Errors in Stream Water Quality Data due to Diurnal Variations in a Karst Watershed in Central Kentucky

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Abstract. Studies that quantify error introduced into a water quality data set by diurnal variations under a given sampling regimen are rare. The objective of this study was to determine the errors associated with sampling at different times of the day and determine the sampling time(s) that minimized error in pH, nitrate-nitrogen, electroconductivity, and temperature data collected from a small stream in karst terrane. Utilizing data collected at short intervals over more than a three-year period, it was concluded that diurnal variations should be considered when developing sampling strategies. Error analysis revealed that the morning hours near noon were optimal for estimating daily means, as well as period mean values under weekly, biweekly, or monthly sampling regimens. Diurnal error in temperature data was significant throughout the year. Also, the time of day a sample is collected should be considered when endeavoring to estimate NO_3-N mass loads and yield.

Index Terms: Surface water quality, Chemistry of fresh water, Miscellaneous

Keywords: Diurnal, Water Quality, Karst, Error, Mass Load

1. Introduction

Diurnal variations in stream flow and water quality have been observed and reported in the

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literature for some time. Daily variations in stream flow have been attributed to evaporation and evapotranspiration (Constanz, 1998; Bren, 1997; Kobayashi et al., 1990, 1995) as well as the affect of water temperature upon the stream/groundwater exchange rate (Constanz, et al., 1994; Constanz, 1998). Daily variations in stream water quality have been attributed to several factors, including, but not limited to, air temperature, solar radiation, plant uptake, photosynthesis, reaeration, and respiration (e.g., Hessen, et al., 1997; Guasch, et al., 1998; Odum, 1957). Significant research has been reported on the dynamics of diurnal stream temperature variations (Sinokrot and Stefan, 1993; Polehn and Kinsel, 1997; Younus et al., 2000; Lowney, 2000). Other studies have focused on the dynamics of nitrate (Burns, 1998; Meuller et. al., 1997) and total solutes (Taylor and Hamilton, 1994). However, studies that quantify error introduced into a water quality data set by diurnal variations under a given sampling regimen are rare.

Taylor and Hamilton (1994) examined diurnal variability of total solute concentrations in the Saskatchewan River and concluded that one sample per day was sufficient to represent the daily average dissolved solutes concentration during stable (non-storm) flow conditions. However, this conclusion was based on samples collected for all or most of one spring or summer day, with sample intervals of one hour or less. Coefficients of variation (CV) were calculated from these data and the CVs were always less than 0.1 of the total solutes daily mean, hence their conclusion. Taylor and Hamilton did not check for diurnal variations in other seasons.

Preud'homme and Stefan (1992) performed an error analysis by randomly sampling a continuous time-series (hourly or bi-hourly) temperature record from three Upper Mississippi River watershed streams during different periods of the day. In an attempt to determine an optimal time to collect a temperature sample that would reflect the daily mean, they could not identify an optimal sampling period between 0600 hours and 1800 hours. They did find that the worst estimates of daily mean temperature were obtained when measurements were only taken in the morning (between 0600 and 1200 hours).

Stream water quality variables are often measured at regularly scheduled intervals; i.e., daily, weekly, biweekly, monthly, or quarterly; and conclusions are drawn about period mean values (e.g. average annual mean, quarterly mean, etc.) based upon the collected data. Many mass load estimation methods use biweekly, monthly, or even quarterly data to develop regression estimates of daily load. 'Actual' or 'true' mass loadings are often determined from data collected on a daily basis. Sample collection times tend to be somewhat randomly distributed during a certain period of the day, such as the workday (0800 to 1700 hours), mornings, or afternoons, depending on the sampler's work schedule. More often than not, studies that involve regular sampling regimens ignore diurnal variations or assume that they are an insignificant source of error.

The objective of this study was to determine the errors associated with sampling at different times of the day and determine the optimal sampling time to minimize error when sampling pH, nitrate-nitrogen (NO_3-N), electroconductivity (E. C.), and temperature within a small Central Kentucky karst stream.

2. Methods

2.1 Study Area

The University of Kentucky Animal Research Center (ARC; Figure 1) lies within the Inner Blue Grass physiographic region of Kentucky and is characterized by broad, shallow sinkholes, low relief, broad valleys and ridges, sparse rock outcrops and thick, fertile, limestone and shale residual soils (Keagy et al., 1993). Portions of the ARC are used for precision and site-specific agriculture operations, as well as tobacco, row crops, small grains, and animal research plots. The ARC is approximately 597.5 ha in area; with the majority of the farm located in the 771 ha Camden Creek watershed with the outlet located at stream site ST-1 (Figure 1). The area is typical Central Kentucky karst where topographic divides and groundwater divides have been found to be non-coincident (Thrailkill, 1985; Thrailkill et al., 1982). The significance of non-coincident divides was illustrated by the results of Coffey (1999), who determined that the basin drainage area required to produce optimum runoff volume predictions from the SWAT hydrologic model at stream site ST-1 was 1600 ha, an increase in drainage area of over 100 percent of the Camden Creek watershed surface area.

The basin hydrologic response is characterized as flashy. Table 1 summarizes various means of quantifying the hydrologic response of the basin. The Flashiness Index (Robertson and Roerish, 1999) was computed as the ratio of Q_{95}/Q_5 ($95^{th}/5^{th}$ percentile of flow). Discharge variability (Preston et al., 1992) was determined by the coefficient of variation (standard deviation/mean) of discharge. The Base Flow Index was computed after the method described by Jordan et al. (1997). Hydrologic response is closely associated with rainfall. Seasonal and yearly rainfall amounts are given in Table 2 for comparison purposes.

2.2 Basin Monitoring

Beginning in 1994, a water-quality monitoring network was installed at the ARC over a period of years. Flow data collection began at four sites in November 1994, and expanded to seven sites in September 1997. Grab sampling began in October 1996. In June 1997, a YSI 6000UPG Multi-Parameter Water Quality Monitor* was installed at stream site ST-1 (Figure 1). The YSI 6000 was outfitted with temperature, dissolved oxygen (D.O.), E. C., pH, turbidity,

*Use of trade names does not imply endorsement.

and NO_3-N sensors. Data were collected by the YSI at 15-minute intervals until September 17, 1999, when logging was switched to 10-minute intervals to match the flow meter data collection interval. The YSI was removed from the stream and re-calibrated every 3 to 4 weeks, which caused a discontinuity in the data record each time.

Plotting the YSI data revealed strong diurnal variations in water temperature, E. C., pH, and NO_3-N (Figure 2) at stream site ST-1. Although the YSI was completely submerged in the flow and positioned 20 feet into a culvert, where it was in continuous full shade, the variations were held in suspicion of being an artifact of temperature variations on logger electronics. Two steps were taken to determine if the diurnal variations were real or simply electronic artifacts. First, the YSI was placed in spring SP-2 and then in spring SP-7 (see Figure 1). Data were collected for 27 days at each site beginning at 0000 hours on August 12, 1997, at SP-2 (day one for SP-2 in Figure 2), and starting at 0000 hours on October 10, 1997, at SP-7 (day one for SP-7 in Figure 2). As can be seen in Figure 2, water temperature and E.C. at the two springs vary little over the period, especially in comparison to stream site ST-1. There is some variation in pH at spring SP-7, but it is not diurnal. The behavior of temperature, pH, and E. C. in this karst hydrologic system appear to be similar to the phenomena reported to occur in regulated rivers by Polehn and Kinsel (1997) and Lowney (2000), where water is released from a reservoir at a nearly constant temperature.

To make certain of the reality of the diurnal variations, another brief study was conducted. An ISCO 3700 sampler was placed at stream site ST-1 and water samples were collected every hour for 48 hours from August 20, 1997 to August 22, 1997. Results of the sample analyses are shown in Figure 3 along with the values obtained from the YSI during the same period. A diurnal pattern exists for both E. C. and pH in both the YSI data and the ISCO collected samples. Discrepancy in YSI and ISCO sample pH values can be attributed to the lag time of 48 hours in collecting and measuring the pH in the ISCO samples. The YSI NO_3-N spike that occurred late on August 22 was due to an observed application of ammonia nitrate to the pasture bordering the stream below spring SP-7. The YSI detected the concentration of NO_3-N from the fertilizer granules that entered the stream and dissolved. It was concluded that the observed diurnal variations in temperature, pH, E. C., and NO_3-N were genuine.

YSI data were collected at stream site ST-1 from June 25, 1997 to December 29, 2000. Data were retrieved at each re-calibration of the instrument. Grab samples were collected biweekly throughout the period as well. Because YSI sensors are subject to drift, the data were linearly compensated for drift by utilizing the compensation software provided with the YSI 6000 and the biweekly grab samples, per the YSI 6000 instruction manual (YSI, undated).

After compensation for drift, data that were obviously erroneous were removed from the dataset. This included data where sensor failure was apparent or the data were especially erratic. Days where the full daily suite of 10- or 15-minute interval data was incomplete were also removed from the dataset. Table 3 contains the details of the extent of the modified data set.

