A Rapid Approach to Characterize Natural Organic Matter in Water

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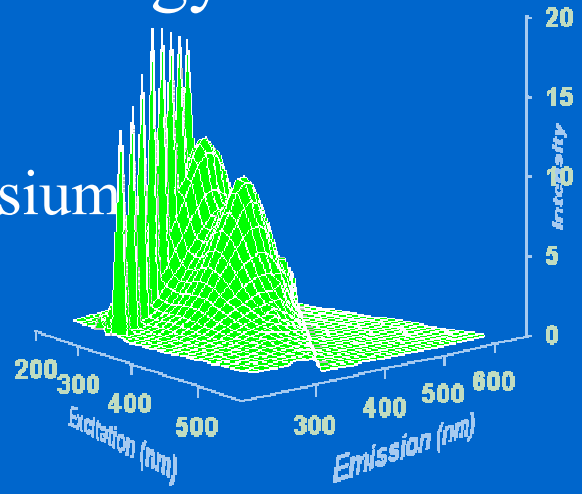

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Methods

NOM ISOLATION & FRACTIONATION (Marhaba et. al, 2002):

- Basis: Leenheer (1998)
- Amberlite DAX-8 resin (macroporous methylmethacrylate copolymer-Supelco, Bellefonte, PA)
- AG-MP-50 strong acid (sulfonated, polystyrene macroporous resin-BioRad, Hercules, CA)
- Duolite A7 weak base (phenol formaldehyde condensation macroporous resin-Supelco, Bellfonte, PA)

TOC: O.I. Analytical 700 system (Sodium Persulfate Oxidation *SM 5310-D).*

FLUORESCENCE: Hitachi F-3010, Ex225nm-525nm, Em249nm-633nm.

Trihlomethanes (THMs): 3400 Varian GC, *EPA551.1 & 552.2*

THM Formation Potential: *Standard Methods, 7-day*

Sampling

SOURCEWATERS:

Raritan & Millstone Rivers, Delaware & Raritan Canal

Others: Passaic River Basin, Rahway river, Oradel Reservoir.

WATER TREATMENT PLANTS:

Ozonation: Canal Rd. (CR) Water Treatment Plant

Chlorination: Raritan Millstone (RM) Water Treatment Plant (Elizabethtown Water Co., Wesfield, NJ)

Others: Passaic Valley Water Commission, North Jersey Distric Water Supply Commission, United Water.

