Effect of Stream Diurnal Variations on Mass Loads in a Small Agricultural Karst Watershed

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ABSTRACT

The University of Kentucky Animal Research Center is located in a karst-dominated terrain in Central Kentucky. Continuous monitoring revealed strong diurnal variations in stream water quality constituents at the water shed pour point throughout the year. The time of the day that a stream sample is collected for the determination of stream mass load has been shown to have a significant influence on the estimated stream mass load in a small karst watershed. The mass load estimation bias of the sample time of day is comparable to mass load estimation bias found by other research results using water quality data that is not identified by a sampling time of day.

KEYWORDS. Stream, diurnal, concentration, mass load, karst.

INTRODUCTION

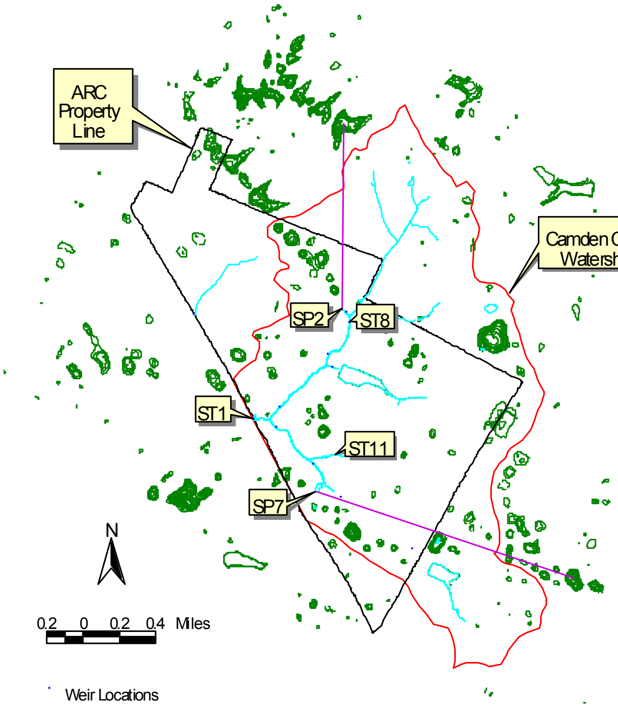

Figure 1. UK Animal Research Center.

Research Watershed

The 583 ha 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 with caverns and underground drainage ways, low relief, broad valleys and ridges, sparse rock outcrops and thick, fertile, limestone and shale residual soils (Keagy et al., 1993). The geology of the area is characterized as Lexington Limestone, high in phosphorus content, with most member units having minor shale bedding with one significant upper member interbedded with shale.

Soils are moderate to well-drained silt loams derived from the high phosphatic limestone. Maury soils are found on broad ridgetops and cover 70% of the area. They are fertile and deep (3-4.5 m over bedrock) with a silty-clay subsoil. McAfee soils cover 15% of the area and are located on moderately steep slopes. They are shallow

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(< 1 m over bedrock) with a silty-clay subsoil. Parts of the ARC are used for precision agriculture operations and include tobacco, row crops, small grains, and animal research grazing plots. The predominant land use outside the ARC boundary is pasture for horse and cattle farms.

Water Quality Monitoring

An intensive water quality monitoring network was begun at the ARC in October 1996 that has provided background data for comparing post-BMP implementation results with pre-BMP water quality values. Implementation of the nutrient management program at the ARC begins the Spring of 2002 as the Beef and Swine Research Units populate their facilities with animals. A problem with assessing the success of a BMP in reducing pollution is the inability of controlling the practices of other landowners within a watershed. The network established at the ARC is capable of separating pollution loads that originate from sources other than the ARC. This has been demonstrated by the detection of spikes of triazines and nutrients (Taraba, et al, 1999) from springs, SP2 and SP7 (See Figure 1).

