Estimating Tributary Phosphorus Loads Using Flow-Weighted Composite Storm Sampling

INTRODUCTION

The quality of the nation's surface water has become an increasing concern as the population has grown and the demand for clean water has increased. Many of man's activities such as land development for agriculture, industrial, or residential use increase the level of plant nutrients entering a water body from runoff and accelerate the process of eutrophication. Eutrophication is defined as the process of increasing productivity of algae and aquatic plant life and the subsequent water quality degradation. Phosphorus is a key nutrient to the water-quality of lakes and reservoirs because it most often is the limiting nutrient for algae growth in fresh waters and, therefore, can often control the rate of eutrophication. This study evaluates several methods for quantifying phosphorus loads entering a lake or reservoir from its tributaries.

Many water quality models use phosphorus loading as a predictor of the in-lake phosphorus concentration. Because phosphorus is often the limiting nutrient, the in-lake phosphorus concentration can be used to estimate the trophic state. Two common models that use a mass balance approach include those of Vollenweider (1975) and Reckhow (1988). These and other predictive models, however, are only as accurate as the phosphorus load estimate that is used in them. Because the results of these models are often used in land-development decisions that can have large financial consequences, the accuracy of the phosphorus load estimate becomes critical.

A large portion of the total phosphorus load entering lakes and reservoirs originate on land and is transported to the impoundments through tributaries. The phosphorus load estimation techniques described in the literature are based either on site-specific data from a monitoring program, or land-use and rainfall data. Monitoring data are more expensive to obtain but they produce a more accurate tributary load estimate than methods based only on land-use and rainfall data. Four phosphorus load techniques were evaluated during this study, three that were based on comprehensive monitoring data and one that was based on land-use and rainfall data.

Study Sites

This study details the results of phosphorus estimation techniques based on data collected from two Virginia sites, Swift Creek Reservoir and Cub Run. The Swift Creek Watershed is drained by nine relatively small, monitored tributaries, and Cub Run is a tributary in another extensively monitored watershed located in a different part of the state. Phosphorus loads carried by Cub Run were considered as controls during this study.

The Swift Creek Reservoir lies outside of Richmond, Virginia, and serves as a drinking water source for Chesterfield County, Virginia. The watershed area is approximately 65 square miles and remains relatively undeveloped. Most urban development during the past few years has occurred in the direct drainage area, which accounts for 12 percent of the watershed. In recent years, local special-interest groups have exerted pressure to develop parts of the upper portion of the watershed as the suburbs of Richmond continue to expand. Development issues have prompted concern over future reservoir water quality because the impoundment is a valued aesthetic addition to the community as well as a drinking water source. In the early 1980's, the Chesterfield County Department of Utilities established, and has since expanded, a monitoring program designed to enable local officials to quantify the current water quality of the Reservoir and detect any adverse water quality trends. Algae in the Reservoir are currently phosphorus limited, so assessing annual phosphorus loads is one of the key goals of the monitoring program.

The Swift Creek Watershed monitoring program employs flow meters and autosamplers on all of its nine major tributaries. Instantaneous flow rates are measured every five minutes and are used in calculations of mean daily flows. Storm event sampling includes flow-weighted composite sampling based on an equal-flow approach. The autosamplers collect water samples during runoff events in such a way that their phosphorus concentrations can be used to determine an event mean concentration (EMC) that is representative of the phosphorus concentration in the entire volume of the storm runoff event. The flow meters use a real-time analysis to quantify the total storm flow volume. Base flow is sampled approximately every two weeks by simple grab sampling.

Cub Run is a tributary to the Occoquan Reservoir, which is a major drinking water supply in northern Virginia. A comprehensive watershed monitoring program was established in 1972 in response to accelerated eutrophication of the Reservoir, and it is conducted by the Occoquan Watershed Monitoring Laboratory (OWML), a component of the Department of Civil and Environmental Engineering at Virginia Tech.

Cub Run data were included as a control in this research project because Cub Run has been extensively monitored by reliable techniques for many years. The Cub Run phosphorus loads determined by OWML were considered to be the "true" loads. In this study, the raw Cub Run data were used to estimate annual phosphorus loads by several other methods, and the results were compared to the "true load" supplied by OWML. Naturally, the actual load is never truly known.

Storm events at Cub Run are routinely monitored by collection of flow-weighted composite samples by techniques similar to those used in the Swift Creek Reservoir monitoring program. The flow meter calculates the total storm flow volume and the autosampler collects a series of samples that are combined and analyzed. The analytical results are expressed as an EMC of phosphorus. The flow meter also provides mean daily flow values. Base flow phosphorus concentrations are determined by analysis of grab samples collected approximately once each week.

Swift Creek Reservoir and Cub Run monitoring data collected during 1996 and 1997 were used for this study. During 1996, rainfall was above average, and during 1997, rainfall was below average at both study sites (Table 1). Flow-weighted composite samples during storm events are collected at both study sites. Most studies of load estimation techniques reported in the literature have not been based on composite sampling and use only grab sample concentrations and instantaneous or mean daily flows to represent storm events. Load estimates based on analyses of flow-weighted composites are more representative of true storm loads than those based on grab-sample analyses. The highest phosphorus concentrations during a runoff event occur on the rising limb of the hydrograph due to the flushing effect. Load estimates based on grab-sample analyses are usually inaccurate because the phosphorus concentration can vary considerably throughout the runoff event.

The tributaries investigated in this study have relatively low flows. Flow characteristics for the nine tributaries to Swift Creek Reservoir and Cub Run during 1996 and 1997 are shown in Table 2. The accuracy of the estimation methods may differ for tributaries with vastly different flow characteristics than the two sites investigated in this study. The Cub Run drainage area is 49.9 sq. mi. which is comparable to the drainage areas of all the tributaries to Swift Creek Reservoir combined, and, therefore, the discharge in Cub Run is greater than that in any individual Swift Creek Reservoir tributary.

TABLE 1. Rainfall Amounts in the Swift Creek Reservoir and Cub Run Drainage Areas.

	Rainfall, inches		
Location	**1996**	**1997**	**Period of Record Average**
Swift Creek	51.5 in.	39.3 in.	41.7 in.
Cub Run	49.4 in.	32.8 in.	38.9 in.

TABLE 2. Mean Daily Flow Characteristics for Tributaries in 1996 and 1997.

