Water Quality Assessment in Connecticut: Evaluation of Current Protocols and Development of Improved Methods

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Statement of Critical Regional or State Water Problem

Connecticut relies on a water quality monitoring program to assess whether state water bodies (e.g., streams and rivers) are meeting water quality standards and supporting their designated uses. This monitoring program is faced with a task both important and difficult: important because of the significant costs and consequences associated with incorrectly listing (or not listing) a water body as impaired; and difficult because of the high temporal and spatial variability in stream water quality, and the limited resources available for assessing large numbers of water bodies. The task of accurate water quality assessment can be made easier by a better understanding of temporal variability and how it affects the results obtained from a limited set of samples.

We propose to carry out pilot research to evaluate how temporal variability in stream conditions affects the results of Connecticut's current water quality assessment program. This research will also be useful more broadly in aiding in the interpretation of water quality measurements taken at infrequent intervals. The underlying question that we hope to address is: **Given a limited set of measurements of pollutant concentration in a stream, how much can one say about concentrations of that pollutant during unsampled periods?** Specific questions that derive from this overall objective are the following:

- Given Connecticut's current sampling scheme, what are the probabilities of making type I and type II errors?
- Given a set of concentration measurements at specific points in time, what is the uncertainty associated with extrapolating these measurements to other times?
- How many samples must be taken in order to reduce this uncertainty to an acceptable level?
- Can the number of samples required be reduced by careful choice of sampling timing (e.g., making sure to cover different flow conditions)?

Statement of Results or Benefits

Our proposal involves collection of a temporally-intensive data set (~200 samples at one site over a 4 month period) to delineate the seasonal, flow-associated, and random variability in levels of bacterial indicators (*E. coli*, fecal coliform), nitrogen, and trace metals. The proposed site is at the USGS gauging station on the Quinnipiac River in Wallingford, where both streamflow (near-real-time) and water quality data (8 times/year) are available from the USGS. We will compare the use support results and other summary measures obtained from the complete data set to those obtained from subsets of the data. These subsets will be derived from Monte Carlo sampling and will mimic different sampling frequencies (e.g., the 8-12 samples per year associated with the current monitoring scheme). This will allow us to begin to answer the questions outlined above.

Results from this project (and a subsequent, larger research program) will allow CT DEP (and other agencies) to redesign its monitoring programs to obtain the greatest amount of water quality information for the lowest cost. Our results will help provide a clearer picture of the health of the state's streams. They will help to prevent costly errors in the state's list of impaired water bodies, and will ultimately help the state direct its resources to those water bodies in greatest need of protection and restoration. They will also be useful in gaining a better estimate of nitrogen loading to Long Island Sound and a fuller understanding of what sampling frequency is required for accurate assessment of nitrogen loading to the Sound from Connecticut rivers.

Nature, Scope, and Objectives

There is a general need for accurate, cost-effective methods of assessing the health of aquatic ecosystems. For example, Section 305(b) of the Clean Water Act requires states to regularly assess whether the state's waters (rivers, lakes, and estuaries) are meeting state water quality standards (WQS). Typically, the resources available for this task are small in comparison to the large number of water bodies for which assessments are required. However, stakes are high: mistaken listing of a water body as impaired (not meeting WQS) can activate the expensive total maximum daily load (TMDL) process for no reason, while a mistaken declaration that a water body is supporting all uses (i.e., meeting WQS) will divert attention from cleaning it up.

The task of assessing riverine health is further complicated by the highly dynamic nature of these ecosystems. The fact that conditions can change quickly in both time and space means that a full assessment of water quality requires a prohibitively large number of samples. Understanding the spatial and temporal variability in water quality is essential for an accurate assessment of whether a given stream meets water quality standards.

