Literature Review

This section will briefly explain the relevant background information for this study. Included are: (1) the importance of phosphorus in surface waters, (2) descriptions of (a) Swift Creek Reservoir and its watershed, (b) Cub Run, a tributary to the Occoquan Reservoir, and (c) their respective current monitoring programs. In addition, two examples of commonly used water quality models that incorporate estimated phosphorus loads are presented, and finally, previous research on phosphorus load-estimation methods as it pertains to the methods used in this study is discussed.

Phosphorus in the Aquatic Environment

Importance of Phosphorus

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 nutrients entering a water body from runoff. As excess nutrients enter a water body a process of enrichment known as eutrophication occurs, the results of which are increased productivity of plant life and water-quality degradation. Some common symptoms of a eutrophic lake or reservoir are anaerobic bottom water, algal blooms, prolific aquatic plants, increased populations of bottom-dwelling fish, and iron and manganese in the water column (Cooke, 1989).

The trophic state describes the condition of a lake or reservoir in terms of its nutrient enrichment. Besides eutrophic, a lake can be considered oligotrophic, mesotrophic, or hypertrophic. An oligotrophic lake is one with clear, pristine water and minimal plant life that would be an ideal drinking water source. Mesotrophic is the lake classification that falls between oligotrophic and eutrophic. Lakes overrun by aquatic plants and algae are considered hypereutrophic.

The influx of excess nutrients, especially nitrogen and phosphorus, to a water body starts a cycle of water-quality degradation that is difficult to break. Algae utilize the nutrients for growth, and when the algae die, they settle to the bottom of the lake or reservoir. The organisms that degrade the dead algae exert an oxygen demand that removes oxygen from the water, and if the bottom water becomes anaerobic, a reducing environment is created and phosphorus that is incorporated in the sediments can be released into the water column. Mixing of this released phosphorus with the entire lake volume starts the process over again, as algae can then use the phosphorus previously bound to the sediments. This process is called "internal loading" or "internal fertilization".

If the water body is a drinking water supply, eutrophication can cause problems during the treatment process. Algae can cause taste-and-odor problems, clog filters, and their extracellular products, if chlorinated, can create trihalomethanes (THMs) and other disinfection by-products (DBPs). Trihalomethanes are believed to be carcinogenic and are by-products of reactions between chlorine and organic matter. Hoehn *et al.* (1980) discovered that algal extracellular products can serve as THM precursors. Currently, the maximum contaminant level (MCL) for THMs is 0.10 mg/L, but the proposed Disinfectant/Disinfection Byproduct (D/DBP) Rule will lower the MCL to 0.080 mg/L. Stage one of the D/DBP Rule is to be promulgated in November, 1998, and compliance will be difficult for water utilities that rely on eutrophic source waters. This rule will make the quality of source water even more important.

Iron and manganese are nuisances but not health threats in drinking water, but they will stain clothing and fixtures and clog pipes if allowed into a distribution system. Manganese is especially difficult and expensive to remove during the treatment process. These problems are most always worse during warm summer months when deep, eutrophic reservoirs are thermally stratified.

Algae in most fresh water supplies are phosphorus limited. In other words, phosphorus is the nutrient that is usually in the shortest supply among the essential nutrients that algae need for growth. For this reason, the phosphorus concentration is crucial for water quality management. One reason phosphorus is often limiting is that it is lost from the water column by sedimentation of both inorganic and organic forms (Cooke, 1989).

Sources of Phosphorus

Phosphorus entering a lake or reservoir can originate from both point and nonpoint sources. In regions where there is no phosphate detergent ban, effluents from laundering and other cleaning operations can be significant inorganic phosphorus sources, usually delivered to receiving streams in domestic wastewater effluents. Domestic wastewater, therefore, is a point source of inorganic phosphorus and organic phosphorus from human excreta and food wastes as well.

Nonpoint phosphorus sources often contribute the majority of the phosphorus load to a reservoir or lake because they are not regulated as stringently as effluents from industries or wastewater treatment plants. Fertilizers often contain large amounts of inorganic phosphorus, and runoff from fertilized agricultural fields or residential land will contain elevated phosphorus concentrations. Fields fertilized with manure and animal feedlots can produce runoff with severely inflated phosphorus concentrations. Concentrations of total phosphorus in runoff from an animal feedlot can be in the range of 47 to 300 mg/L (Novotny, 1994).

Agricultural best management practices (BMPs) are important components of a phosphorus control program. Restricting livestock from entering streams is a good first attempt at control. Livestock walking in a stream can erode the stream-bank soils and add waste directly to the water. Another basic technique is allowing a buffer strip of land that is not plowed along the edge of streams. These strips prevent stream-bank erosion and also provide some filtering of runoff from adjacent fields (Novotny, 1994).

Phosphorus Forms

Phosphorus found in nature consists mainly of phosphates, and the forms are operationally defined. Classification is based on whether a reaction with an ammonium molybdate reagent under acid condition occurs or does not occur. The reaction can be with or without a prior oxidation step during analysis. Filtration through a 0.45 micrometer (μm) membrane filter is defined as the separation of dissolved from particulate forms (APHA, 1995).

Total phosphorus (TP) is the form most commonly measured and, as the name implies, is the total amount, both organic and inorganic, measurable in the water sample. Operationally, TP is the amount of phosphorus that reacts with the molybdate reagent after the oxidation of organic phosphorus to inorganic phosphorus. Some forms of phosphorus are not oxidized, but they are extremely unreactive, and, therefore, are not significant.

Soluble reactive phosphorus (SRP) is a phosphorus form that is often reported and is considered to be the form of phosphorus that is most readily available for biological growth. Operationally, SRP is the phosphorus form that reacts with the molybdate reagent without oxidation and that passes through a 0.45 (μm) membrane filter. It is not uncommon for the SRP concentration to be below detection in a phosphorus-limited system because it is used quickly by algae and higher aquatic plants. In many instances, SRP is reported as orthophosphatephosphorus (OP), but SRP is a more inclusive term because complex inorganic phosphates are usually hydrolyzed during the test and are included in the analysis.

The other forms of phosphorus are not measured as often as TP and SRP and include soluble unreactive phosphorus (SUP), particulate phosphorus, and bioavailable phosphorus (BAP). Soluble unreactive phosphorus is not readily available for plant growth and the analysis is a measure of the organic or colloidal phosphorus. Particulate phosphorus is unable to pass through a 0.45 μm membrane filter. A small fraction of particulate phosphorus can be used by algae for growth. Phosphorus described as "bioavailable phosphorus" includes all the forms that plants can use either directly or indirectly for growth (Cooke, 1989).

