Chlorine Decay Modeling and Water Age Predictions

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OTCO Water Workshop

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Agenda

- Residual Decay in Water
- Experimental Data Collection
- Data Evaluations
- Adjustment for Temperature Variations
- Decay Model Development
- Applications for Decay Evaluations
- Water Age Predictions for Water Systems
- Questions

Residual Decay in Water

- Residual decay generally follows first order reaction

$$C_t = C_o e^{-kt}$$

C_t = concentration at time t
C_o = initial concentration
k = residual decay coefficient
t = decay time in days

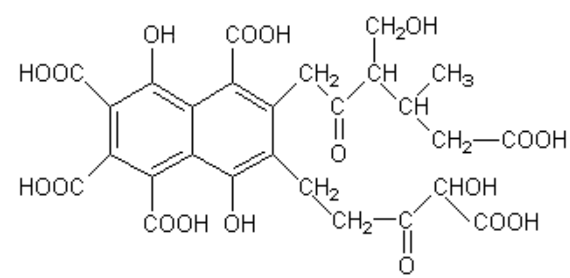
- Calculate decay coefficient (k) from experimental data using reaction equation
- Decay models developed using identified coefficients for free chlorine, total chlorine, and monochloramine

Decay Coefficients

- Decay coefficient (k) contains 2 components
  - $k_t = k_b + k_w$
  - k_w - decay coefficient pipe wall
  - k_b - decay coefficient bulk water
- k_w impacted by contact at pipe wall and presence of biofilms, deposits, corrosion materials
- k_b affected by demand-causing substances in distribution system (water quality)
- k_t dependent on water quality and pipe conditions, site specific

Items Influencing Residual Decay

- Initial residual concentration
- Equilibrium reactions
- Residual half-life
- Water temperature
- Water pH
- Presence of reducing substances
- Water age or residence time
- S/V ratio (surface to volume ratio in pipelines, tanks)



Equilibrium reactions

- Changes residual concentrations based on pH and temperature variations

$$K_i = \frac{[H^+][OCl^-]}{[HOCl]} \qquad HOCl = \frac{[H^+][OCl^-]}{K_i}$$

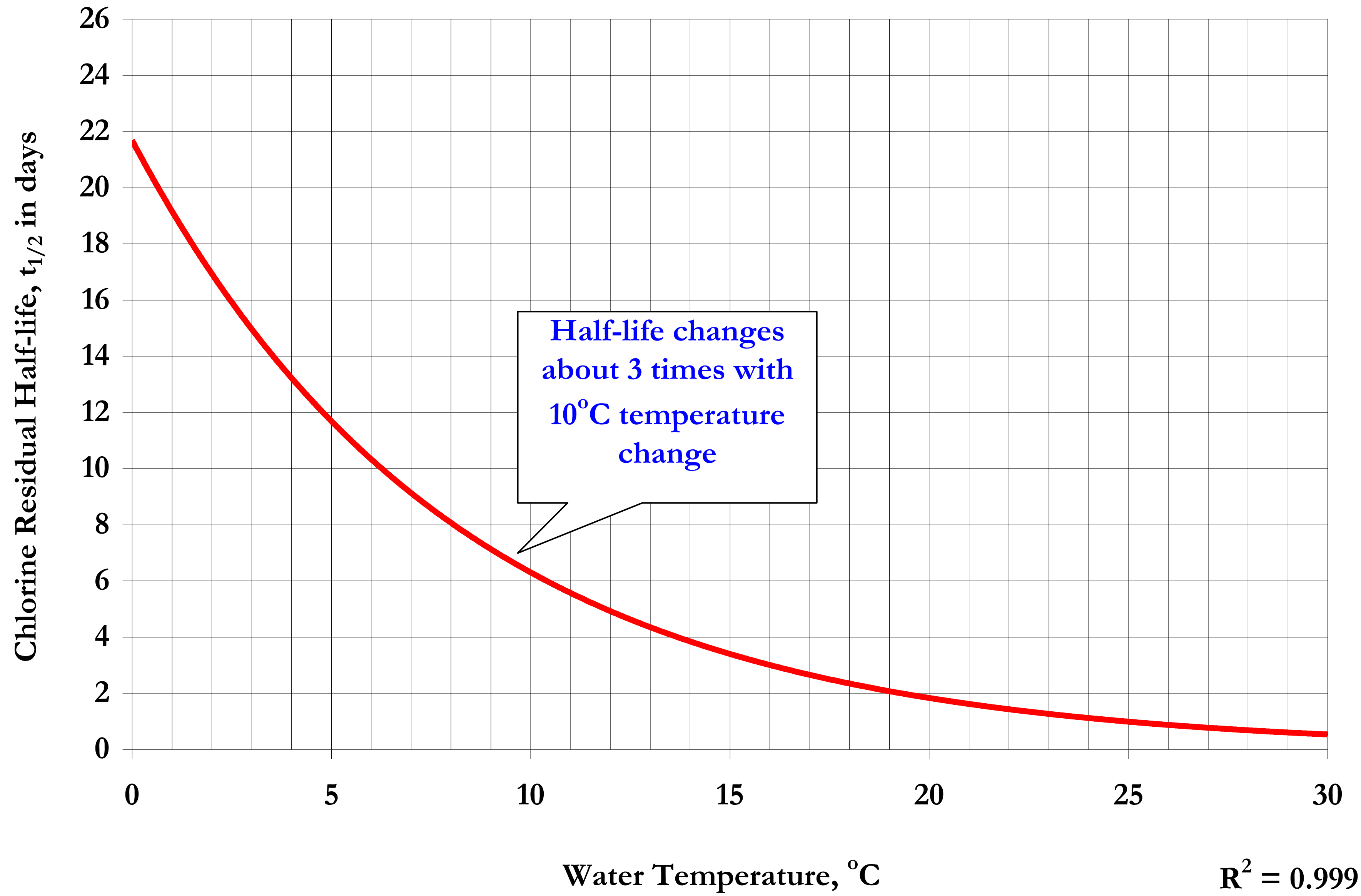
- Free chlorine
  - Hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) remain in solution, but their content may change with pH and temperature according to solubility relationships based on equilibrium chemistry
- Monochloramine
  - Equilibrium chemistry can shift monochloramine levels by simple pH and temperature changes

$$NH_3 + HOCl \Leftrightarrow NH_2Cl + H_2O$$

Residual half-life

- Residual reduces according to half-life reactions for the type of residual
  - ½ concentration reduction each half-life
- Results in depletion over time in distribution and storage

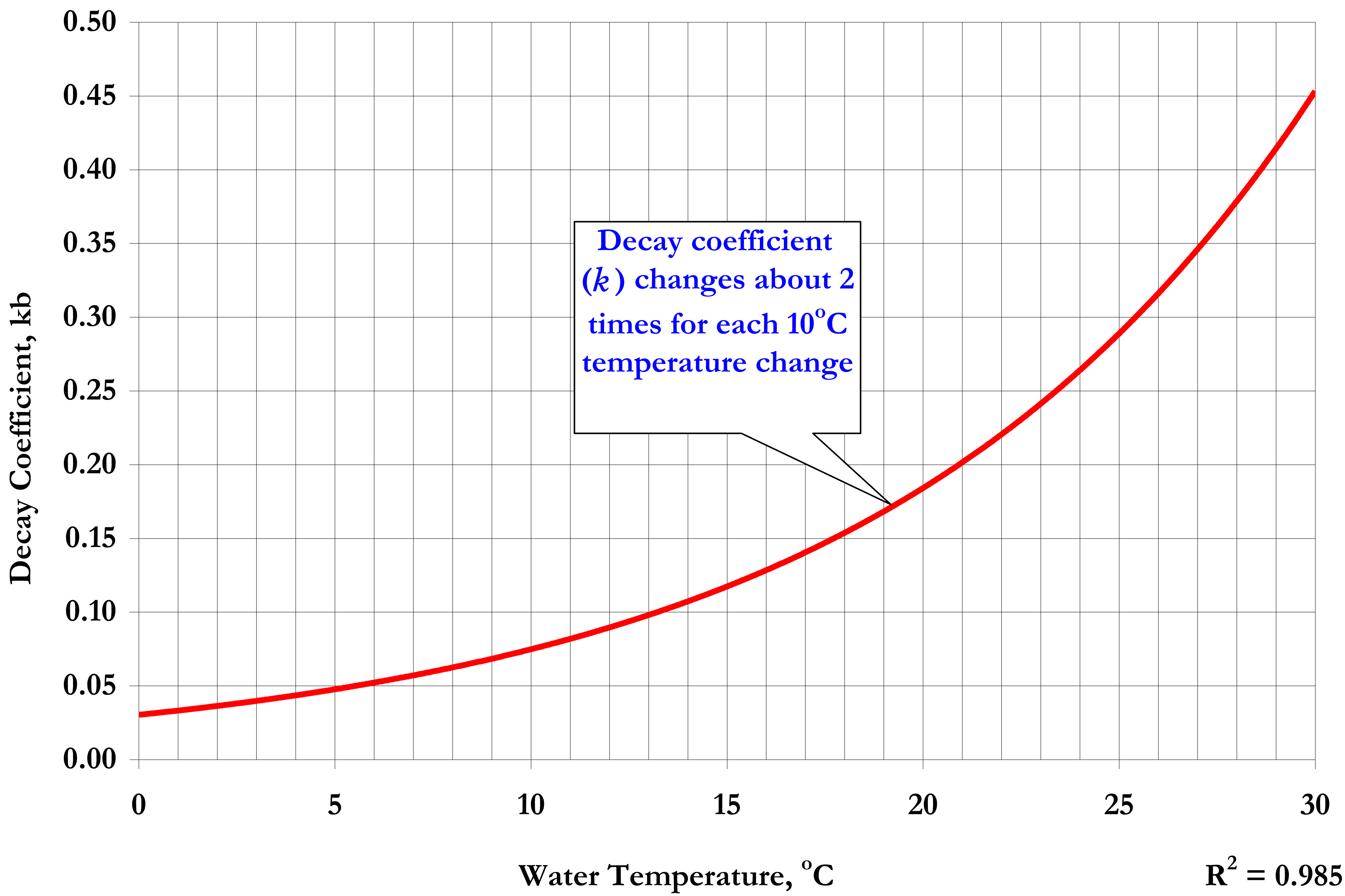
Residual half-life (free chlorine)



Water temperature impacts

- Generally two fold change ***k*** each 10°C change in temperature
- Affects ***k*** and residual decay reactions
- Temperature affects type of free chlorine residual (HOCl or OCl^-)
  - Equilibrium impacts for free chlorine and monochloramine shown earlier
- Increasing temperature increases auto-decomposition of chloramine residuals

