

Fifty Years of Research on Dissolved Organic Material and Drinking Water (1961 – 2011)

Philip C. Singer

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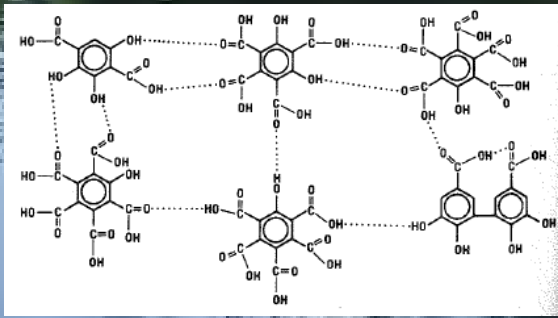
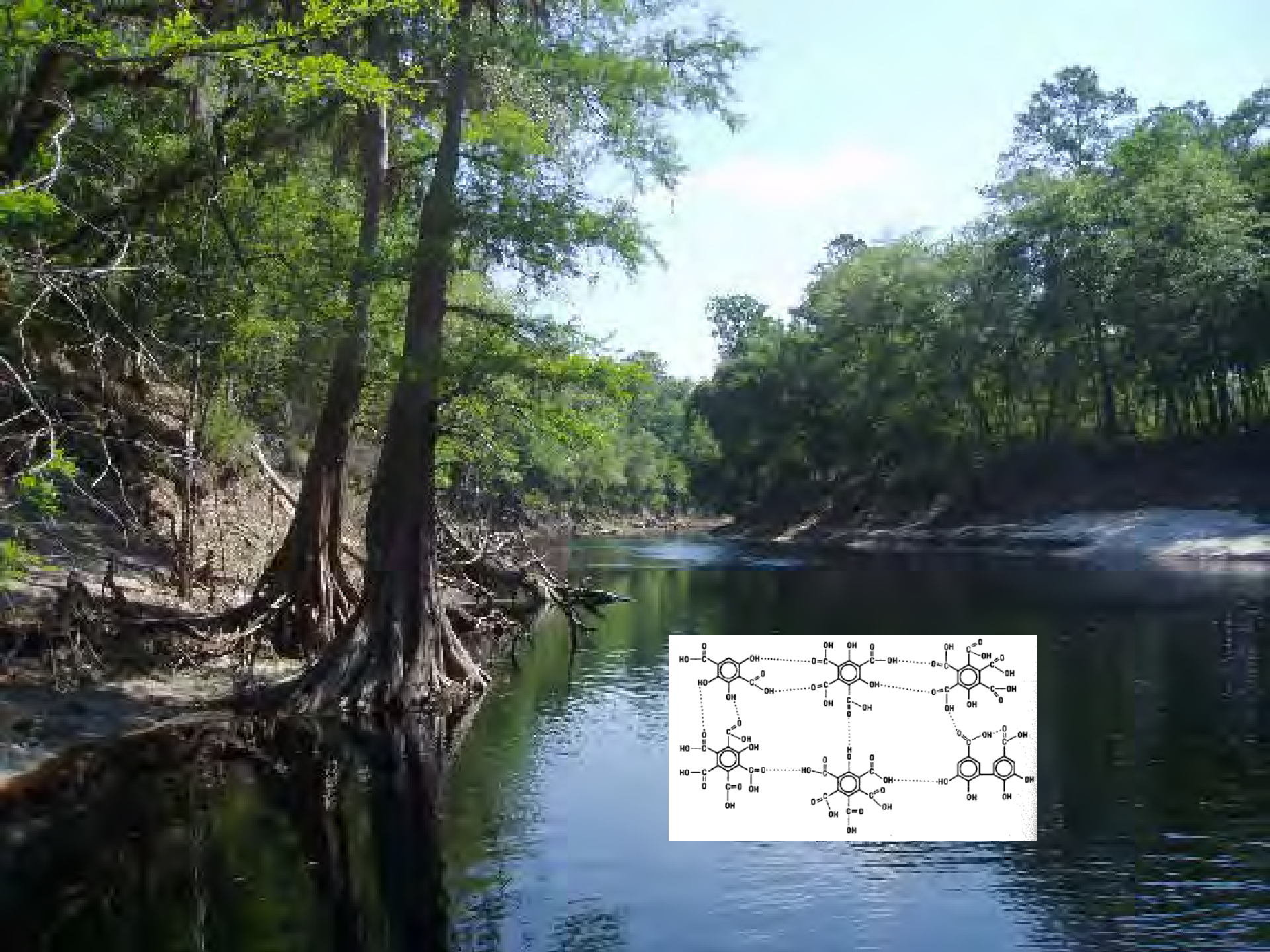
IWA Specialty Conference on Natural Organic Matter

July 2011

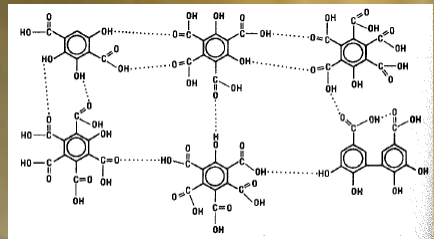
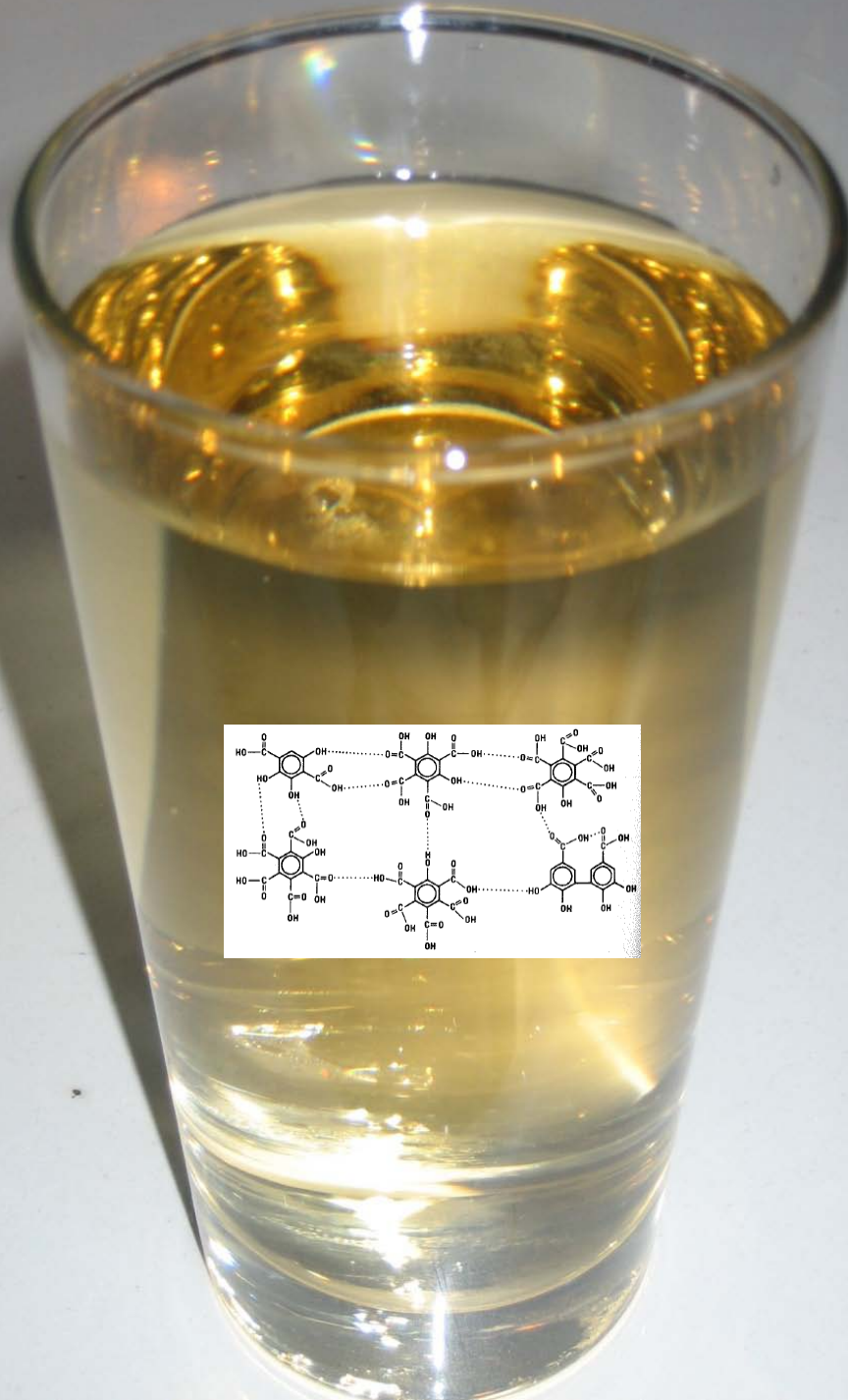


THE UNIVERSITY
of NORTH CAROLINA
at CHAPEL HILL

Disclaimer







Early 1960's – Color in Drinking Water

- Humic substances contribute to the yellow-brown color in raw drinking water.
- Coagulation determined to be an effective method of removing color from water

Color in Drinking Water

- Shapiro, J. *Limnol. Oceanog.*, 2, 161 (1957)
- Black and Willems, *JAWWA*, 53, 589 (1961)
- Black and Christman, *JAWWA*, 55, 753 (1963)
- Black and Christman, *JAWWA*, 55, 897 (1963)
- Black, Singley, Whittle, and Maulding, *JAWWA*, 55, 1347 (1963)
- Hall and Packham, *JAWWA*, 57, 1149 (1965)
- Christman and Ghassemi, *JAWWA*, 58, 723 (1966)

BOOKS IN SOILS AND THE ENVIRONMENT

edited by
A. Douglas McLaren
College of Agricultural Sciences
University of California
Berkeley, California

Soil Biochemistry, Volume 1, edited by A. D. McLaren and G. H. Peterson
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Goring and J. W. Hamaker
Organic Chemicals in the Soil Environment, Volume 2, edited by C. A. I.
Goring and J. W. Hamaker
Humic Substances in the Environment, by M. Schnitzer and S. U. Khan

Volumes in Preparation

Soil Biochemistry, Volume 3, edited by E. A. Paul and A. D. McLaren
Microbial Life in the Soil: An Introduction, by T. Hattori

