



**The Abdus Salam  
International Centre for Theoretical Physics**



**1867-36**

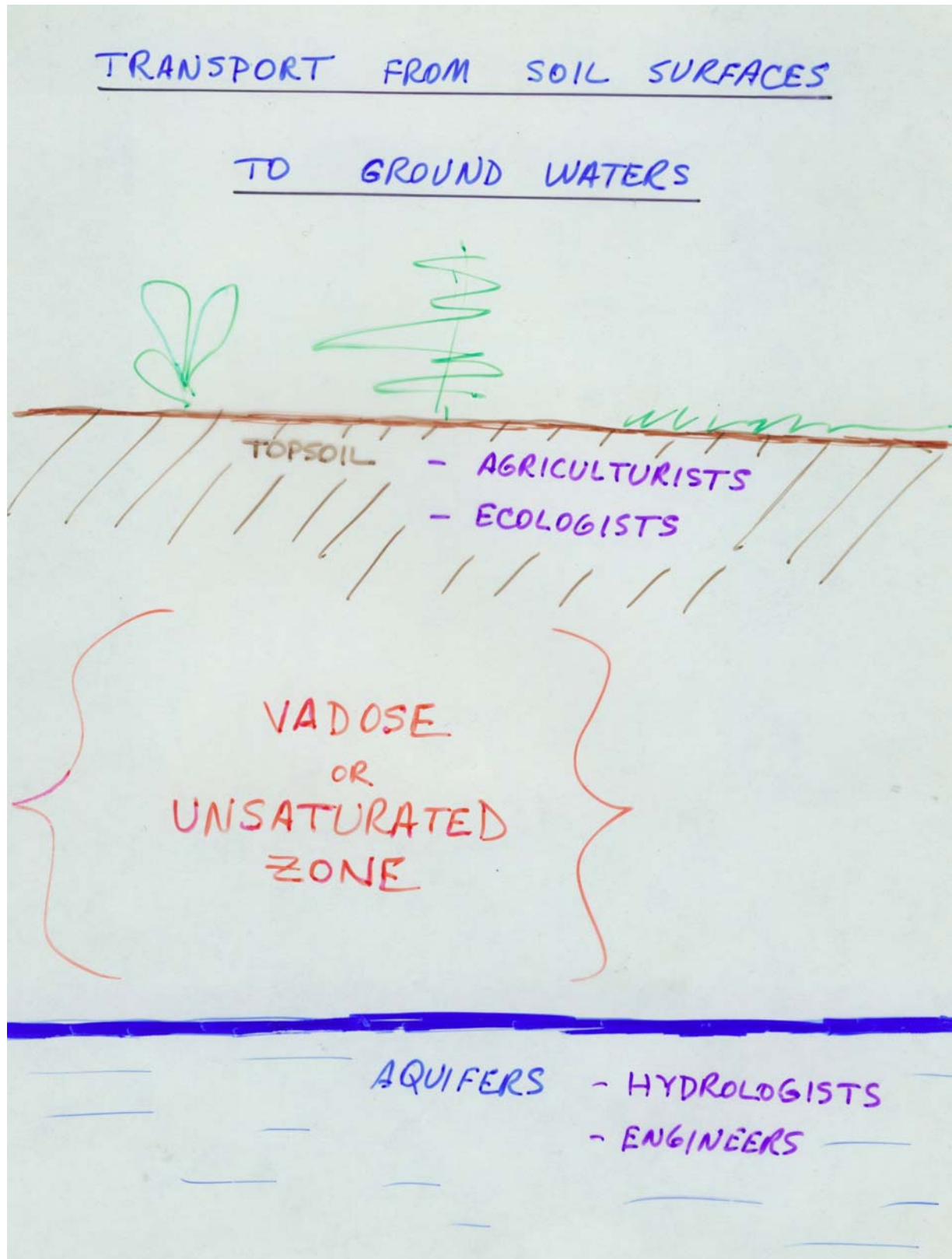
**College of Soil Physics**

*22 October - 9 November, 2007*

**Fundamentals of and analyzing solute transport in soils**

Donald Nielsen  
*University of California  
Davies  
USA*

# Transport from soil to groundwater



# MD Definition

## FLUIDS MOVE AND DISPLACE OTHER FLUIDS WITHIN A GIVEN GEOMETRY

If the fluids do not mix or combine together

### IMMISCIBLE DISPLACEMENT

air and water  
air and oil  
water and oil  
aqueous and nonaqueous fluids

If the fluids are mixable and soluble within  
each other

### MISCIBLE DISPLACEMENT

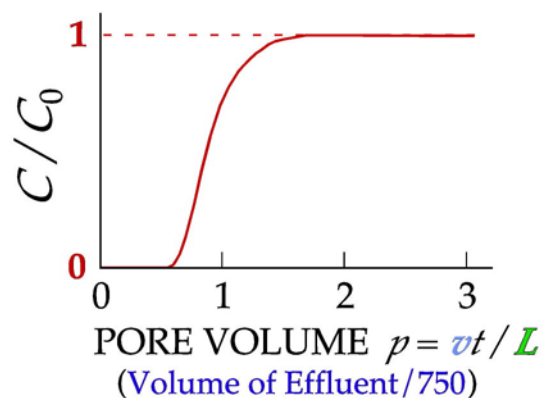
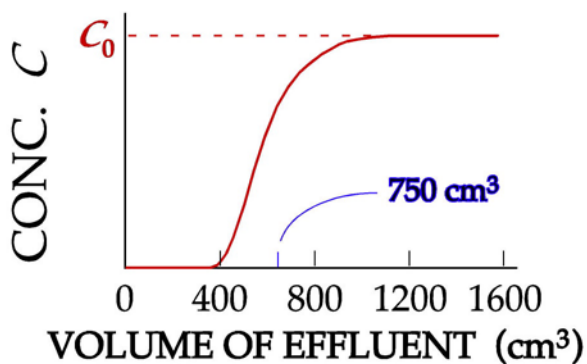
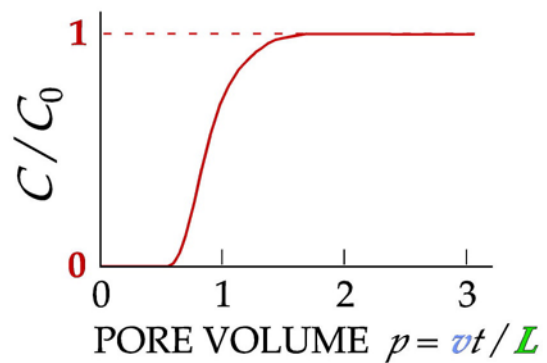
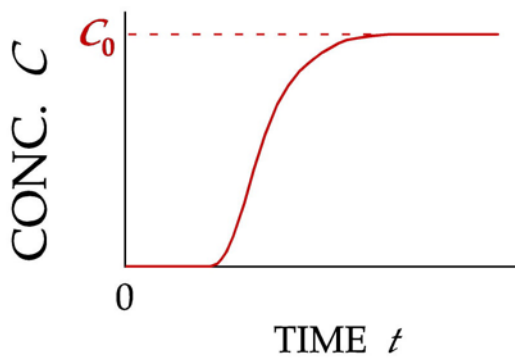
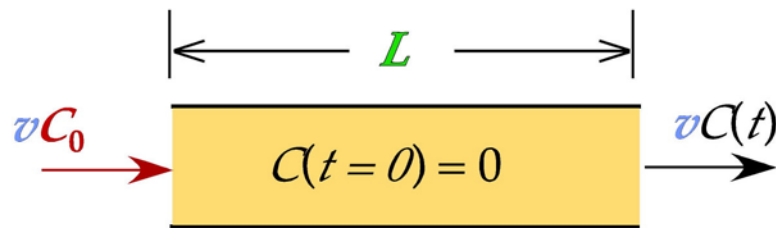
non-saline water and saline water  
rain water and soil solution  
alcohol and water  
paint and turpentine  
fresh air and smoke  
gasoline and oil

# BTC Definition

## MISCIBLE DISPLACEMENT IN FIELD SOILS

- UNDERSTAND LEACHING PHENOMENA
- PREVENT SOIL SALINIZATION
- RETAIN FERTILIZERS FOR PLANT UPTAKE
- MANAGE WASTES, RADIOISOTOPES, ETC.
- PROTECT SURFACE & GROUND WATER QUALITY

## MISCIBLE DISPLACEMENT SOIL COLUMN EXPERIMENT

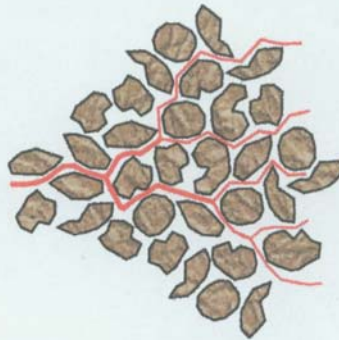




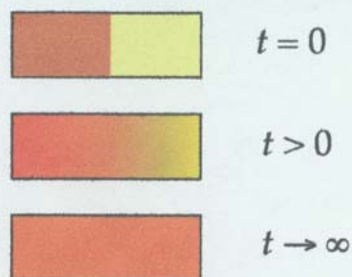
# Interpreting BTC

## INTERPRETING THE SHAPE OF A BREAKTHROUGH CURVE

### DISPERSION CAUSED BY CONVECTION



### DISPERSION CAUSED BY MOLECULAR DIFFUSION



### CHEMICAL REACTIONS

PRECIPITATION  
DISSOLUTION  
HYDROLYSIS, ETC.

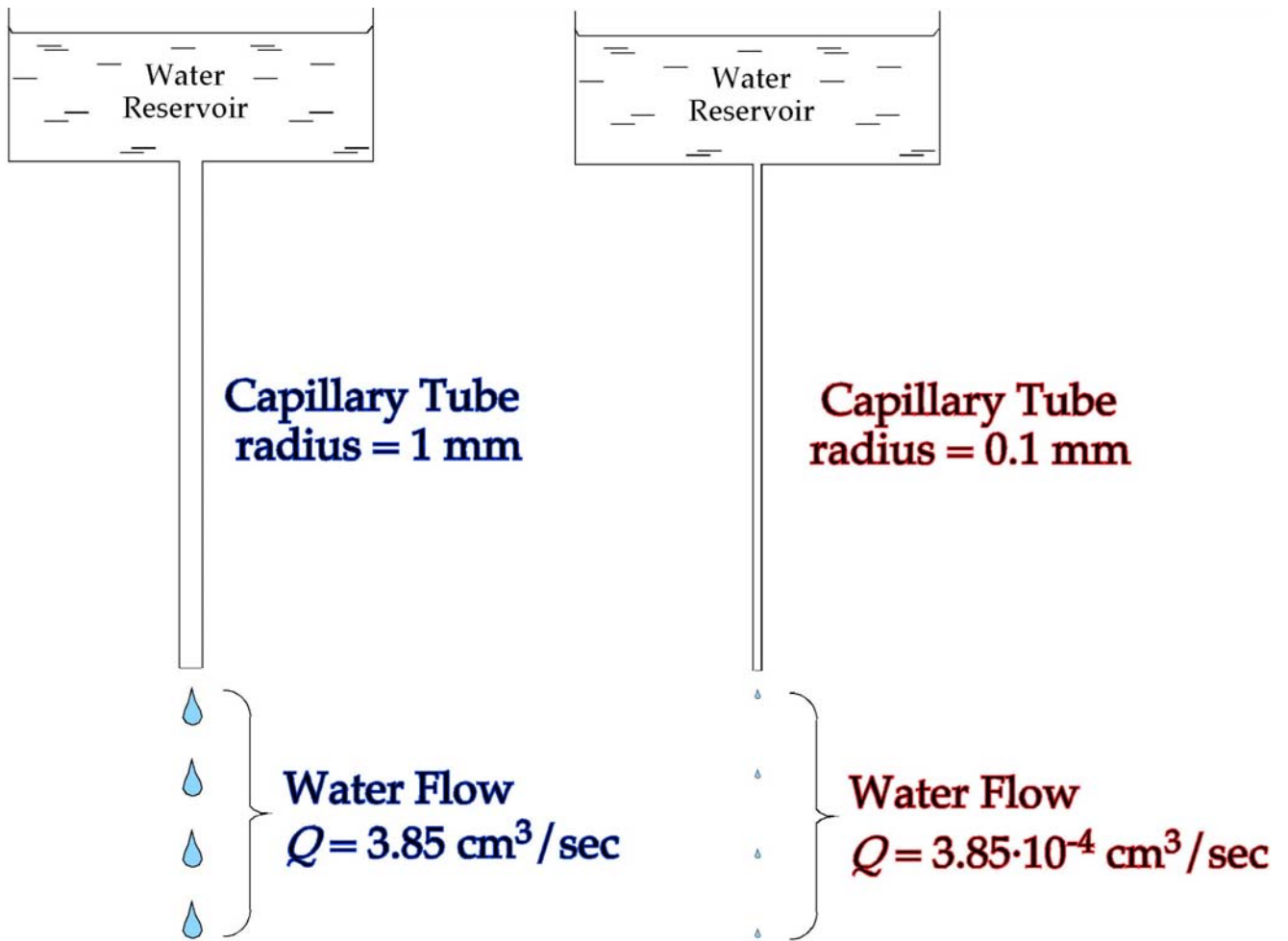
### PHYSICAL REACTIONS

CATION AND ANION EXCHANGE  
SWELLING & SHRINKING, ETC.

### MICROBIOLOGICAL TRANSFORMATIONS

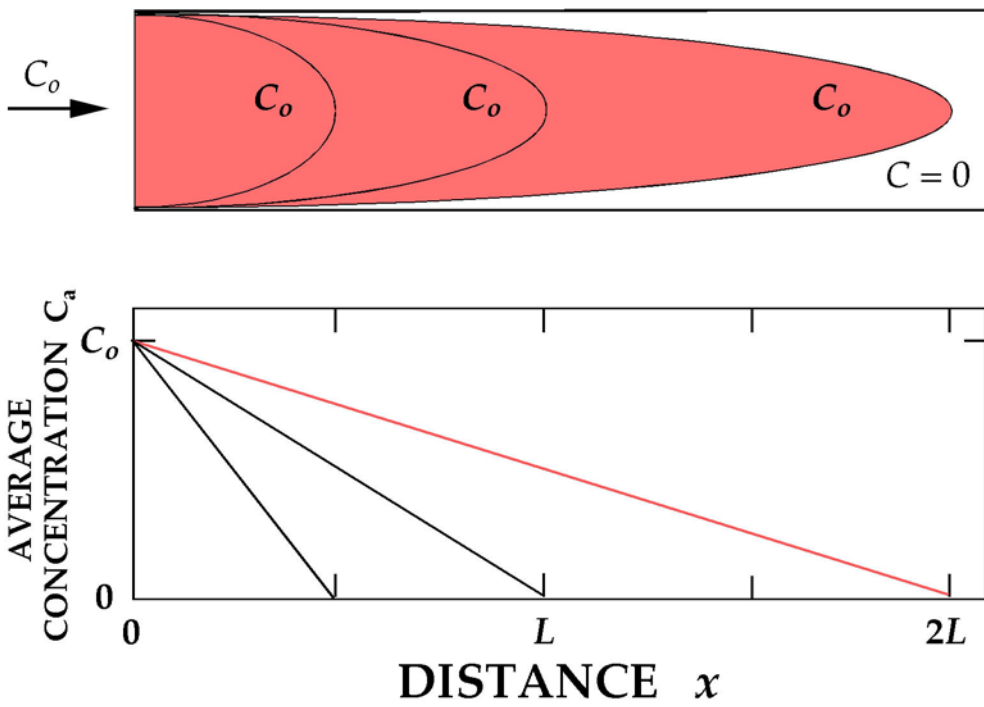
NITRIFICATION  
DENITRIFICATION, ETC.

# Capillary tube flow

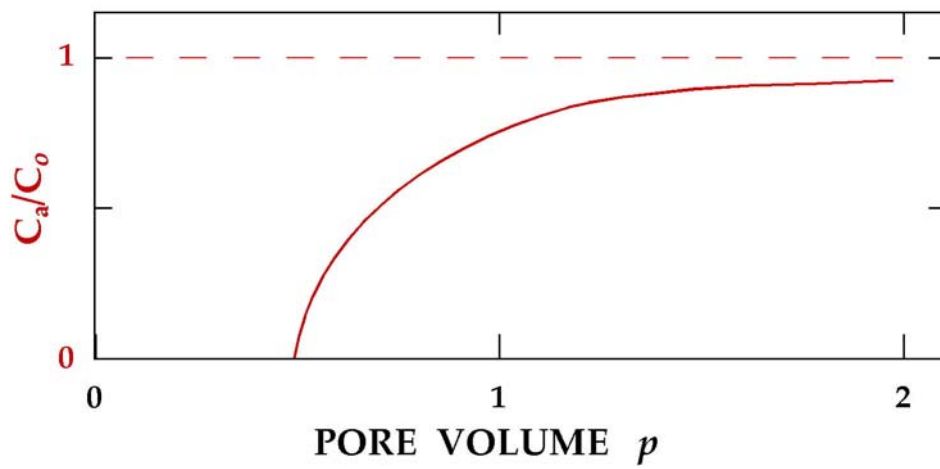
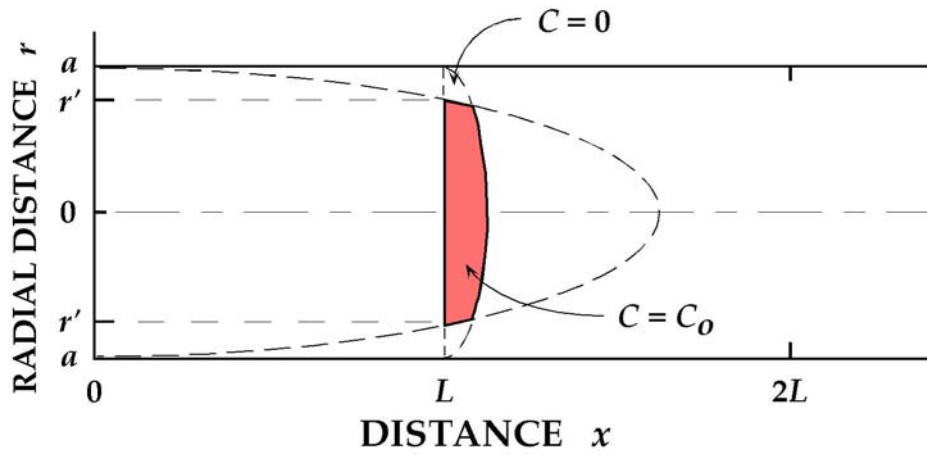


**1 Capillary Tube = 10,000 Capillary Tubes**

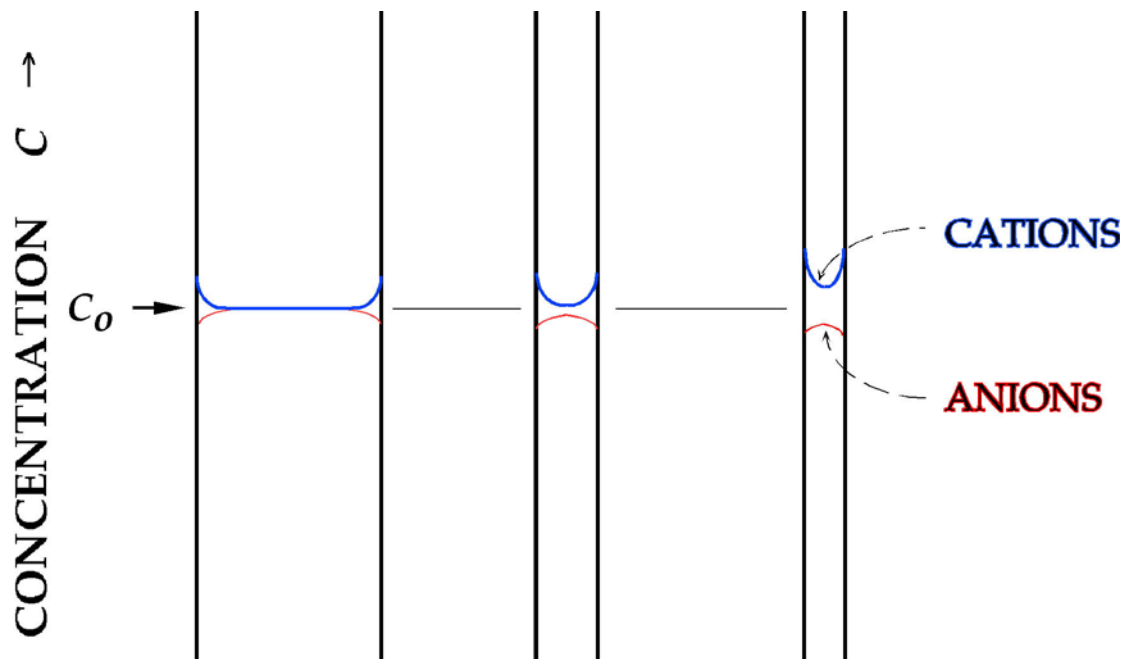
# Parabolic distribution



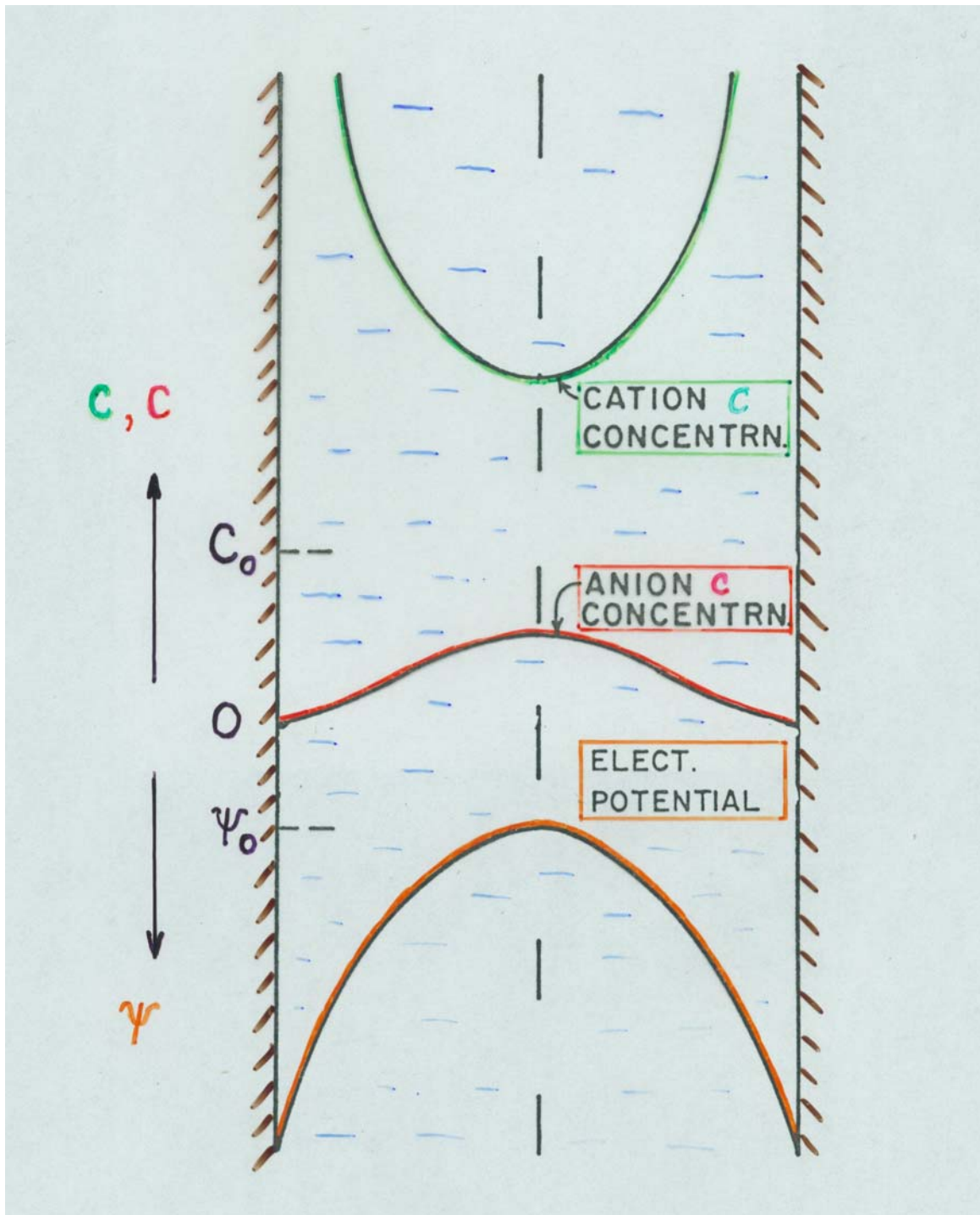
# Calculating Concentration



# Cations & anions in capillary

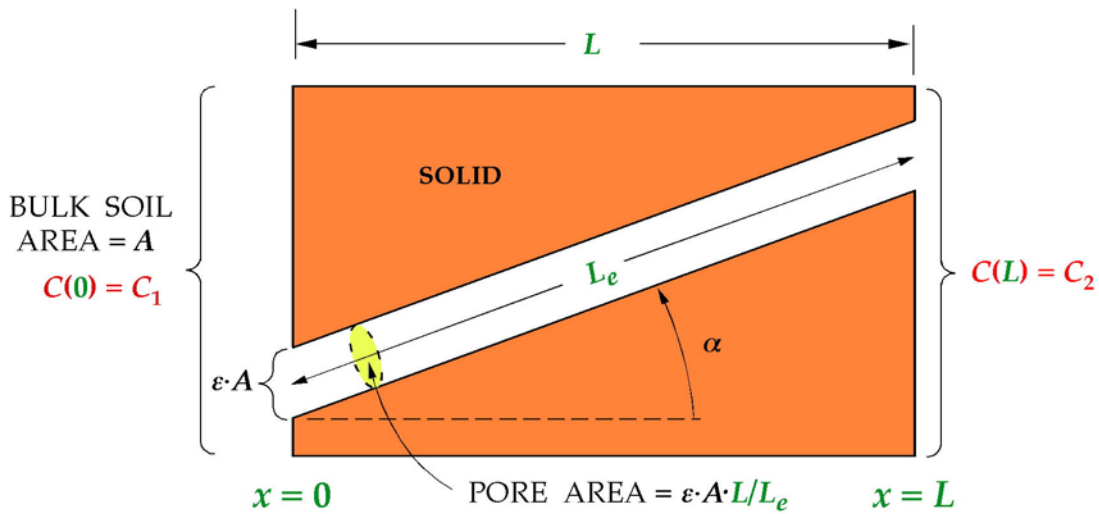


# Ions and pot.field in capillary





# Tortuosity



## FICK'S LAW OF MOLECULAR DIFFUSION

BULK SOIL

$$\left(\frac{Q}{At}\right)_{SOIL} = -D_{SOIL} \frac{C_2 - C_1}{L}$$

SOIL PORE

$$\left(\frac{Q}{\varepsilon A(L/L_e)t}\right)_{PORE} = -D_0 \frac{C_2 - C_1}{L_e}$$

$$\left(\frac{Q}{At}\right)_{PORE} = -D_0 \varepsilon (L/L_e) \frac{C_2 - C_1}{L_e}$$

EQUATING DIFFUSION IN BULK SOIL TO THAT IN SOIL PORE

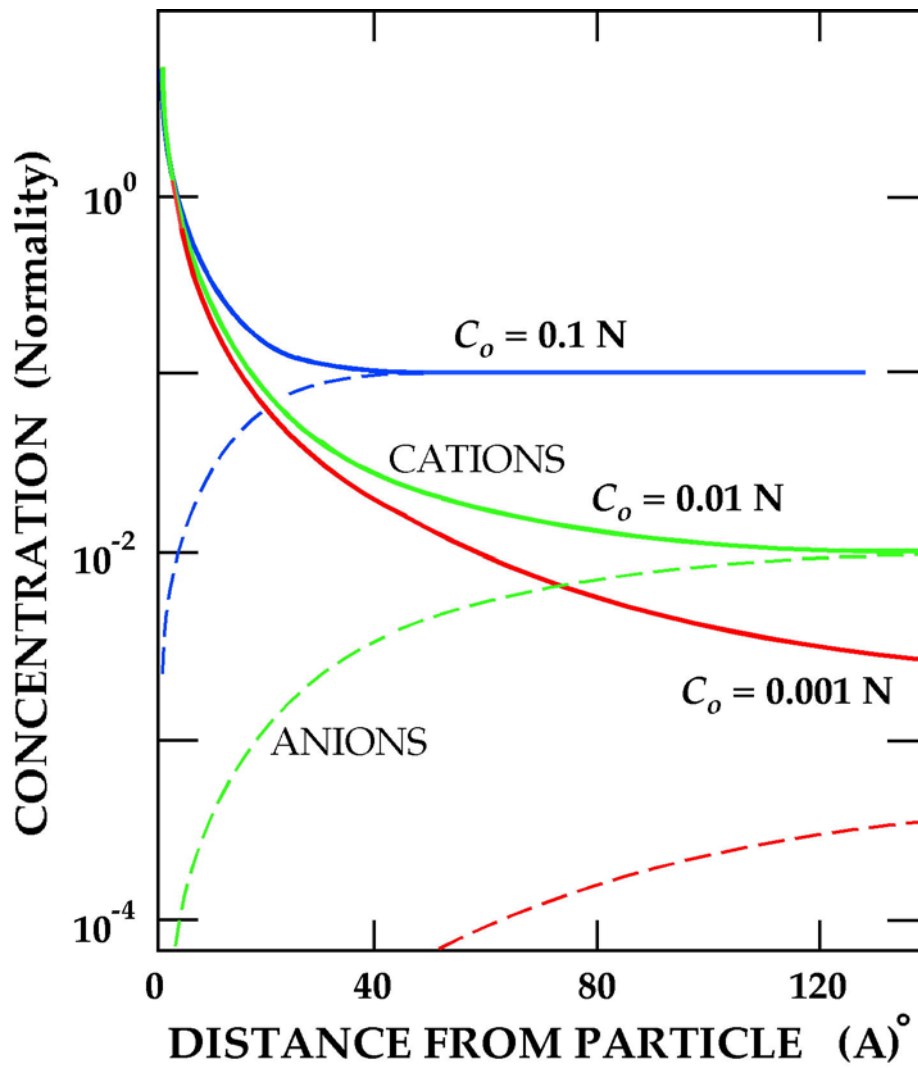
$$D_{SOIL} \frac{C_2 - C_1}{L} = D_0 \varepsilon (L/L_e) \frac{C_2 - C_1}{L_e}$$

$$D_{SOIL} = D_0 \varepsilon (L/L_e)^2 \quad \text{or} \quad D_{SOIL} = D_0 \varepsilon^n$$