Swift Creek Watershed and Reservoir

The Swift Creek Watershed lies outside of Richmond, Virginia, and serves as a drinking water source for Chesterfield County, Virginia. The watershed covers approximately 65 square miles, 85 percent of which lies in Chesterfield County with the remaining in Powhatan County (CDM, 1990).

The Reservoir was constructed in 1966 by an earth fill dam. The most recent Swift Creek Reservoir morphological data (OWML, 1998a) include: surface area, 2.47 square miles (mi^2); volume, 6×10^8 cubic feet (ft^3); and mean depth, 8.73 feet (ft).

Figure L-1 shows a map of the Reservoir and its tributaries. Its two main tributaries are Dry Creek and Swift Creek, which form the two arms of the Reservoir. West Branch, Dry Creek, and Ashbrook Creek all enter the Dry Creek arm, while Little Tomahawk Creek,

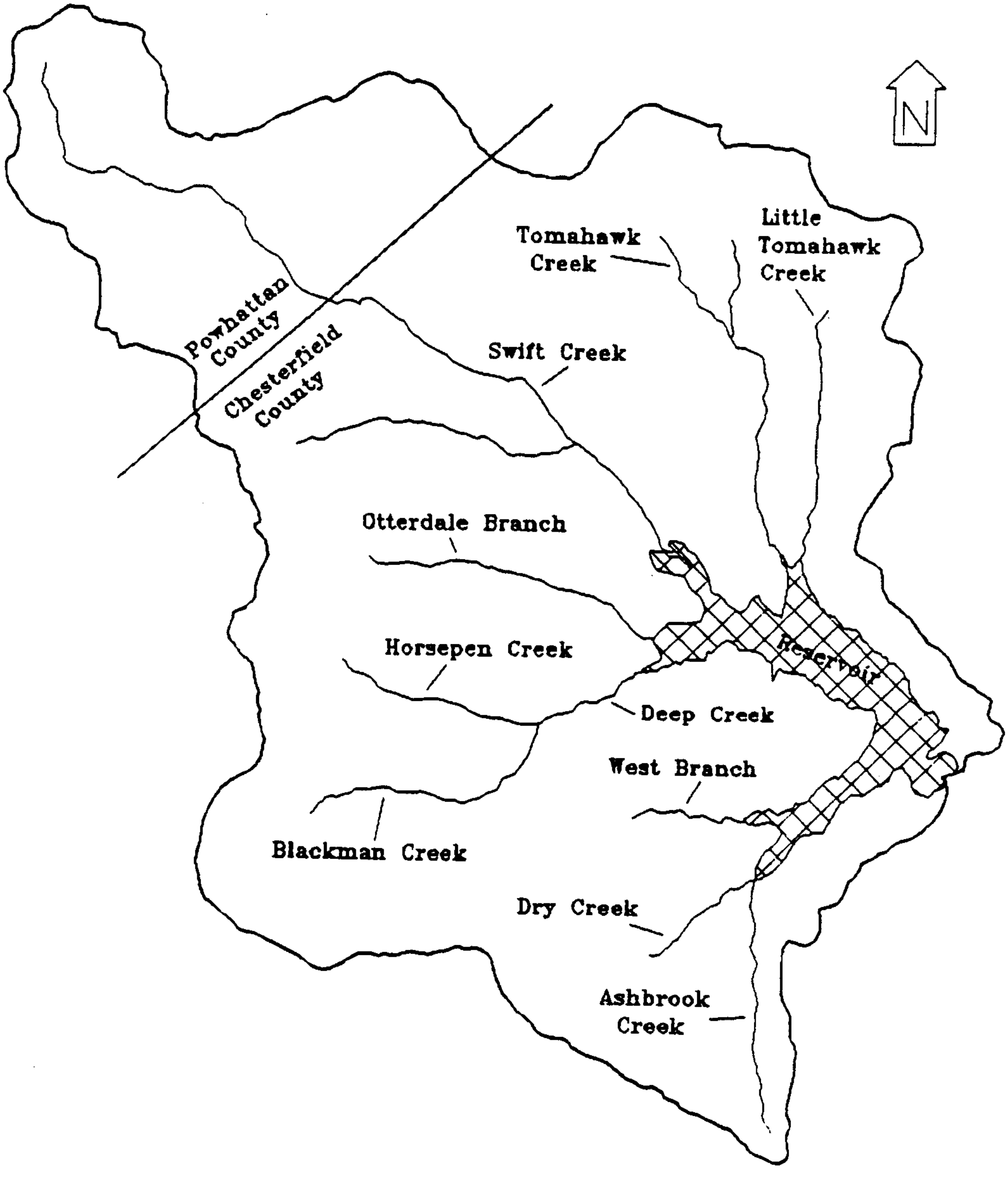

Figure L-1 Swift Creek Reservoir and Watershed (altered from Smock, 1989)

Tomahawk Creek, Swift Creek, Otterdale Creek, and Deep Creek all discharge into the Swift Creek arm. Two tributaries, Horsepen Creek and Blackman Creek, converge to form Deep Creek. These two tributaries have their own sampling stations which represent the drainage area of Deep Creek. The tributaries to the Swift Creek arm (the main stem) drain approximately 75 percent of the watershed, and the tributaries to the Dry Creek arm drain approximately 13 percent. Direct drainage area surrounding the Reservoir accounts for the remaining 12 percent of the watershed area.

Swift Creek is the largest tributary and drains one-third of the watershed. It is considered a perennial stream, meaning it can have flow during drought conditions. However, during 1997, which was a dry year, there was a significant amount of time with no flow in Swift Creek. Flows in the other streams are variable, and during summer months, periods of no flow are to be expected. Base flow accounts for 50 to 60 percent of the annual flow into the Reservoir, with storm flows contributing the remaining discharge (OWML, 1997).