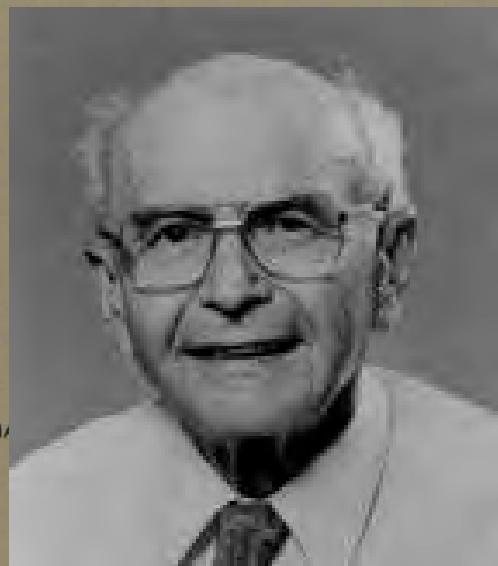
HUMIC SUBSTANCES IN THE ENVIRONMENT

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M/

Aquatic and Terrestrial Humic Materials

Edited by

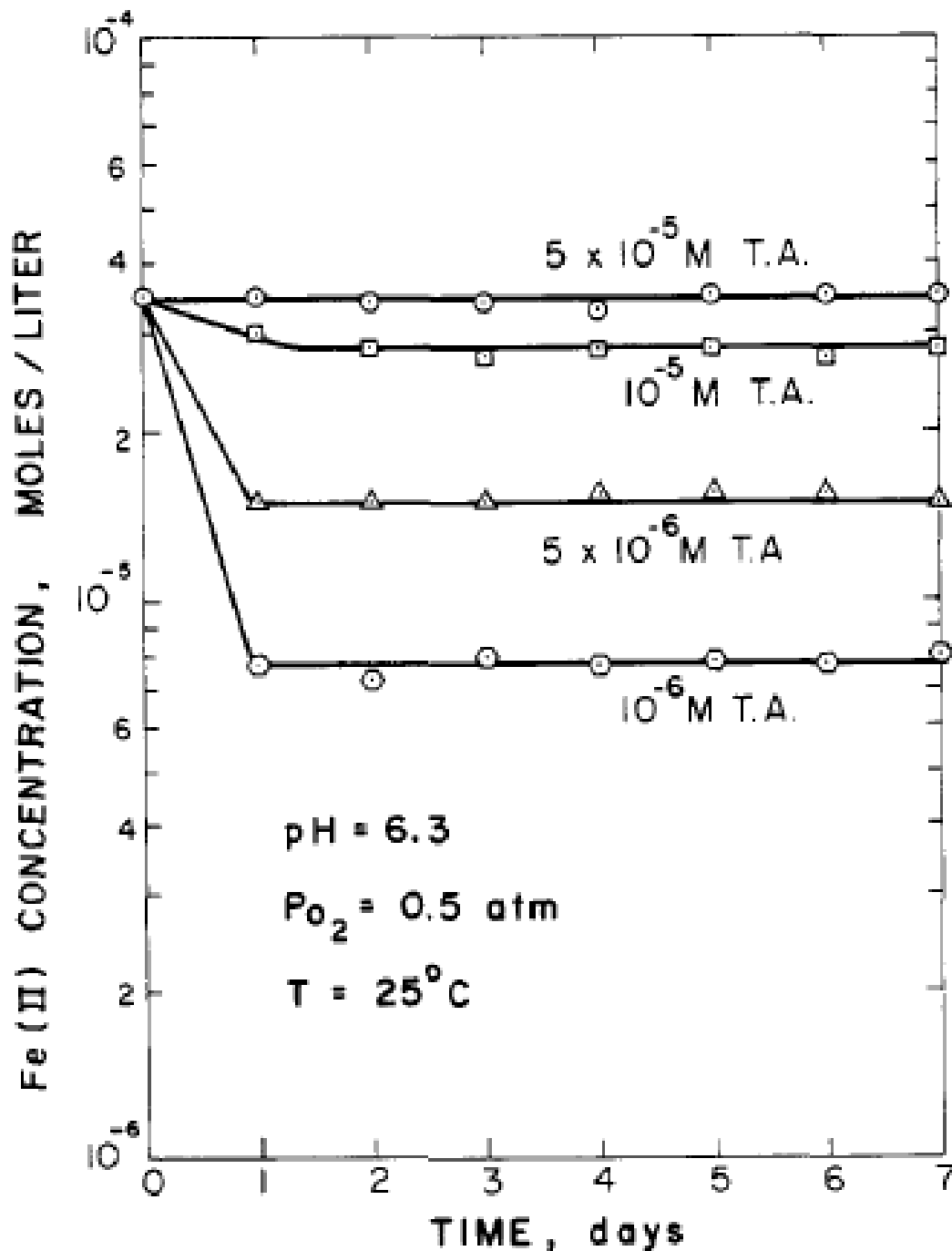
Russell F. Christman
Egil T. Gjessing

 **ANN ARBOR SCIENCE**
THE BUTTERWORTH GROUP





Singer
PhD
1969



Theis and Singer,
 "Complexation of
 Iron(II) by Organic
 Matter and Its Effect
 on Iron(II)
 Oxygenation,"
 Environ. Sci. Tech., 8,
 569 (1974).

Trace Metals and Metal-Organic Interactions in Natural Waters

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1973



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1974

**Formation of Trihalomethanes
During the Disinfection
of Drinking Water**



+ Cl₂



THMs

+

Other Halogenated
DBPs

DOM and Disinfection Byproducts

- The discovery of THMs in drinking water in 1974, and the identification of humic substances as DBP precursors, catalyzed research on the characteristics of DOM that led to DBP formation and to technologies for removing DOM from water

1970's

The Beginning of DBPs

- 1974 – First reports of THMs in chlorinated drinking water
 - Rook
 - Bellar and Lichtenberg
- 1975 – National Organics Reconnaissance Survey
 - Symons, Stevens and co-workers
- 1976 – National Cancer Institute identifies chloroform as a carcinogen
 - Cantor and co-workers

1970's/1980's

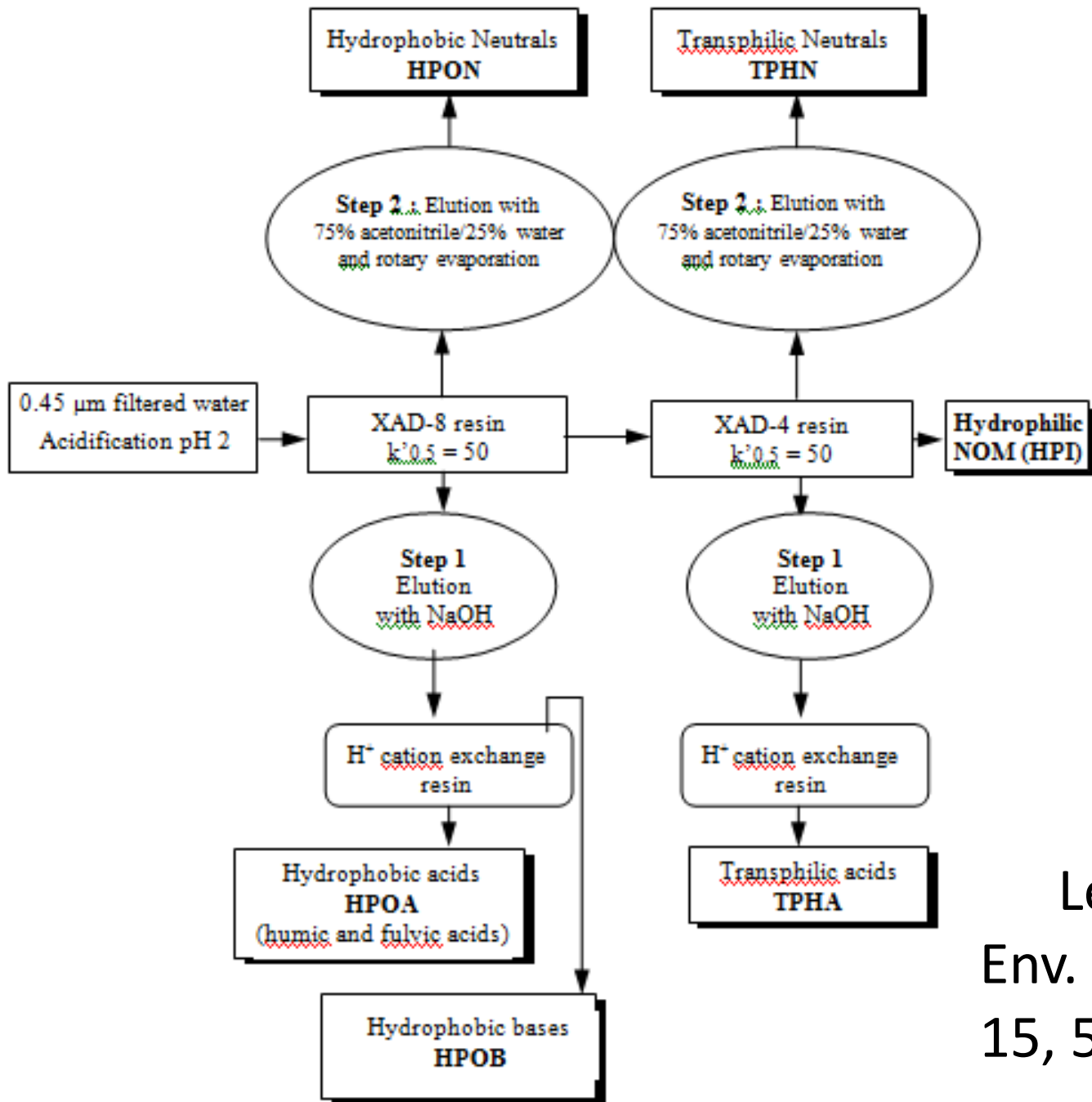
- Hundreds of other halogenated DBPs identified in chlorinated drinking water
- Humic substances identified as primary precursors of DBP formation
- THM/HAA formation linked to specific characteristics of DOM, e.g. aromatic content, SUVA, hydrophobic DOC

