ABSTRACT

Title of dissertation: EVALUATION OF AGRICULTURAL NUTRIENT
                           REDUCTIONS IN RESTORED RIPARIAN BUFFERS

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Efforts to restore the Chesapeake Bay have focused on reducing agricultural

nutrient losses. In particular, riparian buffer restoration has been an important component

of nutrient reduction strategies, and one program used extensively to restore riparian

vegetation on agricultural land is the Conservation Reserve Enhancement Program

(CREP). I evaluated the effect of CREP on water quality on the Delmarva Peninsula by

measuring groundwater nutrients under restored buffers on two farms, monitoring stream

baseflow in 30 small watersheds (or subbasins), and monitoring stream stormflow in two

subbasins. On the farms, nitrate concentrations were lower in the restored buffers than in

the non-buffered sites, suggesting that buffer restoration was successful in filtering

groundwater nitrate. In groundwater under a 7 year old CREP buffer, dilution by

infiltration of rainwater accounted for 56% of the total nitrogen reduction, and

denitrification accounted for 15 to 30%. At the watershed scale, CREP restored 1 to 30%

of total streamline in 15 agriculturally-dominated subbasins in the Choptank River.

However, I did not detect differences in nitrogen concentrations between these subbasins

based on the amount of buffer restoration. Nitrogen concentrations actually increased in

most of the streams since previous monitoring before restoration; therefore, buffers may

not be extensive enough to have measurable affects on baseflow water quality. However, comparison of stormflow between two subbasins revealed significant nutrient differences. Total buffered streamline was greater and more widely distributed in Blockston than in Norwich subbasin. The amount and distribution of CREP may have influenced the stormflow nutrient yields, which were 2 times higher in Norwich versus Blockston. Lastly, I reviewed 20 years of stream monitoring data from German Branch subbasin in the context of all agricultural management practices implemented in the basin. A decade after management, I detected a 33% decrease in phosphorus concentrations in stream baseflow, but no significant changes in nitrogen concentrations. However, the rate of increase of 0.14 mg N L^{-1} yr^{-1} prior to management did not continue to present-day baseflow conditions and may have been suppressed by management practices. While these results are somewhat encouraging, complete understanding of watershed-scale effects of riparian buffers will require further interdisciplinary study.

EVALUATION OF NUTRIENT REDUCTIONS IN
RESTORED RIPARIAN BUFFERS

by

Adrienne J. Sutton

Dissertation submitted to the Faculty of the Graduate School of the
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DEDICATION

This work, the culmination of many years of education is dedicated to my grandmother, Kathryn Bush Tullis, who I miss but who lives in every book I read and every new discovery I make.

ACKNOWLEDGEMENTS

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INTRODUCTION

Humans and coastal ecosystems

Human activity on land has altered downstream coastal ecosystems around the

world, not only affecting the function of habitats for other species but impairing the

natural resources vital to our survival. Nearly half of the land in the contiguous United

States has been converted to cultivation and livestock grazing, which has contributed to

the loss of 50 percent of the country's wetlands and 70 percent of the riparian forests

(Turner et al. 1998). Humans have doubled the rate of reactive nitrogen (N) entering the

N cycle (Vitousek et al. 2002) through the conversion of organic N in fossil fuels to

nitrogen oxides (NO_x) and the production of ammonia (NH_3) fertilizer in the Haber-

Bosch process. More than half the world's human population consumes food produced

using N fertilizer from this process (Galloway and Cowling 2002). The global

phosphorus (P) cycle has also changed by the mining and redistribution of P rich

materials, as fertilizer, on the landscape. Nutrient enrichment of large rivers occurs as

human populations, and their associated agriculture and human waste, increase in the

watersheds (Peierls et al. 1991). Excess N and P inputs to coastal waters is widespread

(Howarth et al. 1995, Beman et al. 2005, Elmgren 1989) and often affects

biogeochemical cycles and species composition of the ecosystems (D'Elia 1987,

Malakoff 1998, Conley et al. 2000). Reducing the amount of nutrients leaking from

human activities on land is crucial to the health of our estuaries and coastal bays.

