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CEE 697z

Organic Compounds in Water and Wastewater

NOM Characterization

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Lecture #6

Outline

- Introduction of NOM
- Water treatment processes for NOM removal
- Introduction of NOM characterization
  - Bulk NOM characterization
  - Factors affecting NOM properties
- NOM characterization methods
  - Size
  - Structure
  - Hydrophobicity

Definition and Origin

- What is NOM?
  - NOM is a heterogeneous mixture of naturally occurring organic compounds.
- Where does it come from?
  - Originates from living and dead plants, animals and microorganisms, and from the degradation products of these sources.
  - Organic compounds enter the water as a result of human activities.
- What's the form?
  - Some occurs as particulate matter or is absorbed to particulate
  - **The majority exists as dissolved compounds (DOM)**

Negative effect on water quality

-- Including color, taste and odor problems

- Increased coagulant and disinfectant dose
    - Increased sludge and DBP formation
- Promoted biological growth in drinking water distribution system
- Increased contents of complexed heavy metals and absorbed organic pollutants
- Caused Fouling problems of membrane

Water treatment processes

- Enhanced coagulation (low pH coagulation)
  - High SUVA water – choose enhanced coagulation process
  - Removal efficiencies 25-70% (TOC)
  - The mechanisms of NOM removal during coagulation
  - Better removal of hydrophobic fraction and high molecular weight NOM

- Adsorption
  - Trace organic compounds or NOM (causes odor and tastes, synthetic organic chemicals)
  - Mechanisms: adsorption and biodegradation (depends on Size and chemical properties of NOM)
  - Lower size of NOM has better removal.

- Ion exchange

  - Electronegativity of NOM

- MF/UF

- Ozonation

The mechanisms of NOM removal during coagulation and flocculation

Contaminants (Particles, NOM) + Coagulants

Destablilizaion

Charge neutralization

Precipitation

(+): coagulant

(-): NOM>Particles

Coagulants

Coagulants with NOM form metal-hydroxide

Introduction of NOM Characterization

- Purpose:
    - -- predicting and perhaps controlling NOM reactivity
- Difficulty:
    - NOM includes hundreds or thousands of distinct chemical species. It is not realistic to evaluate the properties individually.
- Solution:
    - Bulk NOM properties
    - Separate NOM into a limited set of categories
    - Characterize the group of NOM by their similar composition and properties

Bulk NOM characterization

- Bulk NOM concentration: TOC/DOC
    - --- The amount of carbon in the molecules
- Chemical properties:
    - Functional group content
    - Density of electric charge
    - Surface activity toward standard surfaces
    - Hydration energy
    - Affinity for protons or metal ions

NOM properties affected by

- NOM concentration, composition and chemistry are variable and depend on the physicochemical properties of the water:
  - Temperature, ionic strength and pH
  - **Neutralization:** The main cation components present
  - **Adsorption:** The surface chemistry of sediment sorbents (act as the solubility control)
  - **Biodegradation:** The presence of photolytic and microbiological degradation processes

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Size characterization of NOM – introduction

- Most dissolved humic substances have a molecular weight of a few hundred to a few thousand atomic mass units.
- Low-resolution separations:
  - Ultrafiltration using membranes have a specific nominal molecular weight cutoff
  - MW cut-offs of 10KDa, 3kDa and 0.5kDa
- High-resolution separations:
  - size exclusion chromatography (SEC)