Reservoir	Tributary	Year	Minimum Mean Daily Flow	Maximum Mean Daily Flow	Average Mean Daily Flow (cfs)
Swift Creek	Ashbrook	1996	0.0	73.0	3.3
		1997	0.0	43.0	2.0
	Blackman	1996	0.7	227.0	9.4
		1997	0.0	166.0	5.7
	Dry	1996	0.0	86.0	5.0
		1997	0.0	79.0	2.5
	Horsepen	1996	0.1	93.0	5.2
		1997	0.0	77.0	2.8
	Little Tomahawk	1996	0.0	247.0	6.0
		1997	0.0	49.0	1.9
	Otterdale	1996	0.3	142.0	5.4
		1997	0.0	93.0	3.2
	Swift	1996	0.3	161.0	14.6
		1997	0.0	100.0	7.9
	Tomahawk	1996	0.0	69.0	6.7
		1997	0.0	51.0	3.2
	West Branch	1996	0.0	126.0	3.5
		1997	0.0	52.0	2.0
Occoquan	Cub Run	1996	8.4	2,736.0	94.1
		1997	4.1	891.0	42.6

Three of the four methods evaluated during this study employed flow stratification, which means that the mean daily flows were divided into two strata: storm flows and base flows. The cutoff point between the two strata is referred to as the "base flow separation point." The base flow separation point is a selected percentile of the mean daily flows in any given year. Mean daily flows greater than the base flow separation point were considered to be storm flows, and flows smaller than the separation point were considered to be base flows. Only limited information regarding the impact of the base flow separation point on TP load estimates is available in the literature. Dolan *et al.* (1981) stated that the choice of the separation point is a "matter of judgement" and that more research was needed.

The objective of this study was to determine the best method for deriving an estimate of the gaged total phosphorus (TP) load entering a reservoir from its tributaries. An important feature of both watershed monitoring programs included in this study, not found in most others, is the inclusion of flow-weighted composite storm sampling. The impact of the base flow separation point on the results of each method employing flow stratification was also investigated during the project. Each load estimation method was executed over a range of base flow separation points so that its impact on the load estimates could be gauged and an optimum separation point could be selected. The effect of rainfall amounts on the TP estimates was also considered because two years of data were evaluated, one year when the rainfall was above average and one year when the rainfall was below average.

LOAD CALCULATION METHODS

Four methods were used to estimate the tributary phosphorus loads to Swift Creek Reservoir and Cub Run. These methods estimate only the "gaged loads," which are the phosphorus loads in water passing the tributary sampling stations. Contributions to the total load by runoff entering downstream of the stations are considered the "ungaged tributary load." Phosphorus entering in runoff that flows directly into the reservoir is referred to as the "direct runoff load." Ungaged tributary loads and direct runoff loads were not considered in this study, but it should be noted that phosphorus loads contributed by direct runoff can be quite significant.

Monte Carlo Method

Monte Carlo Simulation is a stochastic method that can easily account for the inherent variability of environmental systems by the use of straightforward concepts. A probability distribution is assigned for each variable, such as phosphorus concentration, whose absolute value is uncertain. The assignment can be based on intuition and/or previous data. After the distribution is chosen, the model is executed for a designated number of iterations. During each iteration, the uncertain variable is randomly selected from the assigned distribution, and a new distribution will then be formed from the model results. The distribution of results will include all model uncertainties and is called the "prediction error" (Bobba *et al.*, 1996).

The model used in the Monte Carlo Method during this research project was an equation that was used to calculate the daily phosphorus loads contributed by each tributary from daily flow records and total phosphorus (TP) concentrations:

$$\text{P Load, lb/day} = (\text{Mean daily flow, cfs}) \times (\text{TP, mg/L}) \times (\text{Correction factors})\ldots\ldots (1)$$

The mean daily flow was assumed to represent the flow rate during the entire day, so the total flow volume passing the gage in one day was found by multiplying the flow rate by the number of seconds in a day. Where gaging stations exist, the mean daily flow was recorded by the flow meters each day of the year, but the phosphorus concentrations were determined only on a fraction of the days during the year. The uncertain parameter is the phosphorus concentration on days when no sample was taken.

The input TP concentration distributions were composed of the concentrations that were measured during the year in question. Two data sets were established for each tributary, one consisting of the EMCs measured from storm events and the other consisting of the TP concentrations in base flow grab samples. Depending on the flow designation on a particular day (i.e. base flow or storm flow), a TP concentration was randomly selected from the corresponding data set. The daily TP load was then calculated according to equation 1. The procedure was repeated for every day of the year, and the sum of the daily loads equaled the annual load. The final annual load estimate derived by the Monte Carlo Method, was the median (50th percentile) of the results of the 1,000 iterations. Each year's distribution of 1,000 results tested positively for normality, so the median and mean values were similar.

Regression Method

The Regression Method developed during this research required the collection and chemical analysis of flow-weighted composite storm samples. Most regression estimators are based on a rating-curve approach and are dependent on the relationship between grab sample TP concentration and instantaneous flow rate (Young *et al.*, 1988). Because both the total storm flow volume and phosphorus EMC during storm runoff events were determined during the Swift Creek Reservoir and Cub Run monitoring programs, a rating curve between the TP concentrations and instantaneous discharges would not utilize this potentially valuable information. The relationship developed for use in this study, therefore, related the total phosphorus load to the total flow volume.

Six relationships between the sampled TP loads and the total flow volumes from Swift Creek Reservoir tributaries and Cub Run were analyzed for goodness of fit. Linear and log-log relationships were developed including the following data: storm flows alone, base flows alone, and base and storm flows combined. The R square (R^2) values, statistical measures of fit, for the log total phosphorus load vs. log total flow volume equation were generally highest when both the sampled storm and base flow data were combined. All the regression relationships used during this study, therefore, was a log-log relationship developed from the combination of sampled storm and base flow data for the year in question.

Flows on days when no samples were taken were divided into unsampled base flows and unsampled storm flows according to the base flow separation point. The mean daily flow on base flow days when no sample was collected was used to calculate the total flow volume, which was then used in the log-log relationship to determine the daily phosphorus load. The mean daily flows were also used to find the flow volume on days with unsampled storm flows, except adjacent days with unsampled storm flow first had their flow volumes added before the equation was applied to find the load. The annual load estimate determined by the Regression Method is the sum of the sampled and unsampled storm and base flow loads.

Ratio Estimator Method

Dolan *et al.* (1981) evaluated a method that is well-suited for use in the common situation when ample flow data exist with only limited concentration data. The method is an unbiased ratio estimator developed by Beale (1962). Ratio estimator methods are more precise than averaging methods because the observations, in essence, are flow-weighted (Young *et al.*, 1988). The ratio estimator method of mean daily loading described here has been used extensively on tributaries to the Great Lakes (Dolan *et al.*, 1981; Lang *et al.*, 1988; Preston et. al, 1989; Preston *et al.*, 1992; Richards and Holloway, 1987).

