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FLOW PROPORTIONAL AND TIME COMPOSITE ESTIMATES OF NUTRIENT LOADING FROM AN EASTERN COASTAL PLAIN WATERSHED

by

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Summary: The balance between resources expended and information obtained is an integral aspect of water quality investigations. As part of a Water Quality Demonstration Project in the eastern Coastal Plain, we monitored stream water quality at the watershed outlet. Four methods of assessing stream water quality were compared. These methods were time-composite sampling with continuous flow measurements (TC), flow-proportional sampling with independent measurement of flow (FP), grab sampling with instantaneous flow measurements (IG), and grab sampling for quality assurance/quality control checks using daily USGS flow measurements (UG). Flow measurements using the TC and IG methods were highly correlated (r^2=0.97). Because of more intensive measurements during high flow, the FP method measured higher flow rates during the sampling period. For all four methods, nitrate-N and ammonia-N concentrations were not correlated to stream flow. Because of the significantly higher flow, the FP method predicted significantly higher mass loading rates for both nitrate-N and ammonia-N. Grab sampling (IG and UG) and the TC methods were not significantly different for the entire study period, however a few monthly differences were significantly different. These results suggest that an appropriate sampling method should adequately weight sampling of both storm and base flows.

Keywords: Water Quality, Nitrate-N, Flow-Proportional, Time-Composite Sampling

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INTRODUCTION

Nonpoint source (NPS) pollution of streams and groundwater is a major concern in the US. To assess NPS problems, water quality demonstration projects have been implemented to accelerate the adoption of improved management practices that can reduce NPS. These water quality projects require methods to measure or monitor the associated improvements in water quality in groundwater and stream water. Monitoring methods in streams involve collecting water samples at periodic intervals and determining changes over time. The collection of these samples of stream water may include simple periodic grab sampling, statistical and probability driven grab sampling techniques, regular time monitoring of the samples, or sampling based on stream flow or stage. In addition to the water samples taken, flow measurements are needed to relate the concentrations of nutrients exported to a mass loading of nutrients exported or removed from the watershed over time.

Previous research has looked at various methods for sampling streams to determine flow-weighted nutrient concentrations and their corresponding loads. Humenik et al. (1980) implemented a probability sampling scheme to quantify rural water quality on a watershed basis in North Carolina. They sampled streams using grab samples and averaged two samples per sampling site in a 28-day period or approximately 26 samples per year. They found that the probability sampling technique produced adequate results for the purposes of their monitoring objectives for state NPS water quality plans. Blivan et al. (1980) used both grab and automated sampling techniques in the Piedmont of Virginia and the Coastal Plain of North Carolina. They concluded that a monitoring program should consist of both base flow measurements and runoff or storm flow events to adequately describe the nutrient fluxes on their studied watersheds. They found runoff concentrations were only marginally greater than base flow concentrations and that loadings were highly correlated to flow.

Shih et al. (1994) studied the accuracy of nutrient load calculations using time-composite sampling. They found that when flow and phosphorous concentrations were positively correlated, computations using the time-composite methods underestimated the load and vice-versa.

Tremwel et al. (1996) developed a program to geometrically sample incremental runoff volumes from ephemeral streams and ditches. They compared this method with standard flow proportional sampling techniques. The geometrically incremental volume sampling technique samples frequently in the early stages of a runoff event while conserving bottles for the tail of a large runoff event.

Rekolainen et al. (1991) evaluated the accuracy and precision of annual phosphorus load estimates from two agricultural basins in Finland. Sampling methods that summed the products of regularly sampled flows and concentrations produced the best precision, but the best accuracy was achieved using a method based on multiplying annual flow by flow-weighted annual mean concentrations. They also found that concentrating sampling in high runoff periods gave better accuracy and precision than strategies based on regular interval sampling through the year.

Swistock et al. (1997) compared six methods for calculating annual stream exports of sulfate, nitrate, calcium, magnesium, and aluminum from six small Appalachian watersheds. The six methods they compared were: 1) monthly grab samples with instantaneous flow, 2) monthly grab samples with continuous stream flow, 3) weekly grab samples with instantaneous flow, 4) weekly grab samples with continuous flow, 5) grab and storm flow samples, and 6) multiple regression equations. They used the regression method as a reference in comparing the six methods. For solutes whose concentrations were not correlated strongly with stream flow, they found that weekly grab samples coupled with continuous flow measurements were sufficient to produce export estimates within 10% of the regression method. They suggested more intensive sampling for solutes that correlated strongly with stream flow.

