Molecular and Colloidal Sizes of DOM

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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

Atmosphere

Photic zone

Carbon cycled

Deep Ocean

Marine snow

Net carbon sink

Sediments
Cycling of Terrestrial Organic Matter (OM)

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

**Colloidal Pumping:** Enhanced concentration of metals and pollutants in colloids

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).

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.

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

## Micrometers (Log Scale)

<table>
<thead>
<tr>
<th>Ionic Range</th>
<th>Molecular Range</th>
<th>Macromolecular Range</th>
<th>Micro Particle Range</th>
<th>Macro Particle Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>1000</td>
<td>10000</td>
<td>100000</td>
</tr>
</tbody>
</table>

## Angstrom Units (Log Scale)

<table>
<thead>
<tr>
<th>Approx. Molecular Wt. (Saccharide Type-No Scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

## Relative Size of Common Materials

- Aqueous Salt
- Carbon Black
- Endotoxin/Pyrogen
- Virus
- Albumin Protein
- Tobacco Smoke
- Latex/Emulsion
- Colloidal Silica
- Paint Pigment
- Asbestos
- Gelatin
- Blue Indigo Dye
- Red Blood Cell
- Mist
- Granular Activated Carbon

## Process For Separation

- REVERSE OSMOSIS (Hyperfiltration)
- ULTRAFILTRATION
- NANOFILTRATION
- MICROFILTRATION
- PARTICLE FILTRATION

**Note:**
- 1 Micron (1 x 10^4 Meters) = 4 x 10^3 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

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

(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

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Molecular weight (Daltons)</th>
<th>Diffusivity ($\times 10^8$ cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>1,000,000</td>
<td>25</td>
</tr>
<tr>
<td>6.2</td>
<td>100,000</td>
<td>50</td>
</tr>
<tr>
<td>2.9</td>
<td>10,000</td>
<td>110</td>
</tr>
<tr>
<td>1.3</td>
<td>1,000</td>
<td>250</td>
</tr>
<tr>
<td>0.62</td>
<td>100</td>
<td>700</td>
</tr>
</tbody>
</table>
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)
- $k_B$ = Boltzmann’s constant = $1.38 \times 10^{-23}$ kgm$^2$/s$^2$K
- $\mu$ = dynamic viscosity = 1 cp = 0.01 g/s-cm
- $T$ = temperature [K]
- $r$ = molecule radius

At 20°C in water \[D_{cw} [\text{cm}^2/\text{s}] = 2.14 \times 10^{-9} r^{-1} [\mu\text{m}]^{11}\]
Diffusivities from Structure: **MOLECULES**

**Wilke-Chang Correlation**

Where: [these units must be used]

- \( D_{cw} \) = diffusion coefficient [cm\(^2\)/s]
- \( T \) = temperature [K]
- \( \Phi_l \) = association parameter [ ]
- \( M_l \) = molecular weight of liquid [g/mol]
- \( \mu \) = dynamic viscosity [cp]
- \( V_{C,b} \) = molal volume at normal boiling point [cm\(^3\)]

\[
D_{cw} = \frac{7.4 \times 10^{-8} \ T \ (\Phi_lM_l)^{1/2}}{\mu \ V_{C,b}^{0.6}}
\]

Only if:

\[
V_{C,b} < 0.27 (\Phi_lM_l)^{1.87}
\]

For chemicals in water:

For chemicals in water: \( D_{cw} \) [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$_6$H$_{12}$O$_6$)

\[ V_{G,b} = (6 \times 14.8) + (12 \times 3.7) + (5 \times 7.4) + (1 \times 11) - 15 \]

\[ V_{G,b} = 166.2 \text{ [cm}^3/\text{g]} \]

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

\[ D_{Cw}[cm^2/s] = 1.48 \times 10^{-4}(166.2)^{0.6} \]

\[ D_{Cw}[cm^2/s] = 6.90 \times 10^{-8} \]

Reported \[ D_{Cw}[cm^2/s] = 7.80 \times 10^{-8} \text{ (13\% error)} \]
Diffusivities from Size: **MACROMOLECULES**

**PROTEINS**

Polson Correlation

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

Only if: M>1 kD

**POLYSACCHARIDES**

(Dextran)