The following are the equations used in the Ratio Estimator Method (Dolan *et al.*, 1981):

$$\mu_y = \mu_x \frac{m_y}{m_x} \left(\frac{1 + \frac{1}{n} \frac{S_{xy}}{m_x m_y}}{1 + \frac{1}{n} \frac{S_x{}^2}{m_x{}^2}} \right) \quad \text{(2)}$$

Where:

$$S_{xy} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i y_i - n m_x m_y \quad \text{(3)}$$

$$S_x{}^2 = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i{}^2 - n m_x{}^2 \quad \text{(4)}$$

μ_y = The estimated daily load, (kg)

μ_x = Mean daily flow during the year, (cubic meters per second, cms)

m_y = Mean daily loading on the days on which concentrations were determined, (kg)

m_x = Mean daily flow during the days on which concentrations were determined, (cms)

n = Number of days on which concentrations were determined

x_i = Individual measured flows, (cms)

y_i = Daily loading during each day on which concentrations were determined, (kg)

The estimate is further improved if flow stratification is used. The strata are divided into storm flow and base flow by the base flow separation point (Dolan *et al.*, 1981). According to Richards and Holloway (1987), when stratification is used, a mean daily load is calculated for each stratum. The annual load is found by multiplying the number of days in each stratum during the year by the stratum's corresponding estimated daily load and adding the results.

Schueler's Simple Method

The Simple Method introduced by Schueler (1987) is the only method investigated during this research that does not require any tributary monitoring data. It was formulated by utilizing the comprehensive database that was collected as part of the Washington, D.C. area Nationwide Urban Runoff Program (NURP) study. Unlike the other methods, it can predict loadings under future planning strategies.

Because the method is simplified for easy application, it is not the most precise method, but it has been able to produce order-of-magnitude estimates of phosphorus loadings to aid planners in making their decisions. Cohn-Lee and Cameron (1992) and Houlahan *et al.* (1992) used Schueler's Simple Method to estimate the urban runoff loadings from selected areas within the Chesapeake Bay drainage area. Schueler's Simple Method was developed primarily for use on sites with areas less than one square mile. It should be noted that the Schueler's Simple Method predicts loads produced only from storm runoff, and base flow loads are not considered (Schueler, 1987). The method also estimates the load from the entire tributary drainage area, not from only the areas above the gages. For this reason, loads predicted by Schueler's Simple Method and the other methods in this study cannot be directly compared. As a result, the accuracy of the method was evaluated during this study only with Cub Run data because only a small fraction of the Cub Run drainage area is located downstream of the sampling station. Application of Schueler's Simple Method, therefore, will approximate the Cub Run's gaged load. The method was not applied to Swift Creek Watershed data because of the large portion of its watershed that is either ungaged tributary drainage area or direct drainage area.

The primary equation in Schueler's Simple Method is the following (Schueler, 1987):

$$L = \left[\frac{(P)(P_j)(R_v)}{12}\right](C)(A)(2.72) \qquad (5)$$

Where:

L = TP load from development site, (pounds)

P = Rainfall depth over the desired time period, (inches)

P_j = Factor that corrects P for storms that produce no runoff

R_v = Runoff coefficient, fraction of rainfall that turns to runoff

C = Flow-weighted mean concentration of phosphorus in runoff, (mg/L)

A = Area of the site, (acres)

The variable P_j is to be set to 0.9 when an annual load is being estimated (Schueler, 1987). The runoff coefficient can be found by the following relationship:

$$R_v = 0.05 + 0.009(I) \qquad (6)$$

Where: I = Site imperviousness, (percent)

The flow-weighted mean TP concentration (C) was given by Schueler (1987) for the following land uses: new suburban NURP sites, older urban areas, and hardwood forest. The national NURP study average value was suggested for any land use that is not described by the other three (Schueler, 1987).

ANALYSIS AND DISCUSSION

Flow Stratification and Method Accuracy

The range of base flow separation points to be analyzed was chosen after the cumulative probability distributions of mean daily flows in each tributary were plotted. Figure 1 is an

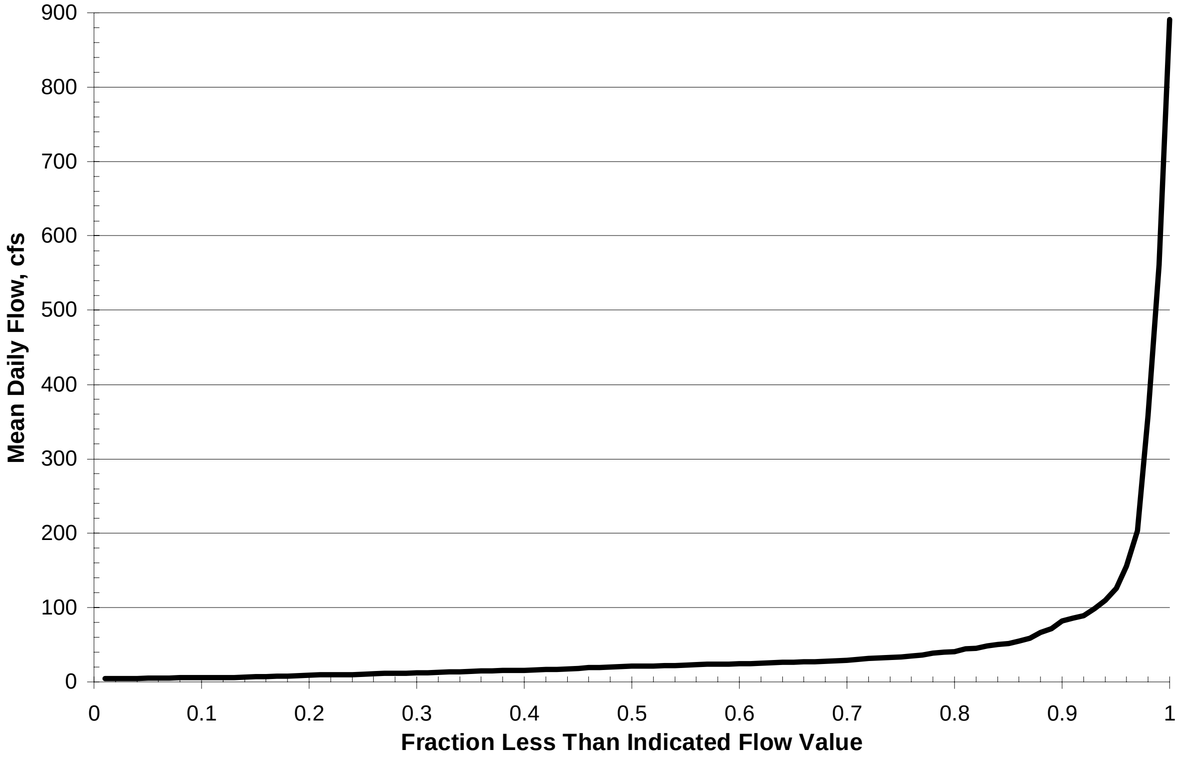

Figure 1. Cumulative Probability Distribution of Cub Run's 1997 Mean Daily Flows.