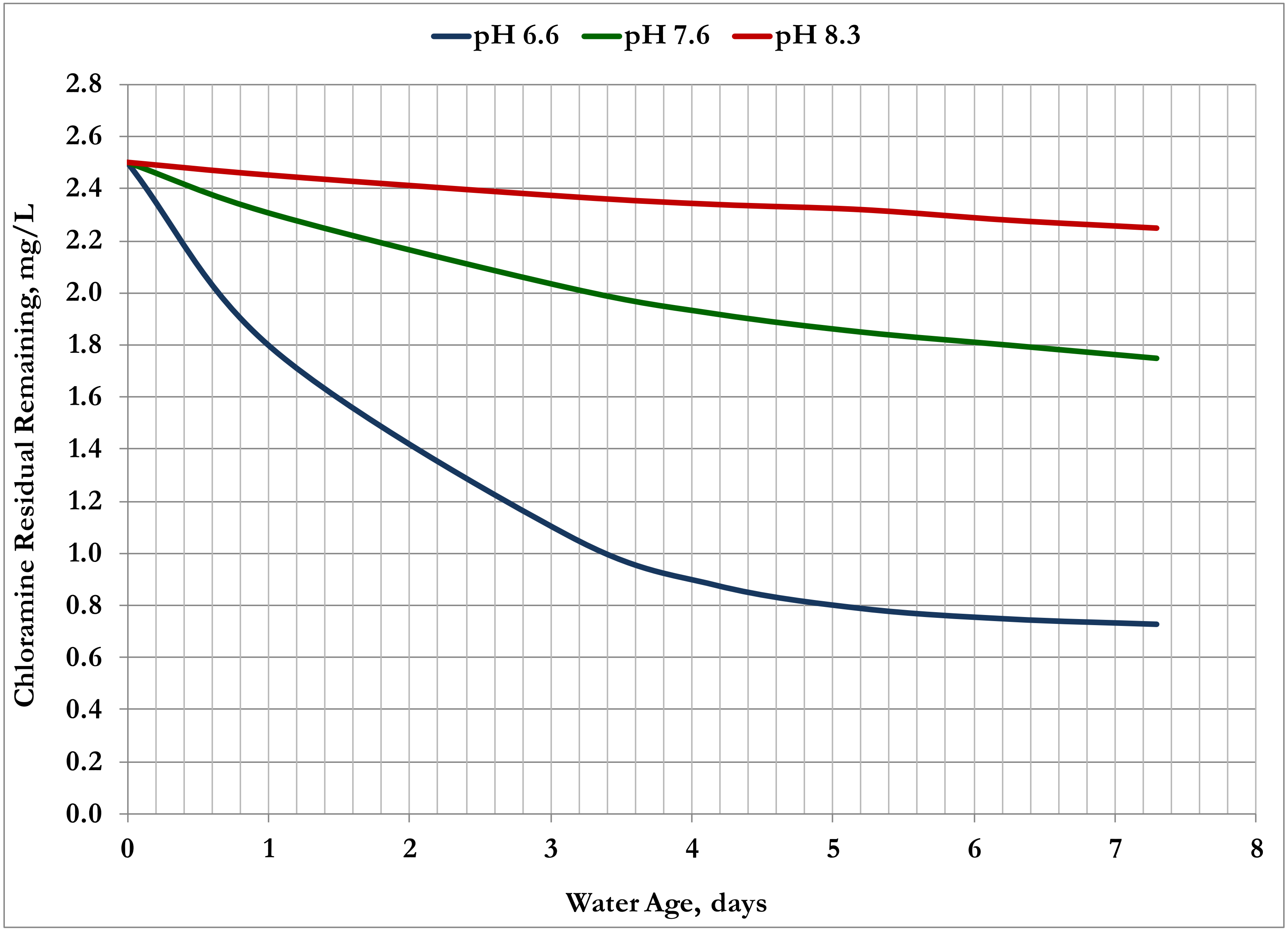
Water temperature impacts



Water pH effects

- pH affects type of residual based on equilibrium
  - Free chlorine (HOCl or OCl^-)
  - Monochloramine balance with ammonia and free chlorine
- Decay of system residuals dependent on pH level and type of residual
  - pH levels above 8 slow auto-decomposition of chloramine residuals
  - pH levels above 8 predominantly OCl^- rather than HOCl

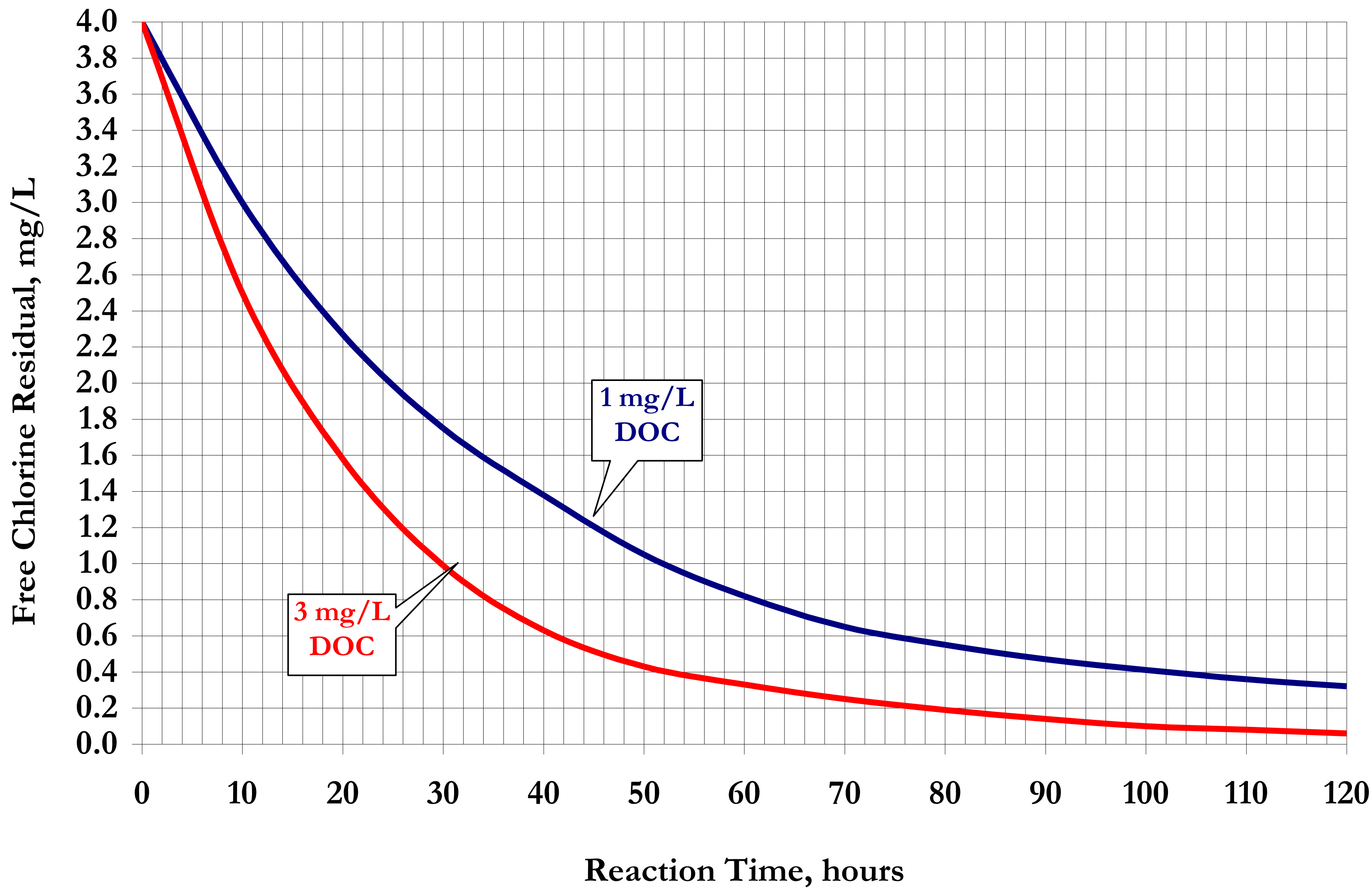
Water pH effects



Reducing substances

- Water quality parameters cause depletion of residual
  - Iron, manganese, ammonia, sulfides, bromide, organic matter, nitrite, cyanide
- Reactions at pipe wall cause depletion of residual
  - Pipe Deposits
  - Corrosion Reactions
  - Biofilms

Reducing substances - DOC



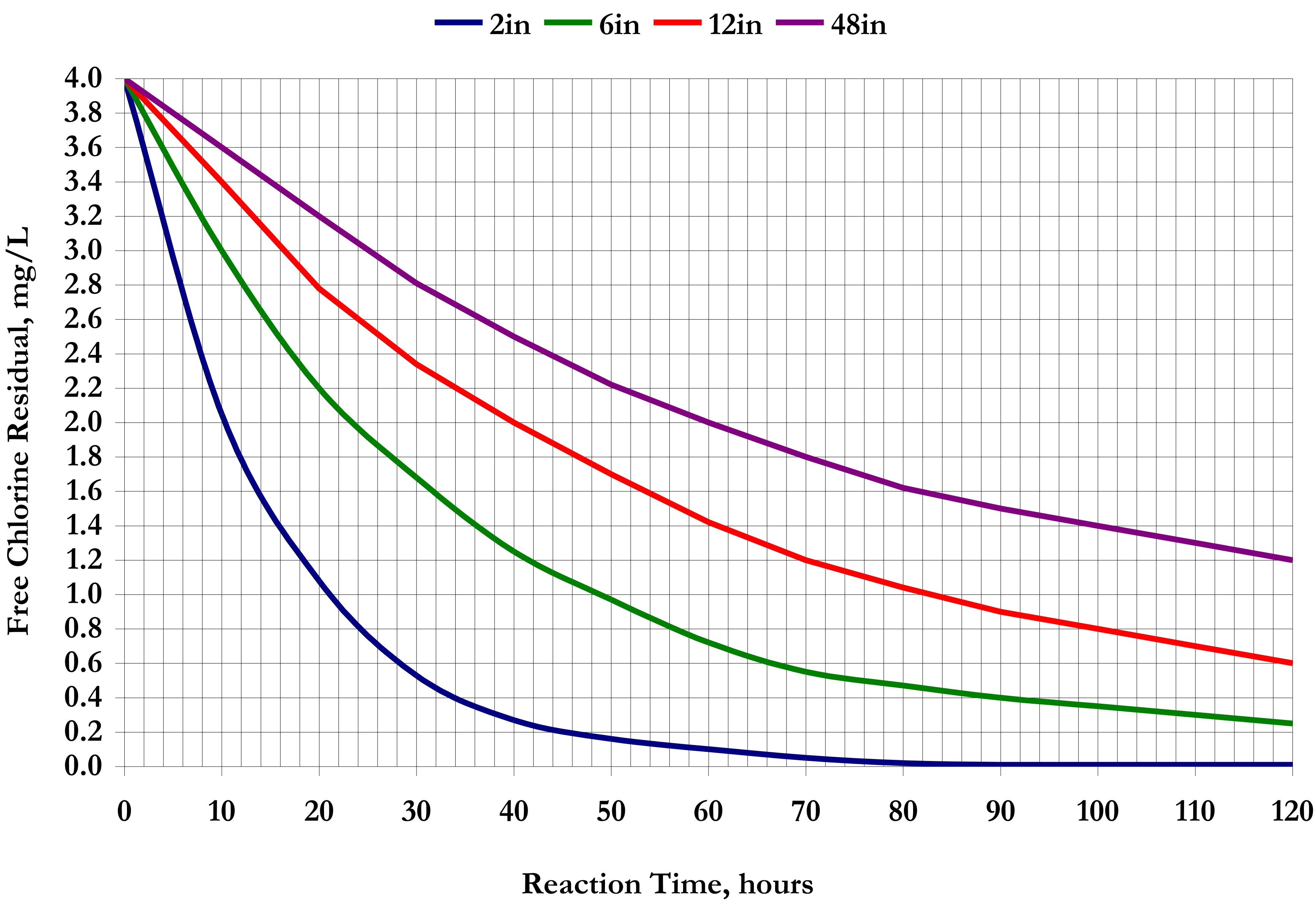
Water age / residence time

- Most significant effects on residual decay
  - Exponent in first order reaction
  - Longer residence time reduces residuals
    - More reaction time with reducing substances
    - More decay reaction based on time
    - More reaction with pipe wall materials
  - Water storage affects water age and residence times
  - Affects water temperature variations in storage tanks
    - Water temperature impacts given earlier
    - Stagnant water conditions erode residual concentrations