Izuno et al. (1996) compared time and flow composite sampling methods for comparing total phosphorous concentrations and loads in the Everglades Agricultural Area of South Florida. They used regression analysis and found a one to one relationship between the two methods when considering potential measurement and analytical errors. Based on their findings, they reported that either method would be adequate for regulatory monitoring programs.

In the eastern Coastal Plain of North Carolina, a Water Quality Demonstration Project (WQDP) was implemented to assess the changes in water quality associated with the voluntary adoption of improved management practice by farmers and land owners. As part of this WQDP, we installed a water quality monitoring station at the outlet of Herring Marsh Run (HMR) watershed. The monitoring stations consisted of a U. S. Geological Survey (USGS) flow measurement station and an automated water sampler to collect timed interval water quality samples. Later, an automated flow proportional sampler was installed adjacent to the timed sampler. Grab samples were taken periodically both for a QA/QC check on the automated samplers and for a separate study.

The objective of this study is to compare results of four stream monitoring methods to determine if the concentrations and mass loading of nutrients exported from the watershed are similar or if they vary greatly based on the sampling techniques utilized. The four sampling methods were: 1) Time-composite sampling with continuous flow measurements (TC), 2) Flow-proportional sampling with independent measurement of flow (FP), 3) Grab sampling with instantaneous flow measurements (IG), and 4) Grab sampling for quality assurance/quality control checks using daily USGS flow measurements (UG).

METHODS

The HMR watershed is located in the Coastal Plain region of eastern North Carolina (longitude, 77°54′50″ W; latitude, 35°04′25″ N). The HMR is a 2050-ha watershed located within the Cape Fear river basin. The watershed is 43% forested while most of the remaining 57% consists of crop land or pasture.

A stream water quality monitoring station was established at the HMR watershed outlet in 1990 as part of a WQDP. The monitoring station consisted of a USGS gaging station and an automated water sampler. Time-based water (TC) sampling began in September of 1990. An automated water sampler with an integral flow meter was placed at the site in July of 1994 to collect flow-proportional samples (FP).

Time Composited (TC) Samples

Flow measurements with the time composited (TC) sample method were collected in cooperation with the USGS in Raleigh, NC. A USGS gaging station consisted of a stilling well located in the side of the stream bank and a stage recorder used to measure and record the stream stage. The stream stage was recorded at 15-min intervals. A stage-discharge relationship, developed from water velocity measurements taken at various stream stages, was used to calculate the stream flow. Velocity measurements and corresponding stage readings were taken every 6 to 8 weeks.

An automated water sampler, installed in 1990, was programmed to collect daily time-based composite samples. In October 1993, the automated sampler was reprogrammed to collect 2-day composite samples comprised of 24 sub-samples taken at 120-min intervals. Beginning in November 1994, the sampler was reprogrammed to collect 3.5-day composite samples. Each composite sample was comprised of 42 sub-samples collected at 120-min intervals. Later, in March 1997, the sampler was reprogrammed to collect 7-day composite samples consisting of 42 sub-samples taken at 240-min intervals. Diluted sulfuric acid was placed in the sampler bottles prior to sample collection to avoid nutrient losses. The acidified samples were collected each week for nutrient analysis.

Flow-proportional (FP) Sampler:

A refrigerated automated water sampler with an integral flow meter was placed at the watershed outlet in July 1994. A pressure transducer, connected to the integral flow meter, was installed in the USGS gaging station stilling well. A stage versus discharge table was adapted from the USGS stage-discharge rating curve. The table was entered into the flow meter for flow determination based on measured stage and the sampler was programmed to collect samples based on a flow interval.

The flow-proportional sampler was programmed, in July 1994, to collect 7 sub-samples per bottle at a flow interval of 875 m^3 (30,900 ft^3). A timed override was added to the sampler program to allow a maximum time of 240-min between sub-samples. The flow interval was changed to 1314 m^3 (46,400 ft^3) in August 1994. Later in August 1994, the number of sub-samples collected per bottle was changed from 7 to 14. In June 1996, the sampler was programmed to only sample storm flow defined as discharge greater than 0.2 m^3/s (7 ft^3/s). The flow interval was changed to 354 m^3 (12,500 ft^3) and 10 sub-samples were collected in each bottle. During this period, the timed override was not used. In January 1997, the sampler was reprogrammed to operate on both timed and flow basis collecting time based samples when discharge was less than 0.42 m^3/s (15 ft^3/s). Sample collection was based on flow when the discharge was above this threshold. Ten subsamples were collected in each bottle. A time interval of 504 minutes was used to collect a 3.5-day composite sample in the timed mode. A flow interval of 2124 m^3 (75,000 ft^3) was used when collection was based on flow. Samples from the refrigerated sampler were not acidified.

