TECHNICAL NOTE:

COMPARISON OF TIME-BASED SAMPLING STRATEGIES TO DETERMINE NITROGEN LOADING IN PLOT-SCALE RUNOFF

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ABSTRACT. *Water quality loadings are generally calculated without knowledge of the relationship of the calculated loads to the total loads. A laboratory runoff study was designed and conducted to compare total loads with loads calculated from time-based sampling strategies. Total loads were measured by capturing all the runoff from 2.2 m^2 Bermuda grass (*Cynodon dactylon *L. Pers.) sod plots with 5% slope and analyzing for NO_3+NO_2-N and NH_4-N. Runoff samples were also manually collected on 1 min intervals during 2 h overland flow events. Total loads were compared to time-discrete and time-composite sampling strategies. The strategies included time-discrete sampling at 1, 2, 3, 4, 5, 10, 15, and 30 min and composite sampling that included 2, 3, 4, and 5 aliquots per composite sample based on the same time-discrete intervals. In addition, loads were also calculated from a composite sample derived from aliquots collected at 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 min intervals. The calculated load of NO_3+NO_2-N and NH_4-N was not significantly different (α = 0.05) from the total load when using time-discrete sampling at 1, 2, or 3 min time intervals. No significant difference (α = 0.05) from the total load was found when using a composite approach with 2, 3, 4, or 5 aliquots collected at 1, 2, or 3 min time intervals or when using a composite sample with aliquots collected on a 1 min interval. To preserve the total load from plot-scale studies, more intensive sampling is required. The results from this study will facilitate the selection of time-based sampling strategies for plot-scale studies.*

Keywords. *Bermuda grass, Concentration, Monitoring, Water quality.*

The U.S. Environmental Protection Agency (U.S. EPA, 1995, 2000) continues to identify surface water quality as a primary concern. This concern has led to numerous initiatives aimed at quantifying pollutant loadings from different sources and management practices at a range of spatial scales. Quantification of loadings implies sampling. Sampling strategies are often selected with one or more of the following constraints: the goals of the project (loads versus concentrations) (Tate et al., 1999), budgetary concerns (Shih et al., 1994), and accuracy with respect to the total load (King and Harmel, 2003). Determining an appropriate sampling scheme is difficult due to a lack of information on performance of different strategies. A few studies exist that have documented the need and use of discrete and composite flow- and time-based sampling strategies (Harmel et al., 2003; King and Harmel, 2003; Kladivko et al., 2001; Stone et al., 2000; Izuno et al., 1998; Tremwel et al., 1996; Thomas and Lewis, 1995; Shih et al., 1994; Smith et al., 1985; Clark et al., 1981; Stevens and Smith, 1978).

Time-based sampling is simple since time is easy to measure. Discrete sampling implies the collection of one aliquot per sample, while composite sampling involves combining more than one aliquot to form a sample. Composite sampling offers an economic advantage, in that fewer samples are analyzed, permitting events of longer duration and larger magnitude to be sampled. Drawbacks of composite sampling are the difficulty in associating the concentration with flow quantity, and time-based composite sampling increases the relative and absolute error in calculated load when compared to the total load (King and Harmel, 2003).

Water quality concerns have resulted in several studies designed to compare different sampling strategies using a Monte Carlo approach (Richards and Holloway, 1987) and measured data (Stone et al., 2000; Robertson and Roerish, 1999; Thomas and Lewis, 1995; Shih et al., 1994; Yaksich and Verhoff, 1983; Stevens and Smith, 1978). These studies have generally been accomplished on large watersheds. Issues of discrete (one aliquot per sample) versus composite sampling (several aliquots per sample), and flow-proportional (based on flow volume) versus time-based sampling (generally equal time intervals) for larger watersheds have been addressed by King and Harmel (2003) and Shih et al. (1994). The findings of these studies can be summarized as follows: for larger watersheds, more intensive sampling generally results in more accurate estimates of the total load.