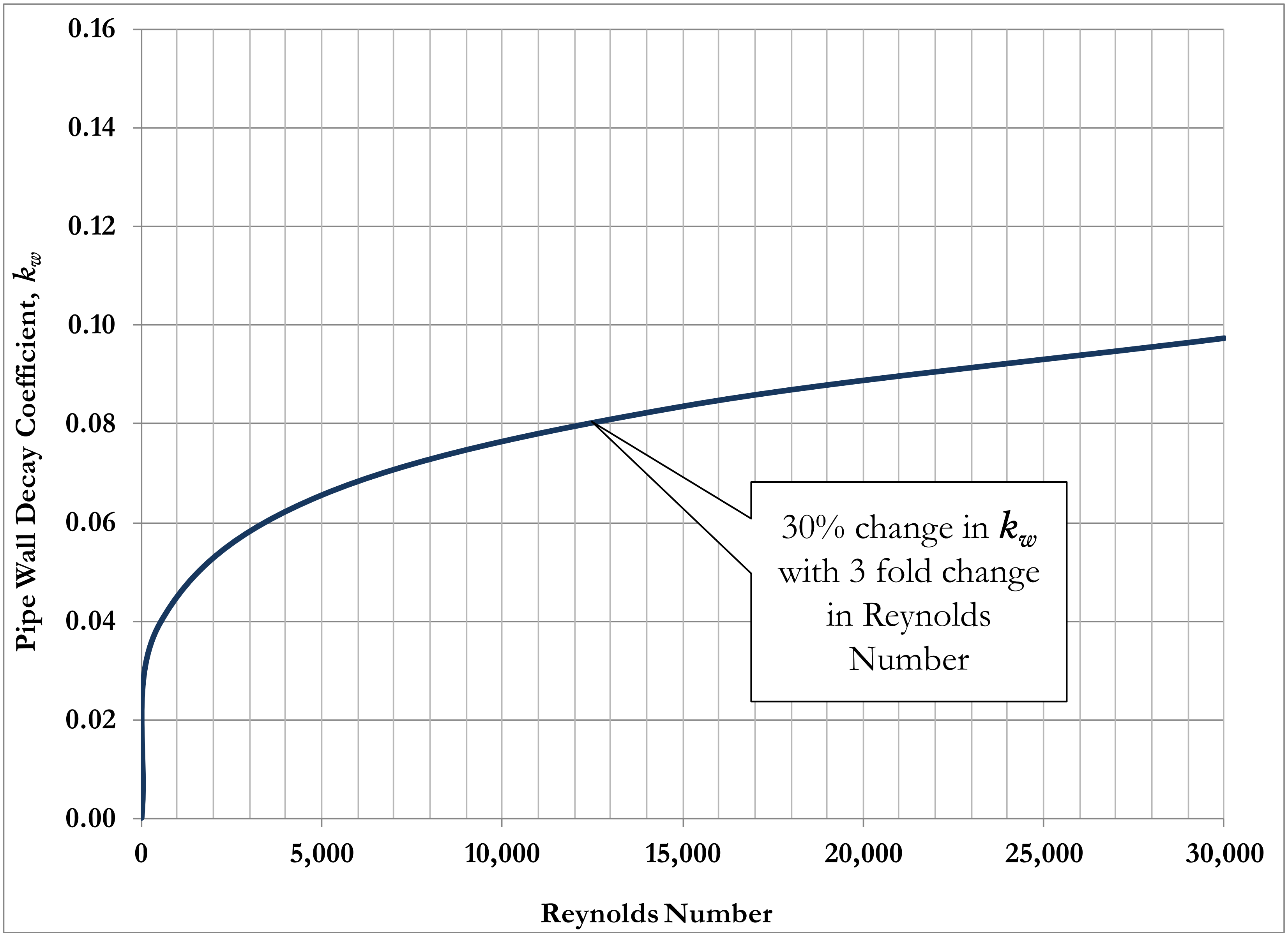
S/V ratio

- Affects volume of water reacting with pipe wall or tank wall
  - Smaller diameter increases bulk volume of water contacting pipe surface
    - Increases residual decay (k_w)
- Affected by flow velocity
  - Increased Reynolds number increases residual decay (k_w)
  - Affects volume to surface area ratio in pipelines increasing decay (k_w)

S/V ratio


2in
6in
12in
48in
Free Chlorine Residual, mg/L
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
Reaction Time, hours

Flow velocity effects



Experimental Data Collection

Experimental Data Collection

- Representative sample with known residual concentration
  - Plant tap collected for experimental evaluation
    - Single sample for entire test period
    - May need to spike sample with disinfectant for evaluation
  - Glass container, brown or amber
    - Rinsed with chlorine and lab water to remove demand on container wall
    - Dried prior to decay evaluation testing
    - Stored in dark conditions
  - Sample capped to simulate pipe conditions
    - No evaporation or off gassing
  - Maintained at room temperature or incubator controlled

Daily observations

- Time, temperature, residual concentration
  - Record observations at nearly same time each day
- Conduct decay testing until maximum residence time achieved
  - Estimate of water system residence time (8 days to 21 days common)

    \- OR -
  - Until residual falls below 0.2 mg/L <u>free</u> chlorine or 1.0 mg/L <u>total</u> chlorine
- Record observations for evaluation and ***k*** determination

Data Evaluations

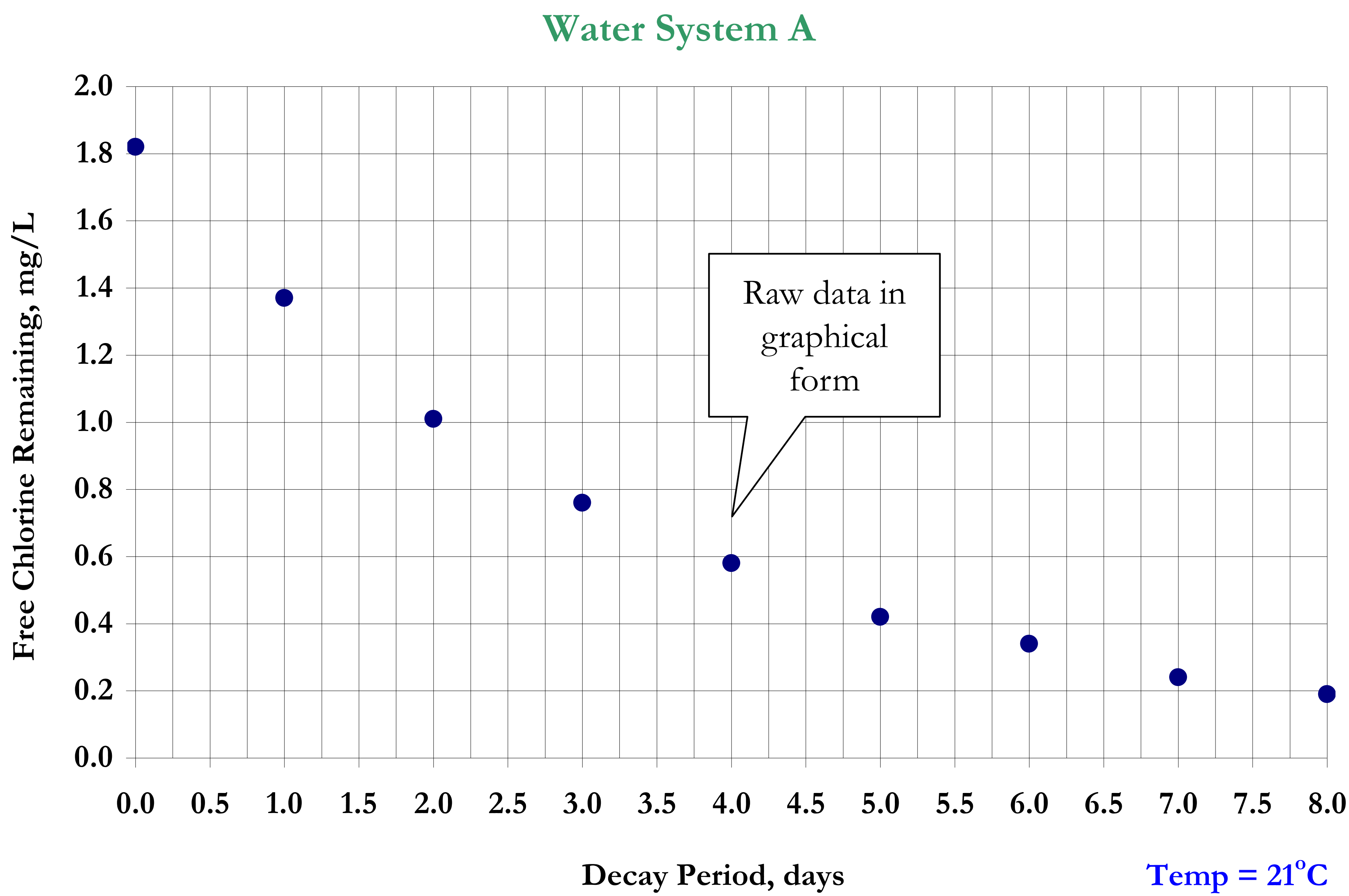
Day 0	1.82
Day 1	1.37
Day 2	1.01
Day 3	0.76
Day 4	0.58
Day 5	0.42
Day 6	0.34
Day 7	0.24
Day 8	0.19

