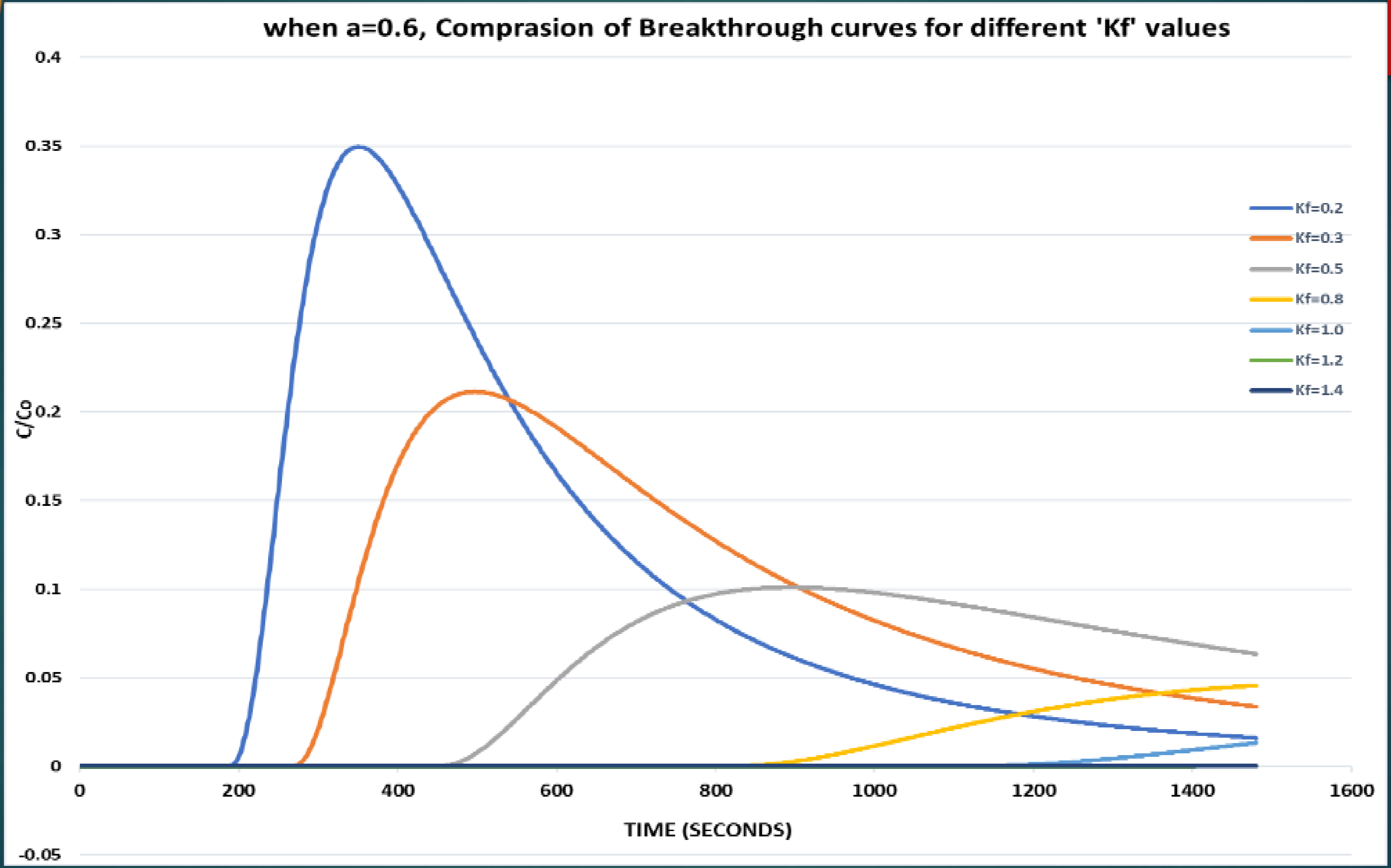

when a=0.6, Comprasion of Breakthrough curves for different 'Kf' values
C/Co
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0
200
400
600
800
1000
1200
1400
1600
TIME (SECONDS)
Kf=0.2
Kf=0.3
Kf=0.5
Kf=0.8
Kf=1.0
Kf=1.2
Kf=1.4

