Molecular and Colloidal Sizes of DOM

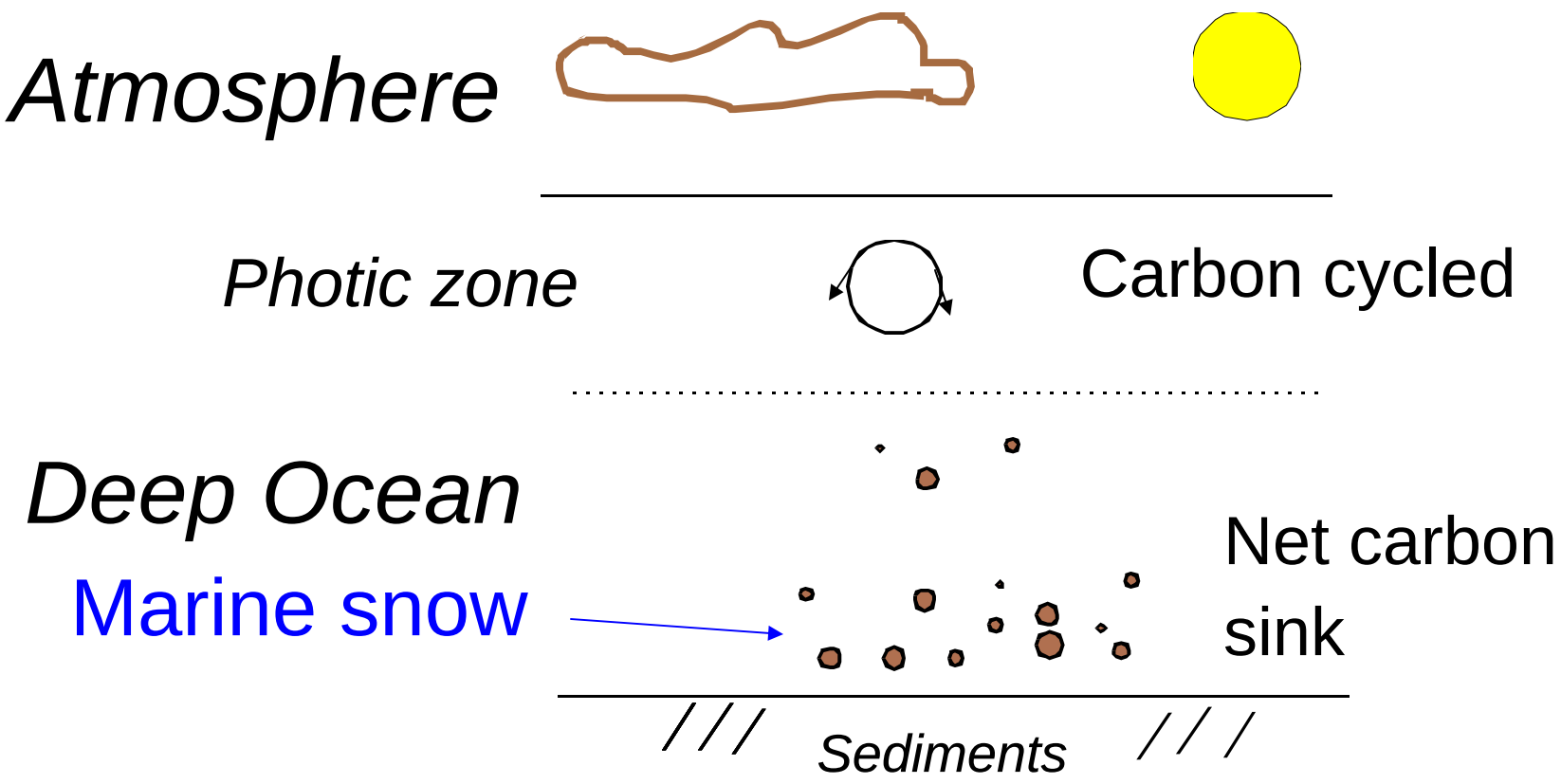
Bruce E. Logan
Department of Civil & Environmental Engineering
The Pennsylvania State University

Email: blogan@psu.edu
http://www.engr.psu.edu/ce/enve/logan.htm

Particle dynamics are important for:

- Water Quality
  - -Clear (non-turbid water)
  - -Treatment by flocculation/clarification
- Bioengineered Systems
  - Fermentation processes (beer, wine)
    - -floc formation for cell separation
- Natural Systems
  - Sedimentation in estuaries (salting-out)
  - Global carbon cycles
  - Fate of chemical pollutants

Global Carbon Cycling



Cycling of Terrestrial Organic Matter (OM)

- POM- particulate organic matter
- COM- colloidal organic matter
- DOM- dissolved organic matter

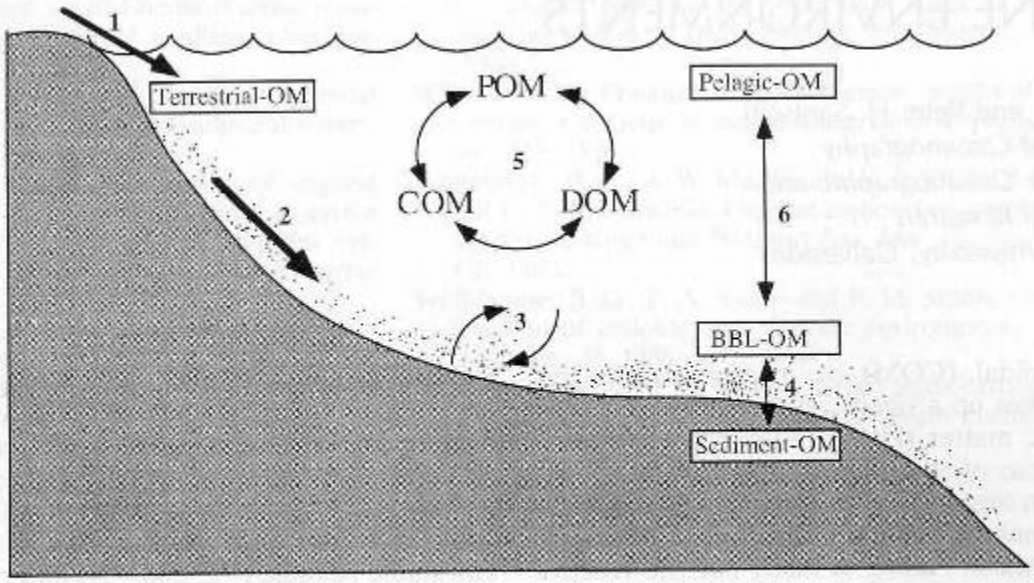


Figure 1. Schematic of processes governing the transport and cycling of dissolved organic matter in marine environments. Processes indicated by arrows include terrestrial inputs (1); lateral transport in the benthic boundary layer (BBL) (2); resuspension and sediment-water exchange (3 and 4); and biological, chemical, and physical processes in the upper water column (5 and 6).

Colloidal Pumping: Enhanced concentration of metals and pollutants in colloids

Figure From: Guo and Santschi (1997, *Rev. Geophys*, 35,1)