The watershed remains relatively rural and undeveloped. In 1990, 85 percent of the watershed was still classified as either forest or idle land (CDM, 1990). Most of the urban development during the past few years has occurred in the direct-drainage area to the Reservoir. Pressure to develop parts of the upper portion of the watershed has increased in recent years as the Richmond suburbs continue to grow. Potential development has prompted concern over future reservoir water quality because the Reservoir is valued as both an aesthetic addition to the community and a valuable drinking water source. In the early 1980's, the Chesterfield County Department of Utilities established a monitoring program designed to document water-quality changes in the Reservoir and provide the basis for rational decisions regarding future watershed development. The County has vastly improved the monitoring program over the years because it recognized that development decisions can have large financial impacts, and therefore, the decisions must be based on sound, reliable data.

Swift Creek Reservoir is phosphorus limited, meaning that phosphorus is the nutrient in the shortest supply among the nutrients that algae need to grow. Phosphorus limitation is evident by total nitrogen to total phosphorus ratios greater than 10:1 by weight (Cooke, 1989). Smock (1989) concluded that phosphorus was limiting in Swift Creek Reservoir after performing tests on algae and water taken from the Reservoir in 1989. He used *Selenastrum capricornutum* for the algal assays and followed the Algal Assay Procedure (National Eutrophication Research Program, 1971.) After adding phosphate, nitrate, or the combination of the two, he observed the algae growth response. With phosphate addition, the population growth showed a statistically significant increase compared to the population growth when nitrate was added. When both nutrients were added together, the growth was at its maximum indicating that nitrogen levels are also important to the algae population in Swift Creek Reservoir (Smock, 1989).

Monitoring Program

Because Swift Creek Reservoir is phosphorus limited, one of the main objectives of the monitoring program has been to quantify the phosphorus mass entering it from its watershed. Phosphorus inputs can originate from the tributaries or directly either as dryfall, wetfall, or through direct runoff; the largest source is from the tributaries. This research involved determining the best technique for quantifying the phosphorus load entering Swift Creek Reservoir from its tributaries. Regular tributary monitoring began in 1991, and the monitoring program has improved greatly since then.

Originally only grab samples were collected for both storm water runoff and base flow analyses, but since 1995, automated sampling techniques have been used to collect composite samples during runoff events. Each of the nine tributaries has a flow meter that measures the instantaneous flow rate at five-minute intervals. The flow values measured during these five-minute intervals are used in calculations of the mean daily flows in each tributary.

The United States Geological Survey (USGS), under contract with Chesterfield County, developed water budgets for Swift Creek Reservoir in 1996 and 1997, and improved the rating curves at each tributary station. A rating curve is the relationship between the stage or water level in a stream to the flow rate. Several areas of the streambeds in the tributaries to Swift Creek Reservoir consist of sand, which makes the cross-sections unstable. These conditions make the development of accurate rating curves quite difficult.

Beginning in May, 1995, flow-weighted composite samples were collected by autosamplers at all nine major tributaries as part of a program to improve the estimate of phosphorus entering the Reservoir during storm events. The autosamplers operate with an "equal-flow" approach. After a designated volume of water passes the sampler during a runoff event, an aliquot is automatically collected and stored in a bottle housed within the autosampler. This process is repeated until the end of the storm event. A composite of all the samples collected during the runoff event will contain phosphorus (and other constituents) at a concentration that is representative of the concentration over the entire storm event. This concentration is called the event mean concentration (EMC). The flow meters calculate the total storm flow volume by a real-time analysis of the instantaneous flow. The EMC can then be multiplied by the calculated total storm flow volume to find the total phosphorus load for that storm event.

Storm flow load estimates based on flow-weighted composite analyses are more accurate than those based on grab sample analyses. The highest concentrations of phosphorus during a runoff event usually occur on the rising limb of the hydrograph as the flow continues to increase and nutrients are flushed from the watershed. Analyses of grab samples can give inaccurate storm load estimates if it is unknown what portion of the hydrograph the sample represents. Base flow phosphorus concentrations in Swift Creek Reservoir's tributaries continue to be determined by analyses of grab samples collected approximately every two weeks.

Prior to October, 1996, phosphorus loads from direct runoff areas surrounding Swift Creek Reservoir were estimated from phosphorus concentration in grab samples collected at only four locations. After October, 1996, twelve sites deemed to be more representative of the direct runoff area were established by USGS, and grab samples were taken only quarterly from then on. In addition, permanent weirs were constructed in two ditches that carry a significant portion of the direct runoff into the Reservoir. Autosamplers were placed at these two sites, and beginning in early 1997, flow-weighted composite samples were collected during stormwater runoff events.

The monitoring program provided the data necessary for calculating the phosphorus loads. Event mean phosphorus concentrations, mean daily flows, and total storm flow volumes were determined for storm runoff events. Grab sample concentrations and mean daily flows were found for base flows.

Cub Run

Cub Run is a tributary to the Occoquan Reservoir, which is a major drinking water supply in northern Virginia. Due to rapid development within its watershed and the addition of wastewater treatment plants whose effluents entered its basin, Occoquan Reservoir was found to be highly eutrophic by the mid to late 1960's, and was in danger of being irreversibly damaged. As a result, a comprehensive watershed monitoring program was mandated by the Virginia State Water Control Board in 1971, and the program was established in 1972. This program is conducted by the Occoquan Watershed Monitoring Laboratory (OWML), which is part of the Charles E. Via Department of Civil and Environmental Engineering at Virginia Tech (OWML, 1998).

The Cub Run drainage area is 49.9 mi^2, an area that is comparable to the entire drainage area of all the tributaries to Swift Creek Reservoir. As a result, the discharge in Cub Run is much greater than the discharge in any single tributary to Swift Creek Reservoir. Cub Run monitoring data served as a control during this research project because they were derived from a comprehensive, highly reliable monitoring program. The Cub Run phosphorus loads that OWML determined by its estimation method was considered to be the "true" load. In this thesis, 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.

Phosphorus loadings during Cub Run's stormwater runoff events were calculated on the basis of EMC concentrations determined from the analysis of flow-weighted composite samples by a method similar to the method used in the Swift Creek Reservoir monitoring program. The flow meter calculated the total storm flow volume and the autosampler collected a sample from which the event mean phosphorus concentration could be determined. The flow meter also provided mean daily flow values. Base flow concentrations were determined by analyses of grab samples collected approximately weekly during 1996 and 1997.

The numbers of sampled runoff events and base flow sampling events in Cub Run far exceeded those in the Swift Creek Watershed during 1996 and 1997. Obviously, the more data that are available, the more reliable the phosphorus load estimate will be. Table L-1 shows the numbers of sampled storm events and base flow grab samples collected during both years.