At the end of the 2001 water year (October 1), four years of surface water flow and surface and ground water quality data have been collected. In addition two years of storm flow data have been collected. The ARC monitoring network data has indicated that the ARC has had a negative impact on surface water quality, relative to incoming water quality, under current crop and animal production practices (Taraba, Ross, and Fogle, 1999). The introduction of BMP practices, such as injecting swine manure into ARC cropland, composting solids wastes before surface land application, and the establishment of riparian zones, is theorized not to have an impact on the surface water quality before it exits the ARC.

Preliminary analysis of the water quality data has shown that sampling strategies can introduce statistical error or bias into a data set due to the existence of diurnal variations in stream water quality parameters. Implications of this analysis are that an unacceptable level of Type I and Type II statistical errors can be introduced to the watershed assessments of the nutrient management BMPs when based on water quality concentrations (Fogle and Taraba, 2001). Significantly different pH values could be obtained from a biweekly sampling regimen with as little as two hours between sampling times, especially if the sampling was only conducted during a particular season. Comparison of temperatures also produced significantly different values, whereas NO_3-N and electroconductivity did not vary significantly with different time of day sampling. This would imply that a significant difference could be found, where none exist, between two identical watersheds when sampling at different times of the day, a Type II error.

The water quality database, containing both pre- and post-BMP implementation data, will be used to develop sampling strategies and methods for use in karst terrains and small watersheds that reduce error and optimize the utility of data gathered. Errors associated with the sampling protocols need to be minimized to avoid the masking of statistically significant positive or negative impacts when assessing agricultural watershed nutrient loads and water concentrations, as well as pre- and post BMP implementation, between the six ARC subwatersheds.

SAMPLING STRATEGIES FOR STREAM NUTRIENT LOAD ESTIMATION

The USEPA Protocol for Developing Nutrient TMDLs (USEPA, 1999) does not provide guidance for a stream sampling strategy to estimate stream nutrient loads. Stream sampling strategies for determination of stream nutrient loads have varied widely and each has its associated error and bias when compared to the “true” or observed stream nutrient load. Stream water quality data bases range from intensive sampling of flow and concentration every 15 minutes (Christensen, et al. 2000) where “true” stream load was calculated by the integration method to infrequent sampling (one per month plus high flow sampling) with daily flow (Robertson and Roerish, 1999). The regression, or rating curve, is used to estimate daily concentration based on daily flow plus other variables. Robertson and Roerish (1999), in a study utilizing subsampling to represent different sampling strategies, found that the most effective sampling strategy to estimate loads in small streams depended on the length of the study. Fixed-period monthly sampling with storm chasing appeared to be the most effective and resulted in the most precise annual loads but still resulted in overestimations of 25-50%. For longer studies, Robertson and Roerish found semimonthly sampling provided the least biased and most precise estimates of constituent loads. Our baseline data at ST-1 can be used as the basis for “true” nutrient flux to compare sampling strategies (subsamples created from database). Richards and Holloway (1987) noted that smaller streams are more volatile in their responses than larger ones and required more intensive sampling to achieve load estimates of a given accuracy. Small watersheds of several square miles would require hourly sampling during runoff events. They found that flow stratified sampling and load calculation utilizing the Beale Ratio Estimator provided the most precise load estimations. They noted that bias was strongly related to sampling frequency and decreased fairly rapidly with increased sampling frequency. Also, Richards and Holloway stated that sampling strategies based upon sampling theory tended to overestimate the number of samples required to achieve a given precision. Currens (1997), studying a karst spring in southwestern Kentucky, recommended biweekly sampling supplemented by bihourly samples from storm flows. Work has also been done on the design of sampling strategies to determine mass loads (e.g. Preston, et al.,1989; and Cohn, et al., 1989).

Another problem that has not been adequately addressed in the literature is the effect of diurnal variations on sample error and bias. Research has gone into the study of diurnal variations in temperature (e.g. Jacobs, et al., 1997; Lowney, 2000; Younus, et al., 2000), electroconductivity (e.g. Kobayashi, et al., 1990) and NO_3-N (e.g. Hessen, et al., 1997; Christensen, et al, 1990; and Jordan, et al., 1997). Loftis, et al (1991) discouraged the collection of fixed interval and fixed time of day because this strategy would fail to expose concentration dynamics within the sampling interval even though random collection would result in a higher variance. Nothing could be located in the literature that dealt with the possibility of the introduction of error and bias into a data set due to diurnal variations.