The Connecticut Department of Environmental Protection (CT DEP) relies increasingly on biological monitoring for its assessments, in large part as a way of dealing with temporal variability in stream water quality (Connecticut Department of Environmental Protection 1999). Biological monitoring presumably integrates the effects of water quality over a relatively long period of time (weeks to months), so that it may give a more accurate reflection of whether water quality is limiting to the biological community than would a small set of water chemistry measurements made at specific points in time. However, biological monitoring has several shortcomings, including our limited understanding of the relationship between water chemistry and biotic health, and difficulties in interpretation of results, especially when an adequate reference site does not exist. In addition, biological monitoring is restricted to assessment of aquatic life use support, not of other uses. Thus, for example, a stream with a healthy macroinvertebrate community could be regularly violating WQS for indicator bacteria (a standard based on protecting human health, not aquatic life support).

In its direct assessments of water quality (i.e., those not based on biotic monitoring), CT DEP relies on three types of monitoring programs:

- a long-standing cooperative program with the USGS, in which 33 sites throughout the state (mostly on large, waste-receiving rivers) are sampled 8-12 times per year;
- a rotating basin program, in which a different basin is selected each year for spatially intensive sampling; samples are collected from these sites 4 times per year (Connecticut Department of Environmental Protection 1999);
- intensive water quality surveys of specific watersheds.

(DEP also analyzes fish tissue samples for toxic bioaccumulative compounds.) Because of the limited budgets and consequently small sample numbers collected per site, these programs – with the exception of the intensive water quality surveys – are very limited in their ability to delineate the temporal variability in water quality.

EPA guidance acknowledges the role of temporal variability by permitting a certain fraction of the samples taken at a particular site to be above WQS before requiring the site to be listed as

impaired (e.g., for temperature standards for aquatic life use support, the site can be considered fully supporting if up to 10% of measurements exceed the standard (US Environmental Protection Agency 1997)).

However, the small number of samples currently used for assessment may greatly increase the chances of either:

- a type I error: a site is declared impaired when it is not (i.e., the samples happened to be taken under unusually bad conditions); or
- a type II error: a site is declared healthy when it is in fact impaired (i.e., the samples happened to be taken under unusually good conditions).

We propose to carry out pilot research to evaluate how temporal variability in stream conditions affects the results of Connecticut's current water quality assessment program. This research will also be useful more broadly in aiding in the interpretation of water quality measurements taken at infrequent intervals. The underlying question that we hope to address is: **Given a limited set of measurements of pollutant concentration in a stream, how much can one say about concentrations of that pollutant during unsampled periods?**

Specific questions that derive from this overall objective are the following:

- Given the current sampling scheme, what are the probabilities of making type I and type II errors?
- Given a set of concentration measurements at specific points in time, what is the uncertainty associated with extrapolating these measurements to other times?
- How many samples must be taken in order to reduce this uncertainty to an acceptable level?
- Can the number of samples required be reduced by careful choice of sampling timing (e.g., making sure to cover different flow conditions)?

Note that the answer to the first question clearly depends on the measured concentrations: If these greatly exceed WQS on the sampling dates, then it is very likely that the stream is truly impaired, while if measurements exceed WQS only slightly or not on all dates, then the true impairment status of the stream may be more difficult to ascertain. We hope to use the answer to question 2 (an estimate of the uncertainty associated with extrapolation of a given set of measurements) to provide managers with the tools to quantitate the probability of type I and II errors in specific situations.

We will focus our analysis on three types of water quality parameters, namely, indicator bacteria, nitrogen, and trace metals, for three reasons:

- these parameters are not captured well by biological monitoring;
- temporal variability tends to be particularly high for these parameters (e.g., in response to storm events);
- current assessment techniques have found many CT rivers to be in violation of WQS for bacteria: the 2000 305(b) report found indicator bacteria impairment for 67 out of 194 segments representing 239 out of 673 miles of river (Connecticut Department of Environmental Protection 2000);

- the accuracy of estimates of N loading to Long Island Sound from Connecticut watersheds is dependent on the uncertainty associated with extrapolating from limited sampling dates.

