ABSTRACT

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This study quantified the effect of hydric soils on the hydrology and biogeochemistry of sub-watersheds across the Delmarva Peninsula. For hydrology, long-term data were compiled for 13 United States Geological Survey sites and evaluated for hydric soil effects. Results show that hydric soils reduce baseflow by increasing ponding and subsurface water storage, resulting in greater evapotranspiration. In contrast, hydric soils were unrelated to stormflow, which was instead driven by topography. During sampling of 18 storms in the Choptank Basin, most forms of nitrogen and phosphorus increased in concentration due to erosion and re-suspension of sediments. Nitrate, however, decreased during storms due to dilution of nitrate-rich groundwater by runoff. Baseflow nitrate concentrations decreased with forested hydric soils, likely due to greater denitrification in forested hydric areas. Annually, much of the total nitrogen and phosphorus export occurred during storms, emphasizing the need to sample a wide range of flows to improve estimates of nutrient losses.

HYDROLOGIC AND BIOGEOCHEMICAL STORM RESPONSE IN CHOPTANK BASIN HEADWATERS

By

Antti I. Koskelo

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Evaluation of Precipitation Inputs

Abstract

This chapter evaluates a 17-station precipitation network in the Choptank River region (coastal plain) with a mixture of instrumentation. The premise of this chapter is that no spatial differences in rainfall occur over an approximately annual time scale within the 60 km x 60 km region inscribed by this network. Errors at each station were quantified by assuming that deviations in annual rainfall totals relative to a reference station mean were due to measurement errors. The reference stations consisted of Wye Research and Education Center, part of the National Atmospheric Deposition Program, and two National Weather Service observing stations, Royal Oak and Dover Quality Controlled. Eight of the sites were significantly different from the reference station mean, while six were not statistically different. Corrections were applied at the eight sites which differed significantly, either at the daily scale or the event scale depending on data availability. Observed monthly rainfall during the June 2006 – August 2007 study period varied about the long-term averages and was characterized by both summer droughts (<5 cm month^{-1}) and wet periods (>15 cm month^{-1}) driven by moderate to large events. Among all 17 sites, the average annual equivalent rainfall was 107 ± 2 cm y^{-1}, which is about normal for this region. An analysis of network density suggests that the 17 stations are adequate for resolving both event and annual totals. Corrected rainfall data will be used in subsequent chapters for the calculation of water budgets and event analysis.

Introduction

Precipitation is a critical part of our lives. It nourishes the crops we eat, sustains our drinking water supplies, affects our physiology and moods, and in some areas can cause severe economic damage and loss of life (Kalkstein and Valimont 1987). Quantitative measurements of precipitation are an important component of water resources management, flash flood predictions, stormwater drainage planning, precipitation forecasting, and hydrologic studies. Mankind has sporadically attempted to measure rainfall dating back to the 4^{th} century BC in India, but it was not until 17^{th} century Europe that people started developing a more rigorous, scientific approach (Strangeways 2007).

Today, the measurement of precipitation is ingrained in our society. Everyone from government agencies to schools to interest groups to ordinary citizens are participating in this task. Worldwide, there are an estimated 150,000 manual (i.e. can-type) gauges in use, consisting of over 50 different models (Sevruk and Klemm 1989), not to mention additional automated and mechanical type gauges. The United States National Weather Service (NWS) alone has well over 10,000 gauged locations (Kuligowski 1997). Developments in radar and satellite technology over the last few decades (especially the WSR-88D Doppler Radar [NEXRAD] and the GOES-8 and GOES-9 satellites) have allowed increasingly accurate estimates of precipitation depths (cm), intensities (cm h^{-1}), spatial distributions (m^2), and movement (km h^{-1}). Forecasters often use a variety of techniques to provide the clearest possible picture of atmospheric conditions. The NWS, for example, uses an integrated approach that combines weighing, tipping bucket, and manual gauges, as well as satellite and radar observations (Kuligowski 1997).

While clearly the measurement of precipitation has come a long way, it is far from being an exact science. One major drawback is the lack of standardization. Each basic approach (i.e. radar, satellite, gauges) has its own associated error. Neither radars nor satellites, for example, directly measure rainfall. The former emits radio waves which bounce off the rain drops and return to the instrument as a reflectivity reading. These values are then converted into precipitation rates using certain assumptions which are not always valid (Kuligowski1997). Satellites are an even more indirect way to measure rainfall. They take infrared and visible images of clouds. Forecasters then interpret the clouds and infer certain precipitation rates based on their irradiances. Again, because the actual rainfall is not measured (only the clouds), this method is inherently prone to error (Kuligowski 1997).

Even among different types of gauges, the errors can be substantial. Tipping bucket gauges, for example, tend to under-catch during high rainfall intensities. This occurs because during each "tip" of the bucket, some precipitation is lost. Therefore, as rainfall intensifies and more "tips" occur, more of the rainfall goes unmeasured. Manual gauges may also have errors. As summarized by Sumner (1988) and Kuligowski (1997), these fall into three basic categories: 1) Errors associated with the instrument itself (e.g. evaporation, condensation, wetting of the cylinder walls), 2) Errors associated with the siting of the instrument (e.g. over- or under-exposure, disturbances to the local wind field, ground slope variations), and 3) Errors associated with how representative individual gauges (and the network as a whole) are of actual rainfall in that area. In summary, it is almost impossible to obtain a truly accurate measurement of rainfall (Sumner 1988), and adequate sampling is essential.

Given this potential for bias, the best approach is usually an integrated one which plays to the strengths of the various techniques. Mechanical and automated type gauges, for example, are useful for rainfall *timing* and *intensity*, while manual gauges are useful for rainfall *totals* (Strangeways 2007). Similarly, over broad spatial areas, radar and satellite imagery provide tremendous spatial and temporal resolution, and are able to reach remote, ungauged areas.

The purpose of this chapter is to provide an estimate of precipitation inputs over the Choptank River Basin on the eastern shore of Maryland (Delmarva Peninsula) for a study of storm and baseflow hydrology and chemistry. The Choptank basin lies entirely within the coastal plain in the mid-Atlantic region and falls within the Chesapeake Bay drainage. Rainfall amounts are used in subsequent chapters of this thesis to address the major research questions, namely 1) How do hydric soils affect the stream flow component of quickflow? and 2) How do hydric soils affect nitrate export? While an integrated approach would be ideal for optimal quantification of rainfall, such methodology is beyond the scope of this thesis. However, I provide a reasonable estimate using the available data and the methods described below.

Regional Climate

In general, precipitation in Maryland is evenly distributed throughout the year, with an average of 5 – 10 cm (2 – 4”) per month and a maximum of 10 – 14 cm (4 –

5.5”) in the late spring and/or summer (Maryland State Climatologist). Precipitation occurring in the summer is variable compared to the winter and is characterized by 23 – 24 days (on average) of convective thunderstorm activity from May – August (Maryland State Climatologist), although the frequency may vary from site to site. Rainfall in the summer is also accompanied by high evapotranspiration, which often exceeds rainfall, resulting in summer drought conditions such as occurred during the summer of 2007.

Frontal precipitation also occurs, usually in the spring and fall, when cold air from the north meets warm air from the south. This is facilitated by the rapid succession of cyclones and anticyclones (i.e. low and high pressure systems) that typically move in from the west during these seasons. Indeed, the most favorable situation for rainfall in Maryland is when a high pressure system forms over the northeast US, and a low pressure system forms over the southeast US or the Ohio River Valley (Maryland State Climatologist). Frontal precipitation is also aided by Maryland’s approximate position at the confluence of the maritime polar and maritime tropical air masses. Both of these factors contribute to atmospheric turbulence and mixing, which often leads to rainfall. Usually, frontal precipitation occurs as either light showers/drizzle (in the case of a warm front), major rainfall (in the case of a cold front), or variable rainfall (in the case of an occluded front; Ahrens 2001).

Among the more destructive storms in Maryland are Nor’easters, a type of low pressure system which usually originates in the Gulf of Mexico and brings torrential rainfall, typically during the winter or early spring. Good examples of

Nor'easters occurred in mid-April, 2007 when about 10 – 11 cm of rain fell over the Choptank region over three days (see Chapter 2), and more recently in mid-May 2008. Tropical cyclones marked by easterly winds may also bring heavy rains to the area in the late summer or early fall.

Description of Network

Precipitation inputs into the Choptank Basin were available from 17 stations spanning a 60 km x 60 km region with the sub-basins at the approximate center (Fig. 1-1). The sites were marked by a mixture of instrumentation, and included: 1) Six 4" diameter manual sub-basin gauges installed as part of this thesis, 2) A tipping bucket gauge operated by Horn Point Laboratory (HPL), part of the University of Maryland Center for Environmental Sciences (www.hpl.umces.edu), 3) Seven stations associated with the Weather Underground (WU, www.wunderground.com), and 4) Three reference stations using either an 8" Belfort tipping bucket rain gauge, or a standard 8" diameter copper gauge (Fig. 1-1).

The 4" manual gauges (Productive Alternatives, Inc.) were installed near the hydrologic gauging stations at the outlets of each of the six sub-basins (Fig. 1-1) as part of a 15-month monitoring effort (June 2006 – August 2007). The rain gauges are named after their sub-basins. Originally, seven gauges were installed (one for each catchment), but the one at the forested site was stolen and was therefore not included in the analyses. The transparent plastic gauges have an 11" capacity. The NWS also uses this type of gauge as part of its supplementary rainfall networks (NWS 2008b). The gauges were sited with a moderate exposure (i.e. ~ 45° cone of open sky above

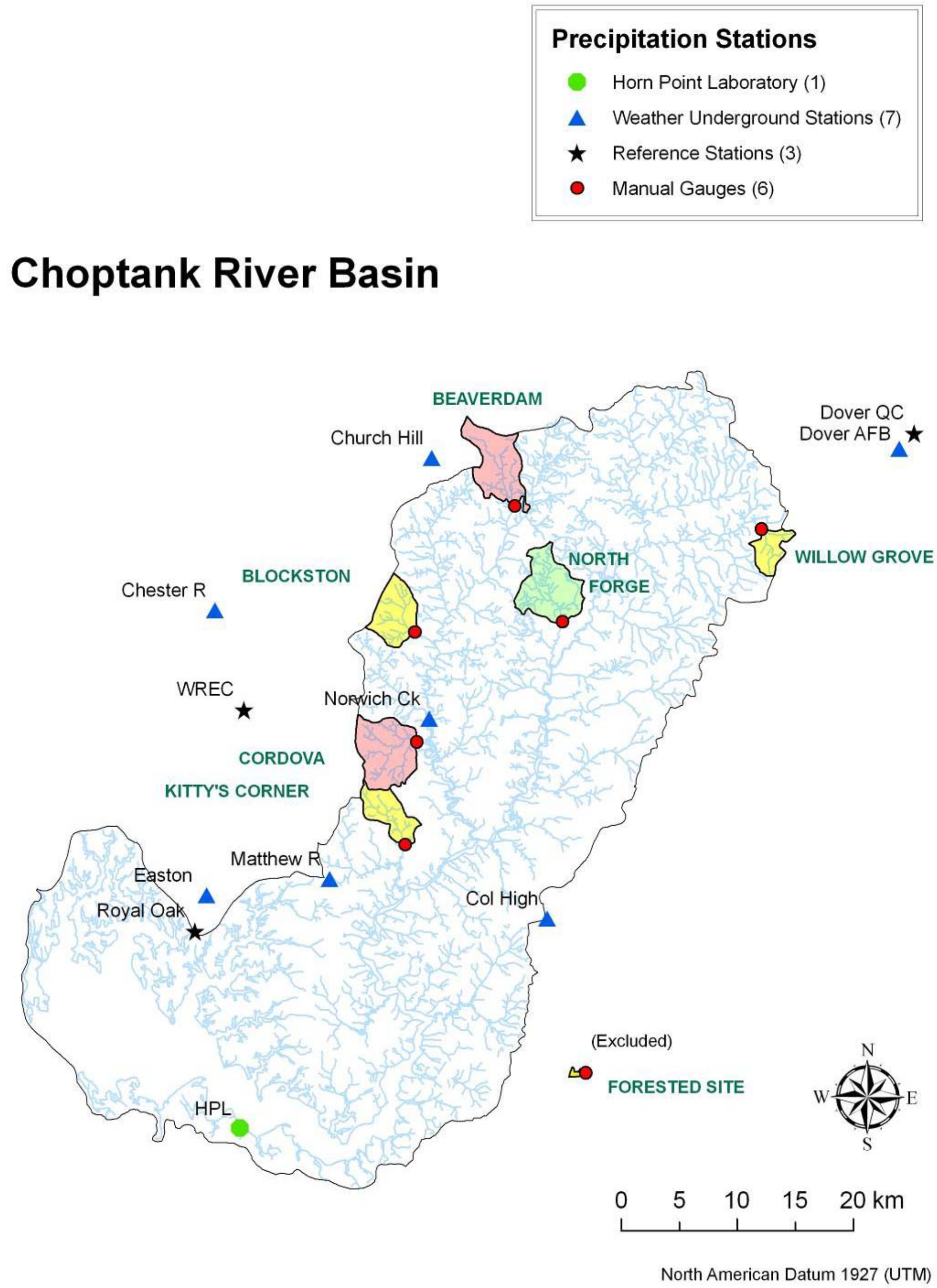

Figure 1-1. Location of the 17 precipitation stations described in the text. The seven Choptank sub-basins are highlighted (names in CAPS). The six manual rain gauges (dark circles) are named after their sub-basin, and are located near the hydrologic gauging stations at the outlet of each catchment. The manual gauge at the forested site was excluded. The three reference stations (stars) are associated with either the National Weather Service (in the case of Royal Oak and Dover QC) or the National Atmospheric Deposition Program (in the case of WREC). The seven Weather Undergound sites (triangles) are operated by volunteers and the data are reported on the internet. Horn Point Laboratory (HPL, light circle) is part of the University of Maryland Center for Environmental Sciences.

them) to minimize errors associated with both under-exposure (blockage of rain by obstructions) and over-exposure (wind eddies altering raindrop trajectories), in accordance with NWS standards (NWS 2008a).

The seven WU stations included Church Hill, Dover AFB, Colonel High, Norwich Creek, Easton, Matthewstown Run, and Chester River. The WU provided free access to the data as part of their "Personal Weather Station" project which allows anyone to purchase an automated weather station (from a vendor of their choosing) and deploy it "in their backyard" (The Weather Underground, Inc., 2008). Hence, rain gauges were not standardized among the WU stations, and the quality of the data were unknown. The three reference stations included Wye Research and Education Center (WREC; station MD13 in the National Atmospheric Deposition network, http://nadp.sws.uiuc.edu) and two NWS (www.nws.noaa.gov) observing sites: Dover Quality Controlled (QC) and Royal Oak. WREC uses an 8" Belfort tipping bucket rain gauge, whereas the two NWS sites use a standard 8" diameter copper rain gauge. Unlike the WU sites, the reference stations were part of a national network and were assumed to be accurate (hence "reference" stations). The Dover QC data were purchased online through the National Climatic Data Center (www.ncdc.noaa.gov/oa/ncdc.html). See Table 1-1 for a summary of the 17 stations and their data sources.

Methods

The basic premise of this chapter is that, at the annual time scale, there are no significant spatial differences in rainfall within the 60 km x 60 km coastal plain area

Table 1-1. Summary of the 17 precipitation stations described in this chapter, with reference stations marked in gray. For each non-reference station, the table lists the % difference from the reference station average (RSA) based on comparisons over a variety of time periods (see Fig. 1-2). If differences were significant at P <0.05, corrections were applied. Equivalent annual rainfall (right-most column) means the data were scaled to a common 365-day period. WREC = Wye Research and Education Center; NWS = National Weather Service; HPL = Horn Point Laboratory, University of Maryland Center for Environmental Sciences, www.hpl.umces.edu; WU = Weather Underground (www.wunderground.com); RSA = reference station average; NS = not significant; * = P <0.05; ** = P<0.01.

No.	Station	Data Source	% Difference from RSA	Significant Difference	Equiv. Annual Rainfall (cm y^{-1})
1	WREC	WREC	-	-	109
2	Dover QC	NWS	-	-	111
3	Royal Oak	NWS	-	-	124
4	HPL	HPL website	-15	NS	98
5	Church Hill	WU website	28	*	106
6	Dover AFB	WU website	-17	NS	95
7	Colonel High	WU website	20	*	98
8	Norwich Ck	WU website	-17	*	98
9	Easton	WU website	-38	**	87
10	Matthews. Run	WU website	-9	*	125
11	Chester River	WU website	-27	**	117
12	Kitty's	thesis research	-6	NS	102
13	Cordova	thesis research	9	*	108
14	Blockston	thesis research	-1	NS	108
15	Beaverdam	thesis research	-2	NS	106
16	Willow Grove	thesis research	-26	**	101
17	North Forge	thesis research	7	NS	110

inscribed by this network. Undoubtedly, there are real spatial and temporal variations at shorter time scales; however, at the annual time scale, I am assuming that these differences average to zero. We therefore used statistically significant differences between reference stations and individual stations to estimate measurement errors. Based on this assumption, the various non-reference stations (WU, HPL, manual sub-basin gauges) were compared to a common benchmark, in this case the average of the three reference stations (WREC, Dover QC, and Royal Oak) during a time period of about 1.5 years (608 days, 1/1/06 – 8/31/07). Rainfall totals were calculated as the sum of daily depths (cm d^{-1}) within that period. Six of the stations (the three reference stations, HPL, Church Hill, and Dover AFB) had continuous data for the full 608 days. However, many of the sites (WU, manual sub-basin gauges) had gaps in the rainfall record, and the size and timing of the gaps differed among the sites. For example, at the Colonel High, Norwich Creek, and Easton sites, only 342 days of data were available (9/7/06 – 8/31/07, with 17 daily gaps). Similarly, Matthewstown Run and Chester River had only 312 days (7/9/06 – 8/31/07, with 107 daily gaps). In these cases, rainfall totals for the non-reference stations were calculated (again, as the sum of daily depths) over whatever time period was available for comparison with the reference stations.

Data availability was especially limited for the six manual sub-basin gauges installed for this thesis project. At these sites, precipitation was *not* available on a daily basis because only about 40 observations were made per site over the 15-month monitoring period, or about one reading every 11 days. Consequently, rainfall totals at these sites were assumed to be representative of the time period over which the observations were made, i.e. the sum of 40 observations over 15 months was assumed to represent the sum of *continuous* daily observations over 15 months. This allowed the manually gauged data to be compared to the reference stations, which reported daily depths. For the Kitty's, Cordova, Blockston, Beaverdam, and Willow Grove sub-basins, the observation period was 357 days (9/7/06 – 8/29/07). The observation period at the North Forge sub-basin was even shorter at 298 days (11/5/06 – 8/29/07). Rainfall totals were calculated as the sum of the 40 observations, again over whatever time period was available for each particular site. In summary, among all 17 stations, five different time periods ranging from 298 – 608 days were used to calculate the annual rainfall totals.

The rainfall totals at each station were compared to the average rainfall total of the three reference stations (WREC, Dover QC, and Royal Oak) to quantify potential measurement biases among the various sites. To make the comparison valid, the rainfall totals at the reference stations were calculated *over the same exact time period* as the non-reference stations (i.e. with data gaps in all the same places). Hence, rainfall totals at the reference stations were also calculated over five different time periods. See Table 1-2 for a more detailed description of the comparison procedure and also Figure 1-2 for a graphical illustration of how the comparisons were made.

Table 1-2. Procedure for comparing the annual rainfall totals at each non-reference station to the reference station average.

Step	Description
1	Sum the daily rainfall depths (cm d^{-1}) from 1/1/06 – 8/31/07 (608 days) for the first non-reference station. If gaps occur in the data, sum all of the available data. This sum is known as “A”
2	Sum the daily rainfall depths for each of the three reference stations (WREC, Dover QC, and Royal Oak) *over the same time period as for the non-reference site above.* If any gaps occurred in the non-reference station data, make sure the same gaps occur in the reference station data to ensure a suitable basis for comparison.
3	Calculate the average of the three reference station sums. This average is known as “B”
4	Calculate a % difference between “A” and “B”
5	Compare “A” and “B” using the *t* statistic to check for significant differences.
6	Repeat steps 1 – 5 for each of the 14, non-reference stations.

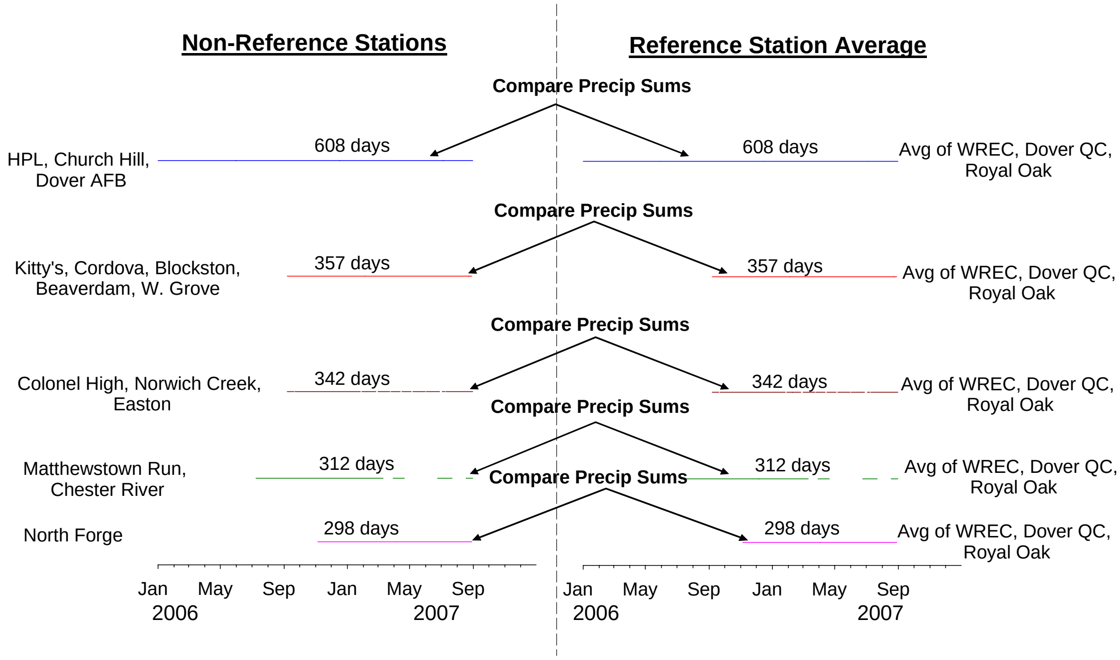

Figure 1-2. Conceptual diagram of the comparisons of annual precipitation sums. Rainfall totals at each non-reference station (left-hand side of figure) were compared to the average rainfall total of the three reference stations (WREC, Dover QC, and Royal Oak; right-hand side of figure) *over the same exact time period.* The comparisons were made over five different time periods ranging from 298 days (bottom-most horizontal line) to 608 days (top-most horizontal line) depending on data availability at a particular site. Data gaps are noted with breaks in the horizontal lines.

The *t* statistic (also called the Student's *t*) was used to test for significant differences with respect to the reference station average. This parameter is useful for comparing one sample mean to another when sample sizes are small. In this case, the reference stations were one sample (n = 3) and each non-reference station was a second sample (n = 1). Equal variance was assumed for both samples. For each site, *t* was calculated as the observed non-reference station value minus the reference station average, divided by the standard error of the reference stations. Calculated *t* values equal to or greater than a "critical" *t* value of 4.3 ($\alpha = 0.05$, $\nu = 2$ degrees of freedom; Zar 1999) were considered significantly different. Note that this method of calculating the 't statistic' is distinct from a two-sample 't-test' which is traditionally used to compare two sample means. In this case, the t statistic is being used to test whether the non-reference station data fit within a 95% confidence interval for the mean of the three reference stations.

For sites with significant annual rainfall differences, the % difference in the annual mean was applied at the daily time step to compensate for measurement errors. For the manual sub-basin gauges, however, corrections were applied to the *event* totals since daily data were not available. Monthly precipitation was calculated as the average of the 11 non-manually gauged stations after corrections had been applied, and compared to long-term monthly averages for the region based on a 24-year record (1983 – 2007) at WREC, and a 28-year record (1971 – 1999) at Federalsburg. The latter site is part of the National Weather Service's Cooperative Observer Program (COOP ID# 183090), and is located <10 km southeast of the Choptank Basin. Annual equivalent rainfall was calculated by first normalizing the 17 stations to a common annual time period [i.e. (rainfall sum over *n* observations) / *n* * 365], and then averaging the corrected rainfall totals among the sites.

Results

The average daily precipitation for the three reference stations (WREC, Royal Oak, Dover QC) over the 608 day period (1/1/06 – 8/31/07) is shown in Fig. 1-3. Daily rainfall varied substantially and was marked by a variety of storm sizes. The two largest storms in the record occurred in June 2006 (up to 10 cm d^{-1}) and April 2007 (up to 8 cm d^{-1}), and are marked in Fig. 1-3 for future reference. Both events were sampled for hydrology and chemistry (see Chapters 2, 3). Also shown in Fig. 1-

3 is the 15-month study period (June 2006 – Aug 2007) for the hydrology and chemistry portion of this thesis (see Chapters 2, 3). Over the 608 day period, the average annual equivalent rainfall for the reference sites was 115 cm y^{-1}, with the lowest total at WREC (109 cm y^{-1}) and the highest total at Royal Oak (124 cm y^{-1}; Table 1-1).

The results of the annual rainfall comparisons are shown in Figure 1-4. The following sites were *not* significantly different from the reference station mean: HPL, Dover AFB, Kitty's, Blockston, Beaverdam, and North Forge (Table 1-1). Eight of the sites, however, were significantly different, including the Cordova and Willow Grove sub-basins, and six of the seven WU sites (Fig. 1-4, Table 1-1). Among the latter sites, the % difference ranged from -38 to 28%, with most of the sites under-reporting. Daily corrections were applied at the six WU sites. For example, since the annual rainfall total at the Colonel High station was found to be 20% greater than the reference station average, each *daily* rainfall depth at that site was divided by 1.2. For the Cordova and Willow Grove sub-basins, daily corrections were not possible, so corrections were applied at the event scale instead. For example, because the annual rainfall total at the Cordova sub-basin was 9% greater than the reference station mean, each event total measured at Cordova (10 storms total during the study period) was divided by 1.09. This approach preserves the short-term spatial and temporal variability while ensuring that the annual means are comparable.

Monthly rainfall was compiled for each of the 15 months in the June 2006 – August 2007 study period and compared to long-term averages based on the WREC and Federalsburg stations (Fig. 1-5). The long-term averages show that rainfall in this

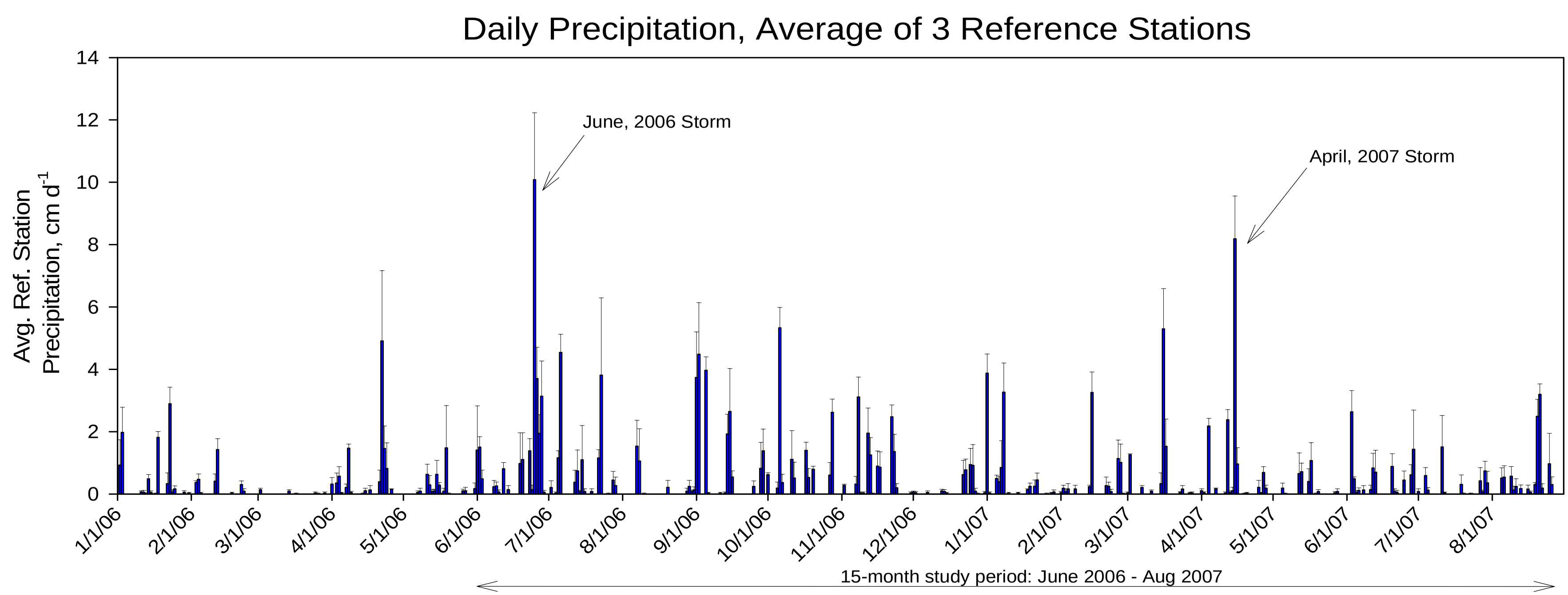

Figure 1-3. Average daily precipitation for the three reference stations (WREC, Royal Oak, Dover QC) over the 608 day period from 1/1/06 – 8/31/07. Shown is the daily mean ± standard error. The two largest storms occurring over this time period (in June 2006 and April 2007) are marked for future reference (see Chapter 2). Also shown is the 15-month study period for the hydrology and chemistry portion of this thesis (see Chapters 2, 3).

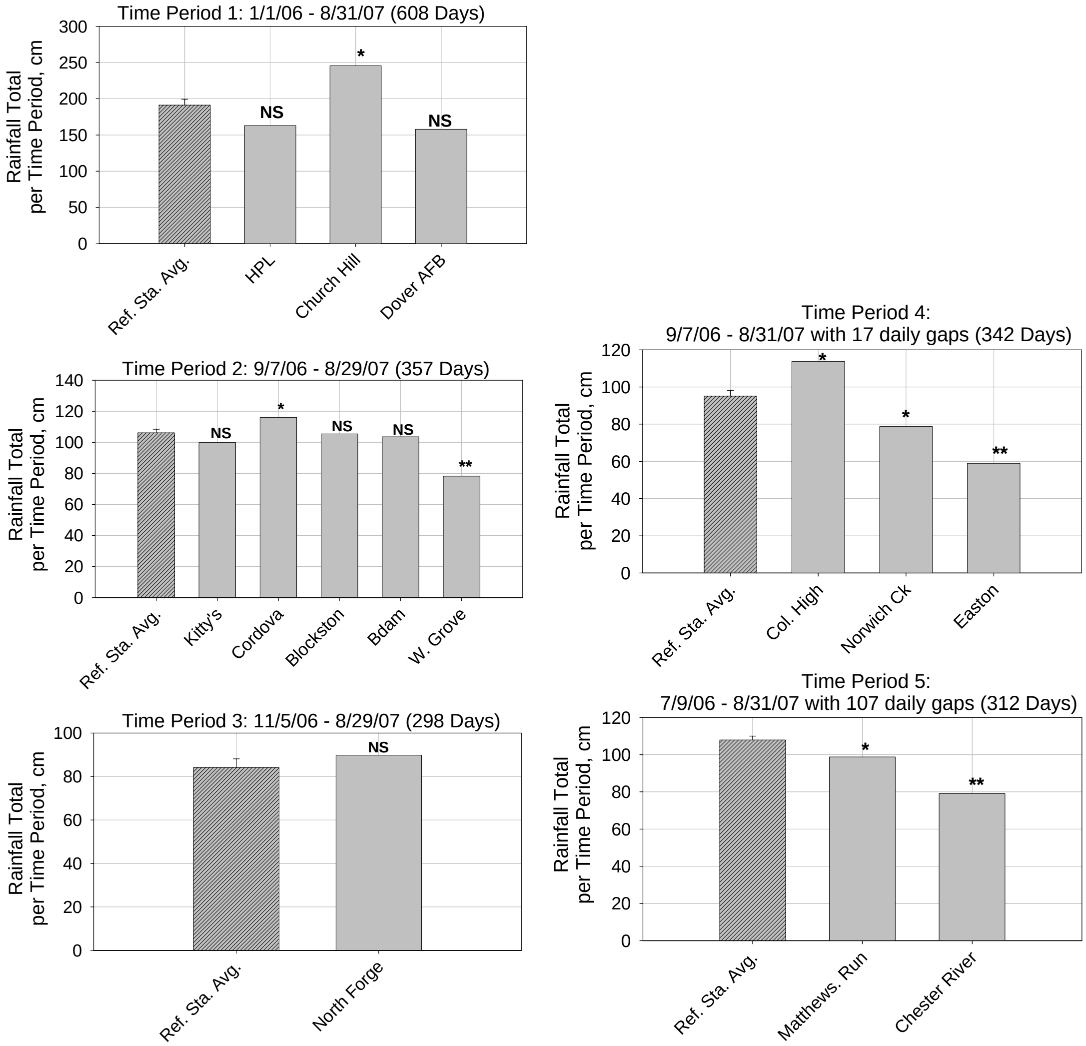

Figure 1-4. Results of the comparisons of annual rainfall totals. Each non-reference station (light gray bars) was compared to the reference station average (dark hashed bar) over five different time periods ranging from 298 – 608 days (see graph headings). Note that the graphs cannot be compared to each other because of the varying time periods used. NS = not significantly different; * = significantly different (P< 0.05); ** = significantly different (P<0.01).

region is relatively evenly distributed throughout the year (Fig. 1-5). Although stream discharge is typically lower in the summertime, this is mainly because of higher evapotranspiration, not lower rainfall. The observed monthly precipitation varied about the long-term averages, ranging from 3 – 25 cm. Several months had above average rainfall (e.g. June 2006) and several months had below-average rainfall (e.g.

Aug 2006). The single wettest month by far was June 2006 with 25 cm of rain, largely due to one 19 cm event which occurred late in that month. Other wet months such as April, 2007 and September, 2006 (both greater than 15 cm $month^{-1}$) also experienced moderate to large events. Several of these storms were sampled in the hydrology and chemistry portions of this thesis (see Chapters 2, 3). Droughts occurred during the summers of 2006 and 2007, as well as December 2006, with monthly totals of <5 cm during these periods. The summer 2007 drought was especially acute with both July 2007 and August 2007 being drier than normal (Fig. 1-5). Across all 15 months, the average monthly rainfall was 9.9 ± 1.5 cm, which is similar to the long-term monthly average of the WREC and Federalsburg stations (9.1 ± 0.4 cm).

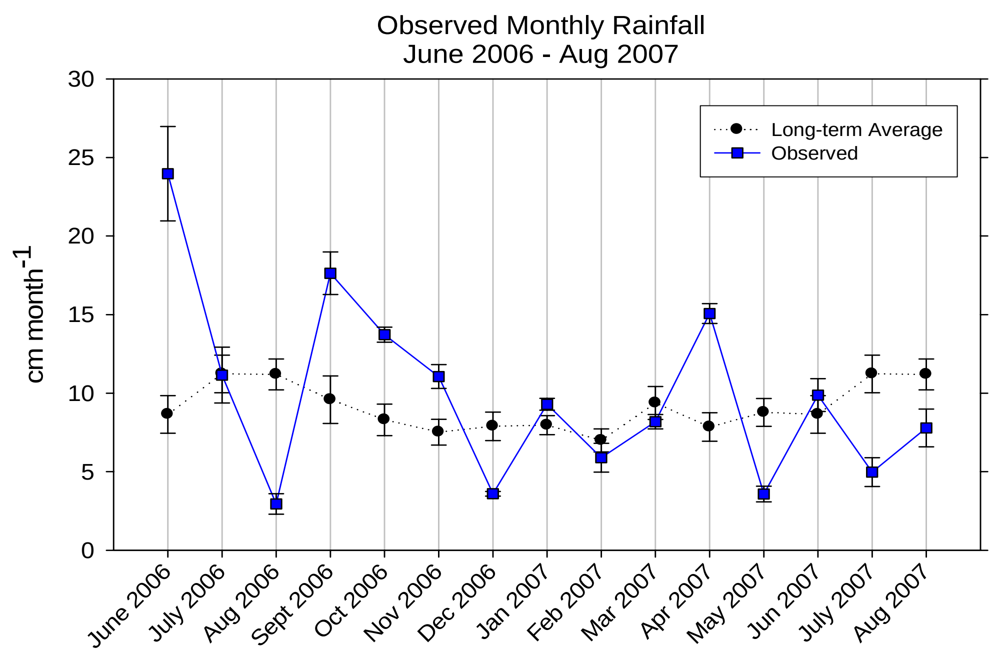

Figure 1-5. Observed monthly rainfall (solid line) for the 15-month study period from June 2006 – August 2007, shown as the average of all available stations ± standard errors. Monthly precipitation varied about the long-term averages (dotted line) based on long-term records at WREC and the National Weather Service's Federalsburg station. Droughts occurred during the summers of 2006-7 and Dec 2006 (all with < 5 cm $month^{-1}$). Wet periods (>15 cm $month^{-1}$, e.g June 2006) were driven by large events in those months.

The annual equivalent rainfall ranged from 87 cm y^{-1} at Easton to 125 cm y^{-1} at Matthewstown Run, with an average of 107 ± 2 cm y^{-1} (Fig. 1-6). The calculated average is comparable to long-term means reported elsewhere for the Choptank region, including 110 cm y^{-1} (Lee et al. 2001) and 107 – 112 cm y^{-1} (Spatial Climate Analysis Service 2000). This suggests that precipitation over the study period, although marked by monthly fluctuations, was about average at the annual scale. See Table 1-1 for a summary of results for all 17 stations.

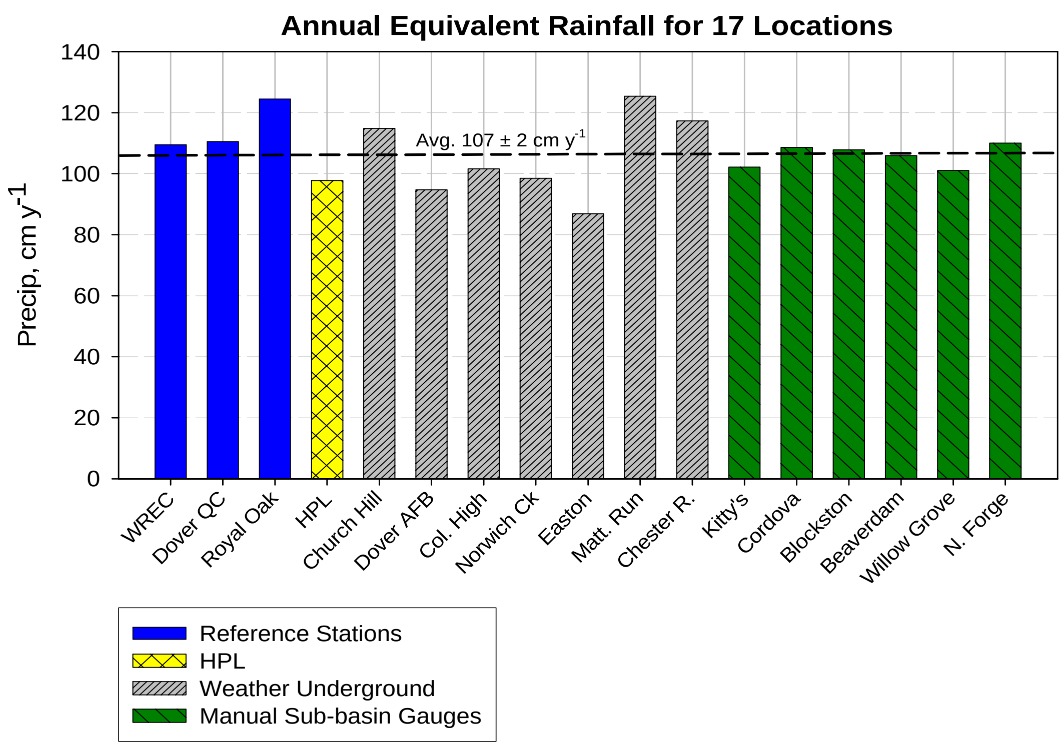

Figure 1-6. Annual equivalent rainfall for all 17 stations in the precipitation network *after* corrections were made at eight of the sites. The term "annual equivalent" means the data, which were available over multiple time periods, were scaled to a common annual time period (365 days) so that the sites could be compared. The average of all stations (107 ± 2 cm y^{-1}) is shown as a dashed horizontal line.

Discussion

As stated earlier, the major premise of this chapter is that annual rainfall does not vary over the 60 km x 60 km region of the precipitation network. Significant differences were assigned to measurement errors. This assumption is supported by the fact that several stations in close proximity had widely divergent rainfall totals. For instance, the Dover AFB and Dover QC stations showed a 26 cm difference in precipitation over 608 days despite being only about 2 km apart (Fig. 1-1). Similarly, the Easton and Royal Oak stations, which are ~ 3 km apart, recorded a 42 cm difference over 342 days. While some of this could be small-scale spatial heterogeneity due to localized summer thunderstorms, it is more likely due to systematic measurement errors.

One additional factor to consider is the density of the stations. Gauges which are too far apart do not adequately resolve the precipitation field, which can vary over distances of 1 km or less (Singh 1997). The basic question is, how many gauges are enough? The answer depends on the duration of rainfall being considered. Over shorter time scales (e.g. daily), the network should be finer, whereas over longer time scales (e.g. annual), the network may be more coarse. As suggested by Sumner (1988) and O'Connell et al. (1977), a simple way to test for the appropriate rain gauge density is to do a correlation among the gauges (termed a "network density validation"). If a strong correlation is found between a majority of the gauges, the network may be considered suitably dense (Sumner 1988).

To address this issue, a correlation was performed between the same event totals as measured by two different sources: 1) the manual sub-basin gauges, and 2) the reference stations. Correlations were done on a pair-wise basis (i.e. each manual sub-basin gauge was paired with the average of the reference sites) because the event time periods differed slightly among the sub-basins. The duration of an event was partially based on the observed discharge record at each site (see Chapter 2). For example, one particular storm at the Blockston sub-basin in April, 2007 was measured to have 11.34 cm of rain based on the manual gauge there. That number was then paired with the average rainfall of the three reference stations *for the same storm*, which in this case was 9.30 cm. Each paired value (e.g. 9.30, 11.34) was then plotted for a variety of different storms, and repeated for each of the sub-basins. All of the available event totals from June 2006 – August 2007 for each manual sub-basin gauge was used in this comparison, with the number of storms ranging from 10 – 17 depending on the site (Fig. 1-7). In general, among the sub-basins, the correlations were highly significant (r^2 = 0.72 – 0.95, $P < 0.001$ for all sites), with an average r^2 of 0.84. These relationships are consistent with Hershfield's (1965) recommendation of $r^2 > 0.81$ to adequately resolve event totals. Furthermore, the slopes of the regressions varied about 1.0 (0.9 – 1.2), suggesting a good match between the reference stations and the manual sub-basin gauges.

The WU sites were also compared to the reference stations in this fashion (Fig. 1-8). In this case, since the WU sites did not have a discharge record, the event time periods were estimated using the discharge record at the Blockston sub-basin (see Chapter 2). All 93 events occurring at the Blockston site between June 2006 and

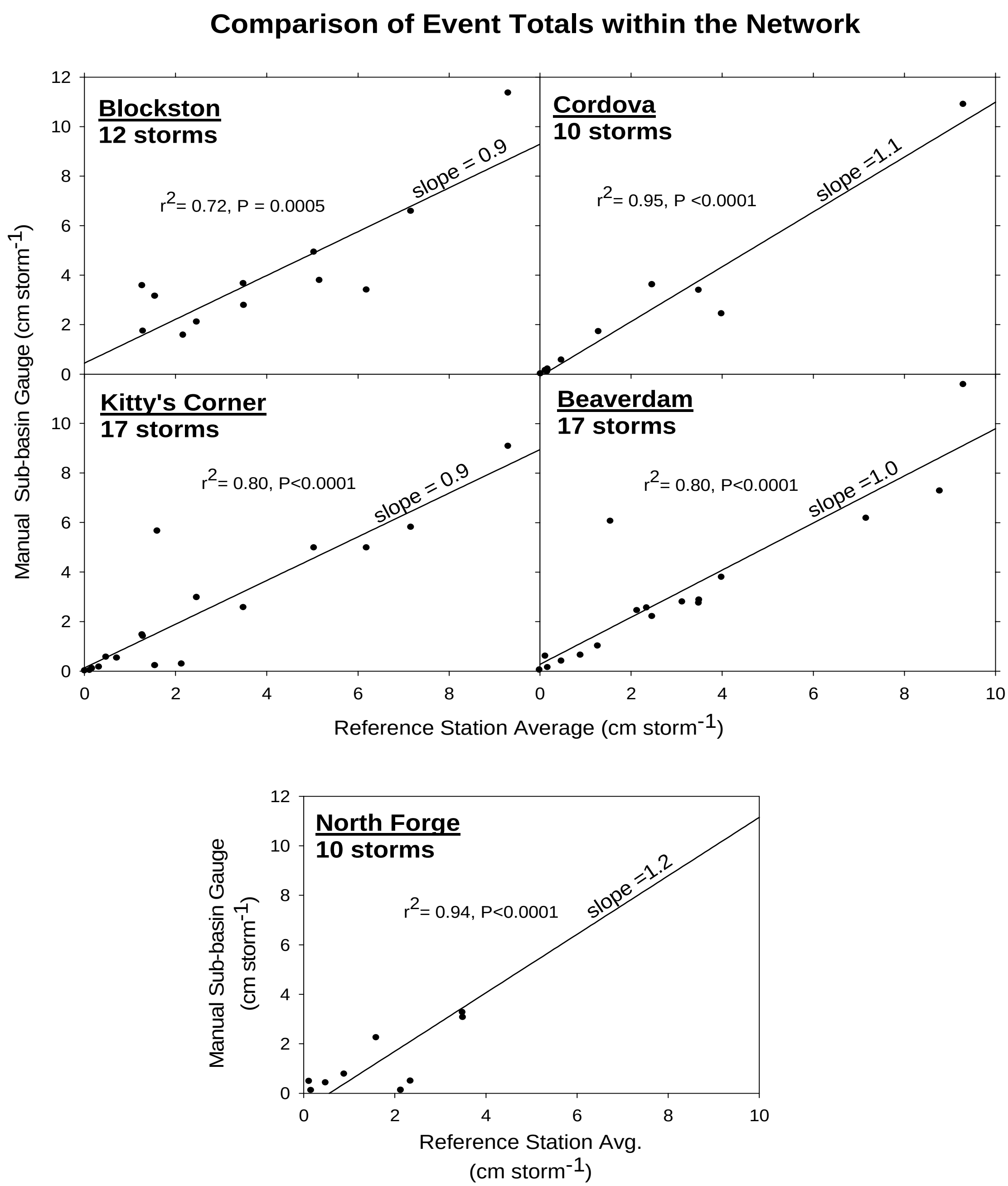

Figure 1-7. Results of the network density validation. These graphs show a comparison of the same event totals as measured by two different sources: 1) the manual sub-basin gauges (y-axes), and 2) the reference stations (WREC, Royal Oak, and Dover QC), shown on the x-axes. Each point on the graphs is a unique storm. All of the available event totals for the sub-basin gauges were used in this comparison, with the number of storms shown in the upper left-hand corner of each panel. The slopes are also shown for reference, with 1.0 being a perfect match. The generally strong correlations (r^2 = 0.72 – 0.95, P <0.001 for all plots) and slopes varying about 1.0 suggest a good match between the manual sub-basin gauges and the reference stations. This supports the idea that the network has an adequate rain gauge density for measuring event totals.

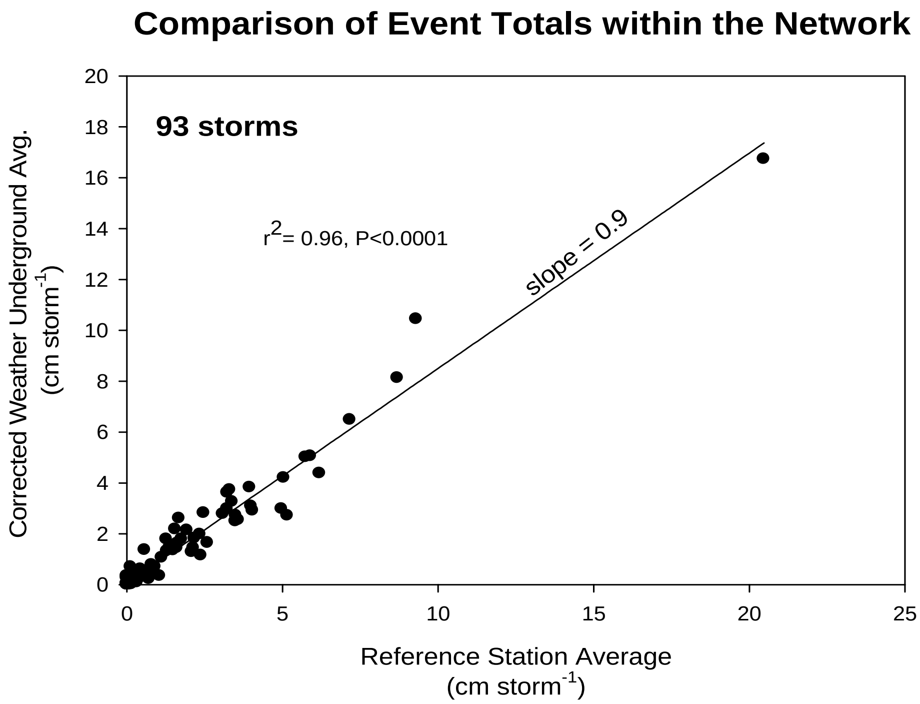

Figure 1-8. Additional results of the network density validation. Comparison of the same event totals as measured by two different sources: 1) the corrected Weather Underground sites (y-axis), and 2) the reference stations (WREC, Royal Oak, and Dover QC), shown on the x-axis. Each point on the graphs is a unique storm. The event time periods were estimated using the Blockston sub-basin. All 93 storms occurring during the June 2006 – Aug 2007 study period at Blockston are plotted on the graph. The slope is also shown for reference, with 1.0 being a perfect match. The strong linear regression (r^2 = 0.96, P <0.0001) and slope of 0.9 suggest that the two groups of gauges (WU sites and reference stations) agree well with each other. This supports the idea that the network has an adequate rain gauge density for measuring event totals.

August 2007 were used for the comparison. The results were similar to the previous analysis, with a strong linear relationship (r^2 = 0.96, P<0.0001) and a slope (0.9) close to 1.0 (Fig. 1-8). While this type of correlational approach is not without statistical problems (Sumner 1988), it does support the idea that the network used here is suitably dense at the *event* scale.

On the other hand, this chapter also compares annual totals. As stated, gauges which are used to measure annual totals (or approximately annual, in this case) may be relatively coarse (Sumner 1988). According to Stephenson (1968), a gauged network covering an area of 3900 km^2 (about the size of this network) would require a minimum of 13 – 17 gauges to adequately estimate *monthly* rainfall. Presumably, in comparing *annual* totals, the number of required gauges would be fewer. This suggests that the current network of 17 gauges is somewhat greater than the minimum required to reasonably estimate spatial variations at the annual scale. One final concern is how well-*distributed* the gauges are *within* a network. Ideally, all of the gauges should be evenly-spaced in a grid pattern, but in this case, it was not possible. While there tends to be more stations along the western side of the Choptank, the distribution is otherwise reasonably well-dispersed (Fig. 1-1).

As stated, one of the assumptions made in this chapter was that the relatively infrequent measurements (once every 11 days) at the manual sub-basin gauges did not affect the rainfall totals at those sites. This assumes zero evaporation in the gauge between readings. While it is possible that some evaporation may have occurred, particularly over long dry spells during the summer, the gauges are designed with caps over the collecting cylinders to minimize evaporative water loss. Furthermore, the fact that the manual gauges and the reference stations agree well in their measurements of annual rainfall totals (Fig. 1-4) supports the idea that evaporation was minimal (otherwise the manual gauges would consistently under-report rainfall). In support of this point, Sevruk (1985) found that evaporation was a relatively minor source of measurement error for manual gauges.

However, this is not to say that manual gauges are free of measurement error. In fact, a preliminary study from Colorado State University suggests that the 4” gauges used in this study slightly over-estimate rainfall depths (101 – 105%) relative to the standard 8” NWS gauges. This is because the copper material in the 8” gauges absorbs a small fraction of the precipitation before it enters the collection cylinder (Community Collaborative Rain Hail and Snow Network 2005). There is also some concern over the collection efficiency of the 4” gauges when rainfall rates are high (NWS 2008b). Nevertheless, the 4” gauge meets NWS accuracy standards (NWS 2008b) and, as stated previously, every type of measuring instrument has it own associated error, even the 8” NWS gauges. Furthermore, small changes in the rainfall totals of 1 – 5% would not change the major findings of this chapter.

Chapter Summary

In summary, this chapter evaluated measurement error within a 17-station gauged network with non-standardized rainfall instrumentation. Errors were quantified by comparing approximately annual rainfall totals at each station to a reliable benchmark, namely the average of three reference stations. Data gaps at some of the sites necessitated the use of five different time periods ranging from 298 – 608 days to calculate rainfall totals. About half of the sites (eight) significantly deviated from the benchmark. In particular, all but one of the Weather Underground stations had significant measurement errors. This underlines the importance of using standardized measuring equipment to collect rainfall totals. Corrections were applied at the eight sites, either at the daily time scale for the WU stations or at the event scale for the Cordova and Willow Grove sub-basins.

Annual equivalent rainfall was 107 cm y^{-1} on average, which compares well to other estimates for the Choptank region. Monthly rainfall varied about the long-term averages, with a range of 3 – 25 cm and an average of 9.9 ± 1.5 cm. A network density validation suggests that the 17-station network, which encompasses about 3900 km^2, is suitable for resolving spatial variation in rainfall at both the event and annual time scales. While it is virtually impossible to measure precipitation with 100% accuracy, the network presented in this chapter likely provides reasonable estimates of rainfall depths. The corrected precipitation data will be used in later chapters to calculate water budgets and perform event analysis.