Example of size characterization and the result

- **Hua, G., Reckhow, D.A., (2007)** Environ. Sci. Technol.**, 41, 3309-3315**

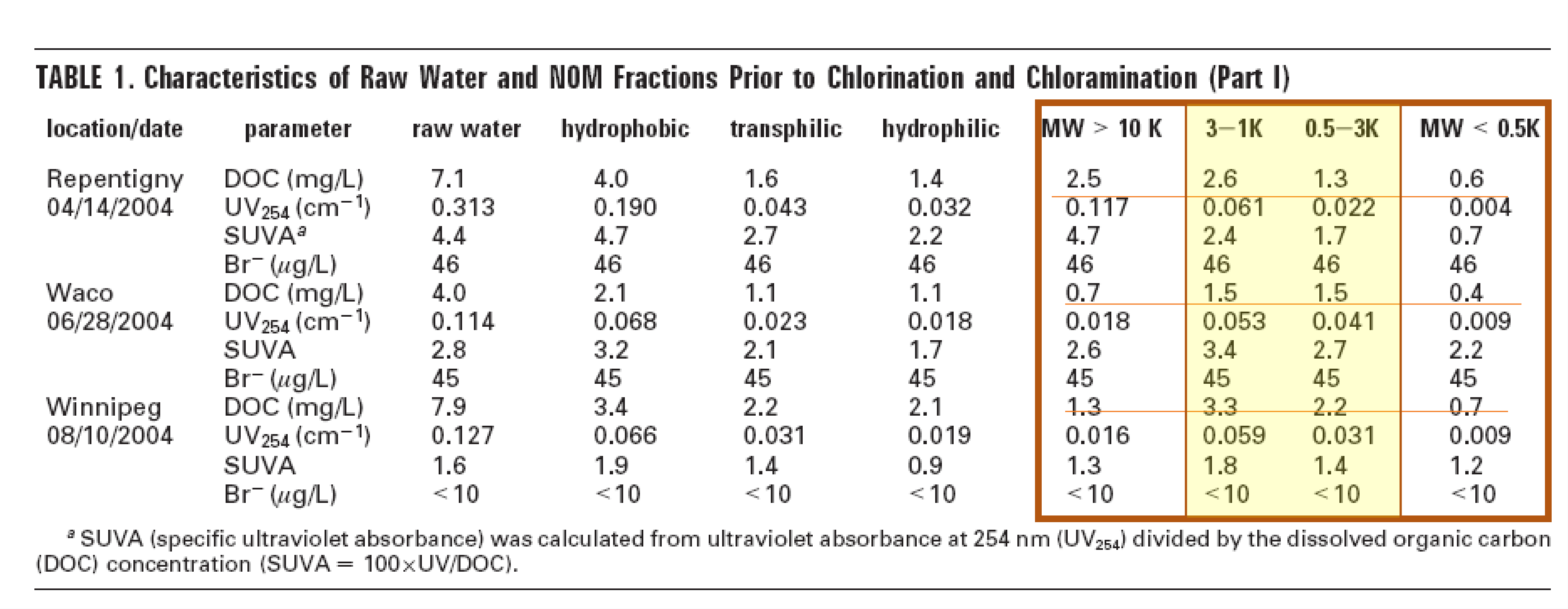


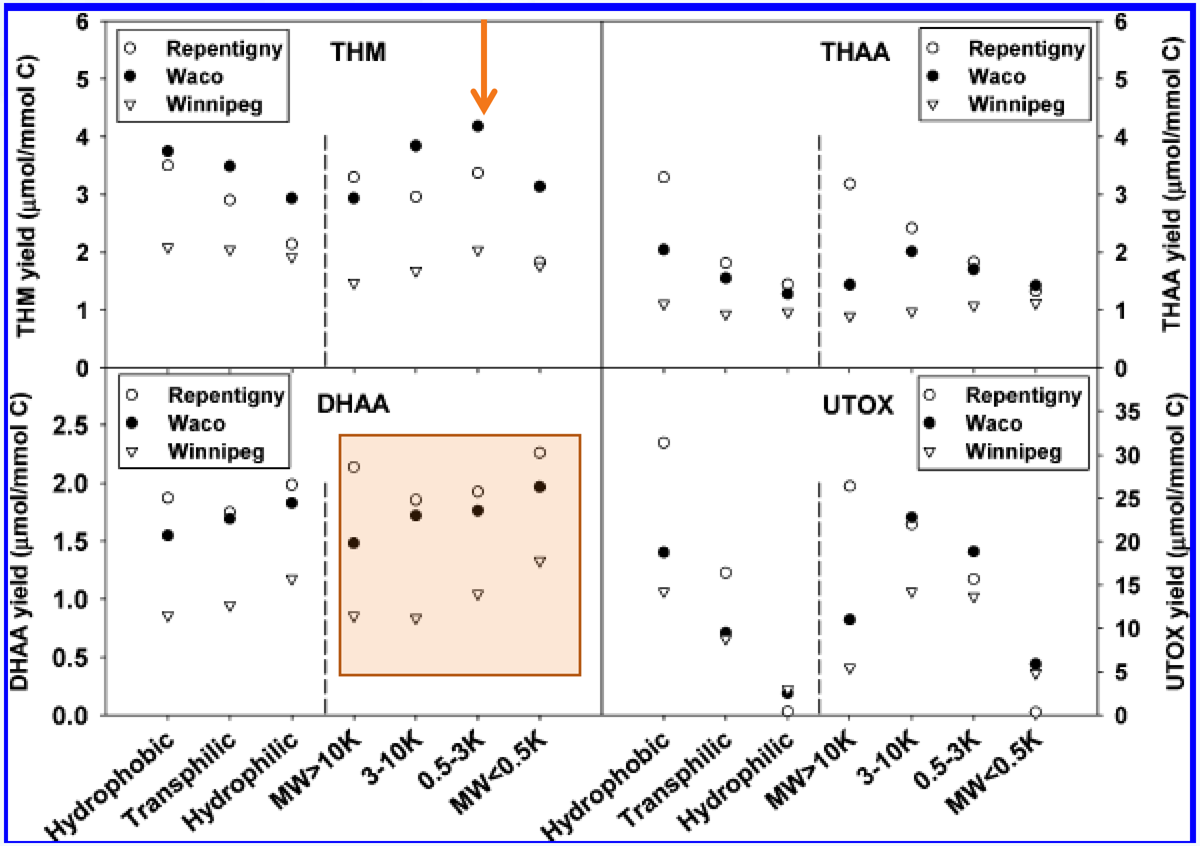
TABLE 1. Characteristics of Raw Water and NOM Fractions Prior to Chlorination and Chloramination (Part I)

location/date	parameter	raw water	hydrophobic	transphilic	hydrophilic	MW > 10 K	3−1K	0.5−3K	MW < 0.5K
Repentigny 04/14/2004	DOC (mg/L)	7.1	4.0	1.6	1.4	2.5	2.6	1.3	0.6
	UV_{254} (cm^{-1})	0.313	0.190	0.043	0.032	0.117	0.061	0.022	0.004
	SUVA[a]	4.4	4.7	2.7	2.2	4.7	2.4	1.7	0.7
	Br^- (μg/L)	46	46	46	46	46	46	46	46
Waco 06/28/2004	DOC (mg/L)	4.0	2.1	1.1	1.1	0.7	1.5	1.5	0.4
	UV_{254} (cm^{-1})	0.114	0.068	0.023	0.018	0.018	0.053	0.041	0.009
	SUVA	2.8	3.2	2.1	1.7	2.6	3.4	2.7	2.2
	Br^- (μg/L)	45	45	45	45	45	45	45	45
Winnipeg 08/10/2004	DOC (mg/L)	7.9	3.4	2.2	2.1	1.3	3.3	2.2	0.7
	UV_{254} (cm^{-1})	0.127	0.066	0.031	0.019	0.016	0.059	0.031	0.009
	SUVA	1.6	1.9	1.4	0.9	1.3	1.8	1.4	1.2
	Br^- (μg/L)	<10	<10	<10	<10	<10	<10	<10	<10

[a] SUVA (specific ultraviolet absorbance) was calculated from ultraviolet absorbance at 254 nm (UV_{254}) divided by the dissolved organic carbon (DOC) concentration (SUVA = 100×UV/DOC).

1. DOC and UV254 indicated the NOM properties of each reservoirs.
2. Majority of DOC and most of UV254 distributed in 3K -500 Da of molecules.

The relationship between size characterization and DBP formation potential



1. Different size of NOM has different DBPFP.
2. The 500-3k NOM produced the most THM.
3. The smaller the size of NOM produced greater amount of DHAA.