Connecticut is currently in transition from a reliance on fecal coliform as an indicator of the possibility of pathogen contamination to the use of *E. coli*, a more accurate indicator of the potential for human health effects. Samples collected by the USGS are analyzed for fecal coliform and enterococci, but not *E. coli*. We will analyze our samples both for *E. coli* (for comparison to the new water quality standard) and for fecal coliform (for comparison to USGS data).

Methods, Procedures and Facilities

Approach:

Our approach to answering the questions outlined above involves collection of a temporally-intensive data set on *E. coli*, fecal coliform, nitrogen, and trace metal levels, followed by comparison of this data set to the more limited data collection typical of DEP and USGS sampling in Connecticut. This will be done at one site: the USGS gauging station on the Quinnipiac River in Wallingford. The streamflow data that we need for data analysis (and for determining sample collection timing; see below) is available on a near-real-time basis for this site from the USGS. In addition, the USGS collects 8 water quality samples per year at this site, which will serve as the basis for our comparison. Generally, four of these samples are collected during the summer (monthly, June-September), while the other four samples are collected during the remainder of the year (semi-monthly, October-May). As a pilot project, our sampling will be limited to June-September (which is the period of greatest concern, especially over bacteria levels).

Sample collection and analysis:

The proposed frequency of sample collection is limited by the fact that samples must be collected manually (due to the need for sterile sampling and the short holding time for analysis of fecal coliform and *E. coli*). However, sample collection would take place at a frequency sufficient to capture the great majority of the seasonal and flow-induced variability in conditions during the summer months. Specifically, we envision the following sample collection scheme:

- baseflow samples collected every 3 days (total over 4 months = 40 samples);
- stormflow samples collected over the course of every stormflow event during these 4 months (total = ~20 samples/storm x ~8 storms = ~160 samples), as follows:
    - rising limb: samples collected every 3 hours from the beginning of the stormflow event until 3 hours after the peak in streamflow
    - falling limb I: samples collected every 6 hours until the point at which flow has fallen 50% of the way to pre-storm levels
    - falling limb II: samples collected every 12 hours until the point at which flow has fallen 75% of the way to pre-storm levels.
    - Note: For these purposes, we will consider a stormflow event to commence when 0.5 in of rain have fallen within a 24-hour period (recorded at a rain gauge near Greeley Laboratory, New Haven).

The "complete" data set at this site will thus consist of a total of ~200 samples over a 4 month period (not including QA samples; see below). In addition, twice during these 4 months, we will collect baseflow samples every 3 hours over a 24 hour period, in order to assess the diurnal and random variability in concentrations during baseflow.

Grab samples will be collected for analysis of *E. coli*, fecal coliform, nitrogen, and trace metals. Samples will be collected and analyzed using standard techniques (Clesceri et al. 1999). Three grab samples will be collected. The first, collected into a sterile sample bottle, will be returned to the laboratory and analyzed for *E. coli* and fecal coliform using the standard EPA membrane filtration methods (US Environmental Protection Agency 2000). The second sample bottle will be filtered in the field using trace metal "clean techniques," while the third sample will be a raw (unfiltered) sample collected using clean techniques (Benoit 1994). These sample bottles will be returned to the laboratory, where an aliquot from the raw sample will be frozen for later analysis of nitrogen. The remainder of the raw and filtered samples will be acidified and stored in the refrigerator for later analysis of trace metals.

Nitrogen samples will be thawed within 30 days of collection and analyzed for NO_3^- (ion chromatography; Clesceri et al. 1999) and total N (alkaline persulfate digestion, followed by ion chromatography; D'Elia et al. 1977). Both raw and filtered trace metal samples will be concentrated by evaporative concentration within 90 days of collection and analyzed for Pb, Ag, Cu, and Cd by graphite furnace atomic absorption spectoscopy.

All of these measurements are familiar to the PI and are routinely carried out in our laboratory. Careful attention will be paid to quality control measures, including thorough training and supervision of all personnel, colony confirmation, and analysis of blanks and replicates (one blank and one replicate per sample). A Quality Assurance Project Plan will be prepared prior to the commencement of sampling.

