Chlorine + Organic Matter

Formation of
Disinfection By-Products

Formation of DBPs

Chlorine + Precursors (TOC) ⇨ DBPs

This reaction is affected by

- TOC concentration
- TOC source / type
- chlorine dose
- bromide ion
- pH
- time (distrib. system)
- temperature
- sunlight - UV

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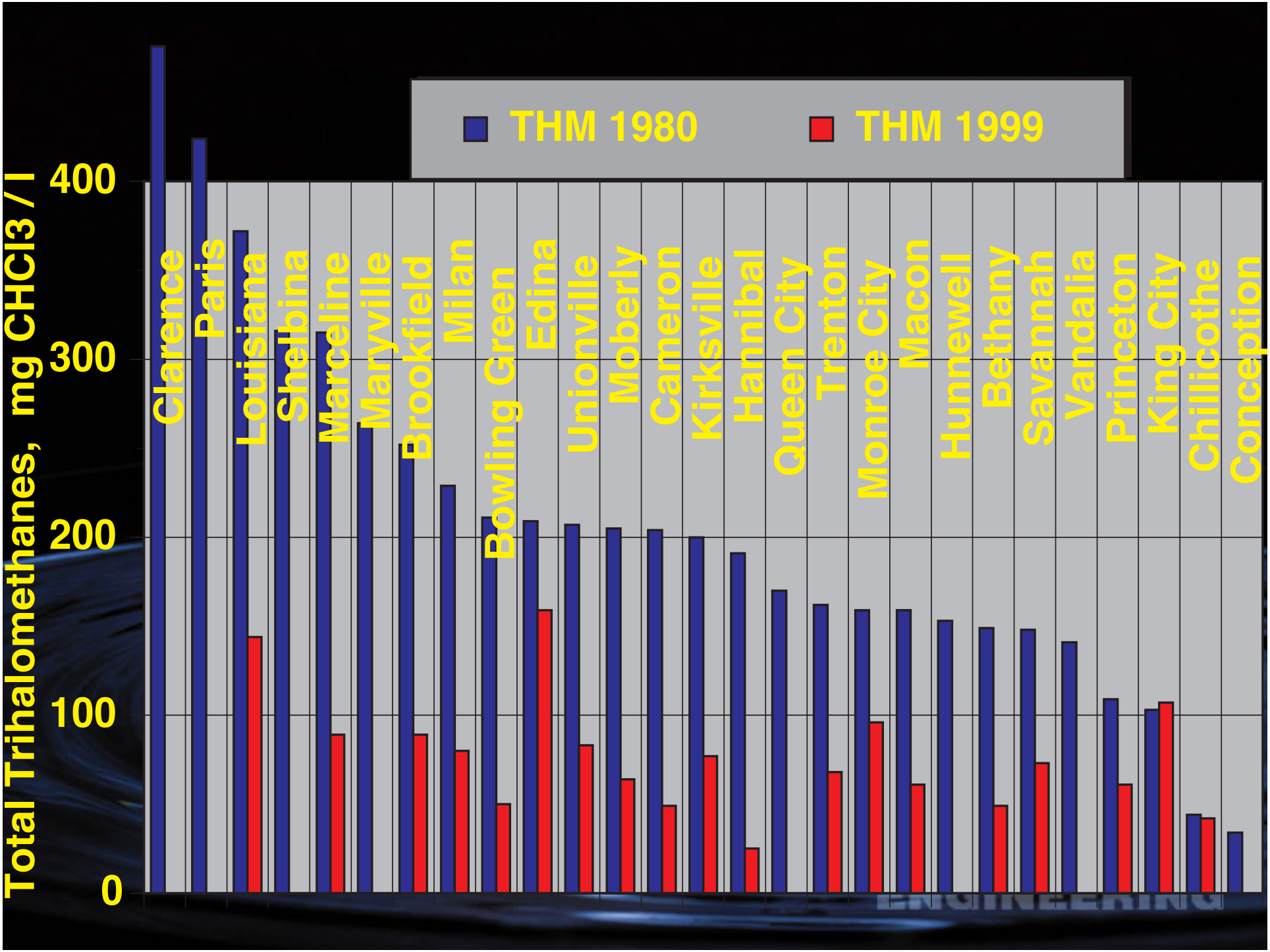
THM and HAA

