

MONITORING IMPACTS OF ANIMAL RESEARCH CENTER ON SURFACE AND GROUNDWATER QUALITY

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Brief Project Summary

An ongoing water quality monitoring program was instituted in October of 1996 to determine the impact of ARC operations on surface water and ground water quality. All relevant water quality, flow, well, and spatial data have been archived on BAE computer systems. The data is readily available for teaching, research, and planning use and have been utilized by several researchers and departments with interests at the ARC.

Studies that quantify error introduced into a water quality data set by diurnal variations under a given sampling regimen are rare. This report presents the results of a study 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 $\text{NO}_3\text{-N}$ mass loads and yield.

Project Objectives

1. Continue building water quality database for the ARC.
2. Assess impacts/improvements produced by the animal waste management BMPs.
3. Support ongoing and future water quality research needs utilizing monitoring network.
4. Develop sampling strategies that minimize error and bias and optimize productivity.
5. Develop ARC WEB page to summarize environmental research results.

Methods

Introduction

Diurnal variations in stream flow and water quality have been observed and reported in the literature for some time. Daily variations in streamflow have been attributed to evaporation and evapotranspiration as well as the affect of water temperature upon the stream/groundwater exchange rate. 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. Significant research has been reported on the dynamics of diurnal stream temperature variations. Other studies have focused on the dynamics of nitrate and total solutes. 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).

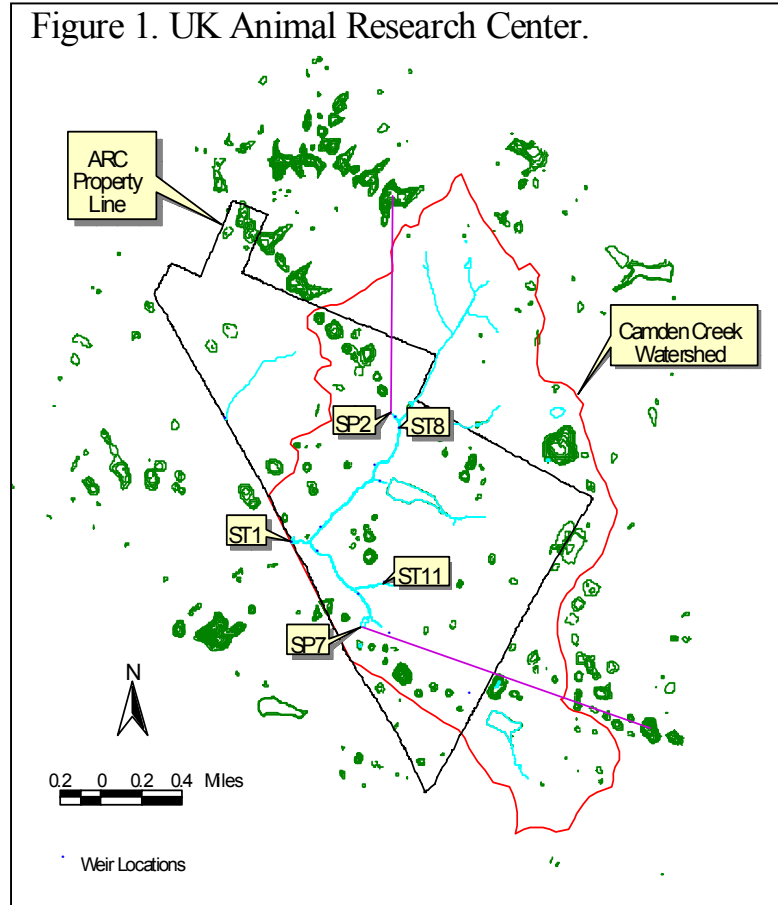
Stream water quality variables are often measured at regularly scheduled intervals; i.e., daily, weekly, biweekly, monthly, or quarterly; and conclusions are drawn about period mean values (e.g. average annual mean, quarterly mean, etc.) based upon the collected data. Many mass load estimation methods 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 progress report is to report on the assessment of 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 ($\text{NO}_3\text{-N}$), electroconductivity (E. C.), and temperature within a small Central Kentucky karst stream.

Study Area

The University of Kentucky Animal Research Center (ARC; Figure 1) lies within the Inner Blue Grass physiographic region of Kentucky which is karst terrain characterized by broad, shallow sinkholes, low relief, broad valleys and ridges, sparse rock outcrops and thick, fertile, limestone and shale residual soils. Portions of the ARC are used for precision and site-specific

Figure 1. UK Animal Research Center.