Equipment necessary for these analyses, including two incubators, filtration apparatus, ion chromatograph, clean room, graphite furnace atomic absorption spectrometer, etc. are all available in Greeley Laboratory and the Environmental Science Facility.

Data analysis:

Analysis of the data will be aimed at addressing the questions outlined above. First, we will use our complete data sets to derive the "true" continuous records (hourly time step) of *E. coli*, fecal coliform, nitrogen, and trace metals at each site. This will be done by interpolation between our measurements, with incorporation of a random noise component. Once the "true" record is in place, we will summarize pollutant levels in several ways:

1. mean of entire record
2. median of entire record
3. geometric mean of entire record
4. maximum of entire record
5. minimum of entire record
6. range of entire record

7. interquartile range of entire record
8. fraction of time WQS exceeded
9. impairment status
10. total pollutant load (kg) over entire record (for nitrogen and trace metals).

Determination of impairment status will follow EPA guidance (US Environmental Protection Agency 1997) and DEP procedures (Lisa Wahle, CT DEP, pers. comm.). For pathogens, this will involve comparison of our data to both the geometric mean standard and the single sample standard:

- fully supporting = neither geometric mean nor single sample standards exceeded;
- partially supporting = either single sample or geometric mean standard exceeded;
- not supporting = both single sample and geometric mean standards exceeded.

We will then carry out Monte Carlo sampling of this complete data set in a manner designed to simulate several different sampling schemes:

- the 4 samples per summer collected by the DEP/USGS cooperative program
- sampling which is conducted at the same frequencies as the above (4 times per summer), but which specifically tries to capture the range of flow conditions
- sampling at higher frequencies (e.g., that suggested by the Long Island Sound Study: twice monthly; LISS 1994).

The Monte Carlo sampling will be stratified to simulate actual sampling patterns, e.g., once per month. For each sampling scheme, we will produce 10,000 synthetic data sets.

For each synthetic data set, we will determine the same 10 parameters listed above. We will then compare these parameters to the "true" values of these parameters, in order to assess both the accuracy and the precision of each sampling scheme. For each sampling scheme, accuracy will be determined by how close the mean of the synthetic data sets is to the true value, while precision will be determined by the standard deviation of the synthetic data sets. For some of the parameters analyzed, we expect to see a clear "bias" associated with the simulated sampling schemes. In particular, we expect that the maximum and minimum values observed (and the range) will be more extreme in the complete data set than in any of the synthetic data sets. However, the degree of this deviation, and its import for water quality assessment, are of interest. More importantly, we will use this approach to assess the accuracy and precision of each sampling scheme's estimates of the other parameters listed above, especially mean, median, geometric mean, fraction of time WQS exceeded, impairment status, and load. These results will speak directly to the degree of uncertainty associated with these limited-frequency sampling schemes.

<u>Personnel and responsibilities</u>:

Two masters' level graduate students at Yale School of Forestry & Environmental Studies will be involved in this project. They will both be employed full time during the summer months and 10 hours/week during the fall semester. It is anticipated that this project will serve as the required "master's project" for both students, and that they will also work on it in the context of a project course taken with the PI. The students will carry out the bulk of the sample collection and analysis. During a typical stormflow event, one student will collect daytime samples, while the other will collect night samples. Each student will also process the samples that he or she

collects, where sample processing includes analysis of the *E. coli* and coliform samples, freezing of the nitrogen samples, and acidification of the trace metal samples. Sample analysis for nitrogen and trace metals will be carried out by the students partly during the summer months (between storms) and partly during the fall semester. The PI will train both graduate students and will also be involved directly in the field and lab work. The PI will also be responsible for site selection, data analysis, and communication of results.

Relationship to future projects:

This project is viewed as a preliminary pilot project, which is by necessity limited in scope and statistical power. Given the small number of sites (1) and the short time frame to be sampled (4 months), we will not be able to provide definitive answers to the questions outlined above. We will, however, be able to provide suggestive results which will be the foundation for further research.