VALUES OF TORTUOSITY  $(L/L_e)^2 = \cos^2 \alpha$

PENMAN	$(L/L_e)^2 = 0.66$	$\alpha \sim 36^\circ$
VAN BAVEL	$(L/L_e)^2 = 0.58$	$\alpha \sim 40^\circ$
MARSHALL	$n = 3/2$	$\alpha \sim 37^\circ$
MILLINGTON	$n = 4/3$	$\alpha \sim 31^\circ$

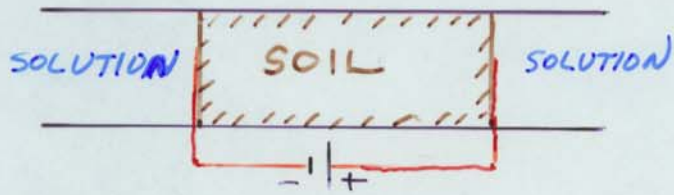
0.1, 0.01, 0.001 N



# Electrokinetic processes

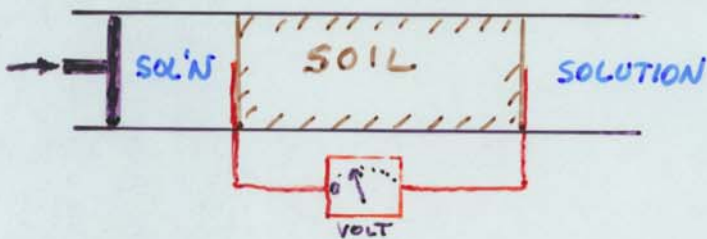
## ELECTRO-KINETIC FLOW PHENOMENA

ELECTRO-OSMOSIS (SOLIDS ARE FIXED, SOLUTION MOVES)



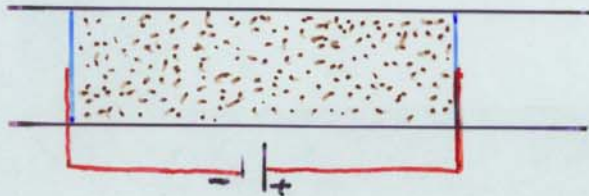
APPLY ELECTRICAL POTENTIAL,  
MEASURE WATER VELOCITY

STREAMING POTENTIAL (SOLIDS ARE FIXED, SOLUTION MOVES)



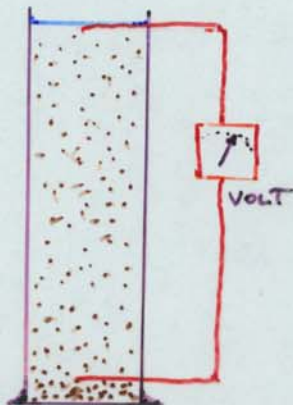
CREATE WATER VELOCITY,  
MEASURE ELECTRICAL POT.

ELECTROPHORESIS (SOLIDS MOVE, SOLUTION FIXED)



APPLY ELECTRICAL POTENTIAL,  
MEASURE PARTICLE VELOCITY

SEDIMENTATION POTENTIAL (SOLIDS MOVE, SOLUTION FIXED)



CREATE PARTICLE VELOCITY,  
MEASURE ELECTRICAL POT.