When setting up a sampling program, one question that inevitably arises is: what is an acceptable interval for collecting samples to accurately estimate the total load? The primary objective of this study was to evaluate some time-based sampling strategies that may be used to calculate loads from plot-scale studies. Specifically, the objective was to measure the total soluble load resulting from a simulated overland flow runoff event and compare that load to

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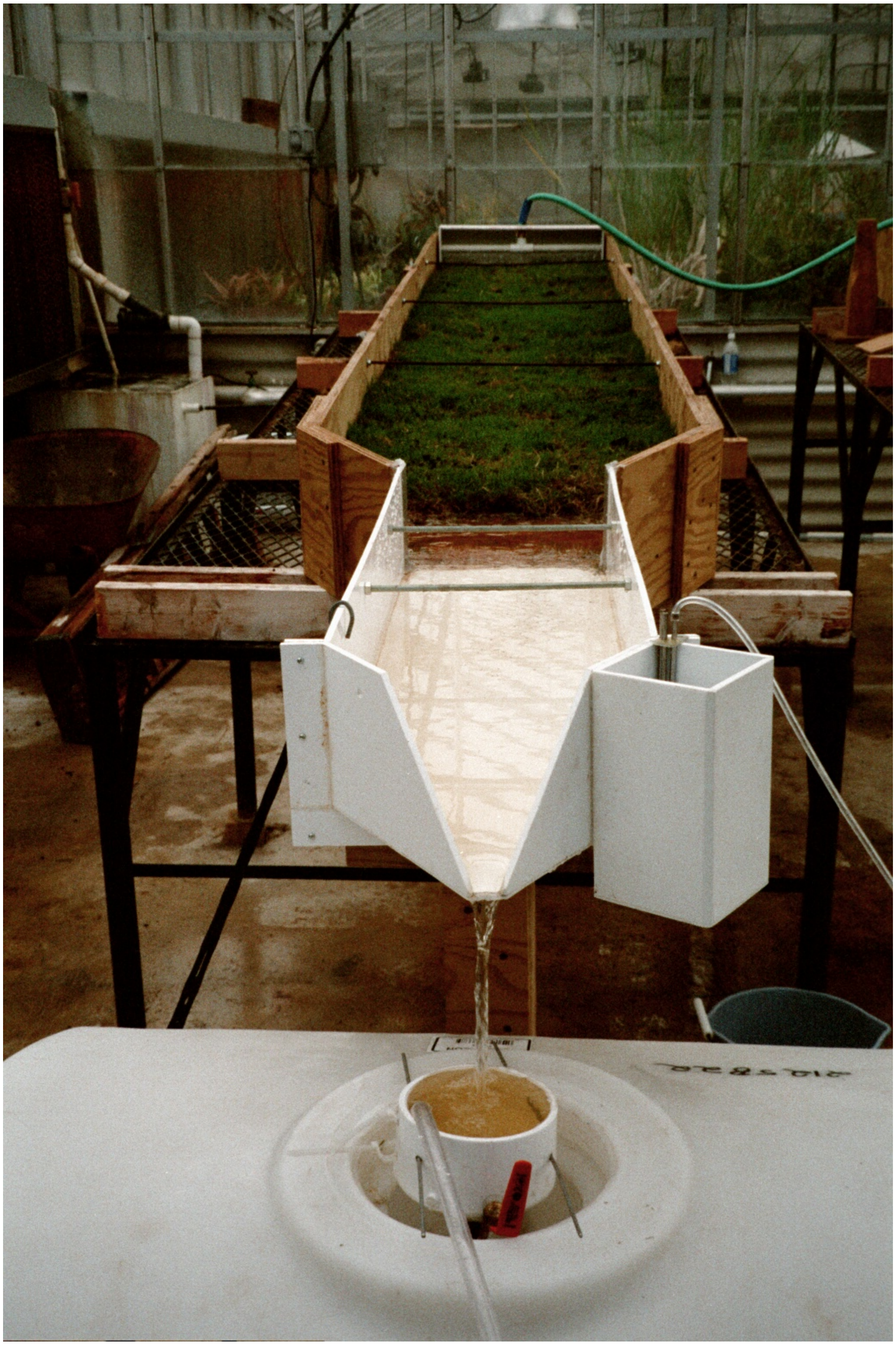

