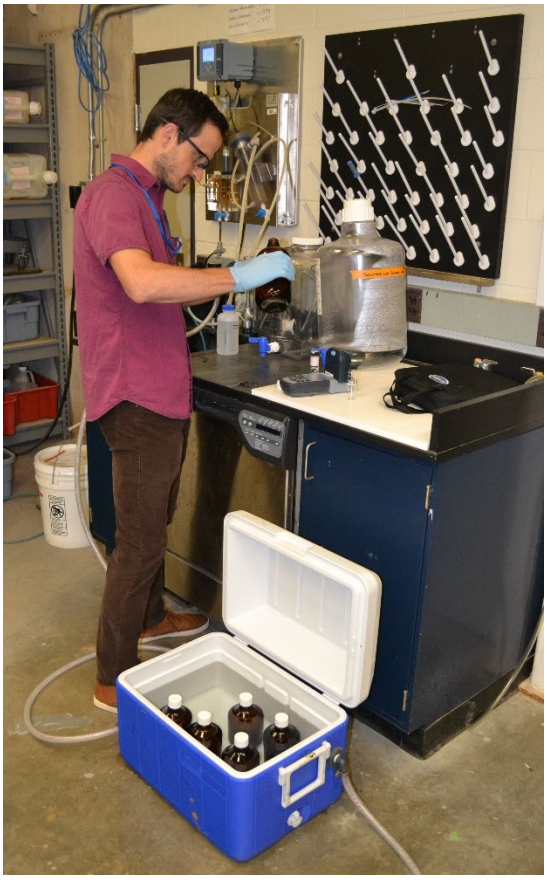
Free Chlorine Distribution System Influent Hold Study Protocol



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OVERVIEW:

The Free Chlorine Distribution System Influent Hold Study protocol provides an approach that a drinking water system may use to simulate free chlorine decay (and/or disinfection by-product formation (DBP)) in the distribution system. For a system that chooses to conduct this study, water entering the distribution system (i.e., treatment plant effluent, through a master meter, etc.) will be collected in bottles and held at distribution system temperature in the dark, to simulate distribution system conditions. Chlorine residual analysis from each of the bottle samples will be used to estimate the bulk chlorine decay of the water (not pipe wall demands). If analytical capability is available, DBP data can be collected to estimate the DBP formation potential of the water. Drinking water systems can use the *DS Influent Hold Study SpreadsheetV5.xlsx* file as a tool to support this study. These optimization tools were developed in partnership with state drinking water programs through the EPA's Area-Wide Optimization Program (AWOP).

STUDY OBJECTIVES:

This study can be used to accomplish various objectives:

- Assess the reactivity (as measured by chlorine residual) of the bulk water; if the water is extremely reactive, additional treatment may be needed.
- Assess regulated DBP formation (i.e., total trihalomethane (TTHM) or haloacetic acid (HAA5)) at the system's estimated maximum residence time (MRT).
- Assess whether chlorine entering the system is adequate to maintain a residual over a defined study period (i.e., few days); if not, the system influent residual may need to be increased.
- Estimate water age in the distribution system by comparing chlorine residual measured in the field with those from the hold study; if distribution system samples have a significantly lower residual, this may be due to distribution system conditions (e.g., pipe material/age, tank operations) and/or high water age in the distribution system.
- Identify HAA biodegradation by comparing hold study results with those in the distribution system at similar chlorine residuals.
- Assess whether a treatment change (e.g., lowering plant effluent chlorine residual) will impact chlorine demand and/or DBP formation.
- Determine the chlorine decay rate for a distribution system water quality or tank mixing model, which may be used to assess the impact of operational changes on distribution system performance.
- Assess seasonal impacts on water quality (chlorine decay, DBP formation, etc.), when repeated throughout the year.