example of one such plot. Plots of 1996 and 1997 Swift Creek Reservoir tributary data and Cub Run data were similarly shaped. A significant deviation from the common base flow appears to begin between the 80th and 90th percentile. During this project, flow separation points selected for evaluation of their impact on the total load predictions were the 75th, 80th, 85th, 90th, and 95th percentiles.

Varying rainfall amounts in the Cub Run watershed during 1996 and 1997 (Table 1) affected the accuracy of each method. Figures 2 and 3 show Cub Run's gaged TP load estimates as a function of the flow separation point during 1996 and 1997, respectively. As was noted earlier, the value reported by OWML was the assumed "true" value.

Load predictions by the Monte Carlo Method were sensitive to the base flow separation point. The average Cub Run TP concentrations in storm flows were more than five times higher than the average for those in base flows during 1996 and 1997. As a result, selection of lower base flow separation points causes more days when TP concentrations are randomly selected from the list of higher storm flow values. The greater the number of flows considered to be storm flows, the higher the estimated load. The Monte Carlo estimates of the 1996 Cub Run TP load were more accurate at the lower percentile flow separation points, and the load was underestimated by 18% when the 95th percentile separation point was selected (Figure 2). As shown in Figure 3, the Monte Carlo Method was the most inaccurate method for predicting TP loads at all base flow separation points, especially at the 95th percentile. These data suggest that the lower base flow separation points should be selected when the Monte Carlo Method is used.

The Ratio Estimator Method also appears to be quite sensitive to the base flow separation point. During 1996, which was a year of higher precipitation, Cub Run TP loads were overestimated by the Ratio Estimator Method, when the lower percentile separation points (75th

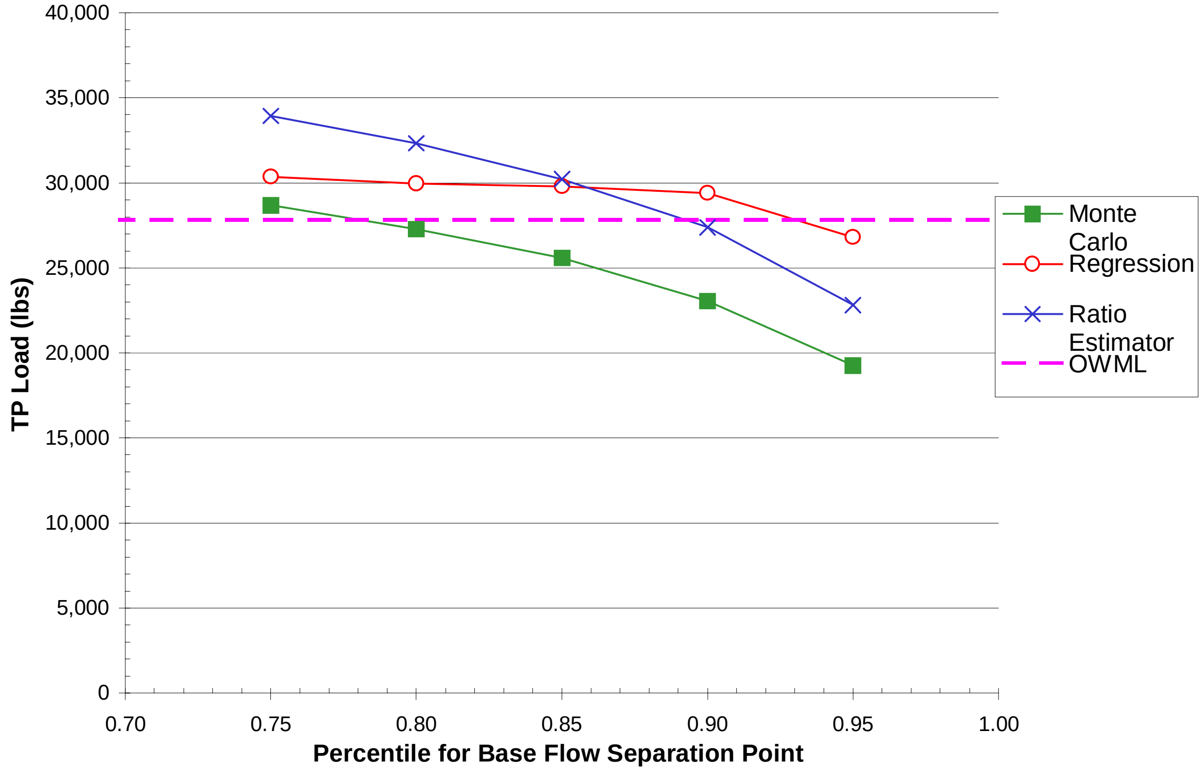

Figure 2. Cub Run's 1996 Gaged TP Load with Varying Base Flow Separation Point.