Trihalomethanes (THM) - 1979

trichloromethane (chloroform)	$CHCl_3$
bromodichloromethane	$CHCl_2Br$
dibromochloromethane	$CHClBr_2$
tribromomethane (bromoform)	$CHBr_3$
	TTHM

Haloacetic Acids (HAA_9)

monochloro-acetic acid,
dichloro-, trichloro-,
bromochloro-, bromodichloro-,
dibromochloro-, monobromo-,
dibromo-, and tribromoacetic acid


THM 1980
THM 1999
Total Trihalomethanes, mg CHCl3 / l
400
300
200
100
0
Clarence
Paris
Louisiana
Shelbina
Marceline
Maryville
Brookfield
Milan
Bowling Green
Edina
Unionville
Moberly
Cameron
Kirksville
Hannibal
Queen City
Trenton
Monroe City
Macon
Hunnewell
Bethany
Savannah
Vandalia
Princeton
King City
Chillicothe
Conception

Health Effects

"… while EPA cannot conclude there is a causal link between exposure to chlorinated surface water and cancer, these studies have suggested an association, albeit small, between bladder, rectal, and colon cancer and exposure to chlorinated surface water."

"As with cancer, EPA cannot conclude at this time there is a causal link between exposure to DBPs and reproductive and developmental effects."

"While EPA recognizes there are data deficiencies in the information on the health effects from the DBPs and the levels at which they occur, the Agency believes the weight-of-evidence presented by the available epidemiological studies on chlorinated drinking water and toxicological studies on individual DBPs support a potential hazard concern and warrant regulatory action at this time to reduce DBP levels in drinking water."

[Federal Register: December 16, 1998 (Volume 263, Number 2410]

Microbial-DBP Rules

- Interim Enhanced Surface Water Treatment Rule
- Stage 1 Disinfection Byproducts Rule
- Filter Backwash Recycling Rule
- Long Term 1 Enhanced Surface Water Treatment Rule
- Ground Water Rule
- Long Term 2 Enhanced Surface Water Treatment Rule
- Stage 2 Disinfection Byproducts Rule

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Stage 1 D/DBP Rule

MRDL (Maximum Residual Disinfectant Level)

Chlorine	4 mg Cl_2 / l
Chloramine	4 mg Cl_2 / l
Chlorine Dioxide	0.8 mg ClO_2 / l

MCLs for Disinfection Byproducts

Total THM	80 µg / l
HAA_5	60 µg / l
Chlorite ion, ClO_2^-	1 mg/ l (from ClO_2)
Bromate ion, BrO_3^-	10 µg / l (from ozone)

New Drinking Water Hazard

Monochloramine + Dimethylamine

⊥ N-nitrosodimethylamine (NDMA)

- nitrogen in agricultural runoff
- nitrogen-bearing exchange resins
- 20 nanograms/liter (CA action level)
- UV oxidation

DBP Removal and Control

1. Control of Precursors (TOC) at the Source
2. Removal of DBP Precursors and Control of DBP Formation
3. Removal of DBP after Formation (Stripping)
4. Use of Alternative Disinfectants
   - Chlorine Dioxide
   - Chloramines
   - Ozone
   - UV

DBP Removal and Control

1. Control of Precursors (TOC) at the Source

   Selective withdrawal from reservoirs

   Plankton control

   Alternative sources

Organic Constituents

Total Organic Carbon (TOC) =

Purgeable (methane, VOC)
Non-Purgeable (NPOC)

Dissolved (fulvic, humic matter)
Particulate (bacteria, algae, …)