Metals (and other pollutants) can partition onto particles to different extents

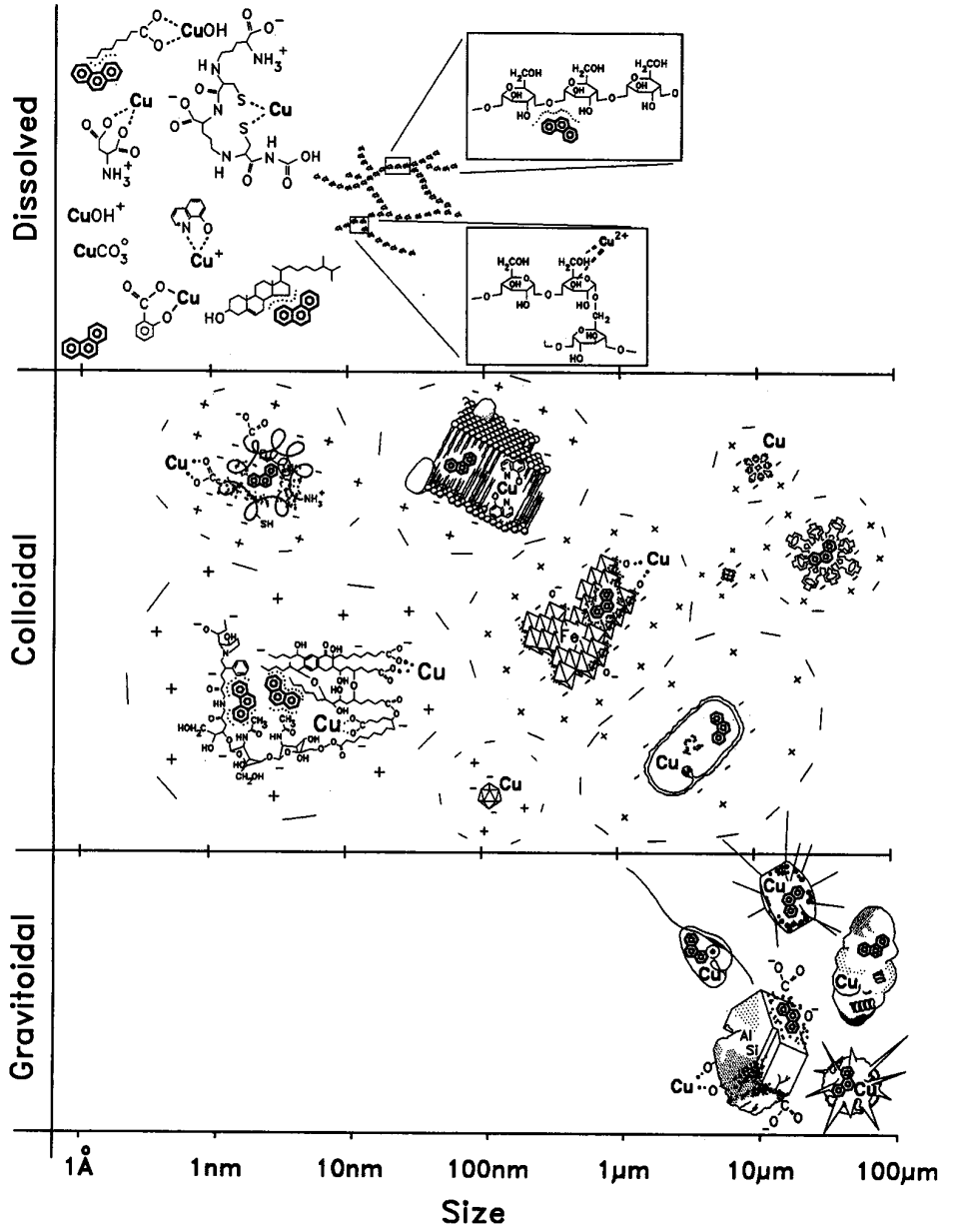


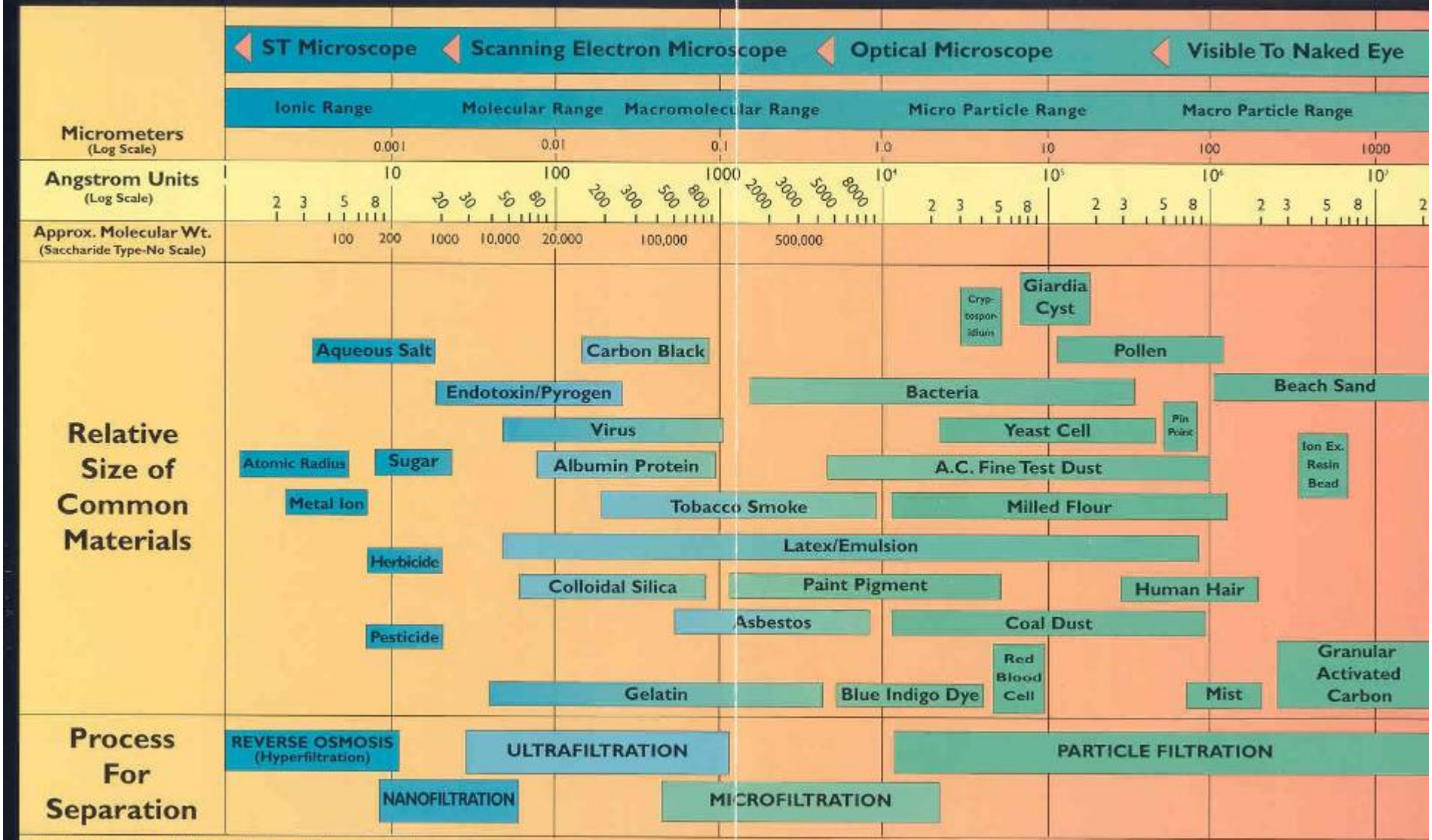
Fig. 3. A chemcentric speciation diagram. Two trace substances, phenanthrene and copper, are used to illustrate how such chemicals' interactions with various constituents may affect their functional speciation.

Gustafsson&Gschwend, Limnol. Oceanogr. 1997, 42, 519.

OVERVIEW

1. Molecular size spectra
   - Range of molecule/particle sizes
   - Relating sizes to diffusion coefficients
2. Molecular size distributions
   - Different methods to measure size spectra
   - Size spectra using ultrafiltration
3. Particle size spectra in the ocean- final analysis

The Filtration Spectrum



Note: 1 Micron (1×10^{-6} Meters) = 4×10^{-5} Inches (0.00004 Inches)
1 Angstrom Unit = 10^{-10} Meters = 10^{-4} Micrometers (Microns)

Molecular Size Distributions

- Molecules: approximately <1000 Daltons (<1 kD)
  - Known structure
  - Tabulated values, correlations, measurements
- Macromolecules: >1 kD
  - Colloids of known properties; sometimes known structure
  - Proteins, polysaccharides, etc.
  - Humic and fulvic acids sometimes included
  - Correlations and measurement
- Colloids: >1 kD to < 0.2 um
  - Unknown properties
  - Must be experimentally measured.

A diffusion coefficient is the fundamental property needed for particle transport

- Chemical flux (J) is related to the concentration gradient according to

$$J = -D\,\nabla c \qquad J = -D\,\frac{dc}{dx}$$

(General Form) (One dimension)

- Flux is in the opposite direction to the gradient
- Diffusion coefficient in water is primarily a property of molecule size and shape.

Relating Molecule Size, Molecular Weight, and Diffusivity

Diameter (nm)	Molecular weight (Daltons)	Diffusivity ($\times 10^{8} cm^{2} s^{-1}$)
13.	1,000,000	25
6.2	100,000	50
2.9	10,000	110
1.3	1,000	250
0.62	100	700

Diffusion Coefficients: Relating Molecule Size to Diffusivity

Most important factors:

- Size of molecule
- Viscosity of water
- Intermolecular forces

Stokes-Einstein equation

$$D_{Cw} = \frac{k_B T}{6\pi\mu\, r}$$

Where:

D_{Cw}= diffusion coefficient of chemical C in water (cm^2/s)

k_B=Boltzman's constant= 1.38×10^{-23} kgm^2/s^2K

μ= dynamic viscosity= 1 cp = 0.01 g/s-cm

T= temperature [K]

r = molecule radius

Assumptions

- Creeping flow (Re<<1)
- Spherical particles
- No slip at surface

At 20°C in water → $D_{CW}\,[cm^2/s] = 2.14\times10^{-9}\, r^{-1}\,[\mu m]$

Diffusivities from Structure: **MOLECULES**

Wilke-Chang Correlation

$$D_{Cw} = \frac{7.4 \times 10^{-8}\ T\ (\Phi_l M_l)^{1/2}}{\mu\ V_{C,b}^{0.6}}$$

Only if:

$$V_{C,b} < 0.27\ (\Phi_l M_l)^{1.87}$$

Where: [these units must be used]

D_{Cw}= diffusion coefficient [cm^2/s]

T= temperature [K]

Φ_l= association parameter [ ]

M_l= molecular weight of liquid [g/mol]

μ= dynamic viscosity [cp]

$V_{C,b}$= molal volume at normal boiling point [cm^3]

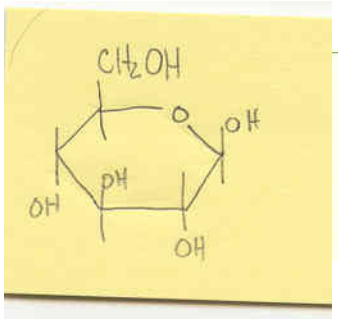
For chemicals in water:
20°C, Φ=2.6, M=18 g/mol

$$D_{Cw}[cm^2/s] = 1.48 \times 10^{-4}\ V_{C,b}^{-0.6}$$

Only if: $V_{C,b} < 359$

The atomic volume can be estimated knowing the structure of the molecule

Example: Glucose ($C_6H_{12}O_6$)



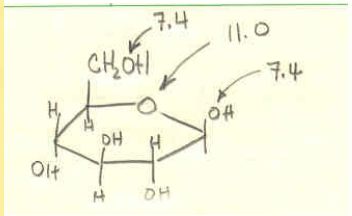
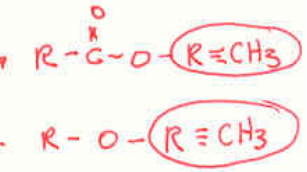
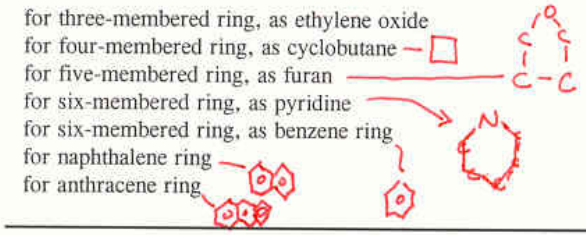


Table 3.4. Atomic Volumes for Complex Molecular Volumes for Simple Substances (Welty *et al.* 1976; p. 490)

Element	$V_{A,b}$ (cm³/g-mole)	Element	$V_{A,b}$ (cm³/g-mole)
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers and other esters	11.0
Iodine	37.0	Oxygen, in acids	12.0
Nitrogen, double bond	15.6	Sulfur	25.6
Nitrogen, in primary amines	10.5		
Nitrogen, in secondary amines	12.0		

for three-membered ring, as ethylene oxide	deduct 6
for four-membered ring, as cyclobutane	deduct 8.5
for five-membered ring, as furan	deduct 11.5
for six-membered ring, as pyridine	deduct 15
for six-membered ring, as benzene ring	deduct 15
for naphthalene ring	deduct 30
for anthracene ring	deduct 47.5





$V_{G,b}=(6\times14.8)+(12\times3.7)+(5\times7.4)+(1\times11)-15$

$V_{G,b}= 166.2$ [cm3/g]

$$D_{Cw}[cm^2/s] = 1.48\times10^{-4}\, V_{C,b}^{-0.6}$$

$$D_{Cw}[cm^2/s] = 1.48\times10^{-4}(166.2)_{G,b}^{-0.6}$$

$$D_{Cw}[cm^2/s] = 6.90\times10^{-8}$$

Reported → $D_{Cw}[cm^2/s] = 7.80\times10^{-8}$ (13% *error*)

Diffusivities from Size: **MACROMOLECULES**

PROTEINS

Polson Correlation

$$D_{Cw}[cm^2/s] = 2.74 \times 10^{-5}\ M_p^{-1/3}$$

Only if: M>1 kD

POLYSACCHARIDES

(Dextrans)

Frigon Correlation

$$D_{Cw}[cm^2/s] = 7.04 \times 10^{-5}\ M_D^{-0.47}$$

Only if: M>1 kD

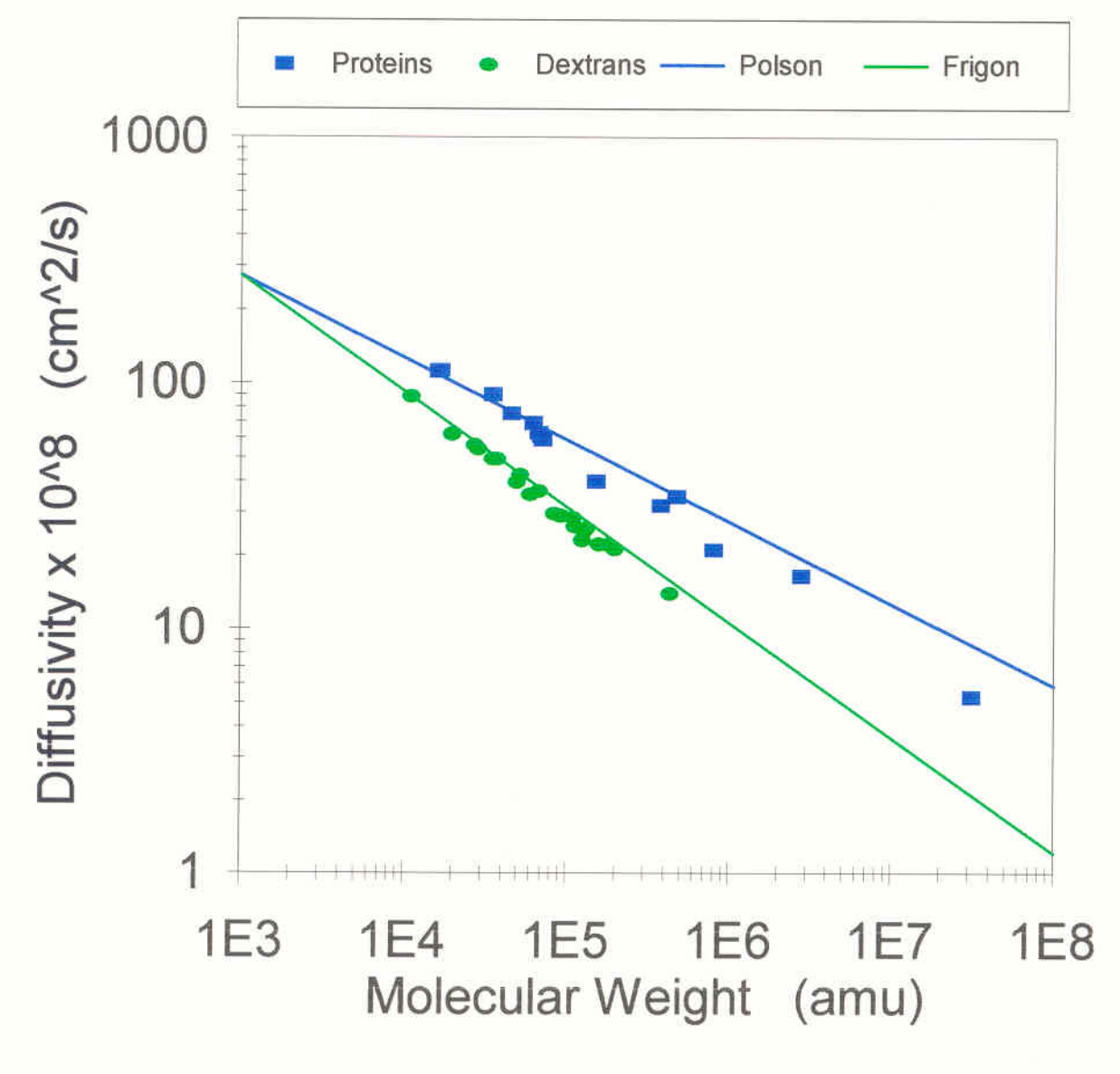
HUMIC & FULVIC ACIDS

Beckett Correlation

$$D_{Cw}[cm^2/s] = 1.42 \times 10^{-4}\ M_H^{-0.422}$$

Natural organic matter (NOM)

Comparison of Diffusion coefficients for Polysaccharides (Dextrans) and Proteins



How do we easily account for temperature?