Some other aspects need to consider before using UF membrane

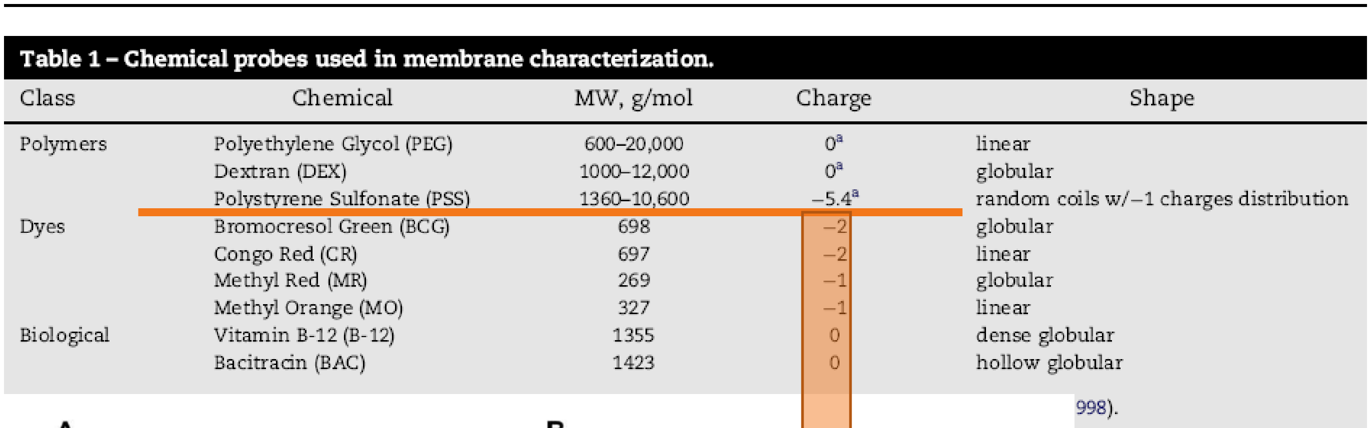
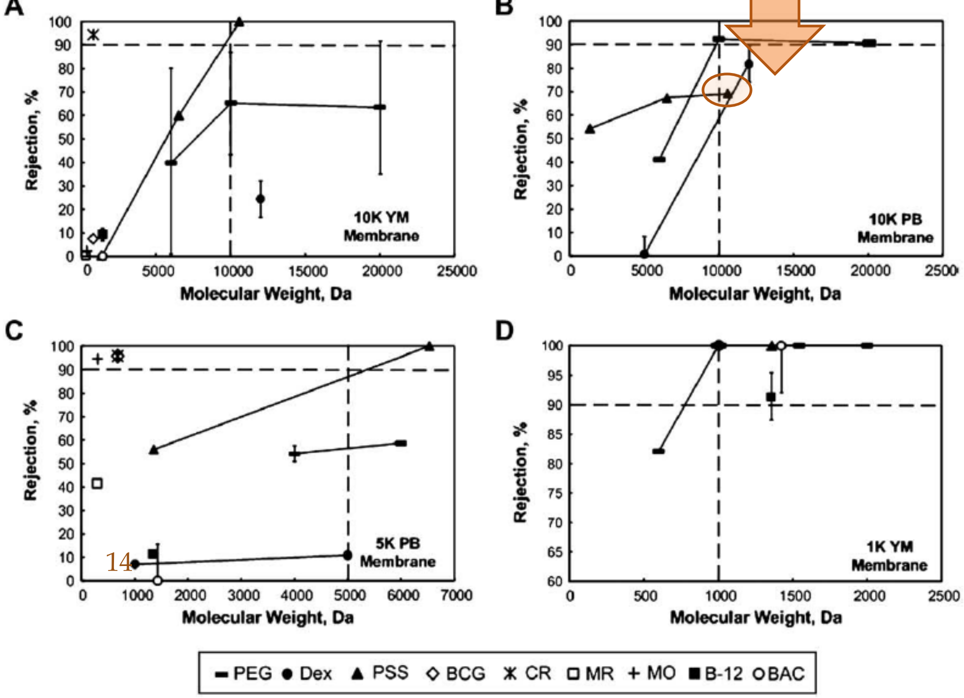


Table 1 – Chemical probes used in membrane characterization.

Class	Chemical	MW, g/mol	Charge	Shape
Polymers	Polyethylene Glycol (PEG)	600–20,000	0[a]	linear
	Dextran (DEX)	1000–12,000	0[a]	globular
	Polystyrene Sulfonate (PSS)	1360–10,600	−5.4[a]	random coils w/−1 charges distribution
Dyes	Bromocresol Green (BCG)	698	−2	globular
	Congo Red (CR)	697	−2	linear
	Methyl Red (MR)	269	−1	globular
	Methyl Orange (MO)	327	−1	linear
Biological	Vitamin B-12 (B-12)	1355	0	dense globular
	Bacitracin (BAC)	1423	0	hollow globular

998).



Revchuk, A., Suffet, I.E., water research 43 (2009) 3685 – 3692

- The study demonstrates that ultrafiltration is not a simple mechanical sieving process,
- but that charges on the membrane and the constituent play a significant role in the rejection process.

NOM characterization by Structure – introduction

- In general, this is a kind of NOM characterization approach without fractionation.
  - ^{13}C-NMR,
  - Fourier Transform Infrared (FTIR) spectroscopy and
  - pyrolysis-gas chromatography-mass spectrometry (Pyr-GC-MS).
  - UV absorbance
  - Fluorescence spectroscopy
- We should consider:
  - Concentrated NOM
  - Change of NOM structure during these processes