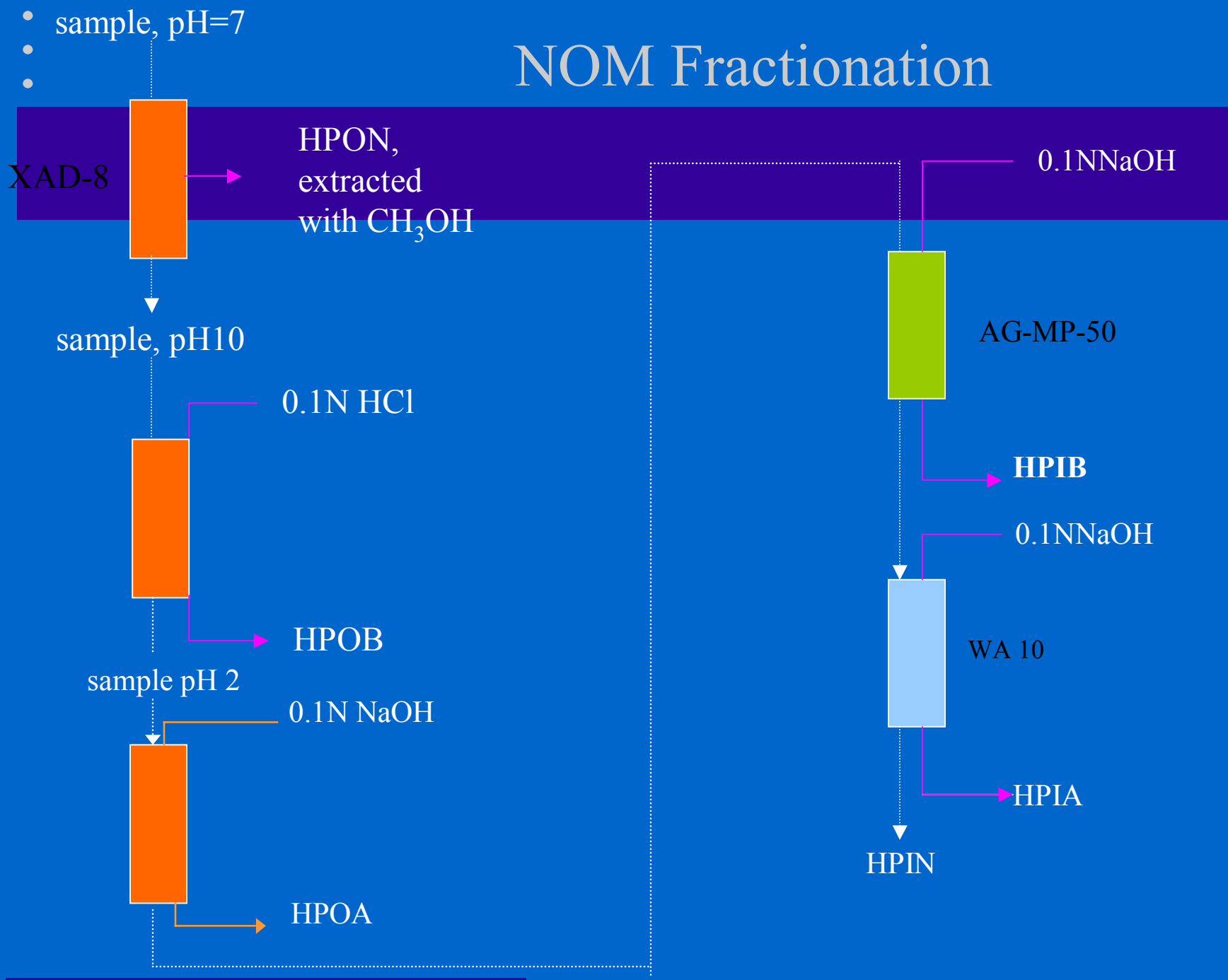
Isolation & Fractionation

HYDROPHOBIC & HYDROPHILIC SUBSTANCES

HYDROPHOBIC & HYDROPHILIC SUBSTANCES

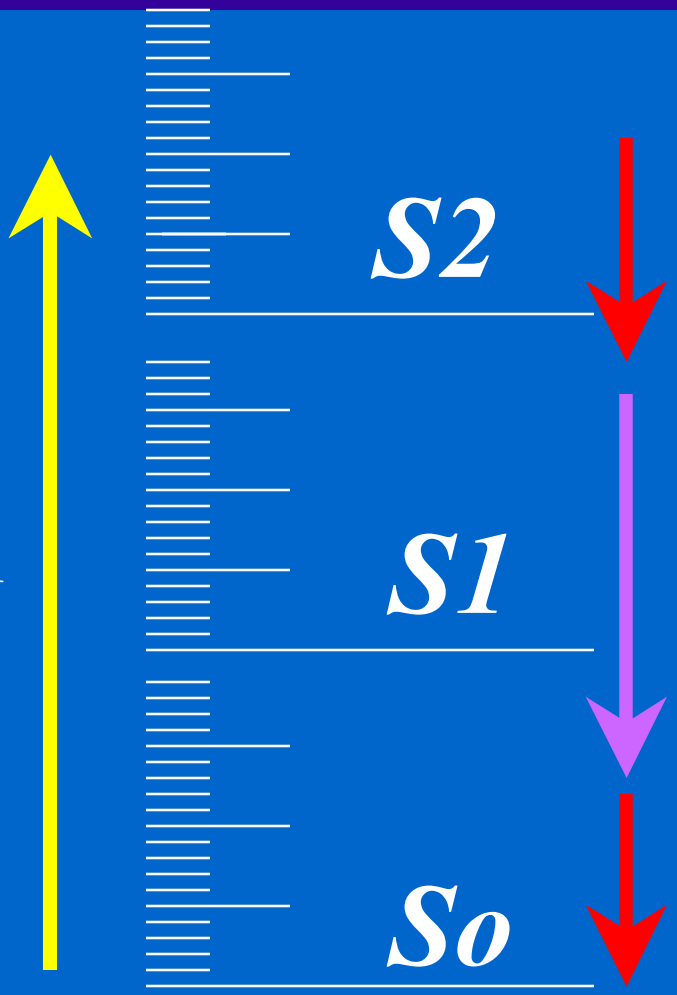
- hydrophobic base— a Humic substance containing amino acids, proteic materials, sugars and polysaccharides (Bruchet et al., 1990)
- hydrophobic acid— a soil fulvic (Schnitzer, 1978)
- hydrophobic neutral— a mix of hydrocarbon and carbonyl compounds such as sugars and Humic substances (Leenheer, 1981)
- Hydrophilic base— a amphoteric proteinaceous materials containing amino acids, amino sugars, peptides and proteins (Leenheer, 1981)
- Hydrophilic acid— an organic compound of the hydroxyl acid group (Leenheer, 1981). And finally,
- Hydrophilic neutral— an organic compound made up of polysaccharides (Tipson, 1968)

NOM Fractionation



What is Fluorescence?