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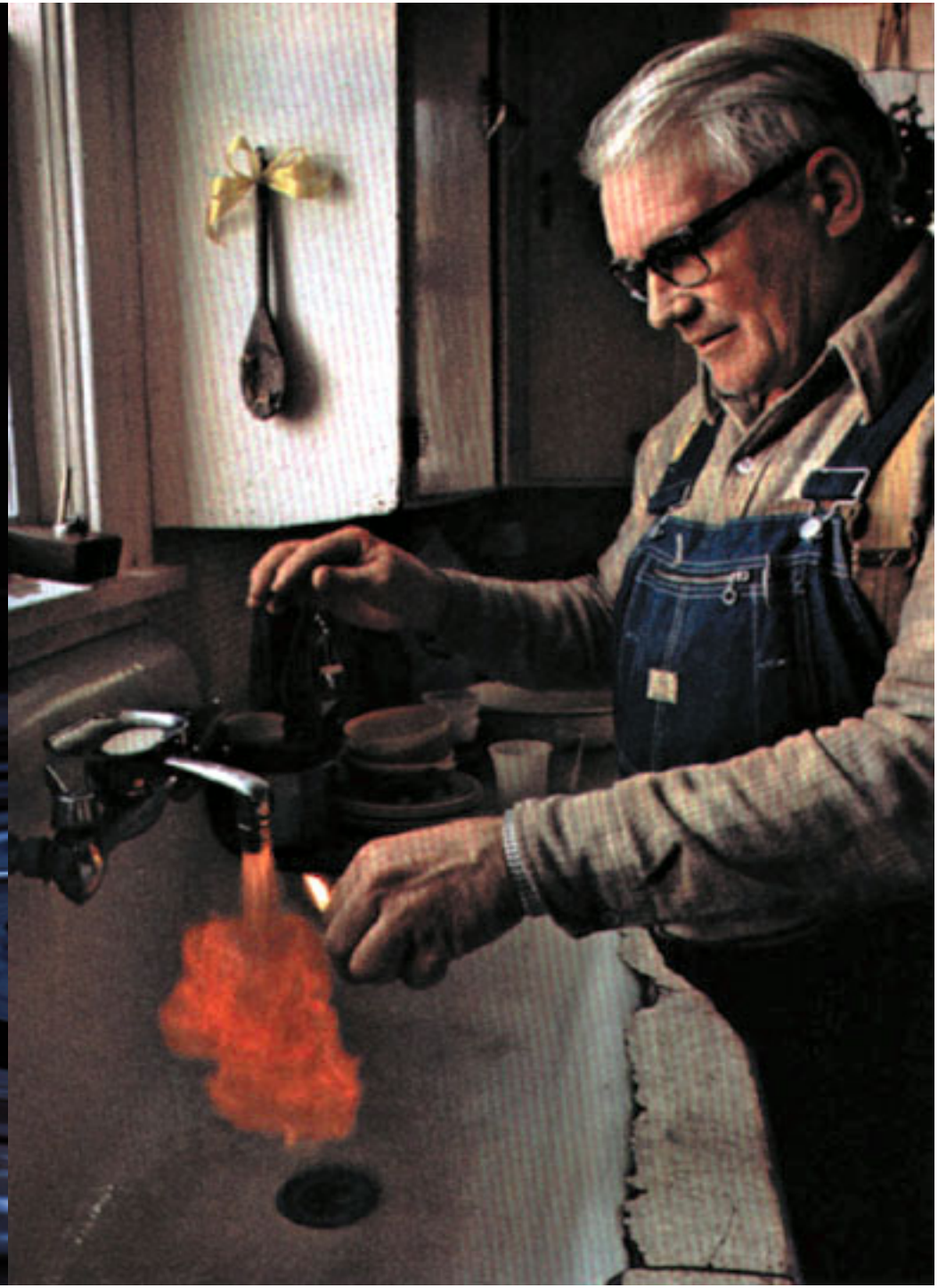
Total Organic Carbon

DISSOLVED		PARTICULATE	
Purgeable	*Non-Purgeable*	*Cell Mass*	*Organic Detritus*
• methane	• humic materials	• algae	• woody fibers
• volatile organic matter	• fulvic and humic acids	• bacteria	• pollen