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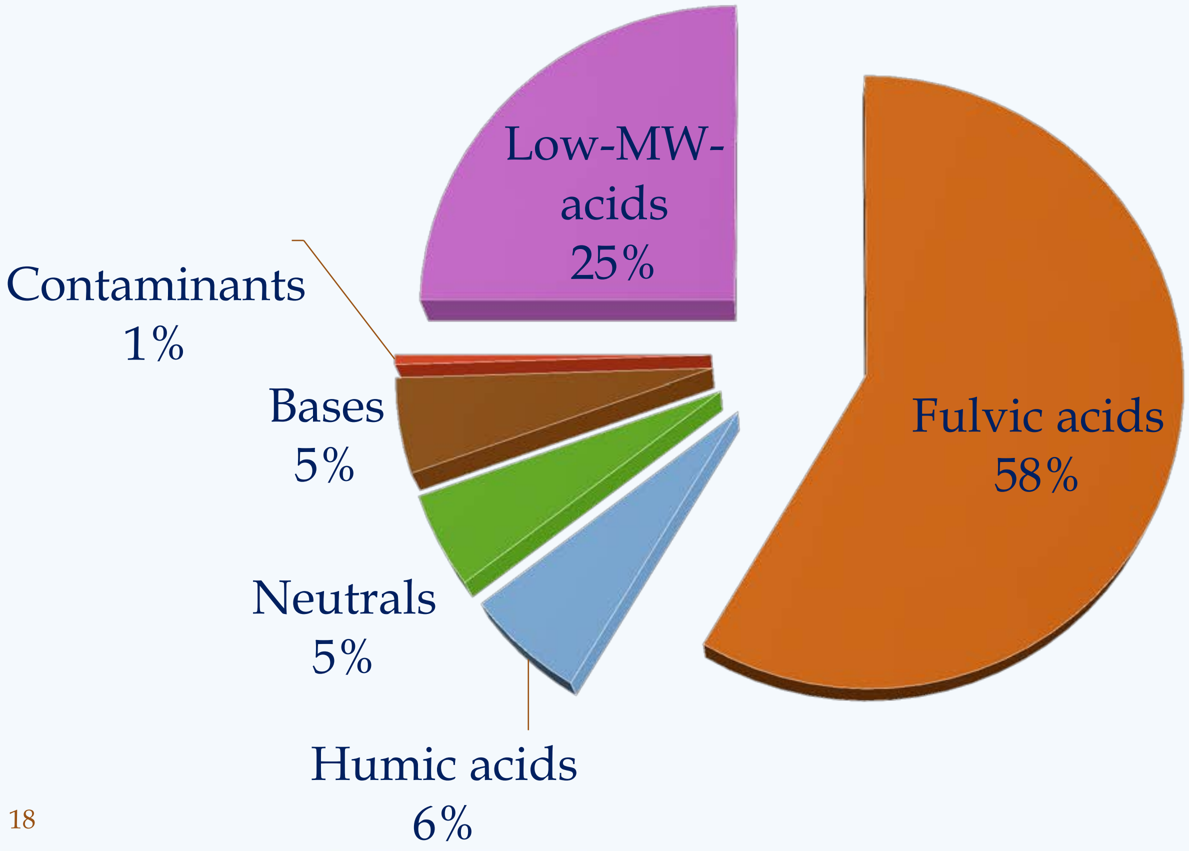
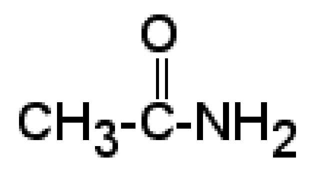
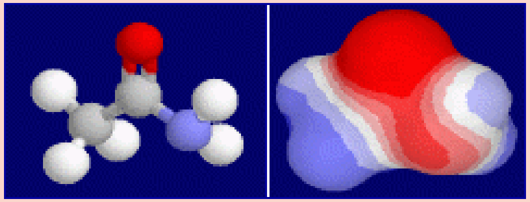
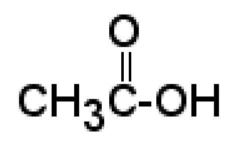
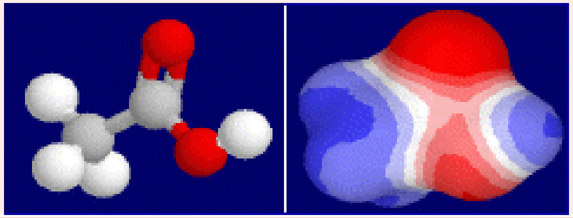
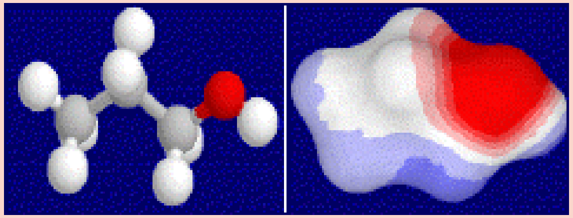
From previous research – literature review

- Hydrophobic fractions: contributing from nearly 50-90% of the DOC in most natural waters.
- Hydrophobic NOM: humic acids and fulvic acids
- ~90% of Humic species are fulvic acids
- Dominant structures of stream humic species are aliphatic and but aromatic.
- Only 12-16% of the carbon in fulvic acid is aromatic carbon.

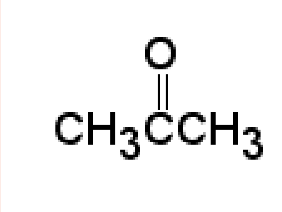
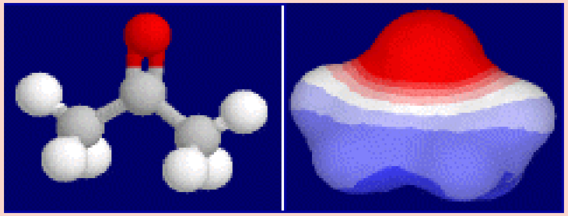
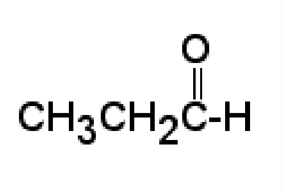
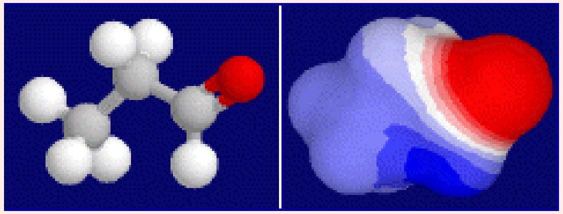
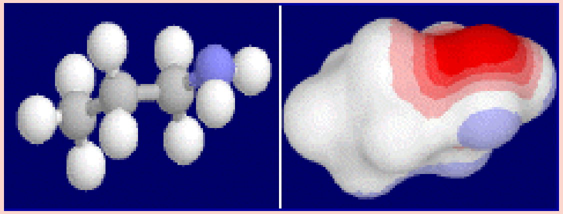
Distribution of surface water DOC