$$E = \frac{hc}{\lambda}$$



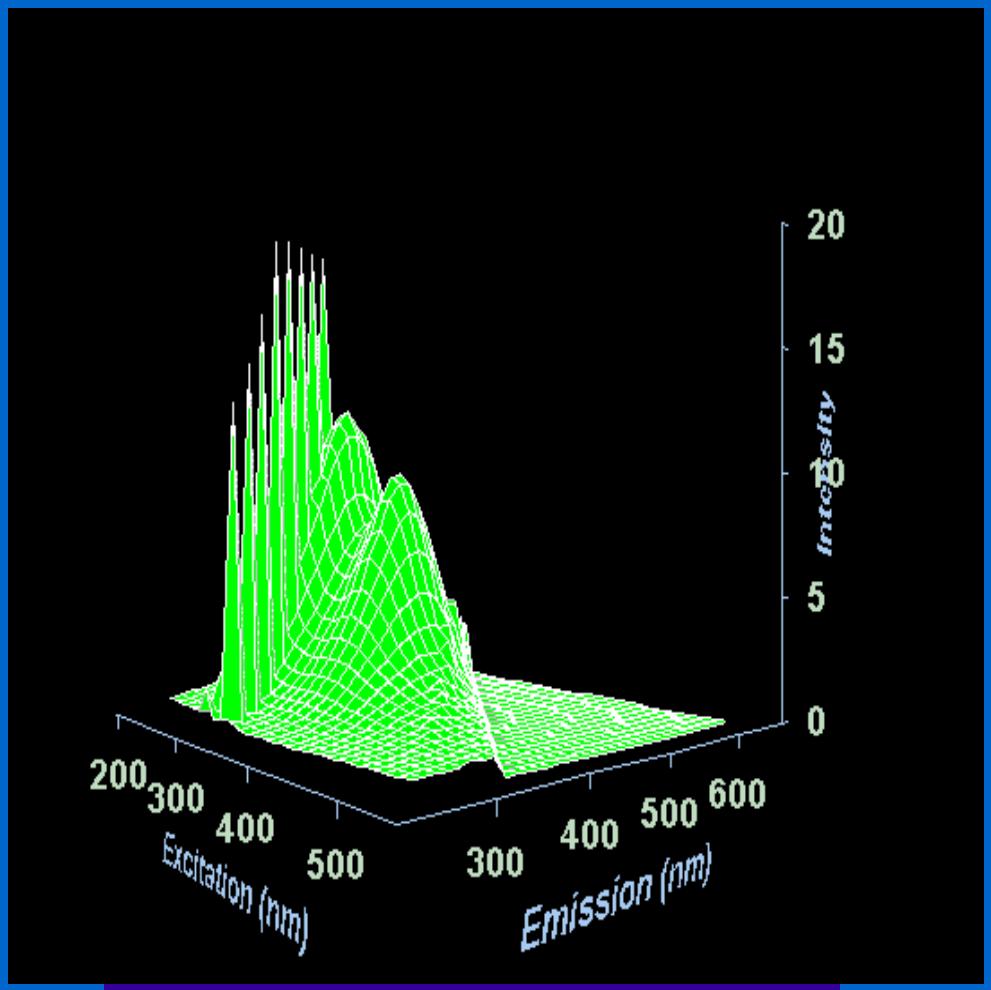
Excitation

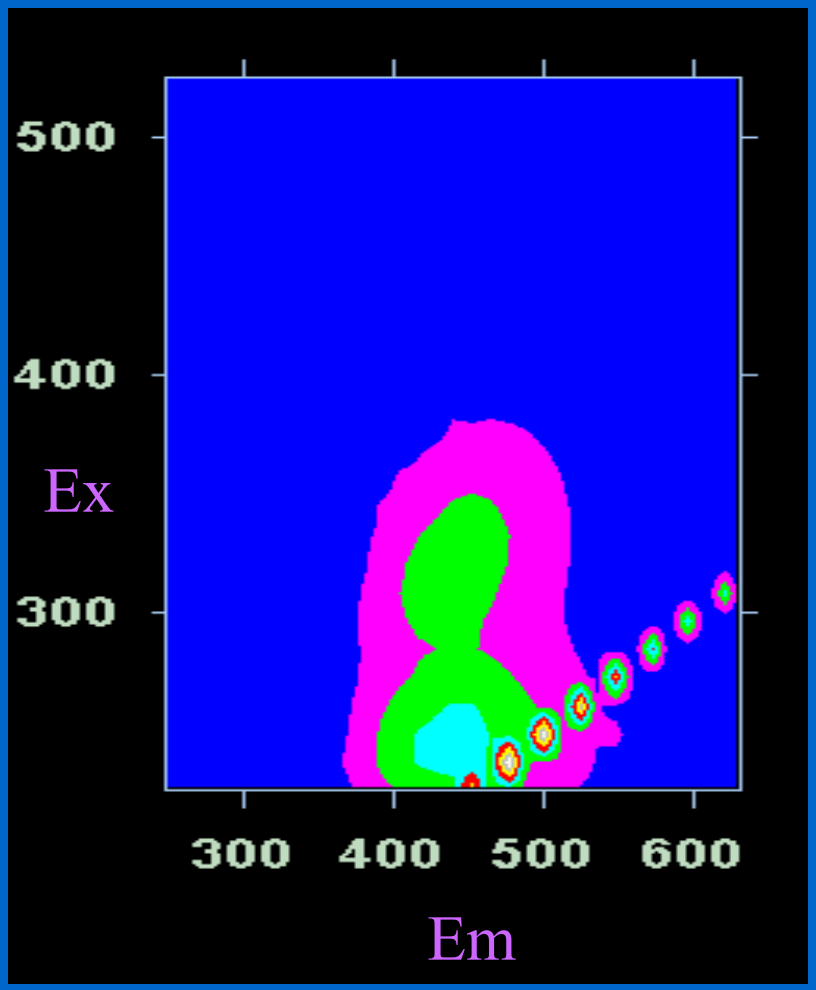
Heat Dissipated

Fluorescent Emission

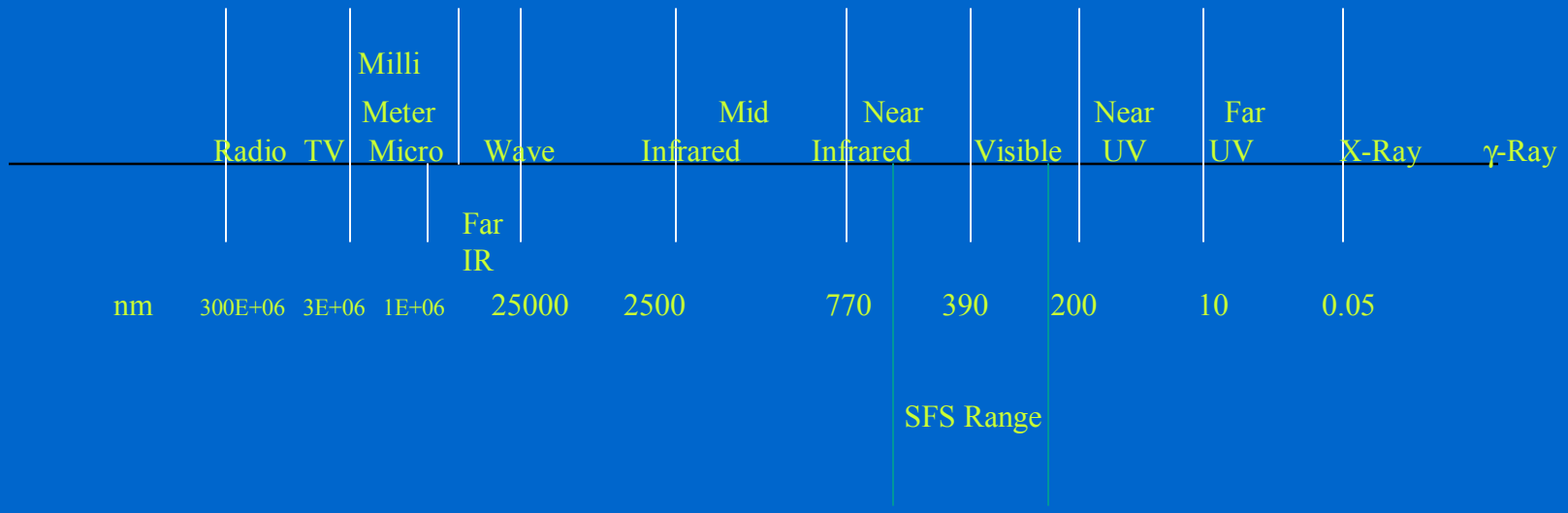
Heat Dissipated

SFS- Determination of Problematic Fractions

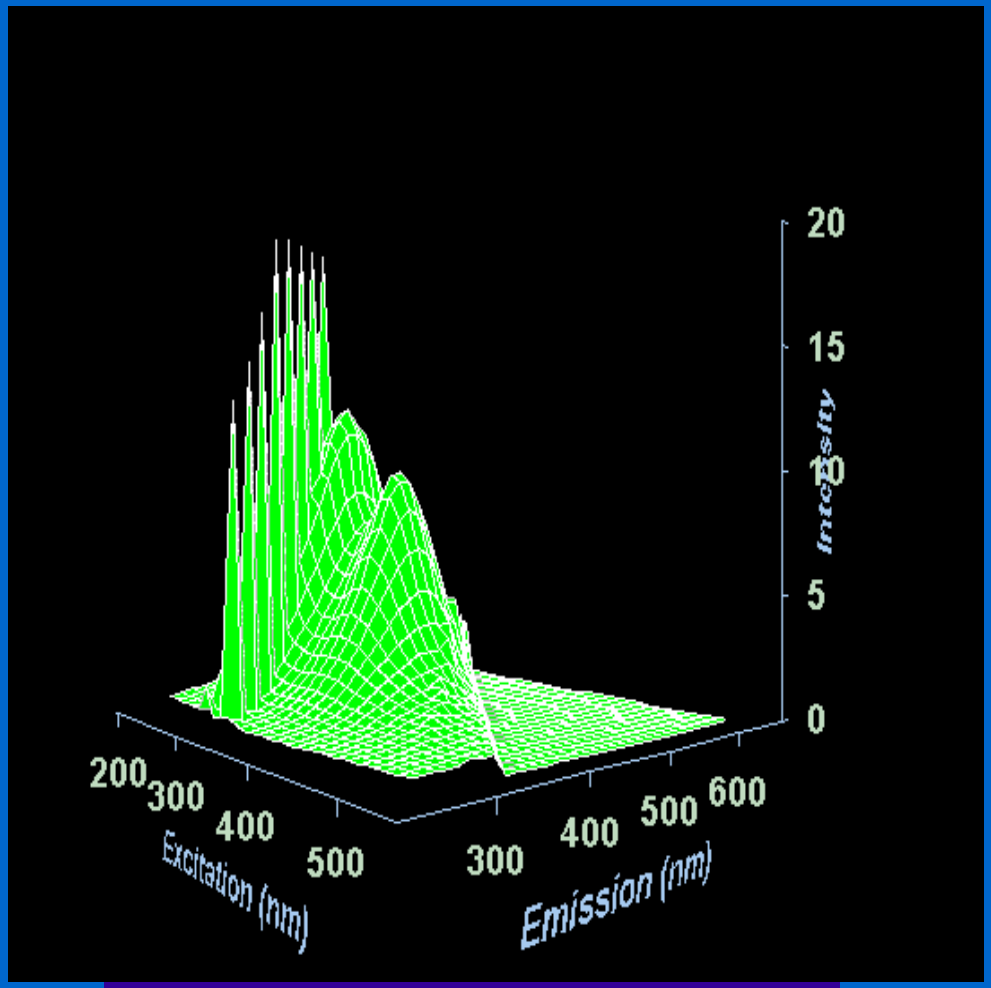


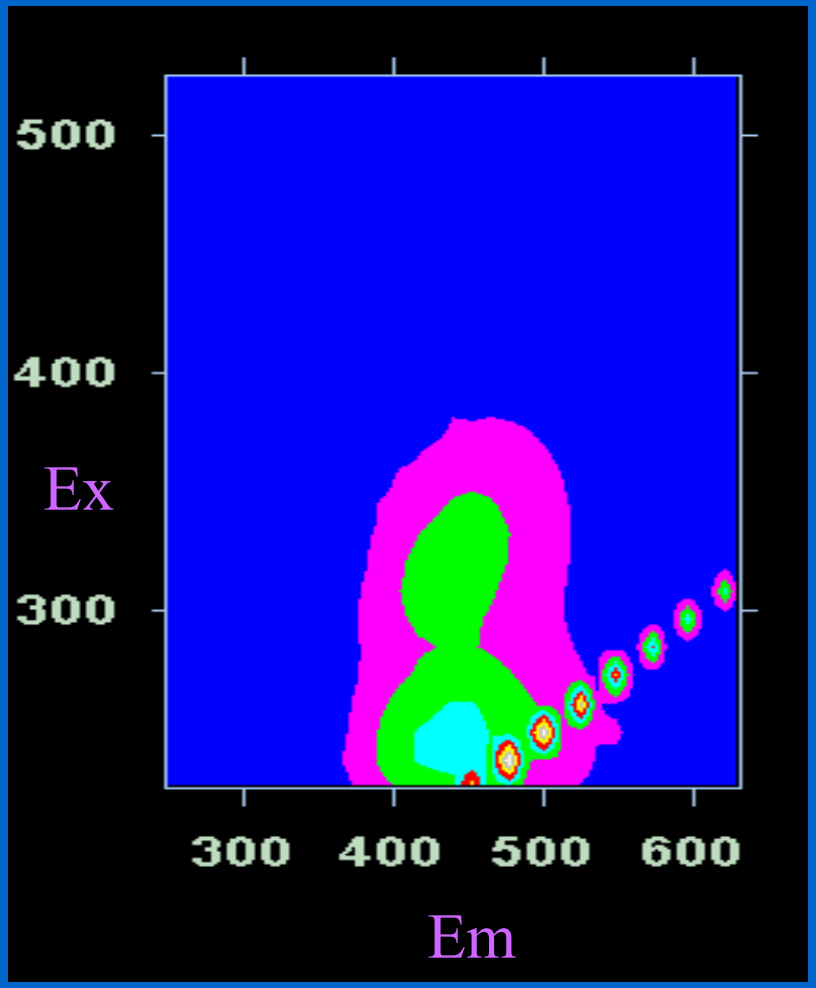


Electro-Magnetic Spectrum

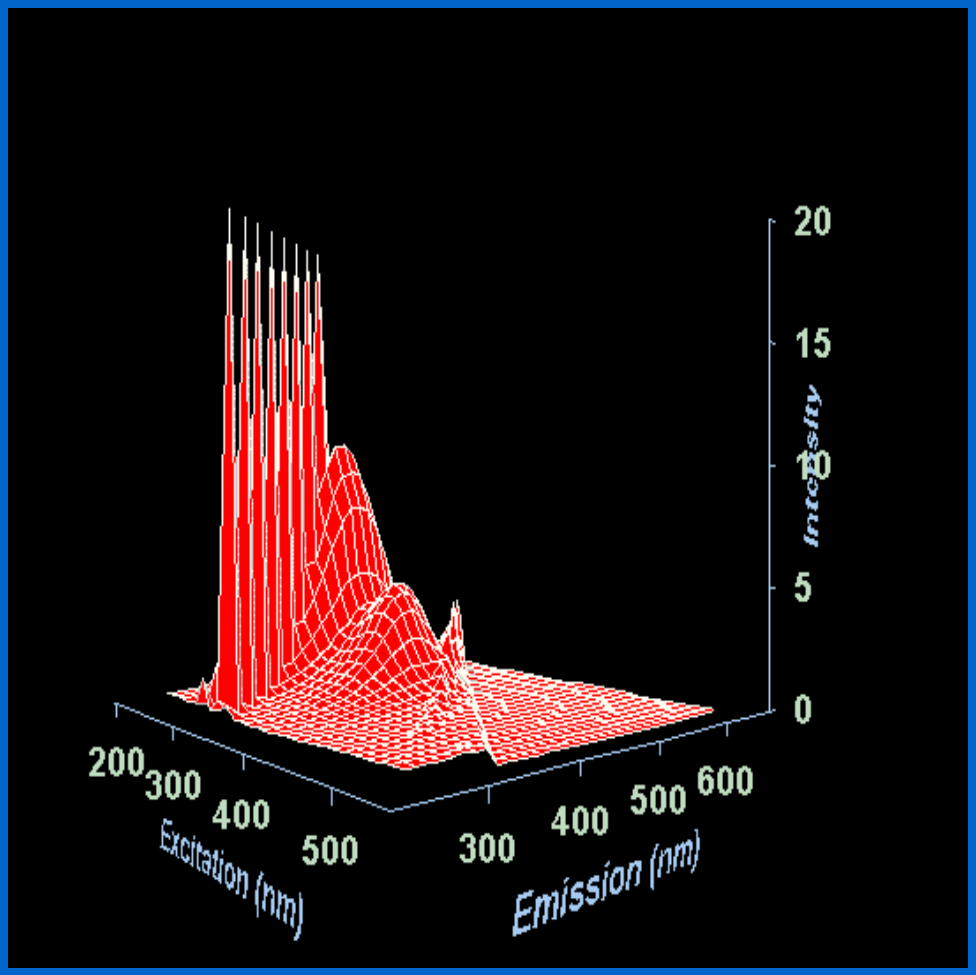


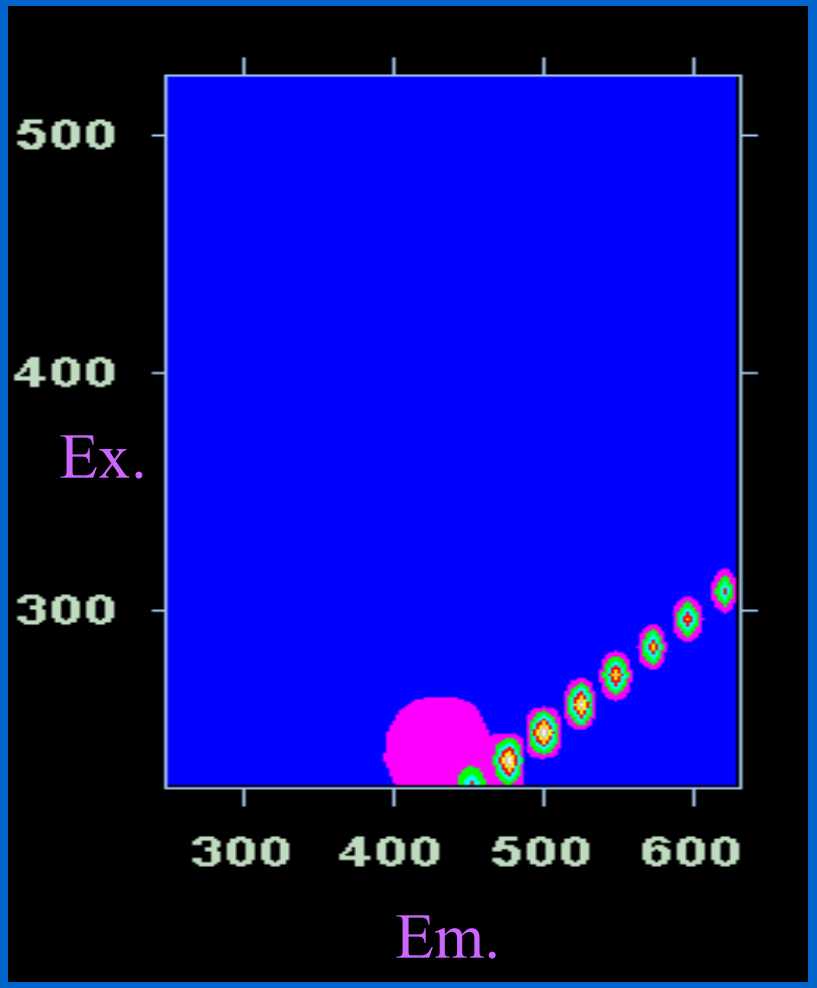
SFS of Non-Chlorinated River Sample





SFS of Chlorinated River Sample





Advantages of SFS Method

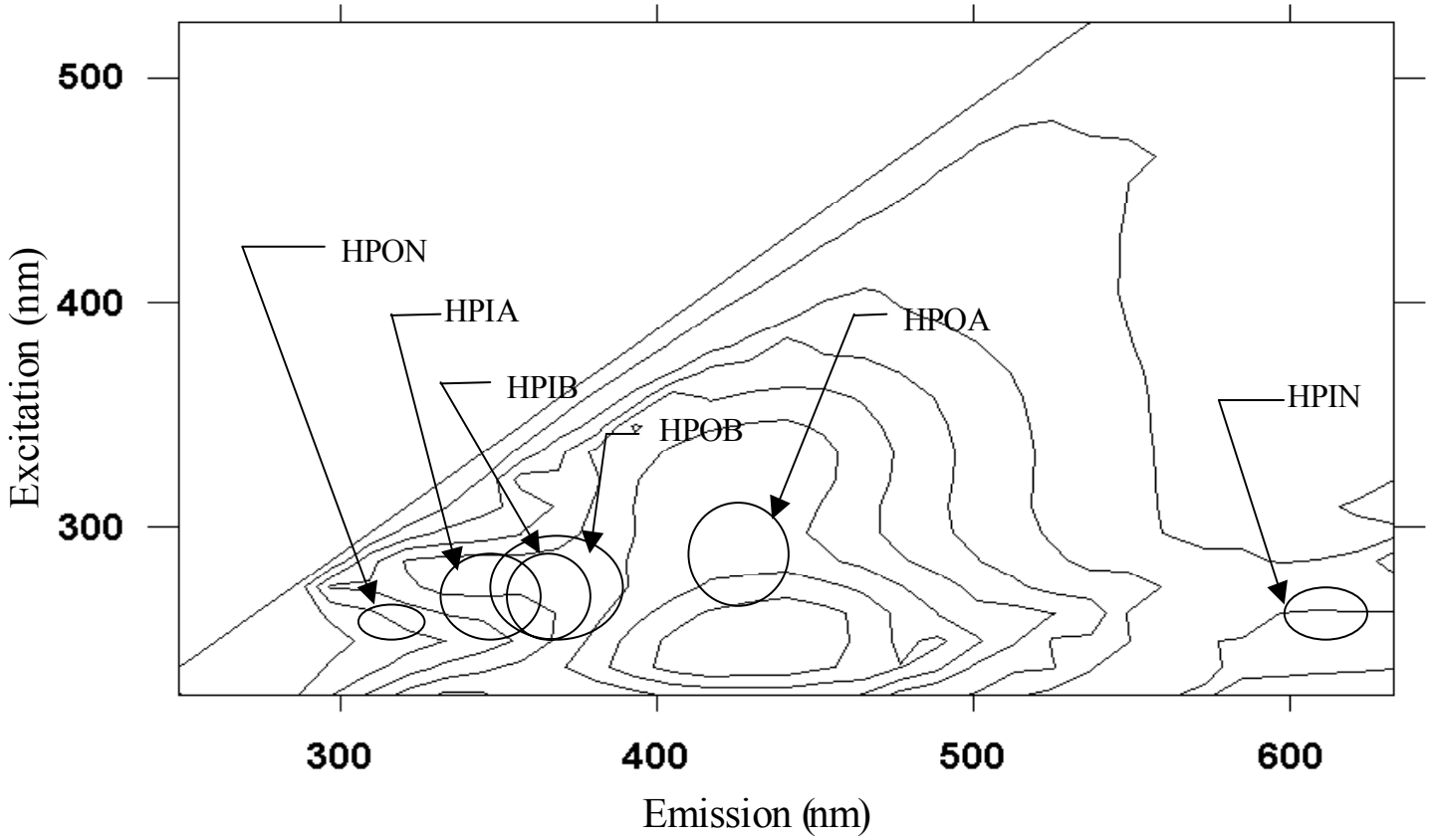
- Better Sensitivity than other spectrophotometric methods
- SFS Contains Chemical specific information
