EVALUATION OF TIME PROPORTIONAL SAMPLING STRATEGIES FOR ESTIMATING ANNUAL NUTRIENT FLUXES AT THE OUTLETS OF COASTAL PLAIN WATERSHEDS

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ABSTRACT

Excess nutrient loads have been recognized to be the major cause of serious water quality problems recently encountered in the North Carolina estuaries and coastal waters. There has been a particular concern in coastal watersheds because agricultural and forested lands are located in close proximity to recreational and environmentally sensitive. Best Management Practices have been proposed to reduce nutrient emissions at the field and the watershed scale. BMP implementations have been coupled with nutrient flux monitoring programs for effectiveness assessment purposes.

Nutrient fluxes are usually estimated from continuous flow measurements and discontinuous concentration values obtained after laboratory analysis from discrete water samples. Because of the discontinuity on the concentration information, there is an error made in flux estimations compared to the actual fluxes. This error may be, in some cases, within the same range as the expected water quality improvements. Actual improvements may thus very well remain undetected because of unsuited sampling strategies.

To our knowledge, there are no existing references to 1) estimate those errors and 2) propose sampling guidelines for minimizing those errors. In this paper, we have examined, using reference databases, the possible errors that can be made on the estimation of annual nutrient fluxes at the outlet of the lower coastal plain watersheds, using time proportional sampling. Our results show that significant errors can be made using even weekly sampling. To detect water quality improvements, our results suggest it is desirable to design sampling on at least a 3-day basis for nitrate and total nitrogen, between 1- to 2-day basis for TOC and less than 1-day for total phosphorus. However, our results also show that there can be significant differences between watersheds. One should expect the magnitude of errors to decrease with increasing watershed size, as long as there is a significant correlation between flow and concentration. One should also expect annual nutrient fluxes to be underestimated for nutrients or chemicals exhibiting a concentration effect during flow events, the opposite being true for nutrients or chemical exhibiting dilution effects. Time proportional sampling thus seems relatively ill designed for monitoring, with reasonable uncertainties, annual nutrient flux at the outlets of small coastal plain watersheds. In particular, increasing sampling frequencies from monthly to biweekly or even weekly does not decrease significantly possible errors on flux estimations.

KEYWORDS. Best Management Practices, sampling strategies, time proportional sampling, sampling errors, nutrient fluxes, water quality, watersheds, diffuse pollution

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INTRODUCTION

Best Management Practices have been drawn to reduce excess nutrient concentrations and fluxes at the outlets of agricultural and forested watersheds. The success of such measures depends in part on the ability to show that nutrient concentrations and fluxes clearly decrease when BMPs are implemented. This evaluation is subject to many factors, some of which can be controlled, others not. An uncontrolled factor is the climate. Indeed, nutrient fluxes and concentrations may vary widely from year to year as a response to differential rainfall amounts and periods during the year. It thus becomes difficult to attribute an increase or a decrease in nutrient export to BMPs implementation.

A factor over which one potentially has control is the method used to measure nutrient fluxes. Fluxes are not directly measured but instead calculated from flow and concentration data. Flow rates are commonly measured and recorded automatically using electronic equipment. The period between consecutive records is thus usually small enough (down to several minutes or even seconds in some applications) so that a linear interpolation between consecutive measurement points closely approaches actual flow variations. Such small measurement intervals are very uncommon for most water quality parameters. In most cases nutrient concentrations are obtained from water samples after analysis in the laboratory. The cost to obtain samples and to conduct analyses in the laboratory intrinsically limits the number of concentration data available for flux calculations.

This limitation would not be a problem if nutrient concentrations varied little with time. Indeed, calculating fluxes requires associating a concentration value to each flow data point. In the case of a parameter which concentration would vary little with time, a linear interpolation between two data points would closely approximate actual concentration values. In most agricultural and forested watersheds however, nutrient concentrations are closely linked to flow rates and vary accordingly. A linear interpolation between two concentration data becomes problematic because during the period of time between two consecutive (often weekly or even monthly) samples, flow may have varied widely and thus the concentrations.