Stream Grab Samples with Instantaneous Flow Measurement (IG):

A survey of water quality was initiated in January 1994. The survey was conducted by collecting grab samples for nutrient and pesticide analysis. Stream flow was also measured at each site when adequate flow was present. Samples were collected weekly except during the months of December, January, and February. During these three months, samples were collected twice a month.

The stream grab samples were collected by hand using individual sample bottles. The sample was collected on the upstream side of the person who collected the sample with the mouth of the bottle pointing upstream. This procedure minimized the collection of sediment disturbed when wading into the stream. Sample bottles were rinsed three times using the stream water before collecting each sample.

Stream flow was determined from velocity measurements. Velocity measurements were taken using a Scientific Instruments model 1205 Price type mini current meter*. The meter consisted of a propeller type device that rotates at a speed proportional to the water velocity. The width of the stream was measured and the stream was divided into equal partial sections. The mean velocity of each section was measured at the midpoint. Measurements were made at a depth of 0.6 times the total water depth when the depth of water was less than 0.76 m (2.5 ft). If the depth of water was greater than 0.76 m (2.5 ft), current measurements were made at a depth of 0.2 and 0.8 times the water depth. The average of these two measurements was then used as the mean velocity. A top-setting wading rod was used to position the current meter at the measurement depth and to measure the depth of water of each section. The cross-sectional area of each section was multiplied by the corresponding velocity to determine discharge for each section. The partial discharge values were summed to determine the total discharge for the stream.

Stream grab sampling for QA/QC using daily USGS flow measurements (UG)

A second set of grab samples was collected beginning in October 1994. The samples were collected at the same time as the IG samples. These samples were collected using the sample bottle as described in the stream survey or using a polyethylene sample dipper (sample cup with a 1.8 m (6 ft.) handle). When the sample dipper was used, it was rinsed with the stream water three times before final sample collection. Then the bottle was rinsed with the stream water as previously described.

All water samples were refrigerated and transported to the USDA-ARS, Soil, Water, and Plant Research Center in Florence, SC, for analysis. Water samples were analyzed using

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* Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the USDA and does not imply approval of a product to the exclusion of others that may be suitable.

a TRAACS 800 Auto-Analyzer for nitrate-N, ammonia-N, and ortho-phosphorus using EPA Methods 353.2, 350.1, and 365.1, respectively (U.S. EPA, 1983). EPA-certified quality control samples were routinely analyzed to verify results.

Statistical Analysis

Statistical analyses on the collected stream water samples were performed using the SAS system (SAS, 1990). A regression analysis of stream water data was performed to determine if any significant relationships existed between nutrient concentrations and stream flow. An LSD test was performed to determine statistical differences in nutrient concentrations in the stream water samples by the different collection methods.

RESULTS

The frequency and magnitude of the peaks in stream flow were related to the rainfall (Figure 1). The rainfall data were obtained from the North Carolina Climatological weather station in Goldsboro, NC. The stream flow data was typical of an eastern Coastal Plain watershed with increased flow in the spring and reduced flow in the summer months except for occasional events related to tropical storms and hurricanes such as those that occurred in June 1995, September 1996, and October 1996.

Flow measurements recorded by the FP and the IG sampling methods were strongly correlated to the USGS flow measurements (Figures 2-3). The FP measurements tended to be larger than the USGS measurements. This could be attributed to the more frequent measurements taken during storms by the FP method compared to a daily value obtained from the USGS sampler (Figure 2). The IG measurements were highly correlated (r^2=0.97) with USGS flow measurements (Figure 3).

Mean nutrient concentrations and flow for the entire study period from January 1994 to December 1997 are shown in Table 1. These findings were similar to other research results in Coastal Plain watersheds in Georgia and Maryland (Hubbard et al. 1983, and Jordon et al. 1997a, b, and c). Flow, nitrate, mass nitrate, and mass ammonia measurements for the FP sampler were significantly ($P<0.05$) higher compared to the TC measurements. Mean ammonia-N concentrations were significantly lower for the FP method compared to the TC method. The higher flow measurements with the FP sampler was attributed to more frequent sampling during storm events and during 1996, the FP sampler was programmed to monitor only larger storm flows. Higher nitrate-N mass loading measurements with the FP sampler was a result of the higher flows. Nitrate-N concentrations were significantly higher for the FP sampler than for the TC sampler. Neither grab sampling methods (IG and UG) was significantly different from the TC method.