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.

Basin Monitoring

A water-quality monitoring network was installed at the ARC over a period of years. 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, and NO₃-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 NO₃-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. It was determined that the observed diurnal variations in temperature, pH, E. C., and NO₃-N were genuine.

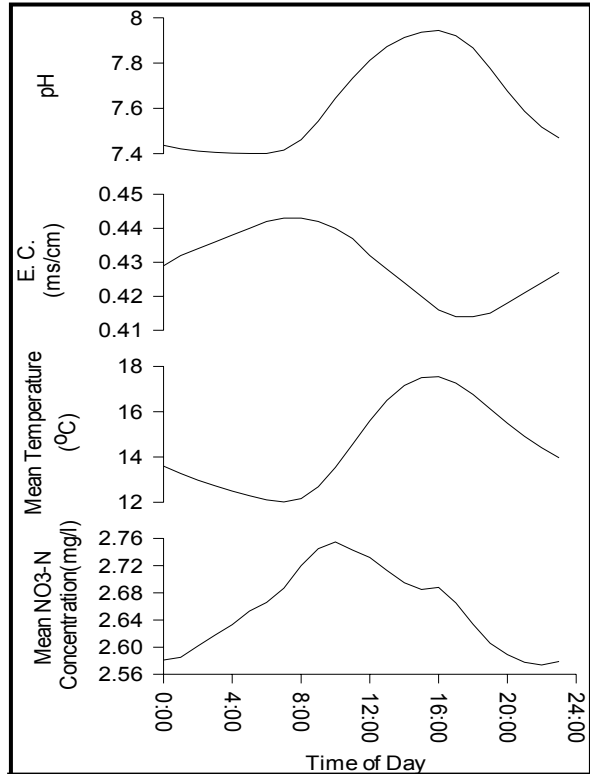


Figure 2. Mean values of temperature, pH, NO₃-N, and E. C. at each hour of the day.

YSI data were collected at stream site ST-1 beginning in June 25, 1997 and were retrieved at each re-calibration of the instrument. Water quality grab samples were collected biweekly as part of the ongoing monitoring strategy and were used for drift compensation of the YSI sensors. 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. Table 1 reports the number of days in the data record with no missing data for each water quality parameter.

Table 1. Extent of the modified data set for each water quality variable.

Variable	Temperature	pH	NO ₃ -N	E.C.
No. of Complete Days in Data Record	1066	1066	786	1003

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, NO₃-N, and pH were determined from the modified data set and are given in Table 2. Means determined for each of the seasons and for three trimesters are also reported. The trimester periods were chosen because noticeable trends within the ARC water quality data and hydrology tended to fall into these three trimesters.

Table 2. 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

^awinter = January – March

^bspring = April – June

^csummer = July – September

^dfall = October – December

^eAMJJ = April – July

^fASON = August – November

^gDJFM = December – March

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

$$\mu_x = \sum X_i/n$$

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

$$v_x = (n\sum X_i^2 - (\sum X_i)^2)/(n(n-1))$$

where v_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

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

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. 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.

Results and Discussion

The basin hydrologic response is characterized as flashy. Table 3 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 (95th/5th 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 4 for comparison purposes.

Table 3. 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 4. Seasonal and total rainfall amounts for each year of the study period.

Year	Rainfall (cm)				Yearly Total
	Season				
	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