Table L-1. Numbers of Sampling Events in Cub Run and Swift Creek Watershed during 1996 and 1997.

Event	1996	1997
Storms Sampled		
Cub Run	29	16
Swift Creek	16	8-12*
Base flows Sampled		
Cub Run	31	40
Swift Creek	15-16*	12-15*

* Number varied depending on the tributary

The method used by OWML to find Cub Run's "true" load included multiplying the EMC by the total storm flow volume to find the storm flow loads. Base flow loads were calculated by multiplying the average of two consecutive sample concentrations and flows, then multiplying the product by the sampling interval:

$$BaseTPload = \frac{(C_1 + C_2)}{2} \times \frac{(Q_1 + Q_2)}{2} \times (t_2 - t_1) \text{ .... (1)}$$

Where:

C_1 and C_2 = P concentrations

Q_1 and Q_2 = Instantaneous flow rate when grab sample was taken

t_1 and t_2 = Times when base flow samples were taken

If a storm occurred between base flow samples, its duration was subtracted from the time interval between grab samples, (t_2 - t_1) (Post, 1998).

Water Quality Models

Several predictive techniques (models) have been developed to evaluate the effect of phosphorus loads on the in-lake phosphorus concentration, and they are often used in watershed development decisions. As noted earlier, if phosphorus is the limiting nutrient, the in-lake phosphorus concentration will control algal growth. The input-output or mass-balance approach is the most common, but as in all modeling efforts, the results are only as accurate as the phosphorus load data that are used in them.

Input-output models are simple and easy to apply. This section will describe two of the most common input-output models, both of which have been previously applied to Swift Creek Reservoir. In these models, the water quality of the lake is estimated on the basis of the phosphorus flux into and out of the system. The lake is assumed to be well-mixed and the concentration of phosphorus is assumed to be constant throughout. In terms of reactor theory, the lake is considered a continuously stirred tank-reactor (CSTR). Two additional assumptions are: (1) that any load is instantaneously mixed throughout the lake and (2) the output flow has the same concentration as the in-lake concentration. If the effluent from a point source discharges directly into the lake, the "well-mixed" assumption may be violated. The control volume for the input-output models is the entire lake. Figure L-2 is a schematic of the control volume of a lake represented as a CSTR. The mass balance for any given time can be written as:

Accumulation of P = Input of P - Output of P - Reactions .... (2)

Examples of reactions that result in a loss of phosphorus are sedimentation, plant uptake, and biological transformation. The reaction term also encompasses the addition of P from internal sources. There may in fact be a net increase of phosphorus in the lake caused by internal loading from the sediments.

Vollenweider

Vollenweider (1969) developed a steady-state solution to a phosphorus mass balance equation that is the basis for many other models. He utilized the inverse relationship between water quality and a lake or reservoir's mean depth. He plotted the annual areal phosphorus load vs. the mean depth of several water bodies from which he dilineated trophic states based on observations of the water bodies' water quality characteristics. The annual areal phosphorus load is the mass of phosphorus entering the water body in a year divided by its surface area.

Vollenweider (1975) modified his original input-output model to include the effect of the hydraulic residence time of a reservoir on the water quality. A water body with a shorter hydraulic residence time can assimilate larger phosphorus loads without exhibiting water quality

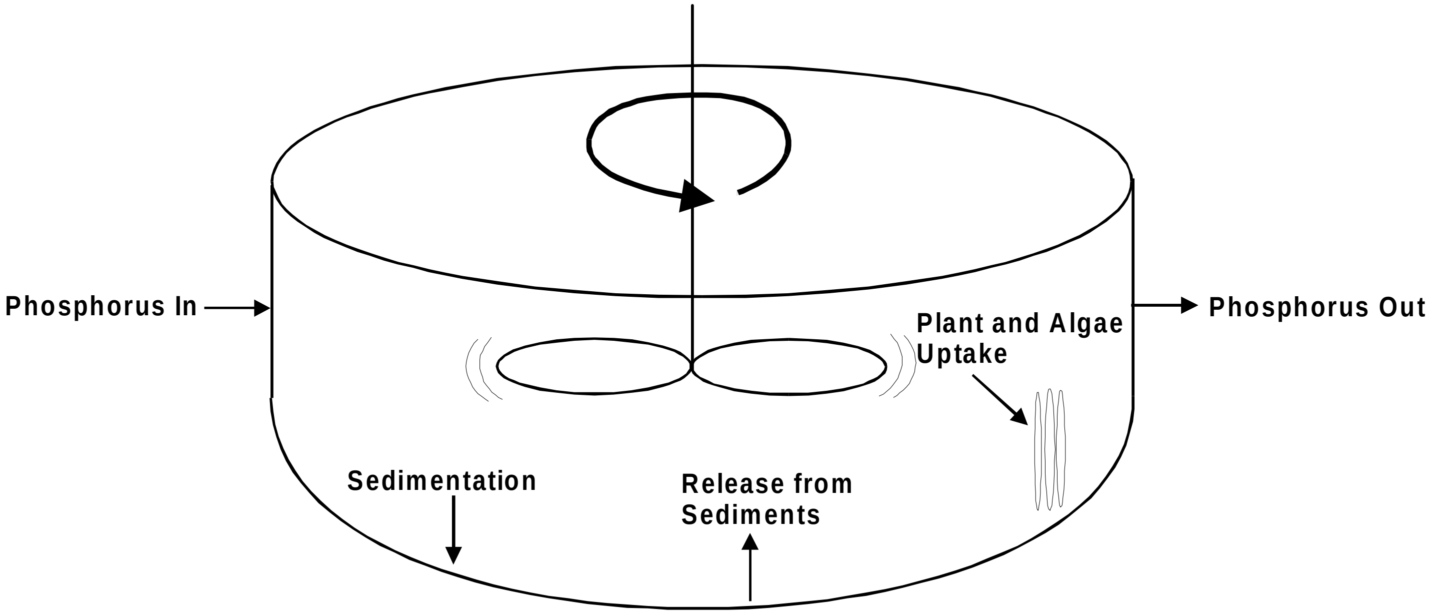

Figure L-2. Schematic of Phosphorus Balance Used in Input-Output Models.

