Work Plan: UMass Testing for Laboratory Chloramination

(Task 3.3.4.a.1)

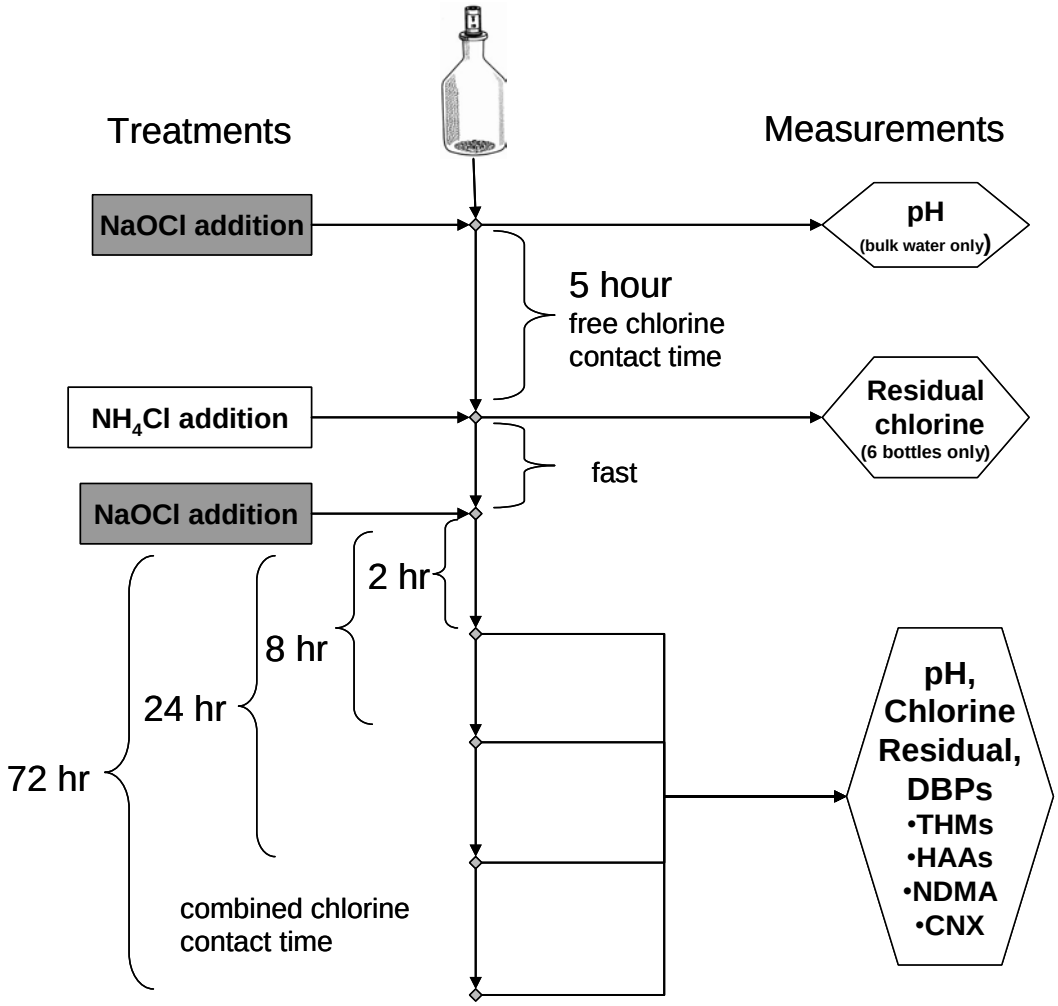
This task will use a semi-factorial design. It is factorial in time and orthogonal in the remaining variables (see table below). This is to be repeated every quarter for 2 years.

Raw water from Kensico is transported to UMass:

- Two samples (small and large) sent 3-4 days apart
  - First: Small, preliminary sample: 4 liters
  - 3-4 Days later: Large, full-sample: 120 liters (six 20L carboys) plus a travel blank (one 20L carboy)
- Quarterly, at time of regulatory compliance sampling
- Large sample Driven to UMass (3 hr transit time); by UMass team or by H&S or DEP personnel
- Small sample may be sent by overnight carrier
- DI water for travel blank (~2-liters) must be transported from UMass to Kensico prior to each large volume sampling event

Summary of UMass treatment protocol

- Addition of sodium hypochlorite
  - Ambient or optimal dose
  - Hold for 5 hours
- Addition of ammonia
  - Based on final target chloramine dose an d Cl_2/N ratio
- Addition of sodium hypochlorite
  - To reach desired chloramine dose
  - Hold for 2-72 hours
- Measure residual and quench
  - Analyze for chlorine and chloramine DBPs