Consequently, using linear interpolation (other interpolation methods as well) induces an error while calculating fluxes. It is crucial to evaluate the magnitude of this potential error for common water sampling strategies. Indeed actual water quality improvements associated with BMP implementation may well remain undetected because of this error. Other errors may be induced due to e.g. flow and concentration measurements themselves. These are not examined in the paper.

The need for evaluating errors made using common sampling strategies is widely recognized in the literature (e.g. Littlewood, 1995; Kronvang and Bruhn, 1996; Webb et al., 1997, 2000; Littlewood et al., 1998; Horowitz, 2003; Moatar and Meybeck, 2003, 2005). Such evaluation is mostly conducted for rather large watersheds and is mostly focused on suspended solids and not as much on dissolved matter and ions (Crawford, 1991; Phillips et al., 1999; Webb et al., 2000; Horowitz, 2003). In this paper we examine errors made in calculating nutrient flux using time proportional sampling strategies for different nutrients and different land uses in the coastal plain.

MATERIAL AND METHOD

Three reference databases obtained from two coastal plain watersheds were used to calculate errors (Appelboom, 2004; Birgand, 2000). Both watersheds are located near the town of Plymouth and are included into a larger heavily instrumented 10,000 ha watershed. The first watershed, 1532 ha in size drains both agricultural (25% of the area) and managed forested lands. The second watershed drains exclusively managed forested land and covers around 4000 ha. Both watersheds are artificially drained by 80-m apart open ditches. Discharge was measured on a continuous basis and nutrient concentrations were obtained after analysis in the laboratory of automatically sampled water. Water was sampled at strategic times along the hydrographs so that a linear interpolation between consecutive samples would closely approximate the actual chemographs. Collected nutrient data included nitrate (NO$_3^-$-N), ammonium (NH$_4^+$-N), organic
nitrogen (ON), phosphate (PO$_4$-P), total phosphorus (TP), dissolved organic carbon (DOC), total dissolved carbon (TOC), Total Suspended Solids (TSS) and Chloride (Cl) (Appelboom, 2004; Birgand, 2000). For our analysis, we only used results from nitrate, total nitrogen, total phosphorus and total organic carbon, as they are the main nutrients of interest.

In the forested watershed, data were recorded during two consecutive years in 2001 and 2002. Water only flowed during the first four months of both years. Thus the errors computed for annual nutrient loads were calculated using four months of data only, each year. Nitrate concentrations were relatively low compared to the other watershed. They varied between 0 and 4.2 mg NO$_3$-N/L, were below 2.0 mg NO$_3$-N/L 80% of the time and varied between 0.1 and 3.4 mg NO$_3$-N/L, 90% of the time. Total nitrogen concentrations varied between 1.1 and 6 mg N/L, were below 4 mg N/L, 80% of the time and varied between 1.8 and 5.2, 90% of the time. Total dissolved Carbon concentrations were relatively high, varying between 13 and 50 mg C/L. Most values (80%) were below 31 mg C/L and varied (90% of the time) between 14 and 36 mg C/L. Total phosphorus concentrations were always very low, that is below 0.04 mg P/L 80% of the time, below 0.08 mg P/L 90% and reached 0.17 mg P/L during one event (Appelboom, 2004).

Data for the mix land use watershed were recorded in 1998 and 1999 where flow never stopped although the vast majority of the cumulative flow (over 95%) occurred in about six cumulative months (not adjacent) of the year. Nitrate concentrations reached much higher values than for the forested watershed, 5% of the values ranging from 10 to 27 mg NO$_3$-N/L, 45% ranging from 1.3 to 10 mg NO$_3$-N/L and half of the time were below 1.3 mg NO$_3$-N/L. Because of the relatively high nitrate concentrations, total nitrogen values were also relatively high ranging from 10 to 28 mg N/L 5% of the time, while the vast majority of the other values ranged between 1.5 and 10 mg N/L. Total dissolved carbon concentrations were even higher than for the forested watershed. Half of the values were comprised between 12 and 37 mg C/L, corresponding to high flow periods while the other half linearly ranged from 37 to 160 mg C/L, corresponding to low flow periods. Total phosphorus concentrations were above 0.08 mg P/L 60% of the time, ranged between 0.08 and 0.38 mg P/L 55% of the time and were above the latter value 5% of the time, reaching 0.71 mg P/L (Birgand, 2000).