Figure 1. Photo of plot P4 with trough, runoff distributor, flume, and reservoir. Not shown are bench scale, datalogger, and laptop computer.

calculated loads resulting from the time−based sampling strategies. Understanding the relationship between total load and loads calculated using various time−based sampling strategies should result in more accurate load estimates and could translate into economic savings with respect to need for laboratory supplies, personnel requirements, and time.

Methods and Materials

Laboratory Setup

Three 0.61m (2 ft) wide by 3.66 m (12 ft) long by 0.08 m (0.25 ft) deep troughs identified as P2, P3, and P4 were constructed, filled with soil, sodded with Bermuda grass (*Cynodon dactylon* L. Pers.), and set at 5% slope (fig. 1). The plots were sodded to minimize sediment−bound pollutants.

The troughs were designed so that overland flow could be introduced at the upslope end. The outlets of the troughs were fitted with a 0.15 m (0.5 ft) H−flume and a 0.91 m (3 ft) approach. The flow exiting the H−flume was channeled to a 0.38 m^3 (13.4 ft^3) storage tank. The storage tank was weighed continuously at 15 s intervals using a 454.5 kg (1000 lb) capacity floor scale connected to a datalogger. Thus, flow rate/volume was measured on a 15 s time interval.

Ammonium nitrate (NH_4NO_3) (33−0−0 applied at a rate of 93.6 kg ha^{-1} actual N to all plots) and composted dairy manure (P2, 4.9 t ha^{-1}; P3, 9.9 t ha^{-1}; and P4, 14.8 t ha^{-1}) were broadcast applied to the plots approximately 4 h prior to the simulation of overland flow. The dairy manure contained 1.24% total nitrogen. The different rates of manure application were used to accommodate a concurrent study. The plots were wetted by sprinkling with 6.4 mm of water prior to introducing overland flow. Overland flow was introduced at the upland portion of the troughs. Overland flow was continued for 120 min. The source of overland flow was tap water. The rate of the runoff was controlled manually by the gate valve on the input flow source.

Sampling Strategies

Time−discrete sampling at 1, 2, 3, 4, 5, 10, 15, and 30 min intervals was evaluated. Composite samples comprised of aliquots collected at 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 min intervals were also investigated. In addition, time−based composite samples (2, 3, 4, and 5 aliquots per sample) using the same time intervals as those used for the discrete sampling were also tested. This approach was a compromise between discrete and single composite sampling. Compositing more than 5 aliquots per sample, while possible, was not deemed practical (the more aliquots used to comprise a sample, the less the volume per aliquot allowed to avoid exceeding sample bottle capacity).

Load Calculations

Manual sampling of the water exiting the H−flume was conducted at 1 min intervals throughout the 2 h overland flow simulation. Each sample was analyzed for NO_3+NO_2−N and NH_4−N concentration. The concentration of each analyte was multiplied by the weighed flow volume during each 1 min interval to calculate the load of each analyte. The summation of the incremental loads resulted in a load estimate. Similarly, the nutrient load for all the sampling schemes (2, 3, 4, 5 min, etc.) was calculated as the concentration for each sample multiplied by the weighed flow during collection of that sample and summed over the event period. For composite samples, loads were calculated as the average concentration of aliquots collected during the composite period multiplied by the weighed volume during that period. At the conclusion of the 2 h simulated runoff event, the water in the 0.38 m^3 (13.4 ft^3; 100 gal) storage tank was stirred, and three water samples were collected from the tank for analysis. Once analyzed, the resulting concentration and total volume of runoff were used to calculate a total load. The calculated load associated with each strategy was compared to the total load.