# Chemico-physico interactions

## CHEMICO-PHYSICO INTERACTIONS

pH → SOIL PARTICLE SURFACE CHARGE DENSITY

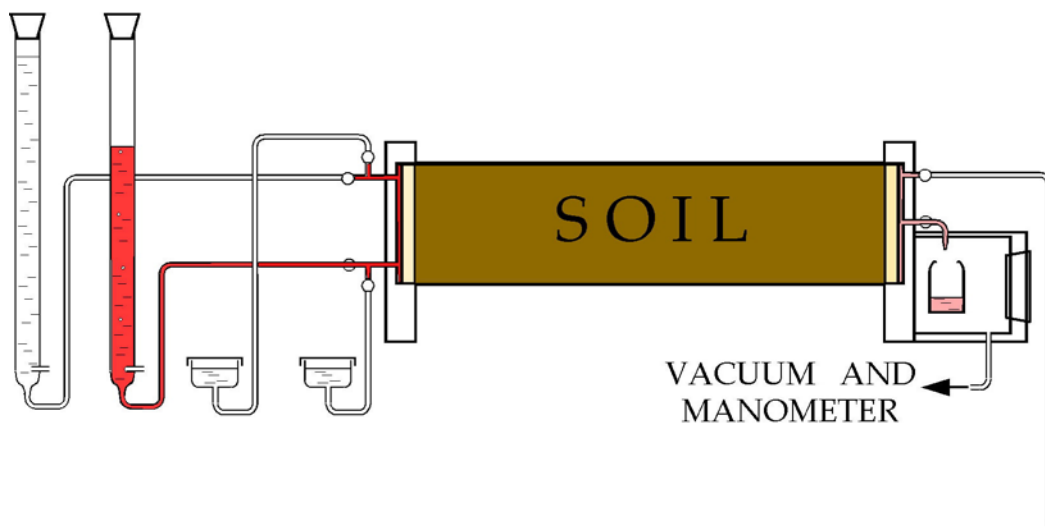
CHARGE DENSITY → ELECTRICAL FIELD

ELECTRICAL FIELD → ORIENTS CATIONS & ANIONS

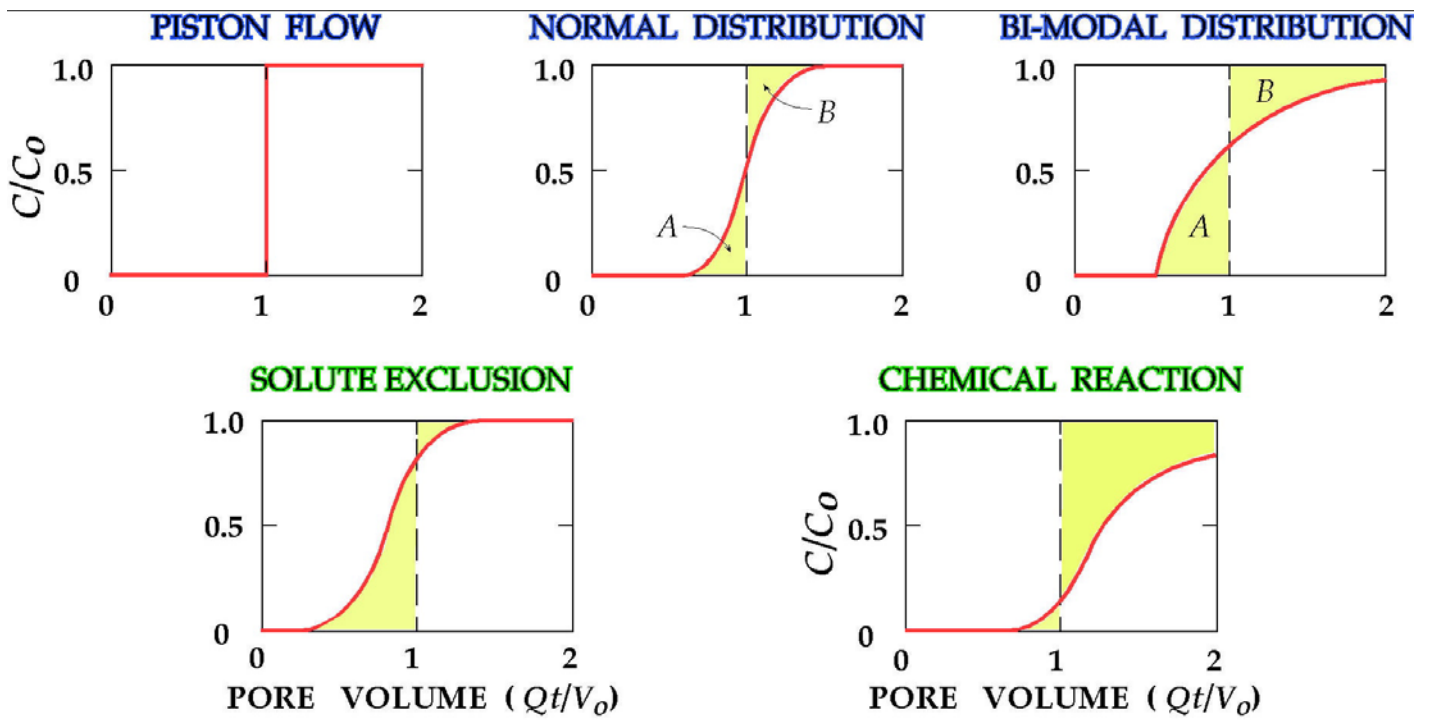
CATIONS & ANIONS → WATER MOLECULE CONFIGURATIONS

WATER CONFIGURATIONS → HYDRAULIC CONDUCTIVITY

# Lab apparatus

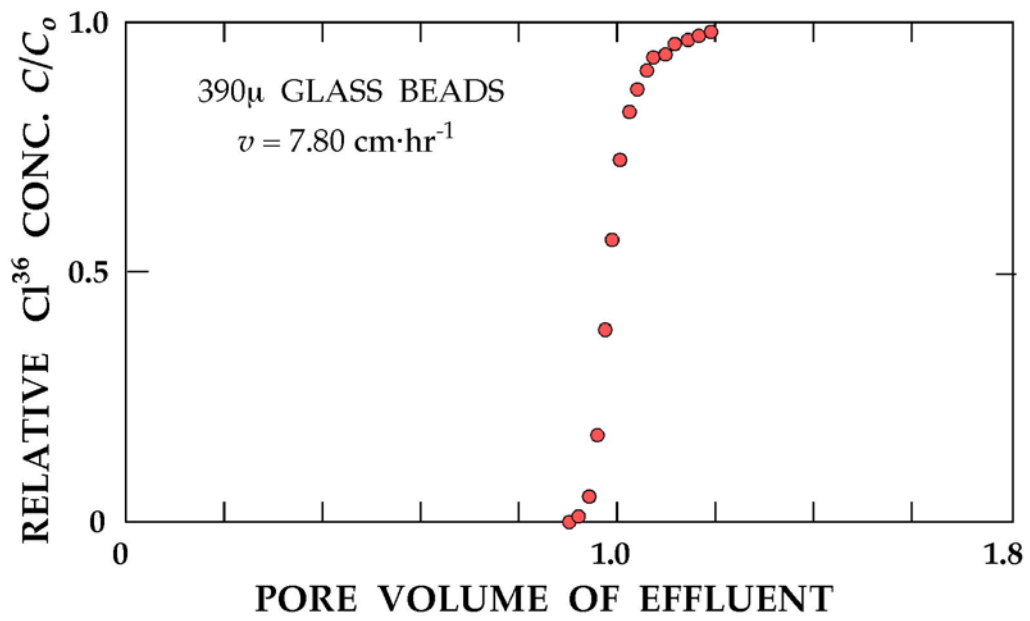


# Five BTCs

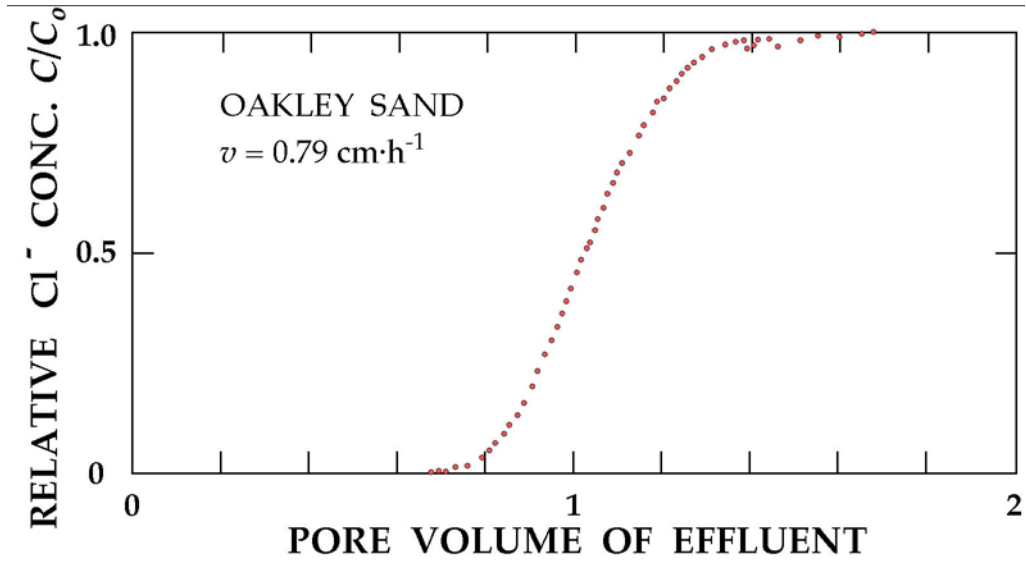




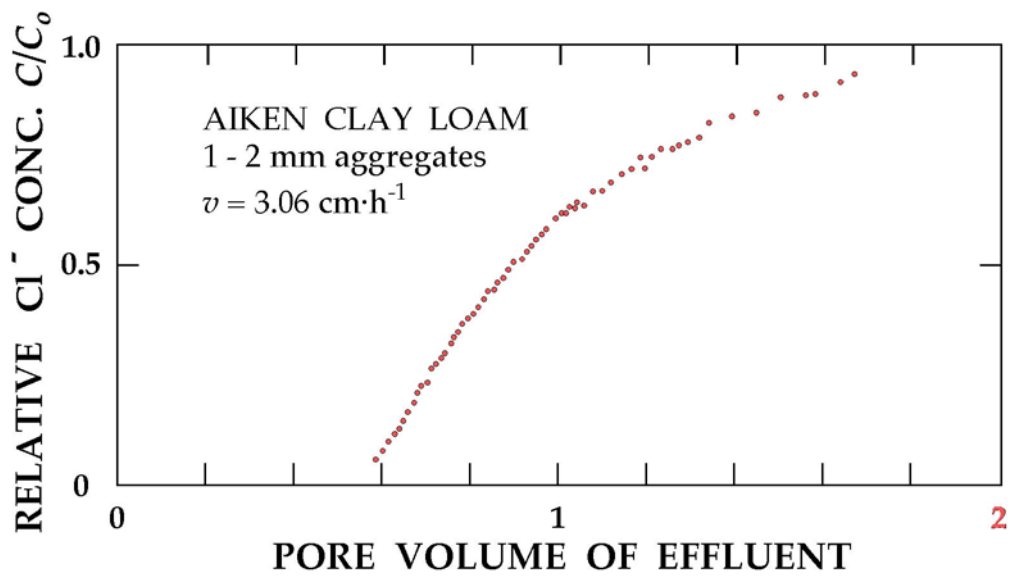
# Piston BTC



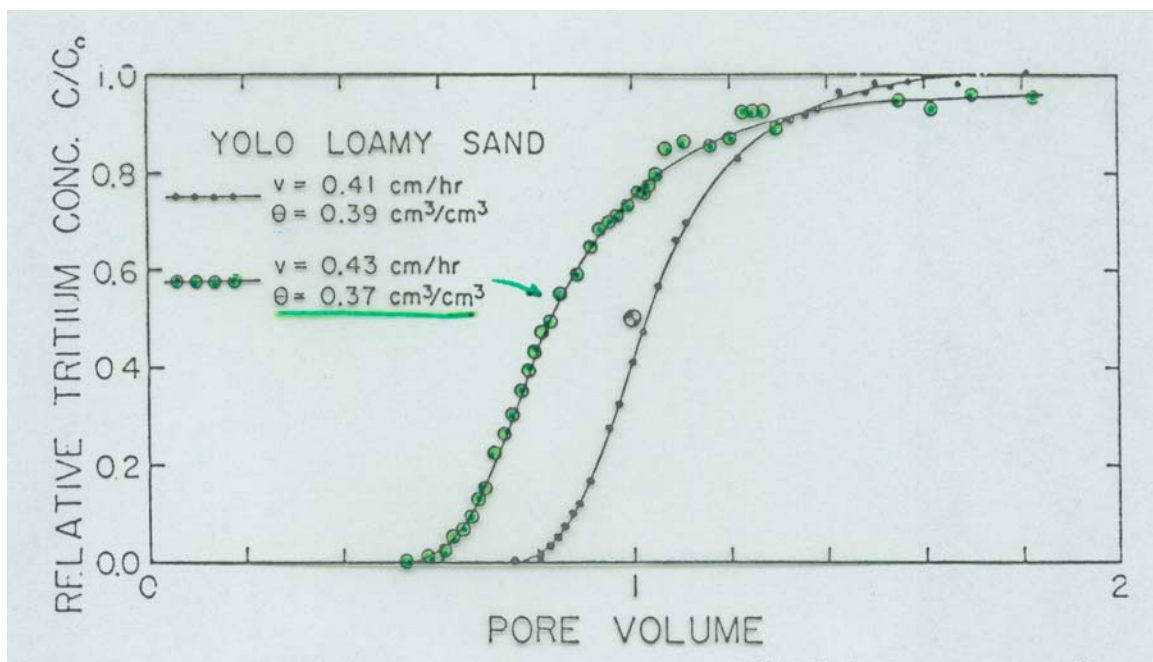
# BTC 2



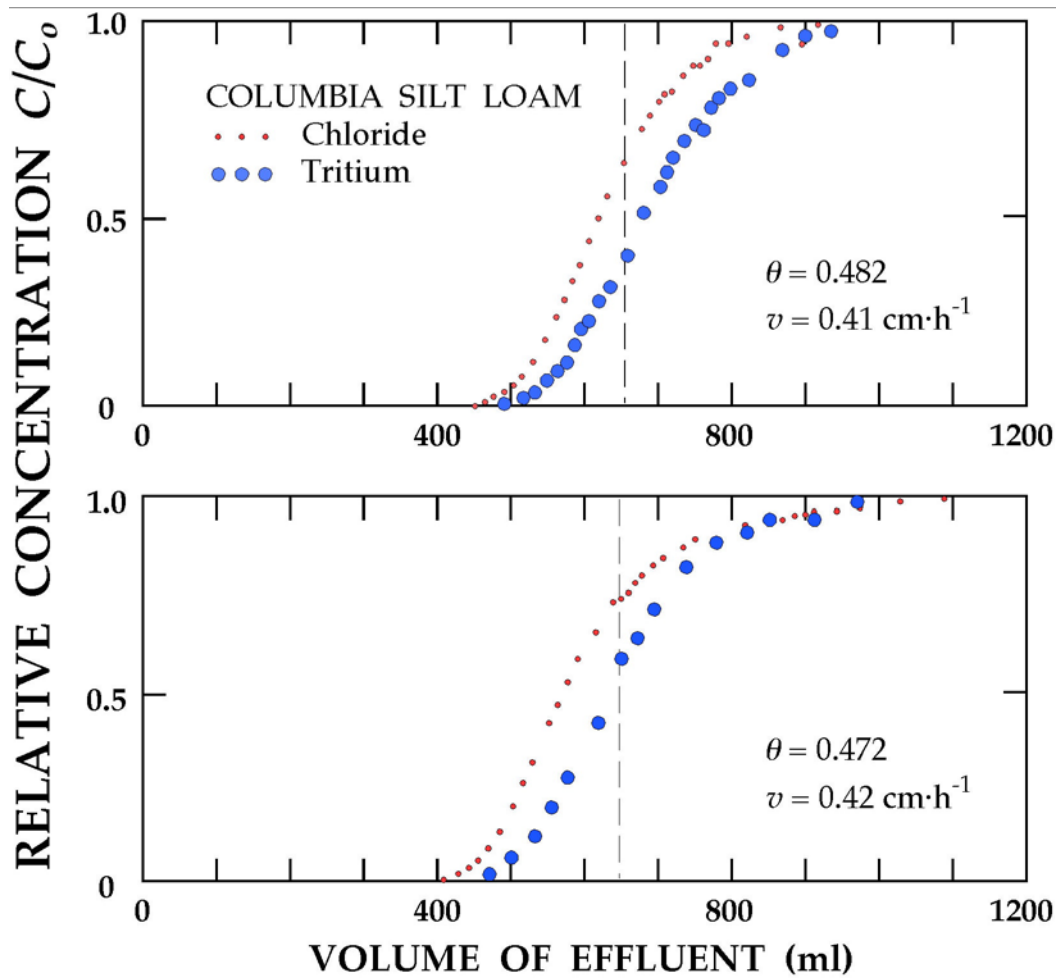
# BTC 3



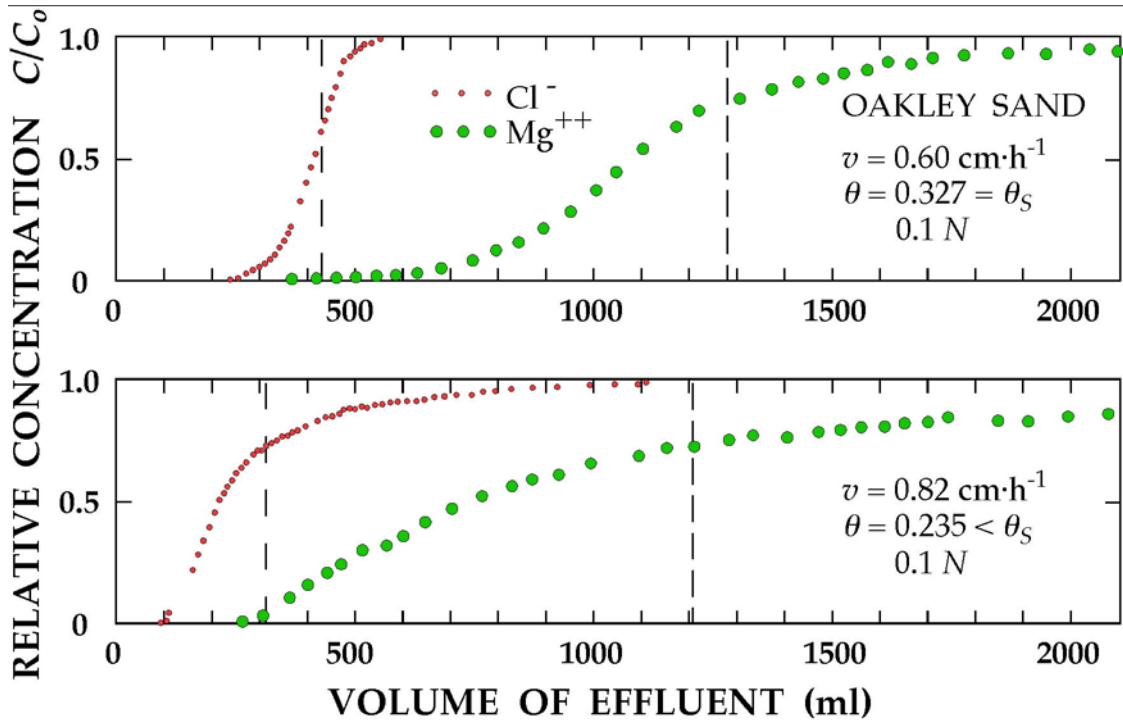
# Small theta change 1



## Small theta change 2

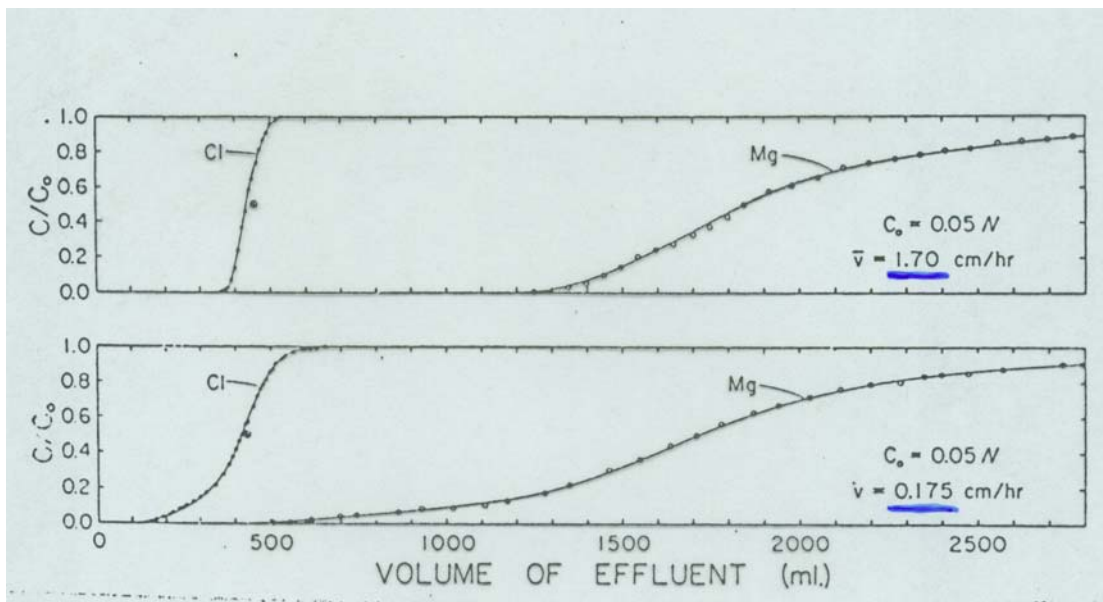


# Exchange delta theta

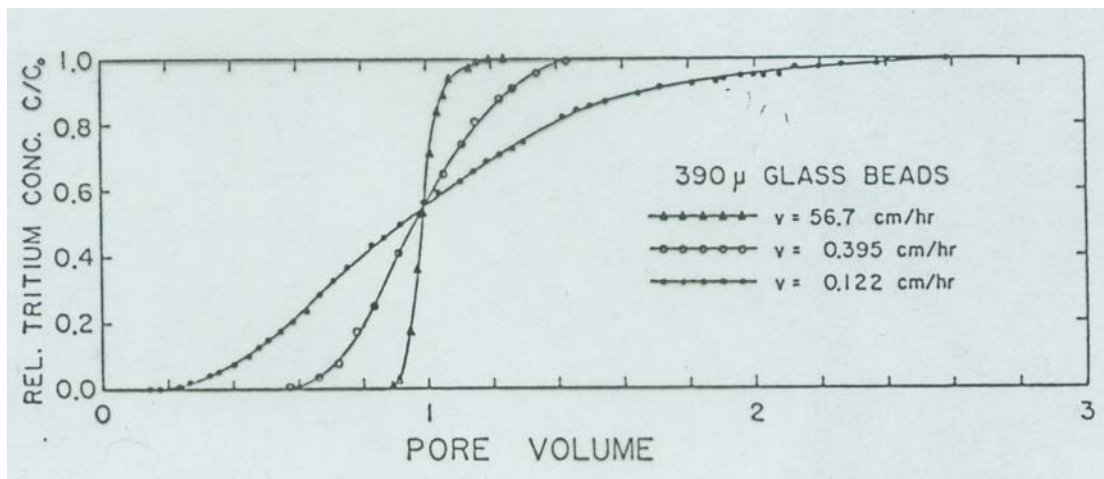




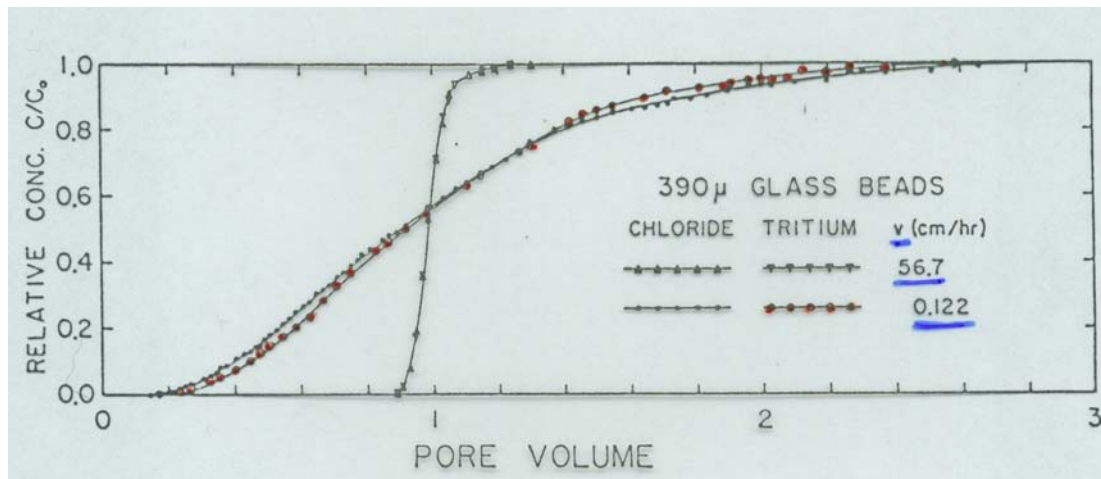
# Exchange delta vel



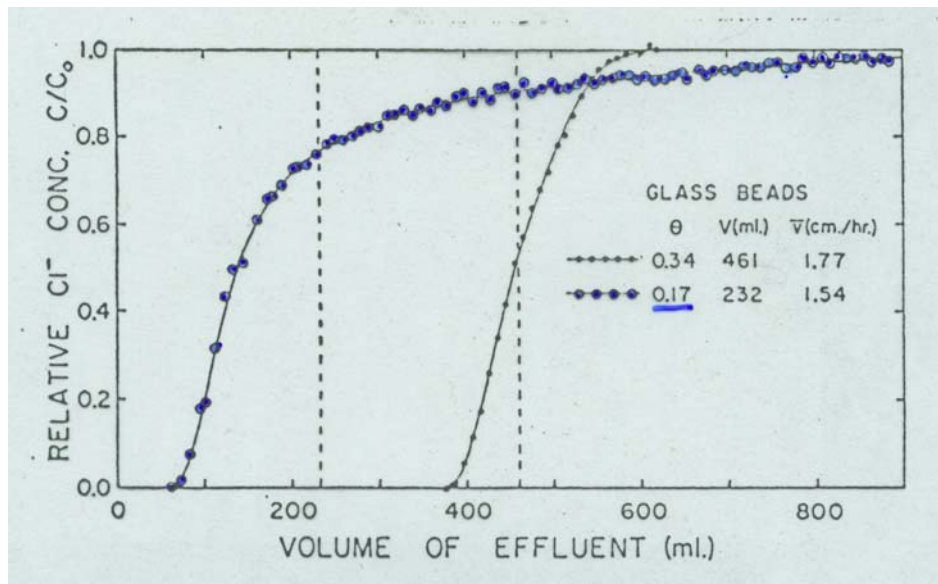
# Tritium 3 velocities



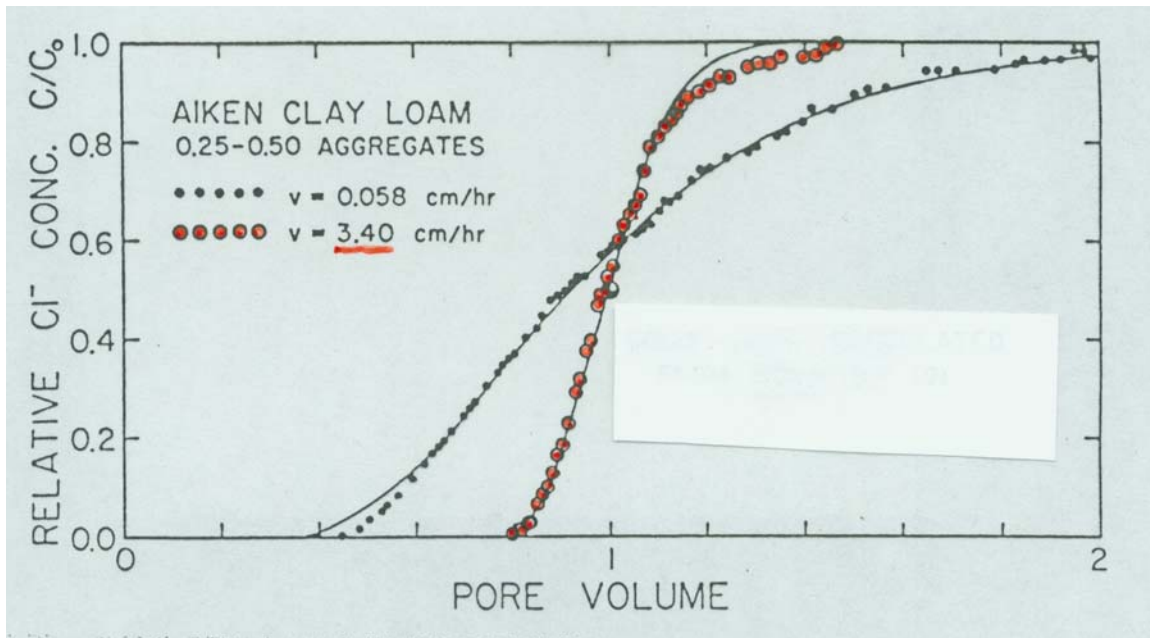
# Cl & Tritium 2 velocities



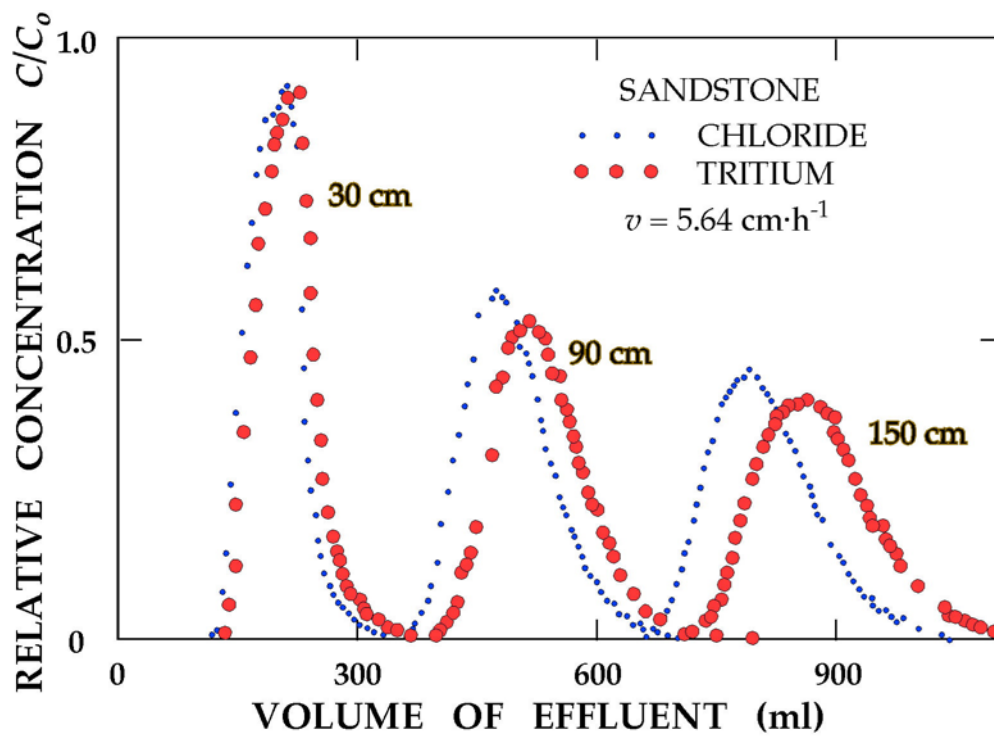
# Sat & Unsat beads



# Aiken 2 velocities

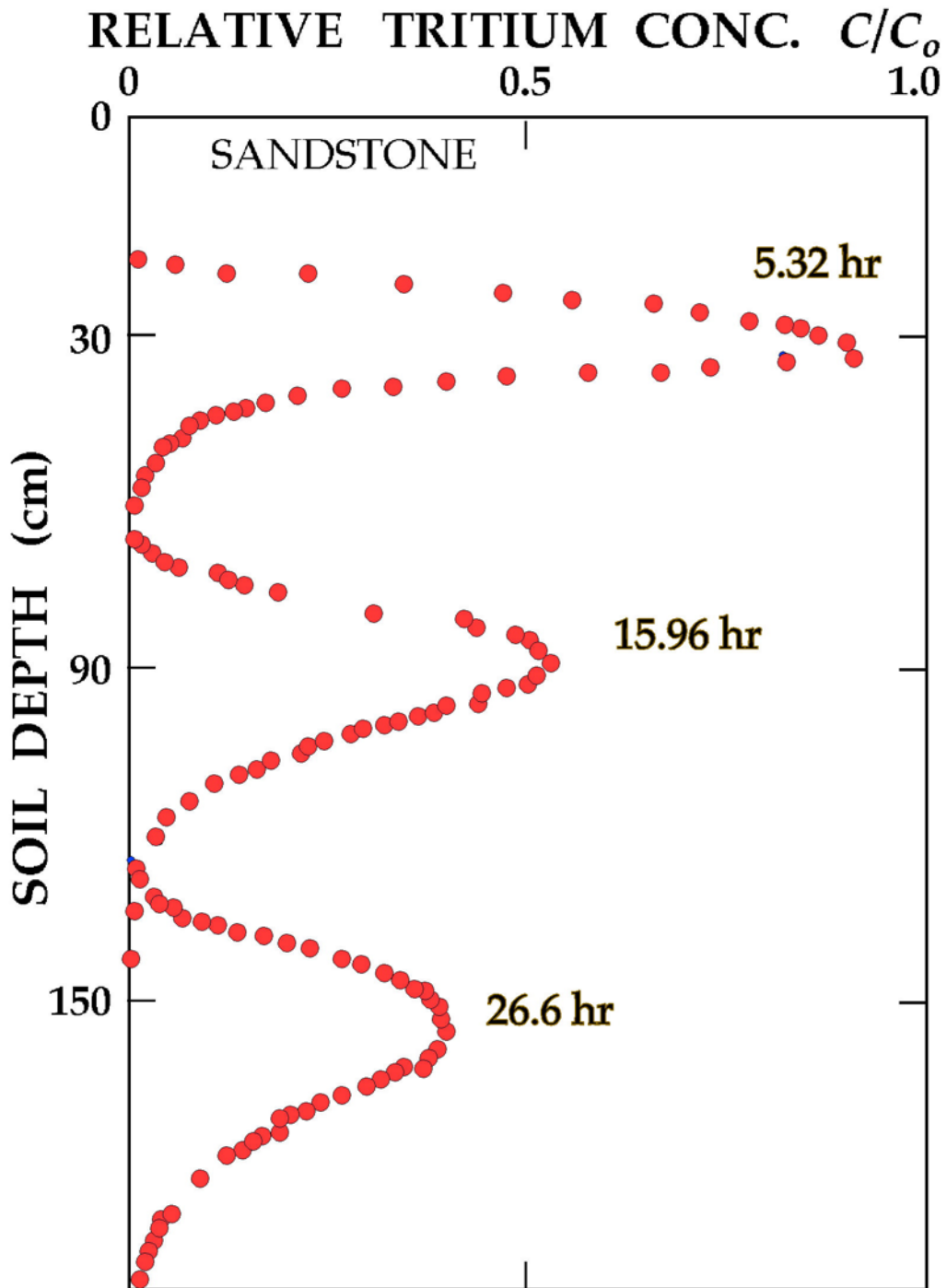


# 30, 90 and 120 cm

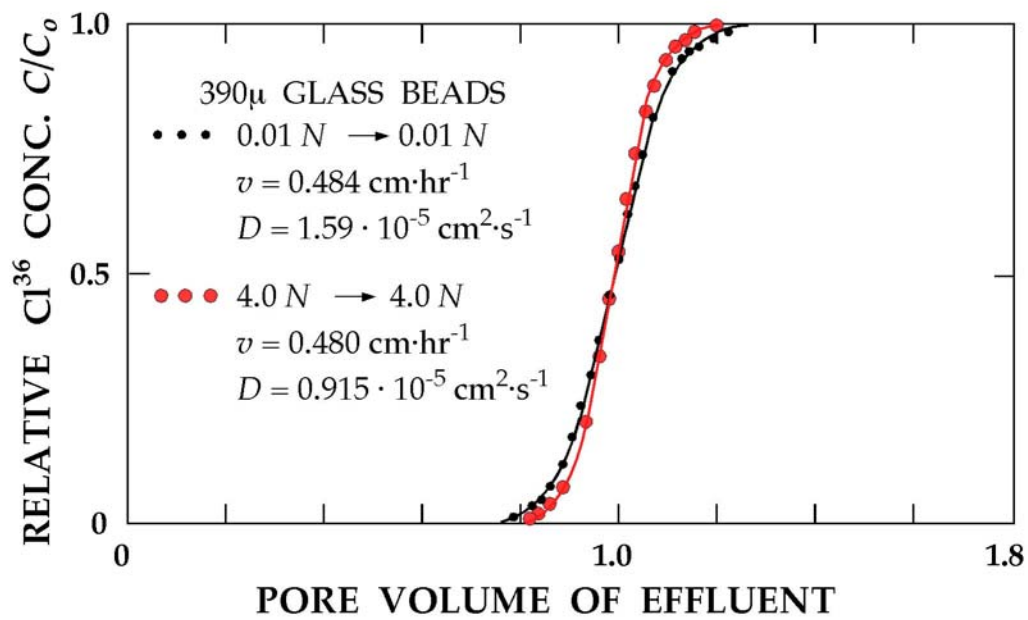




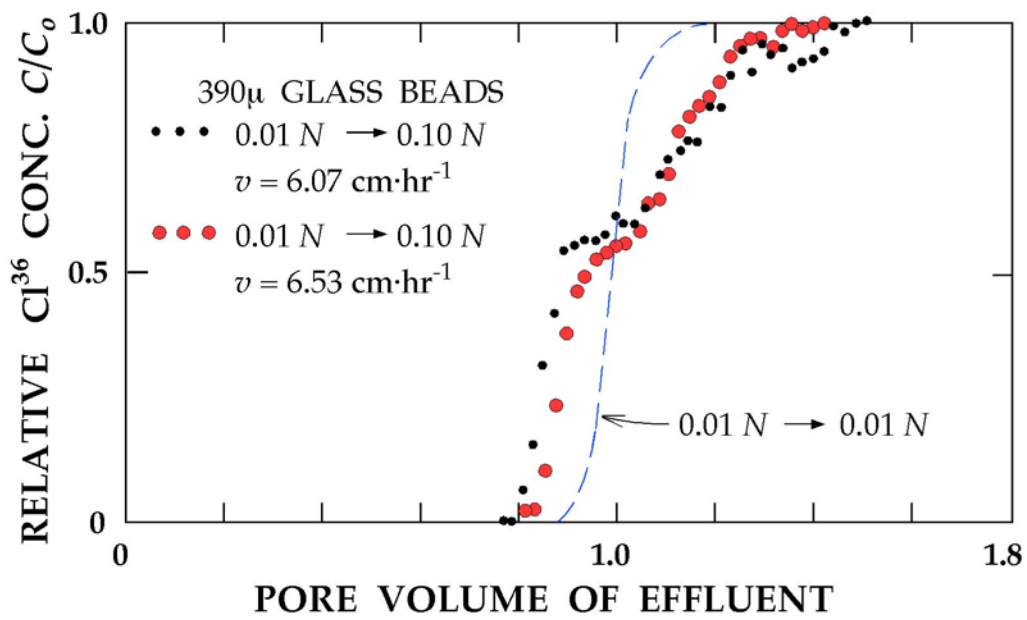
# Tritium profile



# Liquid density

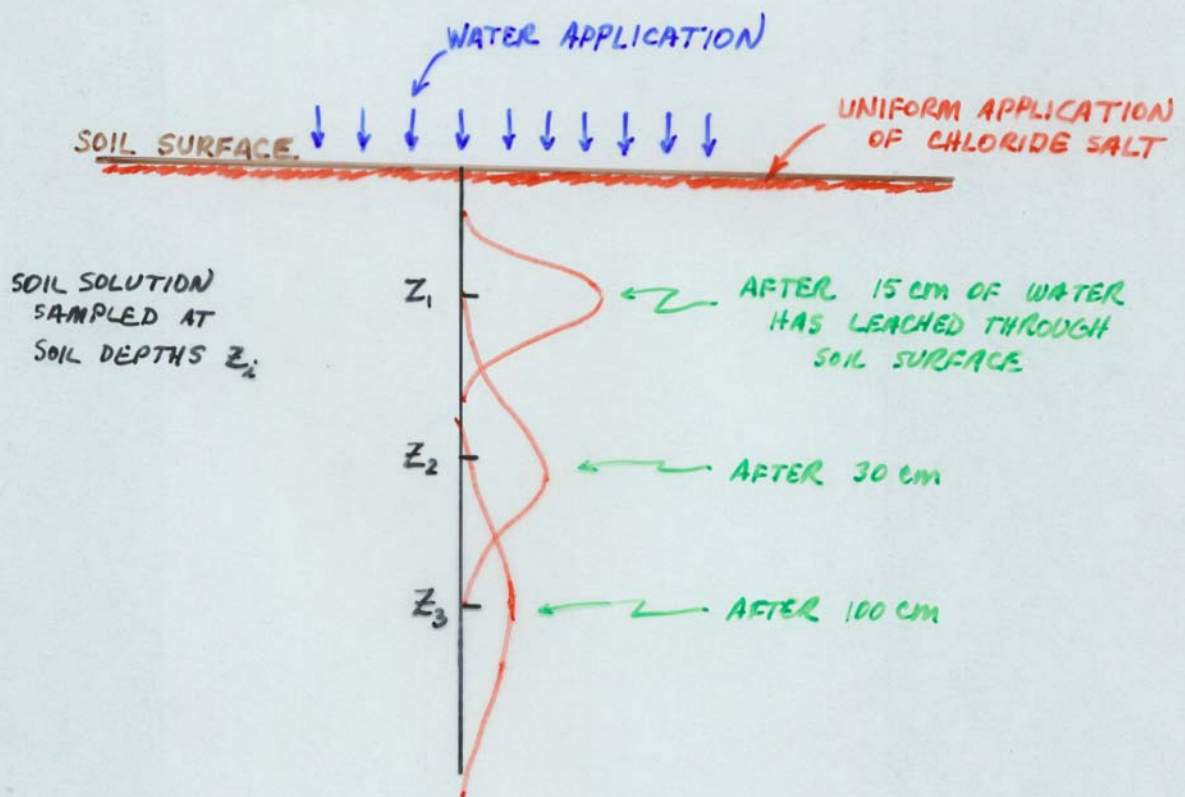


# Heavy over light



# Field Leaching Expt

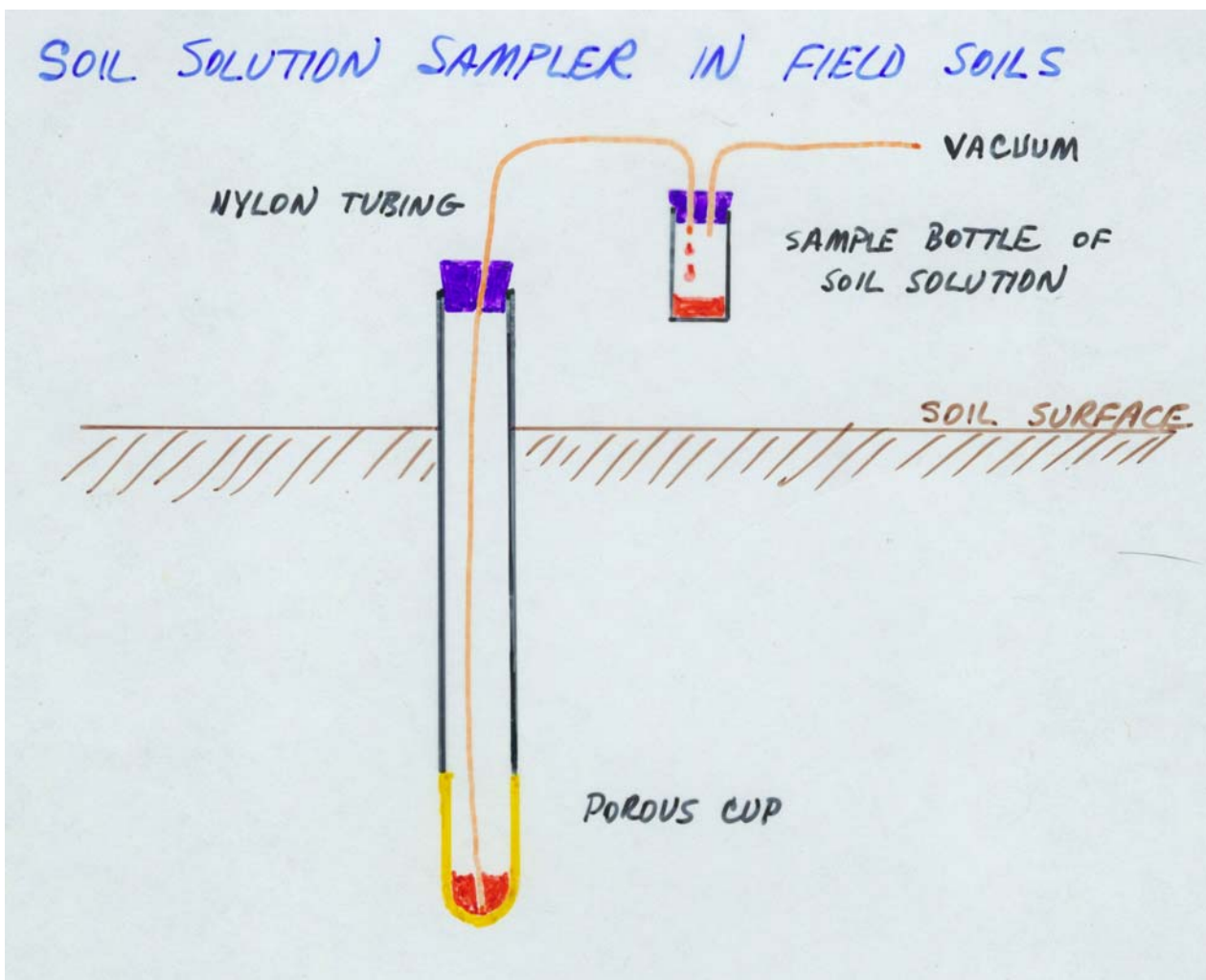
## FIELD LEACHING EXPERIMENT



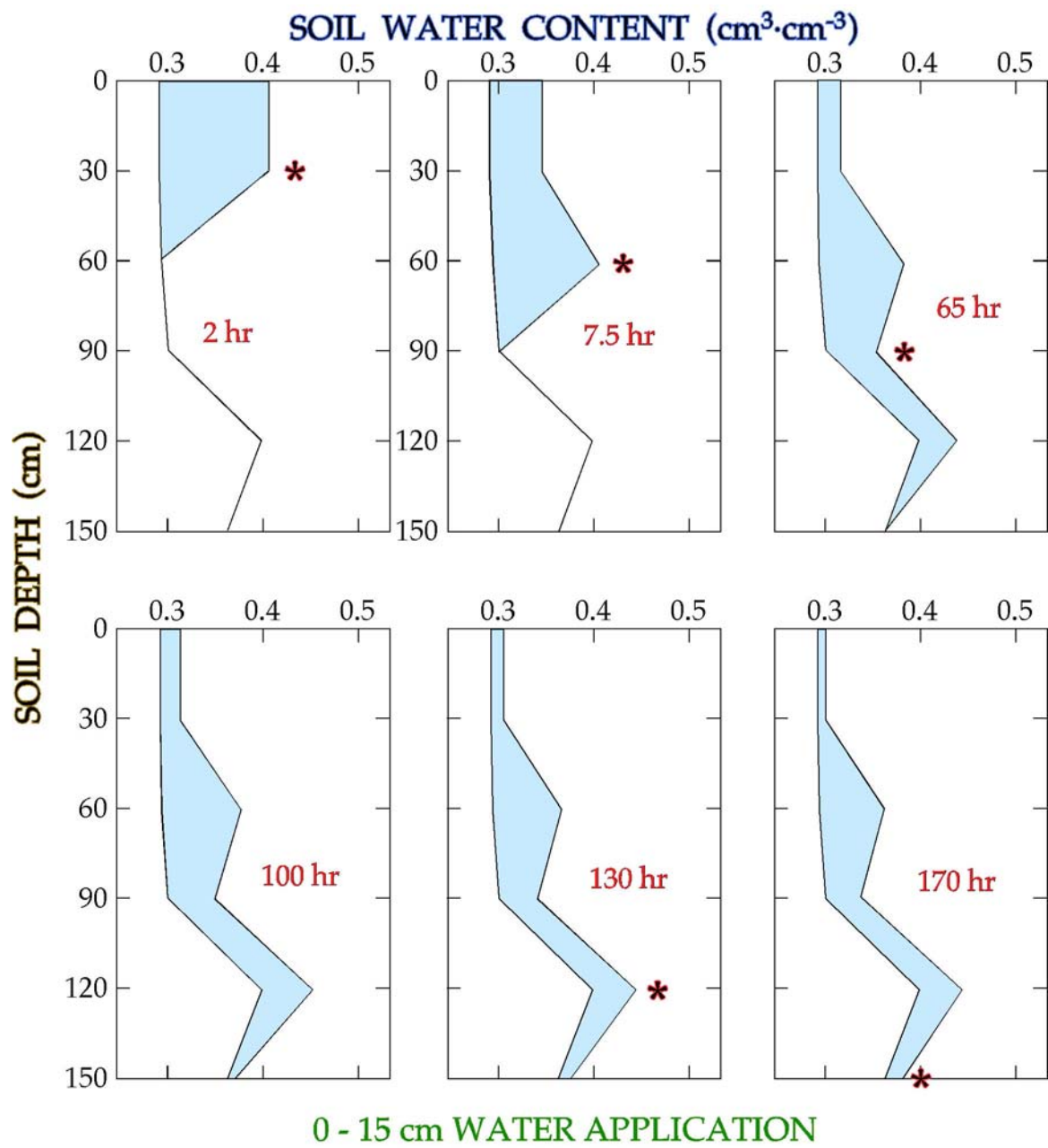
## FIELD LEACHING EXPERIMENTAL CONDITIONS

- CONTINUOUS PONDING OF WATER ON SOIL SURFACE
- INTERMITTENT PONDING WITH 5 CM OF WATER ONCE EVERY WEEK
- INTERMITTENT PONDING WITH 15 CM OF WATER ONCE EVERY WEEK