Reference nutrient annual fluxes were calculated from these three databases. We numerically simulated time proportional sampling from the databases and calculated new annual fluxes. To do so, we used measured flow rate data and concentration data linearly interpolated from sampled concentration data. For each year database, errors were calculated as the percentage difference between the “simulated” flux and the reference one.

### RESULTS AND DISCUSSION

#### Infinite number of possible errors for a set sampling period

For a set sampling frequency, the choice of the first data and time determines the shape of the simulated chemograph since all further sampled concentrations occur exactly at the initial date and time modulo the sampling period (3-day in Figure 1). For a different initial date and time, the shape of the new simulated chemograph may actually be quite different from another one (Figure 1). It should also be noted that depending on the actual sampling period chosen, the simulated chemographs may be quite different from the reference one (Figure 1), the difference between the two increasing with the sampling period. As a result, the probability that the calculated annual fluxes be different from the reference flux is elevated. Thus, for each sampling frequency and for each initial date, we have called this possible difference an evaluation “error” of the annual nutrient flux. Theoretically, there is an infinite number of possible chemographs for a given sampling frequency (Figure 1 shows 2 of them). Consequently, there theoretically is an infinite number of errors for a particular sampling frequency. Nonetheless, the errors are actually bounded in an interval for a particular sampling frequency (see below). The number of simulations was defined by the ratio between the sampling period divided by the time interval of the reference file. When this number was below 150, reference databases were adjusted to shorten the time interval.
This was also done by linear interpolation. Indeed, it was found that above 150 sampling simulations, the results on the errors did not change (data not shown).

The finite number of errors found for each sampling period simulated were then put in increasing order and a cumulated probability was associated to each error value (Figure 2).

In the example presented in Figure 2, using 3-day or weekly sampling tend to always underestimate the annual fluxes compared to the reference one. To better characterize cumulative probability functions, and obtain a representation of the error as a function of the sampling periods, particular statistical values were withdrawn including, the median, the 16.7 and 83.3 percentiles (as 2/3 of the values are included between these two limits), the 2.5 and 97.5 percentiles (as 95% of the values are included between these two limits), as well as the extreme values (referred to as “Inf” and “Sup” in the Figures). Simulations were conducted on an hourly increment from 1-hour sampling interval to 30-day sampling intervals. The previous statistics have then been graphed as a function of sampling periods and are reported from Figure 3 to Figure 4. For lack of space in this paper, results from only one reference database (2002) for the forested watershed have been plotted.

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**Figure 1:** Comparison between measured (thick line) and extrapolated nitrate chemographs from two simulated 3-day sampling (square and triangle series) from the mix land use watershed

**Figure 2:** Cumulative probability function of the error, expressed as the percentage difference with the reference annual flux, made by sampling on a 3-day or weekly basis for the mix land use watershed

**Significant errors rapidly induced by time-proportional sampling**

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Figure 3: Range of errors made while calculating nutrient annual loads using time-proportional sampling for the mix land use watershed
Figure 4: Range of errors made while calculating nutrient annual loads using time-proportional sampling for the Forested watershed using the 2002 reference year

Two clear and opposite patterns appear from the mix land use watershed results: there is a high probability that nitrate, total nitrogen and total phosphorus annual fluxes would be underestimated when calculated using time proportional sampling, the opposite being true for dissolved organic carbon (Figure 3). For the forested watershed, there is a clear tendency to
underestimate nitrate and total nitrogen annual fluxes. There seems to be a similar tendency for dissolved organic carbon, which would be the opposite of the one observed for the mix land use watershed. Errors made for total phosphorus in the forested watershed seem relatively unbiased, the probability of underestimating annual fluxes being essentially equivalent to overestimating it, although the magnitude of overestimating the flux may be higher (Figure 4).