Sample Analysis

All samples were analyzed colorimetrically for NO_3+NO_2−N and NH_4−N concentrations using a Technicon Autoanalyzer IIC and methods published by Technicon Industrial Systems (1973a, 1973b, 1976). The samples were unfiltered and non−digested. Sediment leaving the plots was negligible. Laboratory quality assurance analyses resulted in blank concentrations less than the published Technicon procedure detection limits. Replicates (precision limits) were all within 5%, and measured laboratory spikes (accuracy limits) were all within 8% of known concentrations; most were well below the 5% and 8% values.

Results and Discussion

The simulation of overland flow resulted in a hydrograph and two concentration graphs for each of the three plots (fig. 2). Calculated loads of NO_3+NO_2−N and NH_4−N for the 50 different time−based (time−discrete and time−composite) sampling strategies were compared to the total load (table 1). In general, calculated loads from the different sampling strategies were underestimated when compared to total load.

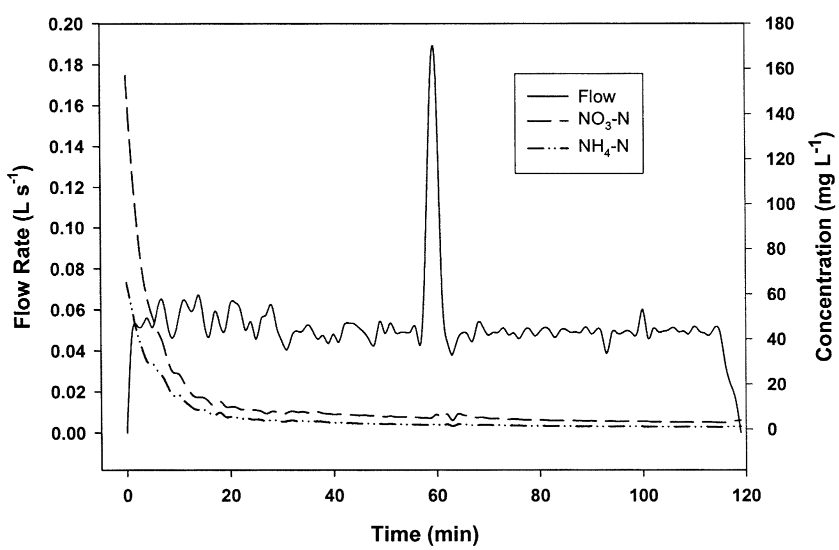

Figure 2. Representative hydrograph with concentration of NO_3+NO_2−N and NH_4−N from plot P3.

Table 1. Total and calculated loads for each constituent at each plot for all investigated sampling strategies.