2.3 Error Analysis

True daily means were determined by averaging the YSI data for each day in the record, utilizing the 10- and 15- minute interval data. Mean values of E. C., Temperature, NO_3-N, and pH were determined from the modified data set and are given in Table 4. Means determined for each of the seasons and for three trimesters are reported in Table 4 as well. The trimester periods were chosen because noticeable trends within the ARC water quality data tended to fall into these three trimesters.

Errors were determined by using error statistics for bias, variance, and root mean square error. Bias is defined as the difference between a sample value and the true value and is determined from

$$\mu_x = \Sigma X_i/n$$

and

$$X_i = V_i - V_m$$

where μ_x is the mean bias of the sampled values, X_i is the individual sample bias, calculated as the difference between the sample value, V_i, and the true mean value, V_m, and n is the number of samples. Optimal sampling, or sampling to minimize error, depends not only on the mean error or bias, but also on the variability of the samples. Variance is the measure of the spread of the sampled values and is determined by

$$\upsilon_x = (n\Sigma X_i^2 - (\Sigma X_i)^2)/(n(n-1))$$

where υ_x is the variance. The standard deviation, σ_x, is determined as the square root of the variance. A biased estimate with low variability may be better than an unbiased estimate with high variability. Therefore, the root mean squared error (RMSE), an error term that combines bias and variance, was calculated to make comparisons. RMSE is given by

$$RMSE = (\mu_x^2 + \sigma_x^2)^{1/2}$$

2.4 Data Subsampling

To determine the error associated with diurnal variations in a sampling regimen, the data were subsampled in several ways. For one method, samples were selected every hour on the hour for each day in the modified data set for comparison with daily mean values. Another method was to select samples on the hour for each day under weekly (7 days between samples), biweekly (14 days), and monthly (28 days) sampling regimens. The weekly, biweekly, and monthly regimens were replicated seven times by starting the sampling regimens on days one through seven, respectively, of the modified data set. If data were not available when a weekly, biweekly, or monthly sample was to be selected, the date was ignored and no selection was made.

2.5 Mass Load and Yield Determination

Electroconductivity and NO_3-N are the only parameters considered here that lend themselves to mass load calculations. NO_3-N concentration was taken directly from the YSI. The YSI E. C. values were converted to Total Solutes (TS) concentration by the following formula (Evangelou et al., 1981):

$$TS = 0.014*E.C.$$

where TS is in moles/liter.

Mass load of NO_3-N and TS were calculated or estimated for each day within the modified data set by four different methods. First, the 'true' load was determined by integrating the 10- or 15- minute interval concentration data in concert with the 10-minute flow data, or

$$L_i^t = \sum_i \sum_j c_{ij} q_{ij} t_{ij}$$

where L_i^t is the ith 'true' daily load, c_{ij} is the jth concentration of the ith day, q_{ij} is the corresponding flow rate, and t_{ij} is the corresponding time interval. The second method of estimating daily load utilized the mean daily concentrations and mean daily flows, calculated as

$$L_i^m = \Sigma c_i^m q_i^m$$

where L_i^m is the ith estimated daily load, c_i^m is the corresponding mean daily concentration, and q_i^m is the corresponding mean daily flow. The third and fourth methods are similar. Concentration and flow for each day were selected at the time of day that when the minimum and maximum RMSE values occurred as shown in Figures 12 and 14, respectively. The daily load estimate was determined by the following:

$L_i^{min} = \Sigma c_i^{min} q_i^{min}$

$L_i^{max} = \Sigma c_i^{max} q_i^{max}$

where L_i^{min} is the estimate of *i*th daily load utilizing concentration and flow values at the time of day, t_i^{min}, when the RMSE is at a minimum (1200 hours for E. C. and 1100 hours for NO_3-N; see Figures 12 and 14). c_i^{min} and q_i^{min} are the concentrations and flow rates corresponding to t_i^{min}. L_i^{max} is the estimate of daily load utilizing concentration and flow values at the time of day, t_i^{max}, when the RMSE is at a maximum (1800 hours for E. C. and 1600 hours for NO_3-N; see Figures 12 and 14). Accordingly, c_i^{max} and q_i^{max} are the concentrations and flow rates corresponding to t_i^{max}.

Yields were determined by summing the daily loads calculated from each method, or

$$Yield^k = \sum_i L_i^k$$

where k equals t, m, min, or max, referring to the methods described above. Table 5 contains the resulting yield values for all data within the modified data set, partitioned by year.

3. Results and Discussion

To determine the distribution of the diurnal variations throughout the day, relative frequency distributions of daily maxima and minima were developed (Figures 4 and 5). Time of day when temperature and pH maxima and minima tended to occur are more readily discernable than for NO_3-N and E. C. Maxima for pH and temperature tended to occur around 1600 hours. Minima for temperature tended to occur at 0700 hours, whereas minima for pH were somewhat distributed throughout the early morning hours. Minima for E. C. occurred around the same time as the maxima for pH and temperature: approximately 1600 hours. NO_3-N maxima and minima were distributed throughout the day, although the maxima tended to occur around 1200 hours and the minima around 0000 hours. Daily mean values occurred somewhere between these times.

Figure 6 is a plot of stream-variable mean values at each hour of the day. Times of occurrence of the mean maxima and minima were easier to discern from Figure 6 than Figures 4 and 5. Mean daily maxima for temperature and pH occurred at 1600 hours. Mean temperature minima occurred at 0700 hours but the mean pH minima occurred around 0500 hours. Mean E. C. maxima occurred at 0700 hours and the minima occurred at about 1730 hours. NO_3-N maxima occurred at 1000 hours and the minima at 2300 hours. Obviously, over a period of over three years, sampling consistently at times near the maxima or minima would introduce some bias from the daily mean, as compared to consistently sampling at times when the daily mean is more likely to occur.

According to Taylor and Hamilton's (1994) criteria, diurnal variations should create minimal error if the daily coefficient of variation is less than 0.1. Figures 7 through 10 are box whisker plots of the distribution of daily coefficients of variation for temperature, E. C., pH, and NO_3-N, respectively. The 0.1 CV threshold was consistently exceeded for all variables except pH, which exceeded the threshold only twice in 1066 days. From this analysis, it is concluded that diurnal variations should be considered when planning sample collection times.

Bias from daily means and the root mean square errors produced by sampling on the hour each day are given in Figures 11 through 14. Sampling at 1100 hours produced the smallest RMSE in daily mean estimates of temperature, pH, and NO_3-N. The smallest E. C. RMSE was produced at 1200 hours. Minimum bias was produced at 1100 hours and 2200 hours for temperature, midnight and 1300 hours for E. C, 1000 hours for pH, and 0500 hours for NO_3-N. The optimal time, based on RMSE, for sampling all variables at one time was around 1100 hours. Although this time produced near maximum bias in NO_3-N, the majority of the error in

NO_3-N was due to variability and not bias. RMSE more than doubled when samples were collected at times near daily maxima or minima, excepting NO_3-N. Sampling in the afternoon produced the largest RMSE in all variables and the largest bias in temperature, E. C., and pH.

Figures 15 through 18 plot the bias and RMSE that resulted from the weekly, biweekly, and monthly sampling regimens. Period means for each plot are given in Table 4. Times of minimum bias were comparable with those in Figures 11 through 14. Optimal sampling time, based on minimum RMSE, was in the morning hours. There were not significantly different levels of error between the different sampling regimens, except for bias in NO_3-N. When sampling NO_3-N, monthly sampling tended to underestimate the period mean at all times of the day and was larger than the bias obtained from weekly or biweekly regimens except during the midday period.

Bias from period means under weekly, biweekly, and monthly regimens was comparable to those obtained by daily sampling. However, the RMSE was increased significantly for all variables but pH. This increase was due to the use of constant period means as opposed to daily means in the error calculations. The variability within one day was significantly less than the variability observed over a longer period, thus the increased values of RMSE.

Given the variability of each of the water quality parameters under weekly, biweekly, and monthly regimens, do differing sample collection times produce significantly different amounts of error in the estimates of the period means? To answer this question, the normalized bias and RMSE for each parameter and sampling regimen were calculated by dividing them by the appropriate period mean. This resulted in normalized bias and RMSE values expressed as a fraction or percentage of the mean. The range (difference between maximum and minimum) of normalized error yields a measure of the difference in error that sampling at the worst time produced as opposed to sampling at the optimal time. Although arbitrary, but comparable to the reasoning used by Taylor and Hamilton (1994), a difference of 10 percent in maximum and minimized error was chosen as the threshold of significance.

The minimum, maximum, and range of the normalized bias and RMSE as a percentage of the period means are given in Table 6. Temperature was the only variable where the difference in normalized minimum and maximum bias and RMSE (given as the range in Table 6) exceeded 10 percent of the period mean. For the other variables, the difference in bias was consistently under 10 percent and the difference in RMSE was consistently under 5 percent. We concluded that sample collection time need only to be considered when sampling for temperature on a weekly, biweekly, or monthly basis.