Take the Wilke-Chang correlation, $D_{Cw} = \dfrac{7.4\times10^{-8}\ T\ (\Phi_l M_l)^{1/2}}{\mu\ V_{C,b}^{0.6}}$

Rearranging, so that for one chemical all constants are on one side of the equation $\dfrac{D_{Cw}\mu}{T} = \dfrac{7.4\times10^{-8}\ (\Phi_l M_l)^{1/2}}{V_{C,b}^{0.6}} =$ constant

So know we can write that at some new temperature T, we have from knows at a previous temperature,

$$\frac{D_{Cw}\mu}{T} = \frac{D_{Cw,T}\mu_T}{T_T} = \text{constant}$$

Or more simply, $\boxed{D_{Cw,T} = D_{Cw}\dfrac{\mu}{\mu_T}\dfrac{T_T}{T}}$

Molecular Size Distributions: **COLLOIDS**

- We know the structure of a very small fraction of dissolved organic matter (DOM)
- Most oceanographers classify colloids as DOM >1 kD
- Does size of molecules matter? YES
  - Biodegradability (bacteria must hydrolyze if >1 kD)
  - Removal in water treatment processes (adsorption)
- To relate size to diffusivity, use Stokes-Einstein (SE) equation.
- To relate molecular weight to size (or diffusivity), must have calibration standards (i.e. synthentic molecules, proteins, dextrans, etc.)

Diffusion coefficients: homogeneous particle size

Ultracentrifugation

- Force on a particle of mass m_c due to gravity is $F=m_c g$
- In a centrifuge spinning at ω, $F=m_c\omega^2 r$, where r=distance from center
- From the velocity of particle during centrifugation (incorporated int the "s" term), it is possible to calculate the diffusivity :

$$D_{Cw} = \frac{RTs}{m_c(1-V_C\ \rho_w)}$$

Light Scattering

- Analysis of the particle is used to determine the radius of gyration, r_g
- Modified form of SE equation is used.

$$D_{Cw} = \frac{k_B T}{6\pi\mu c_g\ r_g}$$

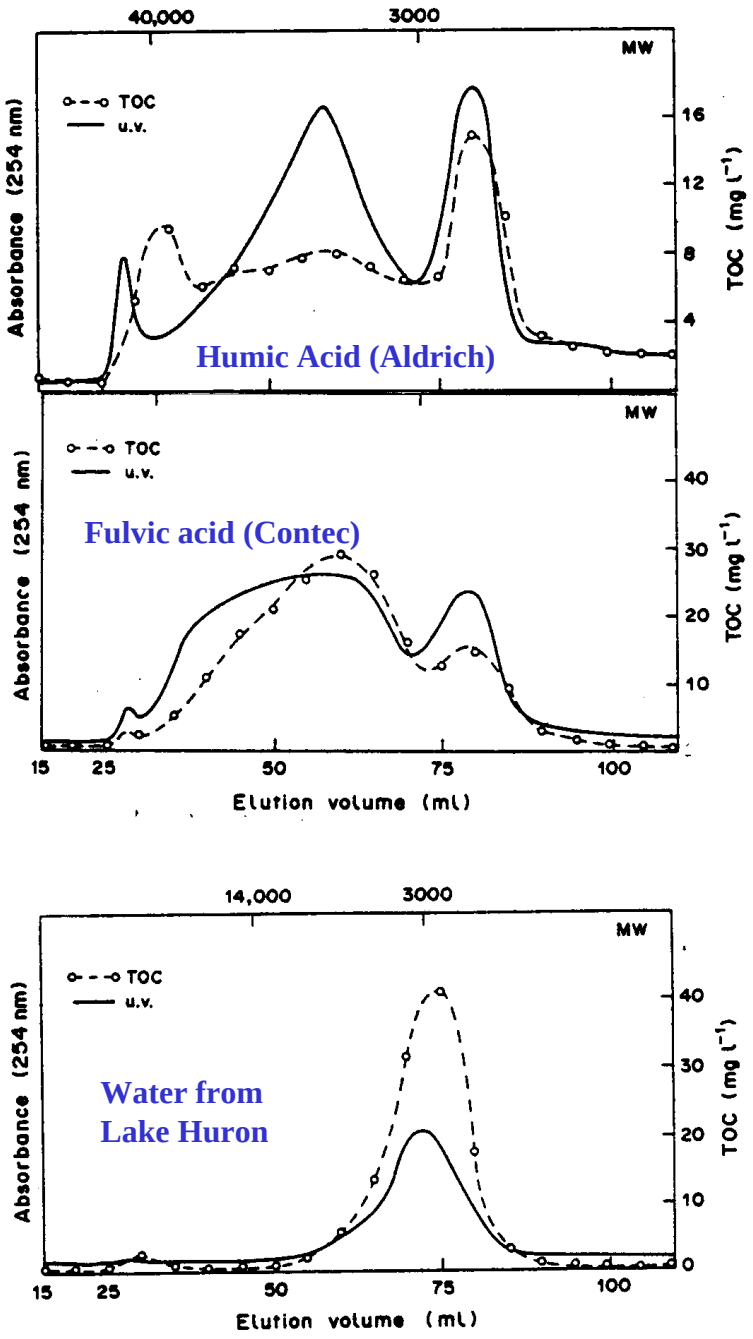
c_g is a new coefficient

- For DOM in water, we have:

$$D_O[cm^2/s] = 1.69\times10^{-5}\ r_O^{-1}$$

Size Exclusion Chromatography (SEC)

- Molecules separated by exclusion of larger particle
- Smaller particles diffuse into porous particles in column, and are delayed
- Can use low pressure (gel permeation chromatography; GPC) or high pressure chromatography (HPLC-SEC).



Field Flow Fractionation

Molecules are separated using two methods, based on:

- Molecule size (like SEC)
- Another method acting perpendicular to the direction of flow, such as an electric or fluid field

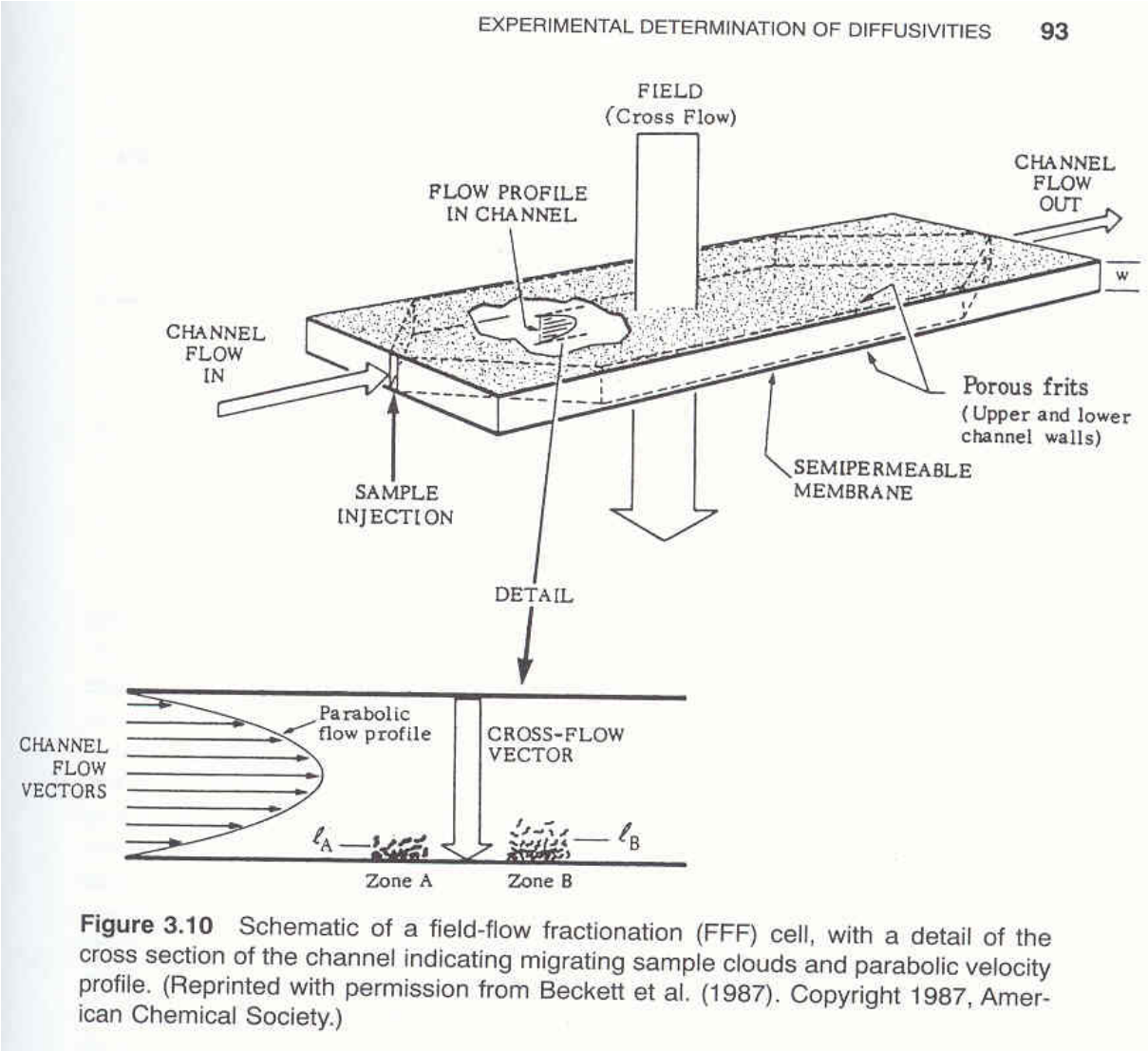


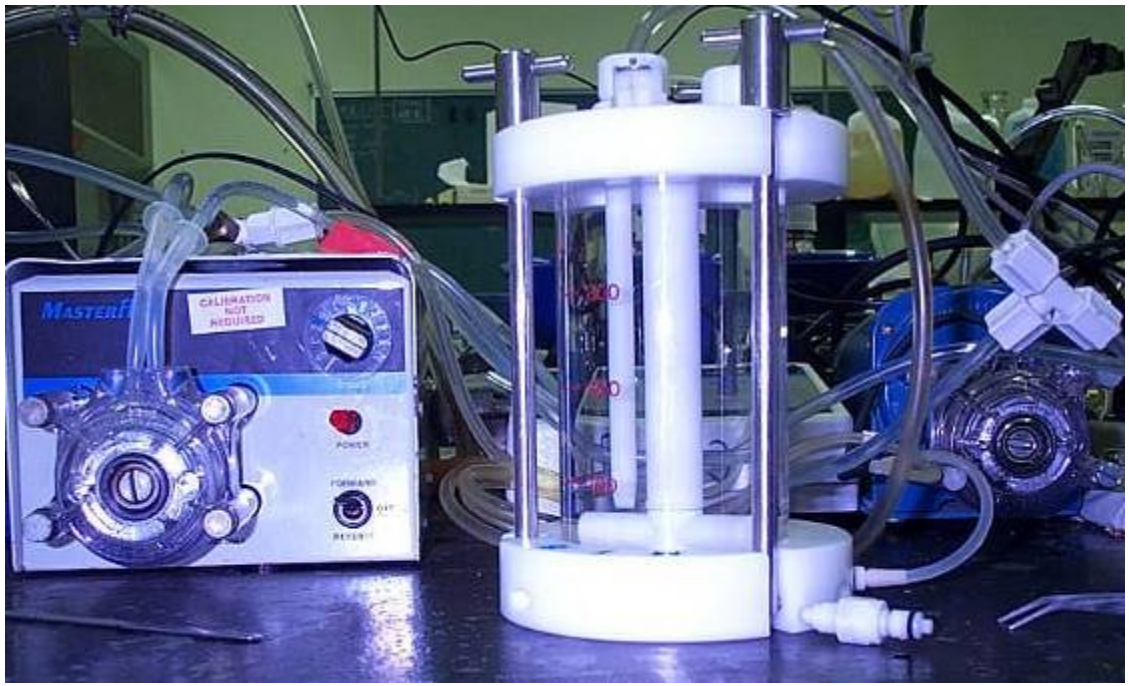
Figure 3.10 Schematic of a field-flow fractionation (FFF) cell, with a detail of the cross section of the channel indicating migrating sample clouds and parabolic velocity profile. (Reprinted with permission from Beckett et al. (1987). Copyright 1987, American Chemical Society.)