Early Experiments with Humic Acid

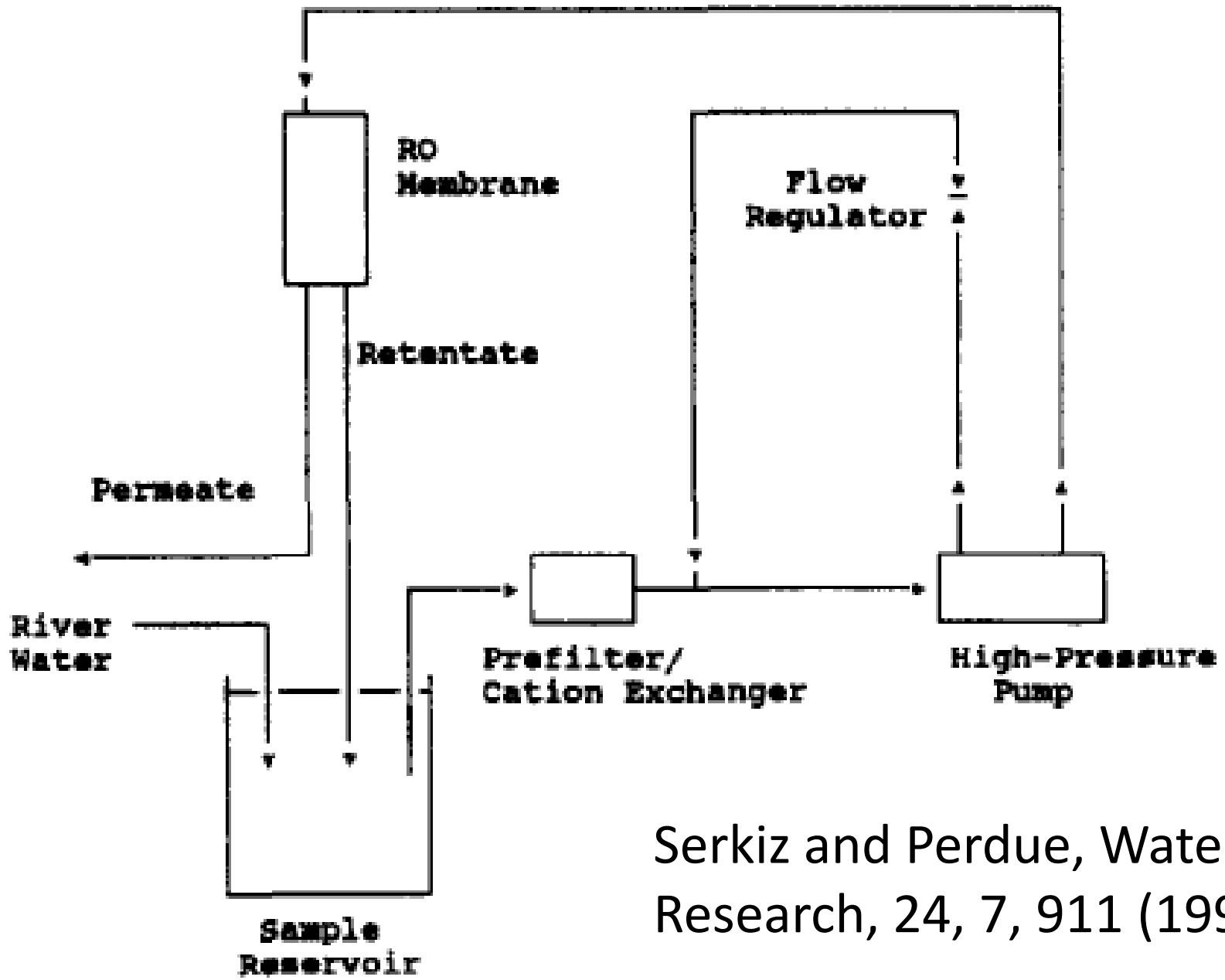
- Aldrich Humic Acid
- Fluka Humic Acid

Isolation and characterization of DOM

- XAD-based isolation and fractionation schemes –
USGS : Aiken, Leenheer, Malcolm, Thurman
- RO concentration - Perdue
- Elemental analysis, NMR, structural and functional group analysis
- Pyrolysis GC/MS – Bruchet et al.
- HPSEC – Frimmel and co-workers, Amy and co-workers
- SUVA
- EEMs, FI, PARAFAC
- DON



Leenheer,
 Env. Sci. Tech.,
 15, 578 (1981)



Serkiz and Perdue, Water Research, 24, 7, 911 (1990)

Fig. 1. Portable reverse osmosis system.

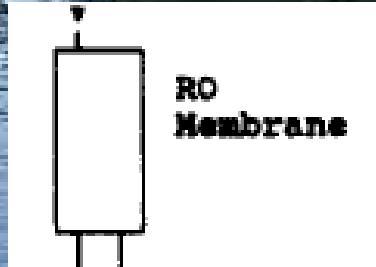
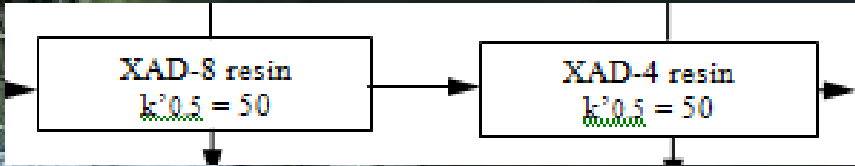
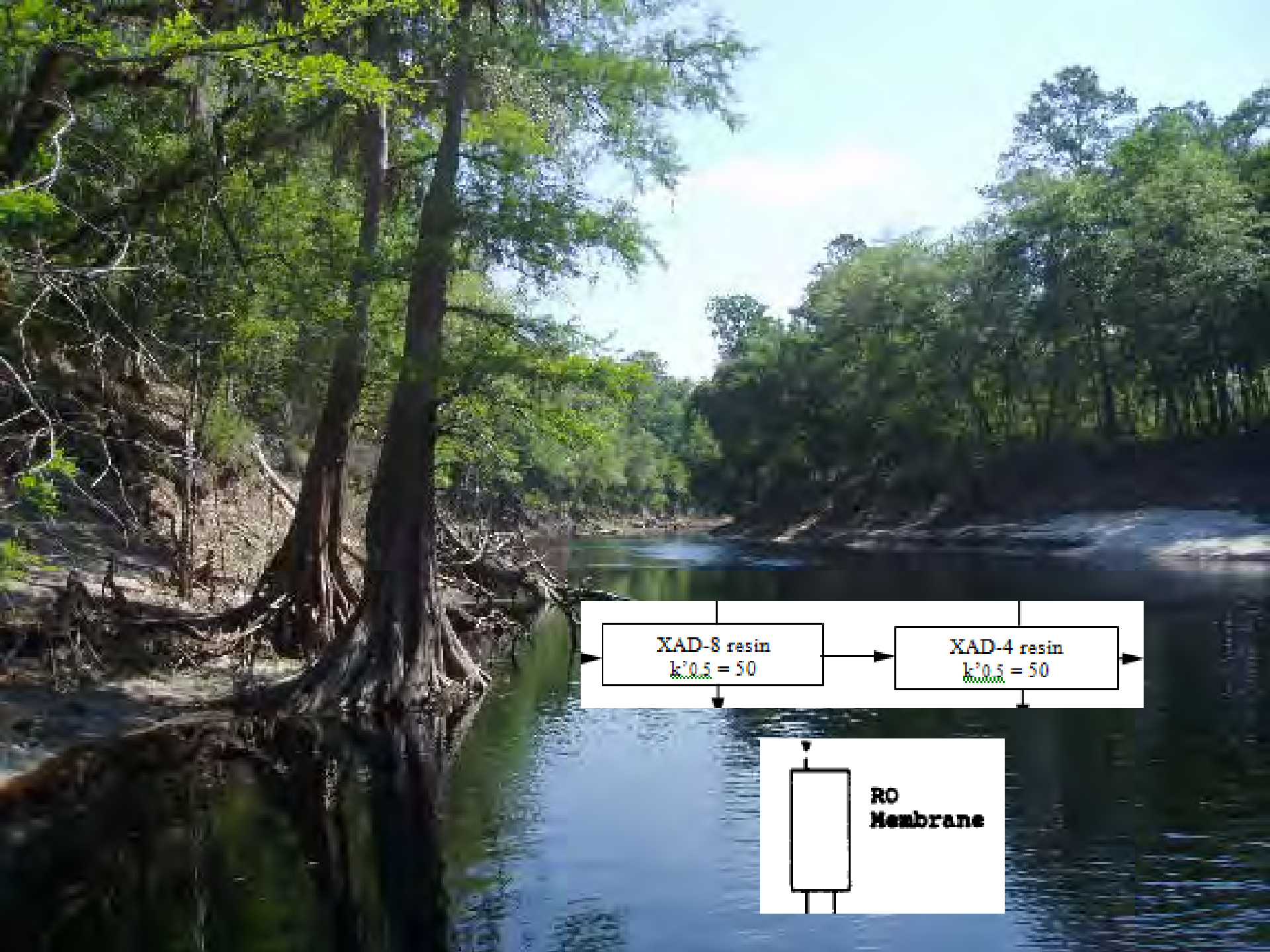


Table V. Elemental Analyses of Humic Concentrates from Freshwaters

sample	C	H	N	O	P	S	ash
Suwannee River fulvic acid (22 mg C/L)	54.65	3.71	0.47	39.28	0.20	0.50	0.95
Suwannee River humic acid (8 mg C/L)	57.24	3.94	1.08	39.13	0.20	0.63	0.56
Biscayne groundwater fulvic acid (6 mg C/L)	55.44	4.17	1.77	35.39	0.20	1.06	0.43
Biscayne groundwater humic acid (2.5 mg C/L)	58.28	3.39	5.84	30.14	0.22	1.43	0.10
Laramie-Fox Hills groundwater fulvic acid (0.050 mg C/L)	62.67	6.61	0.42	29.14	0.20	0.44	1.09
Laramie-Fox Hills groundwater humic acid (0.030 mg C/L)	62.05	4.92	3.21	23.45	0.46	0.96	5.12

Thurman and Malcolm, Env. Sci. Tech., 15, 463 (1981)