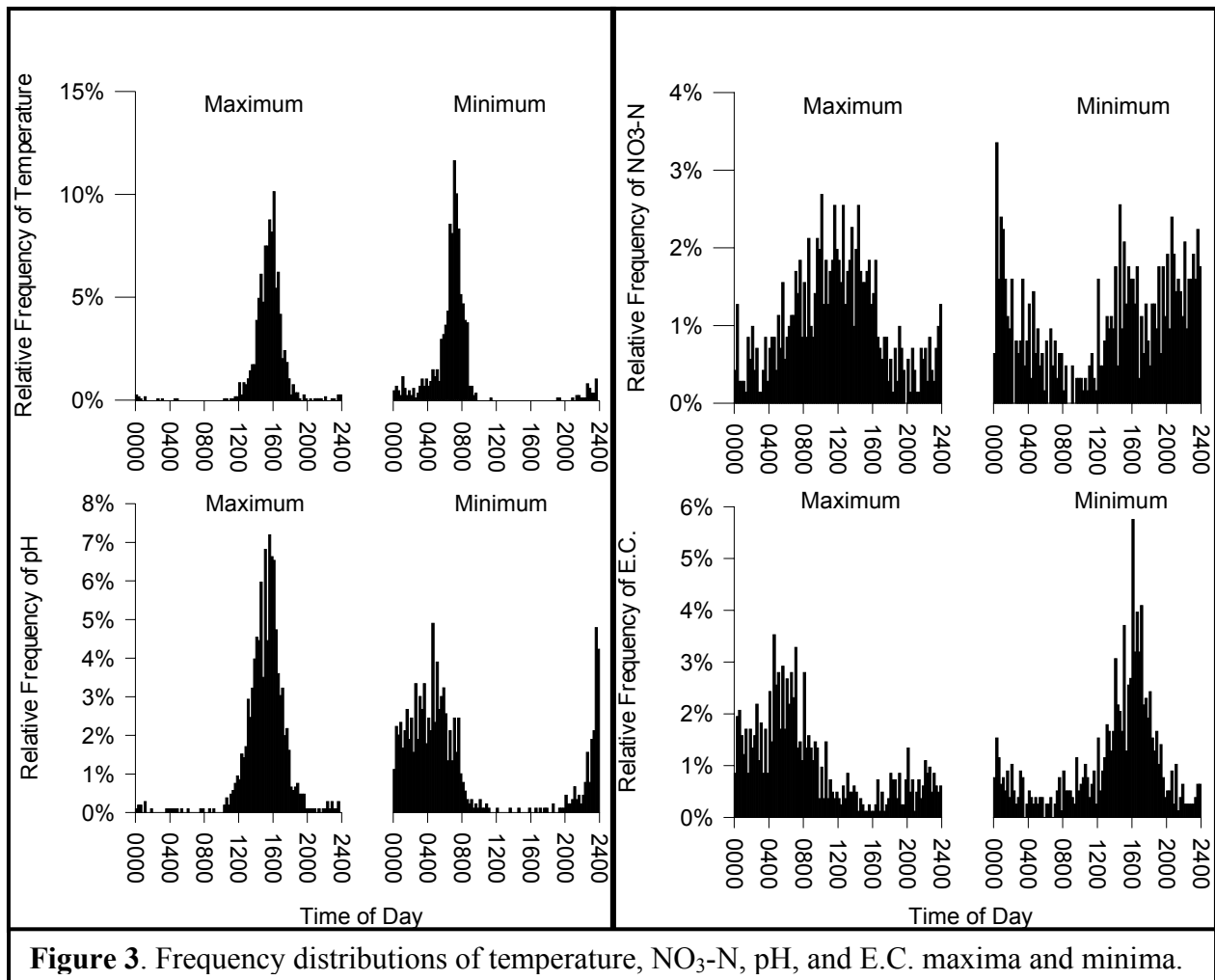
^awinter = January – March

^bspring = April – June

^csummer = July – September

^dfall = October – December

To determine the distribution of the diurnal variations throughout the day, relative frequency distributions of daily maxima and minima were developed (Figure 3). Time of day when temperature and pH maxima and minima tended to occur are more readily discernable than for NO₃-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. NO₃-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. Times of occurrence of the mean maxima and minima were easier to discern from Figure 2 than Figure 3. 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. NO₃-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. Figure 4 contains box whisker plots of the distribution of daily coefficients of variation for temperature, E. C., pH, and NO₃-N.