Eutrophication and the resulting ecosystem degradation is a global problem affecting

estuaries and coastal systems such as the Gulf of Mexico (Malakoff 1998), the Baltic Sea (Elmgren 1989), and southeast Asia ( ).

Chesapeake Bay is an estuary with nearly a century of intensive anthropogenic disturbance contributing to recent ecosystem degradation. Chesapeake Bay is the largest and one of the most biologically diverse estuaries in North America. In the early 1600's when Europeans were colonizing the region, they witnessed extensive meadows of seagrass, massive oyster reefs that posed a threat to navigation, and an abundance of fish and marine life. These resources of the bay and its tributaries provided high biological productivity for European settlers and have defined the tradition and cultures of human populations around the bay for over 300 years (CBP 2000). This productivity has contributed to supporting an increasing human population, along with increasing agriculture and industry around urban centers. Unfortunately, this human success often fouls the same environment that is supporting the human population. Point sources, from industry and urbanization, contribute approximately thirty percent of the nutrient load to the Chesapeake Bay (Boynton et al. 1995). Non-point sources from plant and animal agriculture dominate nutrient inputs at around sixty percent, and atmospheric deposition within the airshed contributes another ten percent (Boynton et al. 1995). Eutrophication has resulted in extensive algal blooms, oxygen depletion in bottom waters, increased turbidity, loss of submerged aquatic vegetation, and loss of habitat (Carpenter et al. 1969, Orth and Moore 1983, Officer et al. 1984, Seliger et al. 1985, Fisher et al. 1988).

Important to Chesapeake Bay restoration is the widespread concern for the bay's biological health and natural resources. Early scientific evidence of ecosystem degradation and political support led to the formation of the Chesapeake Bay Program in

1984 and its current large-scale restoration effort (Malone 1993). Excess nutrients from

anthropogenic land use throughout the 167 000 km^2 watershed represent the bay's most

important pollution problem and a challenge to improving water quality (CBF 2001).

Restoration of riparian buffers is one of several solutions proposed by the Chesapeake

Bay Program to trap agricultural nutrients in the landscape before entering streams

draining into the bay.   This management decision was based on twenty-five years of

research, which revealed that elevated groundwater nitrate (NO_3) is reduced nearly

completely under riparian buffers (Fig 1-1) and evidence for substantial ability to trap

sediment-bound P during runoff events (Peterjohn and Correll 1984, Magette et al. 1989).
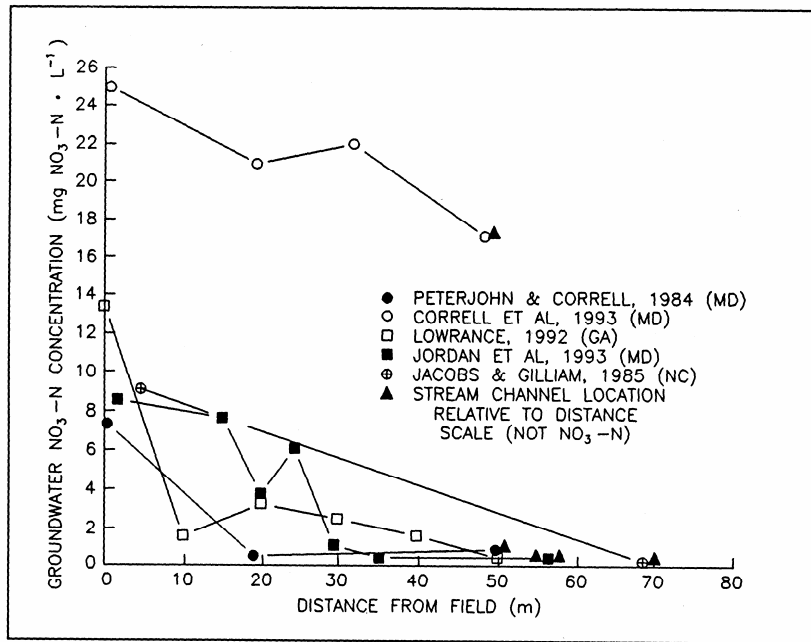
Figure 1-1. Nitrate concentrations in groundwater under established riparian forests in the
Coastal Plain region of the US east coast. In all 5 studies, groundwater nitrate
concentrations decrease from the agricultural field edge to the stream (represented by a
triangle). From Lowrance et al. 1997.