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Chapter 2:
Hydrologic Storm Response in the Choptank River Basin

Abstract

This chapter evaluates the hydrologic storm response of six sub-basins (14 – 27 km^2) of the Choptank River watershed (2057 km^2) on the Delmarva Peninsula (coastal plain). Five of the sub-basins were agriculturally dominated while one all-hydric (and mostly forested) control site was used for reference. The sites were selected to have a wide range of hydric soils (15 – 97%). Discharge data were gathered at 30-min intervals over a 457-day period (Jun 2006 – Aug 2007). Baseflow was separated using a new approach called the 1-day **S**liding **A**verage with **R**ain **R**ecord (SARR) developed for this thesis. Unlike previously published methods, the 1-day SARR is based on both the discharge *and* the precipitation record and is thought to be more physically meaningful than other, more arbitrary baseflow separation techniques. Between 93 and 100 events were identified over the study period depending on the sub-basin. About 69% of the events were small (<2 cm rainfall). One of the sub-basins (Kitty's Corner) had about twice as much quickflow on average (19% of precipitation) as the other sites (9- 10%). Storms occurring during the cool season (Oct – April) generated significantly ($P<0.05$) higher quickflow on average than similar-sized storms occurring during the warm season (May – Sept) due to seasonal cycles of evapotranspiration and soil moisture. Greater than zero quickflow occurred ~2/3 of the time, although annual discharge was only ~1/3

quickflow because of the frequent occurrence of small storms which generated little hydrologic response. Among the Choptank sites, quickflow was compiled over event, monthly, and annual time scales, but in all cases was not related to % hydric soils in the sub-basins. However, a secondary analysis of 13 regional USGS sites with long-term records showed that hydric soils were negatively related to both mean annual water yield and mean annual baseflow on decadal time scales. In addition, hydric soils were positively related to surface ponding/root zone water storage. This suggests that hydric soils decrease baseflow (and total water yield) because they promote larger evaporative losses along the surface and shallow subsurface, resulting in less infiltration to groundwater. Hydric soils, on the other hand, were not related to mean annual quickflow, which instead appeared to be driven by topography, specifically the average slope of the watershed.

Introduction

The Choptank River Basin, a central coastal plain tributary of the Chesapeake Bay (Fig. 2-1), is located in the single most concentrated grain- and poultry-producing region of the 164,000 km^2 Bay drainage (Staver and Brinsfield 2001). Here, the acreage of farmed land is about twice that of forested land. Agriculture and its associated fertilizer use facilitate high rates of erosion and nutrient losses during rain events, resulting in negative impacts downstream. The relative lack of forested acreage means little buffering of nutrient flows. The negative impacts are visible in the Choptank estuary, where chlorophyll *'a'* (a measure of algal growth) and total suspended solids have increased, while water clarity has decreased, over the last two decades (Fisher et al. 2006). The Choptank estuary is a microcosm of the Bay itself, where deep-water hypoxia, loss of submerged aquatic vegetation, poor water quality, excessive plankton production, and declines in fisheries yields have been a problem for decades (Kemp et al. 2005, Fisher et al. 2006).

Many of these problems originate in the headwaters of the Bay's drainage, in this case the upper Choptank River Basin. Headwater streams are highly connected to the landscape and often constitute up to 85% of stream length within a drainage network (Peterson et al. 2001). They also provide key ecosystem services such as flood attenuation, sediment trapping, and processing of carbon, nitrogen, and phosphorus (Meyer et al. 2003), all of which mitigate downstream impacts. The physical flow of water, in particular, is often a "master variable" that controls stream temperature, channel morphology, the rates of energy transfer and material cycling,

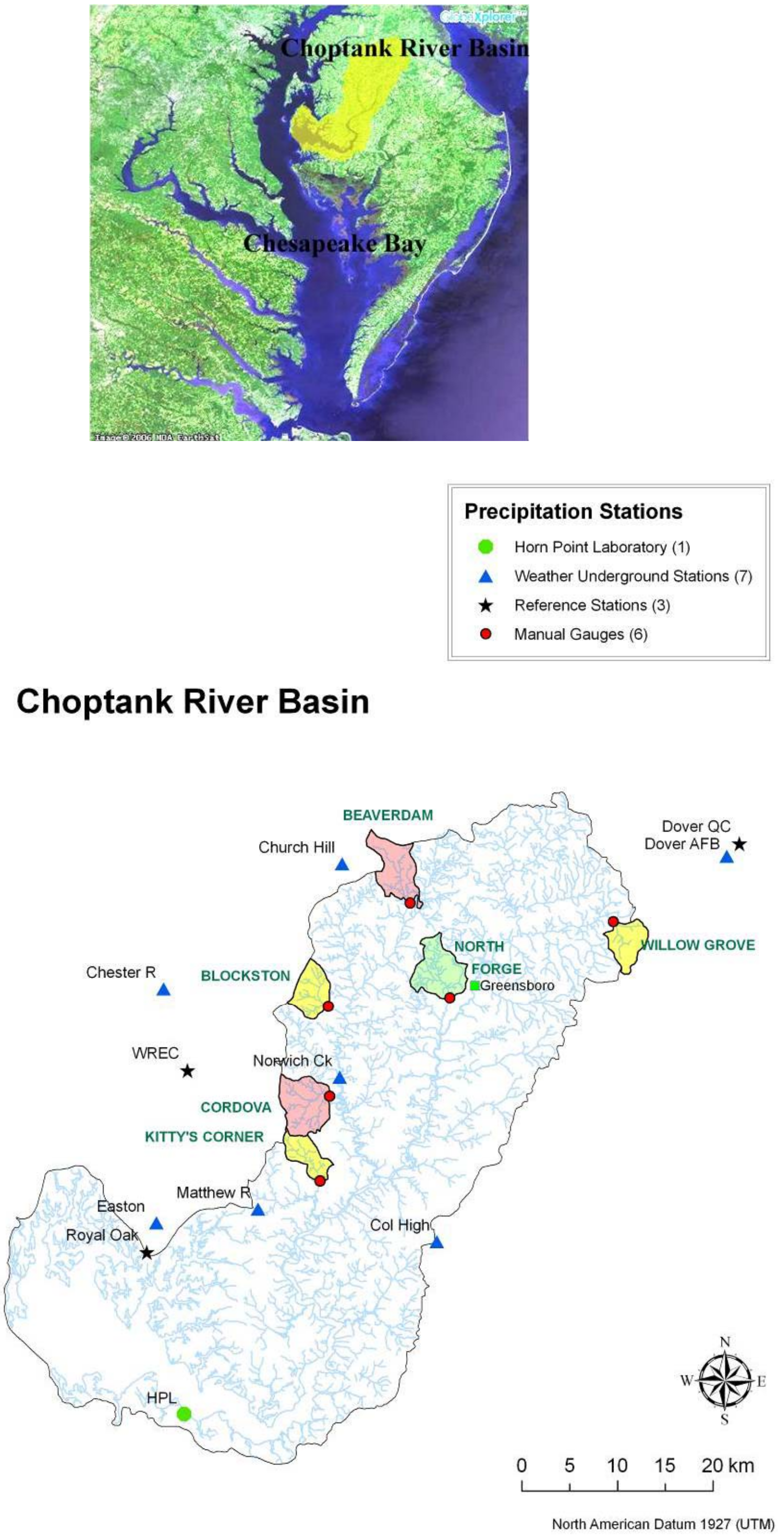


Figure 2-1. <u>Top</u>: Location of the Choptank River Basin relative to the Chesapeake Bay. <u>Bottom</u>: The location of the six Choptank study sub-basins (highlighted polygons), including the all-hydric control site (Willow Grove). Also shown are the USGS' Greensboro station (square) and the 17-station precipitation network (see Ch.1 for a detailed description). The names of the sub-basins are written in CAPS.

habitat diversity, the distribution of biota, and the ecological integrity of the system (Poff et al. 1997, Hart and Finelli 1999).

During precipitation events, the flow of water is at its most dynamic. As discharge increases, a stream's capacity to transport sediment and nutrients also increases. The routing of precipitation through watersheds, including the pathways taken and interactions with soils, geology, and vegetation along the way, is a critical research topic in hydrology. This research can help quantify human impacts on hydrologic and biogeochemical cycles. The purpose of this chapter is to assess hydrologic storm response in various sub-watersheds of the upper Choptank Basin. In particular, this chapter will test the hypothesis that hydric soils, which are common in this region, increase quickflow volume by enhancing lateral overland and shallow sub-surface flow.

Hydric soils are also known as "wetland soils." They are defined as soils "that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part" (NRCS 1998). Both anaerobic and saturated conditions must persist for at least 14 consecutive days for the soil to be considered hydric (National Technical Committee for Hydric Soils 2000). Hydric soils can be broadly grouped into three basic categories: 1) Fine-textured soils with a low infiltration capacity, 2) Soils of any infiltration capacity that are underlain by an aquiclude that impedes vertical water percolation, and 3) Soils that form in topographic lows, for example near a stream channel. Human-induced changes to the hydrology of a hydric soil do not affect its hydric status (NRCS 1998).

This is important for the Choptank region, where many agricultural fields are former wetland sites that have been ditched and drained for agricultural purposes (Norton and Fisher 2000).

Relatively few studies focus on the effects of hydric soils on event hydrology at the small watershed scale (<25 km^2). Most hydrologic studies focus either on land use (e.g. Kochenderfer et al. 1997, Kim et al. 2005), modeling of rainfall-runoff relationships (e.g. Scanlon et al. 2000, Schneiderman et al. 2007), fluvial geomorphology (e.g. Woltemade and Potter 1994, Robinson et al. 1995), the pattern and movement of rainfall (e.g. Singh 1997, de Lima and Singh 2003), riparian zone characteristics (e.g. Tabacchi et al. 2000, Angier et al. 2005), plot-scale measurements of runoff (e.g. Dunne and Black 1970, Needelman et al. 2004), or the effects of single large events (e.g. Smith et al. 1996, Kendall et al. 2001). The studies that do explore soil effects tend to focus either on soil moisture (e.g. McNamara et al. 2005, Zehe et al. 2005) or on physical properties of the soil such as macropores (e.g. Beven and Germann 1982), fragipans (e.g. Gburek et al. 2006) and soil thickness (e.g. Maeda et al. 2006). Studies on hydric soils in particular often concentrate on either hydric soil field indicators (e.g. Thompson and Bell 1998, Vepraskas et al. 2004), wetlands (e.g. Arndt and Richardson 1988, Clausnitzer et al. 2003), or hillslopes (e.g. Thompson et al. 1998) without regard for the larger watershed perspective. Hence, the current study is unique and is intended to increase our understanding of how soils influence hydrology.

Methods

This thesis is part of a larger effort by the United States Department of Agriculture's (USDA) Conservation Effects Assessment Project to monitor various sub-basins in the Choptank River Basin (2057 km^2). As part of this project, 17 sub-basins have been monitored for hydrology since 2003. For this chapter, six of the sites (14 – 27 km^2) were chosen for more intensive study over a 15-month, or 457 day, period (June 2006 – August 2007). Five of the sub-basins are roughly 2/3 agriculture and 1/3 forested, and one (Willow Grove) is an all-hydric, mostly forested control site (97% hydric soils, 58% forest, Table 2-1). Land use has been previously mapped by other researchers, and is based on 1990 aerial photos. Although the sites have relatively simple land uses, they were selected to vary substantially in the percentage of hydric soils (15 – 97%; Table 2-1). Urban land is <5% for each sub-basin. The % of blue-line streams classified as "ditched" ranged from 0 – 24% based on the USGS' National Hydrography Data Set (http://nhd.usgs.gov/). Pivot irrigation pumps do not occur in these sub-basins except at Cordova, which has six, as determined from 2005 aerial photos. Finally, the sub-basins have a wide range of hydrologic soil groups A – D, as determined from the USDA's Soil Survey Geographic Database (http://soildatamart.nrcs.usda.gov/). 'A' soils have a relatively high infiltration rate and a low runoff potential, while 'D' soils have a relatively low infiltration rate and a high runoff potential (Soil Survey 1993).

Precipitation data were gathered from a 17-station network spanning a 60 km x 60 km area surrounding the sub-basins (Fig. 2-1). The stations included 1) Six 4"-

Table 2-1. Characteristics of the six Choptank sub-basins in this study, in order from least to most % hydric soils (same order as in other tables). The all-hydric control site (Willow Grove) is marked in gray.

Sub-basin	Size (km^2)	% Hydric Soils	% Agriculture	% Forest	% soil A	% soil B	% soil C	% soil D	Ditched km	Total Stream km	% Ditched	# Pivot Irrig. Pumps
Cordova	27	15	76	18	60	22	17	1	0.0	41.8	0.0	6
Kitty's Corner	14	26	65	32	52	22	23	3	0.5	20.9	2.6	0
Blockston	17	34	71	28	2	40	20	38	0.0	26.5	0.0	0
North Forge	24	51	67	31	33	17	30	21	0.7	52.0	1.4	0
Beaverdam	22	64	67	32	1	28	6	66	1.9	32.0	5.9	0
Willow Grove	15	97	34	58	0	1	2	97	4.8	20.0	24.1	0

diameter, manual sub-basin gauges (one per watershed), 2) Three reference stations (Wye Research and Education Center and two National Weather Service observing sites), 3) Horn Point Laboratory, and 4) Seven stations associated with the Weather Underground (www.wunderground.com). Rainfall data were generally available as daily depths (cm d^{-1}), except at the manual sub-basin gauges, where data were available about once every 11 days on average. The manual gauges (Productive Alternatives, Inc.) were installed at the outlet of each catchment (Fig. 2-1). As part of an earlier evaluation of the precipitation network (Ch. 1), daily corrections were applied at eight of the 17 sites to compensate for measurement errors. Throughout this chapter, precipitation is reported as the daily, spatially averaged mean (cm d^{-1}) of all 11 stations where daily data were available. If data were missing for a particular station, a subset of the sites was used to calculate the daily mean. The manually gauged data at each sub-basin were averaged in with the rest of the sites on an *event* basis, although for most storms, the data were not available. At the Blockston sub-basin, for example, the manual gauge data were available for only 12 of the 93 measured events. For a detailed assessment of the precipitation data, see Chapter 1.

Stream stage and temperature were measured at each site for the entire 15 months. The data were collected at 30-min intervals with Solinst Model 3001 Leveloggers (Solinst Canada Ltd.) equipped with a thermistor (±0.1 C accuracy) and a pressure transducer (± 0.3 cm accuracy). Each logger was mounted inside an anchored cinder block and positioned ~5 cm above the streambed at the discharge point of the catchment. The cinder blocks were chained to an earth anchor screwed into the bottom ~0.5 m upstream of the logger. The goal of this set-up was to minimize logger movement and protect the instrument from debris during flood events. The loggers were left in-situ for 15 months except for periodic downloading of the data at 3 – 4 month intervals using Solinst Levelogger software. Corrections for variations in barometric pressure were applied using a second reference logger that was not submersed in the stream. Corrected stage data were converted into discharge using a rating curve developed separately for each site (see below). At the annual scale, baseflow was separated from total flow using the 5-day smoothed minima approach of Gustard et al. (1992). At the event and monthly scales, however, baseflow was separated using a new technique developed for this thesis called the 1-day SARR (see below). Throughout this chapter, flow is reported in the same units as precipitation (cm d^{-1}) for ease of comparison, and is normalized for basin area [i.e. (m^3 d^{-1}) / (m^2 of basin area) * 100 cm m^{-1} = cm d^{-1}].

Rating curves were developed incrementally over ~ 2 years by measuring discharge during various flood stages. The rating curves were deemed sufficient when enough discharge points had been collected to adequately describe 65% of the full spectrum of stage conditions, ranging from summer baseflow to major storm flooding. On average, about 10 storms were needed per site to define the spectrum of stage conditions. The rating curves were approximated as 3-parameter exponential functions, with r^2 values in the 0.94 – 0.99 range among the sub-basins (see example in Fig. 2-2). For each site, stage and discharge were measured at, or near, bridge abutments, which provided an excellent “control section” where the stage-discharge relationship was not likely to change from year to year (Hornberger et al. 1998). Discharge was measured using an acoustic doppler current profiler (model no. 70B-

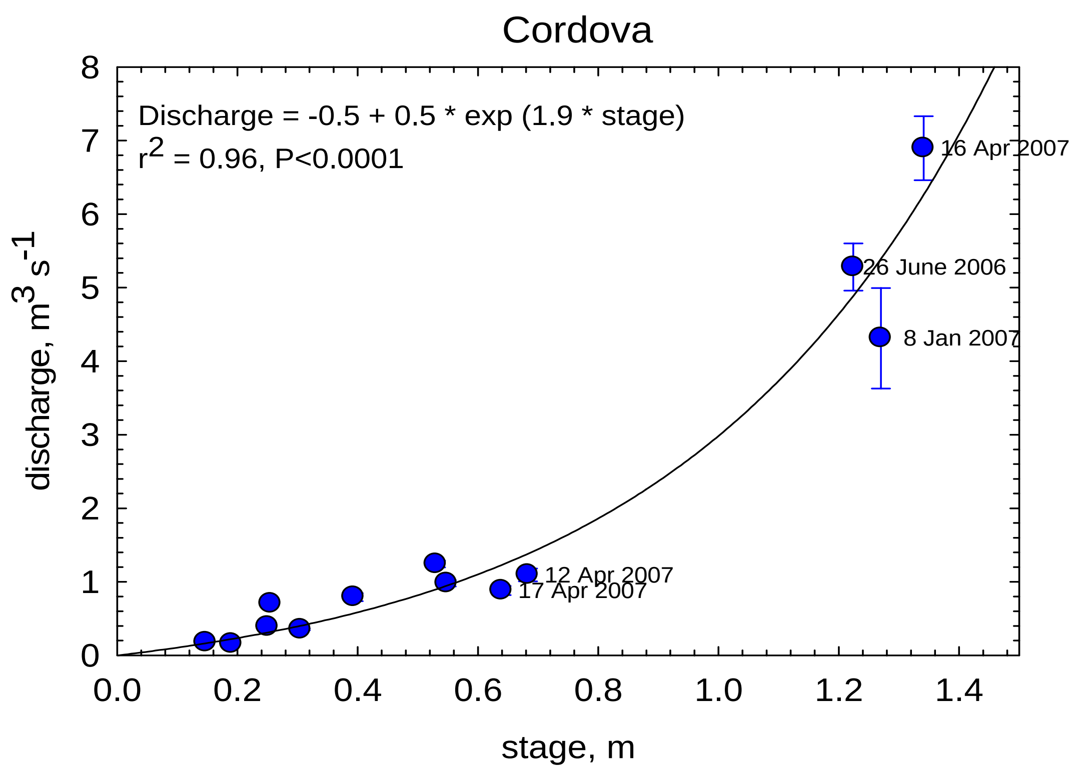


Figure 2-2. An example of a rating curve developed for the Cordova sub-basin. Discharge was measured during a variety of flood stages over ~2 years. For clarity, storm dates are only shown for the larger events.

4001-00, RD Instruments, San Diego, CA) during high flows and a Gurley flow meter (model no. 625, Troy, NY) during low to moderate flows. During very low flows in the summer months, a “stick and leaf” method was used in which velocities were estimated by timing the movement of a leaf along a meter stick.

Baseflow Separation

This section describes the two methods of baseflow separation used in this thesis. The first method was the 5-day smoothed minima approach (or simply “5-day method”) of Gustard et al. (1992), a continuous separation technique designed to estimate baseflow over long time periods (e.g. annual). This approach was chosen due to: 1) its simplicity and lack of assumptions (Jordan et al. 1997), 2) the fact that it has been widely applied in the literature (e.g. Jordan et al. 1997, Vanni et al. 2001, Villar et al. 2002, Schoonover and Lockaby 2006) and is therefore useful as a comparative tool, and 3) it has been shown to be more stable than other low-flow techniques (Gustard et al. 1992). The intention of the 5-day smoothing is not to give an absolute measure of the proportion of baseflow, but rather to obtain a ranking of baseflow proportions *among* watersheds (Jordan et al. 1997). Thus, the 5-day method gives a first approximation of long-term groundwater contributions, but not necessarily an exact quantity. For this chapter, the 5-day method is used at the *annual* scale for making general comparisons among the sub-basins.

The second baseflow separation method was the 1-day SARR, a new technique developed for this thesis to address the limitations of the 5-day method at shorter time scales (e.g. event). Continuous baseflow separation techniques such as the 5-day method are not intended to simulate baseflow for individual events (Smakhtin 2001). The 1-day SARR was also used at the monthly time scale. The remainder of this section provides background information on baseflow separation and describes how the 1-day SARR method was developed, including the various alternative approaches that were considered along the way.

Background

All storm hydrographs consist of “quickflow” and “baseflow” components. Quickflow, so named because it occurs immediately after precipitation begins, is the excess water that drains off a catchment during storms. Quickflow is empirically defined as the non-baseflow portion of the total flow hydrograph (Hornberger et al. 1998), and includes contributions from 1) Direct precipitation onto the stream channel and nearby saturated areas, 2) Overland flow, which is composed of both infiltration excess (also called Hortonian overland flow) and saturation excess, 3) Shallow subsurface stormflow (also called interflow), and 4) Groundwater flow. Quickflow is often referred to as “runoff.” However, that term is not used here because it implies an association with overland flow, and it has conflicting definitions in other disciplines. For example, runoff refers to river flow in oceanography, and to *total* streamflow per unit area in USGS studies (e.g. Wieczorek 2008). Baseflow is the relatively stable flow between storms, and includes contributions from: 1) Groundwater flow, and 2) Return flow. Groundwater is the dominant source, and return flow is groundwater that has re-emerged onto the surface after hitting soils or rocks with a low hydraulic conductivity, whereupon it flows downhill as overland flow. The latter typically occurs close to streams as a seepage face or spring. As a practical matter, quickflow and baseflow are often distinguished based on the time of arrival in the stream since it is difficult to measure the actual flow paths in a basin.

Baseflow separation is largely an arbitrary exercise (Linsley et al. 1975). Ultimately, it is impossible to know the portion of base flow during a recharge event (Jordan et al. 1997). Yet, various separation techniques exist, some dating back to Horton (1933). Most are based on arbitrary extrapolations under the hydrograph peak with the assumption that quickflow and baseflow reservoirs actually exist in nature (Hornberger et al. 1998). For example, one of the most widely used techniques, the “fixed base method,” is to project the pre-event groundwater recession curve to a point underneath the peak, then draw a straight line to a point 'N' days after the peak where $N = A^{0.2}$ ($A = mi^2$ of drainage area). However, there is no scientific basis for assuming that groundwater recession is the same both before and during an event (Linsley et al. 1975). Many current techniques for estimating baseflow are automated; examples include USGS' SWGW (Mayer and Jones 1996), RORA (Rutledge 1993), and PART (Rutledge 1998) computer programs. Although they simplify the process, the algorithms are still based on arbitrary rules. Ultimately, there is no objective reason for picking one method over another because none of them have any physical meaning, and the results would be comparable regardless of which technique is used (Dr. Keith Eshleman, pers. communication).

An alternative hydrochemical method was developed in the 1970s using conservative tracers (e.g. Cl^-) to partition hydrographs into "old" (i.e. pre-event) and "new" (i.e. event) water. This method would yield very different results compared to the non-hydrochemical methods mentioned above. Often, the "old" water component is dominant and may provide nearly 100% contribution on the falling limb (Dr. Keith Eshleman, pers. communication). However, this method is not applicable for the current research since chemical tracer data were not available for most of the storms.

The 30-min Method

Initially, baseflow separation was attempted using the 30-minute discharge data. This involved grouping every five points together, resulting in a flow window of 2.5 hours. (Note: The term "flow window" is used throughout this section to refer to the time interval of the data segregation, i.e. a flow window of five days means dividing a long data set into groups of five days each.) The 30-min method was keeping in spirit with the 5-day approach of Gustard et al. (1992) by preserving the number of data points in the flow window (5), although the time scale was very different. Otherwise, the 30-min method was the same. The advantage of this method was that it preserved the resolution of the data. However, this approach was not feasible because short-term variability (i.e. barometric pressure and logger error), and diel cycles of water flow driven by radiative heating and evapotranspiration (ET), were mistakenly considered storm events. An example is shown in Figure 2-3, which shows a hydrograph from June 15 – 18, 2006 at the North Forge sub-basin. No rain fell during this time period, yet the 30-min method shows frequent baseflow separation consistent with storm events. Clearly, the 30-min approach was overly sensitive to micro-fluctuations in the stream discharge record.

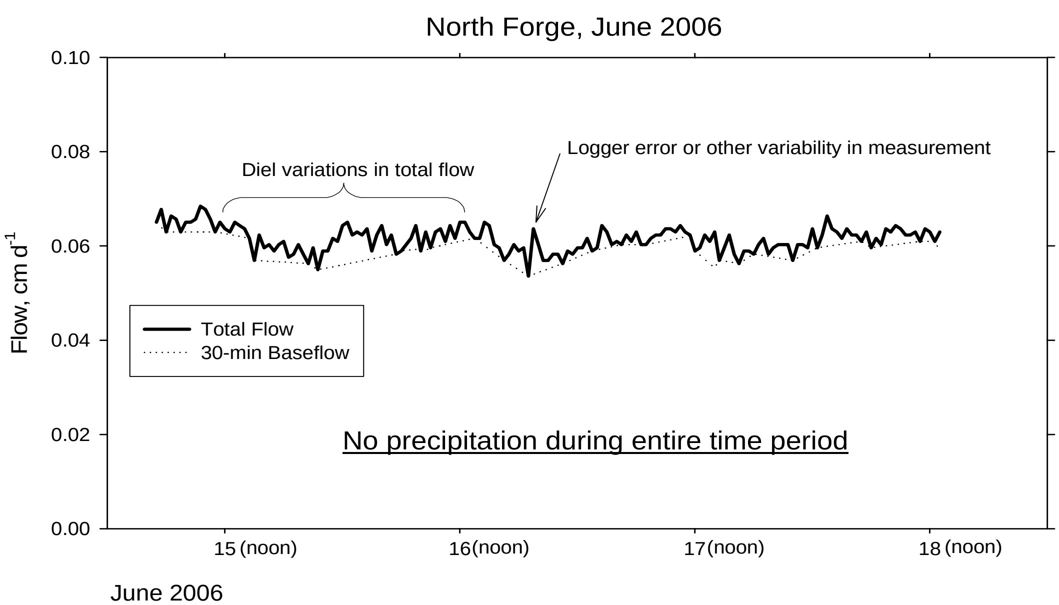


Figure 2-3. An example of the 30-min method of baseflow separation. Shown are 30-min total flow (solid line) and baseflow (dotted line) for the North Forge sub-basin during June 15 – 18, 2006. Using the 30-min approach, logger noise (arrow) and diel cycles of stream flow (bracket) were mistakenly considered "storm" events. No rain fell during this period.

The 5-day Method

The next approach was the 5-day method of Gustard et al. (1992), which is based on mean daily flow values. To follow their technique, the 30-min discharge values were first aggregated as mean daily flow by summing every 48 points (48 x 30 min = 1 day). The daily flow values were then processed according to the rules outlined in Table 2-2. The result was a baseflow index, a simple non-dimensional ratio equal to the volume of baseflow out of the total flow. Note the use of the term "time step" in Table 2-2, which is defined as the time period between flow windows. The calculations for the 5-day method are based on calculating the minimum of each 5-day flow window (Fig. 2-4a). As noted, this method has been widely used in the literature (e.g. Jordan et al. 1997, Vanni et al. 2001, Villar et al. 2002, Schoonover and Lockaby 2006).

In general, the 5-day method had mixed results with the observed data. Over the 15-month study period (June 2006 – Aug 2007), the 5-day method calculated a base flow index of 0.49 for the Blockston sub-basin (Fig. 2-5), which is comparable to values reported by Jordan et al. (1997) for the coastal plain. However, while it gave reasonable results over long time periods, it was generally not sensitive enough at the event scale. For example, during a small (20 cm stage increase) event at the North Forge sub-basin in June 2006, the 5-day method projected 19 continuous days of quickflow despite only intermittent, light rain (<1.4 cm d^{-1}) during this period, including one four day period (June 15 – 18) with zero rain (Fig. 2-6a). This result is counter to field observations of the streams returning to baseflow 1 – 2 days after

Table 2-2. Procedure for baseflow separation using the 5-day method of Gustard et al. (1992). The term "flow window" refers to the size of each data block, i.e. a flow window of 5 days means dividing a long data set into non-overlapping groups of 5 days each. The term "time step" is defined as the time period between the start of each flow window. For the 5-day method, both the flow window and the time step were 5 days (see Fig. 2-4a).

Step No.	Description
1	Divide daily flow into non-overlapping blocks of 5 days (i.e. flow window = 5 days). Find the minimum for each flow window.
2	If 0.9 times the minimum in flow window '*n*' is less than the minima in flow window '*n-1*' AND in flow window '*n+1*', then the minimum in flow window '*n*' is considered "baseflow." Otherwise, the minimum is "quickflow."
3	Repeat the above for the next flow window in the sequence. The time period between flow windows is called the "time step." For the 5-day method, the time step is 5 days. Continue repeating steps #1 -2 for the whole time series.
4	Perform linear interpolation between daily baseflow measurements to fill in the rest of the baseflow points for each day. If the interpolated baseflow exceeds the total measured flow on any given day, then re-define baseflow as equal to the total flow. If the interpolated baseflow is less than the total measured flow for that day, the difference is quickflow.
5	Calculate a baseflow index (BFI) for the entire time series as the sum of the daily baseflow measurements divided by the sum of the daily total flow measurements. The scale for the BFI is 0 -1, with 1 being 100% baseflow and 0 being 100% quickflow.

events of this size. In over-estimating quickflow, the 5-day method also failed to resolve additional events occurring within the June 1 – 19 time period (see arrows in Fig. 2-6a). The entire 19-day period was lumped into "one storm." Baseflow was calculated to be 84.0% of the total flow over the time period shown in Fig. 2-6a (May 29 – June 21). While this is not unreasonable for this time of year when ET is high, the continuous integration of quickflow during periods of zero or light rain (<1.4 cm d^{-1}) was clearly under-estimating baseflow and over-estimating quickflow.

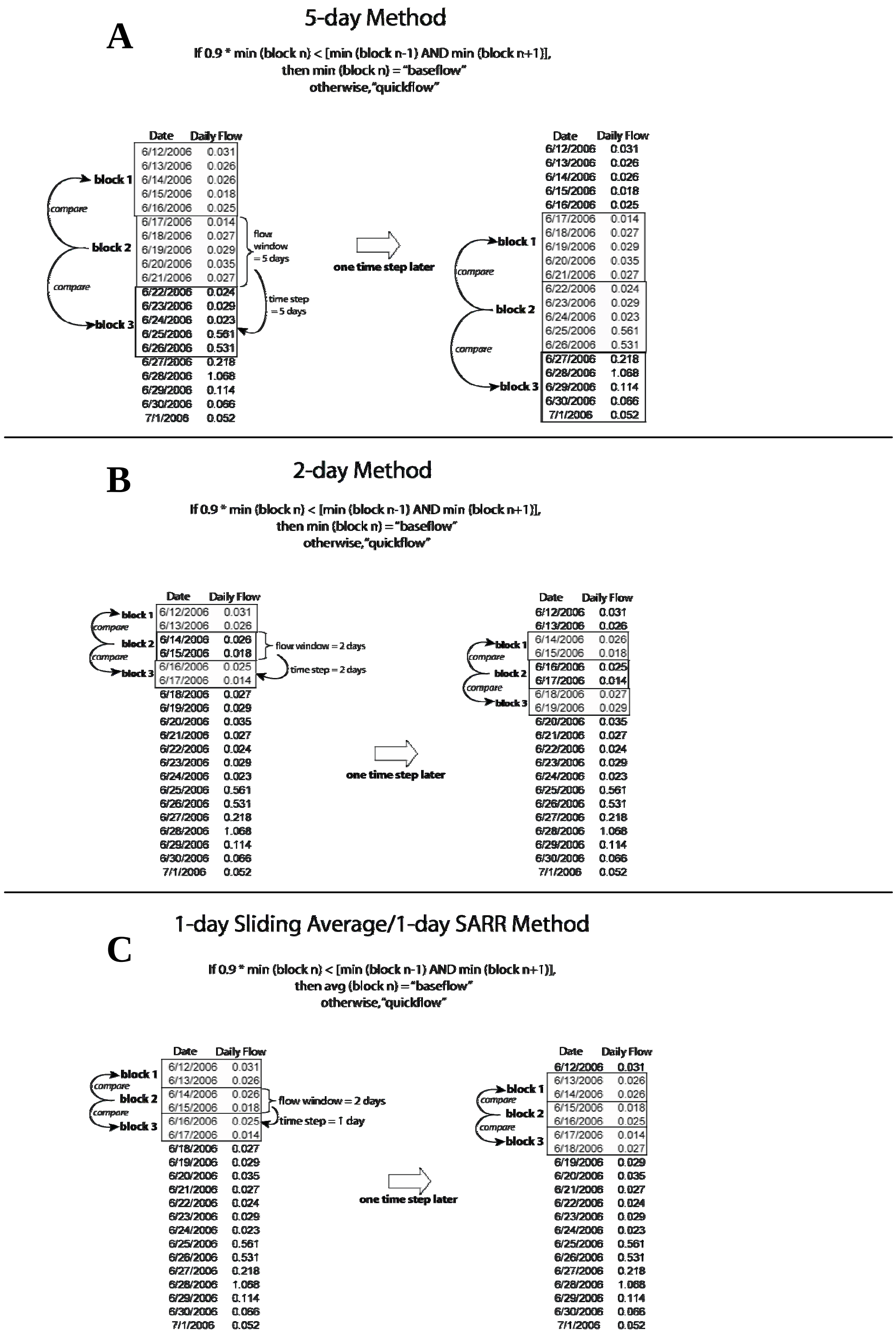


Figure 2-4. Comparison of the calculations for the 5-day (A – top panel), 2-day (B – middle panel), and 1-day (C – bottom panel) methods of baseflow separation. The data is divided into non-overlapping flow windows (see rectangles) of varying size. Each flow window is compared to the one before and after it using the formulas listed for each method. One time step later, the same is done for the next flow window in the sequence, and so on for the entire time series. The 1-day methods (panel C) are the only ones that use an average, not a minimum.

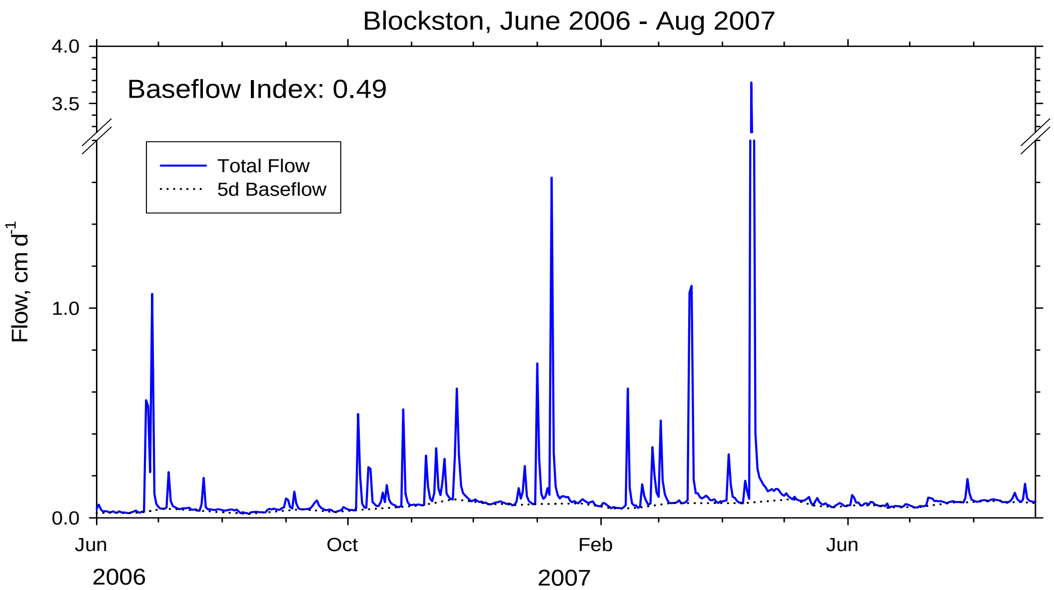


Figure 2-5. Daily total flow (solid line) and baseflow (dotted line) for the June 2006 – Aug 2007 study period at the Blockston sub-basin. Baseflow was separated using the 5-day method of Gustard et al. (1992). At this long time scale, the 5-day method gave reasonable results. The baseflow index of 0.49 is comparable to values reported by Jordan et al. (1997).

The 2-day Method

To address these limitations, a third method was developed called the 2-day method. This approach was identical to the 5-day method except the flow window was changed from five days to two days to match more closely the response time of the streams. This modification made the baseflow separation more sensitive to rainfall. The calculations were again based on the minimum of each flow window, although now the flow window was shorter (Fig. 2-4b). In general, the 2-day approach gave better results. For example, looking at the same event at North Forge as described above, the 2-day approach estimated a faster return to baseflow following the end of rainfall, and was able to resolve additional events which the 5-day approach failed to resolve (Fig. 2-6b). The % baseflow increased from 84.0 % to 90.4 % because of the improved sensitivity and the faster return to baseflow.

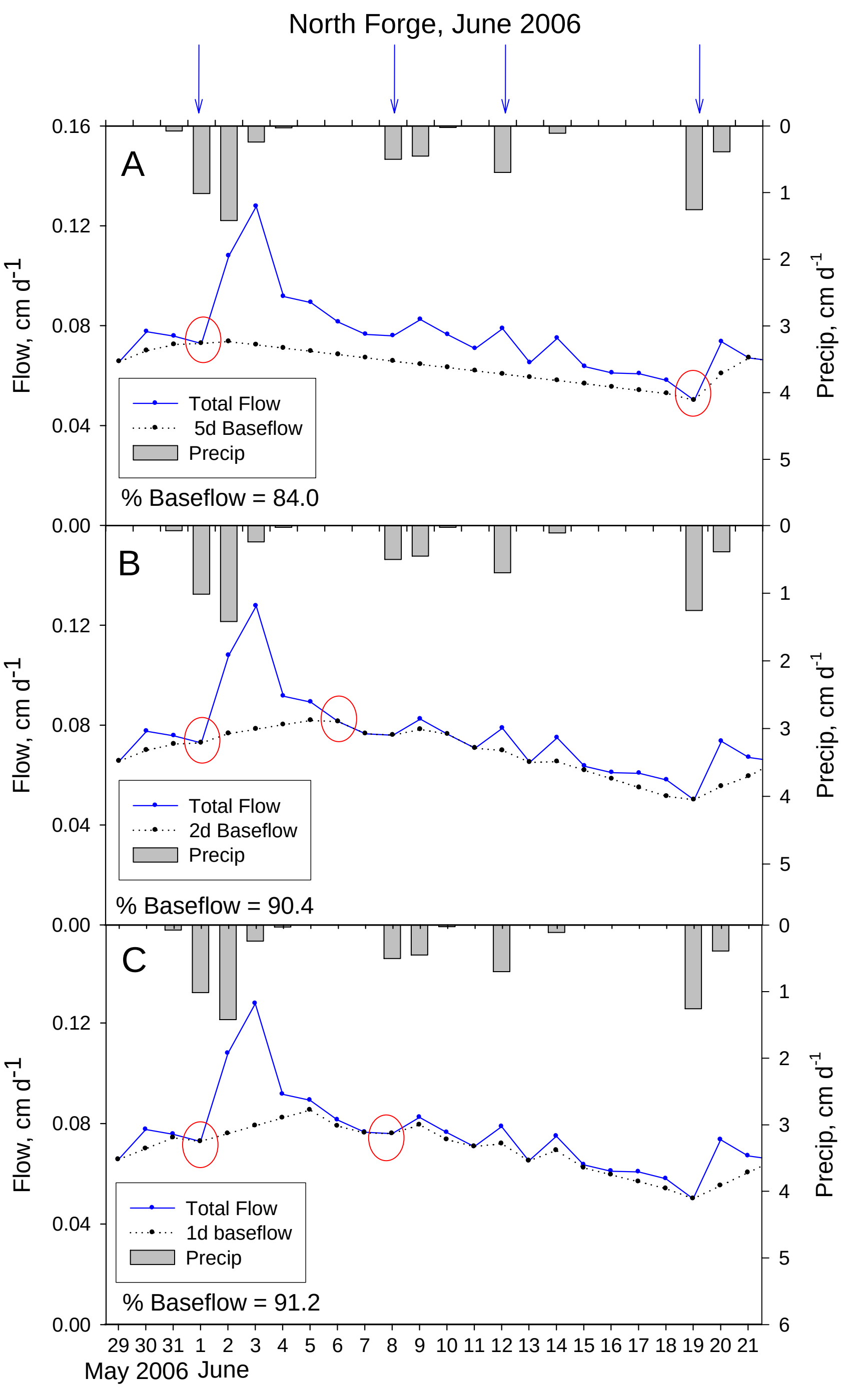


Figure 2-6. Comparison of the 5-day (A – top panel), 2-day (B – middle panel), and 1-day sliding average/1-day SARR (C – bottom panel) methods of baseflow separation. This example is for the North Forge sub-basin during a small event (+ 20 cm stage increase) in June, 2006. Event integration periods are shown with circles. The % baseflow, shown in the lower left-hand corner of each panel, is calculated for each method across the time period shown (May 29 – June 21). The 5-day method fails to resolve multiple events (see arrows), whereas the more sensitive 2-day and 1-day methods are able to distinguish among them. As method sensitivity improves, the % of baseflow increases.

Although the 2-day method was an improvement, it still occasionally over-estimated quickflow. For example, during a small event at the Blockston sub-basin in 2006, the 2-day method estimated 12 continuous days of quickflow (May 24 – June 4) despite relatively little rain during this period (<1.4 cm d^{-1}; Fig. 2-7b). This over-estimation of quickflow was likely due to the use of a minimum function to interpolate the baseflow curve. This point underlines the weakness of the 2-day method. By taking the minimum of every two daily flow measurements, the method systematically classifies 50% of the data (i.e. one daily measurement out of every two) as quickflow. Hence, the 2-day method also under-estimated baseflow, primarily because the minimum of each 2-day flow window was chosen to represent baseflow.

The 1-day Sliding Average Method

To correct this issue, a fourth method was developed: the 1-day sliding average. This approach was the same as the 2-day except: 1) It reduced the time step to one day, hence the term "sliding," which means a contiguous movement from one day to the next, and 2) It calculated the *average* of every two daily flow measurements instead of a minimum to eliminate the under-estimation of baseflow described above (Fig. 2-4c). Results show that the 1-day sliding average method resolved very small events better than either the 5-day or the 2-day methods. For example, at the Blockston sub-basin, the 1-day approach was the only one able to resolve both of the tiny events (<7 cm stage increase) occurring on May 26 – 27 and May 31 – June 4, 2006 (Fig. 2-7c). This improved resolution resulted in the highest %

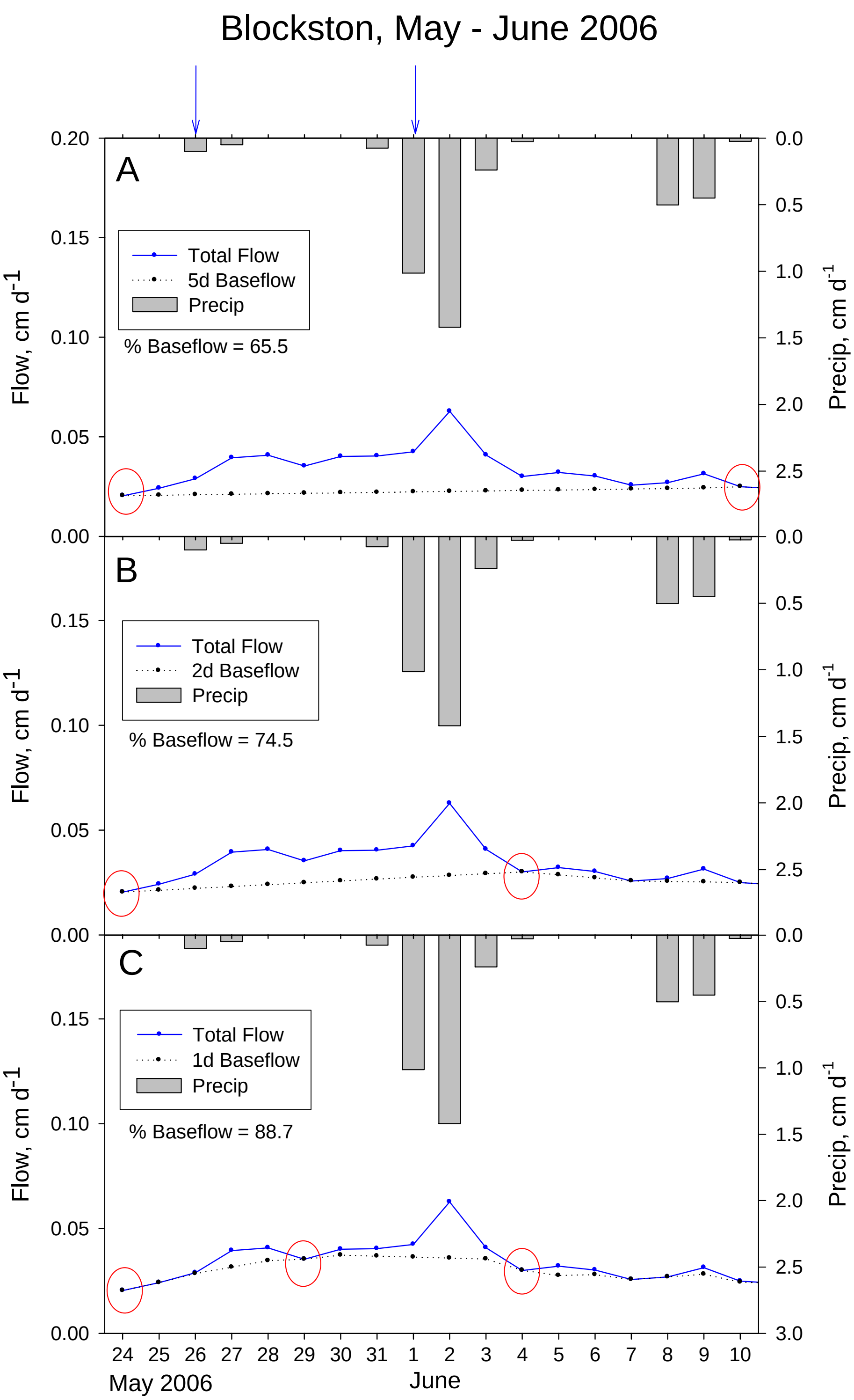


Figure 2-7. Comparison of the 5-day (A – top panel), 2-day (B – middle panel), and 1-day sliding average/1-day SARR (C – bottom panel) methods of baseflow separation. This example is for two very small events (< 7 cm stage increases) during May-June, 2006 at the Blockston sub-basin. Event integration periods are shown with circles. The % baseflow, shown in the left side of each figure, is calculated for each method across the time period shown (May 24 – June 10). Both the 5-day and 2-day methods under-estimate baseflow and fail to isolate both events (see arrows).

baseflow estimate for this sub-basin (88.7%) of any of the methods (Fig. 2-7c), suggesting that baseflow was no longer being under-estimated as it was for the 5-day and 2-day methods. Again, this is because the average (not the minimum) was used to determine the baseflow curve.

However, even the 1-day sliding average method was not perfect. A major drawback was that it occasionally identified quickflow despite the absence of rain at *any* of the precipitation stations. For example, at the Blockston sub-basin, the 1-day sliding average method calculated an event on August 15 -16, 2006 despite minimal (<0.04 cm d^{-1}) or zero rain during the previous five days (Fig. 2-8). While it is possible that all of the rain stations missed a small localized event, it is more likely that this "event" was a mis-classification of quickflow. These errors are called "inconsistencies" and are defined as the number of days on which quickflow occurs despite the absence of rain at any of the stations. Among the six sub-basins, the number of inconsistencies ranged from 13 – 43 days, or 3 – 9% of the study period. These discrepancies cause baseflow to be under-estimated and lead to misidentification of events.

The 1-day SARR Method

To fix the inconsistencies, the discharge data were cross-referenced with the rainfall record. This new, precipitation-linked method was called the 1-day SARR ("1-day **S**liding **A**verage with **R**ain **R**ecord"). It was the only approach which used the precipitation data to help define events. The 1-day SARR method had several advantages over the other methods. Unlike the 5-day and 2-day approaches, it

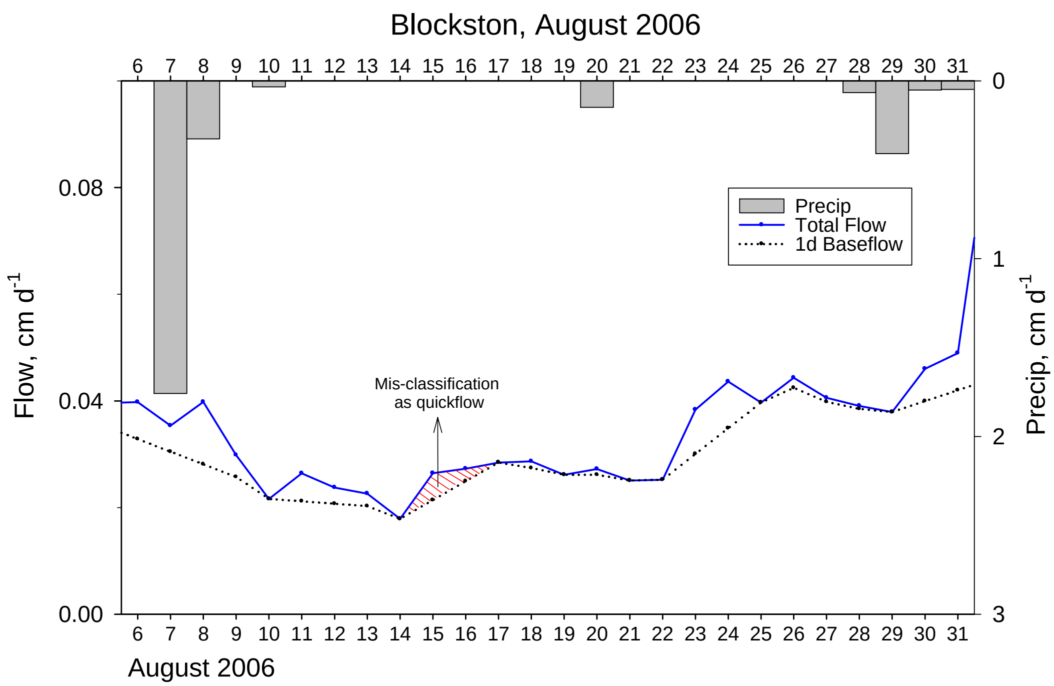
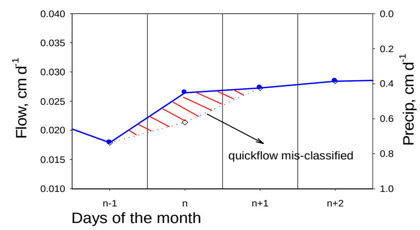
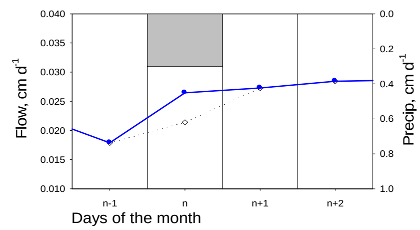
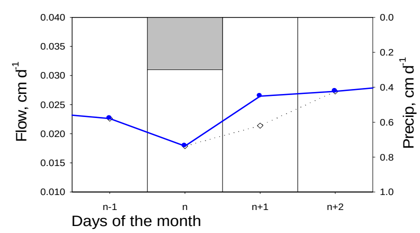
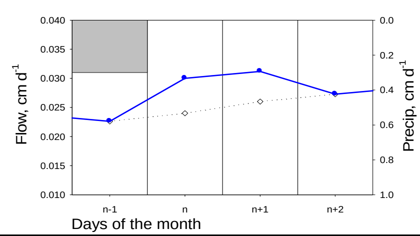
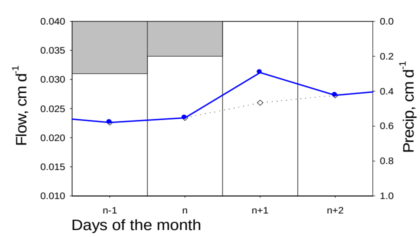


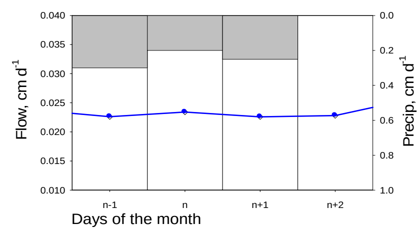
Figure 2-8. This graph shows an example of an inconsistency in the 1-day sliding average method of baseflow separation. Shown are daily total flow (solid line), baseflow (dotted line), and precipitation (gray bars) for the Blockston sub-basin during August, 2006. No rain fell from Aug 11-13, yet the baseflow separation method shows quickflow (dashes) occurring on Aug 15 – 16.

calculated an *average* instead of a minimum to eliminate any under-estimates of baseflow (Fig. 2-4c), and used a 1-day flow window for improved sensitivity to rainfall. Also, unlike the 1-day sliding average method, it was consistent with the rainfall record.

In linking the 1-day SARR method to precipitation, it became necessary to develop rules to govern the relationship between rainfall and quickflow (Table 2-3). The intention of these rules was to mimic field observations of the sub-basins and avoid common sense errors. In doing so, they eliminated inconsistencies (rule 1), established a basis for legitimate quickflow (rule 2), allowed for time lags between rainfall and stream response (rules 3-4), and acknowledged the possibility that

Table 2-3. Rules for cross-referencing precipitation and quickflow, as developed for the 1-day SARR method of baseflow separation to remove inconsistencies in the discharge record.

