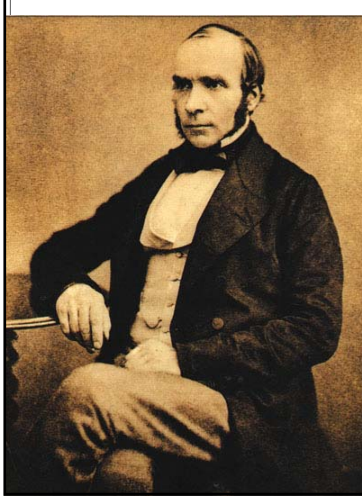
CEE/EHS 597B

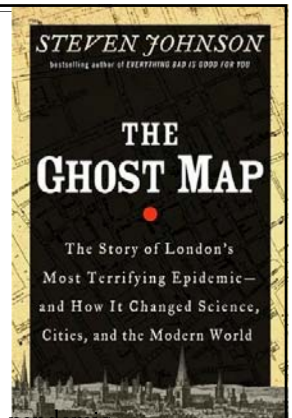
Class #15:

Special Treatment Issues: DBPs

Dave Reckhow

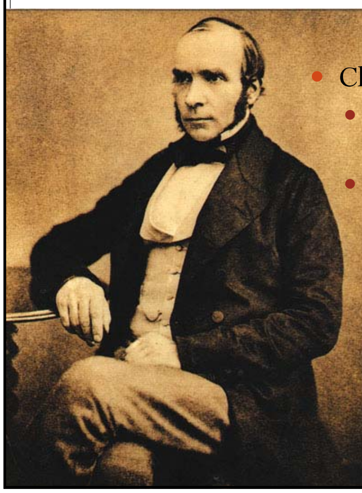


2007



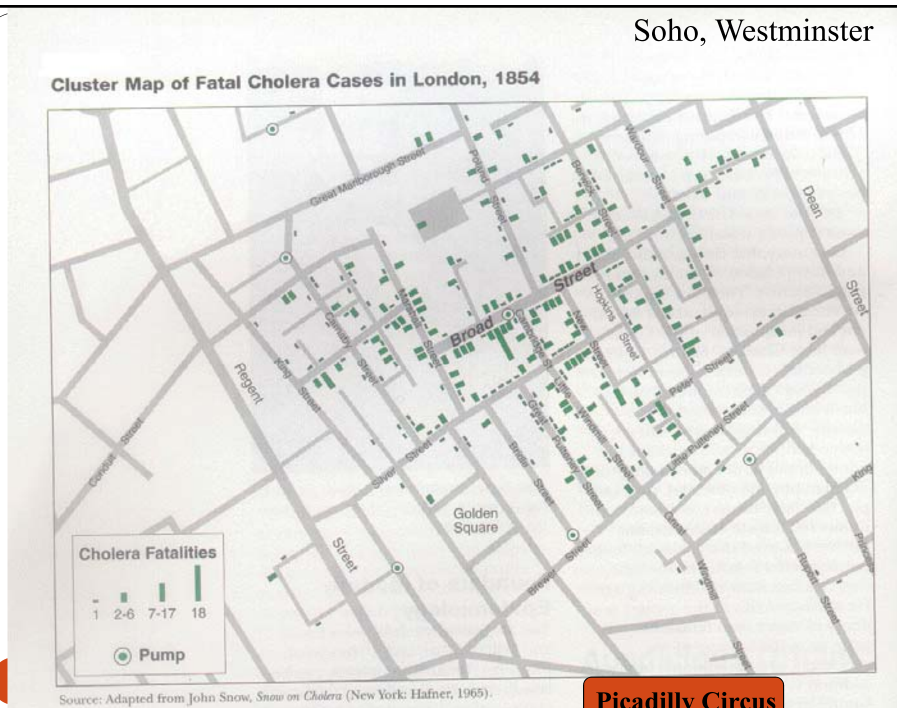
John #1: Dr. John Snow

1813-1858



- Cholera
  - First emerged in early 1800s
  - 1852-1860: The third cholera pandemic
    - Snow showed the role of water in disease transmission
      - London's Broad Street pump (Broadwick St)
    - Miasma theory was discredited, but it took decades to fully put it to rest

Soho, Westminster



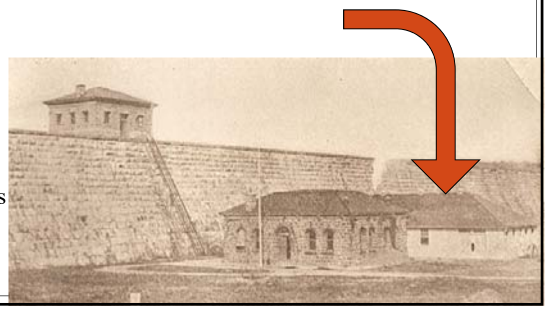
Picadilly Circus

Photo courtesy of the Leal family and Mike McGuire

1858-1914

John #2: Dr. John L. Leal

- Jersey City's Boonton Reservoir
- Leal experimented with chlorine, its effectiveness and production
  - George Johnson & George Fuller worked with Leal and designed the system (1908)



"Full-scale and continuous implementation of disinfection for the first time in Jersey City, NJ ignited a disinfection revolution in the United States that reverberated around the world"

M.J. McGuire, JAWWA 98(3)123

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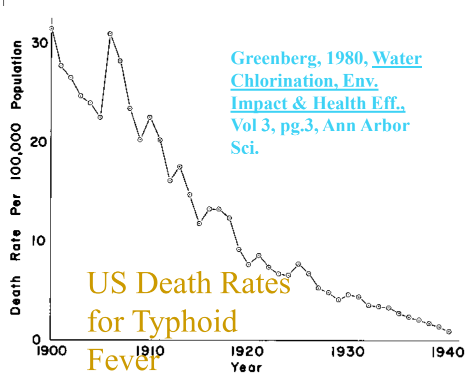
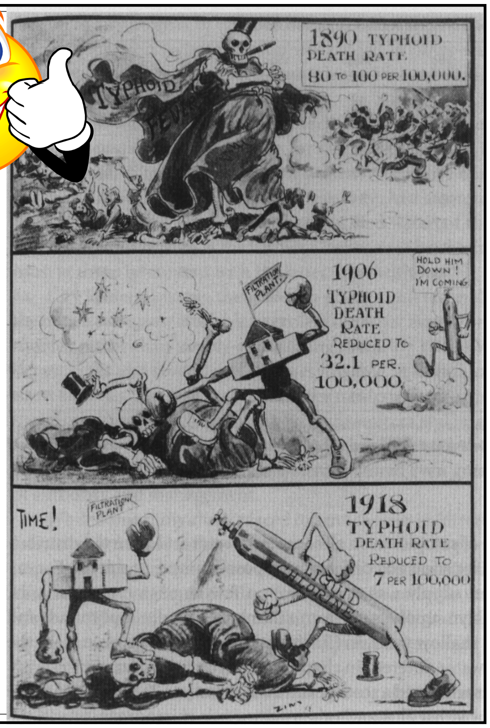
Chlorination

- 1-2 punch of filtration & chlorination



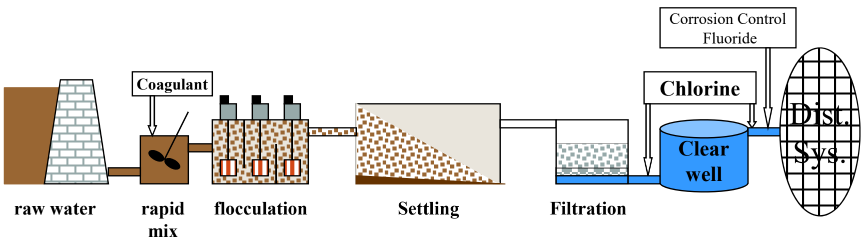
Greenberg, 1980, Water Chlorination, Env. Impact & Health Eff., Vol 3, pg.3, Ann Arbor Sci.



Melosi, 2000, The Sanitary City, John Hopkins Press

Conventional Treatment: 1910-present

- Coagulation & solids separation
  - rapid mix, flocculation, settling, filtration
- Disinfection
  - including clearwell for contact time
- Most common for surface water



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John #3: Johannes J. Rook

1921-2010

- Short Biography
  - Education
    - PhD in Biochemistry: 1949
  - Work experience
    - Technological Univ., Delft (~'49-'54)
      - Laboratory for Microbiology
    - Lundbeck Pharmaceuticals in Copenhagen, (~'55-?)
    - Noury Citric acid Factory (in Holland)
    - Amstel Brewery
    - Rotterdam Water Works by 1963, chief chemist (1964-1984).
    - 1984-1986; Visiting Researcher at Lyonnaise des Eaux, Le Pecq.
- Early Research
  - 1955, Microbiological Deterioration of Vulcanized Rubber
    - Applied Micro.
  - 1964, secured funds for a GC at Rotterdam
    - Carlo Erba with gas sample loop

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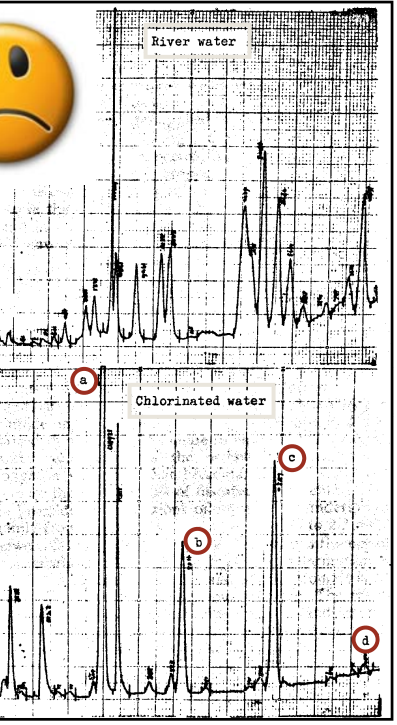
John Rook & DBPs

- Major Contributions
  - Brought headspace analysis from the beer industry to drinking water
    - T&O problems
  - Found trihalomethanes (THMs) in finished water
    - Carcinogens !?!
  - Published in Dutch journal H2O, Aug 19, 1972 issue
  - Deduced that they were formed as byproducts of chlorination
  - Proposed chemical pathways