STUDY DURATION:

The duration of the study will be based on the study objective, which should be defined prior to planning the study. For example:

- To assess the reactivity of the bulk water, the study may be run for less than a week. If the chlorine decays rapidly and/or the initial chlorine residual is very low, the chlorine residual may be completely depleted and the study may end within a few days.
- To assess DBP formation at the system's estimated MRT, the study may need to be run for a few weeks. If the MRT is unknown and cannot be determined by a hydraulic model or tracer study, plan to conduct an initial study for a two-week period.

RESOURCES:

Personnel

- Typically, one to two investigators are needed to set-up the study, collect and analyze the samples through the study, and analyze the data.
- Samples should be analyzed more frequently at the beginning of the study to characterize chlorine decay (and DBP formation trends, if applicable) and less frequently as the study progresses (e.g., sampling at time 0, 6 hours, 12 hours, 24 hours, 48 hours, ≈4 days, ≈7 days, ≈10 days, etc.); based on those results another study may be merited which will likely increase the resources needed.
- The sample schedule, including the study start date, should account for the availability of personnel who are supporting the study; for example, if samples are to be collected at 48 hours, ≈4 days and ≈7 days, it may not be practical to start the study at the end of a work week or immediately before a holiday.
- Required Equipment:
    - Amber glass bottles with PTFE-lined caps (preferably open-top with PTFE-lined septum, as shown in Figure 1).
        - Number: depends on how many samples are desired (i.e., a minimum of five bottles needed for samples collected at 6, 12, 24, 48, and 96 hours) plus an extra bottle in case of breakage.
        - Size: depends on volume needed for sample analysis (i.e., as little as 125 mL is needed for chlorine, pH and temperature; however, 500 or 1000 mL may be needed if DBPs are collected).
        - All glassware should be pretreated to be chlorine demand-free using the following, or similar, procedure:
            1. Each bottle should be filled headspace free with a 10-20 mg/L sodium hypochlorite solution[1].
            2. Soak the bottles for at least 24 hours.
            3. Thoroughly rinse each bottle three times with water[2].

Figure 1: Open-Top Amber Glass Bottle with PTFE-lined Septum

    - Water quality monitoring equipment and necessary sample bottles, including
        - Chlorine test kit, with reagents for free and total residual analysis
        - pH meter
        - Thermometer
        - Optional: bottles (with preservative, if applicable) for additional water quality parameters, which might include total organic carbon (TOC, raw and finished water), bromide (raw water), total trihalomethane (TTHMs, up to six samples if modeling is desired), haloacetic acids (HAA5, up to six).

[1] Approximately ¼ mL of 6% bleach; confirm that product contains only sodium hypochlorite and does not include other chemicals or fragrances.

[2] Water used to prepare glassware chlorine demand-free should be of the highest quality available. If laboratory clean water (RO/IX/GAC, distilled, or deionized) is not available, treatment plant effluent water may be used.

- A water bath, or alternative approach, to maintain bottles at a constant temperature, such as:
  - Laboratory water bath or incubator
  - Container designed (or modified) for continuous flow-through of study water (i.e., plant effluent, system influent, sink (cold) tap) (see Figure 2)
  - Cooler filled with system-entry-point tap water that's replaced periodically to maintain a constant temperature (the rate at which water must be exchanged will depend on the ambient and water temperatures)
  - A room that maintains a desired temperature.

Figure 2: Flow-Through Water Bath

- The Hold Study Spreadsheet (*DS Influent Hold Study SpreadsheetV5.xlsx*); Microsoft Excel is needed to run this.
- A Hold Study Data Collection Log Sheet (printed from the *Log Sheet* worksheet in *DS Influent Hold Study SpreadsheetV5.xlsx*)

Approach:

1. Study set-up and initial (*Hold Time ≈ 0 hrs.*) sample
   a. Label the Sample ID on applicable sample bottles (e.g., TOC, bromide, TTHM and HAA5 vials). The sample ID should be the hold study sample time ("0 hrs").
   b. Prepare the water bath, which will serve as an incubator for the hold study bottles. The temperature of the water bath should be the same as the temperature of the distribution system (or plant effluent water).
   c. Fill the chlorine-demand free amber glass bottles with DS influent water (see Figure 3). It is very important that all the bottles have uniform water quality; if the sample tap is immediately downstream of a chemical feed (i.e., chlorine, pH adjustment), collect a batch of water into a larger container, mix, and then add the composite sample to the bottles and analyze water quality for the *time = 0 hours* sample. Other considerations:
      - Bottles should be filled headspace-free (i.e., no air bubbles) and capped tightly.
      - It is recommended to fill one extra bottle in case a bottle breaks during the study.
      - Place the bottles in the water bath. The level of the water bath should be no higher than the neck of the bottle. Do not submerge the bottles. Cover the water bath container (i.e., bottles should be in the dark).
   d. Record the time and date on the first set of TTHM and HAA5 (and optional bromide and TOC) sample vials.
   e. Collect applicable samples and analyze water quality for the initial (time=0) sample. These should be collected from the DS influent sample tap (or composite sample) - not from an incubated bottle (see Figure 3):
      i. If applicable, fill the TTHM, HAA5 and finished TOC sample vials headspace free and refrigerate.
      ii. Measure free chlorine residual (in duplicate), total chlorine residual, pH, and temperature.
      iii. If applicable, collect raw water bromide and TOC samples and refrigerate.
   f. Record all sample data and study information on the Log Sheet.

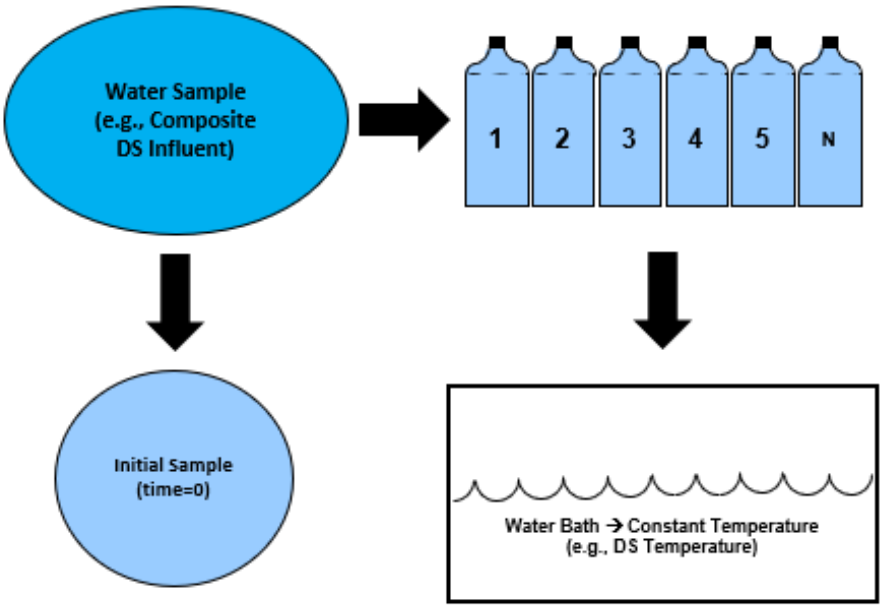

Figure 3: Schematic of Initial Hold Study Sampling

2. Bottles #1 through #5 (Hold Times ≈ 6, 12, 24, 36-48, and 60-72 hrs.)

a. Measure the temperature of the water bath and record reading on the Log Sheet. If necessary, replace the water in the water bath to maintain the distribution system temperature.

b. Label the time, date, and sample ID on one set of TTHM and HAA5 vials. The sample ID should be the sample hold time (e.g., "6 hrs").

c. Remove and open one hold study bottle from the water bath.

d. Fill the TTHM and HAA5 sample vials headspace free and refrigerate.

e. Measure free chlorine residual (in duplicate), total chlorine residual, pH, and temperature.

f. Record all sample data on the Log Sheet.

g. Repeat *Step 2* until five bottles have been analyzed.