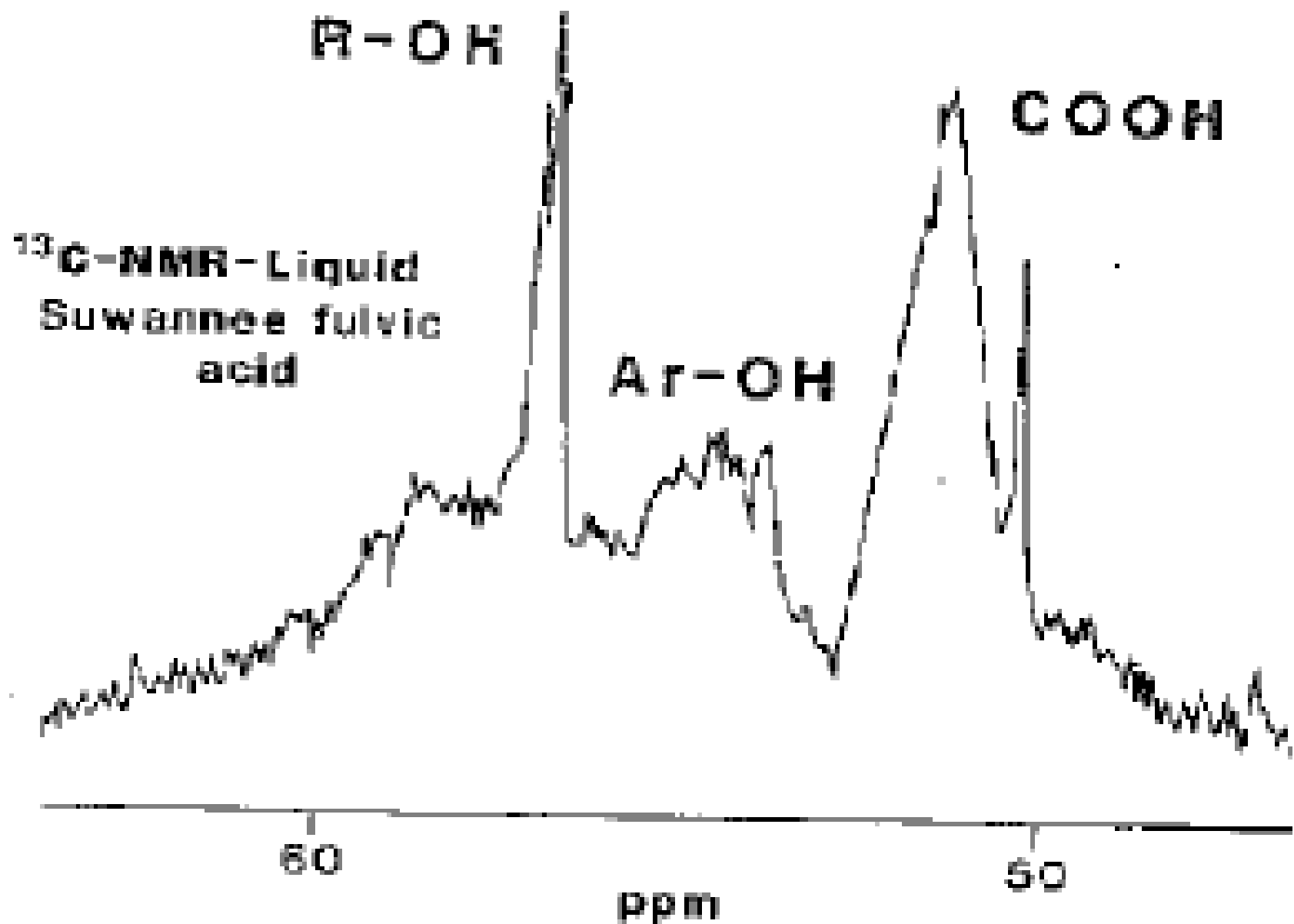


Table I. Elemental Composition of Ten Extracted Aquatic Humic Substances^a

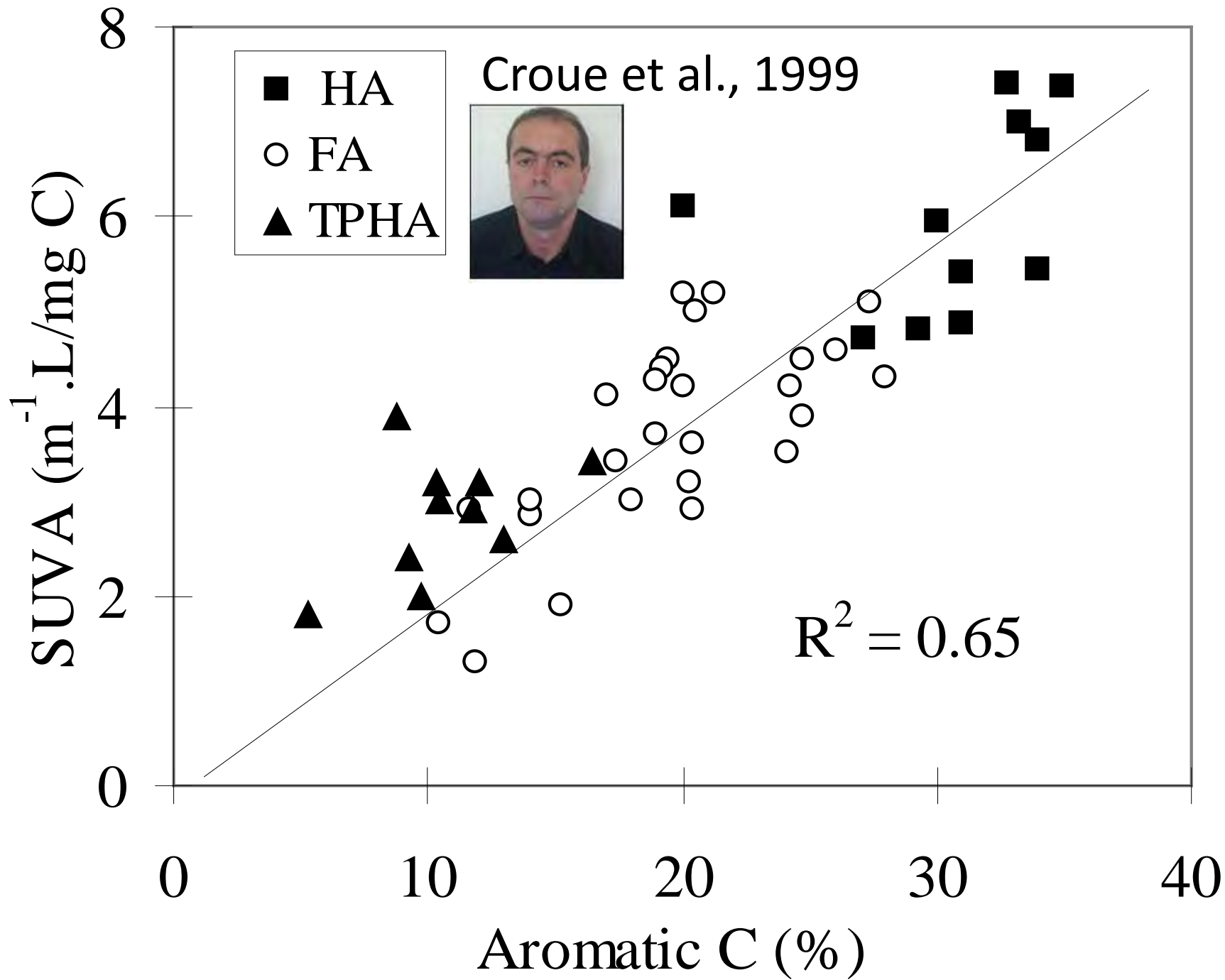
source		ash, %	elemental analysis, ^b %						
			C	H	O	N	S	P	X
Black Lake	F	0.47	55.01	4.58	38.43	1.16	0.57	ND	0.11
	H	5.54	55.63	4.13	35.43	1.97	0.58	ND	0.25
Coal Creek	F	1.26	52.80	4.45	38.39	0.95	0.70	ND	0.06
	H	5.61	56.09	4.01	36.47	1.38	1.45	0.05	0.07
Ogeechee River	F	0.39	54.08	4.82	38.49	0.93	1.27	0.20	0.05
	H	3.85	54.61	4.90	36.80	1.56	1.78	0.36	0.08
Ohio River	F	0.38	55.03	5.24	36.08	1.42	2.00	0.34	0.18
	H	1.49	54.99	4.84	33.64	2.24	1.51	0.06	0.13
Missouri River	F	0.26	54.55	5.17	36.94	1.39	1.64	0.64	0.10
	H	41.80	52.46	5.57	39.75	2.46	2.22	1.45	0.02

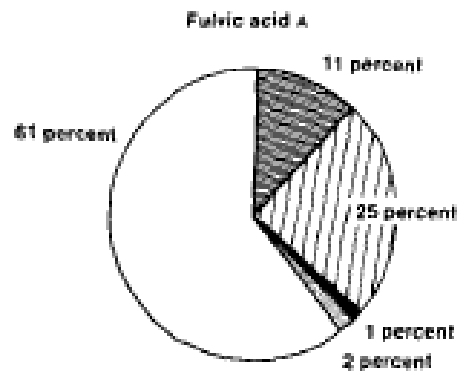
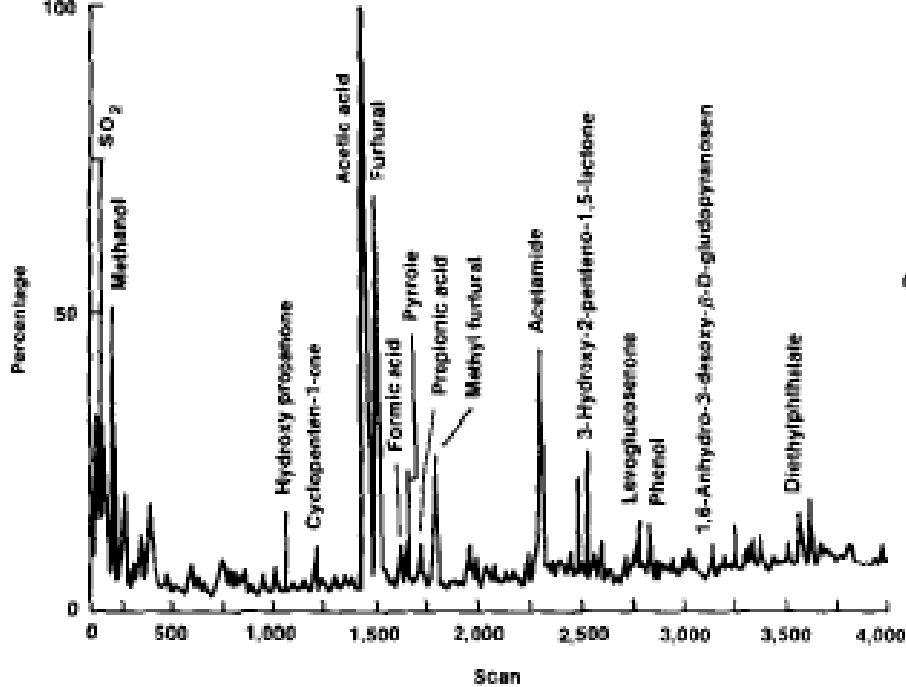
^aF, fulvic acid; H, humic acid. ^bND, not determined.