The group of curves representing the statistics of the errors as a function of the sampling periods may be described as a “beam” of curves. The shape of each curve is actually rather “wavy” or “noisy”, the range of errors varying rapidly from an hourly increment to the next. For the forested watershed, however, curves become less wavy as sampling period increases. This may be linked to the relatively short period of data available to compute the annual loads (4 months of data).

In all cases, the beam of curves tends to spread open as the sampling period increases, suggesting that the errors may reach higher absolute values with increasing sampling period. The narrowness of the beam and its deviation compared to the X-axis, may be quite different from one nutrient to another and from one watershed to the other.

Controlled drainage has been shown to potentially reduce total nitrogen and total phosphorus exports by as much as 50 and 35%, respectively, at the field scale in the coastal plain of North Carolina (Evans et al., 1991; Gilliam et al., 1999). At the watershed scale, one would expect a maximum nutrient load reduction to reach lower values than those figures. Indeed, BMPs are rarely (never) implemented on 100% of the surface area at the same time, and when implemented, they may not be implemented with an optimal efficiency. A 10 to 20% improvement seems to us to be a reasonable figure for an expected decrease of the nutrient loads in the rather small coastal plain watersheds. Consequently, the intrinsic error made by the chosen sampling strategies should, to have chance to detect improvements, not exceed half of this expected improvement.

Table 1 shows the computed desirable sampling periods to restrict errors on annual nutrient fluxes within ±5% and ±10% difference compared to the reference one. Most values are below 3-day sampling, but vary from 16 hours for total phosphorus for the smaller mix land use watershed to over a week for total organic carbon for the larger forested watershed. These values are rarely reported in the literature. In four watersheds of similar sizes in Brittany, France, Birgand et al. (2005) did find similar results for nitrate and total phosphorus loads for the 5% thresholds, although desirable sampling frequency for total phosphorus loads was estimated at 10-hour. Sampling on a 1- to 3-day frequency obviously implies heavy efforts both on the field and in the laboratory, especially if monitoring must be conducted on a number of stations. Proper conservation of samples can also be problematic as it may differ depending on the nutrient considered. Time-proportional sampling is thus probably ill designed for detecting water quality change in rather small watersheds. Nonetheless, this technique is still commonly used without, it seems, much knowledge about the errors possibly made using it. Several factors influencing on the magnitude and the range of errors can be drawn from our results, however. They are discussed below.

As previously mentioned, there is a negative percent bias for nitrate, total nitrogen and total phosphorus in the errors made. These three nutrients exhibit a positive correlation between flow rates and their concentrations during flow events (Appelboom, 2004; Birgand, 2000), sometimes referred to as a “concentration effect” (e.g. Webb and Walling, 1985). This result is expected as

### Table 1: desirable sampling periods to restrict errors on annual nutrient loads due to infrequent sampling to 5 and 10%. The two values for the forested watershed correspond to the results from the two years of data

<table>
<thead>
<tr>
<th>Error Thresholds</th>
<th>NO₃-N</th>
<th>TN</th>
<th>TOC</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>10%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>Mix land use watershed (1500 ha)</td>
<td>1.6 d</td>
<td>3 d</td>
<td>2 d</td>
<td>4 d</td>
</tr>
<tr>
<td>Forested watershed (4000 ha)</td>
<td>2.3-2.4 d</td>
<td>3.4-4.7 d</td>
<td>2.5-3.6 d</td>
<td>5.5 - 8.7 d</td>
</tr>
<tr>
<td></td>
<td>3-16 d</td>
<td>9 d</td>
<td>1.2 -1.6 d</td>
<td>1.5-2.1 d</td>
</tr>
</tbody>
</table>