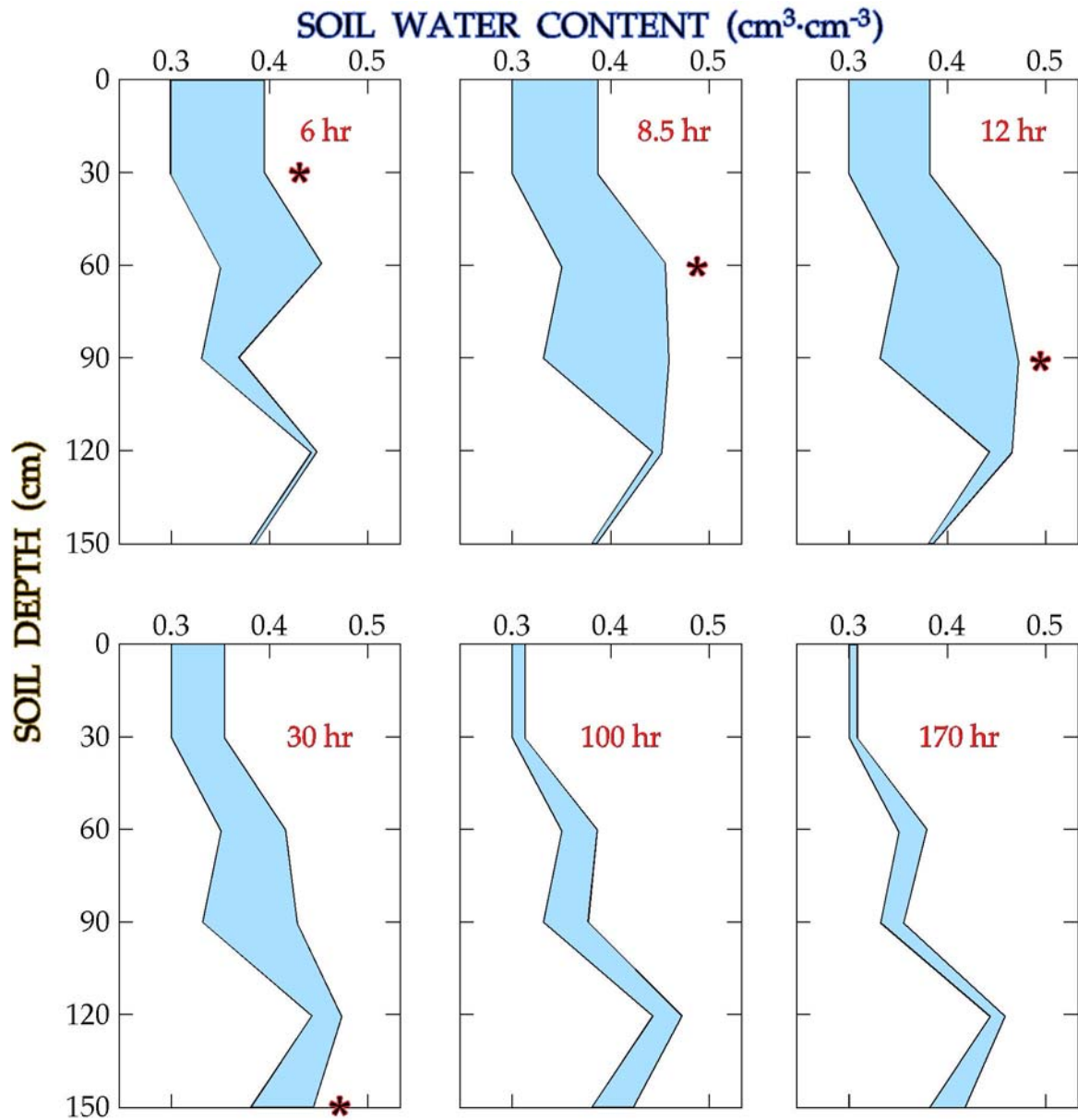
# Solution sampler



# 0-15cm applic

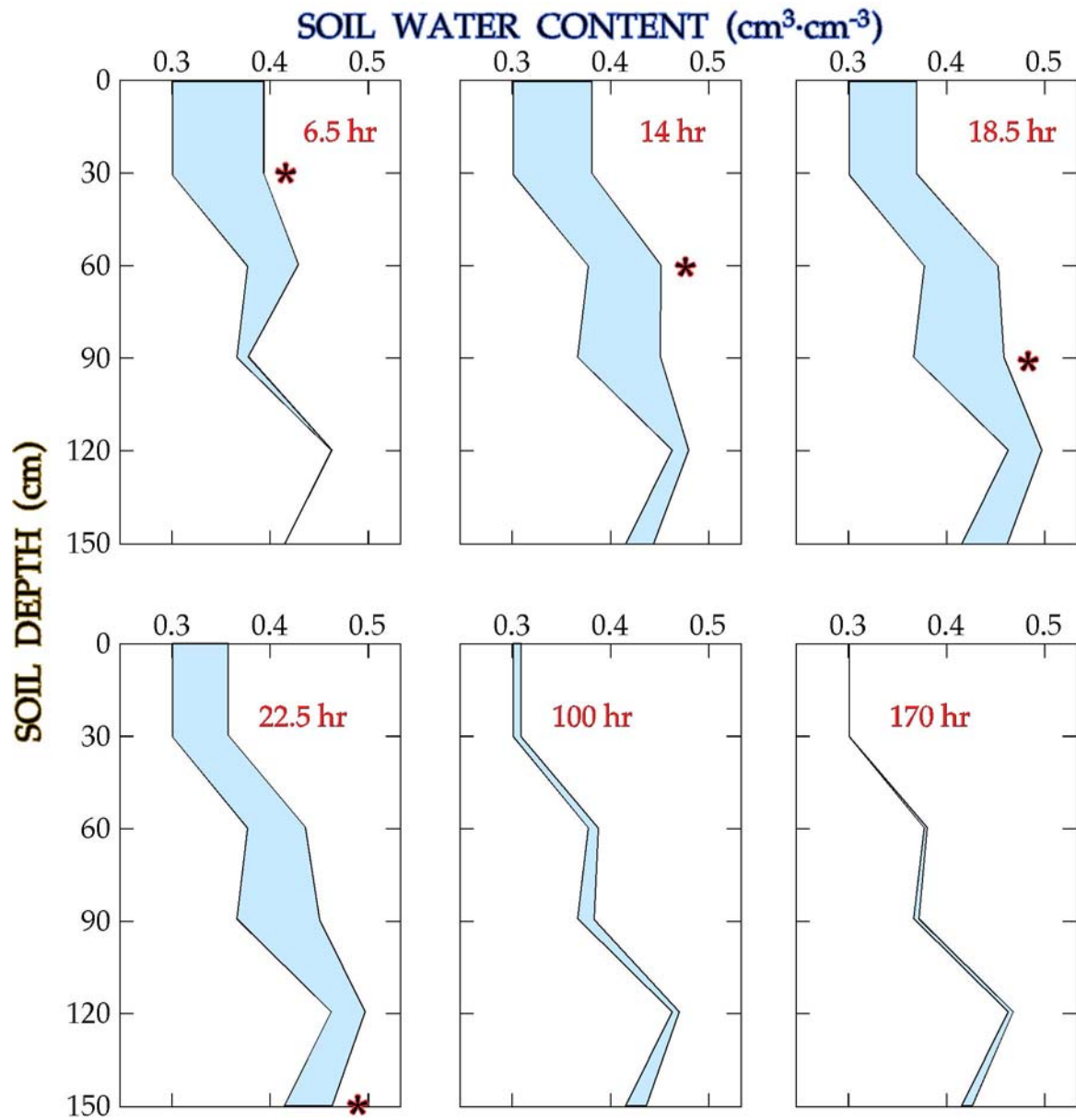


# 15-30cm appl



15 - 30 cm WATER APPLICATION

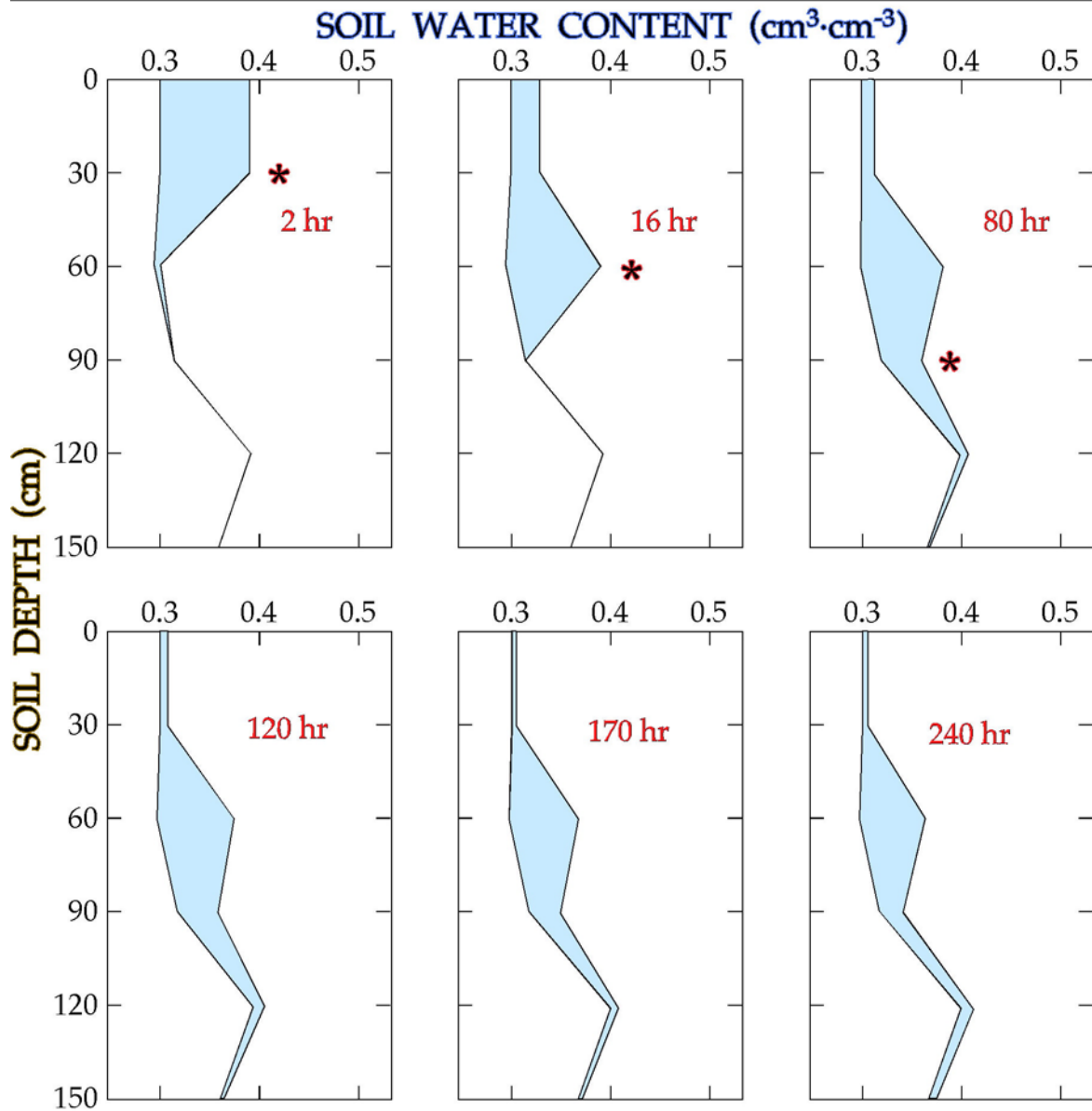
# 75-90cm appl



75 - 90 cm WATER APPLICATION

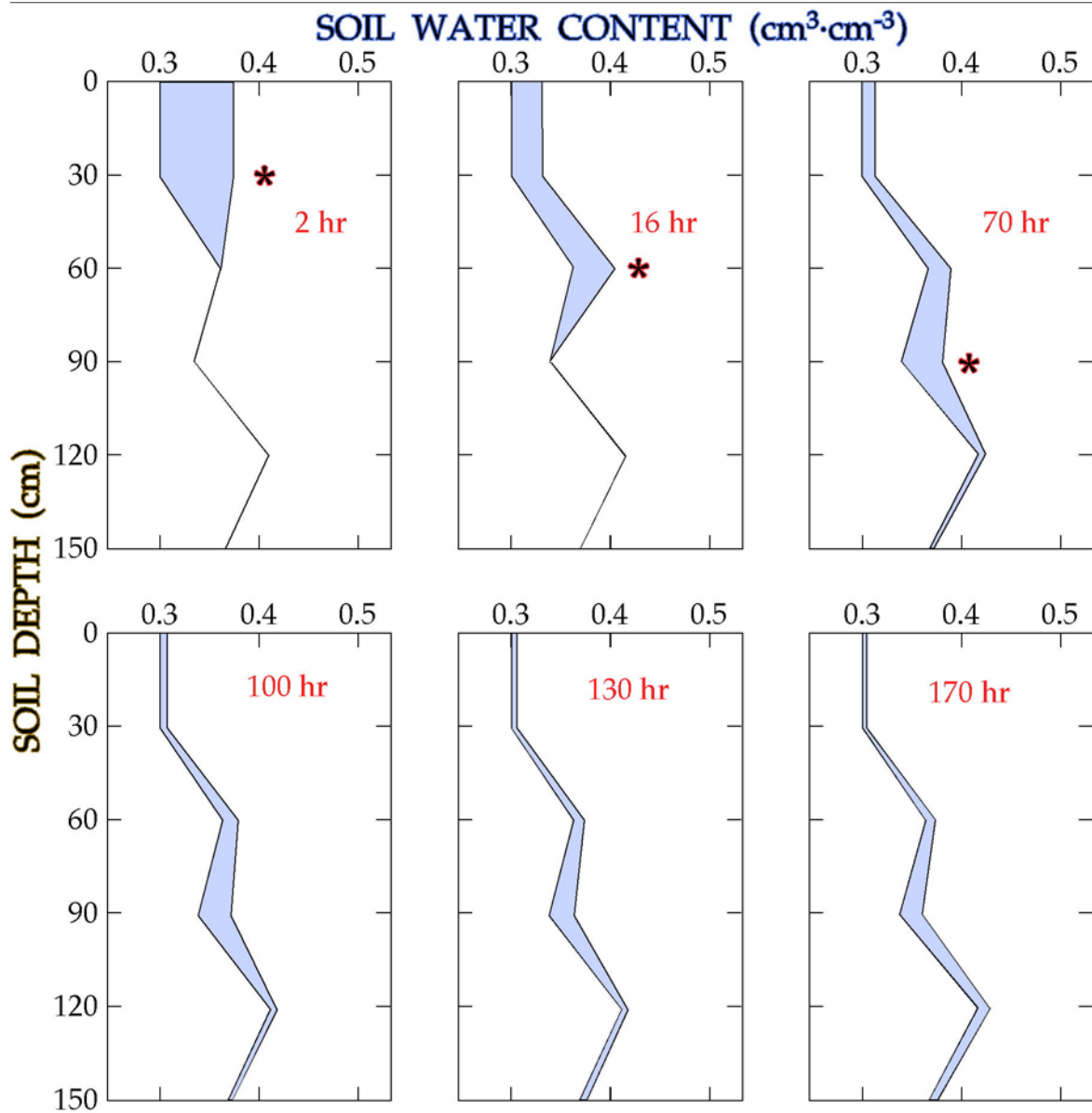


# 0-10cm appl



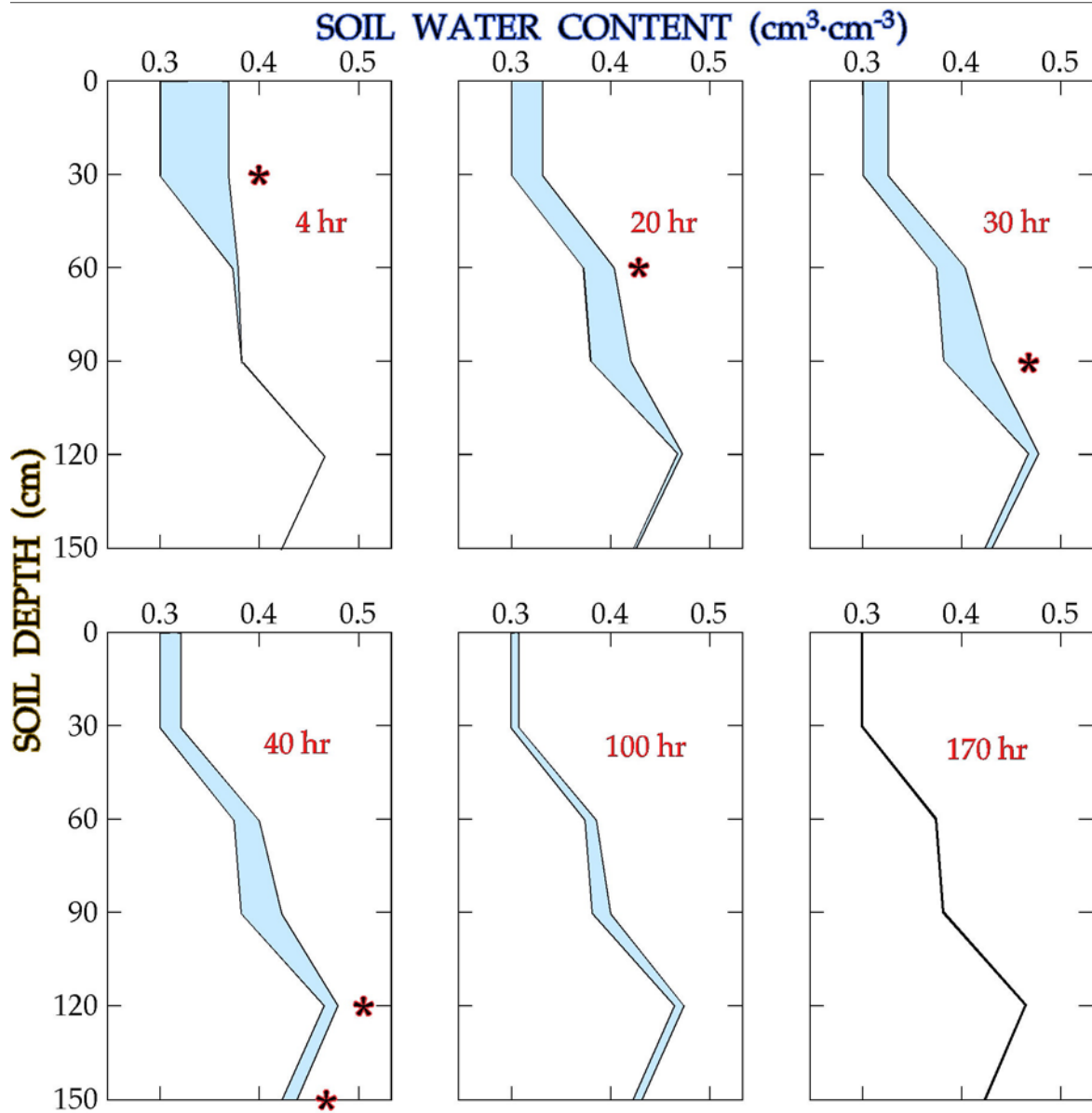
0 - 10 cm WATER APPLICATION

# 10-15cm appl



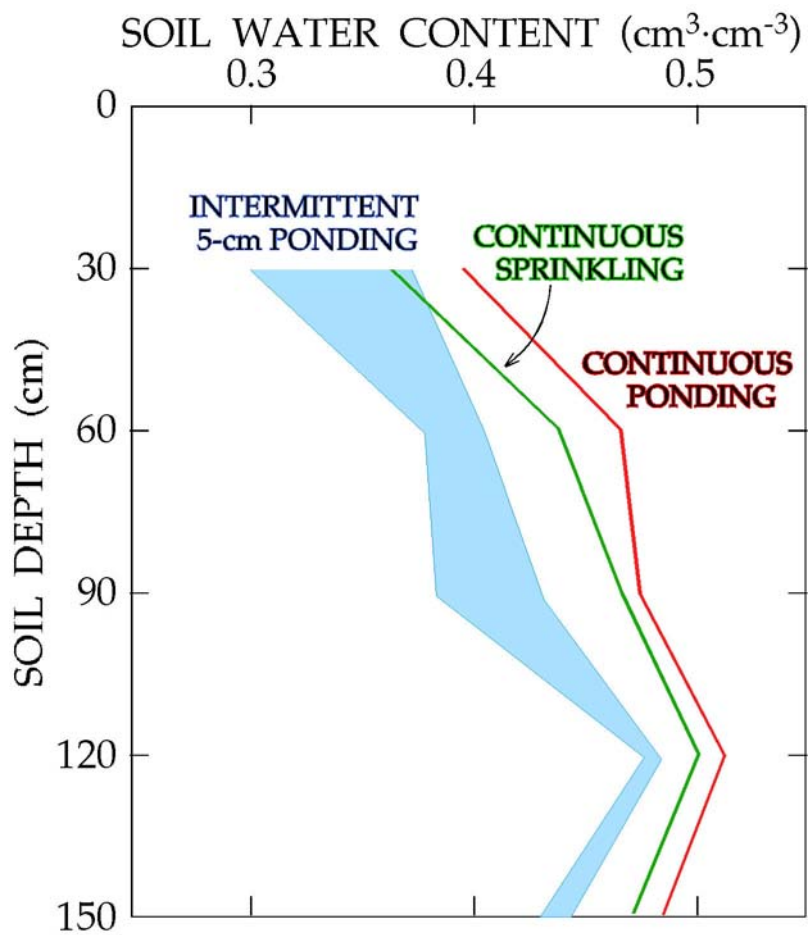
10 - 15 cm WATER APPLICATION

# 65-70cm appl

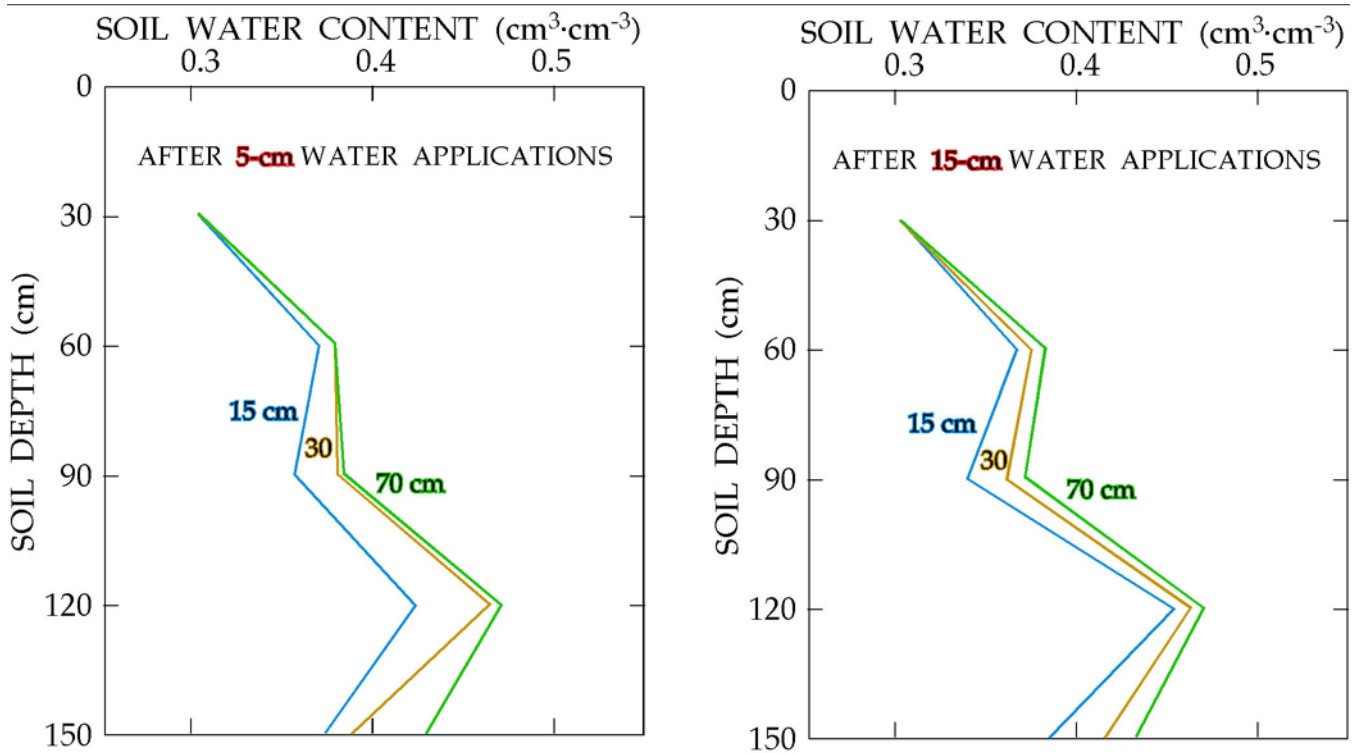


65 - 70 cm WATER APPLICATION

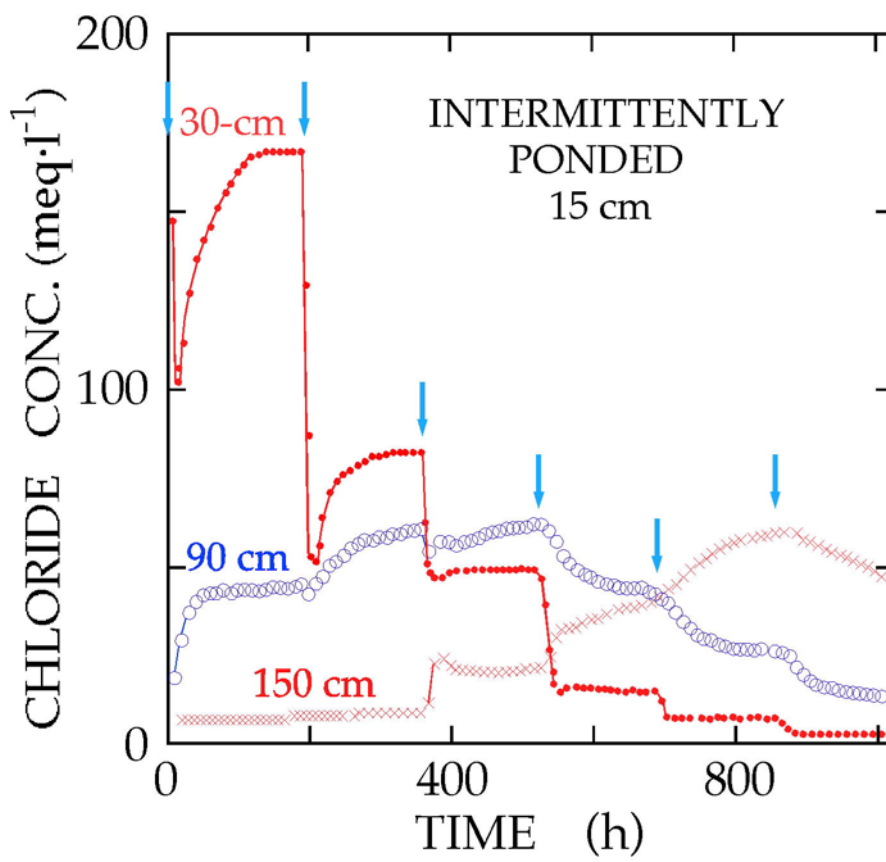
# Theta profiles



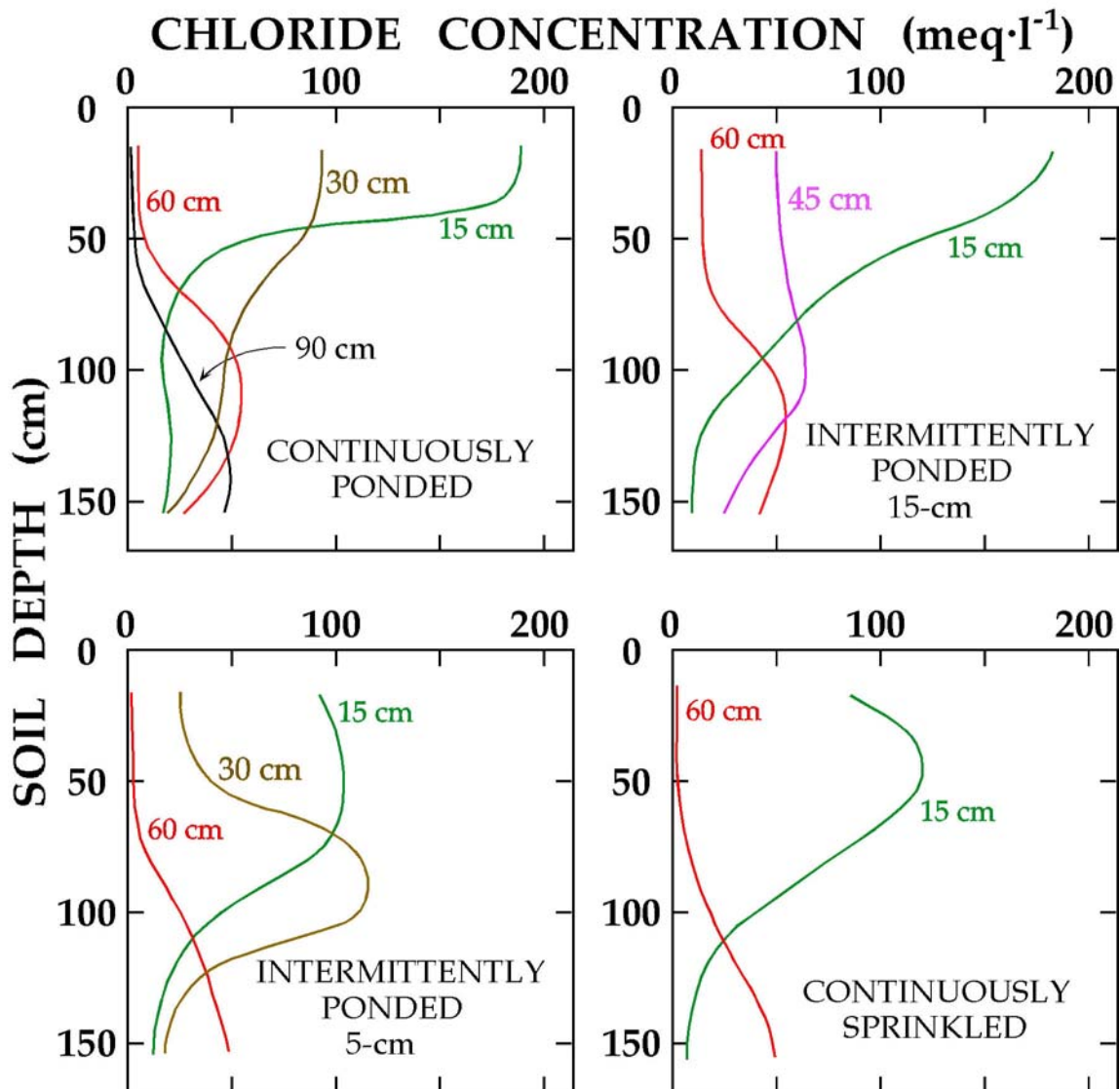
# Theta increases



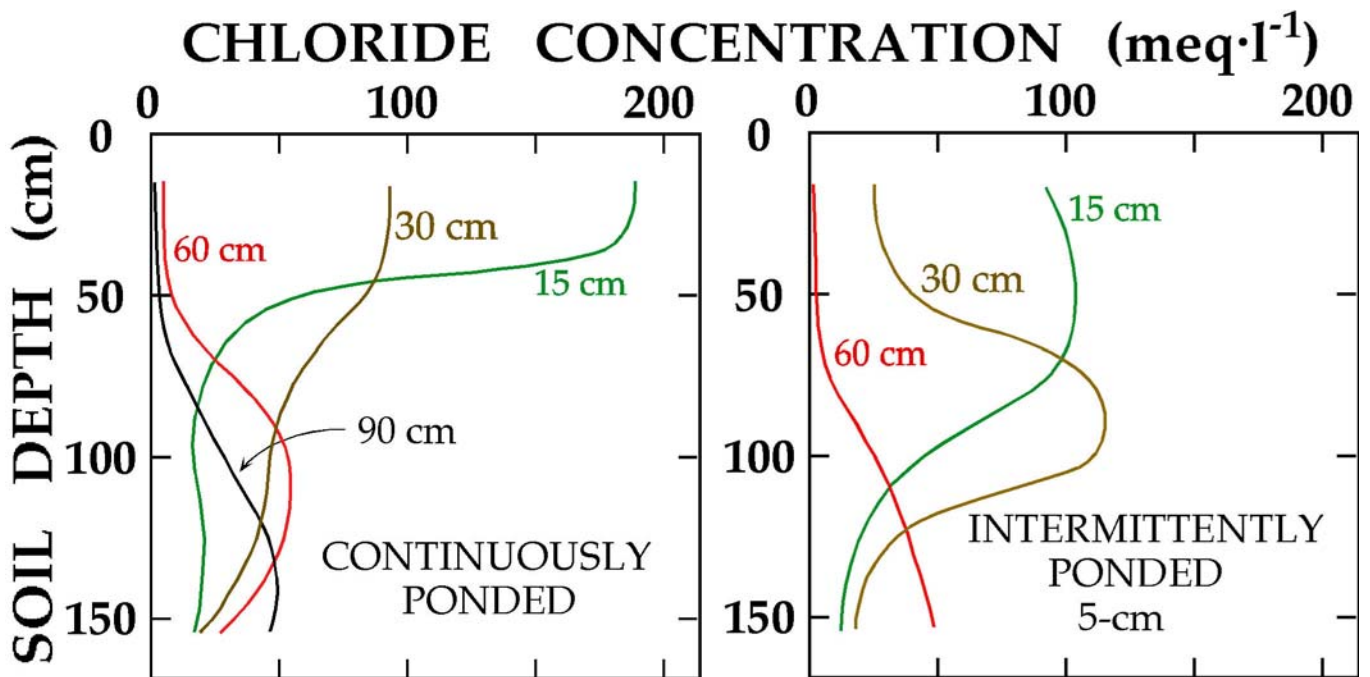
# Cl at 30, 90 & 150



# Conc profiles 1

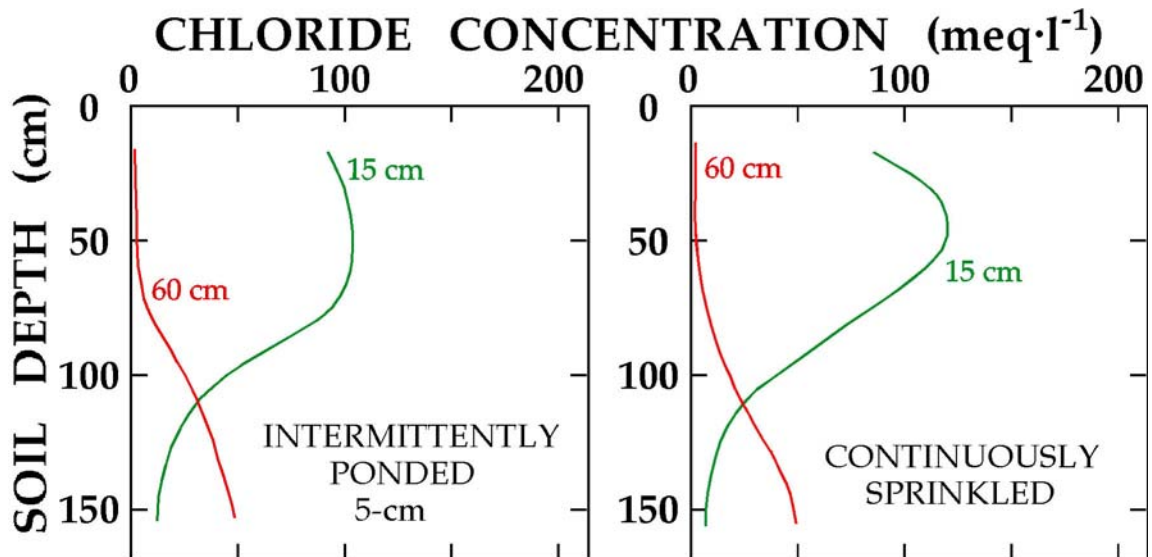


## Conc profiles 2

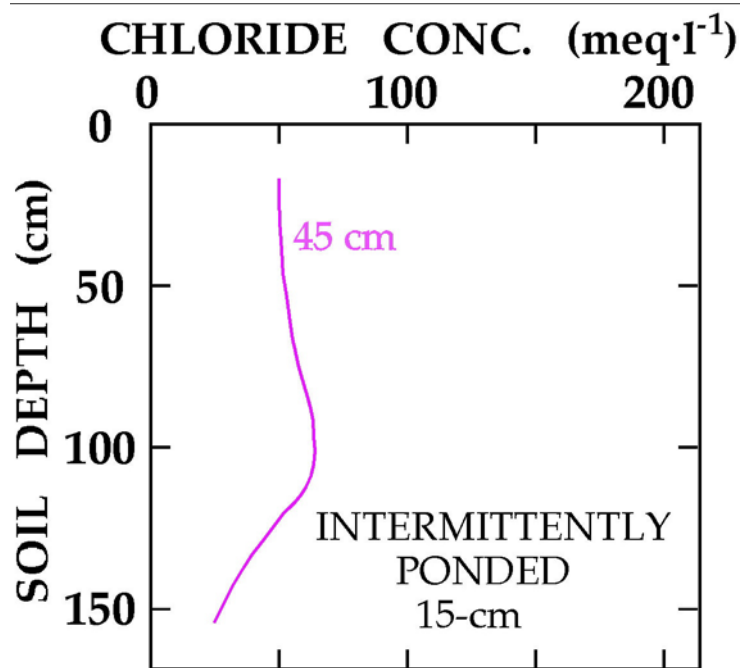




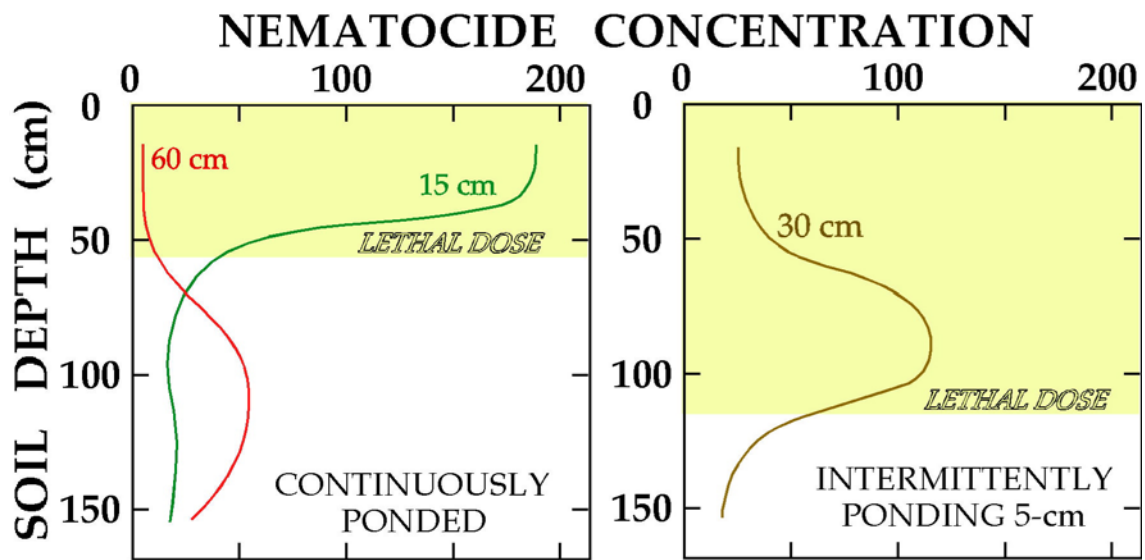
# Conc profiles 3



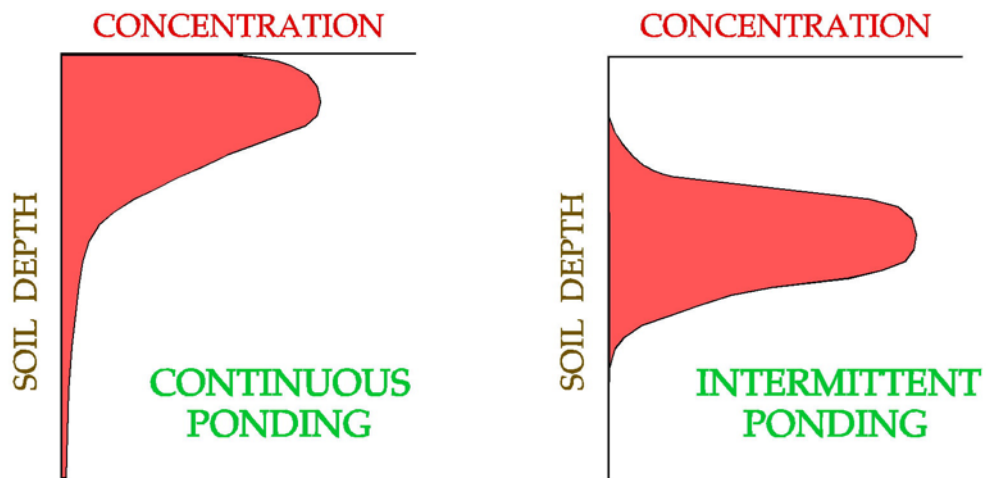
# Conc profiles 4



# Conc profiles 5



# conclusions



SOIL SALINITY CAN BE MANAGED BY CONTROLLING THE FREQUENCY AND AMOUNTS OF IRRIGATION WATER

SOLUTE TRANSPORT DEPENDS UPON:

- LEACHING VELOCITY OF SOIL WATER
- SOIL WATER CONTENT DURING LEACHING

# Convective Diffusion Eq.

## CONVECTIVE - DIFFUSION EQUATION

**INFLUX**

$$J_{\text{CONVECTION}} = J_{\text{WATER}} C$$

$$J_{\text{DIFFUSION}} = -D \frac{\partial C}{\partial x}$$

$\Delta x$

**OUTFLUX**

$$J_w C + \frac{\partial J_w C}{\partial x} \Delta x$$

$$-D \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \left( -D \frac{\partial C}{\partial x} \right) \Delta x$$

TIME RATE OF CHANGE OF AMOUNT OF SOLUTE IN VOLUME OF BOX = INFLUX - OUTFLUX