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Riparian Zones

Background

The word "riparian" comes from the Latin *rip*, meaning bank of a stream. Lowrance et al. (1985) defines a riparian ecotone as a complex assemblage of organisms and their environment existing adjacent to flowing water. A term commonly used for this unique environment is riparian buffer because of its role at the land-water interface as a natural filter of water moving over and through the land into nearby streams. This ecotone's role is especially important adjacent to land highly impacted by human use and disturbance (e.g., agriculture or high density urban land uses); riparian buffers may have the potential to minimize human effects before contaminated water enters streams.

Riparian buffers serve a variety of different roles and processes in the natural and disturbed environment (Lowrance et al. 1985, Osborne and Kovacic 1993, Hill 1996, Fennessy and Cronk 1997, Lowrance et al. 1997, Naiman et al. 2005). Buffers contribute to landscape diversity, especially in many coastal plain areas where they provide a break in the pattern of row crops, pastures, and upland pine forests. Riparian ecotones often consist of an abundance and high diversity of plants and animals, making them a critical wildlife habitat. This habitat is not restricted to the land; old trees in the riparian forest will fall, some into the adjacent stream providing woody debris. Woody debris is known to create important habit for stream life and is important in stream morphology by dissipating water flow velocity and creating pools. Streamside vegetation shades and cools the water, which would otherwise be uninhabitable for many organisms at high temperatures and low oxygen levels characteristic of summer. During storm events, riparian buffers dissipate runoff energy as overland flow moves over the soils and

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vegetation. This serves the process of sediment trapping, which is especially important in

agricultural areas with the capacity of providing large sediment loads to waterways.

Sediment can also enter streams, rivers, and estuaries by bank erosion. The roots and

cover of established streamside vegetation stabilize the stream bank and reduce erosion

potential.

Nutrient filtering

The filtering role of riparian buffers is often cited as the basis for its nutrient

retention and removal capacity. Riparian buffers have the potential to reduce terrestrial

export of N and P in four processes: soil trapping during runoff events, denitrification in

groundwater, plant uptake, and rainwater dilution. Soil accumulation within the buffer

traps eroded soil and removes particle-borne phosphorus from surface runoff (Peterjohn

and Correll 1984, Lowrance et al. 1986, Cooper et al. 1987, Magette et al. 1989, Dillaha

et al. 1989, Vought et al. 1994). Nitrate is water-soluble and moves to streams primarily

via groundwater contribution to base flow but also in overland flow during storms. For

example, Magette et al. (1989) found that 9 m grass buffers reduce surface runoff N and

P up to 50%. In an established forest buffer, Peterjohn and Correll (1984) measured

larger nutrient reductions in surface runoff at 75% of N and 70% of P.

Denitrification in anoxic, carbon rich soils of riparian zones may be a dominant

process in removing elevated groundwater nitrate (NO_3) in agricultural landscapes.

Measurements of N removal in groundwater are consistent among many studies (e.g., Fig

1-1), ranging from 60 to nearly 100% (Lowrance et al. 1984, Peterjohn and Correll 1984,

Correll et al. 1992, Lowrance 1992, Jordan et al. 1993, Jacobs and Gilliam 1985). In

anoxic soils, the microbial process of denitrification can permanently remove nitrate as N_2 gas:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