Nutrient concentrations and stream flows were not correlated (Table 2). Strong correlations between flow and nutrient concentrations may be an important cause of variation between export calculations by different methods (Swistock et al., 1997). When flow and concentrations were positively correlated, Shih et al. (1994) found that time composited sampling tended to overestimate the stream loading.

The sampling period with the most simultaneous and corresponding measurements among the four collection methods was in 1995. For this year, mean flow and nutrient concentrations and nutrient loadings are shown in Table 3. These data were similar to the overall results for the entire sampling period. Flow measurements with the FP method were significantly higher that with the TC method. Measurements with the FP method were not significantly higher than with the UG grab sample using the corresponding day's USGS flow measurement. Nitrate-N concentrations were not significantly different among the four methods. Mass nitrate-N concentrations were significantly higher with the FP method than with the TC method. This was mainly attributed to the increased flow because the nitrate-N concentrations were not significantly different. Ammonia-N concentrations were significantly smaller for the FP method than for the TC method. Both grab sampling methods (IG and UG) were not significantly different from the TC method for flow, nutrient concentrations, or mass loadings.

Flow for 1995 was high during the late winter and during the summer when storms produced large stream flows in June and early July (Figure 4). The FP sampler tended to have higher flows than the timed sampler. Using the LSD test, the FP measurements were significantly different from the other methods in four months (Figure 4). Flow using the instantaneous (IG) measurements were not significantly different from the TC method throughout the year.

Monthly mean nitrate-N concentrations using the FP and TC samples were not statistically different for 1995. Both grab sample methods had nitrate-N concentrations statistically different from the FP and TC samples for three months (Figure 5). The December nitrate-N concentration using the UG sampling method was extremely higher than that using the other methods and may have been caused by laboratory or sampling error.

The FP mass nitrate-N was significantly different from the TC samples in four months (Figure 6). The FP loadings were highest in the months with the highest overall exports, but they were not significantly different from the TC samples or the grab (IG and UG) samples.

The UG grab samples using the USGS flow were significantly different from the TC samples for two months (Figure 6). These grab samples were taken on days that had higher than average flows for the month and may have biased the results. The December loading rate was probably skewed because of laboratory or sampling error. This may be of concern when sampling with only a few points during the month.

Ammonia-N concentrations were significantly higher for the IG grab samples than for the other methods during the first few months of 1995. After May, this method had concentrations generally lower but not significantly different from the FP and TC methods. The UG grab sample method had significantly higher concentrations during November and December, but was not significantly different from the other methods during the rest of the year. Ammonia-N concentrations for the FP and TC methods varied from month to month.

The IG mass ammonia-N was significantly higher than the other methods in two months (Feb. and Apr.). After the first four months of the year, mass ammonia-N for this method was generally the lowest loading. FP mass ammonia-N loading was significantly higher than TC method in three months (May, Sept, and Oct). TC mass ammonia-N loadings were highest in

June, November and December, but were not significantly different from the other methods. The UG mass ammonia-N loadings were significantly different from the FP and IG loadings in November and December. The December UG grab sample measurement corresponded to the same sample that was suspected to be influenced by laboratory or sampling error for the nitrate-N measurements.

SUMMARY AND CONCLUSIONS

Stream flow measurements were taken independently using four different sampling methods. These four sampling methods were 1) time-composited (TC) with continuous flow measurement using a USGS monitoring station, 2) flow-proportional (FP) sampling with independent flow measurement, 3) grab sampling with instantaneous stream flow measurements (IG) , and 4) grab sampling with corresponding daily flow from a USGS flow monitoring station (UG).

The FP method generally predicted higher flows than the TC method and both grab sampling (IG and UG) methods. These higher flows were a result of the more intensive monitoring during high flows. Flow measurements with the TC and both grab (IG and UG) sampling methods were not significantly different.

Nitrate and ammonia-N concentrations were not correlated to flow rate. If nutrients were positively correlated to flow, alternative monitoring strategies would be required to accurately estimate nutrient loadings.

The FP method predicted significantly higher mass loadings of nitrate and ammonia-N for the entire sampling period. These higher mass loading rates were related to the significantly higher flows observed with the FP method.