1) Related Research

Much effort has gone into the task of determining how the limited frequency of sample collection affects the results of water quality monitoring programs; this research will be briefly summarized below. Our proposal differs from this previous work in several ways:

- Much previous research was focused on estimating fluxes, rather than concentrations. Flux data are useful for many purposes, including understanding sources, apportioning loads (e.g., for TMDL calculation), determining trends, etc. However, compliance with state WQS is related to pollutant concentrations, not fluxes.
- Previous studies have looked at suspended sediment (SS), nutrients, major ions, and trace elements, but have not generally measured indicator bacteria, despite the significance of this parameter as a source of WQS violations.
- Many of the analyses carried out by previous studies dealt with levels of sampling effort (typically, semi-monthly to sub-daily sample collection) substantially greater than that used on a routine basis for water quality assessment in Connecticut (8-12 samples per year).

When pollutant loads need to be determined from continuous discharge data and intermittent concentration measurements, as is often the case, several methods are available. Interpolation of concentrations between measurements is the simplest method and works well when sample collection is frequent enough to delineate all the changes in concentration. More commonly, simple log-log regression of concentration against flow (the "rating curve method") often produces good fits to the data and allows extrapolation of measured to unmeasured conditions. However, the bias introduced during the retransformation from log space into linear space can be substantial (Ferguson 1986). Several methods exist to eliminate this bias, including use of the minimum variance unbiased estimator (MVUE; Cohn et al. 1989; Cohn et al. 1992) and the smearing estimator (Duan 1983). In addition, estimates can be improved by incorporation of other predictive variables into the regression, such as a seasonal component (Cohn et al. 1992) or separate classes for different flow ranges. Regression approaches can provide fairly good results for large rivers if sampling frequency is fairly high, but tend to be substantially less precise and more biased for small streams, especially at low sample frequency (Robertson and Roerish 1999; Richards and Holloway 1987).

For the purposes of determining compliance with WQS, however, one is interested in the distribution of concentrations, rather than the loads. Estimation of concentrations for unmeasured dates can be obtained using the MVUE (Cohn et al. 1989; Cohn et al. 1992) or by using rating curves with different lags between hydrographs and chemographs (Webb et al. 2000). In addition, Holtschlag has recently developed an optimal estimator for suspended sediment concentrations, which takes into account streamflow, the direction of change of streamflow, seasonal changes, measurement uncertainty, and a dynamic error component (Holtschlag 2001). While this optimal estimator provided much more accurate results than regression or interpolation techniques for high-frequency sampling (up to every 3 days), this difference was much smaller for lower sampling frequencies (every 48 days). Smith et al. (2001) have recently suggested new statistical approaches for dealing with the effects of limited data on type I and II errors in the water quality assessment process.

In terms of the design of sample collection timing, Robertson and Roerish (1999) found that when using regression estimators, the most effective sampling strategy for small streams was either monthly sampling supplemented by storm chasing or semimonthly sampling, depending on the length of the study. Various methods of stratified random sampling have been proposed for unbiased estimates of sediment loads, but these generally require intensive effort and the availability of automated flow or turbidity data (Thomas and Lewis 1995; Richards and Holloway 1987).

Principal Findings and Significance:

We were able to carry out our intensive sampling regime (see Methodology) for a period of over 6 months. *E. coli* data from this sampling, together with streamflow (from USGS) are shown in Figure 1 below. We have similar results for fecal coliform, NO_3^-, and total N. Several observations can be made:

•*E. coli* concentrations are quite variable, with a total range of ~3 orders of magnitude during the sampling period.

•Much of this variability is associated with storm events.

•Our sampling frequency appears adequate to capture most of the variability during both baseflow and stormflow (note that most trends are represented by more than one point), but lower sampling frequencies would miss much of this variability.

•Indicator concentrations are not a simple function of streamflow, but rather vary in complex ways with storm patterns. Some small storm events have surprisingly high bacterial concentrations.