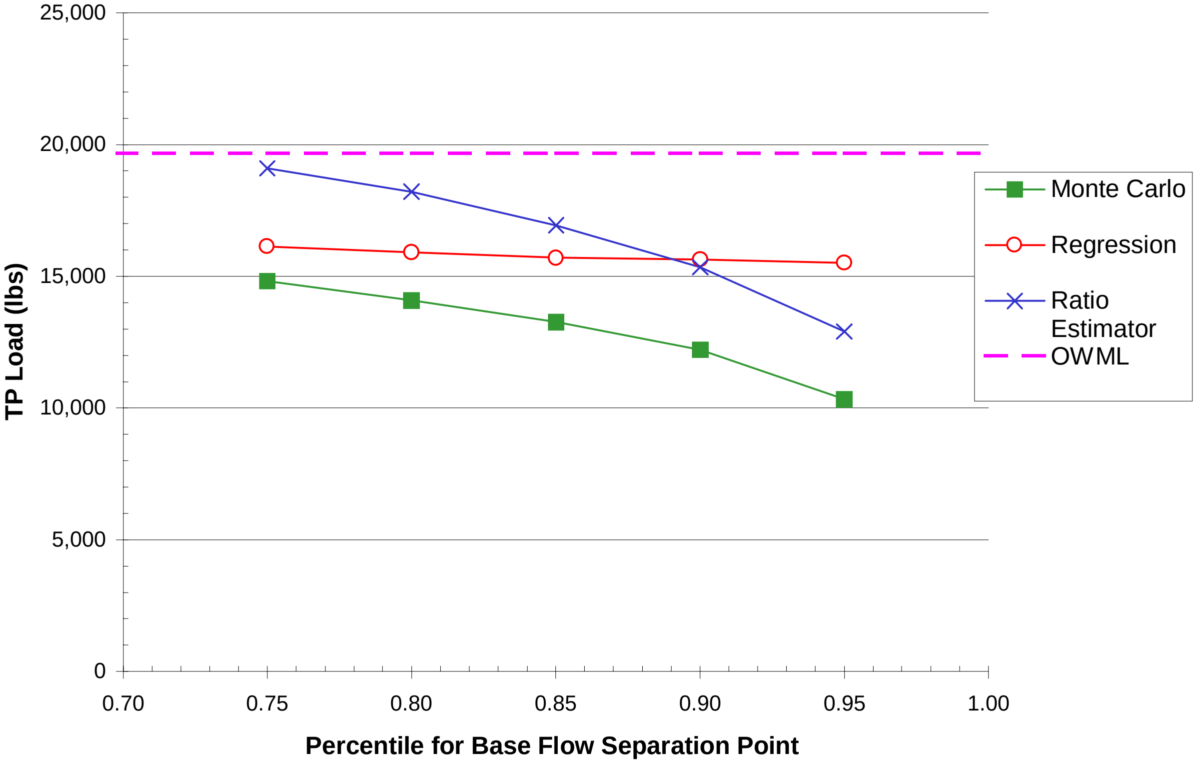

Figure 3. Cub Run's 1997 Gaged TP Load with Varying Base Flow Separation Point.

and 80th percentiles) were selected. Figure 4 shows the gaged TP loads for Swift Creek Watershed during 1996. As can be seen, TP loads estimated by the Ratio Estimator Method were much greater than those estimated by the other two methods. Rainfall during 1996 was greater than average, so it appears that the Ratio Estimator Method overestimates loads during wet years. The reason for the overestimation involves the calculation of the estimated daily load for storm flows. During 1996, the average of flows greater than the 85th percentile exceeded that of the average of flows when storm samples were measured ($\mu_x > m_x$). This occurrence led to an estimated daily storm load (μ_y) that was greater than the average TP load observed during sampled storms (m_y), which in turn, inflated the annual load estimate. Because the Swift Creek Reservoir TP load includes nine individual tributary load estimates, the effect was even more pronounced. During 1997, a year when rainfall was below average, the Ratio Estimator Method was the most accurate method for predicting TP loads in Cub Run when lower base flow separation points (i.e. $\leq$ 85th percentile) were selected (Figure 3). The data suggest that the most accurate separation point for use with the Ratio Estimator Method varies with the amount of precipitation in any given year.

The Regression Method was the method that was least affected by the base flow separation point, which is an attractive feature, in that a wrong choice of base flow separation point will not decrease the accuracy of the estimate significantly. The only change that occurs in the Regression Method with the selection of base flow separation point is a shift in the designation of unsampled storm and unsampled base flows. Regardless of the designation, the unsampled flow volume during any particular day is entered into the same equation; the only difference is that the unsampled storm flow volumes on adjacent days are added. The Regression Method was the most consistently accurate method for predicting the 1996 Cub Run

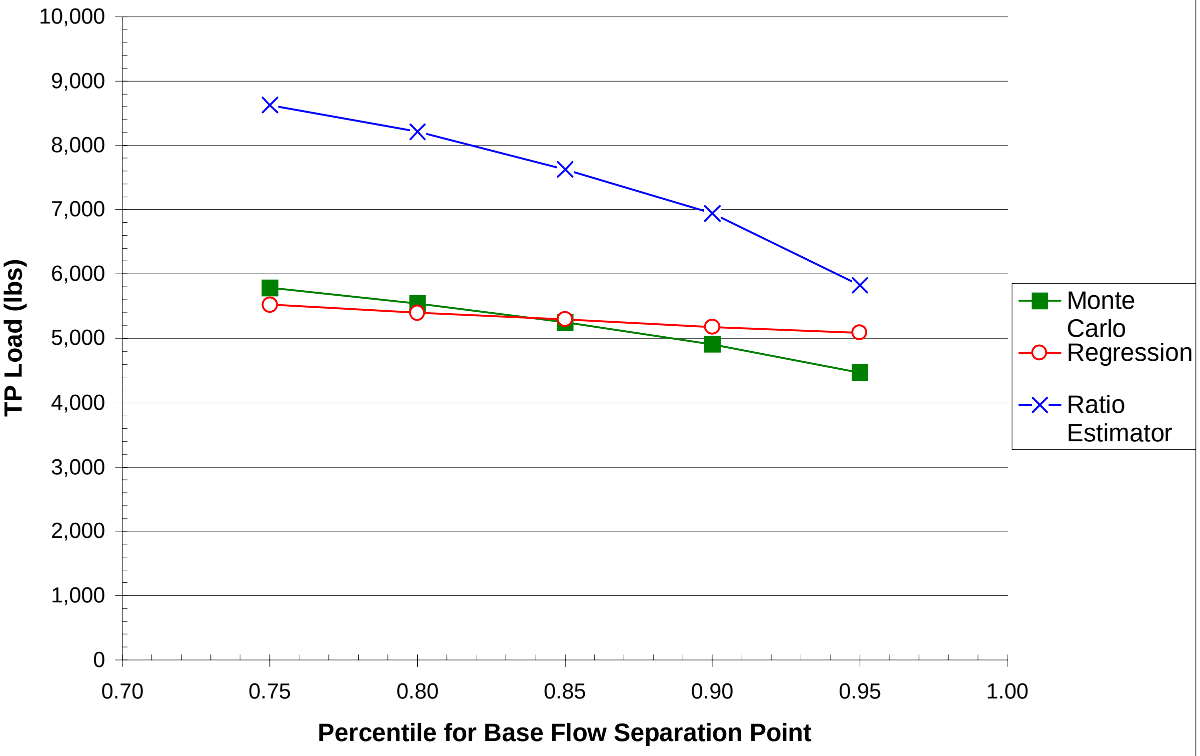

Figure 4. Swift Creek's 1996 Gaged TP Load with Varying Base Flow Separation Point.