The effect of the diurnal variations found in the ARC stream data set at ST-1 can be seen in Table 1. A comparison of randomly selected daily water variables and their “true” daily means is shown. The “true” daily means were determined from data collected at 10-minute intervals with a YSI 6000 Water Quality Datalogger by averaging the 144 data points collected each day. Random values were selected from the data record within given periods of the day, such 8 am to 5 pm, or noon to 5 pm. Table 1 contains the means, standard deviations, and root mean square errors (RMSE) of the differences between the random sample and the daily mean. Samples

Table 1. Comparison of True Mean and Randomly Selected Daily Water Variables

Variable	No. of Days in Data Record	Sampling Period	Mean	Standard Deviation	RMSE
Temp	1066	24 hour	-0.090	2.453	2.455
		8 am - 5 pm	0.949	2.406	2.586
		8 am - noon	-0.858	1.655	1.864
		noon - 5 pm	2.527	1.752	3.075
		max - min	0.326	0.412	0.525
pH	1066	24 hour	-0.004	0.294	0.294
		8 am - 5 pm	0.158	0.264	0.308
		8 am - noon	0.012	0.192	0.192
		noon - 5 pm	0.286	0.255	0.383
		max - min	0.063	0.056	0.084
NO3-N	786	24 hour	0.005	0.437	0.437
		8 am - 5 pm	0.056	0.352	0.357
		8 am - noon	0.087	0.309	0.321
		noon - 5 pm	0.035	0.449	0.450
		max - min	0.050	0.272	0.276
E.C.	1003	24 hour	0.000	0.025	0.025
		8 am - 5 pm	0.000	0.024	0.024
		8 am - noon	0.009	0.020	0.022
		noon - 5 pm	-0.008	0.022	0.024
		max - min	-0.003	0.013	0.013

collected between noon and 5 pm were the worst at estimating the daily mean for temperature, pH, and NO_3-N. Averaging the daily minimum and maximum values produced the best estimates of the daily means. In a long term study, with a goal of estimating average annual loads or concentrations emanating from a watershed, it would seem reasonable that collecting data that was sampled as near the daily mean as possible would produce better results. Conversely, it would seem that consistently collecting data near maximum or minimum values could produce bias in the data.

Mean water variable values at each hour of the day, taken from the same data collected to produce Table 1, are plotted in Figure 2. It is plain from Figure 2 that if one researcher consistently sampled at, say, 6 am and another consistently sampled at 4 pm, they would arrive at different values for pH within the same stream. Significantly different results can be obtained by sampling at different times within the day within a given sampling strategy (Fogle and Taraba, 2001).

The differences between the minimum and maximum values for NO_3-N and E.C. are small for the total data set averages shown in Figure 2. McBride, et al. (1993) would have asked the question "Is this of practical significance?" even though there is statistical significance found between sampling times of the day. Two of the three years were dry. The minimum to maximum range for each of these two parameters was found to be the highest during summer of 1998. Rainfall was normal preceding and during this season. The E.C. had a range of about 0.15 mS/cm or about 3 times the range in Figure 2, while NO_3-N had a range of 1.0 mg/l which was is more than 5 times the range in Figure 2 (Taraba, et al. 1999).The stream flow at ST-1 is in Figure 3 and presents both the mean daily flow and the mean daily base flow which was calculated by the method found in Jordan, et al. (1997).