In this process, nitrate is used by denitrifying bacteria as an alternate electron acceptor in the absence of oxygen. There have been increasing concerns that in some cases, denitrification does not go to completion resulting in N_2 gas but may result in the release of N_2O to the atmosphere (Groffman et al. 2000). As it rises into the stratosphere N_2O acts as a greenhouse gas and also contributes to depletion of the ozone layer. It appears that decreasing pH and the presence of some O_2 tend to decrease the rate of denitrification while increasing N_2O production relative to N_2, but other factors such as differences in the bacterial communities and bacterial enzyme production may also contribute to the relative amounts of denitrification end products (Knowles 1982, Zumft 1997). Ideally, denitrification results in NO_3 conversion to N_2, which accumulates in groundwater and is ultimately returned to the atmosphere. Microbial denitrification is a permanent removal of nitrate from groundwater, but it will only occur if there is a sufficient hydrologic connection between the NO_3-enriched subsurface groundwater flow and the riparian zone. If the contaminated groundwater does not flow through an anoxic zone of riparian soil, denitrification may not take place on a large scale. However, denitrification can take place in anoxic microenvironments and appear to play a significant role in soil denitrification overall, even in largely aerobic soils (Russell 1973, Knowles 1982). Typical denitrification rates in riparian buffers range from 30 to 40 kg N ha^{-1} yr^{-1} and rates as high as 295 kg ha^{-1} yr^{-1} have been recorded (Naiman and Decamps 1997, Naiman et al. 2005).

Plant uptake can be an important nutrient reduction process in riparian buffers. The deep roots of mature riparian vegetation will take up and assimilate nutrients into plant material if intercepting the groundwater flow. However, if the vegetation is not periodically harvested and removed, much of the biomass may return to downstream aquatic systems as organic N and P through tissue sloughing, litter production, plant senescence, and in the products of decomposition (Fennessy and Cronk 1997). For example, total N uptake by coastal plain riparian forests was estimated at 77 to 84 kg N ha^{-1} yr^{-1} with only an average of 20% of the N stored in woody tissue, and similarly, only 30% of total P uptake of 1.7 to 3.8 kg P ha^{-1} yr^{-1} uptake remained in woody tissue (Peterjohn and Correll 1984, Fail et al. 1986). In this case, the riparian vegetation is transforming the inorganic N and P into organic forms and slowing the fluxes from land to water.

Recharge of low nutrient precipitation through the buffer can also play a significant role in reducing groundwater N (Speiran et al. 1998). Nutrient reduction may still occur in buffers with limited ability for trapping soil runoff, denitrification, and plant uptake. Dilution of groundwater may be significant in agricultural landscapes where N-rich groundwater recharged from fertilized fields moves through wide buffers where low N rainwater recharges through unfertilized soils.

Groundwater flow

Hydraulic connectivity within riparian zones is important for nutrient reduction processes, especially denitrification and plant uptake. Lowrance et al. (1995) conducted a detailed review of potential hydrologic connection between riparian buffer systems and