Ultrafiltration (UF)

- Membranes fabricated that have set average pore size
- Rated in terms of atomic mass units (amu) or Daltons based on >99% rejection of molecules larger than the stated amu.
- UF separations provide discrete (not continuous) molecular size distributions
- There is no “perfect” membrane. Problems are:
  - Some materials are rejected due to charge repulsion
  - Build up of material on membrane can cause rejection of smaller sized molecules
  - Most researchers incorrectly report sizes by not considering membrane rejection (**Apparent size distribution**)
  - The **Actual size distribution** can be determined using a permeation coefficient model.

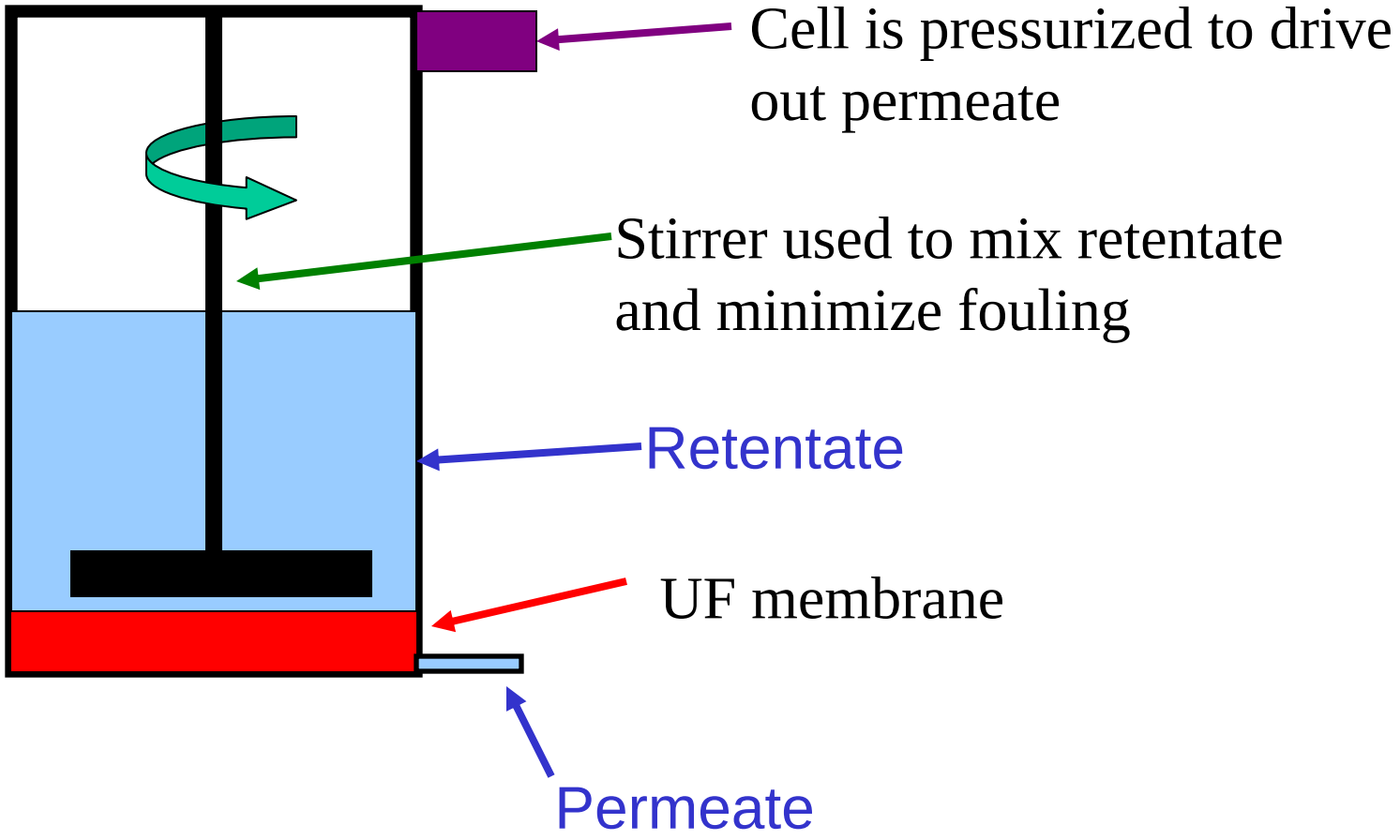
Ultrafiltration Cells

FIGURE 12. Stirred cells.

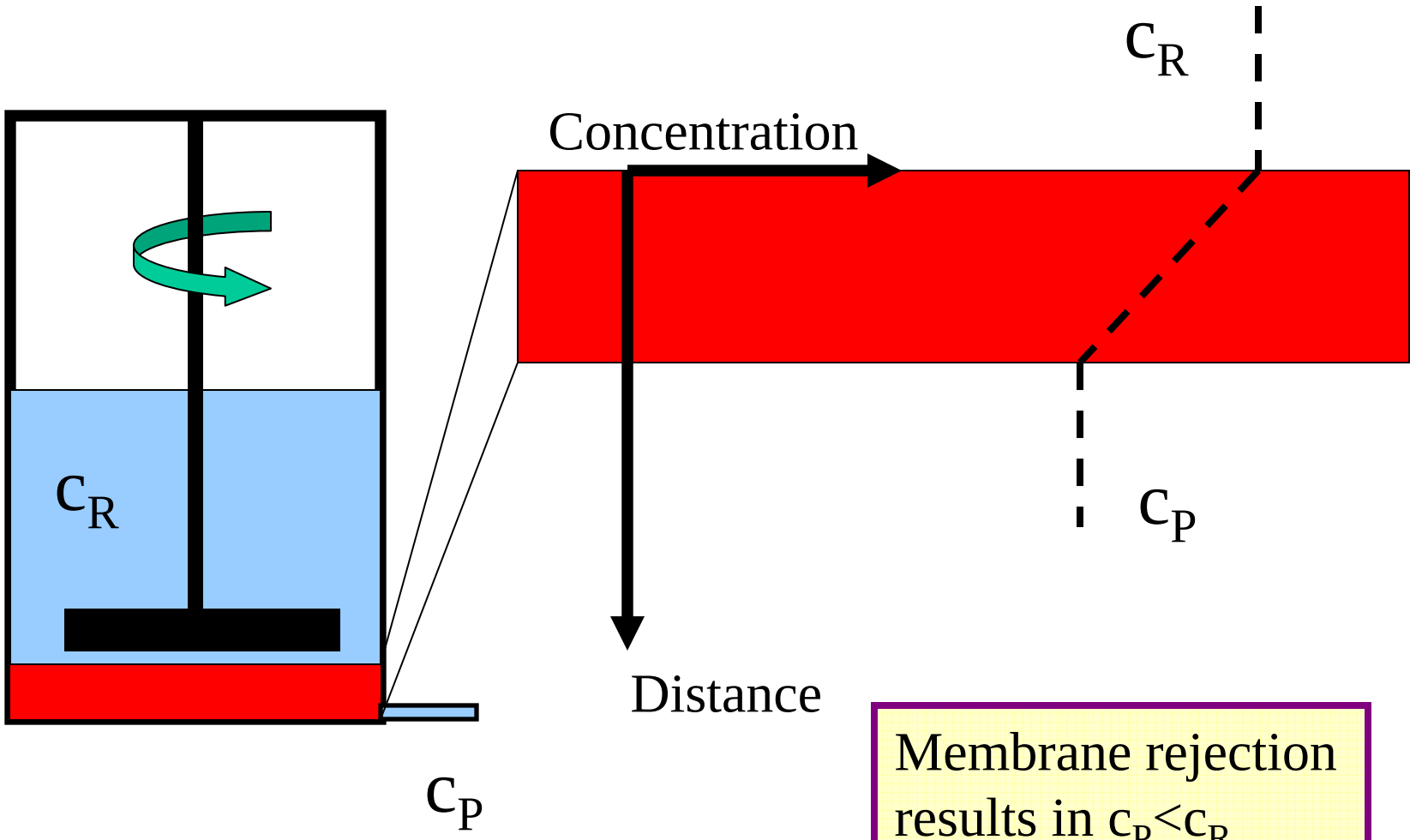


UF Cell Components

Ultrafiltration cell body



Effect of membrane rejection on permeate concentration



Membrane rejection results in $c_P < c_R$

Mass Balance Equations Produce Fundamental Relationships

Permeate concentration at at any time

$$c_P = p_c \, c_{r,0} \, F^{\,p_c - 1}$$

Filtrate Concentration (all of the permeate is collected)

$$c_f = c_{r,0} \, \frac{(1 - F^{\,p_c})}{(1 - F)}$$

$c_{r,0}$= concentration of material able to pass the membrane

F= fraction of filtrate removed [$F=1-(V_f/V_{r,0})$]

p_c= permeation coefficient

…derivation of equations…

Examples of UF Size Separations

• Example permeation coefficient model calculation to determine concentration of material <1K in sample using UF size separation.

•Separation of compounds having a known molecular weight using a 1000 amu membrane

- Vitamin B-12: MW=1192 Daltons
- Sucrose: MW=342 Daltons

•Errors for values of the permeation coefficient

•Effect of parallel versus serial filtration

Example: UF Separation, 1K amu

• You wish to determine the concentration of DOC (ppb) in seawater that is <1000 Daltons (C<1K). You use a 1K cell filled with 100 mL of sample.

•Permeate concentrations are measured at 6 times during separation.

Based on the following approaches, what would you conclude is the concentration of material <1K in the sample (C<1K)?

a) **Apparent C<1K** based on the first measurement (the instantaneous permeate sample at 5 mL)?
b) **True C<1K** based on the permeate coefficient model?
c) **Apparent C<1K** based on collecting 90 mL?

Permeation Coefficient Model Calculations

c_p	V_f
5.9	5
6.1	10
6.4	20
7.5	50
9.0	70
12.9	90

Answer part (a)

C<1K = **5.9 ppb**
based on first 5 mL

Permeation Coefficient Model Calculations

c_p	V_f	F
5.9	5	0.95
6.1	10	0.90
6.4	20	0.8
7.5	50	0.5
9.0	70	0.3
12.9	90	0.1

$$F = 1 - (V_f / V_{r,0})$$

$$V_{r,0} = 100 \text{ mL}$$

Permeation Coefficient Model Calculations

c_p	V_f	F
5.9	5	0.95
6.1	10	0.90
6.4	20	0.8
7.5	50	0.5
9.0	70	0.3
12.9	90	0.1

Next step:

Take natural log of F and c_p

Permeation Coefficient Model Calculations

c_p	V_f	F	ln c_p	ln F
5.9	5	0.95	1.77	-0.57
6.1	10	0.90	1.81	-1.05
6.4	20	0.8	1.86	-0.22
7.5	50	0.5	2.01	-0.69
9.0	70	0.3	2.19	-1.20
12.9	90	0.1	2.56	-2.30

Permeation Coefficient Model Calculations

The true C<1K is equal to $c_{r,0}$.