Researchers, in order to conserve funds, will often only sample during certain periods of the year, such as the spring when, for example, NO_3-N levels may be elevated due to fertilization. Figures 19 through 22 are comparisons of the RMSE for daily sampling, stratified by season and trimester, for temperature, E. C., pH, and NO_3-N, respectively. Sampling during different seasons or periods only produced different levels of error. The largest error in NO_3-N was produced in the fall of the year, but the largest error was produced in summer when sampling for E. C. and in spring when sampling for pH. The best time to sample temperature and pH occurred in late morning for all periods. The optimal time of day for sampling NO_3-N and E. C. shifted with period of the year.

Table 7 gives the normalized minimum, maximum, and range of the RMSE, stratified by period, as a percentage of the period means. Again, sampling time produced significant differences (>10 percent) in error in estimates of mean temperature during all periods. Other than temperature, the 10 percent threshold was exceeded only by NO_3-N during the summer, fall, and the ASON trimester (see Table 7). During these periods, sample collection time should be considered in order to minimize error produced by diurnal variations.

The effect of diurnal variations on mass yield estimations generally produced less that 10 percent differences from true yields (Table 5). The only exception was for NO_3-N in the year 2000 when estimating yield with values collected at the time of day, t_i^{max}, when the RMSE was at the maximum value. Percent differences in NO_3-N yield greater than 5 percent were produced in 1997 for both the t_i^{min} and t_i^{max} time of day. Although flow rate is usually the dominant variable in estimating mass load and yield, it is concluded that diurnal variations should be examined as a possible source of error and sampling times considered when designing a sampling regimen to collect data for estimating NO_3-N mass load and yield.

4. Conclusions

The objective of this study was to determine the errors associated with sampling at different times of the day and determine the optimal sampling time to minimize error in estimates of pH, NO_3-N, E. C., and temperature in a small karst watershed in Central Kentucky. Utilizing the criteria used by Taylor and Hamilton (1994), it was concluded that when sampling for temperature, E. C., and NO_3-N, sampling time should be a consideration. Taylor and Hamilton's 0.1 CV threshold was consistently exceeded by all variables, except pH, which exceeded the threshold only twice in 1066 days.

Sampling at 1100 hours produced the smallest RMSE in daily mean estimates of temperature, pH, and NO_3-N. The smallest E. C. RMSE was produced at 1200 hours. Minimum temperature bias was produced at 1100 hours and 2200 hours, minimum E. C. bias at midnight and 1300 hours, minimum pH bias at 1000 hours, and minimum NO_3-N at 0500 hours. The optimal time for collecting one aliquot and analyzing for all variables was near 1100 hours.

When sampling weekly, biweekly, or monthly, optimal sampling time, based on minimum RMSE, was in the morning hours. Error was not significantly different between the differing regimens, except for bias in NO_3-N. Monthly sampling tended to under-predict the period NO_3-N mean and produce more bias than weekly or biweekly sampling. Temperature was the only variable where the difference in minimum and maximum normalized bias and RMSE exceeded 10 percent of the period mean. For the other variables, normalized bias was consistently under 10 percent and normalized RMSE consistently under 5 percent. Sample collection time was significant only for temperature when sampling on a weekly, biweekly, or monthly basis.

When sampling during seasons or certain periods of the year only, sample collection time should always be a consideration when measuring temperature. NO_3-N exceeded the 10 percent threshold during the summer, fall, and ASON trimester. During these periods, the time of day that the NO_3-N sample is collected should be a consideration in order to minimize error due to diurnal variations. Also, it is concluded that diurnal variations should be examined as a possible source of error and sampling times considered when designing a sampling regimen to collect data for estimating mass load and yield.

Notation

μ_x mean bias of sampled values.

X_i individual sample bias.

V_i sample value.

V_m true mean value.

n number of samples.

υ_x variance.

σ_x standard deviation.

RMSE root mean square error.

CV coefficient of variation.

c concentration.

q flow rate.

t time interval.

L daily mass load

Yield total mass yield.

References

Bren, Leon J., Effects of slope vegetation removal on diurnal variations of a small mountain stream, *Water Resources Research, 33*(2), 321-331, 1997.

Burns, D. A., Retention of NO_3^- in an upland stream environment: A mass balance approach. *Biogeochemistry*, *40*, 73-96, 1998.

Coffey, M. E., Characterization of a small karst watershed with the SWAT model, M.S. thesis, University of Kentucky, Lexington, Kentucky, 111 p., 1999.

Constanz, Jim, Carole L. Thomas, and Gary Zellweger, Influence of diurnal variations in stream temperature on stream flow loss and groundwater recharge, *Water Resources Research, 30*(12), 3253-3264, 1994.

Constanz, Jim, Interaction between stream temperature, stream flow, and groundwater exchanges in alpine stream, *Water Resources Research, 34*(7), 1609-1615, 1998.

Evangelou, V. P., F. Rawlings, J. D. Crutchfield, and E. A. Shannon, A simple chemo-mathematical model as a tool in managing surface mine sediment ponds. Proceedings, 1981 Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation, *UKY BU 126*, College of Engineering, University of Kentucky, Lexington, pp. 49-58, 1981.

Guasch, H., J. Armengol, E. Marti, and S. Sabater, Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams, *Wat. Res. 32*(4), 1067-1074, 1998.

Hessen, D. O., A Henriksen, and A. M. Smelhus, Seasonal fluctuations and diurnal oscillations in nitrate of a heathland brook, *Wat. Res. 31*(7), 1813-1817, 1997.

Jordan, T. E., D. L. Correll, and D. E. Weller, Relating nutrient discharge from watersheds to land use and streamflow variability, *Water Resources Research, 33*(11), 2579-2590, 1997.

Keagy, D. M, J. S. Dinger, A. W. Fogle, and L. V. A. Sendlein, Interim report on the occurrence of pesticides, nitrate, and bacteria on groundwater quality in a karst terrain—the inner Bluegrass Region, Woodford County, Kentucky, *Kentucky Geological Survey Open-File Report, OF-93-04,* Kentucky Geological Survey, Lexington, 1993.

Kobayashi, D., K. Suzuki, and M. Nomura, Diurnal fluctuations in stream flow and in specific conductance during drought periods, *J Hydrol., 115,* 105-114, 1990.

Kobayashi, D., Y. Kodana, Y. Ishii, Y. Tanaka, and K. Suzuki, Diurnal variations in stream flow and water quality during the summer dry season, *Hydrol. Proc., 9*(7), 833-841, 1995.

Lowney, C. L., Stream temperature variation in regulated rivers: Evidence for a spatial pattern in daily minimum and maximum magnitudes, *Water Resources Research, 36*(10), 2947-2955, 2000.

Meuller, D. K., B. C. Ruddy, and W. A. Battaglin, Logistic model of nitrate in streams of the Upper-Midwestern United States, *J. Environ. Qual*., *26*, 1223-1230, 1997.

Odum, H. T., Trophic structure of Silver Springs, Florida, *Ecol. Monogr*., *27*, 396-413, 1957.

Pohlen, R. A., and W. C. Kinsel, Transient temperature solution for stream flow from a controlled temperature source, *Water Resources Research, 33*(1), 261-265, 1997.

Preston, S. D., V. J. Bierman, and S. E. Silliman, Impact of flow variability on error in estimation of tributary mass loads, *Journal of Environmental Engineering*, *118*(3), 402-419, 1992.

Preud'homme, E. B., and H. G. Stefan, Errors related to random stream temperature data collection in upper Mississippi River watershed, *Water Resources Bulletin*, *28*(6), 1077-1082, 1992.

Robertson, D. M, and E. D. Roerish, Influence of various water quality sampling strategies on load estimates for small streams, *Water Resources Research*, *35*(12), 3747-3759, 1999.

Sinokrat, B. A., H. G. Stefan, Stream temperature dynamics: Measurement and modeling, *Water Resources Research, 29*(7), 2299-2312, 1993.

Taylor, B. R., and H. R. Hamilton, Comparison of methods for determination of total solutes in flowing waters, *Journal of Hydrology*, *154*, 291-300, 1994.

Thrailkill, J., Flow in a limestone aquifer as determined from water tracing and water levels in wells, *Journal of Hydrology*, *78*, 123-136, 1985.

Thrailkill, J., L. E. Spangler, W. M. Hopper, M. R. McGovern, J. W. Troester, and D. R. Gouzer, Groundwater in the Inner Bluegrass karst region, Kentucky. Research Report 136, *Kentucky Water Resources Research Institute*, Lexington, 136 p. 1982.

Younus, M., M. Hondzo, and B. A. Engel, Stream temperature dynamics in upland agricultural watersheds, *Journal of Environmental Engineering, 126*(6), 518-526, 2000.

YSI, Incorporated, 6000UPG Multi-parameter water quality monitor: Instruction Manual. YSI Incorporated, Yellow Spring, OH, Undated.

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Table 1. Summary of Basin Hydrologic Response Indices.

Year	Base Flow Index	Flashiness Index			Discharge Variability		
		Q5 (m^3/s)	*Q95* (m^3/s)	*FI*	*Mean* (m^3/s)	*Std* (m^3/s)	*CV*
1998	0.268	0.005	0.632	131.2	0.197	0.383	1.95
1999	0.385	0.001	0.555	980.0	0.114	0.218	1.91
2000	0.298	0.012	0.501	41.2	0.115	0.248	2.16

Table 2. Seasonal and total rainfall amounts for each year of the study period.