Protocol for Laboratory Treatment of Kensico Water

Test #	First Chlorine Dose (mg/L)	Second Chlorine Dose[1] (mg/L)	Cl_2/N Ratio (mg/mg)	pH	Temp (^oC)	Times (hr)
1	Amb	None	0	Amb	Amb	2, 8, 24, 72
2	Amb	None	0	Amb	Amb±10	2, 8, 24, 72
3	Opt	None	0	Amb	Amb	2, 8, 24, 72
4	Opt	None	0	Amb	Amb±10	2, 8, 24, 72
5	Amb	Mid	4.0	Amb	Amb	2, 8, 24, 72
6	Amb	Mid	4.9	Amb	Amb	2, 8, 24, 72
7	Amb	Mid	6.0	Amb	Amb	2, 8, 24, 72
8	Amb	Low	4.9	Amb	Amb	2, 8, 24, 72

[1] This is the desired chloramine residual after addition of the second hypochlorite dose. The value of these residuals is listed in the "Chloramine Dose" table below

9	Amb	High	4.9	Amb	Amb	2, 8, 24, 72
10	Amb	Mid	4.9	Amb	Amb±10	2, 8, 24, 72

Key:

Amb = ambient or current chlorine dose, pH, Temperature, etc.
Amb±10 = 10C above ambient in cold weather, or 10C below ambient in warm weather
Opt = optimized chlorine dose
Mid = mid-level chloramine residual
Low = low-level chloramine residual
High = high-level chloramine residual

Protocol for Laboratory Treatment of Travel Blank Water

Test #	Chlorine Dose (mg/L)	Chloramine Dose (mg/L)	Cl_2/N Ratio (mg/mg)	pH	Temp (^oC)	Times (hr)
1tb	Amb	None	0	Amb	Amb	72
10tb	Amb	Mid	4.9	Amb	Amb±10	72

Chlorination doses

Type	Target Free Residual	At contact time	NaOCl dose
Ambient	0.8±0.3 mg/L	48 hrs	From demand test
Optimal	0.2±0.1 mg/L	48 hrs	From demand test

Ammonia doses

Test #	Nitrogen	NH_4Cl dose[2]
5	0.50 mg/L	1.91 mg/L
6, 10	0.41 mg/L	1.56 mg/L
7	0.33 mg/L	1.27 mg/L
8	0.20 mg/L	0.78 mg/L
9	0.82 mg/L	3.12 mg/L

[2] Values are expressed as NH_4Cl. Concentration of NH_4Cl stock solution is selected so that volume added to each 300 mL BOD bottle is in the range of 50-500 µL

Chloramination doses

Type	Target Residual (initial level)	NaOCl dose[3]
Low	1 mg/L	1 mg/L - 5hr FRC
Mid	2 mg/L	2 mg/L - 5hr FRC
High	4 mg/L	4 mg/L - 5hr FRC

Based on the above table, UMass will run 10 separate sets of chlorination/chloramination tests resulting in 40 separate sets of DBP analyses of each type for each quarter. The DBP analyses to be conducted on each of the 40 quarterly samples include:

- THMs
- Iodo-THMs
- Haloacetic acids
- Cyanogen Halides
- Nitrosamines including NDMA

In addition, combined and free chlorine residuals are to measured on all.

DBP formation models will be selected and calibrated based on these data. This will involve work by the PhD student under close supervision of the lead PI (Reckhow).

Sequence

1. Set the 2 controlled temperature chambers to desired level
2. Determine "Ambient" and "Optimal" chlorine doses from the small preliminary sample as soon as it arrives
    a. Measure UV absorbance and TOC on this sample
    b. Prepare 8 BOD bottles filled with this sample and chlorinate duplicates at 60%, 80%, 100% and 120% of the full system chlorine dose
    c. Measure chlorine residual in duplicate for each sample at the end of 48 hours.
    d. Interpolate dose required to achieve the target residuals based on these preliminary data. This dose can be linearly adjusted based on the relative UV absorbance of the full sample to the preliminary sample.
3. Assess each large-volume samples as soon as they arrive at UMass.
    a. Measure UV absorbance of each large-volume sample container (e.g., carboy)
    b. If UV abs values are similar, proceed to the next step. If not, consult immediately with PIs and sampling team to discuss possible need to discard one outlier (carboy).