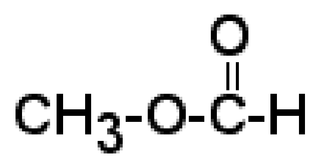
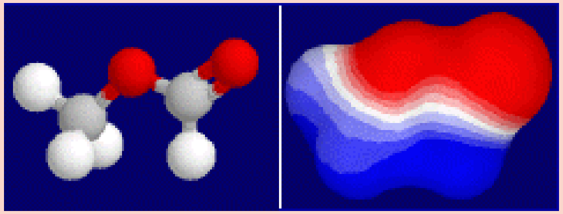
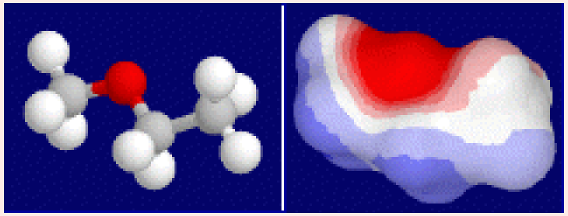
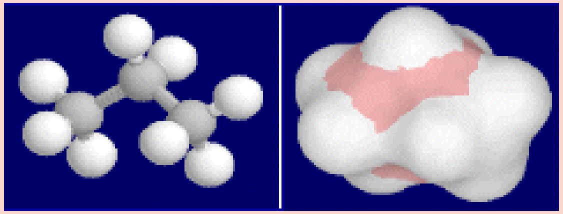


Chemical structure polarity – background information

Functional Group Name	Polarity Rank	Structure Name	
Amide	1	 $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$	
Acid	2	 $CH_3\overset{O}{\overset{\|}{C}}-OH$	
Alcohol	3	$CH_3CH_2CH_2OH$	

The more areas of red and blue that you see, the more polar is the compound and the functional group in the compound. Look at the amide, and acid.

Functional Group Name	Polarity Rank	Structure Name	
Ketone	4, 5	 $CH_3\overset{\overset{O}{\|}}{C}CH_3$	
Aldehyde	4, 5	 $CH_3CH_2\overset{\overset{O}{\|}}{C}\text{-}H$	
Amine	6	$CH_3CH_2CH_2NH_2$	

Functional Group Name	**Polarity Rank**	**Structure Name**	
Ester	7	 $CH_3\text{-O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-H}$	
Ether	8	$CH_{3\text{-O-CH2CH3}}$	
Alkane	9	$CH_3CH_2CH_3$	

The more areas of gray and lighter shades of red and blue, the more non-polar properties are being depicted. Look at the amine, ether, and alkane.

Alkyl

Alkylene

Ether

Ester

Amine

Aldehyde/ Ketone

Alcohol/ Phenol

Acid

Amide

Polar

One of the method – reverse-phase high-pressure liquid chromatography (RP-HPLC)

- 1). Choose appropriate **non-polar column** and **polar elution**
- 2). Calibrate the method with organic compounds of known **octanol-water partition coefficient**
- 3). octanol-water partition coefficient ≈ NOM retention times.

reverse-phase high-pressure liquid chromatography (RP-HPLC) cont.

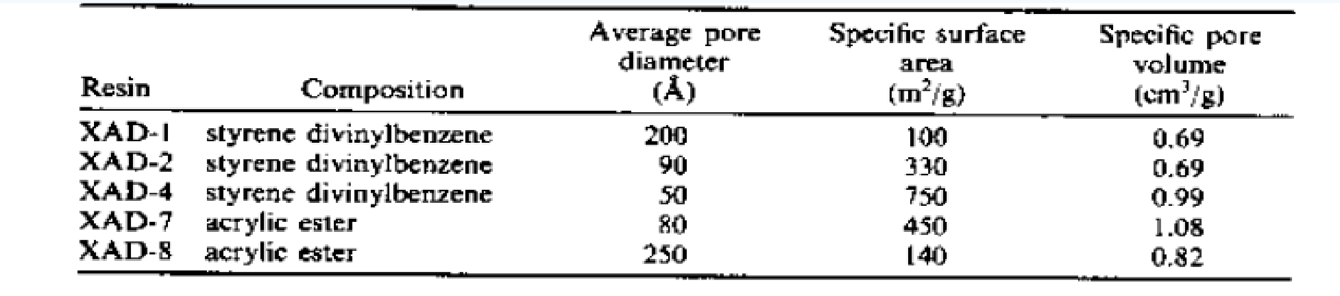
- Reverse phase HPLC Advantages:
  - **“full” spectrum of NOM polarity** based on various standards.
  - Lower time and labor-intensive
  - Feasibility of **in situ** monitoring
  - **Stable and reliable**: A very good logarithmic correlation between RP-HPLC capacity factor and NOM molecule solubility (expressed as octanol-water partition coefficient).
- Disadvantages:
  - Not be able to directly measure the reactivity
  - appropriate detector? (e.g. UV absorbance at wavelength 254nm)
  - Irreversible adsorption of NOM onto the hydrophobic stationary phase in the column

Introduction to XAD resins

- Amberlite XAD resins
  - These resins are nonionic, macroporous polymers which possess large surface areas.
- Use of XAD resins for isolation, concentration, and chromatographic separation of many chemically distinct classes of compounds.
- Pros:
  - Compared with activated carbon:
    - easier to elute and
    - are free from the risk of chemical alteration of the humics.
  - Compared with alumina, silica gel, nylon, and polyamide powder,
    - XAD resins have greater adsorption capacities and
    - are easier to elute.

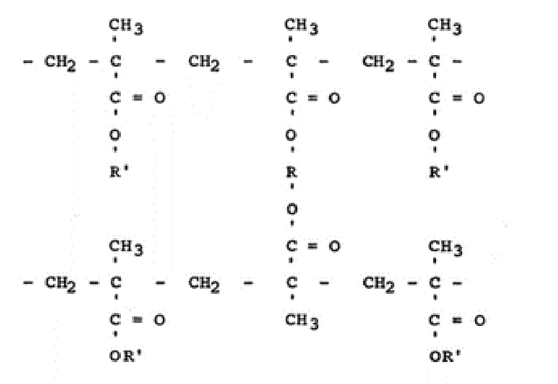
Introduction to XAD resins (cont.)