Water System A

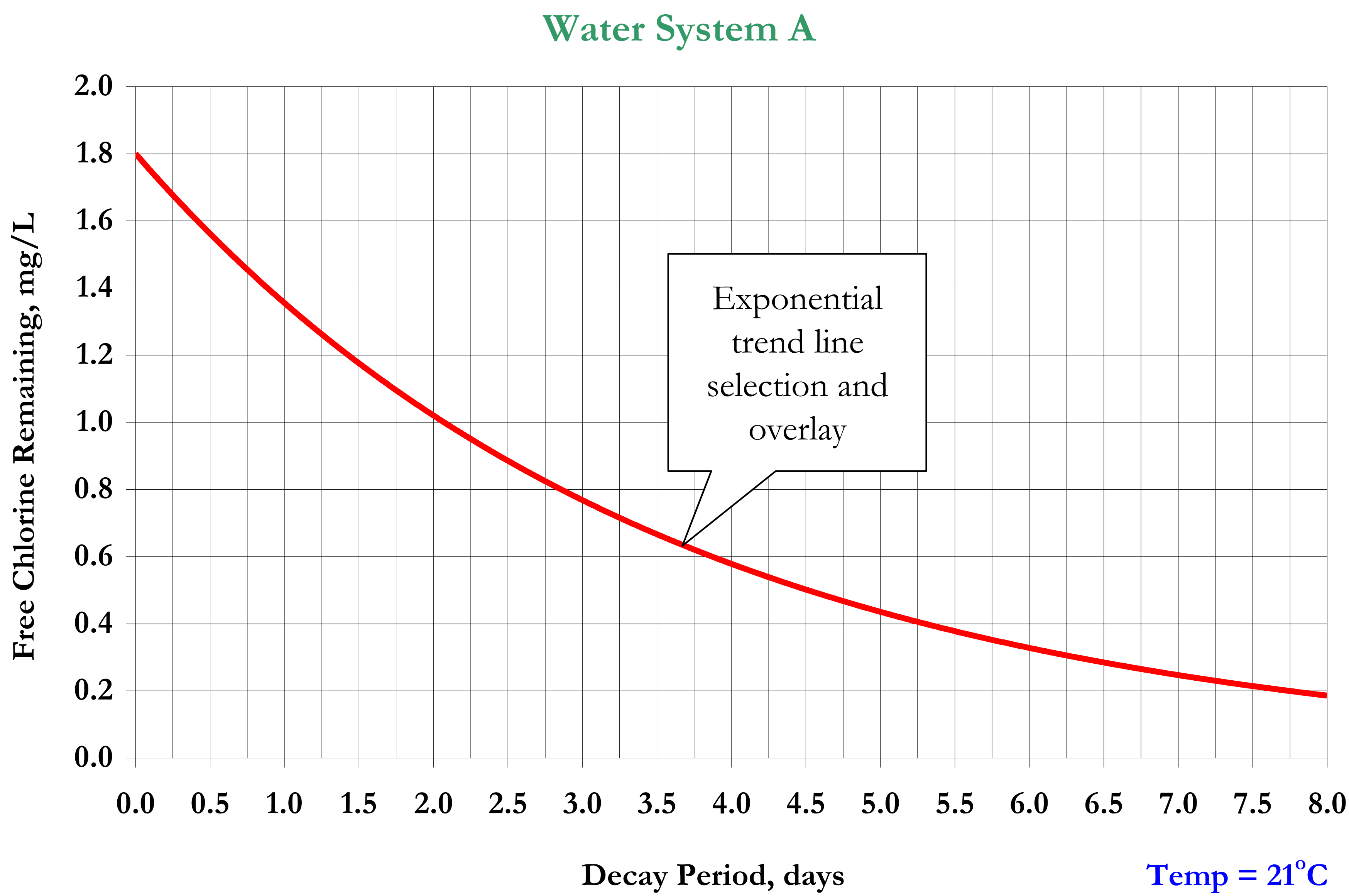
- Free chlorine decay for 8 days (max residence time)
- Graph data in Excel™
  - Select scatter graph
  - Add trend line to data points
  - Select exponential graph type
  - Display equation and R^2 options
- Determine decay coefficient (*k*) from equation