3. Enter hold study data into the *Data Entry* worksheet in the *DS Influent Hold Study SpreadsheetV5.xlsx* file as shown in Figure 4 (user input is in red text). DBP, bromide, and TOC data can be entered when it becomes available.

Distribution System Influent Hold Study Data Entry Worksheet

Enter data into red columns.

Raw Bromide		mg/L as Br
Raw Total Organic Carbon		mg/L as C
Finished Total Organic Carbon		mg/L as C

Target Free Chlorine Concentration at End of Study = 0.20 mg/L as Cl_2

Sample Identification	Sample Time & Date	Elapsed Time (days)	Free Chlorine #1 (mg/L as Cl_2)	Free Chlorine #2 (mg/L as Cl_2)	Avg Free Chlorine (mg/L as Cl_2)	Chlorine Demand (mg/L as Cl_2)	Total Chlorine (mg/L as Cl_2)	Sample Temperature (°C)	Bath Temperature (°C)	pH	TTHM (µg/L)	HAA5 (µg/L)	Comments
Initial Sample		#N/A			#N/A	#N/A							
Bottle #1		#N/A			#N/A	#N/A							
Bottle #2		#N/A			#N/A	#N/A							
Bottle #3		#N/A			#N/A	#N/A							
Bottle #4		#N/A			#N/A	#N/A							
Bottle #5		#N/A			#N/A	#N/A							
"Model Predicted" Bottle #6		#N/A			#N/A	#N/A					#N/A		
"Model Predicted" Bottle #7		#N/A			#N/A	#N/A					#N/A		
"Model Predicted" Bottle #8		#N/A			#N/A	#N/A					#N/A		
"Model Predicted" Bottle #9		#N/A			#N/A	#N/A					#N/A		
"Model Predicted" Bottle #10		#N/A			#N/A	#N/A					#N/A		

Figure 4: Screenshot of the *Data Entry* Worksheet from *DS Influent Hold Study SpreadsheetV5.xlsx*

Based on the data collected from the six samples during the hold study (i.e., time = 0 hours and five bottles), the spreadsheet will predict the time it will take for the chlorine to decay to a final concentration and the corresponding TTHM formation (if TTHM data are collected as part of the hold study).

The *Model Predicted Free Chlorine Concentration at End of Study* is entered by the user (in cell P4). The spreadsheet will generate data from five "model predicted" bottles (i.e., #6 through #10), predicting average free chlorine concentrations at various times. The "desired final concentration" is typically the minimum free chlorine residual optimization goal (0.2 mg/L) or the minimum allowable residual that is required to be in compliance (state specific). In the example in Figure 4, the concentration entered was 0.20 mg/L and the "Model Predicted" Bottle #10 was 12.9 days.

TTHM formation is predicted using an algorithm based on chlorine demand and measured TTHM concentrations during the hold study. The example in Figure 4 shows the final predicted TTHM concentration was 62.2 µg/L at 12.9 days (i.e., for "Model Predicted" Bottle #10).

4. Review graphical results on *Cl2DecayGraph*, *TTHMFormationGraph*, and *Cl2DBPGraph* worksheets. Example chlorine decay and TTHM formation graphs is shown in Figures 5 and 6 (below).