- Properties of XAD resins

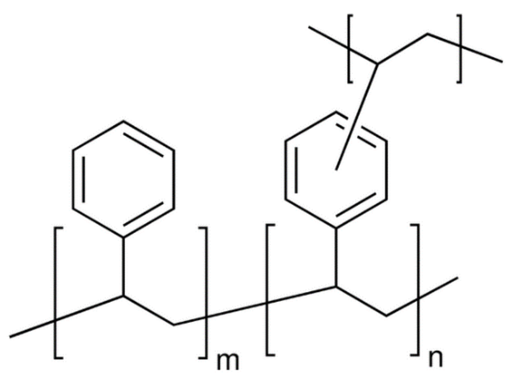


Resin	Composition	Average pore diameter (Å)	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)
XAD-1	styrene divinylbenzene	200	100	0.69
XAD-2	styrene divinylbenzene	90	330	0.69
XAD-4	styrene divinylbenzene	50	750	0.99
XAD-7	acrylic ester	80	450	1.08
XAD-8	acrylic ester	250	140	0.82

- XAD-8 Structure:



XAD-4 Structure

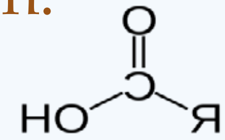


Introduction to XAD resins (cont.)

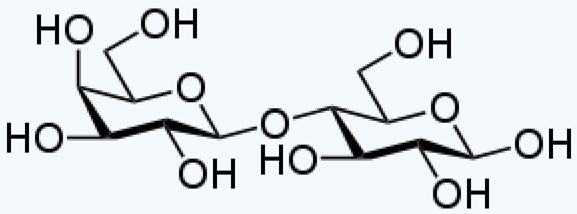
- The capacity factor is k′, where
  - k′ = grams of solute on resin/grams of solute in column void volume
- Divides the NOM mixture into Hydrophobic and hydrophilic fractions
  - Hydrophobic: adsorbable on XAD-8 resins
  - Hydrophilic: non-adsorbable on XAD-8 resins

Hydrophilic and hydrophobic Fraction components

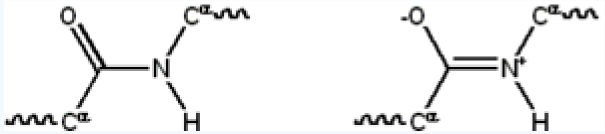
- Hydrophilic fraction:
  - carboxylic acids,

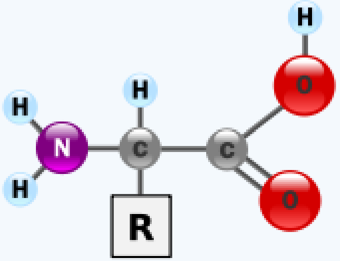


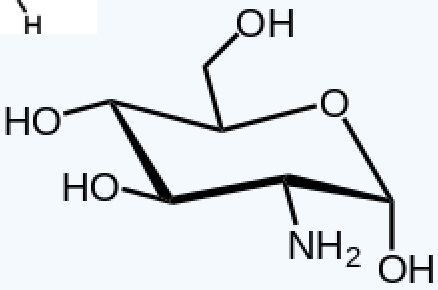
  - carbohydrates,



  - amino acids and amino sugars and
  - proteins.



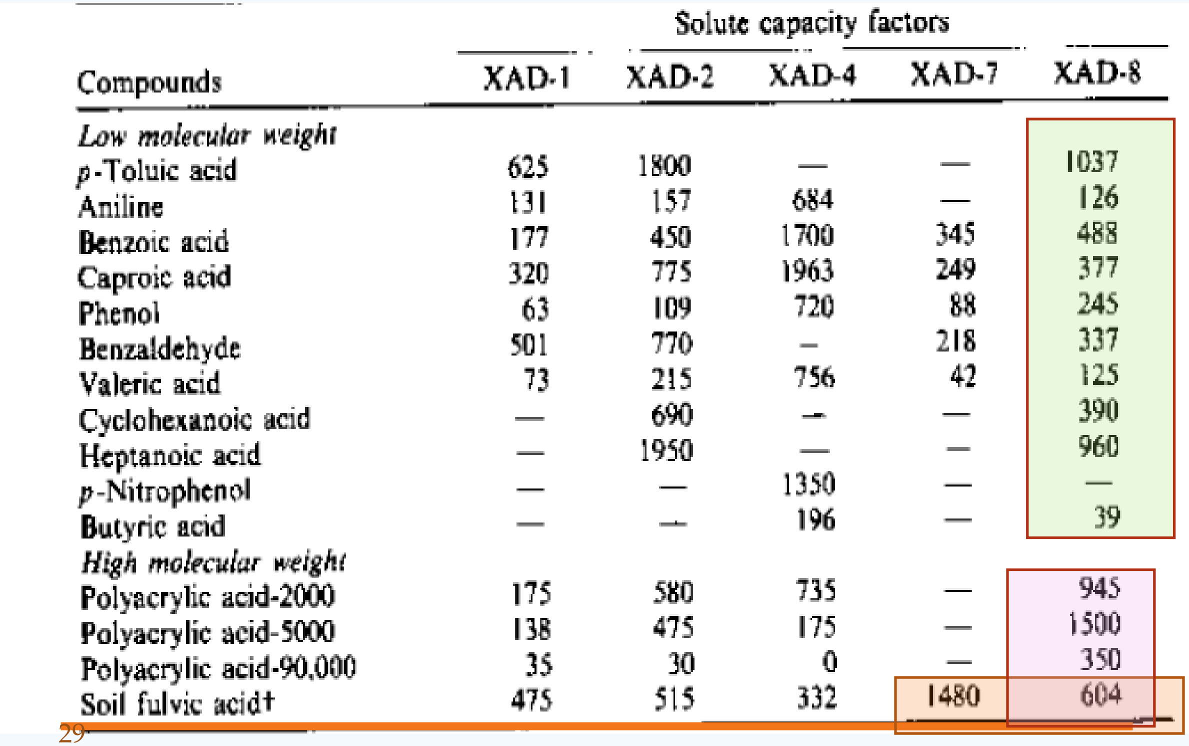




- Hydrophobic fraction: humic species

Solute capacity factors

- Organic matter capacity factors can be determined by surrogates. (Aiken et al., 1992)