An appropriate sampling program would sample both base and storm flows and should be adapted to the needs and purpose of the project. A sampling program that concentrated on storm flows would tend to overestimate the stream loadings. A sampling program based solely on base flow would underestimate the stream loadings. A grab sampling strategy should have samples taken frequently (2-3/month) and at varying stream flows so that erroneous samples would not bias the results. A fixed interval sampling with more frequently collected composite appear to be an appropriate method to accurately estimate stream nutrient loadings.

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Table 1. Mean flow, nutrient concentrations, and mass loadings for the Herrings Marsh Run Watershed for the four sampling methods from January 1994 to December 1997.

Method	Flow (m^3/s)			Nitrate-N (mg/L)			Ammonia-N (mg/L)			Mass Nitrate-N (kg/ha)			Mass Ammonia-N (kg/ha)		
	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.
FP	698	0.60	0.57	538	1.02	0.69	538	0.16	0.23	516	9.65	9.70	516	1.63	2.97
UG	69	0.33	0.48	70	0.89	0.70	64	0.20	0.15	69	5.18	8.38	63	0.77	1.03
IG	83	0.16	0.31	83	0.85	0.58	83	0.27	0.25	82	2.75	6.16	82	0.49	0.80
TC	1448	0.26	0.38	1228	0.85	0.59	1128	0.24	0.27	1218	3.50	5.79	1118	0.72	1.25
$LSD_{0.05}$		0.11			0.15			0.06			1.71			0.46	

Table 2. Regression correlation coefficients for estimating nutrient concentration based on stream flow rate.

Method	r^2	
	Nitrate-N	Ammonia-N
FP	0.0046 ns	0.0108
UG	0.0751	0.0327 ns
IG	0.1324	0.0106 ns
TC	0.0859	0.0038

ns - indicates that the regression was not significant at the $P<0.05$ level.

Table 3. Mean flow, nutrient concentrations, and mass loadings for the Herrings Marsh Run Watershed for the four sampling methods in 1995.

Method	Flow (m^3/s)			Nitrate-N (mg/L)			Ammonia-N (mg/L)			Mass Nitrate-N (kg/ha)			Mass Ammonia-N (kg/ha)		
	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.	n	Mean	Std. Dev.
FP	191	0.45	0.44	153	0.93	0.73	153	0.15	0.11	153	7.49	9.42	153	0.72	0.87
UG	40	0.33	0.54	40	0.90	0.79	39	0.23	0.17	40	5.75	9.96	39	0.76	1.13
IG	41	0.24	0.42	42	0.81	0.64	42	0.21	0.18	41	4.09	8.26	41	0.63	0.99
TC	365	0.26	0.37	307	0.79	0.63	291	0.26	0.24	307	4.13	8.23	291	0.81	1.49
LSD		0.14			0.23			0.70			2.95			0.43	

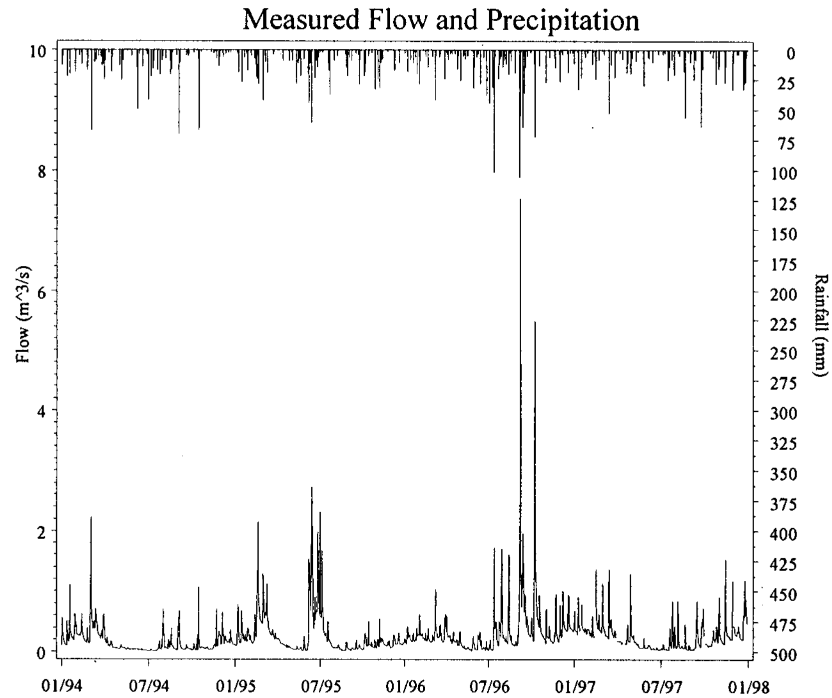

Figure 1. USGS stream flow and rainfall for the Herring Marsh Run Watershed.

