CEE/EHS 597B

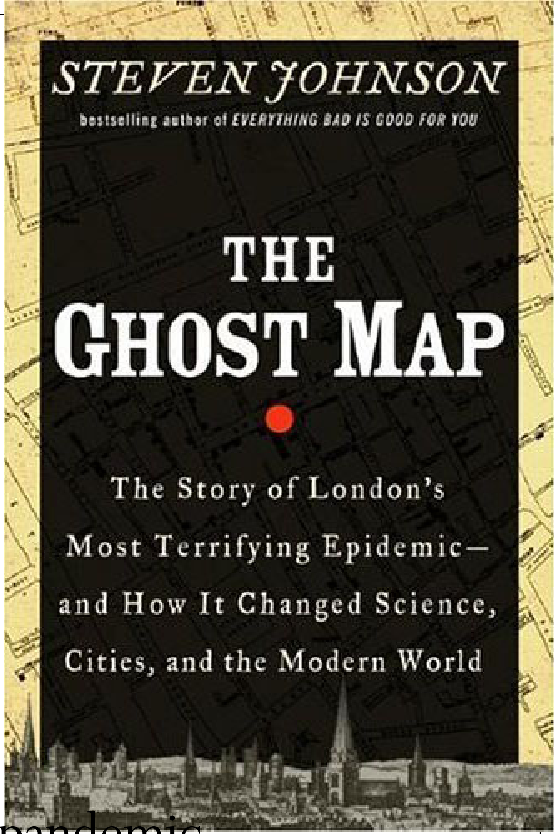
Class #15:

Special Treatment Issues: DBPs

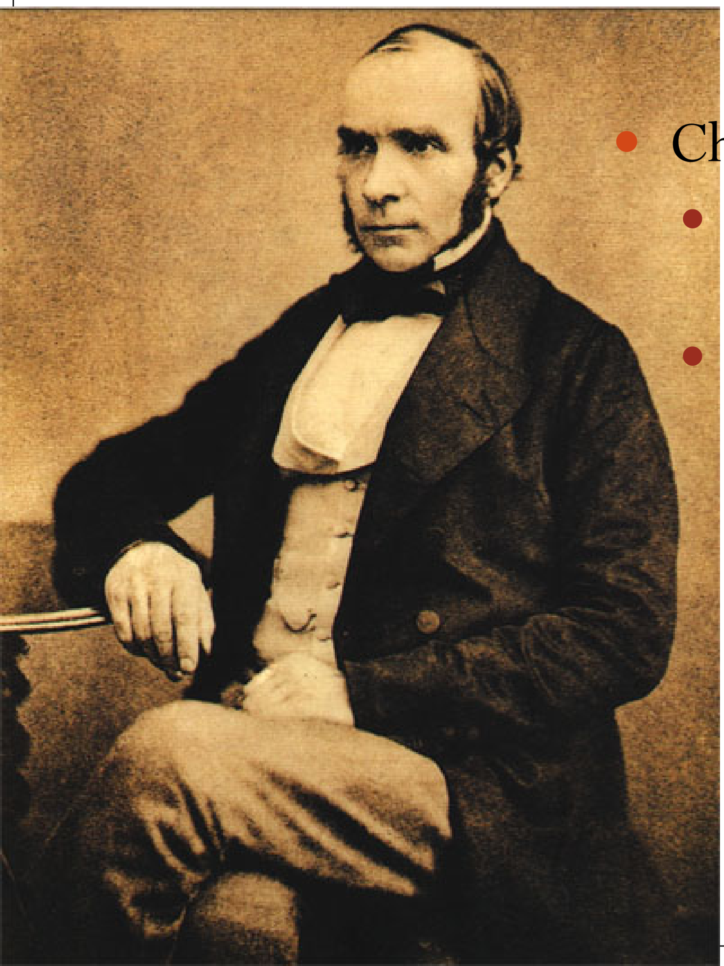
Dave Reckhow

John #1: Dr. John Snow

2007



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 pu it to rest

Soho, Westminster

Cluster Map of Fatal Cholera Cases in London, 1854

Source: Adapted from John Snow, *Snow on Cholera* (New York: Hafner, 1965).

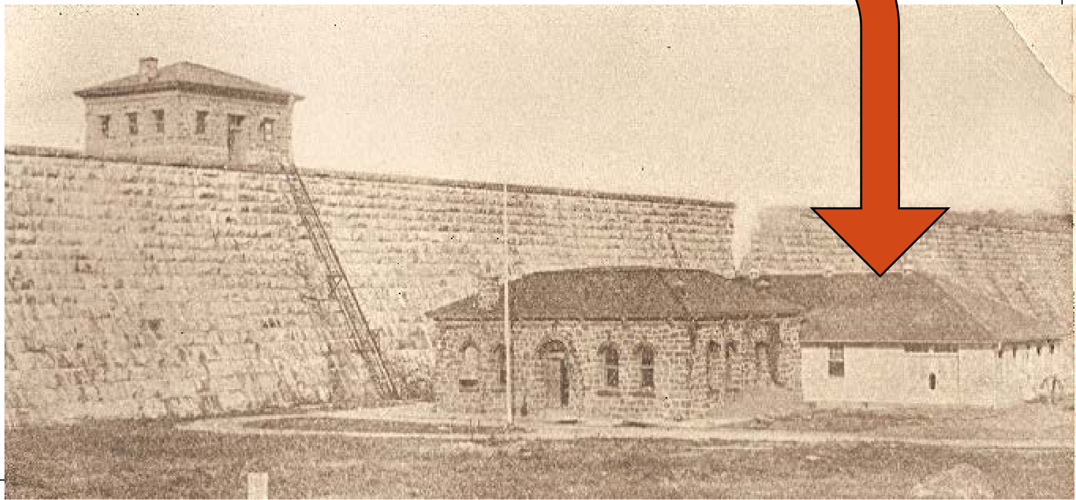
Picadilly Circus

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)

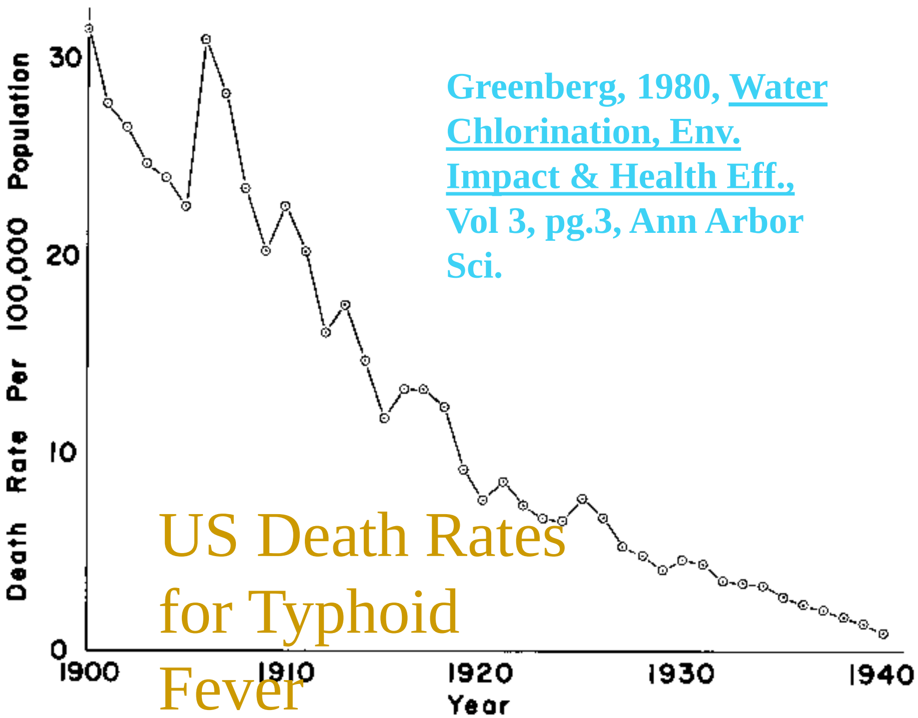


"Full-scale and continuous implementation of disinfection for the first time in Jersey City, NJ ignited a disinfection revolution in the United States that reverberated around the world"

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

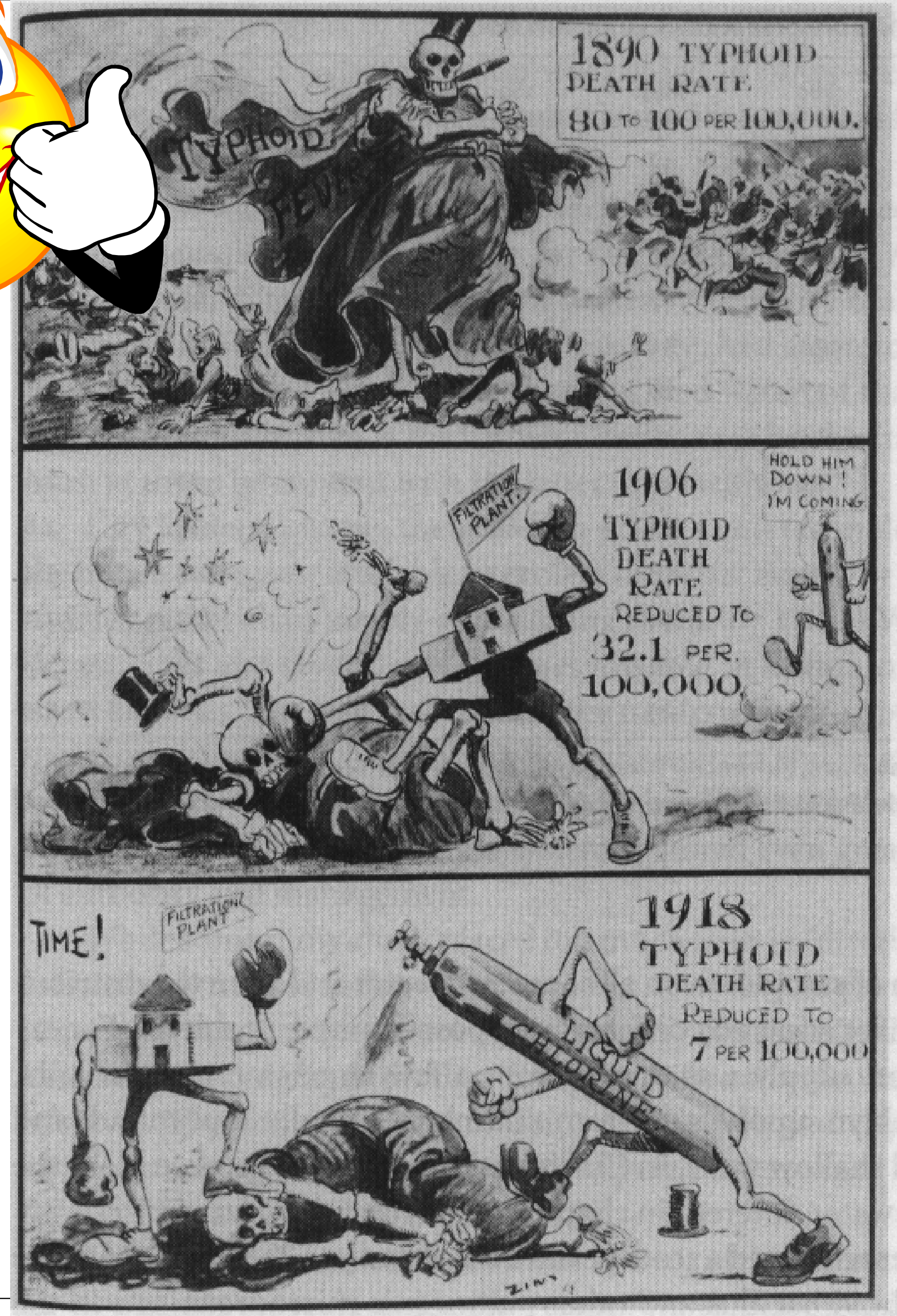
Chlorination

- 1-2 punch of filtration & chlorination



US Death Rates for Typhoid Fever

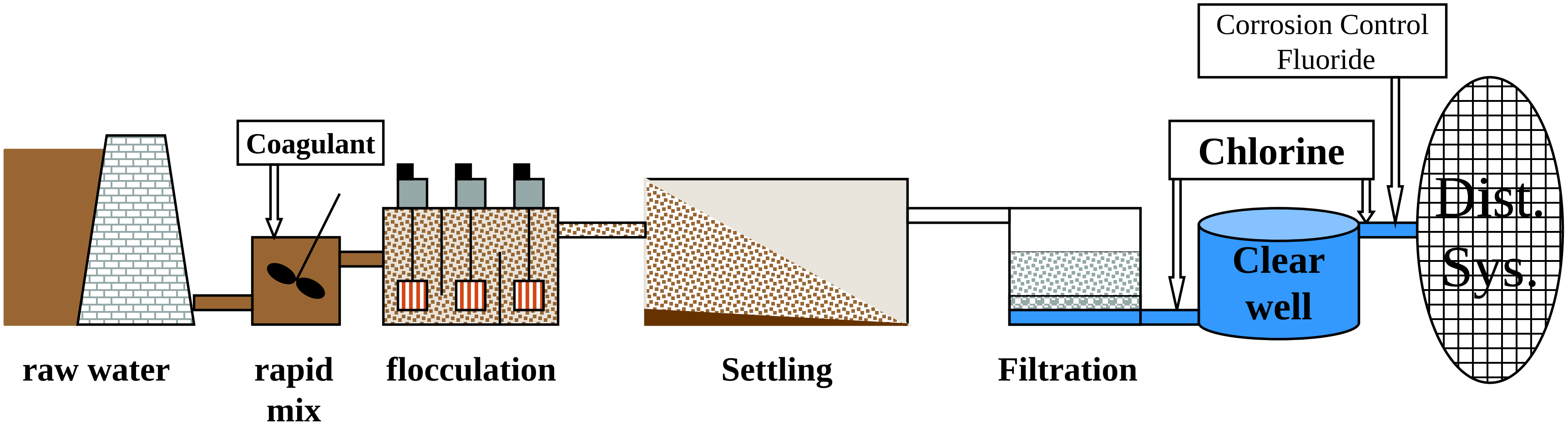
Greenberg, 1980, Water Chlorination, Env. Impact & Health Eff., Vol 3, pg.3, Ann Arbor Sci.



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



John #3: Johannes J. Rook

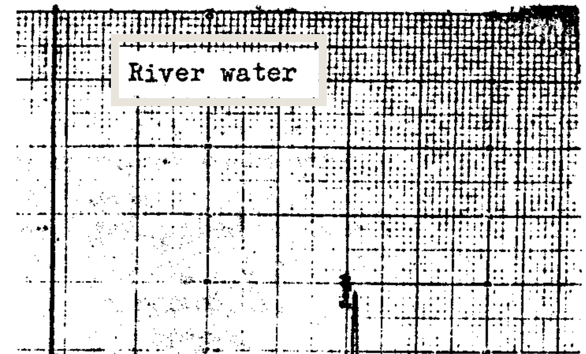
1921-2010

- 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

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



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

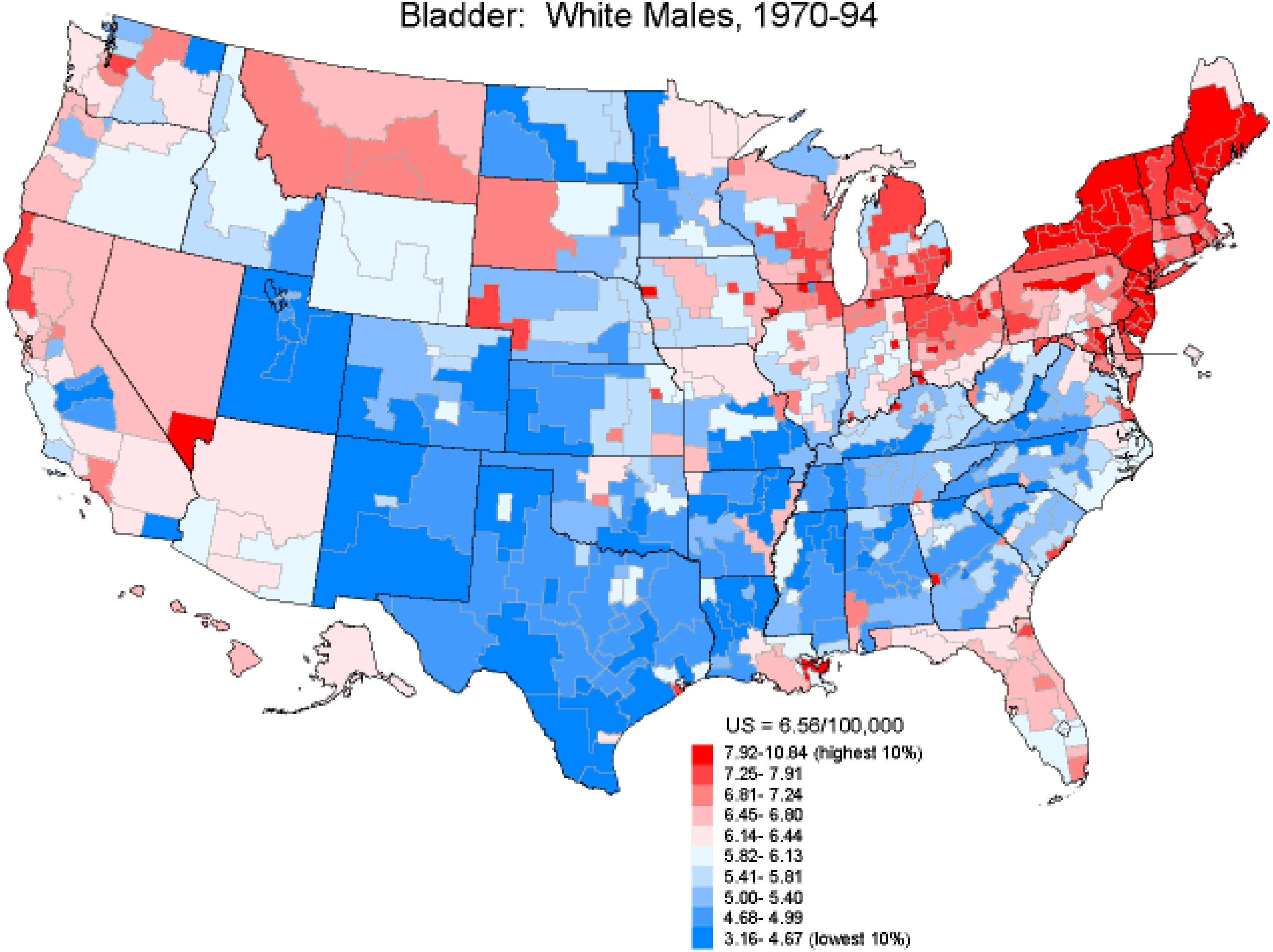
DBP Epidemiology

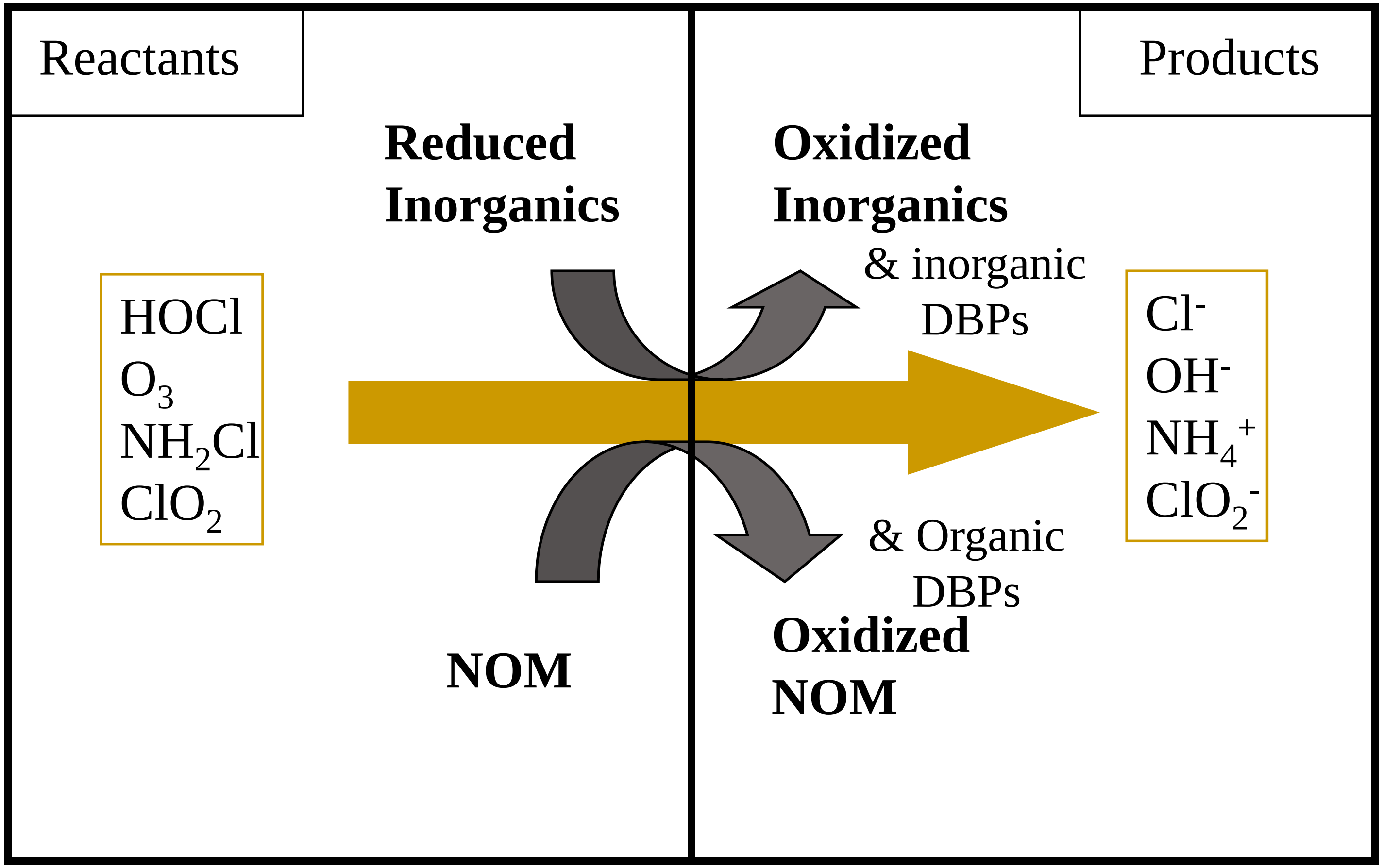
- Bladder Cancer
  - DBPs linked to 9,300 US cases every year
- Other Cancers
  - Rectal, colon
- Reproductive & developmental effects
  - Miscarriages & Low birth weight
  - Birth Defects
    - e.g., Cleft palate, neural tube defects
- Other
  - Kidney & spleen disorders
  - Immune system problems,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