problems. The assumptions for the mass balance according to Thomann and Mueller (1987) are the following: the lake is completely mixed, steady state conditions exist, phosphorus is the limiting nutrient, and total phosphorus can be used to gauge the trophic state. Despite these simplifying assumptions, the Vollenweider model (1975) is quite useful. The equation that Vollenweider used to determine the in-lake concentration based on the loading is the following:

$$P = \frac{L}{10 + \frac{z}{\tau}} \quad (3)$$

Where:

P = In-lake phosphorus concentration (g/m^3)

L = Areal phosphorus loading rate using the surface area of the lake (g/m^2/yr)

z = Mean depth of lake (m)

τ = Hydraulic residence time (years)

Equation 3 incorporates the loss of phosphorus by sedimentation only, and the net effective settling velocity is assumed to be 10 m/yr. The areal phosphorus loading rate is the parameter that is affected by the phosphorus load estimation technique. Vollenweider proposed certain concentrations of phosphorus that he deemed "acceptable" or "excessive." The acceptable level is 0.010 mg-P/L and was set as the boundary between oligotrophy and mesotrophy. The excessive level is 0.025 mg-P/L and separates what are considered mesotrophy and eutrophy. The upper boundary between eutrophy and hypereutrophy is 0.06 mg-P/L (EPA, 1988). From these values, the areal phosphorus loading rate for acceptable or excessive in-lake phosphorus levels can be found:

$$L_{10} = 0.01(10 + z/\tau) \quad (4)$$

$$L_{25} = 0.025(10 + z/\tau) \quad (5)$$

$$L_{60} = 0.06(10 + z/\tau) \quad (6)$$

A log-log plot of the areal loading rate vs. the mean depth/residence time gives a graphical representation of the trophic state of the lake or reservoir. Figure L-3 is an example of the Vollenweider plot (OWML, 1997). The required phosphorus load reduction to change the lake from eutrophic to mesotrophic can be determined directly from the chart. This graphical representation is the most valuable attribute of the Vollenwieder (1975) model, but some caution should be taken not to consider the result as an absolute indication of trophic state. This model is only as accurate as the phosphorus loading estimate, and these estimates are often quite poor. Also, eutrophication is affected by other variables such as sunlight, climate, and mixing.

Reckhow

Reckhow (1988) developed a phosphorus input-output model that incorporated data from lakes and reservoirs in the southeastern U.S. Previously, most lake studies were performed in northern temperate climates. Both Swift Creek Reservoir and the Occoquan Reservoir fall in the geographical area considered by Reckhow. The mass balance equation for Reckhow's model is:

$$V(dP/dt) = M - QP - kPV \quad (7)$$

Where:

$V(dP/dt)$ = Phosphorus accumulation

V = Lake volume (m^3)

P = Phosphorus concentration (mg/L)

M = Annual phosphorus loading (g/yr)

Q = Annual hydraulic loading (m^3/yr)

k = Nutrient trapping parameter (yr^{-1})

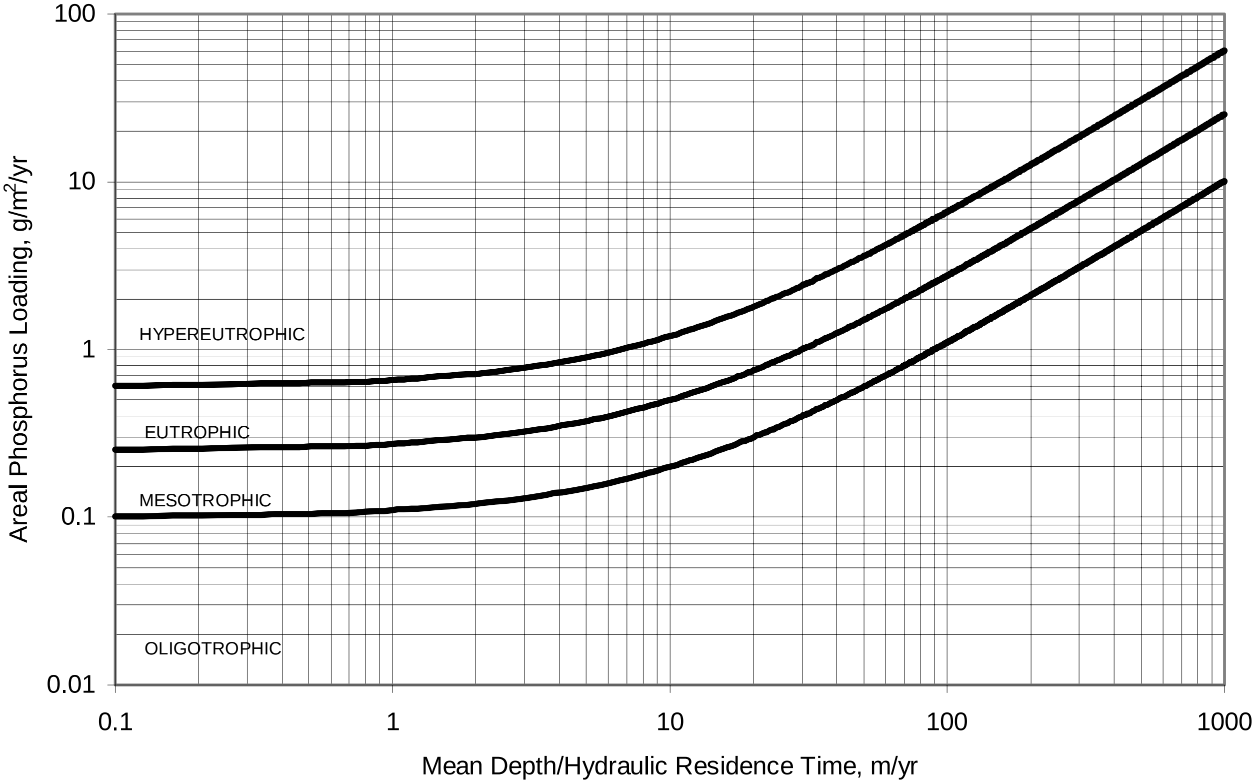

Figure L-3. Vollenweider Model (1975) Plot (altered from OWML, 1997)

At steady state, the accumulation equals zero, so equation 7 can be written as:

$$M = QP + kPV \quad (8)$$

From this, the in-lake phosphorus concentration can be expressed as:

$$P = \frac{M}{Q + kV} \quad (9)$$

Note that M/Q = P_{in}, the phosphorus concentration in influent (mg/L) and V/Q = T_w, the hydraulic retention time (yr). When these relationships are substituted into equation 9, the final result is:

$$P = \frac{P_{in}}{1 + kT_w} \quad (10)$$

The nutrient trapping parameter, k, was calibrated to fit data sets from 70 lakes and reservoirs in the southeast obtained from the U.S. Environmental Protection Agency's National Eutrophication Survey. The statistical best fit for k was found to be:

$$k = 3.0(P_{in})^{0.53}(T_w)^{-0.75}(z)^{0.58} \quad (11)$$

The phosphorus-trapping coefficient was, therefore, found to be a function of the influent P concentration, the hydraulic retention time in the lake, and the mean depth (z) (Reckhow, 1988).