To calculate $c_{r,0}$, use the equation:

$$c_P = p_c \, c_{r,0} \, F^{\,p_c - 1}$$

And linearize it, to obtain

$$\ln c_P = \ln (p_c \, c_{r,0}) + (p_c - 1) \ln F$$

y-intercept

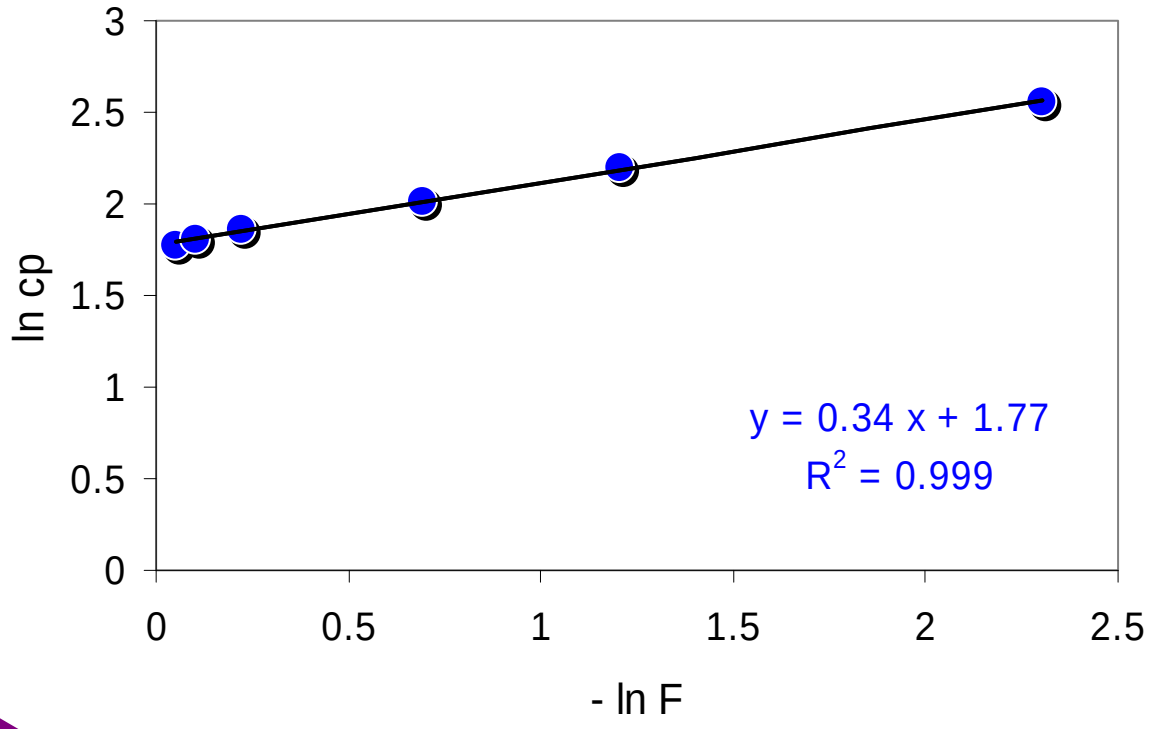
slope

ln c_p	ln F
1.77	-0.57
1.81	-1.05
1.86	-0.22
2.01	-0.69
2.19	-1.20
2.56	-2.30

Permeation Coefficient Model Calculations

$$\ln c_P = \ln (p_c \; c_{r,0}) - (1 - p_c) \ln F$$

(Note sign change on ln F term)



Slope= 0.34

p_c=(1-0.34)=0.66

y-intercept=1.77

$C_{r,0}$=$e^{1.77}$/0.66=9.0

$$c_P = 5.94 \; F^{0.34}$$

Answer part (b)

Actual C<1K = **9.0 ppb**

Permeation Coefficient Model Calculations

What if the first 90 mL are used to determine C<1K?

$$c_f = c_{r,0}\frac{(1-F^{p_c})}{(1-F)} = 9.0\frac{(1-F^{0.66})}{(1-F)}$$

If 90 mL are collected, then F is:

$$F = 1-(V_f/V_{r,0}) = 1-(90/100) = 0.1$$

$$c_f = 9.0\frac{(1-(0.1)^{0.66})}{1-(0.1)}$$

$$c_f = 7.8$$

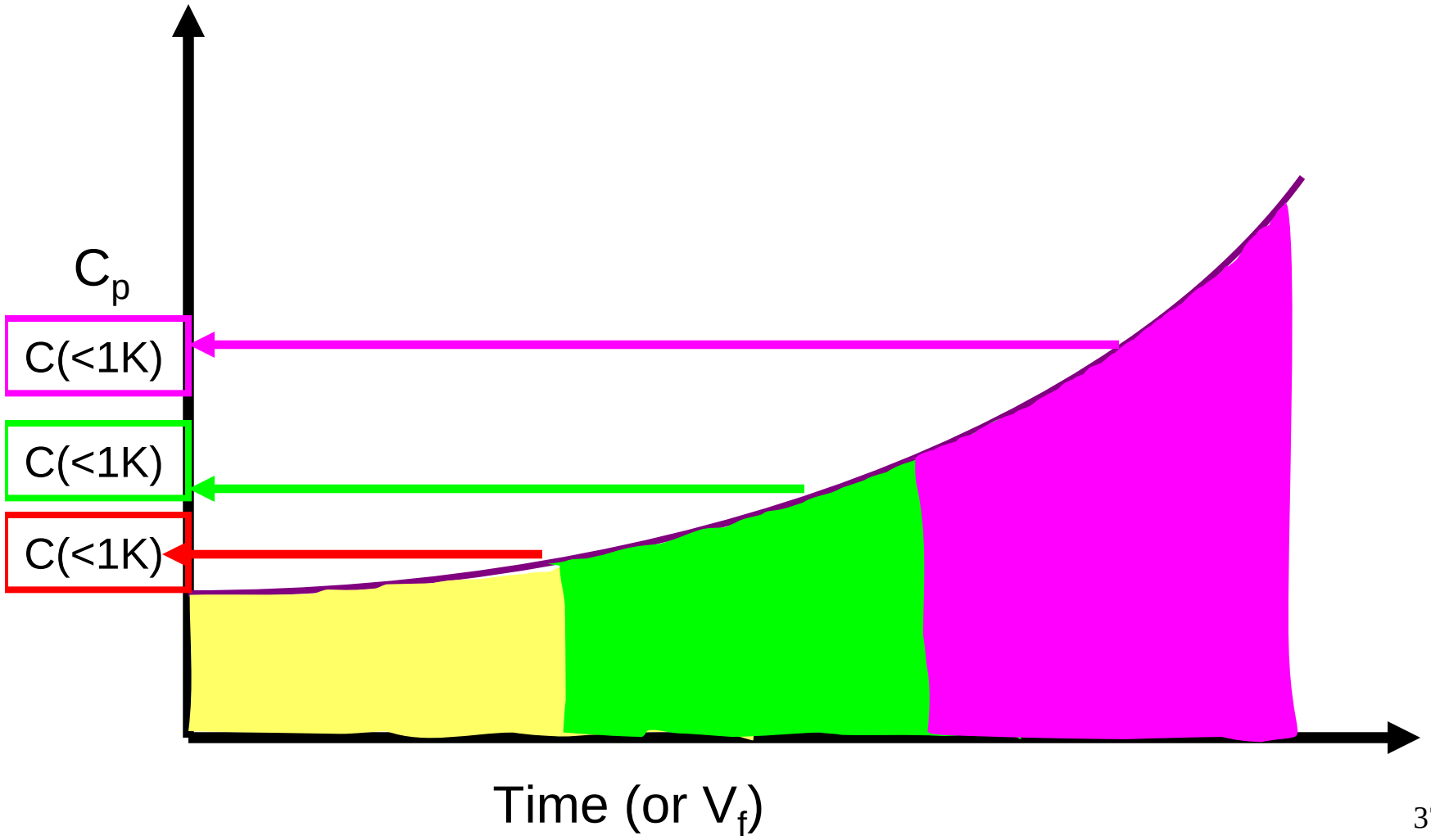
Answer part (c)

C<1K = 7**.8 ppb** based on 90 mL

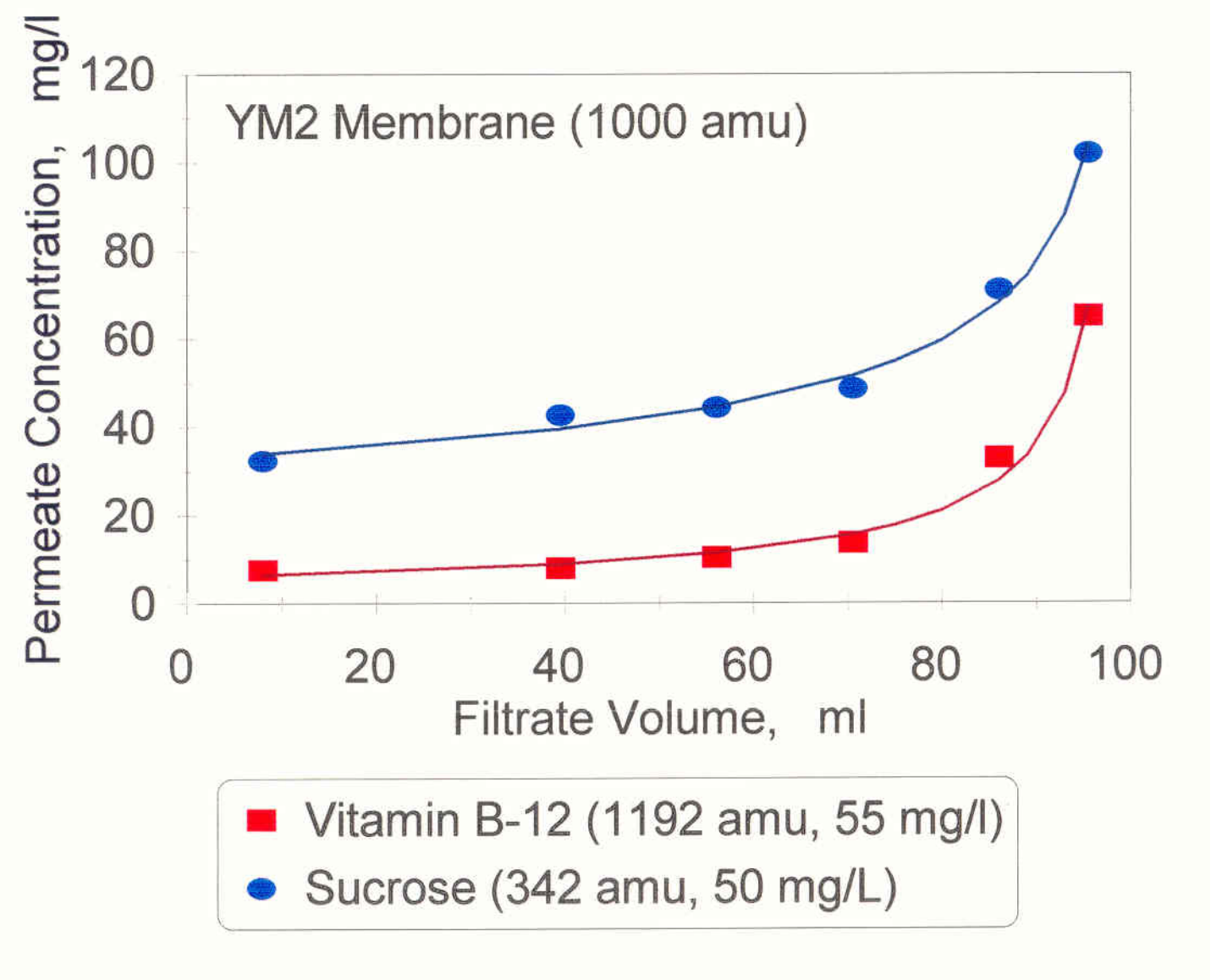
Permeation Coefficient Model: Comparison

Method	C <1K (ppb)	Error
Collect 5 mL	5.9	44%
Permeation Coefficient Model	9.0	---
Collect 90 of 100 mL	7.8	13%

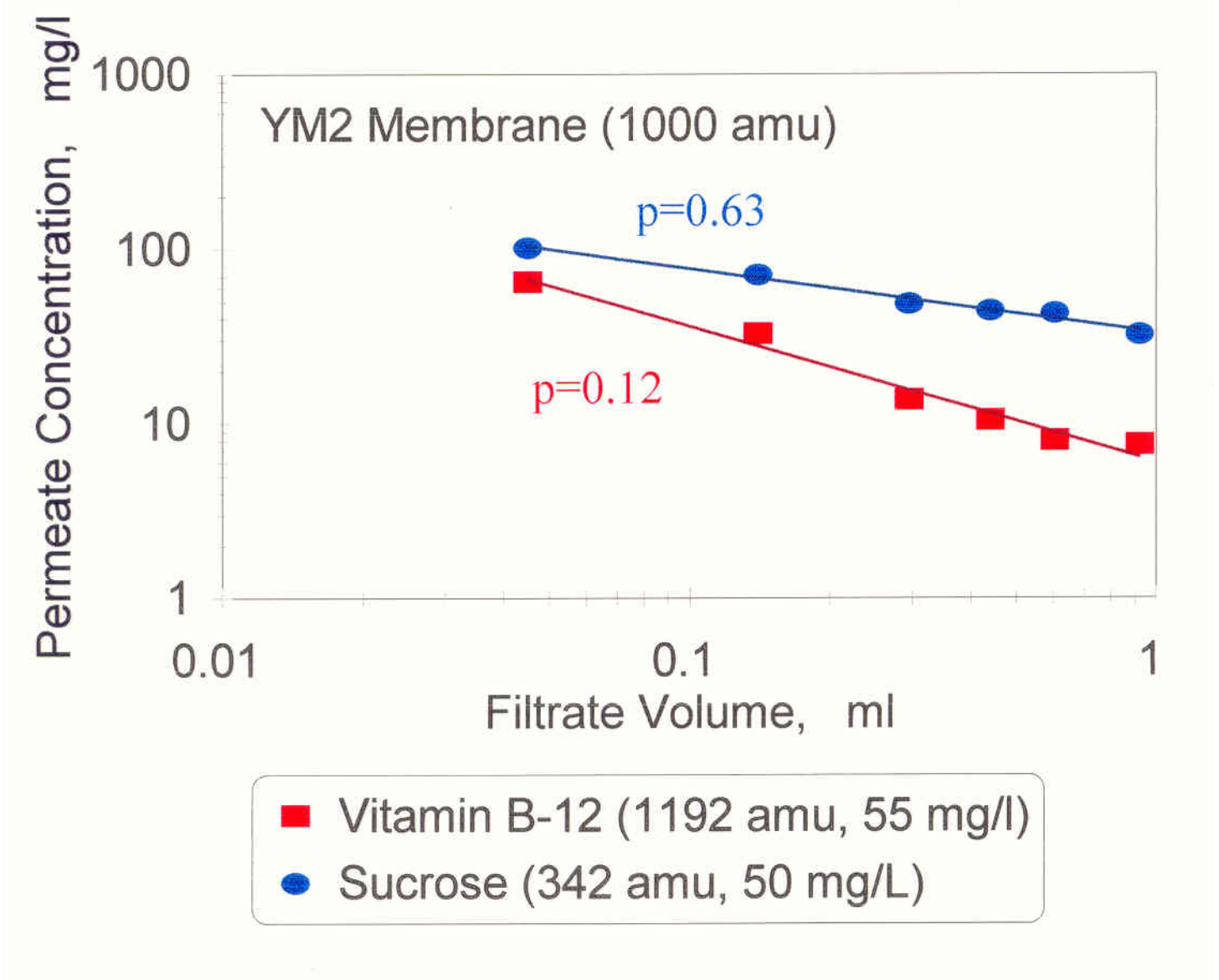
Effect of different filtration volumes on apparent C (<1k)