$$\frac{\partial \epsilon G}{\partial t} + \frac{\partial \rho S}{\partial t} + \frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - \frac{\partial J_w C}{\partial x} + \text{SOURCE} - \text{SINK}$$

ASSUME :

NO SOLUTE IN GASEOUS PHASE

NO SOURCES OR SINKS

BULK DENSITY  $\rho$  IS CONSTANT

SOIL WATER CONTENT  $\theta$  IS CONSTANT

SOIL WATER FLUX  $J_w$  IS CONSTANT

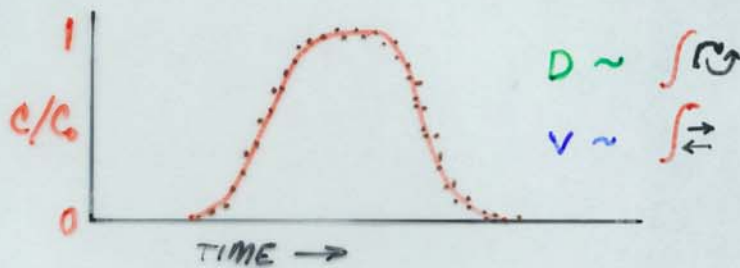
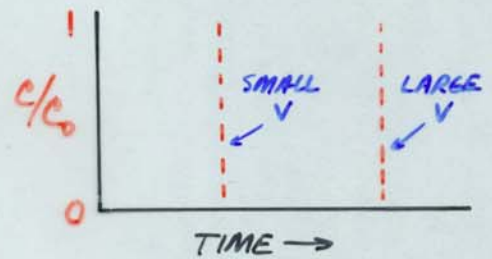
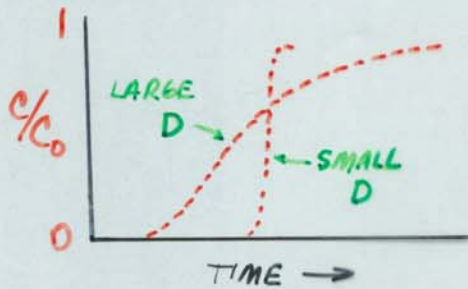
APPARENT DIFFUSION COEFFICIENT IS CONSTANT

SOIL IS HOMOGENEOUS

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad \text{WHERE} \quad v = \frac{J_w}{\theta}$$

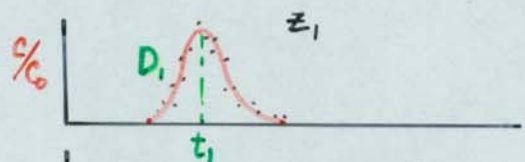
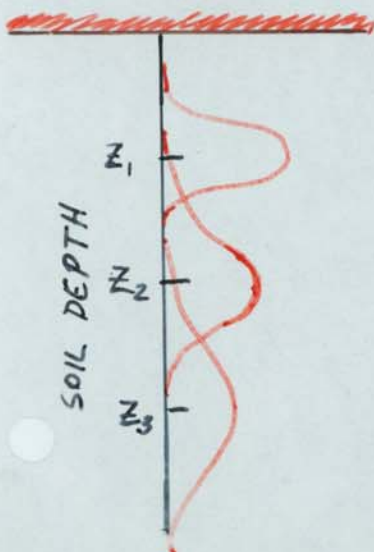
# Estimating D & v field

ESTIMATING THE VALUES OF D & v FROM FIELD-MEASURED BREAKTHROUGH CURVES

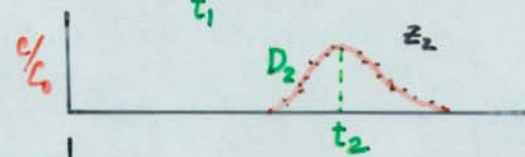


$$\frac{c}{c_0} = \frac{1}{2} \left[ \operatorname{erfc} \left( \frac{x-vt}{\sqrt{4Dt}} \right) + \exp \left( \frac{vx}{D} \right) \operatorname{erfc} \left( \frac{x+vt}{\sqrt{4Dt}} \right) \right] -$$

$$\frac{1}{2} \left[ \operatorname{erfc} \left( \frac{x-v(t-t_1)}{\sqrt{4D(t-t_1)}} \right) + \exp \left( \frac{vx}{D} \right) \operatorname{erfc} \left( \frac{x-v(t-t_1)}{\sqrt{4D(t-t_1)}} \right) \right]$$



$$\frac{z_1}{t_1} = v_1$$



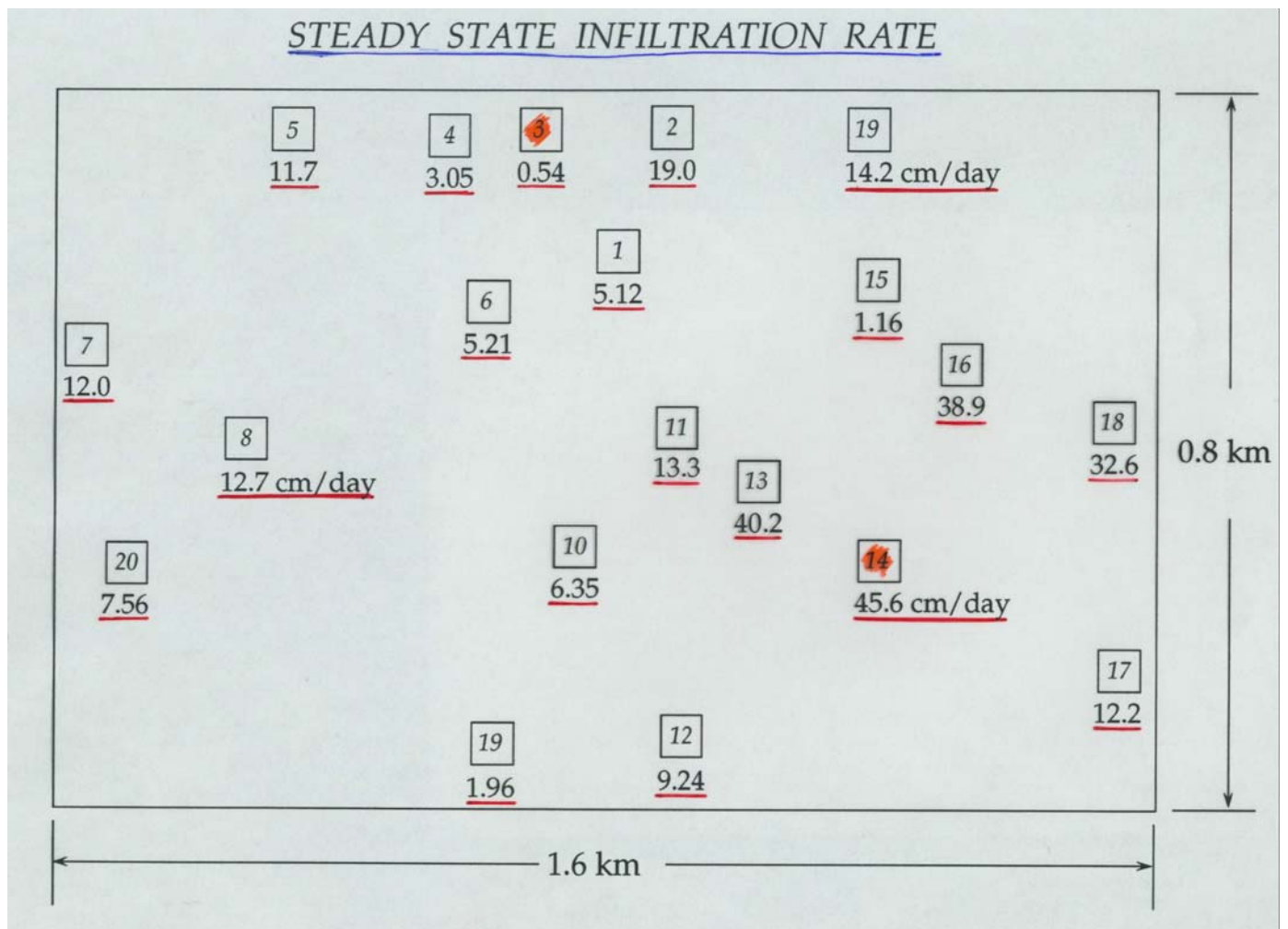
$$\frac{z_2}{t_2} = v_2$$



$$\frac{z_3}{t_3} = v_3$$

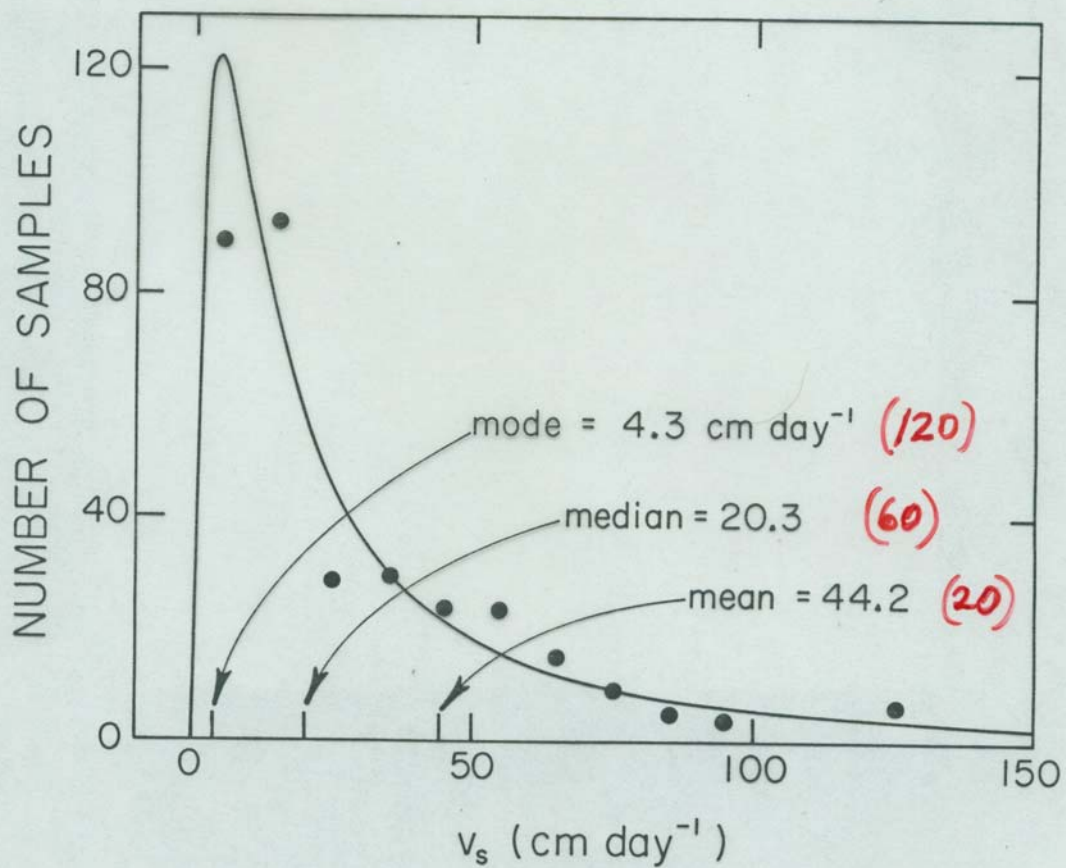


# 20 Field plots



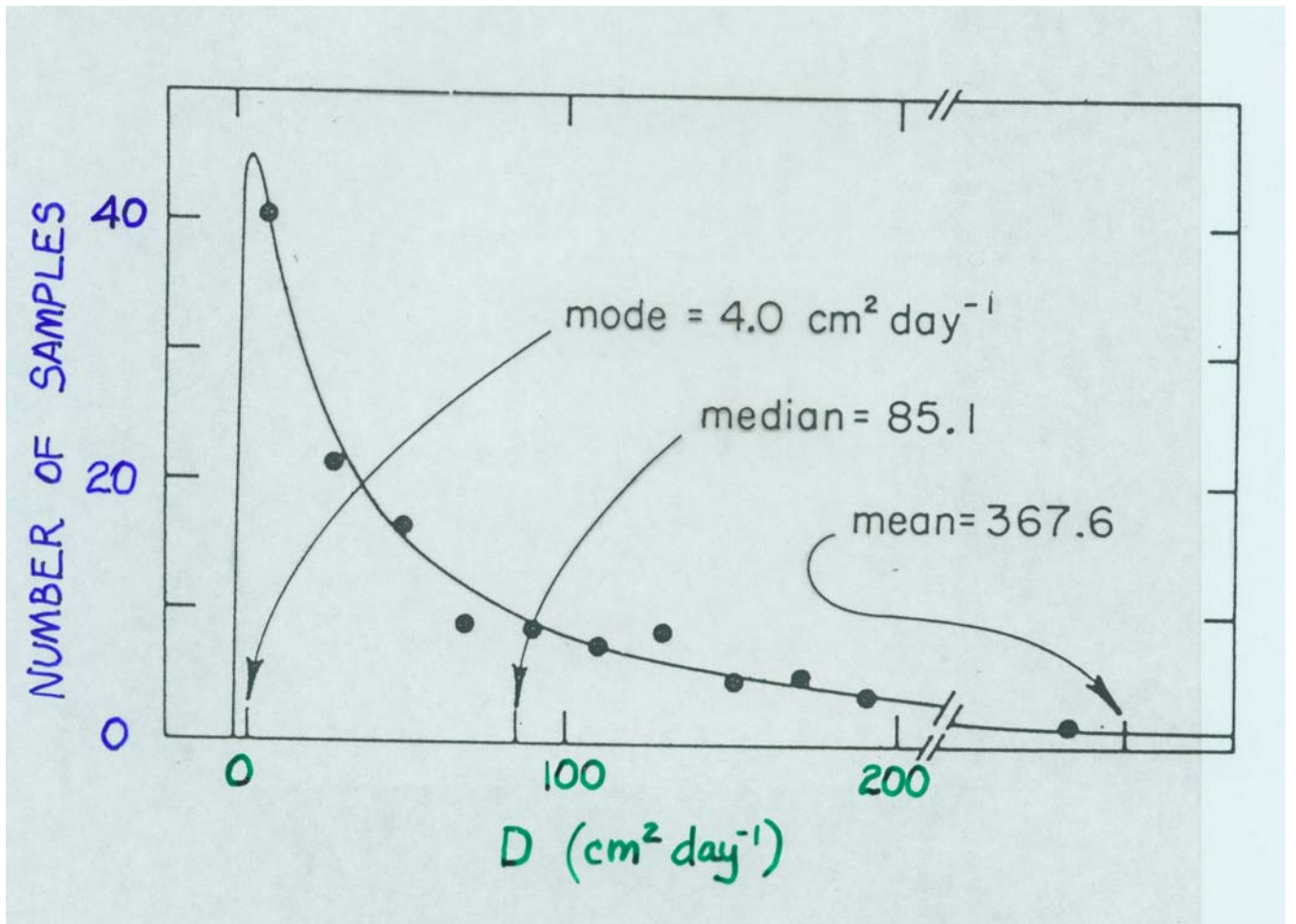
# Distrib of v

360 OBSERVATIONS TAKEN IN 150 ha. FIELD

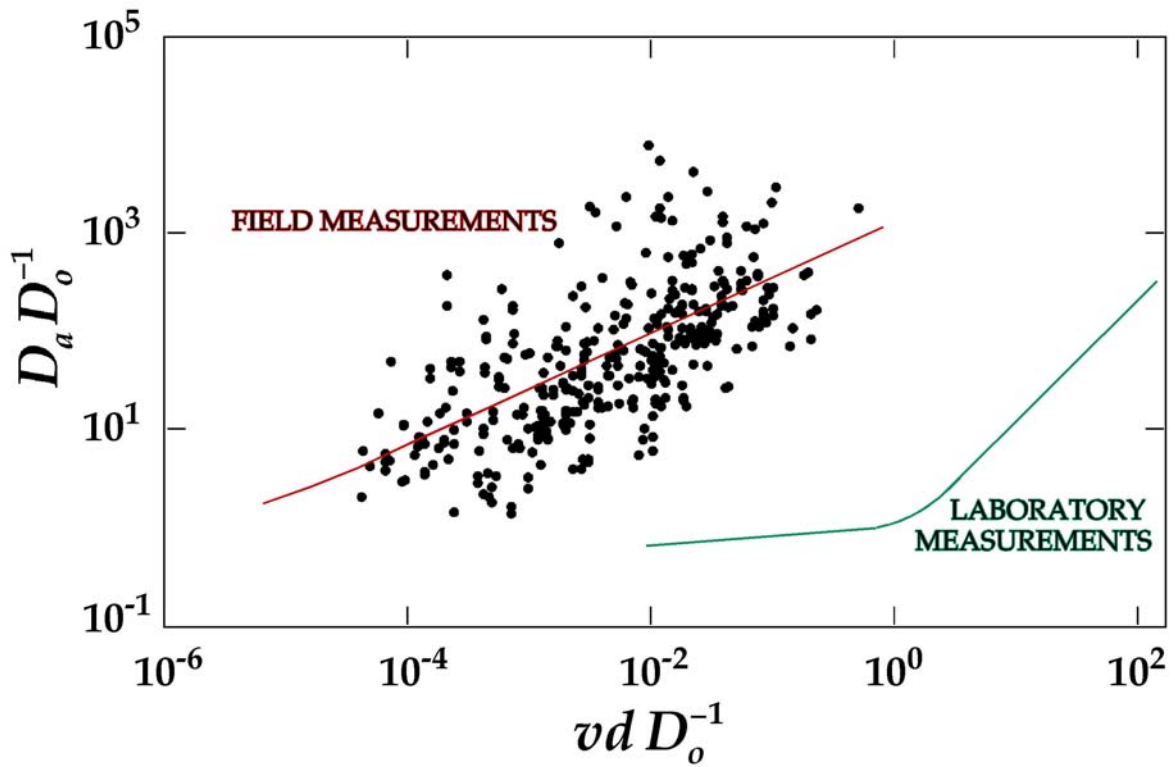
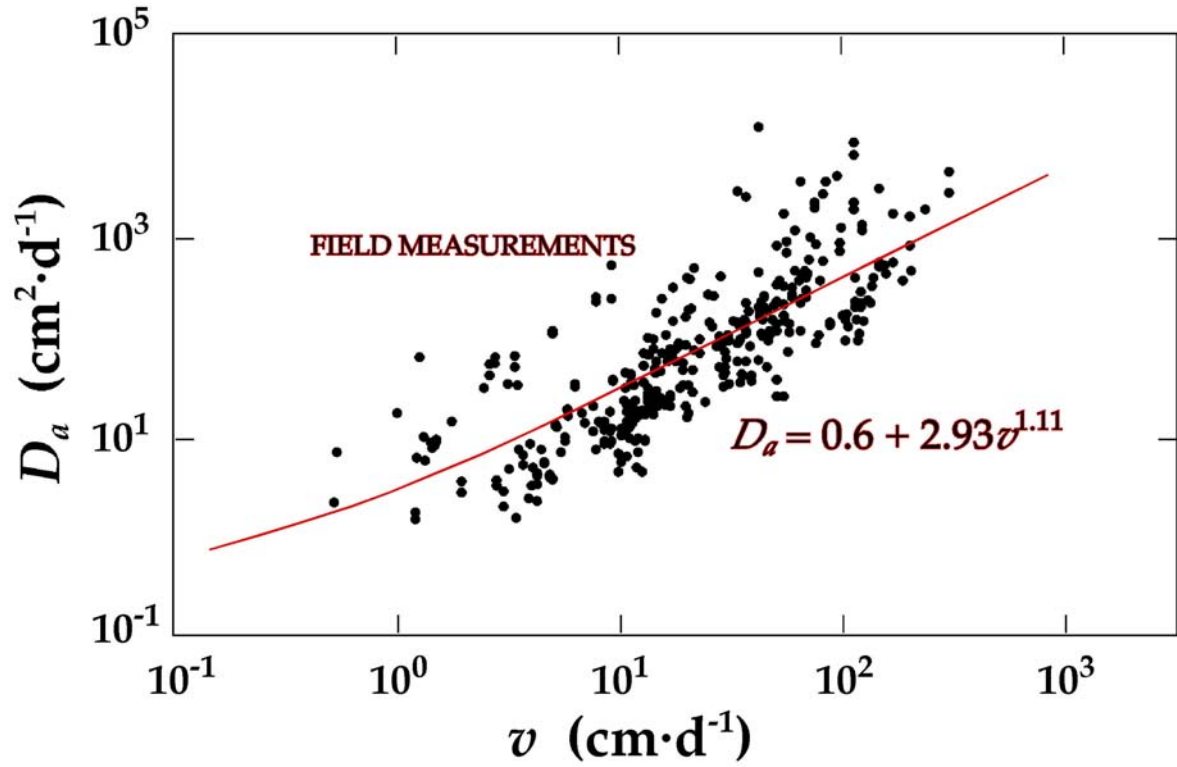