Frigon Correlation

\[
D_{CW} \left[ cm^2/s \right] = 7.04 \times 10^{-5} \ M_D^{-0.47}
\]

Only if: M>1 kD

**HUMIC & FULVIC ACIDS**

Beckett Correlation

\[
D_{CW} \left[ cm^2/s \right] = 1.42 \times 10^{-4} \ M_H^{-0.422}
\]

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,

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

Rearranging, so that for one chemical all constants are on one side of the equation

\[ \frac{D_{cw} \mu}{T} = \frac{7.4 \times 10^{-8} \ (\Phi_l M_l)^{1/2}}{V_{C,b}^{0.6}} = \text{constant} \]

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,

\[ D_{cw,T} = D_{cw} \frac{\mu}{\mu_T} \frac{T_T}{T} \]
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 $\omega$, $F = m_c \omega^2 r$, where $r =$ distance from center
- From the velocity of particle during centrifugation (incorporated into 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:

$$D_O [cm^2/s] = 1.69 \times 10^{-5} r_O^{-1}$$
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
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

- Cell is pressurized to drive out permeate
- Stirrer used to mix retentate and minimize fouling
- Retentate
- UF membrane
- Permeate
Effect of membrane rejection on permeate concentration

Membrane rejection results in $c_p < c_R$
Mass Balance Equations Produce Fundamental Relationships

Permeate concentration 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

<table>
<thead>
<tr>
<th>$c_p$</th>
<th>$V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9</td>
<td>5</td>
</tr>
<tr>
<td>6.1</td>
<td>10</td>
</tr>
<tr>
<td>6.4</td>
<td>20</td>
</tr>
<tr>
<td>7.5</td>
<td>50</td>
</tr>
<tr>
<td>9.0</td>
<td>70</td>
</tr>
<tr>
<td>12.9</td>
<td>90</td>
</tr>
</tbody>
</table>

Answer part (a)

$C < 1K = 5.9 \text{ ppb}$ based on first 5 mL
### Permeation Coefficient Model Calculations

\[
F = 1 - \left( \frac{V_f}{V_{r,0}} \right)
\]

\[
V_{r,0} = 100 \text{ mL}
\]

<table>
<thead>
<tr>
<th>(c_p)</th>
<th>(V_f)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9</td>
<td>5</td>
<td>0.95</td>
</tr>
<tr>
<td>6.1</td>
<td>10</td>
<td>0.90</td>
</tr>
<tr>
<td>6.4</td>
<td>20</td>
<td>0.8</td>
</tr>
<tr>
<td>7.5</td>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>9.0</td>
<td>70</td>
<td>0.3</td>
</tr>
<tr>
<td>12.9</td>
<td>90</td>
<td>0.1</td>
</tr>
</tbody>
</table>
### Permeation Coefficient Model Calculations

<table>
<thead>
<tr>
<th>$c_p$</th>
<th>$V_f$</th>
<th>$F$</th>
</tr>
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<tbody>
<tr>
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<td>0.95</td>
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<td>0.8</td>
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<td>0.5</td>
</tr>
<tr>
<td>9.0</td>
<td>70</td>
<td>0.3</td>
</tr>
<tr>
<td>12.9</td>
<td>90</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Next step:
Take natural log of $F$ and $c_p$
Permeation Coefficient Model Calculations

<table>
<thead>
<tr>
<th>$c_p$</th>
<th>$V_f$</th>
<th>$F$</th>
<th>$\ln c_p$</th>
<th>$\ln F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9</td>
<td>5</td>
<td>0.95</td>
<td>1.77</td>
<td>-0.57</td>
</tr>
<tr>
<td>6.1</td>
<td>10</td>
<td>0.90</td>
<td>1.81</td>
<td>-1.05</td>
</tr>
<tr>
<td>6.4</td>
<td>20</td>
<td>0.8</td>
<td>1.86</td>
<td>-0.22</td>
</tr>
<tr>
<td>7.5</td>
<td>50</td>
<td>0.5</td>
<td>2.01</td>
<td>-0.69</td>
</tr>
<tr>
<td>9.0</td>
<td>70</td>
<td>0.3</td>
<td>2.19</td>
<td>-1.20</td>
</tr>
<tr>
<td>12.9</td>
<td>90</td>
<td>0.1</td>
<td>2.56</td>
<td>-2.30</td>
</tr>
</tbody>
</table>
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