Table II. Characterization of Ten Extracted Aquatic Humic Substances^a

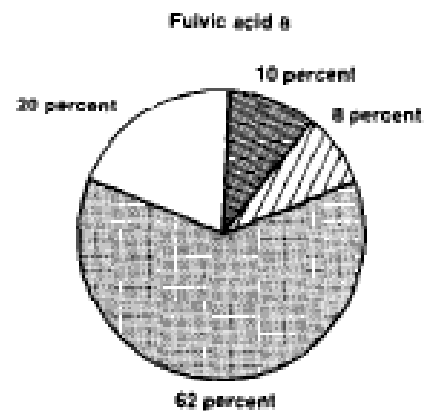
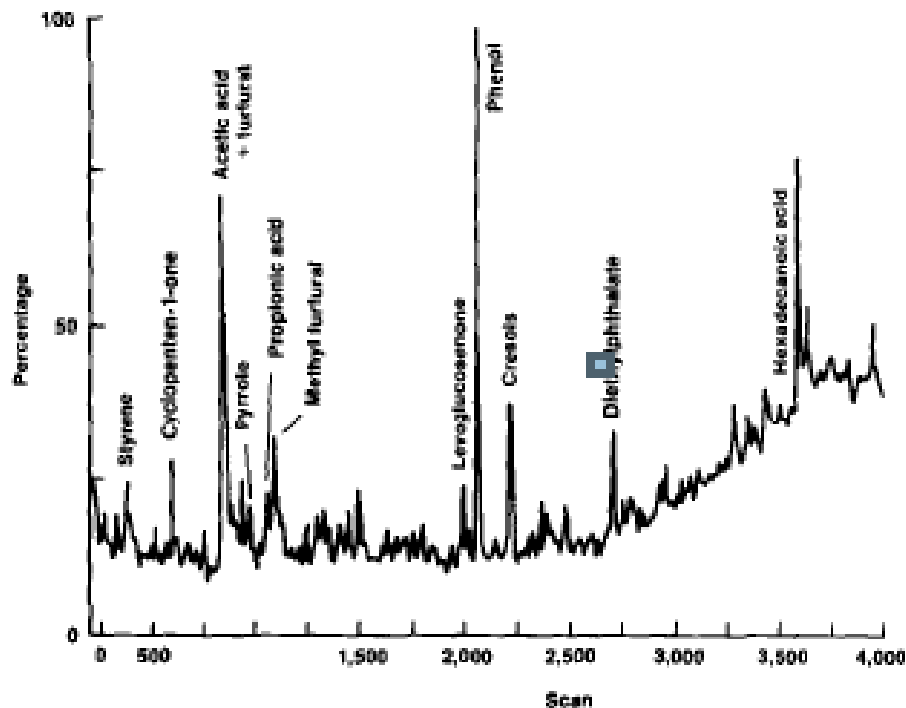
source		¹³ C NMR		mol size, Å	acidic groups, mequiv/g		specific absorbance, nm	
		% arom	% aliph		carboxyl	phenolic	254	400
Black Lake	F	17	83	6.1	5.7	1.5	0.0412	0.0039
	H	35	65	11.2	4.4	1.6	0.0736	0.0147
Coal Creek	F	19	81	7.3	6.1	2.1	0.0428	0.0047
	H	31	69	10.3	5.0	2.6	0.0540	0.0084
Ogeechee River	F	19	81	9.2	5.8	1.8	0.0370	0.0038
	H	31	69	12.3	4.0	2.0	0.0486	0.0071
Ohio River	F	14	86	5.5	5.0	1.0	0.0286	0.0026
	H	34	66	9.0	3.8	1.5	0.0544	0.0081
Missouri River	F	14	86	7.3	5.7	0.8	0.0300	0.0029
	H	30	70	9.2	2.8	5.4	0.0594	0.0089

^aF, fulvic acid; H, humic acid.





Bruchet,
Rousseau,
Mallevalle,
JAWWA, 82,
9, 66 (1990)



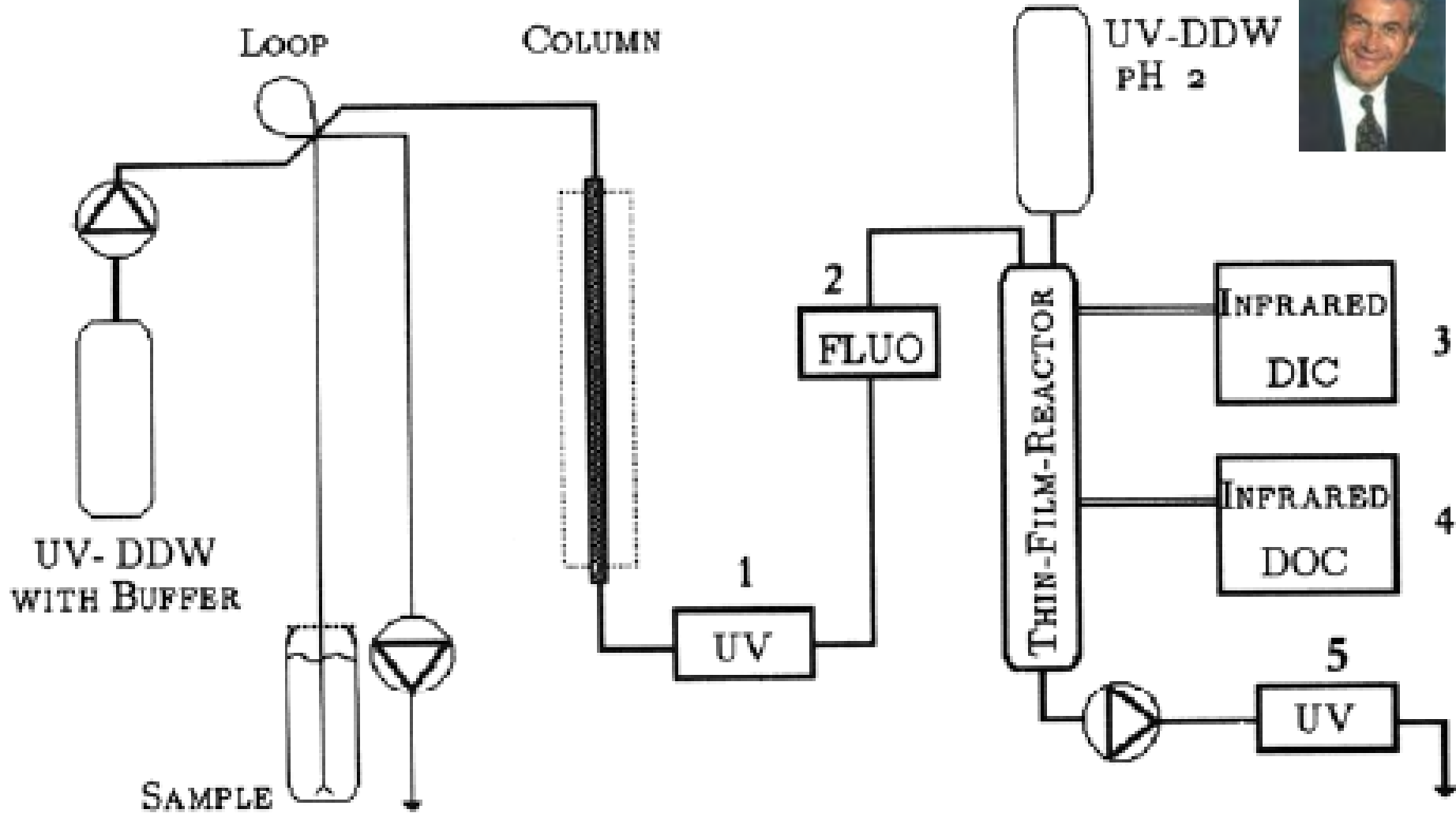
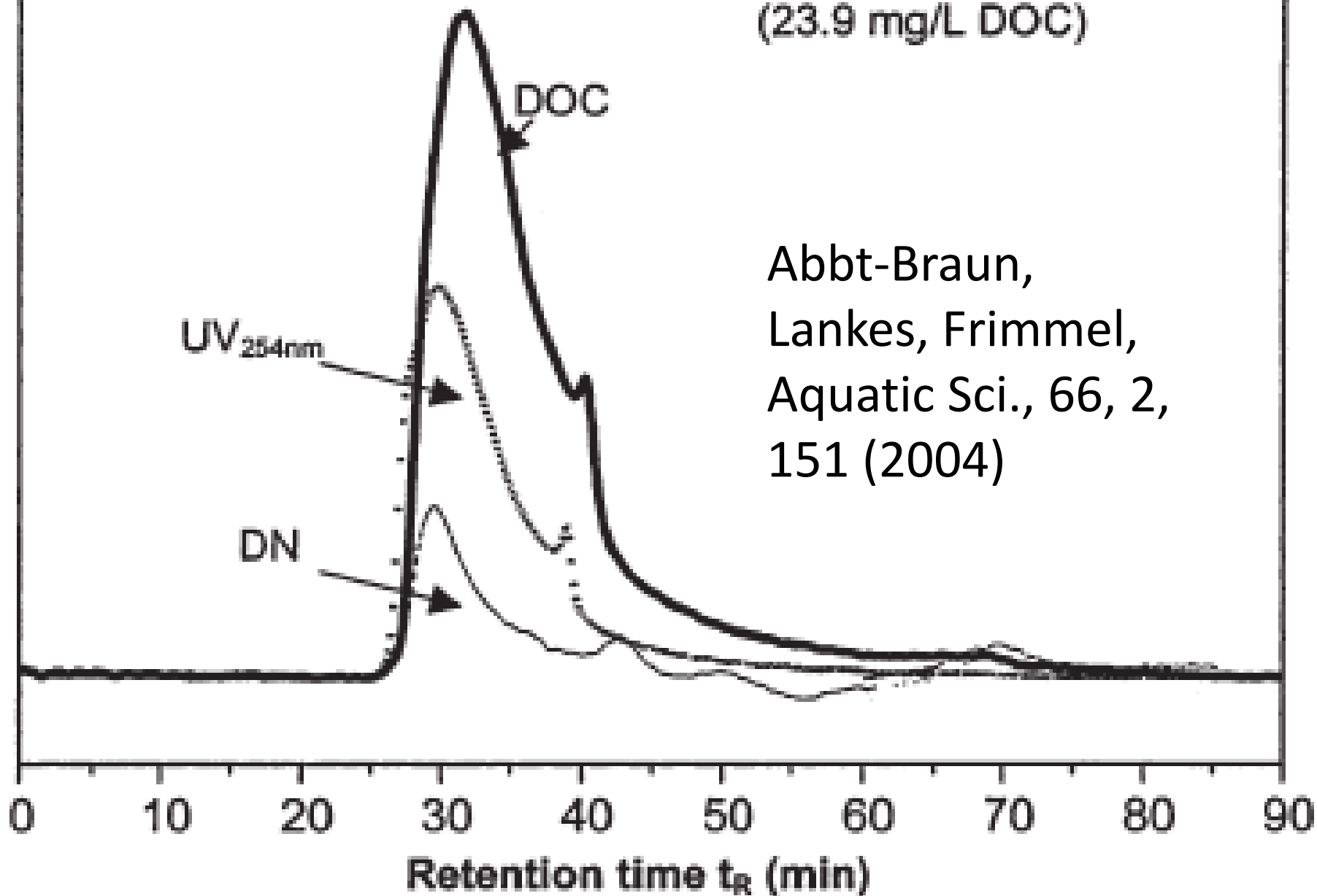