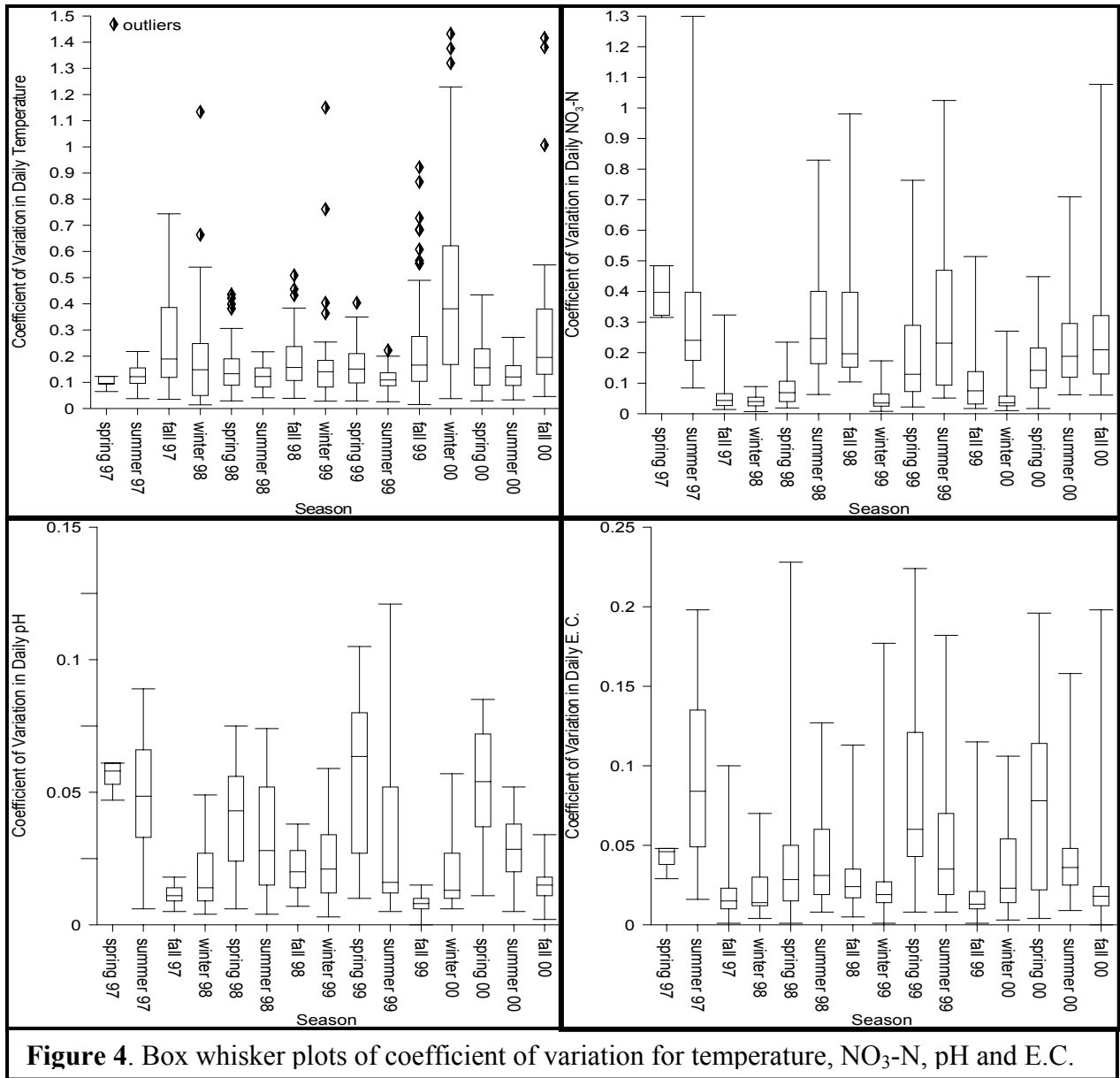