Year	Rainfall (cm)				
	Season				Yearly Total
	winter[a]	spring[b]	summer[c]	fall[d]	
1997	44.83	39.45	20.93	20.93	126.14
1998	26.26	54.48	20.29	24.56	125.60
1999	32.82	29.11	13.46	22.17	97.56
2000	31.29	35.03	29.51	21.18	117.02
normal	29.77	33.05	30.86	28.60	122.28

[a] winter = January – March
[b] spring = April – June
[c] summer = July – September
[d] fall = October – December

Table 3. Extent of the modified data set for each water quality variable.

Variable	Temperature	pH	NO3-N	E.C.
No. of Complete Days in Data Record	1066	1066	786	1003

Table 4. True mean values for each water quality variable for the modified data set as well as the seasons and selected trimesters utilizing the modified data set.

	Mean Values							
	entire record	winter[a]	spring[b]	summer[c]	fall[d]	AMJJ[e]	ASON[f]	DJFM[g]
E.C.	0.435	0.427	0.393	0.419	0.485	0.392	0.456	0.452
NO_3-N	2.639	4.486	2.553	1.422	2.279	2.260	1.316	4.215
pH	7.596	7.745	7.564	7.614	7.500	7.584	7.521	7.698
Temperature	14.168	7.996	17.212	21.536	9.320	19.044	15.965	7.169

[a] winter = January – March
[b] spring = April – June
[c] summer = July – September
[d] fall = October – December
[e] AMJJ = April – July
[f] ASON = August – November
[g] DJFM = December – March

Table 5. Yields resulting from determining daily load by four different methods: 1) Integration; 2) Mean daily concentration and flow; 3) Concentration and flow at time of minimum RMSE; and 4) Concentration and flow at time of maximum RMSE.

Total Solutes								
		Yield (kmoles)				Percent Differences		
Year	# of days in record	Integrated[a] (1)	Means[b] (2)	Min RMSE[c] (3)	Max RMSE[d] (4)	(2) - (1)	(3) - (1)	(4) - (1)
1997	111	2373.1	2372.2	2320.7	2199.0	-0.04%	-2.21%	-7.34%
1998	241	16638.9	16811.1	16205.3	16695.9	1.04%	-2.61%	0.34%
1999	305	17671.9	17799.4	16717.9	17176.4	0.72%	-5.40%	-2.80%
2000	265	12393.8	12371.0	11537.2	11900.8	-0.18%	-6.91%	-3.98%

NO_3-N								
		Yield (kg)				Percent Differences		
Year	# of days in record	Integrated[a] (1)	Means[b] (2)	Min RMSE[c] (3)	Max RMSE[d] (4)	(2) - (1)	(3) - (1)	(4) - (1)
1997	91	1348.4	1340.5	1474.5	1461.0	-0.58%	9.35%	8.35%
1998	200	17519.0	17660.2	17787.8	17858.6	0.81%	1.53%	1.94%
1999	212	8609.5	8589.7	8720.6	8344.8	-0.23%	1.29%	-3.07%
2000	229	10213.6	10171.3	9579.3	8825.0	-0.41%	-6.21%	-13.60%

[a] Yield determined as the sum of each day's load, calculated by integrating the short interval YSI and flow data .
[b] Yield determined as the sum of each day's load, calculated by daily mean concentration • daily mean flow.
[c] Yield determined as the sum of each day's load, calculated by concentration • flow at time of day when RMSE is at minimum value.
[d] Yield determined as the sum of each day's load, calculated by concentration • flow at time of day when RMSE is at maximum value.

Table 6. Minimum, maximum, and range of bias and RMSE as a percentage of the period mean for weekly, biweekly, and monthly sampling regimens. Mean values are given in Table 3.

Sampling Regimen		weekly		biweekly		monthly	
		Normalized		Normalized		Normalized	
		bias	RMSE	bias	RMSE	bias	RMSE
pH	min	-2.6%	4.8%	-2.7%	4.9%	-2.7%	5.2%
	max	4.6%	8.6%	4.5%	8.6%	4.8%	8.8%
	range	7.2%	3.8%	7.2%	3.7%	7.5%	3.6%
E. C.	min	-4.9%	14.9%	-5.0%	15.5%	-6.3%	15.2%
	max	1.9%	19.1%	1.5%	19.7%	0.9%	20.0%
	range	6.8%	4.2%	6.5%	4.2%	7.2%	4.9%
NO_3-N	min	-2.5%	65.4%	-2.8%	65.7%	-9.3%	64.5%
	max	4.4%	68.2%	4.0%	69.1%	-1.2%	67.8%
	range	6.9%	2.8%	6.8%	3.4%	8.0%	3.3%
Temperature	min	-15.2%	45.9%	-14.6%	45.9%	-14.7%	45.8%
	max	23.8%	60.2%	24.7%	60.4%	26.6%	59.2%
	range	39.0%	14.3%	39.3%	14.6%	41.2%	13.4%

Table 7. Minimum, maximum, and range of bias and RMSE as a percentage of the period mean under a daily sampling regimen stratified by different periods within the year.

		Normalized RMSE as a Percentage of Period Mean							
		entire record	winter	spring	summer	fall	DJFM	AMJJ	ASON
E. C.	min	14.8%	12.5%	12.4%	16.6%	9.1%	13.1%	13.1%	13.8%
	max	19.0%	15.0%	20.1%	22.0%	9.6%	15.3%	20.2%	17.5%
	range	4.2%	2.5%	7.7%	5.5%	0.6%	2.1%	7.1%	3.6%
NO_3-N	min	0.3%	0.0%	0.1%	0.4%	0.5%	0.0%	0.1%	0.5%
	max	7.7%	2.8%	5.9%	14.8%	13.6%	3.3%	7.8%	14.3%
	range	7.3%	2.7%	5.8%	14.3%	13.2%	3.3%	7.7%	13.7%
pH	min	0.1%	0.1%	0.1%	0.2%	0.0%	0.0%	0.3%	0.0%
	max	2.5%	1.3%	5.0%	2.9%	1.3%	1.4%	4.9%	1.5%
	range	2.5%	1.2%	4.9%	2.8%	1.2%	1.3%	4.7%	1.5%
Temperature	min	45.8%	40.7%	21.4%	13.6%	50.1%	48.1%	21.4%	36.7%
	max	60.1%	61.7%	35.0%	25.5%	60.2%	67.5%	34.6%	47.1%
	range	14.3%	21.0%	13.6%	11.9%	10.1%	19.4%	13.2%	10.4%

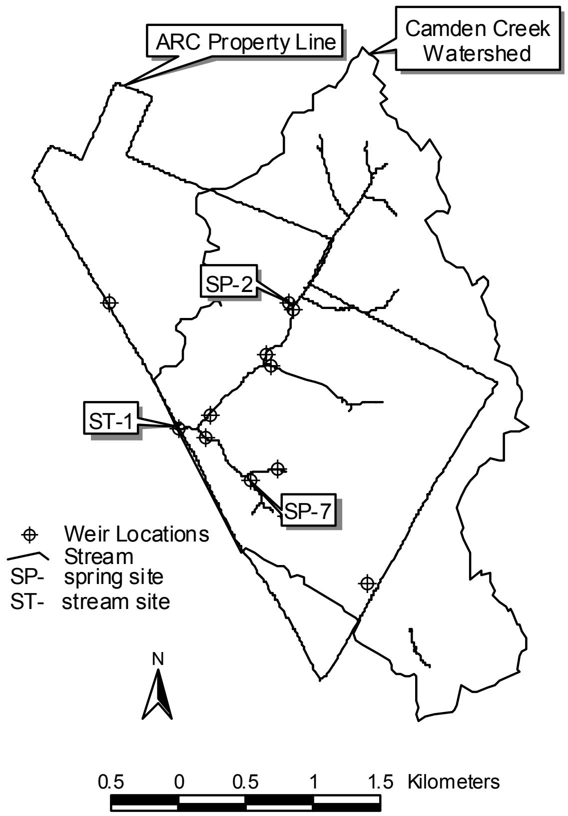

Figure 1. Study Area: University of Kentucky Animal Research Center (ARC).

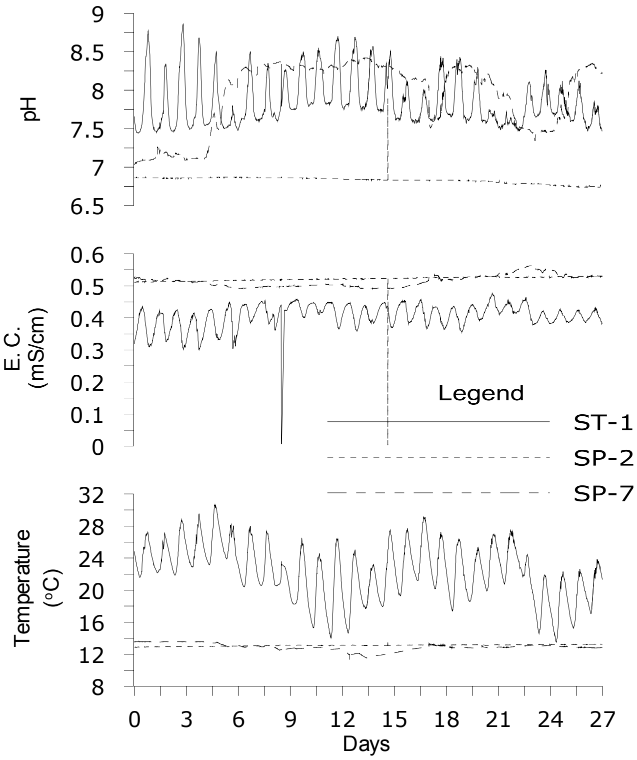

Figure 2. Example of YSI data from stream site ST-1, spring SP-2, and spring SP-7.