$$C_t = C_o e^{(-kt)}$$

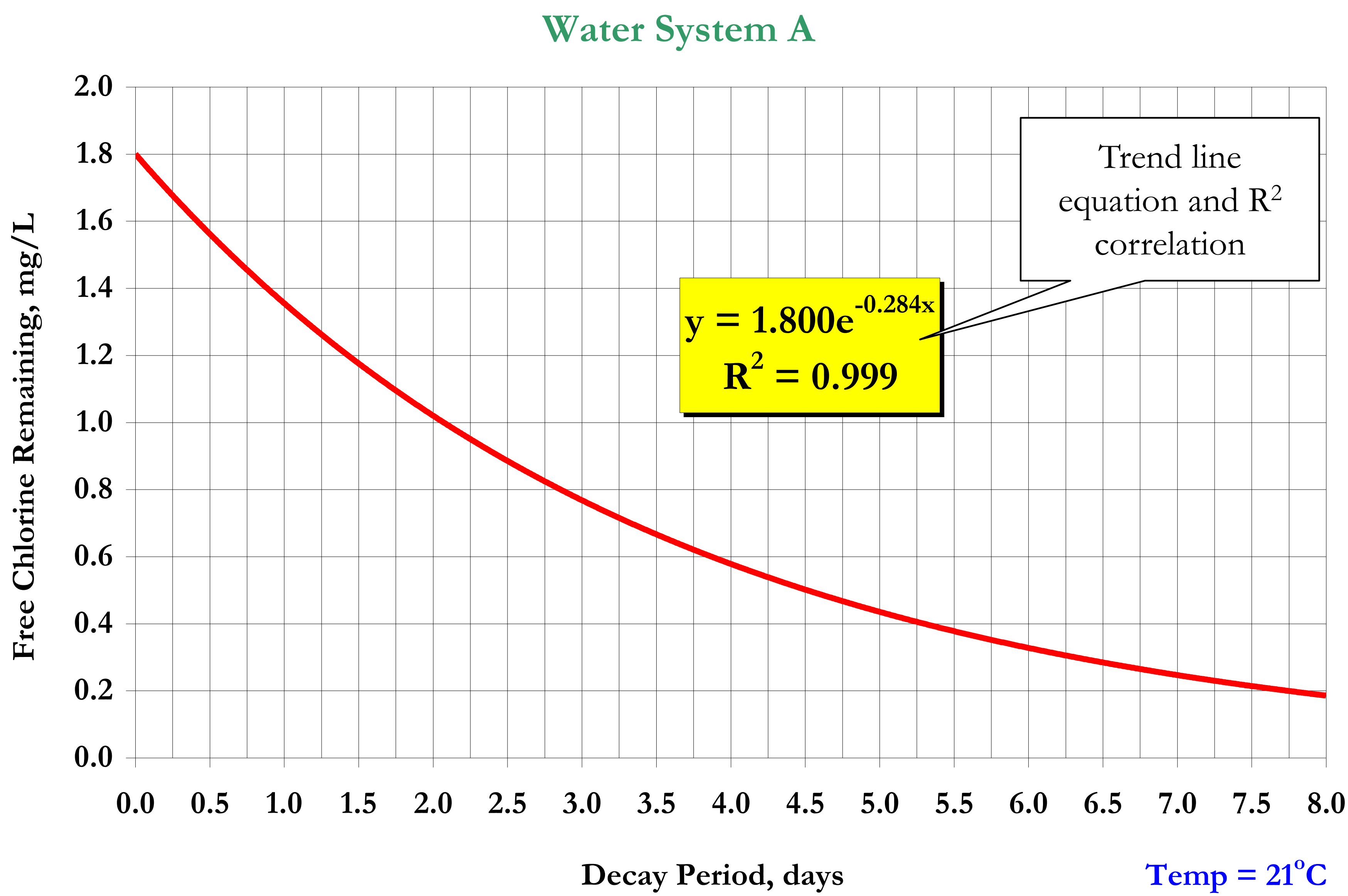
Water System A



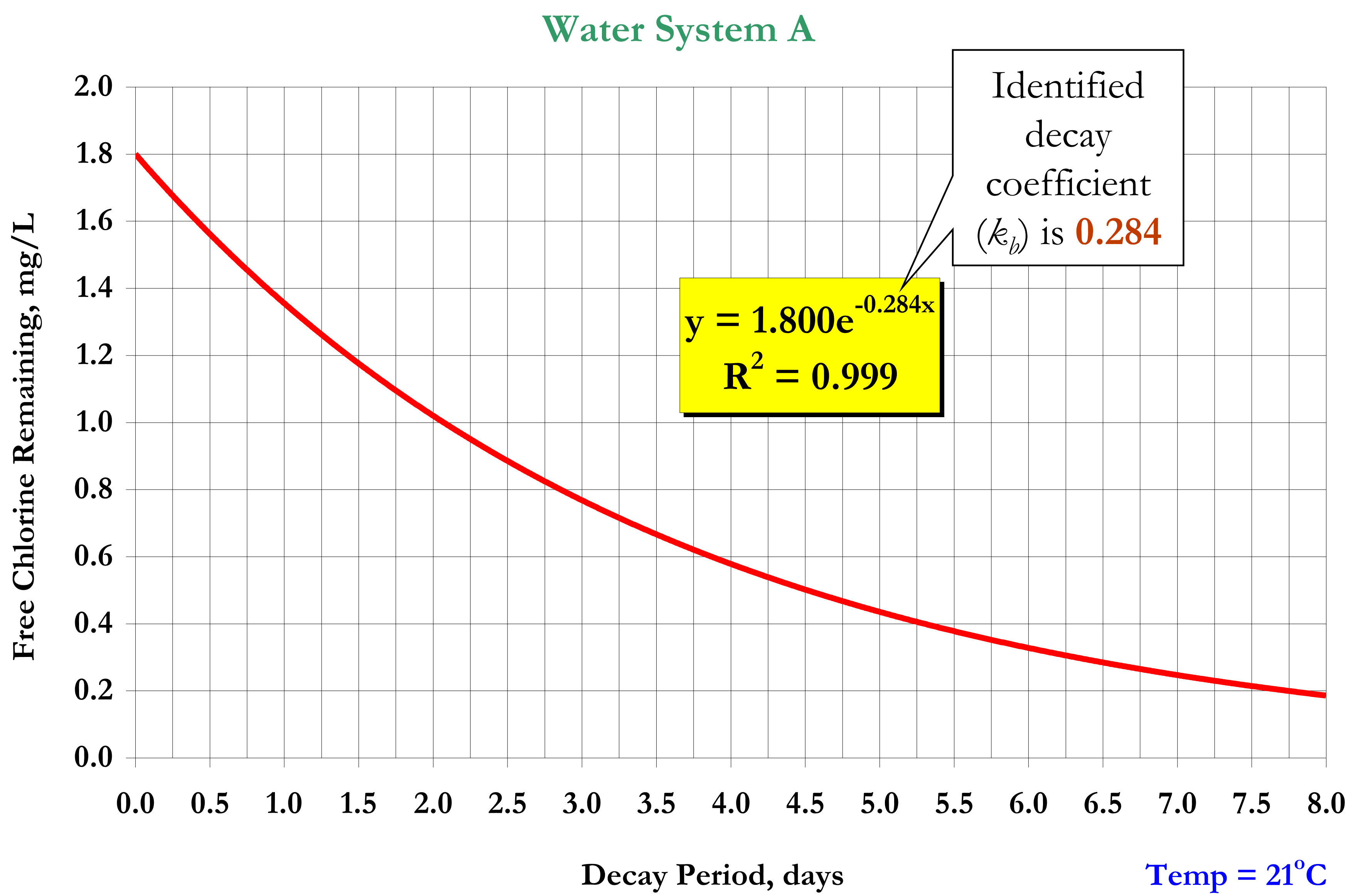
Water System A



Water System A



Water System A



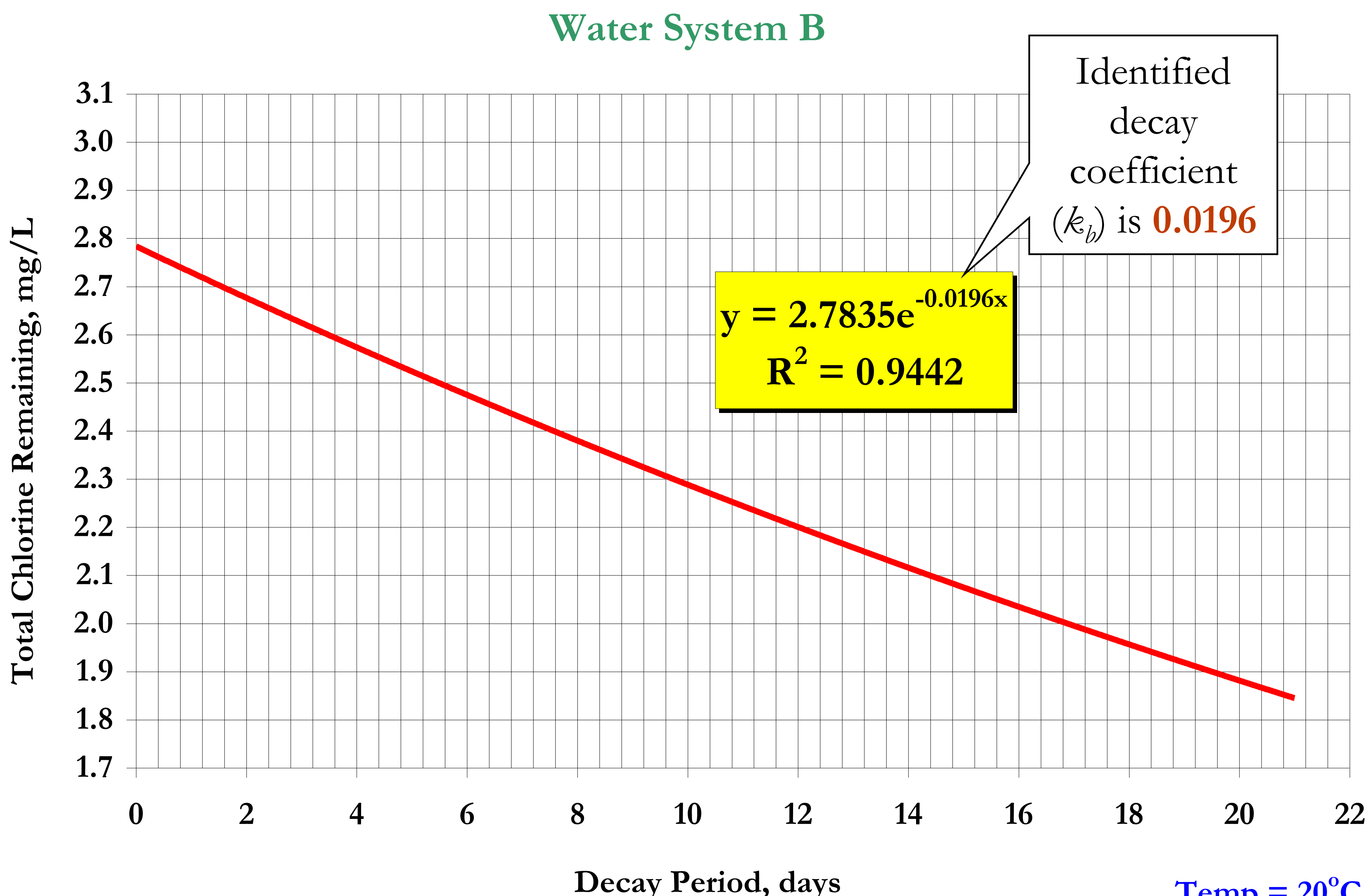
Day 0	3.05	Day 11	2.20
Day 1	2.70	Day 13	2.15
Day 3	2.55	Day 15	2.05
Day 5	2.45	Day 17	2.00
Day 7	2.38	Day 19	1.95
Day 9	2.30	Day 21	1.90

Water System B

- Total chlorine decay for 21 days (depletion minimized)
- Graph data in Excel™
  - Select scatter graph
  - Add trend line to data points
  - Select exponential graph type
  - Display equation and R^2 options
- Determine decay coefficient (*k*) from equation

$$C_t=C_o e^{(-kt)}$$

Water System B



Temp = 20°C

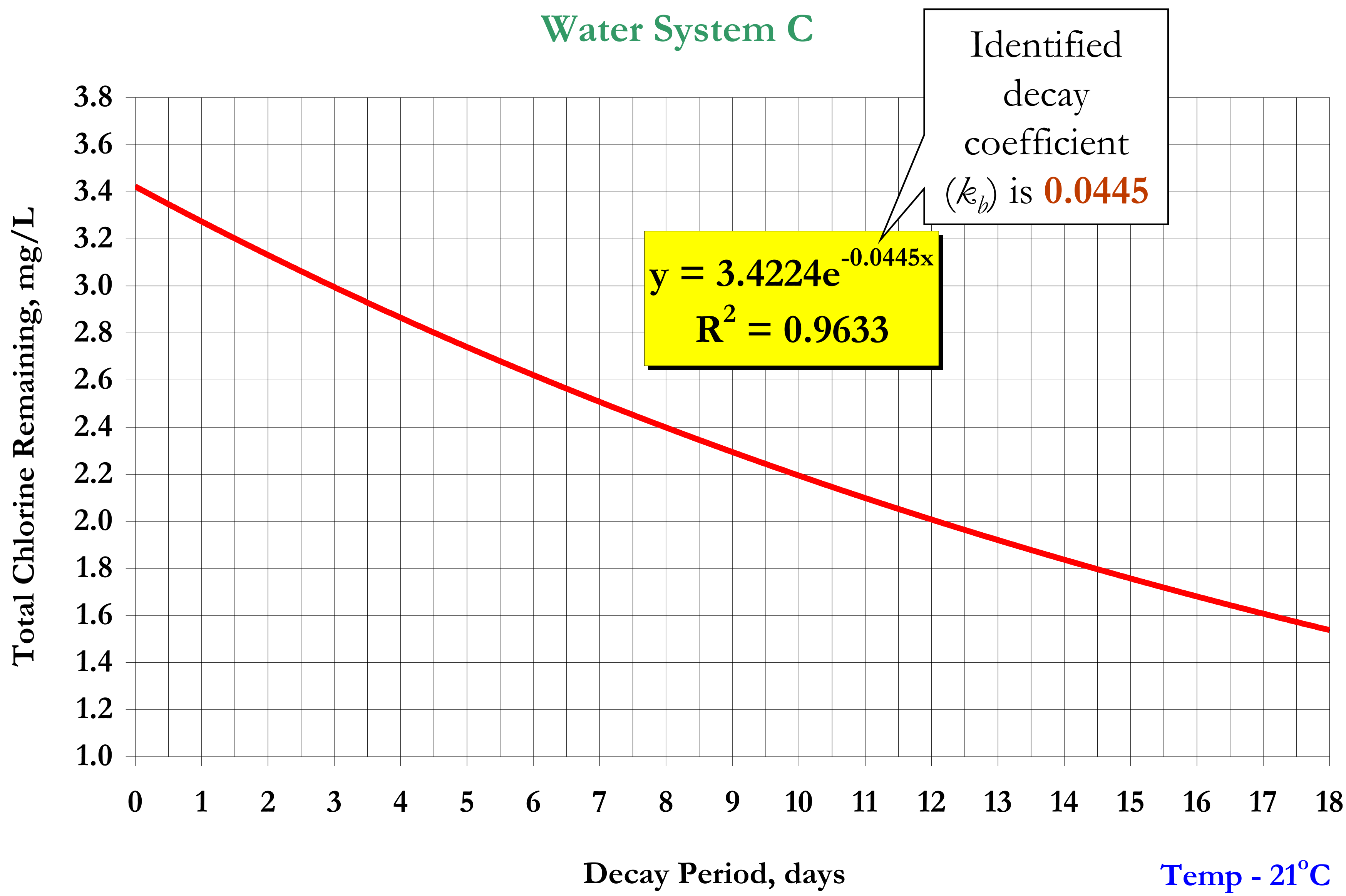
Day 0	3.6	Day 12	1.90
Day 2	3.3	Day 14	1.80
Day 4	2.9	Day 16	1.7
Day 6	2.6	Day 18	1.7
Day 8	2.3		
Day 10	2.1		

Water System C

- Total chlorine decay for 19 days (depletion minimized)
- Graph data in Excel™
  - Select scatter graph
  - Add trend line to data points
  - Select exponential graph type
  - Display equation and R^2 options
- Determine decay coefficient (*k*) from equation

$$C_t = C_o e^{(-kt)}$$

Water System C



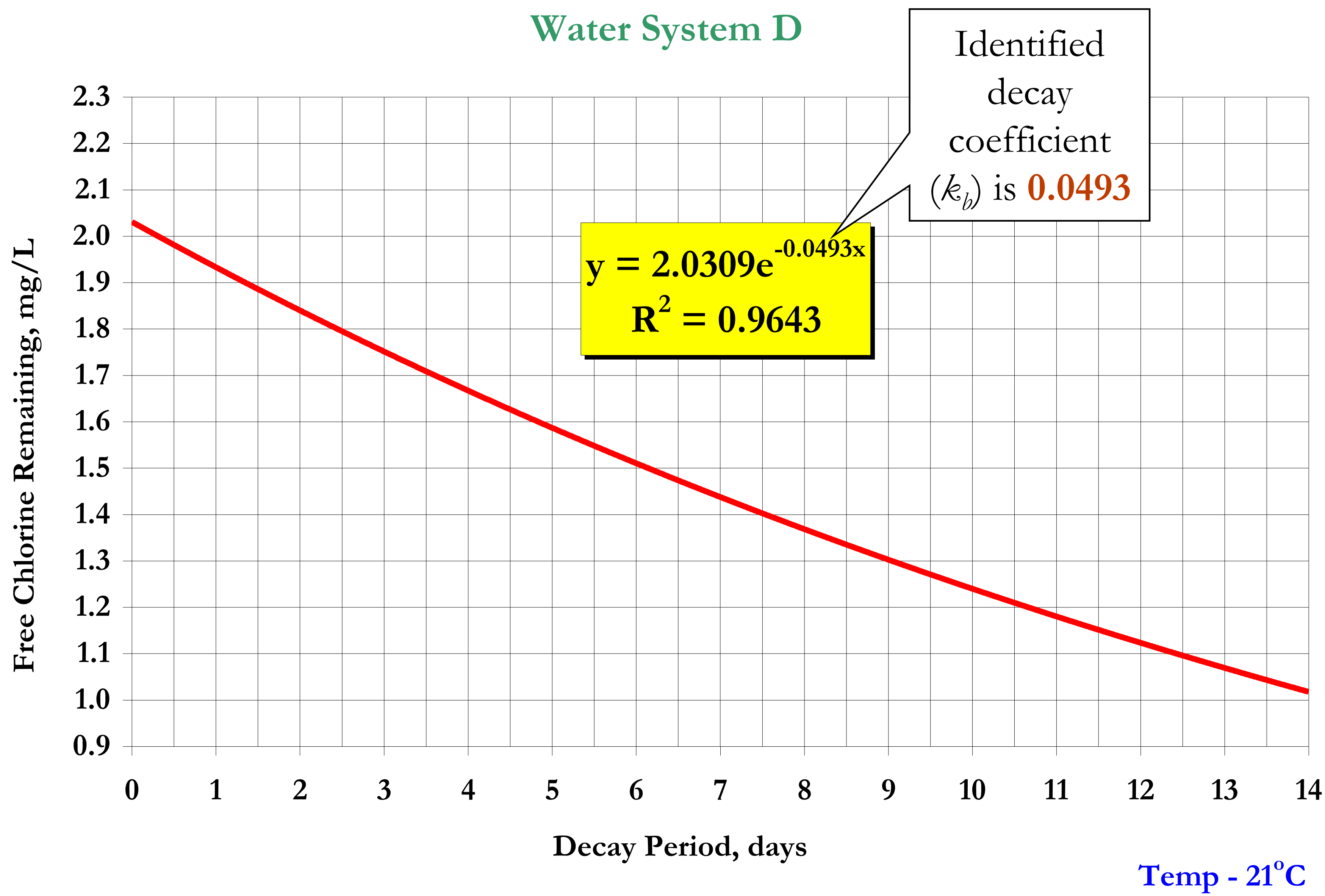
Day 0	2.17	Day 10	1.23
Day 1	1.94	Day 12	1.12
Day 2	1.86	Day 14	1.08
Day 4	1.62	Day 15	1.07
Day 6	1.40		
Day 8	1.34		