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

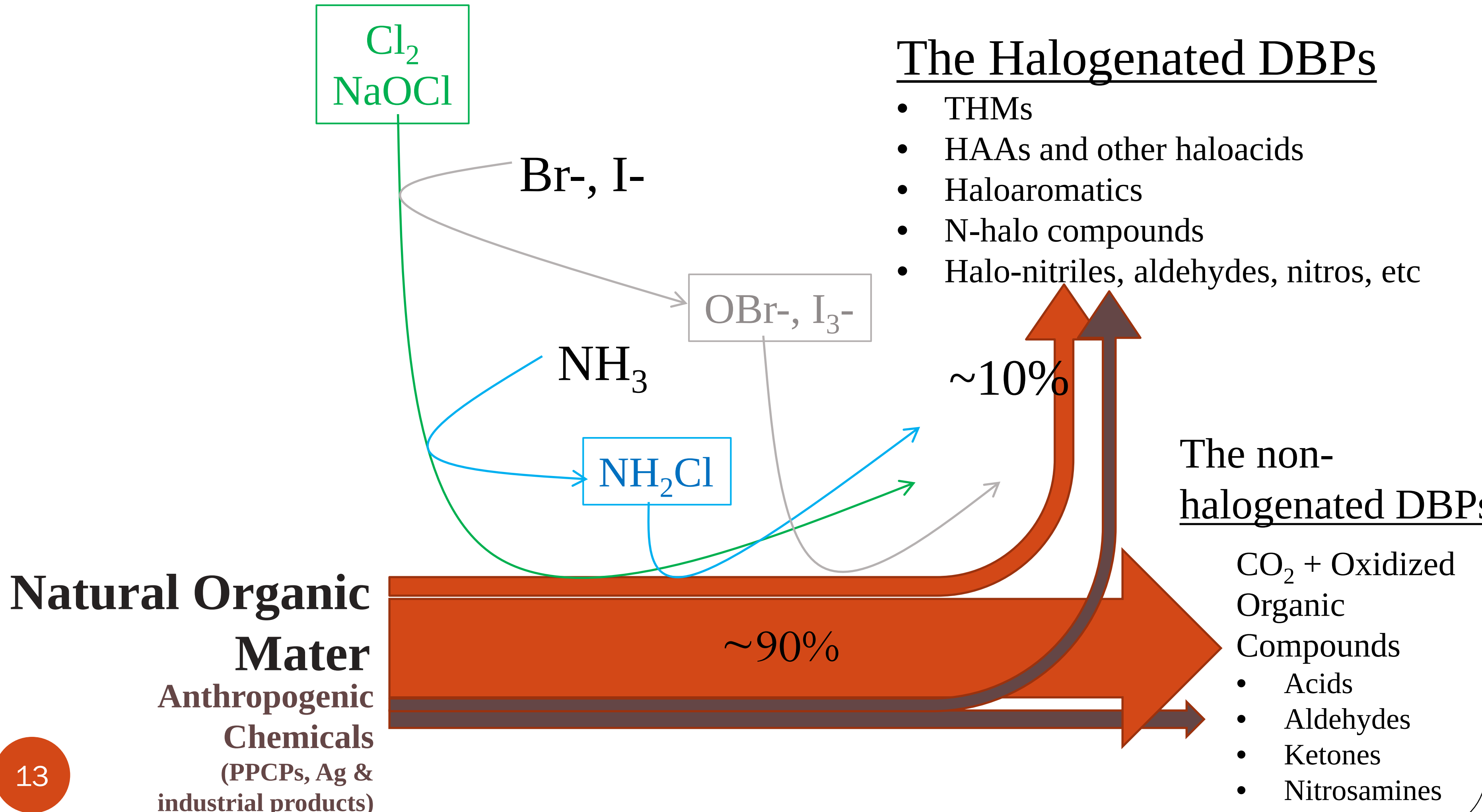
20 µg/L THMs - high risk
Hwang et al., 2008

Cancer Mortality Rates by State Economic Area (Age-adjusted 1970 US Population)
Bladder: White Males, 1970-94




Reactants
Products
Reduced
Inorganics
Oxidized
Inorganics
& inorganic
DBPs
HOCl
O_3
NH_2Cl
ClO_2
Cl^-
OH^-
NH_4^+
ClO_2^-
& Organic
DBPs
Oxidized
NOM
NOM

Formation of Cl_2-driven DBPs



Reactions with Disinfectants: Chlorine

The Precursors!

HOCl

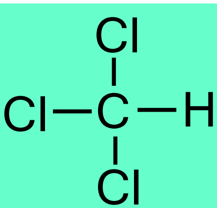
+ natural organics

(NOM)

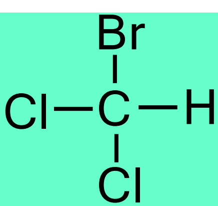
Oxidized NOM
and inorganic chloride
- Aldehydes

Chlorinated Organics
- TOX
- THMs
- HAAs

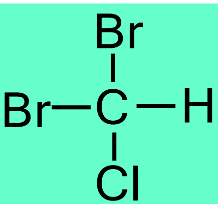
The THMs



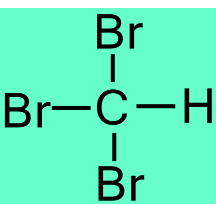
Chloroform



Bromodichloromethane



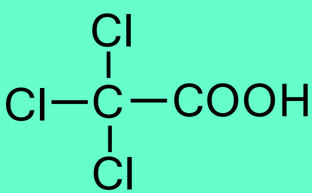
Chlorodibromomethane



Bromoform

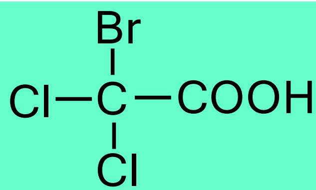
The Haloacetic Acids

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

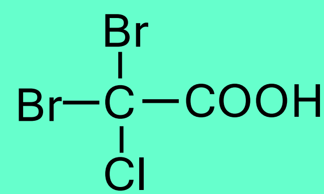


Trichloroacetic Acid

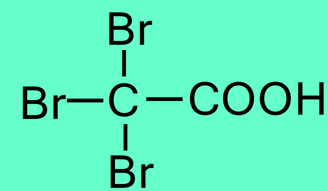
(TCAA)



Bromodichloroacetic Acid

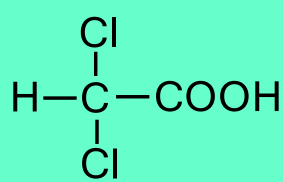


Chlorodibromoacetic Acid



Tribromoacetic Acid

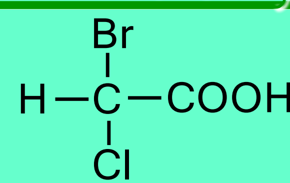
  - And 2 or 3 of the dihaloacetic acids



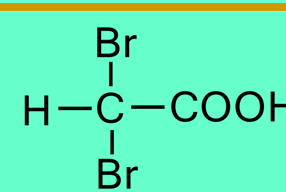
Dichloroacetic Acid

(DCAA)

HAA6 only



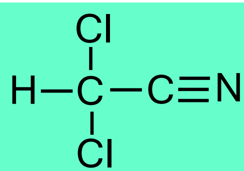
Bromochloroacetic Acid



Dibromoacetic Acid

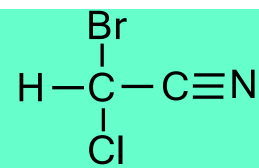
Haloacetonitriles

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



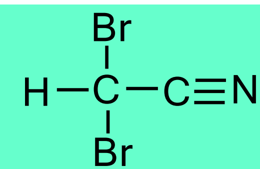
Dichloroacetonitrile

(DCAN)



Bromochloroacetonitrile

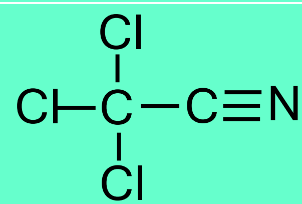
(BCAN)



Dibromoacetonitrile

(DBAN)

  - Trihaloacetonitriles

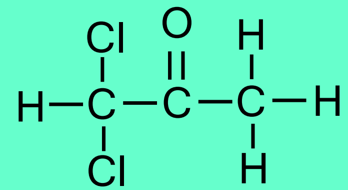


Trichloroacetonitrile

(TCAN)

Halopropanones

- As well as the:
    - dihalopropanones

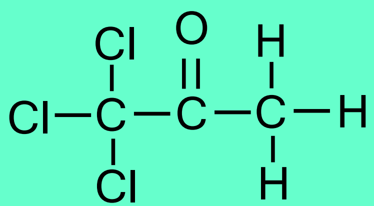


etc

1,1-Dichloropropanone

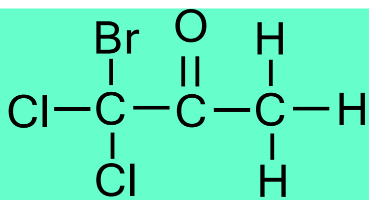
(DCP)

    - trihalopropanones



1,1,1-Trichloropropanone

(TCP)

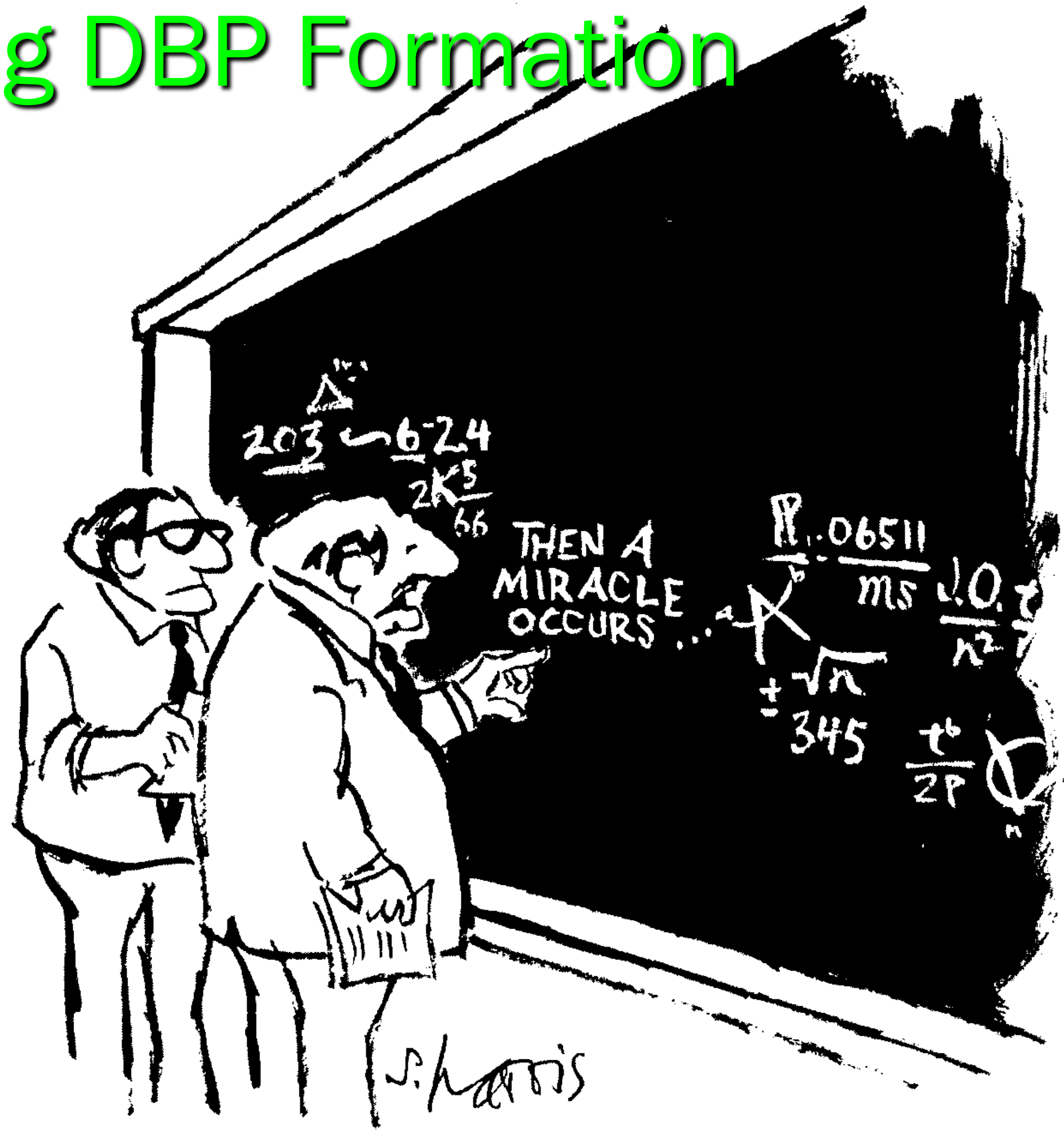


1,1,1-Bromodichloropropanone

etc.

Factors Affecting DBP Formation

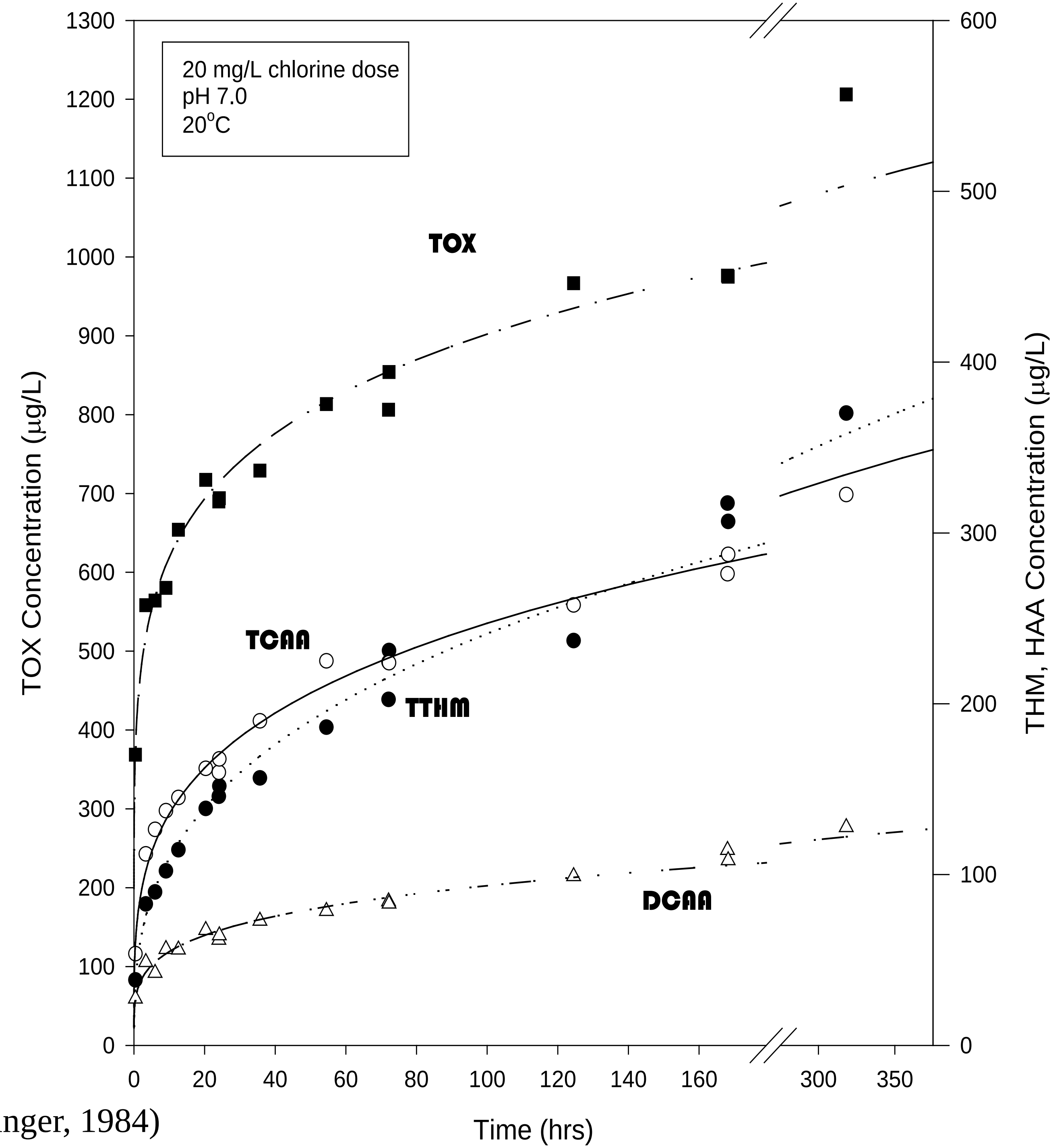
- Time
- pH
- Dose
- Temperature
- Bromide/Ammonia
- Pretreatment
- Reactions with pipe walls & attached materials



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

Time

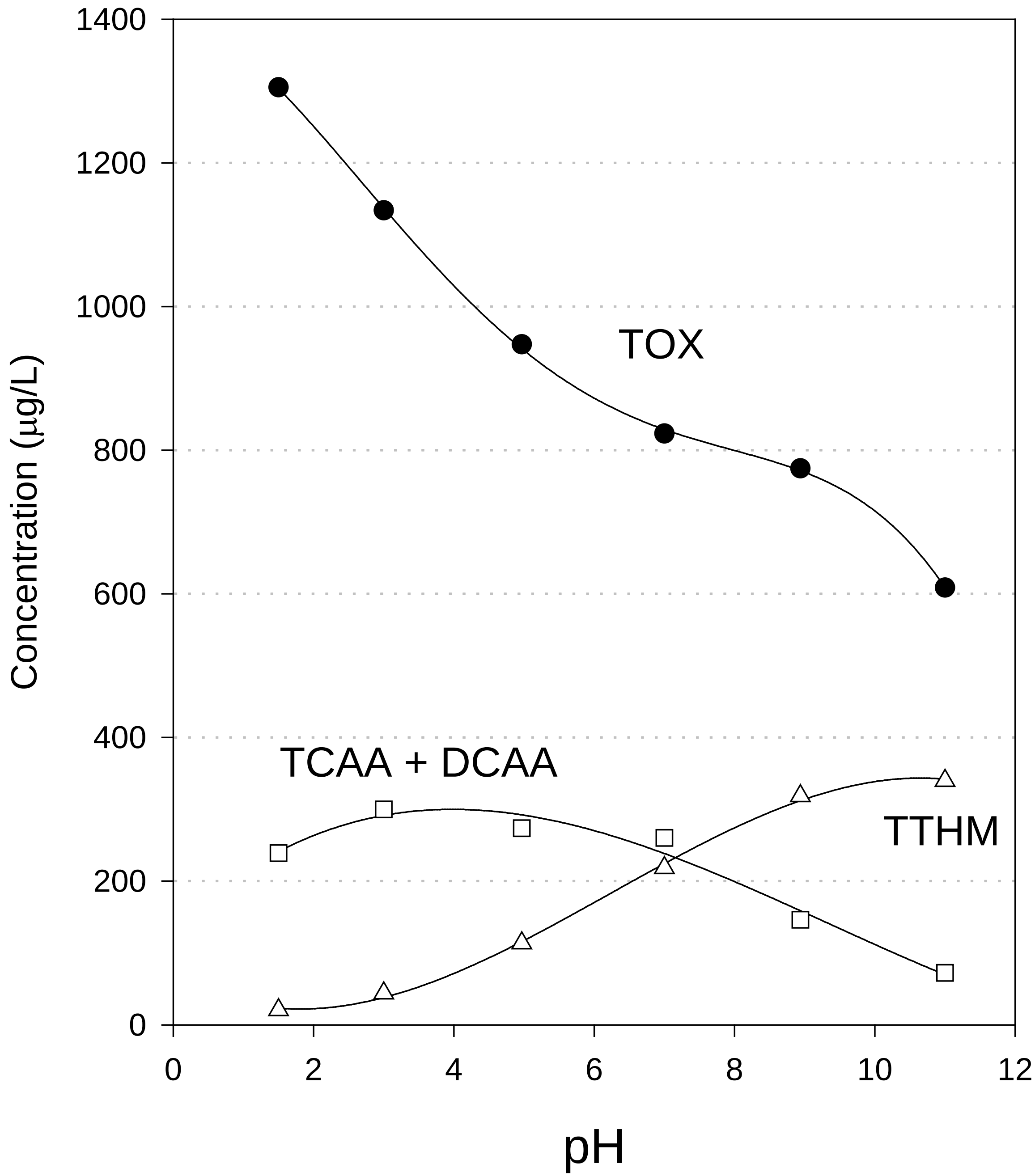
- Major Byproducts



Aquatic NOM

(after Reckhow & Singer, 1984)

pH Effects



Concentration (µg/L)
1400
1200
1000
800
600
400
200
0
TOX
TCAA + DCAA
TTHM
0
2
4
6
8
10
12
pH