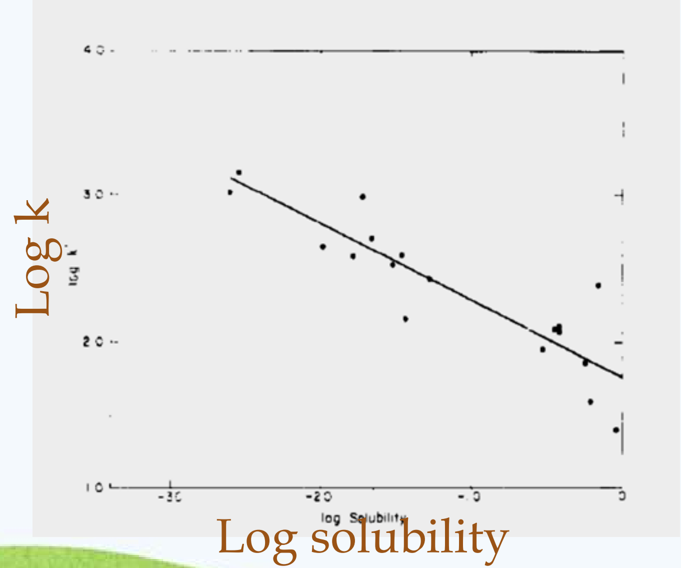
Compounds	XAD-1	XAD-2	XAD-4	XAD-7	XAD-8
	Solute capacity factors				
Low molecular weight					
p-Toluic acid	625	1800	—	—	1037
Aniline	131	157	684	—	126
Benzoic acid	177	450	1700	345	488
Caproic acid	320	775	1963	249	377
Phenol	63	109	720	88	245
Benzaldehyde	501	770	—	218	337
Valeric acid	73	215	756	42	125
Cyclohexanoic acid	—	690	—	—	390
Heptanoic acid	—	1950	—	—	960
p-Nitrophenol	—	—	1350	—	—
Butyric acid	—	—	196	—	39
High molecular weight					
Polyacrylic acid-2000	175	580	735	—	945
Polyacrylic acid-5000	138	475	175	—	1500
Polyacrylic acid-90,000	35	30	0	—	350
Soil fulvic acid†	475	515	332	1480	604

Soil fulvic acid have a higher capacity factor onto XAD7 and 8 resins.

The low MW compounds have a smaller adsorption on XAD8 compared with the high MW ones.

Relation between solubility and capacity factor

- Polarity (of low MW NOM)
  - Can be quantitatively expressed as the aqueous molar solubility
  - A linear relationship between the log solute solubility and log capacity factor on XAD8 resins.

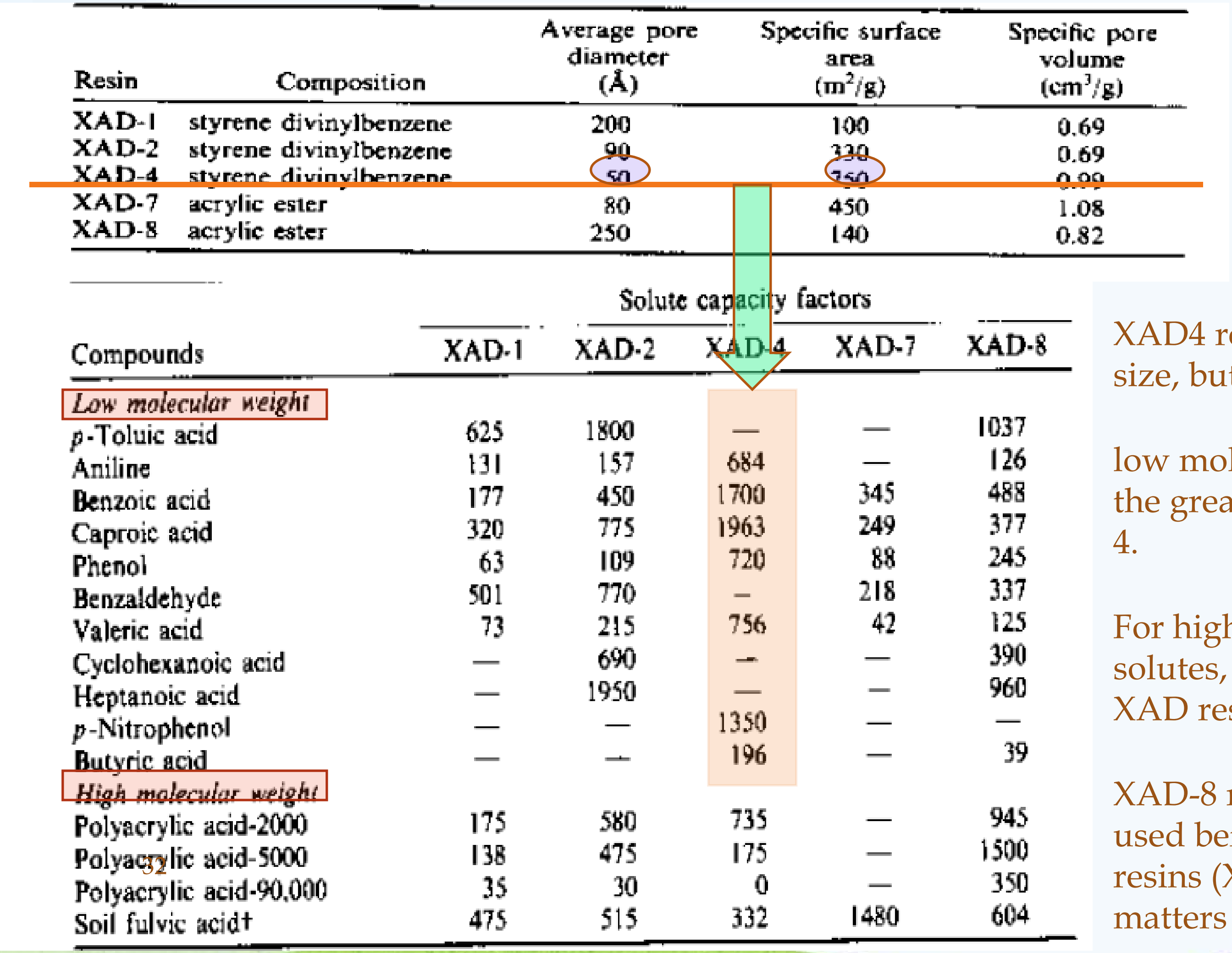


As the solubility increasing, the adsorption capacity onto the resins decreases.