Water System D

- Free chlorine decay for 15 days (depletion minimized)
  - Sample spiked with NaOCl
- Graph data in Excel™
  - Select scatter graph
  - Add trend line to data points
  - Select exponential graph type
  - Display equation and R^2 options
- Determine decay coefficient (*k*) from equation

$$C_t = C_o e^{(-kt)}$$

Water System D



Adjustment for Temperature Variations

Water temperature changes

- ***k*** changes by factor of 2 each 10°C change in temperature
  - Each 1°C changes ***k*** about 10%
    - Increasing temperature increases ***k***
    - Decreasing temperature decreases ***k***
  - Calculate ***k*** at various temperatures to bracket range of water temperatures experienced in distribution
- Initial experimental data System B
  - ***k*** = 0.0196 @20°C
  - 10°C - 0.0098
  - 20°C - **0.0196**
  - 30°C - 0.0392

Water temperature changes

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    - Increased temp increases ***k***
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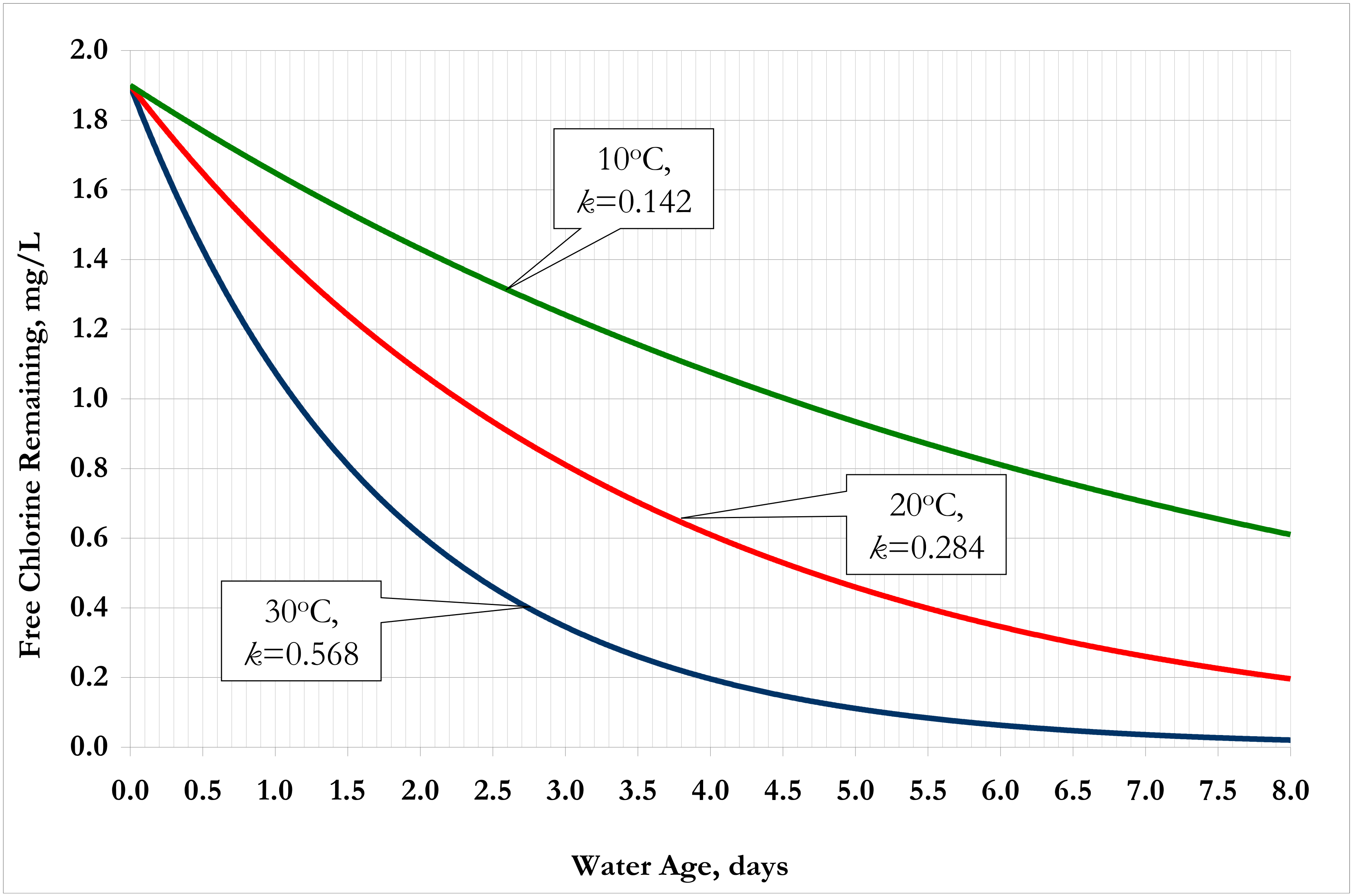
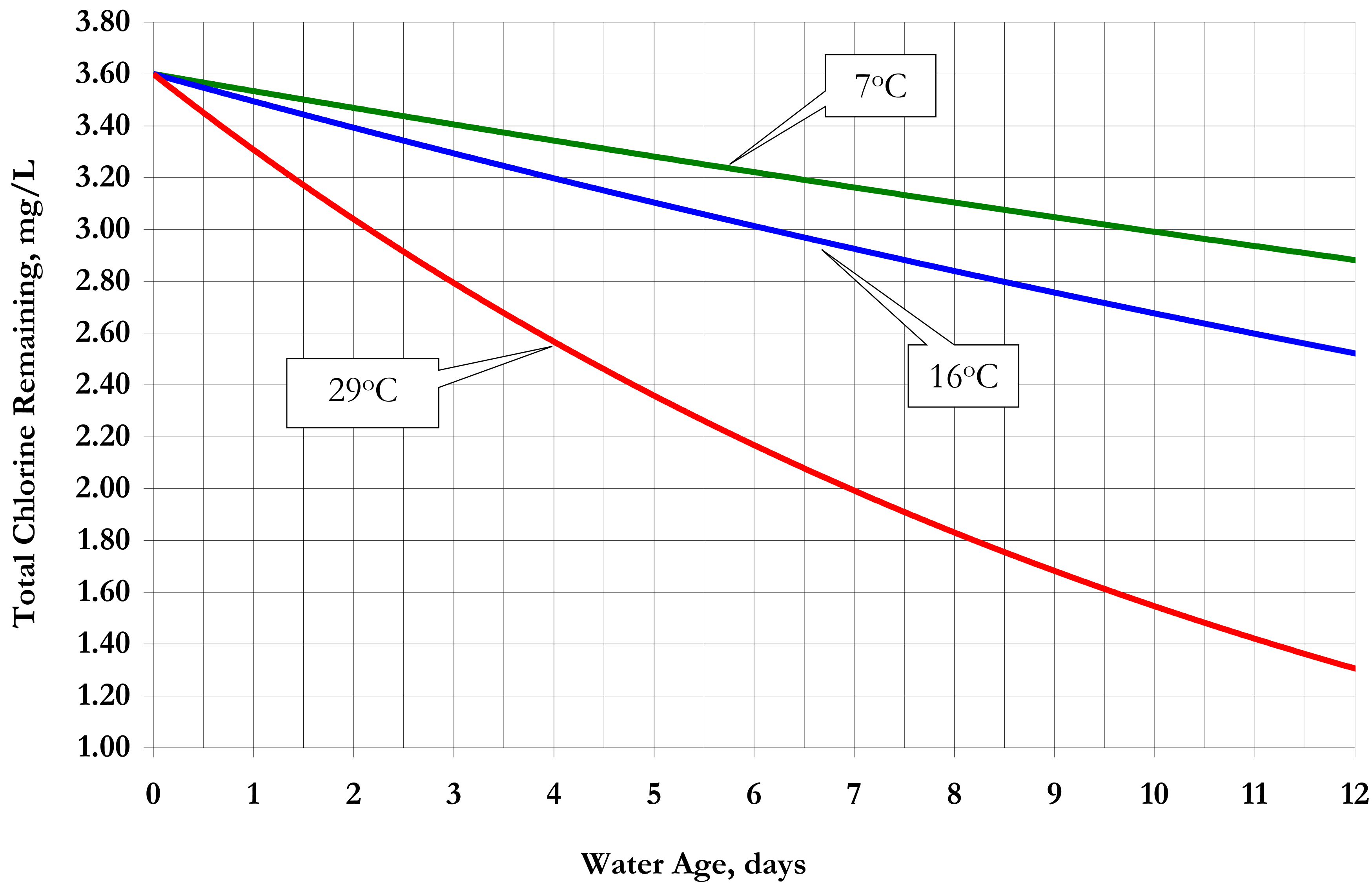
  - Calculate ***k*** at various temperatures to bracket range of water temperatures experienced in distribution system
- Initial experimental data System B
  - ***k*** = 0.0196 @20°C
  - 10°C - 0.0098
  - 20°C - **0.0196**
  - 30°C - 0.0392

3°C	0.0070	13°C	0.115
4°C	0.0073	14°C	0.122
5°C	0.0075	15°C	0.131
6°C	0.0078	16°C	0.140
7°C	0.0082	17°C	0.151
8°C	0.0085	18°C	0.163
9°C	0.0089	19°C	0.178
10°C	0.0098	**20°C**	**0.0196**
11°C	0.0103	21°C	0.0215
12°C	0.0109	22°C	0.0225