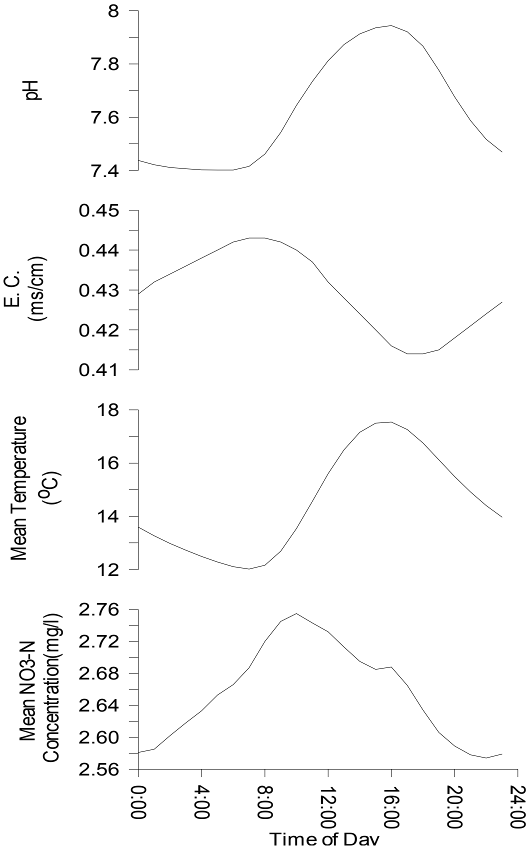

Figure 2. Mean Parameter Values at Each Hour

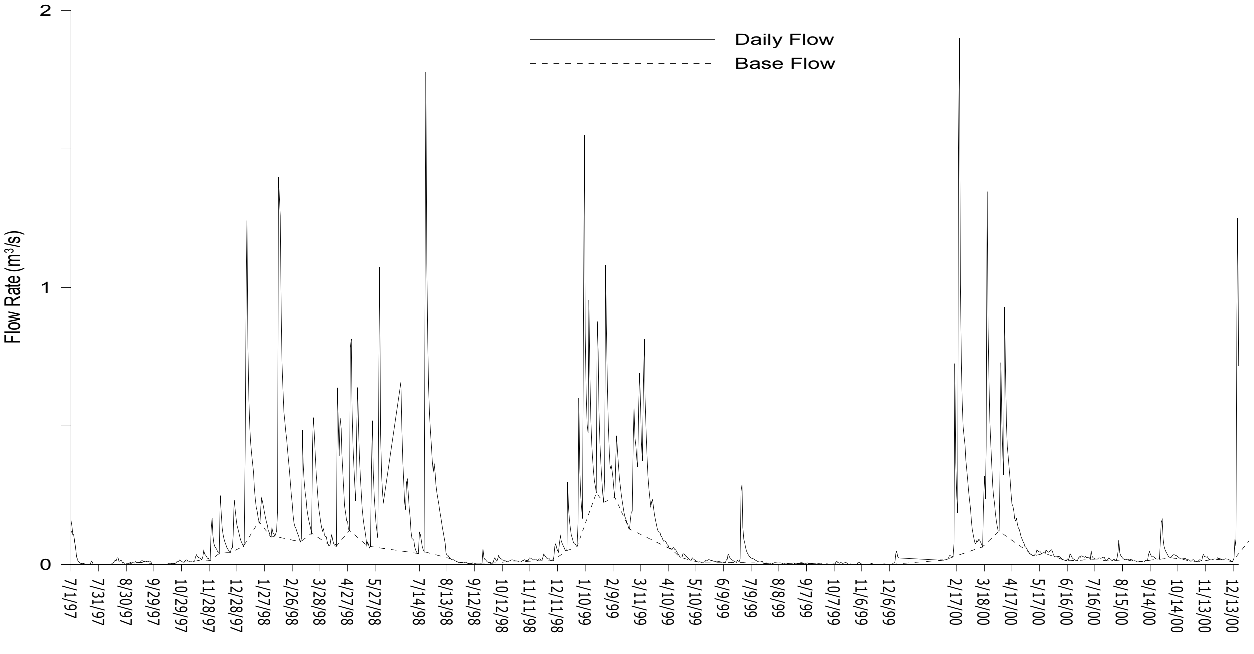

Figure 3. Mean Daily Flow and Mean Daily Baseflow at the UKARC Pour Point (ST-1).