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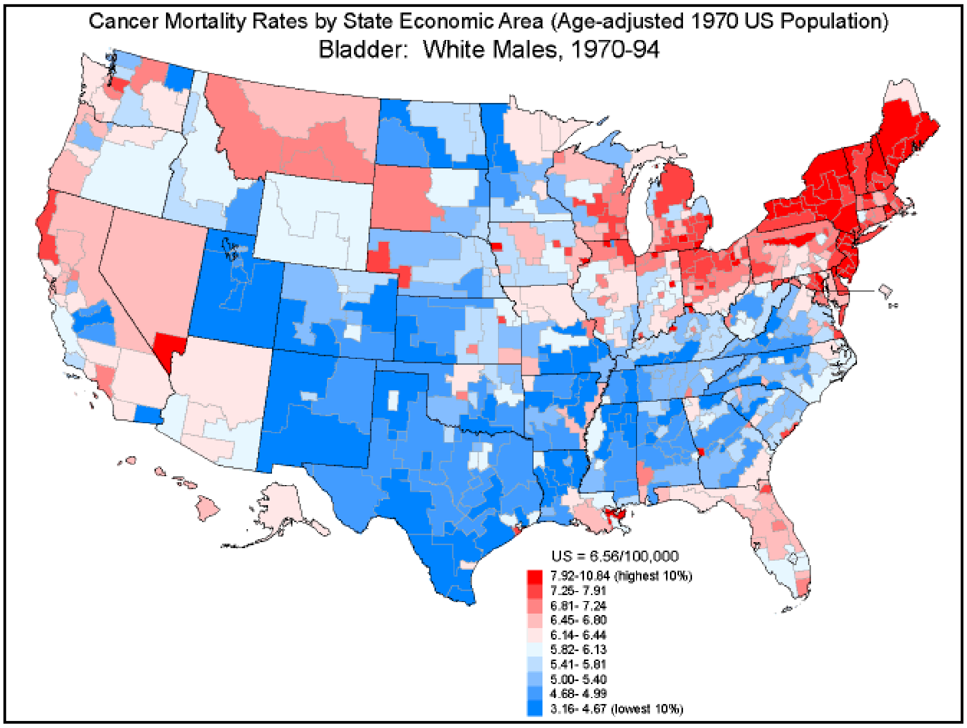
Rook, 1974, Water Treat. & Exam., 23:234

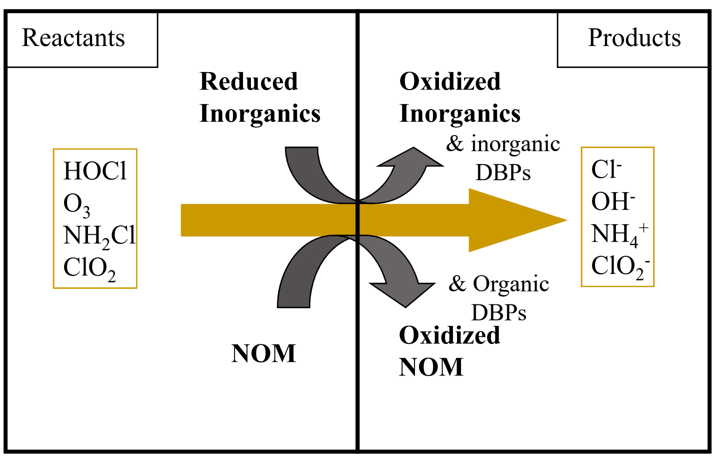
DBP Epidemiology

- Bladder Cancer
  - DBPs linked to 9,300 US cases every year
- Other Cancers
  - Rectal, colon
- Reproductive & developmental effects
  - Miscarriages & Low birth weight
  - Birth Defects
    - e.g., Cleft palate, neural tube defects
- Other
  - Kidney & spleen disorders
  - Immune system problems, neurotoxic effects

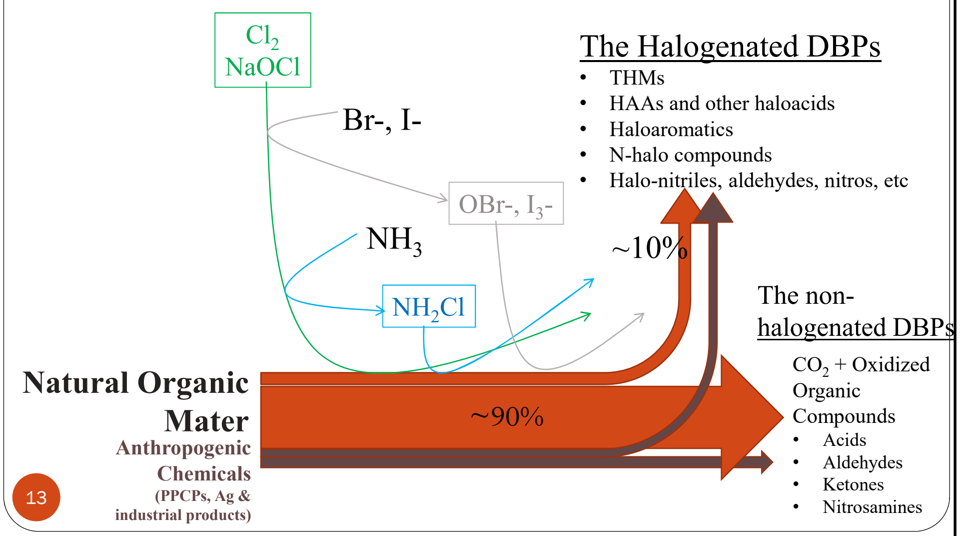
Basis for current EPA regulation
80 µg/L THMs
60 µg/L HAAs

20 µg/L THMs - high risk
Hwang et al., 2008

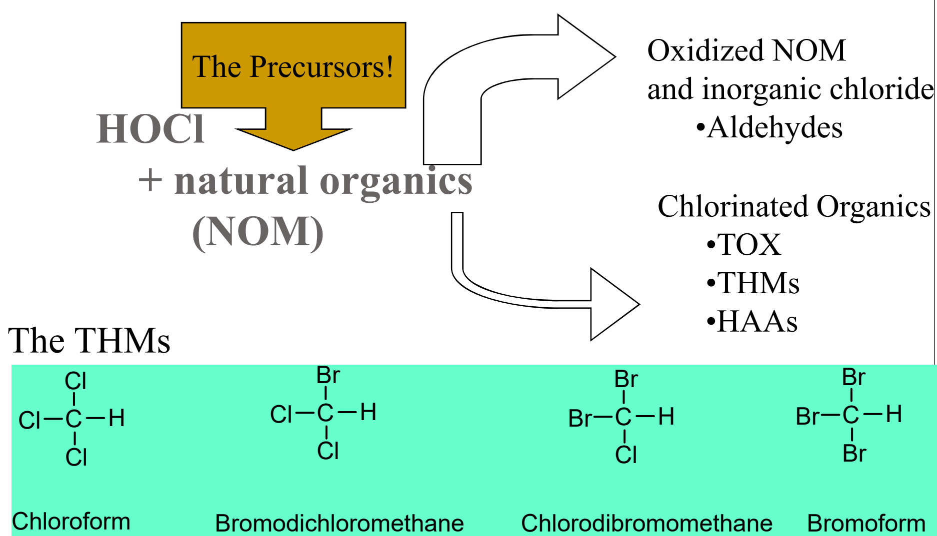

Cancer Mortality Rates by State Economic Area (Age-adjusted 1970 US Population)
Bladder: White Males, 1970-94
US = 6.56/100,000
7.92-10.84 (highest 10%)
7.25- 7.91
6.81- 7.24
6.45- 6.80
6.14- 6.44
5.82- 6.13
5.41- 5.81
5.00- 5.40
4.68- 4.99
3.16- 4.67 (lowest 10%)


Reactants
Products
Reduced Inorganics
Oxidized Inorganics
& inorganic DBPs
HOCl
O3
NH2Cl
ClO2
Cl-
OH-
NH4+
ClO2-
& Organic DBPs
NOM
Oxidized NOM

Formation of Cl_2-driven DBPs

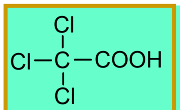


Reactions with Disinfectants: Chlorine

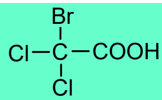


The Haloacetic Acids

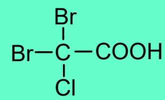
- HAA5 & HAA6 include the two monohaloacetic acids (MCAA & MBAA) plus
  - One of the trihaloacetic acids:



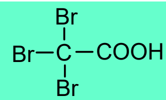
Trichloroacetic Acid *(TCAA)*



Bromodichloroacetic Acid

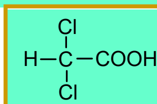


Chlorodibromoacetic Acid



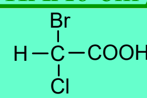
Tribromoacetic Acid

- And 2 or 3 of the dihaloacetic acids

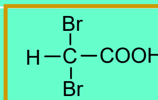


Dichloroacetic Acid *(DCAA)*

HAA6 only



Bromochloroacetic Acid



Dibromoacetic Acid

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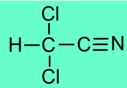
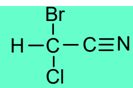
Haloacetonitriles

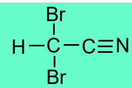
- Others that are commonly measured, but not regulated include the:
  - Dihalo-acetonitriles



Dichloroacetonitrile *(DCAN)*

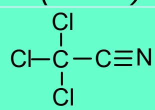


Bromochloroacetonitrile *(BCAN)*



Dibromoacetonitrile *(DBAN)*

  - Trihaloacetonitriles



Trichloroacetonitrile *(TCAN)*

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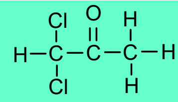
Halopropanones

- As well as the:
  - dihalopropanones

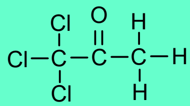


etc

1,1-Dichloropropanone

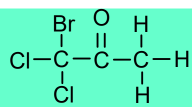
(DCP)

  - trihalopropanones



1,1,1-Trichloropropanone

(TCP)



1,1,1-Bromodichloropropanone

etc.