Seasonal Decay Variations



Seasonal Variations Water System C



Decay Model Development

Decay Model Development

- Using ***k*** values established decay calculations are made using first order equation
  - ***k*** varies with temperature (vlookup function in Excel™)
  - Bracket water age 0 days to X days
  - Use typical initial residuals in plant effluent (t=0)
  - Bracket residual concentration variations
  - Insert equations for each residual and water age into table
- Table becomes decay model for individual water systems
  - Known water age predicts residual at that location
  - Known residual concentration predicts water age at that location
  - Predict tap residuals needed to meet minimum system residuals
    - Temperature variations often illustrate loss of residual due to decay reactions

Example Decay Model Table

Chlorine Decay Model

Temp, oC	21
k	0.284

	Residence Time, Days															
mg/L Tap	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**	**3.0**	**3.5**	**4.0**	**4.5**	**5.0**	**5.5**	**6.0**	**6.5**	**7.0**	**7.5**	**8.0**
2.8	2.43	2.11	1.83	1.59	1.38	1.19	1.04	0.90	0.78	0.68	0.59	0.51	0.44	0.38	0.33	0.29
2.7	2.34	2.03	1.76	1.53	1.33	1.15	1.00	0.87	0.75	0.65	0.57	0.49	0.43	0.37	0.32	0.28
2.6	2.26	1.96	1.70	1.47	1.28	1.11	0.96	0.83	0.72	0.63	0.55	0.47	0.41	0.36	0.31	0.27
2.5	2.17	1.88	1.63	1.42	1.23	1.07	0.93	0.80	0.70	0.60	0.52	0.45	0.39	0.34	0.30	0.26
2.4	2.08	1.81	1.57	1.36	1.18	1.02	0.89	0.77	0.67	0.58	0.50	0.44	0.38	0.33	0.29	0.25
2.3	2.00	1.73	1.50	1.30	1.13	0.98	0.85	0.74	0.64	0.56	0.48	0.42	0.36	0.32	0.27	0.24
2.1	1.82	1.58	1.37	1.19	1.03	0.90	0.78	0.67	0.59	0.51	0.44	0.38	0.33	0.29	0.25	0.22
2.0	1.74	1.51	1.31	1.13	0.98	0.85	0.74	0.64	0.56	0.48	0.42	0.36	0.32	0.27	0.24	0.21
1.9	1.65	1.43	1.24	1.08	0.93	0.81	0.70	0.61	0.53	0.46	0.40	0.35	0.30	0.26	0.23	0.20
1.8	1.56	**1.35**	1.18	1.02	0.88	**0.77**	0.67	0.58	0.50	**0.44**	0.38	0.33	0.28	0.25	0.21	**0.19**
1.7	1.47	1.28	1.11	0.96	0.84	0.73	0.63	0.55	0.47	0.41	0.36	0.31	0.27	0.23	0.20	0.18

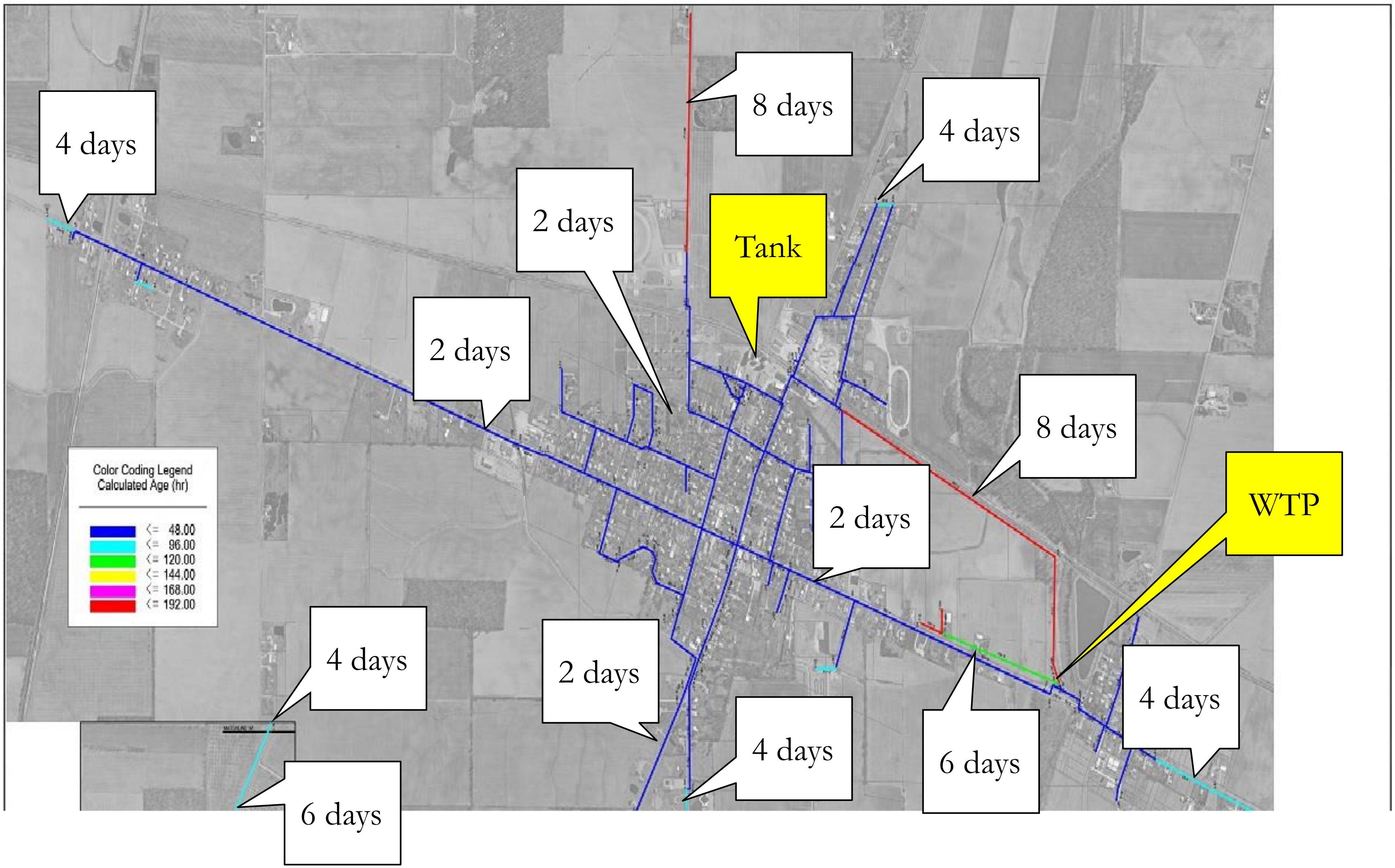
Applications for Decay Evaluations

Applications for Decay Evaluations

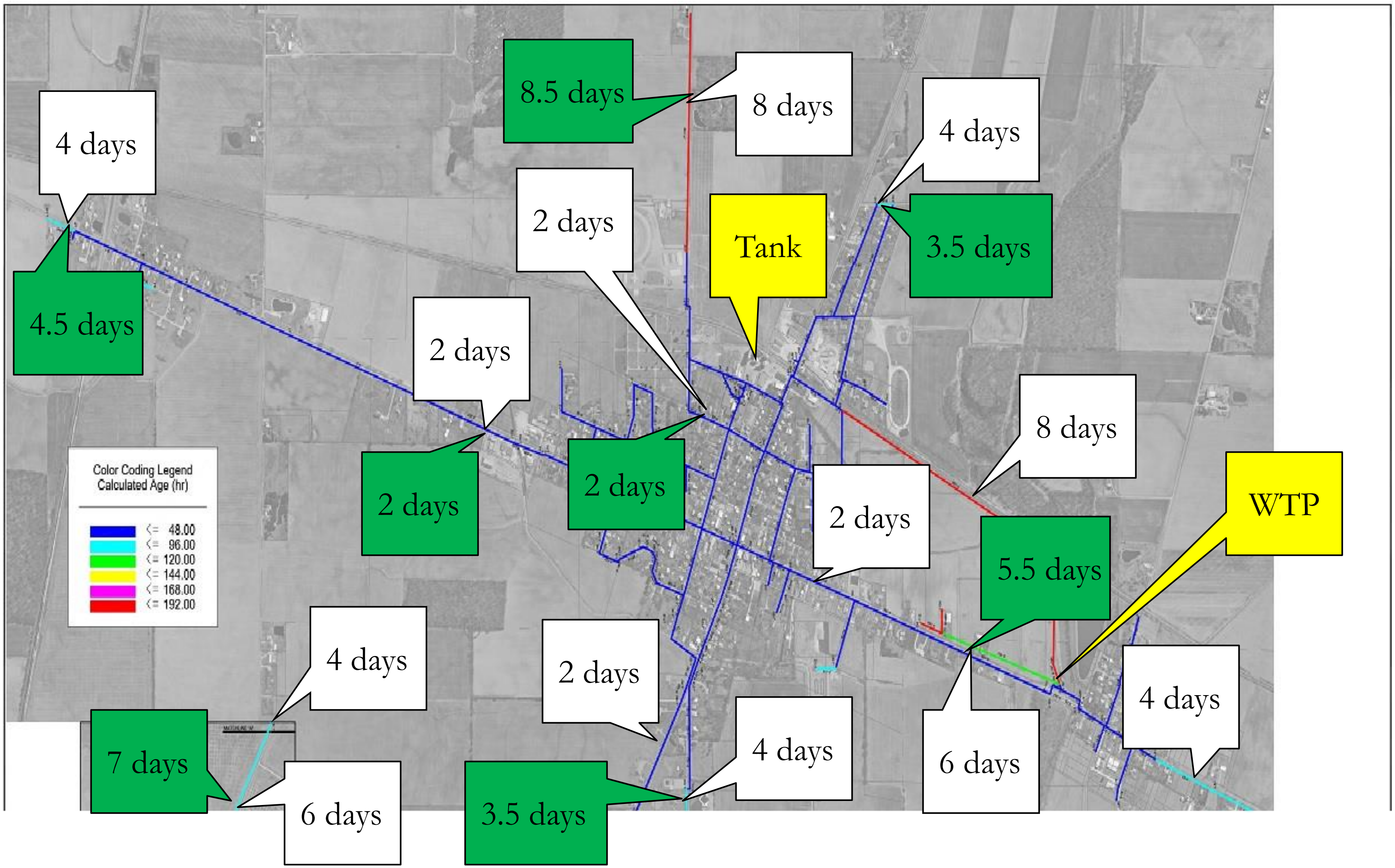
- Define residuals in areas that are not monitored
- Evaluate seasonal impacts to meet system residual requirements
- Define problem areas in storage and pipelines where persistent low residuals exist
  - Extended water age due to lack of mixing
  - Discover water age issues within distribution system
- Match decay evaluations with hydraulic modeling
- Relate other water quality issues in distribution

Water Age Predictions

Water System A (Hydraulic Model)