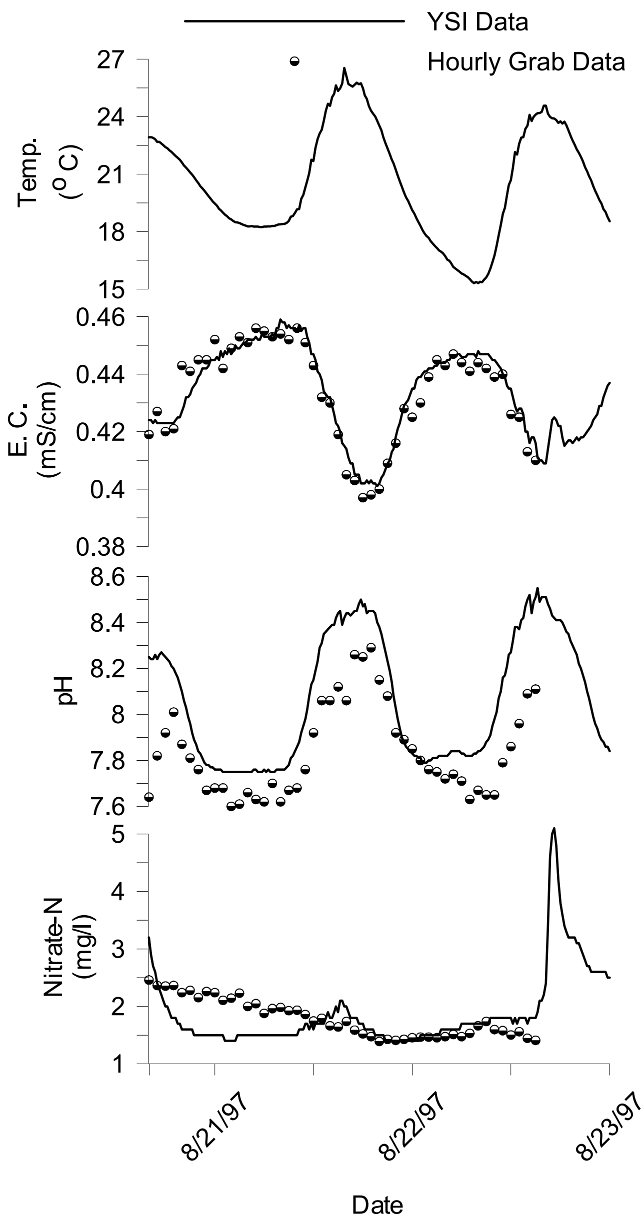

Figure 3. Comparison of YSI 6000 data to hourly grab sample data at stream site ST-1.

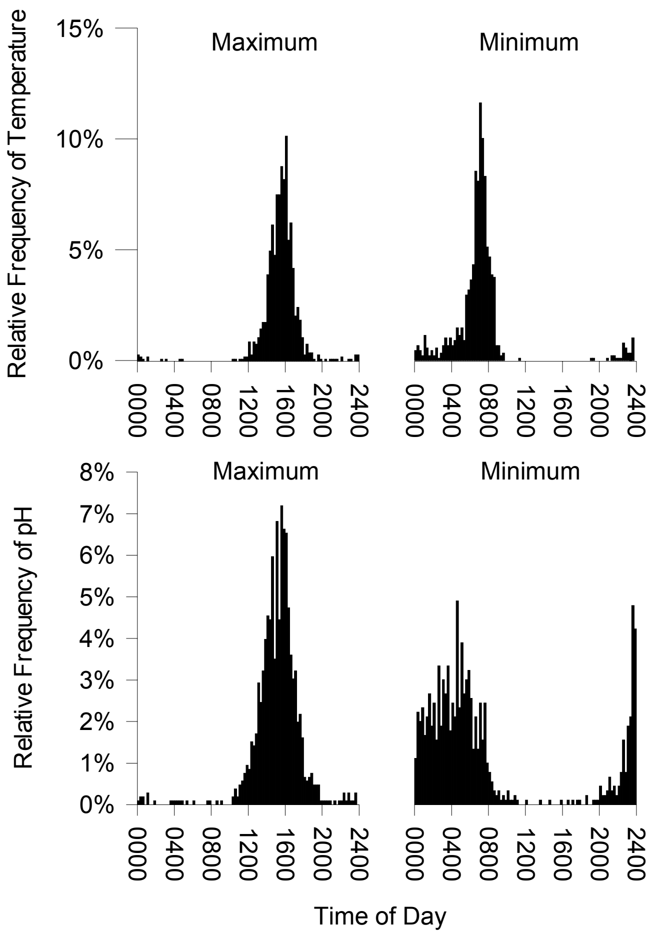

Figure 4. Frequency distributions of Temperature and pH maxima and minima.

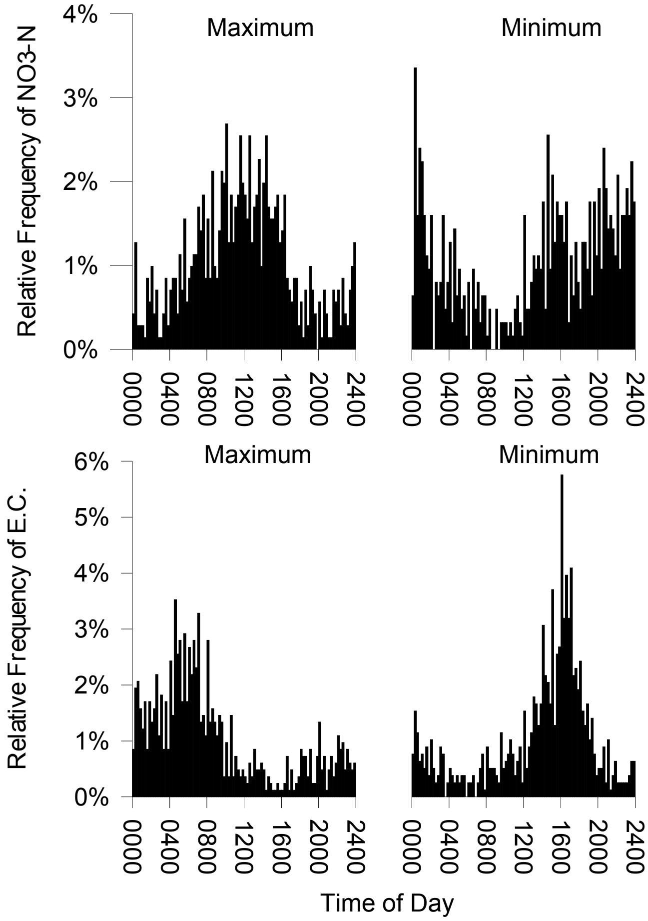

Figure 5. Frequency distributions of NO_3-N and E.C. maxima and minima.

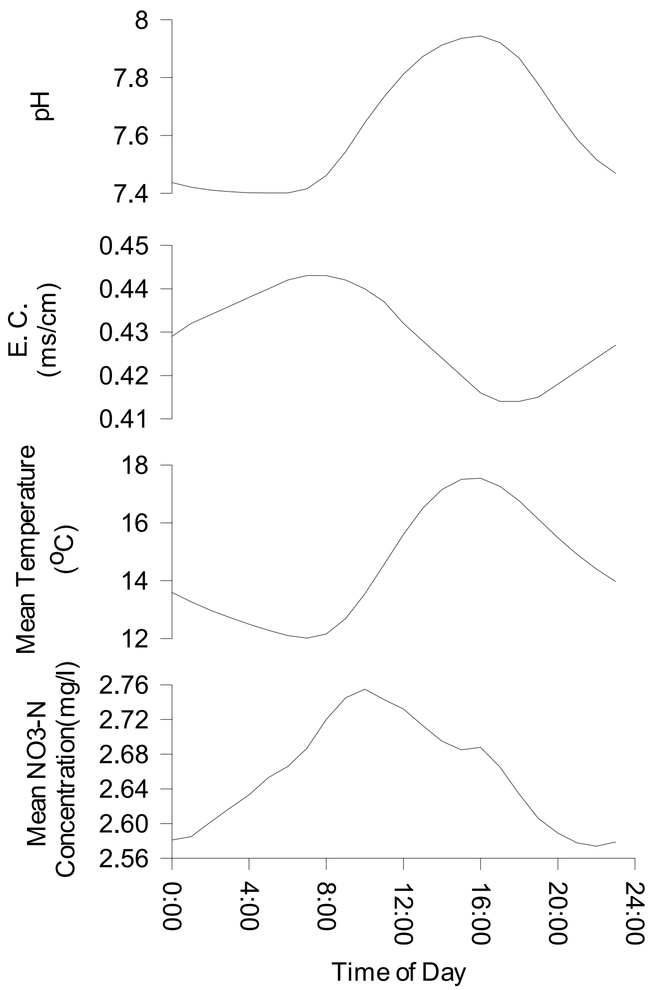

Figure 6. Mean values of temperature, pH, NO_3-N, and E. C. at each hour of the day.