Significance of Bromide

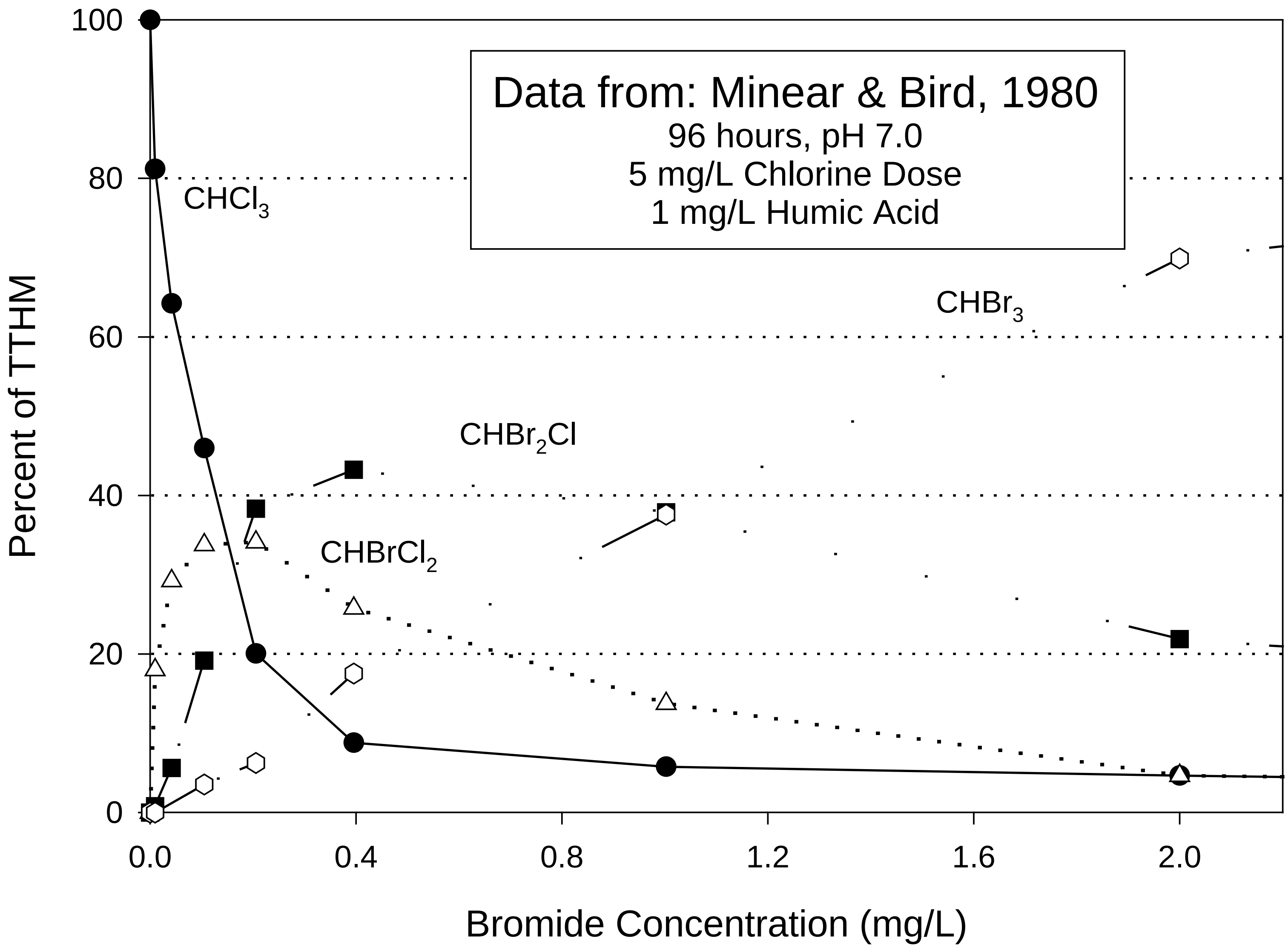
- Present in surface and groundwaters
- Concentrations are highly variable
- Not removed by most treatment processes
- Readily oxidized by chlorine

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

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

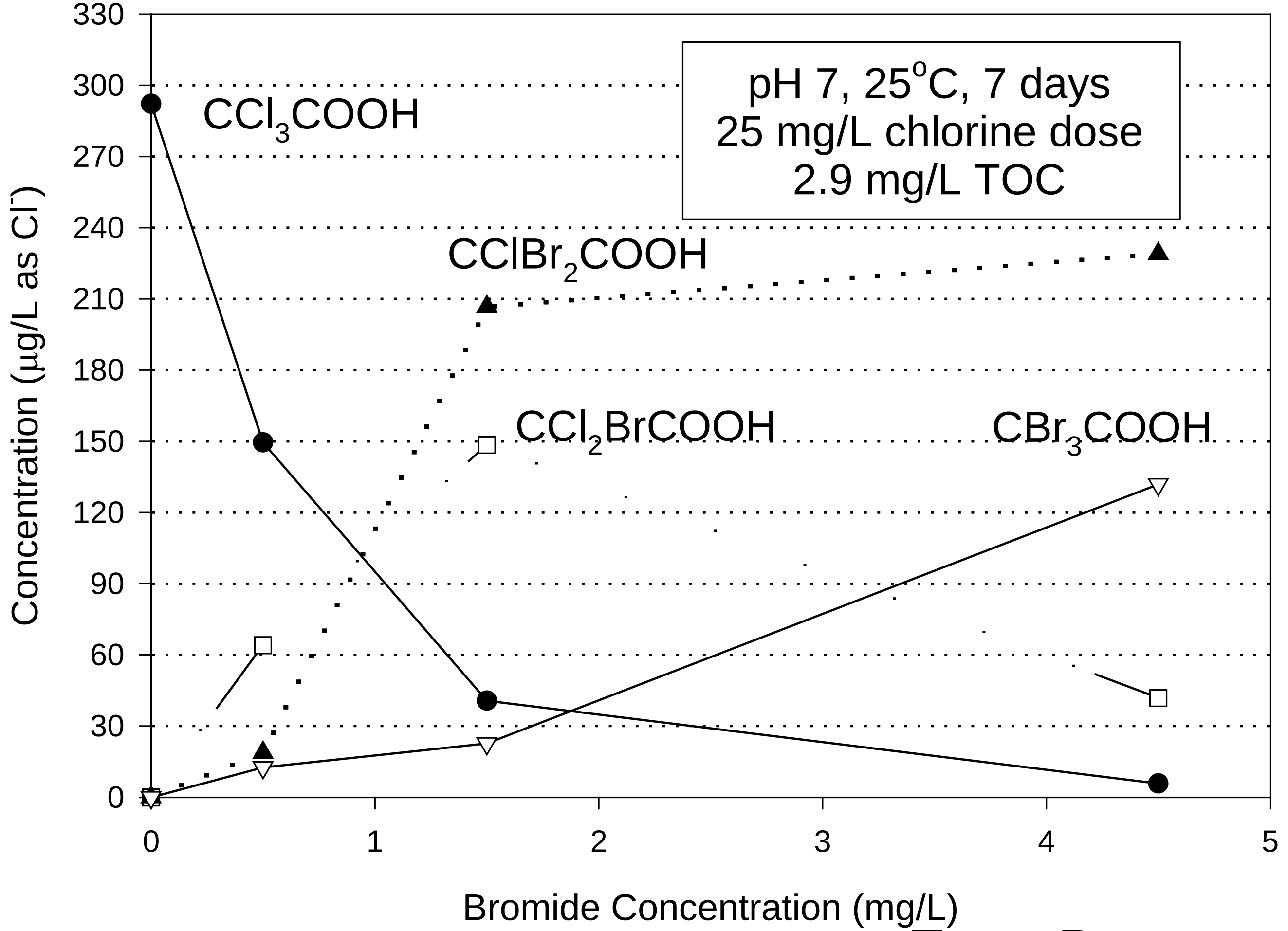
Therefore, bromide has a **13 second** half life at pH 7, and 1 mg/L residual chlorine

Impact of Bromide on THM Formation



Bromide: THAA Formation

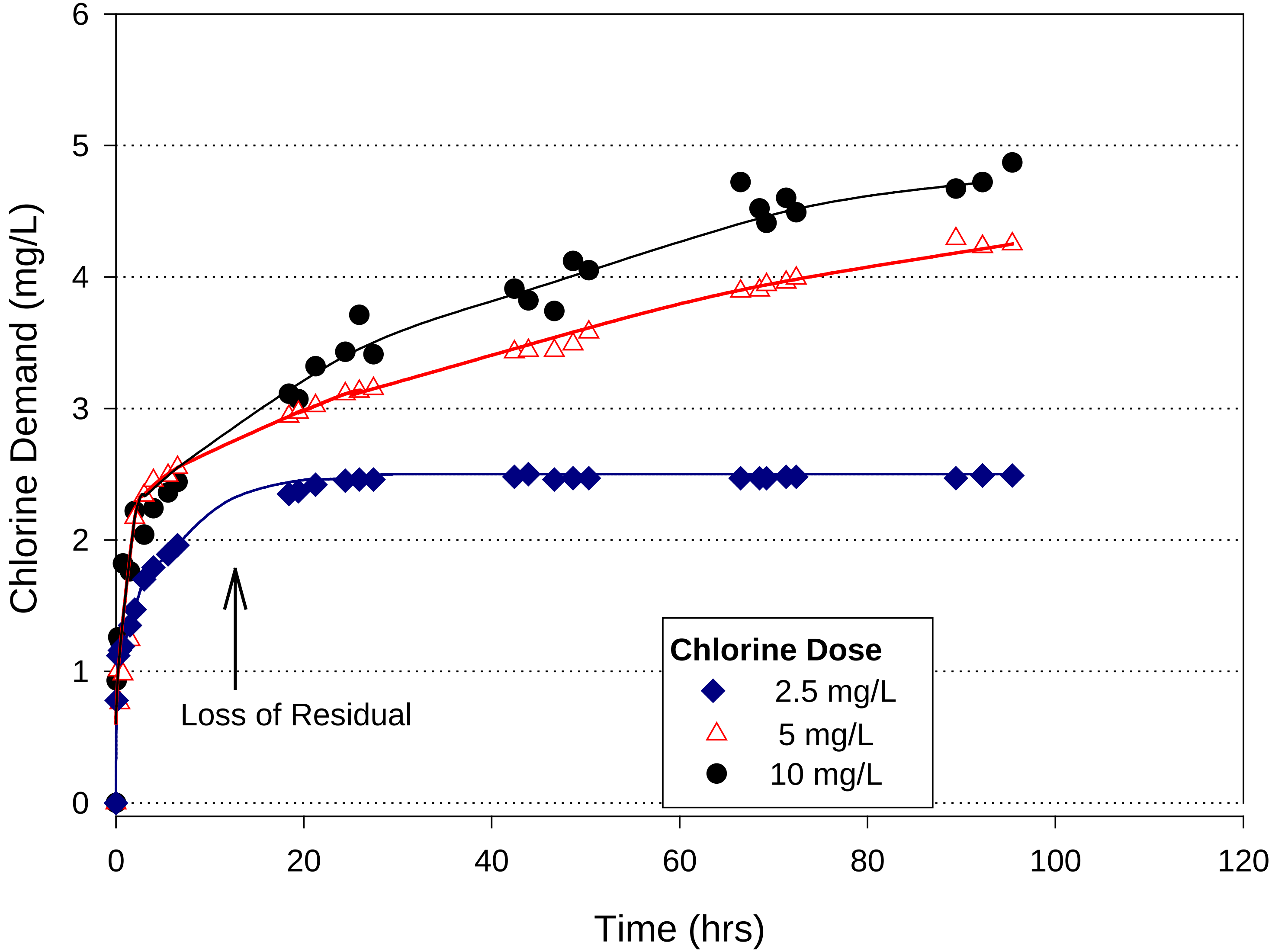
Note that TCAA is the only regulated THAA



From Pourmoghaddas, 1990

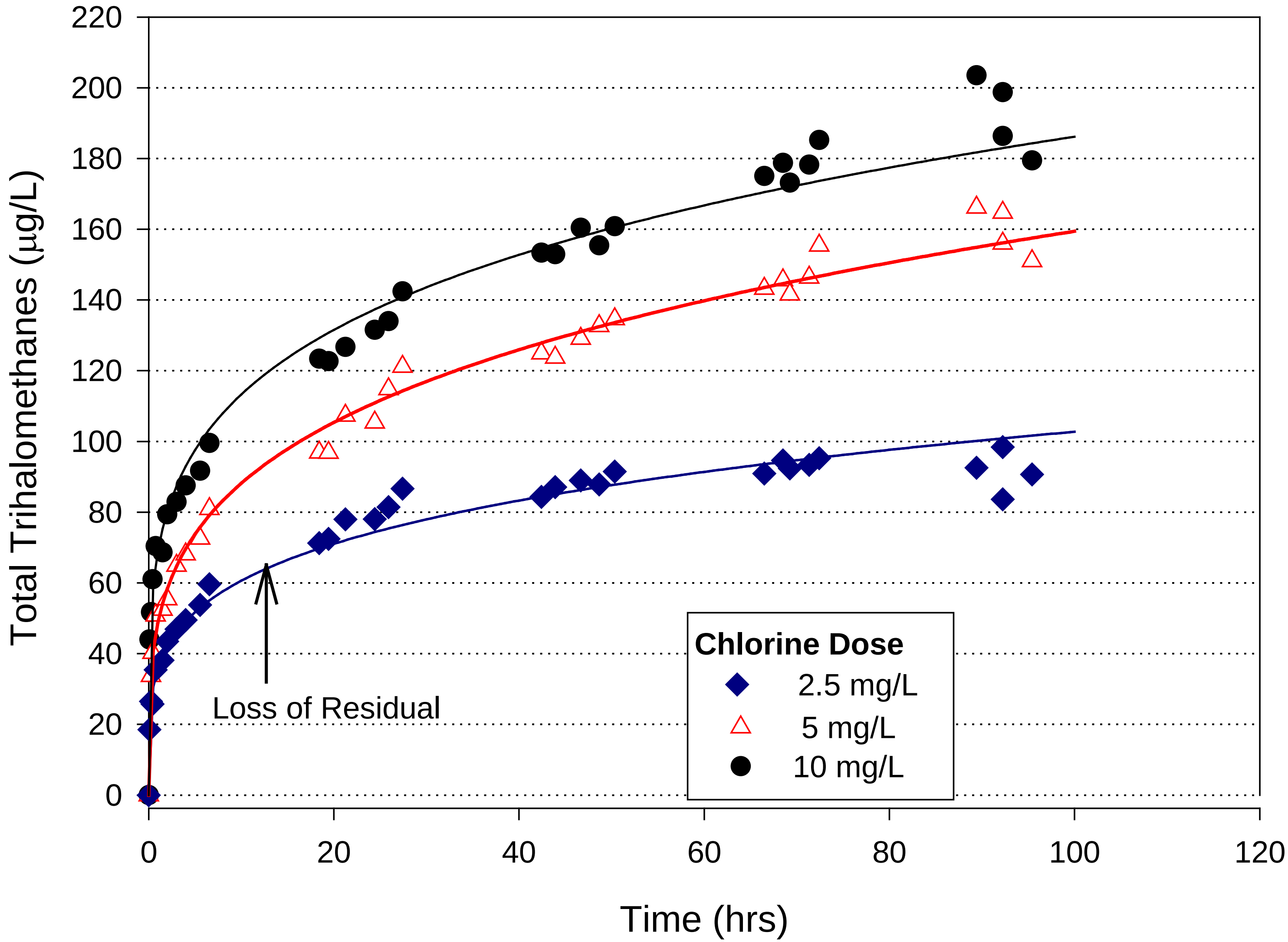
Case Study: Impact of time & chlorine dose

Cl_2 Demand



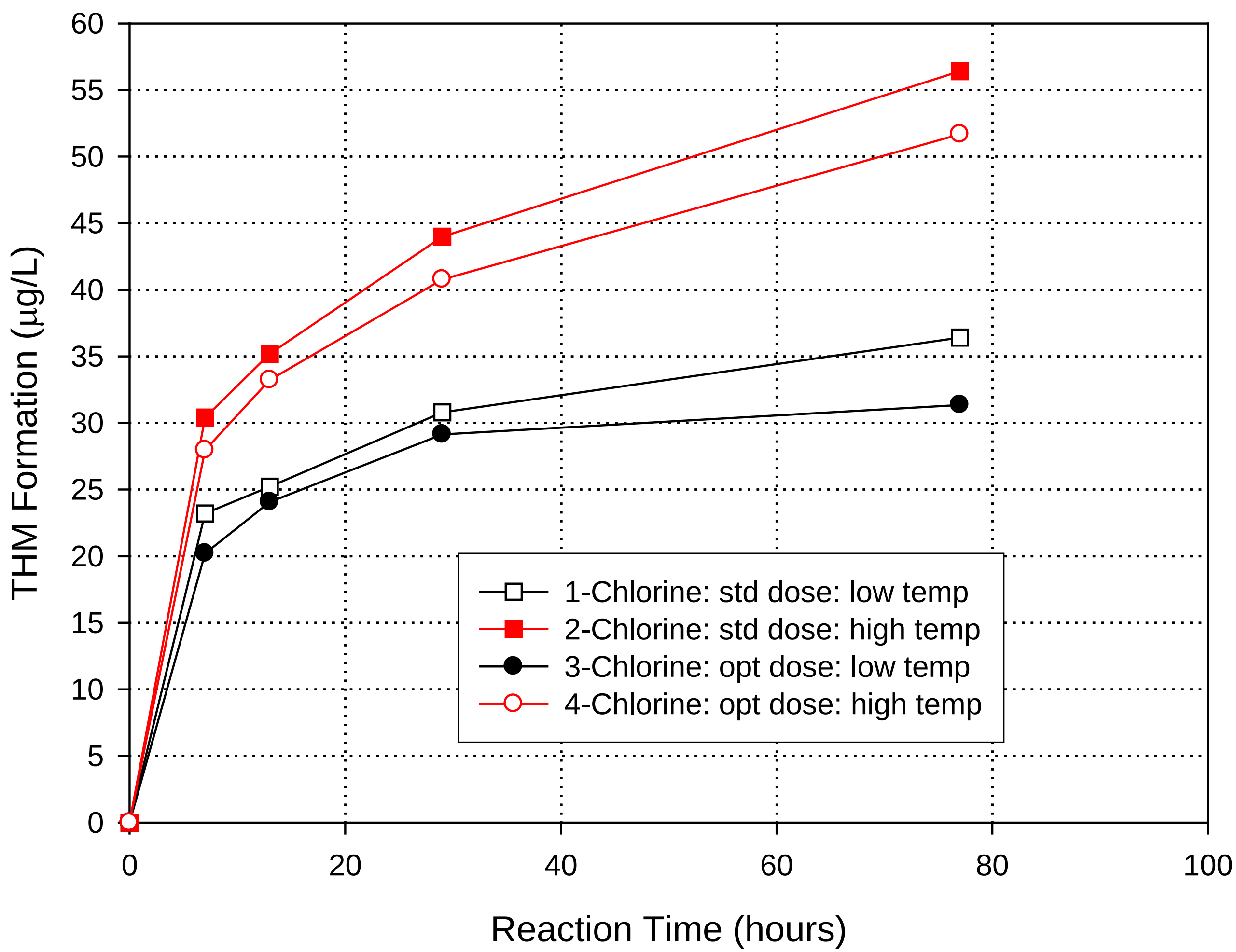
Case Study: Impact of time & chlorine dose