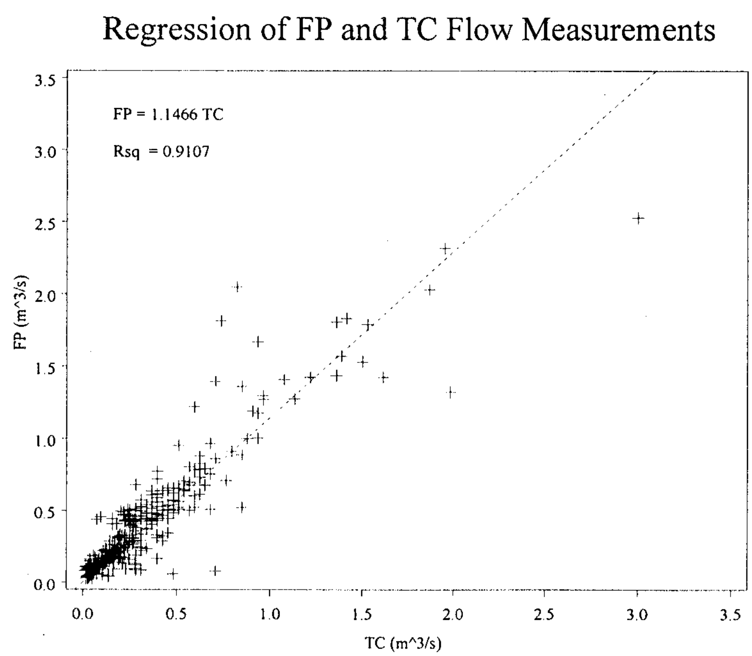

Figure 2. Regression of Flow-Proportional (FP) and Time Composited (TC) flow measurements.

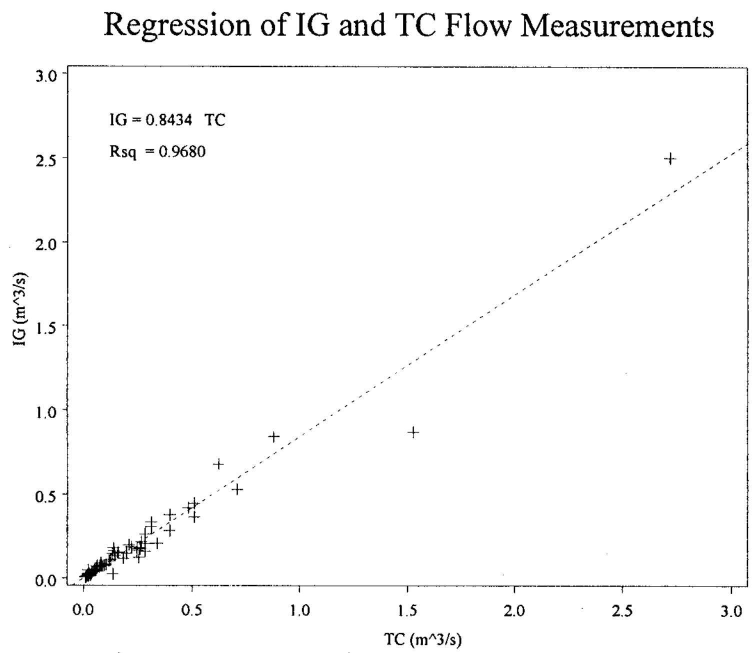

Figure 3. Regression of Instantaneous Grab Sample (IG) and Time Composited (TC) flow measurements.