TP load over a wide range of separation points (Figure 2). During 1997, a year of lower precipitation, the Regression Method underestimated the gaged load (Figure 3), which was also true for the 1997 Swift Creek Reservoir load prediction.

The sums of the 1996 and 1997 TP loads predicted by all four estimation methods are shown in Figure 5 in comparison to the value reported by OWML (i.e. the assumed "true load). Because of the inclusion of data from a year with high precipitation and one with low precipitation, the comparison shown in Figure 5 is useful in that it suggests which method may provide the best TP load estimates under a variety of rainfall conditions.

Loads predicted by Schueler's Simple Method are not shown to vary with base flow separation point (Figure 5) because the method does not utilize flow data. Schueler's Method underestimated Cub Run's load combined 1996 and 1997 TP load; the underestimates during 1996 and 1997 were 15.7 percent and 20.6 percent, respectively. Underestimation is the expected result because loads resulting only from storm flows are considered by this method. Despite the fact that the load estimates are based on land-use data rather than monitoring data, this method shows potential for providing rough estimates of phosphorus loadings. In the absence of sophisticated monitoring programs, planners may discover that Schueler's Simple Method provides an inexpensive tool for estimating the impacts of future land-use changes on downstream water quality. Schueler's Method was developed using data from the Washington D.C. area, and it should be noted that the accuracy of the estimates may vary when the method is used in a different geographic region.

The Monte Carlo Method consistently underestimated the combined 1996 and 1997 TP loads. As the percentile flow separation point increased, the TP load estimate decreased, as did the accuracy. The Ratio Estimator Method overestimates the load at the 75th and 80th

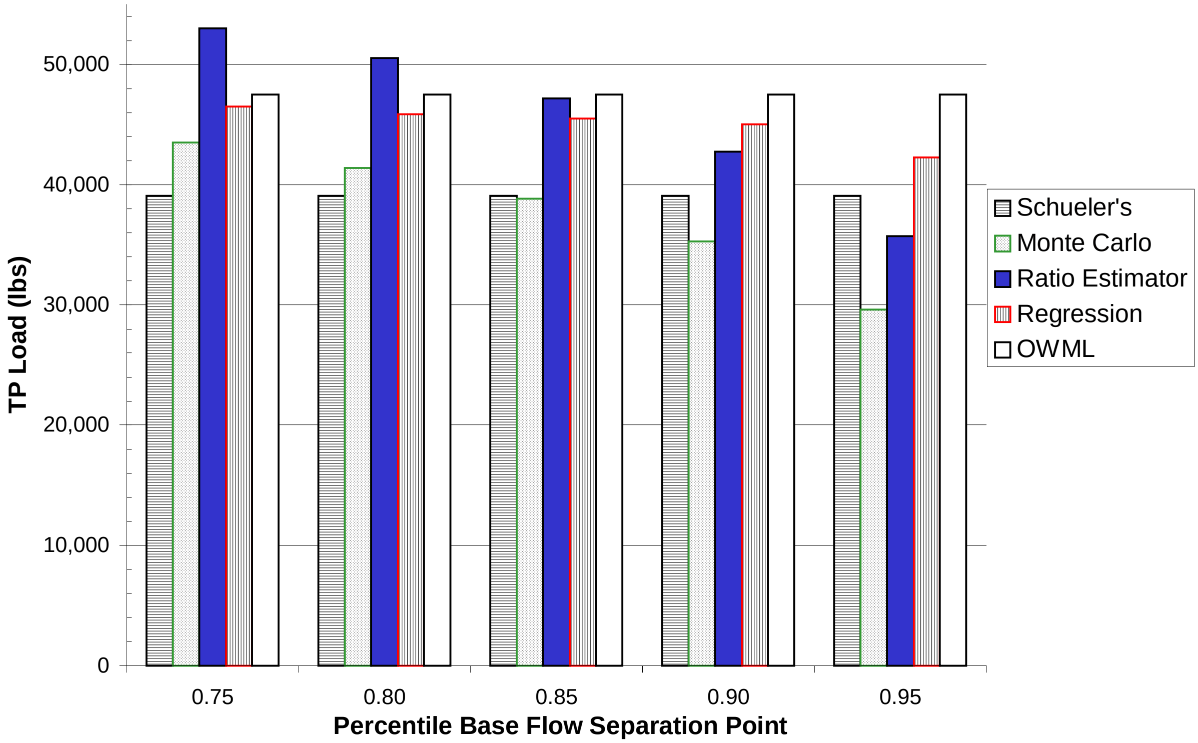

Figure 5. 1996 and 1997 Combined Cub Run Gaged Total Phosphorus Estimation Method Comparison.

percentiles, was most accurate at the 85th percentile, and underestimated the load at the 90th and 95th percentiles. The sensitivity of this method to the flow separation point is easily seen by the data in Figure 5.

The Regression Method consistently provided the best TP load estimate and was insensitive to the flow separation point; it appears to be slightly more accurate at the lower percentile flow separation points. The data suggest that the 85th percentile flow cutoff point is appropriate for use with both the Ratio Estimator Method and the Regression Method.

The optimum base flow separation point for general use in flow stratification is difficult to discern. It appears that the Monte Carlo Method provides more accurate estimates at the lower cutoff points. The best base flow separation point for use with the Ratio Estimator Method appears to depend on the annual rainfall. Also, because the Ratio Estimator Method results are extremely sensitive to the base flow separation point, a wrong choice can lead to inaccurate estimates. The Regression Method, therefore, apparently is the only method among the three that is not significantly impacted by the choice of the base flow separation point.