METHODS AND RESULTS

Results from ARC baseline data, collected at ST-1 from June 1997 through 2000, indicate that biweekly sampling with a continuous flow record may provide acceptable estimations of annual load. Flow, NO_3-N and E.C. data was collected continuously (10 minute intervals). Grab samples were also collectedly biweekly through the period. Loads were calculated three ways: "True" loads utilizing the continuous flow and concentration data and estimated loads using 1) grab sample concentrations and a "grab flow" and 2) grab sample concentrations and the average flow rate for 1, 2 and 4 week periods. The average flow was determined by using the continuous flow record for 3.5 (1 week), 7 (2 week), and 14 (4 week) days, respectively before and after the grab sample collection time. This procedure is repeated to obtain an estimated load at 5 sample times during a day: 8:00 am, 10:00 am, noon, 2:00 pm, and 4:00 pm. Replications were obtained by using a different starting day within the continuous data series to develop the subsample data set that is used to compute the stream load. Wet and dry weather periods were roughly equally represented (56% wet, 44% dry, determined from Figure 2). A percent bias was calculated for the difference between the "true" load and the estimated load. Table 2 presents the median and the maximum and minimum values of these percent biases for NO_3-N and Total Solutes. The median percent bias for NO_3-N and Total Solutes mass loads for all sample times and sampling frequency are comparable and in the range of –2.27& to 7.65% and –2.16% to 1.57% respectively. These percent biases compare favorably with those of dissolved stream component mass load estimates of Cohn, et al., (1989) and Christensen, et al. (2000). The range of the percent biases for monthly sampling frequency is nearly three times that of the weekly and biweekly sampling frequency for the average flow method. The percent bias for the grab flow method indicate somewhat higher median values for NO_3-N mass load for weekly sampling frequency and weekly and biweekly frequency for Total Solutes. The range of the median biases for NO_3-N and Total Solutes stream mass loads for all sample times and sampling frequencies were -17.89% to 12.22% and –8.07% to 7.44% respectively. The medians were below the median bias of mass load predictions of Robertson and Roerish (1999) for the sampling strategies they utilized. There appears to be time of day median differences for the grab flow method. The grab flow method median range was much higher than the average flow method.

An examination of the influence of the diurnal concentrations of NO_3-N and Total Solute were conducted using the percent bias differences between paired sampling time of day (e.g. 8:00 am and 10:00 am or 8:00 am and 3:00 pm) for each replication. This created nine data sets for the paired comparisons. The resulting differences in percent biases due to the sampling time of day ware comparable to the bias found by Cohn, et al., 1989 when estimating mass load from stream data with no time of day designation. A Kruskal-Wallis non-parametric test was utilized to determine if there were significant differences among the paired sampling times which would imply an influence on the estimate of the NO_3-N and Total Solutes mass loads. Table 3 summarizes these results. The grab flow method for mass load estimation was found to be significantly influenced by the time of day sampling except for the weekly NO_3-N sampling frequency. The average flow method of estimating NO_3-N mass flow was found to be significantly affected by the time of day for only the monthly sampling frequency, while estimating the Total Solutes mass load was significantly affected for biweekly and monthly sampling frequency.

CONCLUSIONS

The time of the day that a stream sample is collected for the determination of stream mass load has been shown to have a significant influence on the estimated stream mass load in a small karst watershed. The mass load estimation bias of the sample time of day is comparable to mass load estimation bias found by other research results using stream water quality that is not identified by a sampling time. Although the average diurnal range of some stream water quality parameters in this study was small and any significance findings could be concluded as practically insignificant, the implications are that there are periods during the year when the diurnal ranges would be considered practically significant.