What about molecule sizes near the membrane cut off? B-12 should be 100% rejected…



p_c-values are very low for B-12



Error analysis of p_c values

Error of concentration of chemical A in a two component (A, B) system,

p_c (A) is fixed as shown

p_c (B) varies (0.1, 0.3, 0.5, 0.7, 0.9)

Errors are large when p_c=0.1

Only use pc correction if $p_c \geq 0.2$

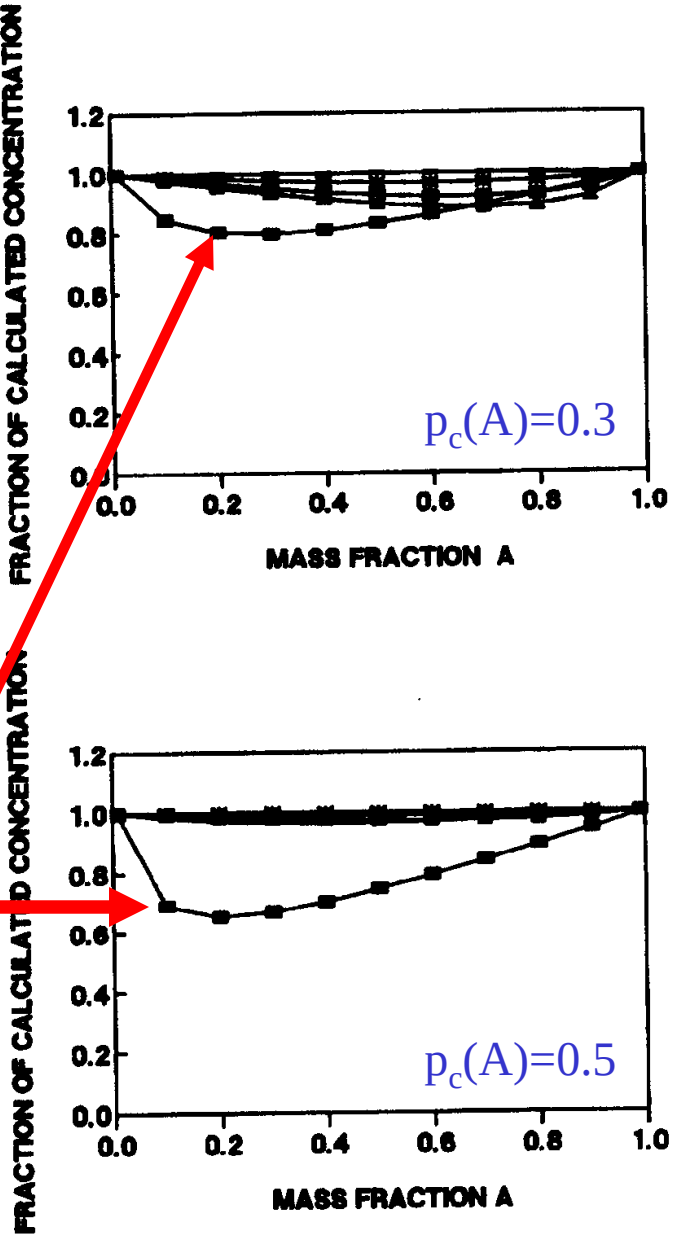
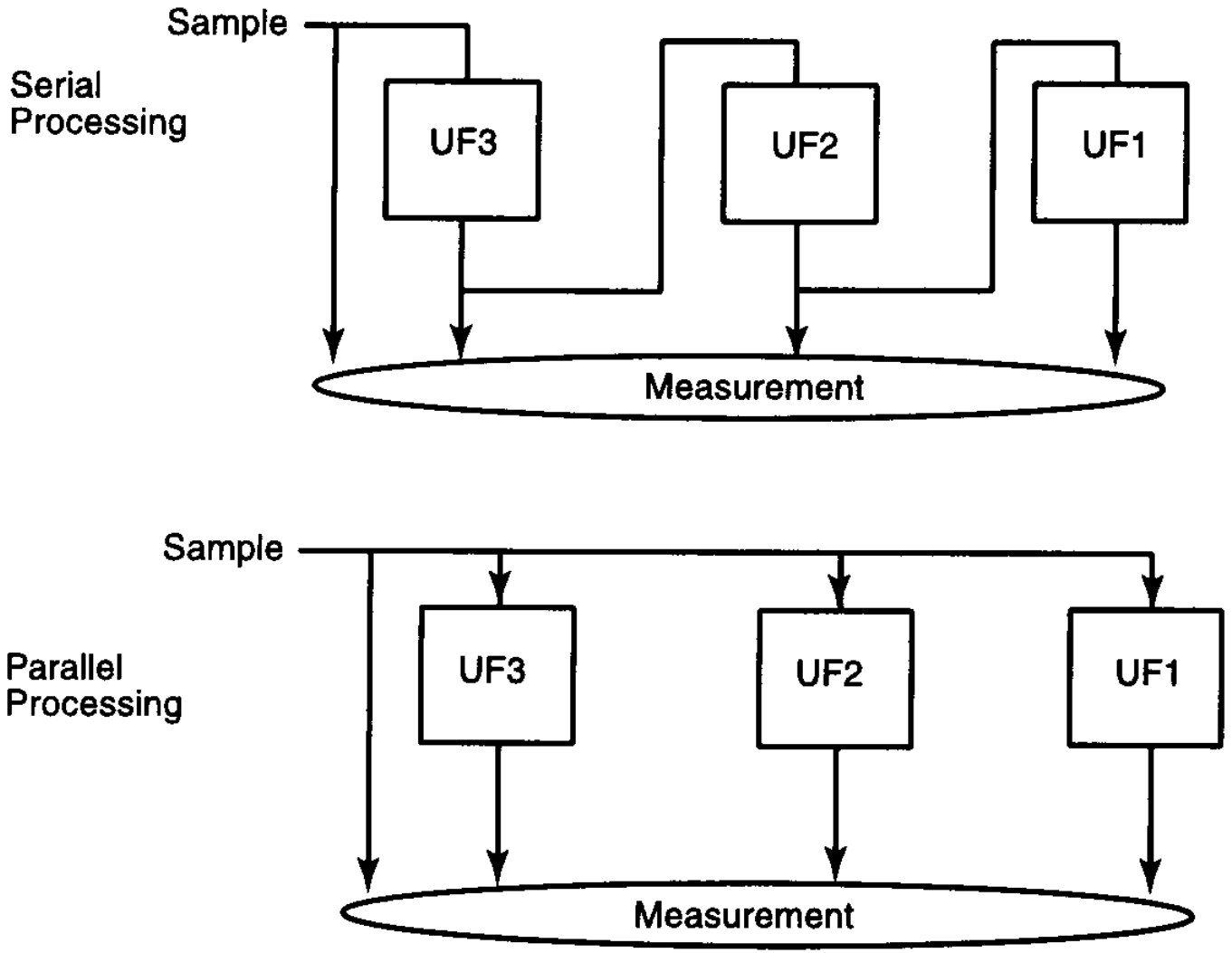


FIG. 10. Errors in Estimating Initial Concentration of Component *A* in Two-Component System Calculated as Function of Mass Fraction of *A* [$C_{A0}/C_{A0} + C_{B0}$] for: (*a*) $p_A = 0.3$; (*b*) $p_A = 0.5$ (Values of p_B: ■ = 0.1, ▲ = 0.3, □ = 0.5, * = 0.7, and − = 0.9)

Series versus Parallel Separations



Series versus Parallel Separations

- Examine separations through membranes UF1, UF2, and UF3, each one having a different molecular weight cut off (UF3 has the highest cut off, for example 100K).
- Assume there is 10 mg/L of DOC in each size fraction.
- Compare results for series versus parallel analysis of the sample.

Series versus Parallel Separations

RESULTS:

Note that “Actual” means what would be found if p_c model used; Series & Parallel means what is found if no p_c model is used

Size class	DOC (mg/L)		
	Actual	Series	Parallel
>UF3	10	15.7	15.7
<UF3 to >UF2	10	11.2	8.1
<UF2 to >UF1	10	7.8	8.1
<UF1	10	5.3	8.1

Notes on UF size separations

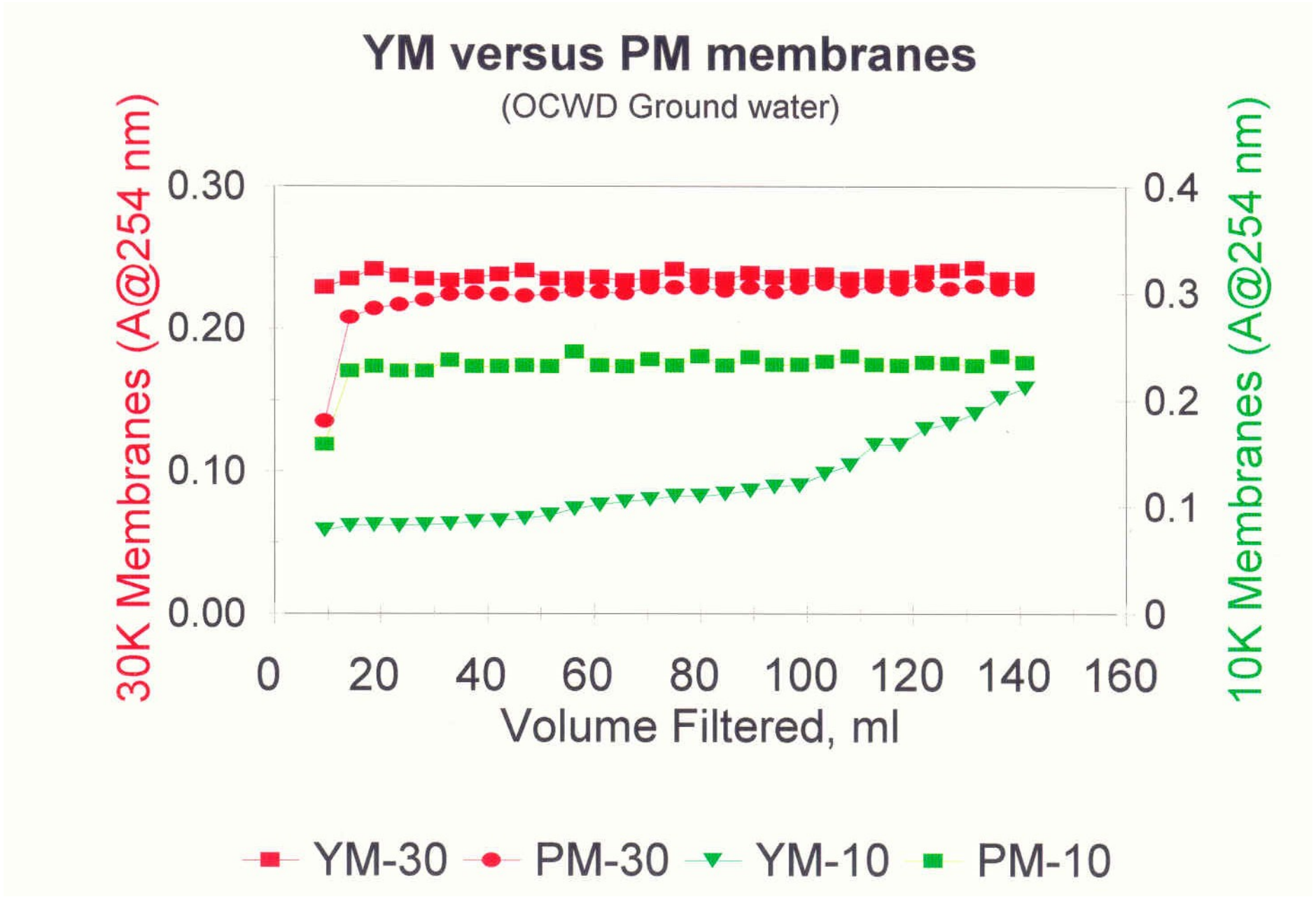
- Apply the permeation coefficient model unless:
  - p_c>0.9 (little rejection by membrane)
  - p_c<0.2 (sizes are too close to membrane cutoff)
- Prepare size fractions in parallel, not serial
- When size distributions are adjusted for membrane rejection, mass will be shifted to smaller size fractions