	NO_3+NO_2−N (g)			NH_4−N (g)		
	P2	P3	P4	P2	P3	P4
Total load	3.05	4.53	9.73	1.54	2.20	4.25
td1[a]	2.26	4.13	10.35	1.12	1.99	4.96
td2	2.18	3.89	8.94	1.07	1.88	4.45
td3	2.20	3.74	8.75	1.08	1.83	4.35
td4	2.22	3.62	7.79	1.09	1.75	4.08
td5	2.12	3.55	8.16	1.04	1.80	3.83
td10	1.86	3.01	4.52	0.92	1.51	2.78
td15	1.83	2.58	3.62	0.87	1.24	2.31
td30	1.50	2.12	2.56	0.67	0.88	1.58
tc2_1[b]	2.18	3.94	9.41	1.07	1.90	4.57
tc2_2	2.28	3.85	9.04	1.12	1.86	4.49
tc2_3	2.32	3.68	8.72	1.13	1.81	4.34
tc2_4	2.29	3.54	7.62	1.12	1.72	4.01
tc2_5	2.19	3.45	7.76	1.08	1.75	3.71
tc2_10	2.19	3.28	4.78	1.05	1.59	2.90
tc2_15	1.37	1.92	2.81	0.70	0.98	1.91
tc2_30	1.48	2.13	2.47	0.65	0.86	1.48
tc3_1	2.20	3.93	9.66	1.08	1.90	4.66
tc3_2	2.39	3.83	9.12	1.17	1.86	4.53
tc3_3	2.40	3.63	8.65	1.17	1.79	4.31
tc3_4	2.36	3.49	7.51	1.15	1.70	3.96
tc3_5	2.22	3.40	7.61	1.10	1.73	3.66
tc3_10	1.87	2.87	4.24	0.92	1.41	2.61
tc3_15	1.79	2.41	3.38	0.85	1.13	2.12
tc3_30	1.45	2.05	2.37	0.63	0.82	1.40
tc4_1	2.26	3.93	9.74	1.11	1.90	4.69
tc4_2	2.47	3.82	9.15	1.21	1.85	4.54
tc4_3	2.48	3.62	8.62	1.21	1.79	4.30
tc4_4	2.41	3.50	7.51	1.18	1.71	3.96
tc4_5	2.23	3.38	7.49	1.11	1.71	3.62
tc4_10	1.85	2.74	4.16	0.91	1.34	2.55
tc4_15	1.83	2.45	3.34	0.87	1.14	2.09
tc4_30	1.37	1.95	2.27	0.58	0.76	1.28
tc5_1	2.35	3.93	9.88	1.15	1.90	4.76
tc5_2	2.56	3.80	9.17	1.25	1.84	4.55
tc5_3	2.53	3.61	8.58	1.24	1.78	4.28
tc5_4	2.42	3.45	7.34	1.19	1.68	3.88
tc5_5	2.24	3.33	7.35	1.11	1.68	3.55
tc5_10	1.98	2.76	4.20	0.95	1.32	2.58
tc5_15	1.80	2.41	3.30	0.85	1.12	2.05
tc5_30	1.37	1.95	2.27	0.58	0.76	1.28
tc1_1	3.23	3.63	9.99	1.62	1.73	4.75
tc1_2	2.96	3.50	8.57	1.48	1.67	4.23
tc1_3	2.74	3.22	8.00	1.37	1.56	3.98
tc1_4	2.50	3.19	6.61	1.24	1.52	3.47
tc1_5	2.33	3.15	6.84	1.17	1.56	3.30
tc1_6	2.19	3.09	5.95	1.10	1.51	2.98
tc1_7	2.30	2.75	5.10	1.18	1.37	2.74
tc1_8	2.03	2.36	4.50	1.04	1.13	2.51
tc1_9	2.10	2.26	4.42	1.05	1.09	2.50
tc1_10	1.90	2.83	3.66	0.93	1.35	2.22

[a] td*a* represents time−discrete sampling at an interval of *a* minutes.
[b] tc*a_b* represents time−composite sampling, where *a* is the number of aliquots combined to create the sample, and *b* is the number of minutes between each aliquot.

Calculated loads of NO_3+NO_2−N and NH_4−N responded similarly to like sampling strategies, discrete (fig. 3) and composite (fig. 4). Average deviation from the total load increased as the time between samples increased. Total loads

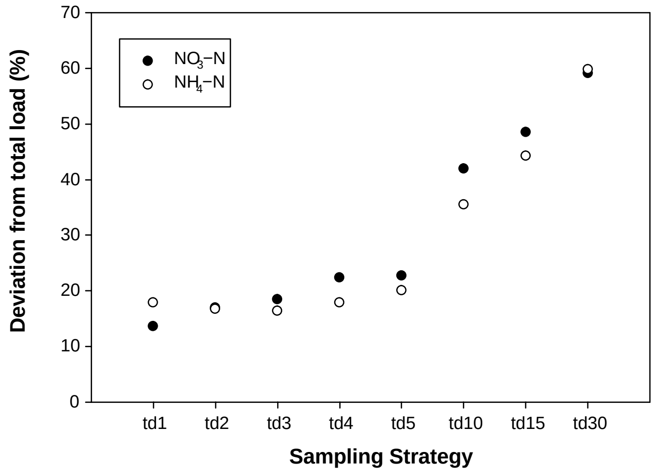

Figure 3. Average (n = 3) deviation of estimated NO_3+NO_2−N and NH_4−N loads from total loads using different time−discrete sampling intervals (e.g., td3 = time−discrete samples collected at 3 min intervals).