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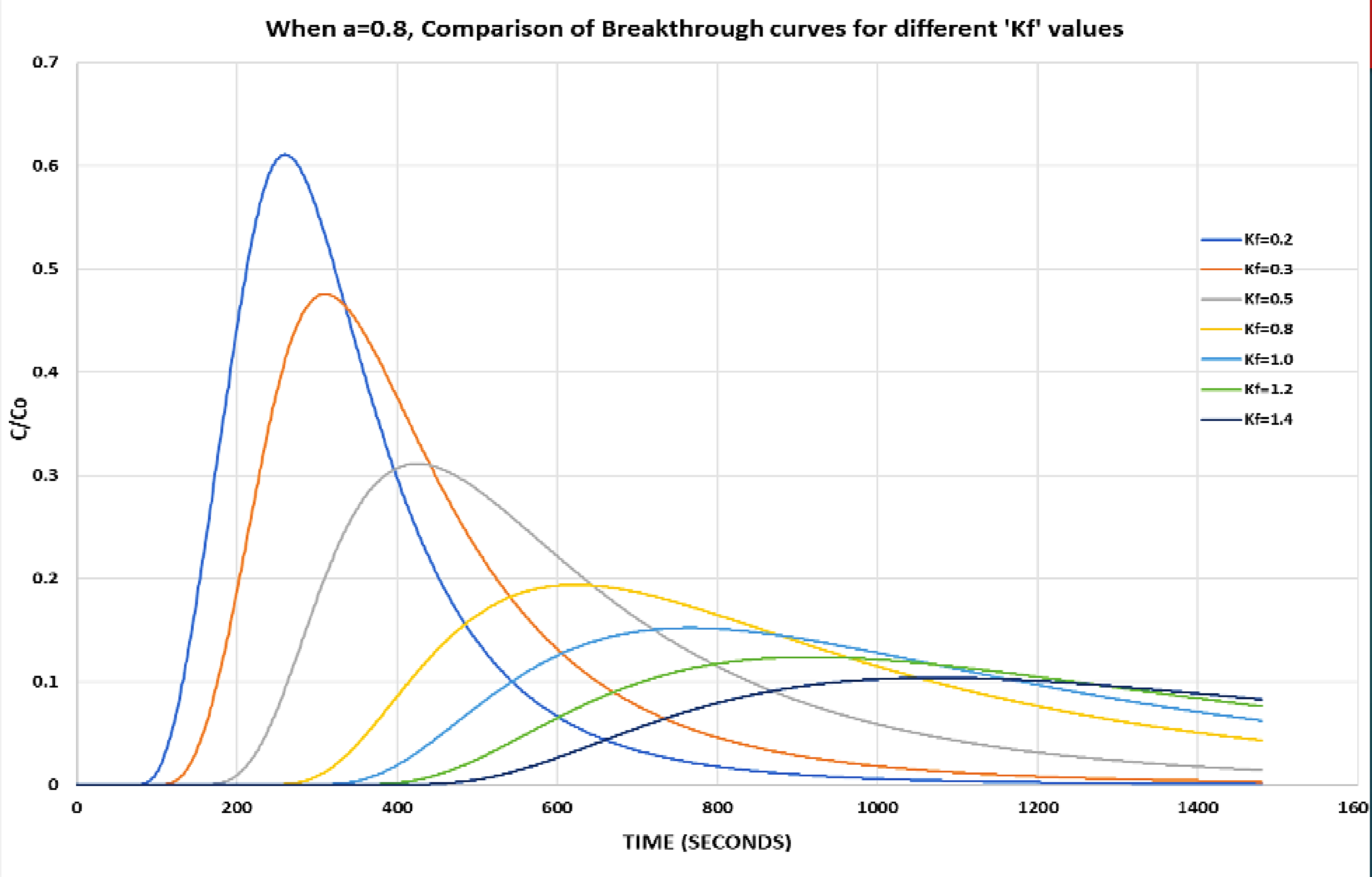
When a=0.8, Comparison of Breakthrough curves for different 'Kf' values
C/Co
TIME (SECONDS)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
1200
1400
160
Kf=0.2
Kf=0.3
Kf=0.5
Kf=0.8
Kf=1.0
Kf=1.2
Kf=1.4

Comparison of Relative concentration values at a point 8 cm from the input source for different K_f and a Values.

K_f	Maximum relative concentration (C/Co) at 8 cm distance from the source in aqueous dissolved phase within the simulation time.		
	When, a=0.6	When, a=0.7	When, a=0.8
0.2	0.35	0.5	0.6
0.3	0.21	0.37	0.45
0.5	0.10	0.20	0.32
0.8	0.045	0.11	0.22
1.0	0.012	0.08	0.15
1.2	Negligible	0.06	0.13
1.4	negligible	0.040	0.10

CONCLUSION

- A porous medium has ability to adsorb contaminants from an aqueous solution is directly proportional to its adsorption capacity. As a result, the concentration of contaminants in the aqueous phase decreases when the adsorption capacity of the porous medium is higher, since more of the contaminant is adsorbed onto the solid phase. This leads to a reduction in the peak relative aqueous phase concentration and a slower rate of pollutant migration.
- However, a higher adsorption intensity can have an adverse effect on pollution migration. When the adsorption intensity is high, the concentration of contaminants in the aqueous phase increases compared to the concentration for a lower adsorption intensity, even when the adsorption capacity is the same. These critical parameters can be used to design a customized media with a suitable pollution removal process to treat targeted pollution.

Future scope

In the same problem we can take high initial pulse input concertation and check how the solute transport behaves also 3-D modelling will help in better understanding the plume spreading behaviour rather than 1-D.

Also the effect of pressure and temperature may be incorporated in model for better analysis and predicting and simulating actual GW solute transport process.

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Thank you!