RESULTS of Actual Water Samples

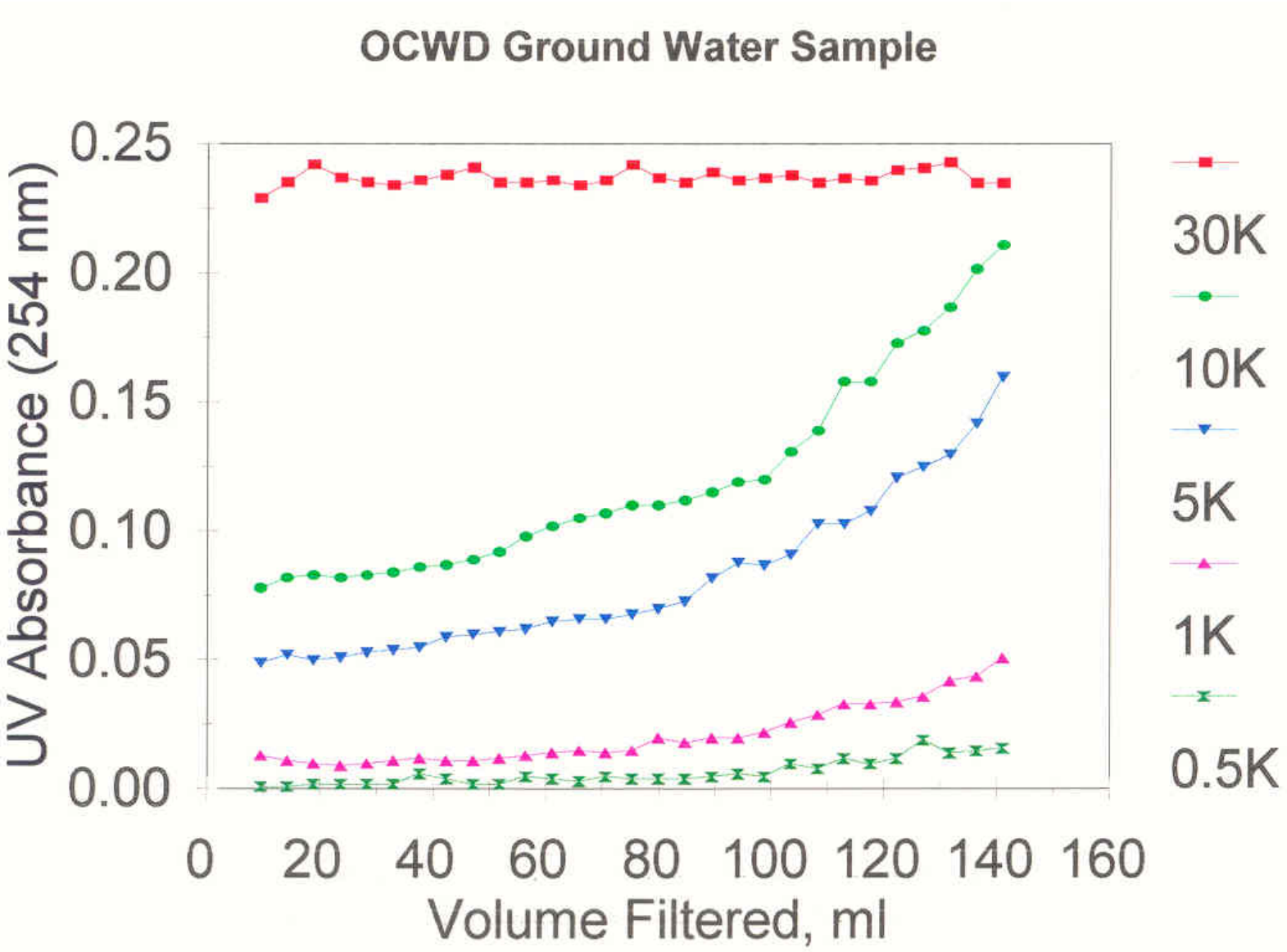
- Size distributions of NOM in groundwater using UV-absorbance (indicating concentration of humic and fulvic acids)
  - Orange county ground water (OCWD)
  - Biscayne aquifer ground water

- Dissolved Organic Carbon in Wastewater

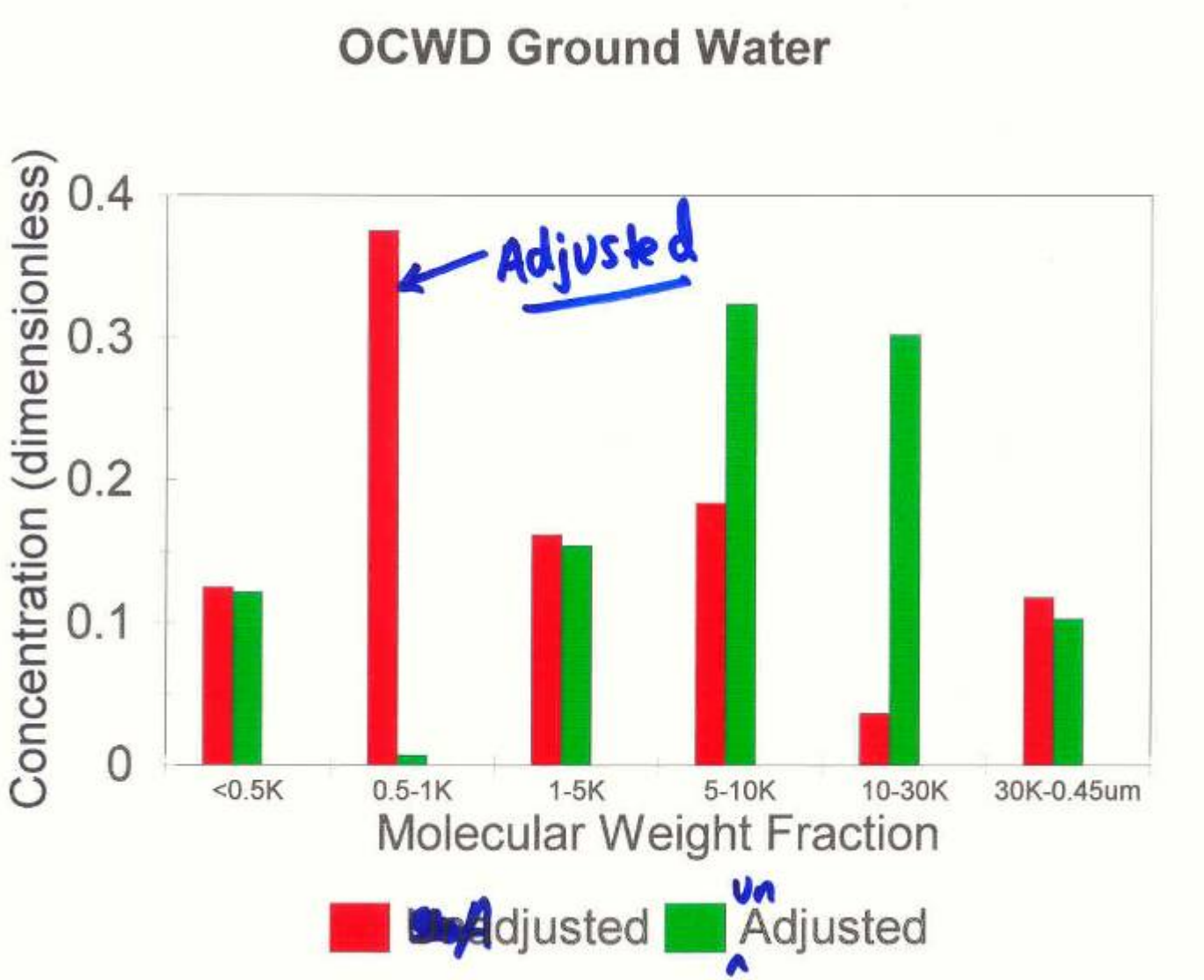
- Molecular weight distributions of pure compounds during bacterial degradation in pure and mixed cultures.


YM versus PM membranes
(OCWD Ground water)
30K Membranes (A@254 nm)
10K Membranes (A@254 nm)
0.30
0.20
0.10
0.00
0.4
0.3
0.2
0.1
0
0 20 40 60 80 100 120 140 160
Volume Filtered, ml
YM-30
PM-30
YM-10
PM-10

High rejection of samples for <10K sizes

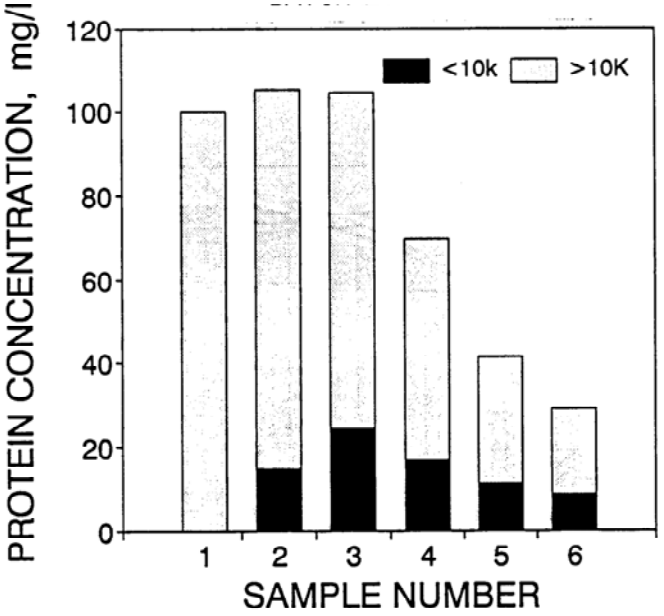


Adjusting the size distribution with the pc model shifts the distribution to smaller MW



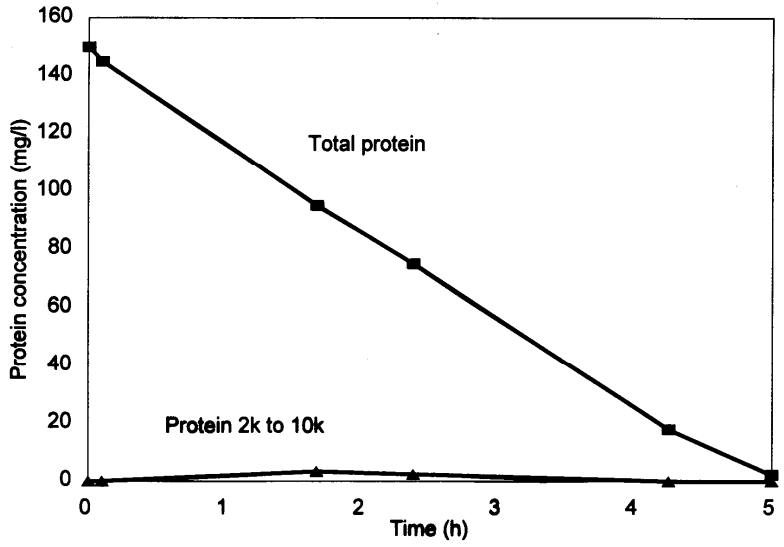
Size distributions during bacterial degradation of Protein macromolecules