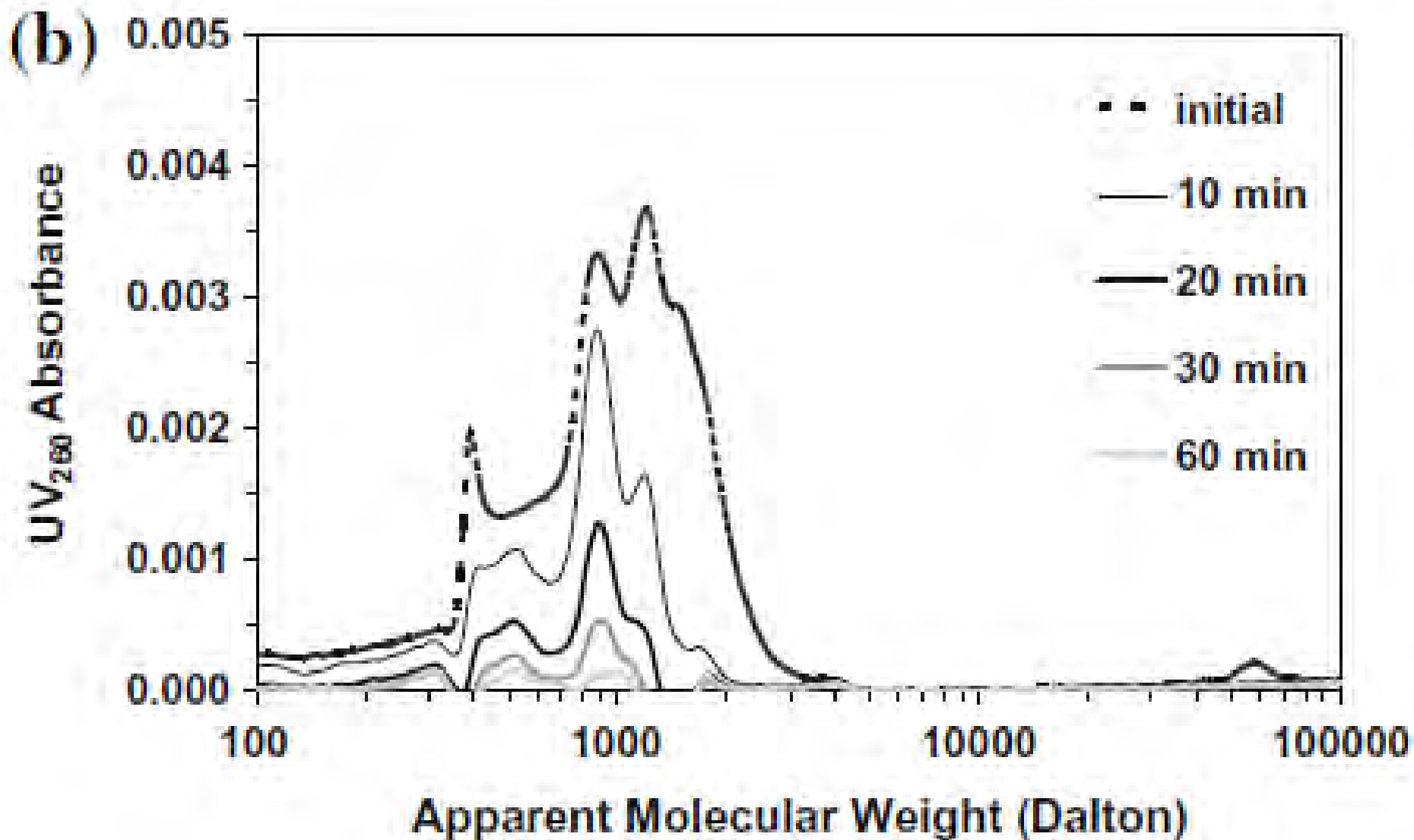
Figure 1. Schematic diagram of the liquid chromatographic system with a total of five detectors (UV-DDW: UV-irradiated double-distilled water).

gel chromatography

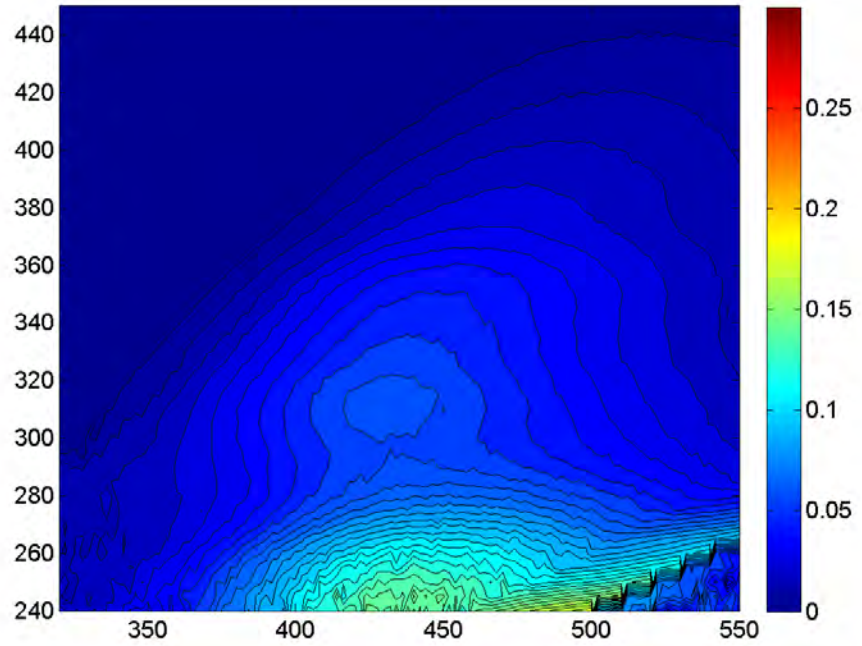
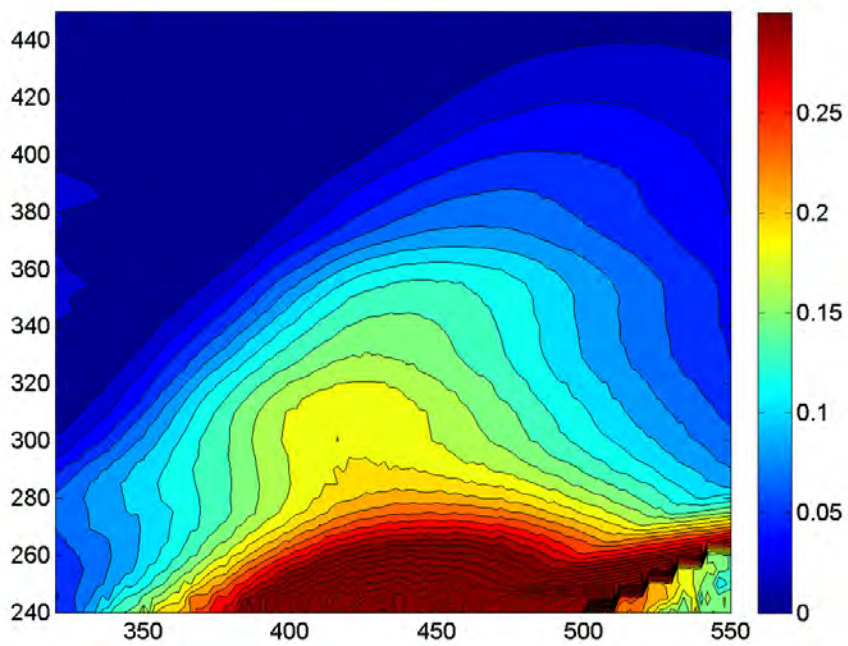
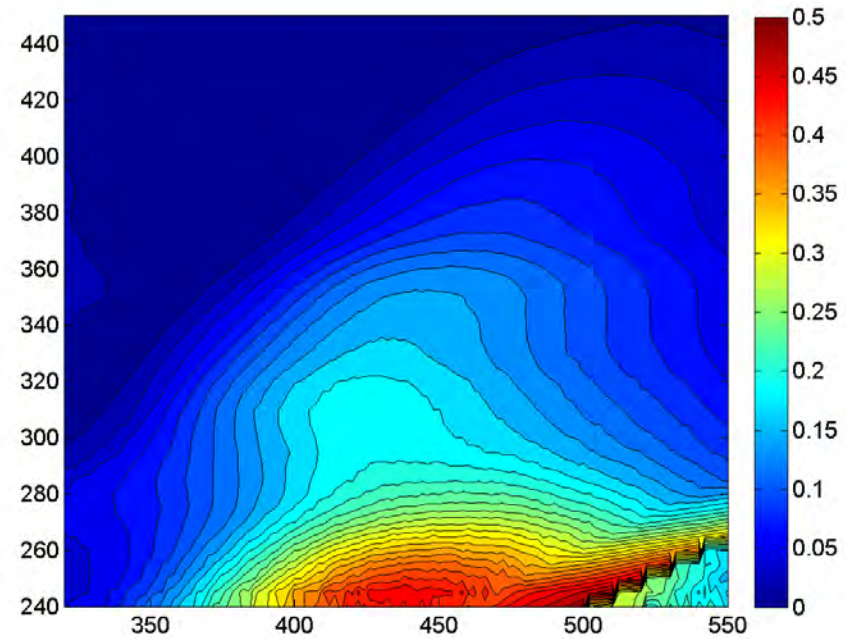
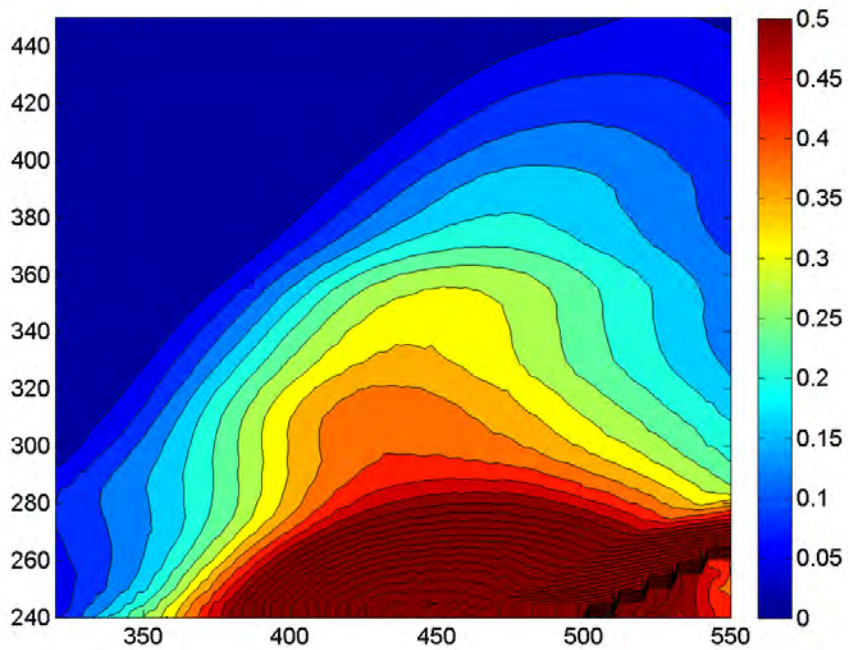
brown water (lake Hohloh)
(23.9 mg/L DOC)