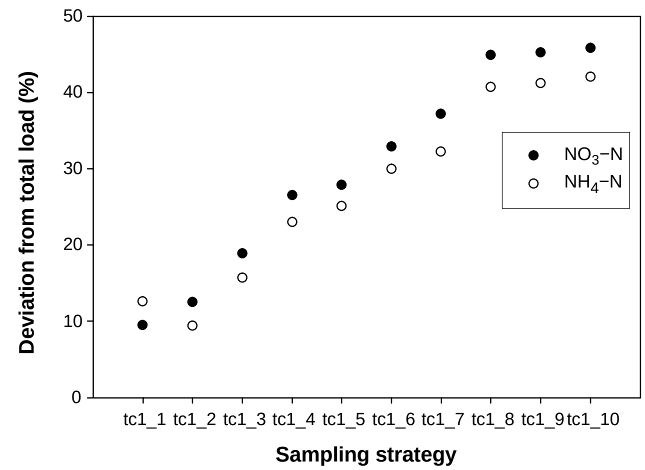

Figure 4. Average (n = 3) deviation of estimated NO_3+NO_2−N and NH_4−N loads from total loads using different time−composite sampling strategies, where tc*a_b* represents *a* composite samples with aliquots collected every *b* minutes (e.g., tc1_3 is a single composite with aliquots collected every 3 min).

of NO_3+NO_2−N and NH_4−N for each plot were paired with the calculated load from each sampling strategy. The residuals (total load − calculated load) of the paired values were not normally distributed (Anderson−Darling test for normality). Thus, the signed rank test (nonparametric equivalent of the t−test) was run with the six paired loads (NO_3+NO_2−N and NH_4−N for P2, P3, and P4) to compare the median residual to zero (H_0: median residual equals 0; H_A: median residual does not equal 0). Loads calculated using discrete sampling intervals of 1, 2, and 3 min were not significantly different (α = 0.05) from the total loads. Loads calculated using a composite strategy of 2, 3, 4, or 5 aliquots per sample collected at 1, 2, or 3 min time intervals were not significantly different (α = 0.05) from the total load. Likewise, loads estimated using a single composite approach, i.e., aliquots collected on a 1 min interval, were not significantly different (α = 0.05) from the total loads. All other sampling strategies produced calculated loads that were significantly different from the total loads. These results are similar to those of a recent field study investigating flow−proportional sampling strategies, specifically that

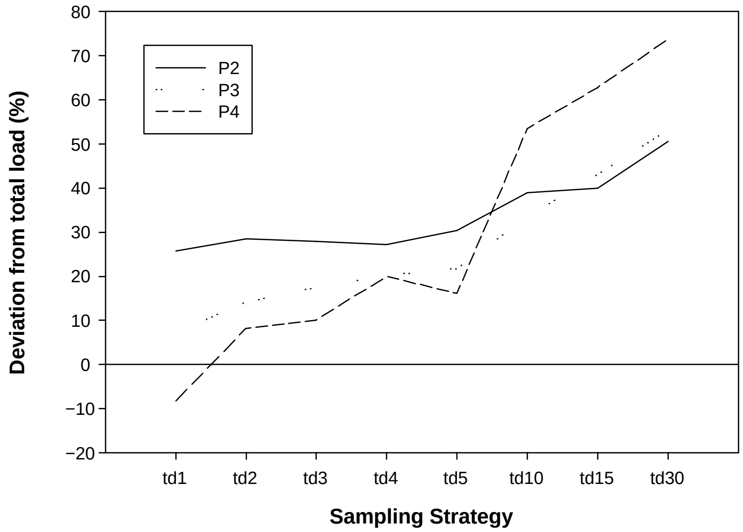

Figure 5. Deviation of NO_3+NO_2−N calculated loads from total loads for three application rates (P2, P3, and P4) using time−discrete sampling.

increasing the sampling interval resulted in greater error from total load than did increasing the number of composite samples (Harmel and King, unpublished data).