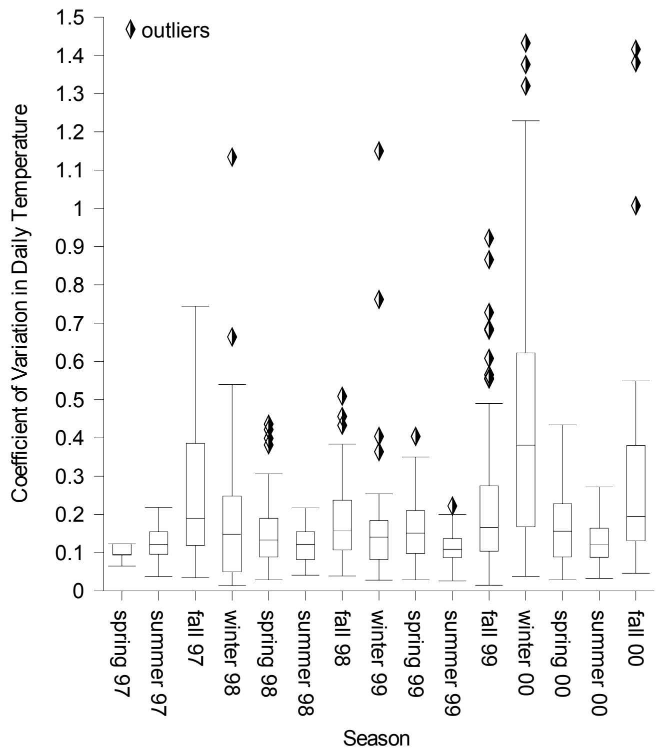

Figure 7. Box whisker plot of daily temperature coefficient of variation.

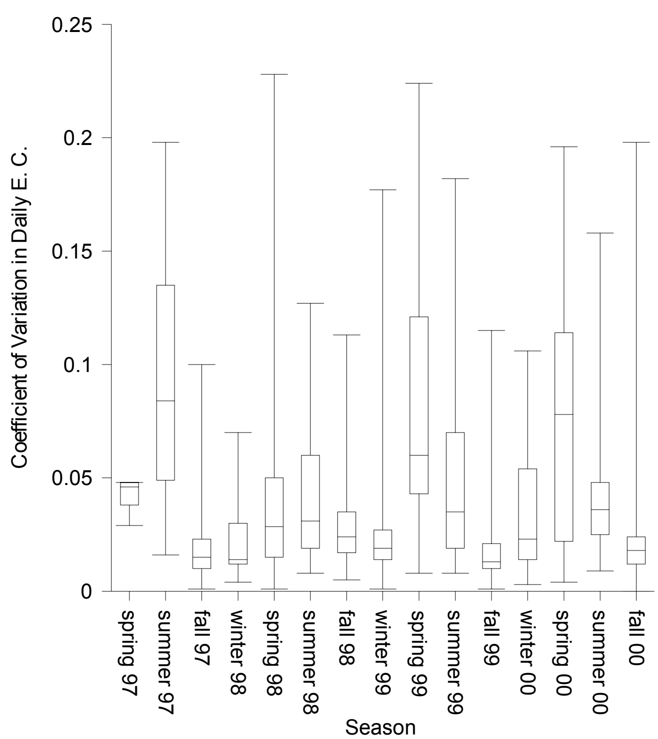

Figure 8. Box whisker plot of daily E. C. coefficient of variation.

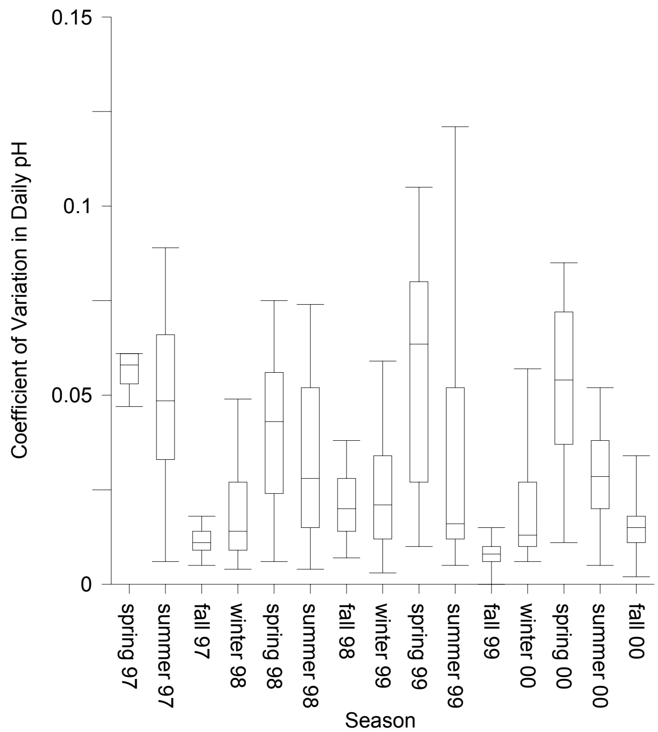

Figure 9. Box whisker plot of daily pH coefficient of variation.

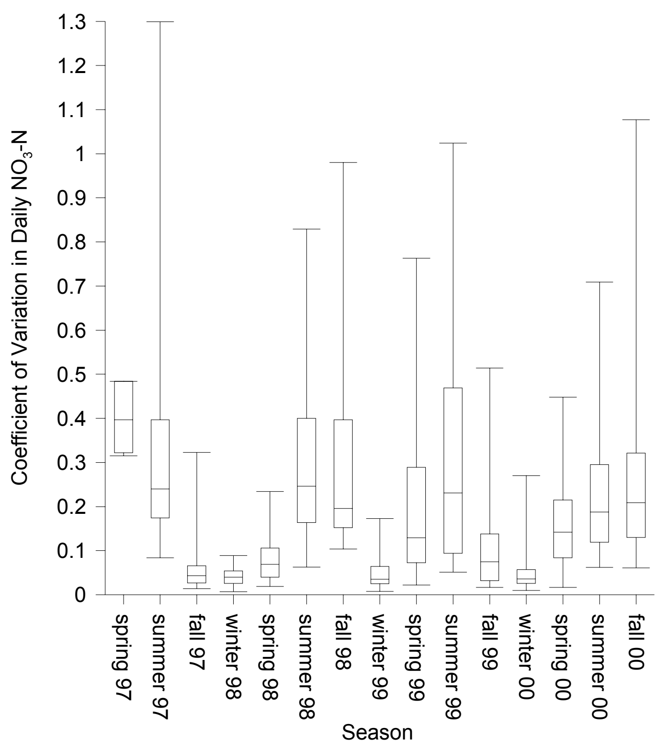

Figure 10. Box whisker plot of daily NO_3-N coefficient of variation.

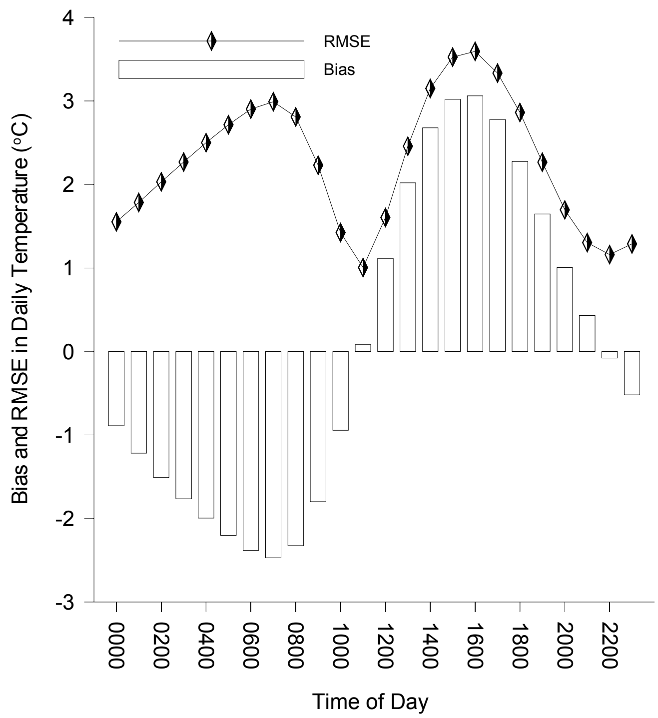

Figure 11. Bias and RMSE in daily temperature at each hour of the day.