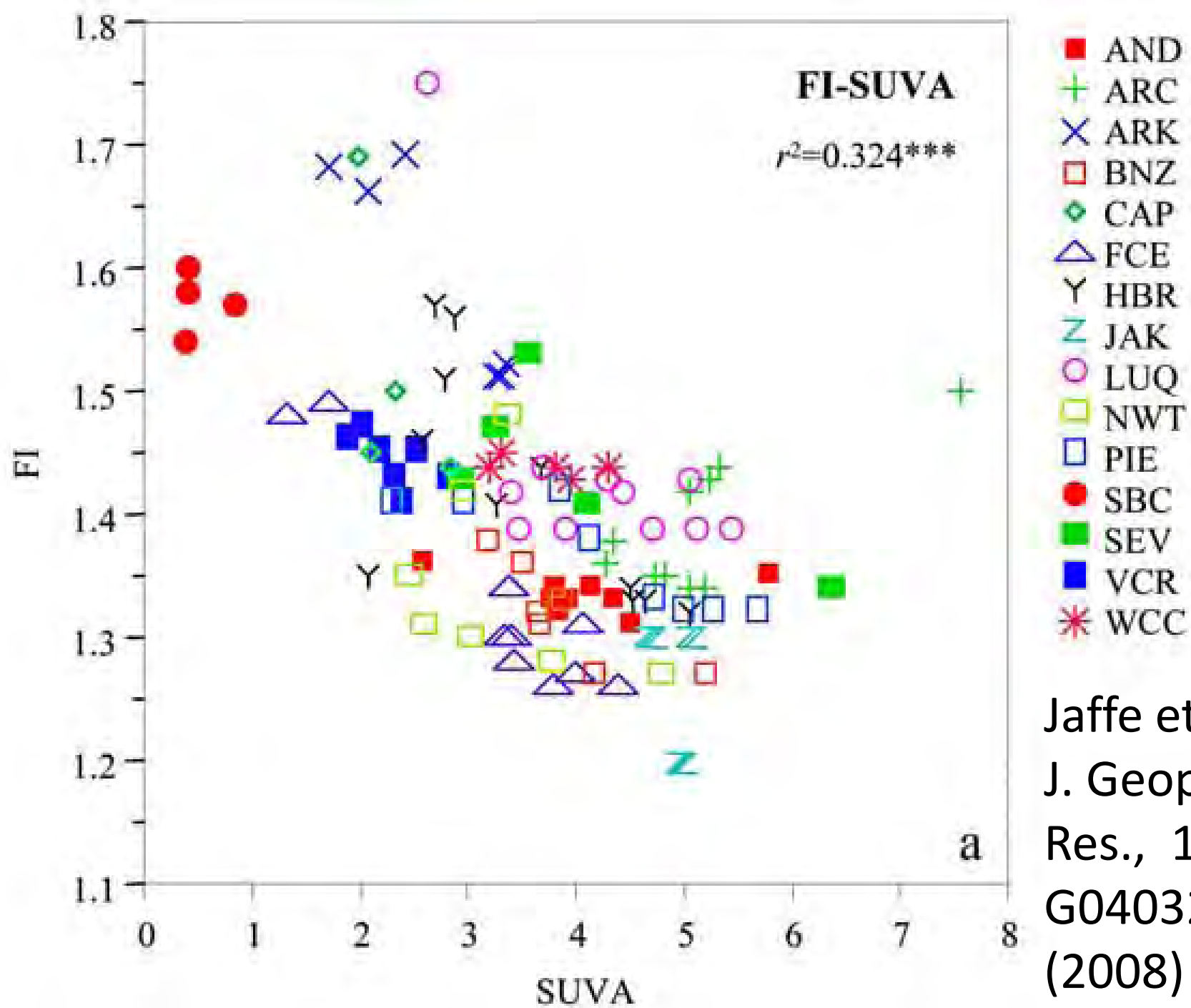
Relative intensity





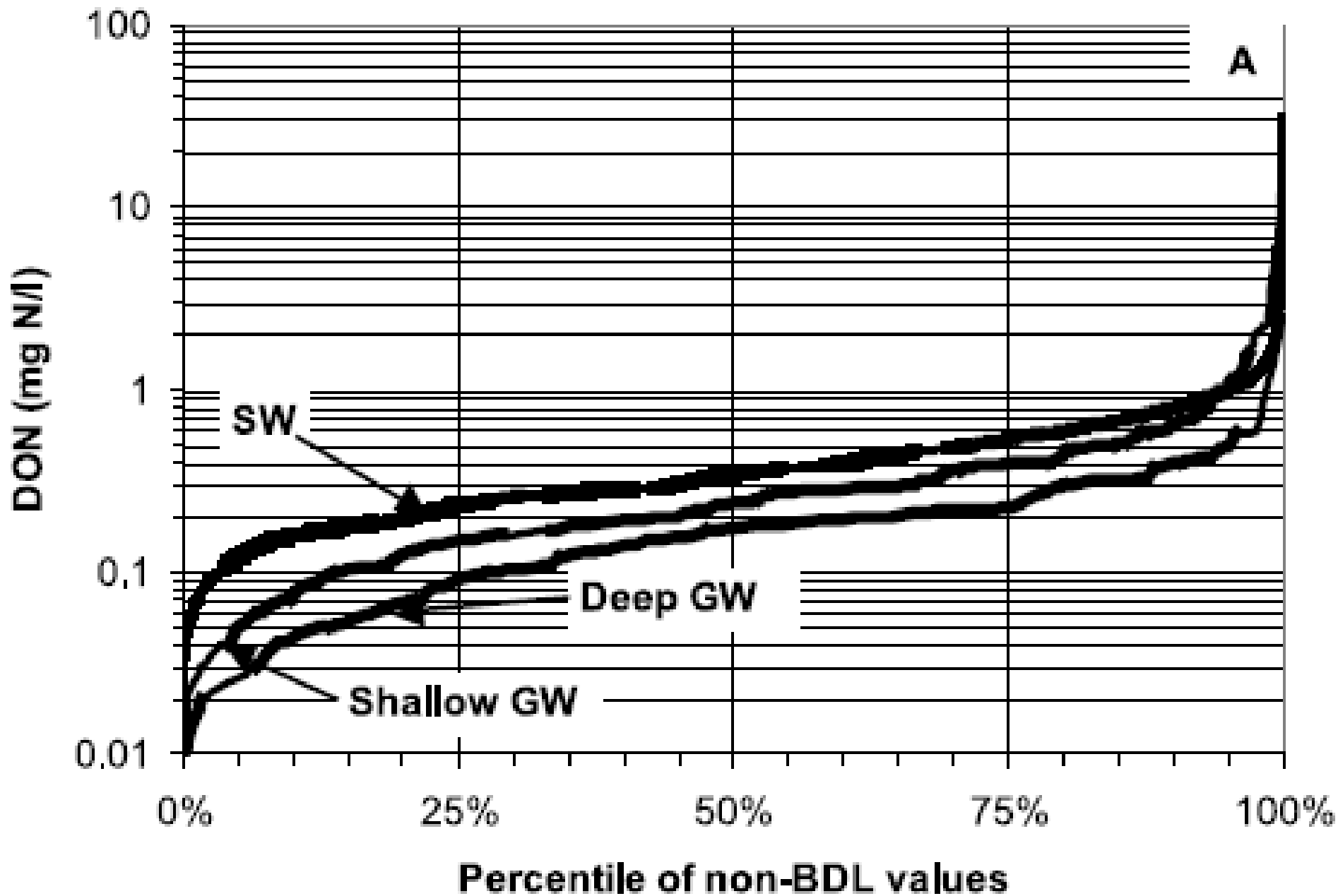
Liu, et al., Org. Geochem., 41, 2, 124 (2010)