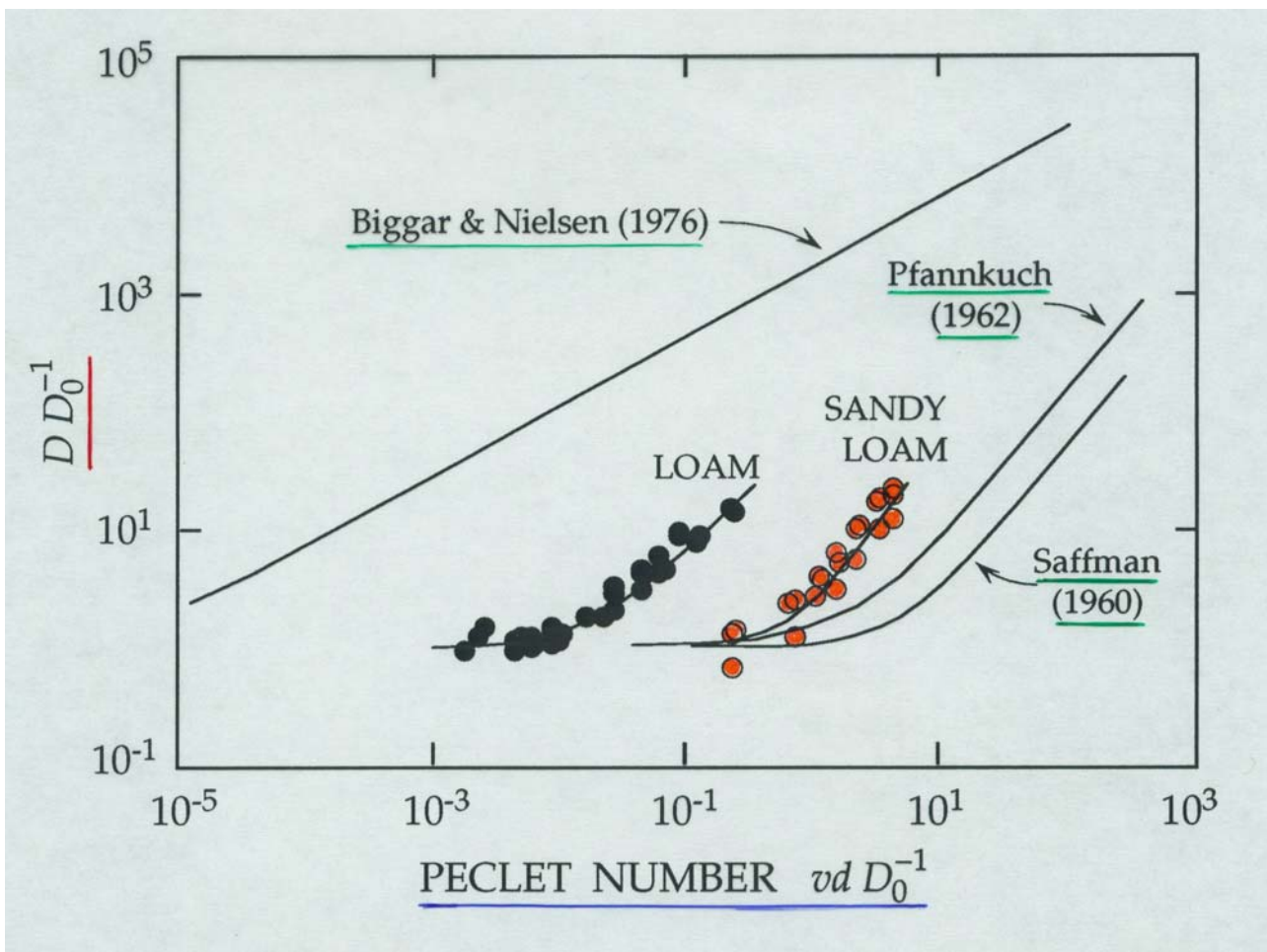
# Distrib of D



# D versus v



# D versus Peclet

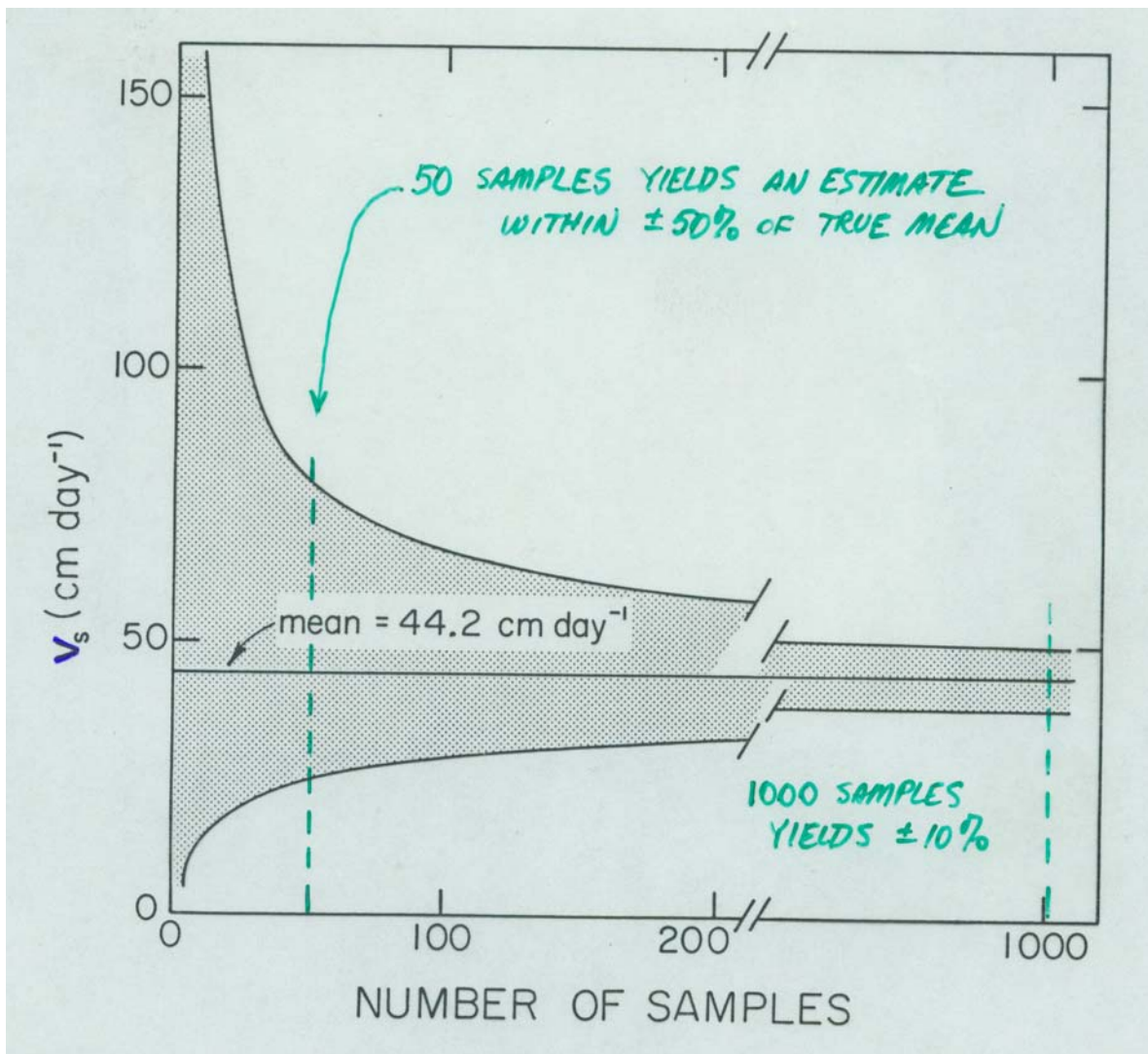


No. of samples

NUMBER OF SAMPLES  
FOR  
EQUALLY RELIABLE VALUES

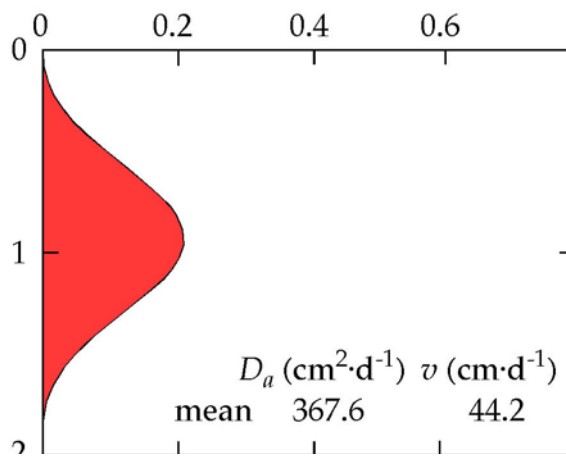
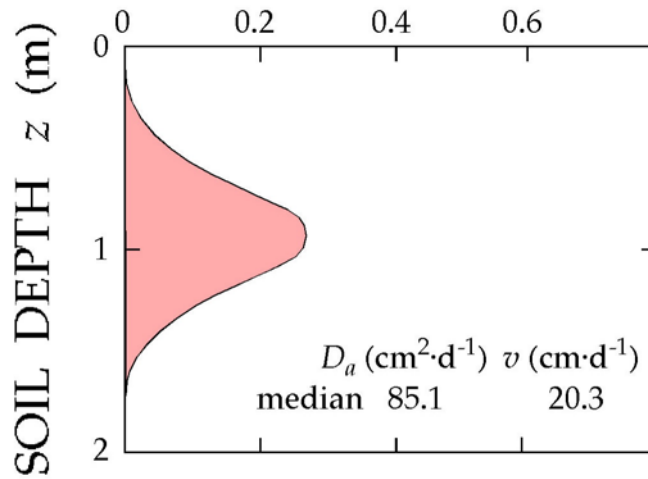
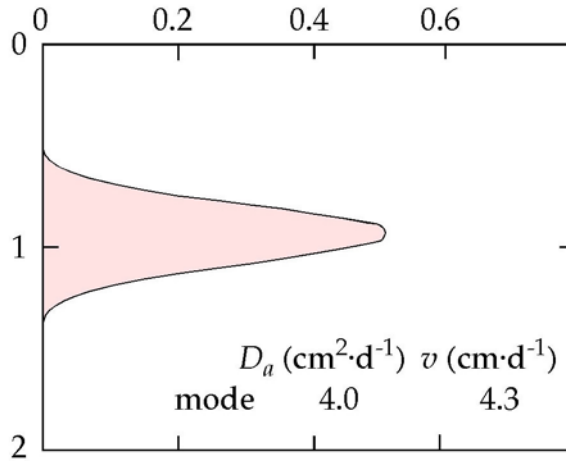
$$\frac{\overset{10}{\partial}(\overset{400}{\theta C})}{\partial t} + \frac{\overset{10}{\partial}(\overset{50}{\rho S})}{\partial t} = \overset{500}{D} \frac{\partial^2 C}{\partial z^2} - \frac{\overset{200}{\partial}(\overset{200}{v C})}{\partial z}$$

# Estimating $v$

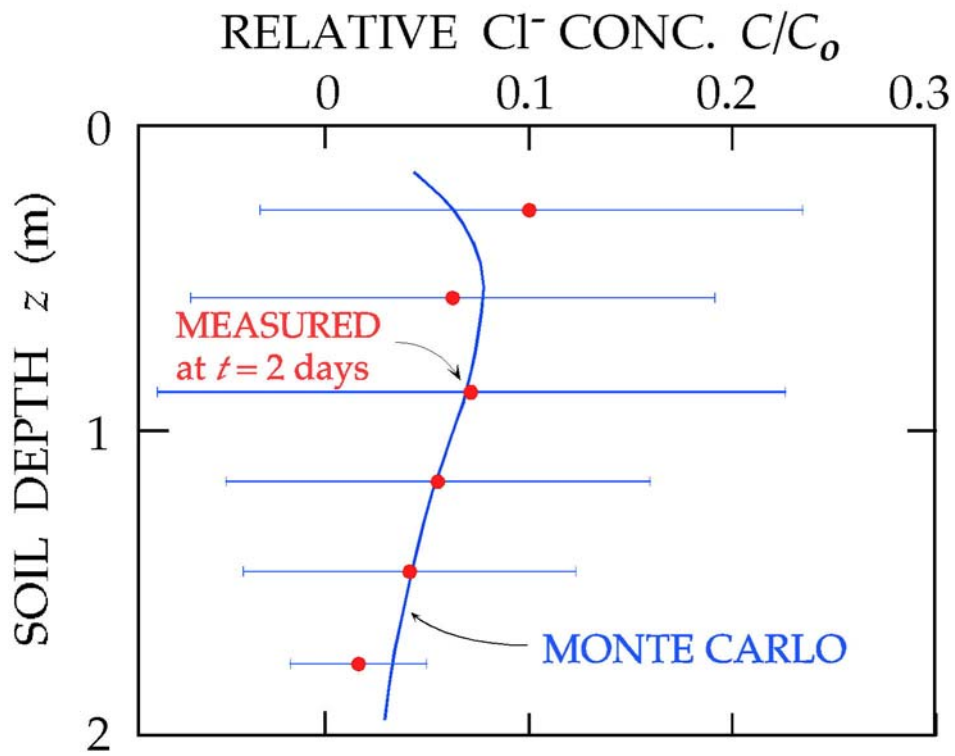


# Modmedmean

RELATIVE Cl<sup>-</sup> CONC.  $C/C_0$



# Field ave. C

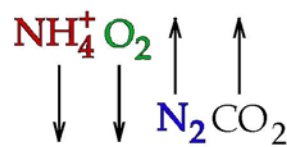




# Lab column

## NITRIFICATION & DENITRIFICATION STEADY-STATE SOIL COLUMN EXPERIMENT

0.01N CaSO<sub>4</sub> containing 50μg NH<sub>4</sub><sup>+</sup>-N per ml  
infiltrating the soil column  
at a water flux density of 2 cm·day<sup>-1</sup>



WATER UNSATURATED

WATER SATURATED





# Steady lab eqns

## STEADY-STATE CONVECTIVE DIFFUSION EQUATIONS

$$\text{AMMONIUM N} \quad D_1 \frac{d^2 C_1}{dz^2} - v \frac{dC_1}{dz} - k_1 C_1 = 0$$

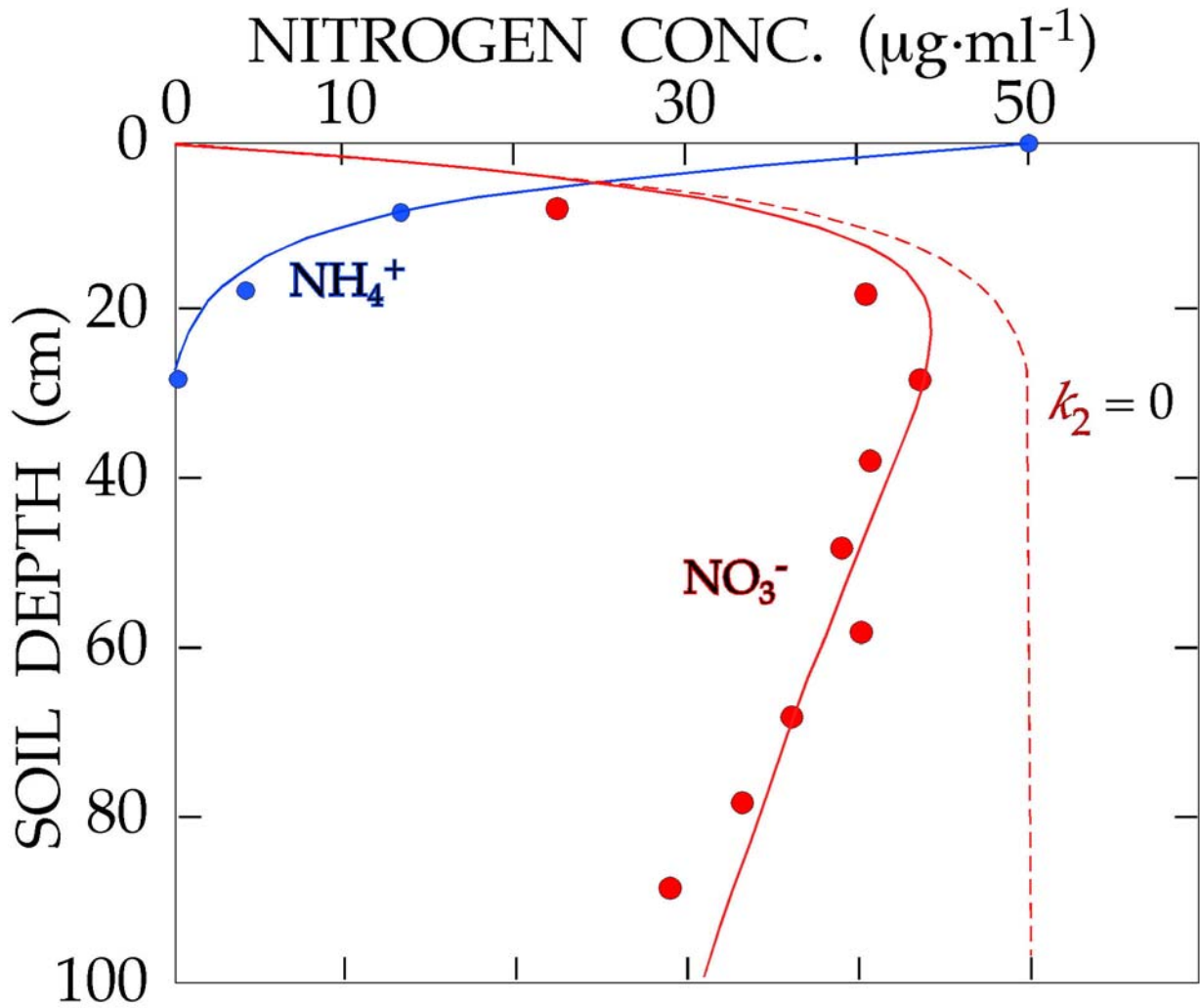
$$\text{NITRATE N} \quad D_2 \frac{d^2 C_2}{dz^2} - v \frac{dC_2}{dz} + k_1 C_1 - k_2 C_2 = 0$$

$$\text{GASEOUS N}_2 \quad D_3 \frac{d^2 C_3}{dz^2} + k_2 C_2 = 0$$

$$\text{AMMONIUM N} \quad C_1(z) = C_1^0 \exp\left[\frac{z}{2D_1} \left(v - \sqrt{v^2 + 4D_1 k_1}\right)\right]$$

$$\text{NITRATE N} \quad C_2(z) = \frac{k_1 C_1^0}{k_1 - k_2} \left\{ \exp\left[\frac{z}{2D_2} \left(v - \sqrt{v^2 + 4D_2 k_2}\right)\right] - \exp\left[\frac{z}{2D_1} \left(v - \sqrt{v^2 + 4D_1 k_1}\right)\right] \right\}$$

# NH<sub>4</sub>+NO<sub>3</sub>



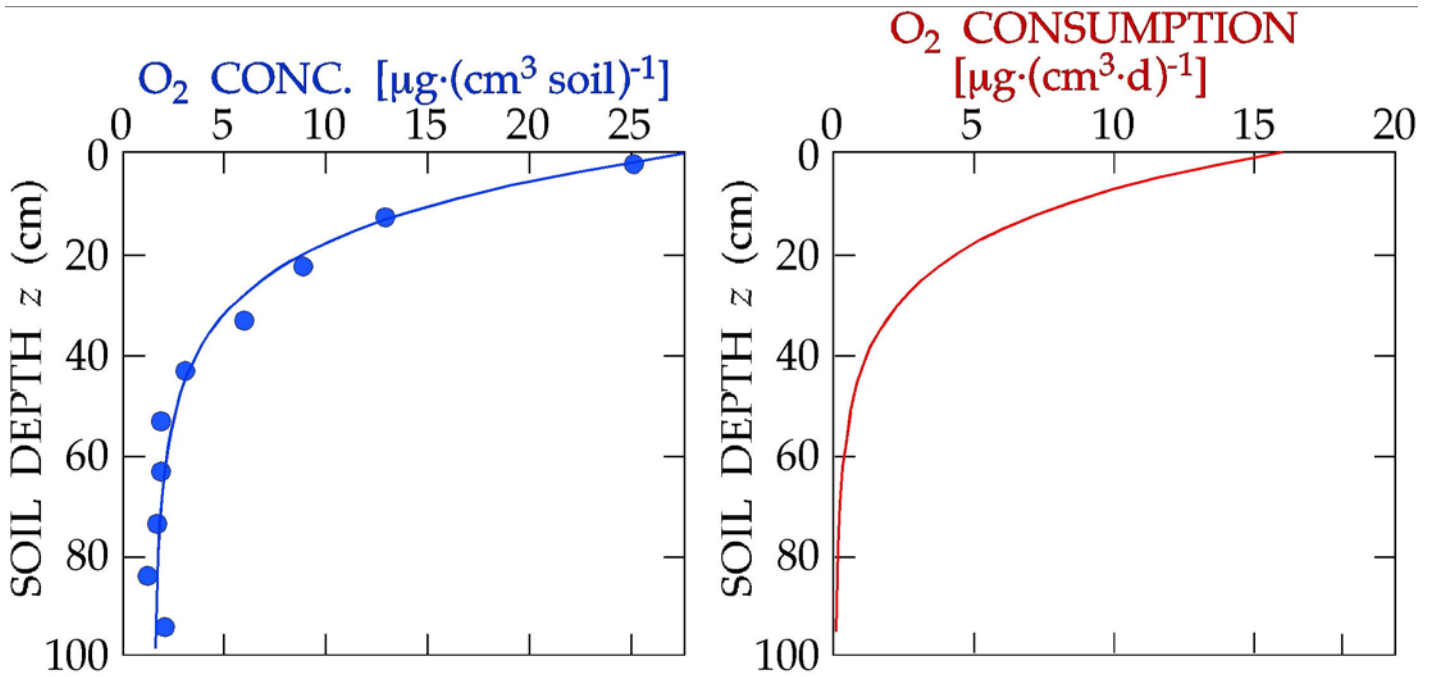
$$k_1 = 1.025 \text{ day}^{-1}$$

$$v = 6 \text{ cm}\cdot\text{day}^{-1}$$

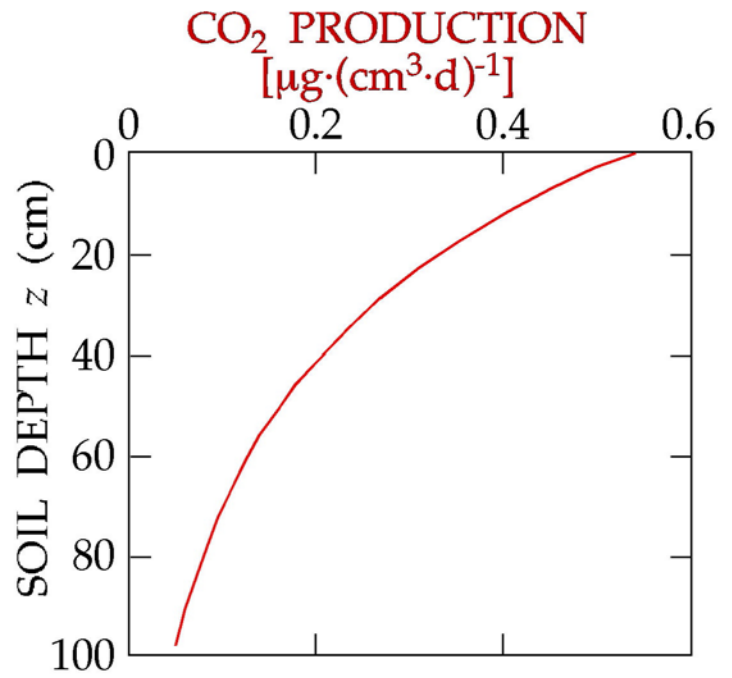
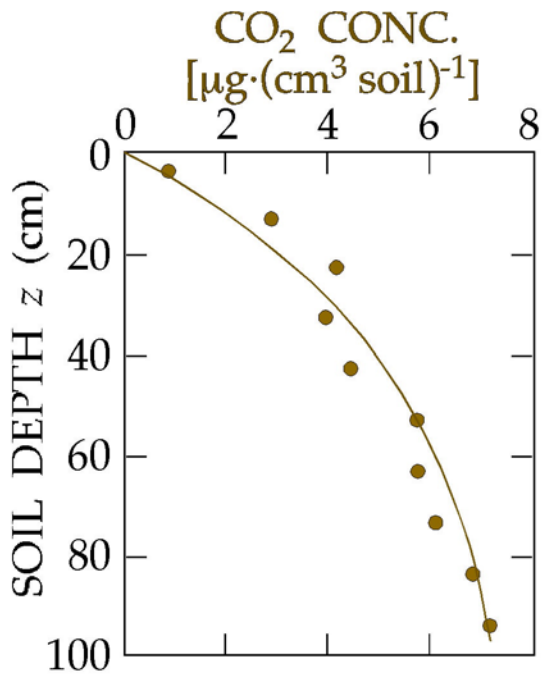
$$k_2 = 0.0304 \text{ day}^{-1}$$

$$D_1 = D_2 = 2.3 \text{ cm}^2\cdot\text{day}^{-1}$$

# O<sub>2</sub> profiles

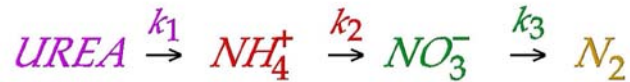


# CO<sub>2</sub> profiles



# Nonstedy equations

## NONSTEADY-STATE CONVECTIVE DIFFUSION EQNS.

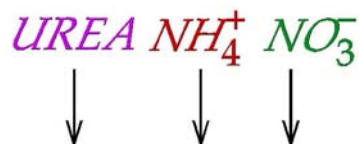


$$\text{UREA} - N \quad \frac{\rho}{\theta} \frac{\partial S_1}{\partial t} + \frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial z^2} - v \frac{\partial C_1}{\partial z} - k_1 C_1$$