Rule	Purpose	Example Figure
1.) If no rainfall occurs at any of the 11 regional stations on day *n*, or on day *n-1*, and quickflow is estimated to occur on day *n*, then that quickflow is mis-classified. To resolve this, baseflow was set equal to the observed total flow.	Corrects inconsistencies (i.e. where quickflow occurs without accompanying rainfall)	
2.) If rain occurs at any of the 11 regional stations on day *n*, and quickflow also occurs on day *n*, then that quickflow is considered to be part of a "real event."	Establishes a basis for legitimate quickflow	
3.) If rain occurs at any of the 11 regional stations on day *n*, and quickflow does not occur on day *n*, but does occur on day *n+1*, then that quickflow is considered to be part of a "real event." This rule allows for a one day time lag between the time of rainfall and the response of the stream.	Allows for a one-day time lag in hydrologic response	
4.) Multiple, contiguous days of quickflow are left intact as long as the initial day of quickflow is correctly classified as a "real event" per rules 2 & 3 above.	Allows for multiple days of quickflow	
5.) If rain occurs *continuously* on days *n-1* and *n* with no accompanying quickflow, but quickflow does occur on day *n+1*, then the rain is considered part of the event. This rule allows for 2 days of rain without quickflow. The *initial* rainfall is assumed to enter soil storage or be lost via ET. Note that if rainfall were not continuous (i.e. occurs on day *n-1* but not day *n*), then the quickflow would be mis-classified per rule #1.	Allows for partial soil storage/ET and a delayed hydrologic response	

6.) If rain occurs continuously for up to 3 days with no accompanying quickflow, it is considered a "real event" in which 100% of the precipitation is absorbed by the basin, or lost due to evapotranspiration. No instances of rainfall occurring for > 3 days without quickflow were observed in the dataset.	Allows for 100% soil storage/ET and zero hydrologic response	

precipitation might not reach the stream due to soil storage and ET (rules 5-6). The latter is especially likely during the summer when soils are dry and ET rates are high.

In comparing the 1-day SARR with the 5-day and 2-day approaches, it was clearly the optimal method. For events ranging from very small (< 7 cm stage increase) to moderate (20 cm stage increase), it was the most sensitive to rainfall, the least biased in terms of under-estimating baseflow, the most capable of resolving events, and the only method fully consistent with the observed basin response times (Figs. 2-6a-c, 2-7a-c). However, for large events (e.g. 75, 180 cm stage increases), no major differences were observed among the methods (Fig. 2-9a-c).

Methods Comparison

The differences among the baseflow separation methods are summarized in Table 2-4 using the Blockston sub-basin as an example. At the 15-month time scale, the differences were fairly small. Baseflow varied from 25.0 to 29.4 cm, and increased with each method as sensitivity improved. Indeed, sensitivity was really the driving factor in the baseflow estimates. The more sensitive 1-day methods had relatively short event integration periods (see circles in Figs. 2-6a-c, 2-7a-c), resolved

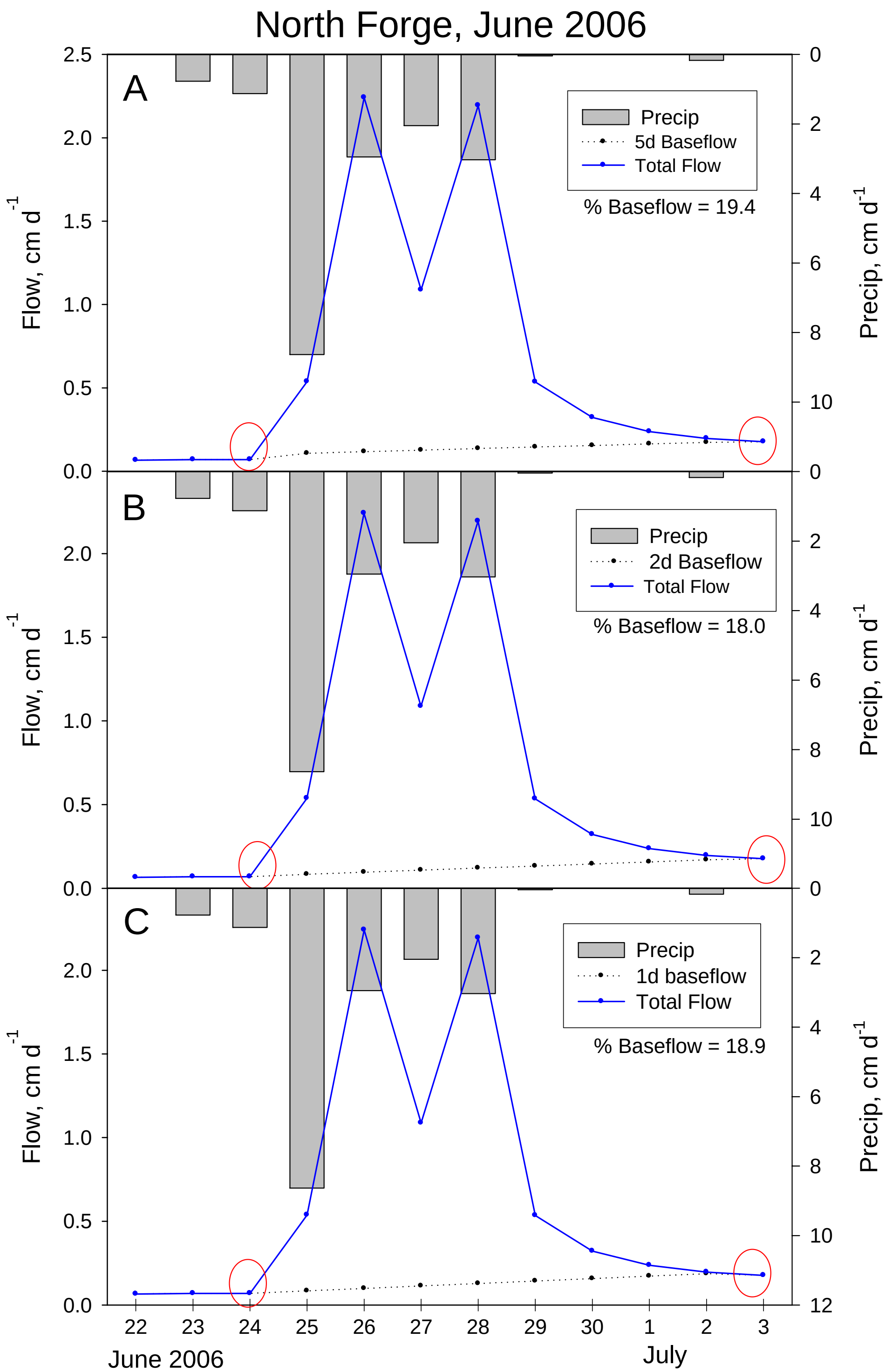


Figure 2-9. Comparison of the 5-day (A – top panel), 2-day (B – middle panel), and 1-day sliding average/1-day SARR (C – bottom panel) methods of baseflow separation. This example is for the North Forge sub-basin during a large event (+ 180 cm stage increase) in June, 2006. Event integration periods are shown with circles. The % baseflow, shown on the right side of each panel, is calculated for each method across the time period shown (June 22 – July 3). Differences among the baseflow curves are minor, and changes in the % baseflow are negligible. For all three methods, the event starts on 6/24/06 and ends on 7/3/06.

Table 2-4. Quantitative comparison of the various baseflow separation methods over the 15-month study period (Jun 2006 – Aug 2007). This example is for the Blockston sub-basin. Units are cm per study period except where noted. BFI = Baseflow Index.

	5-day Method	**2-day Method**	**1-day Sliding Avg. Method**	**1-day SARR Method**
Total flow	51.1	51.1	51.1	51.1
Baseflow	25.0	28.0	29.0	29.4
Quickflow	26.1	23.1	22.1	21.7
BFI (unitless)	0.49	0.55	0.57	0.58
Calc. # events	45	91	94	93

the full spectrum of event sizes, and *averaged* the baseflow to avoid under-estimates. The less sensitive 5-day and 2-day methods, on the other hand, had longer event integration periods (see circles in Figs. 2-6a-c, 2-7a-c), a limited resolution of very small and small events, and calculated the *minimum* baseflow, which created a systematic negative bias. Consequently, the more sensitive 1-day methods had higher estimates of baseflow (29.0 cm or greater), whereas the coarser 5-day and 2-day methods had lower estimates of baseflow (25.0 and 28.0 cm, respectively). Baseflow increased most dramatically from the 5-day to the 2-day method (25.0 cm to 28.0 cm). This jump illustrates how changing the flow window from five to two days has a large effect on method sensitivity, which leads to big improvements in baseflow estimates. Quickflow ranged from 21.7 - 26.1 cm (Table 2-4), and was inversely related to baseflow, since baseflow + quickflow = total flow. The baseflow index varied from 0.49 – 0.58 (for the same sub-basin) depending on which method was used (Table 2-4). This range is comparable to values reported by Jordan et al. (1997) for the coastal plain.

Among the various approaches, the calculated number of events ranged from 45 – 94 (Table 2-4) with higher estimates for the more sensitive methods. For the 5-day, 2-day, and 1-day sliding average methods, events were counted as the number of unique separations of the hydrograph, whereas for the 1-day SARR, events were counted based on both the number of unique separations *and* the rainfall record. As expected, the coarser 5-day and 2-day methods estimated relatively few events (45 and 91, respectively), whereas the more sensitive 1-day methods estimated higher numbers (93 – 94). Again, the large jump in the number of events from the 5-day to the 2-day method (45 to 91) underlines the importance of the flow window size. The number of events for the 1-day sliding average and 1-day SARR methods differed by only one (94 versus 93). However, the event *time periods* were different for these two approaches because the latter used the rainfall record to help define events, whereas the former did not.

Summary of Baseflow Separation

At the event scale, the 1-day SARR method gave the optimal results. It was the only method that was fully consistent with the observed basin response times. It was the most sensitive to rainfall, yet not so sensitive that it mis-classified logger noise and diel cycles as “events.” It was the only approach able to resolve the full spectrum of event sizes, including very small events which the other methods could not resolve. It calculated an average instead of a minimum to avoid under-estimating baseflow. Finally, it cross-referenced the rain record to correct any inconsistencies where apparent quickflow occurred in the absence of precipitation. Again, the 1-day SARR was the only method linked to rainfall.

The differences among the methods are summarized in Fig. 2-10. This conceptual graph shows how method sensitivity changes over different event sizes,

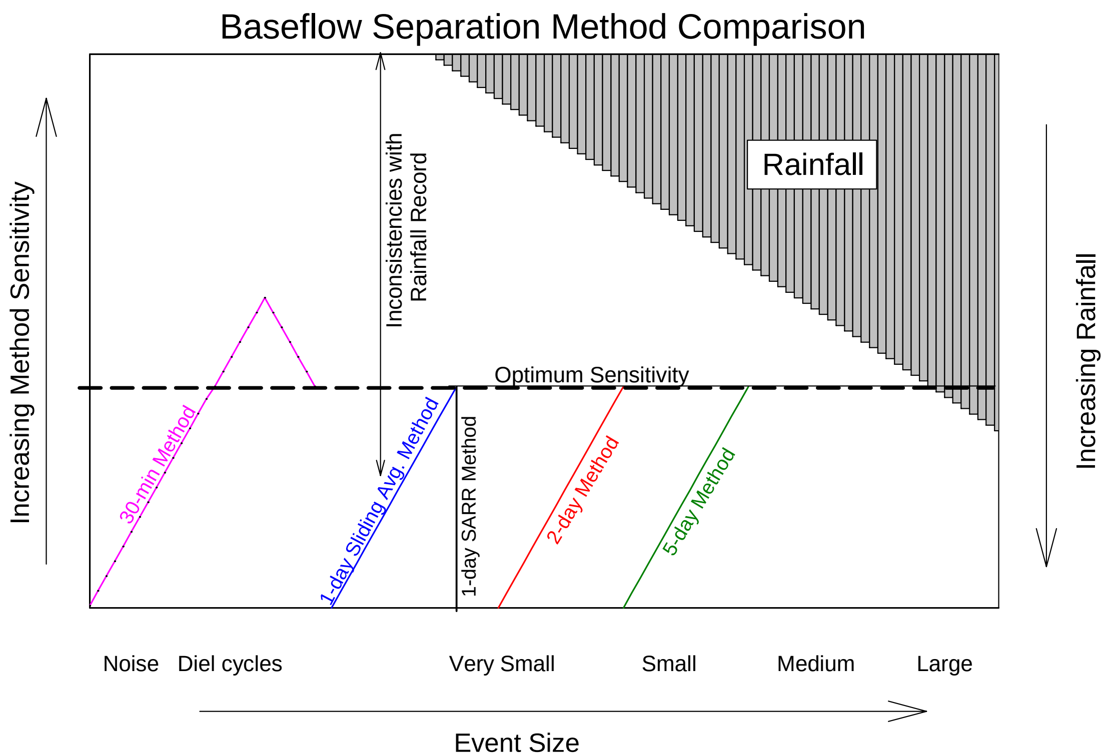


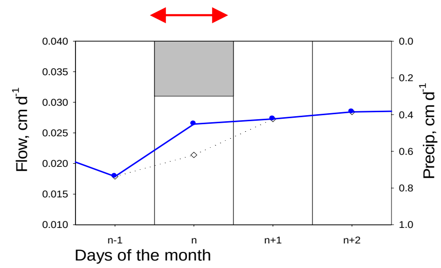
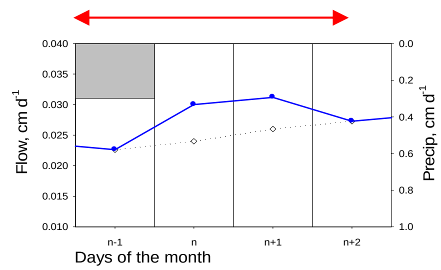
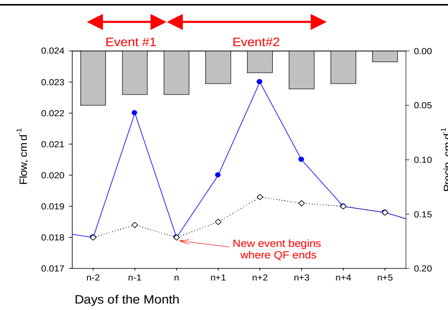
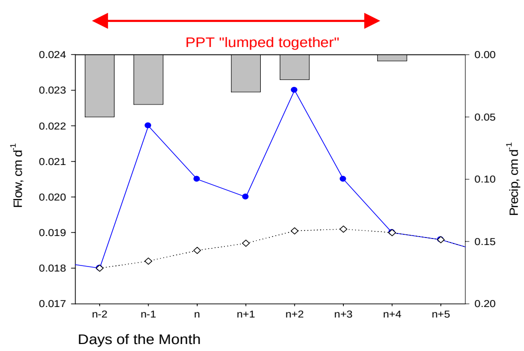
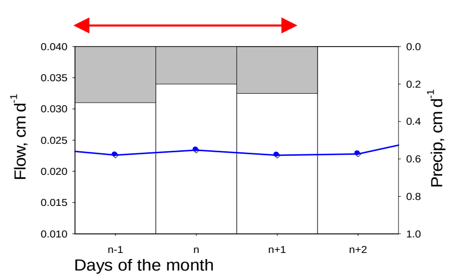
Figure 2-10. Conceptual comparison of the various baseflow separation methods. The 30-min approach is overly sensitive at the noise end of the event size spectrum. For the other methods, sensitivity drops below optimum (horizontal dotted line) for a certain size class. The 1-day sliding average method has optimum sensitivity for all size classes but is inconsistent with the rainfall record. The 1-day SARR approach is ideal: it resolves all event size classes, does not mistake noise and diel cycles for "events," and is fully consistent with the rain record.

ranging from micro-fluctuations (e.g. logger noise, diel cycles) to large events. As discussed earlier, the 30-min approach was overly sensitive at the noise end of the spectrum, while at the other end, the 5-day method was not sensitive enough to resolve anything but medium and large events. The rest of the methods fell between these extremes. Sensitivity for the 2-day method dropped below optimum for very small events. The 1-day sliding average resolved all storm sizes ranging from very small to large, but this method was not linked to precipitation and therefore it calculated inconsistencies where quickflow occurred without accompanying rainfall. The 1-day SARR method had optimum sensitivity for the full range of events *and* was fully consistent with the rain record. Clearly, of all the baseflow separation techniques, the 1-day SARR was the most effective at the event scale, and was therefore used for the event analysis component of this thesis (see below).

Event Identification

Events were identified at each sub-basin using a combination of precipitation data and discharge data. To define the event time periods, the total daily discharge was first separated into quickflow and baseflow components using the 1-day SARR method. Quickflow was defined as total flow minus baseflow. The daily quickflow values were then cross-referenced to the daily precipitation record, resulting in five possible scenarios (Table 2-5). In the simplest case (scenario 1), the precipitation period was the same as the quickflow period, resulting in an event time period equal to either one or the other (since they were equivalent). Oftentimes, however, quickflow extended past the end of precipitation due to time lags in the stream's response. In these cases (scenario 2), the duration of the event was identified by the two extremes---the first day of rainfall through the last day of quickflow. Occasionally, multiple separations of the hydrograph occurred within a continuous period of rainfall. For these situations (scenario 3), the precipitation was divided into separate events along the breaks in each quickflow period. On the other hand, when quickflow was continuous but precipitation was not, the latter was aggregated as one event (scenario 4). Finally, for some events, precipitation occurred but no quickflow was observed. For these cases (scenario 5), the event time period was equal to the precipitation time period. Event precipitation was calculated by summing the daily

Table 2-5. Methods for defining event time periods. Each event time period is indicated by:

Scenario No.	Scenario description	Event time period defined as:	Example Figure
1	Precipitation contiguous with quickflow	Precipitation or quickflow period (they are equivalent)	
2	Quickflow extends past precipitation	1st day of precipitation to last day of quickflow	
3	Multiple quickflow periods for 1 continuous precipitation period	quickflow period (each quickflow period is a unique event)	
4	Multiple precipitation periods for 1 continuous quickflow period	Quickflow period (precipitation is "lumped together" as one event)	
5	precipitation but no quickflow	precipitation period	

precipitation values over each event time period. Similarly, event quickflow was calculated as the sum of the daily quickflow values over each event time period. The % quickflow for each event was calculated as: (event quickflow / event precip) * 100 = % quickflow.

Quickflow Analysis at Multiple Time Scales

Quickflow was compiled over three different time scales: event, monthly, and annual. At the event scale, precipitation and quickflow were integrated for individual storms as described above. The average event quickflow was also calculated for each of two seasons: warm (May – Sept) and cool (Oct – Apr). Monthly quickflow was compiled by summing all of the daily quickflow values for each of the 15 months in the study period. Annual quickflow was calculated by summing the daily quickflow values over the 15-month study period and then normalizing to 365 days. At the event and monthly time scales, the 1-day SARR method was used to separate baseflow, while at the annual scale, the 5-day method of Gustard et al. (1992) was employed to be consistent with its intended use.

Annual Water Budgets

Annual water budgets were also estimated for each sub-basin. Annual precipitation was calculated as the annual equivalent average of the 17 stations in the precipitation network with corrections at eight of the sites to adjust for measurement errors (Ch. 1). The term "annual equivalent" refers to scaling the different time periods at each station to a common annual time period of 365 days (Ch. 1). Annual water yields (cm y^{-1}) were calculated as the sum of all 30-min discharge observations over the 15-month study period, divided by the sub-basin area, and then normalized to 365 days. The amount of precipitation entering soil storage or lost due to ET was estimated as precipitation minus water yield. Deep recharge (>15 m) was assumed to be zero due to the presence of a continuous aquiclude in the Choptank region (Norton and Fisher 2000). In previous hydrologic modeling of the Choptank Basin, Lee et al. (2001) estimated deep recharge as <3% of rainfall. Annual quickflow was estimated by summing all of the daily quickflow values over the 15 months, and then normalizing to 365 days. Annual baseflow was calculated in the same way except using the daily baseflow values. Baseflow was separated using the 1-day SARR method. Finally, to help quantify potential errors in the hydrologic data, water yields were compared to the nearest USGS gauging station, which is located in the upper Choptank Basin near Greensboro, MD (USGS site no. 1491000), just east of the North Forge sub-basin (Fig. 2-1). Daily data for the Greensboro station were downloaded from the USGS website (http://waterdata.usgs.gov). Water yields at Greensboro were calculated as the annual sum of the daily flow values normalized to sub-basin area.

Flow Frequency Analysis

Flow frequency was analyzed using two basic approaches: 1) Flow duration curves, and 2) Histograms. A flow duration curve (FDC) is a plot of flow magnitude versus frequency, and is a useful way of displaying the entire range of flow conditions, although it does not show *when* the different flows occurred. The shape of an FDC is a function of watershed attributes when flow is normalized by sub-basin area (Smakhtin 2001). In previous studies, FDCs have been used to demonstrate the effects of afforestation (Lane et al. 2005), geology (Searcy 1959), and climate change (Wilby et al. 1994) on the flow regime of streams and rivers. In this context, the FDCs are used to characterize the hydrology of the study sub-basins, and to detect any effects of hydric soils.

FDCs were generated for each sub-basin by arranging the 30-min total flow record during the study period (June 2006 – August 2007) in order of increasing magnitude, and then calculating every 5th percentile (e.g. 5th, 10th, etc). Each percentile was then plotted against the % of time that value was exceeded. The flow values along the curve are referred to as "Qnth" where *n* is the % of time exceeded, e.g. Q50 is the flow equaled or exceeded 50% of the time. Once the FDCs were constructed, three indices were calculated based on the shape of the curves, including 1) Q20/Q90, a measure of streamflow variability (Arihood and Glatfelter 1991), 2) Q50/Q90, a measure of baseflow variability (Smakhtin 2001), and 3) Q90/Q50, a measure of groundwater contributions (Smakhtin 2001).

Histograms were generated by grouping the daily flow data into various size classes, and then counting the number of days in each class. The size of the classes was arbitrarily chosen as 0.2 cm d^{-1} (e.g. 0.0 – 0.2, 0.2 – 0.4, etc). The number of days with >0 quickflow (as separated using the 1-day SARR method) were also counted and plotted on the same histogram. Unlike FDCs, histograms have the advantage of showing the absolute frequency of the different flow magnitudes (i.e. the number of days instead of a percentage of time) and of showing the relative contributions of baseflow and quickflow for each size class.

Regional Analysis of Delmarva USGS Data

To generate a second test of the hypothesis that hydric soils increase quickflow volume, another data set was compiled for 13 USGS gauging sites across Delmarva. Hydrologic data were downloaded from the USGS website (http://water.usgs.gov/) as both average daily and average annual flow for the longest time period available. The sites were selected based on three criteria: 1) They were located in central Delmarva, 2) They had a minimum of a 7-year flow record, 3) They were non-tidal, and 4) Soil Survey Geographic Database (SSURGO) soils data were available for the county(s) in which the sub-basin was located. The sub-basins were delineated with ArcGIS software using established HUC12 boundaries as a guideline. HUC 12 watersheds were available from the Maryland Department of Natural Resources Geospatial Data website (http://dnrweb.dnr.state.md.us/gis/data/index.asp), the University of Delaware's Spatial Analysis Lab (www.udel.edu/FREC/spatlab), and the Delaware Data Mapping and Integration Laboratory (http://datamil.delaware.gov/). Unfortunately, USGS gauging stations do not coincide exactly with HUC 12 sub-basin boundaries, although in many cases only a minor adjustment to the watershed boundary was necessary. Adjustments were made with the help of a blue-line stream coverage available through the USGS' National Hydrography Dataset (http://nhd.usgs.gov/). In general, the HUC 12 sub-basin boundaries were adjusted so that they ran precisely halfway between adjacent blue-line streams draining in opposite directions. The size of each USGS sub-basin was available from the USGS website (http://waterdata.usgs.gov/nwis), though not the actual sub-basin boundaries. In general, the size of the delineated watersheds agreed well with the published USGS sub-basin sizes, generally within ± 5%, suggesting that the delineated watershed boundaries were largely correct.

Once the sub-basins were defined, the county-level soils data (SSURGO) were downloaded from the USDA's website (http://soildatamart.nrcs.usda.gov/). These coverages were then clipped by each sub-basin to calculate the percentage of hydric soils in each watershed. In SSURGO, hydric soil attributes are listed as "all," "partial," and "none" for each soil mapping unit in the database. For the purposes of this analysis, "all" and "partial" were grouped together. As a practical matter, even map units which are classified as "all" hydric have inclusions of non-hydric soils because of the coarse resolution of the mapping (Schaetzl and Anderson 2005). In fact, at the scale of these watersheds (9 – 195 km^2), it is virtually impossible to have a map unit which is 100% hydric. In addition to soils data, two other coverages were also downloaded, including land use from the 2001 National Landcover Database (www.mrlc.gov) and elevation data from the USGS' National Map Seamless Server (http://seamless.usgs.gov/). The purpose of these downloads was to explore any potential effects of land use and slope on quickflow, baseflow, and total flow at these 13 USGS sites. In addition, the extent of ditches in each sub-basin was available through the previously mentioned National Hydrography Dataset.

The availability of the flow data varied among the sites. Three of the sites had <10 years of record (but no less than 7 years) while the remainder had >30 years of record. As mentioned, flow data were downloaded as both mean annual flow and mean daily flow. The availability also varied somewhat depending on which time scale was involved. For example, one of the sites (Chicamacomico River near Salem, MD, USGS Site No. 1490000) had 36 years of annual data available but only 7.3 years of daily data. However, for the vast majority of sites, there were only slight discrepancies in the availability of the daily and annual data. For each sub-basin, the annual flow was averaged over all available years and normalized by sub-basin area to get the average long-term water yield. The daily flow, on the other hand, was entered into a SAS software program (courtesy Dr. Tom Jordan) to separate daily baseflow and daily quickflow per the 5-day method of Gustard et al. (1992). Daily quickflow was equal to total flow minus baseflow. Each block of 365 daily baseflow and quickflow values (or 366 in the case of leap years) was summed to get annual baseflow and annual quickflow. This was repeated for each year in the record. The average of all the years was then calculated to get the mean long-term annual baseflow and quickflow for each site. The baseflow index was also calculated for each site per the method of Gustard et al. (1992).

Some of the sites had gaps in the flow data. In the case of the annual flow, years without data were simply excluded. However, for the daily data, years containing daily gaps were not excluded unless >180 of the days in that year had missing data. If a year had <180 days of missing data, the annual quickflow and baseflow were scaled to 365 days (i.e. sum of *n* observations/*n* * 365). For example, if a site had 63 daily flow gaps for the year 2003, leaving 302 days (365 – 63 = 302) *with* baseflow and quickflow data, then the sum of those 302 observations was divided by 302 and then multiplied by 365 to get the annual baseflow (or quickflow) for the year 2003. The choice of 180 days (~0.5 year) is somewhat arbitrary but seemed reasonable given that scaling to one year is probably not a good idea if <0.5 year of data is available.

The USGS sub-basins ranged from 7 – 195 km^2 (Table 2-6). The published sizes from the USGS website (http://water.usgs.gov/) were used, *not* the sizes of the delineated watersheds, although again the differences were generally small (± 5%). The calculated % of hydric soils (all + partial) ranged from 52 – 99 % among the sub-basins (Table 2-6). Land use among the sites was generally similar to the Choptank watersheds with ~2/3 agriculture, ~1/3 forest, and <3% urban. Other watershed attributes, including % of surface ponding on 75 – 100% of the map units, average sub-basin slope, length and % of ditches, and % wetland are shown in Table 2-6.

Results

Summary of Rain Events

Among the six Choptank sub-basins, the calculated number of events during the study period ranged from 63 – 100 (Table 2-7). However, four of the sites (Kitty's Corner, Cordova, North Forge, and Willow Grove) considerably under-estimated the storm population because of gaps in the discharge data (see "Daily Flow Record" section below), which again were used to help identify events. Only the Blockston and Beaverdam sub-basins, with 93 and 100 storms, respectively, represented true estimates of the storm population because they had no gaps in their discharge records (Table 2-7).

Table 2-6. Summary of sub-basin attributes for the 13 USGS sites. Included from left to right are the USGS site name and number, the sub-basin size, two soil metrics (% hydric and % of surface ponding on 75 – 100% of the map units), average sub-basin slope, length and % of ditches, and land use information. With the exception of sub-basin size, which was available through the USGS website (http://water.usgs.gov/), all of the data were calculated using GIS software.

USGS sub-basin name	USGS Site No.	Size, km^2	% hydric, all + partial	% Ponding on 75 - 100% of Map Units	Avg. Sub-basin Slope, % Rise	Ditched Length, km	% Stream Length Ditched	% Urban	% Forest	% Agriculture	% Wetland
Unicorn	1493000	51	52	0.0	0.8	3	4	1.3	22	68	8
Manokin	1486000	12	96	87.5	0.5	2	15	0.6	48	35	14
Beaverdam Ck near Salisbury	1486500	51	61	43.8	1.1	5	13	8.3	36	50	3
Chicamicomico	1490000	39	60	0.4	0.7	17	30	0.3	31	62	4
Pocomoke	1485000	157	97	68.7	0.5	147	50	0.5	37	52	10
Nassawango	1485500	116	91	42.9	0.8	18	16	0.6	59	28	9
South Fork	1484983	7	97	73.3	0.9	5	39	1.8	27	68	2
North Fork	1484981	9	99	70.9	0.8	6	29	1.1	29	65	4
Green Run	1484985	33	98	76.8	0.8	25	35	0.9	26	70	2
Beaverdam at Houston	1484100	8	59	43.1	0.4	0	0	0.1	37	62	1
Nanticoke	1487000	195	64	39.5	0.4	67	26	3.0	31	63	2
Marshyhope near Adamsville	1488500	121	90	72.3	0.5	60	26	0.5	35	62	2
Murderkill	1484000	33	56	42.6	0.6	7	11	2.4	33	62	3

Table 2-7. Summary of hydrologic data for the six Choptank sub-basins over the 15-month study period (Jun 2006 – Aug 2007). Outliers are defined as events where quickflow > precipitation. They were not used to calculate the averages (columns E - G) because they greatly skewed the data. In columns E – G, data are displayed as: *mean (standard error, sample size)*. Baseflow was separated using either the 1-day SARR method to calculate the number of quickflow days (columns H – J), or the 5-day method of Gustard et al. (1992) to calculate the baseflow index (column K). The all-hydric control site (Willow Grove) is marked in gray. The average % of time and flow which quickflow contributed is shown on the last row of the table (columns I – J). BFI = baseflow index, W.Y. = water yield, QF = quickflow.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
					Units are % of Precipitation									
	Length of Record (d)	Missing Data d (% of record)	Calc. # Events	# Outliers Excluded	(All Seasons) Avg. Event QF	(May - Sept) Avg. Event QF	(Oct - Apr) Avg. Event QF	# Days w/ QF	% Time	% Flow	BFI	Annual W.Y.	Greensboro W.Y.	% Diff.
Cordova	396	61 (13%)	68	1	10.2 (1.7, 67)	6.9 (1.8, 30)	12.8 (2.7, 37)	263	66	29	0.61	42	53	-20
Kitty's Corner	371	86 (19%)	63	1	18.6 (2.2, 62)	8.0 (2.3, 30)	28.6 (2.5, 32)	265	71	53	0.34	57	52	9
Blockston	457	-	93	1	9.0 (1.3, 92)	4.2 (1.1, 51)	15.0 (2.2, 41)	321	70	43	0.49	40	47	-15
North Forge	401	56 (12%)	60	1	9.1 (1.3, 59)	6.4 (1.7, 32)	12.2 (1.8, 27)	291	73	28	0.61	48	53	-9
Beaverdam	457	-	100	4	8.8 (1.6, 96)	9.9 (2.7, 49)	7.7 (1.7, 47)	273	60	20	0.71	59	47	25
Willow Grove	386	71 (16%)	67	2	8.5 (2.1, 65)	3.5 (2.2, 30)	12.8 (3.3, 35)	258	67	14	0.77	60	45	33
								Avg:	68	31				

The distribution of storm sizes followed a log-normal pattern where smaller events were relatively common and larger events were increasingly rare (Fig. 2-11). As shown in this figure, storms with < 2 cm of rainfall represented 69% of the observed values. In contrast, events with >4 cm of rainfall represented <10% of the observed values. The largest single event took place in June 2006, when ~19 cm (7.5”) of rain fell over several days, causing widespread flooding across Delmarva (Fig. 1-3 in Ch. 1). The second largest event was in April 2007, when a major Nor’easter brought 9 – 11 cm (3 – 4”) of rain to the area. In general, among the sub-basins, the event totals varied slightly for the same storm because, as explained above, the events were identified with the help of the discharge record, which varied from site to site. For example, the large June event at the Blockston sub-basin (event #7) lasted 9 days (6/23/06 – 7/1/06) and had a rainfall total of 18.61 cm. In contrast, the same event at the Cordova sub-basin (event #5) lasted 10 days (6/23/06 – 7/2/06) and had a rainfall total of 18.79 cm. A full list of events occurring at each site is given in the Appendix.

Daily Flow Record

The daily flow record over the 15-month study period (Jun 2006 – Aug 2007) was characterized by frequent event flows up to 4.2 cm d^{-1} super-imposed onto baseflows that were typically < 0.3 cm d^{-1} (Fig. 2-12). Due to logger failures, data gaps of 1 – 3 months occurred at the Kitty’s Corner (Fig. 2-12a), Cordova, and North Forge sub-basins. In addition, the Willow Grove logger was not installed until August 2006, resulting in a 2.5-month gap at that site. The summer drought of 2007 was an

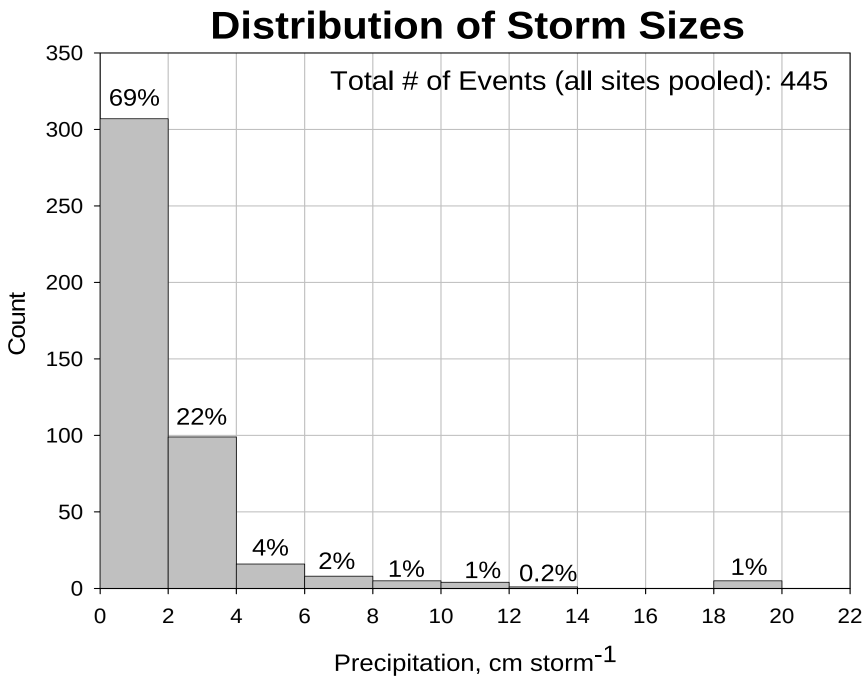


Figure 2-11. Event precipitation histogram for all storms occurring at all six Choptank sub-basins over the study period (Jun 2006 – Aug 2007). Precipitation totals for each storm were calculated by summing the mean daily rainfall for 11 regional stations over each event time period (see Ch. 1). Event time periods were defined as each unique separation of the hydrograph and its associated rainfall. All six sites are pooled for this graph, resulting in 445 total events. Shown above each bar is the percentage of the total number of storms.

especially low flow period for many of the sites. At Kitty's Corner, in particular, discharge was measured as either zero or negative (i.e. flow upstream) during much of the season (Fig. 2-12a), probably due to a tidal effect from the Choptank estuary, which is ~ 4 km downstream (Fig. 2-1). The Kitty's Corner site is only 0.71 m above sea level (USGS 2008).

The sub-basins varied more than two-fold in their groundwater contributions based on the baseflow index (BFI). The differences among the sub-basins can be illustrated by comparing the extreme cases. The Kitty's Corner site, with the lowest baseflow index (0.34), had relatively small groundwater inputs and large event peaks (Fig. 2-12a). In contrast, the Beaverdam sub-basin, with a baseflow index of 0.71,

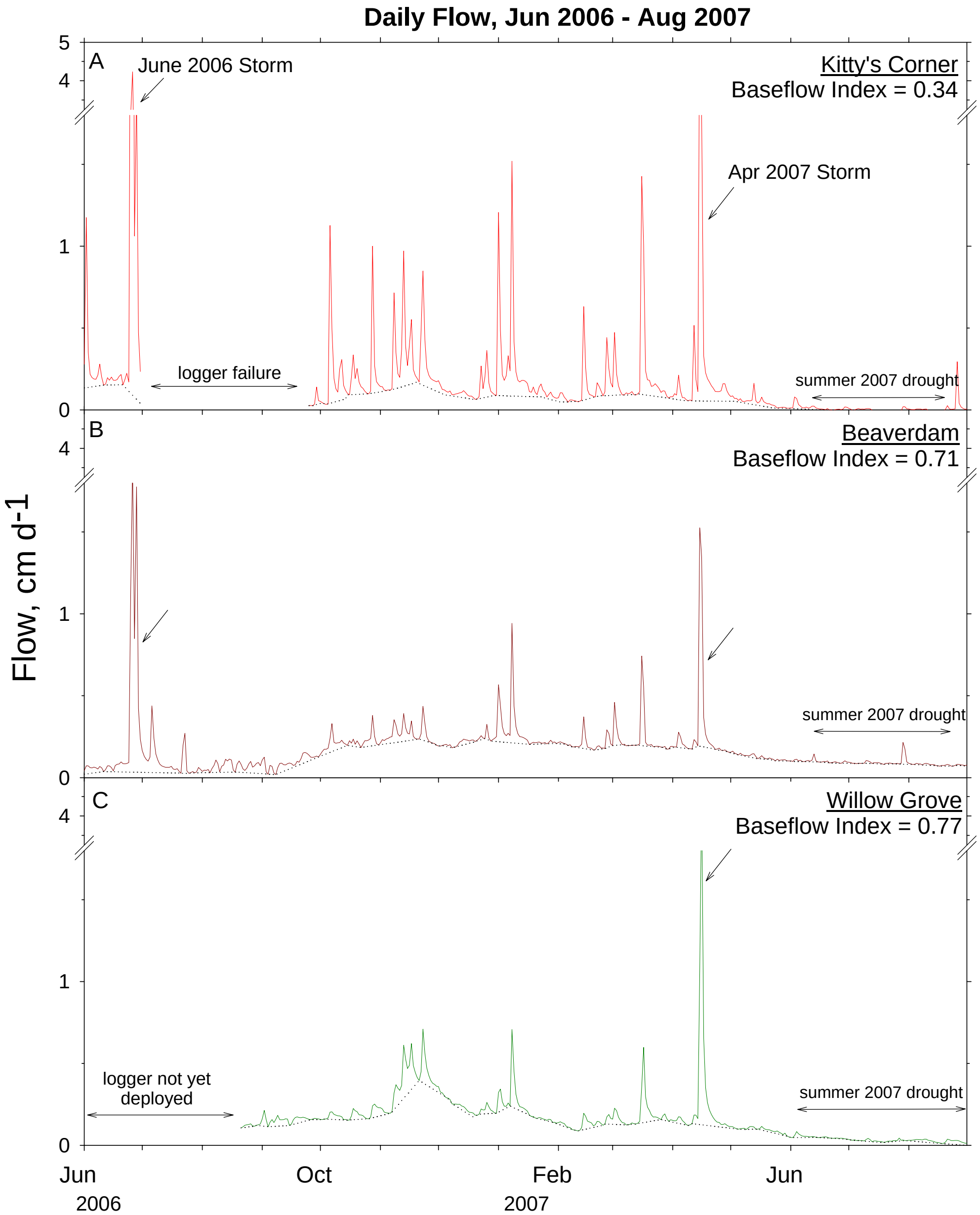


Figure 2-12. Examples of mean daily total flow (solid line) and baseflow (dotted line) for a stormflow-dominated site (Kitty's Corner, A – top panel), a groundwater-dominated site (Beaverdam, B – middle panel), and the all-hydric reference site (Willow Grove, C – bottom panel) for the 15-month study period (Jun 2006 – Aug 2007). Baseflow was separated using the 5-day method of Gustard et al. (1992), resulting in a baseflow index (right-hand side of each panel) which indicates the relative contribution of groundwater on a 0 – 1 scale. Note the three month gap at the Kitty's Corner sub-basin due to logger failure and the very low flows during the summer 2007 drought (horizontal arrows). The two largest events, in June 2006 and April 2007, are marked with diagonal arrows.

had large groundwater inputs and small event peaks (Fig. 2-12b). Willow Grove, the all-hydric control site, was similar to Beaverdam in its baseflow index (0.77) and behavior (Fig. 2-12c). However, unlike either Beaverdam or Kitty's Corner, Willow Grove had a large increase in discharge during late November 2006, probably related to leaf-fall from this mostly forested site (Fig. 2-12c). Baseflow indices for the other sites ranged from 0.49 – 0.61 (Table 2-7). Among all the sites, the baseflow index did not vary significantly (P>0.05) with either % hydric soils or hydrologic soil group.

Baseflow generally followed a seasonal trend with higher flows from fall to spring (approx. Oct – May) and lower flows during the summer, coinciding with reduced ET during the cooler months. This seasonal pattern was most pronounced at the groundwater-dominated sites such as Beaverdam and Willow Grove. At Beaverdam, for example, baseflows were about 10-fold higher from fall to spring (Fig. 2-12b).

Hydrologic Responses to Storm Events

Stream discharge responses to precipitation were typically characterized by a steep rising limb (<12 h), a brief peak (< 2 h), and a gradual exponential decay usually lasting 1 – 3 days, although occasionally up to 10 days for very large storms (Fig. 2-13). Some event hydrographs were marked by multiple peaks due to an intermittent rainfall pattern (e.g. June 2006 storm in Fig. 2-12a, b). As shown in Fig. 2-13, the stream temperature record was marked by large (~5 ° C) diel cycles driven by radiative heating during the daytime and cooling at night. During events, stream temperature often dropped suddenly with the passage of cold fronts.

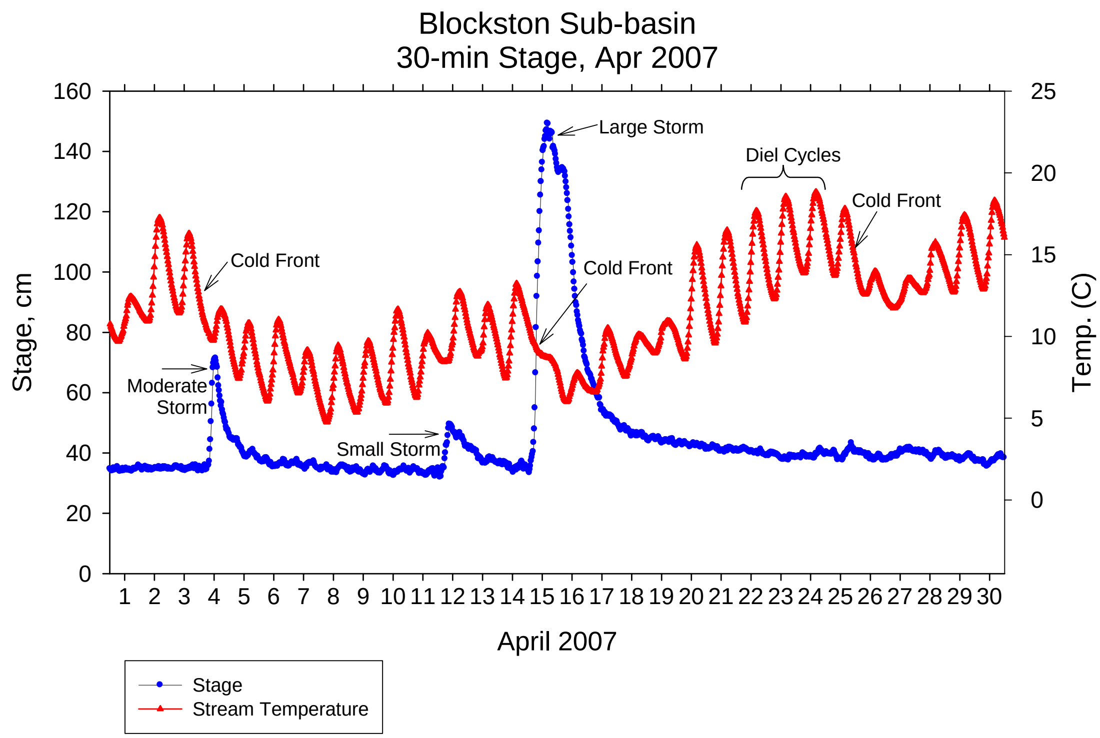


Figure 2-13. 30-min stage (circles) and stream temperature (triangles) at the Blockston sub-basin during April 2007. Shown are examples of different-sized events (arrows), including a small, moderate, and large- sized storm with stage increases of about +15, +35, and +115 cm, respectively. The stream temperature record shows large (~5° C) diel cycles (bracket) due to radiative heating of the stream during the daytime and cooling at night. The passage of cold fronts (arrows) during events caused 5 – 10 °C decreases in stream temperature.

Across all storms, the average quickflow per event was about 9 – 10 % of precipitation for each sub-basin except Kitty's Corner, which had an average of 19% (Table 2-7). Virtually all storms had a reasonable quickflow response (i.e. 0 – 100% of precipitation) except for the occasional outlier where quickflow was greater than rainfall. The outliers were usually associated with very small, barely measurable, storms. For example, event 43 at the Blockston sub-basin had 189.5% quickflow (Appendix). For this storm, the precipitation and quickflow totals were both <0.01 cm, and no stage increase was discernable in the 30-min record. This suggests that the daily rainfall and 30-min discharge data were not precise enough to capture the micro-fluctuations in flow that are associated with the smallest events. In general, the outliers were excluded from the data set because they greatly skewed the averages. Most sites had only one outlier out of >60 events (Table 2-7). In addition, the quickflow data were expressed as a percentage of precipitation (instead of cm storm^{-1}) because normalizing the quickflow to rainfall reduced the uncertainties about the mean, and helped to distinguish statistical differences among the sub-basins (Fig. 2-14).

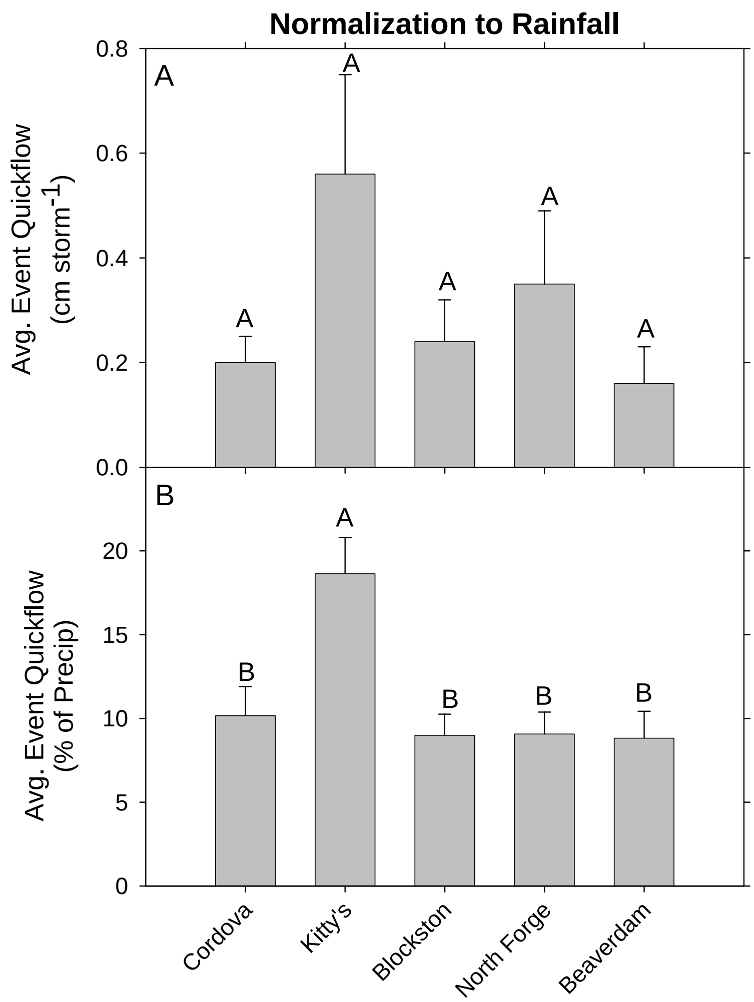


Figure 2-14. An example of how normalizing the quickflow data to precipitation reduces the uncertainties about the mean and helps to distinguish statistical differences among sites. In the top panel (A) is the average event quickflow shown in absolute units of cm storm^{-1}. In the bottom panel (B) is the same data expressed in relative units, i.e. % of precipitation. In both cases, the values shown are the means ± standard errors. When the quickflow is normalized to precipitation, the error bars decrease, and it becomes possible to distinguish among the means (i.e. Kitty's Corner has a higher event quickflow response than any other site) based on a one-way analysis of variance. Significant differences at $P<0.05$ are marked with letters.

Finally, event quickflow showed a strong seasonal trend. At four of the sites (Kitty's Corner, Blockston, North Forge, and Willow Grove), the average event quickflow was significantly higher (P<0.05) during the cool season (Oct – Apr) than it was during the warm season (May – Sept, Fig. 2-15a), likely because of reduced ET during the cooler months. In pooling across all sites, the average event quickflow was twice as high (14% vs. 7% of precipitation) during the cool season, and this difference was significant at P<0.001 (Fig. 2-15b).

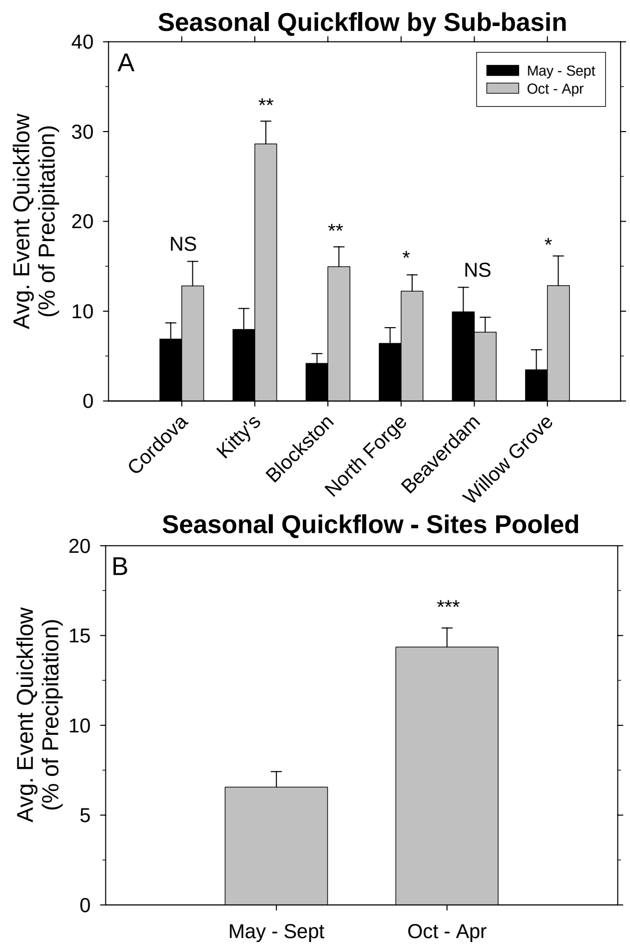


Figure 2-15. The top panel (A) shows the seasonal differences in average event quickflow (± standard errors) for each sub-basin during warm (May – Sept) and cool (Oct – Apr) seasons. Data includes all storms occurring in each season. For four of the six sites (Kitty's Corner, Blockston, North Forge, and Willow Grove), the average event quickflow was significantly higher (P<0.05) during the cool season. The bottom panel (B) shows the same data only with the sites pooled, showing a significantly higher average event quickflow during the cool season. For both panels, a one-way analysis of variance was used to test for significant differences between the means. NS = not significant (P>0.05), * = P<0.05, ** = P<0.01, *** = P<0.001.

Flow Duration Curves

The flow duration curves (FDCs) for each sub-basin were generally similar in shape, although some differences were noted in scaling (Fig. 2-16). For example, the Cordova and Blockston sub-basins, because of smaller water yields (see section 3.6 below), had consistently lower flows for the same frequencies compared to the Beaverdam and North Forge sub-basins. The Willow Grove all-hydric site followed a virtually identical curve as Beaverdam, except it had lower flows > Q80 (Fig. 2-16). This is not surprising given that both Willow Grove and Beaverdam are groundwater-dominated sites with similar baseflow indices (0.77 and 0.71, respectively). The only anomalous behavior occurred at the Kitty's Corner sub-basin, which had a very different curve marked by extreme high flows and an obvious decrease in flows >Q70 (Fig. 2-16). This suggests a highly variable flow regime at this site. Indeed, the Kitty's Corner sub-basin had the largest Q20/Q90 and Q50/Q90 ratios, and the lowest Q90/Q50 ratio (Table 2-8). This indicates that this site had the largest streamflow and baseflow variability, and the smallest groundwater contributions. In contrast, the rest of the sites had no major differences in their flow indices, although Willow Grove had slightly elevated streamflow and baseflow variabilities (Table 2-8) due to a period of high discharge in Nov 2006 (Fig. 2-12c).

Flow Frequency Analysis

As shown in Table 2-7, days containing >0 quickflow were surprisingly common, occurring 60 – 73% of the time among the six sub-basins (avg. 68%). However, quickflow only contributed 14 – 53% of the total annual discharge (avg.