THM



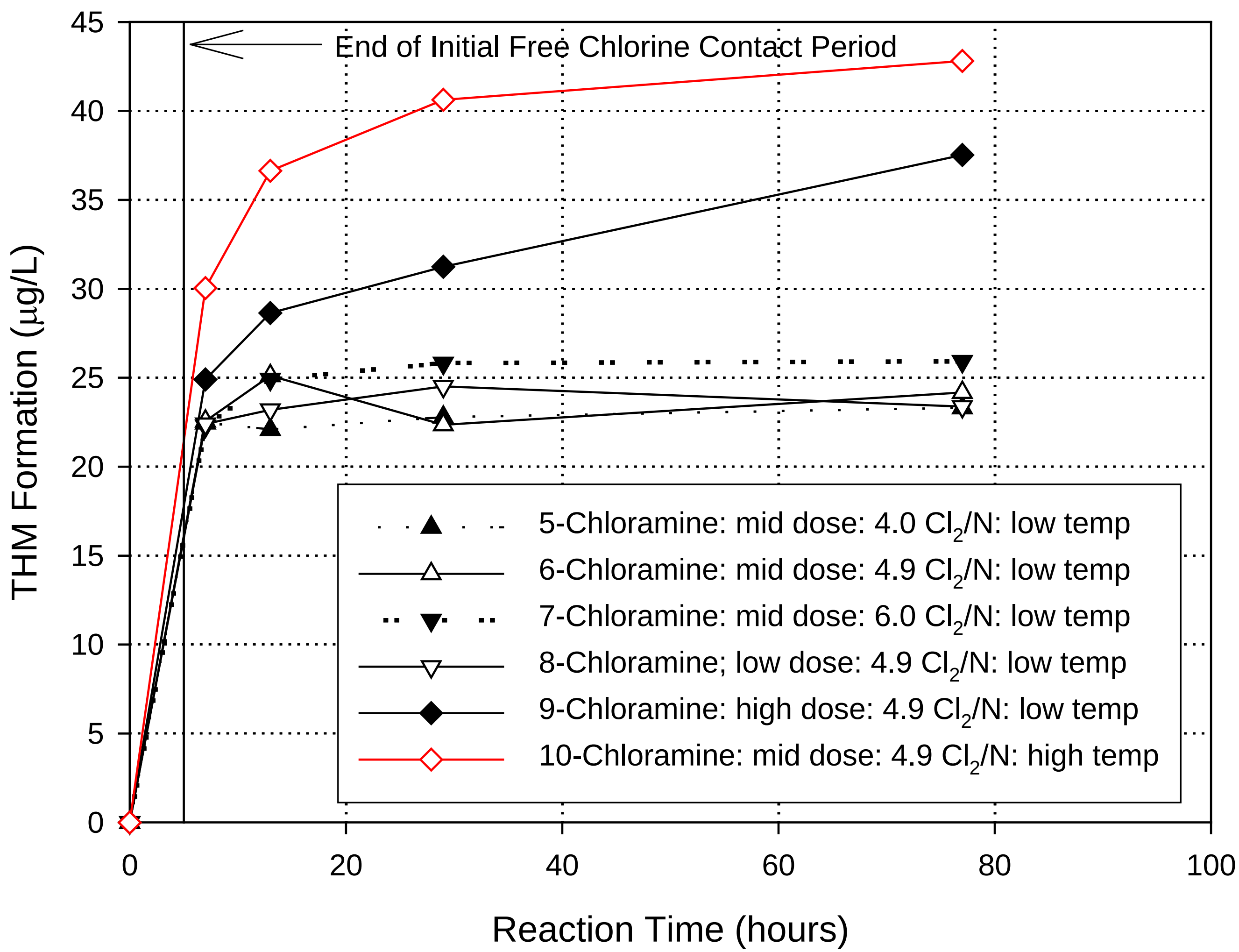
THMs from Chlorination

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



THMs from Chloramination

- Addition of ammonia after 5 hrs free contact time



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

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

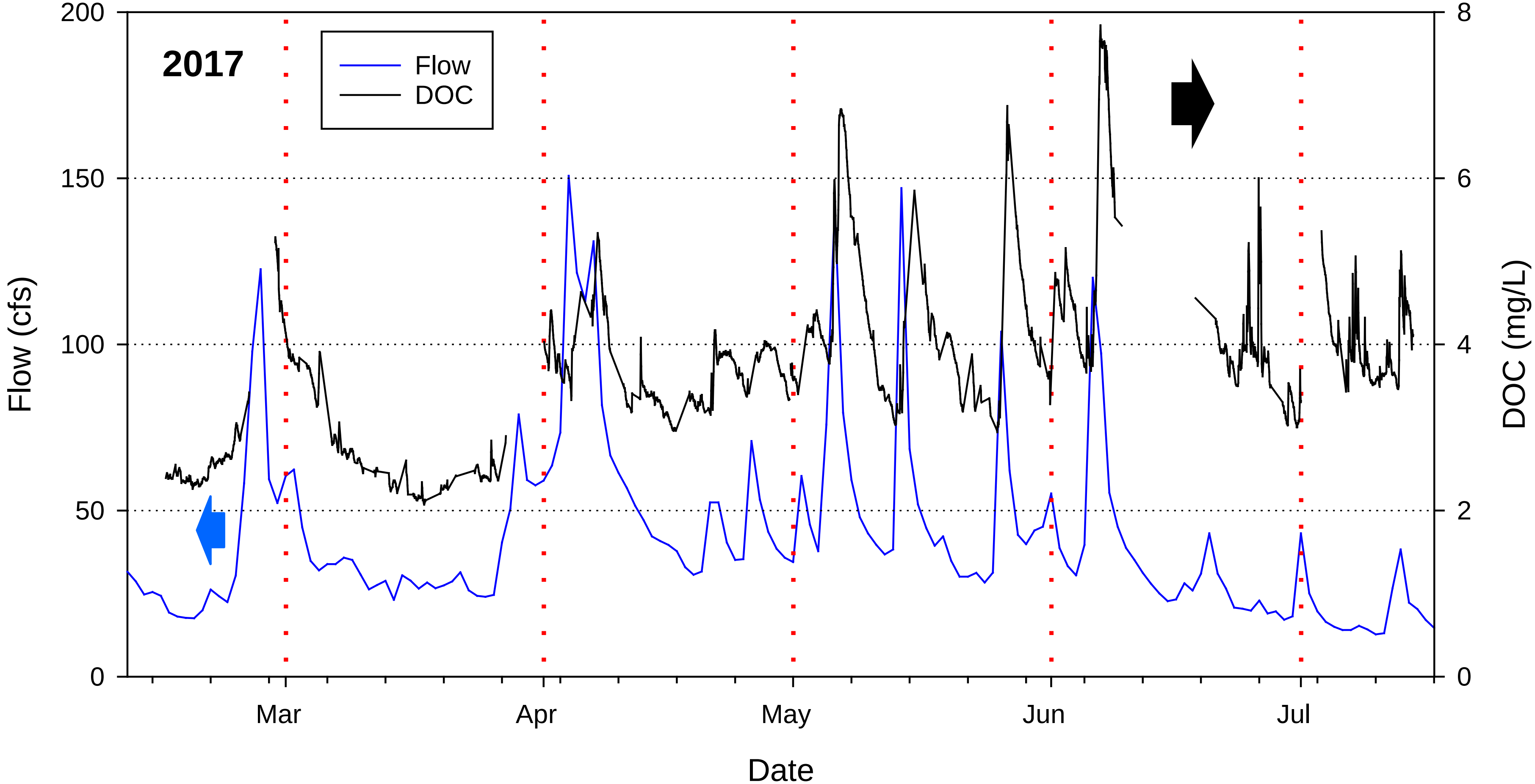
Descriptive, but not much insight

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

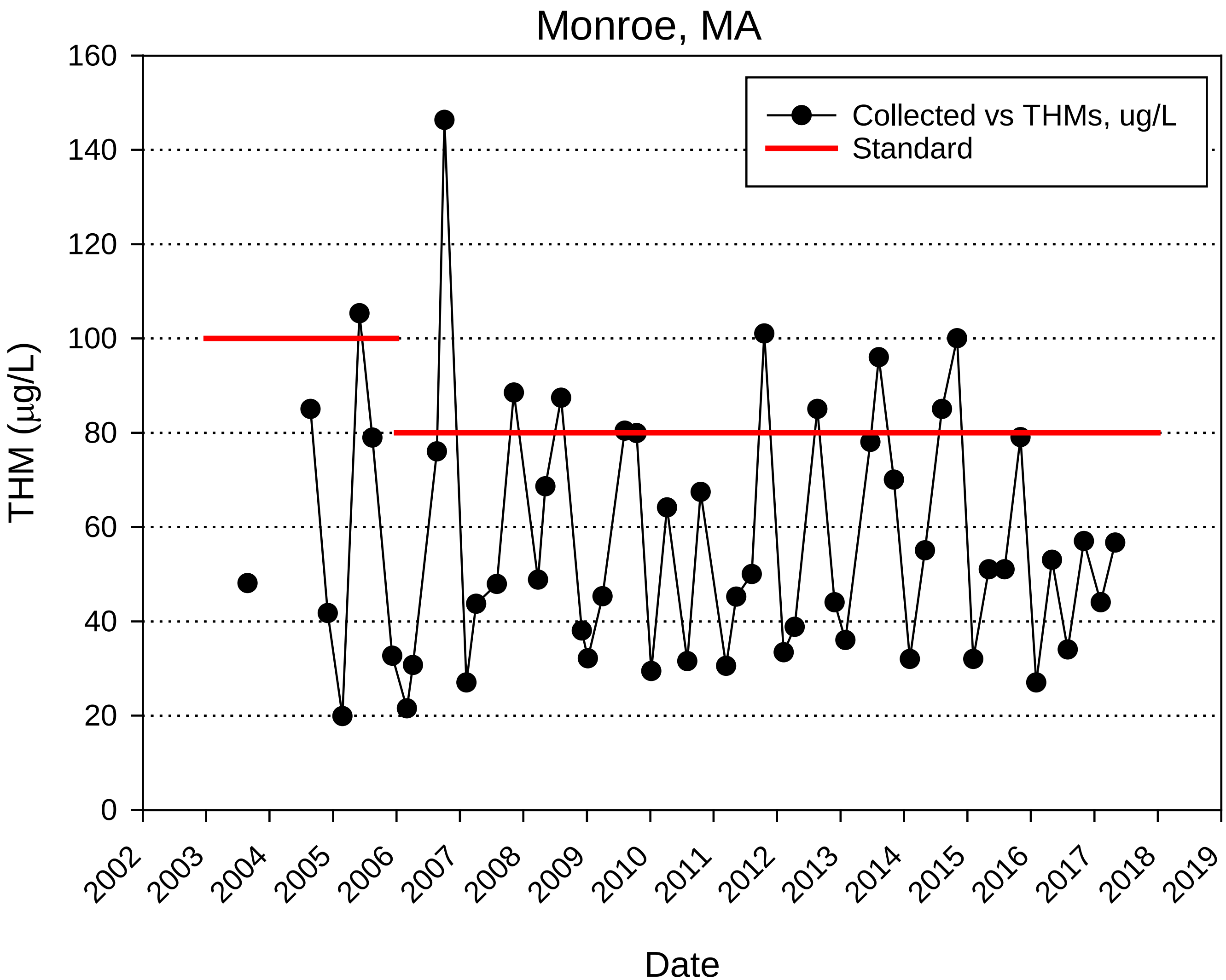
[1] $Cl_2/Br < 75$; [2] $Cl_2/Br > 75$; [3] $Cl_2/Br < 50$; [4] $Cl_2/Br > 50$