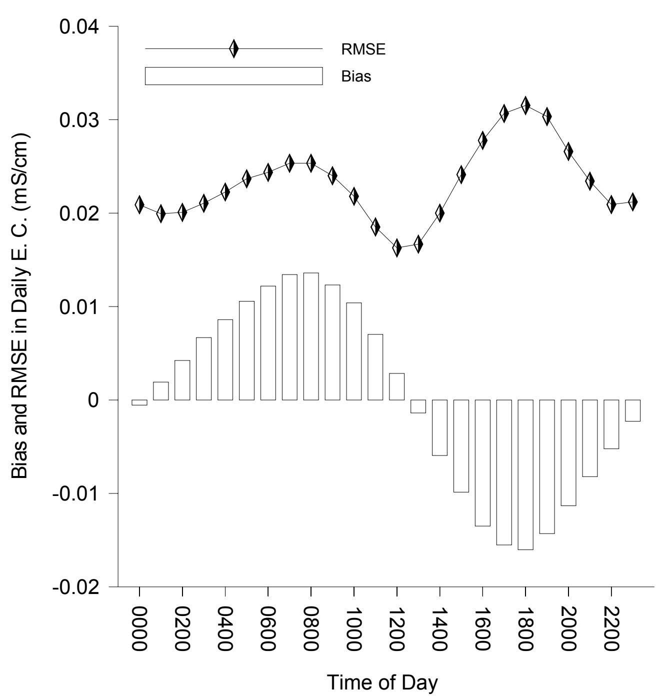

Figure 12. Bias and RMSE in daily E. C. at each hour of the day.

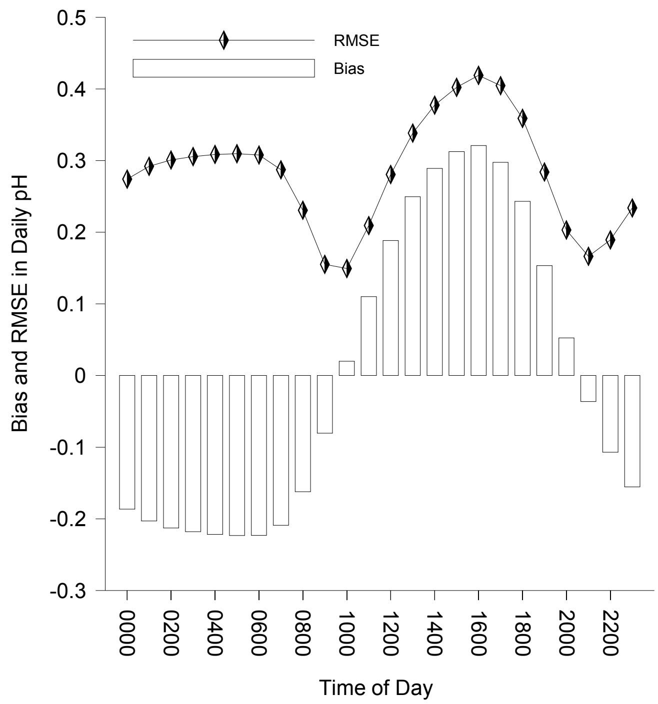

Figure 13. Bias and RMSE in daily pH at each hour of the day.

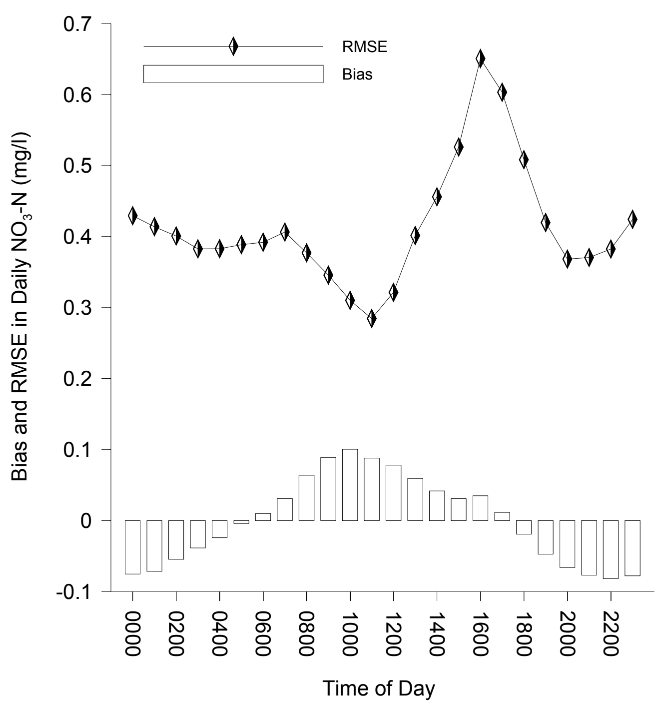

Figure 14. Bias and RMSE in daily NO_3-N at each hour of the day.

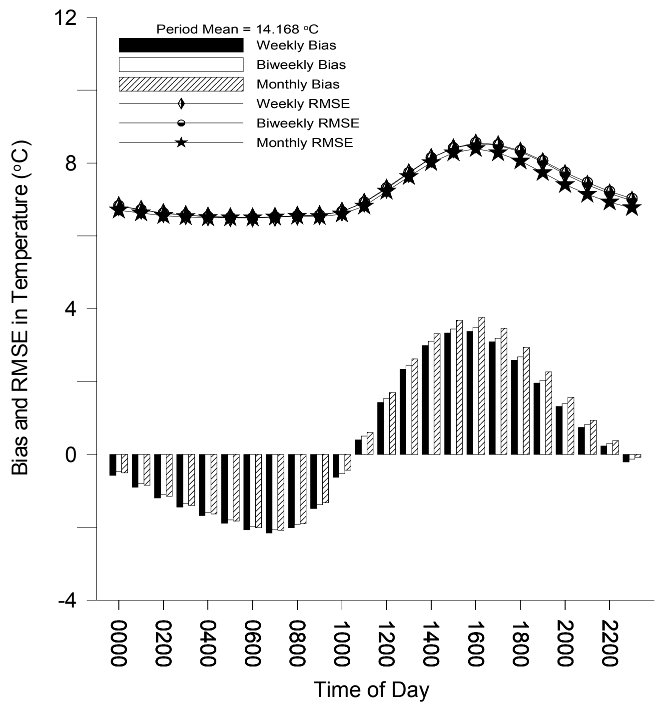

Figure 15. Bias and RMSE produced by diurnal variations in weekly, biweekly, and monthly sampling regimens of temperature. Plotted values are the means of seven replications of each regimen.

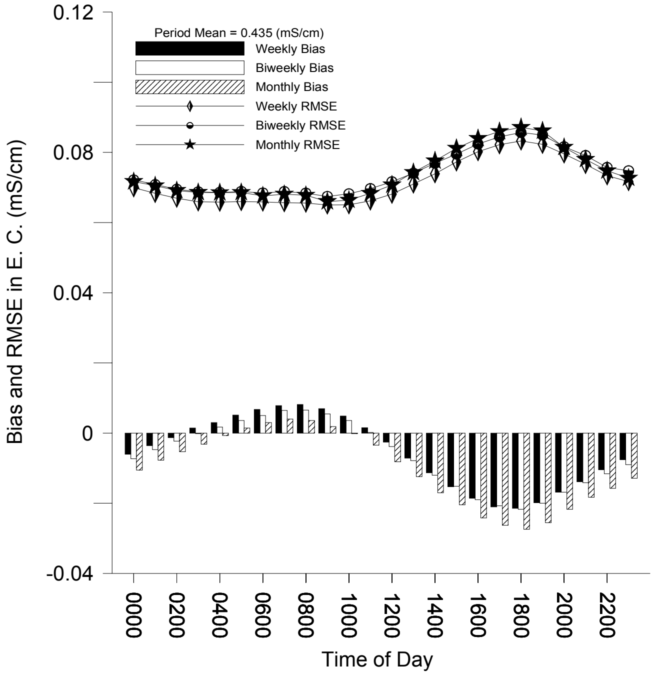

Figure 16. Bias and RMSE produced by diurnal variations in weekly, biweekly, and monthly sampling regimens of E. C. Plotted values are the means of seven replications of each regimen.

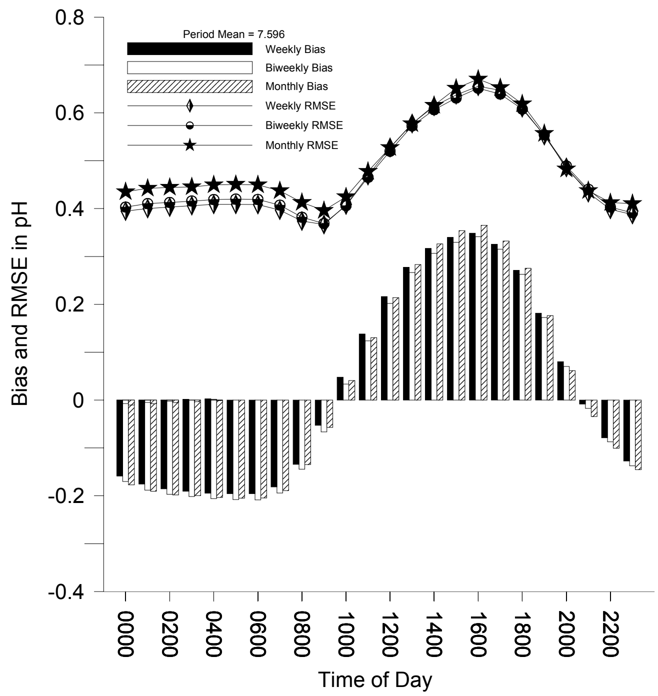

Figure 17. Bias and RMSE produced by diurnal variations in weekly, biweekly, and monthly sampling regimens of pH. Plotted values are the means of seven replications of each regimen.