- Easy to Use
- Inexpensive Technique conducive to process monitoring

SFS Characteristics of DOM Fractions
(Marhaba *et al, 2000*)

Fraction	Major Peak Location	Minor Peak Location
Hydrophilic Acid	(225-237 Ex, 345-357 Em)	(273 Ex, 357-369 Em)
Hydrophilic Base	(225-237 Ex, 357-369 Em)	(273-285 Ex, 357-381 Em)
Hydrophilic Neutral	(225 Ex, 609-621 Em)	-
Hydrophobic Acid	(237-249 Ex, 417-429 Em)	(297-309 Ex, 417-429 Em)
Hydrophobic Base	(225-237 Ex, 369-381 Em)	(273-285 Ex, 369-381 Em)
Hydrophobic Neutral	(225-237 Ex, 309-321 Em)	-

Major Peak Locations of DOM Fractions

(Marhaba *et al, 2000*)



SFS Model (Marhaba, 2000)

$$C(f) = a + b * P(f) + c * A(f) + d * S(f) + e * S(f) * A(f) \qquad (1)$$

$$S(f) = \frac{[P(f) - P(f)_i]}{[Em(f)_p - Em(f)_i]} \qquad (2)$$

Where,

C(f) = Predicted fraction concentration (mg/L)

P(f) = Intensity at the location of the fraction major peak (intensity units).

$P(f)_i$ = Spectrum intensity at Em_i (intensity units).

$Em(f)_i$ = Starting Em of spectrum = Ex +24 (nm).

$Em(f)_p$ = Em at fraction major peak location (nm).

*A(f) = Area of emission spectrum where the fraction major peak exists (intensity units*nm).*

*S(f) = Rising slope of the corresponding fraction spectral major peak (intensity units*nm).*

a, b, c, d and e are regression coefficients different for each fraction.

SFS Model Verification

	R/M WTP (sampled May 21, 1998)			PVWC WTP (sampled April 16, 1998)			