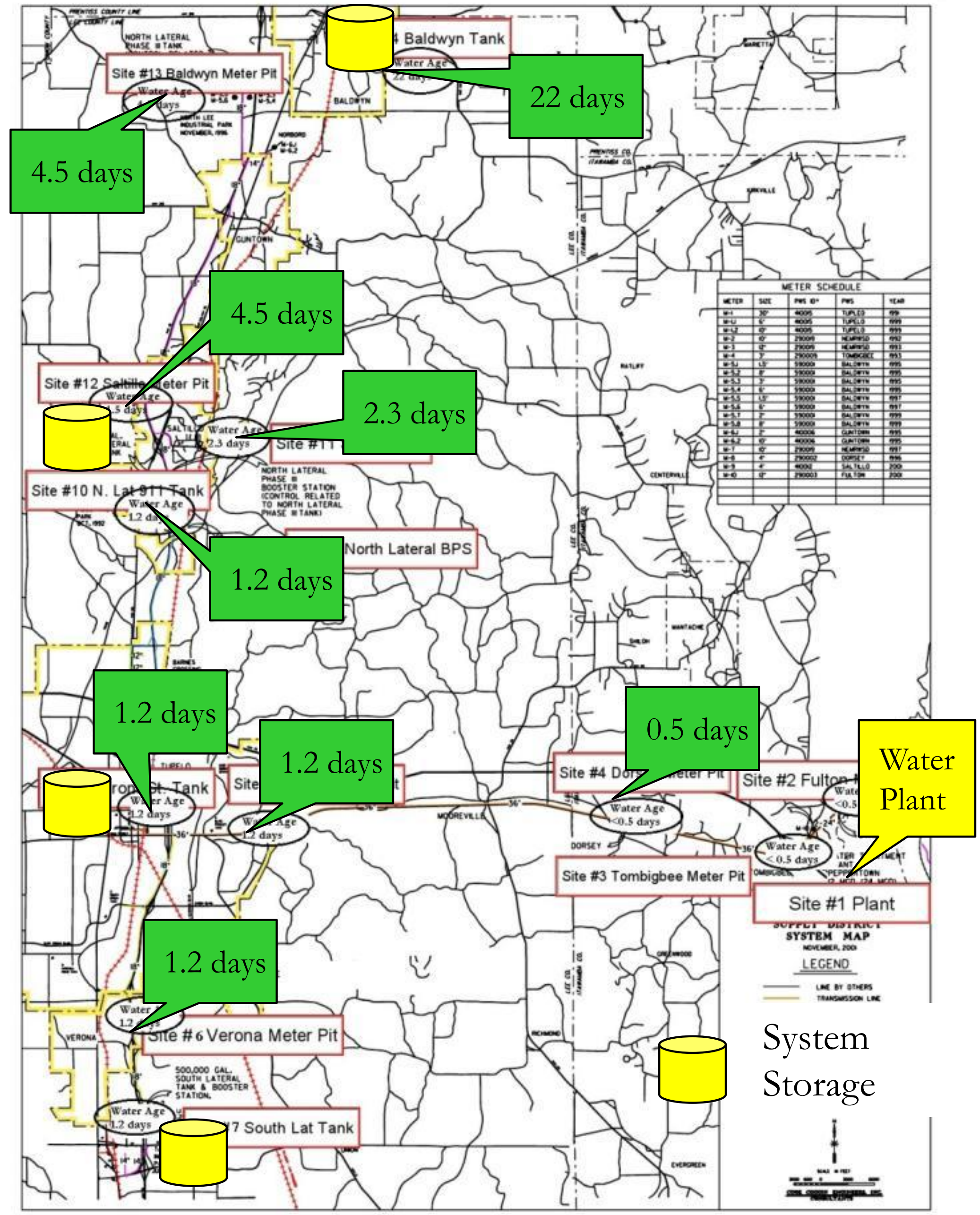


Water System A (Hydraulic Model vs. Decay)

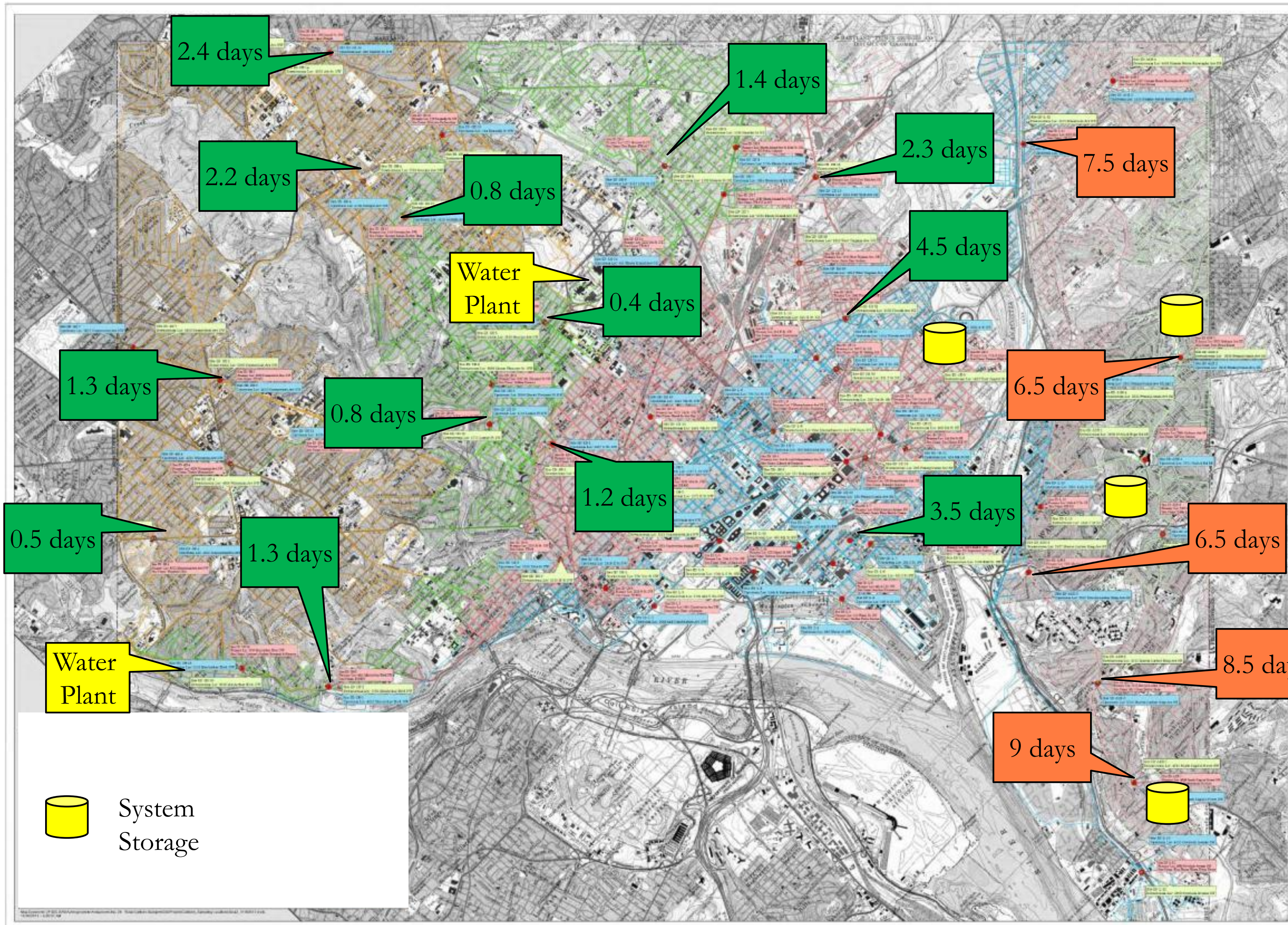


Water System B

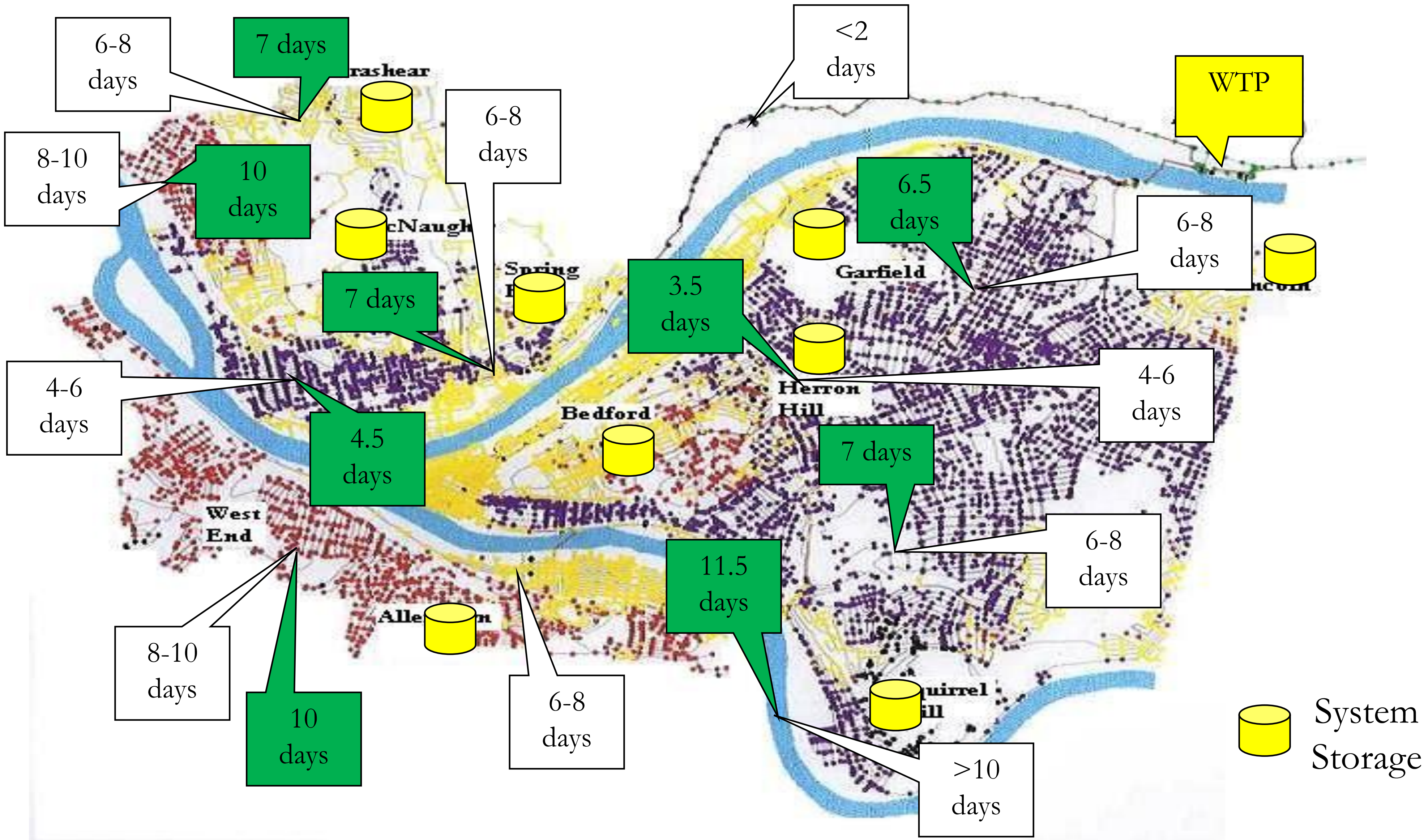
- Northern most tank contributes significant water age
  - Total chlorine depleted less than 1.0 mg/L
  - Study underway for tank mixing



Water System C



Water System D -Hydraulic Model vs. Decay



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Questions

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