•The peak in bacterial concentrations often follows the peak in streamflow; there is no evidence of a "first-flush" effect.

•*E. coli* concentrations are often above the single-sample standard (406/100 mL) for class B waters not designated as bathing areas, especially during storms. *E. coli* concentrations are above the geometric mean standard (126/100 mL) for most of the sampling period.

•*E. coli* and fecal coliform concentrations appear to co-vary at this site (r^2 of 0.76 for a linear correlation between the two parameters). These observations have significant implications, both for understanding the temporal variability in health risk, and for assessing the uncertainty associated with the current sampling regime.

We have carried out Monte Carlo subsampling on our interpolated *E. coli* and fecal coliform data, in order to assess the loss of information with limited sampling. We simulated 3 sampling regimes:

- sampling once per month
- samping once per month, baseflow only
- sampling once per month, weekdays 8AM-5PM only.

For each scenario, our complete data set was re-sampled 10,000 times. The calculated geometric means (i.e., for each scenario, the distribution of 10,000 geometric means, each of 7 sample points (corresponding to the 7 months of data)) are shown below (Figures 2-4) and are compared to the "true" geometric mean of the entire data set. As can be seen, there is considerable loss of precision with all 3 sampling regimes (broad distribution) and a substantial bias towards low results, especially with the baseflow-only sampling.

We are continuing to investigate these results and analyze other scenarios.

Figure 1. *E. coli* results (with streamflow data from USGS)