	S_e	F_e	E	I_n	S_e	F_e	E
P(HPOA)	0.20	0.23	0.22	0.71	0.34	0.28	0.36
A(HPOA)	0.34	0.20	0.19	0.53	0.34	0.32	0.24
P(HPOB)	0.24	0.26	0.30	0.42	0.42	0.42	0.42
A(HPOB)	0.18	0.12	0.12	0.33	0.29	0.20	0.21
P(HPON)	0.72	0.42	0.62	0.58	0.56	0.70	0.28
A(HPON)	0.65	0.50	0.49	0.45	0.51	0.37	0.34
P(HPO)	1.38	0.94	1.16	1.68	1.18	1.60	0.90
A(HPO)	1.17	0.83	0.79	1.31	1.13	1.02	0.78
P(HPIA)	1.78	1.62	1.28	2.60	1.48	0.74	0.90
A(HPIA)	1.66	1.40	1.11	2.34	1.37	0.92	0.81
P(HPIB)	0.34	0.22	0.20	0.40	0.40	0.34	0.17
A(HPIB)	0.21	0.14	0.15	0.25	0.25	0.28	0.23
P(HPIN)	0.24	0.18	0.15	0.64	0.58	0.40	0.38
A(HPIN)	0.30	0.15	0.20	0.60	0.40	0.20	0.20
P(HPI)	2.36	2.02	1.63	3.64	2.46	1.48	1.45
A(HPI)	2.17	1.69	1.46	3.19	2.02	1.39	1.23