Annual TOC Cycles: Small NE Tributary

- Mill River in Amherst

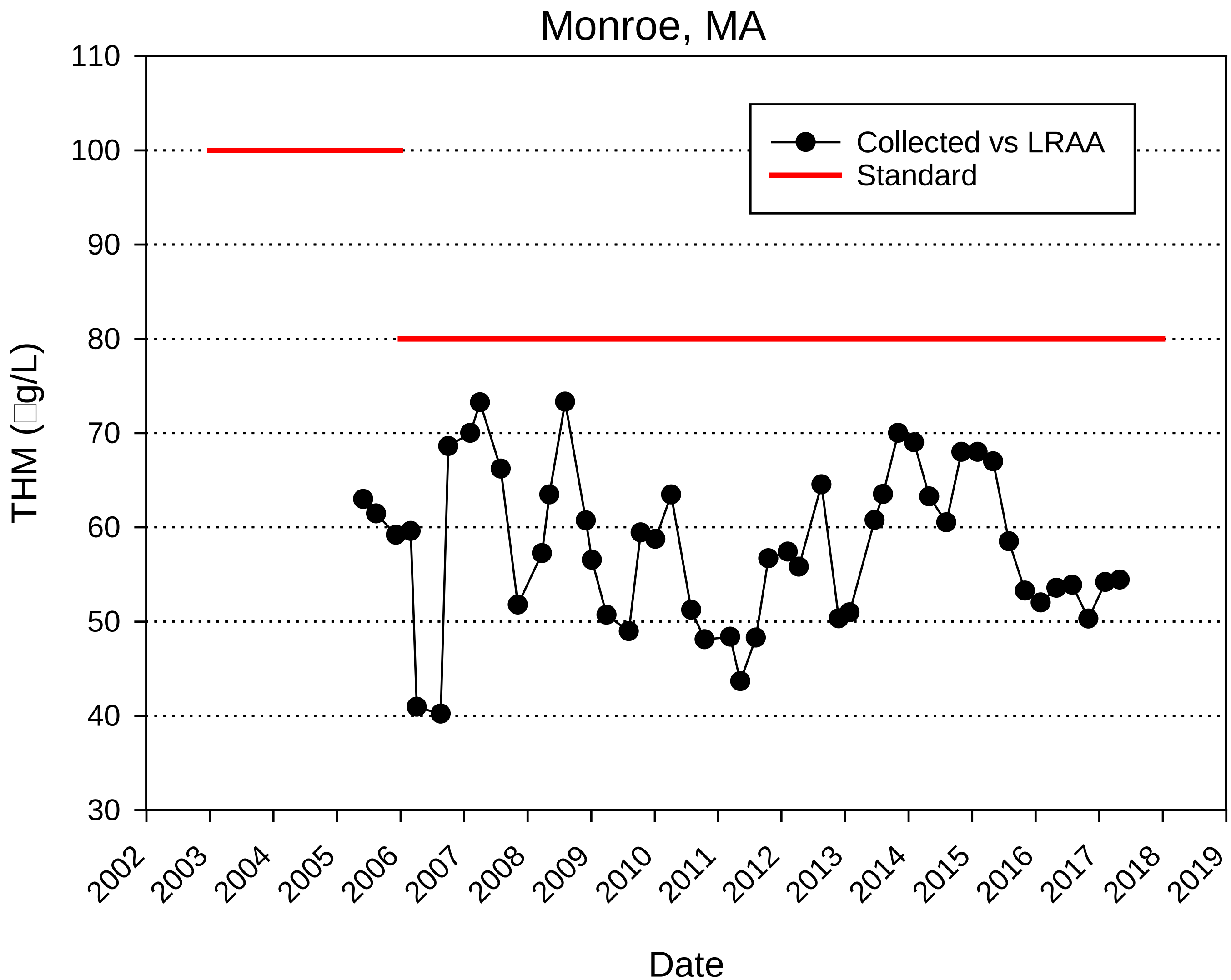


Monroe: quarterly THMs



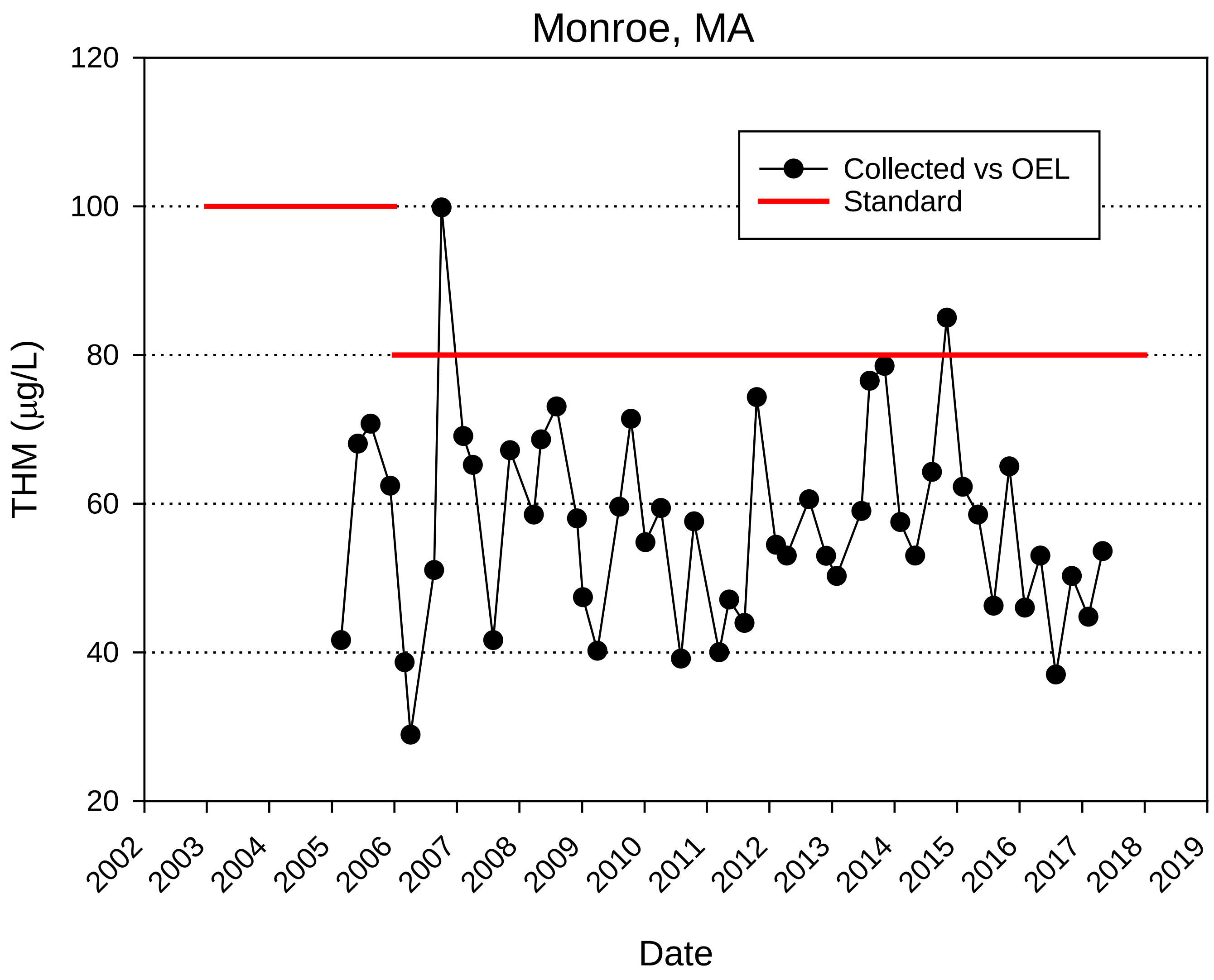
Monroe: THMs LRAA

- XCV



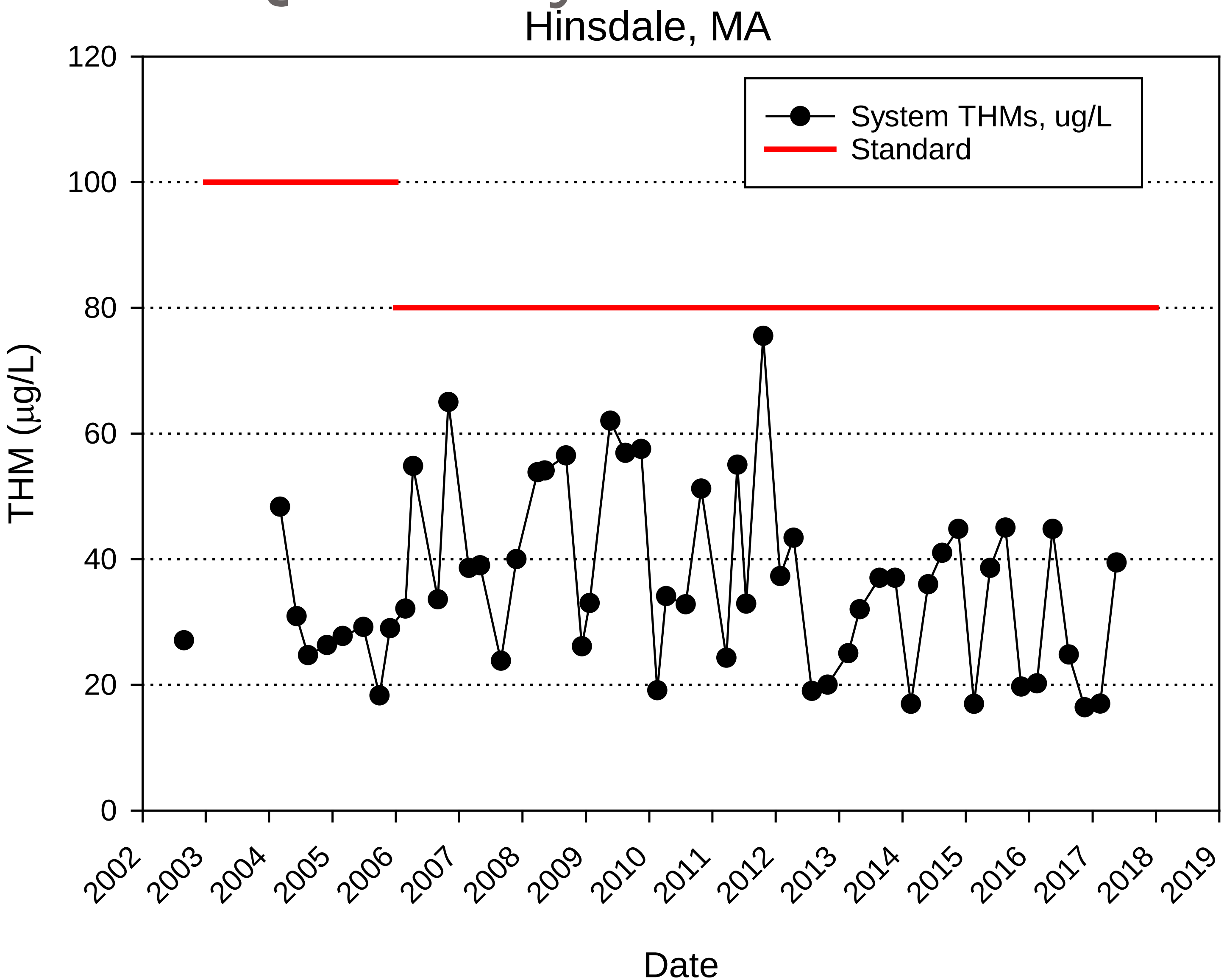
Monroe: THMs OEL

- dsf

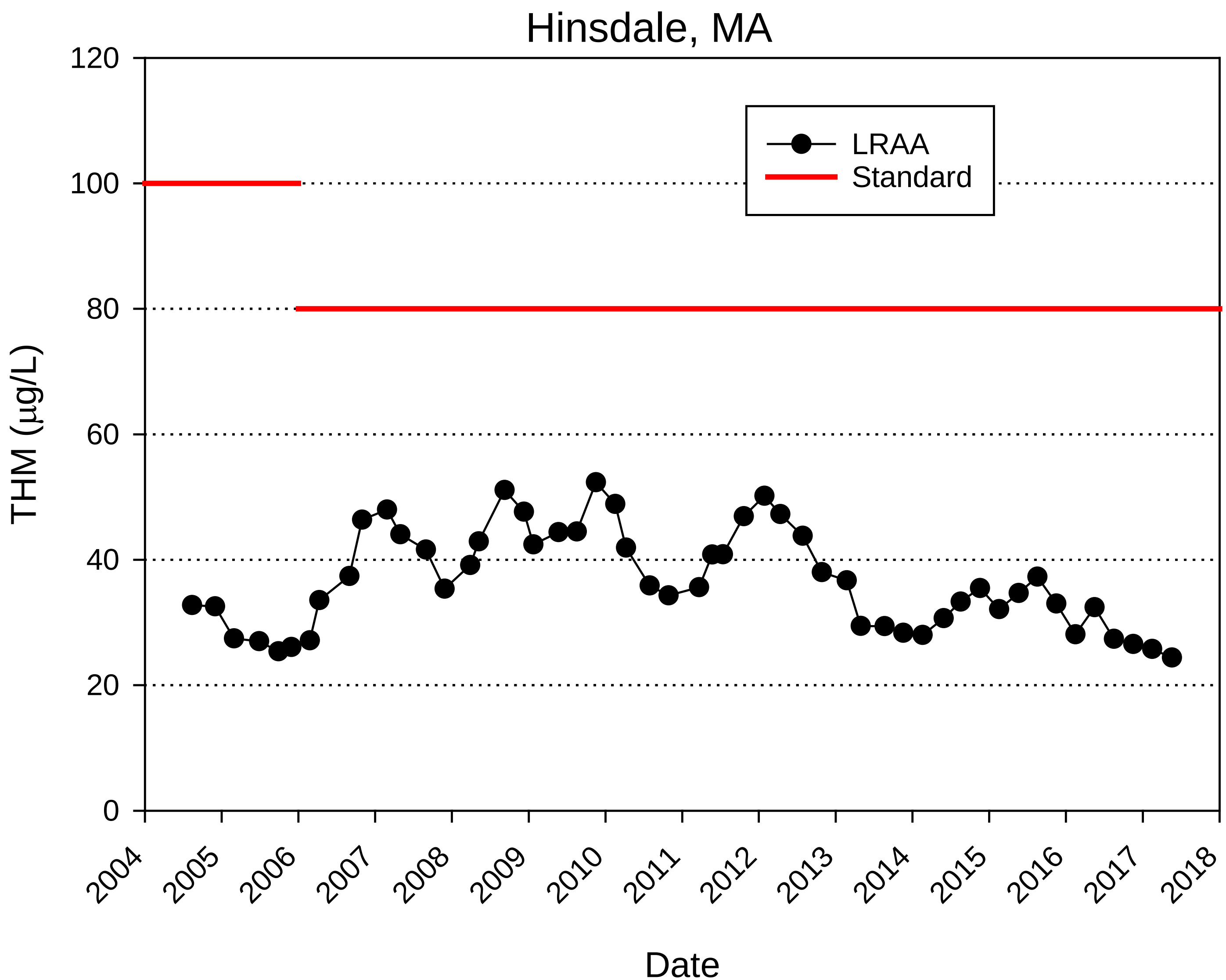


Hinsdale: Quarterly THMs

- sd

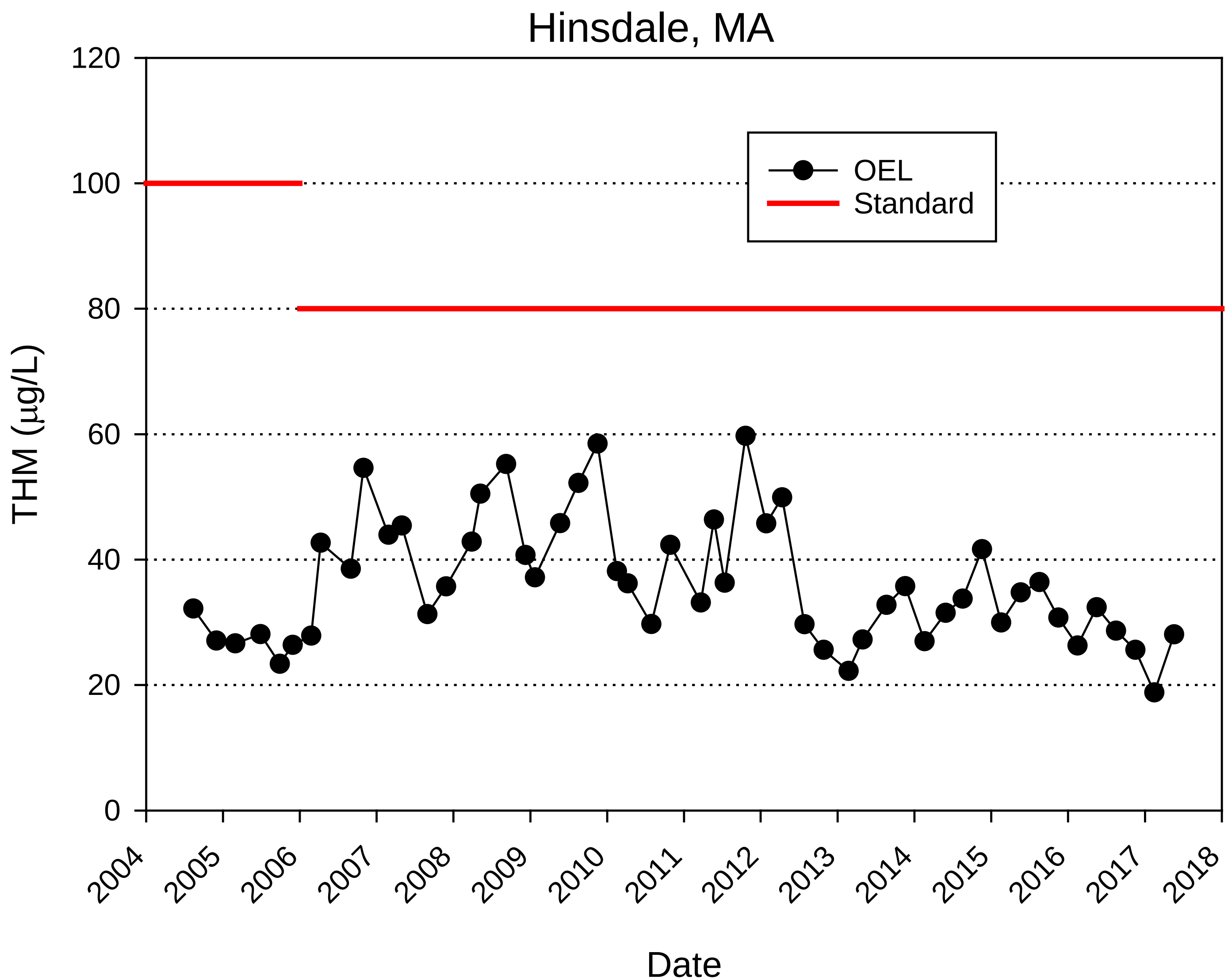


Hinsdale: THM LRAA



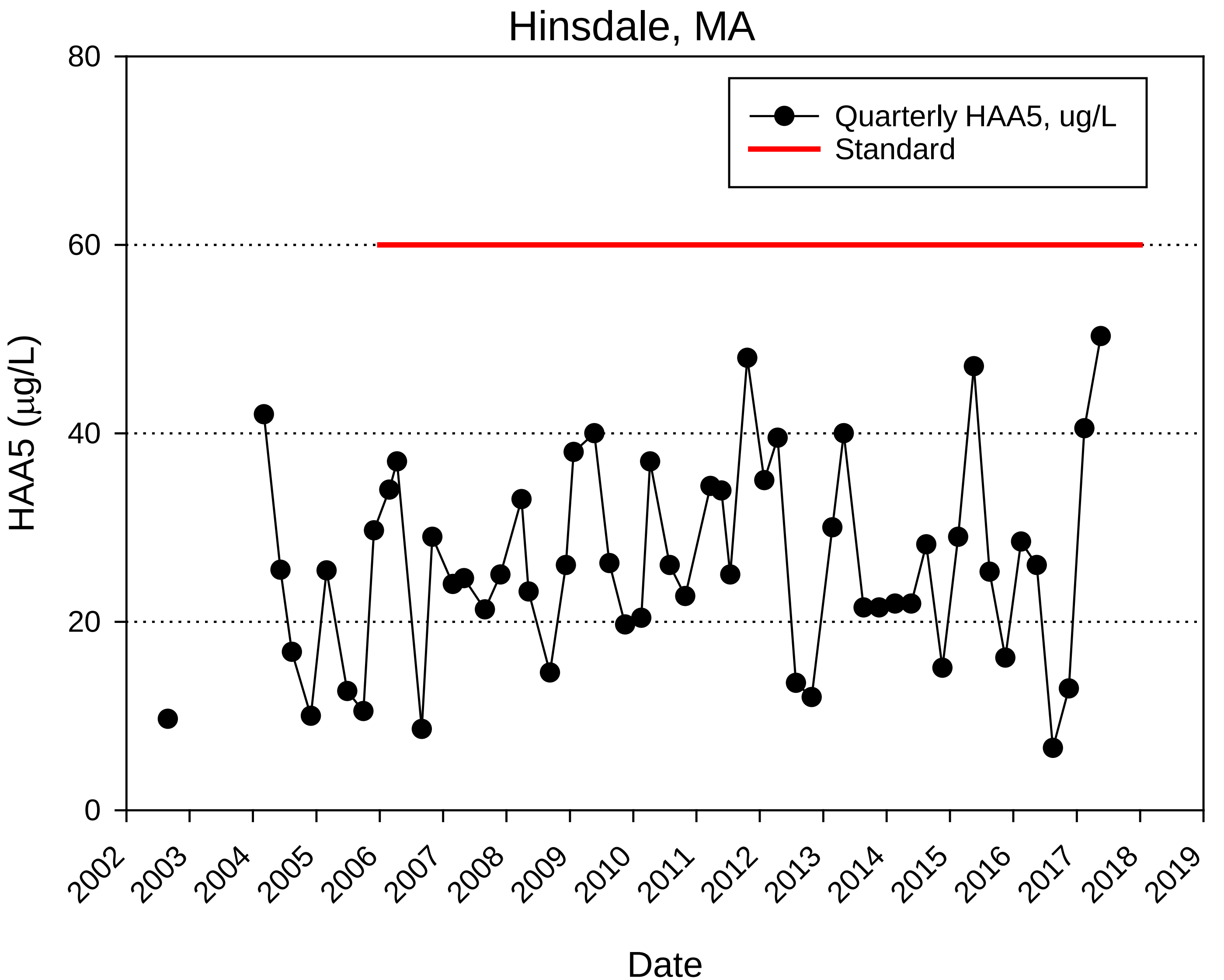
Hinsdale: THM OEL

- sd

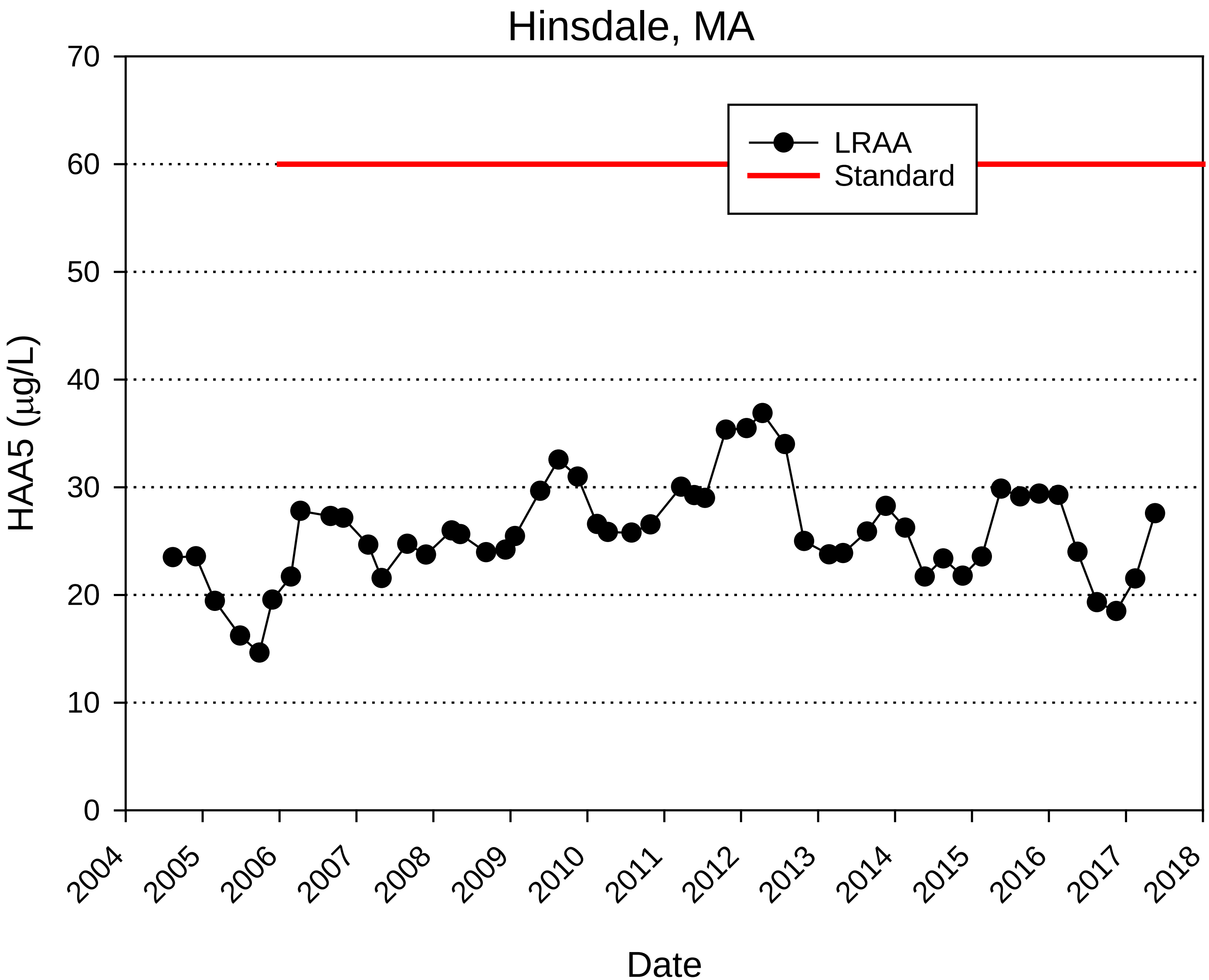


Hinsdale: Quarterly HAA5

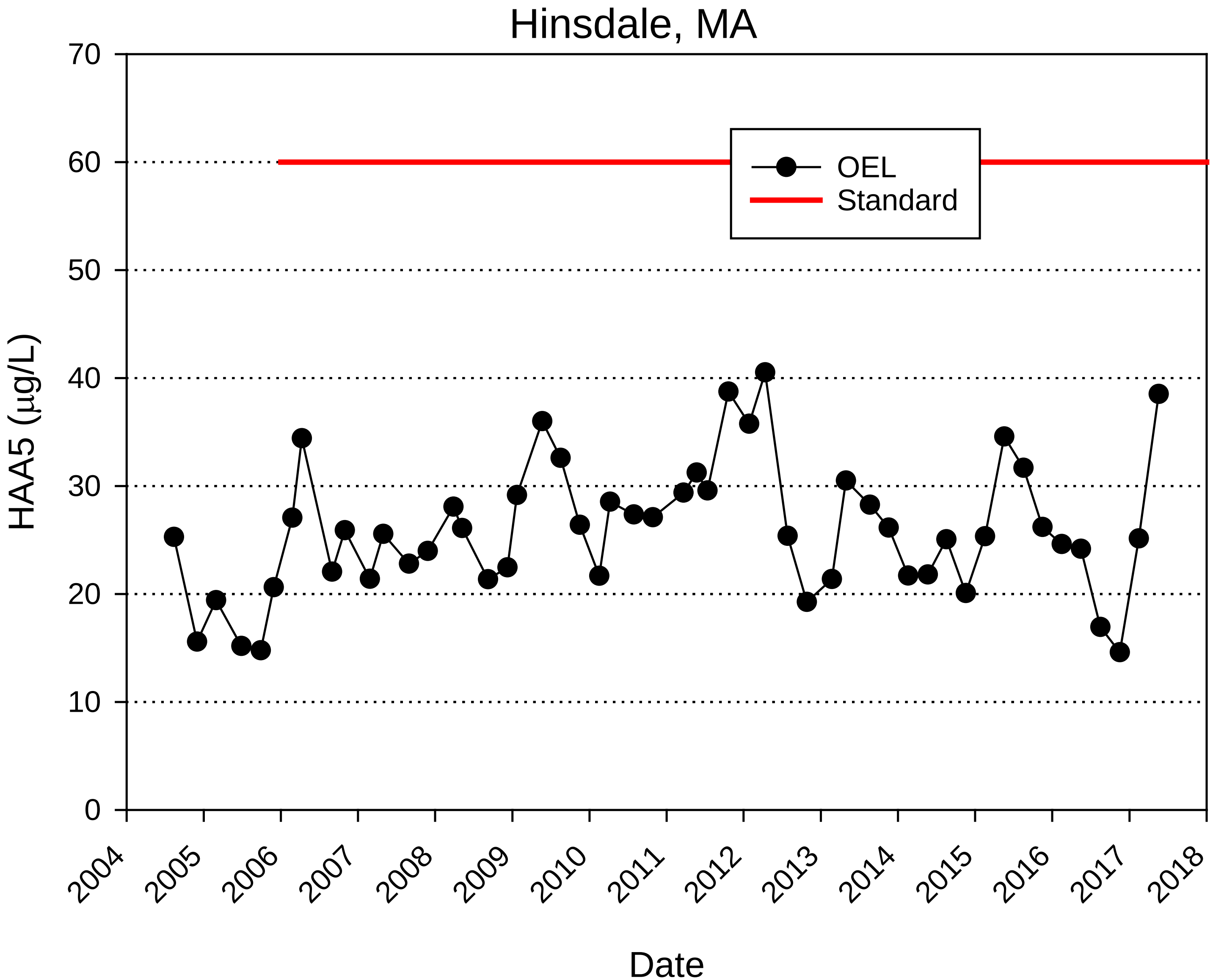
- ad



Hinsdale HAA5 RAA

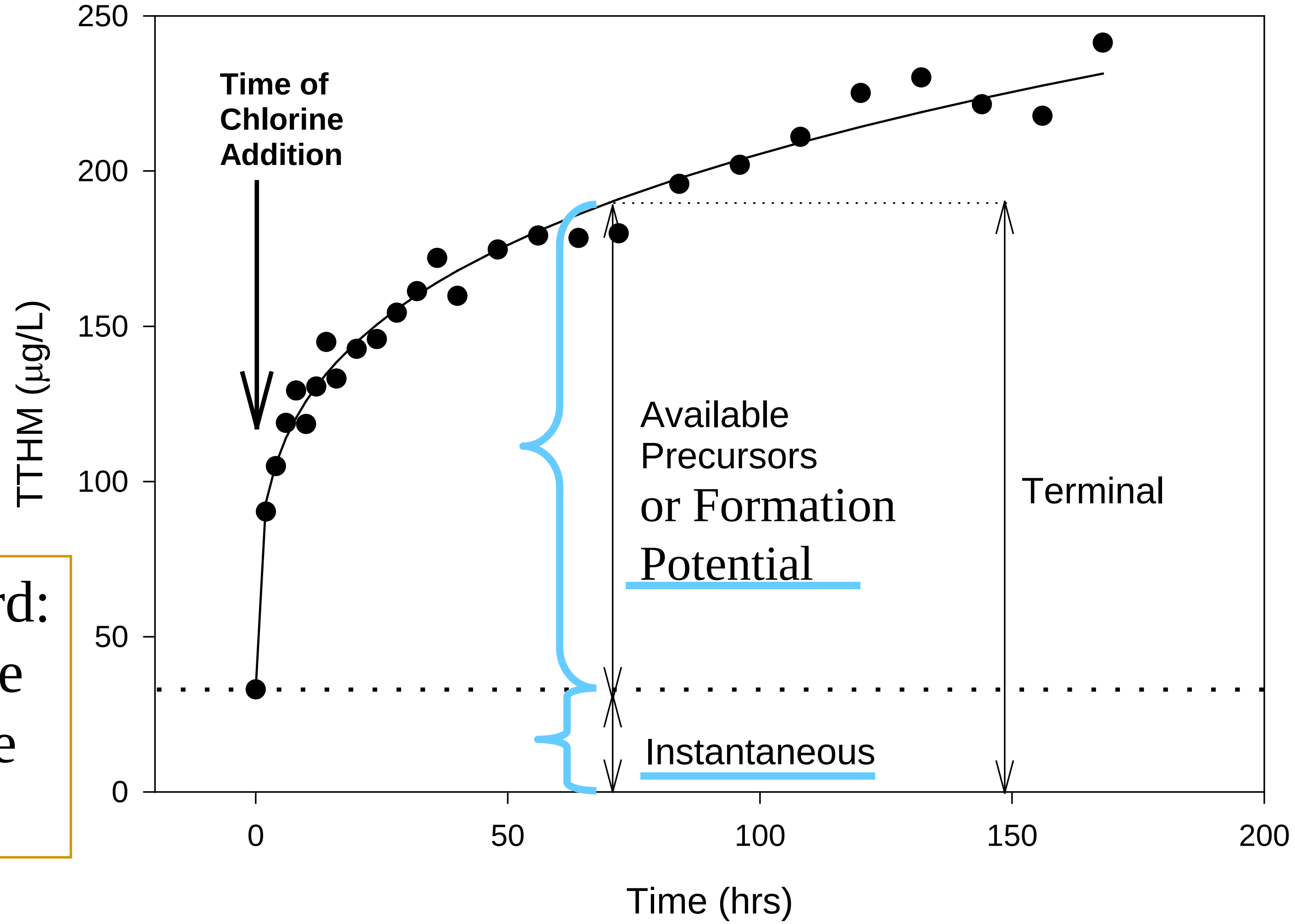


Hinsdale: HAA5 OEL



Analysis of DBP Precursors

Laboratory Precursor Test



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

Significance

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

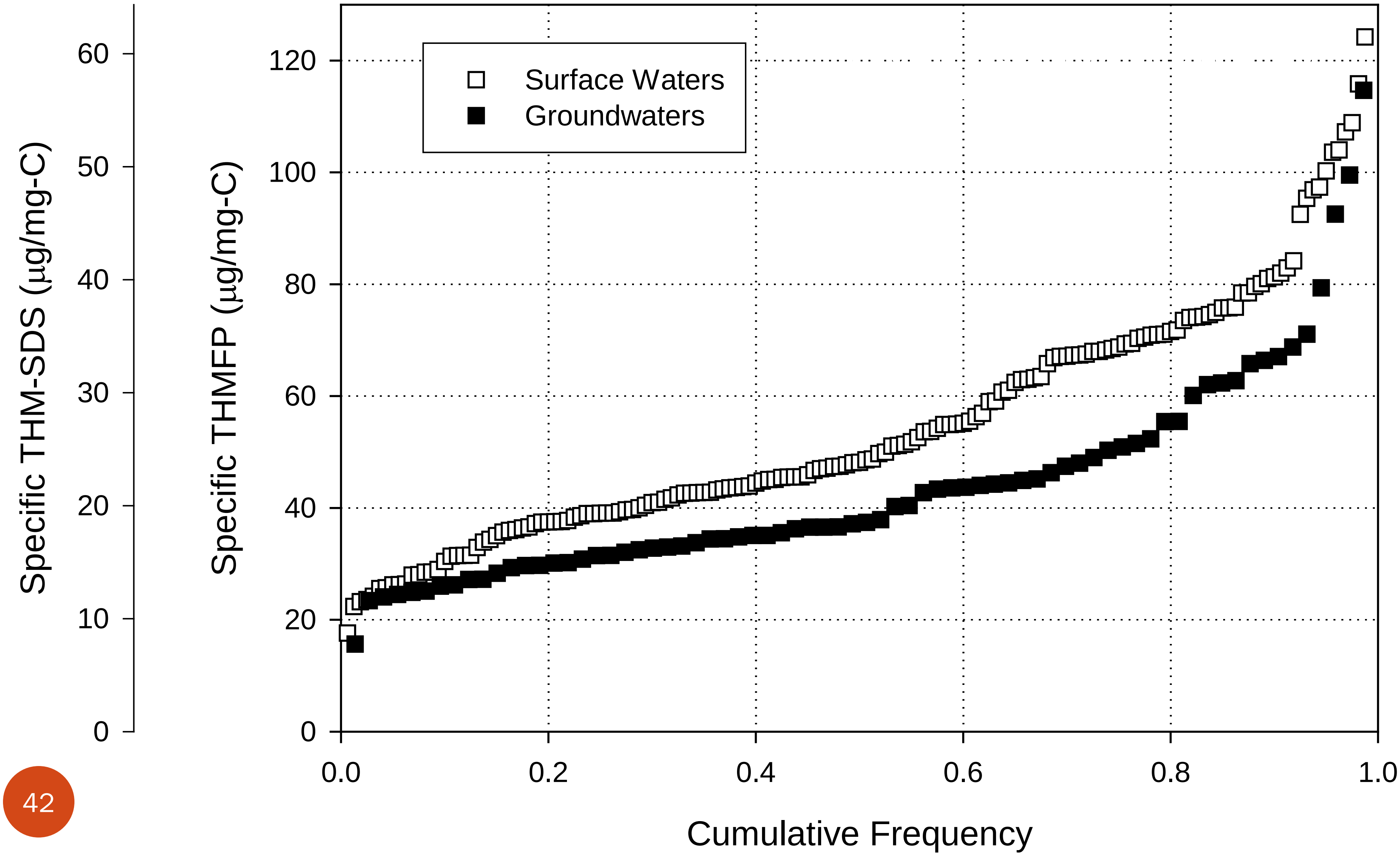
	THMs	HAAs
Stage 1&2	0.080	0.060

(mg/L)