The Swift Creek Reservoir and Cub Run TP estimates determined by the Monte Carlo, Regression, and Ratio Estimator Methods when the 85th percentile flow separation point was used are shown in Figure 6. The 85th percentile was chosen because the TP estimates by the Regression and Ratio Estimator Methods for the combination of 1996 and 1997 loads were accurate and because it is a conservative choice based on the cumulative distributions of mean daily flows. The 1996 Swift Creek Reservoir load predicted by the Ratio Estimator Method was approximately 50 percent greater than the loads predicted by other two methods. The 1997 Swift Creek Reservoir loads predicted by the Monte Carlo Method and the Ratio Estimator Method

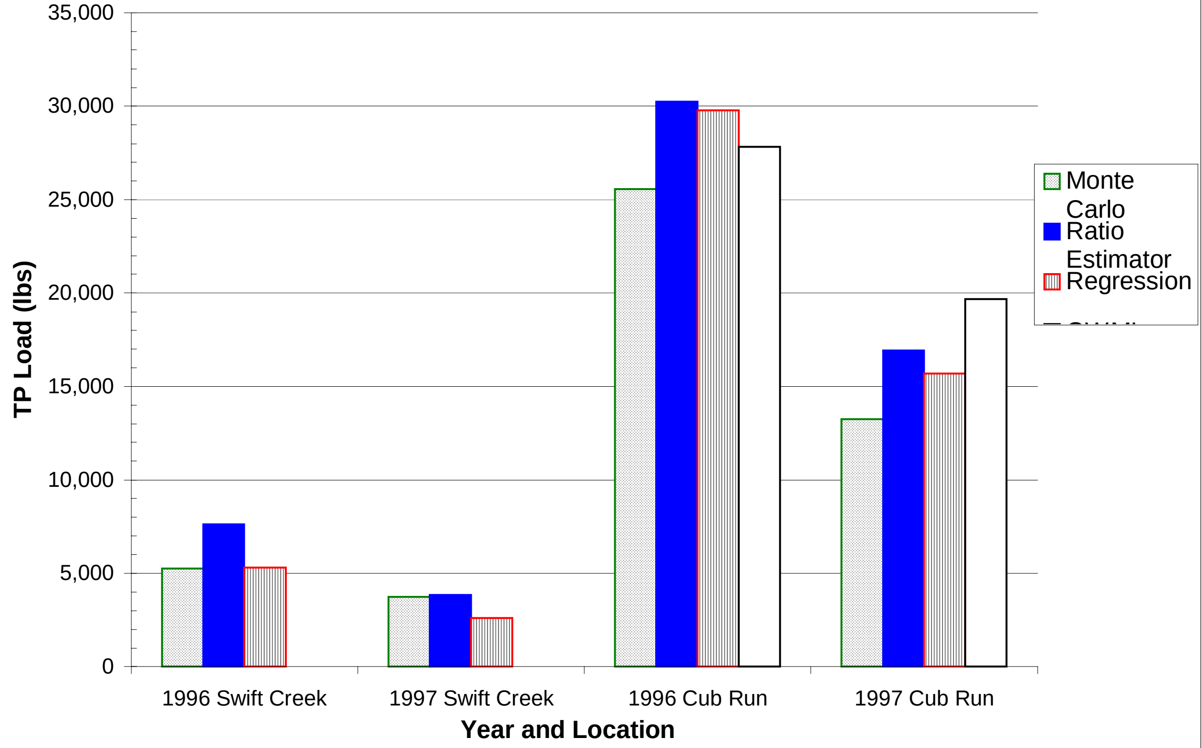

Figure 6. Gaged Total Phosphorus Estimation Method Comparison using the 85th Percentile as the Base Flow Separation Point.

were similar, but the load predicted by the Regression Method was much smaller, perhaps reflecting the influence of low rainfall on the estimate.

During 1996, the Ratio Estimator Method and the Regression Method overestimated the Cub Run load, but the load predicted by the Monte Carlo Method was much less than the "true" value. All of the methods underestimated the 1997 Cub Run load, but relative to one another, the Monte Carlo Method was the least accurate and the Ratio Estimator Method was the most accurate. The likelihood of large errors in TP load predictions appears to be greater in years with low precipitation.

Error Analysis

The standard error was the statistic used to indicate the uncertainty of each estimate; the lower the standard error, the greater the confidence that can be placed on the estimate. In general, the standard error is equal to the standard deviation of the sampling distribution of a statistic (McClave and Dietrich, 1991). Table 3 summarizes the standard errors associated with each method when the 85th percentile flow separation point was used.

For the Monte Carlo Method, the distribution of the statistic is composed of the results from the 1,000 iterations, so the standard deviation of these values is equivalent to the standard error. The standard error of the prediction by the Regression Method for one use of the developed relationship is defined as follows (McClave and Dietrich,1991):

$$s_p = s\sqrt{1+\frac{1}{n}+\frac{\left(x_p-\bar{x}\right)^2}{SS_{xx}}} \quad \ldots\ldots (7)$$

$$s = \sqrt{\frac{SSE}{n-2}} \quad \ldots\ldots (8)$$

$$SS_{xx} = \sum_{i=1}^{n} \left(x_i - \bar{x}\right)^2 \quad \text{..........} \quad (9)$$

Where:

SSE = The sum of the squared errors, (lbs of P)^2

n = Number of observations

x_i = ith observed total flow volume, (cf)

x_p = Total flow volume used for prediction, (cf)

$\bar{x}$ = Average of observed total flow volumes, (cf)

The *s* value units are log(TP, pounds) so it was first converted to pounds of TP before equation 7 was applied. Multiple uses of the regression equation in each annual estimate are accounted for by the following equation:

$$s_a = s\sqrt{n_p\left(1+\frac{1}{n}\right)+\frac{1}{SS_{xx}}\sum_{p=1}^{n_p}\left(x_p-\bar{x}\right)^2} \quad \text{..........} \quad (10)$$

Where:

s_a = Standard error of prediction of the annual load, (lbs of P)

n_p = Number of uses of the regression equation

Loads in nine tributaries comprise the total Swift Creek Reservoir load, so the values of s_a were determined for each and squared to express the variances. The variances were then added together and the square root was calculated to find the standard error associated with the combined annual tributary loads.

TABLE 3. Load Estimates and Standard Errors in Pounds of TP using the 85th Percentile Base Flow Separation Point.