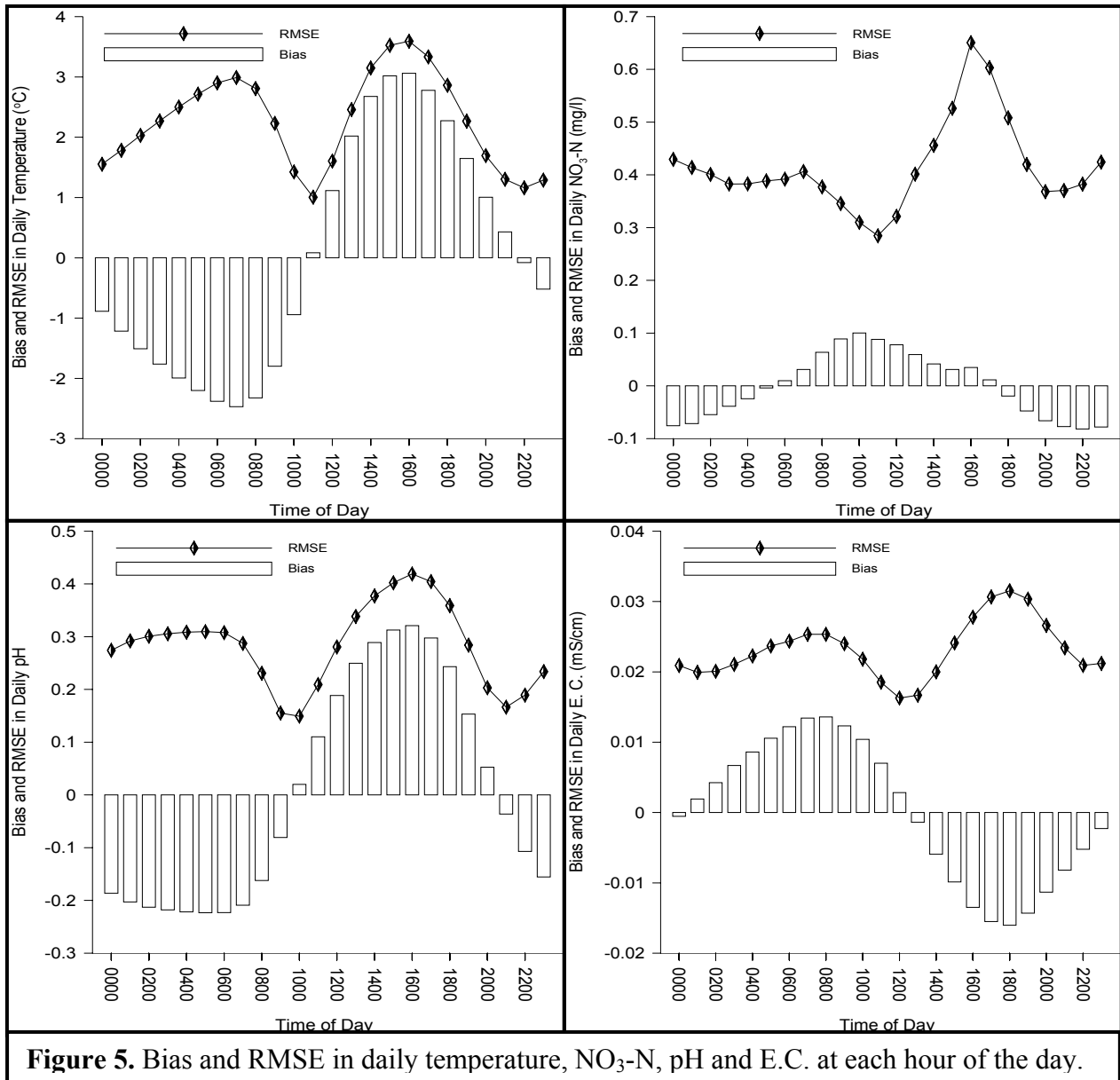