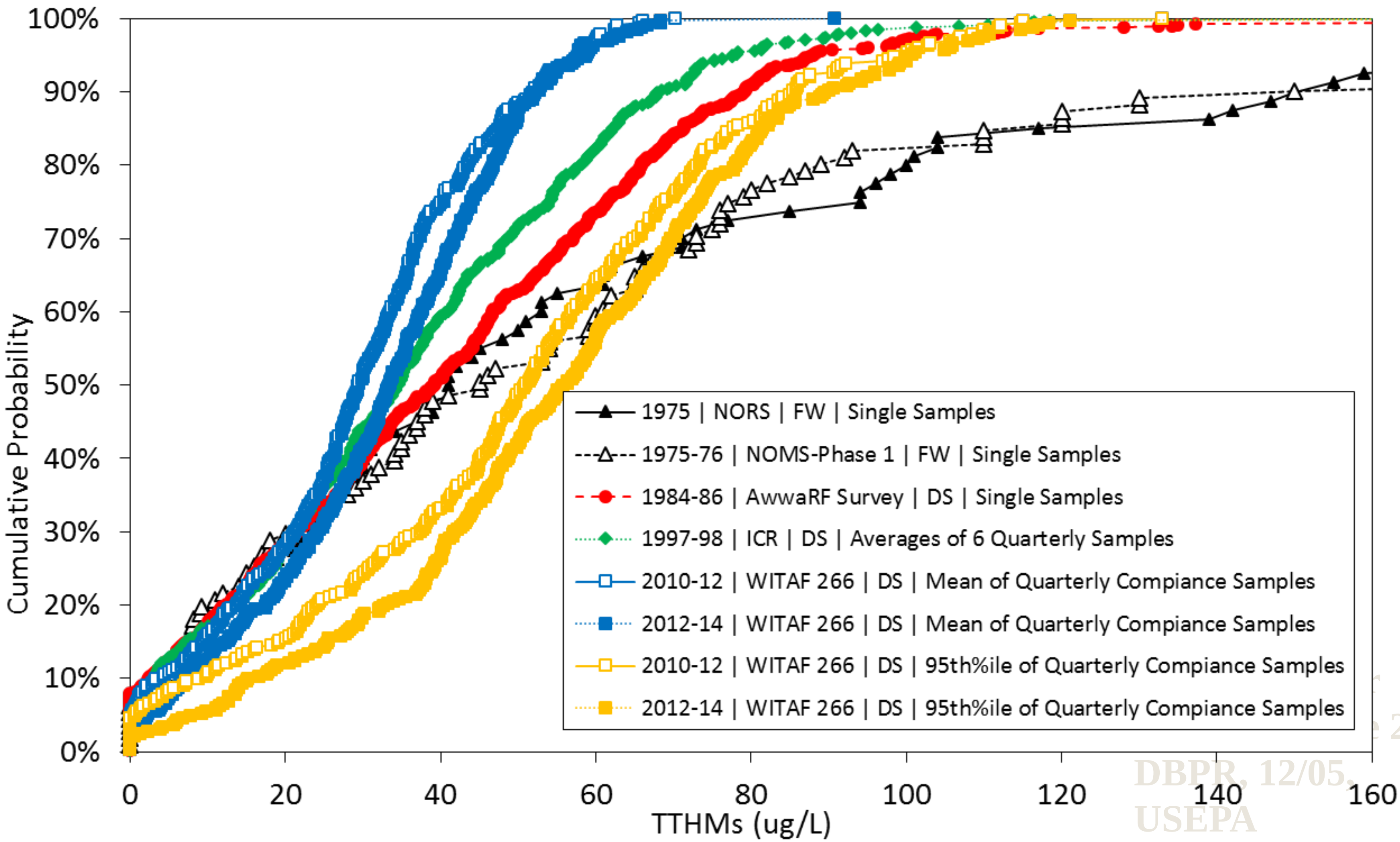
- Formation potential are important for controlling organic precursors
  - assess process performance
  - compare waters

National Database

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



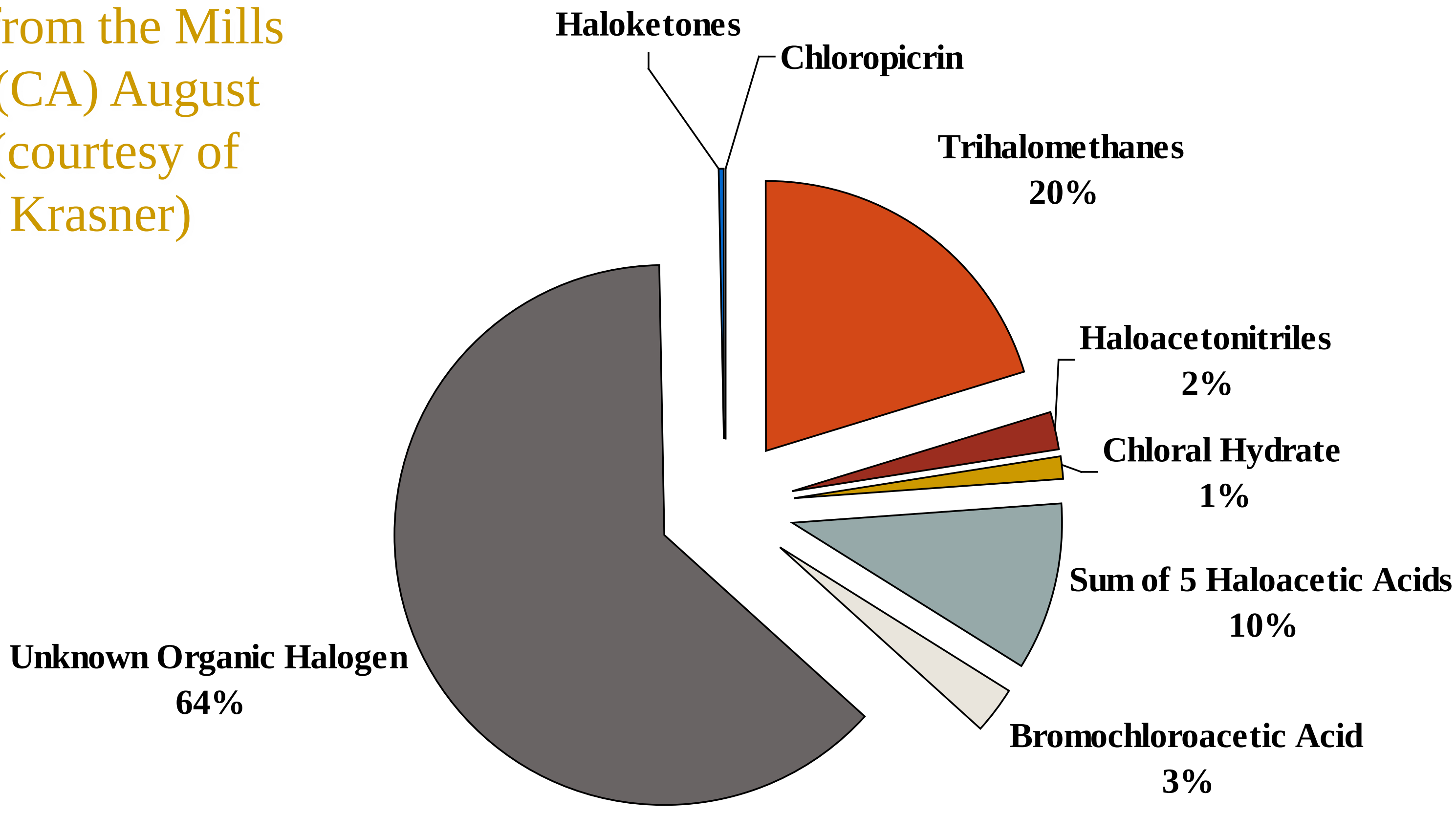
Mean TTHMs from US Surveys



From Seidel et al., 2016

TOX: Known & Unknown

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



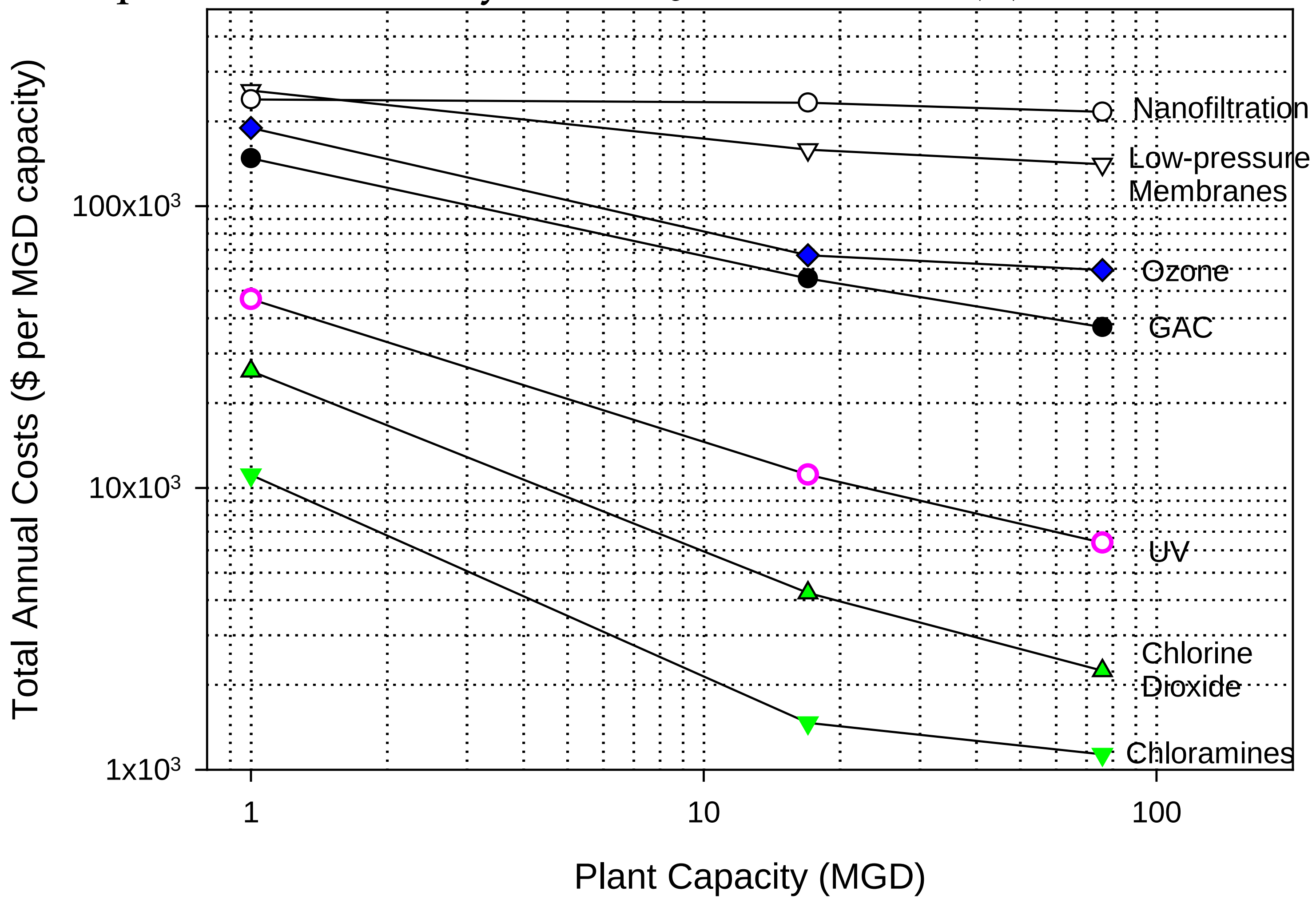
DBP Control Strategies

- 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 <u>Water Quality and Treatment</u>; 6th edition; 2011

Some 2009 Projected Costs

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



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

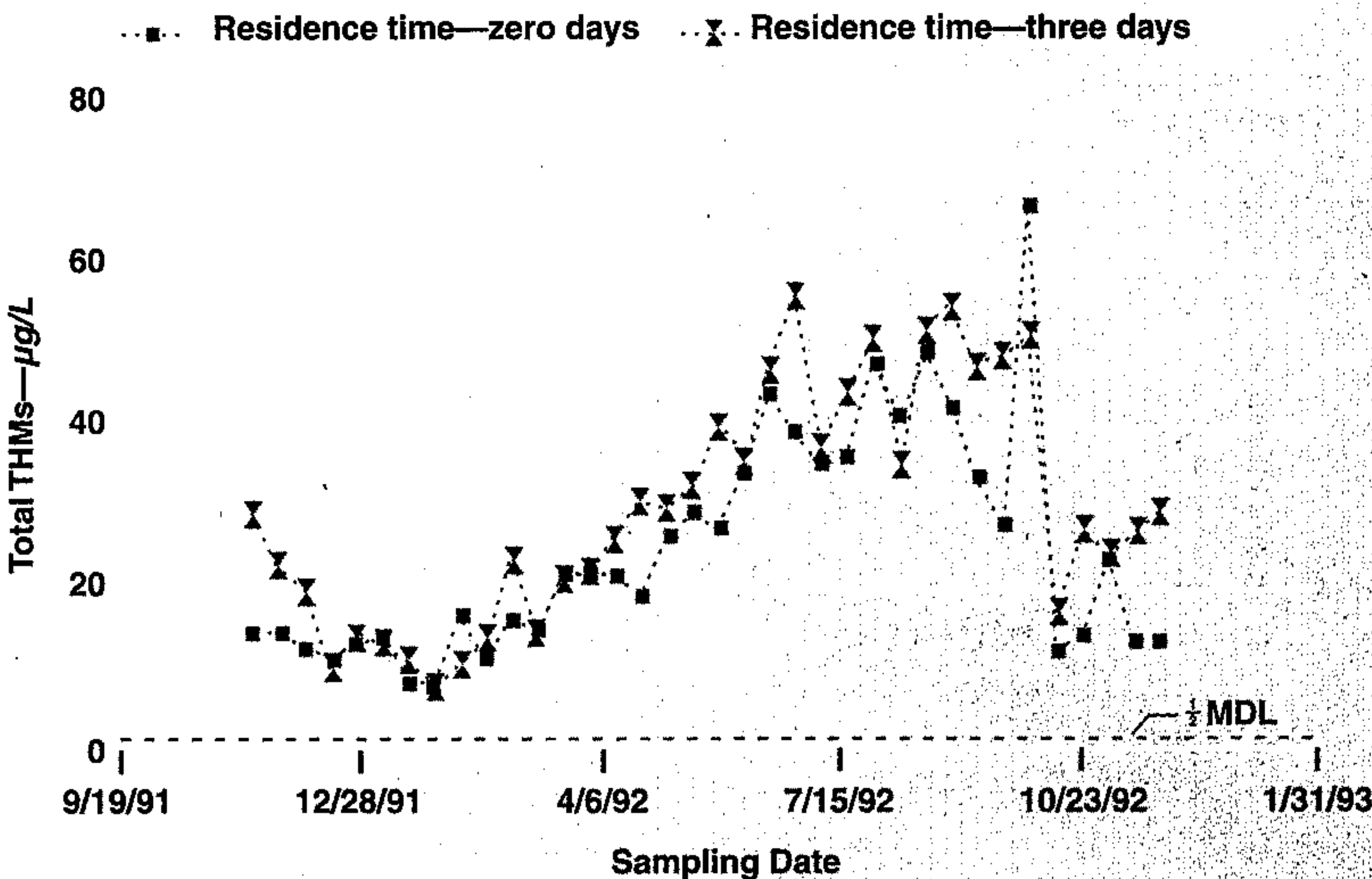
Utility Case Studies

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

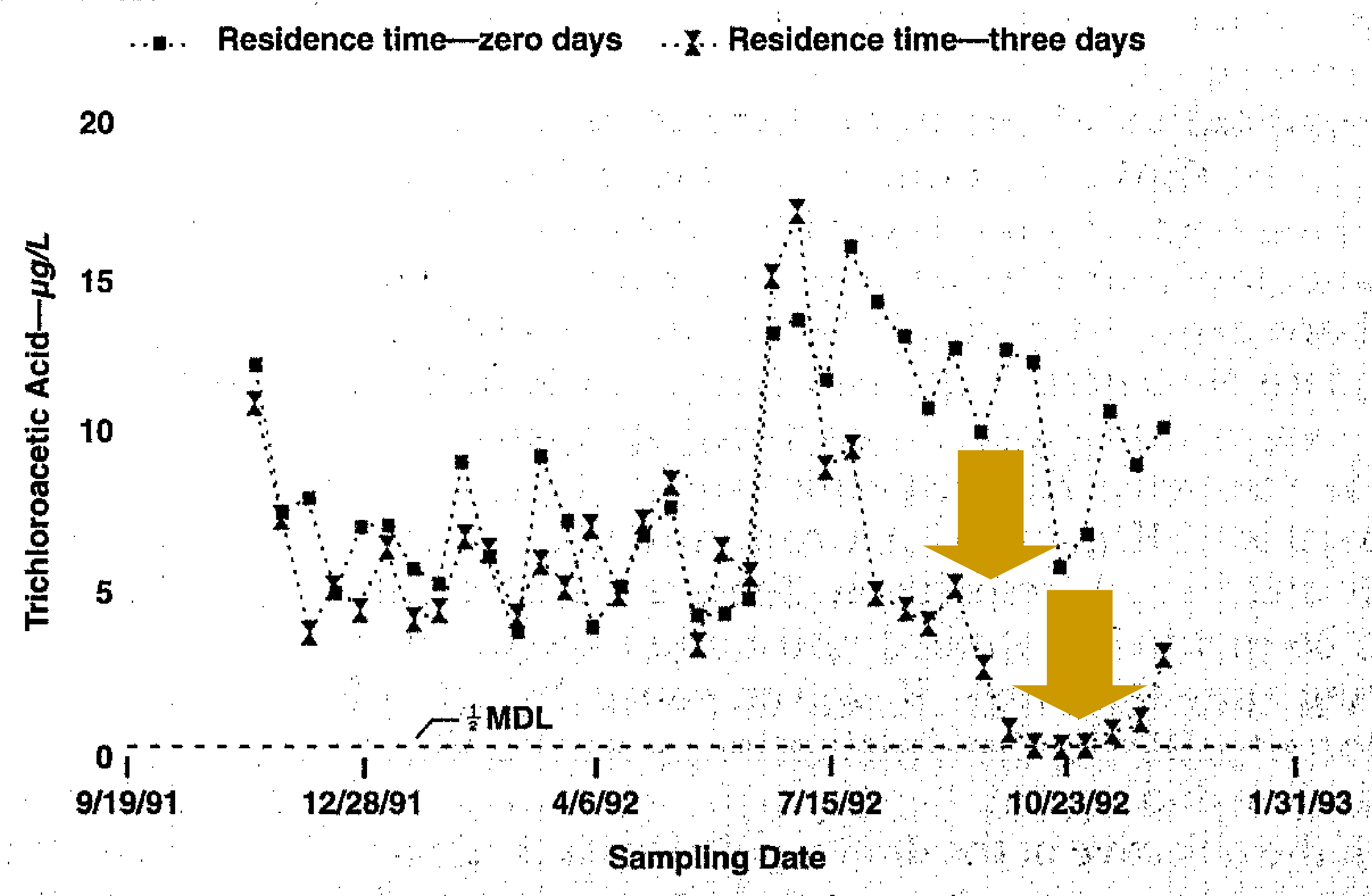
Seasonal Variability & Biodegradation

- 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

Elizabethtown, NJ: THMs



Elizabethtown, NJ: TCAA

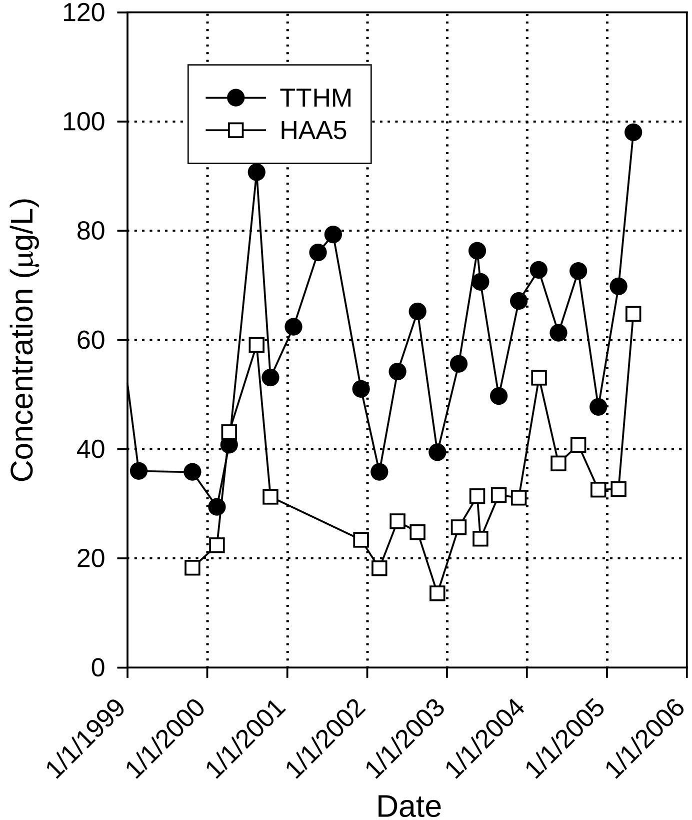


HAA Degradation

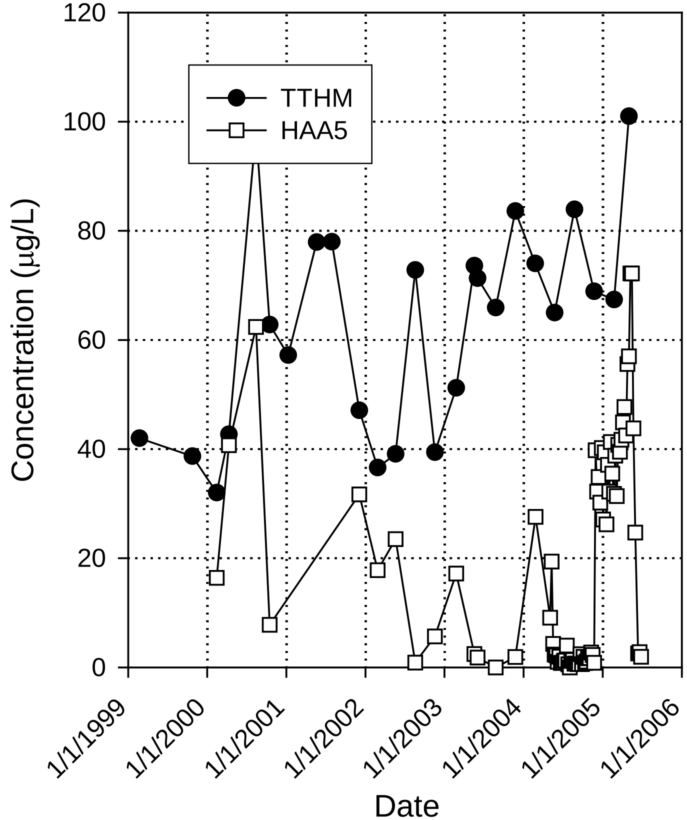
- Biodegradation:
  - dihaloacetic acids degrade more readily than trihaloacetic acids
  - On BAC
    - MHAA>DHAA>THAA
      - Wu & Xie, 2005 [JAWWA 97:11:94]
  - In distribution systems
    - DHAA>MHAA>THAA
      - Many studies