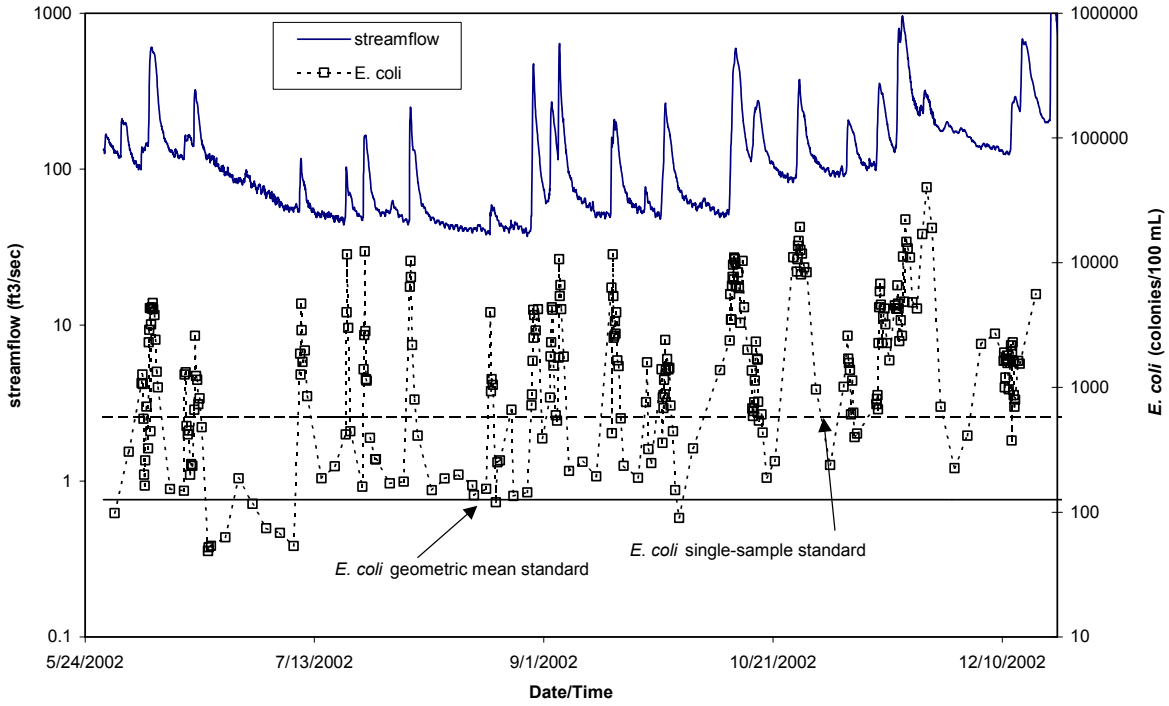


Figure 2: Resampling data: one sample per month, all data included

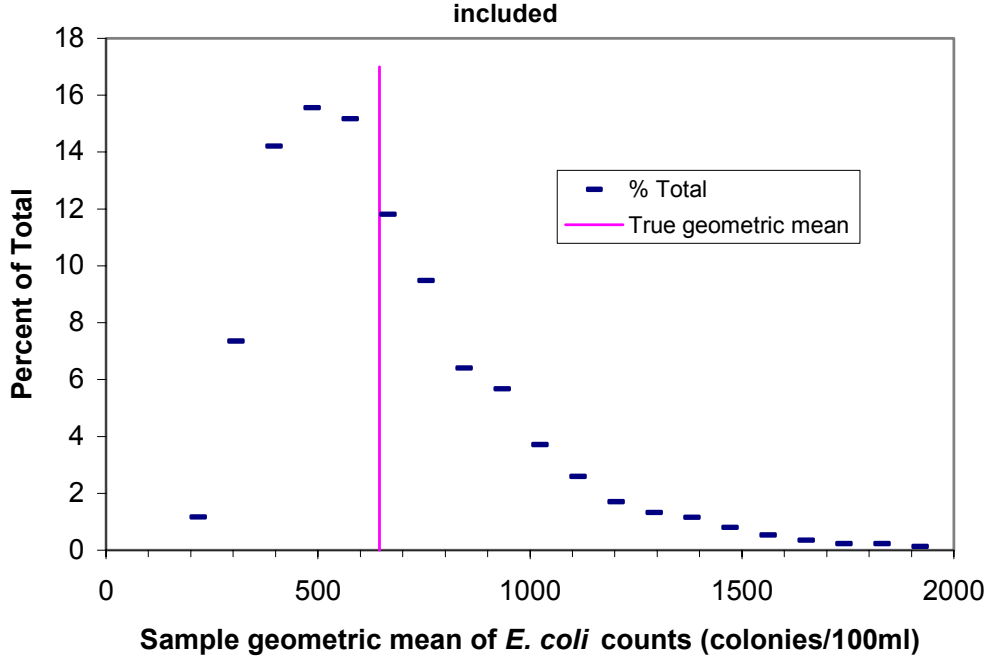
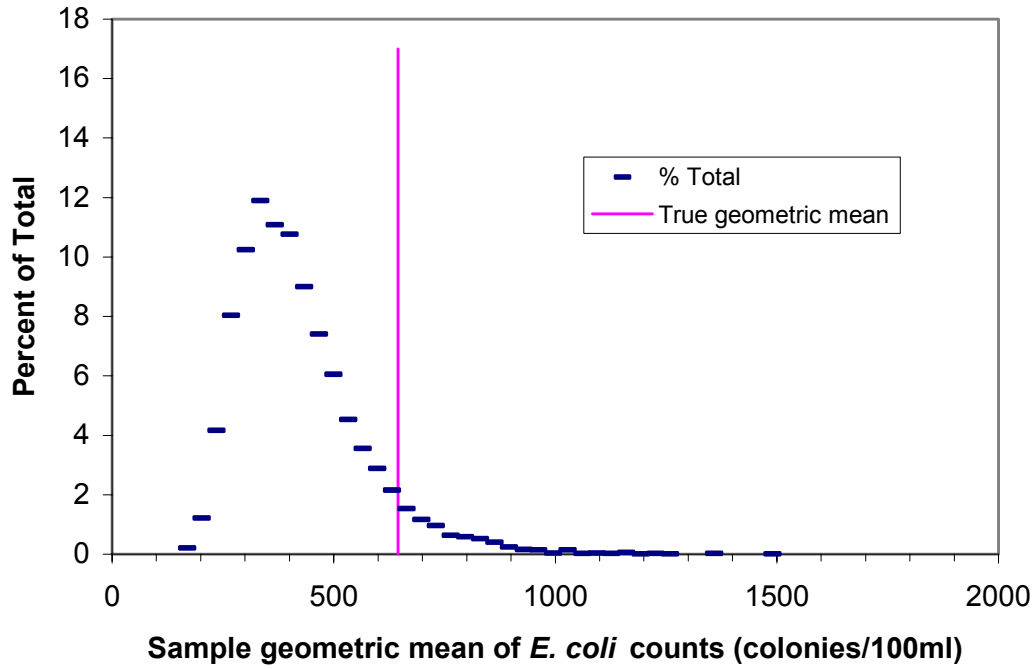