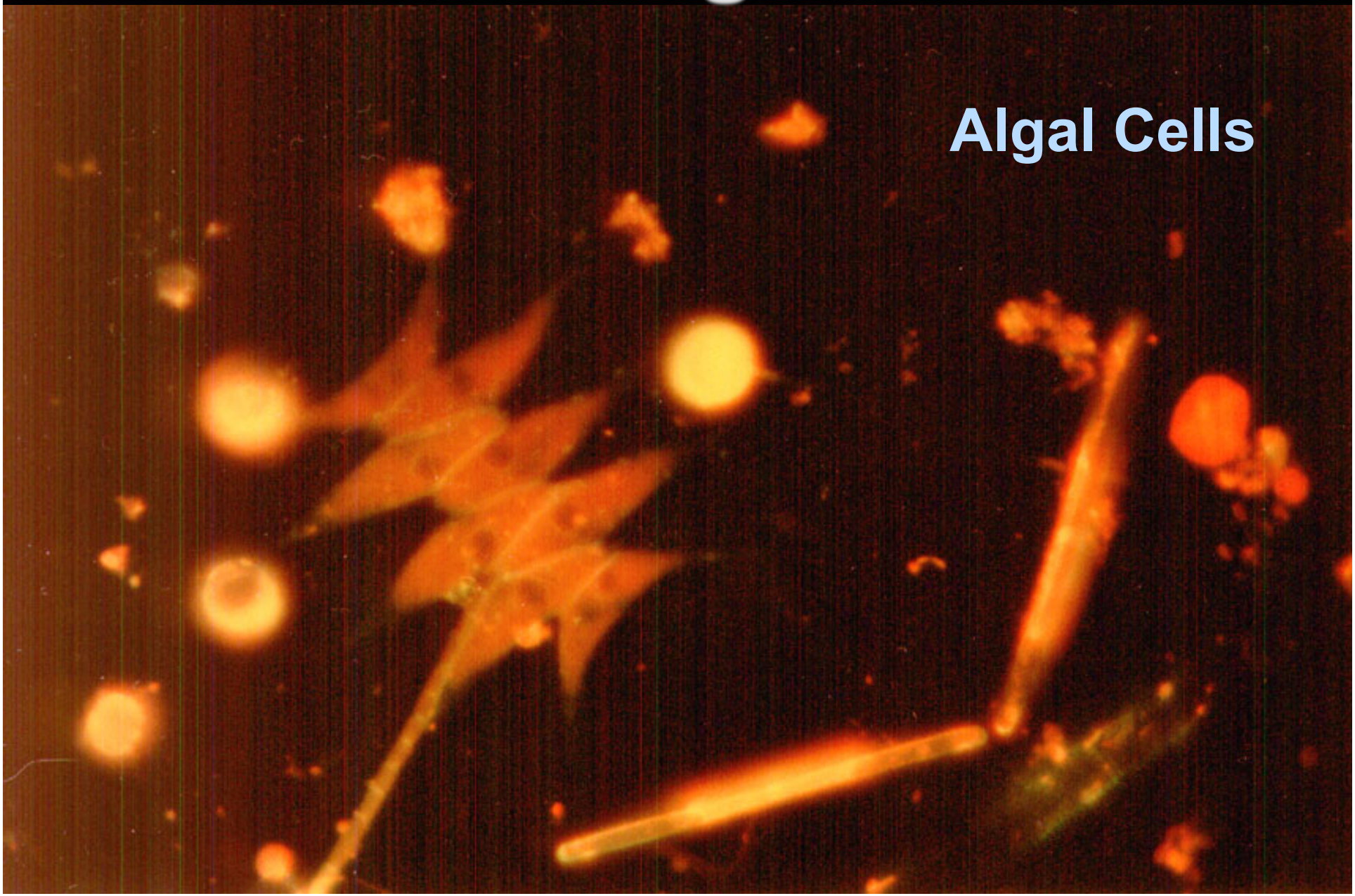
Purgeable

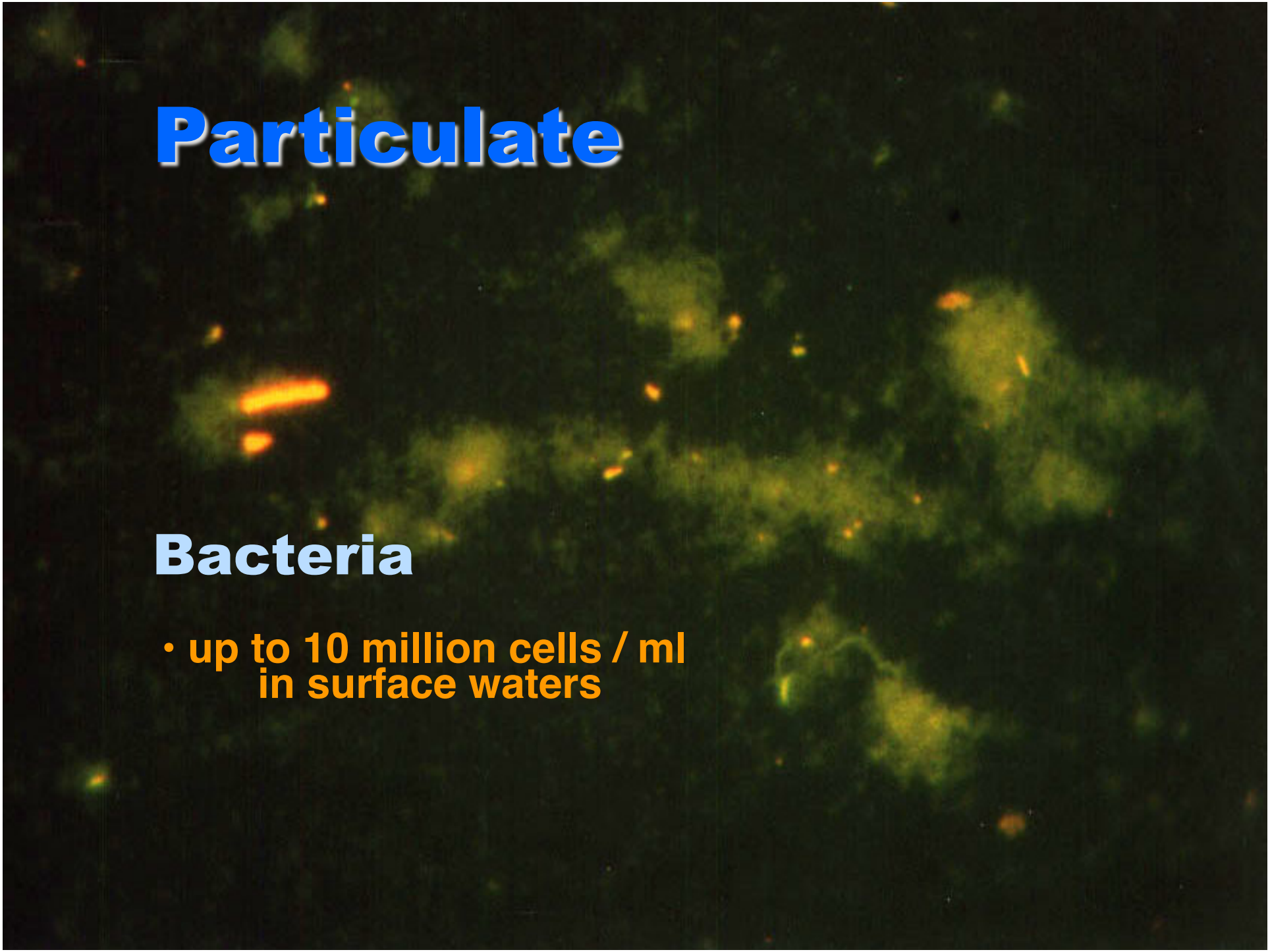
Methane

- up to 77 mg CH_4/l
- wells used for home heating, cooking
- wellhouse explosion