Some of the mechanisms

- The ordering of water molecules around the non-polar organic solutes produced an unfavorable entropy of solution.
  - This negative entropy is a driving force both for aggregation of the non-polar solutes and its adsorption onto the hydrophobic resins.
- According to Traube's rule, the addition of the CH_2 group to the aliphatic acid molecule reduces its solubility (Wang et al. 1979).
  - Therefore, the relation of solubility and capacity can also be applied on the high MW NOM.

Factors influence hydrophobicity of NOM – MW Size



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Benzaldehyde	501	770	—	218	337
Valeric acid	73	215	756	42	125
Cyclohexanoic acid	—	690	—	—	390
Heptanoic acid	—	1950	—	—	960
p-Nitrophenol	—	—	1350	—	—
Butyric acid	—	—	196	—	39
High molecular weight					
Polyacrylic acid-2000	175	580	735	—	945
Polyacrylic acid-5000	138	475	175	—	1500
Polyacrylic acid-90,000	35	30	0	—	350
Soil fulvic acid†	475	515	332	1480	604

XAD4 resins have the smallest pore size, but highest specific surface area.

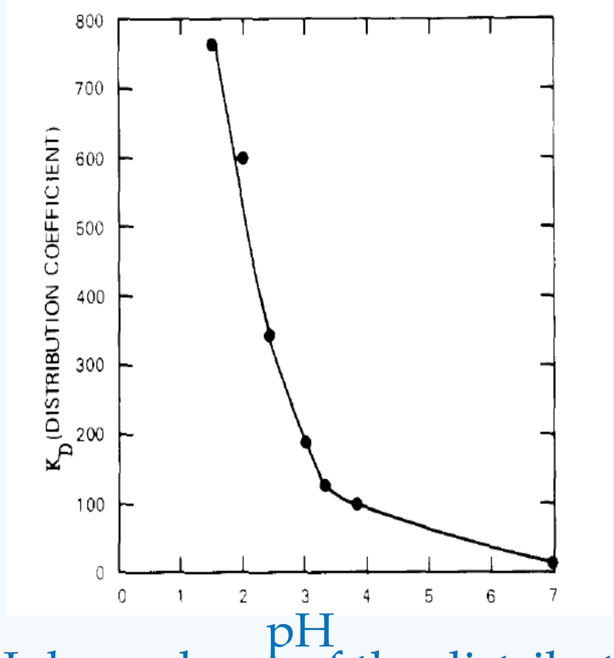
low molecular weight solutes have the greatest capacity factors in XAD-4.

For high molecular weight organic solutes, size exclusion occurs on XAD resins

XAD-8 resins were suggested to be used before the smaller pore size resins (XAD-4) to prevent the organic matters clogging.

Factors influence hydrophobicity of NOM – NOM molecular charge

- K_D decreases as pH raising from 1.5 to 3.
- K_D = mg material adsorbed by resin per gram of resin/mg material in solution per mL of solution
- pH of solution can affect the charge of the organic acids, and consequentially has an effect on the partitioning coefficient.



pH dependence of the distribution coefficient of fulvic acid on XAD-8

Factors influence hydrophobicity of NOM – NOM charge (cont.)

- Adsorption of fulvic or humic acids on XAD-8 resins is favored when they are in the **undissociated form** under low pH condition.
  - XAD-8 resins, composed by acrylic ester, have a **measurable cation exchange capacity** (Aiken et al., 1992).
- The adsorption result, in part, from **intermolecular forces** between the undissociated acid molecules and the acrylic ester resins.
- There is also an **excellent elution efficiency** (approximate 90%) of the XAD-8 resins for humic substances using 0.1N sodium hydroxide as the elution solvent (Aiken et al., 1979).
  - This is attributed to **the charge repulsion** when both the resin and the fulvic acid are anionic at pH 13 (Aiken et al., 1992).
- The **similar carbon arrangement** could be another reason for humic acids to be favoringly absorbed on XAD-8 resins based on "like dissolves like" principle.
  - Malcolm (1985) indicated that the dominant structures of stream humic species are aliphatic and not aromatic. ^{13}C NMR analysis in Aiken (1992)'s research proved this, and found the carboxyl groups were the third largest components after aliphatic and aromatic carbons in fulvic acids.

Other factors

- *Effect of pH:* −
  - Fulvic acids dissociate under high pH conditions (pH>12), and detach from the anionic acrylic ester resins due to negatively charge repulsion.
  - On the other hand, at sufficiently low pH (pH=2), the carboxylic acid groups on fulvic acid become protonated, and it can be exchanged with the cationic ions released from the XAD-8 resins.
- *NOM concentration:* +
  - Adsorption of NOM molecule could be explained by two theoretical models: **site-binding model** and **phase transfer model** (Benjamin and Lawler).
  - the dominant principle of NOM adsorption on XAD resins could be the **non-site specific phase transfer model.**
  - **The adsorption density on XAD resins increases as the dissolved concentration of NOM increasing.**

Other factors (cont.)

- ***Ionic strength:*** ✚
  - Curtis and Rogers (1981) found that there is no effect on retentions of aromatic acids on XAD-8 resins when ionic strength increases.
  - However, I think high ionic strength could enlarge the pH range for NOM adsorption onto the XAD resins, since the cationic ions may **neutralize** some dissociated humic acids and improve its removal by negatively charged XAD-8 resins when pH is high.
    - Gray and others (2007) found that at high ionic strength, the hydrophobic NOM fraction seemed to contribute most to flux decline of UF membranes. There could be a similar phenomena for XAD-8 adsorption.
- ***Effect of flow rate and specific throughput.*** −
  - A high flow rate or throughput could decrease the efficiency of NOM adsorption on XAD resins.
  - It takes nearly 8 hours to reach the adsorption equilibrium between fulvic acids and XAD-8 resins. This slow rate of adsorption caused by slow diffusion of fulvic acid into the beads, it is also another effect of small pore diameter and large fulvic acid molecules (Aiken et al., 1979).
  - The intraparticle diffusion was concluded to be the rate limiting step (Aiken et al., 1992).

- To next lecture