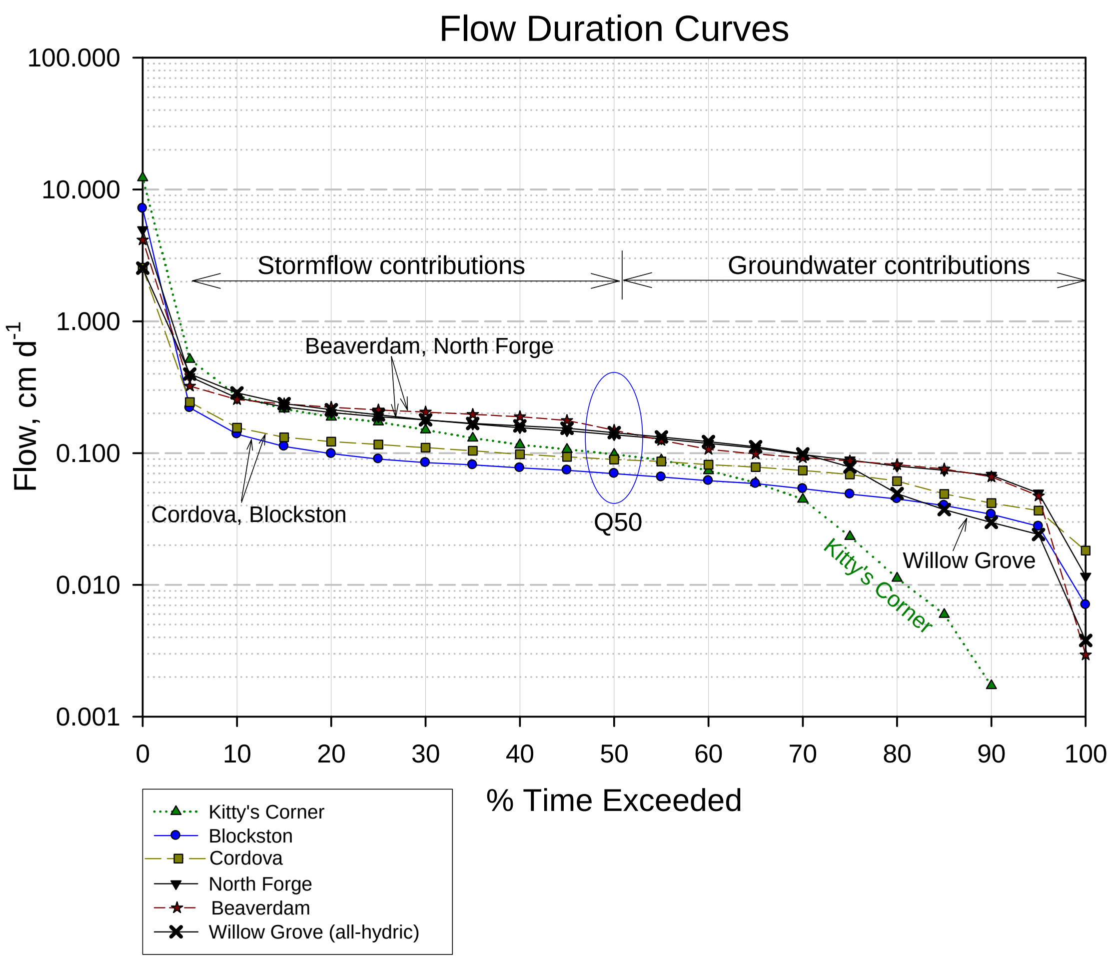


Figure 2-16. Flow duration curves for each of the six Choptank sub-basins, showing the relation between magnitude of flow (y-axis) and frequency (x-axis). Flows > Q50 (the flow equaled or exceeded 50% of the time; see circle) represent groundwater contributions to streamflow while flows <Q50 represent stormflow contributions (horizontal arrows). The Kitty's Corner sub-basin (triangles) has an obvious drop-off in flows >Q70, suggesting a small and/or variable groundwater input.

31%). These data are consistent with the frequent occurrence of small storms (Fig. 2-11) which generate relatively little quickflow but are common enough to sustain the stream at "quickflow conditions" for a majority of the time. As shown in Fig. 2-17, most of the measured events consisted of tiny "slivers" of quickflow. Again, on a volume basis, these types of storms contribute very little to annual discharge, but on a frequency basis, they are very common.

Table 2-8. Summary table of three flow indices based on the flow duration curve for each sub-basin (see Fig. 15). The Q20/Q90 ratio is a measure of streamflow variability, Q50/Q90 is a measure of baseflow variability, and Q90/Q50 is a measure of groundwater contributions. Most of the sub-basins have similar values for each index with the exception of Kitty's Corner, which has higher streamflow variability, higher baseflow variability, and lower groundwater contributions. The all-hydric control site (Willow Grove) is marked in gray.

Sub-basin	streamflow variability Q20/Q90	baseflow variability Q50/Q90	groundwater contributions Q90/Q50
Cordova	3	2	0.47
Kitty's	109	57	0.02
Blockston	3	2	0.49
North Forge	3	2	0.49
Beaverdam	3	2	0.44
Willow Grove	7	5	0.21

Low flows (<0.2 cm d^{-1}) among the five Choptank sites were by far the most common whereas larger flows (> 0.4 cm d^{-1}) were rare (Fig. 2-18a). Again, days containing >0 quickflow were quite common, and represented a majority of the total number of days in each of the size classes (Fig. 2-18a). As expected, low flows had relatively fewer days containing quickflow whereas higher flows (> 0.4 cm d^{-1}) all contained some quickflow. A similar pattern was observed for the Willow Grove all-hydric site (Fig. 2-18b), although at this sub-basin, high flows (>0.8 cm d^{-1}) were much less common because this site was dominated by groundwater inputs (BFI = 0.77). Note that this type of analysis does not imply anything about the *magnitude* (i.e. cm d^{-1}) of quickflows, only the *frequency* (i.e. 75 out of 100 days).

Finally, high flows, although less common, contributed disproportionately to annual discharge. For example, at the Blockston sub-basin, flows > 0.4 cm d^{-1} occurred only 3% of the time, yet contributed 32% of the annual discharge. Similarly, the two largest storms (in June 2006 and Apr 2007), although they only lasted for <4% of the study period, exported 11 – 26% of the total annual discharge (avg. 19%)

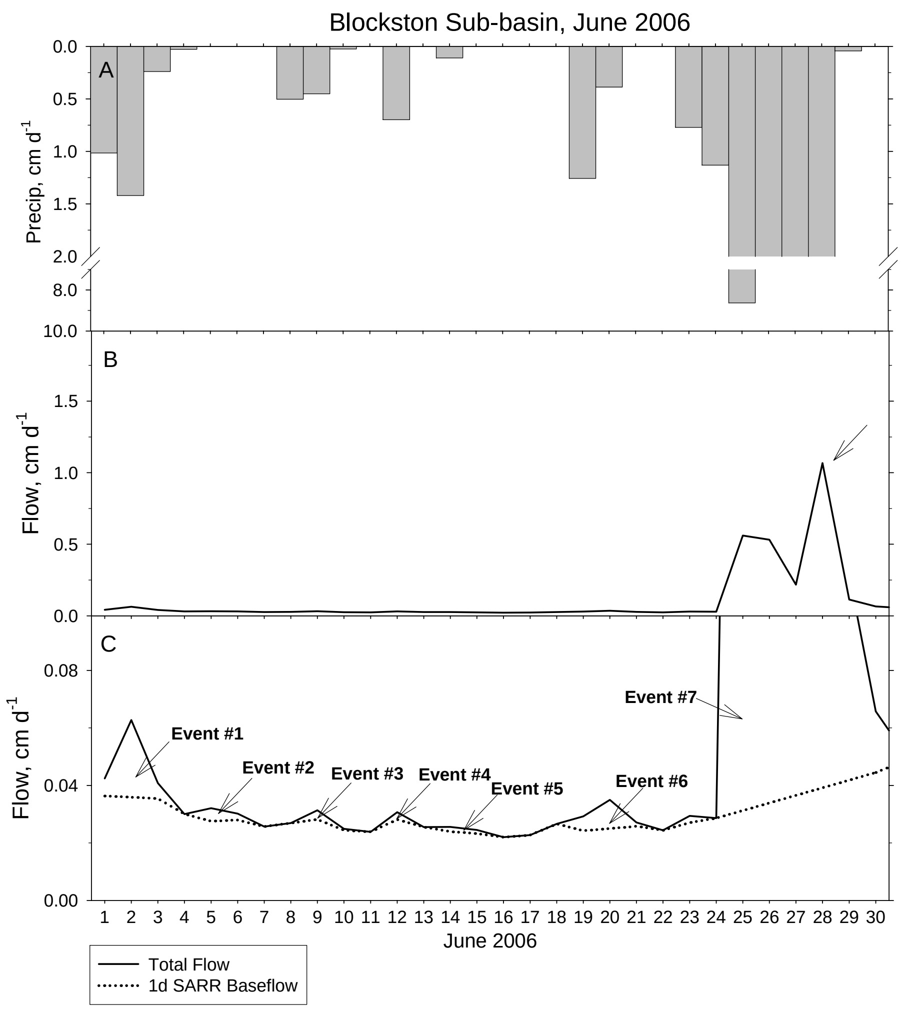


Figure 2-17. An example of how the 1-day SARR method of baseflow separation identified numerous very small events. In the top panel (A) is the daily precipitation record (bars on inverse y-axis) for the month of June 2006. In the middle panel (B) is the daily total flow record (solid line) at the Blockston sub-basin showing what appears to be only one large storm (arrow). However, upon closer inspection (C – bottom panel, note change in y-axis), seven unique events (arrows) occurred during this period, as shown by the various baseflow separations (dotted line) projected by the 1-day SARR method. Each unique separation of the hydrograph and its associated rainfall (panel A) were defined as "events" (see text for details).

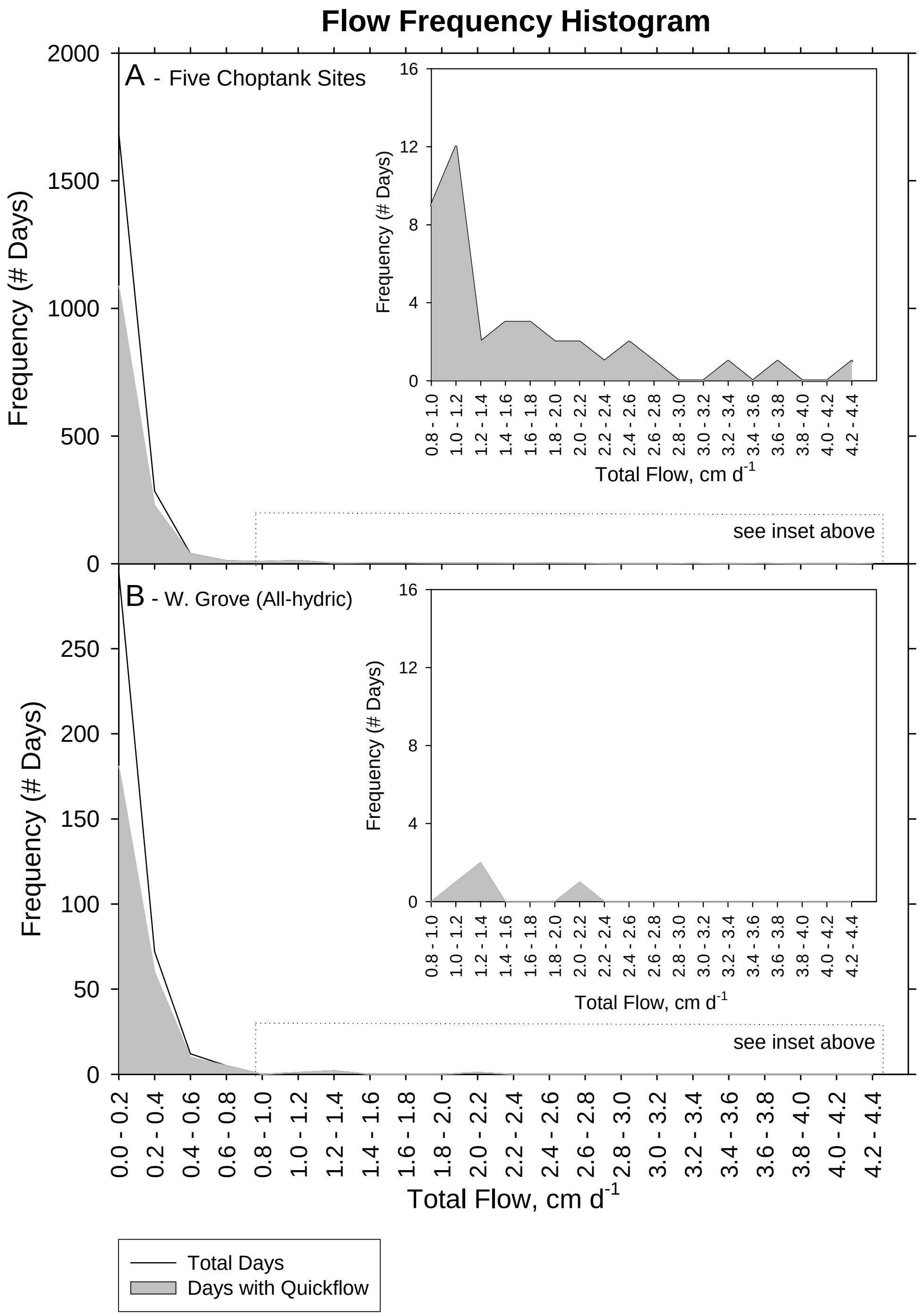


Figure 2-18. Combined flow frequency histogram for the five Choptank sub-basins (A - top panel) and Willow Grove, the all-hydric control site (B – bottom panel) during the 15-month study period (Jun 2006 – Aug 2007). Shown are the total number of days (solid lines) and days with >0 quickflow (gray area plot) for various size classes (x-axis). Baseflow was separated using the 1-day SARR method. Note: for clarity, the occurrence of negative flow (i.e. flow moving upstream) at the Kitty's Corner sub-basin was omitted (see text).

among the five agricultural sites (Table 2-9). This underlines the importance of large, rare events in driving the hydrologic budgets of these sub-basins.

Table 2-9. The two largest storms, occurring in June 2006 and April 2007, had a disproportionately large effect on total annual water budgets. As shown, among the five Choptank sub-basins, these two events combined contributed 11 – 26% of the total annual discharge (right-most column), with an average of 19%. The all-hydric control site (Willow Grove) is also shown in gray. However, at this sub-basin, the logger was not deployed during the June 2006 event, and therefore it was not averaged in with the others.

	units are cm QF storm^{-1}		units are cm		
	June 2006	April 2007	∑	Total Annual Discharge	%
Cordova	2.5	2.0	4.5	42	11
Kitty's	10.3	4.6	14.9	57	26
Blockston	2.3	6.7	9.0	40	22
North Forge	6.3	5.1	11.3	48	24
Beaverdam	5.8	2.8	8.6	59	15
				Avg:	**19**
Willow Grove	n/a	3.8	3.8	60	6

Annual Water Budgets

On average among the six Choptank sites, 52% of annual precipitation entered soil storage or was lost due to ET while 48% was discharged as stream flow (Fig. 2-19). The baseflow component of stream flow was 33% of rainfall while quickflow was 14% of rainfall. Within individual sites, Kitty's Corner had the most quickflow at 28% of precipitation, while at the other extreme, Willow Grove had the least quickflow at only 8% of precipitation. Again, the disparity is due to the differences in hydrology between the sub-basins; Kitty's Corner was dominated by storm flows

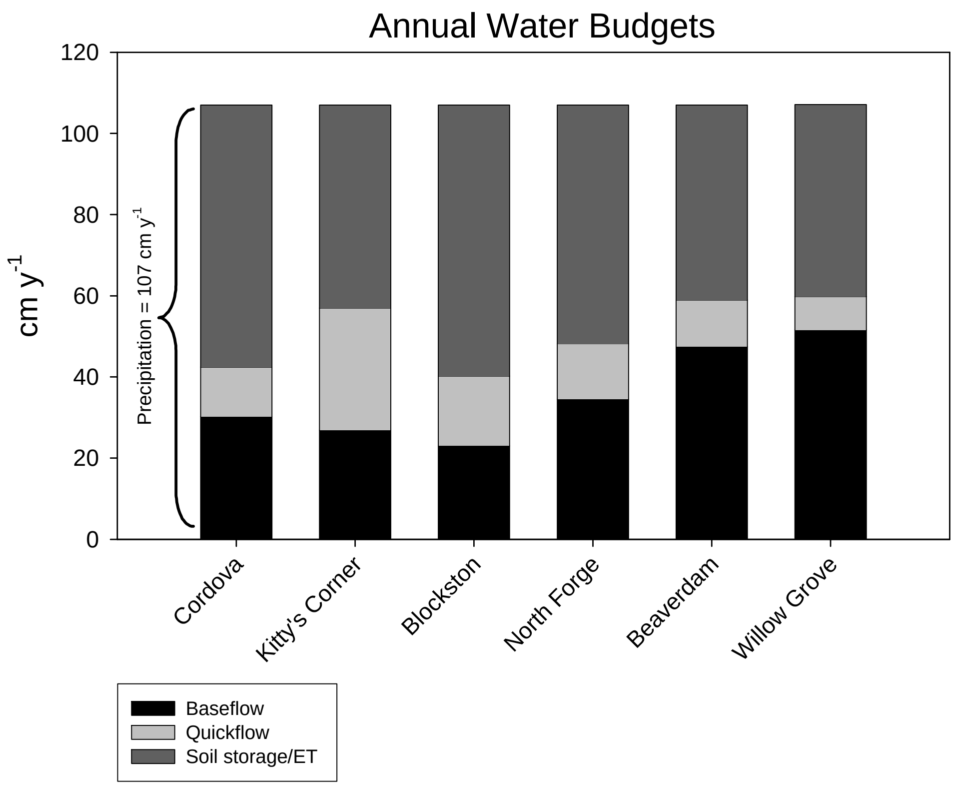


Figure 2-19. Annual water budgets for the six Choptank sub-basins over the study period (Jun 2006 – Aug 2007) showing the components of baseflow (dark bars), quickflow (light bars), and soil storage/evapotranspiration (ET, medium gray bars). The sum of all three equals the annual precipitation (107 cm y^{-1}, see bracket), which is a spatially averaged mean of 11 regional stations (Ch. 1). Total annual discharge equals baseflow + quickflow, and was calculated from the 30-min discharge record. Annual baseflow was calculated by summing the daily baseflow values (as separated using the 1-day SARR method) during the study period and then normalizing to 365 days. Annual quickflow was calculated in the same way only using the daily quickflow values. Soil storage/ET was estimated as precipitation minus total discharge.

(BFI = 0.34) while Willow Grove was dominated by groundwater (BFI = 0.77). Annual water yields varied over a large range, from 40 cm y^{-1} at the Blockston sub-basin to 60 cm y^{-1} at Willow Grove, or within ± 25% of the water yields at the USGS' Greensboro station over the same time period (Table 2-7). Because of data gaps at four of the Choptank sites, the water yields at Greensboro were calculated over the same exact time period as each individual sub-basin (i.e. with gaps in all the same places) to ensure a suitable basis for comparison.

Hydric Soils

No significant relationship (P>0.05) was found between percent hydric soils and quickflow. This was true for all three of the time scales assessed: event, monthly, and annual (Fig. 2-20).

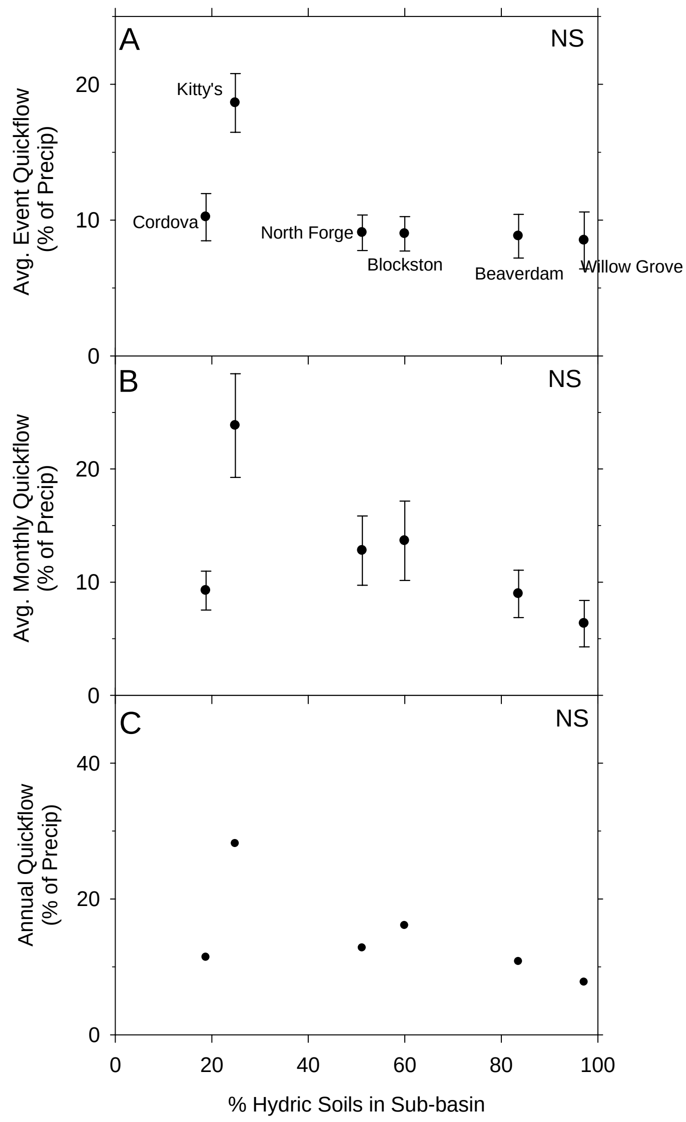


Figure 2-20. Average event (A – top panel), monthly (B – middle panel), and annual (C – bottom panel) quickflow (± standard errors) across a gradient of % hydric soils in the six Choptank sub-basins during the 15-month study period (Jun 2006 – Aug 2007). The sites are marked in panel A and are the same in the other panels. NS = no significant trend (P>0.05).

Regional Analysis of Delmarva USGS Data

Hydrologic results for the 13 USGS regional sites varied. Average annual baseflow ranged from 16.7 – 31.8 cm y^{-1} while average annual quickflow ranged from 10.5 – 30.3 cm y^{-1} among the sub-basins (Table 2-10). As shown in this table, baseflow indices varied from 0.41 – 0.75, which is about the same range observed for the Choptank watersheds, and indicates a similar mix of both stormflow and groundwater-dominated sites. Average annual water yields were < 49 cm y^{-1} (Table 2-10), which is generally less than the Choptank sites (40 – 60 cm y^{-1}). In addition, the USGS annual water yields varied over a smaller range despite a broader range of land uses (compare Table 2-6 with Table 2-1).

Among the USGS sites, the mean annual water yield decreased significantly with increasing hydric soils in each sub-basin (r^2 = 0.61, P<0.01, Fig. 2-21a). Mean annual baseflow also decreased significantly with increasing hydric soils (r^2 = 0.80, P<0.0001, Fig. 2-21b). However, no significant relationship was found for mean annual quickflow (Fig. 2-21c). Hydric soils were positively related to % surface ponding on 75 – 100% of the map units (r^2=0.69, P<0.001, Fig. 2-21d). However, in ditched agricultural areas, surface ponding would probably not occur since most of the excess rain water would be drained off via ditches. In these areas, precipitation is likely stored in the root zone of fine-textured soils, where it provides sustenance for crops during dry periods. Hence, the y-axis in Fig. 2-21d reflects not only surface ponding but also shallow subsurface water storage in soils. In addition, mean annual quickflow increased with average sub-basin slope (r^2= 0.61, P<0.01, Fig. 2-21e). There was no relationship between % hydric soils and average sub-basin slope,

Table 2-10. Summary of hydrologic results for each of the 13 USGS sub-basins. Both daily flow (top table) and annual flow (bottom table) were available from the USGS website (http://water.usgs.gov/). Shown are the length of records (excluding gaps) for each type of data (i.e. daily or annual), the period of record, and the # of gaps in the record. In general, the availability of the daily and annual data was similar (compare top and bottom tables), although for some sites, discrepancies occurred (e.g. Chicamacomico). Also shown are mean annual baseflow, mean annual quickflow, baseflow index, and mean annual water yields (with standard errors). BFI = baseflow index, exc = excluding.

Daily Data

				units are cm y^{-1}				
USGS Sub-basin Name	Length of Record (y)*	Period of Record	# Gaps (d)	Avg. Annual Baseflow	Std. Error	Avg. Annual Quickflow	Std. Error	BFI
Nassawango	58.5	12/10/1949 - 5/30/2008	12	21.0	0.9	23.0	1.6	0.44
Beaverdam at Houston	49.4	5/14/1958 - 9/14/2007	0	30.8	1.4	10.5	0.9	0.75
Green Run	8.0	5/10/1994 - 9/25/2002	141	19.7	2.4	19.8	3.9	0.50
South Fork	8.0	6/8/1994 - 6/17/2003	384	17.3	2.1	29.3	6.5	0.41
Nanticoke	65.2	4/8/1943 - 5/28/2008	0	31.8	1.1	11.2	0.8	0.74
Unicorn	59.5	1/10/1948 - 5/29/2008	354	28.0	1.1	17.3	1.2	0.62
Manokin	54.1	5/9/1951 - 5/30/2008	1096	16.7	0.9	19.9	1.4	0.46
Beaverdam Ck near Salisbury	7.6	10/7/2000 - 5/30/2008	7	28.1	3.5	30.3	4.8	0.49
Chicamacomico	7.3	9/14/2000 - 5/30/2008	161	26.1	3.6	18.7	3.6	0.58
Pocomoke	57.1	12/6/1949 - 5/30/2008	524	21.1	0.8	20.4	1.4	0.51
North Fork	6.6	6/12/1994 - 6/3/2003	865	17.7	1.4	20.1	4.8	0.47
Marshyhope near Adamsville	60.9	4/8/1943 - 5/8/2008	1552	21.2	0.9	19.5	1.4	0.52
MurderKill	31.8	7/2/1931 - 5/30/2008	16496	25.4	1.3	22.1	2.1	0.53

Annual Data

				units are cm y^{-1}	
USGS Sub-basin Name	Length of Record (y)*	Period of Record	# Gaps (y)	Avg. Annual Water Yield	Std. Error
Nassawango	57	1951 - 2007	0	41.9	2.2
Beaverdam at Houston	49	1959 - 2007	0	41.7	2.1
Green Run	8	1995 - 2002	0	37.5	5.6
South Fork	8	1995 - 2002	0	40.4	7.2
Nanticoke	64	1944 - 2007	0	43.0	1.8
Unicorn	57	1949 - 2007 exc.2003, 2006	2	44.6	2.2
Manokin	53	1952 - 2007exc.1972-74	3	36.6	2.1
Beaverdam Ck near Salisbury	47	930 - 2007 exc.1933-38, 1976-200	31	44.8	2.4
Chicamicomico	36	1952 - 2007 exc. 1981 - 2000	20	43.6	2.4
Pocomoke	55	1951 - 2007, ex. 2005-06	2	42.1	2.1
North Fork	7	1995 - 2002 exc. 1996	1	34.3	6.9
Marshyhope near Adamsville	59	1944 - 2007 exc. 1969-71, 2003-04	5	40.7	2.0
Murderkill	30	1932 - 1999 exc. 1934-60, 1986-96	38	48.9	3.2

* The length of record excludes gaps

suggesting that the relation with quickflow was due to a topographic effect unrelated to hydric soils. Finally, a variety of other sub-basin attributes (besides hydric soils) were also explored, including land use (% agriculture, % forest, % wetland), sub-basin size, and ditches (both % ditched and ditched length). However, none of these attributes varied significantly with either mean annual baseflow, mean annual quickflow, or mean annual water yield.

Some of the Choptank sites fit along the USGS regression lines, while others did not. For example, in Fig. 2-21e, most of the sites (Blockston, Beaverdam, Willow Grove, and North Forge) followed the same trend as the USGS data. Similarly, in Fig. 2-21a, the Kitty's Corner, Cordova, North Forge, and Blockston sub-basins fit along the USGS regression line. On the other hand, in Figs. 2-21a and 2-21b, both the Willow Grove and Beaverdam sub-basins were well above the expected range based on the USGS trend line. These types of discrepancies underline the differences in record lengths (15 months for the Choptank sites versus >7 years for the USGS sites) and the uncertainties of the Choptank rating curves and stage records. There may be significant errors in the computed discharges for the Choptank sub-basins, and these are evaluated below (see "Error Analysis" section below).

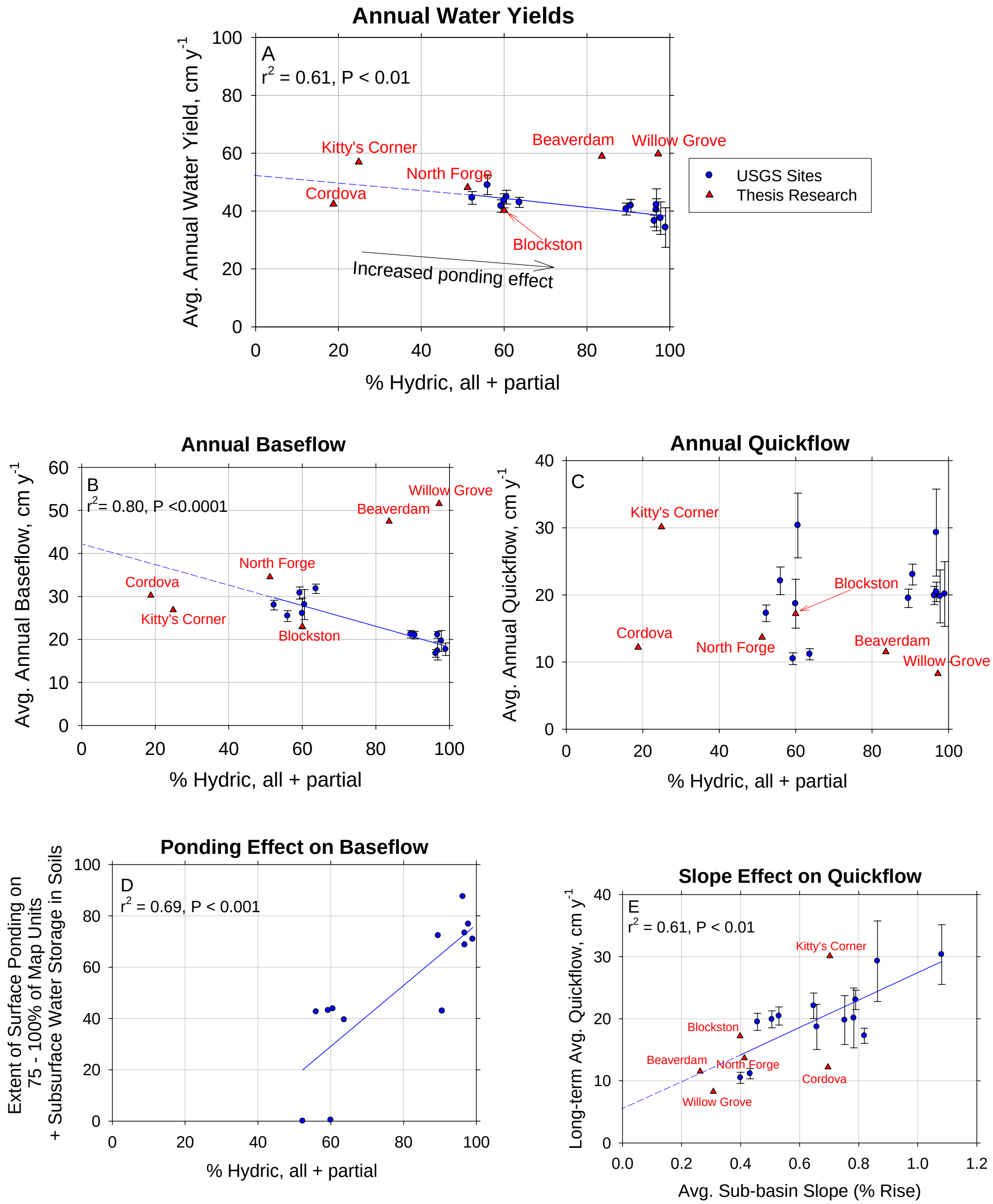


Figure 2-21. Results of the regional analysis of Delmarva USGS data, showing the six Choptank sub-basins (triangles) alongside the 13 USGS sites (circles). In the top-most panel (A), water yields decreased with increasing % hydric soils in the sub-basins, largely due to the baseflow component (B - middle left panel). The decrease in baseflow was due to the positive association between hydric soils and surface/shallow subsurface ponding (D - lower left panel). Conversely, no significant relationship was found between hydric soils and quickflow (C - middle right panel). Quickflow, however, was positively related to slope (E - lower right panel). Extrapolations of trend lines are shown with a dotted line.

Discussion

This study found that groundwater contributions varied among the six Choptank sub-basins as indicated by baseflow indices (BFI) ranging from 0.34 – 0.77. These values bracket the range calculated by Jordan et al. (1997; 0.44 – 0.54) for four watersheds with similar land uses in the nearby Chester River Basin (located just north of the Choptank). Vanni et al. (2001) calculated BFIs of 0.29 – 0.44 for three catchments with >90% agriculture, while Villar et al. (2002) calculated a BFI of 0.47 for a single catchment with 37% agriculture. Schoonover and Lockaby (2006) found widely varying BFIs among four pasture-dominated watersheds, with values of either <0.30 or >0.80.

Although the baseflow index is a robust metric over short time periods of 1 – 2 years, interpretation becomes difficult when >2% of the discharge record contains gaps (Gustard et al. 1992). For this study, four of the sites (Kitty's Corner, Cordova, North Forge, and Willow grove) had gaps of 12 - 19% of the record (Table 2-7), suggesting that the variation in the BFIs may be due to under-sampling rather than real baseflow differences among the sub-basins. Nonetheless, the Blockston and Beaverdam sites, both of which had continuous records with no gaps, had major differences in their BFIs (0.49 for Blockston versus 0.71 for Beaverdam), although with a sample size of two it is hard to speculate on potential trends related to hydric soils. A study by Angier et al. (2005) found that groundwater contributions to a stream were largely a function of macropores in the riparian zone which allowed for discrete zones of groundwater upwelling. In this case, it may be that Beaverdam has more of these upwelling zones than Blockston does, although this was not measured in the current study.

Both baseflow (Fig. 2-12) and quickflow (Fig. 2-15) exhibited a strong seasonal trend with higher amounts of each from fall to spring. Similar seasonal trends have been reported elsewhere (e.g. Owens et al. 1991, Jordan et al. 1997 & 1997a, Burges et al. 1998). This finding is consistent with reduced ET and higher soil moisture during the cooler months. Soil moisture, in particular, is well-established as one of the primary controls on quickflow (e.g. Aubert et al. 2003, Zehe et al. 2005). McNamara et al. (2005) found that increases in soil moisture during the fall – spring can improve the hydraulic connectivity along a hillslope, leading to greater quickflow from previously disconnected sources. In addition, the seasonal nature of the annual hydrographs (Fig. 2-12) coincide well with the "major rise" (Oct – Mar) and "major recession" (Apr – Sept) periods typical of coastal plain streams (Mayer and Jones 1996).

This study found that some quickflow occurred on ~2/3 of the days in the study period, yet quickflow contributed only ~1/3 of the total annual discharge (Table 2-7). This finding agrees well with Norton and Fisher (2000) and Lee et al. (2001), both of whom also found that quickflow was about 1/3 of the total annual flow in the Choptank Basin. Again, as discussed earlier, frequent small storms in this region (Fig. 2-11) generate small amounts of quickflow on a fairly regular basis, yet the cumulative contribution of quickflow from these "slivers" is relatively small (Fig. 2-17). The relative occurrence of quickflow and baseflow has major implications for nutrient export because of differences in baseflow and quickflow chemistry. This will be discussed more in Chapter 3.

The flow duration curves summarize the hydrology of the sub-basins (Fig. 2-16). The generally flat nature of the curves from Q10 – Q90 suggests that rain water is able to infiltrate and replenish the surficial aquifer, resulting in sustainable groundwater reservoirs and a steady streamflow (Gustard et al. 1992). The only exception was the Kitty's Corner site, which had sharply declining flows in the Q70 – Q90 range. According to Smakhtin (2001), this indicates a small and/or variable groundwater contribution, which is consistent with Kitty's Corner having the lowest baseflow index (0.34, Table 2-7) and the highest baseflow variability (Table 2-8). In contrast, the ends of the FDCs (at Q0, Q100) had much steeper slopes, which illustrates how the maximum and minimum flows associated with the large June 2006 storm and summer 2007 drought, respectively, caused the greatest flow variability during the study period.

However, the interpretation of FDCs is complicated by several factors. The first is that the curves only indicate the hydrologic conditions over the period of record, which in this case was a 457-day period from 2006 – 07. Natural changes in the flow regime (e.g. inter-annual variability in rainfall) or anthropogenic changes in the watershed which may alter the flow regime (e.g. urbanization, digging ditches) are not captured in a 1 - 2 year time window. Other researchers have used several years of FDCs to show the effects of watershed changes on hydrology (e.g. Brown et al. 2005, Lane et al. 2005). Along these lines, Vogel and Fennessey (1994) suggest that multi-annual interpretation of FDCs can improve confidence in one's hydrologic results. However, this approach is beyond the scope of the current study. The second factor which limits the interpretation of FDCs is spatial variability in rainfall within a single year. For the study sub-basins, the observed annual rainfall varied from 102 – 110 cm y^{-1} during the study period (Ch. 1). It is not clear what effect these spatial differences have on the shape of the FDCs, if any. Lane et al. (2005) developed a method to normalize the annual FDCs by the long-term precipitation mean. However, this approach is also beyond the scope of this study. The third and final factor which makes it difficult to interpret FDCs is potential errors in the flow data. This will be discussed in section 4.1 below.

Annually, 52% of precipitation entered soil storage/ET and 48% was discharged as streamflow based on averages among the sites (Fig. 2-19). Baseflow represented 33% of rainfall, while quickflow was 14% of rainfall (or, expressed in different terms, total annual flow was 69% baseflow and 31% quickflow). Long-term water budgets have been compiled previously by Norton and Fisher (2000) and Lee et al. (2001) for the Choptank Basin. In comparing the observed values to theirs, the major differences are: 1) They have slightly higher estimates for ET (55 - 65% of rainfall) and lower estimates for discharge (34 – 35%), and 2) They have slightly lower estimates for both baseflow (24 – 25% of rainfall) and quickflow (10 – 11%). These discrepancies are due to differences in methodology. Both Norton and Fisher (2000) and Lee et al. (2001) based their discharge calculations on the USGS gauging station at Greensboro and separated baseflow using either USGS' PART software or the General Watershed Loading Function model. In contrast, for the current study, discharge was measured independently of the USGS and baseflow was separated using the 1-day SARR method, a new technique developed for this thesis which incorporated precipitation. As a proportion of rainfall, the ratio of baseflow to quickflow calculated here (2:1) is about the same as the ratio calculated by them. However, the absolute amount of total flow measured in this study is about 1.5 times higher than their values, hence the baseflow and quickflow numbers are also higher here. Finally, it should be noted that the water budgets presented in this study, unlike those in Norton and Fisher (2000) and Lee et al. (2001), are *not* long-term averages and only reflect conditions during the 457-day study period, which was slightly drier than normal (Ch. 1).

Error Analysis

The largest uncertainties in the hydrologic data are associated with two factors: 1) The rating curves, and 2) The 30-min stage records. The rating curves have many potential sources of error, including: weed growth, pools, riffles, under-sampling of large events, changes in channel roughness, backwater effects, channel scouring during storms, and instrument limitations (Cole et al. 2005, Trumbauer 2007, Smith 2007). A detailed assessment of the rating curves is beyond the scope of this chapter. However, as a first approximation, the ± 25% discrepancy between the Choptank sub-basin water yields and the USGS' Greensboro station (Table 2-7) over the same time period suggests that the computed discharges may have uncertainties that are greater than the accuracy needed to measure the effects of hydric soils. Although the rating curves were developed very carefully over ~2 years, additional sampling of flows, particularly high flows, may be necessary to improve the stage-discharge relationship for these sub-basins.

The second factor is the 30-min stage records. As mentioned earlier, stage was monitored continuously using loggers. The loggers were mounted within the cavity of a cinder block that was chained to the stream bed. While this approach helped to stabilize and protect the logger, it did not prevent scouring underneath the cinder block during high flows. Indeed, at many of the sites, abrupt shifts in the stage record occurred on multiple occasions which were obviously not related to storm flows. Instead, they indicated that the cinderblock had moved from its original position (again, this usually occurred during the highest flows). These shifts were corrected by manipulating the stage record. However, the corrections likely introduced significant uncertainties into the annual water yields since they propagated through all parts of the stage record occurring after the shift. In retrospect, a better way of monitoring stage would be to install the loggers in stilling wells adjacent to the streams but with an under-ground connection to the main channel, similar to the USGS' gauging houses. This way, the logger would be protected from the turbulence associated with high flows.

Regional Analysis of Delmarva USGS Data

The analysis of regional USGS data showed that total flow, especially the baseflow component, was negatively related to hydric soil abundance. This finding is the opposite of Latron and Gallart (2007), who found that the extent of saturated areas (analogous to hydric soils) was *positively* related to baseflow. In contrast, Loucks

(1998) found no relationship between hydric soils and baseflow. For this study, hydric soils appear to decrease baseflow by facilitating surface ponding, which leads to larger evaporative losses from the free water surface and less infiltration to groundwater. This is not surprising given that ponding is part of the definition of a hydric soil. In this case, the ponding effect is *not* related to topography since hydric soils do not vary with slope. In other words, hydric soils appear to have an inherent ability, irrespective of their position in the landscape, to hold water at the surface. As mentioned previously, hydric soils are not only associated with topographic lows; they can also be fine-textured soils with a low infiltration capacity, or soils that are underlain by an aquiclude. In either case, these properties would tend to limit the infiltration of rainfall and support the ponding of water on the surface.

Unlike baseflow, quickflow did not vary with hydric soils. Even when integrated over decadal time scales, quickflow was too variable to show a consistent trend. The standard errors about the mean for annual quickflow were generally much higher than for annual baseflow (compare Figs. 2-21b, c) due to inter-annual variability in precipitation. This suggests that, even over climatic time scales, spatial variations in rainfall and differing storm paths among the sub-basins are overcoming the effects of hydric soils on quickflow, if in fact there is any effect at all. Plot-scale studies have demonstrated the importance of soil drainage class, soil parent material, and soil texture on quickflow volume (Whipkey 1965, Needelman et al. 2004), suggesting that at smaller spatial scales, it may be possible to measure the effects of hydric soils on quickflow. At the watershed scale, long-term data are needed to overcome inter-annual variability in rainfall and measurement errors (Fig. 2-21c).

Although quickflow did not vary with hydric soils, quickflow was positively related to average sub-basin slope ($r^2 = 0.61$, $P<0.01$, Fig. 2-21e). Slope is a well-established control on quickflow, particularly when antecedent soil moisture is high (Haggard et al. 2005). Again, since slope was *not* related to hydric soils, this is a topographic effect, not a soils effect. As slope increases, more overland and shallow subsurface flow occurs. Previous studies have demonstrated the importance of the variable source area concept, which states that quickflow, primarily as shallow subsurface flow, only occurs in a small portion of the watershed (<10% of the area) which expands and contracts during storms (Freeze 1974, Chow et al. 1988). Given this context, it is likely that most of the quickflow in these sub-basins is generated in a few, relatively steep areas, probably adjacent to the stream channel where the incision of the flowing water often creates a strong slope gradient. Hortonian overland flow (also known as infiltration excess), on the other hand, is probably *not* occurring in these sub-basins due to the permeability of the soils. Hortonian overland flow is more typical for arid or semi-arid climates where the lack of organic matter creates soils with a relatively low infiltration capacity.

Hypothesis Testing

The ultimate goal of this chapter is to test the hypothesis that hydric soils increase quickflow volume by enhancing lateral overland and shallow sub-surface flow. This hypothesis was tested over event, monthly, annual, and decadal time scales using a combination of six Choptank sub-basins and 13 regional USGS sites with a combined range of 19 – 99% hydric soils. No significant relationships were found between hydric soils and quickflow at any of the time scales (Figs. 2-20, 2-21c). Consequently, the hypothesis was rejected. Hydric soils, at least within the scope of this study, are not related to quickflow. However, hydric soils were found to strongly reduce baseflow (Fig. 2-21b) by increasing both surface and shallow subsurface water retention, resulting in higher ET (Fig. 2-21d).

Effects of Irrigation and Ditches

Finally, two factors which may affect water discharges, outside of soil and land use effects, are agricultural irrigation and ditches. Irrigation recycles groundwater back into the root zone of a watershed. If the water is drawn from above a gauging site, it can potentially reduce water yields due to higher ET losses. In contrast, if the water is drawn from below a gauging site, it may potentially inflate water yields because the recycled water is double-counted. An additional factor is whether the farmer is drawing from the surface unconfined aquifer or the deeper confined aquifer. Water drawn from the deeper confined aquifer introduces “new” water into the watershed which would normally never enter the stream channel. This would tend to increase water yields. In contrast, water drawn from the surface unconfined aquifer simply recycles “old” water, which could either increase or decrease water yields depending on where the water was drawn from, as discussed above.

In general, irrigation effects are very difficult to quantify. In the current study, the number of pivot irrigation pumps in each sub-basin were counted using 2005 aerial photographs (Table 2-1). However, this data was not very useful since no pumps were found in any of the sub-basins except Cordova. Usually, the pumps draw from groundwater wells and spray water in a circle, leaving a conspicuous ring ~500 meters wide visible in aerial photos. However, simply counting the number of rings does not account for the movement of pumps across watershed boundaries, or the occurrence of other forms of irrigation, i.e. smaller-scale, localized withdrawals of surface waters which do not show up in aerial photos. Indeed, such smaller-scale irrigation has been visually confirmed in the stage record as sharp, downward spikes in the 30-min stage record. In addition, small-scale irrigation has been anecdotally confirmed at at least one site (Beaverdam) based on conversations with local farmers.

In contrast, ditches had a clear, measurable effect on annual water yields among the six Choptank sub-basins. Indeed, annual water yields increased exponentially with the % of total stream length ditched (r^2= 0.96, P <0.01, Fig. 2-22a). Ditches enhance surface water discharge because they channelize water which would otherwise pond on the surface and evaporate, or slowly infiltrate to groundwater. However, among the regional USGS sites, ditches were not related to annual water yields (Fig. 2-22a), probably because the extent of ditches is under-estimated in these sub-basins. The National Hydrography Data Set (NHD), which was used to calculate the % of ditched stream length, is part of a broader effort to map the blue-line streams and ditches for the entire Chesapeake region. As such, the resolution is fairly coarse, and smaller channels, which are often dug by farmers in their fields to help with drainage, are not included. Indeed, many of these small channels, which are probably <3' deep, are visible in high-resolution aerial photos but are not mapped in the NHD. Alternatively, the trend line among the six Choptank sub-basins could simply be due to errors in the stage records and discharge computations, and/or the short length of the records (15 months), as discussed above.

Finally, ditches were found to increase linearly with hydric soils (r^2= 0.49, P <0.001, Fig. 2-22b) among both the Choptank and the USGS sites. This is not

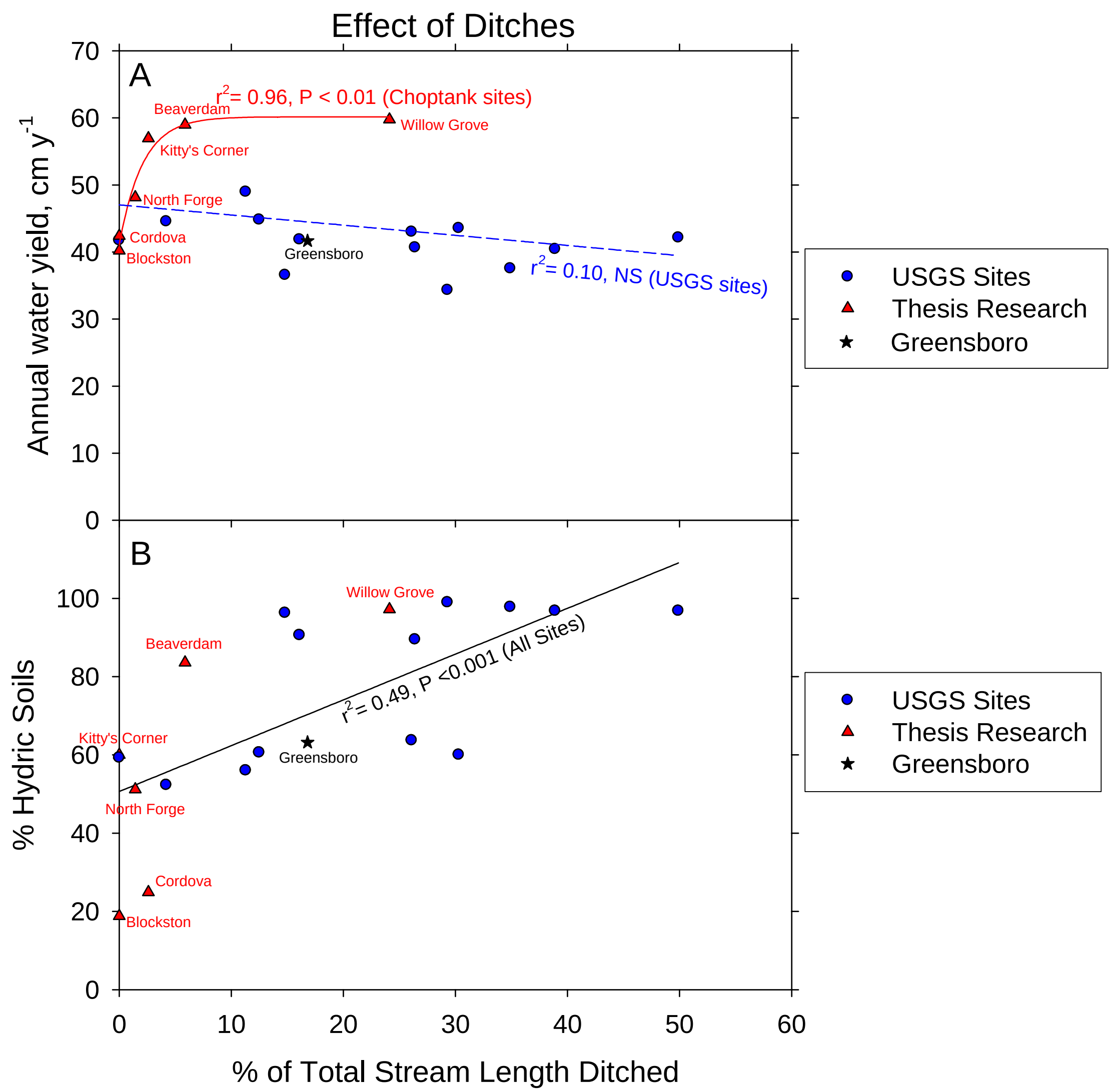


Figure 2-22. In the top panel (A), annual water yields increased exponentially with the % of total stream length ditched among the six Choptank sub-basins (triangles). However, there was no significant relationship for the 13 regional USGS sites (circles and dotted line). Also shown for reference is the USGS' Greensboro station (star). In the bottom panel (B), % hydric soils increased linearly with the % of total stream length ditched among all sites, including the six Choptank sites, the 13 regional USGS sites, and the USGS' Greensboro station (same symbols as panel A). NS = not significant (P > 0.05).

surprising since hydric soils, by definition, are either poorly drained or very poorly drained, and therefore extensive ditching is most likely to occur in these soils. As shown previously for the USGS sites (Fig. 2-21a), hydric soils decrease annual water yields because they enhance surface and shallow subsurface water storage, resulting in greater evaporative losses (Fig. 2-21d). Ditches, in contrast, work to counteract this effect by augmenting baseflows. In other words, ditches may be obscuring the effects of hydric soils.

Chapter Summary

This chapter explored the effect of hydric soils on the streamflow components of baseflow and quickflow in various sub-watersheds across the Delmarva Peninsula. During a 15-month period from June 2006 – Aug 2007, 93 events were identified at the Blockston sub-basin, while 100 were identified at the Beaverdam sub-basin. Most events were small (< 2 cm of rainfall), although two large ones (in June 2006 and April 2007) had >10 cm of rainfall. The hydrology of the Choptank sites was dominated by low flows (<0.4 cm d^{-1}). Larger flows were rare, occurring <8% of the time, but contributed disproportionately to total annual discharge. The sub-basins were generally marked by flat flow duration curves which indicate a stable hydrology with continuous groundwater inputs and permeable soils. Kitty's Corner, with a baseflow index (BFI) of 0.34, was the "flashiest" site with lower low flows and higher high flows than the other sub-basins. Baseflow among the sites exhibited a seasonal trend with higher discharges from fall to spring, especially at groundwater-dominated sites like Beaverdam (BFI = 0.71) where a 10-fold increase was observed.

Days with >0 quickflow occurred ~2/3 of the time. Nonetheless, quickflow only contributed ~1/3 of the total annual discharge because many of the occurrences of quickflow were tiny "slivers" associated with small storm events.

On average, the Kitty's Corner sub-basin had about twice as much quickflow (19% of precipitation) as the others (9 -10 %). On a seasonal basis, storms occurring during the cool season (Oct – Apr) had stronger hydrologic responses (15% of precipitation) than similar-sized storms occurring during the warm season (May – Sept, 7%) due to seasonal differences in ET and soil moisture. Annually, ~50% of rainfall entered soil storage or was lost due to ET while ~50% was discharged as stream flow. Total flow was composed of ~2/3 baseflow and ~1/3 quickflow. These numbers differ somewhat from the long-term water budgets compiled by Norton and Fisher (2000) and Lee et al. (2001) due to differences in methodology, although the ratio of baseflow to quickflow (2:1) is the same.

For the Choptank sites, hydric soils were not related to quickflow at either the event, monthly, or annual time scales. However, potential uncertainties in the rating curves and stage records made it difficult to interpret the findings. Consequently, a secondary analysis of 13 USGS sites was undertaken, which did find a significant, negative relationship between hydric soils and baseflow. This correlation was likely due to increased surface ponding and subsurface water storage in hydric areas, which resulted in greater evaporative losses, less infiltration to groundwater, and hence less baseflow discharge. In contrast, quickflow varied with slope, not hydric soils. As slopes became steeper, overland and shallow subsurface flows increased. Slope and hydric soils were not related. In conclusion, baseflow was driven by a soils effect while quickflow was driven by a topographic effect.