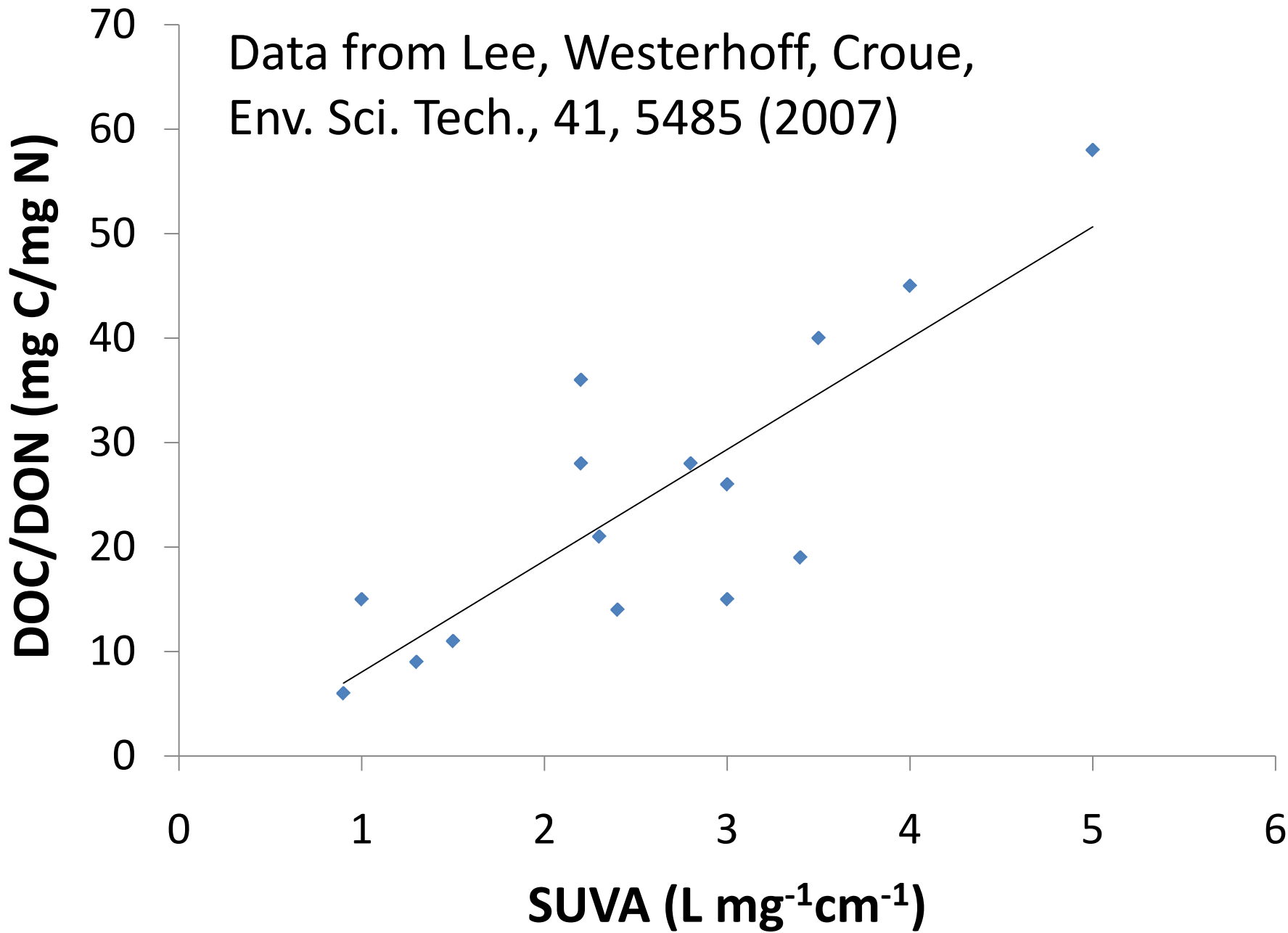


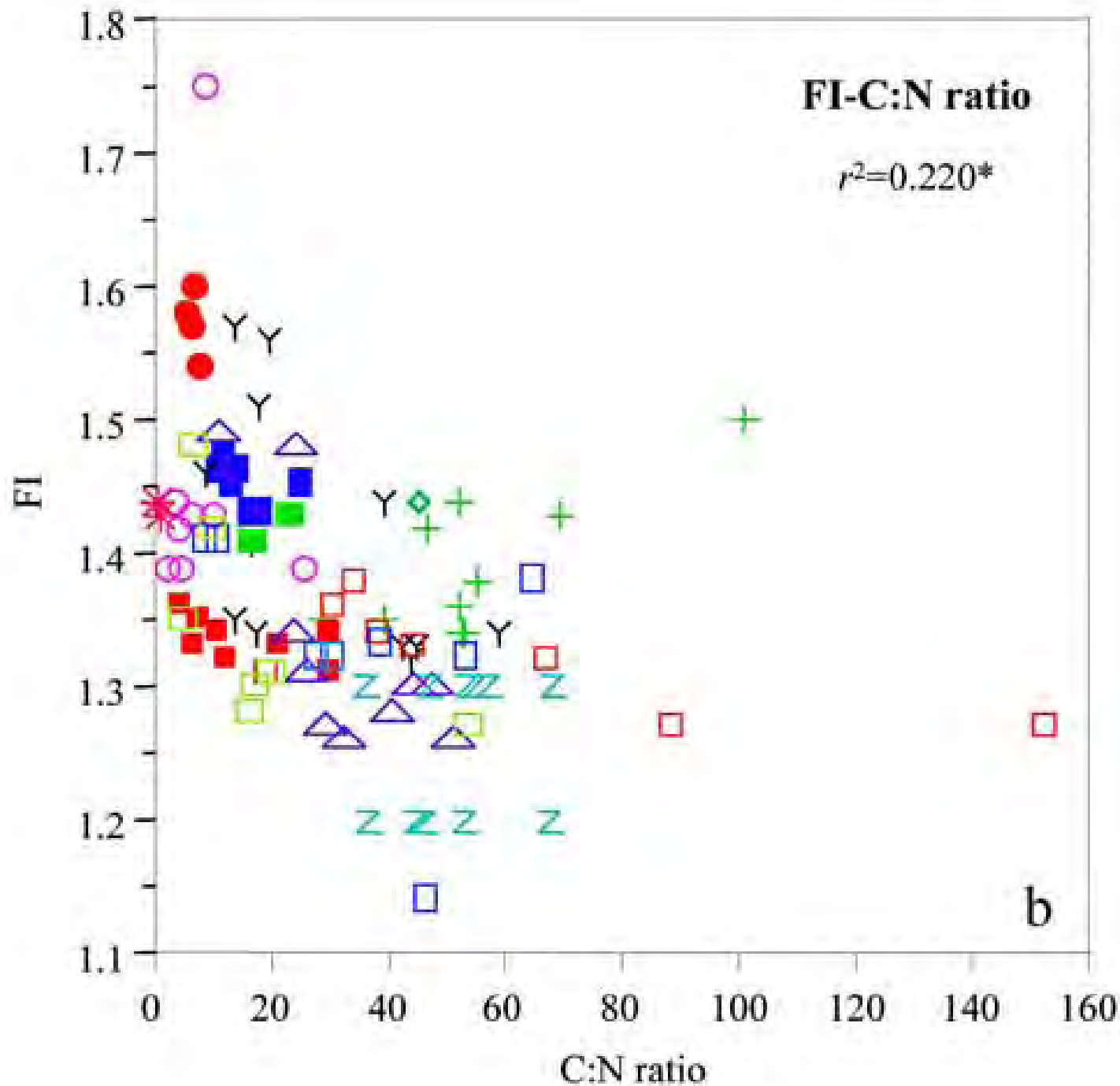
Jaffe et al.,
 J. Geophys.
 Res., 113,
 G04032
 (2008)

Westerhoff and Mash, Aqua, 51, 28, 415 (2002)



Data from Lee, Westerhoff, Croue,
Env. Sci. Tech., 41, 5485 (2007)





Jaffe et al.,
J. Geophys.
Res., 113,
G04032
(2008)

Dissolved Organic Material and Drinking Water

- DOM is source of yellow-brown color in drinking water
- DOM can be removed by coagulation
- DOM stabilizes particulate material and inhibits coagulation of particles
- DOM concentration typically controls the required coagulant dose for turbidity removal
- DOM exerts a significant oxidant demand
- DOM interferes with Fe and Mn oxidation and removal
- DOM interferes with oxidation of organic micropollutants
- When oxidized, DOM contributes to biological growth

Dissolved Organic Material and Drinking Water (cont'd)

- DOM can be removed by activated carbon adsorption but inhibits the removal of taste and odor compounds and organic micropollutants
- DOM can be removed by NF and RO, but causes membrane fouling
- DOM can be removed by anion exchange
- DOM inhibits precipitative softening
- DOM impacts corrosion in distribution systems
- DOM reacts with chlorine to form halogenated disinfection byproducts

2000's

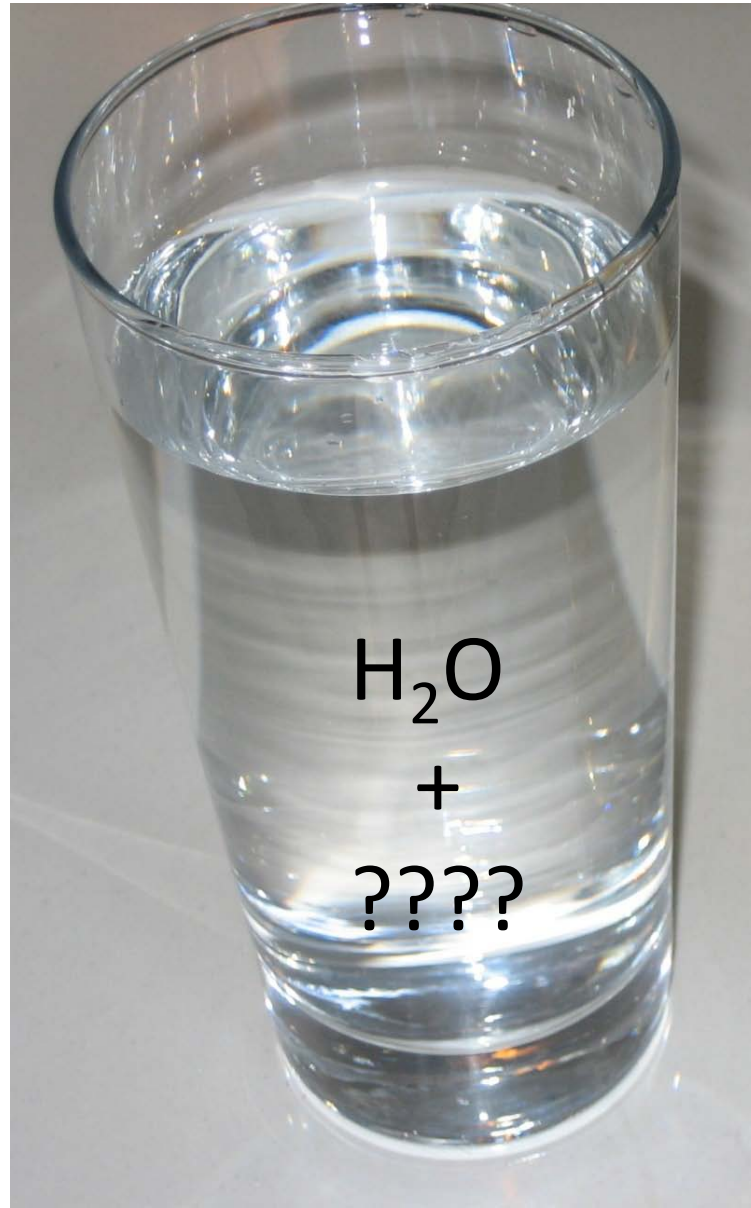
- Enhanced technologies for removing DOM from water
 - Optimized membrane treatment
 - Tailored adsorbents
 - Optimized oxidation coupled with engineered biological treatment

- Emerging DBPs



- Importance of DON
- Continuing characterization of DOM

The Next Fifty Years???



H_2O

+

????

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