Particulate Organic Carbon



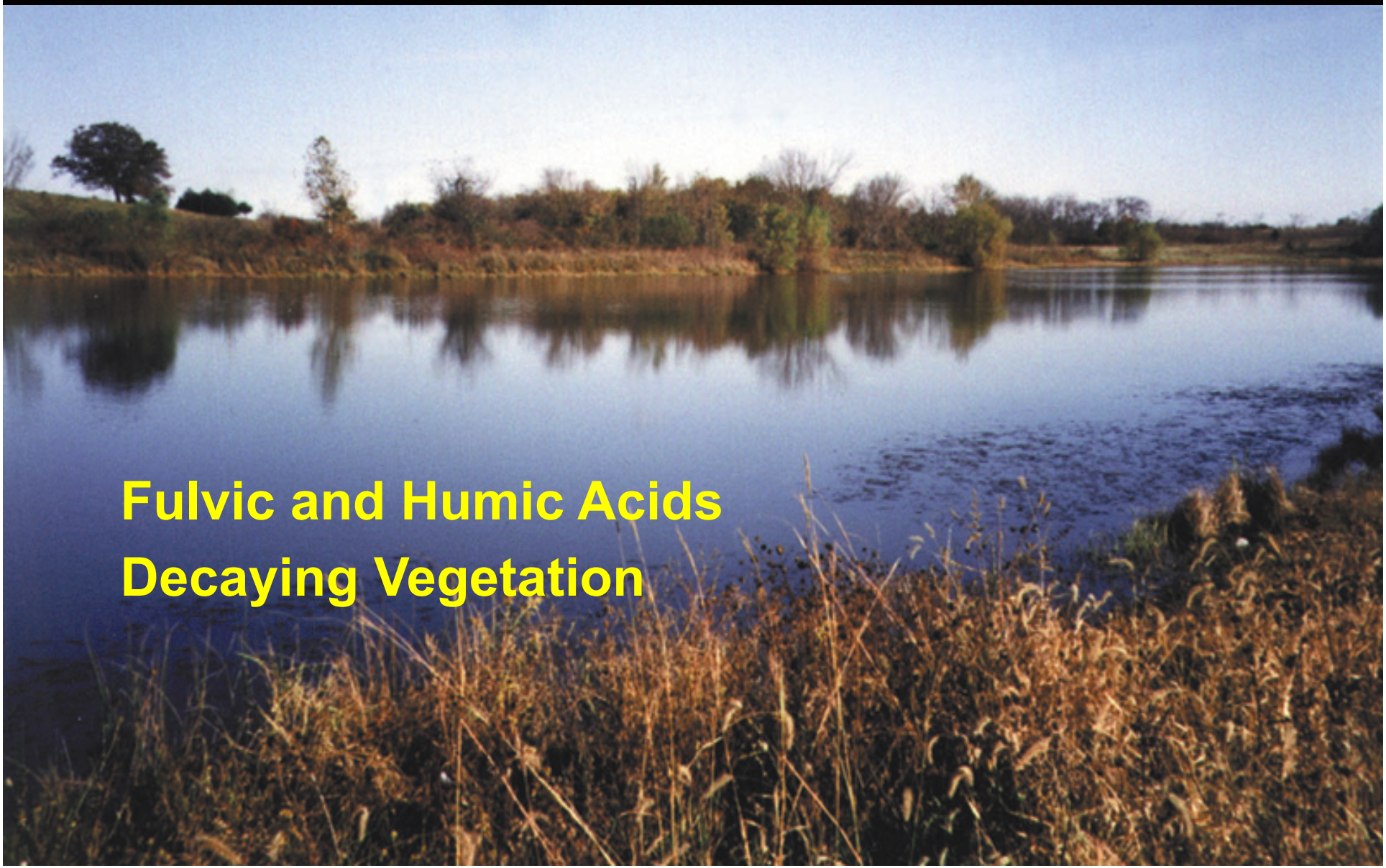


Particulate

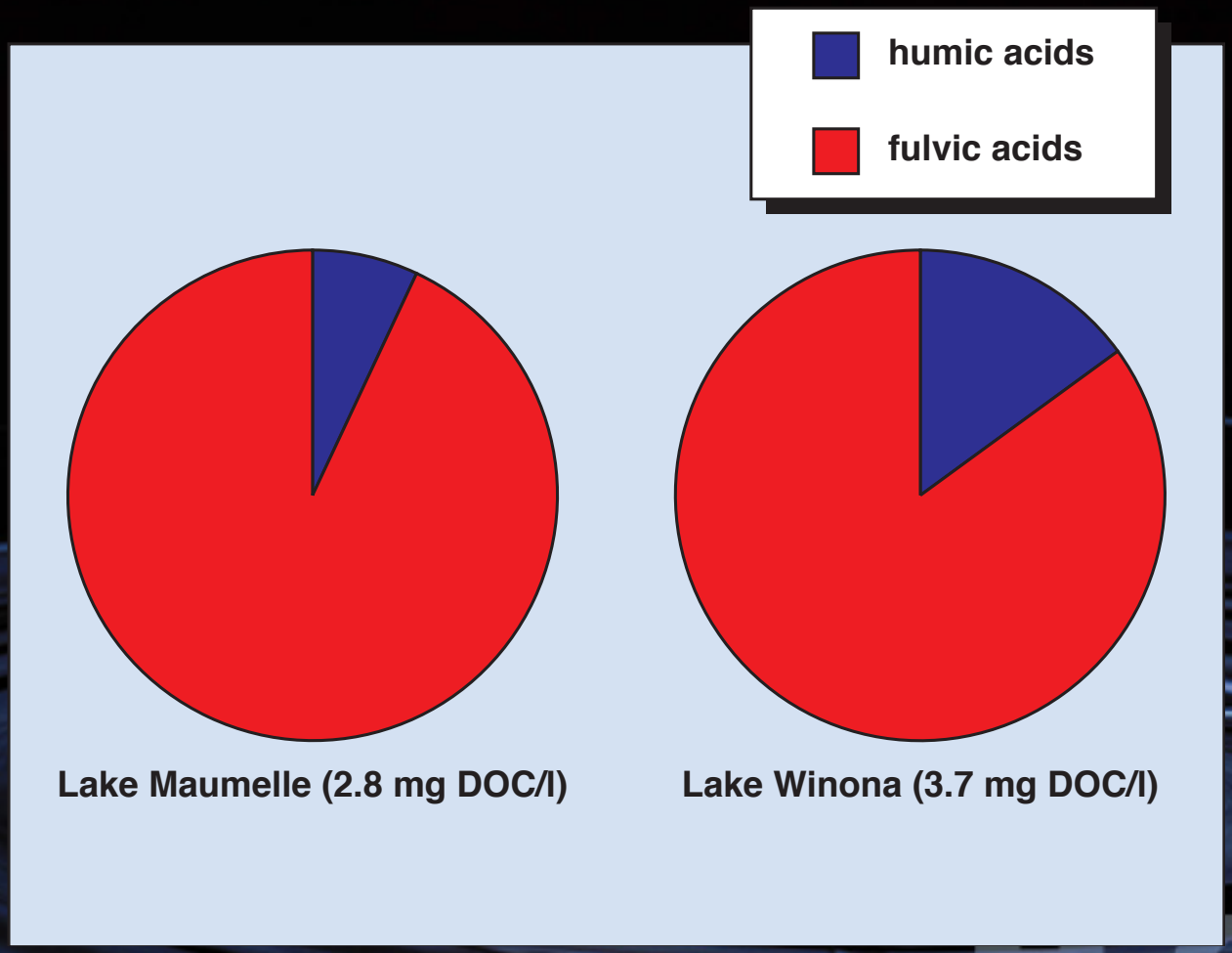
Bacteria

- up to 10 million cells / ml in surface waters

Dissolved Organic Carbon



Humic and Fulvic Acids



Cameron, MO Lakes

TOC in Missouri Waters

Source Water	TOC (avg)
MO Lakes	4.8
MO Rivers	3.6
Wells < 100 feet	1.2
Wells > 100 feet	0.2