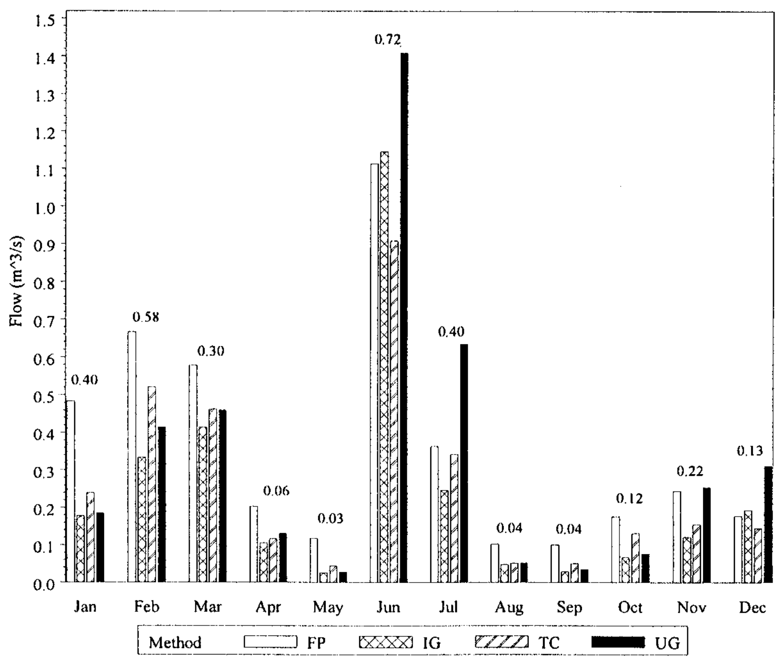

Figure 4. Mean 1995 monthly flow measurements for the Herring Marsh Run Watershed for the four sampling methods ($LSD_{0.05}$ values are shown above each month).

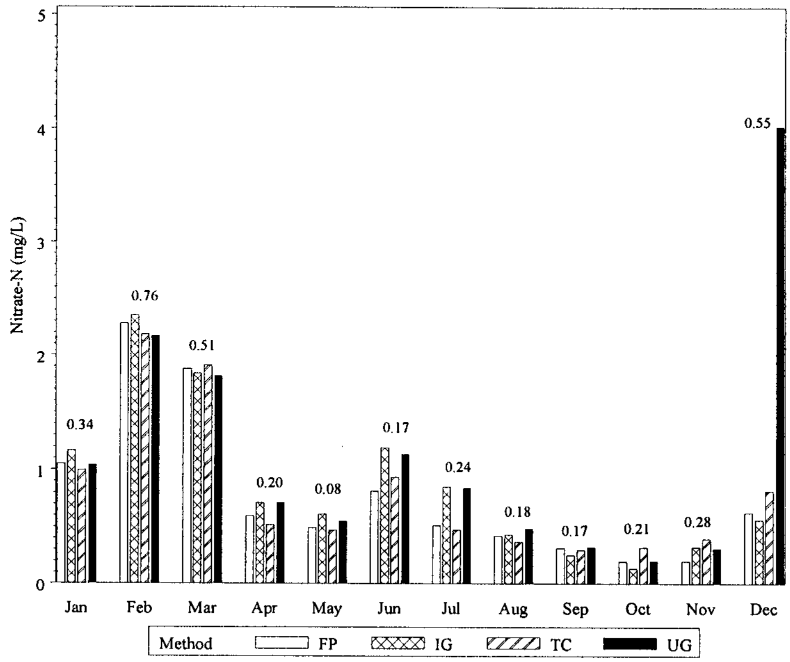

Figure 5. Mean 1995 monthly nitrate-N concentrations for the Herrings Marsh Run Watershed for the four sampling methods ($LSD_{0.05}$ values are shown above each month).

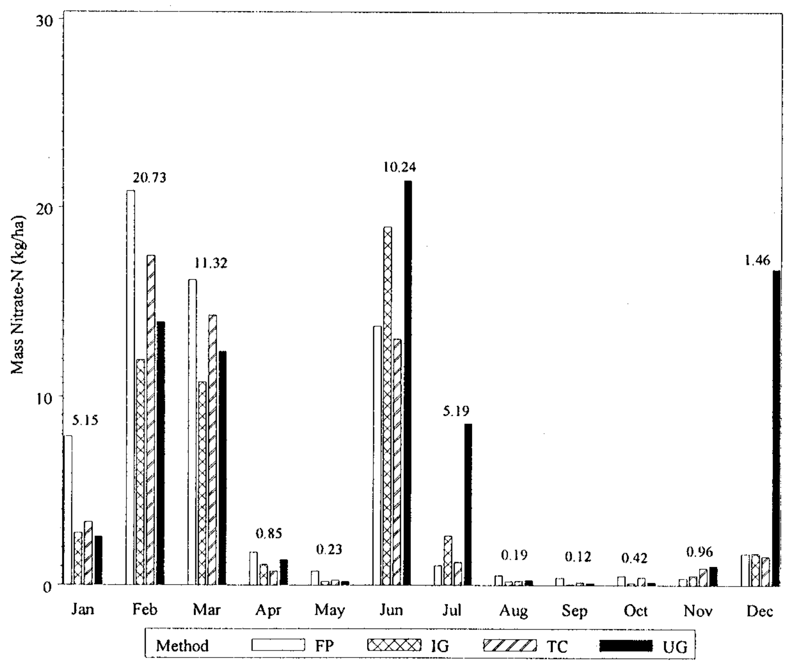

Figure 6. Mean 1995 monthly mass nitrate-N loading for the Herrings Marsh Run Watershed for the four sampling methods ($LSD_{0.05}$ values are shown above each month).