Table 2. Median and Range of Percent Bias between "True" Observed Mass Load and the Estimated Mass Load Based on Sampling Strategy

Total NO3-N Mass Discharged										
Sample	**"True"-Avg Flow**					**"True" - Grab Flow**				
Time	8:00 AM	10:00 AM	12:00 noon	2:00 PM	4:00 PM	8:00 AM	10:00 AM	12:00 noon	2:00 PM	4:00 PM
weekly										
Median	3.39%	2.54%	-2.27%	-1.21%	-0.97%	-0.59%	1.45%	3.27%	5.70%	5.16%
Minimum	-3.29%	-5.03%	-4.83%	-4.17%	-4.10%	-13.17%	-20.67%	-29.00%	-24.33%	-22.38%
Maximum	10.09%	7.60%	1.08%	2.95%	2.80%	18.94%	20.80%	19.70%	20.40%	21.05%
biweekly										
Median	4.44%	3.82%	4.83%	4.92%	4.73%	3.99%	7.50%	12.22%	11.30%	11.99%
Minimum	0.29%	-1.25%	-2.96%	-2.74%	-1.88%	-26.78%	-22.07%	-15.94%	-21.70%	-31.85%
Maximum	9.14%	9.29%	10.92%	12.81%	12.62%	23.81%	26.42%	28.26%	30.89%	31.26%
monthly										
Median	2.83%	3.32%	4.65%	7.65%	5.58%	-17.89%	-11.92%	-4.23%	-0.35%	-3.58%
Minimum	-11.94%	-12.25%	-8.81%	-8.48%	-8.82%	-185.27%	-166.83%	-145.64%	-138.86%	-172.75%
Maximum	17.63%	15.53%	15.37%	17.36%	17.60%	29.26%	34.21%	36.55%	40.36%	39.74%

Total Solutes Discharged										
Sample	**"True"-Avg Flow**					**"True" - Grab Flow**				
Time	8:00 AM	10:00 AM	12:00 noon	2:00 PM	4:00 PM	8:00 AM	10:00 AM	12:00 noon	2:00 PM	4:00 PM
weekly										
Median	-0.59%	-0.24%	-2.09%	-1.10%	-0.98%	1.27%	5.05%	7.44%	7.11%	4.11%
Minimum	-5.54%	-4.80%	-3.87%	-2.36%	-1.63%	-10.22%	-7.66%	-4.87%	-0.94%	-5.24%
Maximum	16.28%	17.10%	0.20%	0.97%	1.65%	10.79%	14.35%	9.21%	12.69%	14.45%
biweekly										
Median	-2.07%	-0.91%	0.56%	1.57%	1.48%	-7.49%	-4.31%	1.84%	3.15%	1.21%
Minimum	-5.76%	-4.70%	-3.86%	-2.05%	-1.40%	-26.20%	-21.70%	-16.14%	-12.31%	-18.26%
Maximum	7.66%	8.11%	8.88%	8.47%	6.46%	2.38%	5.78%	10.59%	13.46%	6.80%
monthly										
Median	-2.16%	-1.08%	-0.24%	-0.27%	0.99%	-8.07%	-3.37%	-2.22%	-2.97%	-2.61%
Minimum	-6.47%	-5.26%	-4.51%	-4.08%	-3.65%	-52.29%	-40.08%	-30.13%	-26.38%	-49.21%
Maximum	24.01%	25.44%	26.48%	26.76%	27.66%	27.18%	31.00%	35.06%	36.81%	38.85%

Table 3. Kruskal-Wallis Test on Percent Bias Differences of Paired Sampling Times.

Sample Frequency	**Parameter**	**Sampling Strategy**	**H Statistic**
weekly			
	NO3-N	"True" - Avg Flow	15.53
		"True" - Grab Flow	2.29
	Total Solutes	"True" - Avg Flow	9.43
		"True" - Grab Flow	**17.62
biweekly			
	NO3-N	"True" - Avg Flow	10.54
		"True" - Grab Flow	**48.26
	Total Solutes	"True" - Avg Flow	**21.12
		"True" - Grab Flow	**29.35
monthly			
	NO3-N	"True" - Avg Flow	**41.84
		"True" - Grab Flow	**36.39
	Total Solutes	"True" - Avg Flow	**32.88
		"True" - Grab Flow	**55.31

** = Significant at alpha=0.05

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