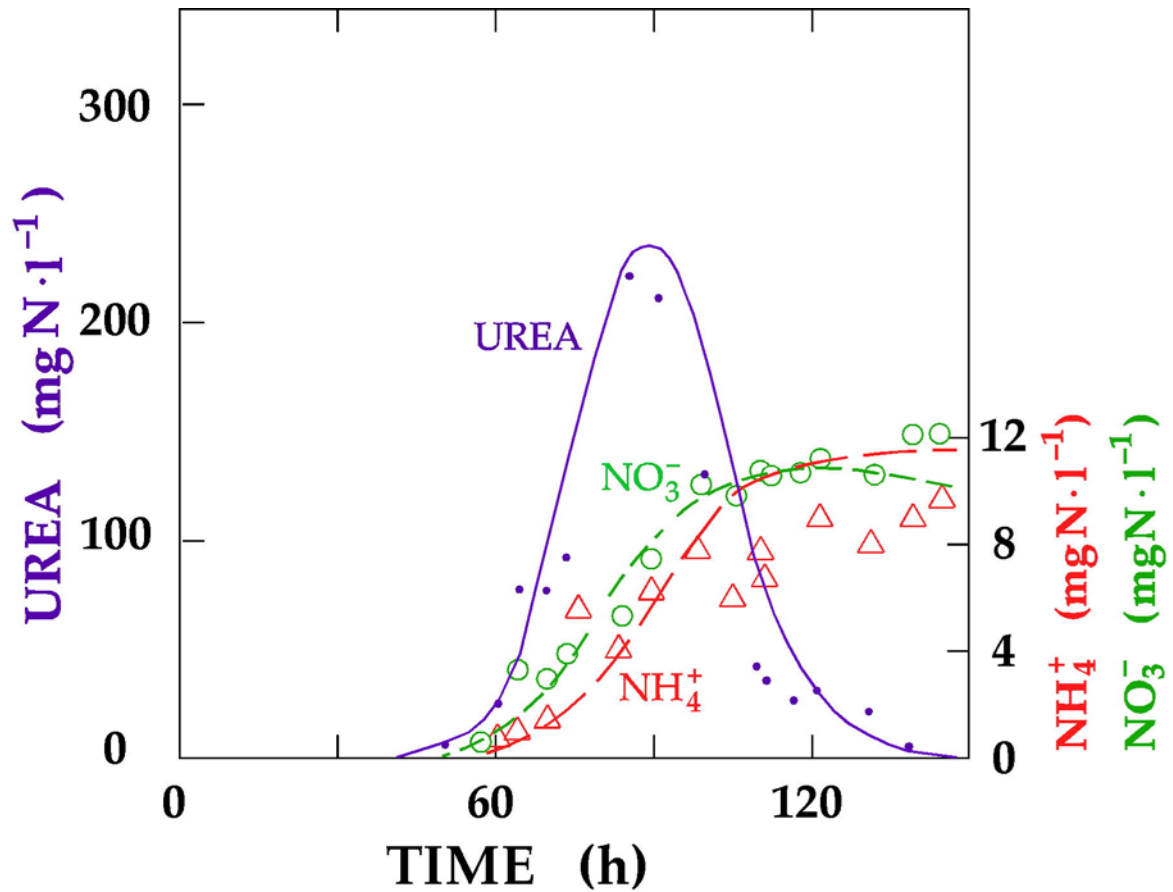
$$\text{NH}_4^+ - N \quad \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} + \frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial z^2} - v \frac{\partial C_2}{\partial z} + k_1 C_1 - k_2 C_2$$

$$\text{NO}_3^- - N \quad \frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial z^2} - v \frac{\partial C_3}{\partial z} + k_2 C_2 - k_3 C_3$$

$$\text{N}_2 - N \quad \varepsilon \frac{\partial C_4}{\partial t} = D_4 \frac{\partial^2 C_4}{\partial z^2} + k_3 C_3$$



# Urea, NH<sub>4</sub>, NO<sub>3</sub>



$$C_1^0 = 1000 \text{ mg} \cdot \text{l}^{-1}$$

$$C_2^0 = 0$$

$$C_3^0 = 0$$

$$k_1 = 0.016 \text{ h}^{-1}$$

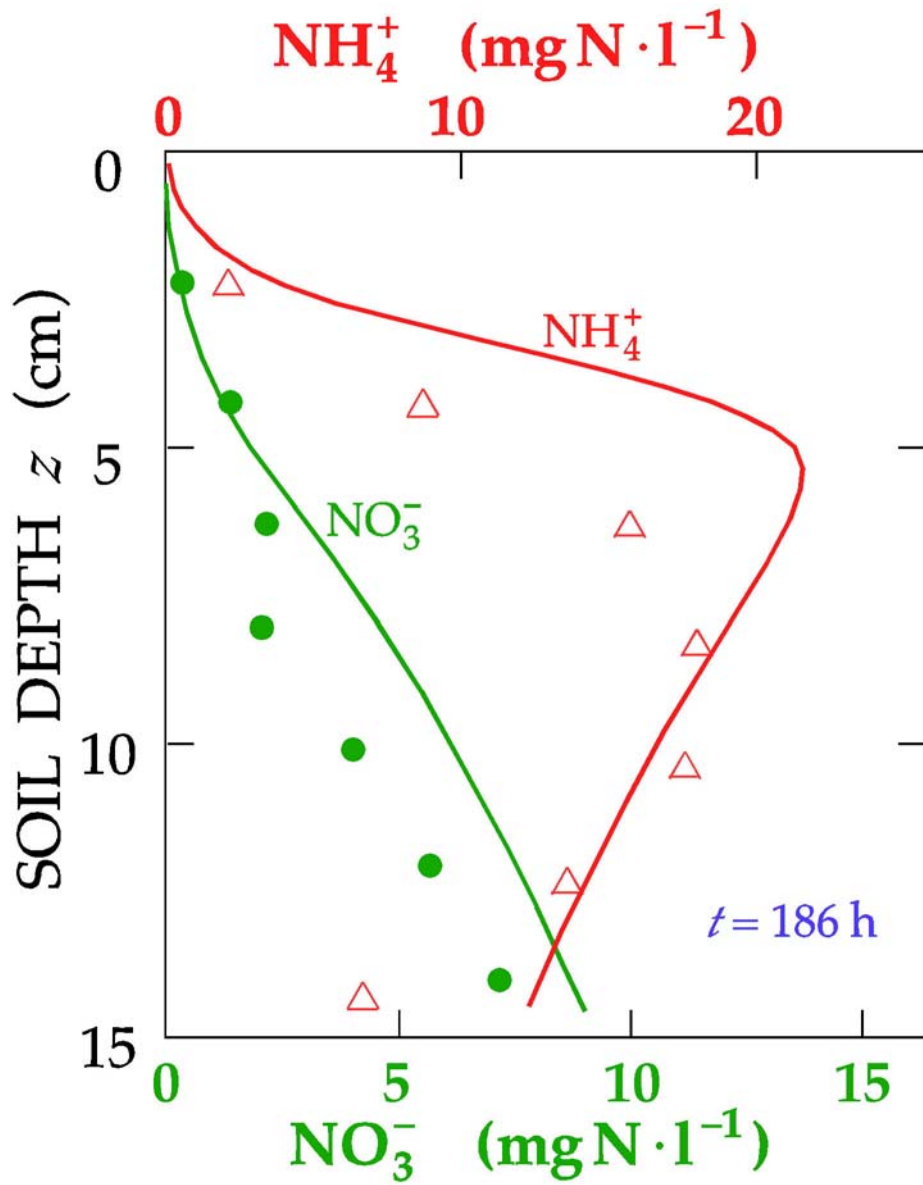
$$k_2 = 0.010 \text{ h}^{-1}$$

$$k_3 = 0.001 \text{ h}^{-1}$$

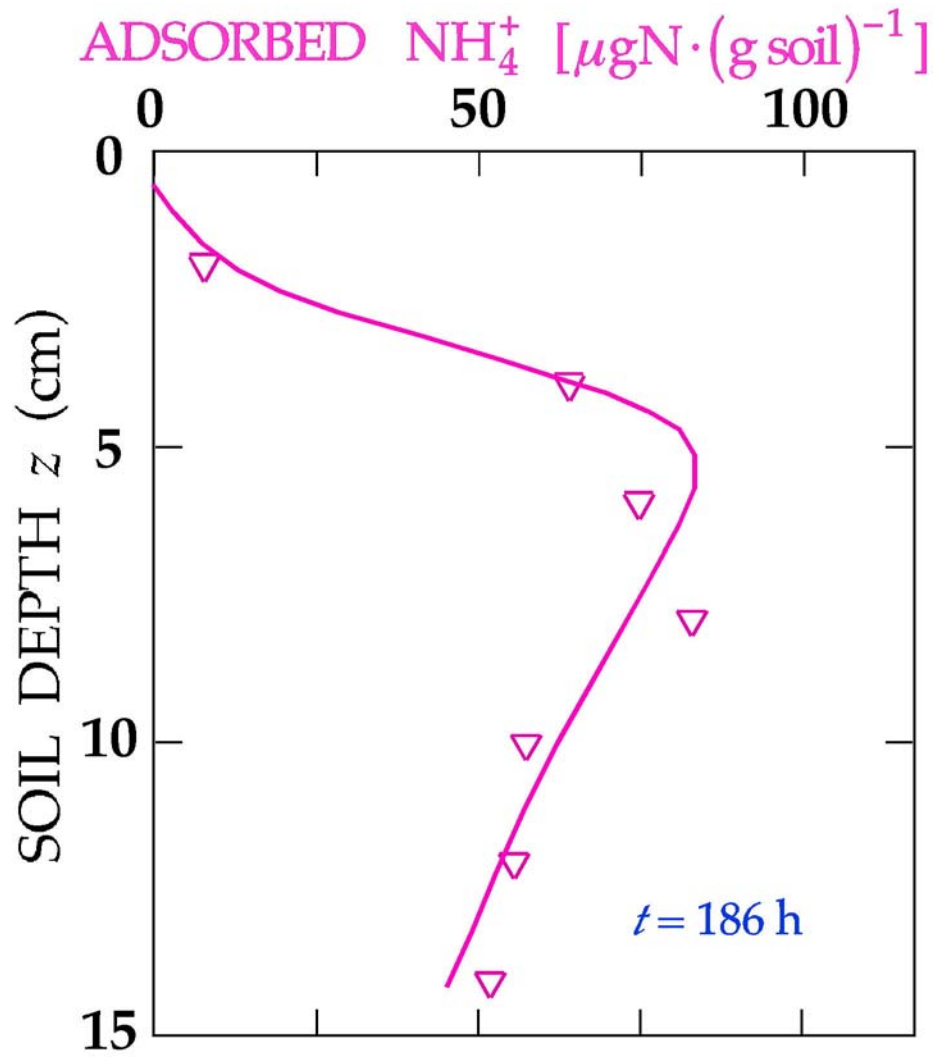
$$v = 0.24 \text{ cm} \cdot \text{h}^{-1}$$

$$D = 0.05 \text{ cm}^2 \cdot \text{h}^{-1}$$

# NO<sub>3</sub> profile

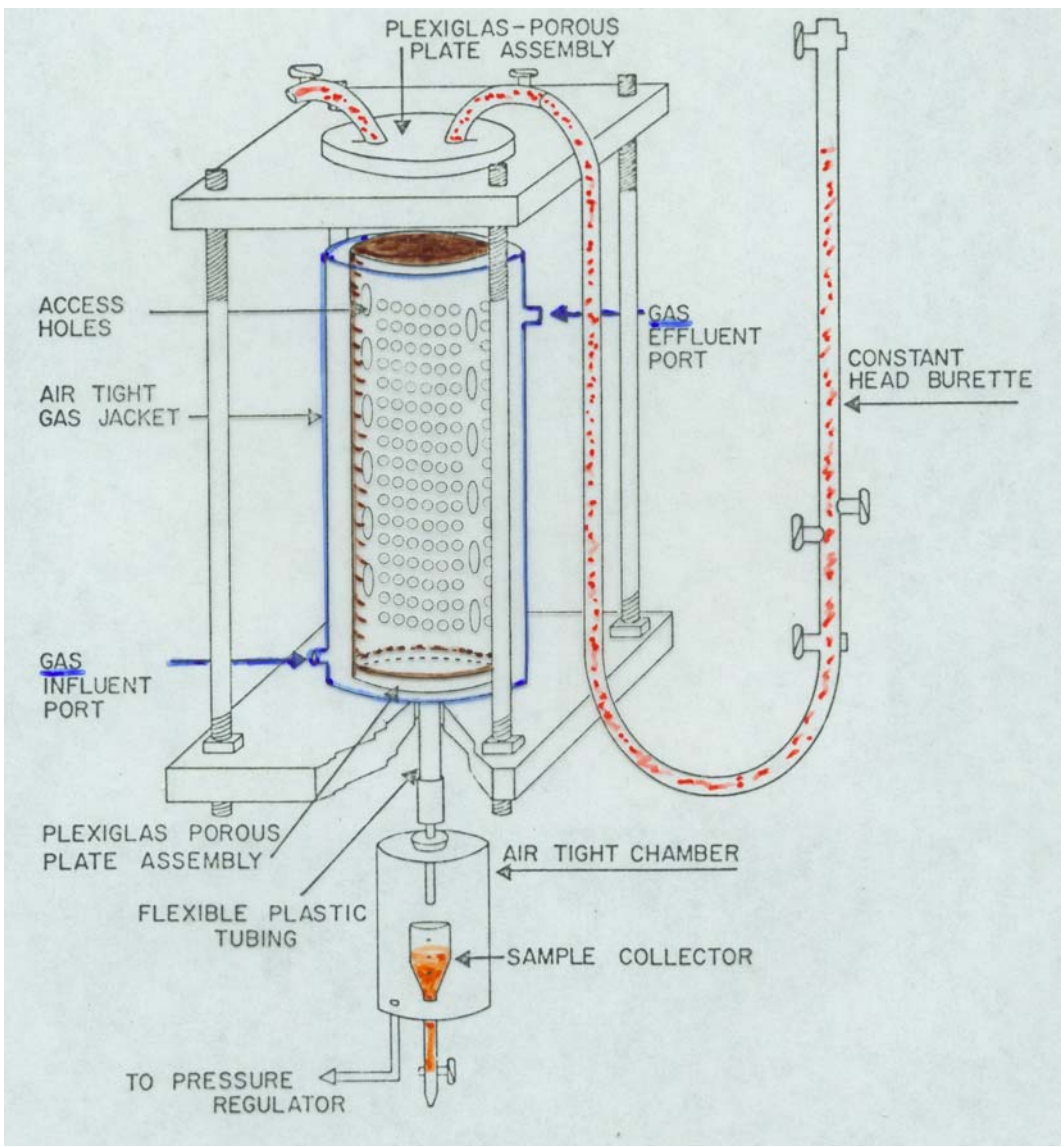


# Adsorbed NH<sub>4</sub>

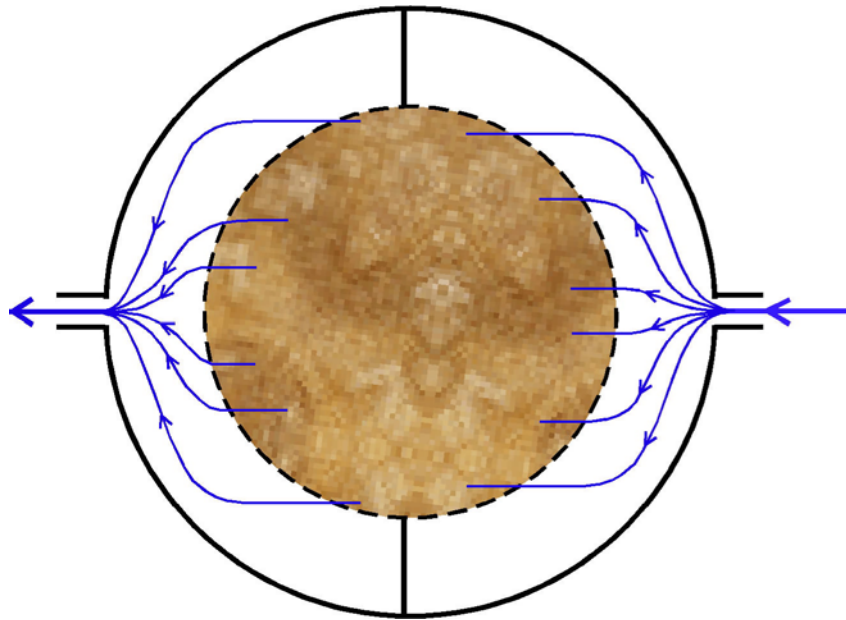




# Control soil air



# Soil air flow



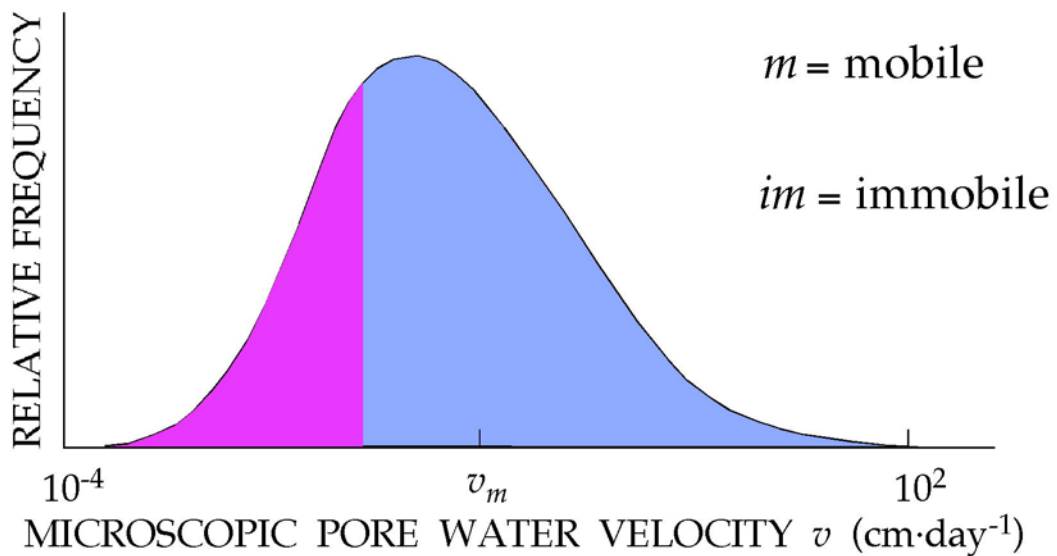
# Different disciplines

MISCIBLE DISPLACEMENT PHENOMENA  
ARE NOT WELL UNDERSTOOD  
OWING TO DIFFERENCES  
IN SCIENTIFIC DISCIPLINARY VIEWPOINTS

$\frac{\partial \rho S}{\partial t} + \frac{\partial \theta C}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - \frac{\partial J_w C}{\partial z} \pm \phi$			
<p><b>CHEMISTS</b>  <math>S = f_1(C)</math> EQUILIBRIA  <math>\frac{\partial S}{\partial t} = f_2(S, C)</math> KINETIC</p>	<p><b>MATHEMATICIANS</b>            PARABOLIC            HYPERBOLIC</p>	<p><b>PHYSICISTS</b>  <math>D = D_0 + \beta v^n</math>            MOBILE-            IMMOBILE WATER</p>	<p><b>GEOHYDROLOGISTS</b>            IRREVERSIBLE REACTIONS    <b>PLANT PHYSIOLOGISTS</b>            PLANT ROOT RELATIONS    <b>MICROBIOLOGISTS</b>            MICHAELIS-MENTEN            REACTIONS</p>

# Mobile-immob.

## CONCEPT OF MOBILE-IMMOBILE SOIL WATER



$$\theta_m \frac{\partial C_m}{\partial t} + \theta_i \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - v_m \theta_m \frac{\partial C_m}{\partial x}$$

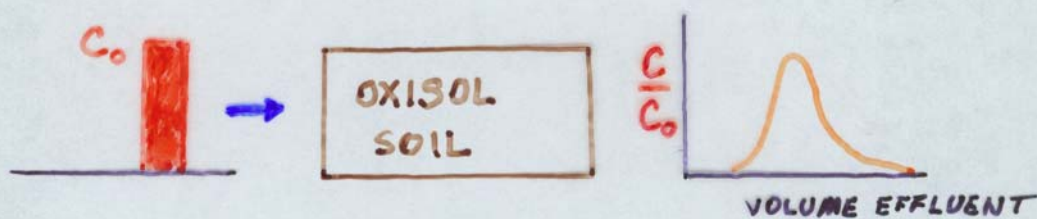
$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im})$$