groundwater flow in various hydrogeomorphic regions of the Delmarva Peninsula (Fig 1-2). The functions of riparian zones in similar regions can be assessed by grouping these regions by landforms and hydrologic characteristics. The three regions applicable to this study are well-drained uplands, poorly-drained lowlands, and poorly-drained uplands.
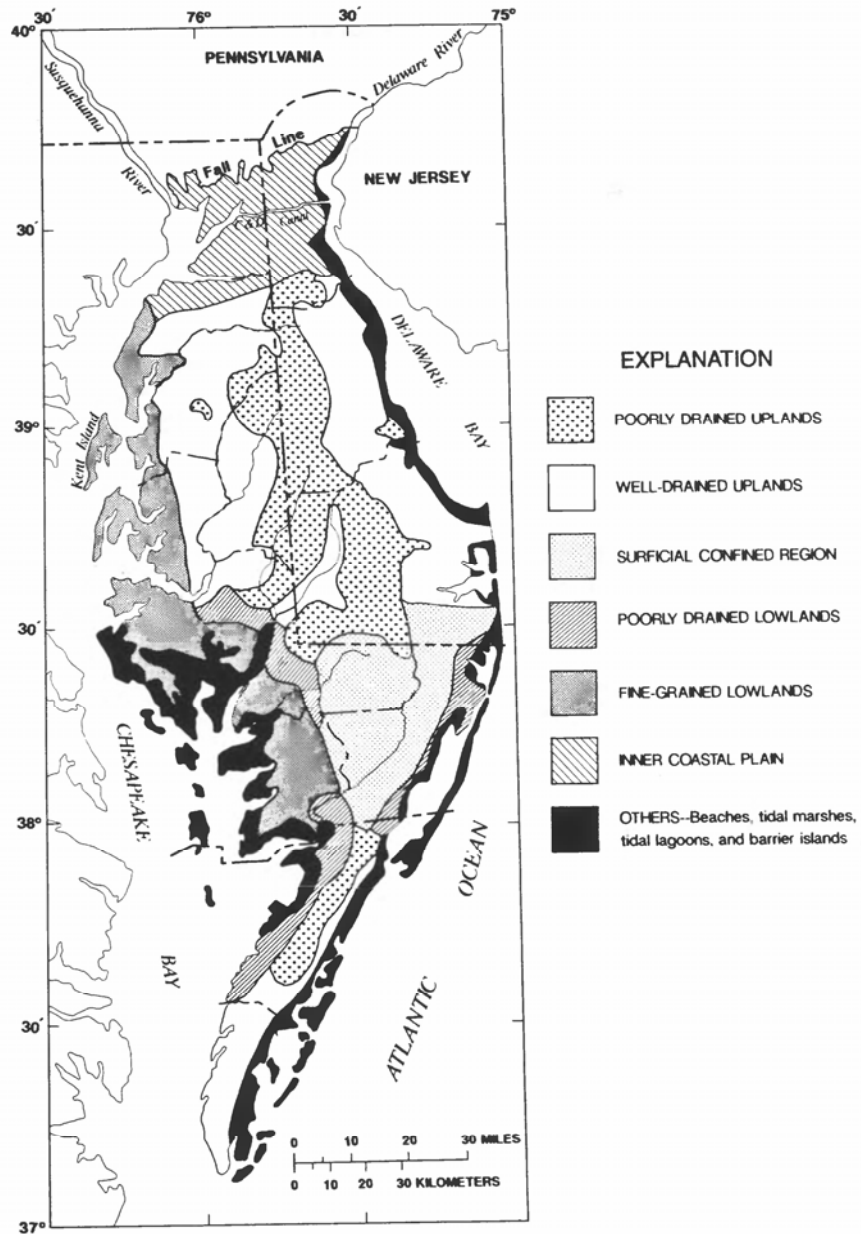
Fig 1-2. Hydrogeomorphic regions of the Delmarva Peninsula (from Hamilton et al. 1993).

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In the well-drained uplands, denitrification is possible in the short flow paths of young

groundwater originating in near-stream recharge areas connected to the riparian zone.

Denitrification may be an important process in these areas because these shorter flow

paths are the main source of baseflow to low order streams (Lowrance et al. 1997), and

low order streams account for most of the total streamlength as a whole. However, the

longer flow paths of older groundwater may bypass the riparian zone and discharge

directly through the stream bottom, or hyporheic zone (Fig 1-3). In this case, there may

be no hydrologic connection to anoxic, organic rich areas or roots of vegetation in the

riparian zone. Bohlke and Denver (1995) confirmed that in relatively thick surficial