Nutrient application rate had an impact on calculated loads of NO_3+NO_2−N (fig. 5) and NH_4−N (fig. 6) when using a time−discrete sampling strategy. Smaller applications (P2) resulted in greater deviations of the calculated load from the total load for intervals up to 5 min. When using a composite approach, deviations from the total load of NO_3+NO_2−N (fig. 7) and NH_4−N (fig. 8) were, in general, more consistent. This consistency is a result of the deviations in concentrations averaged out over the period of the composite.

Based on the data collected and analyzed in this study, if there exists interest in collecting information about the distribution of concentration throughout an event and a requirement that the load estimate not be significantly different from the total load, then time−discrete sampling at 1, 2, or 3 min intervals is required. If information about the distribution throughout an event is not required, then a single time−composite sample, i.e., aliquots collected at a 1 min interval, would be adequate for capturing the total load. This strategy would also be more practical and economical with respect to laboratory supplies, personnel, and time when compared to time−discrete sampling (1 sample versus 40 samples at the 3 min collection interval for a 2 h event as used in this study).

Limitations

The data used in this study were collected from small plots in a laboratory environment. Only one general concentration shape (concentration declining with time) and hydrograph shape were evaluated. The results should be applicable to plot−scale studies, small rainfall simulation studies, or simulated runoff studies with similar hydrograph and concentration shapes. Extrapolation of results to significantly different hydrograph or concentration graph shapes or to spatial scales greater than 2.2 m^2 should be done with caution.

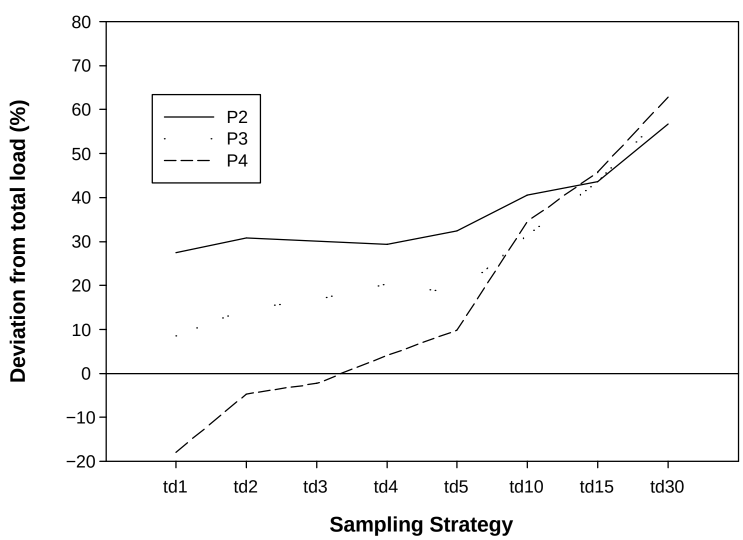

Figure 6. Deviation of NH_4−N calculated loads from total loads for three application rates (P2, P3, and P4) using time−discrete sampling.