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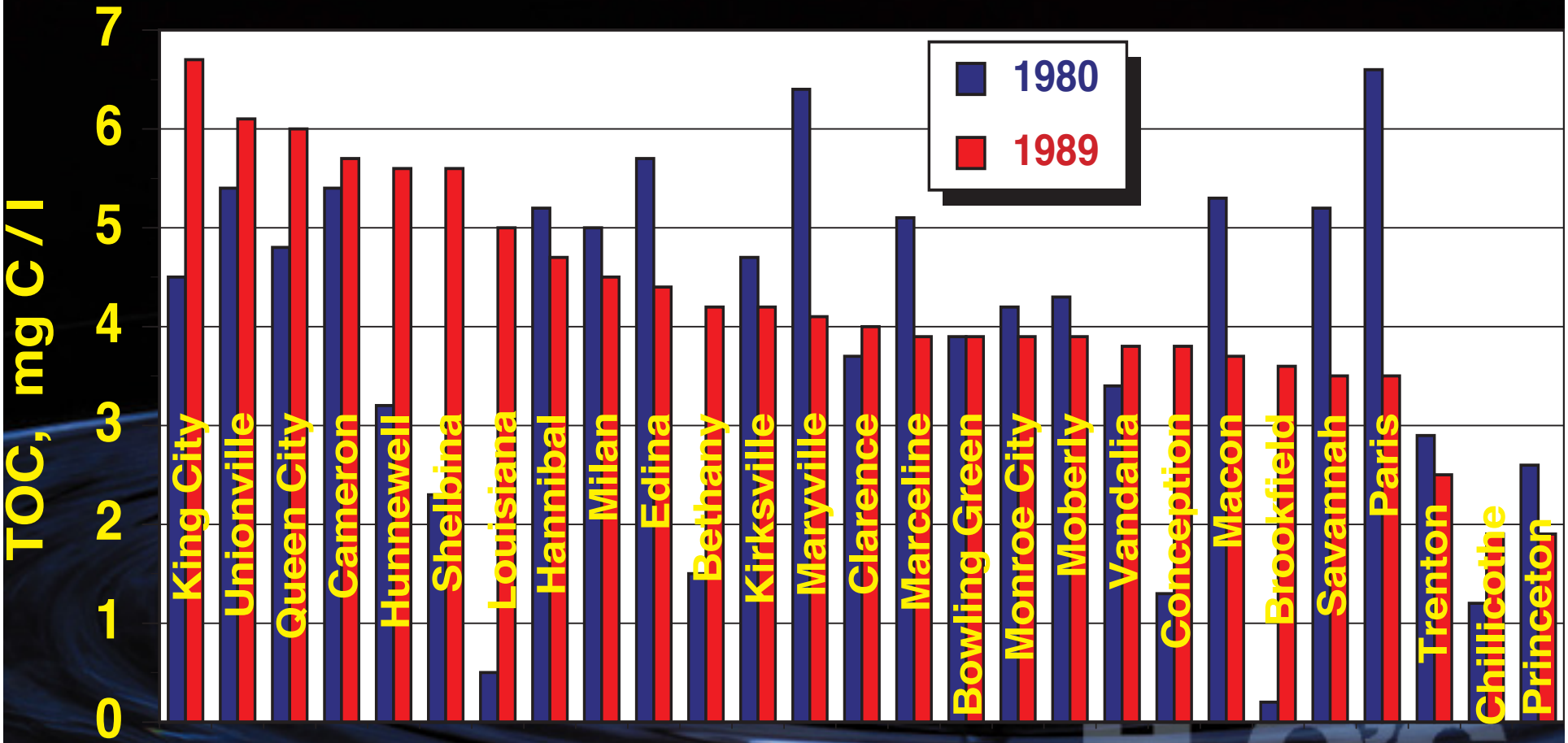
Historical TOC Data



Mississippi River DOC

Mississippi River & Tributaries	DOC, mg C/l	Discharge, m3/s
Minneapolis, MN	12	410
La Crosse, WI	10	1,600
Dubuque, IA	9.9	2,300
Davenport, IA	8.5	2,600
Quincy, IL	6.4	3,900
Missouri River	3.7	1,800
St. Louis, MO	5.0	7,300
Cairo, IL	5.2	7,800
Ohio River	2.4	4,000
Memphis, TN	4.4	13,400
Greenville, MS	4.1	15,600
Natchez, MS	3.8	17,600
Baton Rouge, LA	3.8	16,000
New Orleans, LA	3.7	4,340

DBP Precursor Removal Requirements by Enhanced Coagulation or Softening

Percent TOC Removal Required = (TOC raw - TOC treated / TOC raw) x 100%

Source Water TOC, mg C / l	Alkalinity 0 - 60 mg $CaCO_3$ eq./l	Alkalinity 60 - 120 mg $CaCO_3$ eq./l	Alkalinity >120 mg $CaCO_3$ eq./l
> 2 - 4	35	25	15
> 4 - 8	40	35	25
> 8	50	40	30

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