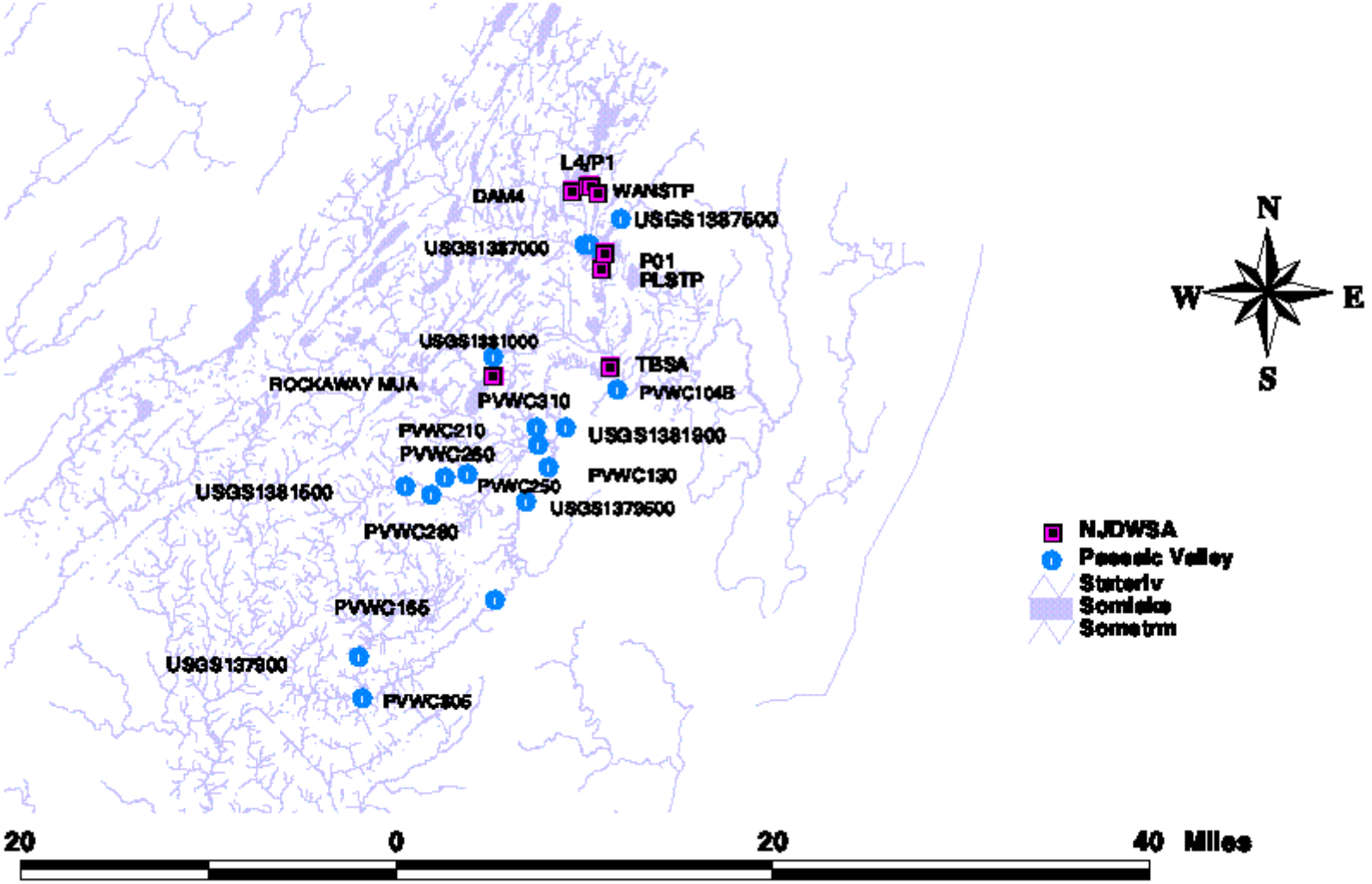
P, predicted value; A, actual value; I_n, plant influent; S_e, sedimentation basin effluent; F_e, filter effluent; E, plant effluent; HPO, sum of hydrophobic substances; HPI, sum of hydrophilic substances.