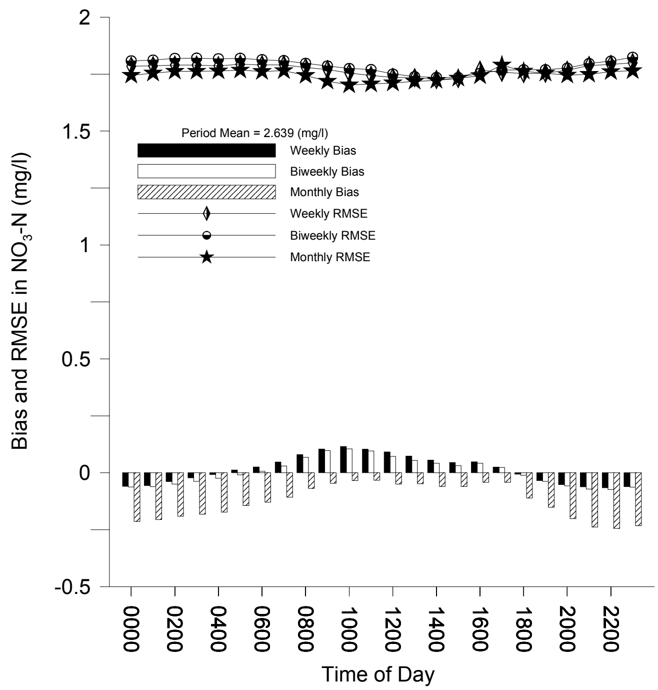

Figure 18. Bias and RMSE produced by diurnal variations in weekly, biweekly, and monthly sampling regimens of NO_3-N. Plotted values are the means of seven replications of each regimen.

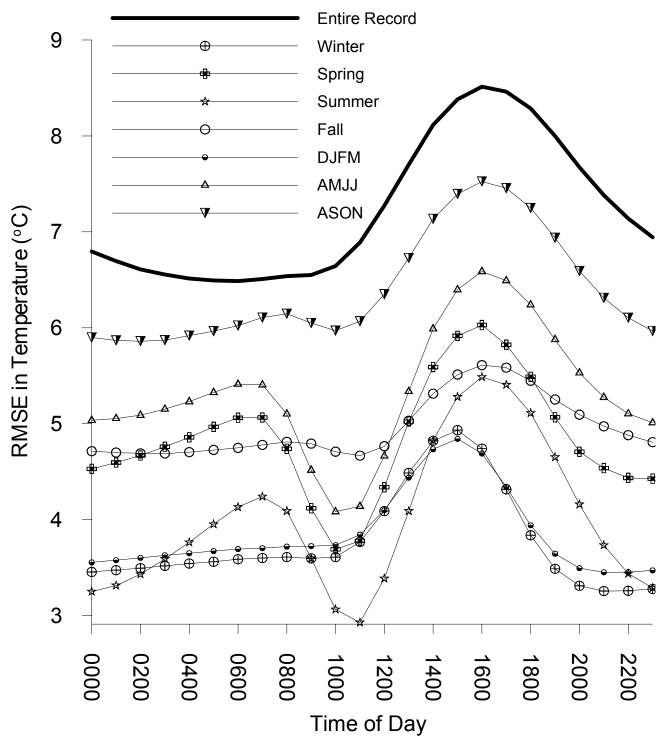

Figure 19. RMSE in temperature under a daily sampling regimen within given seasons or trimesters. Means for seasons and trimesters are given in Table 3.

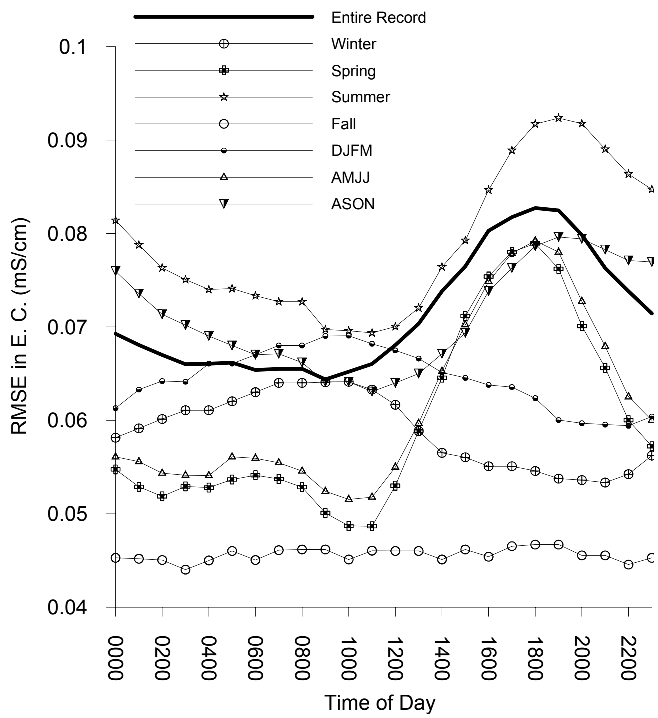

Figure 20. RMSE in E. C. under a daily sampling regimen within given seasons or trimesters. Means for seasons and trimesters are given in Table 3.

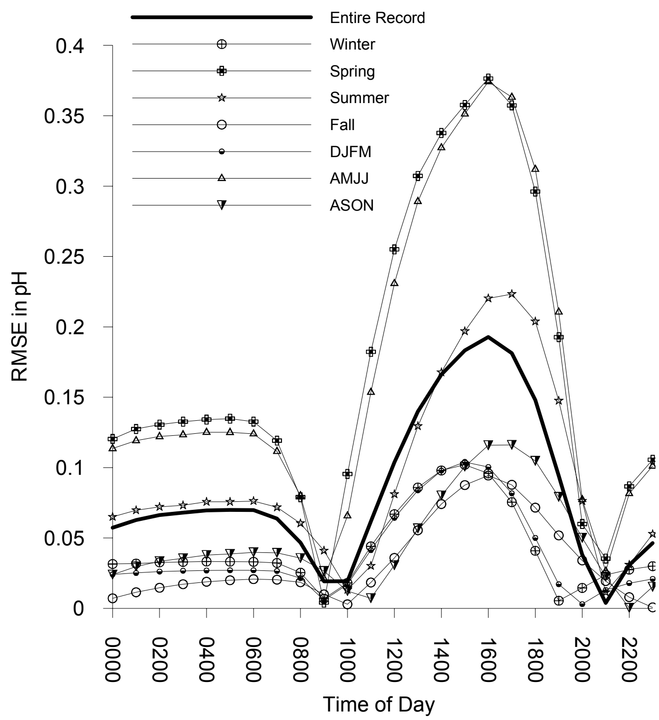

Figure 21. RMSE in pH under a daily sampling regimen within given seasons or trimesters. Means for seasons and trimesters are given in Table 3.

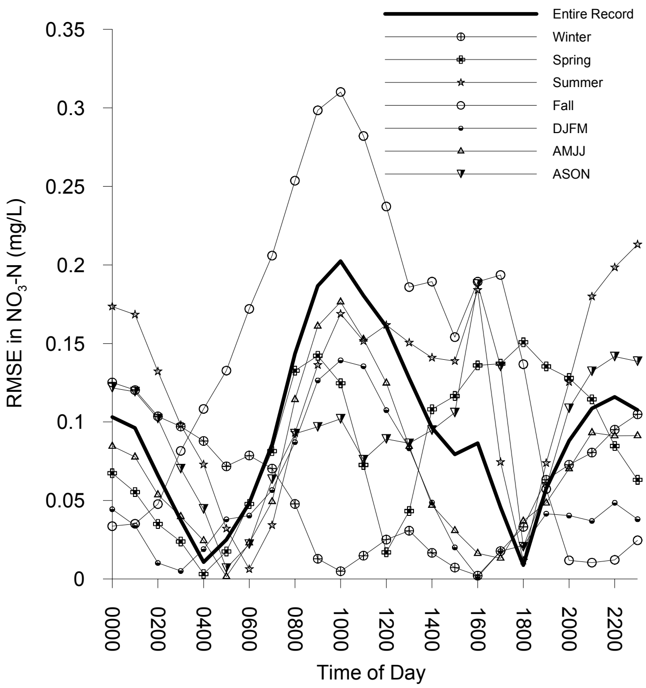

Figure 22. RMSE in NO_3-N under a daily sampling regimen within given seasons or trimesters. Means for seasons and trimesters are given in Table 3.