Pure cultures



Small MW compounds do accumulate with proteins with pure cultures

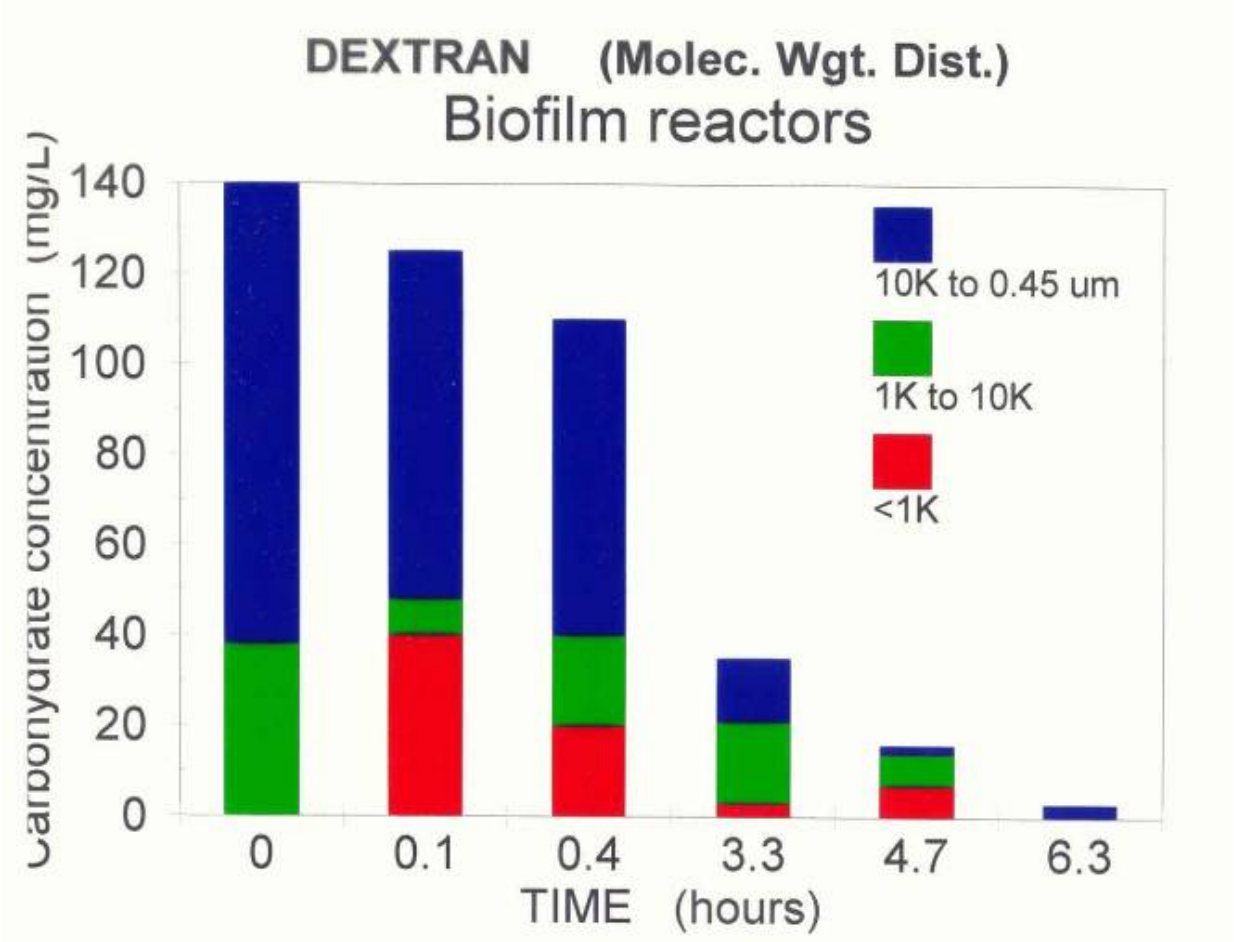
Mixed cultures



Small MW compounds do not accumulate with proteins with mixed cultures

Size distributions during bacterial degradation of dextran macromolecules: Mixed cultures

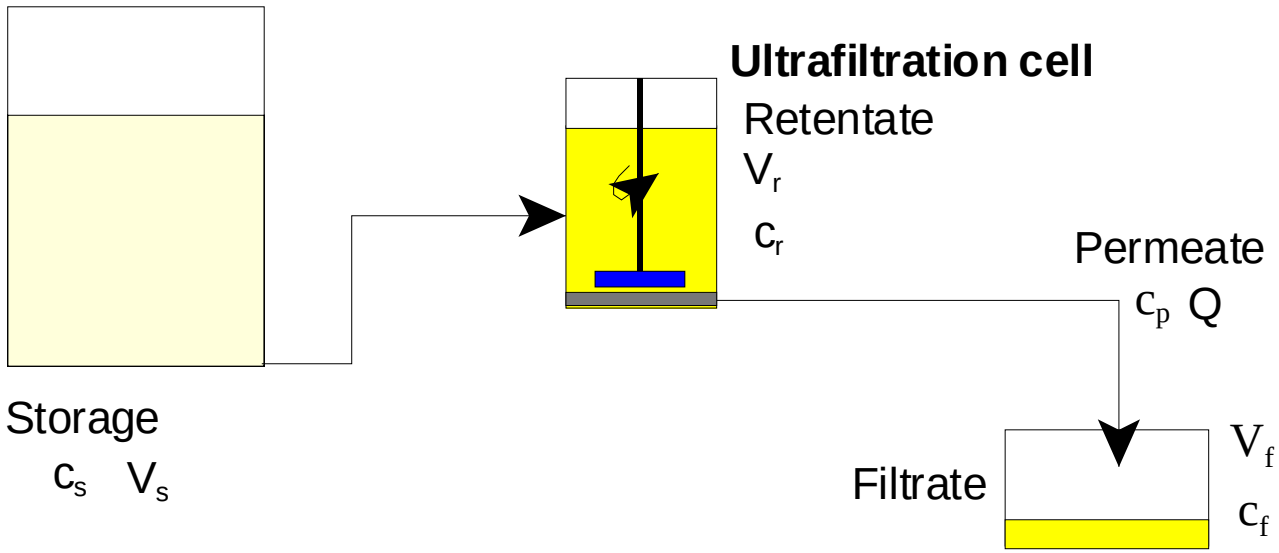
Small MW compounds do accumulate with dextrans (mixed or pure cultures)



Continuous flow method for molecular size distributions

- In some systems, organic matter concentrations are very low (e.g. seawater) and must be conentrated to be measured.
- A continuous flow method was developed for this situation.

UF Analysis when samples must be concentrated



A control volume around the storage and retentate cells produces the equation:

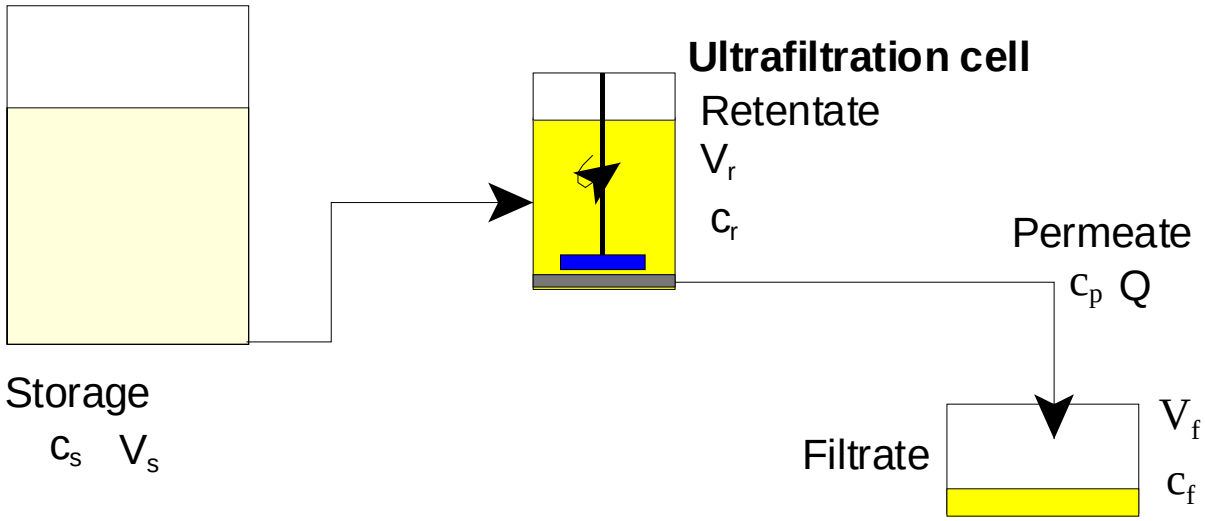
$$\frac{dm_T}{dt} = c_p Q$$

Problem: Derive an expression for c_p and c_f as a function of the permeate coefficient, $p_c=c_p/c_r$ and $F_s=(V_{s0}-V_s)/V_r$ and $V^*=V_{s0}/Vr$

Where:

- $m_T=m_s + m_r$
- M_s= mass in storage cell
- M_r= mass in retentate cell
- Q, $c_{r0}=c_{s0}$ and V_r are all constant

UF Analysis when samples must be concentrated



ANSWERS

$$c_p = c_{s0}\left[1+(p_c-1)\,e^{-p_c F_s}\right]$$

$$c_f = \frac{c_{s0}}{V*}\left[V*+1-\frac{1}{p_c}-\frac{1}{p_c(p_c-1)\,e^{-p_c F_s}}\right]$$

UF Results: Comparison of Storage Reservoir vs Batch Approaches

Storage Reservoir

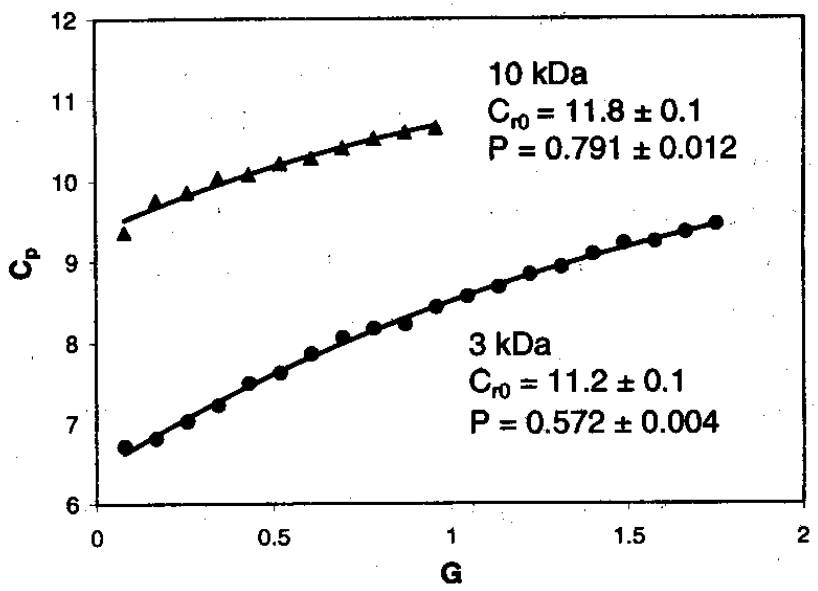


Fig. 2. Permeation concentration (C_p) as a function of G $[(V_0-V_r)/V_{cell}]$ for the model proposed in this paper (3 and 10 kDa membranes).

Batch Sample

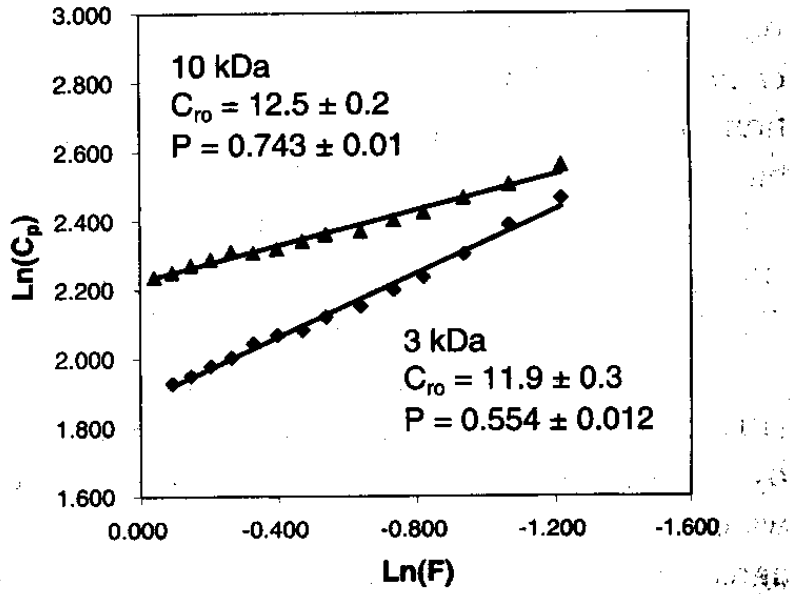


Fig. 3. Ln (permeation concentration, C_p) as a function of F $[1-(V_f/V_0)$ for the model reported by Logan and Jiang (3 and 10 kDa membranes).

Figures from: Cai, 1999, Water Res., 33, 13.