aquifers of coastal plain watersheds of the Delmarva Peninsula, groundwater can flow
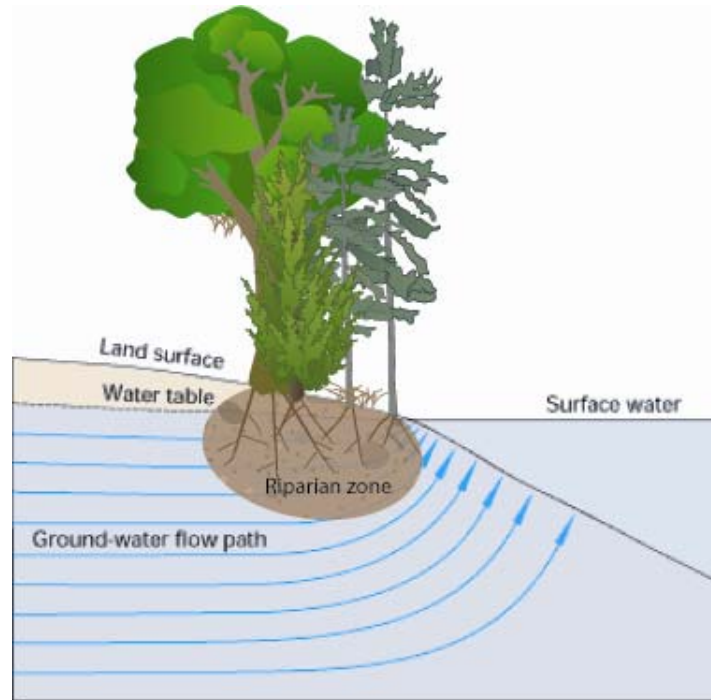
Figure 1-3. Cross section of subsurface groundwater. Flow paths vary in length and time
between groundwater recharge and discharge to the stream depending on
hydrogeomorphic characteristics of the region. On the Delmarva Peninsula, groundwater
flow paths in areas with deep aquicludes may bypass the riparian zone located in
shallower depths. Adapted from Winter et al. 1998.

beneath the riparian zone and nitrate discharges upward into streams relatively

unmodified. Poorly-drained lowlands in tidally influenced areas also have the potential

for denitrification if tidal movements are not too strong to restrict discharge from

groundwater and if groundwater flow paths move through the riparian zone. The poorly-

drained uplands in this region have the highest potential for denitrification (Lowrance et

al. 1997). In these areas, the water table is usually within 3 meters of the surface and is

often connected to the riparian zones.

Residence time in the upper several meters of the surficial aquifer is usually less

than 15-20 years (Dunkel et al. 1993, Bohlke and Denver 1995), and in most cases local

and recent land use effects may be detected in the groundwater chemistry. Other research

has indicated that in the Chesapeake Bay watershed overall, groundwater age varies from

modern (0-4 years) to 50 years old, and 75% of the groundwater is less than 10 years old

(Focazio et al. 1998). Samples from this study were collected from springs, which are

discharge points for converging groundwater flow paths and can be considered an

average of the water in an aquifer. If nutrient removal capabilities of riparian buffers

throughout the Chesapeake Bay watershed are comparable to past studies (e.g., Fig 1-1),

reductions in young groundwater entering streams may occur over relatively short time

spans. These ecotones are the last portion of the landscape the groundwater contacts

before entering the stream and when restored, may have the potential for immediate

improvement in water quality.

Contemporary research

The nutrient removal and retention capacity of riparian buffers has gained much

attention in the past fifteen to twenty years. This attention has paralleled the acknowledgement that anthropogenic nutrient loading to fresh waters, estuaries, and the coastal ocean has greatly impacted water quality and the organisms inhabiting these environments (Howarth et al.1996 and Vitousek et al. 1997). Scientific research on riparian buffers began with this interest in the late 1970's to mid 1980's with many pivotal studies in agriculturally dominated coastal plain areas (Asmussen et al. 1979, Schlosser and Karr 1981, Lowrance et al. 1984, Peterjohn and Correll 1984, Jacobs and Gilliam 1985, Cooper et al. 1987). These studies defined the nutrient retention and removal processes that can occur in riparian buffers and stressed the importance of this land-water interface, especially in watersheds dominated by agriculture. But these studies focused on individual established, or "naturally occurring", riparian zones. Very few studies have assessed the impact of riparian buffers at a watershed scale. Landscape models have produced mixed results on the importance of buffer location in the watershed, connectivity of buffers along stream corridors, and width of buffers on stream water quality (Omernik et al. 1981, Hunsaker and Levine 1995, Weller et al. 1998, Perry et al. 1999). US Department of Agriculture scientists have developed a Riparian Ecosystem Management Model (REMM) that predicts nutrient reductions in riparian buffers based on empirical data, estimations, or predictions from other models of hydrology, sediment and nutrient inputs, and vegetative growth (Stone et al. 2001, Altier et al. 2002). Some empirical studies have sought to assess the effect of established riparian forests on nutrient concentrations in streams but without consistent results (Johnson et al. 1997 and Norton and Fisher 2000). In general, the importance of riparian zones at the watershed scale is poorly understood.