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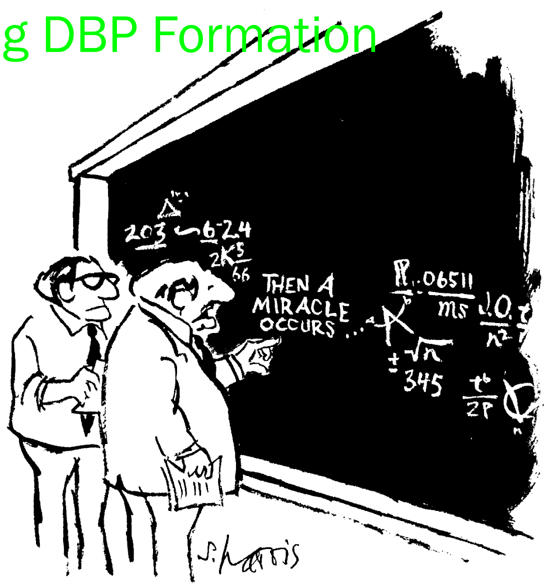
Factors Affecting DBP Formation

- Time
- pH
- Dose
- Temperature
- Bromide/Ammonia
- Pretreatment
- Reactions with pipe walls & attached materials



"I think you should be more explicit here in step two"

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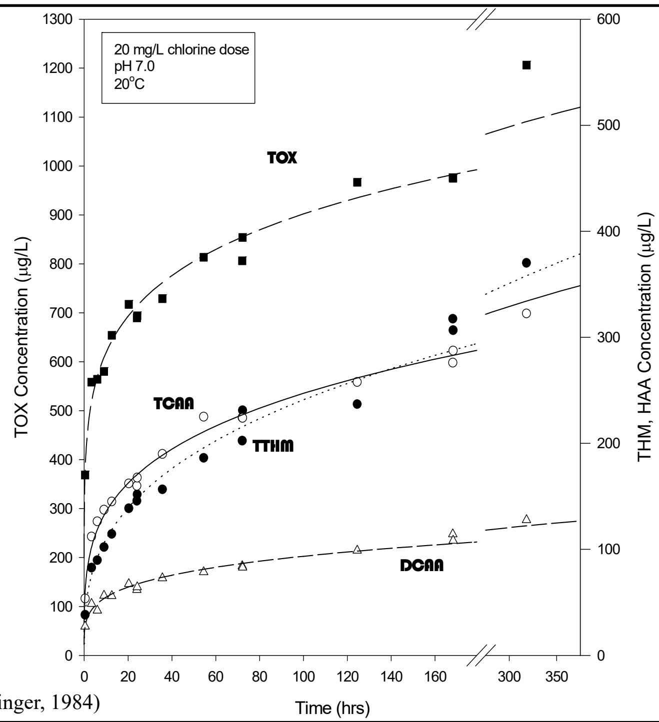
Time

- Major Byproducts



Aquatic NOM

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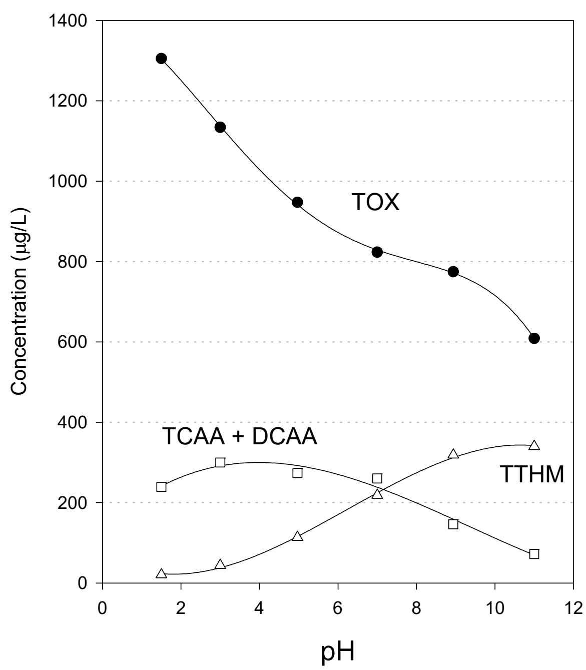
(after Reckhow & Singer, 1984)

pH Effects



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Significance of Bromide

- Present in surface and groundwaters
- Concentrations are highly variable
- Not removed by most treatment processes
- Readily oxidized by chlorine

$$HOCl + Br^- \xrightarrow{k} HOBr + Cl^-$$

$$k = 4.7x10^{-2}[\exp(^{-754.9}/_T)]M^{-1}s^{-1}$$
$$= 3.7x10^3 M^{-1}s^{-1} \qquad @25° C$$

Therefore, bromide has a **13 second** half life at pH 7, and 1 mg/L residual chlorine

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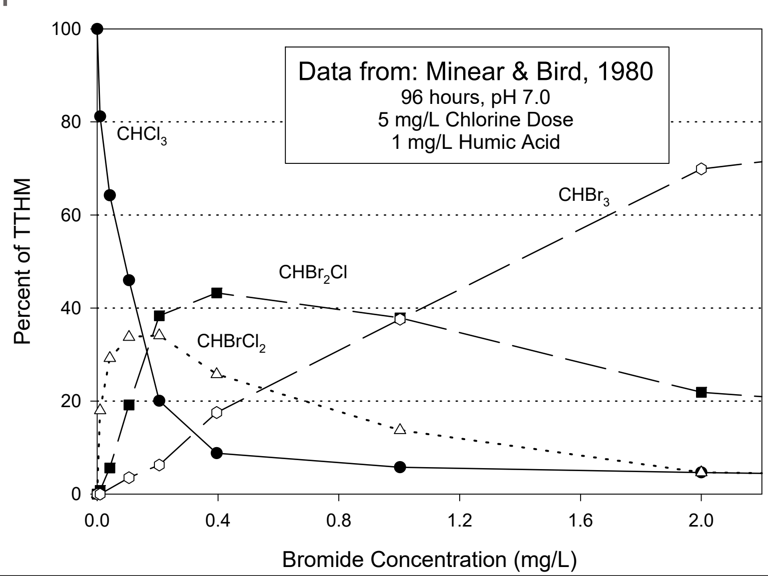
Impact of Bromide on THM Formation



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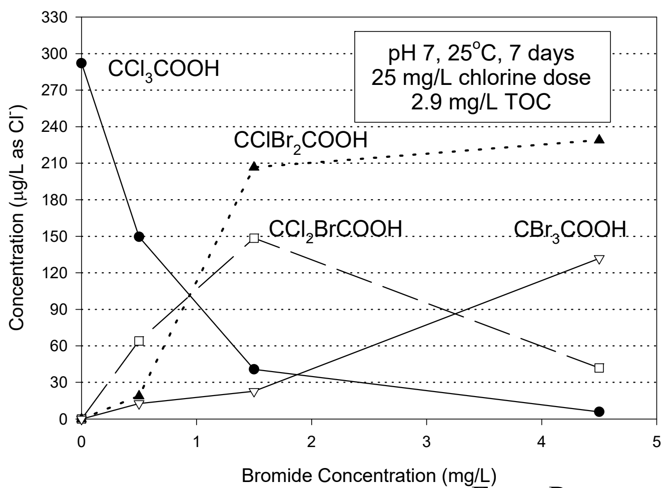
Bromide: THAA Formation

Note that TCAA is the only regulated THAA



From Pourmoghaddas, 1990

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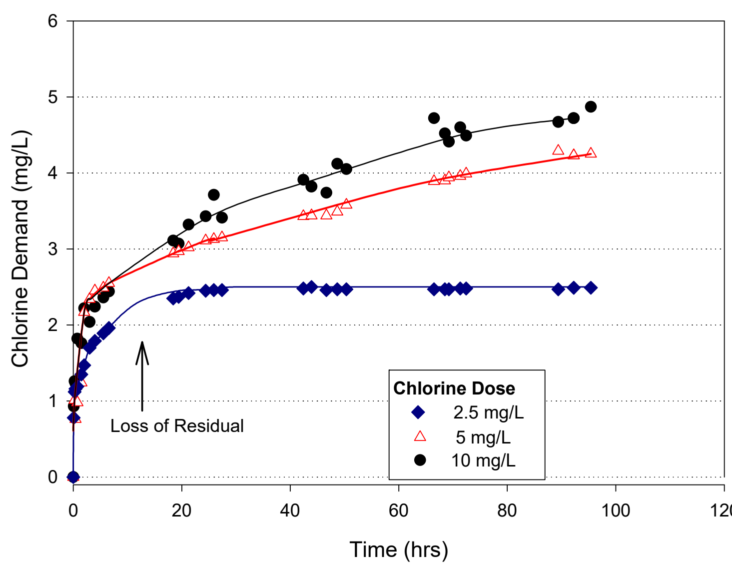
Case Study: Impact of time & chlorine dose

Cl_2 Demand



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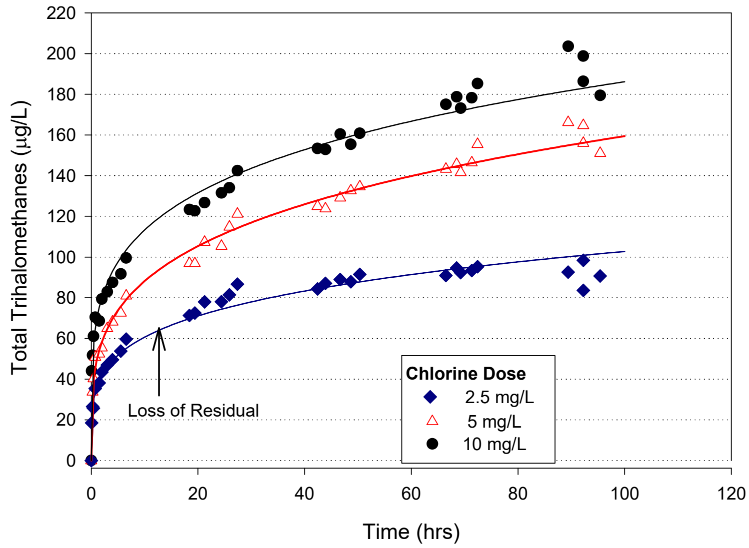
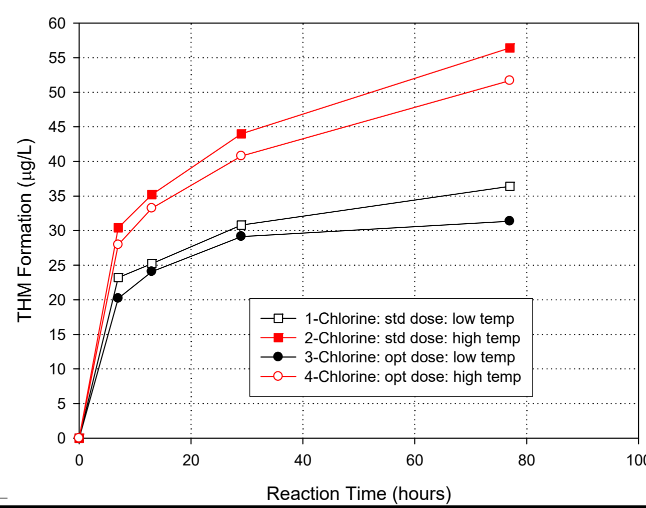
Case Study: Impact of time & chlorine dose

THM



THMs from Chlorination

- Chlorine Residual @ 48 hrs
  - std = 0.8 mg/L
  - opt = 0.2 mg/L
- Temp
  - Low = 13 C
  - High = 23 C



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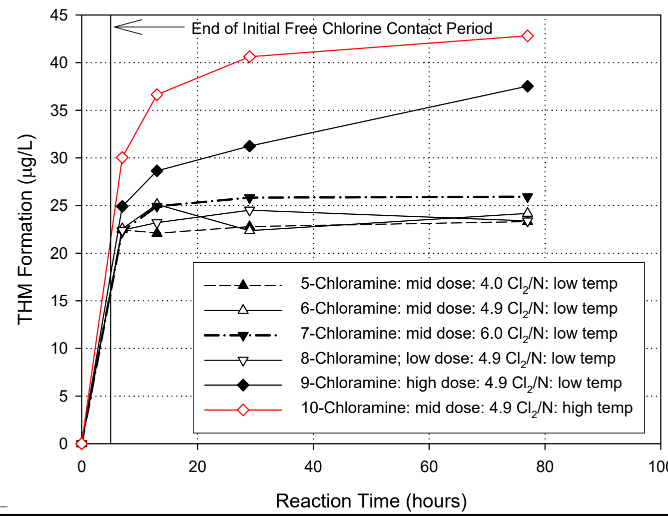
THMs from Chloramination