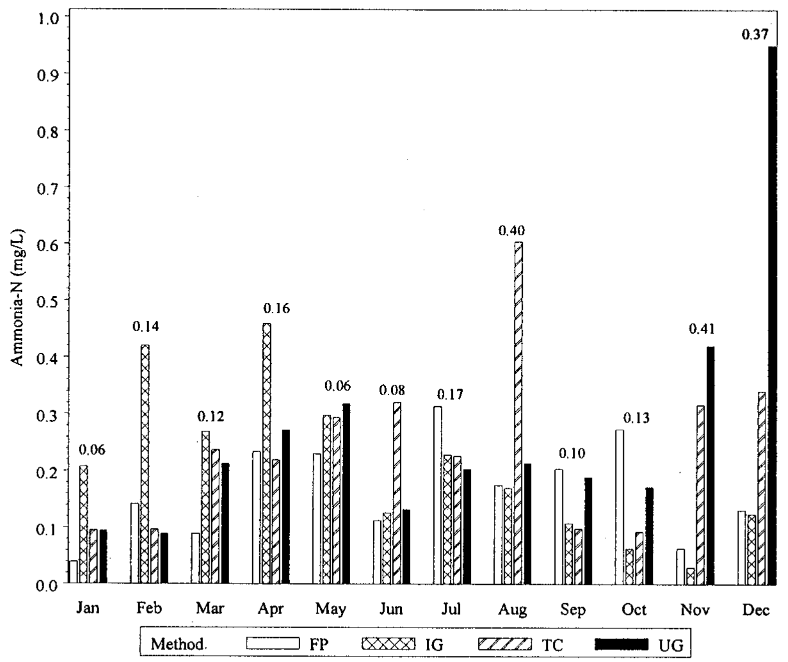

Figure 7. Mean 1995 monthly ammonia-N concentrations for the Herrings Marsh Run Watershed for the four sampling methods ($LSD_{0.05}$ values are shown above each month).

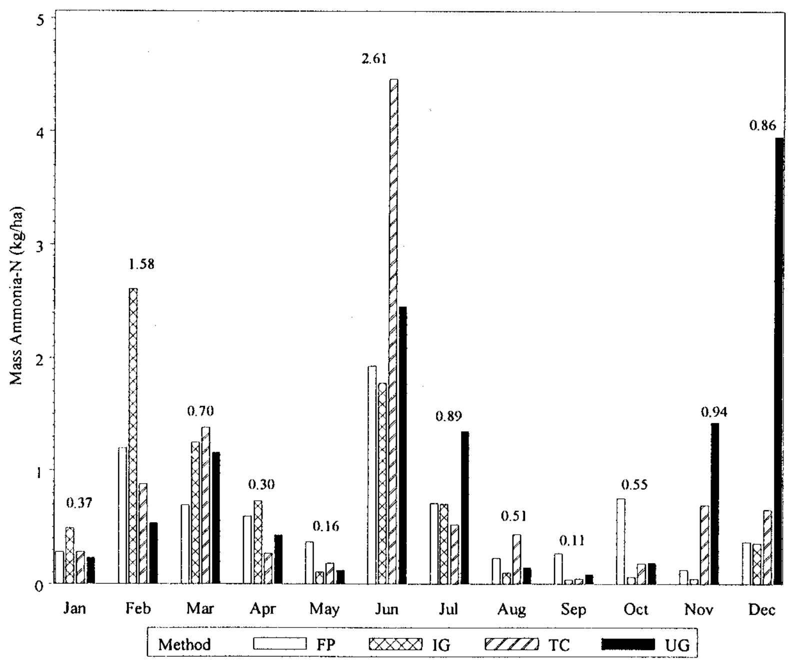

Figure 8. Mean 1995 monthly mass ammonia-N loading for the Herrings Marsh Run Watershed for the four sampling methods ($LSD_{0.05}$ values are shown above each month).