Location and Year		**Ratio Estimator**	**Monte Carlo**	**Regression**
Swift Creek 1996	TP Load	**7,627**	**5,248**	**5,295**
	Standard Error	**58.3**	**347.4**	**173.2**
Swift Creek 1997	TP Load	**3,834**	**3,753**	**2,620**
	Standard Error	**40.6**	**155.5**	**103.3**
Cub Run 1996	TP Load	**30,233**	**25,573**	**29,797**
	Standard Error	**108.7**	**3,080.4**	**47.3**
Cub Run 1997	TP Load	**16,934**	**13,259**	**15,701**
	Standard Error	**182.3**	**1,435.0**	**34.0**

The estimated mean square error for the Ratio Estimator Method is defined by the following equation (Lang *et al.*, 1988):

$$E = m_y{}^2 \cdot \left[\begin{array}{l} \dfrac{1}{n} \cdot \left(\dfrac{S_x{}^2}{m_x{}^2} + \dfrac{S_y{}^2}{m_y{}^2} - 2\dfrac{S_{xy}}{m_x m_y} \right) + \\ \dfrac{1}{n^2} \cdot \left(2 \cdot \left(\dfrac{S_x{}^2}{m_x{}^2} \right)^2 - 4\dfrac{S_x{}^2}{m_x{}^2}\dfrac{S_{xy}}{m_x m_y} + \left(\dfrac{S_{xy}}{m_x m_y} \right)^2 + \dfrac{S_x{}^2}{m_x{}^2}\dfrac{S_y{}^2}{m_y{}^2} \right) \end{array} \right] \qquad (11)$$

The variables are the same as those defined in the Load Calculation Methods section with the addition of:

$$S_y{}^2 = \frac{1}{(n-1)} \sum_{i=1}^{n} y_i{}^2 - n m_y{}^2 \qquad (12)$$

The square root of the estimated mean square error (E) is the estimated standard error of the mean (Lang *et al.*, 1988). Separate estimated mean square errors were found for each flow stratum, E_{high} and E_{low}. The estimated mean square error for the total annual load was found by:

$$E_{total} = d_{high} E_{high} + d_{low} E_{low} \qquad (13)$$

Where:

d_{high} = Number of days in the year when flows were considered to be high

d_{low} = Number of days in the year when flows were considered to be low

The standard error of the annual load estimate is equivalent to the square root of E_{total}. The Swift Creek Reservoir tributaries' E_{total} values were summed and the square root was taken, resulting in the estimated standard error of the total gaged annual load to the Reservoir.

The standard errors associated with the Swift Creek Reservoir estimates were greater relative to the magnitude of the load estimates than those associated with the Cub Run estimates.

The differences were due to the fact that nine Swift Creek Reservoir tributary loads were estimated and combined compared to only one for Cub Run. The standard errors in 1996 were generally higher than those in 1997 because 1996 was a wetter year; therefore, the loads and the flow fluctuations were greater. The only method that generated estimates with relatively high standard errors was the Monte Carlo Method. If only one iteration of this method were used, the result could be quite different from the mean of the distribution of results, which is the reason the median value of 1,000 iterations was used as the final result of the Monte Carlo Method during this study.

Application of Methods

The simplicity of phosphorus load estimation techniques should be considered when one is choosing a method. Some factors important to the method selection include available computing power, the available time for computations, and most importantly, the available data.

Execution of Schueler's Method requires only current land-use data and annual rainfall amounts. If no major land-use changes have occurred from one year to the next, the only change in the predicted loadings will be a result of variations in rainfall. This method, therefore, is the most inexpensive method if land-use information is available because the only measurements required every year is the rainfall. Using a spreadsheet, one can recalculate the load estimates each year by simply changing the rainfall amount.

The Ratio Estimator Method is best set up on a computer spreadsheet. Once the spreadsheet is established, applying the method to a new year's data is straightforward. After a spreadsheet is designed for application of the Monte Carlo Method, it also is easy to apply to a new year's data. The Monte Carlo Method does require more computations than the other three methods, but they can be programmed and performed automatically. As an example of the numbers of computations that may be needed, for every tributary annual-load estimate, 365 phosphorus concentrations are randomly sampled. With the use of 1,000 iterations for nine tributaries, the computations quickly add up.

The Regression Method is more labor intensive on a year-to-year basis. The general structure of the previous year's spreadsheet can be used, but the regression relationship needs to be redeveloped from the new sampled storm and base flow data for each tributary for that year. The new relationship then must be applied to all the unsampled flow volumes to estimate the TP load.

Storm Event Sampling

The key difference between this research and the majority of the studies described in the literature was that the flow-weighted composite storm sampling method was used instead of simple grab sampling. Even in this study, the only method that pairs the total storm flow volume and the phosphorus EMC in calculations of the phosphorus load associated with each storm runoff event is the Regression Method.   Loadings estimated by the Monte Carlo Method involved use of the EMCs in the storm-flow TP concentration database, from which values were randomly selected for calculations of the daily loads. Data used in estimating the mean daily storm flow load by the Ratio Estimator Method included phosphorus concentrations equal to the EMC and a flow equal to the mean daily flow. Grab-sample TP concentrations could have been used instead of the EMC when the Monte Carlo Method and the Ratio Estimator Method were applied; therefore, flow-weighted composite storm sampling is not a requirement for application of these methods. Use of an EMC instead of a grab-sample concentration, however, is still beneficial because it is more representative of the overall concentration in the entire flow volume on any given day.

CONCLUSIONS

1. Schueler's Simple Method gave reasonable rough estimates of gaged phosphorus loads in Cub Run during 1996 and 1997 without the use of monitoring data. This method can be a valuable tool to complement an existing monitoring program for the prediction of loads from future development scenarios. Schueler's Method was developed based on data in the Washington D.C. area, so the estimates resulting from applications in other geographic regions may not be as accurate as those found in this study.

2. The Monte Carlo Method underestimated loads for a year with above average rainfall and for a year with below average rainfall in this study; this method most likely underestimates TP loads for years with all levels of rainfall amounts. The Monte Carlo Method is sensitive to the base flow separation point, and the selection of lower percentile base flow separation points (e.g. $\leq$ 85th percentile) helps reduce the degree of underestimation.

3. The Ratio Estimator Method also is sensitive to the base flow separation point, and the optimum point depends on the amount of rainfall. Application of a lower cutoff point produces a more accurate estimate in years when rainfall is below normal. In contrast, application of a higher cutoff point produces a more accurate estimate in years when rainfall is above average.

4. The Regression Method is the least sensitive of those tested to the base flow separation point. This is an attractive feature because a wrong choice will not significantly affect the load estimate. This is the only method that takes full advantage of flow-weighted composite

data by pairing the total storm flow volumes and the associated total phosphorus EMCs for calculation of TP loads from sampled storm events. Predictions of the combined loads during 1996 and 1997 were more consistently accurate than either of those predicted by the Monte Carlo or Ratio Estimator Methods over a range of base flow separation points. The Regression Method, however, does tend to underestimate loads during years when precipitation is below normal.

5. No clear optimum base flow separation point for flow stratification could be identified. Selection of the 85th percentile seemed to produce reasonable TP load estimates when the Regression Method and the Ratio Estimator Method were used to estimate the combined Cub Run load during 1996 and 1997. Also, the cumulative probability distribution plots of mean daily flows seemed to change drastically at approximately the 85th percentile indicating that the flows were no longer base flow.

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