- Addition of ammonia after 5 hrs free contact time



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DBP Modeling

- Power function models (Empirical)
  - simple to use
  - greater experience
- Chemical kinetic models (Semi-mechanistic)
  - depends on time-varying concentrations of the precursors (reactants)
  - better adapted for use with a more integrated framework
    - combine with degradation terms
    - combine with hydraulic/reactor models
    - Chlorine boosting

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DBP Formation: Empirical Model

- Montgomery Watson, 1992

$$DBPs = a(TOC)^b (UV_{254})^c (Br + d)^e (pH)^f (Cl_2dose)^g (Time)^h (Temp)^i$$

DBPs in μg/L, UV_{254} in cm^{-1}, Time in hrs, Temp in °C, all others in mg/L

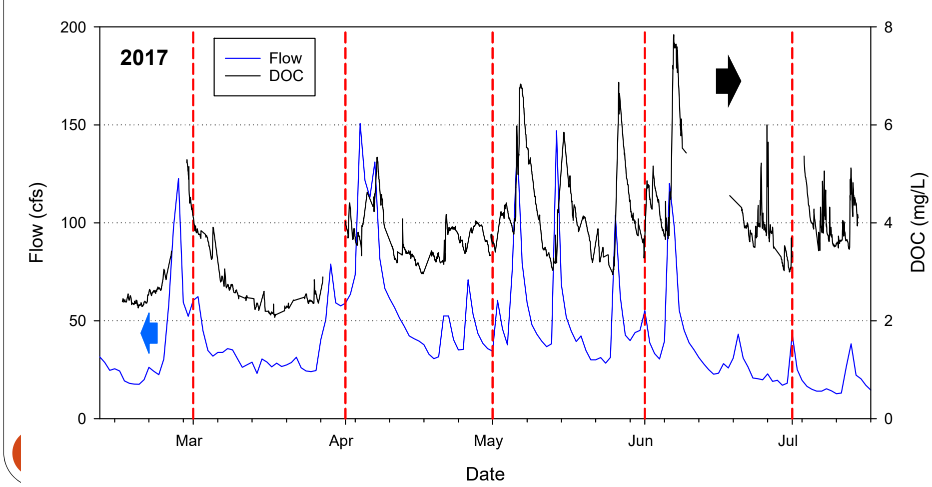
Descriptive, but not much insight

Compound	a	b	c	d	e	f	g	h	i
Chloroform	0.064	0.329	0.874	0.01	-0.404	1.161	0.561	0.269	1.018
Bromodichloromethane[1]	0.0098			0	0.181	2.55	0.497	0.256	0.519
Bromodichloromethane[2]	1.325	-0.725		0	0.794		0.632	0.204	0.519
Chlorodibromomethane[3]	15.0	-1.67		0	1.24		0.73	0.261	0.989
Chlorodibromomethane[4]	0.028	-1.08	-1.18	0	1.57	1.97	1.07	0.200	0.596
Bromoform	6.53	-2.03		0	1.39	1.60	1.06	0.136	
Monochloroacetic Acid	1.63	0.75		0.01	-0.085	-1.12	0.51	0.300	
Dichloroacetic Acid	0.605	0.29	0.73	0.01	-0.57		0.48	0.239	0.665
Trichloroacetic Acid	87.2	0.36	0.90	0.01	-0.70	-1.73	0.88	0.264	
Monobromoacetic Acid	0.176	1.66	-0.62	0	0.80	-0.93		0.145	0.450
Dibromoacetic Acid	84.9	-0.62	0.65	0	1.07		-0.20	0.120	0.657

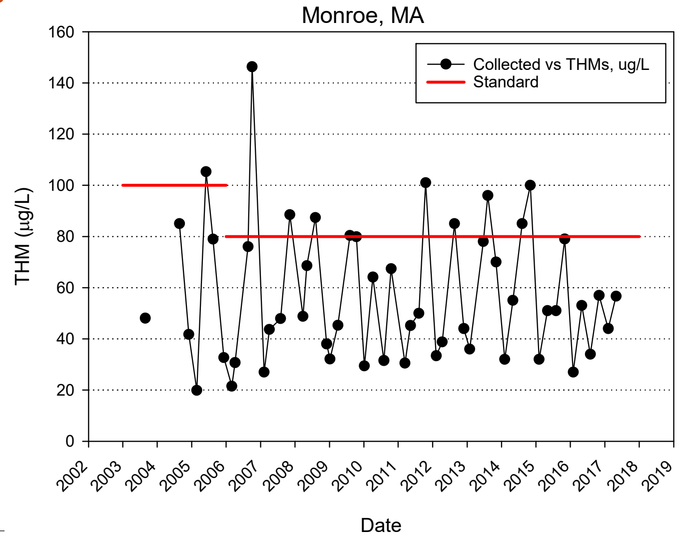
[1]Cl_2/Br <75; [2]Cl_2/Br >75; [3]Cl_2/Br <50; [4]Cl_2/Br >50

Annual TOC Cycles: Small NE Tributary

- Mill River in Amherst



Monroe: quarterly THMs



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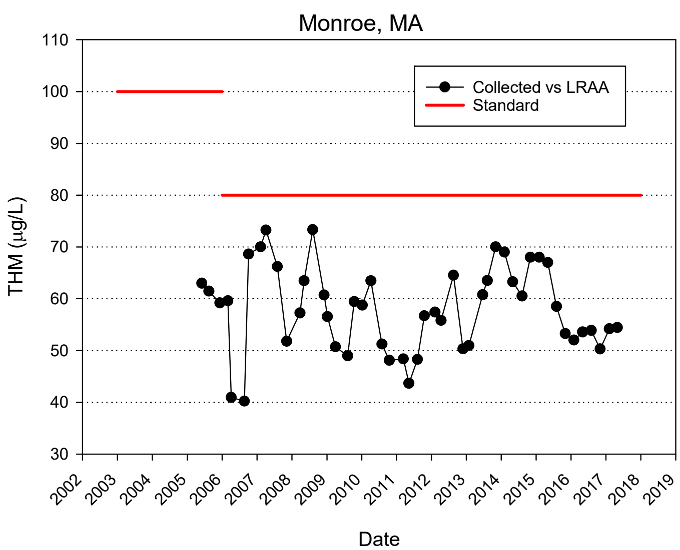
Monroe: THMs LRAA

- xcv



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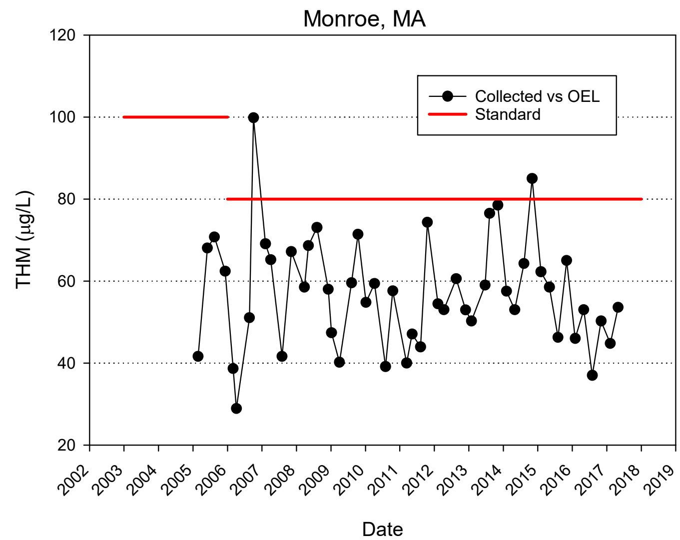
Monroe: THMs OEL

- dsf



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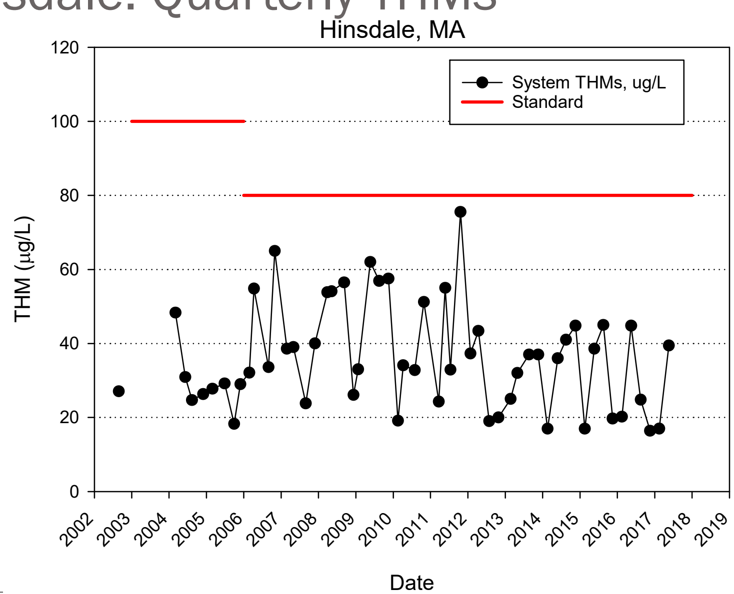
Hinsdale: Quarterly THMs

- sd



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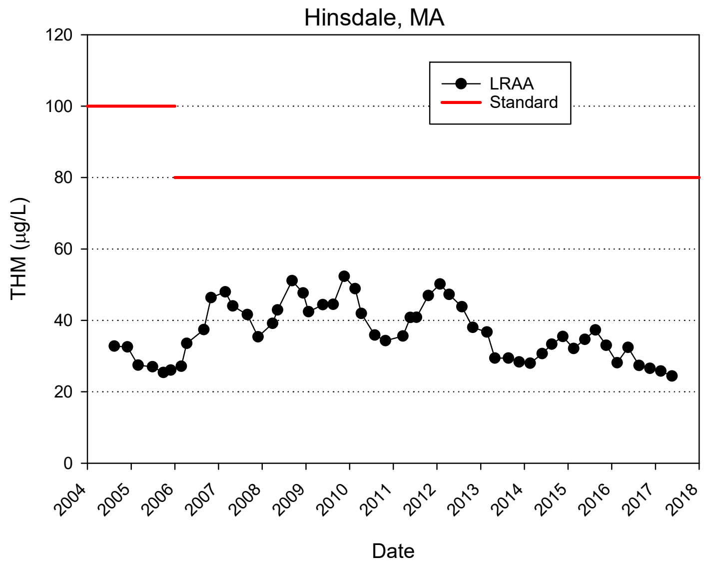
Hinsdale: THM LRAA