The resulting in-lake phosphorus concentration derived from Reckhow's model can be compared to literature values of typical phosphorus concentrations for determination of the trophic state. Reckhow's model is most likely more accurate for finding the in-lake P concentration in Swift Creek Reservoir and Occoquan Reservoir than Vollenweider's model because Reckhow's model was calibrated on lakes with similar climates.

Phosphorus Load-Estimation Techniques

The phosphorus load-estimation techniques described in the literature fall into two major categories; those which utilize site-specific data derived from a monitoring program, or those which utilize land-use information. After a monitoring program is established at a significant financial cost, it is hoped that the use of the monitoring program data leads to a more accurate estimate than methods based on land use alone. Four phosphorus load techniques will be discussed, three that incorporate monitoring data and one that relies on land-use data.

Monte Carlo Method

Monte Carlo Simulation (MCS) methods were first developed in the 1940s as a numerical technique. They were used to solve complex sets of equations that could not be solved by hand. Now that personal computers are more common and powerful, MCS has become more popular (Bobba *et al.*, 1996).

Monte Carlo Simulation is most often used in model error analysis. It is a stochastic method that can easily account for the inherent variability of environmental systems with straightforward underlying concepts. A probability distribution is assigned to each parameter whose value is uncertain. This assignment can be based on intuition and/or previous data. For environmental problems, the following distributions are most often appropriate: Normal, Log Normal, Gumbel, Log-Gumbel, Gamma, Log-Pearson Type-III, Beta, Weibull, and Uniform (Bobba *et al.*, 1996).

After a distribution is chosen, the model is executed numerous times. Bobba *et al.* (1996), citing Malone (1983), stated that one method for determining how many iterations are required is to iterate until the sample statistic converges to its historical or population value. For each iteration, the uncertain variable is randomly chosen from the assigned distribution. A distribution will then be formed from the model results. This distribution will include all of the uncertainties in the model and is called the prediction error (Bobba *et al.*, 1996).

First-order error analysis is another common method used to quantify model error and is based on the first-order terms of the Taylor series. It is a linearization procedure dependent on the first two moments. First-order analysis requires fewer calculations than MCS for simple models, but MCS does have advantages over first-order error analysis in that MCS is not limited to the first two moments and the complete error distributions can be used. Linearization of the model is also not required in MCS. The choice of the best error analysis is dependent on the computing power available and the complexity of the model (Chapra and Reckhow, 1983).

The Monte Carlo Method used in this research can be considered an error analysis. The model used is the calculation of the daily phosphorus loads for each tributary:

P Load = (Mean daily flow, cfs) x (86,400 sec/day) x (TP, mg/L) ....(12)

The two parameters needed to find the phosphorus load are the mean daily flow and the phosphorus concentration. The mean daily flow is assumed to represent the flow rate for the whole day, so the total volume is found by multiplying this value by the number of seconds in a day. The mean daily flow during each day of a year is determined by the flow meters, but the phosphorus concentration is measured only on a fraction of the days in a year. The uncertain parameter is the phosphorus concentration on day's when no sampled was taken. The input distribution for phosphorus concentrations includes the concentrations that were measured during the year in question. For each iteration, a phosphorus concentration value is randomly chosen from this distribution, and the daily phosphorus load is then determined from equation 12. In this research, separate phosphorus concentration databases were formed for concentrations measured from base flows, storm flows, and flows from direct runoff areas.

Regression Methods

The high costs associated with the collection and analysis of water samples forces one to minimize the number of samples collected during any given year. For this reason, log-linear models are often used to relate phosphorus concentration to discharge so that phosphorus concentrations on days when no samples were collected can be estimated. Advantages these models offer are that the standard estimators are well understood and they are easy to apply (Cohn *et al.*, 1992).

Most regression estimators are dependent on the relationship between TP and flow. A regression analysis is performed on measured values of both flow and the corresponding phosphorus concentration. The resulting relationship is then used to estimate the phosphorus concentration when the flow is known but no phosphorus measurement was taken (Young *et al.*, 1988).

Cohn *et al.* (1989) pointed out that a major drawback to the simple log-log regression is the introduction of bias. The traditional rating curve method can be severely biased and, as a result, causes the loading to be underestimated. The bias is introduced during the retransformation of the load value from log space to real space. Many of the bias correction methods in some situations actually increase the bias. Use of the minimum variance unbiased estimator (MVUE) process has been recommended as a way of reducing retransformation bias (Cohn *et al.*, 1989).

Dolan *et al.* (1981) found that the relationship between phosphorus concentration and flow with the highest statistical significance for the Grand River was phosphorus concentration vs. the natural log of the discharge. Four versions of this relationship were tested, one with data collected during a single quarter of a year, one with data collected during half a year, one with data collected during an entire year, and one with flow stratification. Flow stratification is the separation of data depending on the magnitude of the flow rates. The two strata in this case were high flow and low flow, and a separate relationship was developed for each of the two strata. The root mean square error (RMSE) was used as the criterion for comparing methods because it allows for tradeoffs between bias and precision. The lowest RMSE was associated with the regression relationship derived from an entire year's data, so it was considered the best of the four (Dolan *et al.*, 1981).

Young *et al.* (1988) tested three regression methods on data collected from tributaries to the Great Lakes. One method involved log phosphorus load vs. log flow to estimate each day's TP load, and the other two methods related log TP concentration to log flow. The first of these used the common least squares regression while the other used a robust, bisquare-weighted regression. The robust method involves an iterative solution that is considered complete after the slope of the regression equation from one iteration to the next varies less than one percent (Young *et al.*, 1988).