Biodegradation in Dist. Systems

Town Hall; Norwood, MA



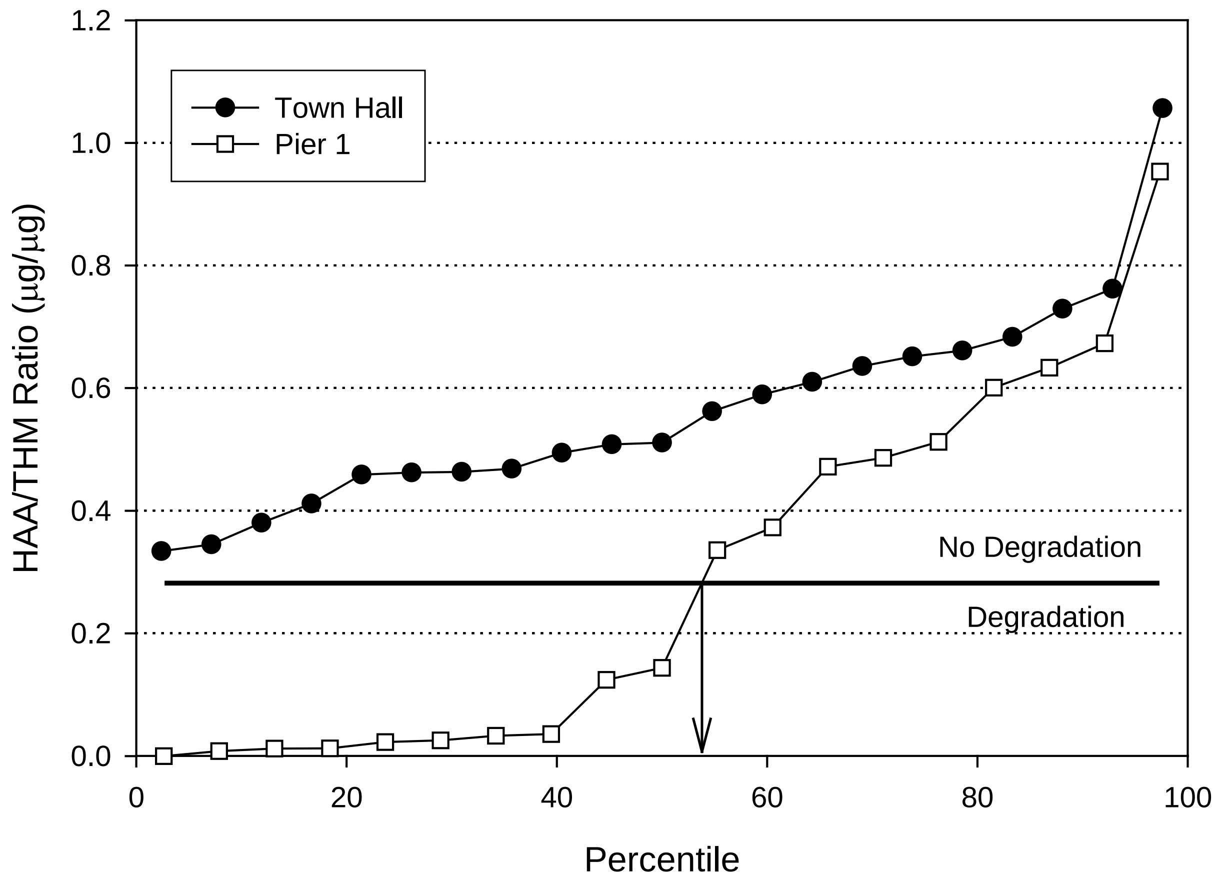
Pier 1; Norwood, MA



Example: Norwood, MA

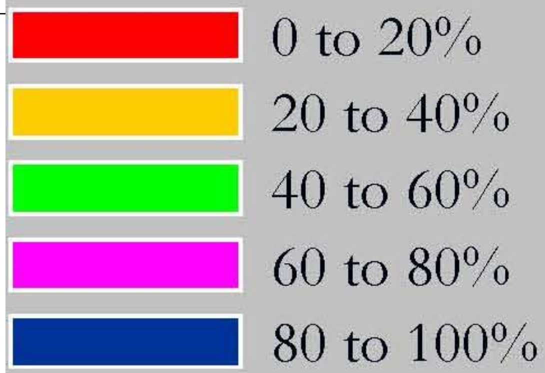
Biodegradation of HAAs

- Norwood, MA example



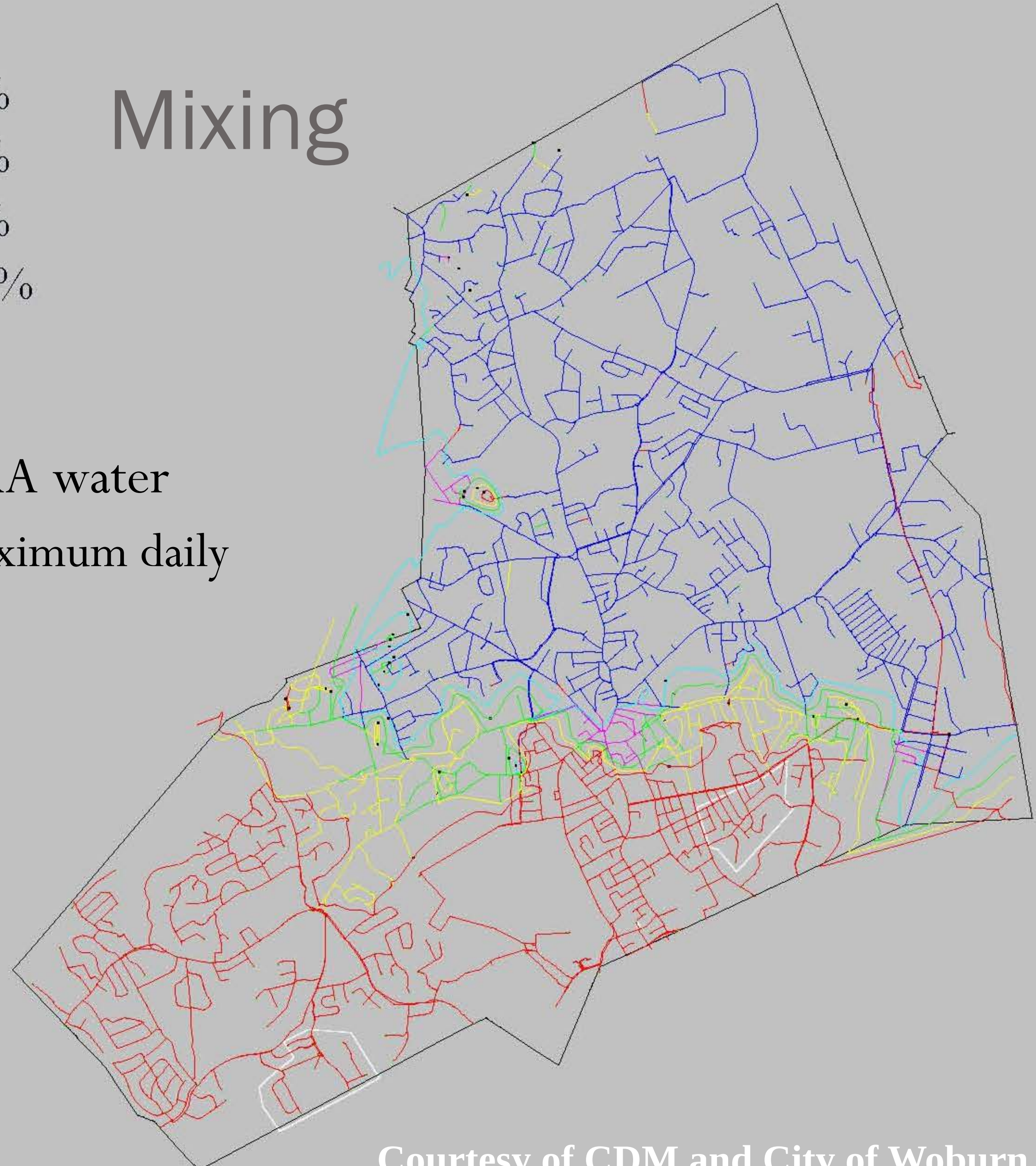
Woburn System Description

- 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



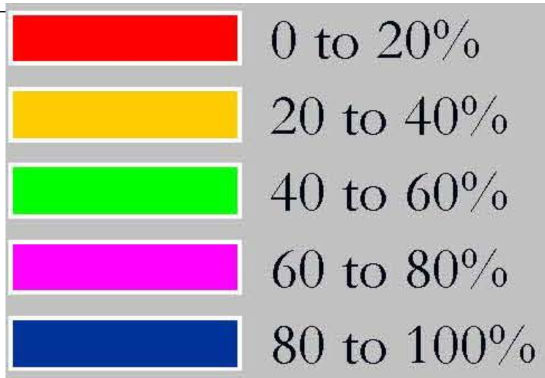
Mixing

- Percent MWRA water
  - Based on Maximum daily demand

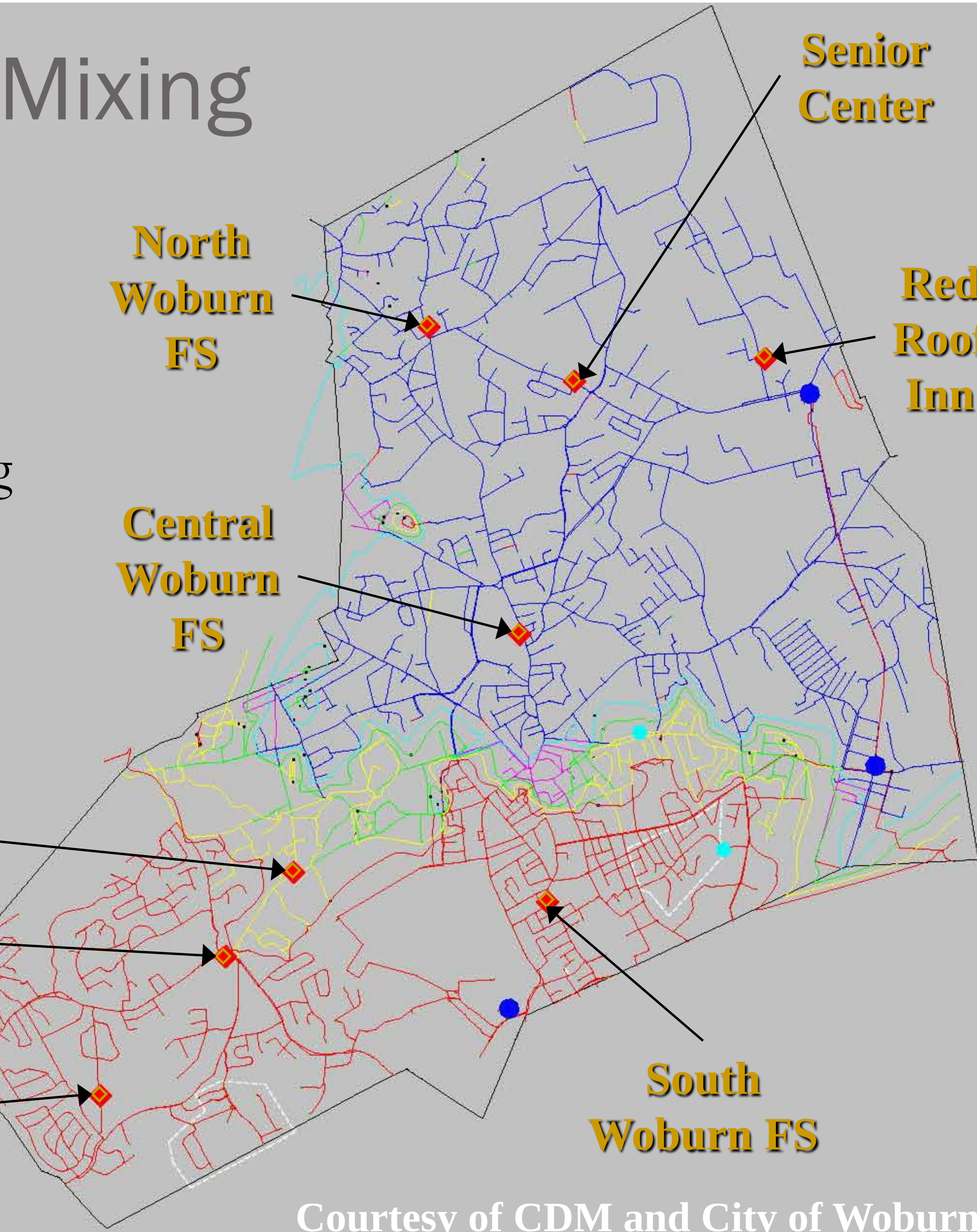


Courtesy of CDM and City of Woburn

Mixing

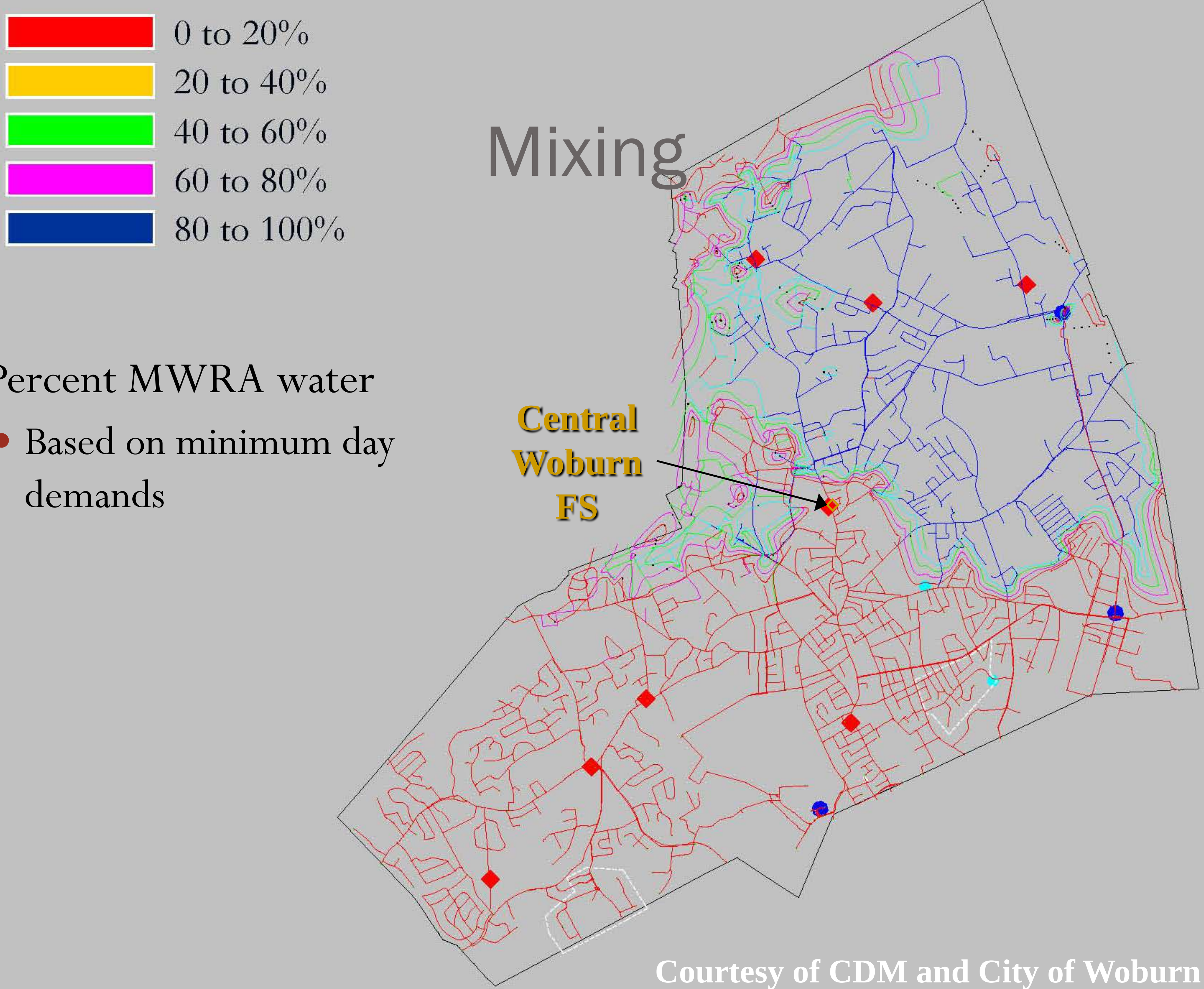


- Same as before, but:
  - Including THM sampling locations



Mixing

- Percent MWRA water
  - Based on minimum day demands

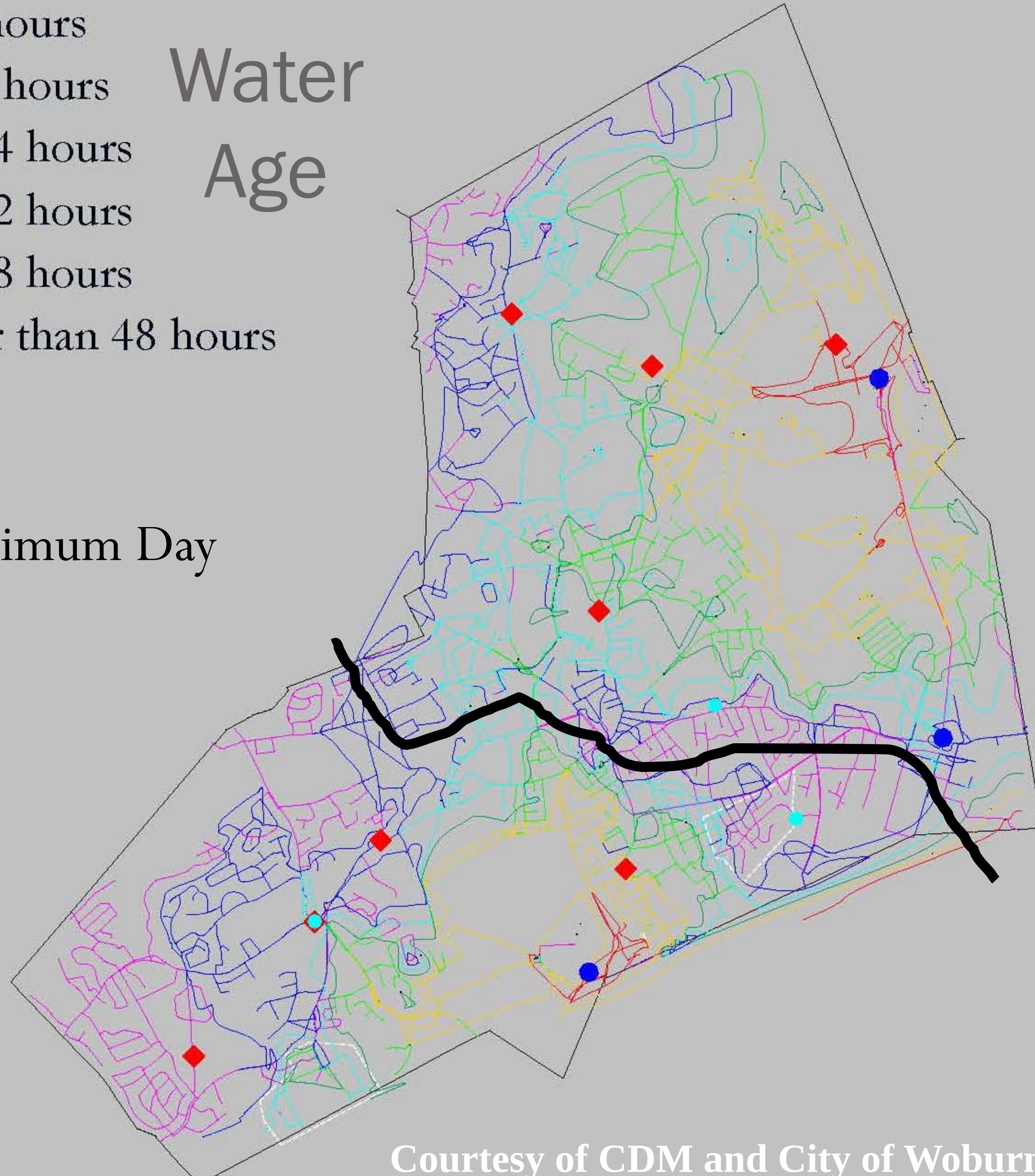


Courtesy of CDM and City of Woburn

Water Age

- 0 to 8 hours (red)
- 8 to 16 hours (yellow)
- 16 to 24 hours (green)
- 24 to 32 hours (cyan)
- 32 to 48 hours (blue)
- Greater than 48 hours (magenta)