Figure 4. Box whisker plots of coefficient of variation for temperature, NO₃-N, pH and E.C.

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 Figure 5. Sampling at 1100 hours produced the smallest RMSE in daily mean estimates of temperature, pH, and NO₃-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 NO₃-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 NO₃-N, the majority of the error in NO₃-N was due to variability and not bias. RMSE more than doubled when samples were collected at times near daily maxima or minima, excepting NO₃-N. Sampling in the afternoon produced the largest RMSE in all variables and the largest bias in temperature, E. C., and pH.

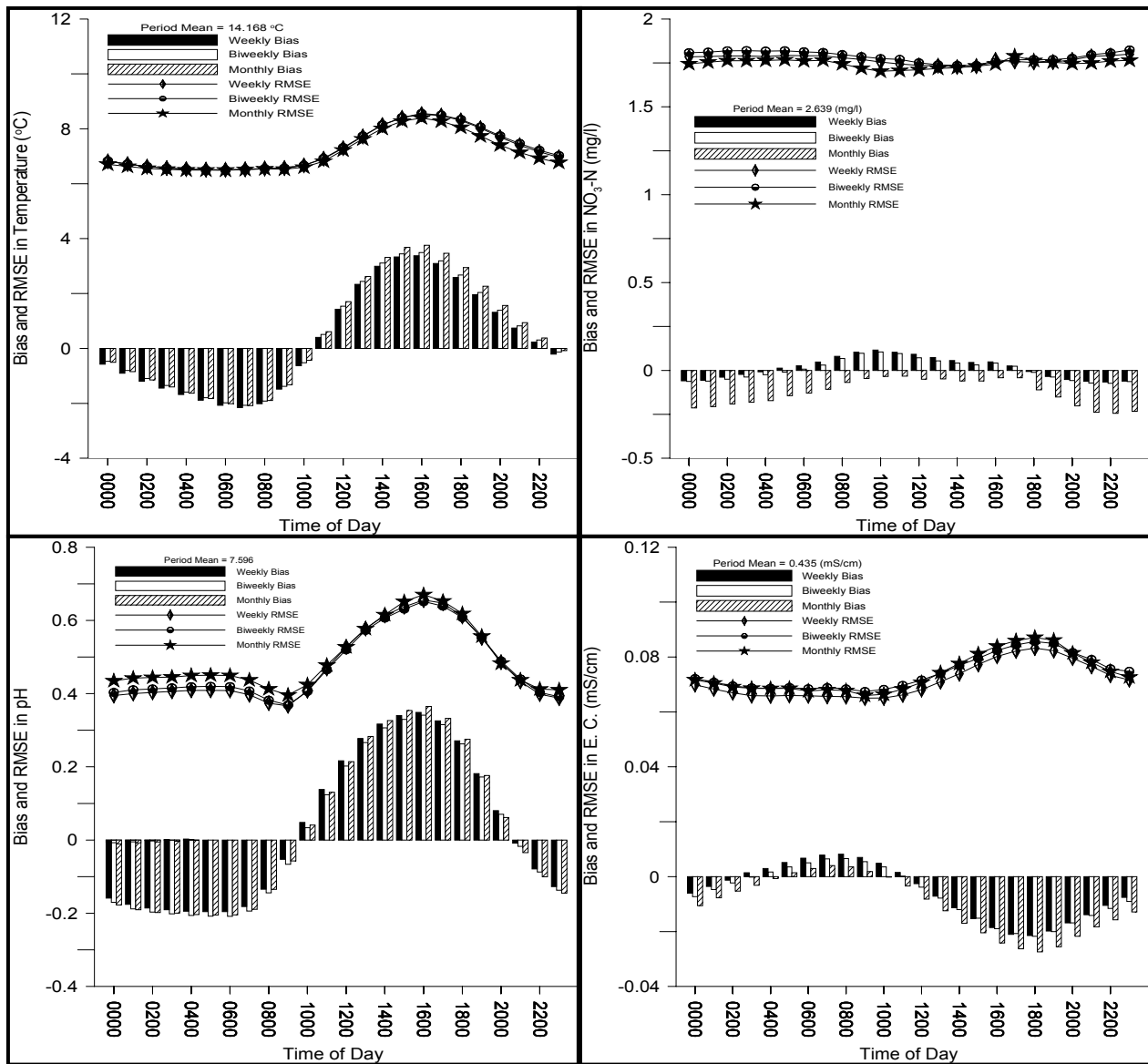


Figure 6. Bias and RMSE produced by diurnal variations in weekly, biweekly, and monthly sampling regimens of temperature, NO₃-N, pH and E.C. Plotted values are the means of seven replications of each regimen.

The bias and RMSE that resulted from the weekly, biweekly, and monthly sampling regimens are shown in Figure 6. Period means for each plot are given in Table 4. Times of minimum bias were comparable with those in Figure 5. 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 NO₃-N. For NO₃-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 5. Temperature was the only variable where the difference in normalized minimum and maximum bias and RMSE (given as the range in Table 5) 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.

Table 5. 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 2.

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%

Researchers, in order to conserve funds, will often only sample during certain periods of the year, such as the spring when NO₃-N levels may be elevated due to fertilization. Table 6 has

Table 6. 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%

comparisons of the RMSE for daily sampling, stratified by season and trimester, for temperature, E. C., pH, and NO₃-N, respectively and gives the normalized minimum, maximum, and range of the RMSE, stratified by period, as a percentage of the period means. 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 NO₃-N during the summer, fall, and the ASON trimester (see Table 6). During these periods, sample collection time should be considered in order to minimize error produced by diurnal variations.

Conclusions

- 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 time should be a consideration when sampling for temperature, E. C., and NO₃-N.
- Sampling at 1100 hours produced the smallest RMSE in daily mean estimates of temperature, pH, and NO₃-N while the smallest E. C. RMSE was produced at 1200 hours.
- Optimal time for collecting one aliquot and analyzing for all variables was near 1100 hours, based on minimum RMSE when sampling daily, weekly, biweekly, or monthly.
- Error was not significantly different between the different sampling regimens, except for bias in NO₃-N.
- Monthly sampling tended to under-predict the period NO₃-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.
- When sampling during seasons or certain periods of the year only, sample collection time should always be a consideration when measuring temperature while NO₃-N exceeded the 10 percent threshold during the summer, fall, and ASON trimester.

References

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