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Chapter 3:
Biogeochemical Storm Response in the Choptank River Basin

Abstract

This chapter evaluates nutrient (N and P) concentrations during a 15-month period (Jun 2006 – Aug 2007) as a function of land use in 15 agriculturally dominated sub-basins of the Choptank River Basin, Delmarva Peninsula, and one all-forested reference site in the adjacent Nanticoke Basin. Baseflow phosphate concentrations increased linearly with the density of concentrated animal feeding operation buildings upstream. Percent agriculture explained 31 – 79 % of the variability in baseflow concentrations of total nitrogen, nitrate, specific conductivity, and pH. Sampling during eight storms at each of four sub-basins over the same time period showed that nutrient concentrations responded to storm discharges in three ways: 1) The particulates (total suspended solids, particulate N and P) had large brief spikes in concentrations and rapidly returned to pre-storm levels, 2) Ammonium and phosphate had modest increases in concentrations, followed by an exponential decay back to initial levels, and 3) Nitrate and conductivity (25) decreased in concentration and slowly returned to pre-storm levels. Most of the analytes followed a clockwise hysteresis when plotted against discharge, indicating either a low affinity for the soil matrix (e.g. nitrate) or soil erosion (e.g. particulates). In contrast, phosphate exhibited a counter-clockwise hysteresis resulting from desorption from upland topsoils and/or bank storage of phosphate. Baseflow concentrations of nitrate, adjusted for agricultural land use, decreased exponentially with % forested hydric soils (r^2= 0.72,

$P < 0.001$), likely due to higher rates of denitrification in forested hydric areas. Baseflows were dominated by dissolved forms. In contrast, quickflows had larger fractions of particulate N (21% of total N) and particulate P (65% of total P). Most of the variability in the volume-weighted means of the 12 measured analytes during storm discharges was explained by either event discharge (L ha^{-1}) or mean event stream temperature. In the four Choptank sub-basins, annual export of TN was estimated at 22 – 33 kg ha^{-1} y^{-1} for TN and <1.4 kg ha^{-1} y^{-1} for TP. On average, 30% and 83% of the annual loads of TN and TP, respectively, were discharged during storm flows. The two largest events alone exported 12% and 51% of the total annual loads of TN and TP, respectively. This has important implications for monitoring groups and underlines the importance of sampling during a range of flows to produce accurate estimates of annual TN and TP export.

Introduction

Eutrophication of the Chesapeake Bay is an ongoing issue. Excessive algal growth, hypoxic bottom waters, loss of submerged aquatic vegetation, poor water quality, and declines in fisheries yields have been problematic for decades (Kemp et al. 2005). Many studies (e.g. Fisher et al. 2006) have identified agricultural fertilizer applications as a major source of nutrients which fuels the over-enrichment of the Bay. Indeed, current estimates suggest that agriculture accounts for 49% of the phosphorus (P) inputs and 38% of the nitrogen (N) inputs to the Chesapeake Bay watershed (Lane et al. 2007).

A good example of the effects of agriculture is the Choptank River Basin on the Delmarva Peninsula (central coastal plain). This basin is an intensive grain- and poultry-producing region where population increases and fertilizer use, especially since the 1950s, has caused increased phytoplankton abundance and decreased water quality in the downstream estuary over the last two decades (Fisher et al. 2006). Nutrient runoff in the Choptank Basin is further exacerbated by several factors, including a general lack of forested buffers, an irregular shoreline, flat topography, and soil drainage characteristics which promote rapid leaching of nutrients (especially nitrate) to groundwater (Staver and Brinsfield 2001, Fisher et al. 2006).

Storm events are the primary mechanism by which agricultural nutrients are flushed off the land and into ground and surface waters. Major storms can transport a large fraction of the available nutrients during brief periods of days or even hours. Pionke et al. (2000), for example, found that 90% of the algal available phosphorus exported from an agricultural watershed occurred during the largest seven storms per year. Similarly, Correll et al. (1999) concluded that a single large spring storm delivered 39% of the total P for that season in a mixed-land-use catchment. In addition, previous work in the upper Choptank River Basin (e.g. Fisher et al. 2006) has demonstrated a large degree of short-term (hourly) variability in nutrient concentrations during brief intervals of stormflow. This suggests that storm events, although relatively infrequent in this region and only lasting for brief periods, have a disproportionately large effect on nutrient discharges.

The major objective of this chapter is to assess the biogeochemical storm response of four agriculturally dominated sub-basins of the Choptank River Basin. In particular, this chapter tests the hypothesis that sub-basins with greater percentages of hydric (i.e. wetland) soils will export less nitrate, primarily because of higher rates of denitrification (see Ch. 2 for definition of hydric soils). This research is unique in three respects. First, it is the only known study which has looked systematically at the effects of hydric soils on stream nutrient (N and P) chemistry at the small watershed scale (<25 km^2). Other studies in the Choptank Basin (Norton and Fisher 2000, Lee et al. 2001) have shown that hydric soils are important in this region for baseflow, but these authors did not directly test their effects on stormflow. Second, this thesis is one of relatively few studies which have measured short-term (hourly) fluctuations in stormflow nutrient chemistry for a large number of storm events, and is the only known study that focuses on soil effects. Other researchers (Correll et al. 1999, McFarland and Hauck 1999, Vanni et al. 2001) have done similar short-term sampling of stormflows, but their focus has been on either land use, storm intensity, or watershed size, not hydric soils. Third and finally, this is the only known study which has examined a very wide range of storm sizes, including two events that were probably ~50-year storms (more on this below).

Notwithstanding the above exceptions, most nutrient monitoring programs do not sample at short intervals during storm events. This is likely because of the logistical demands of sampling storms, which are often 1) unpredictable (especially during the summer), 2) may only last for a few hours, and 3) tend to occur during inconvenient times. For example, the United States Geological Survey (USGS), which maintains a non-tidal water quality database for 1,320 sites in the Chesapeake Bay watershed, collects grab samples on a *monthly* basis without regard for stormflow or baseflow conditions (Langland et al. 2006). Similarly, the Maryland Biological Stream Survey (MBSS), part of the MD Department of Natural Resources' (MD DNR) state-wide monitoring effort of all non-tidal streams, collects grab samples on a seasonal basis during a "spring index period" (about March 1 - May 1) to determine the degree of acidification and organic loading in a stream (Kazyak 2001). Again, as with the USGS, samples are collected without regard for stage levels or the time since the last rainfall. Indeed, according to the MBSS sampling manual, "sampling during turbid conditions or just after heavy rains should be avoided" (Kazyak 2001, pg. 30).

Of course, sampling programs will differ depending on the goals of the researchers involved. However, in reducing the frequency of sample collection to monthly or seasonal grab samples (in the case of USGS and MD DNR), valuable information may be lost, potentially biasing estimates of nutrient fluxes (Correll et al.

1999, Vanni et al. 2001). It is hoped that the more detailed data presented in this chapter will aid future monitoring programs and contribute to better estimates of N and P losses from agricultural watersheds.

Methods

This thesis is part of a larger effort by the United States Department of Agriculture's (USDA) Conservation Effects Assessment Project to monitor stream chemistry in various sub-basins of the Choptank River watershed (2057 km^2). As part of this project, 15 agriculturally-dominated sub-basins (<52 km^2) have been monitored for nutrient chemistry since January 2003 (Fig. 3-1). Most of this monitoring has been during low flow (i.e. baseflow) conditions, yet nutrient concentrations change most dramatically during brief periods of stormflow (e.g. Correll et al. 1999). To better characterize this stormflow (hereafter referred to as quickflow), four of the Choptank sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge) were chosen for more intensive study over a 15-month period (June 2006 – August 2007). The watersheds range from 14 – 25 km^2 in size and are all roughly 2/3 agriculture and 1/3 forested (Table 3-1). Although they have relatively simple land uses, the sub-basins were selected to vary substantially in the percentage of hydric soils (25 – 84%; Table 3-1).

An average of eight storms were sampled for seston, N, and P chemistry at each of the four sub-basins during the 15-month study period (June 2006 – Aug 2007). A total of 31 storms were monitored (Table 3-2), although the same storm was

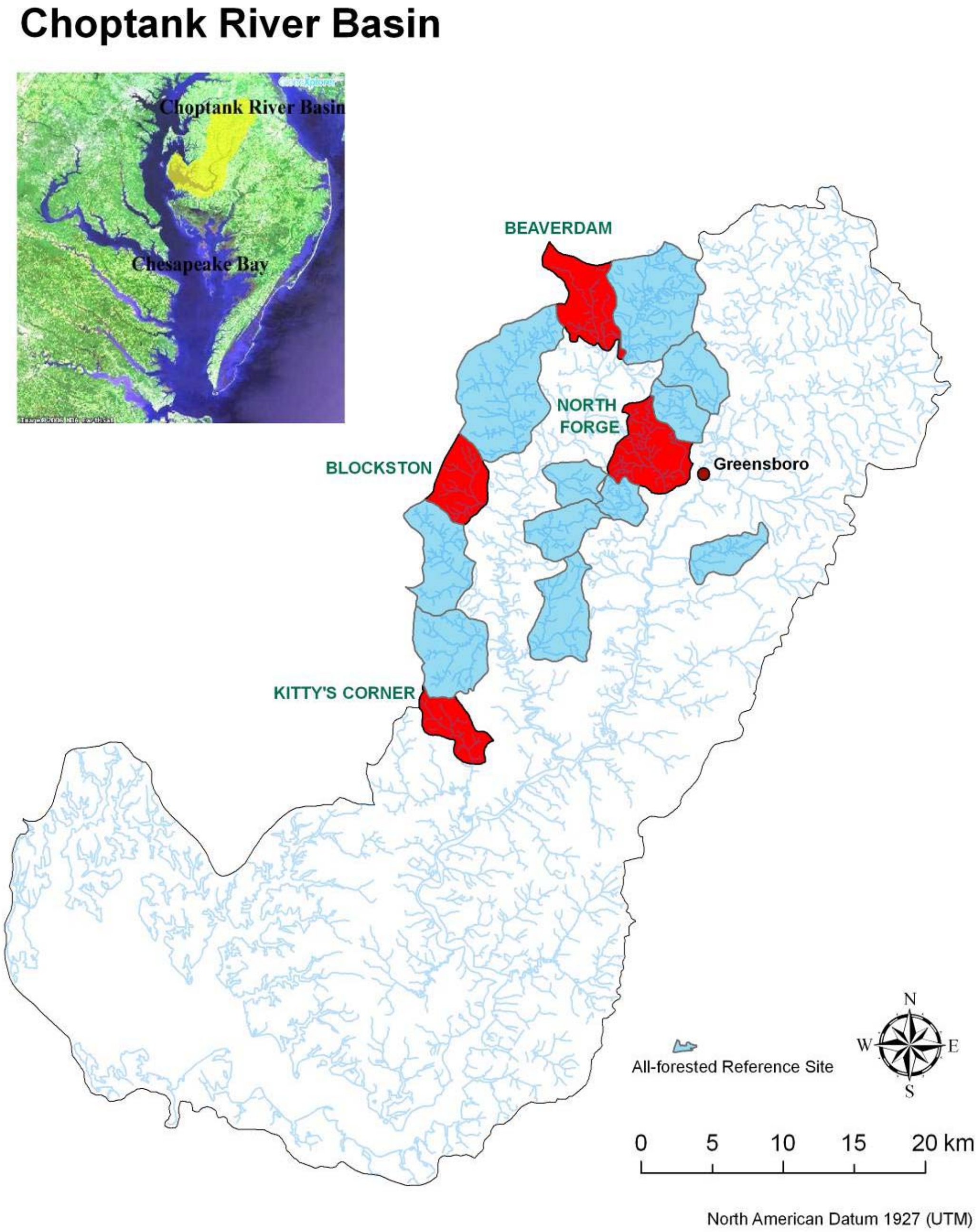


Figure 3-1. Location of the 16 Choptank sub-basins sampled for baseflow chemistry (dark + light polygons), and the four sub-basins sampled for quickflow chemistry (dark polygons). The names of the quickflow sites are shown next to each watershed in CAPS. Also included is the all-forested reference site (small light polygon) located just southeast of the Choptank Basin in the Nanticoke Basin, and the USGS' Greensboro station (circle). The inset shows the regional position of the Choptank Basin relative to Chesapeake Bay.

Table 3-1. Summary of watershed properties for the 15 Choptank sub-basins where baseflow samples were collected, and the forested reference site in the adjacent Nanticoke Basin (marked in gray). The four sub-basins where storm sampling occurred are indicated with X's (right-most column).

Sub-basin	Size (km^2)	% Hydric	% Agriculture	% Forest	Storm Sampling
Kitty's Corner	13.5	24.9	65.1	32.1	X
Cordova	26.5	18.8	76.3	18.4	
Norwich	24.5	32.6	74.7	23.1	
Blockston	17.0	60.0	71.4	28.3	X
Piney	14.7	24.1	78.6	16.2	
Oakland	10.0	16.8	84.0	9.6	
German Branch	51.4	45.2	72.0	26.8	
Beaverdam	23.3	83.6	67.0	32.2	X
Long Marsh	40.5	63.7	58.3	40.8	
Broadway	16.2	58.4	61.8	35.1	
Oldtown	11.6	59.9	58.0	32.3	
Spring	12.2	32.0	77.8	21.6	
North Forge	25.0	51.2	67.0	30.7	X
South Forge	8.5	38.2	65.1	28.2	
Downes	23.4	19.4	77.6	15.6	
Forested Site	1.3	54.5	0.0	95.0	

often sampled at multiple sites. Hence, the number of unique storms was only 18 out of an estimated 93 – 100 occurring over the study period, or 18 – 22% of the total (see Ch. 2 for calculation of total storm population). The sampled events represented a wide range of sizes (Fig. 3-2a) with rainfall totals of 0.66 – 18.61 cm $storm^{-1}$, peak flow responses of <0.01 - 0.51 cm h^{-1}, and integrated stormflows of <0.01 – 10.26 cm $storm^{-1}$ among the sites (Table 3-2). Although the sizes of the sampled events varied somewhat by sub-basin (Fig. 3-2a), there were no statistically significant differences ($P>0.05$) in the average storm size among the sites (Fig. 3-2b), which facilitates comparison of the different watersheds. In addition, a wide range of seasonal conditions was represented with three to four events sampled in each of fall (Sept – Nov), winter (Dec – Feb), and spring (Mar – May). However, a disproportionate number of storms (eight) were sampled in the summer (June – Aug) since this season

Table 3-2. List of storms sampled at each sub-basin during the 15-month study period (June 2006 – Aug 2007). Shown from left to right are the event number (same as in Appendix), the sampling dates, the precipitation totals, the peak flow rate, and the integrated quickflow response for each storm (see Ch. 1, 2). In general, the sampled events represent a wide range of storm sizes and seasonal conditions.

KITTY'S CORNER - 7 STORMS				
Event No.	Sampling dates	Precip, cm storm^{-1}	Peak Q, cm h^{-1}	Integrated Q, cm storm^{-1}
5	June 27-29, 2006	18.61	0.18	10.26
12	November 7-9, 2006	2.88	0.05	0.74
21	January 5-7, 2007	4.71	0.02	1.78
38	April 11-13, 2007	2.81	0.05	0.53
39	April 14-16, 2007	9.47	0.23	4.61
46	June 3-5, 2007	3.07	0.01	0.14
58	July 29-31, 2007	3.75	0.01	0.10

BLOCKSTON - 10 STORMS				
Event No.	Sampling dates	Precip, cm storm^{-1}	Peak Q, cm h^{-1}	Integrated Q, cm storm^{-1}
7	June 25-27, 2006	18.61	0.04	2.34
20	September 1-3, 2006	8.43	0.01	0.10
23	September 14-16, 2006	3.59	0.00	0.12
35	November 7-9, 2006	2.82	0.02	0.31
46	January 8-9, 2007	4.69	0.10	1.87
59	March 15-17, 2007	6.63	0.19	2.12
66	April 14-16, 2007	10.61	0.30	6.70
74	June 2-4, 2007	3.51	0.01	0.09
88	July 27-29, 2007	1.66	0.00	0.12
92	August 20-22, 2007	4.09	0.01	0.06

BEAVERDAM - 7 STORMS				
Event No.	Sampling dates	Precip, cm storm^{-1}	Peak Q, cm h^{-1}	Integrated Q, cm storm^{-1}
32	November 8-10, 2006	2.87	0.02	0.12
67	April 4-6, 2007	2.27	0.01	0.17
68	April 11-13, 2007	2.43	0.01	0.05
69	April 14-16, 2007	10.72	0.51	2.79
79	June 5-7, 2007	0.66	0.00	0.00
85	June 28-30, 2007	1.97	0.00	0.01
94	July 29-31, 2007	1.66	0.02	0.22

NORTH FORGE - 7 STORMS				
Event No.	Sampling dates	Precip, cm storm^{-1}	Peak Q, cm h^{-1}	Integrated Q, cm storm^{-1}
24	November 8-10, 2006	2.97	0.01	0.24
31	January 5-6, 2007	0.81	0.01	0.01
38	February 14, 2007	3.00	0.04	0.42
42	March 16-17, 2007	6.92	0.14	1.80
44	April 4-6, 2007	1.24	0.01	0.12
45	April 11- 16, 2007	13.49	0.24	5.06
51	June 3-5, 2007	3.51	0.01	0.07

occurred twice during the June 2006 – Aug 2007 study period. The two largest events (>10 cm rainfall) took place in June 2006 and April 2007, and were both sampled, although not consistently at every sub-basin (Table 3-2).

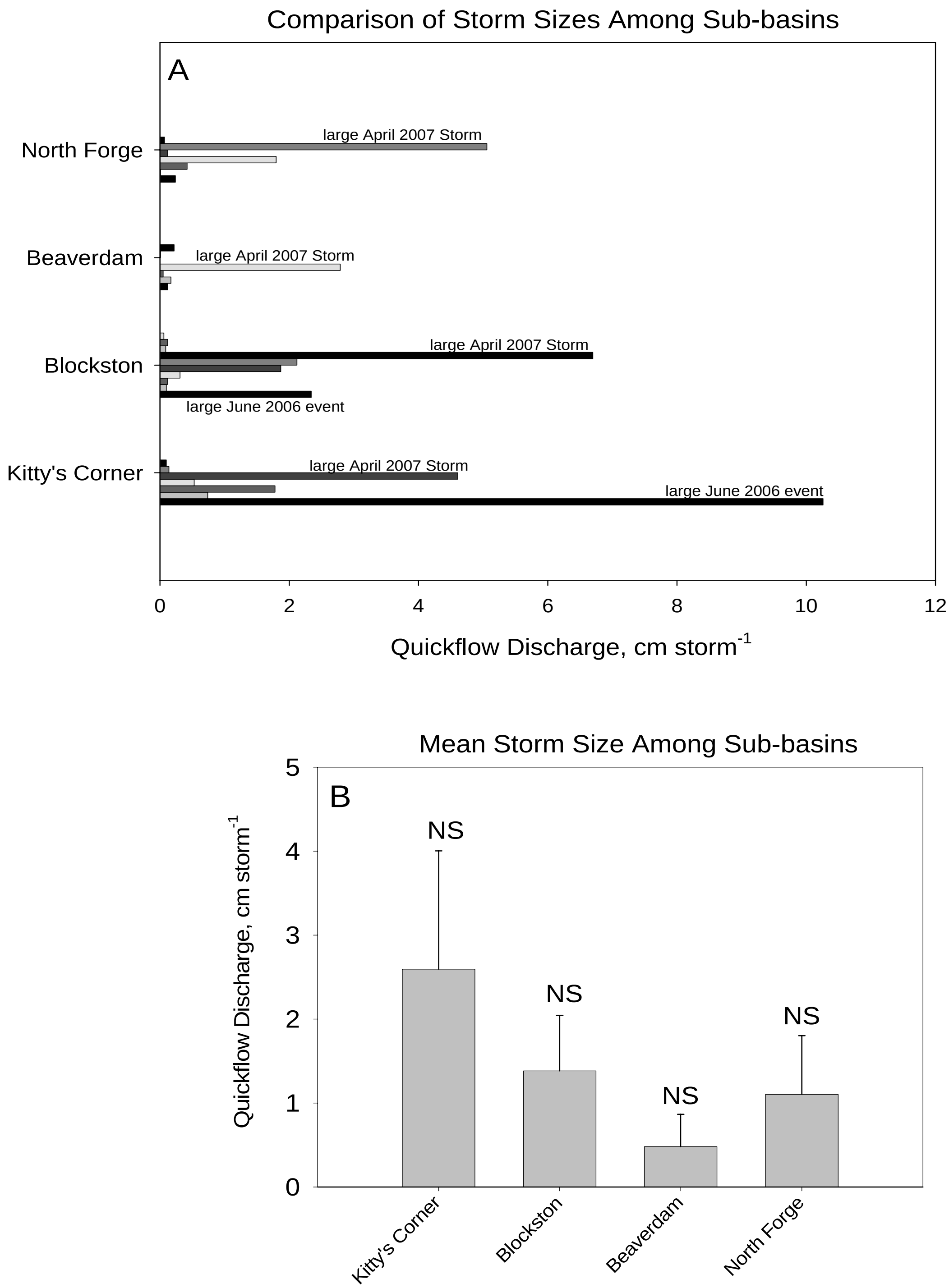


Figure 3-2. The top panel (A) is a comparison of storm sizes for all sampled events at each of the four sub-basins where quickflow chemistry was measured. The two largest events, occurring in June 2006 and April 2007, are shown, although the former was not sampled consistently at every sub-basin. The bottom panel (B) is a comparison of the mean storm sizes (± standard error) at each site. No significant differences (P>0.05) were observed among the means using a one-way analysis of variance due to the large range of storm sizes sampled. NS = not significant.

Discharge (L s^{-1} or m^3 s^{-1}) was monitored at the hydrologic gauging stations located at the outlet of each catchment (Fig. 3-1, see also Ch. 2). The discharge data were used to volume-weight the measured nutrient concentrations (more on this below). Stage and temperature were monitored continuously every 30 minutes using data loggers (Solinst Ltd.) mounted ~5 cm above the stream bottom inside an anchored cinder block which provided protection from storm debris and stabilized the logger in place. The cinder block was chained to the bottom using an earth anchor located ~1 m upstream. Data were downloaded from the loggers approximately every 3 – 4 months.

Corrections were applied for barometric pressure using a second reference logger (Solinst Ltd.) exposed to the air and specially calibrated for atmospheric sensitivity. The corrected stage data were then converted into discharge using rating curves developed separately for each site over a ~2 year period. The rating curves were constructed by measuring velocity and depth along a cross-section of stream during a variety of stage conditions. For a given stage, the measured velocity (m s^{-1}) and depth (m) profiles were integrated along the cross-section (m), resulting in total discharge (m^3 s^{-1}). The rating curves were all highly significant ($P<0.0001$) with r^2 values of 0.94 – 0.99 (see example in Fig. 2-2 of Ch. 2).

Once the discharge data were compiled, baseflow was separated from the total flow using a new method developed for this thesis called the 1-day **S**liding **A**verage with **R**ain **R**ecord (1-day SARR, see Ch. 2). This approach, based on a method by Gustard et al. (1992), was unique in that it incorporated the daily precipitation record, which made the separation more physically meaningful. Quickflow was calculated as total flow minus baseflow. Events were identified by cross-referencing the daily precipitation and daily discharge data (see Table 2-5 in Ch. 2). Briefly, each unique separation of the hydrograph, along with the rainfall associated with that separation, was considered an “event.” Days with >0 precipitation but no quickflow response were also considered “events” since summer rainfall was often absorbed by the soil and had zero hydrologic response. Rainfall and quickflow totals for each individual storm (cm storm^{-1}) occurring in the study period were calculated as the integrated sum of daily rainfall and daily quickflow within each event time period.

Quickflow water samples were collected using automated ISCO (Lincoln, NE, model 3700) water samplers. The ISCOs were programmed to collect one sample every hour during a storm event and composite every two hourly samples into one bottle, resulting in 24 samples over a 48-hour period. Each 24-sample time series of nutrient concentrations is called a “chemograph.” This method of sampling is consistent with the known hydrologic response times of these sub-basins, which is ~1 – 3 days for small to moderate events. Sample collection was triggered by a sensor (ISCO 1640 liquid level actuator) positioned ~1 cm above the stream at baseflow. As the stage increased during a storm event, the rising water tripped the sensor and started the sampling cycle. Samples were pumped through an intake mounted ~ 10 cm above the stream bottom on top of the same anchored cinderblock described earlier. Acid preservatives were not used in the bottles because they dissolve particulate nutrients, which are especially important in storm samples (Jordan et al. 1997). The bottles were retrieved from the field immediately following the end of the sampling cycle.

Once the samples were collected, they were processed in the laboratory as follows. Conductivity and pH were measured on whole samples using digital Yokogawa and VWR probes, respectively. Conductivity measured at a given temperature T [cond(T)] was converted to specific conductivity [cond (25)] using the following formula:

$$cond(25) = cond(T) * \exp(0.023 * 25)/\exp(0.023 * T) \qquad \text{(eq. 1)}$$

This formula was derived from a water sample obtained from the nearby gauging station at Greensboro, MD (Fig. 3-1) and measured at various temperatures (Fisher et al. 1998). Whole samples were filtered using 25-mm (0.025 μM) Whatman glass fiber filters and analyzed for total suspended solids (TSS), particulate nitrogen (PN), and particulate phosphorus (PP). TSS concentrations were estimated using the gravimetric method in which the change in dry weight of a filter is divided by the filtration volume of the sample:

$$[TSS], \text{mg L}^{-1} = \Delta\text{dry weight (mg)} / \text{filtrate volume (L)} \qquad \text{(eq. 2)}$$

PP was measured by first ashing the organic matter on the filter in a high temperature (450°) muffle furnace, and then solubilizing the remaining phosphate residue in boiling hydrochloric acid (Andersen 1976). Finally, the PP (as phosphate) was measured colorimetrically on a spectrophotometer (885 nm) using the ascorbic acid method (Strickland and Parsons 1972). Particulate nitrogen (PN) was estimated using an elemental analyzer at Horn Point Laboratory's Analytical Services Lab. Due to financial and time constraints, only selected samples (corresponding to the baseflow, rising limb, peak, and falling limb portions of the flow hydrograph) were tested for particulates (PP and PN). For some events, this resulted in 4-sample chemographs for these analytes instead of the usual 24 samples.

The filtrate from the particulate (TSS, PP, PN) measurements was frozen and sent to a USDA laboratory in Beltsville, MD for processing. There, phosphate (PO_4), nitrate (NO_3), ammonium (NH_4), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) were all measured colorimetrically with a Lachat autoanalyzer. In the case of TDN and TDP, the samples were first digested using the persulfate autoclave digestion method (Valderrama 1981) prior to being shipped to the USDA. The digestion oxidizes all forms of nitrogen to nitrate, and all forms of phosphorus to phosphate so they can be measured as above. Initially, total nitrogen (TN) and total phosphorus (TP) were also measured on whole samples. However, the high amounts of particulates in the samples led to clogging of the autoanalyzer tubes. Hence, the samples had to be filtered first, resulting in total dissolved nitrogen and phosphorus only (i.e. TDN, TDP). Nonetheless, TN and TP could be calculated as TDN + PN and TDP + PP, respectively, although only if PN and PP data were available. A summary list of all the chemical parameters measured in the quickflow samples is shown in Table 3-3.

Finally, the efficiency of the autoclave digestion for both the TN/TP and TDN/TDP samples was estimated by comparing the expected and calculated values for the same TN/TP (or TDN/TDP) standards. The results of this analysis showed that

Table 3-3. Comparison of chemical parameters measured in monthly baseflow samples (left column) and event-based quickflow samples (right column), showing the overlap of seven analytes (specific conductivity, pH, phosphate, ammonium, nitrate, total phosphorus, and total nitrogen).

BASEFLOW SAMPLING - MONTHLY	QUICKFLOW SAMPLING - PER STORM
Conductivity (25)	Conductivity (25)
pH	pH
Phosphate	Phosphate
Ammonium	Ammonium
Nitrate	Nitrate
Total Phosphorus	Total Phosphorus
Total Nitrogen	Total Nitrogen
	Total Suspended Solids
	Particulate Phosphorus
	Particulate Nitrogen
	Total Dissolved Phosphorus
	Total Dissolved Nitrogen

the efficiency rates were around 80% for TP/TDP, and >95% for TN/TDN. To adjust for this, the data were divided by the efficiency rate, e.g. a TN value of 300 μM with an efficiency of 95% was divided by 0.95.

Baseflow Data

Data on baseflow chemistry were also available within this project (Sutton et al. in press). Grab samples were collected monthly at each of the 15 Choptank sub-basins (one sample per site), as well as one all-forested reference site in the adjacent Nanticoke Basin (Fig. 3-1). To ensure that only baseflow was represented, samples were collected only when 1) a minimum of three days had passed without rainfall, and 2) stage conditions were at normal, non-quickflow levels for that particular month based on observations of the sites over several years. Baseflow samples were tested for seven analytes, including PO_4, NH_4, NO_3, TN, TP, pH, and conductivity (25) using the same methods described above (Table 3-3).

One of the goals of this chapter is to compare quickflow with baseflow chemistry, and to determine the controlling factors of each in these sub-basins. Unfortunately, the sampling methodologies for quickflow and baseflow, as just described, are not the same. Each data set has its own advantages and disadvantages. The baseflow data, for example, are useful for correlating the observed nutrient concentrations to watershed attributes (e.g. land use) because the number of sub-basins (16) is so large. However, a disadvantage is that the number of tested parameters (seven) is relatively small. The quickflow data, on the other hand, is more intensive with 12 tested parameters, yet with a sample size of only four sub-basins, it is difficult to correlate the observed concentrations with watershed properties. To address this issue, the baseflow and quickflow data sets were treated differently, as described below.

The baseflow data were correlated with known watershed attributes as follows. First, the average monthly baseflow concentrations were computed for each of the seven measured analytes over the 15-month study period (June 2006 – Aug 2007). The means were then examined for correlations with the following variables: land use (% agriculture, % forest), soil properties (hydrologic soil group A - D, % hydric soils), % buffered stream length, and the number of concentrated animal feeding operations. Correlations that were significant ($P<0.05$) were further explored, while non-significant correlations ($P>0.05$) were discarded. Where multiple, significant correlations were observed for the same analyte, a forward step-wise linear regression was used to explore the best model fit, and each variable was tested for independence using a Pearson Product Moment test. This is described in more detail in the "Statistics" section below.

Watershed attributes were available from a variety of sources. Land use has been previously interpreted and digitized by other researchers from aerial photos (e.g. Fisher et al. 2006, Sutton 2006). Soil properties, including hydrologic soil group and hydric status, were available from the USDA's website (http://soildatamart.nrcs.usda.gov/) as county-level soil survey geographic databases (SSURGO). Hydrologic soil groups are defined based on a soil's infiltration rate, with 'A' soils having a very high infiltration rate (and hence a relatively low runoff potential) and 'D' soils having a very low infiltration rate (and hence a relatively high runoff potential, Soil Survey 1993). Both the hydrologic soil group and the hydric status of a particular soil type are listed as attributes in the SSURGO database. The % forest buffered stream length was obtained from Sutton (2006). Concentrated animal feeding operations in each sub-basin were counted using imagery derived from 2005 aerial photographs. Watershed boundaries have been previously delineated and digitized based on USGS 7.5' topographic maps (Norton and Fisher 2000).

Volume-Weighting of Quickflow Data

Volume-weighting of quickflow nutrient concentrations is especially important because discharge and chemistry both change rapidly during storm events. Each nutrient concentration in a given chemograph (e.g. μmol L^{-1}) was multiplied by the average of the four closest 30-min discharge values (e.g. L s^{-1}, Fig. 3-3a), resulting in a flux rate (e.g. μmol s^{-1}) for the two-hour time period over which the

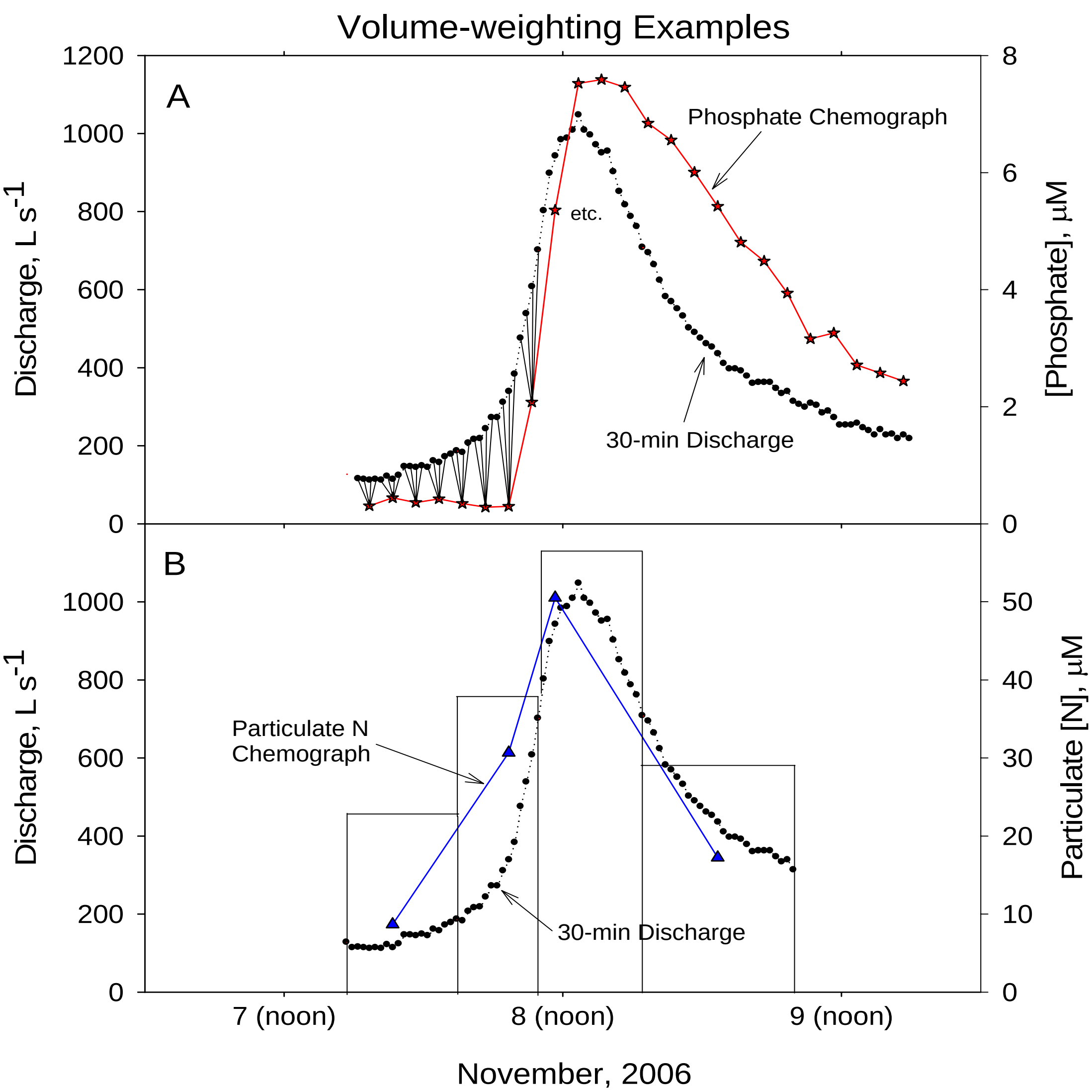


Figure 3-3. Examples of how the nutrient samples were volume weighted by discharge. Most of the time (A – top panel), each nutrient concentration in the chemograph (stars) was weighted by the average of the nearest four 30-min discharge points (circles and dotted line). For clarity, volume-weighting is only shown for the first few points in the phosphate chemograph. For some analytes (e.g. particulate N and P), only selected samples were available, resulting in a more poorly-resolved chemograph. In these cases (B – bottom panel), each point in the chemograph (triangles) was weighted by the average of a wider range of discharge points (boxes), resulting in a larger standard error for the volume-weighted mean.

sample was taken. The midpoint of the sample collection period was used as the time stamp, i.e. a sample collected at 0800 h and 0900 h would have a time stamp of 0830 h. The volume-weighted (v.w.) mean concentration for each storm was calculated as the sum of the two-hour flux rates (e.g. μmol s^{-1}) over the sampling period divided by the sum of the discharges (e.g. L s^{-1}) over the same interval, as follows:

$$\text{v.w. mean} = \frac{\sum (\text{Ci} * \text{Qi})}{\sum Qi} \qquad \text{(eq. 3)}$$

where C_i = i^{th} nutrient concentration in the chemograph and Q_i = avg. of closest discharge measurements associated with C_i (Fig. 3-3). Since pH is on a log scale, each pH sample was de-logged prior to being volume-weighted, and then re-logged. The standard error of the volume-weighted means ($SE_{\text{v.w. mean}}$) was calculated using an equation derived from the sample variance (Zar 1999), as shown below:

$$SE_{\text{v.w. mean}} = \frac{\sqrt{\sum_{i=1}^{n} (Ci - \text{v.w. mean})^2 \Big/ (n-1)}}{\sqrt{n}} \qquad \text{(eq. 4)}$$

where n = sample size and C_i and "v.w. mean" are the same as above.

As mentioned, for some analytes (e.g. PN, PP), fewer samples (usually four) were available in the chemograph. As a result, each concentration was weighted over a broader range of discharge values. The number of discharge measurements used to weight each concentration varied from one chemograph to the next because the time interval between the four samples was not consistent. However, as a general rule, each sample concentration was weighted over a symmetrical discharge interval with the sample as close to the mid-point as possible, with no overlap in the discharge intervals among the samples (Fig. 3-3b). Because of the poorer resolution of having only four samples (instead of the usual 24), the volume-weighted means for these analytes generally had larger standard errors.

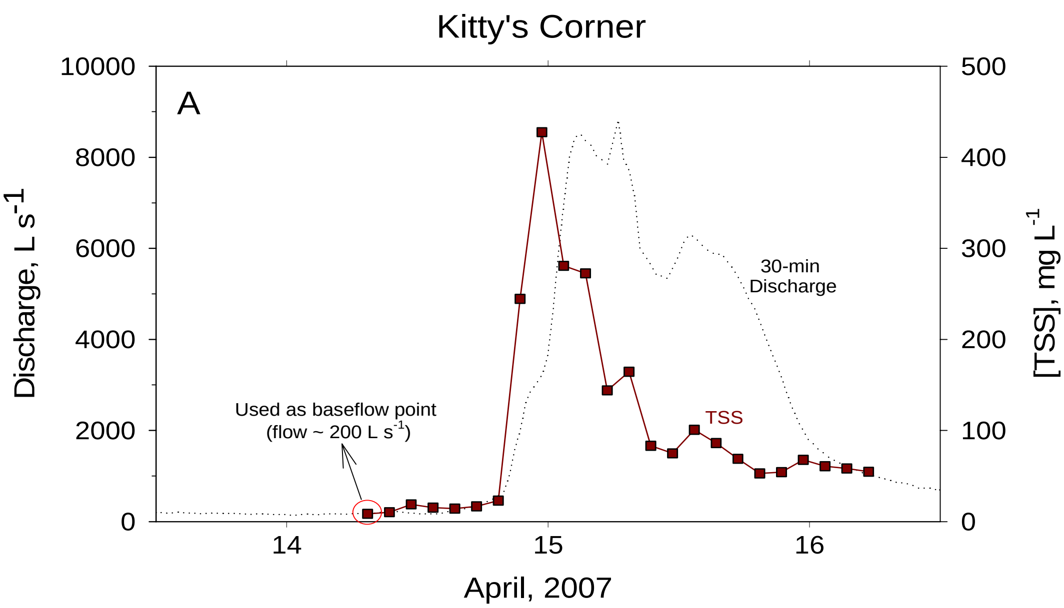
Comparison of Baseflow and Quickflow Nutrient Concentrations

Mean baseflow and v.w. mean quickflow concentrations were compared for the four sub-basins where the two sampling programs overlapped (i.e. Kitty's Corner, Blockston, Beaverdam, and North Forge, Table 3-1). Mean baseflow nutrient concentrations were calculated as the monthly average of all 15 months in the study period. Mean quickflow concentrations were calculated as the average v.w. mean for all sampled events at each sub-basin. In averaging across all sampled events, a "typical" quickflow concentration was estimated, with the standard error of the mean representing the range in sampled storm sizes, which for this study was quite large (Fig. 3-2a). In addition, since the mean storm size for each of the four sites was similar (Fig. 3-2b), the average v.w. mean concentrations could be compared directly among the different watersheds.

For the five analytes not measured in the baseflow samples (Table 3-3), the baseflow data were derived from the measured storm chemographs. Either the first point or the last point in the chemograph (whichever had the lowest flow, usually <500 L s^{-1}) was used as a baseflow sample. Only points which were clearly before the start of the discharge rising limb, or clearly after the end of the discharge falling limb, were used based on visual interpretations of the discharge hydrograph and the nutrient chemograph for each particular storm (Fig. 3-4a). For some events, it was not possible to obtain an adequate baseflow sample because the discharge was too high (usually > 500 L s^{-1}) during the sampling period relative to normal, pre-storm discharge levels for that month (Fig. 3-4b).

N and P Fractions in Baseflows and Quickflows

Average N and P fractions were also compiled for both baseflow and quickflow during the study period. Since particulate nutrients (PN and PP) were not measured in the baseflow samples (Table 3-3), DOP + PP was estimated as TDP – PO_4, and DON + PN was estimated as TDN – NH_4 – NO_3. In both cases, for comparison with the quickflow, it was assumed that the dissolved organic portions (DOP and DON) represented a majority of the DOP + PP and DON + PN, respectively, since concentrations of particulate nutrients (PP and PN) in baseflow are typically minimal (e.g. < 2 μM for PN, Volk et al. 2006).



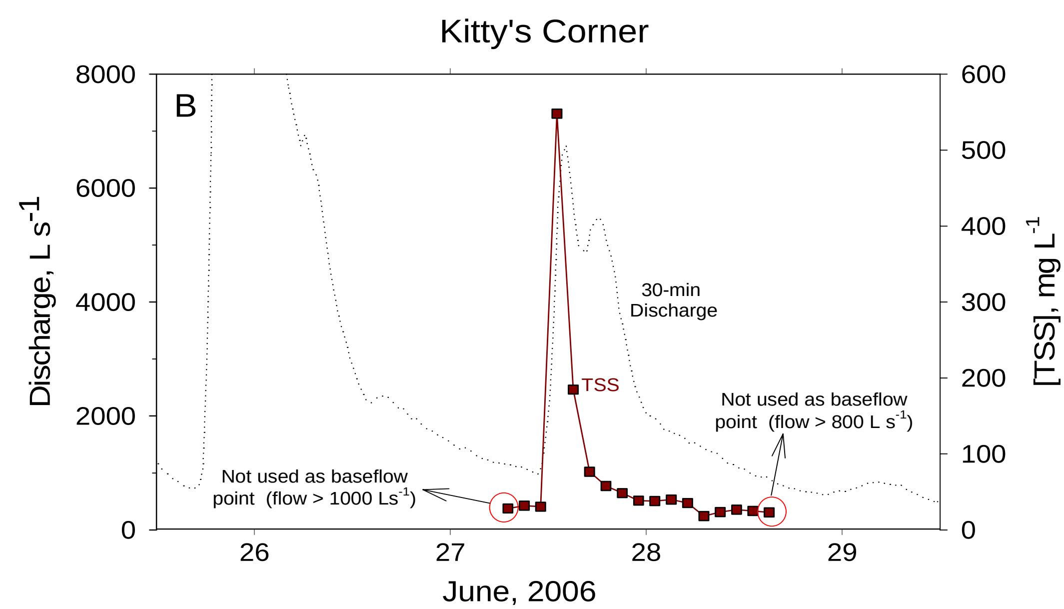


Figure 3-4. Examples of how a portion of the measured quickflow chemographs was used as a "baseflow" sample for comparison with the quickflow chemistry. Two basic scenarios were possible. In the first scenario (A – top panel), the initial sample in the chemograph (arrow) had a flow of (in this example) ~200 L s^{-1}, which is consistent with pre-storm discharge levels for the month of April, 2007. Hence, this sample could be used as a "baseflow" sample. In the second scenario (B – bottom panel), neither the initial nor the final TSS chemograph samples (arrows) could be used as baseflow because both were collected at flows > 800 L s^{-1}, either because of a second, larger flow peak the day before sampling started (for the first chemograph sample), or because the current storm was still receding (for the last chemograph sample). For reference, normal baseflow values for the month of June, 2006 were ~300 L s^{-1} (not shown). Hence, for this particular chemograph, it was not possible to obtain a baseflow sample.

Volume-weighted Means and Peak Concentrations

For each of the 12 measured analytes, v.w. mean quickflow concentrations were examined for correlations with the following two variables: event discharge (L ha^{-1}) and mean event stream temperature. Event discharge (Q_{event}) was calculated for each event as the sum of the 30-minute instantaneous discharge measurements (L s^{-1}) over the sampling interval, multiplied by the interval between measurements (30 min), and then normalized to sub-basin area, as shown below:

$$Q_{\text{event}} = \frac{\sum \text{L s}^{-1} * 60\,\text{s min}^{-1} * 30\,\text{min})}{(\text{watershed area in ha})} \qquad \text{(eq. 5)}$$

Mean event stream temperature was used as a proxy for seasonal changes, and was calculated as the average of the 30-min temperature measurements (obtained using the stream loggers) over the sampling interval. In addition, peak nutrient concentrations for each of the analytes were examined for correlations with peak discharge (L s^{-1}).

Peak Offsets

Peak offsets were calculated for each analyte as the time difference (in hours) between the peak in nutrient concentrations and the peak in discharge (Fig. 3-5a). Multiple peak offsets were calculated for events where both the flow hydrograph and the nutrient chemograph peaked more than once due to variations in rainfall during

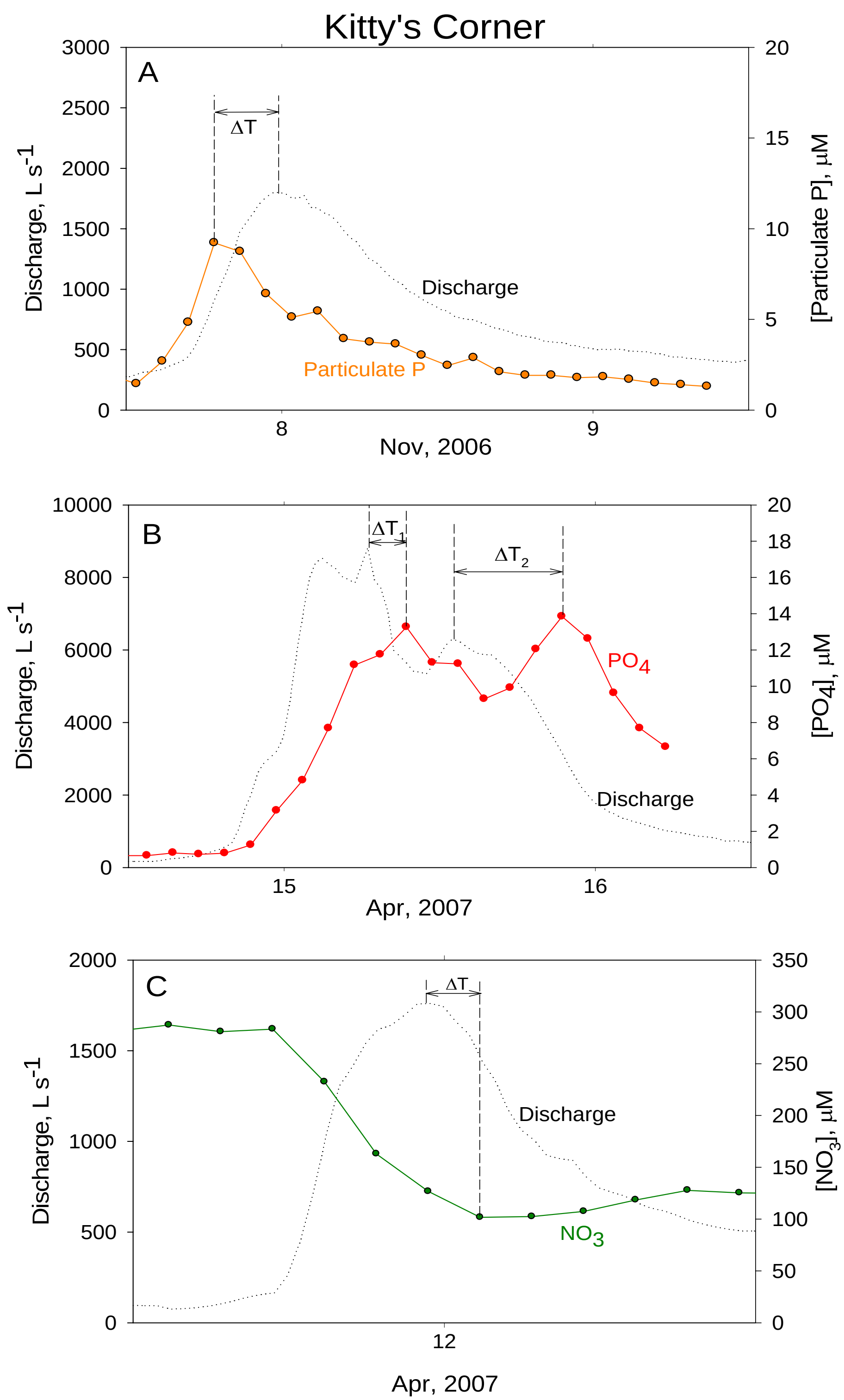


Figure 3-5. Examples of how the peak offsets (ΔT) were determined from the nutrient chemographs and the discharge hydrographs. When one peak occurred (A – top panel), ΔT was calculated as the time difference (in hours) between the peaks. When more than one peak occurred (B – middle panel), a peak offset was calculated for each peak. Some analytes, like NO_3, decreased during storm events. In these cases (C – bottom panel), the peak offset was calculated based on the minimum nutrient concentration, not the maximum.

the event (Fig. 3-5b). For analytes that decreased during storms (e.g. nitrate), the minimum concentration was used instead of the peak concentration (Fig. 3-5c).

Statistics

Curves were fitted to the data using a “forward selection” procedure (Zar 1999). In this process, a simple regression (e.g. linear) was initially fit to the data, followed by more complex regressions (e.g. exponential), which often increased the r^2 value. The “best” fit among the curves was determined using a modified F statistic which measured whether or not the higher-order model was a significant improvement over the lower-order model. F was defined as the difference in the regression sums of squares (SS) for the two models, divided by the residual mean square (MS) of the higher-order model, as shown below (Zar 1999):

$$F = \frac{\text{(regression SS for higher degree model)} - \text{(regression SS for lower degree model)}}{\text{(residual MS for higher degree model)}}$$

F was calculated in a step-wise fashion for each pair of models from the smallest to the largest (e.g. linear versus 2-parameter exponential, 2-parameter exponential versus 3-parameter exponential). If the calculated F was equal to or greater than a critical F (α=0.05, ν = residual degrees of freedom for the higher degree model; Zar 1999), the higher-order model was considered a significant improvement and the lower-order model was discarded. The next higher-order model was then tested, and so on. If, however, the calculated F was less than the critical value, the lower-order model was considered a better fit. The advantage of this approach was that it objectively determined the best model whereas other indicators (e.g. r^2) can be misleading because they do not convey information about the significance of one model over another.

In some cases, multiple correlations were significant ($P<0.05$) for the same analyte. For instance, nitrate concentrations were significantly related to both % agriculture and % hydric soils. In these cases, the most important variable was determined using a forward step-wise linear regression. This analysis involved adding each independent variable incrementally into the regression to see if it significantly improved the predictive ability of the model. A model term was considered significant if the calculated F value was greater than the critical value. Unlike above, where F was used to compare *between* models, F was calculated for each model term individually as the mean square of the regression divided by the mean square of the residual (Zar 1999). Forward step-wise regressions require that one independent variable be forced into the equation as a baseline for comparison with the other terms. In this case, either the correlation with the highest r^2 value or a known driver of nutrient concentrations (e.g. % agriculture) was used as the baseline.

In addition to step-wise regression, a Pearson Product Moment test was used to measure multi-collinearity among the independent variables. This test uses a correlation coefficient (-1 to 1) and a P value which indicates both the direction and strength of the relationship. Correlation coefficients less than zero indicate a negative (i.e. inverse) association, values close to zero indicate no association, and values greater than zero indicate a positive association. It is important to test for multi-collinearity because independent variables that co-vary produce unreliable multiple regression results, and conclusions based on correlated terms may be misleading.

Finally, differences in mean baseflow and mean quickflow concentrations at each sub-basin were tested using a one-way analysis of variance with site as the factor. The differences were considered significant if P was <0.05. Throughout this chapter, the following convention is used to denote significance: NS (not significant) = P >0.05, * = P<0.05, ** = P<0.01, *** = P<0.001.

Results

Summary of Storms

During the 15-month study period (June 2006 – Aug 2007), a total of 93 events were identified at the Blockston sub-basin and 100 events were identified at the Beaverdam sub-basin. The storm population varied by location because, as mentioned above, the discharge data (which was unique for each site) was used to help identify events (Ch. 2). The other sub-basins (Kitty's Corner and North Forge) had much smaller storm populations (<63 events) because of missing logger data at these sites, although they likely would have had similar population sizes if the loggers had not failed. Individual event totals ranged from <0.01 – 18.79 cm rainfall storm^{-1} and <0.01 – 10.26 cm quickflow storm^{-1} (see Appendix). The two largest events (both with >10 cm rainfall) occurred in late June 2006 and mid-April 2007 and caused widespread flooding of local roads and towns. Individual storm hydrographs were characterized by a steep rising limb (<12 h), a brief peak (<2 h), and a long gradual tail generally lasting about 1 – 3 days although sometimes up to 10 days for major events (see example in Fig. 2-13 of Ch. 2). Detailed event analysis is available in Chapter 2, while a full list of storms is shown in the Appendix.