Young *et al.* (1988) found the most accurate of these three regression methods was the least squares regression of log TP vs. log flow. The robust method was the most precise but tended to underestimate the load because outliers were eliminated as the relationship was developed (Young *et al.*, 1988). As Richards and Holloway (1987) noted, it is common for 80 percent of the annual load to be delivered past the monitoring station during only 20 percent of the time, so the elimination of these outliers (high values especially) will greatly affect the final load estimate.

The regression method developed during this research project was based on the phosphorus concentrations in flow-weighted composite storm flow samples. None of the studies mentioned above dealt with entire storm events and included only grab sample concentrations and either mean daily flows or instantaneous flows. Because the total storm flow volume and phosphorus EMC were determined with the use of the flow meters and autosamplers, a rating curve between TP concentration and instantaneous discharge data would not utilize this valuable information. Therefore, the Regression Method in this research related the log of total phosphorus load to the log of total flow volume.

Schueler's Simple Method

The Simple Method introduced by Schueler (1987) is the only method investigated during this research project that does not require any monitoring program data. Schueler used the comprehensive database that was collected as part of the Washington, D.C. area Nationwide Urban Runoff Program (NURP) study in formulating his method. The method is able to predict loadings under many different planning strategies, and is the only one considered that can predict loadings that will result from future land uses.

The method is simplified for easy application, so it is not the most precise method; however, its use has provided order-of-magnitude estimates of phosphorus loadings that planners can use to aid them make planning decisions. Principally, the Simple Method was developed for use on sites of areas less than one square mile. An important characteristic of the Simple Method is that it finds only loads produced from storm runoff, so base flow loads are not considered; therefore, direct comparisons cannot be made between the results of the Simple Method and those of the other methods used in this study. The Simple Method is included in this study primarily because a citizen activist in the Swift Creek Watershed compiled Chesterfield County land use data and used the Simple Method to test various future land use scenarios. In this study the Simple Method's accuracy is tested only on data for Cub Run's present loadings. Because only a small fraction of the Cub Run drainage area is located downstream of the sampling station, Schueler's Simple Method will approximate Cub Run's gaged load. The results of Schueler's Simple Method are not shown for Swift Creek Watershed because of the large portion of its watershed that is either ungaged tributary drainage area or direct drainage area. Schueler's Method, therefore, would not approximate the tributary load.

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

$$L = \left[\frac{(P)(P_j)(R_v)}{12}\right](C)(A)(2.72) \qquad (13)$$

Where:

L = TP load for 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 set to 0.9 when an annual load is being estimated. The runoff coefficient can be found by the following relationship:

$$R_v = 0.05 + 0.009(I) \qquad (14)$$

Where:

I = Site imperviousness (percent)

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

Cohn-Lee and Cameron (1992) used Schueler's Simple Method (1987) to estimate the urban runoff loadings from selected urban areas within the Chesapeake Bay drainage area. They first estimated what the loadings would be without any BMPs in place and then recalculated the loadings taking into account the existing stormwater management programs in Maryland's Prince George's County and Montgomery County. They chose Schueler's method because it considers site-specific factors, it allows for a comparison with other sources of loadings such as industry, and it can be used to estimate the mitigation achieved from control devices. The authors concluded that the stormwater management programs resulted in pollutant reductions, but the net urban-runoff loadings were not reduced. With each new development site, more pollutants are added to the Chesapeake Bay because no BMP is 100 percent effective.

Cohn-Lee and Cameron (1992) addressed two shortcomings of Schueler's Simple Method (1987). First, it does not to take into account fate and transport of the pollutants, so the study assumed that all loads eventually reached the Chesapeake Bay. Some of the loads probably were lost by sedimentation en route to the Bay, but it is difficult to quantify the amount. Second, the availability and accuracy of land-use data also limit the model.

In a similar study, Houlahan *et al.* (1992) used Schueler's Simple Method (1987) to estimate the impact of the Critical Area Act on one of the tributaries to the Cheseapeake Bay. Schueler's Method (1987) was chosen because only a small number of input parameters was required and the model was calibrated in the Washington D.C. and Baltimore area. They compared the results of the method if the maximum development under the Critical Act existed to the loads that would be generated from two different future land use scenarios, total urbanization and suburban expansion.

The Critical Area Act allows for the conversion of 5 percent of the forested land present in 1984 to be developed into residential areas. The Critical Area Act development scenario converted all low-density residential areas in 1984 to either medium density or central business district areas. The Act also mandates the use of urban BMPs and agricultural BMPs. The total urbanization scenario converted all 1984 land uses, including forested and agricultural areas, to older urban areas typified by Annapolis, Maryland. The suburban expansion scenario forecasted future land uses if the present development trends were continued, and the land uses included forest, low density residential, medium density residential, and central business district. The 1984 forest areas were reduced significantly and the agricultural areas were eliminated in the suburban expansion scenario.

No nutrient concentration, C, was given by Schueler (1987) for runoff from wetlands, so Houlahan *et al.* (1992) assumed that it would be the same C as runoff from hardwood forests. They noted that the Simple Method might overestimate loads during years of low rainfall. Impervious surfaces during years with little precipitation may produce less runoff because evaporation rates are increased. The authors concluded that the Critical Area Act will result in a substantial reduction in loadings compared to the other two development scenarios (Houlahan *et al.*, 1992).

Ratio Estimator Method

Dolan *et al.* (1981) evaluated a method that is well suited for use in the common situation when ample flow data but little concentration data are available. The method is an unbiased ratio estimator developed by Beale (1962) and was mandated by the International Joint Commission for Great Lakes for use in estimating loads into the Great Lakes (Young *et al.*, 1988). The method is described as unbiased because the mean of several estimates will move toward the "true" mean. Ratio estimators are more precise than averaging methods because the observations, in essence, are flow-weighted (Young *et al.*, 1988). The following are the equations for the ratio estimator:

$$\mu_y = \mu_x \frac{m_y}{m_x} \left(\frac{1 + \frac{1}{n} \frac{S_{xy}}{m_x m_y}}{1 + \frac{1}{n} \frac{S_x{}^2}{m_x{}^2}} \right) \text{ ....(15)}$$

Where:

$$S_{xy} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i y_i - n m_x m_y \text{ ....(16)}$$

$$S_x{}^2 = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i{}^2 - n m_x{}^2 \text{ ....(17)}$$

μ_y = The estimated daily load of P, (kg)

μ_x = Mean daily flow for the year, (cubic meter per second, cms)

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

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

n = Number of days on which concentrations were determined

x_i = Individual measured flows on days which concentrations were determined (cms)

y_i = Daily loading of P for each day on which the TP concentration was determined, (kg)

The estimate is further improved if flow stratification is employed. Division of the mean daily flows into high or storm flow and low or base flow creates the two strata (Dolan *et al.*, 1981). As described by Richards and Holloway (1987) when stratification is used, a mean daily load is calculated for each stratum and the annual load is determined as follows:

Annual Load = (Number of base flow days x μ_y for base flow) +

(Number of storm flow days x μ_y for storm flow)..................(18)

The cutoff point between high flow and low flow is discussed in the next section.