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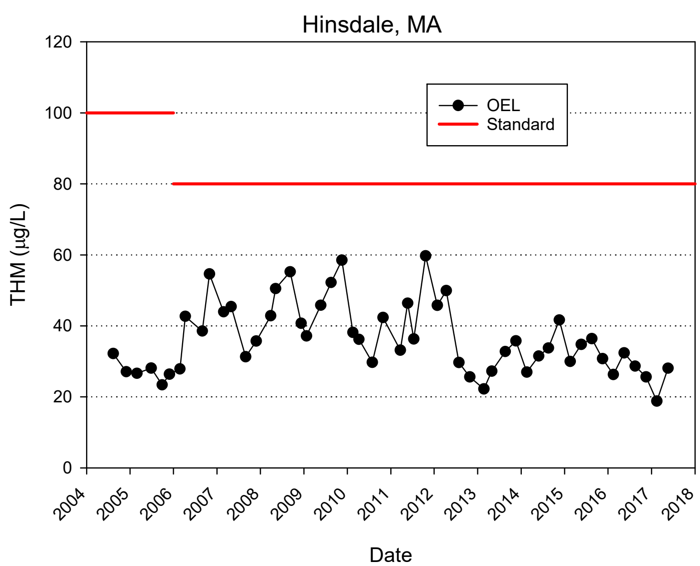
Hinsdale: THM OEL

- sd



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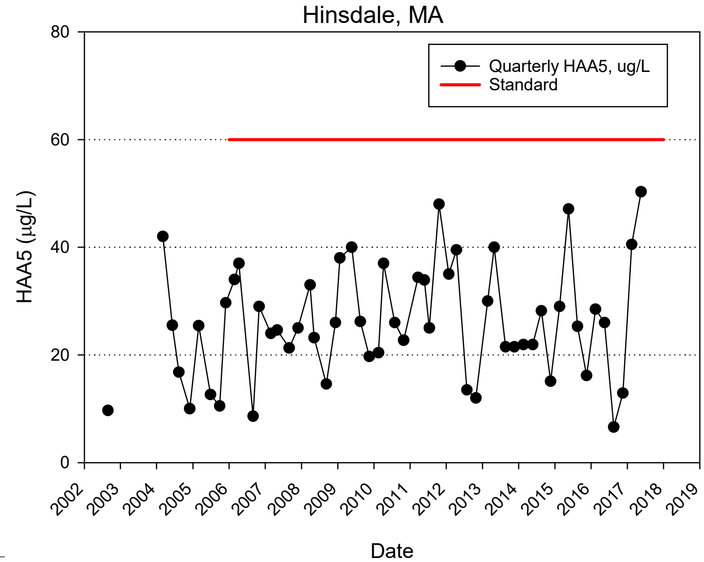
Hinsdale: Quarterly HAA5

- ad



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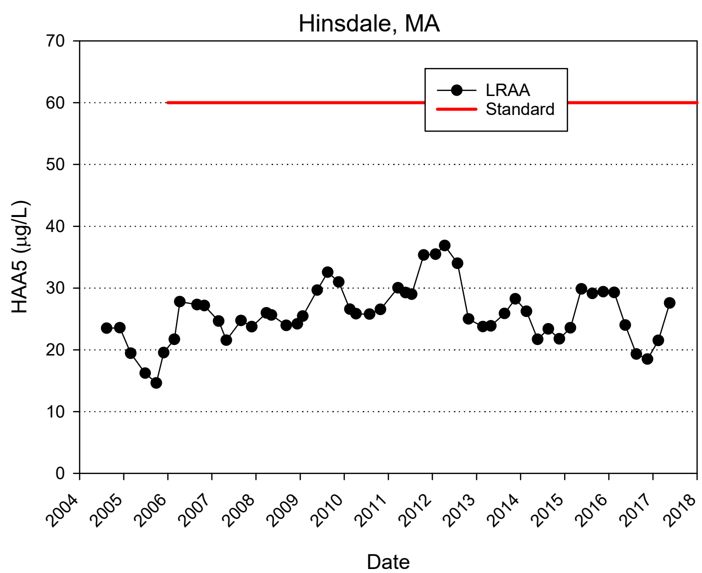
Hinsdale HAA5 RAA



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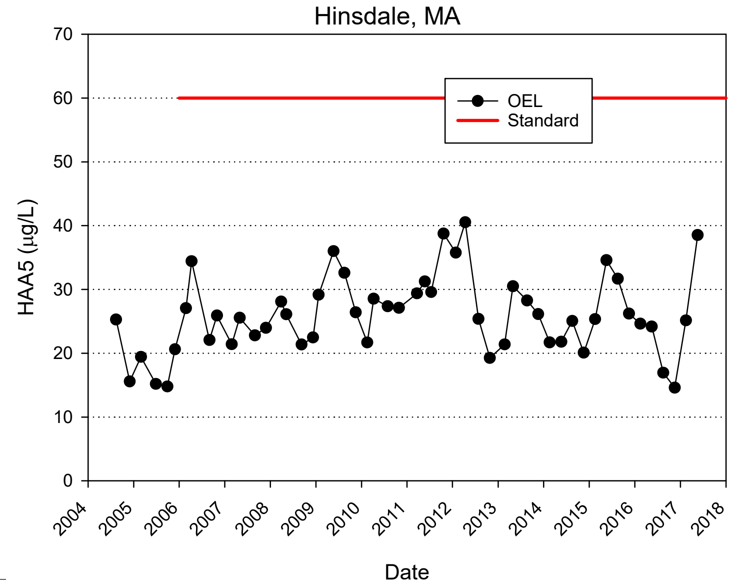
Hinsdale: HAA5 OEL



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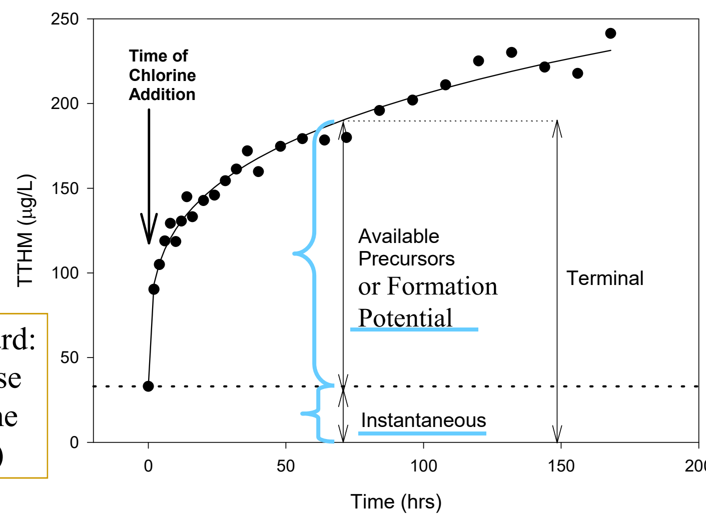
Analysis of DBP Precursors

Laboratory Precursor Test



Use a standard:
- chlorine dose
- reaction time
- pH (maybe)

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Significance

- Only instantaneous concentrations are regulated
- Formation kinetics are important for managing systems

	THMs	HAAs
Stage 1&2	0.080	0.060

(mg/L)

- Formation potential are important for controlling organic precursors
  - assess process performance
  - compare waters

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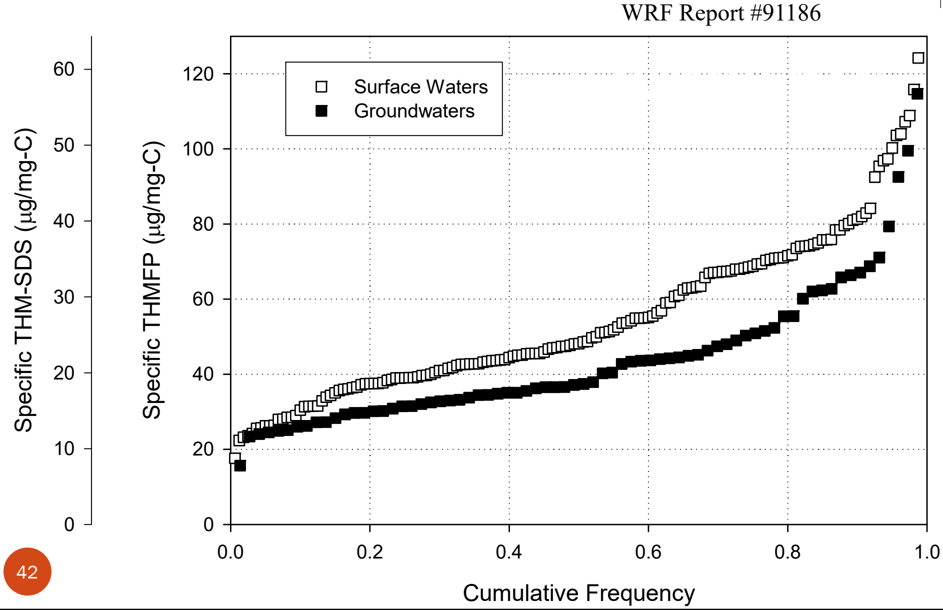
National Database

From: Reckhow et al., 2007
WRF Report #91186



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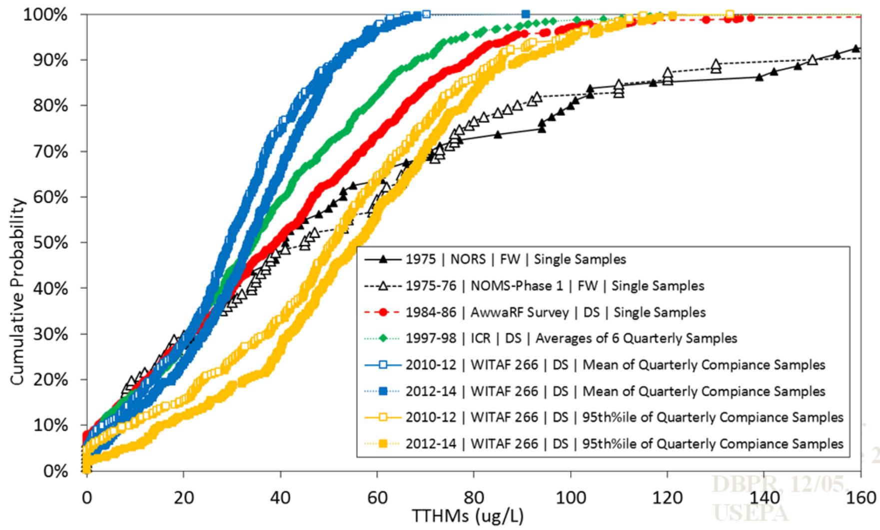
Mean TTHMs from US Surveys