Baseflow Chemistry and Watershed Properties

Baseflow data were correlated to land use in the watershed. In particular, mean phosphate concentrations increased linearly with the number of CAFO farms in each sub-basin ($r^2 = 0.47$, $P<0.01$), from a low of 0.2 μM at the forested reference site up to 2.3 μM at the German Branch watershed (Fig. 3-6a). For this analysis, each CAFO "farm" was defined as one or more buildings in close proximity (i.e. a farm with four buildings and a farm with one building were each counted as "one" farm). However, this method of counting is somewhat misleading because 1) the number of farms is not normalized by watershed area, and 2) not all farms are the same size. To further explore the role of CAFOs, a second method was employed in which the number of *buildings* in each watershed were counted (i.e. a farm with four buildings was counted as "four" whereas a farm with one building was counted as "one"). The total number of buildings in each sub-basin were then divided by watershed area so

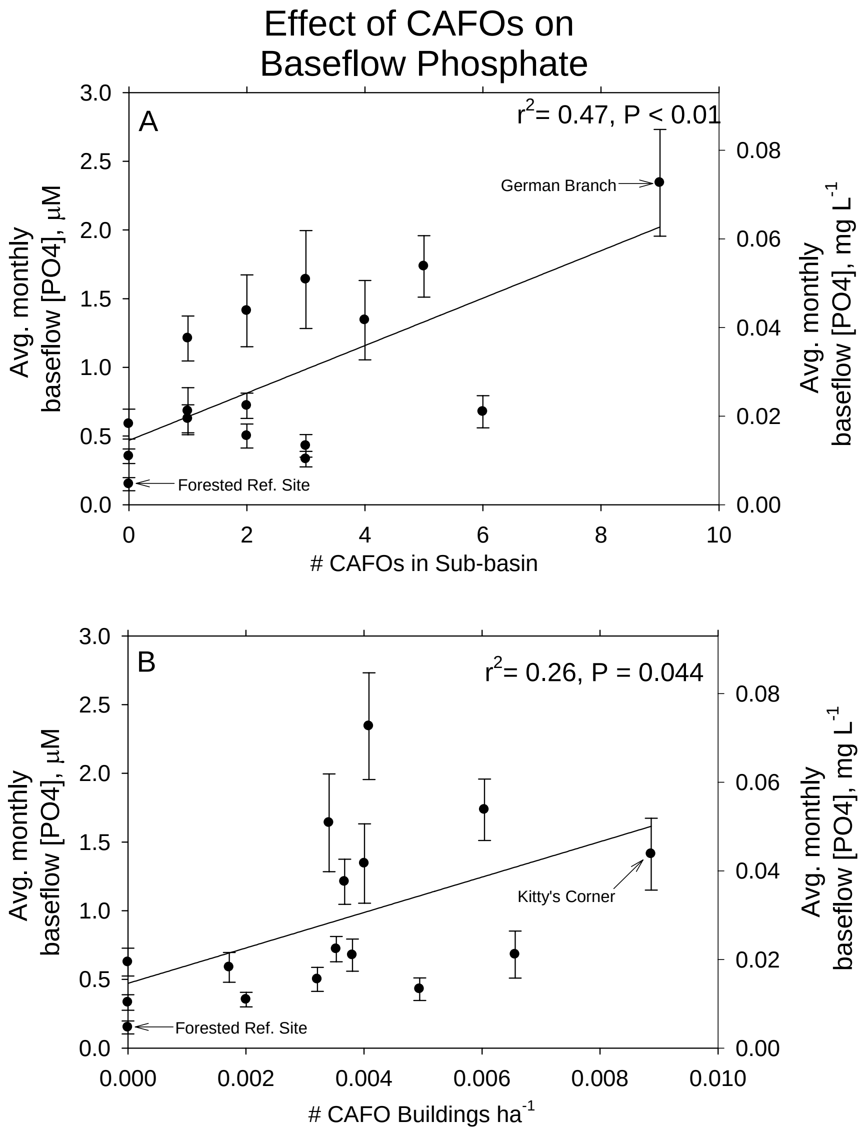


Figure 3-6. In the top panel (A), average monthly baseflow phosphate concentrations increased linearly with the number of concentrated animal feeding operation (CAFO) farms in each sub-basin during the 15-month study period (June 2006 – Aug 2007). In the bottom panel (B) is the same phosphate data plotted against the number of CAFO *buildings* per watershed area. Shown in both panels are the means (as both µM and mg L^{-1}, see both y-axes) ± standard errors.

that sub-basins of different sizes could be compared. This method assumed that the number of CAFO buildings was proportional to the number of chickens, which in turn was proportional to the amount of manure. The results of this analysis show that baseflow phosphate concentrations increased linearly with the density of CAFO buildings (r^2= 0.26, P = 0.044, Fig. 3-6b), although there was more scatter in the data compared to the first counting method (compare Figs. 3-6a, b). Despite this relatively weak correlation, the density of CAFO buildings was still more descriptive than using percent agriculture to explain baseflow phosphate concentrations (r^2= 0.19, P > 0.05, data not shown).

Mean baseflow phosphate was also related to several other variables. These included a negative but weak correlation with % forest (r^2= 0.29, P = 0.03) and % hydric soils (r^2= 0.30, P = 0.03), and a positive but weak correlation with % agriculture (r^2= 0.25, P = 0.047). However, none of these variables significantly improved the model using # CAFOs alone. In addition, the two dominant land uses, % agriculture and % forest, were strongly correlated (correlation coefficient = -0.99, P <<0.0001). Mean total phosphorus concentrations were not significantly correlated with any of the tested variables.

Mean total nitrogen concentrations increased exponentially with % agriculture (r^2= 0.77, P<0.0001, Fig. 3-7a), and were also inversely correlated with % forest (r^2= 0.82, P <0.0001), % hydric soils (r^2= 0.38, P = 0.01), % hydrologic soil group A (r^2= 0.70, P <0.01), and % hydrologic soil group D (r^2= 0.64, P <0.01). However, again, none of these variables significantly improved the regression. The results for nitrate were virtually identical to the results for total nitrogen since baseflow N was almost entirely composed of nitrate (Fig. 3-7b). The USGS' Greensboro station (Fig. 3-1) is also included in Figs. 3-7a, b for reference. It falls on the low end of the agricultural Choptank sub-basins because of the relatively large abundance of forest there (49%). Mean ammonium concentrations were not significantly correlated with any of the tested variables. These results for baseflow nitrogen are similar to those reported previously for the Choptank Basin (Fisher et al. 2006) and elsewhere in the Mid-Atlantic (Jordan et al. 1997).

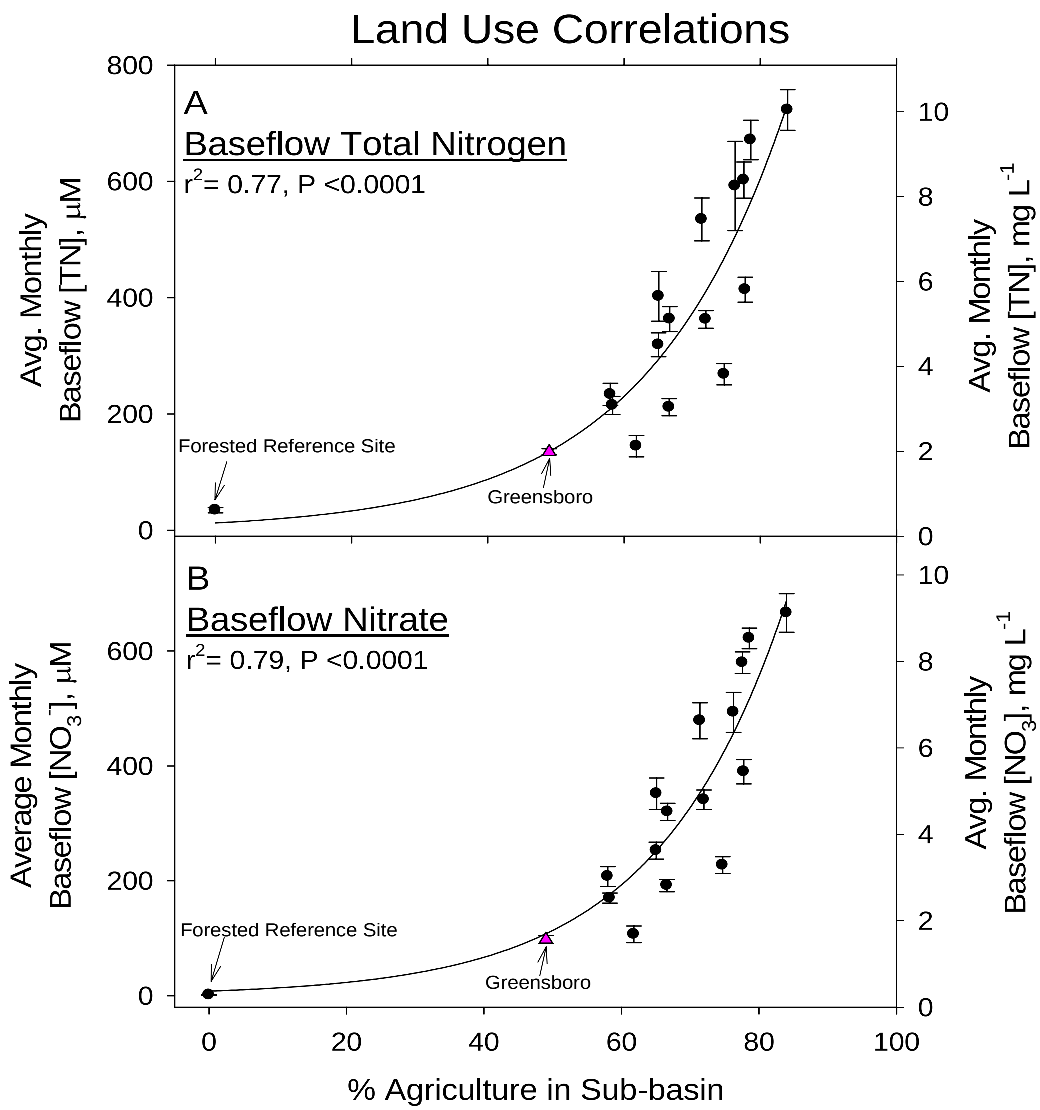


Figure 3-7. Average monthly baseflow concentrations (as both µM and mg L^{-1}, ± standard errors) of total nitrogen (A - top panel) and nitrate (B - bottom panel) increased exponentially with agricultural land use during the 15-month study period (June 2006 – Aug 2007). Almost all of the total nitrogen was composed of nitrate, hence the almost identical trends. Data includes the 15 Choptank sub-basins, the all-forested reference site in the Nanticoke Basin (see text and arrows), and the USGS' Greensboro station (triangles).

Mean conductivity(25) increased linearly with % agriculture (r^2=0.31, P = 0.02), from about 50 µS cm^{-1} at the forested reference site to almost 400 µS cm^{-1} at some of the agricultural sites (Fig. 3-8a). Mean conductivity(25) was also inversely correlated with % forest (r^2= 0.33, P = 0.02) and % hydric soils (r^2=0.25, P = 0.049), although

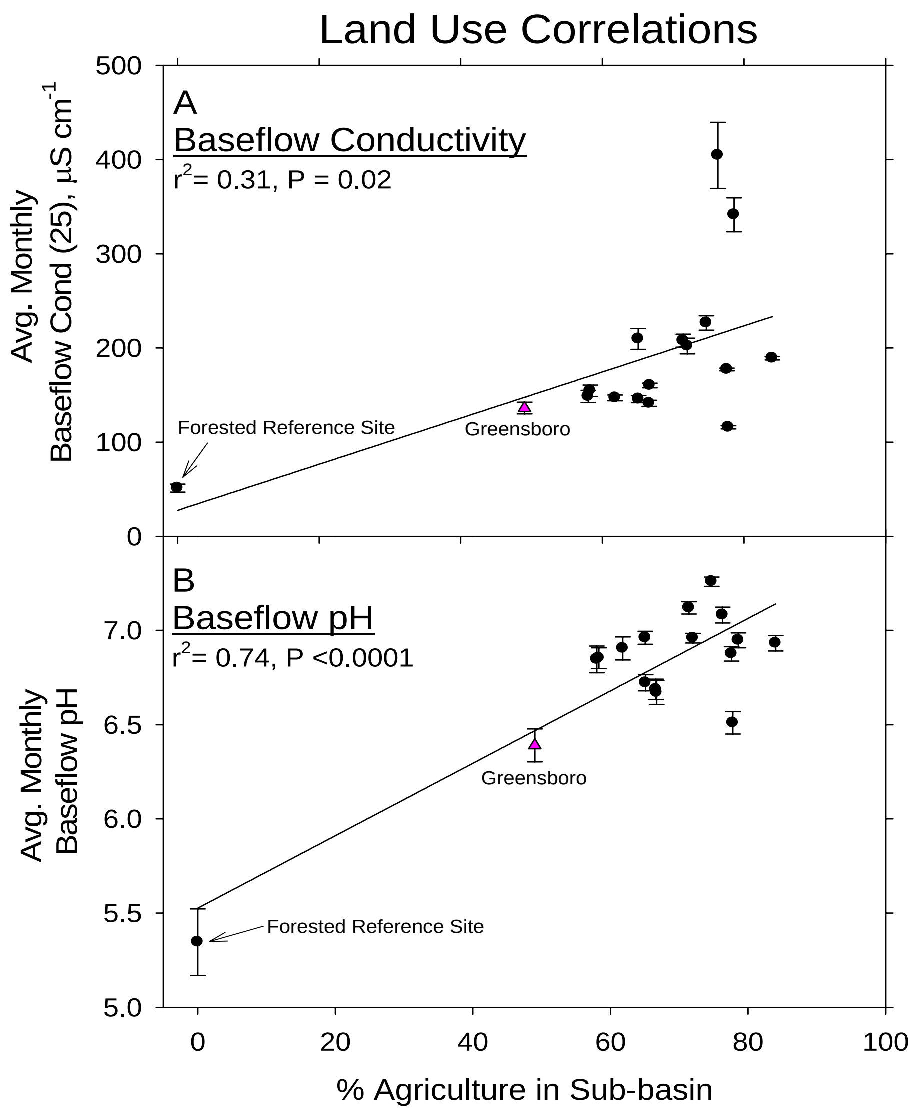


Figure 3-8. Average monthly baseflow conductivity (A - top panel) and pH (B - bottom panel, ± standard errors) increased linearly with agricultural land use during the 15-month study period (June 2006 – Aug 2007). Data includes the 15 Choptank sub-basins, the all-forested reference site in the Nanticoke Basin (arrows), and the USGS' Greensboro station (triangles).

these two variables did not add significantly to the model. Finally, mean pH increased linearly with % agriculture (r^2= 0.74, P <0.0001) from 5.3 at the forested site to a high of 7.3 among the agricultural sub-basins (Fig. 3-8b). Mean pH was also inversely correlated with % forest (r^2= 0.73, P <0.0001) and positively related to the number of CAFO farms (r^2= 0.43, P = 0.03), although these two variables did not significantly improve the model. Again, the USGS' Greensboro station is also shown in Figs. 3-8a, b, and falls roughly half-way between the agricultural Choptank sub-basins and the forested site (data from Fisher et al. 1998). A summary of all the baseflow correlations is presented in Table 3-4.

Table 3-4. Summary of baseflow and quickflow correlation results. Shown for each analyte are the most significant correlation (determined using forward step-wise regressions and the Pearson Product Moment test, see text), the direction and type of relationship (+ = positive correlation, - = negative correlation), the coefficient of determination (r^2), the significance of the regression (P), and the other variables that were also correlated with that analyte (but which were not significant in the model). For analytes where "none" is listed, none of the tested variables (see text for a full list) were significantly (P<0.05) correlated. 'A' soils and 'D' soils refer to hydrologic soil groups.

BASEFLOW					
Analyte	**Most Significant Correlation**	**Relationship**	**r^2**	**P**	**Also Correlated With:**
phosphate	# CAFOs	+, linear	0.47	<0.01	% forest, % agriculture, % hydric
total phosphorus	none				
ammonium	none				
nitrate	% agriculture	+, exponential	0.79	<0.0001	% forest, % hydric, 'A' soils, 'D' soils
total nitrogen	% agriculture	+, exponential	0.77	<0.0001	% forest, % hydric, 'A' soils, 'D' soils
Conductivity	% agriculture	+, linear	0.31	0.02	% forest, % hydric
pH	% agriculture	+, linear	0.74	<0.0001	% forest, # CAFOs

QUICKFLOW					
Analyte	**Most Significant Correlation**	**Relationship**	**r^2**	**P**	**Also Correlated With:**
phosphate	none				
particulate phosphorus	event discharge	+, exponential	0.82	<0.0001	
total dissolved phosphorus	none				
total phosphorus	event discharge	+, exponential	0.93	<0.0001	mean event temperature
ammonium	mean event temperature	-, linear	0.23	<0.01	event discharge
nitrate	event discharge	-, exponential	0.69	<0.0001	mean event temperature
particulate nitrogen	event discharge	+, exponential	0.88	<0.0001	
total dissolved nitrogen	mean event temperature	+, - peak	0.42	<0.01	event discharge
total nitrogen	none				
conductivity	event discharge	-, exponential	0.63	<0.0001	mean event temperature
pH	mean event temperature	+, linear	0.26	<0.01	
total suspended solids	event discharge	+, exponential	0.79	<0.0001	

Changes in Nutrient Concentrations during Storm Discharges

Among the measured analytes, the responses of nutrient concentrations to storm discharges followed three basic patterns, similar to those reported by Sutton (2006). First, the particulates (TSS, PN, PP) were characterized by large brief spikes in concentrations, usually on the rising limb of the hydrograph, followed by a rapid return to pre-storm levels (Fig. 3-9a, f, g). Peak concentrations varied by storm size, but averaged about 219 mg L^{-1} for TSS, 118 µM for PN, and 15 µM for PP. Second,

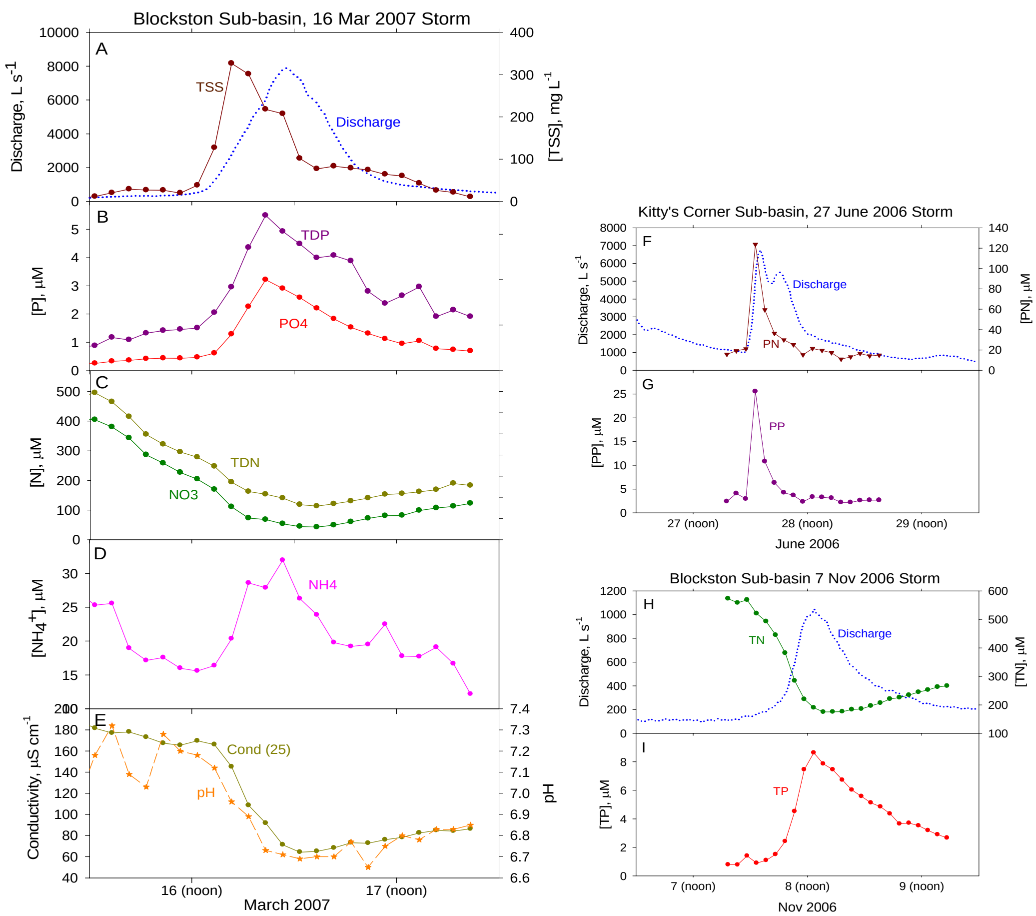


Figure 3-9. Examples of the responses of each of the 12 measured analytes to quickflow. Storm discharges (dotted line) are shown in panels A, F, and H. For the analytes, panels and abbreviations are as follows: TSS = total suspended solids (panel A), TDP = total dissolved phosphorus (panel B), PO_4 = phosphate (panel B), TDN = total dissolved nitrogen (panel C), NO_3 = nitrate (panel C), NH_4 = ammonium (panel D), cond (25) = specific conductivity (panel E, shown with pH), PN = particulate nitrogen (panel F), PP = particulate phosphorus (panel G), TN = total nitrogen (panel H), and TP = total phosphorus (panel I).

PO_4 and NH_4 concentrations increased to moderate levels, then subsided back to initial levels in an exponential fashion (Fig. 3-9b, d). In contrast to the first pattern, the slopes were generally more gradual and the peaks were smaller and broader.

Average peak concentrations were about 8 μM for PO_4 and 38 μM for NH_4. Finally, conductivity (25), nitrate, and to a lesser extent pH, decreased in concentration on the rising limb of the hydrograph and very slowly returned to pre-storm levels (Fig. 3-9c, e). In many cases, even after 48 hours of sampling, nitrate and conductivity (25) still had not returned to initial concentrations, indicating that the recovery time for these analytes generally exceeded the sampling period (though not necessarily the storm period, see "Annual Nutrient Export" section below). The average minimum concentrations for nitrate, conductivity (25), and pH were 139 μM, 129 μS cm^{-1}, and 6.59, respectively. In general, these changes in chemistry during storm discharges are due to different concentrations of these analytes in baseflow versus in quickflow, which originates from direct rainfall, overland flow, and shallow sub-surface flow.

Many of the analytes followed a hysteresis loop during storm discharges, as shown by plots of concentration versus discharge. Nitrate, conductivity (25), and total suspended solids generally followed a clockwise hysteresis (Fig. 3-10a, c, d), indicating that concentrations were lower (for the same discharge) on the falling limb of the flow hydrograph. In contrast, phosphate followed a counter-clockwise hysteresis (Fig. 3-10b), indicating that concentrations were higher on the falling limb. Ammonium, total nitrogen, and particulate phosphorus also showed a clockwise hysteresis, while total phosphorus showed a counter-clockwise hysteresis similar to that of phosphate (data not shown).

For most of the analytes, the peak (or minimum) concentrations were strongly correlated with peak discharge (L s^{-1}). This means that larger storms had a more pronounced effect on either concentrating or diluting nutrient discharges than smaller storms. In the case of the particulates (PN, PP, TSS, Fig. 3-11a), peak concentrations increased exponentially with peak discharge (r^2 >0.77, P<0.0001). In contrast, NH_4

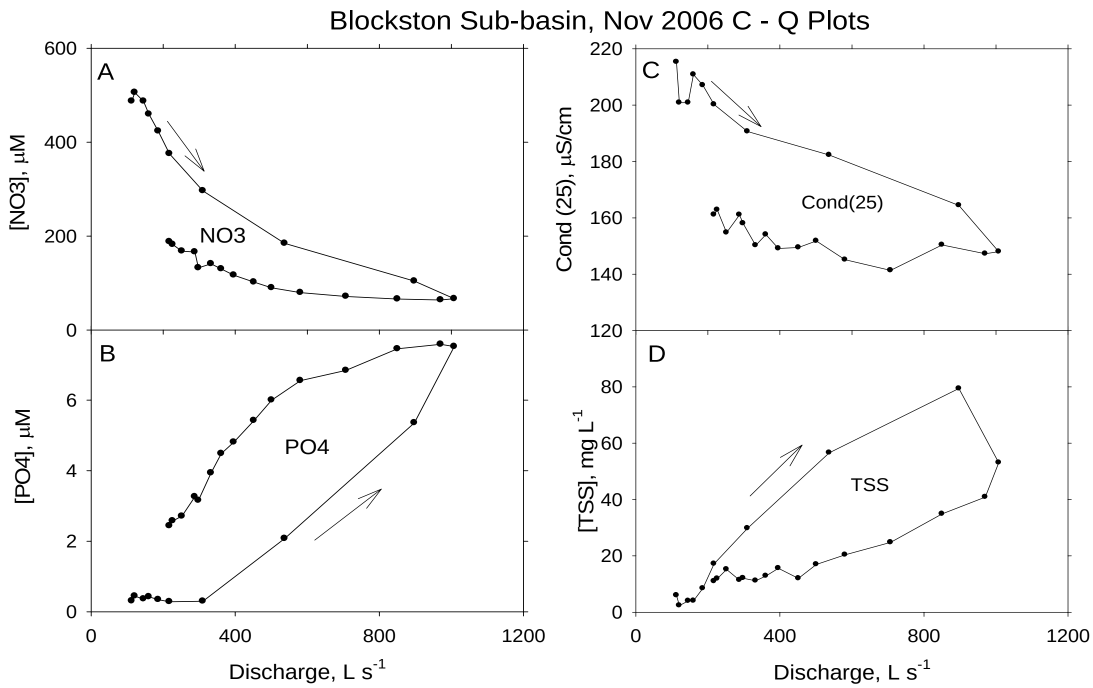


Figure 3-10. Examples of concentration – discharge plots showing clockwise hysteresis for nitrate (NO_3, A – upper left panel), specific conductivity (C – upper right panel), and total suspended solids (TSS, D - lower right panel), and counter-clockwise hysteresis for phosphate (PO_4, B – lower left panel) during a moderately-sized event at the Blockston sub-basin in November, 2006.

increased linearly with peak discharge (r^2= 0.25, P<0.01) while PO_4 had no significant relationship (Fig. 3-11b). Minimum concentrations of nitrate and conductivity(25) decreased exponentially with peak discharge (r^2 >0.58, P<0.0001) and leveled out for larger storms with discharge peaks of >10,000 L s^{-1} (Fig. 3-11c).

Finally, during the summer drought of 2007, nitrate exhibited an unusual behavior. Normally, nitrate decreased steadily during storm flows, as described above. However, for three of the sampled events (two at the Kitty's Corner sub-basin and one at the North Forge sub-basin), nitrate concentrations initially decreased on the rising limb of the hydrograph, but then increased to well above pre-storm levels on the falling limb (Fig. 3-12). These storms took place in early June and late July, 2007 after extended dry periods, with <0.67 cm of rainfall in the previous 16 days for

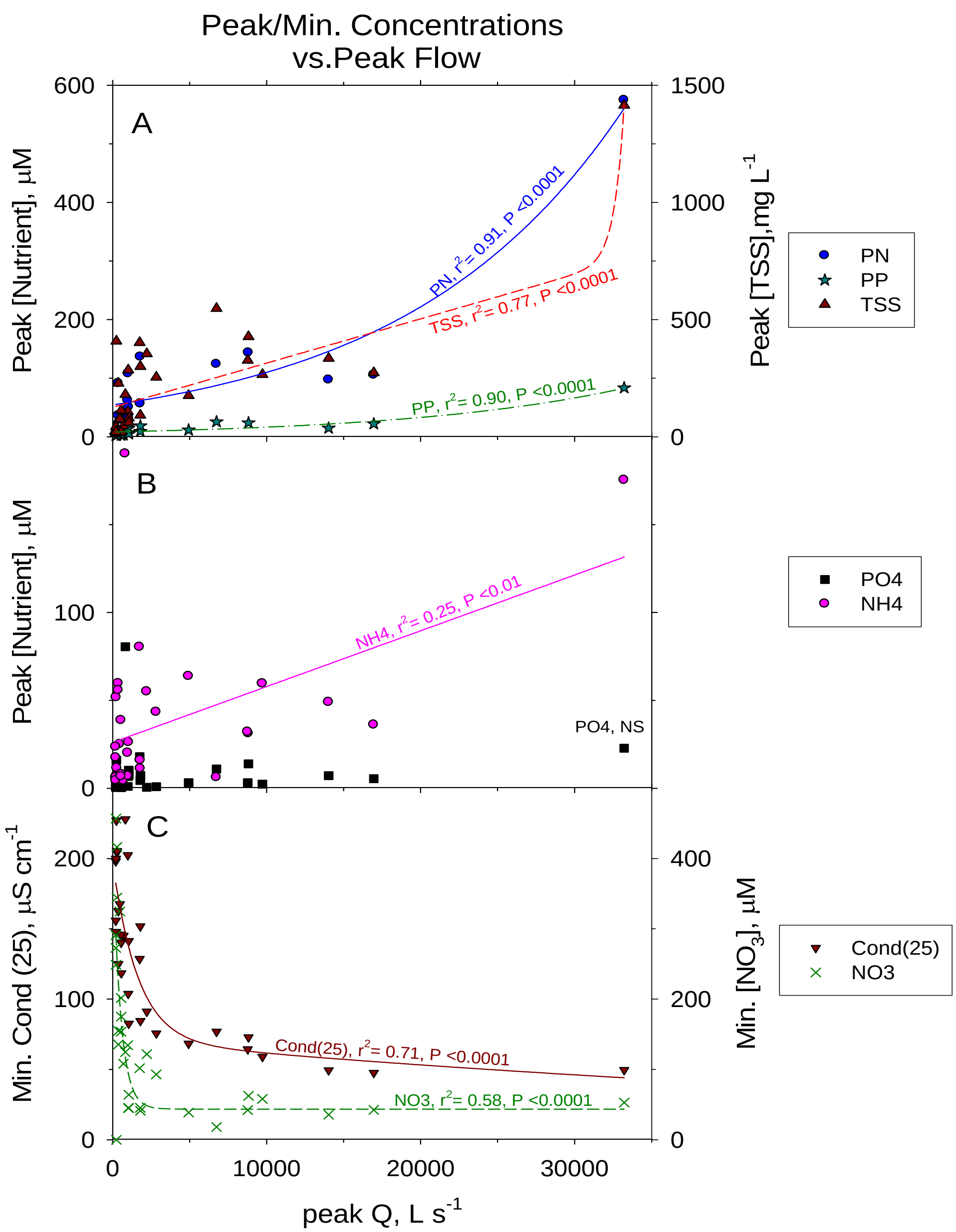


Figure 3-11. Peak (or minimum) concentrations versus peak discharge (L s^{-1}) for the particulates (PN, PP, TSS, A – top panel), the dissolved nutrients (PO_4, NH_4, B – middle panel), and the analytes that decreased during quickflow (specific conductivity and NO_3, C – bottom panel). At the highest discharges, stream conductivity (25) and NO_3 are approaching levels normally found in rainfall. Data includes all storms sampled at each of the four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge) during the 15-month study period (June 2006 – Aug 2007). Significant correlations (P<0.05) are shown with a trend line; only PO_4 was not significant (NS).

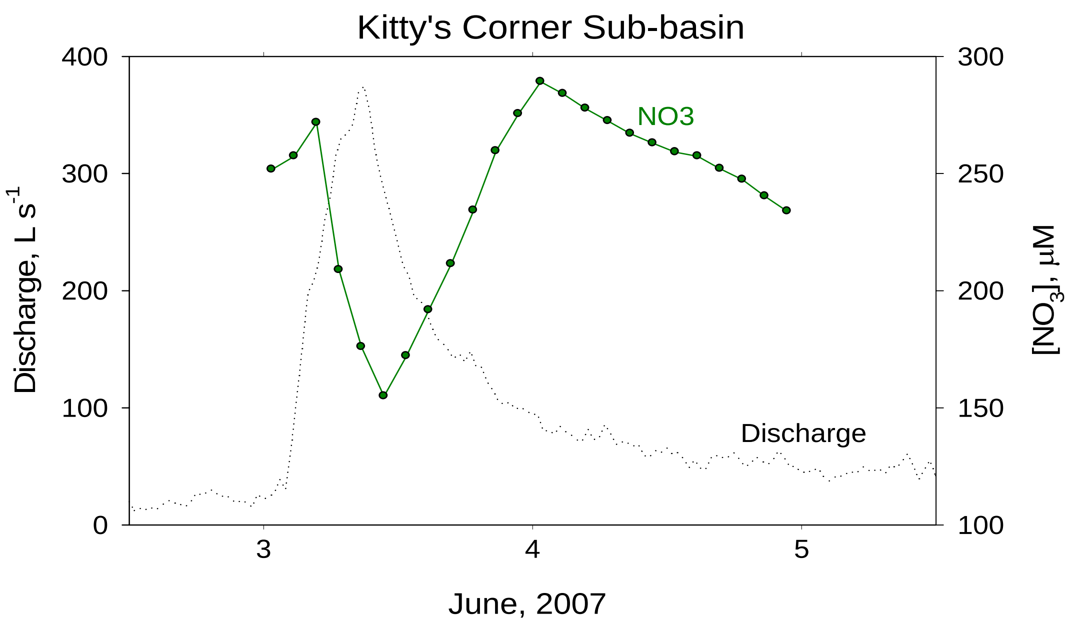


Figure 3-12. Example of some unusual behavior by nitrate (NO_3, circles) in response to increases in discharge (dotted line) during a small event in June 2007 at the Kitty's Corner sub-basin. While nitrate concentrations normally decreased during storm discharges (Fig. 9c), here they decreased initially, then increased on the falling limb of the discharge hydrograph.

each storm. Leaching of soil nitrate derived from excess N fertilizer under dry summer conditions could explain this unusual N chemistry. Alternatively, the large spike in nitrate concentrations on the falling limb could be the result of 1) groundwater forced into the stream by an increased hydraulic head during a storm event and/or 2) pre-storm nitrate concentrations being depleted by in-stream plant uptake, which has a bigger effect on concentrations at low flow rates (Dr. Tom Jordan, pers. communication).

Peak Offsets

Among the analytes, there was considerable variation in the timing of the chemistry peak (either before or after the discharge peak) as well as the number of hours between the nutrient peak (or trough) and the discharge peak (ranging from < 1 h to > 42 h, Table 3-5). However, despite the variability, some patterns emerged. As shown in Table 3-5, phosphate, nitrate, and conductivity (25) generally peaked after the flow peak (with occasional exceptions) by 0.03 – 32.53 h. In contrast, TSS usually peaked before the flow peak (by 0.26 – 12.46 h) for most of the sub-basins. The only exception was the channelized Beaverdam site, where TSS generally followed the flow peak by 0.91 – 24.28 h. Ammonium and pH did not follow a consistent behavior.

The other analytes are more difficult to interpret because of limited data. Nonetheless, PN and PP usually preceded the discharge peak (by 0.28 – 12.46 h), while minima in TDN and TN often followed the discharge peak (by 0.58 – 23.25 h), although exceptions occurred in both cases (Table 3-5). This behavior was consistent with the other, better sampled analytes. For example, the particulate nutrients exhibited the same pattern as TSS (peaking prior to the discharge peak) and had a virtually identical range of peak offsets (0.28 – 12.46 h versus 0.26 – 12.46 h). Similarly, TDN and TN had the same pattern as nitrate (both peaked after the flow peak) and comparable ranges of peak offsets (0.58 – 23.25 h versus 0.03 – 23.25 h). This suggests that, even though these analytes were not as well sampled, the interpretation of the peak offsets is largely correct, again because the patterns compare well to the better-sampled parameters. Finally, TP did not exhibit a consistent behavior, varying from as much as 12 h prior to the discharge peak to 13 h following the discharge peak.

Comparison of Baseflow and Quickflow Nutrient Concentrations

Volume-weighted (v.w.) mean phosphorus concentrations consistently exceeded baseflow phosphorus. Among the four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge), v.w. mean quickflow phosphate concentrations were 3 – 9 times higher than mean baseflow concentrations, increasing from < 2 μM during baseflow up to ~5.0 μM during storm flows (Fig. 3-13a). In this figure, the differences in the means were statistically significant ($P<0.01$) at three of the four sites. V.w. mean quickflow PP concentrations were 4 – 10 times higher than mean baseflow concentrations, increasing from < 1.5 μM during baseflow up to ~15 μM during quickflow (Fig. 3-13b). However, due to the large variability in the v.w. means during storms, the differences were only significant ($P<0.05$) at the Blockston site (Fig. 3-13b). Finally, v.w. mean quickflow TDP concentrations were 3 – 7 times higher than mean baseflow concentrations, increasing from < 2 μM during baseflow up to ~7 μM during quickflow (Fig. 3-13c). In this figure, the differences in the means were significant ($P<0.05$) at three of the sites.

Like phosphorus, NH_4 and PN concentrations were also higher during periods of quickflow. Among the four sub-basins, v.w. mean quickflow NH_4 concentrations were 2-7 times higher than mean baseflow concentrations, increasing from < 3 μM at most of the sites during baseflow, up to ~18 μM during quickflow (Fig. 3-14a). In

Table 3-5. Summary of peak offset results for all sampled storms at each of the four Choptank sub-basins. Peak offset (in hours) was calculated as chemistry – flow for each analyte. Positive numbers indicate that the chemistry peak (or trough) is ahead of the flow peak, while negative numbers indicate that the chemistry is behind the flow peak. Where multiple peaks occurred, two peak offsets were calculated (see Fig. 5). Cells highlighted in gray indicate the calculation was based on a 4-sample chemograph. For each site, means ± standard errors are shown on the last row.

KITTY'S CORNER

Sampling Date	Peak offset (PO4), h	Peak offset (NH4), h	Peak offset (NO3), h	Peak offset (cond), h	Peak offset (pH), h	Peak offset (TSS), h	Peak offset (PP), h	Peak offset (PN), h	Peak offset (TDN), h	Peak offset (TN), h	Peak offset (TDP), h	Peak offset (TP), h
June 27-29, 2006	0.91	-7.09, 4.86	8.90	6.91	4.91	-1.09	-1.09	-1.09	2.90	4.91	4.91	-1.09
November 7-9, 2006	3.05	15.04	9.04	13.04	5.04	-2.96	-4.96	-4.96	9.04	9.04	5.04	-2.96
January 5-7, 2007	0.83, 9.33	-5.17, 7.33	7.33	23.33	-20.67	-2.67	5.33	n/a	9.33	n/a	9.33	3.33
April 11-13, 2007	1.93	1.93	1.93	-0.06	1.93	-4.07	n/a	n/a	-0.06	n/a	3.94	n/a
April 14-16, 2007	2.98, 8.47	-1.02	4.98	2.98	2.98	-7.02	-7.02	-7.02	14.98	n/a	4.98	n/a
June 3-5, 2007	-0.22	17.78	1.78	3.78	-2.22	-4.22	-4.22	-4.22	1.78	n/a	-0.22	n/a
July 29-31, 2007	6.75	2.75	n/a	0.75	-1.25	0.75, -1.24	n/a	n/a	6.75, 12.76	n/a	2.75, 6.76	n/a
mean (std. error)	3.78 (1.17)	4.05 (2.79)	5.66 (1.34)	7.25 (3.16)	-1.33 (3.39)	-2.82 (0.84)	-2.39 (2.15)	-4.32 (1.23)	7.19 (1.89)	6.98 (2.07)	4.69 (0.99)	-0.24 (1.86)

BLOCKSTON

Sampling Dates	Peak offset (PO4), h	Peak offset (NH4), h	Peak offset (NO3), h	Peak offset (cond), h	Peak offset (pH), h	Peak offset (TSS), h	Peak offset (PP), h	Peak offset (PN), h	Peak offset (TDN), h	Peak offset (TN), h	Peak offset (TDP), h	Peak offset (TP), h
June 25-27, 2006	4.72	-0.28	1.72	1.72	-3.28	-4.93, -2.28	-10.80, -2.28	-10.80, -0.28	-0.28	6.72	-4.93	0.07
September 1-3, 2006	15.04	-12.96	11.04	-4.96	1.04	-2.96	-2.96	n/a	n/a	13.04	17.04	11.04
September 14-16, 2006	-0.28	-16.28, -8.28	3.72	1.72	-42.28	-4.28	-2.28, 1.72	n/a	n/a	-0.28	3.72	-4.28
November 7-9, 2006	1.94	-0.06	1.94	5.94	5.94	-2.06	-2.06	-2.06	-2.06	1.94	5.94	-0.06
January 8-9, 2007	-4.46	-14.46	-0.46	-0.46	-14.46	-12.46	-12.46	n/a	1.54	n/a	-10.46	-12.46
March 15-17, 2007	-2.40	-0.40	3.60	1.61	9.60	-6.40	n/a	n/a	3.60	n/a	-2.40	n/a
April 14-16, 2007	14.49	14.49	6.49	6.49	2.49	-7.51	-7.51	-7.51	6.49	14.49	14.49	-7.51
June 2-4, 2007	9.66	11.66	7.66	1.66	1.66	-0.34	-0.34	-0.34	7.66	7.66	9.66	-0.34
July 27-29, 2007	-1.85	-1.85	6.15	0.15	-13.85	-13.85	n/a	n/a	4.15	n/a	-1.85	n/a
August 20-22, 2007	-8.71	-8.71	-0.71	-4.71	-12.71	-0.71	n/a	n/a	-0.71	n/a	-8.71	n/a
mean (std. error)	2.82 (2.54)	-3.38 (3.03)	4.12 (1.18)	0.92 (1.19)	-6.58 (4.79)	-5.25 (1.36)	-4.33 (1.61)	-4.20 (2.11)	2.55 (1.24)	7.26 (2.39)	2.25 (3.00)	-1.93 (2.78)

BEAVERDAM

Sampling Dates	Peak offset (PO4), h	Peak offset (NH4), h	Peak offset (NO3), h	Peak offset (cond), h	Peak offset (pH), h	Peak offset (TSS), h	Peak offset (PP), h	Peak offset (PN), h	Peak offset (TDN), h	Peak offset (TN), h	Peak offset (TDP), h	Peak offset (TP), h
November 8-10, 2006	9.09	1.09	5.09	9.09	1.09	13.09	13.09	13.09	13.09	3.09	7.09	13.09
April 4-6, 2007	2.28	2.28	2.28	2.28	6.28	24.28	n/a	n/a	-1.72	n/a	2.28	n/a
April 11-13, 2007	2.91	2.91	2.91	20.91	8.91	0.91	n/a	n/a	8.91	n/a	2.91	n/a
April 14-16, 2007	-5.42	-5.42	18.58	16.58	-3.42, 12.58	6.58	6.58	6.58	6.58	0.58	-5.42	6.58
June 5-7, 2007	21.53	-16.47	-0.69	-12.47	-16.47	15.53	n/a	n/a	5.53	n/a	21.53	n/a
June 28-30, 2007	16.53	-3.47	-5.47	2.53	-5.47	-5.47	n/a	n/a	-3.47	n/a	32.53	n/a
July 29-31, 2007	17.25	17.25	23.25	3.25	5.25	-0.75	-2.75	-0.75	23.25	-2.75	17.25	5.25
mean (std. error)	9.17 (3.69)	-0.26 (3.86)	6.56 (3.95)	6.03 (4.14)	1.10 (3.30)	7.74 (3.96)	5.64 (4.60)	6.31 (4.00)	7.45 (3.42)	0.31 (1.69)	11.17 (4.98)	8.31 (2.42)

NORTH FORGE

Storm Date	Peak offset (PO4), h	Peak offset (NH4), h	Peak offset (NO3), h	Peak offset (cond), h	Peak offset (pH), h	Peak offset (TSS), h	Peak offset (PP), h	Peak offset (PN), h	Peak offset (TDN), h	Peak offset (TN), h	Peak offset (TDP), h	Peak offset (TP), h
November 8-10, 2006	5.84	-4.16	1.84	-4.16	-8.16	-2.15	-2.16	-2.16	-2.16	-4.16	11.84	-2.16
January 5-6, 2007	4.56	0.56	4.56	0.56	2.56	-1.44	-1.44	n/a	2.56	n/a	2.56	2.56
February 14, 2007	4.02	-1.98	0.03	0.03	2.03	-1.98	n/a	n/a	2.03	n/a	4.02	n/a
March 16-17, 2007	3.86	-4.14	1.86	1.86	-2.14	-2.14	n/a	n/a	3.86	n/a	1.86	n/a
April 4-6, 2007	28.24	-3.76	4.24	-3.76	36.24	-3.76	n/a	n/a	6.24	n/a	-1.76	n/a
April 11-13, 2007	1.74	1.74	3.74	7.74	3.74	-0.26	n/a	n/a	15.74	n/a	3.74	n/a
April 14-16, 2007	10.33	-7.67	2.33	2.33	22.33	-7.67	-7.67	-7.67	2.33	-7.67	10.33	-7.67
June 3-5, 2007	4.91	2.91	0.91	-1.09	-3.09	2.91	8.91	2.91	0.91	2.91	4.91	8.91
mean (std. error)	7.94 (3.03)	-2.06 (1.26)	2.44 (0.57)	0.44 (1.34)	6.69 (5.28)	-2.06 (1.06)	-0.59 (3.46)	-2.31 (3.06)	3.94 (1.89)	-2.97 (3.11)	4.69 (1.57)	0.41 (3.52)

this figure, the differences in the means were significant (P<0.05) at three of the sites. The Kitty's Corner sub-basin had much higher baseflow ammonium concentrations (9.2 μM) than the other sites (<3 μM) due to one anomalously high (61.6 μM) sample

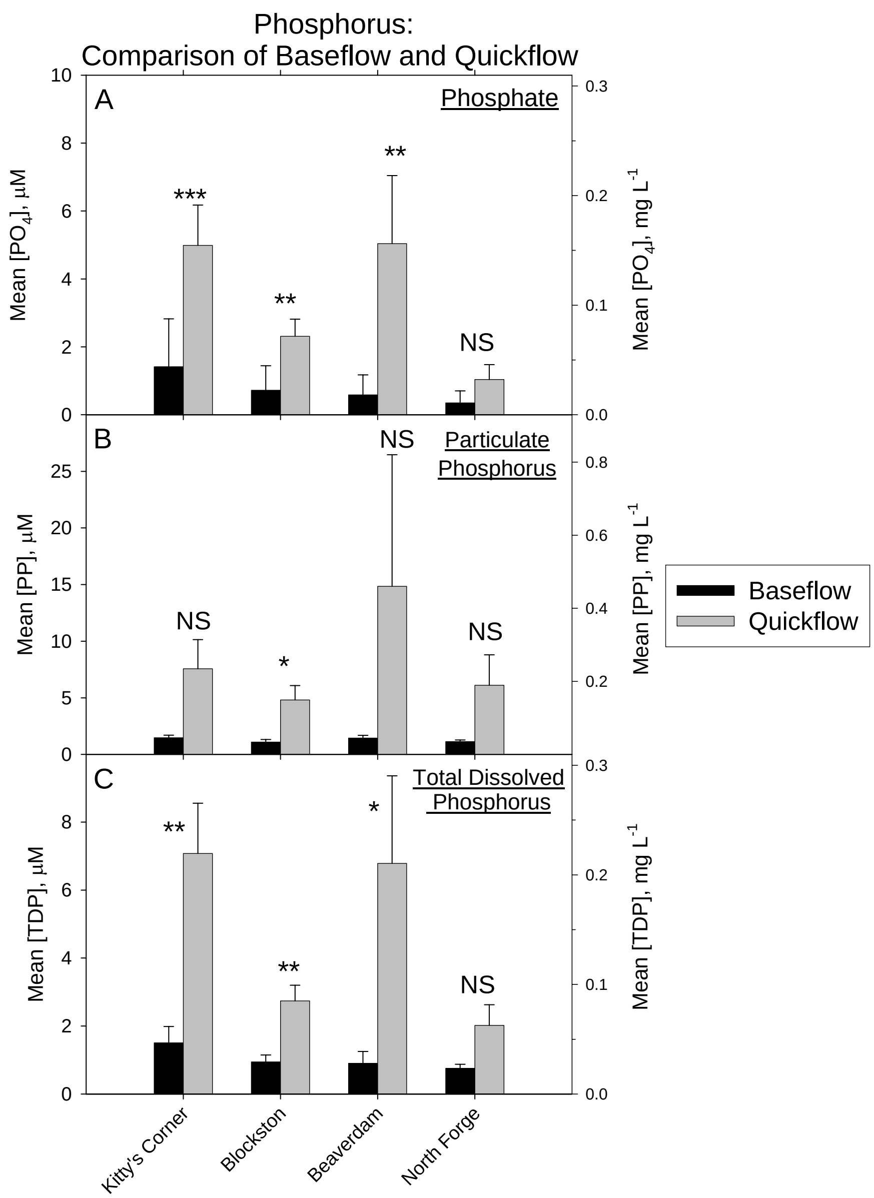


Figure 3-13. Comparison of mean baseflow (dark bars) and mean quickflow (light bars) concentrations (as both μM and mg L^{-1}, ± standard errors) of phosphate (PO_4, A - top panel), particulate phosphorus (PP, B – middle panel), and total dissolved phosphorus (TDP, C – bottom panel) at each of the four sub-basins during the 15-month study period (June 2006 – Aug 2007). Note the different y-axis scale for PP. Baseflow data are either monthly averages (in the case of PO_4) or were derived from portions of the measured quickflow chemographs (in the case of PP and TDP). Quickflow data are volume-weighted averages of all of the sampled events at each of the four sites. A one-way analysis of variance was used to test for significant (P<0.05) differences between the means at each site. NS = not significant, * = P<0.05, ** = P<0.01, *** = P <0.001.

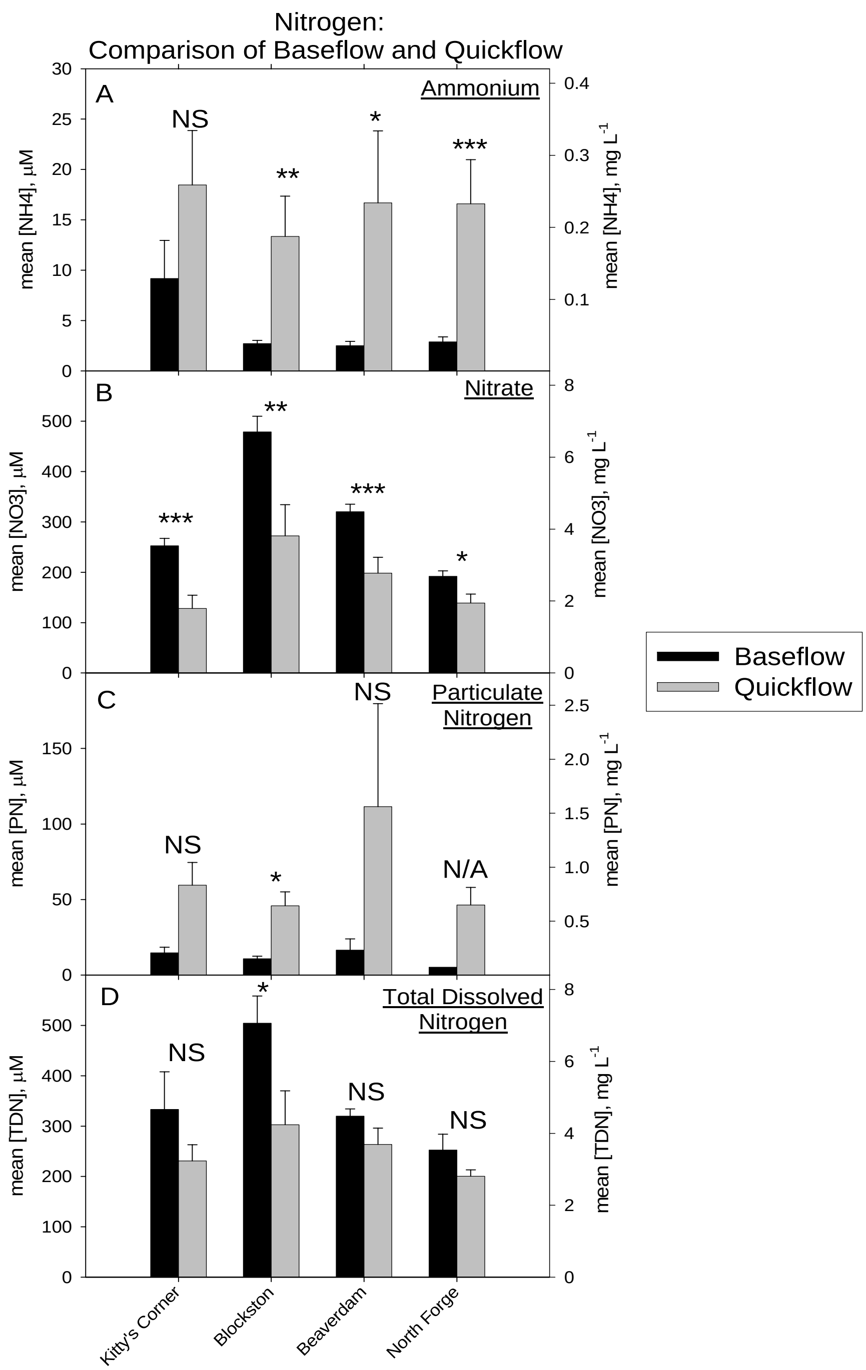


Figure 3-14. Comparison of mean baseflow (dark bars) and mean quickflow (light bars) concentrations (as both μM and mg L^{-1}, ± standard errors) of ammonium (NH_4, A - top panel), nitrate (NO_3, B – second panel from top), particulate nitrogen (PN, C – third panel from top), and total dissolved nitrogen (TDN, D – bottom panel) at each of the four sub-basins during the 15-month study period (June 2006 – Aug 2007). Note the differences in scale among the y-axes. Baseflow data are either monthly averages (in the case of NH_4 and NO_3) or were derived from portions of the measured quickflow chemographs (in the case of PN and TDN). Quickflow data are volume-weighted averages of all of the sampled events at each of the four sites. A one-way analysis of variance was used to test for significant ($P<0.05$) differences between the means at each site. NS = not significant, * = $P<0.05$, ** = $P<0.01$, *** = $P<0.001$, N/A = statistics not available due to low sample size.

collected on 8/16/07. It is not clear if this high reading was real or due to analytical errors. V.w. mean quickflow PN concentrations were 4 – 9 times higher than mean baseflow concentrations, increasing from < 17 μM during baseflow up to 111 μM during quickflow (Fig. 3-14c). However, due to variability in the v.w. means during storms, the differences between the means were only significant ($P<0.05$) at the Blockston site (Fig. 3-14c).

Unlike the other N components, NO_3 and TDN concentrations decreased during quickflow. V.w. mean quickflow NO_3 concentrations were 0.5 – 0.7 times the mean baseflow concentrations (Fig. 3-14b). In this figure, the decrease in the means was significant ($P<0.05$) at all four sub-basins. Blockston had the highest mean baseflow nitrate concentrations (~480 μM) and the highest v.w. mean quickflow nitrate concentrations (~270 μM) of the sites (Fig. 3-14b), probably because it has the most agriculture (71.4%, Table 3-1). V.w. mean quickflow TDN concentrations were also less than mean baseflow concentrations at all four sub-basins. Since TDN was primarily nitrate, the pattern of decrease was almost identical to nitrate (Fig. 3-14d). Due to variability in the v.w. means during storms, the decrease in TDN concentrations was only significant ($P<0.05$) at the Blockston site (Fig. 3-14d).