$$\theta = \theta_m + \theta_i \quad \text{Total Soil Water Content}$$

$$\phi = \frac{\theta_m}{\theta} \quad \text{Fraction of Mobile Water}$$

$$1 - \phi \quad \text{Fraction of Immobile Water}$$

# Oxisol expt



CONCENTRATION 0.1, 0.01, 0.001 N

ISOTOPES

$^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{45}\text{Ca}$

pH

4, 7, 9

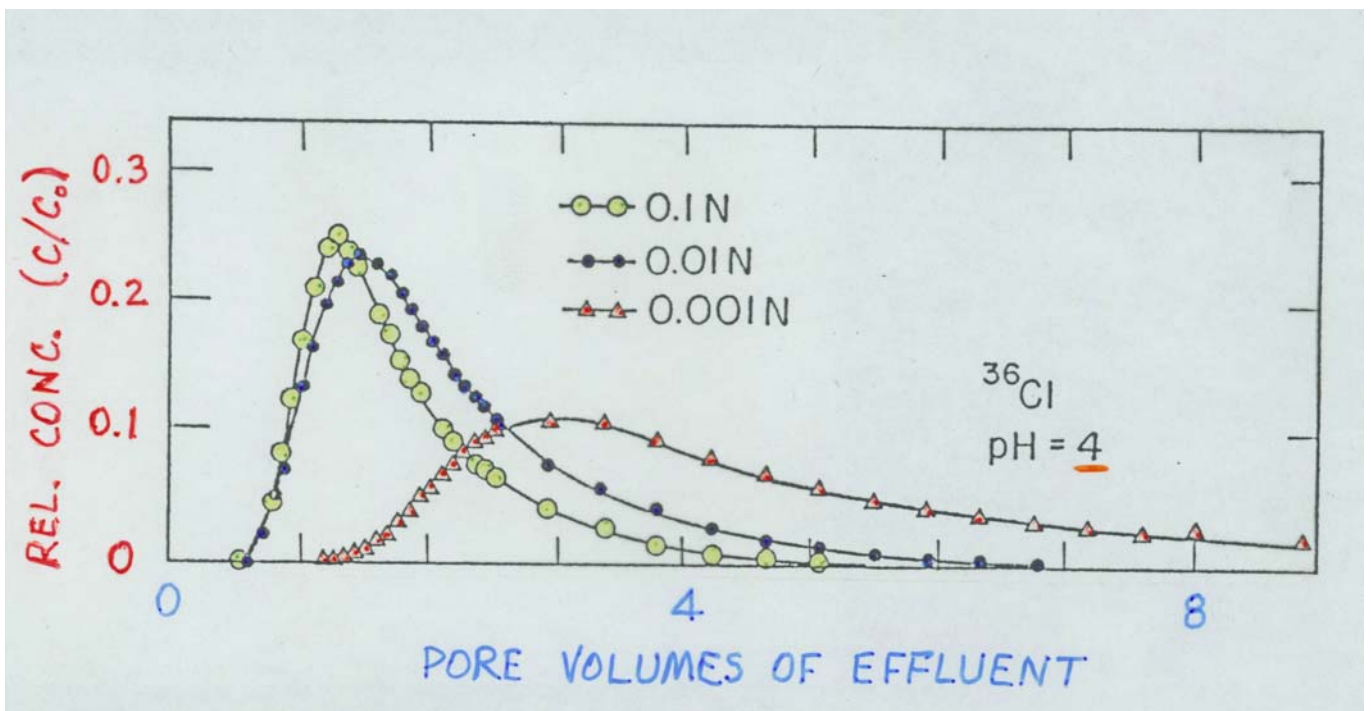
FLUX

0.25, 3.2 cm/hr

AGGREGATE DIAMETER 0.5-1, 1-2, 2-4.7 mm

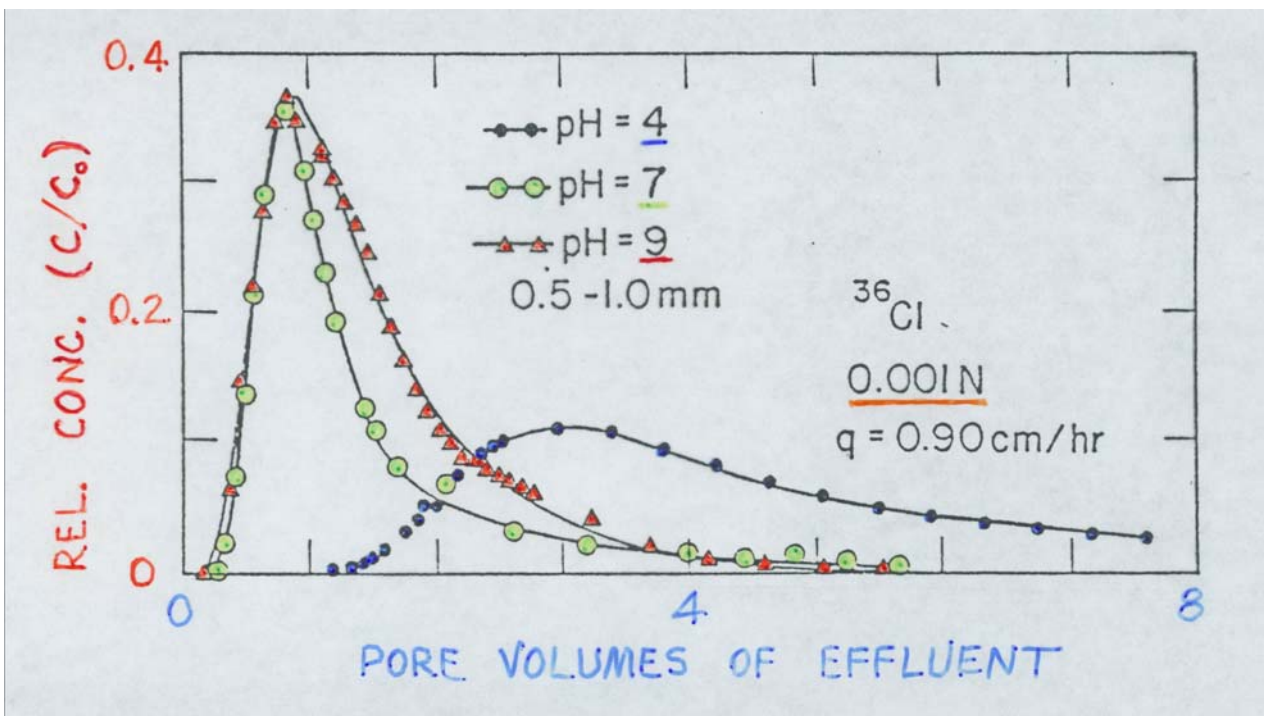
- WATER - SATURATED -

0.1,0.01,0.001

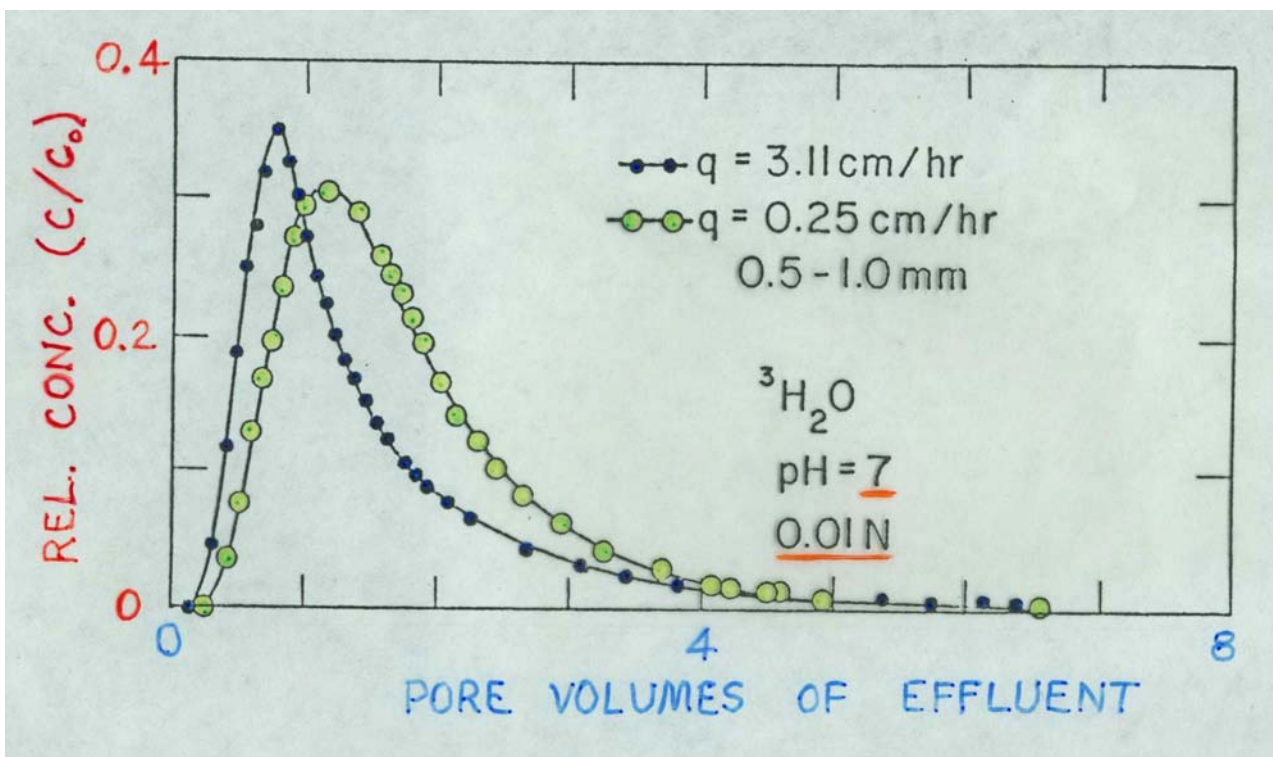




# pH 4, 7, 9

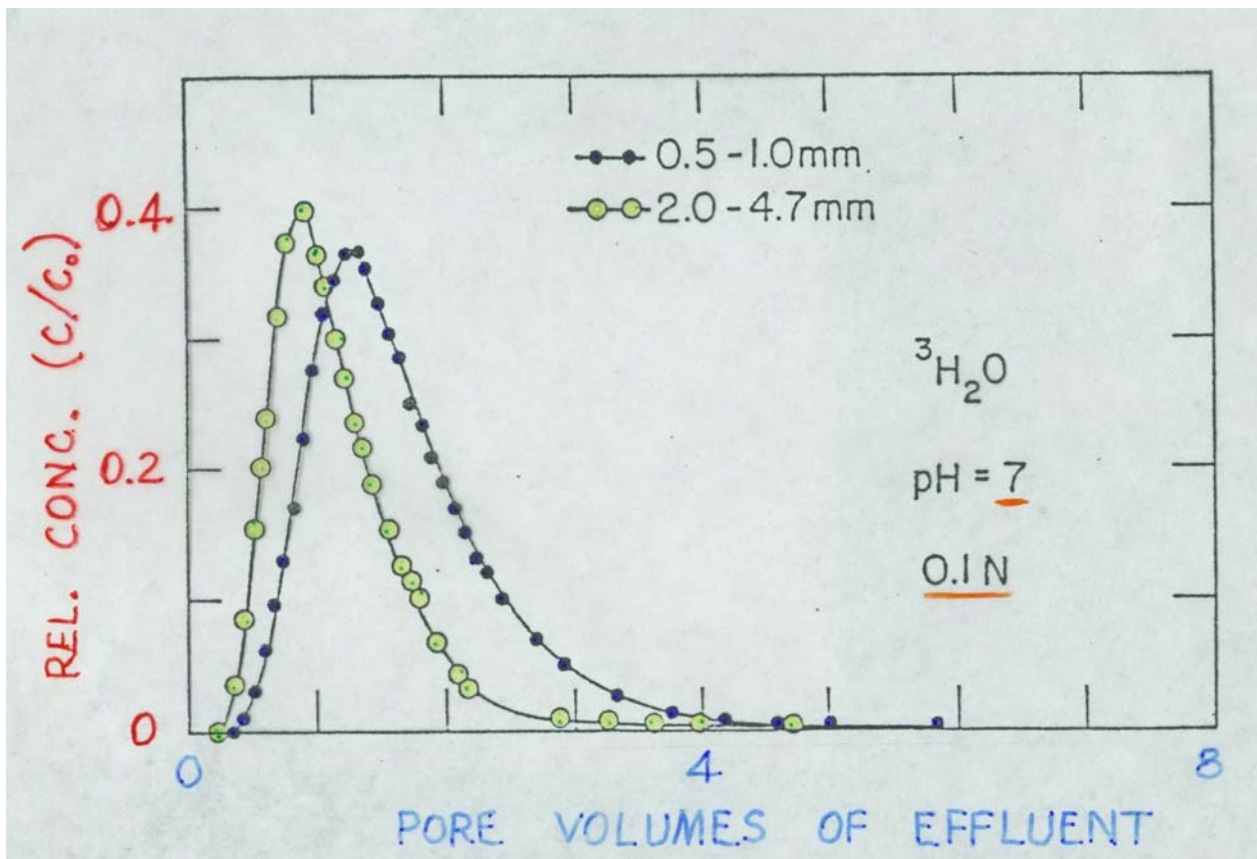


## 2 fluxes

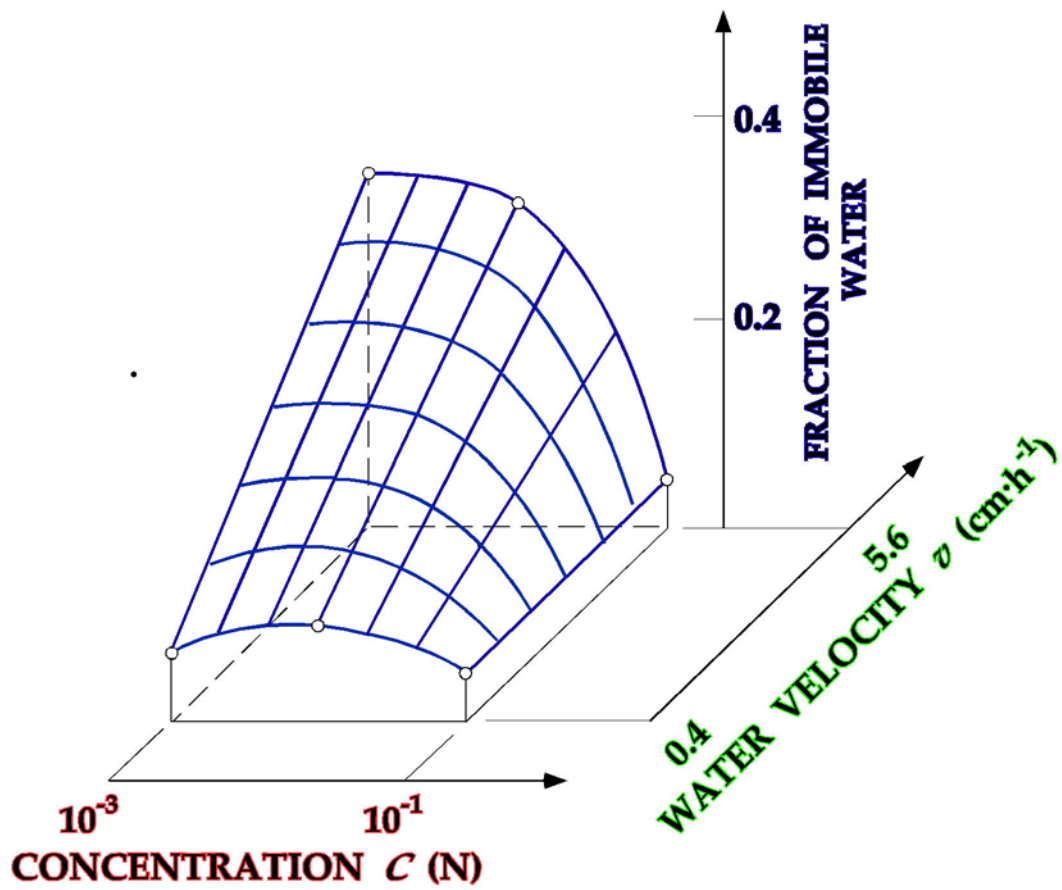




## 2 aggregate size



# Immobile water



# MD Theories

MISCIBLE DISPLACEMENT THEORIES

CONVECTIVE-DIFFUSION EQUATIONS

STOCHASTIC CONTINUUM APPROACHES

STOCHASTIC CONVECTION APPROACHES

TRANSFER FUNCTIONS

CHROMATOGRAPHIC APPROACHES

MARKOV PROCESSES

MONTE CARLO SIMULATIONS

DETERMINISTIC EQUATIONS

KINEMATIC WAVE EQUATIONS

DUAL POROSITY MODELS

•  
•  
•  
•

# Conv-diffusion Eq.

CONVECTIVE - DIFFUSION EQUATION

$$\frac{\partial \theta C}{\partial t} + \frac{\partial \rho S}{\partial t} = \frac{\partial}{\partial z} \left( \theta D \frac{\partial C}{\partial z} \right) - \frac{\partial qC}{\partial z} + f$$

**GEOCHEMISTS**      **HYDROLOGISTS**      **CHEMISTS, GEOBIOLOGISTS**

**MATHEMATICIANS**

# Stoch-continuum

## STOCHASTIC CONTINUUM APPROACH

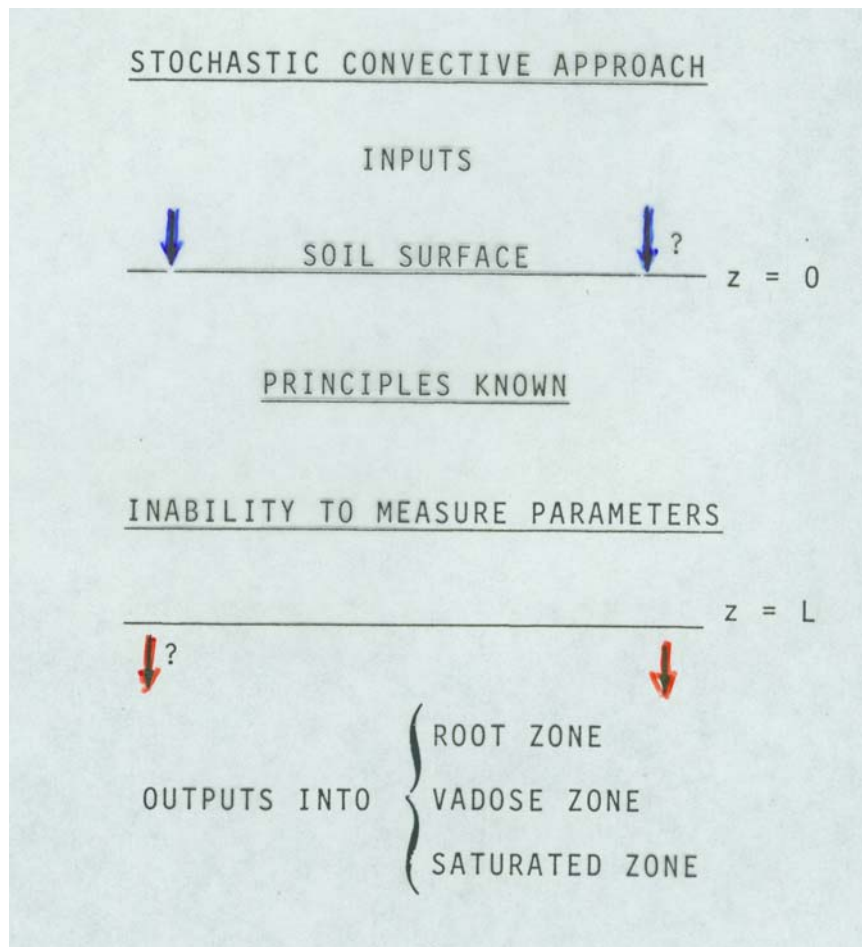
$$\underline{Q} = - \underline{K} \frac{dH}{dz}$$

$$\underline{Q} + \underline{q} = - [\underline{K} + \underline{k}] \frac{d[H+h]}{dz}$$

$$\underline{Q} + \underline{q} = - \underline{K} \frac{dH}{dz} - \underline{K} \frac{dh}{dz} - \underline{k} \frac{dH}{dz} - \underline{k} \frac{dh}{dz}$$

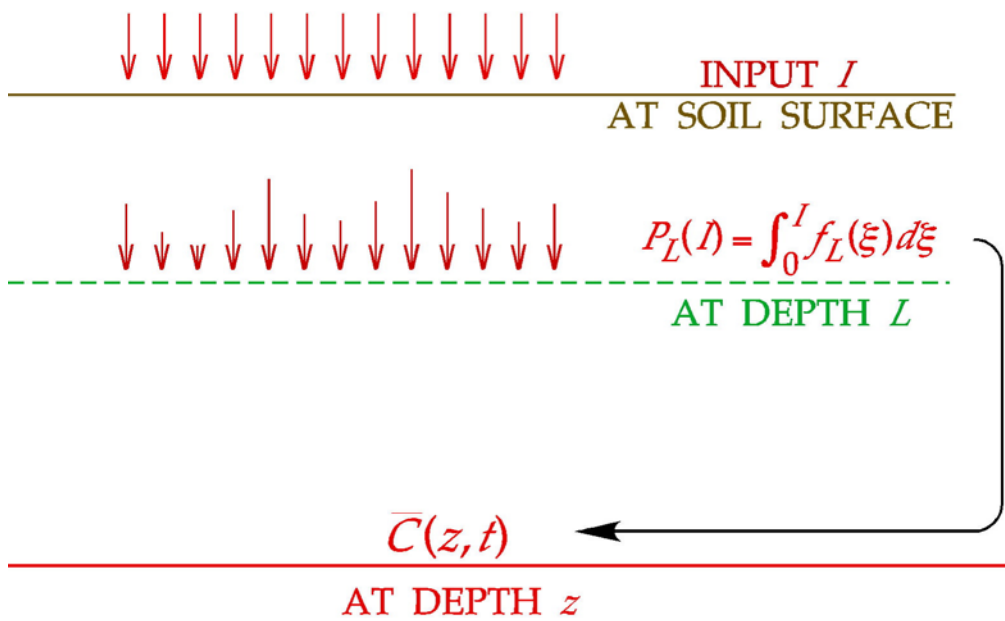
$$\underline{q} = - \underline{K} \frac{dh}{dz} - \underline{k} \frac{dH}{dz} - \underline{k} \frac{dh}{dz}$$

# Stoch-convective

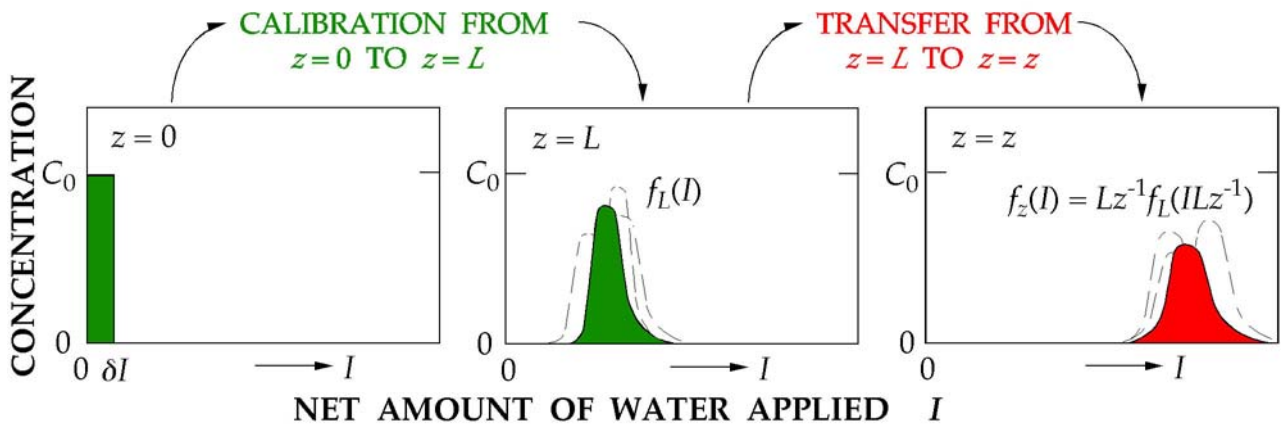


# Transfer function

## TRANSFER FUNCTION

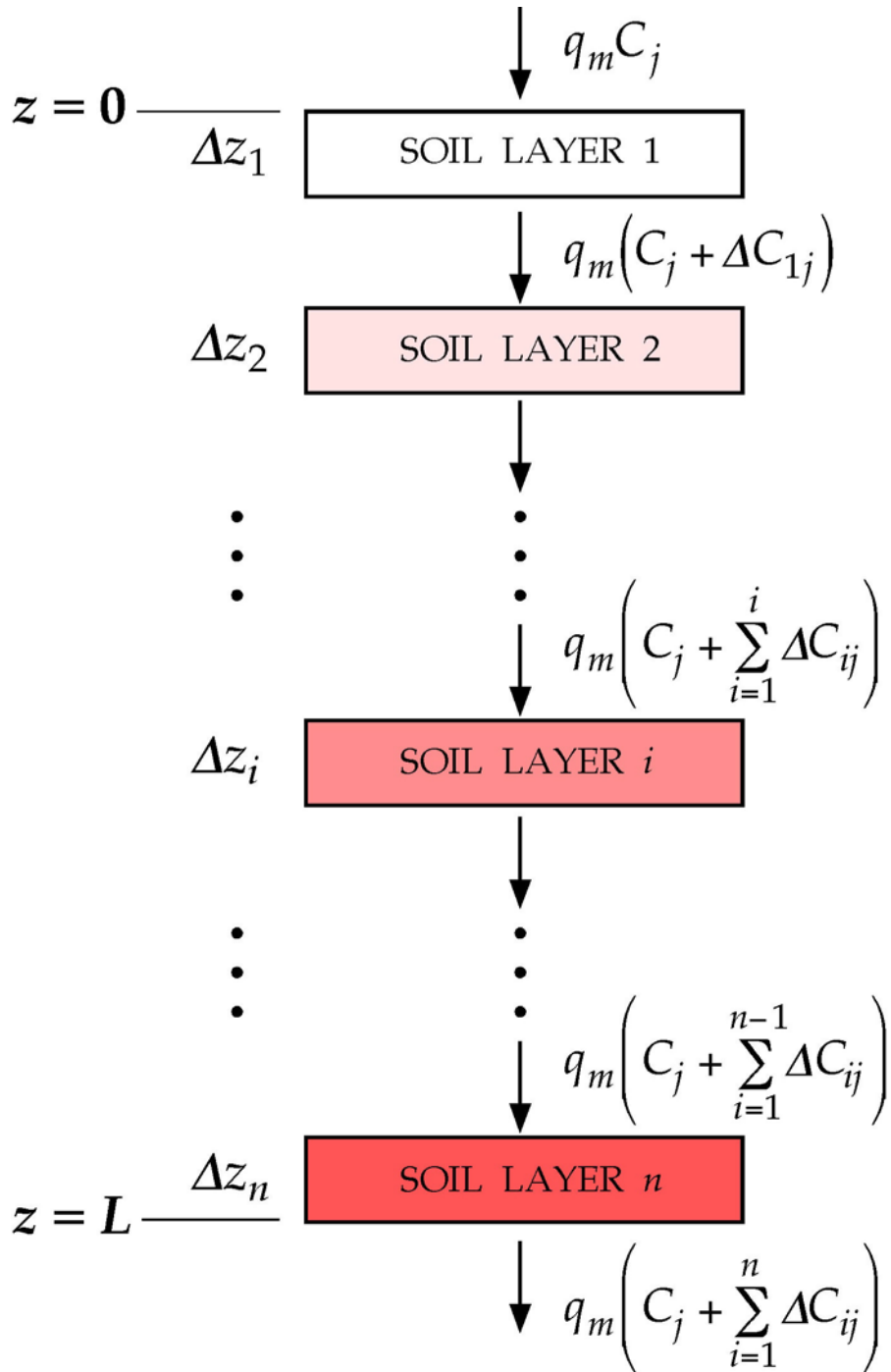


# Trans functions



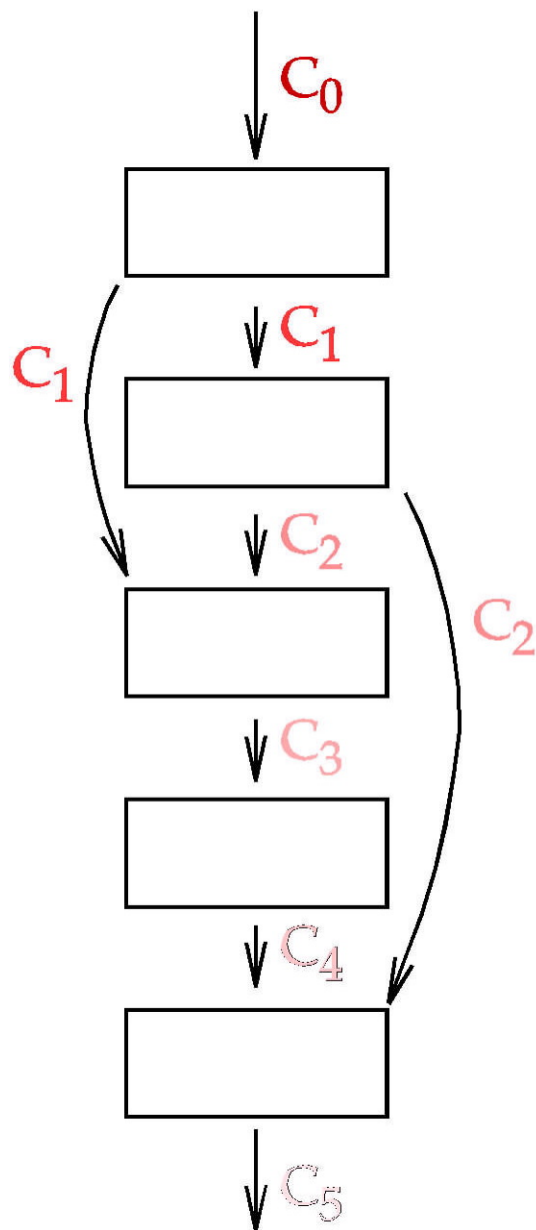


# Chromatogr



# Markov Process

**A RANDOM PROCESS WHOSE FUTURE PROBABILITIES ARE DETERMINED BY ITS MOST RECENT VALUES**



# Monte carlo simulation

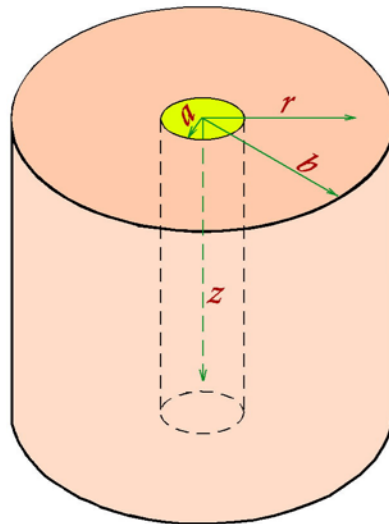
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z}$$

$$C = C(z, t | D, v)$$

$$\bar{C}(z, t) = \int_0^{C_0} f(C | z, t) C dC$$

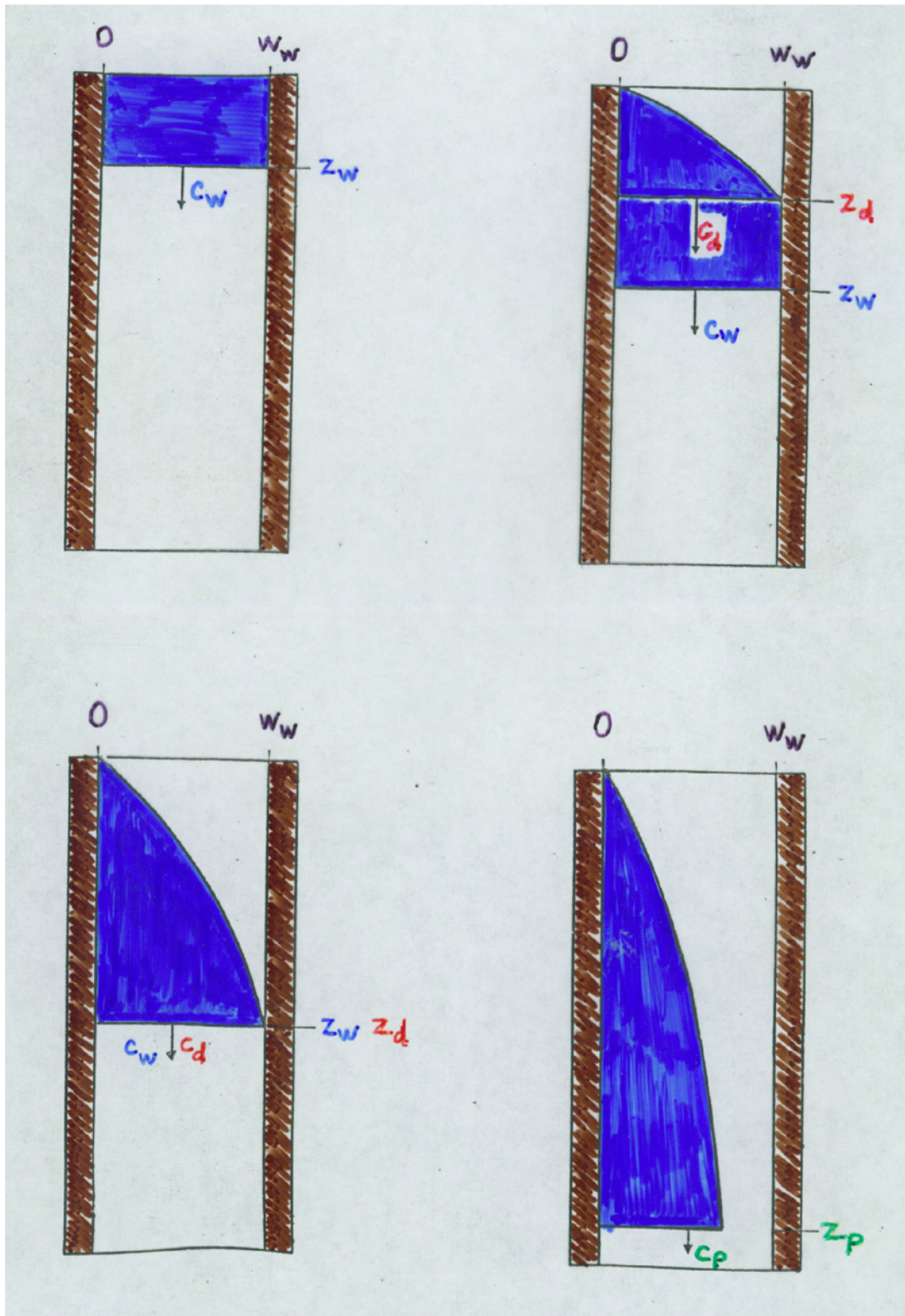
# Deterministic

## DETERMINISTIC PORE GEOMETRY



# Kinematic wave

## KINEMATIC WAVE OF INFILTRATION



# Questions

BECAUSE OF MACROPORES, CAN LEACHING BE DESCRIBED BY THE CONVECTIVE -  
DIFFUSION EQUATION ?

BECAUSE OF SPATIAL VARIABILITY, WHAT IS THE "PROPER" NUMBER OF  
SAMPLES ?

WHAT ARE THE MERITS OF SOIL SOLUTION PROBES, AND DO THEY  
REPRESENT THE ' "REAL" SITUATION ?

WHICH ARE THE BEST MODELS TO DESCRIBE SOLUTE MOBILITY AND  
RETENTION ?

ARE CHEMICAL REACTIONS MORE IMPORTANT THAN PHYSICAL REACTIONS ?

HOW IS A MODEL VERIFIED ?

HOW CAN THE RESULTS FROM A SMALL EXPERIMENTAL PLOT BE EXTEND OVER  
AN ENTIRE FIELD ?



# Important points

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## IMPORTANT POINTS ABOUT LEACHING

As water moves more slowly through a soil, greater opportunity exists for more complete mixing and chemical reactions to take place within the entire pore structure owing to molecular diffusion compared with convection.

Microscopic pore water velocity distributions manifest their greatest divergence for water-saturated soil conditions. Hence, under water-saturated conditions, the greatest proportion of water moves through the soil matrix within the largest pore sequences.

Under water-saturated soil conditions, when the average pore water velocity is large compared with transport by molecular diffusion, the relative amount of solute being displaced depends upon the solute concentration of the invading water.

The concept of preferential flow paths occurs at all degrees of water-unsaturation even though their existence is usually only demonstrated for macropores near water-saturation. At each progressively smaller water content, the larger pore sequences remaining full of water establish still another set of preferential flow paths.

Any attempt to measure the solute concentration based on extraction methods carried out either in the laboratory or the field will depend upon the rate of extraction and the soil water content during the extraction process.

Inasmuch as rainfall infiltration usually occurs at greater soil water contents and greater average pore water velocities than does evaporation, the amount of solutes transported near the soil surface per unit water moving through the soil surface is greater for evaporation than for infiltration.