Application of buffers in the Chesapeake watershed

Riparian buffers are one of the strategies to reduce agricultural nutrient inputs into aquatic ecosystems across the nation. The US Department of Agriculture established the Conservation Reserve Program (CRP) in 1985 in an attempt to encourage farmers to restore former riparian forest buffers on highly erodible agricultural land. The program provides financial incentives to farmers and ranchers to take land out of agricultural production and plant trees, grass, and other vegetation along streams. Early on in the program, the US Department of Agriculture (2001) concluded that areas funded by the CRP have experienced less soil erosion, improvements in air and water quality, and the addition of millions of acres of wildlife habitat.

As a part of its plan to reduce the nutrient load to the bay, the Chesapeake Bay Program established a nutrient subcommittee that later published a document reviewing the ability of streamside forest buffers to act as natural nutrient filters (Lowrance et al. 1997). Many of the principal authors were researchers involved in the early pivotal studies defining riparia as nutrient filters, and in their recommendations, these authors developed a three zone riparian buffer system consisting of a grassed portion for runoff control, a managed forest, and an undisturbed forest (Fig 1-4). This is viewed as the most ideal system for management purposes of the Chesapeake Bay Program and has the potential to control sediment runoff, decrease nutrient input, decrease stream temperature, and create critical wildlife habitat. Their consensus was that riparian buffers can help to remove sufficient amounts of groundwater nitrate from adjacent agricultural fields before flowing to streams (Fig 1-1), while acknowledging that this area of research requires more study. This report, along with other studies revealing the potential of riparian
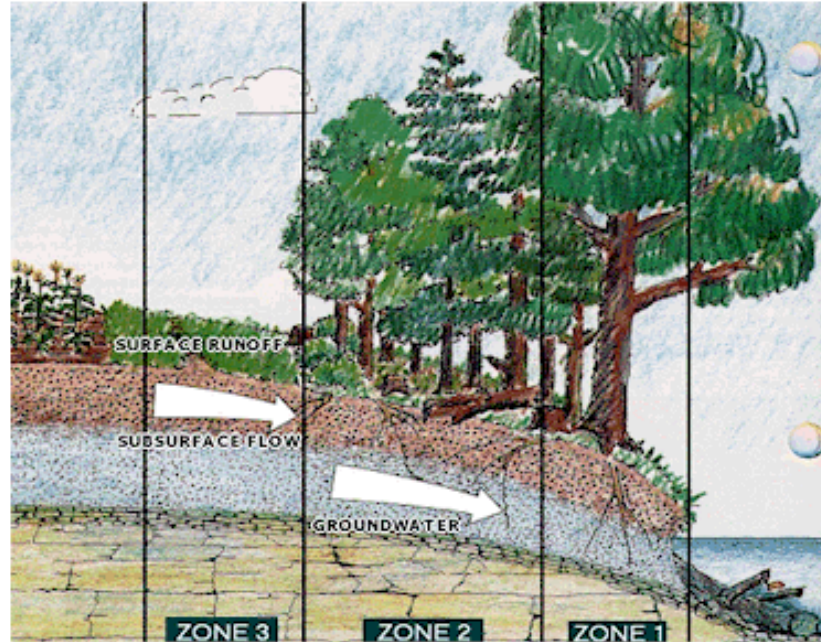
Figure 1-4. Example of a three zone managed riparian forest. Nutrient rich overland flow and groundwater from the agricultural landscape flows through a herbaceous filter strip, then a managed forest that is selectively harvested, and a permanent forest adjacent to the stream. From Chesapeake Bay Program.

buffers to reduce nutrient loads, may have contributed to expanding the CRP into the

Conservation Reserve Enhancement Program (CREP) in 1997. In October of 1997,

Maryland was the first state to establish a CREP. The program allows up to 100,000

acres of environmentally sensitive land along streams and rivers to be removed from

agricultural production and maintained as several kinds of riparian vegetation. Its

support came from the hope that riparian buffers will improve the water quality of

Chesapeake Bay by reducing the nutrient load to its tributaries.