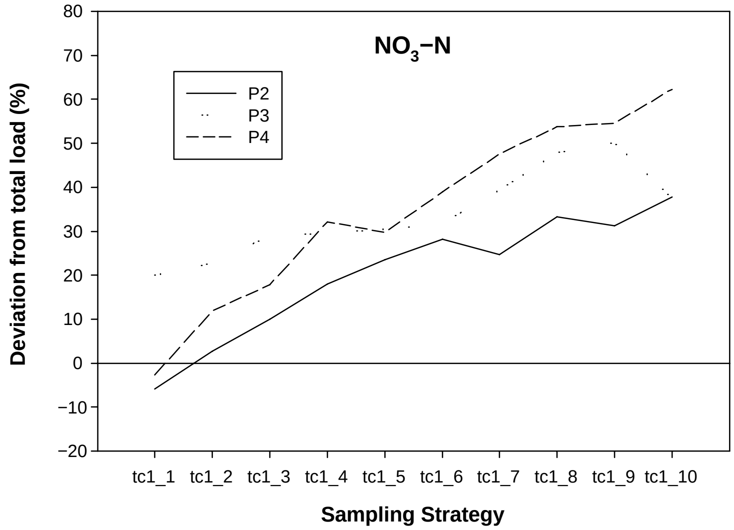

Figure 7. Deviation of NO_3+NO_2−N calculated loads from total loads for three application rates (P2, P3, and P4) using time−composite sampling.

SUMMARY AND CONCLUSIONS

A laboratory test was conceived, designed, and completed to compare and evaluate several time−based sampling strategies for load determination of NO_3+NO_2−N and NH_4−N. Overland flow was simulated for a 2 h period on three plots with differing levels of nutrient application. A total of 50 different time−discrete and time−composite sampling strategies were evaluated. Calculated loads of NO_3+NO_2−N and NH_4−N responded in a similar manner to identical sampling strategies (increasing deviation from the total load with an increase in time interval between sampling).

With respect to NO_3+NO_2−N and NH_4−N, calculated loads using time−discrete sampling at 1, 2, and 3 min intervals were not statistically different (α = 0.05) from the total load. All other tested time−discrete methods produced loads that were significantly less than the total loads. A single composite sample, i.e., aliquots collected at 1 min intervals, was the only single composite strategy that produced load calculations not significantly different from the total loads (α = 0.05). Loads calculated from time−composite strategies that included 2, 3, 4, and 5 aliquots per sample collected at intervals of 1, 2, and 3 min were also not significantly different from the total loads. Application rate also had an impact on the calculated loads from time−discrete sampling strategies for time intervals less than 5 min. The results should be applicable to similarly designed small plot−scale studies. The use of an optimal strategy should result in more accurate load estimates and could also provide economic (laboratory supplies, time, and personnel for sample analysis) savings.

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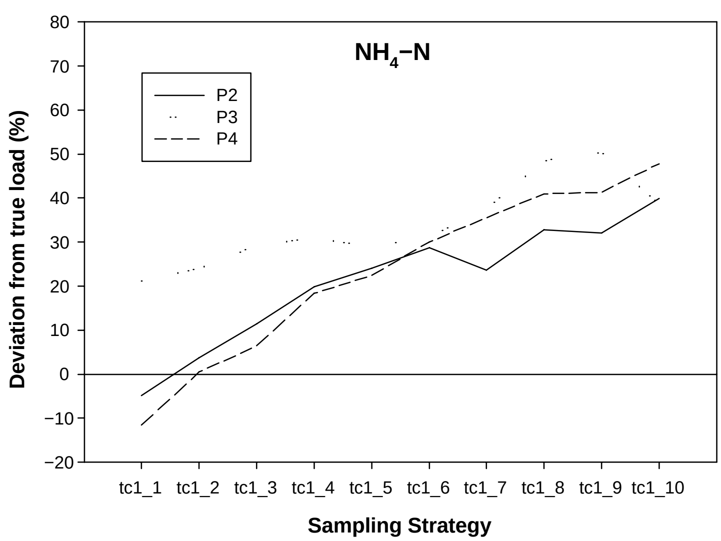

Figure 8. Deviation of NH_4−N calculated loads from total loads for three application rates (P2, P3, and P4) using time−composite sampling.

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