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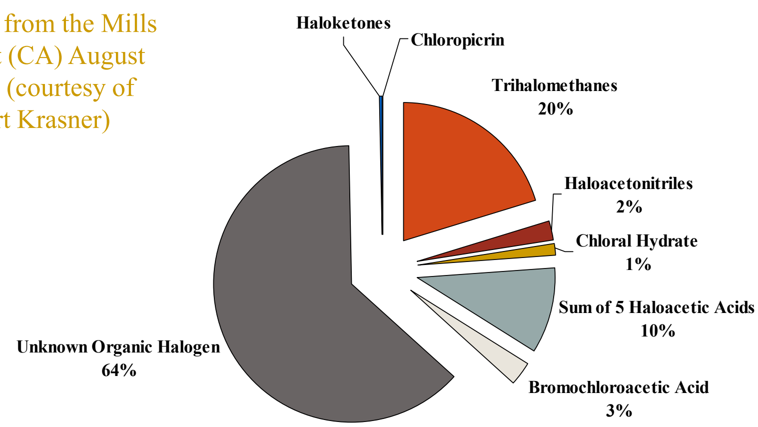
From Seidel et al., 2016

TOX: Known & Unknown

Data from the Mills Plant (CA) August 1997 (courtesy of Stuart Krasner)



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DBP Control Strategies

- Source Selection
- Precursor Removal
  - Most commonly used: better coagulation, GAC, MIEX, membranes
- Changing Treatment Sequence/conditions
- Alternative disinfectants
  - Also common: chloramines, chlorine dioxide, ozone
- DBP removal
- Distribution System Modification

See: Chapter 19 in Water Quality and Treatment; 6th edition; 2011

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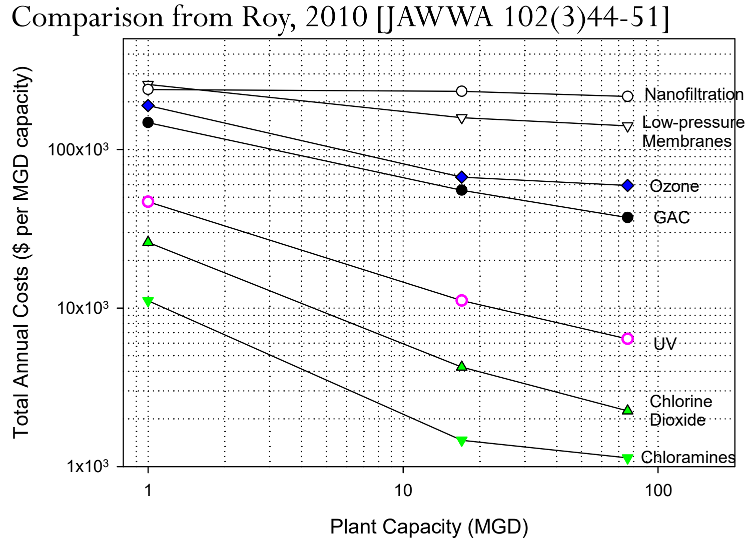
Some 2009 Projected Costs

- Comparison from Roy, 2010 [JAWWA 102(3)44-51]



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Alternative Secondary Disinf.

- Chloramines
  - About 30% now use chloramines
    - Seidel et al., 2005
  - Unique chloramine DBPs
    - Anecdotal reports of health effects
  - Reduction of chlorine DBPs
  - Nitrification and regrowth (free ammonia)
    - Modeling: Fleming et al., 2005; Liu et al., 2005
    - Control techniques: e.g., Rosenfeldt et al., 2009 [JAWWA 101:10:60]
  - Lead solubilization
    - If Pb(IV) controls solubility
      - Lytle & Schock, 2005 [JAWWA 97:11:102]
      - Vasquez et al., 2006 [JAWWA 98:2:144]
  - Possible role in controlling bromate

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Utility Case Studies

- Biodegradation
  - Elizabethtown, NJ
    - Weisel study
  - Norwood, MA
- Distribution System Evaluation
  - Woburn, MA

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Seasonal Variability & Biodegradation

- Chen & Weisel study
- JAWWA, April 1998
- Intensive study of Elizabethtown, NJ system
  - 125 MGD conventional plant
  - 4.9 mg/L DOC (raw water average)
  - pH 7.2

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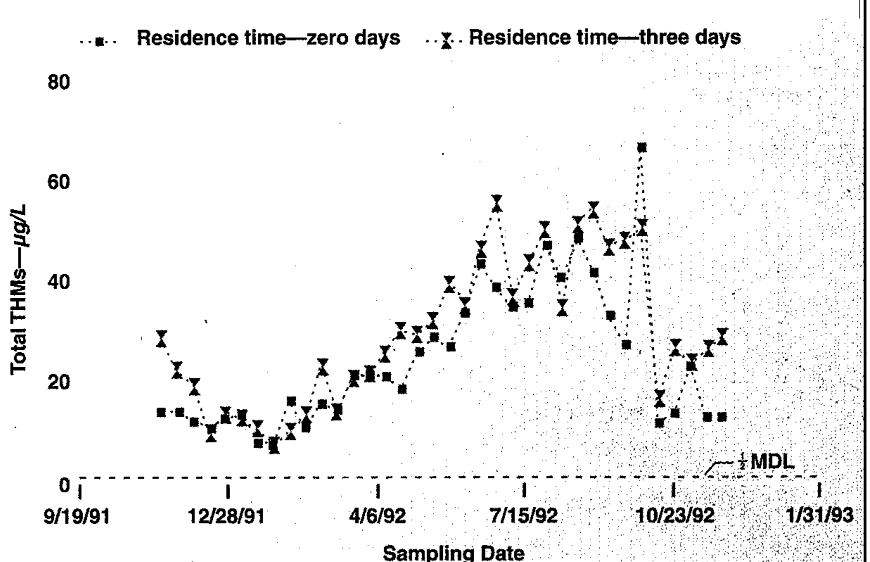
Elizabethtown, NJ: THMs



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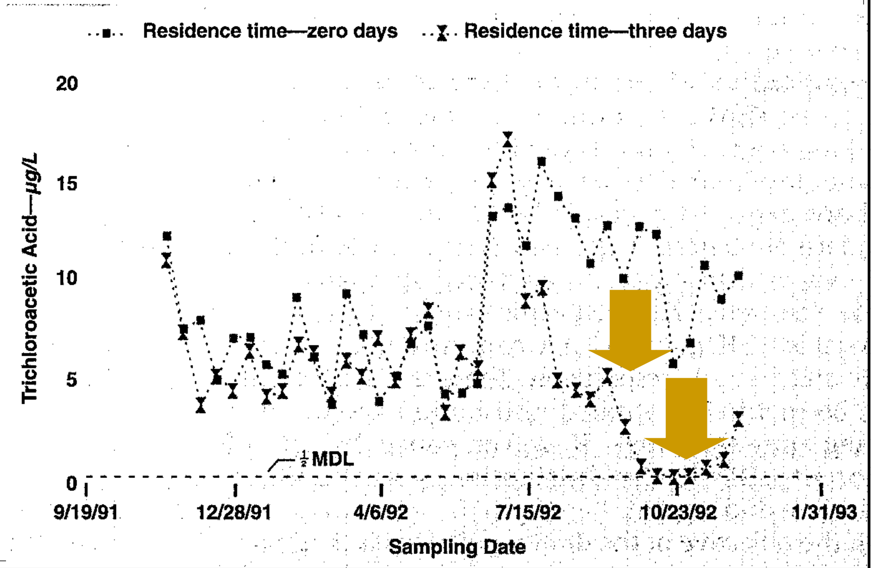
Elizabethtown, NJ: TCAA



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HAA Degradation

- Biodegradation:
  - dihaloacetic acids degrade more readily than trihaloacetic acids
  - On BAC
    - MHAA>DHAA>THAA
      - Wu & Xie, 2005 [JAWWA 97:11:94]
  - In distribution systems
    - DHAA>MHAA>THAA
      - Many studies

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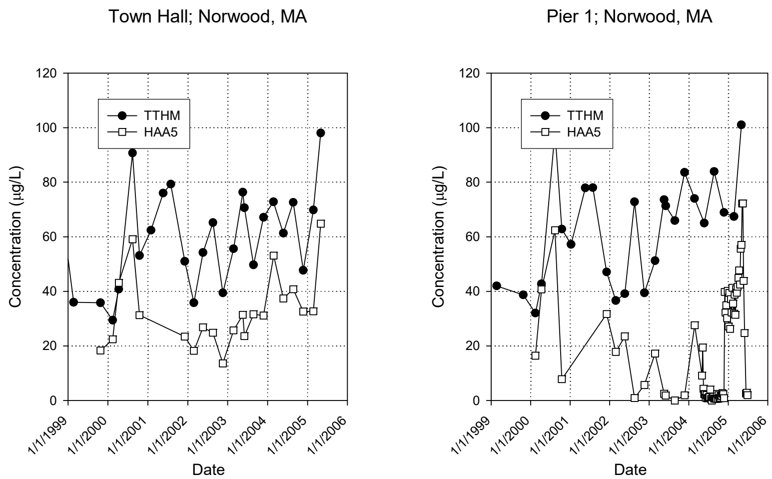
Biodegradation in Dist. Systems



Example: Norwood, MA

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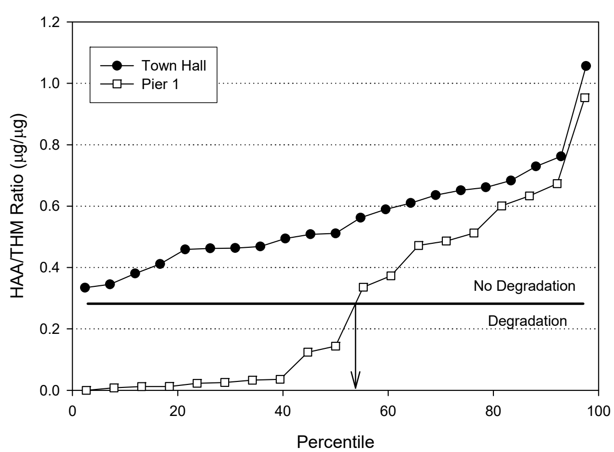
Biodegradation of HAAs

- Norwood, MA example



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Woburn System Description

- Local supplies of 4 MGD from five municipal wells located at Horn Pond
  - Free chlorine
- The MWRA supplies an average of 2.5 MGD through connections at Meter 230 and 200 to supplement local supply
  - chloramines
- Ave day demand is 6.2 MGD
  - Max (summer) is 12.5 MGD
  - Min (winter) is 4.5 MGD