Figure 3: Resampling data: one sample per month, baseflow only



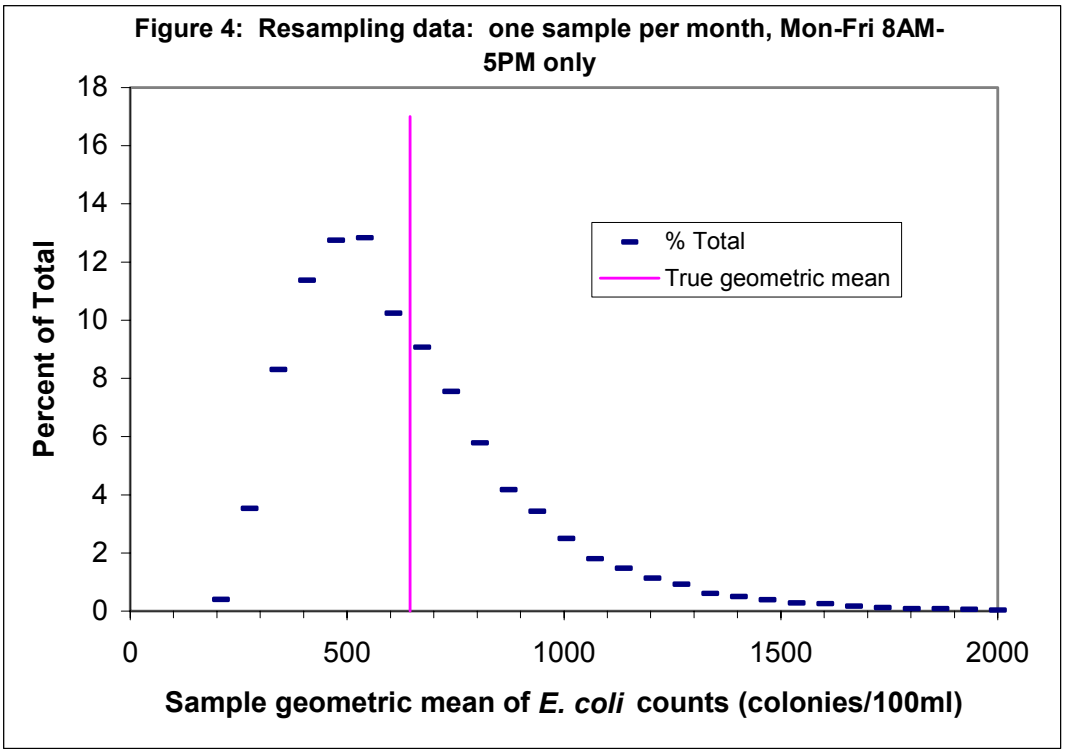


Figure 4: Resampling data: one sample per month, Mon-Fri 8AM-5PM only
Percent of Total
18
16
14
12
10
8
6
4
2
0
0
500
1000
1500
2000
% Total
True geometric mean
Sample geometric mean of E. coli counts (colonies/100ml)

<NOTE: Graphs of these results will be available through the CT IWR web site: www.ctiwr.uconn.edu

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