Similar to NO_3 and TDN, v.w mean quickflow conductivity (25) decreased at all sites, down to 0.7 – 0.8 times the mean baseflow levels. This was likely due to a large reduction in nitrate and other major ions (Fig. 3-15a). In this figure, the decrease in the means was significant ($P<0.05$) at all four sub-basins. Mean baseflow and mean quickflow conductivities were higher at the Kitty's Corner and Blockston sites (>200 $\mu S\ cm^{-1}$) than they were at the Beaverdam and North Forge sites (140 – 160 $\mu S\ cm^{-1}$,

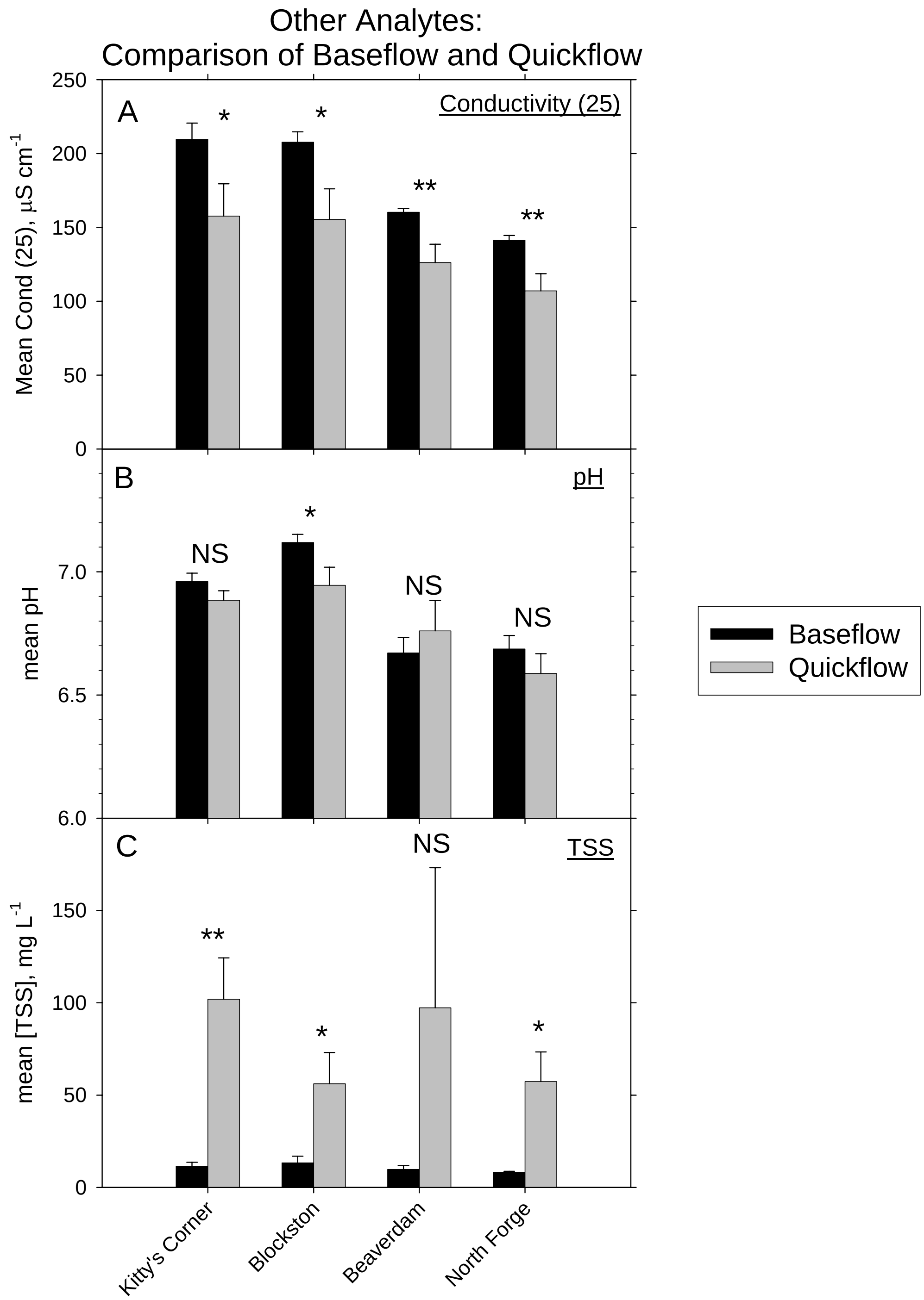


Figure 3-15. Comparison of mean baseflow (dark bars) and mean quickflow (light bars) specific conductivity (A - top panel), pH (B – middle panel), and total suspended solid (TSS, C – bottom panel) concentrations (± standard errors) at each of the four sub-basins during the 15-month study period (June 2006 – Aug 2007). Note the differences in scale among the y-axes. Baseflow data are either monthly averages (in the case of conductivity and pH) or were derived from portions of the measured quickflow chemographs (in the case of TSS). Quickflow data are volume-weighted averages of all of the sampled events at each of the four sites. A one-way analysis of variance was used to test for significant ($P<0.05$) differences between the means at each site. NS = not significant, * = $P<0.05$, ** = $P<0.01$.

Fig. 3-15a). This does not appear to be an agricultural effect since both Beaverdam and North Forge have more agricultural land than Kitty's Corner does (Table 3-1). Conductivity(25) also exhibited a seasonal pattern, with lower levels during the cool season (Oct – Apr) versus the warm season (May – Sept), probably due to reduced evapotranspiration during the cooler months (Fig. 3-16). In addition, v.w. mean quickflow conductivity (25) was significantly less ($P<0.001$) than mean baseflow conductivity (25) during the cool season (Fig. 3-16).

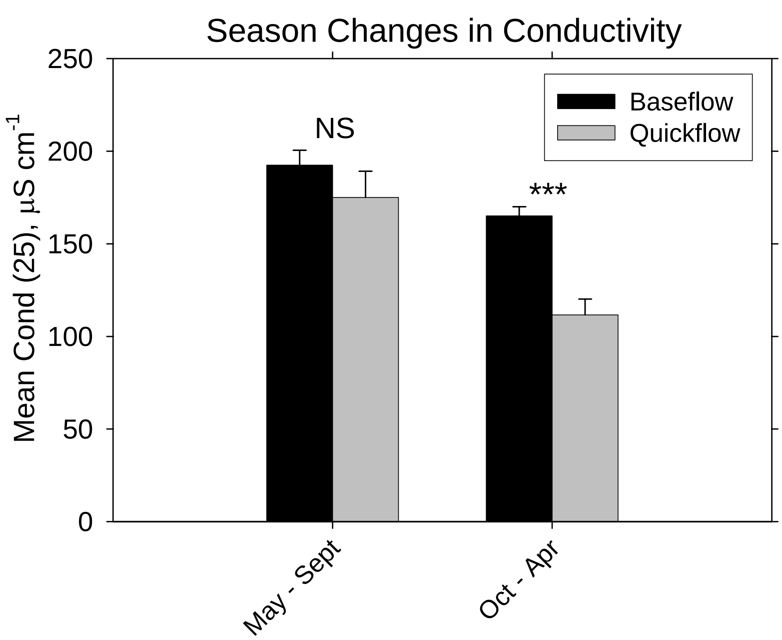


Figure 3-16. Comparison of warm season (May – Sept) and cool season (Oct – Apr) mean baseflow (dark bars) and mean quickflow (light bars) specific conductivity (± standard errors) during the 15-month study period (June 2006 – Aug 2007). Data includes all four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge). Baseflow data are monthly averages, while quickflow data are volume-weighted averages of all sampled events at all sites. A one-way analysis of variance was used to test for significant ($P<0.05$) differences between the means at each site. NS = not significant, *** = $P <0.001$.

Finally, pH generally decreased, while TSS increased, during storm discharges. For pH, because of the subtlety of the changes, the v.w. means were only significantly different ($P<0.05$) at the Blockston site (Fig. 3-15b). As for TSS, v.w. mean quickflow concentrations were about 4 – 10 times higher than mean baseflow concentrations, increasing from <14 mg L^{-1} during baseflow up to ~100 mg L^{-1} during quickflow (Fig. 3-15c). Although there was considerable variability in the v.w. means during storm flows, the differences in the means were still significant ($P<0.05$) at three of the four sub-basins (Fig. 3-15c).

N and P Fractions in Baseflows and Quickflows

Large changes in N and P speciation were observed in comparing baseflows and quickflows. Baseflow phosphorus was dominated by dissolved forms at all four sub-basins. Phosphate represented 28 – 70% (avg. 44%) of the total P, with the rest being DOP + PP (Fig. 3-17a), most of which was assumed to be DOP since PP is typically minimal in baseflows. In contrast, storm discharges at every sub-basin were dominated by PP, which represented 65% of the total P on average (Fig. 3-17c). Phosphate was proportionately less important in quickflow, despite the fact that concentrations increased during storms. On average, phosphate represented only 25% of the total P in quickflow samples. As for nitrogen, baseflows were almost exclusively nitrate, which represented 79 – 91% (avg. 87%) of the total N (Fig 3-17b). DON + PN was only a small fraction and ammonium levels were negligible. Quickflows, however, were a complex mixture of several N forms (Fig. 3-17d). Ammonium, DON, and especially PN forms all generally increased relative to baseflow. Quickflow PN represented 13 – 30 % (avg. 21%) of the total N. Nitrate, however, was still the dominant form, representing 58% of the total N on average,

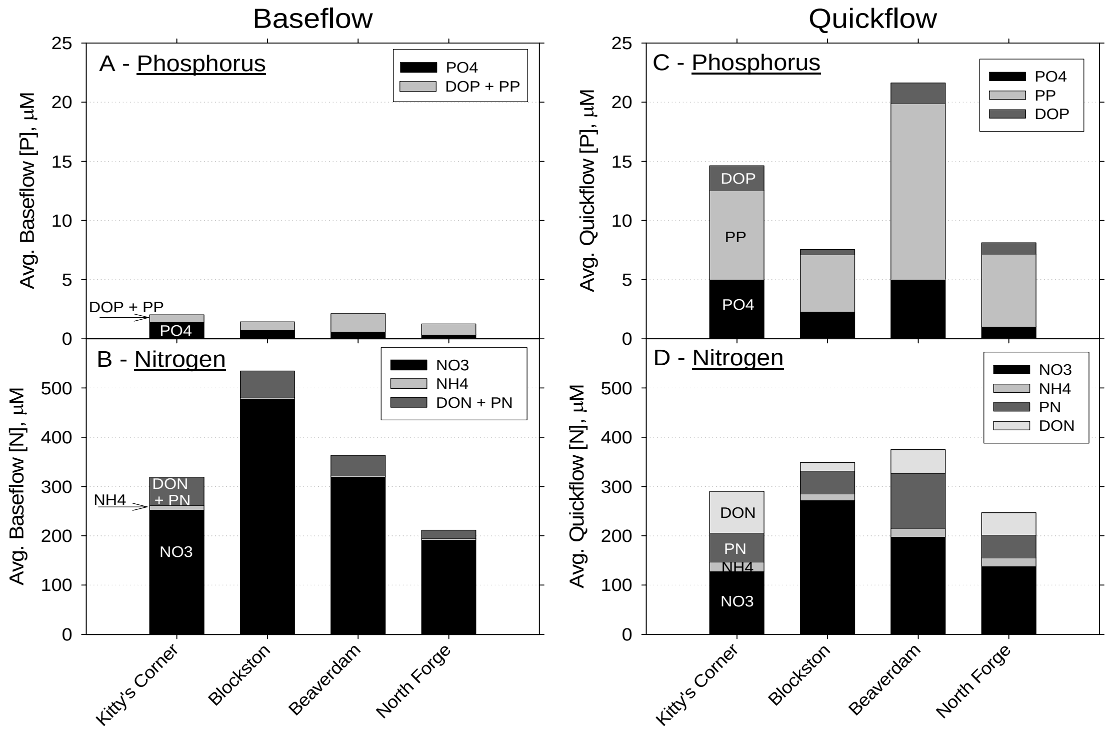


Figure 3-17. Average fractions of N and P in base and quickflows for the four Choptank sub-basins during the 15-month study period (June 2006 – Aug 2007). Shown are baseflow phosphorus (A – upper left panel), baseflow nitrogen (B – lower left panel), quickflow phosphorus (C – upper right panel), and quickflow nitrogen (D – lower right panel). Baseflow data (panels A, B) represent monthly arithmetic averages, while quickflow data (panels C, D) represent average volume-weighted means across all sampled events. For the baseflow data, DON + PN were grouped together because PN was not measured directly (see Table 3-3). Abbreviations are as follows: PO_4 = phosphate, DOP = dissolved organic phosphorus, PP = particulate phosphorus, NO_3 = nitrate, NH_4 = ammonium, DON = dissolved organic nitrogen, PN = particulate nitrogen. DOP and DON were estimated as TDP – PO_4 and TDN – NO_3 – NH_4, respectively.

despite decreasing concentrations during rain events due to dilution of nitrate-rich groundwater by rain and overland/shallow subsurface flows.

Factors Influencing Quickflow Volume-weighted Means

V.w. mean P concentrations were related to event discharge. Total phosphorus concentrations increased exponentially with event discharge (r^2= 0.93, P <0.0001, Fig. 3-18a). [Note in this figure that all four sub-basins were grouped together and fitted to one regression line to improve the statistical significance. The reason this was done is because an initial analysis (data not shown) did not show any significant differences among the four sub-basins. The same holds true for all other figures presented in this section.] Total phosphorus concentrations were also negatively but weakly correlated with mean event stream temperature (r^2 = 0.24, P <0.05). However, this variable (temperature) did not significantly improve the model since it was inversely related to event discharge (correlation coefficient = -0.56, P = 0.02). V.w. mean PP concentrations also increased exponentially with event discharge (r^2= 0.82, P <0.0001), from <10 μM for small storms, up to ~40 μM for the largest event in April 2007 (Fig. 3-18b). Neither v.w. mean phosphate nor v.w. mean TDP concentrations were significantly related to either event discharge or mean event stream temperature.

V.w. mean N concentrations were also influenced by event discharge and temperature. Ammonium concentrations decreased linearly with mean event stream temperature (r^2=0.23, P <0.01) with sampled events in the spring (Mar – Apr) generally falling on the upper end of the curve and sampled events in the summer

(Jun – Jul) generally falling on the lower end of the curve (with some exceptions, Fig. 3-19d). This suggests that spring fertilizer (and/or manure) applications are the

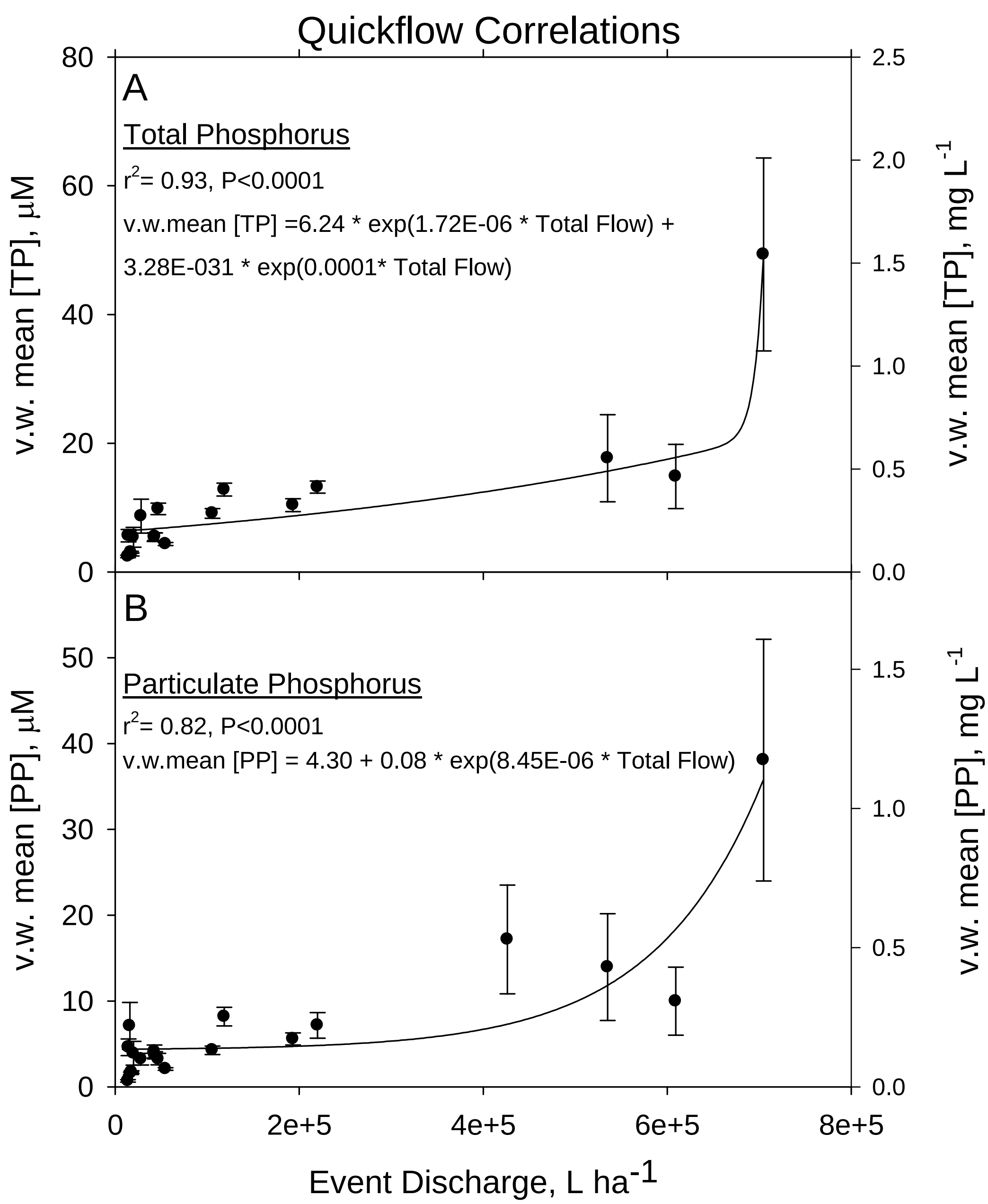


Figure 3-18. Quickflow volume-weighted (v.w.) mean concentrations (as both μM and mg L^{-1}, ± standard errors) of total phosphorus (TP, A – top panel) and particulate phosphorus (PP, B – bottom panel) both increased exponentially with event discharge. Data includes all storms sampled at each of the four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge) during the 15-month study period (June 2006 – Aug 2007).

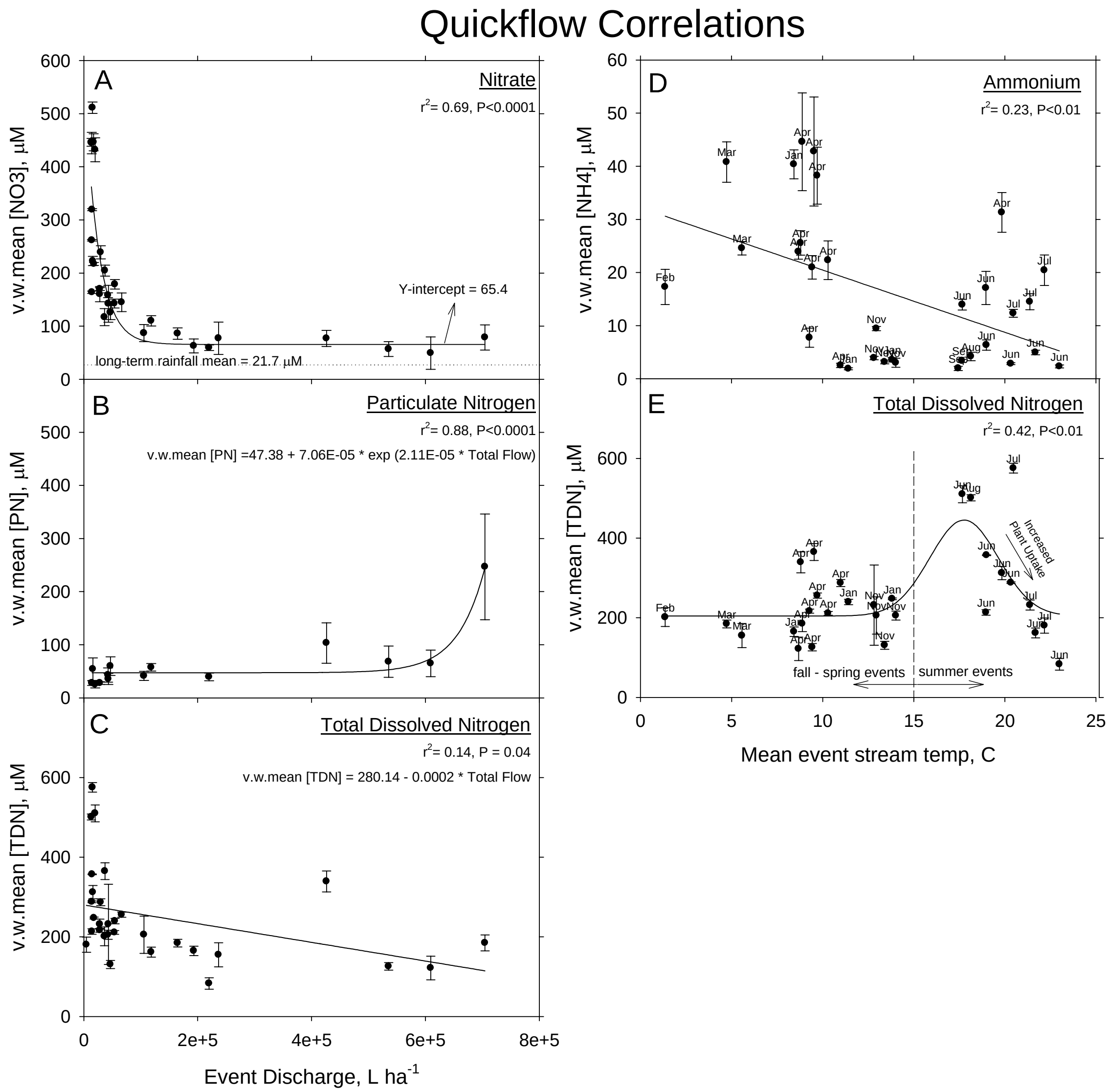


Figure 3-19. Quickflow volume-weighted (v.w.) mean concentrations (± standard errors) of nitrate (A – upper left panel), particulate nitrogen (B – middle left panel), and total dissolved nitrogen (C – bottom left panel) were all correlated with event discharge. Nitrate followed an exponential dilution curve, approaching concentrations about 3x the normal levels in rain water (see arrow, dotted line). In contrast, v.w. mean concentrations (± standard errors) of ammonium (D – upper right panel) and TDN (E – bottom right panel) were correlated with mean event stream temperature. Note the month symbols above each data point in panels D & E, and the fact that TDN is shown twice (panels C & E). The stronger relationship is in panel E. However, panel C is shown for reference because it was used as an extrapolation tool (see text, section 4.5). For all panels, data includes all storms sampled at each of the four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge) during the 15-month study period (June 2006 – Aug 2007).

primary cause of the higher ammonium concentrations at lower stream temperatures. V.w. mean ammonium concentrations were also positively but weakly correlated with event discharge (r^2 = 0.21, P <0.01). However, this variable did not significantly improve the model in Fig. 3-19d because it was inversely related to mean event stream temperature (correlation coefficient = -0.40, P = 0.02). V.w. mean nitrate concentrations decreased exponentially with event discharge (r^2=0.69, P <0.0001, Fig. 3-19a), decreasing from several hundred μM for small to moderate events down to 65.4 μM for the largest events, which is about three times the normal levels in rainwater based on a long-term record at Wye Research and Education Center (Rochelle- Newall et al. in press). V.w. mean nitrate concentrations were also correlated with mean event temperature (r^2= 0.41, P <0.01), although this variable did not add significantly to the model since it was inversely related to event discharge (correlation coefficient = -0.39, P = 0.03). V.w. mean PN concentrations increased exponentially with event discharge (r^2 = 0.88, P <0.0001, Fig. 3-19b) from ~50 μM for small storms up to ~250 μM for the largest event in April 2007.

V.w. mean TDN concentrations were correlated with mean event stream temperature (r^2= 0.42, P <0.01, Fig. 3-19e). As shown in this figure, a prominent peak occurred at ~450 μM and 18°C. The peak was composed almost entirely of nitrate, and is likely *not* due to fertilizer applications since it corresponds to events sampled in the summer (Jun – Aug), not in the spring (Mar – Apr, Fig. 3-19e). However, with no events sampled in May, the peak may simply be under-sampled. For summer storms (right of the dotted line in Fig. 3-19e), increasing temperatures were accompanied by decreasing TDN concentrations, again due to the nitrate fraction which was likely being consumed by plant uptake (see arrow). V.w. mean TDN concentrations were also weakly correlated with event discharge (r^2= 0.14, P =0.04, Fig. 3-19c). Although this variable did not significantly improve the model because it was inversely related to mean event stream temperature (correlation coefficient = -0.38, P = 0.04), the correlation is shown as an extrapolation tool for the un-sampled events (see "Annual Nutrient Export" section below). Finally, v.w. mean TN concentrations were not significantly related to either event discharge or mean event stream temperature.

Like N and P, the other analytes were also related to either event discharge or temperature. V.w. mean conductivity (25) decreased exponentially with event discharge (r^2=0.63, P <0.0001, Fig. 3-20a), decreasing from roughly 200 μS cm^{-1} for small events down to 65.8 μS cm^{-1} for the largest events (in June 2006 and April 2007). This minimum conductivity (25) is about three times the normal levels in rainwater based on a long-term record at Wye Research and Education Center (Rochelle-Newall et al. in prep.). V.w. mean conductivity (25) was also correlated with mean event stream temperature (r^2= 0.36, P <0.001), although this variable did not significantly add to the regression because it was inversely correlated with event discharge (correlation coefficient = -0.40, P = 0.02). V.w. mean TSS concentrations increased exponentially with event discharge (r^2 = 0.79, P <0.0001, Fig. 3-20b) from <40 mg L^{-1} for small events up to ~550 mg L^{-1} for the largest event (April 2007). Finally, v.w. mean pH increased linearly with mean event stream temperature (r^2=0.26, P <0.01, Fig. 3-20c), although there was considerable scatter in the data. A summary of all the quickflow correlations is presented in Table 3-4 (see above).

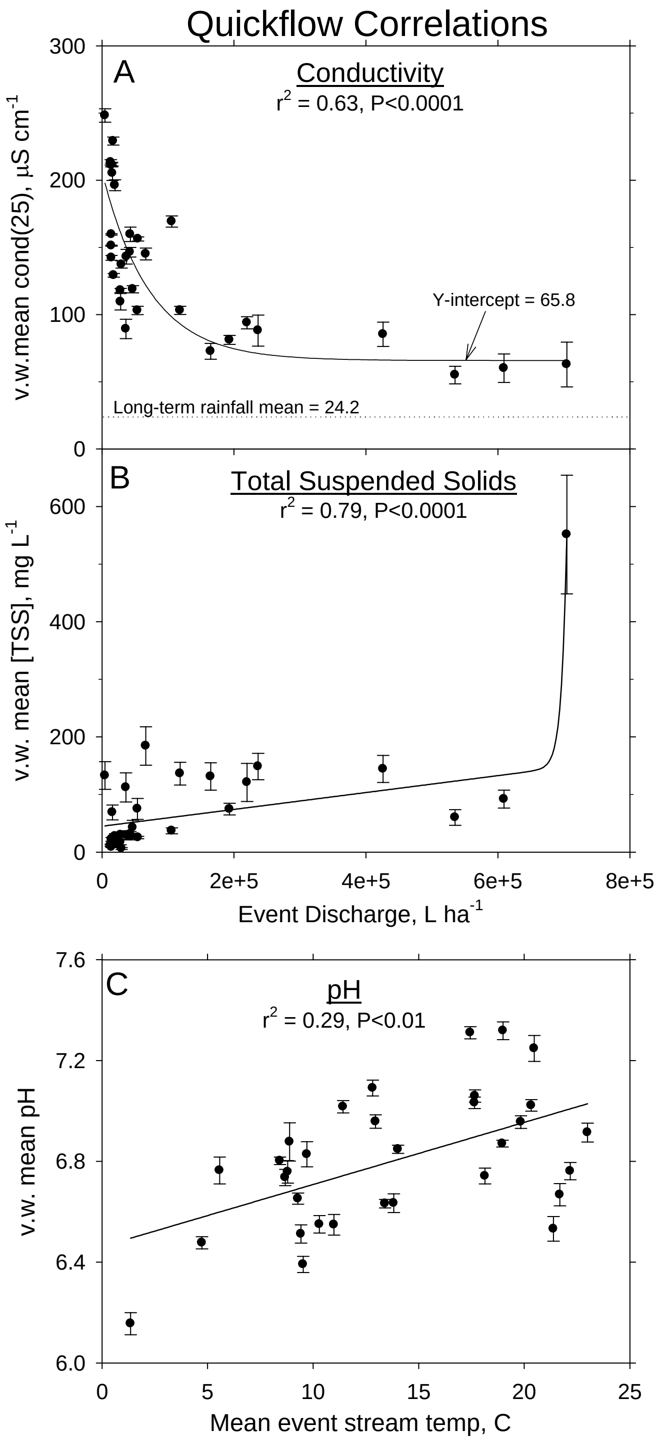


Figure 3-20. Quickflow volume-weighted (v.w.) mean specific conductivity (A – top panel) and total suspended solid (B – middle panel) concentrations (± standard errors) were both strongly correlated with event discharge. Conductivity(25) followed an exponential dilution curve, approaching levels about three times that in rainwater for the largest events (see arrow, dotted line). In contrast, pH (C – bottom panel), also shown with standard error bars, increased linearly with mean event stream temperature. Data includes all storms sampled at each of the four sub-basins (Kitty's Corner, Blockston, Beaverdam, and North Forge) during the 15-month study period (June 2006 – Aug 2007).

Discussion

Land Use Correlations

This study found that baseflow nutrients (N and P) were positively related to agricultural land use and animal husbandry operations upstream. In particular, baseflow phosphate concentrations were higher in areas with larger densities of concentrated animal feeding operation (CAFO) buildings (Fig. 3-6b) McFarland and Hauck (1999), in studying 16 agricultural (mainly dairy farm) watersheds in Texas, reported a similar finding, and attributed the increased phosphate to runoff from dairy waste application fields.

On Delmarva, CAFOs have been recognized as major phosphorus sources for decades because of waste disposal issues. In this area, the industry is mainly broiler-type chickens which are usually slaughtered at ~7 weeks of age (US EPA 2003). CAFO houses are typically long, metal structures divided into three chambers (a brood chamber and two others) corresponding to the different life stages and heating requirements of the chickens (US EPA 2003). The chambers are lined with litter, usually sawdust or other materials which absorb the moisture in the excreted manure (US EPA 2003). When some or all of the chambers are cleaned (once every 1- 3 years), the waste material is either applied to croplands as a means of disposal, or stored temporarily (up to 2 weeks) on site until land becomes available (Staver and Brinsfield 2001, US EPA 2003). Unfortunately, due to high transportation and building costs, oftentimes the material can neither be shipped elsewhere nor kept in a storage structure. Growers usually just use a tarp or store the manure in large, uncovered piles until it can be spread on fields (US EPA 2003). In total, an estimated 1.2 tons of manure are generated annually per 1,000 birds (Lichtenberg et al. 2002).

The disposal of poultry manure on croplands is problematic for water quality because of the imbalance of N and P nutrients in the waste materials. Poultry manure has an N:P ratio of <2:1 (by weight), whereas crops require ratios of roughly 5:1 for optimal growth (Staver and Brinsfield 2001). Consequently, manure applications often exceed the P requirements of the plants, resulting in excessive buildup of P in the top soil. Increases in soil P are generally accompanied by a linear increase in dissolved phosphate in solution due to desorption from the soil matrix (Staver and Brinsfield 2001), which eventually drains into surface waters during periods of runoff. No-till agricultural practices, which have been widely implemented in the Choptank region, often further exacerbate P losses because senescing plant tissues, which would ordinarily be tilled under, release large amounts of phosphate into the soil (Staver and Brinsfield 2001).

This study also found that baseflow concentrations of nitrate (ranging from about 100 – 700 μM) were positively related to the percentage of agricultural land use in the watershed (Fig. 3-7b). Similar findings have been reported for the Coastal Plain (Jordan et al. 1997), the Piedmont (Jordan et al. 1997a), and for agricultural regions well outside the Chesapeake Bay drainage (Ahearn et al. 2005). Nitrate in surface waters is generally derived from the nitrification of ammonia in inorganic fertilizers, usually applied as either anhydrous ammonia (NH_3) or liquid N during the spring (Hamilton et al. 1993). As mentioned, in areas with CAFOs, poultry waste is also applied (typically in the spring, but sometimes in the fall) which provides additional

N to further stimulate nitrification (Hamilton et al. 1993, Staver 2001). Farmers generally tend to apply higher amounts in irrigated areas with well-drained soils where corn is the dominant crop (since corn requires the most N), and lower amounts in non-irrigated areas with poorly drained soils where soy is the dominant crop (since soy, being a legume, does not require N, Hamilton et al. 1993). On average, nitrogen application rates have been estimated at about 300 kg N ha^{-1} y^{-1} for manure and 120 - 250 kg N ha^{-1} y^{-1} for inorganic fertilizer (Weil et al. 1990), although there are likely large differences among individual farmers.

Leaching of nitrate into groundwater, and eventually surface waters, is a major regional problem (Hamilton et al. 1993). Previous studies have shown that nitrate is especially prone to leaching in the "well drained uplands," the hydrogeomorphic region where the southern-most seven sub-basins are located (Hamilton et al. 1993, Hively et al. in press). This area consists of mainly sandy, well drained soils with relatively little silt and clay to impede the percolation of rainwater, resulting in a median groundwater nitrate concentration of 636 μM (Hamilton et al. 1993), which falls on the upper end of the curve in Figure 3-7b. The other hydrogeomorphic region is the "poorly drained uplands," which includes five of the northern-most sub-basins (Hively et al. in press). Here, soils are relatively poorly drained (especially in stream valleys) and groundwater is generally discharged via anaerobic pathways which encourage increased denitrification. Median groundwater nitrate concentrations in this region are only 314 μM (Hamilton et al. 1993), which falls along the middle of the curve in Figure 3-7b. Leaching is relatively less problematic in the poorly drained uplands because a portion of the nitrate is consumed during denitrification. Finally, natural groundwaters in areas of minimal leaching (i.e. areas without agriculture, lawn fertilizer, animal waste, or septic tanks) typically have concentrations of <29 μM, which is closer to the mean concentrations observed at the forested site (<1.3 μM, Fig. 3-7b, Hamilton et al. 1993).

Even in the well drained uplands, however, leaching does not necessarily occur in all areas. Studies have shown, for example, that substantial amounts of nitrate will only leach if 1) It is applied in excess of crop needs, as discussed above, or 2) Microbial conversion to nitrate continues after the crops have ceased nitrate uptake for the year (which occurs in the fall) and no winter cover crops are planted to stimulate additional uptake (Hamilton et al. 1993, Staver 2001). Indeed, without winter cover crops, leaching of nitrate typically occurs with most major rain events from fall to early spring (Staver 2001). In contrast to the agricultural sub-basins, the forested site, as mentioned, had virtually zero nitrate (<1.3 μM). This watershed is dominated by pine trees that were clear-cut in the 1980s but have grown back to ~10 m in height. Forests, especially aggrading forests such as this one, are well-known for being nutrient sinks due to plant uptake, heterotrophic immobilization, and abiotic reactions with soil organic matter (Brady and Weil 2002).

Baseflow conductivity (25) and pH were also positively related to the percentage of agricultural land (Fig. 3-8a, b). No other known studies have reported specific conductivities and pH as a function of land use; these parameters seem to not be reported as often. In this case, because nitrate is such a large fraction of the total dissolved ions in these streams, the trend in conductivity (25) is likely being driven primarily by nitrate, and secondarily by other agricultural ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}. As for pH, the observed correlation is probably less of an agricultural effect and more of a forested effect. Forested soils, and by extension the surface waters draining those soils, are generally rich in organic acids resulting from the decomposition of organic matter (Brady and Weil 2002). Hence, the sites with more forest (or less agriculture) have relatively low pHs. Still, it is surprising that the mean pHs among the agricultural sites are so high (6.5 – 7.3), especially since the optimum soil pH for crop production is 5.0 – 5.6 (Brady and Weil 2002) and the pH of groundwater in this region is typically 5.8 (Hamilton et al. 1993). It is not clear what is causing these high pHs. While over-application of lime could be a contributing factor, this seems unlikely to be the case for all 15 of the agricultural sub-basins.

Nutrient Behavior during Storm Discharges

This study found that nutrient and sediment concentrations fluctuated during brief periods of stormflow. Responses of concentrations to rain events followed three general patterns: 1) The particulates (PN, PP, TSS) increased with storm discharge, typically with large brief spikes in concentrations on the rising limb of the hydrograph, 2) NH_4 and PO_4 also increased with storm flows but with a more gradual slope and a smaller, broader peak compared to the particulates, and 3) Nitrate and conductivity (25) decreased during periods of quickflow and only slowly returned to pre-storm levels (Fig. 3-9). For three sampled events following a dry period during the summer of 2007, nitrate concentrations decreased slightly, then increased to greater than pre-storm levels (Fig. 3-12), although this pattern was the exception not the rule. Similar behaviors for these analytes during storm discharges have been reported elsewhere (e.g. Vanni et al. 2001, Gachter et al. 2004, Volk et al. 2006). Vanni et al. (2001), in particular, also observed the same unusual behavior of nitrate following dry periods for an agricultural watershed (>90%) in the Mid-west. Exceptions include Correll et al. (1999), who detected little to no change in either phosphate or nitrate concentrations, and two reports by Obrien et al. (1993) and Kline et al. (2007), both of which found consistent increases in nitrate concentrations during storm flows among various sites in western Maryland and Virginia.

The storm behavior of phosphate, in particular, has been described previously by Gachter et al. (2004). They determined that quickflow phosphate concentrations were largely determined by the balance of adsorption and desorption in upland topsoils. During dry periods, phosphate is mostly adsorbed to the soil matrix, but during storm events (or irrigation), phosphate enters the aqueous phase via abiotic desorption. For a given soil type, the balance of adsorption/desorption is influenced by the residence time of infiltrating rainwater in the topsoil (Gachter et al. 2004). Consequently, during the initial flushing of the soil during rain events, when residence times are short, desorption is limited and hence phosphate levels are low. However, during slower periods of overland and shallow subsurface flow, when the rain is in contact with the soil for longer periods, desorption is extended, causing phosphate levels to increase. This mechanism is consistent with the observed counter-clockwise hysteresis for phosphate (Fig. 3-10b), which shows higher concentrations on the return limb of the chemograph *after* the discharge peak has passed. In addition to desorption in upland topsoils, stream bank storage of phosphate is another possible contributor to the higher concentrations on the return limb.

Nitrate, on the other hand, behaves very differently from phosphate because it has no sorption affinity for the soil matrix. Consequently, the infiltrating rainwater, which is typically low in nitrate (~21.7 μM, Rochelle-Newall et al. in press), has little interaction with the topsoil and is immediately flushed via macropores into the stream channel, where it begins diluting nitrate-rich baseflows (Gachter et al. 2004). As a result, nitrate exhibits a clockwise hysteresis (Fig. 3-10a) with lower concentrations on the return limb of the chemograph, again because of this dilution effect. The only exception to this pattern occurred during the summer drought of 2007, when nitrate concentrations increased during storm discharges for three of the sampled events, likely due to a build-up of soil nitrate levels over extended dry periods. Most of the nitrate was probably derived from the nitrification of ammonium applied as a fertilizer that spring. For these events, nitrate followed a more complex pattern with *higher* concentrations on the return limb of the chemograph, similar to phosphate. However, unlike phosphate, nitrate only accumulates in the soil in the absence of rain water, which would carry it elsewhere. Phosphate, on the other hand, accumulates in the soil because of an inherent affinity for the soil matrix.

In contrast to both phosphate and nitrate, the particulate fractions (PN, PP, TSS) followed yet another mechanism. Particulates come from a variety of sources, including organic litter on the soil surface, bank erosion, and re-suspended bedload (Correll et al. 1999, Thompson 2008). Agricultural land, in particular, is a major source of fine sediment (Kuhnle et al. 1996), and there is likely a low threshold for detachment and transport of the sediment into stream channels. This view is consistent with the particulates peaking *before* the discharge peak when flow strengths are assumed to be less than their maximum. On the return limb of the chemograph (Fig. 3-10d), the particulate concentrations are lower since the discharge peak has passed and therefore the ability of the water to dislodge additional sediment is reduced.

N and P Fractions in Storm Discharges

This study found that storm discharges were dominated primarily by nitrate (58% of total N on average) and secondarily by particulate N (21% of total N on average, Fig. 3-17d). Other studies have reported the opposite. Correll et al. (1999), for example, in studying a cropland watershed in the Rhode River Basin with similar land use, found that PN was the dominant form of N in storm flows, comprising 84% of the total N flux for one event, while nitrate was only about 27% of the total N. Similarly, Volk et al. (2006), who monitored a mixed-land-use subwatershed of Rehoboth Bay, DE, reported that PN was a dominant component of the total N load, especially for large storms, and that DIN (which includes NO_3) was a relatively minor fraction. For the current study, there is evidence that during the largest sampled events (e.g. mid-April 2007, probably a ~50-year storm), PN concentrations exceeded nitrate concentrations, but only because discharge was so high that dilution of nitrate was allowed to reach its maximum extent.

The discrepancy in N forms in storm discharges between this study and others is likely due to differences in baseflow nitrate chemistry among regions. Correll et al. (1999) and Volk et al. (2006), for example, reported mean baseflow nitrate concentrations of about 120 μM and 278 μM for their Rhode River and Rehoboth Bay sites, respectively. In contrast, the Choptank sites had mean concentrations of about 200 – 500 μM. Land use alone does not explain this variability since the Rhode River watershed had almost identical land use compared to the Choptank sites, whereas the Rehoboth Bay sub-basin had less agriculture (47%) and slightly more forest (41%), which if anything would decrease nitrate concentrations relative to the Rhode River and Choptank sites. Alternatively, other factors may be contributing to the disparities, including differences in historical fertilizer use, size effects (the Rhode River site, at <0.2 km^2, is much smaller than either the Choptank or Rehoboth Bay sites), or variation in soil drainage characteristics.

In contrast, estimates of DON and NH_4 fractions in storm discharges (Fig. 3-17d) agree reasonably well with other studies. Correll et al. (1999), for example, determined that DON and NH_4 were, on average, roughly 9% and 3 – 4 % of the total N in storm flows, respectively (as visually estimated from Fig. 4 in their report). Similar proportions of DON and NH_4 have been reported by Sutton (2006) and Volk et al. (2006) for individual events. These studies are in general agreement that both DON and NH4 represent a small but measurable proportion of the total N during quickflows. By comparison, the current study found that DON and NH_4 were, on average, 16% and 5% of the total N, respectively.

As for phosphorus, storm discharges were dominated by PP, which represented about 65% of the total P on average (Fig. 3-17c). This agrees well with Correll et al. (1999), who reported almost identical mean proportions of PP from a cropland watershed (as visually estimated from Fig. 5 in their report), and individual event fractions as high as 83% of the total P. This finding is also supported by previous work in the Choptank by Sutton (2006), who monitored two of the same watersheds studied here (Blockston and Norwich). Although she did not report mass balances of P fractions during quickflow, an analysis of her data suggests that PP was >50 % of the total P. Other studies, however, disagree. Primrose et al. (1997), for example, found that phosphate (not particulates) accounted for > 50% of the total P losses in the German Branch watershed, the same site monitored for baseflow chemistry in this study (Table 3-1).

Traditionally, storm events are considered an important time for particulate nutrient transport (e.g. Correll et al. 1999). This study found that PN and PP represented, on average, 21% and 65% of the total N and total P in storm discharges, respectively (Fig. 3-17c, d). As suggested earlier, these nutrients are likely derived from organic litter and topsoils during periods of overland and shallow sub-surface flow (Correll et al. 1999) and/or are re-suspended from the streambed as discharge velocities increase during storm events (Volk et al. 2006). In contrast, particulate nutrients in baseflow, although they were not measured directly, were likely minimal, certainly <10% of the total N and P. This shift, from dissolved nutrients during baseflow to particulate nutrients during quickflow, has important implications for downstream loadings. As shown in Chapter 2, total annual flow is only ~1/3 quickflow (F = fraction of annual flow that is quickflow). However, since concentrations (C) of particulate nutrients during quickflow are typically much higher than during baseflow, especially for large events, the total load of PN and PP during storm discharges is disproportionately high (i.e. C * F = total quickflow load). A portion of these particulate nutrients are eventually mineralized to inorganic forms in estuarine sediments downstream, at which point they become available for biotic uptake (Correll et al. 1999).

Hypothesis Testing

One of the major goals of this chapter is to test the hypothesis that sub-basins with greater percentages of hydric soils export less nitrate, primarily due to higher rates of denitrification (although other factors such as different crop rotations and greater plant uptake in hydric areas could also contribute). As shown previously, % agriculture was the main driver of baseflow nitrate concentrations (r^2= 0.79, P <0.0001, Fig. 3-7b), and % hydric soils did not significantly improve the regression (Table 3-4). This suggests that land use has a proportionately larger effect on nitrate discharges than hydric soils. However, combining these two terms (% agriculture and % hydric soils) into the same multiple regression is mis-leading because % agriculture is a source term, and % hydric soils are a sink term. Therefore, to truly test the hypothesis, it is necessary to normalize the baseflow nitrate concentrations by the fraction of agricultural land in the watershed (0 – 1), that is [NO_3] / (Ag. Fraction). This effectively removes the source term, and isolates the sink term. The results of this analysis show that agriculture-normalized nitrate concentrations decrease linearly with % hydric soils (r^2= 0.29, P <0.05, Fig. 3-21a).

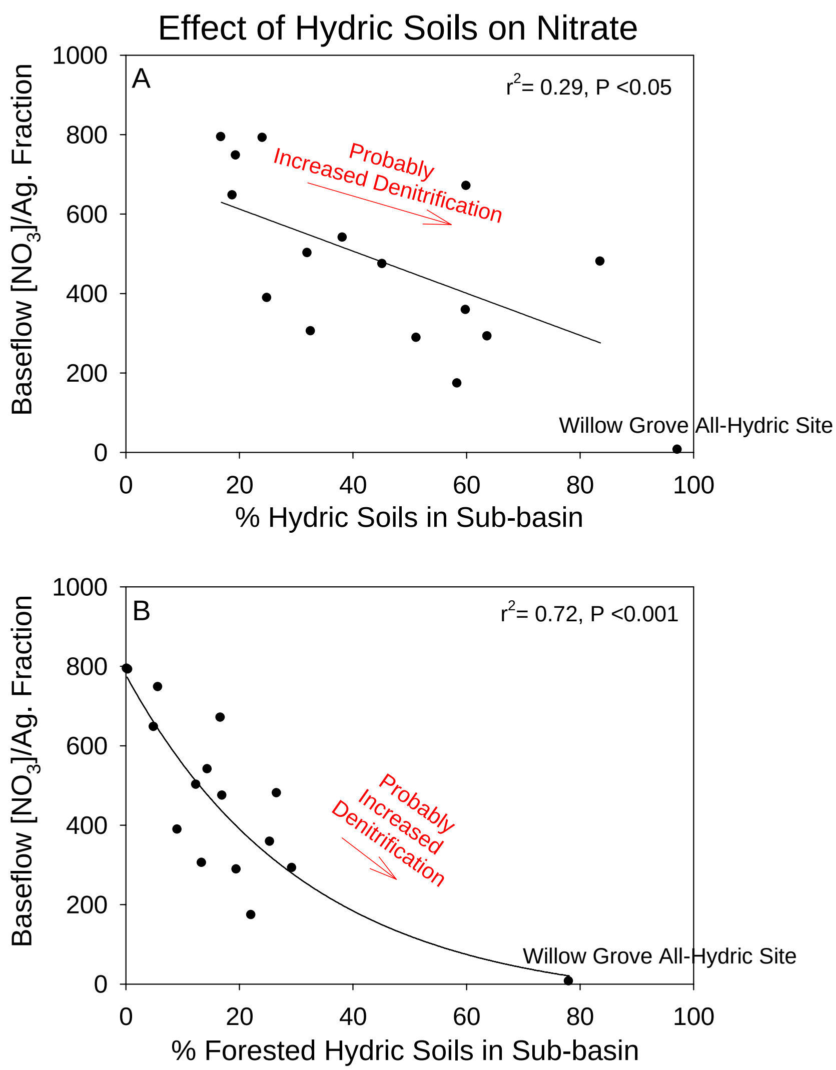


Figure 3-21. In the top panel (A), mean monthly baseflow nitrate concentrations, normalized by the agricultural fraction (y-axis), decreased linearly with % hydric soils (x-axis). In normalizing the nitrate data by the agricultural fraction, the effect of land use is removed. In the bottom panel (B) is the same nitrate data plotted against % forested hydric soils. In both panels, the negative relationship is likely due to enhanced denitrification in hydric areas. The Willow Grove all-hydric (and mostly forested) site is labeled for reference.

However, not all hydric soils behave in a similar manner. Agricultural hydric soils, in particular, which in this region are heavily ditched and drained, are probably no longer functioning as "wetland" soils even though they are technically still classified as hydric. Forested hydric soils, in contrast, which are assumed to *not* be ditched, are likely still functioning as wetland soils because the water has not been artificially drained. To address this issue, the percentage of forested hydric soils in each of the Choptank watersheds was calculated in ArcGIS and plotted against the same agriculture-normalized nitrate concentrations as above. The results show that ag-adjusted nitrate concentrations decrease exponentially with percent forested hydric soils (Fig. 3-21b), and the relationship is statistically stronger (r^2= 0.72, P <0.001) than it was for % hydric soils (compare Figs. 3-21a, b). However, using forested hydric soils as an independent variable is no more statistically descriptive than using % forest (r^2= 0.75, P <0.0001, data not shown), which also has a negative relationship with ag-adjusted nitrate concentrations.

In any case, whether looking at % hydric soils, % forested hydric soils, or % forest, the negative correlation with ag-adjusted nitrate concentrations is probably due to enhanced denitrification in wet forested areas. Although denitrification was not measured directly in this study, other research in the Choptank shows that excess N_2 concentrations (an indicator of denitrification) in groundwater are about an order of magnitude higher in saturated forested hydric soils than they are in drained agricultural hydric soils (Fisher et al. 2007). This disparity underlines the importance of soil water saturation in driving denitrification, and supports the idea that ditched agricultural areas are less functional as wetland soils enhancing denitrification. Again, while other factors could also be contributing to the decrease in nitrate concentrations (e.g. different agricultural management practices in hydric areas), it is likely that at least some of the nitrate is lost via denitrification. In conclusion, the data support the hypothesis. Within the confines of this study, hydric soils, especially forested hydric soils, do appear to decrease stream nitrate levels.

One final consideration is flow paths. While the correlations presented above (Fig. 3-21a, b) do not provide direct evidence of one flow path over another, they do hint at the following plausible mechanism: subsurface nitrate-rich flow from cropland percolates to groundwater, and then flows into anaerobic, forested areas next to the stream channel, where some denitrification occurs before the water is discharged into the stream. This is partly why more forested watersheds have less baseflow nitrate (in addition to having less fertilizer use, Fig. 3-7b). Agricultural ditches circumvent this process. The ditches drain the water off at the source (i.e. at the crop field), thereby preventing the water from being discharged through forested areas where they would normally undergo denitrification. Without this attenuation, nitrate concentrations remain high. This is partly why watersheds with more cropland have higher nitrate concentrations, in addition to the fact that more fertilizer is used.

Annual Nutrient Export

Annual export of TN and TP occurs as both baseflow and quickflow components. As discussed previously, many organizations and research groups (e.g. USGS, DNR) only sample baseflow (Kazyak 2001, Langland et al. 2006), but in this study, we have adequate data to include stormflows. Although only ~20% of the storms were sampled, sufficient data was collected to extrapolate over all events.

Annual export of TN and TP during storm discharges was estimated by using the measured relationships between v.w. mean nutrient concentrations and event discharge to extrapolate v.w. means for the unsampled events. For TP, v.w. means were extrapolated directly using event discharge (Fig. 3-18a). For events where TDP was measured but not PP or TP, the v.w. mean of PP was extrapolated separately (Fig. 3-18b) and added to the measured v.w. mean of TDP. As for nitrogen, TN was not significantly correlated with event discharge. Hence, both TDN and PN were extrapolated separately (Figs. 3-19b, c) and summed together to estimate the v.w. mean of TN. While in general the extrapolations were based on statistically strong relationships (r^2 >0.82, P <0.0001), the correlation for TDN (r^2= 0.14, P = 0.04, Fig. 3-19c) was much weaker, which likely increased the uncertainties in the estimates of annual TN export relative to annual TP export.

In addition to extrapolating for the unsampled events, it was also necessary to extrapolate over the unsampled portions of the sampled events. This is because many of the storms lasted longer than the 48-hour sampling cycle. In examining all events, three types of sampling patterns were identified: 1) “Fully sampled,” defined as storms for which samples were collected on each day of the event (Fig. 3-22a), 2) “Multiple event,” defined as storms with multiple discharge peaks, only some of which were sampled (Fig. 3-22b), and 3) “Partially sampled,” defined as storms with a single peak where the long tail of the hydrograph was not adequately sampled (Fig. 3-22c). For the “fully sampled” and “multiple event” categories, the measured v.w. mean nutrient concentration (μM) was multiplied by the integrated discharge for each storm (L $event^{-1}$), resulting in kg of nutrient per event (i.e. v.w. mean * L $event^{-1}$ = kg of nutrient per event, Fig. 3-22a, b). For “multiple event” storms, it was assumed that the other, unsampled peaks had identical v.w. means as the sampled peak (Fig. 3-22b).