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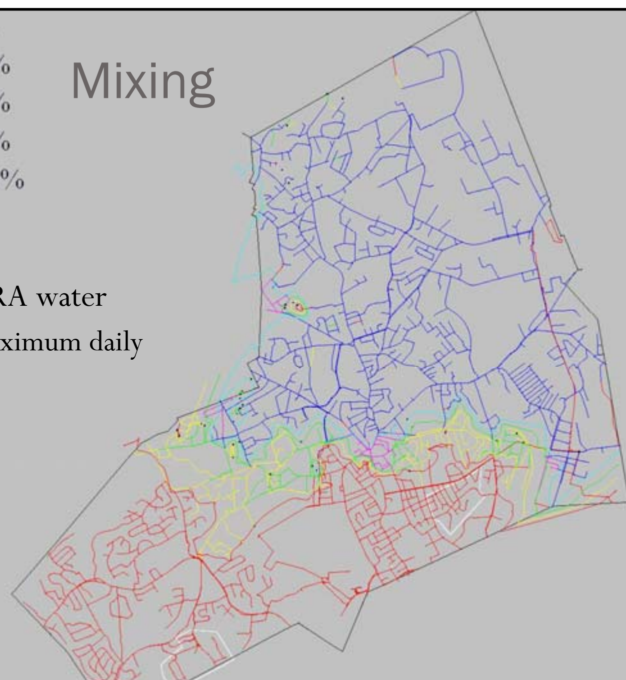
Mixing

- 0 to 20%
- 20 to 40%
- 40 to 60%
- 60 to 80%
- 80 to 100%

- Percent MWRA water
  - Based on Maximum daily demand



Courtesy of CDM and City of Woburn

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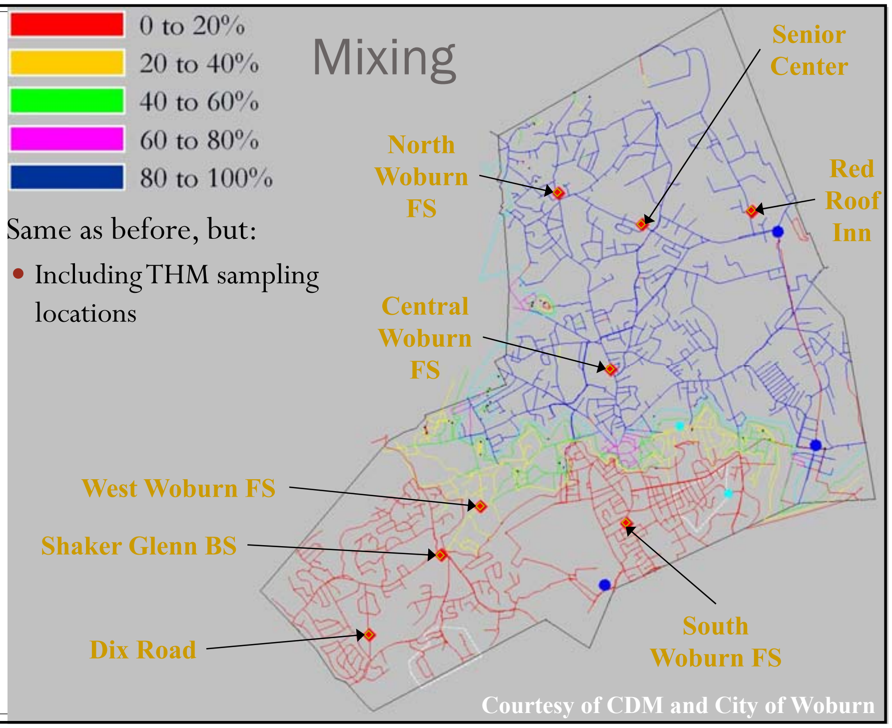
Mixing

- Same as before, but:
  - Including THM sampling locations



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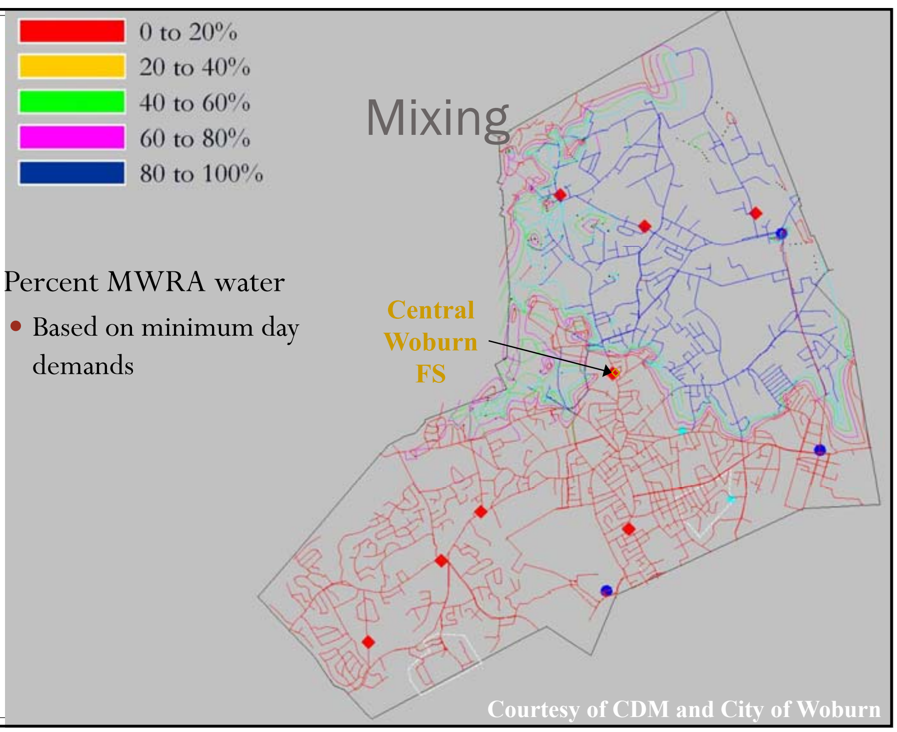
Mixing