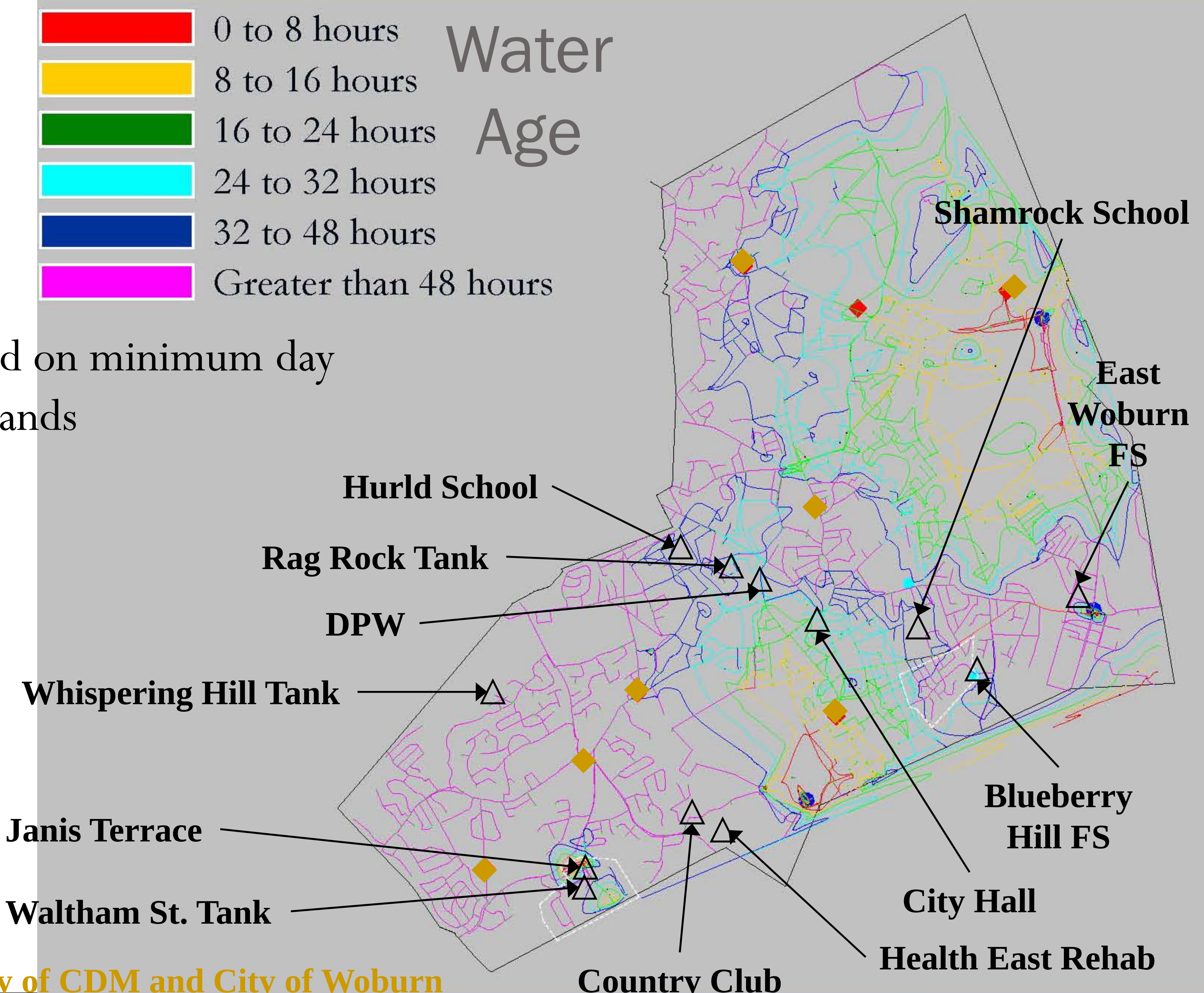
- Based on Maximum Day demands



Courtesy of CDM and City of Woburn

Water Age

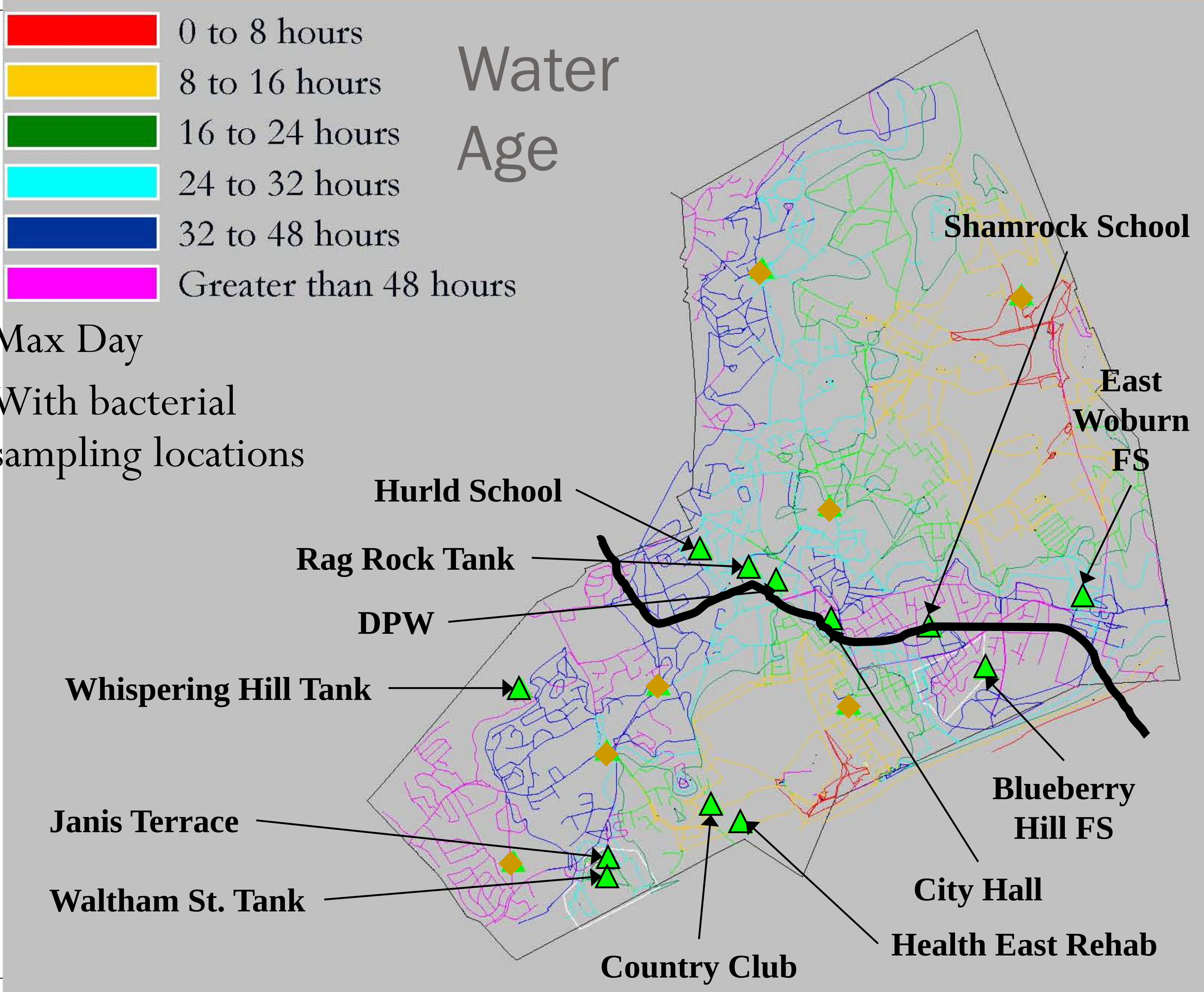
- Based on minimum day demands



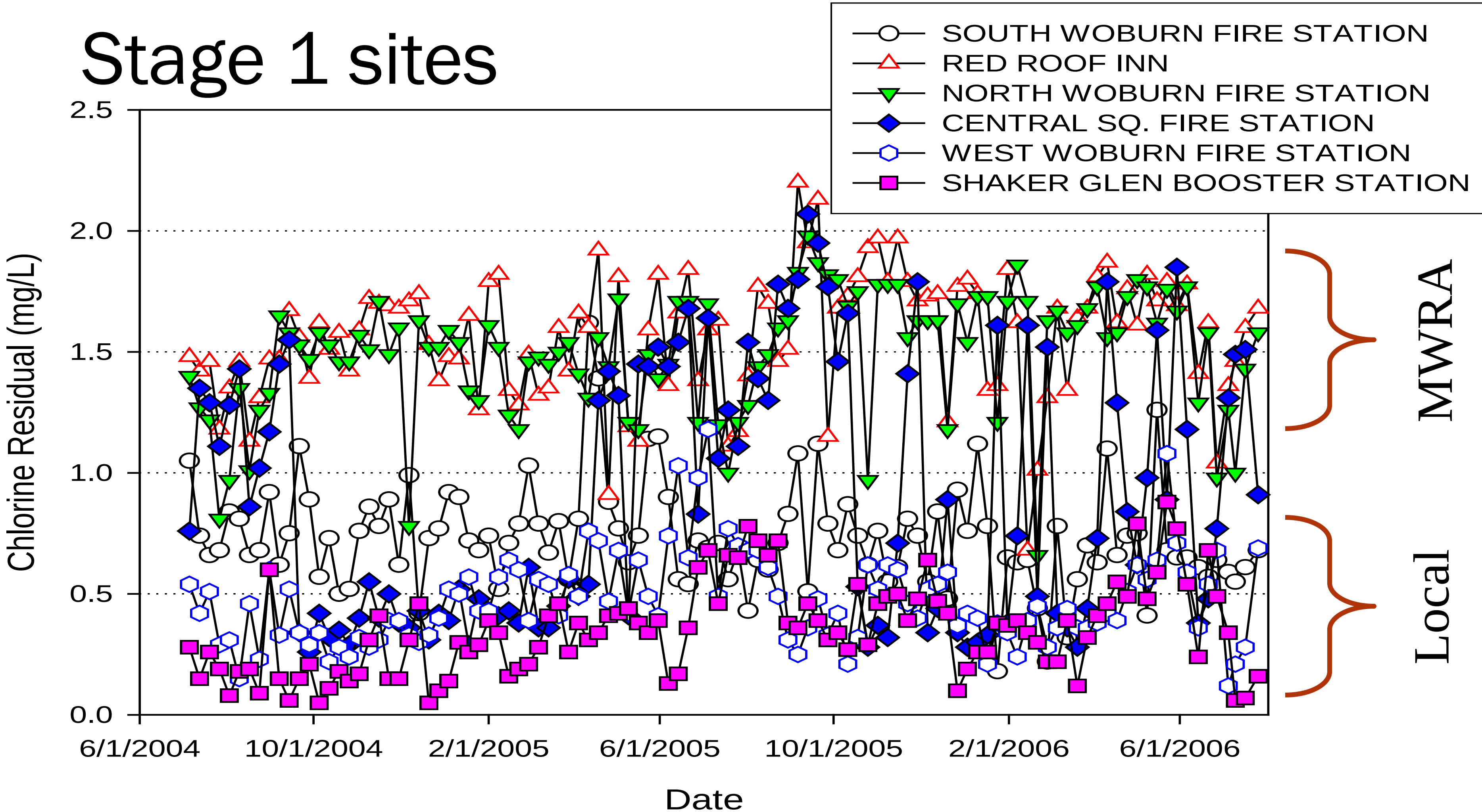
Courtesy of CDM and City of Woburn

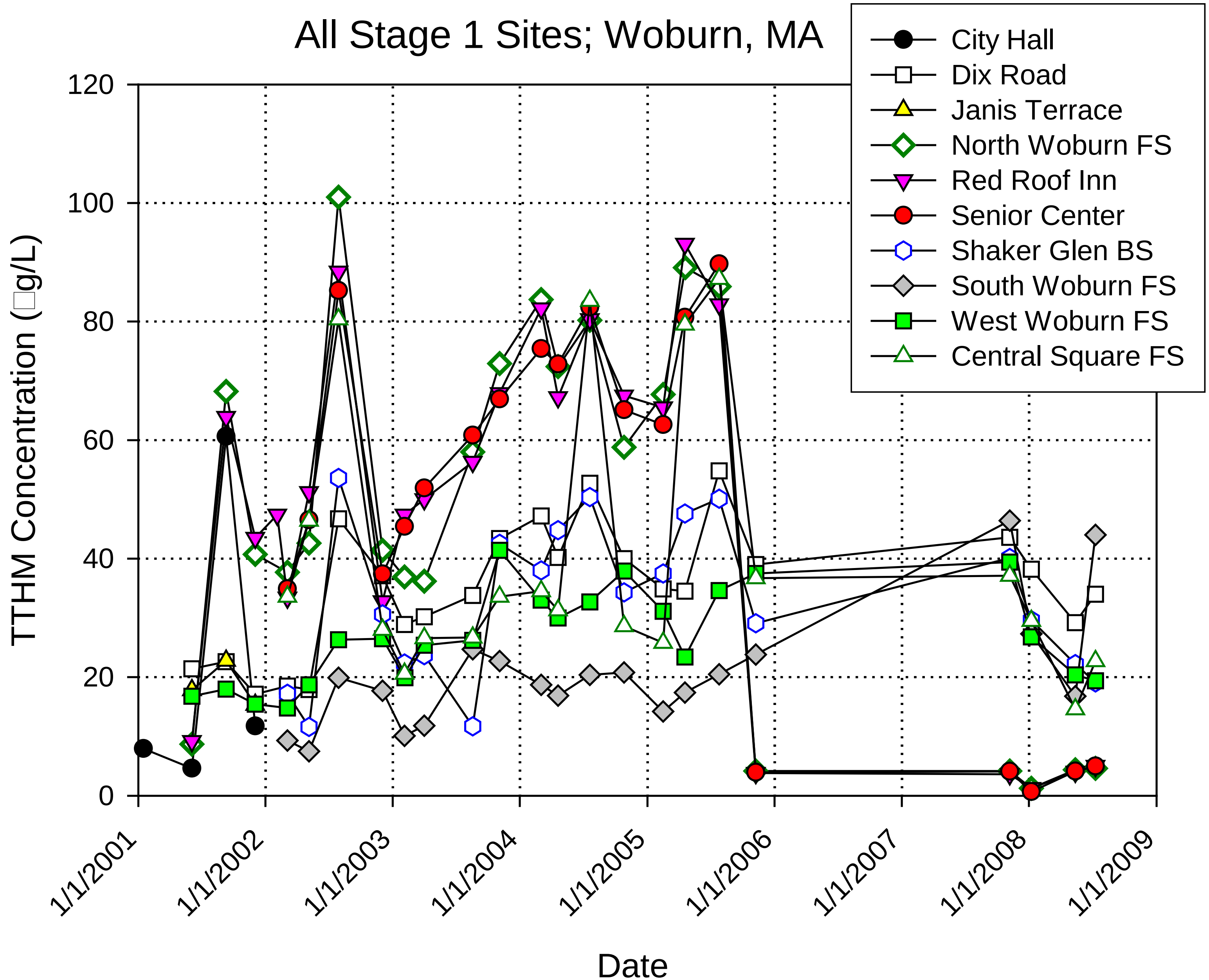
Water Age

- Max Day
- With bacterial sampling locations

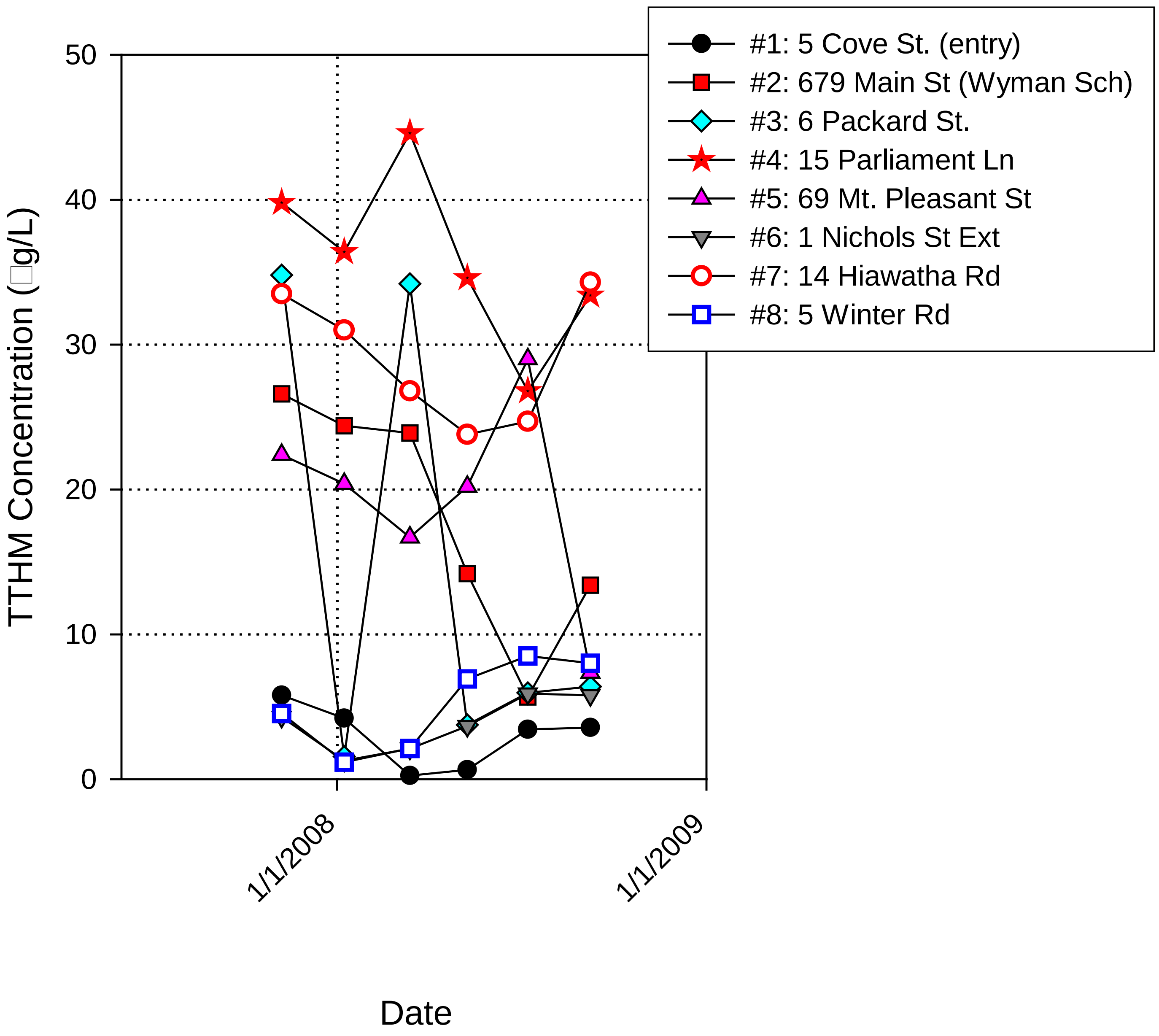


Chlorine Residuals at Stage 1 sites

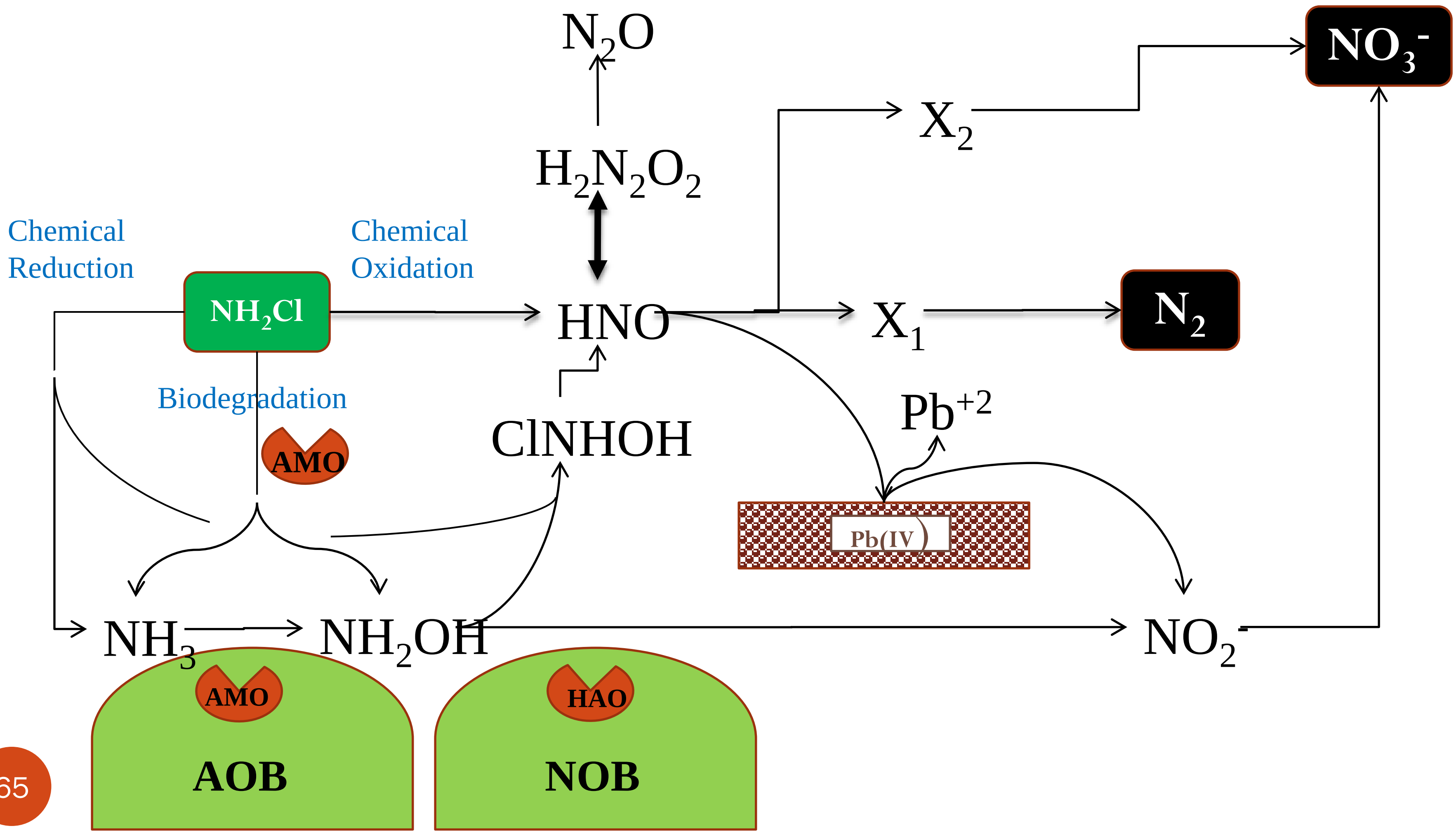



All Stage 1 Sites; Woburn, MA
TTHM Concentration (□g/L)
Date
0
20
40
60
80
100
120
1/1/2001
1/1/2002
1/1/2003
1/1/2004
1/1/2005
1/1/2006
1/1/2007
1/1/2008
1/1/2009
City Hall
Dix Road
Janis Terrace
North Woburn FS
Red Roof Inn
Senior Center
Shaker Glen BS
South Woburn FS
West Woburn FS
Central Square FS

IDSE Sites; Woburn, MA



Chloramines – many more reactions




The End
suva