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

<table>
<thead>
<tr>
<th>$\ln c_p$</th>
<th>$\ln F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.77</td>
<td>-0.57</td>
</tr>
<tr>
<td>1.81</td>
<td>-1.05</td>
</tr>
<tr>
<td>1.86</td>
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<td>2.19</td>
<td>-1.20</td>
</tr>
<tr>
<td>2.56</td>
<td>-2.30</td>
</tr>
</tbody>
</table>
Permeation Coefficient Model Calculations

\[ \ln c_P = \ln \left( p_c c_{r,0} \right) - (1 - p_c) \ln F \]

(Note sign change on \( \ln F \) term)

Slope = 0.34

\[ p_c = (1 - 0.34) = 0.66 \]

\( p_c \) = 0.66

y-intercept = 1.77

\[ C_{r,0} = e^{1.77} / 0.66 = 9.0 \]

\( C_{r,0} \) = 9.0

\[ c_P = 5.94 F^{0.34} \]

Answer part (b)

Actual C<1K = 9.0 ppb
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:

$$F = 1 - \left( \frac{V_f}{V_{r,0}} \right) = 1 - \left( \frac{90}{100} \right) = 0.1$$

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

$$c_f = 7.8$$

Answer part (c)

$C_{<1K} = 7.8$ ppb based on 90 mL
## Permeation Coefficient Model: Comparison

<table>
<thead>
<tr>
<th>Method</th>
<th>C &lt;1K (ppb)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collect 5 mL</td>
<td>5.9</td>
<td>44%</td>
</tr>
<tr>
<td>Permeation Coefficient Model</td>
<td>9.0</td>
<td>---</td>
</tr>
<tr>
<td>Collect 90 of 100 mL</td>
<td>7.8</td>
<td>13%</td>
</tr>
</tbody>
</table>
Effect of different filtration volumes on apparent C (<1k)

Time (or $V_f$)

$C_p$

$C(<1K)$

$C(<1K)$

$C(<1K)$
What about molecule sizes near the membrane cut off? **B-12** should be 100% rejected…

![Graph showing permeate concentration vs filtrate volume for YM2 Membrane (1000 amu). The graph compares Vitamin B-12 (1192 amu, 55 mg/l) and Sucrose (342 amu, 50 mg/l).]
$p_c$-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 $p_c$ correction if $p_c>0.2$

FIG. 10. Errors in estimating initial concentration of component A in two-component system calculated as function of mass fraction of A $[C_A/C_{MB} + C_A]$ 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

Sample

Serial Processing

UF3  \rightarrow  UF2  \rightarrow  UF1

Measurement

Sample

Parallel Processing

UF3  \rightarrow  UF2  \rightarrow  UF1

Measurement
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.

<table>
<thead>
<tr>
<th>Size class</th>
<th>DOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual</td>
</tr>
<tr>
<td>&gt;UF3</td>
<td>10</td>
</tr>
<tr>
<td>&lt;UF3 to &gt;UF2</td>
<td>10</td>
</tr>
<tr>
<td>&lt;UF2 to &gt;UF1</td>
<td>10</td>
</tr>
<tr>
<td>&lt;UF1</td>
<td>10</td>
</tr>
</tbody>
</table>
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)

Volume Filtered, ml

0 20 40 60 80 100 120 140 160

YM-30 PM-30 YM-10 PM-10

10K Membranes (A@254 nm)
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**

**Mixed cultures**

Small MW compounds **do** accumulate with proteins with pure 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 concentrated to be measured.

• A continuous flow method was developed for this situation.
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 $F_s = (V_{s_0} - V_s) / V_r$ and $V^* = V_{s_0} / V_r$

Where:
- $m_T = m_s + m_r$
- $M_s =$ mass in storage cell
- $M_r =$ mass in retentate cell
- $Q$, $c_{r_0} = c_{s_0}$ and $V_r$ are all constant
UF Analysis when samples must be concentrated

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

\[ c_f = \frac{c_{s0}}{V^*} \left[ V^* + 1 - \frac{1}{p_c} - \frac{1}{p_c (p_c - 1) e^{-p_c F_s}} \right] \]
UF Results: Comparison of Storage Reservoir vs Batch Approaches

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

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