- Percent MWRA water
  - Based on minimum day demands



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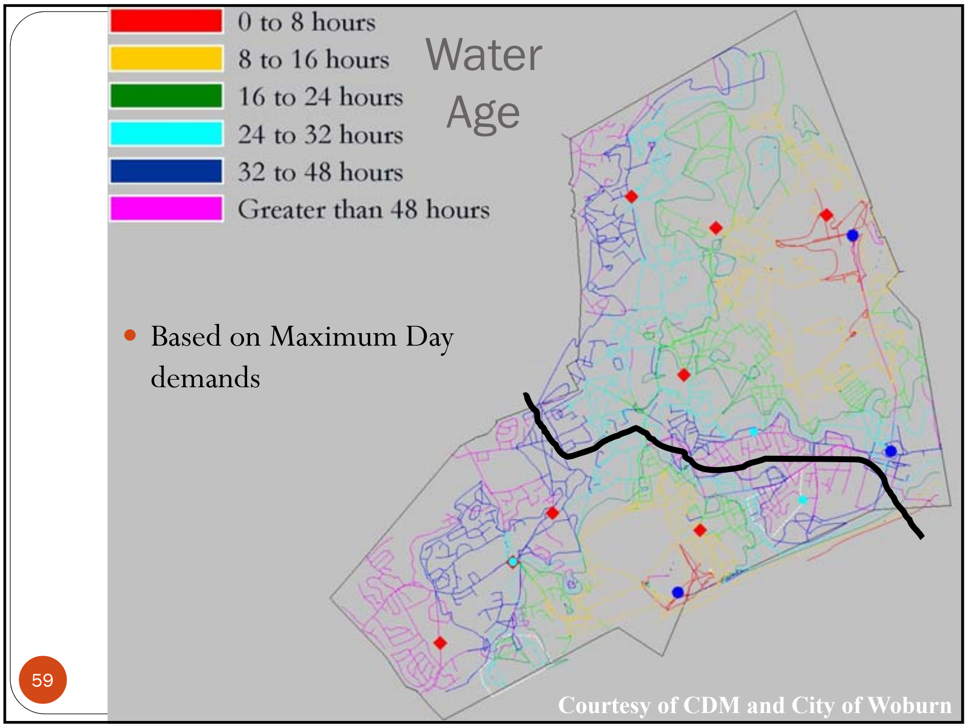
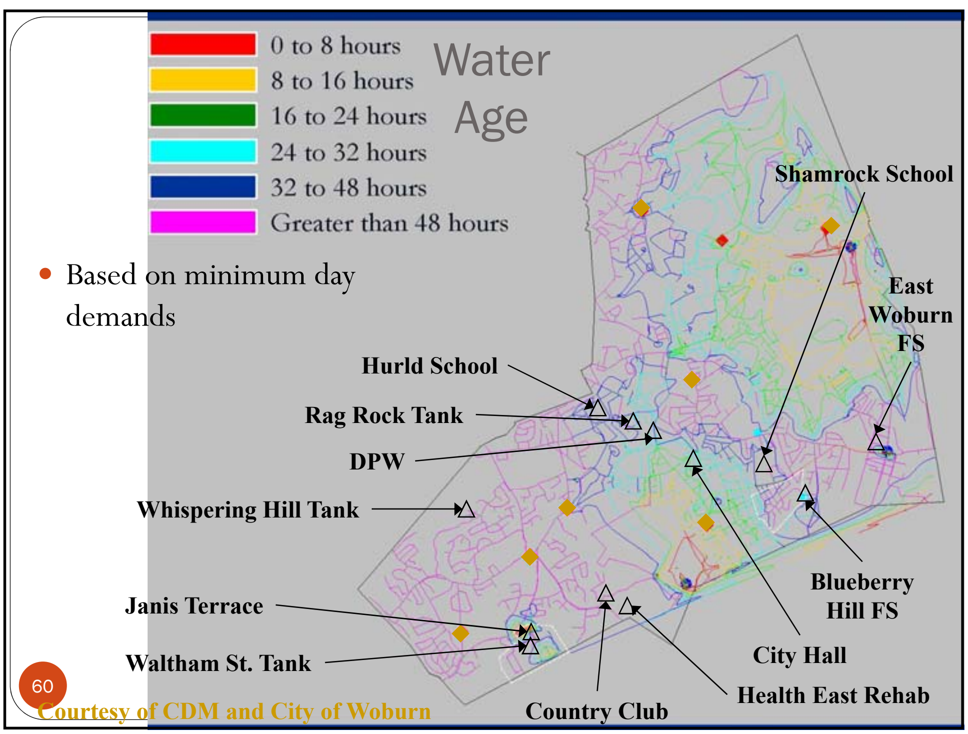
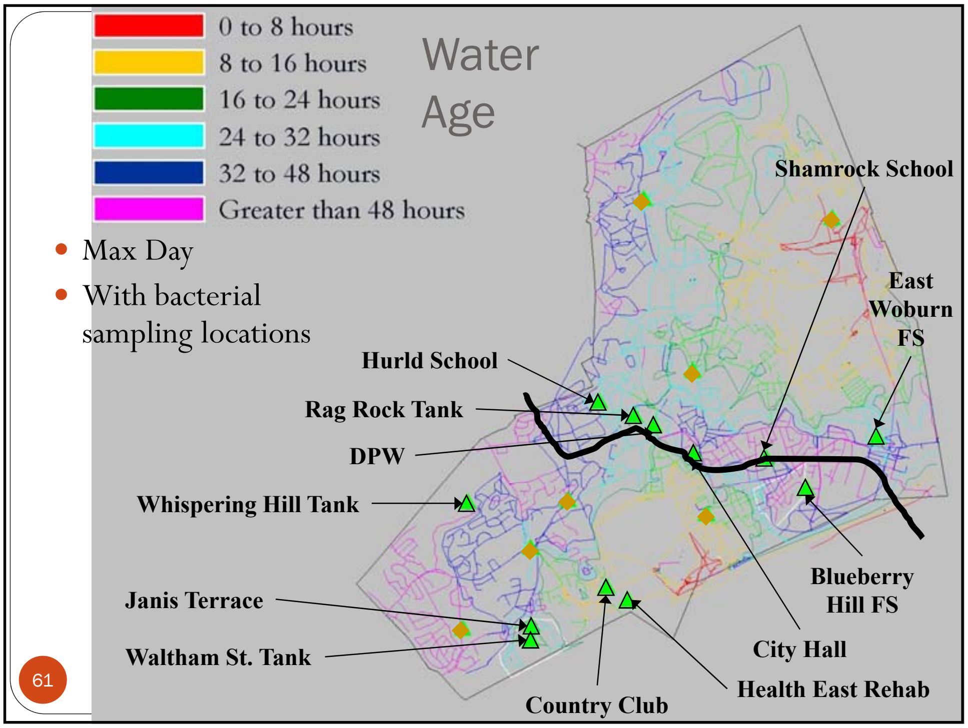
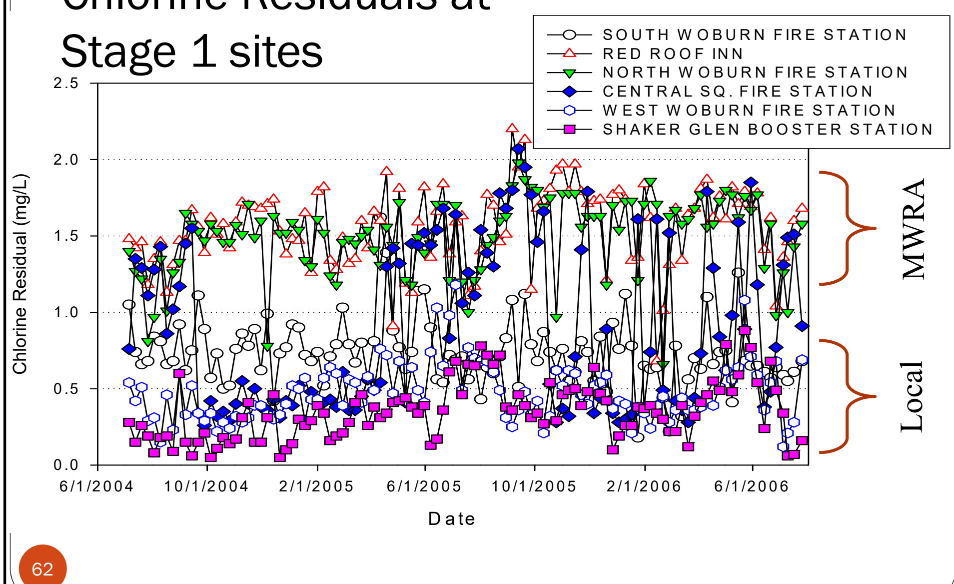
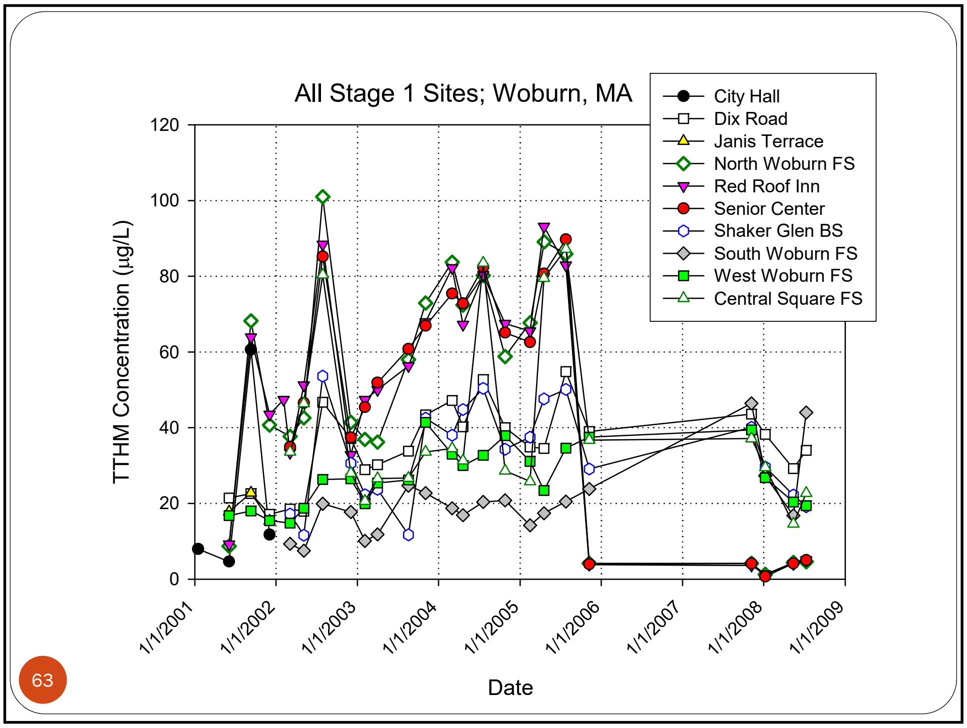

0 to 8 hours
8 to 16 hours
16 to 24 hours
24 to 32 hours
32 to 48 hours
Greater than 48 hours
Water Age
Based on Maximum Day demands
59
Courtesy of CDM and City of Woburn


0 to 8 hours
8 to 16 hours
16 to 24 hours
24 to 32 hours
32 to 48 hours
Greater than 48 hours
Water Age
Based on minimum day demands
Shamrock School
East Woburn FS
Hurld School
Rag Rock Tank
DPW
Whispering Hill Tank
Janis Terrace
Waltham St. Tank
Blueberry Hill FS
City Hall
Health East Rehab
Country Club
60
Courtesy of CDM and City of Woburn



Chlorine Residuals at Stage 1 sites




All Stage 1 Sites; Woburn, MA
TTHM Concentration (µg/L)
120
100
80
60
40
20
0
1/1/2001
1/1/2002
1/1/2003
1/1/2004
1/1/2005
1/1/2006
1/1/2007
1/1/2008
1/1/2009
Date
City Hall
Dix Road
Janis Terrace
North Woburn FS
Red Roof Inn
Senior Center
Shaker Glen BS
South Woburn FS
West Woburn FS
Central Square FS
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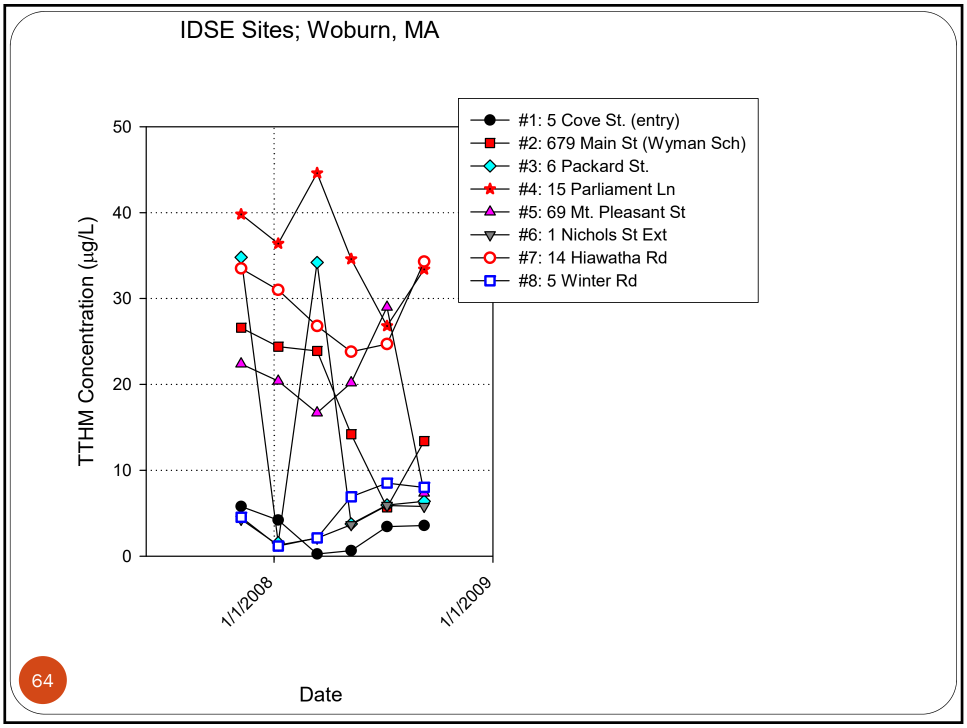
IDSE Sites; Woburn, MA
TTHM Concentration (µg/L)
50
40
30
20
10
0
1/1/2008
1/1/2009
Date
#1: 5 Cove St. (entry)
#2: 679 Main St (Wyman Sch)
#3: 6 Packard St.
#4: 15 Parliament Ln
#5: 69 Mt. Pleasant St
#6: 1 Nichols St Ext
#7: 14 Hiawatha Rd
#8: 5 Winter Rd
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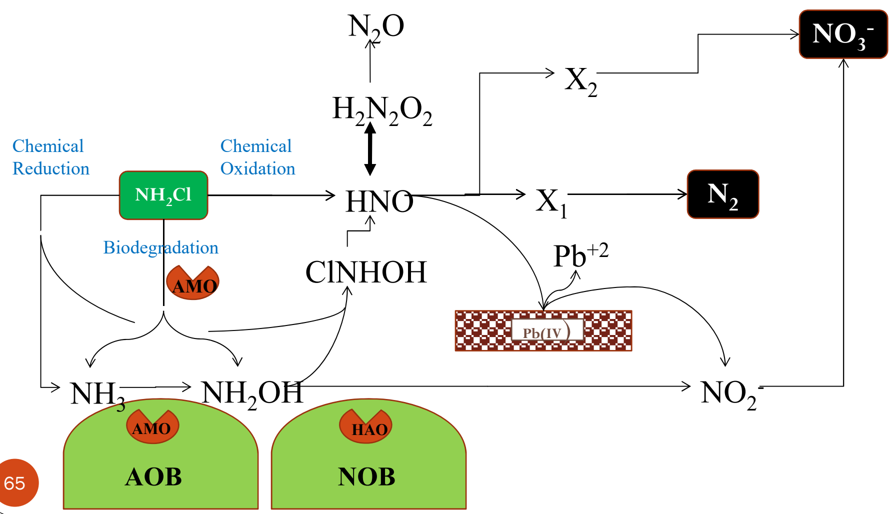
Chloramines – many more reactions



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