Table 1
flow events being relatively rare, a linear interpolation between consecutive infrequent samples will tend to underestimate the actual concentration, the majority of the time, hence the nutrient flux. King and Harmel (2003) found similar results using a set of flow events from 87 watersheds in the US. Similarly, Kronvang and Bruhn (1996) showed a general trend towards an underestimation of total phosphorus annual fluxes using the equivalent of weekly, biweekly and monthly sampling. Littlewood (1995) and Littlewood et al. (1998) did not show any particular bias in one direction or another for their set of data, however. Concentration pattern for TOC exhibited an opposite pattern, sometimes referred to as a “dilution effect” (Webb and Walling, 1985), for the mix land use watershed (Birgand, 2000), and consequently, a positive percent bias was computed (Figure 3). In the forested watershed, a concentration effect was observed (Appelboom, 2004), hence a negative percent bias. Lack of bias for total phosphorus in the forested watershed is most likely due to the absence of a clear correlation between flow and concentrations for this nutrient, the values always remaining very low (Appelboom, 2004).

Threshold values tend to be lower for the smaller mix land use watershed than for the larger forested one (Table 1). The actual beams of curves are also narrower and deviate more from the X-axis for the smaller watershed (Figure 3 and Figure 4). Similar observations were made for different size watersheds in Brittany, France (Birgand et al., 2005). These results are somewhat expected since for smaller times of concentration corresponding to smaller watersheds, and for a set sampling frequency, there will be a tendency to “cut” more of the actual concentrations variations by linear interpolation. In other words the measured chemographs will tend to differ from the actual one, “quicker” for increasing sampling frequency for smaller watersheds. Moatar and Meybeck (2003; 2005) showed no particular bias for nitrate, orthophosphate or total phosphorus in the Loire river at Orléans in France (36970 km²), and this may be due to relative lack of correlation between flow and concentration for this size of watershed.

The same observation can be made for nutrients which concentrations vary on relatively smaller amplitudes, regardless of the actual value around which they vary. Figure 3 and Figure 4 tend to show that the beams of curves corresponding to total nitrogen tend to deviate less from the X-axis than for nitrate. This is very likely due to the smaller amplitudes in the variation of total nitrogen concentrations compared to those of nitrate (Appelboom, 2004; Birgand, 2000). Similarly, the actual errors made on annual total phosphorus loads on both watersheds are quite similar (Figure 3 and Figure 4), although the actual values are much lower for the forested watersheds. However, both the base and maximum values are lower for the forested watershed and the relative amplitude between the two are similar to the one on the mix land use watershed. Range of error for TOC in the forested watershed is clearly smaller than that of other nutrients, and that of the mix land use watershed, illustrating this observation again.

Errors computed for the forested watershed seem to be significantly different for the two sets of annual data (Table 1). This result is somewhat different from what was shown by Birgand et al. (2005), where there seemed to be a relative similarity between results from different years for nitrate. This may be due to the relatively few numbers of flow events corresponding to the short period of data available for each year. Horowitz (2003) has shown that the actual percent error increases with the decrease of the period for the nutrient flux evaluation. King and Harmel (2003) show very large biases in the simulations based on few flow events, confirming this observation. It is thus possible that the errors computed for the forested watershed were overestimated compared to a situation where there would have been a full year of available data.

CONCLUSION

In this paper, we have examined, using reference databases, the possible errors that can be made on the estimation of annual nutrient fluxes at the outlet of the lower coastal plain watersheds, using time proportional sampling. Our results show that significant errors can be made using even weekly sampling. To detect water quality improvements, our results suggest it is desirable to design sampling on at least a 3-day basis for nitrate and total nitrogen, between 1- to 2-day basis for TOC and less than 1-day for total phosphorus. However, our results also show that there can be significant differences between watersheds. One should expect the magnitude of errors to
decrease with increasing watershed size, as long as there is a significant correlation between flow and concentration. One should also expect annual nutrient fluxes to be underestimated for nutrients or chemicals exhibiting a concentration effect during flow events, the opposite being true for nutrients or chemical exhibiting dilution effects. Time proportional sampling thus seems relatively ill designed for monitoring, with reasonable uncertainties, annual nutrient fluxes at the outlets of small coastal plain watersheds. In particular, increasing sampling frequencies from monthly to biweekly or even weekly does not decrease significantly possible errors on flux estimations.

REFERENCES