For “partially sampled” storms (by far the most common, representing 22 of the 31 sampled events), total loading per storm was estimated using a different method. First, a hysteresis diagram, showing discharge versus concentration, was plotted (Fig. 3-22d). Then, a straight line was drawn between the first and last samples in the chemograph and the mid-point of the line was derived using linear extrapolation (Fig. 3-22d). Finally, this point, assumed to represent the v.w. mean (μM) of the unsampled discharge tail, was multiplied by the volume of unsampled discharge (L), and added to the measured v.w. mean (μM) multiplied by the sampled discharge (L, Fig. 3-22c, d). For this approach, it was assumed that nutrient concentrations returned in a linear fashion to the same initial levels. While for large changes in discharge, this assumption would likely not be valid, the extrapolations generally represented only a small portion of the entire hysteresis (Fig. 3-22d).

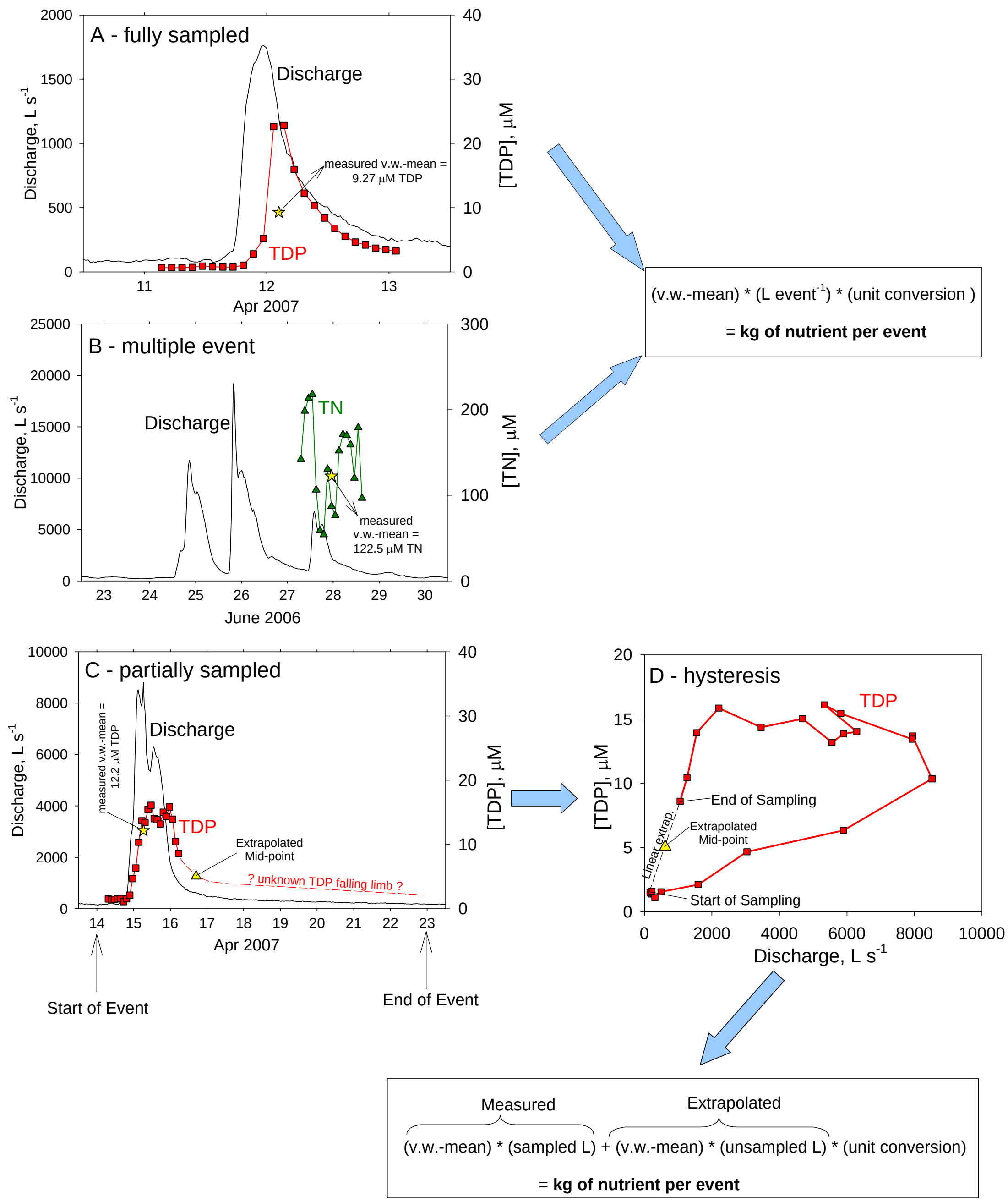


Figure 3-22. For extrapolation purposes, sampled events fell into three categories: those that were "fully sampled" (A – top panel), those in which the discharge hydrograph peaked multiple times ("multiple event", B – middle panel), and those that were "partially sampled" (C – bottom panel). For both the "fully sampled" and the "multiple event" cases, the measured volume-weighted (v.w.) means (stars) were applied to the entire duration of the event to estimate the total kg of nutrient per event (see equation on the right-hand side of panels A and B). However, if the storm was only partially sampled (C - bottom left panel), the unsampled portion was extrapolated from a hysteresis plot (D- bottom right panel) showing the relationship between nutrient concentrations and discharge. In panel D, the linear extrapolation is shown as a dotted line. The mid-point of the extrapolation (triangle, shown in both panels C and D) was used to estimate the v.w. mean for the unsampled portion of the event. For partially sampled events, the total kg of nutrient per event was estimated using both the measured v.w. mean and the extrapolated v.w. mean (see equation under panel D).

Annual export of TN and TP was also estimated for the baseflow samples. Each monthly concentration was weighted by the sum of daily baseflow values occurring in a symmetrical region corresponding to the mid-points between samples (Fig. 3-23). Daily baseflow was separated from total flow using the 1-day SARR method (Ch. 2). A baseflow sample collected on 5/30/06, although outside of the study period (6/1/06 – 8/31/07) was also included because no monthly sample was available for June 2006 due to very high flows in that month. For the 5/30/06 sample, the monthly concentration was volume-weighted by the sum of daily baseflows occurring within a truncated region from 6/1/06 (the start of the study period) to a point halfway to the next sample, collected on 7/5/06 (Fig. 3-23).

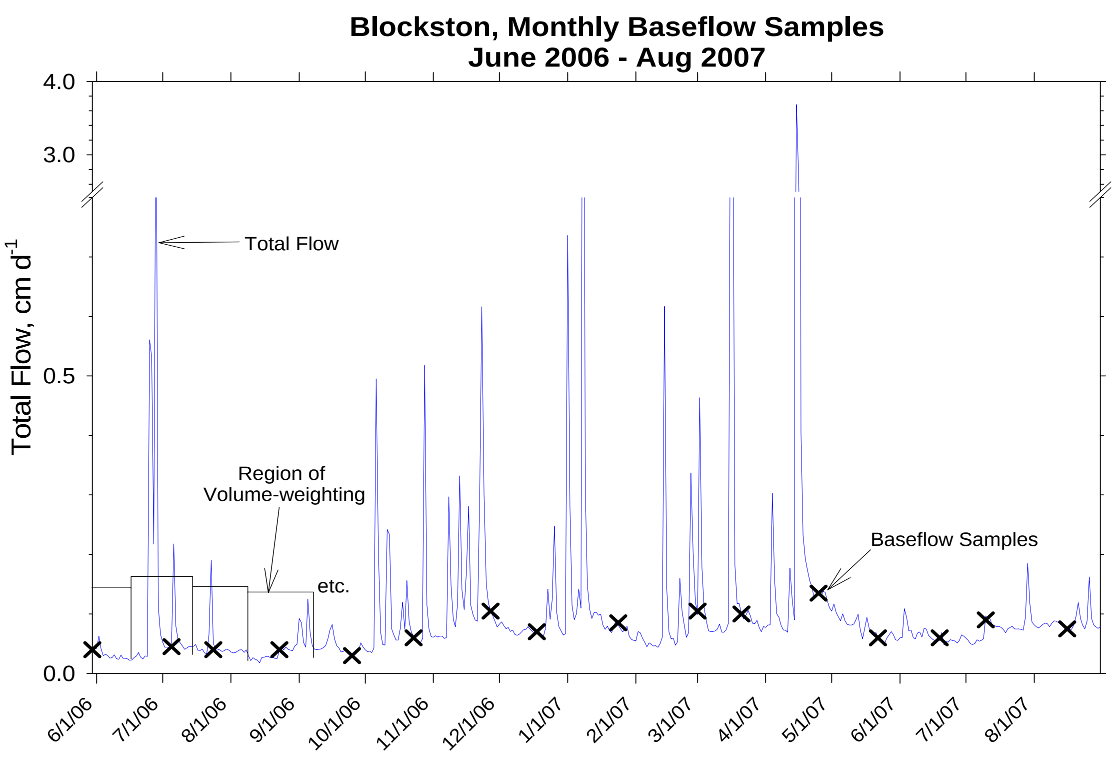


Figure 3-23. To calculate the annual export of baseflow nutrients, monthly samples (X's) were volume-weighted by the sum of daily baseflows occurring from the mid-point of the previous sample to the mid-point of the next sample (rectangular boxes). For clarity, the region of volume-weighting is only shown for the first few samples. Total daily flow is also illustrated as a solid line (arrow).

Total annual export (quickflow + baseflow) among the four sub-basins ranged from 21.9 – 32.8 kg ha^{-1} y^{-1} for TN and 0.9 – 1.4 kg ha^{-1} y^{-1} for TP (Table 3-6a). Annual export estimates vary tremendously among studies, even within a single land use. As described in Vanni et al. (2001), agricultural watersheds may export anywhere from 2.1 – 80 kg ha^{-1} y^{-1} for TN and 0.1 – 18.6 kg ha^{-1} y^{-1} for TP, which puts the calculated values in Table 3-6a on the low to middle portions of the scale.

Table 3-6. The top table (A) shows the annual export coefficients of total nitrogen (TN) and total phosphorus (TP) for each of the four Choptank sub-basins. Also included is the percentage of annual export which occurs during baseflow and during quickflow for both TN and TP, with averages on the last row. The bottom table (B) shows the percentage of the annual export of TN and TP due to the two largest sampled events (in June 2006 and April 2007), again with averages on the last row.

A	Annual Export Coefficients		TN			TP		
	kg TN ha^{-1} y^{-1}	kg TP ha^{-1} y^{-1}	% BF	% QF	total	% BF	% QF	total
Beaverdam	32.8	0.9	84	16	100	29	71	100
North Forge	21.9	0.9	70	30	100	20	80	100
Kitty's	26.9	1.4	52	48	100	11	89	100
Blockston	25.7	1.0	75	25	100	9	91	100
				30			**83**	

B	% of Annual TN	% of Annual TP
Beaverdam	8	58
North Forge	15	60
Kitty's	17	56
Blockston	9	29
	12	**51**

For this study, annual TN losses did not vary significantly with any of the hydrology terms, including baseflow index, annual baseflow, and annual quickflow (see Ch. 2). In contrast, annual TP losses increased linearly with annual quickflow discharge (r^2= 0.96, P=0.02, Fig. 3-24). This finding is consistent with other local studies (e.g. Fisher et al. 2006, Sutton 2006) which have shown that phosphorus is primarily transported via stormflow pathways, not via groundwater. Finally, annual exports of TN and TP did not vary significantly with % hydric soils.

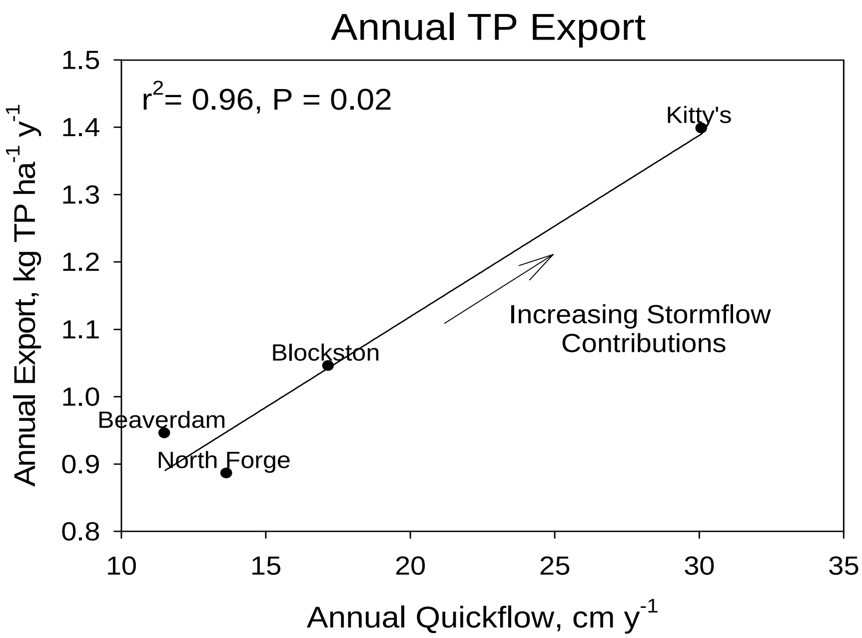


Figure 3-24. Annual export of total phosphorus (TP) increased linearly with annual quickflow discharge, suggesting that TP losses are mainly associated with storm flows.

Among the four sub-basins, a surprisingly large fraction of the annual losses of TN and TP occurred during storm discharges (Table 3-6a). As shown in the table, 16 – 48% (avg. 30%) of the annual TN and 71 – 91% (avg. 83%) of the annual TP load occurred during periods of quickflow. The two largest events alone, occurring in June 2006 and April 2007, both of which were probably ~50-year storms, exported 8 – 17% (avg. 12%) of the annual TN load and 29 – 60% (avg. 51%) of the annual TP load (Table 3-6b).

These results are not simply an artifact resulting from the use of the 1-day SARR method of hydrograph separation. As discussed in Chapter 2, the 1-day SARR was much more sensitive to slight increases in discharge due to small rain events, which the other, coarser methods (e.g. 5-day, 2-day) generally failed to detect. However, over the entire 15-month study period, the 1-day SARR method actually calculated *less* quickflow than the other methods (see Table 2-4 in Ch. 2), primarily because it projected a faster return to baseflow. As shown in the example in Fig. 2-6 of Chapter 2, while the 5-day method predicted 19 continuous days of quickflow in response to a 20 cm stage increase (a fairly small event), the 1-day SARR method, within the same 19-day period, had returned to baseflow four times, resulting in four unique events and a much lower estimate of quickflow. Therefore, if anything, the 1-day SARR method *under*-estimated the percentage of annual TN and TP export occurring during storm discharges.

Finally, as discussed in Chapter 2, total annual discharge was disproportionately affected by brief periods of very high flows, when discharge rates increased by 1 – 2 orders of magnitude. For example, the two largest storms alone (in June 2006 and April 2007) contributed, on average, 19% of the total annual water budget for the four sub-basins (see Table 2-9 in Ch. 2). Furthermore, for large events such as these, there were essentially no differences among the hydrograph separation methods (see Fig. 2-9 in Ch. 2). Again, as described in Chapter 2, the major differences were for small and medium-sized events. Therefore, it does not appear likely that the high export of TN and TP during storm discharges is simply due to the 1-day SARR method of baseflow separation.

Implications for Monitoring Groups

This study has important implications for monitoring groups and other researchers. If storm discharges are not sampled, about 1/3 of the annual TN load and almost all of the annual TP load will be missed. As stated previously, organizations such as the USGS often sample on a monthly basis, while other groups (e.g. Maryland DNR) sample even less frequently, i.e. during the spring only (Kazyak 2001, Langland et al. 2006). Assuming a random, monthly grab sampling scheme (similar to the baseflow monitoring that occurred for this project), one is more likely to sample “quickflow” than “baseflow” because quickflow occurs ~2/3 of the time while baseflow occurs only ~1/3 of the time (Ch. 2). However, this quickflow is most often associated with small events which are much more common than large ones (see Fig. 2-11 in Ch. 2). During small storms, both nutrient concentrations (C) and discharge (Q) are relatively low and hence loading is minimal (i.e. C * Q = nutrient load). This means that random monthly samples, although they are more likely than not to contain *some* storm runoff, only capture a small fraction of the annual nutrient loads. A better, more balanced approach would be to sample baseflow *and* some large storms, which contribute disproportionately to both annual discharge (19% in this case) and annual nutrient export (51% of TP, 12% of TN in this case). During major events, both C and Q are extremely high, resulting in enormous loadings.

Finally, one can imagine a situation where random grab samples are collected monthly and total flow is monitored using a logger, similar to the one used in this study. In this scenario, the researcher could simply multiply the nutrient concentrations in each monthly sample by the average monthly discharge. The problem with this type of monitoring, however, is that 1) The monthly nutrient concentrations (C) are probably not representative of those seen in large storms, when most of the nutrient flux occurs (unless the sampler happens to catch a major event), and 2) Average monthly discharge (Q) is preferentially biased towards low flow conditions, which are much more common than high flows. Hence, both the ‘C’ and ‘Q’ portions of the loading equation are likely to be under-estimated.

Again, this study emphasizes the need to sample during very high flows. For many monitoring groups, this will likely be difficult given the logistical and labor-intensive demands of sampling storm events. However, the extra effort will greatly improve estimates of TN and TP losses from agricultural watersheds.

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Chapter 4:

Thesis Summary

The general purpose of this study was to quantify the hydrologic and biogeochemical storm response of various sub-watersheds of the Choptank River Basin. Within this broader context, a second major goal was to examine the impact of hydric, or wetland, soils on 1) the stream flow components of baseflow and quickflow, and 2) stream nitrate concentrations. No other known study has looked specifically at these relationships, especially quickflow, which is often under-sampled or not sampled at all. In contrast, the current study examined quickflow in great detail, using hourly measurements of total suspended solids, nitrogen (N), and phosphorus (P) to determine the short-term changes in chemistry during a large number of storm events at four Choptank sub-basins. It is hoped that the more detailed data presented in this thesis will contribute to our understanding of storm runoff and help improve estimates of annual losses of N and P from agricultural watersheds. A brief summary of each thesis chapter follows.

In Chapter 1, the precipitation data were evaluated and adjusted for measurement errors where necessary. Errors were quantified by comparing the annual totals at 14 regional stations with unknown measurement errors to the mean annual total of three reference stations, which were assumed to be accurate since they were part of a national network (either the National Weather Service or the National Atmospheric Deposition Program). If the annual total for a given non-reference site was outside the 95% confidence interval of the reference stations, a correction was applied to the non-reference site. This method of calibration was based on the assumption that rainfall within the 60 km x 60 km coastal plain area inscribed by the 17 stations was spatially uniform at the annual time scale. Undoubtedly, at shorter time scales, this would not be the case due to variability in storm paths and rainfall intensity. However, at the annual scale, it was assumed that these differences averaged to zero. In this way, significant measurement errors were quantified at eight of the sites, and the rainfall data were corrected accordingly. The corrections were made by applying the percent difference in the annual totals [i.e. (individual non-reference site / reference station avg.)* 100] at either the daily or event time scales. This approach preserved the temporal and spatial heterogeneity of the rainfall data while ensuring that annual totals among all the stations were comparable.

In Chapter 2, the adjusted precipitation data were used to identify events and assess the hydrologic storm response among six Choptank sub-basins. Ninety three storms were identified at the Blockston sub-basin over a ~1.5 year period (June 2006 – Aug 2007), while 100 were identified at the Beaverdam sub-basin, about 15 km to the north. About 69% of these storms were small (< 2 cm of rainfall), although two large events (in June 2006 and Apr 2007) had > 10 cm of rainfall. Hydrologic responses to storm events were generally about the same among the sites except at Kitty's Corner, which on average generated about twice as much quickflow (19% of precipitation) as the others (9 – 10 % of precipitation). On a seasonal basis, storms occurring during the cool season (Oct – Apr) had stronger hydrologic responses (15% of precipitation) than similar-sized storms occurring during the warm season (May – Sept, 7%) due to seasonal differences in evapotranspiration and soil moisture. Days containing >0 quickflow were surprisingly common, accounting for ~2/3 of the study period. However, most of this quickflow was the result of runoff from very small storms, which on a volumetric basis contributed relatively little to total annual discharge. Consequently, annual flow was only ~ 1/3 quickflow.

In addition to characterizing the hydrology of the Choptank sites, Chapter 2 also explored the effect of hydric soils on baseflow and quickflow. Among the six Choptank sub-basins, hydric soils were not related to baseflow or quickflow at either the event, monthly, or annual time scales. However, a secondary analysis of long-term (decadal) data from 13 regional USGS sites showed that baseflow decreased significantly with hydric soils because of increased surface ponding and shallow subsurface water storage in hydric areas, resulting in greater evaporative losses, less infiltration to groundwater, and hence less baseflow in the stream. Quickflow, on the other hand, increased with slope, not hydric soils. This suggests that baseflow was driven by a soils effect while quickflow was driven by a topographic effect. These relationships were fairly similar to those found for the Choptank sub-basins. However, shorter record lengths (~1.5 years), measurement errors in the stage and discharge computations, and a small sample size (6) at the Choptank sites prevented statistical significance on their own.

Chapter 3 examined the biogeochemistry of baseflow and quickflow among the Choptank sub-basins. Baseflow chemistry was correlated with agricultural land use upstream of the sampling sites. Specifically, baseflow concentrations of nitrate, total nitrogen, conductivity (25), and pH were all positively related to % agriculture while phosphate concentrations were positively related to the density of concentrated animal feeding operation buildings upstream. As for quickflow, most of the variability in the observed volume-weighted (v.w.) mean concentrations during storm discharges was explained by either event discharge (L ha^{-1}) or mean event stream temperature. As event discharge increased, v.w. mean concentrations of particulate N and P, and seston, also increased, probably due to increased sediment loading from the watershed, as well as bank erosion and re-suspension from the stream bed. In contrast, v.w. mean concentrations of nitrate decreased during higher event discharges because nitrate-rich groundwater was being diluted by overland and shallow sub-surface flows. On the other hand, ammonium and total dissolved nitrogen were best explained by stream temperature. Colder temperatures were associated with higher v.w. mean concentrations of ammonium, probably due to fertilizer applications which took place in the spring, when stream temperatures were relatively cool (<10° C). V.w. mean concentrations of total dissolved nitrogen decreased with stream temperature during the summer months only, likely due to increased plant uptake at warmer temperatures.

In general, storm discharges were marked by large changes in both nutrient concentrations and speciation. Phosphorus, ammonium, particulate N, and seston concentrations all increased during storms, and were 2 – 10 times higher in quickflows compared to baseflows. In contrast, nitrate and conductivity(25) levels decreased during storms, down to about half the levels found in baseflows. Among individual analytes, the responses to storm discharges followed three patterns. First, the particulates (total suspended solids, particulate N and P) had large, brief peaks early in the storm and a fast return to pre-storm concentrations. Second, ammonium and phosphate had smaller, broader peaks and a gradual, exponential return to pre-storm concentrations. Finally, nitrate and conductivity (25) both decreased during storm discharges and very slowly returned to pre-storm levels. As for speciation, baseflows were dominated by dissolved inorganic forms of N and P such as nitrate and phosphate, as well as dissolved organic species. In contrast, storm discharges had much higher fractions of particulates, which represented 21% and 65% of the total N and P, respectively.

Chapter 3 also found a significant, negative relationship between baseflow nitrate concentrations (adjusted for agricultural land use) and % forested hydric soils. This trend was likely due to greater denitrification in forested hydric areas, which is supported by other research in the Choptank Basin (Fisher et al. 2007). For this analysis, baseflow nitrate concentrations were divided by the fraction (0 – 1) of agricultural land to remove the effect of agriculture and isolate hydric soils as a sink term for nitrate.

Finally, Chapter 3 found that most of the annual export of TN and TP occurred during storm events. Specifically, 30% and 83% of the annual loads of TN and TP, respectively, took place during periods of runoff. The two largest events alone (in June 2006 and April 2007), when discharge rates increased by 1 – 2 orders of magnitude, accounted for 12% and 51% of the annual TN and TP load, respectively. This underlines the importance of sampling during very high flows, and suggests that monthly baseflow monitoring is likely to under-estimate annual losses of TN and TP from agricultural watersheds.

Appendix

List of storm events identified at each of the six Choptank sub-basin over the 457-day study period (June 2006 – Aug 2007). Outliers, where quickflow > precipitation, are shown with highlights. Quickflow was separated using the 1-day SARR method (see Ch.2 text). For each event, % quickflow was calculated as: (quickflow / precip) *100. Storm populations at the Cordova, Kitty's Corner, North Forge, and Willow Grove sub-basins are under-estimated because of gaps in the discharge records at these sites. As described in Chapter 2, the discharge data were used to help identify events.

Cordova Sub-basin

Event No.	Event Time Period	Precip, cm	Quickflow, cm	% Quickflow
1	5/31/06 - 6/6/06	2.79	0.23	8.2
2	6/7/06 - 6/10/06	0.98	0.02	2.1
3	6/12/06 - 6/17/06	0.81	0.02	2.2
4	6/19/06 - 6/21/06	1.65	0.05	2.8
5	6/23/06 - 7/2/06	18.79	2.51	13.4
6	7/3/06 - 7/12/06	5.59	0.21	3.8
7	7/13/06 - 7/16/06	0.94	0.03	3.5
8	7/17/06 - 7/19/06	0.25	0.01	4.0
9	7/22/06 - 7/24/06	3.41	0.12	3.4
10	7/25/06 - 8/1/06	0.53	0.04	8.5
11	8/7/06 - 8/11/06	2.12	0.02	1.1
12	8/18/06 - 8/24/06	0.15	0.04	29.2
13	8/28/06 - 9/3/06	8.49	0.20	2.3
14	9/4/06 - 9/10/06	2.81	0.08	3.0
15	9/11/2006	0.00	0.00	0.0
16	9/13/06 - 9/20/06	3.42	0.11	3.2
17	9/24/06 - 9/26/06	0.25	0.01	3.7
18	9/27/06 - 10/3/06	2.79	0.07	2.5
19	10/5/06 - 10/9/06	5.25	0.53	10.2
20	10/11/06 - 10/15/06	1.72	0.16	9.4
21	10/17/06 - 10/18/06	2.05	0.06	3.1
22	10/19/06 - 10/21/06	0.77	0.01	1.7
23	10/22/06 - 10/25/06	0.00	0.00	96.3
24	10/27/06 - 10/30/06	3.47	0.41	11.8
25	11/2/06 - 11/3/06	0.25	0.01	2.3
26	11/7/06 - 11/10/06	2.88	0.24	8.4
27	11/12/06 - 11/14/06	2.99	0.31	10.4
28	11/15/06 - 11/20/06	1.72	0.16	9.4
29	11/22/06 - 12/2/06	3.27	0.56	17.2
30	12/3/06 - 12/8/06	0.09	0.01	10.7
31	12/13/06 - 12/16/06	0.15	0.02	10.1
32	12/19/2006	0.0018	0.0022	**116.7**
33	12/22/06 - 12/23/06	1.50	0.04	2.9
34	12/24/06 - 12/30/06	1.74	0.16	9.4
35	12/31/06 - 1/3/07	3.86	0.65	16.9
36	1/5/07 - 1/11/07	4.46	0.94	21.0
37	1/14/07 - 1/20/07	0.30	0.03	9.4
38	1/21/07 - 1/25/07	0.63	0.06	9.3
39	1/26/07 - 1/31/07	0.09	0.01	14.1
40	2/1/07 - 2/5/07	0.48	0.02	5.1
41	2/6/07 - 2/10/07	0.13	0.00	3.7
42	2/13/07 - 2/16/07	2.91	0.37	12.9
43	2/20/07 - 2/23/07	0.56	0.09	16.4
44	2/25/07- 2/28/07	1.95	0.22	11.3
45	3/1/07 - 3/5/07	1.42	0.22	15.6
46	3/7/07 - 3/9/07	0.12	0.00	3.4
47	3/11/2007	0.05	0.00	4.5
48	3/15/07 - 3/25/07	6.90	1.39	20.2
49	3/27/07 - 3/29/07	0.02	0.01	51.1
50	3/30/07 - 3/31/07	0.01	0.00	9.2
51	4/1/07 - 4/2/07	0.13	0.00	0.0
52	4/4/07 - 4/5/07	1.91	0.08	3.9
53	4/7/2007	0.08	0.00	3.3
54	4/11/07 - 4/13/07	2.96	0.28	9.4
55	4/14/07 - 4/22/07	9.87	2.03	20.6
56	4/25/07 - 4/30/07	1.05	0.03	2.9
57	5/5/07 - 5/6/07	0.14	0.00	0.0
58	5/9/07 - 5/10/07	0.03	0.00	11.4
59	5/11/07 - 5/14/07	1.36	0.03	2.1
60	5/16/07 - 5/18/07	1.31	0.02	1.5
61	5/19/07 - 5/26/07	0.12	0.05	44.6
62	5/27/07 - 6/1/07	0.28	0.05	19.3
63	6/3/07 - 6/8/07	3.76	0.14	3.7
64	6/9/07 - 6/10/07	0.01	0.00	21.0
65	6/11/07 - 6/16/07	2.47	0.01	0.3
66	6/17/07 - 6/22/07	0.75	0.04	4.9
67	6/23/07 - 6/28/07	1.44	0.01	0.9
68	6/29/07 - 6/30/07	0.53	0.00	0.9

Kitty's Corner Sub-basin

Event #	Event Time Period	Precip, cm	Quickflow, cm	% Quickflow
1	5/31/06 - 6/6/06	2.79	1.28	46.1
2	6/7/06 - 6/10/06	0.98	0.15	15.7
3	6/11/06 - 6/16/06	0.81	0.04	4.8
4	6/19/06 - 6/20/06	1.65	0.05	3.3
5	6/23/06 - 6/30/06	18.61	10.26	55.1
6	9/25/06 - 9/26/06	0.08	0.00	0.9
7	9/27/06 - 10/3/06	2.79	0.18	6.4
8	10/5/06 - 10/9/06	5.25	1.60	30.5
9	10/11/06 - 10/15/06	1.72	0.39	22.7
10	10/17/06 - 10/25/06	2.82	0.73	25.8
11	10/27/06 - 11/3/06	3.72	1.02	27.4
12	11/7/06 - 11/10/06	2.88	0.74	25.5
13	11/12/06 - 11/04/06	2.99	0.87	29.2
14	11/15/06 - 11/20/06	1.72	0.51	29.6
15	11/22/06 - 12/2/06	3.27	1.35	41.3
16	12/3/06 - 12/5/06	0.08	0.00	6.1
17	12/7/2006	0.02	0.01	69.7
18	12/13/06 - 12/19/06	0.16	0.05	32.4
19	12/22/06 - 12/30/06	3.24	0.76	23.4
20	12/31/06 - 1/3/07	3.86	1.42	36.9
21	1/5/07 - 1/11/07	4.71	1.78	37.7
22	1/14/07 - 1/20/07	0.30	0.13	42.8
23	1/21/07 - 1/25/07	0.63	0.15	24.1
24	1/26/07 - 1/30/07	0.09	0.05	59.4
25	2/1/07 - 2/5/07	0.50	0.10	20.1
26	2/6/07 - 2/10/07	0.09	0.02	25.1
27	2/13/07 - 2/19/07	2.65	0.82	31.0
28	2/20/07 - 2/23/07	0.56	0.15	25.9
29	2/25/07 - 2/28/07	1.95	0.46	23.7
30	3/1/07 - 3/5/07	1.35	0.49	36.0
31	3/7/07 - 3/8/07	0.11	0.00	2.5
32	3/9/07 - 3/12/07	0.05	0.01	23.6
33	3/15/07 - 3/20/07	6.24	2.33	37.3
34	3/23/07 - 3/25/07	0.21	0.06	29.4
35	3/27/07 - 3/29/07	0.02	0.05	**223.1**
36	3/30/07 - 3/31/07	0.01	0.00	5.9
37	4/1/07 - 4/8/07	2.13	0.23	11.0
38	4/11/07 - 4/13/07	2.81	0.53	19.0
39	4/14/07 - 4/23/07	9.47	4.61	48.7
40	4/25/07 - 4/30/07	1.05	0.13	12.3
41	5/5/07 - 5/7/07	0.14	0.01	6.3
42	5/9/07 - 5/10/07	0.03	0.00	2.3
43	5/11/07 - 5/14/07	1.36	0.13	9.2
44	5/16/07 - 5/24/07	1.42	0.10	7.0
45	5/27/07 - 5/30/07	0.23	0.01	3.3
46	6/3/07 - 6/6/07	3.07	0.14	4.7
47	6/7/07 - 6/9/07	0.71	0.00	0.6
48	6/11/07 - 6/17/07	2.48	0.04	1.6
49	6/18/07 - 6/20/07	0.67	0.01	1.2
50	6/21/07 - 6/22/07	0.07	0.00	1.8
51	6/23/07 - 6/26/07	0.51	0.01	1.7
52	6/27/07 - 7/2/07	0.89	0.05	5.0
53	7/3/07 - 7/6/07	0.54	0.01	1.5
54	7/7/07 - 7/8/07	0.00	0.00	13.4
55	7/10/07 - 7/12/07	1.01	0.01	0.9
56	7/18/07 - 7/20/07	0.22	0.00	1.5
57	7/23/2007	0.00	0.00	9.6
58	7/26/07 - 8/2/07	3.75	0.10	2.6
59	8/5/07 - 8/11/07	1.31	0.02	1.4
60	8/13/07 - 8/14/07	0.27	0.01	2.1
61	8/16/07 - 8/17/07	0.15	0.01	4.4
62	8/18/07 - 8/22/07	4.88	0.03	0.7
63	8/25/07 - 9/2/07	1.53	0.37	24.2

Blockston Sub-basin

Event #	Event time period	Precip, cm	Quickflow, cm	% Quickflow
1	5/31/06 - 6/3/06	2.75	0.04	1.5
2	6/4/06 - 6/6/06	0.04	0.01	19.0
3	6/7/06 - 6/10/06	0.98	0.00	0.4
4	6/12/06	0.70	0.00	0.4
5	6/13/06 - 6/15/06	0.11	0.00	2.5
6	6/19/06 - 6/21/06	1.65	0.02	1.0
7	6/23/06 - 7/1/06	18.61	2.34	12.5
8	7/2/06 - 7/3/06	0.18	0.00	0.3
9	7/4/06 - 7/10/06	5.08	0.24	4.7
10	7/12/06 - 7/16/06	1.44	0.01	0.8
11	7/18/06 - 7/20/06	0.25	0.01	2.3
12	7/22/06 - 7/24/06	3.41	0.18	5.3
13	7/25/06 - 7/27/06	0.03	0.00	6.9
14	7/28/06 - 7/31/06	0.50	0.00	0.9
15	8/7/06 - 8/9/06	2.08	0.02	1.0
16	8/10/06 - 8/13/06	0.04	0.01	28.9
17	8/18/06	0.00	0.00	42.3
18	8/20/06	0.15	0.00	0.7
19	8/28/06	0.07	0.00	0.9
20	8/29/06 - 9/3/06	8.43	0.10	1.2
21	9/4/06 - 9/8/06	3.42	0.11	3.2
22	9/10/06 - 9/11/06	0.01	0.00	0.0
23	9/13/06 - 9/19/06	3.59	0.12	3.3
24	9/20/06	0.00	0.00	0.0
25	9/24/06	0.17	0.00	1.0
26	9/25/06 - 10/1/06	2.86	0.02	0.7
27	10/2/06	0.00	0.00	0.0
28	10/5/06 - 10/9/06	5.25	0.61	11.6
29	10/11/06 - 10/15/06	1.72	0.39	22.7
30	10/17/06 - 10/18/06	2.05	0.07	3.2
31	10/19/06 - 10/25/06	0.78	0.12	15.4
32	10/27/06 - 10/31/06	3.47	0.52	15.0
33	11/2/06	0.25	0.00	0.5
34	11/3/06	0.00	0.00	0.0
35	11/7/06 - 11/10/06	2.82	0.31	10.8
36	11/12/06 - 11/14/06	2.99	0.26	8.9
37	11/15/06 - 11/20/06	1.72	0.27	15.7
38	11/22/06 - 11/29/06	3.20	1.09	34.2
39	11/30/06 - 12/3/06	0.11	0.01	5.1
40	12/4/06	0.03	0.00	0.0
41	12/7/06 - 12/8/06	0.02	0.00	26.1
42	12/13/06 - 12/16/06	0.15	0.01	6.1
43	12/19/06	0.002	0.003	**189.5**
44	12/22/06 - 12/29/06	3.23	0.40	12.5
45	12/30/06 - 1/3/07	3.86	0.86	22.3
46	1/5/07 - 1/11/07	4.69	1.87	39.9
47	1/14/07	0.02	0.00	23.7
48	1/18/07 - 1/20/07	0.28	0.01	1.9
49	1/21/07 - 1/26/07	0.64	0.03	4.4
50	1/28/07 - 1/31/07	0.08	0.02	23.8
51	2/1/07 - 2/5/07	0.45	0.05	10.2
52	2/6/07 - 2/8/07	0.08	0.00	3.4
53	2/13/07 - 2/18/07	3.20	0.71	22.1
54	2/20/07 - 2/23/07	0.56	0.15	26.6
55	2/25/07 - 2/28/07	1.75	0.37	21.4
56	3/1/07 - 3/6/07	1.51	0.49	32.6
57	3/7/07 - 3/9/07	0.12	0.00	0.0
58	3/11/07	0.05	0.01	15.3
59	3/15/07 - 3/21/07	6.63	2.12	32.0
60	3/23/07 - 3/26/07	0.21	0.03	13.6
61	3/27/07 - 3/29/07	0.02	0.01	40.4
62	3/30/07	0.01	0.00	0.0
63	4/1/07 - 4/2/07	0.13	0.00	0.0
64	4/4/07 - 4/10/07	2.00	0.32	16.0
65	4/11/07 - 4/13/07	2.38	0.14	6.0
66	4/14/07 - 4/22/07	10.61	6.70	63.2
67	4/25/07	0.30	0.00	1.5
68	4/26/07 - 4/30/07	0.74	0.04	5.2
69	5/5/07 - 5/9/07	0.16	0.01	6.0
70	5/11/07 - 5/14/07	1.36	0.06	4.4
71	5/16/07 - 5/19/07	1.40	0.05	3.4
72	5/20/07	0.03	0.00	0.0
73	5/27/07 - 5/30/07	0.45	0.03	5.7
74	6/3/07 - 6/7/07	3.51	0.09	2.6
75	6/8/07 - 6/10/07	0.26	0.01	3.9
76	6/11/07 - 6/16/07	2.47	0.03	1.3
77	6/17/06 - 6/18/07	0.02	0.00	18.6
78	6/19/07 - 6/20/07	0.67	0.01	1.5
79	6/21/07 - 6/22/07	0.07	0.00	0.4
80	6/23/07 - 6/26/07	0.51	0.00	0.6
81	6/27/07 - 7/3/07	1.59	0.03	1.8
82	7/4/07 - 7/6/07	0.50	0.00	0.3
83	7/7/07	0.00	0.00	0.0
84	7/10/07 - 7/12/07	2.47	0.05	2.1
85	7/18/07 - 7/20/07	0.30	0.00	0.9
86	7/23/07	0.01	0.00	3.6
87	7/26/07	0.20	0.00	0.3
88	7/27/07 - 7/31/07	1.66	0.12	7.4
89	8/5/07 - 8/7/07	0.54	0.00	0.5
90	8/9/07 - 8/14/07	1.03	0.01	0.9
91	8/16/07 - 8/17/07	0.15	0.00	0.4
92	8/18/07 - 8/23/07	4.09	0.06	1.4
93	8/25/07 - 8/29/07	2.58	0.10	3.7

North Forge Sub-basin

Event No.	Event Period	Precip, cm	Quickflow, cm	% Quickflow
1	6/1/06 - 6/7/07	2.71	0.10	3.56
2	6/8/06 - 6/10/06	0.98	0.01	0.60
3	6/12/06 - 6/18/06	0.81	0.03	3.45
4	6/19/06 - 6/21/06	1.65	0.02	1.52
5	6/23/06 - 7/2/06	18.79	6.27	33.36
6	7/3/06 -7/11/06	5.08	0.36	7.04
7	7/12/06 - 7/20/06	1.69	0.04	2.52
8	7/22/06 - 7/31/06	3.95	0.37	9.44
9	8/7/06 - 8/8/06	2.08	0.00	0.13
10	8/10/06 - 8/15/06	0.04	0.01	25.45
11	8/18/06 - 8/21/06	0.15	0.02	14.63
12	8/28/06	0.07	0.00	0.46
13	8/29/06 - 9/3/06	8.43	0.14	1.63
14	9/4/06 - 9/8/06	3.42	0.09	2.61
15	9/10/06 - 9/11/06	0.01	0.00	33.07
16	9/13/06 - 9/20/06	3.42	0.10	2.96
17	9/24/06 - 9/25/06	0.24	0.00	0.72
18	9/26/06 - 10/3/06	2.79	0.01	0.29
19	10/5/06 - 10/9/06	5.25	0.27	5.15
20	10/11/06 - 10/15/06	1.72	0.15	8.43
21	10/17/06 - 10/25/06	2.82	0.33	11.78
22	10/27/06 - 11/2/06	3.71	0.28	7.53
23	11/3/06 - 11/6/06	0.0025	0.0033	**132.84**
24	11/7/06 - 11/10/06	2.97	0.24	8.17
25	11/12/06 - 11/14/06	2.99	0.36	11.90
26	11/15/06 - 11/20/06	1.72	0.24	13.90
27	11/22/06 - 12/10/06	3.36	0.79	23.54
28	12/13/06 - 12/19/06	0.16	0.01	6.45
29	12/22/06 - 12/30/06	3.24	0.22	6.80
30	12/31/06 - 1/4/07	3.86	0.53	13.82
31	1/5/07 - 1/6/07	0.81	0.01	1.52
32	1/7/07 - 1/17/07	3.62	1.31	36.28
33	1/18/07 - 1/20/07	0.28	0.01	2.71
34	1/21/07 - 1/25/07	0.63	0.01	1.38
35	1/26/07 - 1/30/07	0.09	0.01	12.00
36	2/1/07 - 2/6/07	0.43	0.07	16.83
37	2/7/07 - 2/8/07	0.09	0.00	3.77
38	2/13/07 - 2/18/07	3.00	0.42	13.93
39	2/20/07 - 2/23/07	0.56	0.07	13.26
40	2/25/07 - 2/28/07	1.95	0.24	12.51
41	3/1/07 - 3/11/07	1.85	0.35	19.13
42	3/15/07 - 3/29/07	6.92	1.80	26.00
43	3/30/07 - 4/2/07	0.14	0.00	2.68
44	4/4/07 - 4/10/07	1.24	0.12	9.76
45	4/11/07 - 4/25/07	13.49	5.06	37.51
46	4/26/07 - 4/30/07	0.74	0.02	3.09
47	5/5/07 - 5/10/07	0.16	0.01	6.32
48	5/11/07 - 5/14/07	1.36	0.04	2.62
49	5/16/07 - 5/25/07	1.42	0.03	2.15
50	5/27/07 - 5/30/07	0.46	0.02	3.86
51	6/3/07 - 6/7/07	3.51	0.07	2.03
52	6/8/07 - 6/9/07	0.26	0.00	0.00
53	6/11/07 - 6/16/07	2.47	0.11	4.56
54	6/17/07 - 6/18/07	0.02	0.00	30.50
55	6/19/07 - 6/21/07	0.71	0.01	1.07
56	6/22/07 - 6/24/07	0.18	0.00	0.72
57	6/25/07 - 6/26/07	0.36	0.00	0.48
58	6/27/07 - 7/1/07	0.81	0.03	3.64
59	7/3/07 - 7/5/07	0.57	0.02	3.95
60	7/6/07 - 7/7/07	0.01	0.00	0.00

Beaverdam Sub-basin

Event No.	Event Period	Precip, cm	Quickflow, cm	% Quickflow
1	5/31/06 - 6/7/06	2.79	0.05	1.88
2	6/8/06 - 6/10/06	0.98	0.03	3.10
3	6/12/06 - 6/15/06	0.81	0.07	8.84
4	6/19/06 - 6/21/06	1.65	0.01	0.66
5	6/23/06 - 7/3/06	18.79	5.78	30.77
6	7/4/06 - 7/16/06	6.52	0.64	9.88
7	7/18/06 - 7/20/06	0.25	0.03	10.38
8	7/22/06 - 7/24/06	3.41	0.41	12.14
9	7/25/06 - 7/27/06	0.03	0.01	18.32
10	7/28/06 - 7/31/06	0.50	0.03	5.88
11	8/7/06 - 8/9/06	2.08	0.11	5.15
12	8/10/06 - 8/17/06	0.04	0.36	**975.32**
13	8/18/06 - 8/22/06	0.15	0.15	96.33
14	8/28/06 - 9/3/06	7.88	0.17	2.14
15	9/4/06 - 9/7/06	3.60	0.10	2.88
16	9/10/06 - 9/12/06	0.01	0.06	**656.35**
17	9/13/06 - 9/16/06	3.38	0.02	0.67
18	9/17/06	0.01	0.00	0.00
19	9/19/06	0.02	0.01	54.84
20	9/20/06 - 9/26/06	0.25	0.13	51.42
21	9/27/06 - 9/29/06	2.32	0.00	0.13
22	9/30/06 - 10/3/06	0.47	0.03	5.70
23	10/5/06 - 10/8/06	5.25	0.18	3.43
24	10/9/06	0.00	0.00	0.00
25	10/11/06 - 10/14/06	1.72	0.02	0.90
26	10/17/06 - 10/18/06	2.05	0.02	0.75
27	10/19/06 - 10/21/06	0.77	0.02	2.61
28	10/22/06 - 10/24/06	0.00	0.02	**791.69**
29	10/27/06 - 10/30/06	3.47	0.19	5.38
30	11/2/06	0.25	0.01	4.71
31	11/3/06	0.02	0.00	0.00
32	11/7/06 - 11/10/06	2.87	0.12	4.01
33	11/12/06 - 11/15/06	3.00	0.13	4.43
34	11/16/06 - 11/20/06	1.71	0.06	3.23
35	11/22/06 - 12/1/06	3.26	0.36	10.95
36	12/2/06 - 12/5/06	0.09	0.00	4.27
37	12/7/06	0.02	0.01	56.79
38	12/13/06 - 12/16/06	0.15	0.01	4.76
39	12/19/06	0.002	0.005	**265.93**
40	12/22/06 - 12/24/06	1.50	0.01	0.61
41	12/25/06 - 12/27/06	1.73	0.05	2.98
42	12/28/06	0.00	0.00	0.00
43	12/30/06 - 1/4/07	3.86	0.49	12.72
44	1/5/07 - 1/6/07	0.74	0.01	0.90
45	1/7/07 - 1/16/07	3.62	0.90	24.82
46	1/18/07 - 1/19/07	0.28	0.00	0.47
47	1/21/07 - 1/23/07	0.61	0.00	0.66
48	1/24/07 - 1/25/07	0.03	0.00	14.48
49	1/26/07	0.00	0.00	0.00
50	1/28/07	0.06	0.01	10.53
51	1/29/07 - 1/30/07	0.02	0.00	26.21
52	2/1/07 - 2/5/07	0.42	0.01	2.78
53	2/6/07 - 2/8/07	0.11	0.01	6.72
54	2/13/07 - 2/18/07	2.74	0.20	7.27
55	2/20/07 - 2/24/07	0.56	0.02	3.46
56	2/25/07 - 2/28/07	1.95	0.19	9.69
57	3/1/07 - 3/5/07	1.31	0.37	28.12
58	3/7/07	0.07	0.00	6.99
59	3/8/07 - 3/9/07	0.05	0.00	1.60
60	3/11/07	0.05	0.00	1.17
61	3/15/07 - 3/19/07	6.43	0.62	9.71
62	3/23/07 - 3/26/07	0.21	0.00	1.82
63	3/27/07 - 3/28/07	0.02	0.01	38.41
64	3/30/07	0.01	0.00	0.00
65	4/1/07	0.07	0.00	2.66
66	4/2/07	0.06	0.00	0.00
67	4/4/07 - 4/8/07	2.27	0.17	7.66
68	4/11/07 - 4/13/07	2.43	0.05	2.26
69	4/14/07 - 4/22/07	10.72	2.79	26.07
70	4/25/07 - 4/26/07	0.32	0.01	2.26
71	4/27/07 - 4/29/07	0.73	0.01	0.98
72	5/5/07 - 5/7/07	0.14	0.01	4.71
73	5/9/07	0.02	0.00	3.46
74	5/10/07 - 5/14/07	1.36	0.04	2.89
75	5/16/07 - 5/19/07	1.40	0.01	0.72
76	5/20/07 - 5/23/07	0.03	0.01	50.06
77	5/27/07 - 5/30/07	0.52	0.00	0.74
78	6/3/07 - 6/4/07	2.82	0.01	0.42
79	6/5/07 - 6/7/07	0.66	0.00	0.70
80	6/8/07 - 6/10/07	0.26	0.00	0.83
81	6/11/07 - 6/16/07	2.47	0.02	1.00
82	6/17/07 - 6/18/07	0.02	0.00	4.19
83	6/19/07 - 6/20/07	0.67	0.01	0.87
84	6/21/07 - 6/26/07	0.58	0.00	0.81
85	6/27/07 - 7/2/07	1.97	0.01	0.39
86	7/3/07 - 7/4/07	0.48	0.00	0.29
87	7/5/07 - 7/6/07	0.09	0.00	1.08
88	7/7/07	0.00	0.00	0.00
89	7/10/07 - 7/12/07	3.92	0.02	0.46
90	7/18/07	0.01	0.00	45.03
91	7/19/07 - 7/20/07	0.29	0.00	0.04
92	7/23/07	0.01	0.00	28.14
93	7/26/07	0.20	0.00	1.03
94	7/27/07 - 8/2/07	1.66	0.22	13.28
95	8/5/07	0.31	0.00	0.64
96	8/6/07 - 8/7/07	0.23	0.00	1.30
97	8/9/07 - 8/16/07	1.12	0.01	0.76
98	8/17/07 - 8/18/07	0.07	0.00	0.99
99	8/19/07 - 8/22/07	4.79	0.01	0.11
100	8/25/07 - 8/29/07	1.30	0.01	0.59

Willow Grove Sub-basin (All-hydric)

Event No.	Event Period	Precip, cm	Quickflow, cm	% Quickflow
1	8/11/06	0.00	0.00	0.00
2	8/18/06 - 8/20/06	0.15	0.00	2.21
3	8/28/06 - 9/3/06	8.49	0.13	1.54
4	9/4/06 - 9/6/06	3.41	0.05	1.37
5	9/7/06 - 9/9/06	0.00	0.05	1222.00
6	9/10/06 - 9/14/06	2.17	0.04	1.94
7	9/15/06 - 9/20/06	1.26	0.03	2.15
8	9/24/06 - 9/25/06	0.24	0.00	1.41
9	9/26/06 - 10/1/06	2.79	0.00	0.14
10	10/2/06	0.00	0.00	0.00
11	10/5/06 - 10/12/06	6.97	0.07	0.98
12	10/14/06	0.00	0.00	79.24
13	10/17/06 - 10/25/06	2.82	0.11	4.03
14	10/27/06 - 11/5/06	3.72	0.12	3.17
15	11/7/06 - 11/10/06	2.88	0.15	5.21
16	11/12/06 - 11/14/06	2.99	0.31	10.27
17	11/15/06 - 11/20/06	1.72	0.22	12.50
18	11/22/06 - 12/4/06	3.35	0.65	19.55
19	12/7/06 - 12/10/06	0.02	0.01	87.72
20	12/13/06 - 12/20/06	0.16	0.03	21.95
21	12/22/06 - 12/23/06	1.50	0.02	1.53
22	12/24/06 - 12/30/06	1.74	0.06	3.51
23	12/31/06 - 1/4/07	3.86	0.23	6.03
24	1/5/07 - 1/6/07	0.86	0.01	1.11
25	1/7/07 - 1/17/07	3.62	0.79	21.78
26	1/18/07 - 1/20/07	0.28	0.01	2.21
27	1/21/07 - 1/25/07	0.63	0.01	1.34
28	1/26/07 - 1/28/07	0.07	0.02	24.39
29	1/29/07 - 1/30/07	0.02	0.00	17.67
30	2/1/07 - 2/4/07	0.45	0.03	5.68
31	2/6/07 - 2/10/07	0.08	0.01	14.93
32	2/13/07 - 2/18/07	2.76	0.23	8.36
33	2/20/07 - 2/23/07	0.56	0.03	4.63
34	2/25/07 - 2/28/07	1.95	0.07	3.70
35	3/1/07 - 3/7/07	1.38	0.17	12.68
36	3/8/07 - 3/9/07	0.05	0.00	0.00
37	3/11/07 - 3/12/07	0.05	0.00	7.44
38	3/15/07 - 3/21/07	4.78	0.82	17.24
39	3/23/07 - 3/25/07	0.21	0.01	3.87
40	3/27/07 - 3/29/07	0.02	0.04	153.34
41	3/30/07 - 4/1/07	0.07	0.00	4.07
42	4/2/07	0.06	0.00	0.00
43	4/4/07 - 4/8/07	1.71	0.08	4.66
44	4/11/07 - 4/26/07	10.74	3.78	35.21
45	4/27/07 - 5/4/07	0.73	0.02	2.58
46	5/5/07 - 5/6/07	0.14	0.00	0.00
47	5/9/07 - 5/14/07	1.38	0.02	1.68
48	5/16/07 - 6/1/07	1.87	0.07	3.73
49	6/3/07 - 6/10/07	3.78	0.06	1.56
50	6/11/07 - 6/15/07	2.45	0.00	0.11
51	6/16/07 - 6/22/07	0.77	0.01	0.79
52	6/23/07 - 6/25/07	0.50	0.00	0.24
53	6/26/07 - 7/2/07	1.01	0.01	0.77
54	7/3/07 - 7/4/07	0.48	0.00	0.53
55	7/5/07 - 7/8/07	0.10	0.00	1.61
56	7/10/07 - 7/12/07	1.51	0.03	1.83
57	7/18/07	0.00	0.00	67.62
58	7/19/07 - 7/22/07	0.15	0.01	4.83
59	7/23/07	0.00	0.00	0.00
60	7/26/07 - 7/27/07	0.34	0.01	2.06
61	7/28/07 - 7/30/07	1.51	0.00	0.12
62	7/31/07 - 8/1/07	0.01	0.00	0.51
63	8/5/07 - 8/7/07	0.54	0.00	0.30
64	8/9/07 - 8/17/07	1.19	0.04	3.58
65	8/18/07 - 8/23/07	4.79	0.03	0.67
66	8/25/07 - 8/28/07	1.57	0.01	0.91
67	8/29/07	0.04	0.00	0.00

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