Dolan *et al.* (1981) compared the loads determined with the ratio estimator to those determined by nine other estimation methods with data collected from the Grand River, a tributary to Lake Michigan. The other methods included five simple averaging methods and four regression methods. After creating 680 data sets on which to test the methods by random selection of a full year's data, the authors selected the root mean square error (RMSE) as the comparison criterion. This statistic was chosen because it balances the importance of bias and precision. The unbiased stratified ratio estimator outperformed the nine other estimation techniques on the basis of RMSE.

In a similar study with data collected from the Saginaw River, the Grand River, and the Sandusky River, all tributaries to the Great Lakes, Young *et al.* (1988) concluded that the unbiased stratified ratio estimator was the most accurate method of those tested. They evaluated the results obtained with both the stratified and unstratified Beale's ratio estimator and compared them to the results obtained by three regression methods. The ratio estimator method is also robust to the effects of discharge variability, which is an important characteristic for use on an event-responsive system (Preston *et al.*, 1992).

Base Flow Separation Point

The Regression Method, Monte Carlo Method, and Ratio Estimator Method used in this research all incorporate flow stratification. 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", and is a percentile of the mean daily flows in any given year. Mean daily flows greater than the base flow separation point were considered storm flow, and any less than the separation point were considered to be base flow. The loads determined by each estimation method were evaluated over a range of base flow separation points (75th percentile to 95th percentile) in order to gauge the impact this parameter had on the estimation methods and to determine if an optimum separation point could be identified.

The Regression Method used in this research utilized the base flow separation point for classifying unsampled mean daily flows as being either storm flow or base flow. The difference in calculation between days with unsampled base flows and unsampled storm flows is that flow volume on adjacent unsampled storm flow days was combined before the regression equation was applied, whereas individual daily flow volumes were used on days designated unsampled base flow. The flow volumes are combined for days with adjacent unsampled storm flow to approximate the entire storm event's flow volume because the regression relationship was developed using the sampled storms' entire storm event volumes.

The base flow separation point was the basis for designating each mean daily flow as either storm flow or base flow for use in the Monte Carlo Method in this study. Separate databases of phosphorus concentrations in storm flow and base flow samples were created. Depending on the classification of its mean daily flow as either base or storm flow, a given day's TP concentration value was randomly selected from the corresponding database.

The unbiased stratified ratio estimator method produced two daily TP load estimates, one for storm flow days and one for base flow days. The annual load is found using equation 18, shown again below:

$$\text{Annual Load} = (\text{Number of base flow days x } \mu_y \text{ for base flow}) + (\text{Number of storm flow days x } \mu_y \text{ for storm flow})$$

The base flow separation point determined the number of days in the year that were included in each stratum.

The literature contains only limited information about the selection of base flow stratification points. Table L-2 contains some values used in previous studies.

Table L-2. Base Flow Separation Points Found in the Literature.

Load Estimation Method	Source	Percentile Flow Separation Used
A form of Regression Method Ratio Estimator	Dolan et al., 1981	69.6th percentile
Ratio Estimator	Richards and Holloway, 1987	80th percentile
A form of Regression Method Ratio Estimator	Young et al., 1988	50th, 75th, and 85th percentile

Dolan *et al.* (1981) stated that the cut-off between high flow and low flow is a "matter of judgement" and that research is needed in this area. A flowrate of 4,000 cubic feet per second (cfs), which was equivalent to the 69.6th percentile of the mean daily flows, was chosen as the separation point in their study.

Richards and Holloway (1987) used the 80th percentile as the base flow separation point for the ratio estimator method. They stated, without further explanation, that this point adequately separates runoff periods from base flow periods for the particular watersheds in their study.

Young *et al.* (1988) varied the base flow separation point using Beale's ratio estimator (1962) and found no improvement in accuracy as the separation point was increased. They determined that regardless of the cutoff point, the use of flow stratification in the Ratio Estimator Method improved its accuracy.

There is a clear lack of information concerning the best base flow separation point. One objective of this research, therefore, was to evaluate the impact that the cutoff point has on phosphorus load estimates and determine which point is best for each method.

Storm Event Sampling

The key difference between this research and studies previously discussed is the use of flow-weighted composite storm sampling. The storm data used in this study included total storm flow volumes and event mean TP concentrations, whereas other studies have relied on TP concentration in grab samples and either instantaneous flows or mean daily flows.

Even in this study the only method in which the total storm flow volume and the phosphorus EMC were paired to calculate a particular storm's phosphorus load is the Regression Method. The Monte Carlo Method randomly selected the EMCs from the storm flow TP concentration database and used them to calculate the daily loads. When applying the Ratio Estimator Method, any day within a sampled storm event was assumed to have a phosphorus concentration equal to the EMC and a flow rate equal to the mean daily flow. Grab sample concentrations could have been used instead of an EMC in both the Monte Carlo Method and the Ratio Estimator Method; therefore, flow-weighted composite storm sampling is not required if either of these two methods is used. Use of an EMC instead of a grab sample concentration, however, is still beneficial because the EMC is a more representative value of the TP concentration in the entire day's flow.

Summary

Phosphorus is extremely important to surface water quality because it is often the limiting nutrient for algae growth. Many models can be used to predict the in-lake phosphorus concentration and trophic state as a first step in assessing the ecological health of a lake or reservoir. These models are often used in planning decisions but are only as reliable as the phosphorus loading estimate that is used in their execution. Previous research efforts on phosphorus load estimation techniques, for the most part, have been limited to grab-sample analyses, and, in addition, the base flow separation point for flow stratification has not been considered in depth.

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