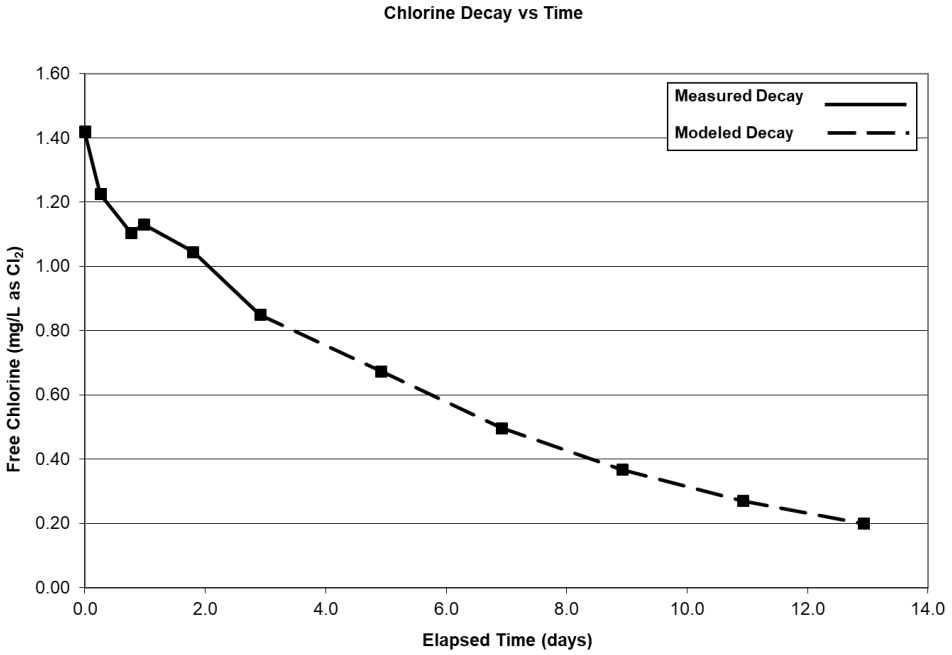

Figure 5: Screenshot of *Cl2DecayGraph* Worksheet from *DS Influent Hold Study SpreadsheetV5.xlsx*

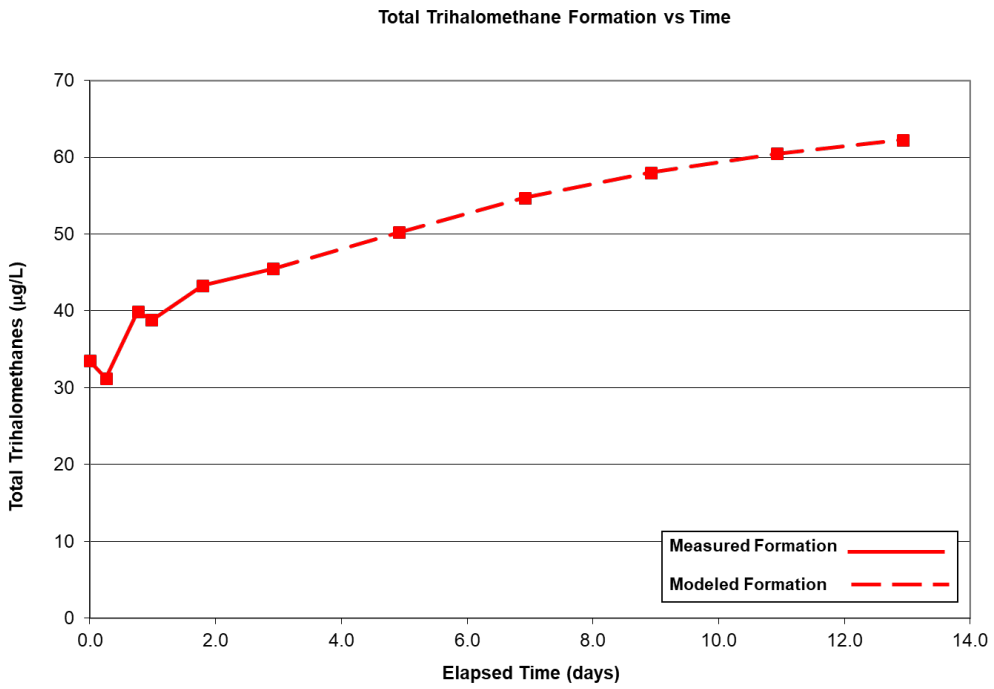

Figure 6: Screenshot of *TTHMFormationGraph* Worksheet from *DS Influent Hold Study SpreadsheetV5.xlsx*

CONCLUSIONS AND FULL-SCALE IMPLEMENTATION:

Documenting the results and conclusions from this study will support the water system's decisions about any treatment changes that are made. That documentation can also serve as a resource for designing future studies.