[3] Concentration of NaOCl stock solution is selected so that volume added to each 300 mL BOD bottle is in the range of 50-500 µL

4. Blend the full, large sample as soon as it arrives and the UV absorbance has been checked.
    a. Pour all containers of Kensico water into a single polyethylene reservoir (>120 L) placed inside one of the cold rooms.
5. Assess full blended large-volume sample as soon as it is mixed.
    a. Measure UV absorbance of the full, large-volume sample. This should be very close to the values observed for the individual samples above.
    b. If UV abs is significantly different from preliminary sample re-calculate "ambient" and "Optimal" doses, assuming that the chlorine demands are linearly related to the UV abs.
    c. Measure TOC and DOC of the full sample
6. Prepare 44 BOD bottles and 44 two-liter bottles for initial chlorine dosing of the large volume-sample, each should contain a magnetic stir bar
    a. number of bottles receiving ambient dose: 72 total[4]
    b. number of bottles receiving optimal dose: 16 total[5]
7. Add "ambient" dose of NaOCl to 6 bottles (3 BOD, 3 two-liter) for assessment of 5 hr residual
8. Add requisite dose of NaOCl to all remaining bottles
    a. This should be done in a time-staggered fashion so that ammoniation and re-chlorination can be done on all in an orderly fashion as they reach the 5 hour mark
9. Place all samples in the appropriate controlled temperature chambers (1,3,5,6,7,8,9 in ambient chamber and 2,4,10 in other)
10. **At 5 hours** retrieve bottles and add requisite level of ammonium chloride to each sample needing chloramination (see table above), using microliter syringes
    a. Open bottle being careful not to disturb surface
    b. place bottle on stir plate and begin stirring
    c. quickly add required volume of NH_4Cl stock (50-500 µL) with syringe needle extending into the main body of the bottle.
11. Immediately add requisite level of sodium hypochlorite to each sample needing chloramination (see table above) using the same microliter syringe technique
12. Replace cap being careful not to cause NaOCl solution to escape around the stopper. Return bottle to the constant temperature chamber.
13. **At 7 hours** of total contact time (2 hrs of chloramine contact time for tests #5-10) remove 2 bottles of each type (2 x 10tests = 20 bottles) and initiate analyses
    a. dispense sample to vials for analysis of DBPs
        i. from BOD bottles: THMs & other neutral extractables, iodo-THMs, HAAs, cyanogen halides
        ii. from 2-liter bottles: THMs & other neutral extractables, iodo-THMs, HAAs, cyanogen halides and nitrosamines

[4] 8 treatments x 4 reaction times x 2 replicates = 64; add 6 more for estimating 5 hr residual, and 2 more for travel blanks, which makes 72. Half of these are to go in BOD bottles (one set of replicates) and the other half in 2-liter bottles. The set in BOD bottles may be dropped in future testing if replicates give similar results.

[5] 2 treatments x 4 reaction times x 2 replicates = 16. Again, half of these are to go in BOD bottles (one set of replicates) and the other half in 2-liter bottles. The set in BOD bottles may be dropped in future testing if replicates give similar results.

b. measure chlorine residual (free, mono, and dichloramine)
c. measure final pH

14. **At 13 hours** of total contact time (8 hrs of chloramine contact time for tests #5-10) remove another 2 bottles of each type (2 x 10tests = 20 bottles) and initiate analyses as done for the earlier time
15. **At 29 hours** of total contact time (24 hrs of chloramine contact time for tests #5-10) remove another 2 bottles of each type (2 x 10tests = 20 bottles) and initiate analyses as done for the earlier time
16. **At 77 hours** of total contact time (72 hrs of chloramine contact time for tests #5-10) remove another 2 bottles of each type plus travel blanks (2 x 10tests = 20; plus 2 equals 22 bottles) and initiate analyses as done for the earlier time
17. Conduct DBP analyses on all samples

Schedule:

	Small Sample[6]	**Large Sample[7]**
1st Run	9 Nov 06	14 Nov 06
2nd Run	1 Feb 07	6 Feb 07
3rd Run	26 Apr 07	1 May 07
4th Run	2 Aug 07	7 Aug 07
5th Run	1 Nov 07	7 Nov 07
6th Run	31 Jan 08	5 Feb 08
7th Run	1 May 08	6 May 08
8th Run	31 Jul 08	5 Aug 08

This lab chloramine sampling task is to be done once every quarter for a 2 year period. It is to coincide with the monthly compliance sampling. The first run date was selected as the earliest date that can be scheduled following execution of the subcontract. The subsequent 7 runs are scheduled based on the quarterly schedule. Collection of large samples is intended to coincide with the City's Tuesday (usually 1st week of the month) DBP sampling date. The small sample is then to be collected on the Thursday of the previous week.

[6] 4 liters sent by overnight carrier in cooler with ice packs
[7] 120 liters transported by car directly to UMass (3 hours) and refrigerated upon arrival