Statistics: R-Square = 0.96; F-ratio = 1.04; F (41,41, α = 0.05) = 1.69

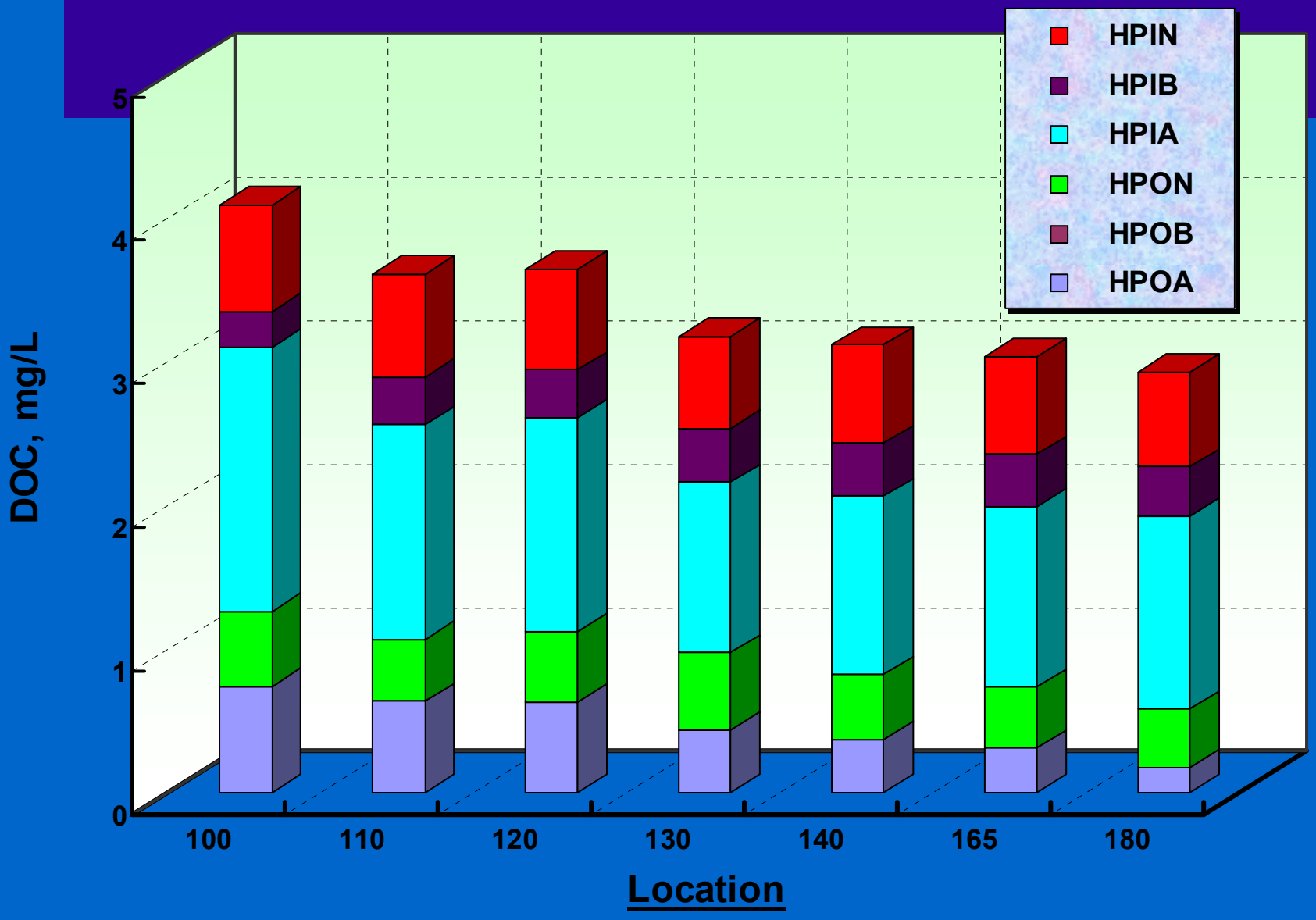
Applications of the SFS Method/Model

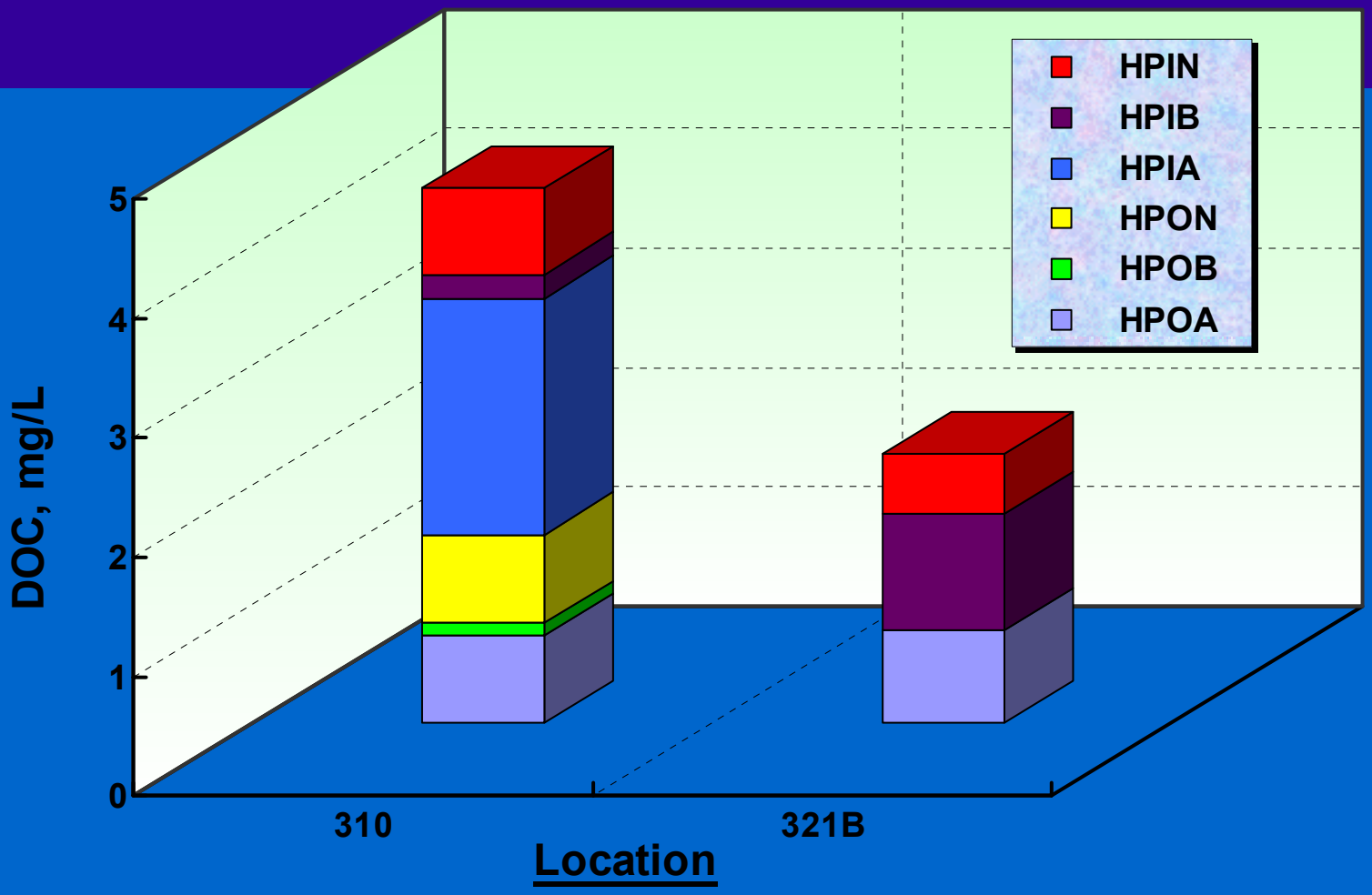
- Water Treatment Optimization
- Source water Characterization

Passaic River Basin Watershed Monitoring Locations



Predicted Fraction Concentrations along the Passaic River




HPIN
HPIB
HPIA
HPON
HPOB
HPOA
DOC, mg/L
0
1
2
3
4
5
310
321B
Location

Conclusions

- SFS method/model analysis can be performed within 3 minutes vs a person-week.
- Can be used for on-line water treatment plant optimization of problematic organics removal.
- Can be used for rapid source water spatial and temporal characterization.

Additional Research

- Additional verification of SFS method/model for application to all regions of NJ and water treatment systems.
- Coagulation studies to determine optimum removal of most problematic precursory fractions to disinfection by-products.
- Application to water treatment plants for optimization of DBP precursors removal.
- Application to source water characterization.

Acknowledgements

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  - Elizabethtown Water Company
  - Passaic Valley Water Commission
  - North Jersey Water Supply Authority
  - United Water
  - 6 STP Authorities