There are questions in the scientific community as to whether implementation of

riparian buffers as a management practice (e.g., CRP and CREP) will be an effective way

to improve water quality. Specific sites are not considered on a case-by-case basis, and a

buffer is added when there is a willing farmer, not when the conditions are especially

conducive for a buffer to act as a nutrient filter. Riparian zones are also one of the last

areas in the landscape with the potential to filter nutrients before groundwater enters the

stream. Some argue more resources should focus on managing nutrients on agricultural

fields with Best Management Practices, BMPs, such as winter cover crops (Brinsfield and

Staver 1990). Nevertheless, much of the environmental management community in the

Chesapeake Bay support riparian buffers as a management tool, and CREP continues to

be a popular conservation practice on farms.

As of 2004, 6100 km of riparian zones have been restored in the Chesapeake Bay

watershed (Fig 1-5). The Chesapeake Executive Council has committed to restore and

conserve at least 70% of the streams and shoreline in the watershed (CBP 2003). This

leaves almost 42 000 km of streamline to be restored and a significant undertaking for

many years to come. Incomplete scientific knowledge on the capacity of restored

riparian buffers to meet nutrient reduction goals in the bay is not a reason to avoid

(a)   **(b)**
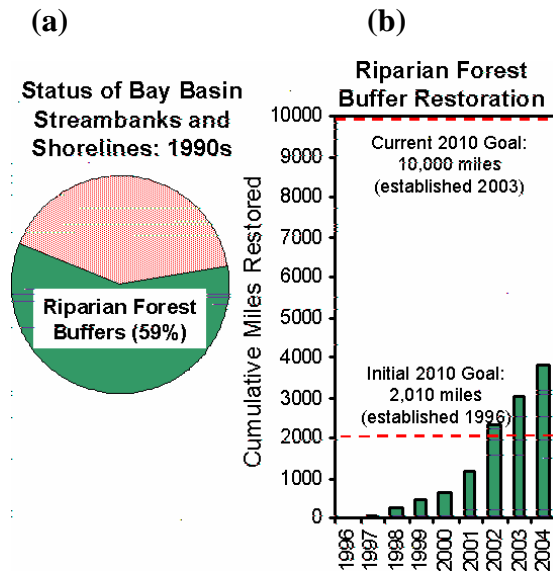
Figure 1-5. (a) Percentage of streamline buffered by riparian forests in the 1990s before
large restoration effort began in Chesapeake Bay watershed. Current goal is to restore an
additional 11% of streamline. (b) Yearly progress of miles of restored riparian buffers
and the 2010 goal. From Chesapeake Bay Program.

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making management decisions, but monitoring the outcome of the restoration can guide continuing efforts to meet nutrient goals. Scientists in the Chesapeake Bay region have the unique opportunity to measure the effects of restored riparian buffers at scales directly applicable to estuarine water quality in the natural environment.

Plot-scale research and watershed-scale restoration goals

Most research on the ability of riparian zones to buffer the impact of N and P inputs from agricultural landscapes has been done on established buffers. Established riparian zones have been preserved in their "naturally occurring" state while the surrounding land was converted to agriculture. Whether restored buffers have the same ability to reduce N in groundwater and P in runoff as demonstrated in established buffers has not been investigated in detail. If restored buffers possess connectivity to the flow paths of nutrient enriched groundwater and overland flow and acquire sufficient levels of soil organic carbon for biological processing of nutrients, the potential for similar reductions nay exist.

Past research has also focused on nutrient reduction in individual riparian zones at the plot scale. Here I use the term plot scale to describe the defined plots on experimental farm fields or transects through one area of riparian buffer. I define field scale as research taking place over an entire farm field and the surrounding buffers and define watershed scale as stream water quality research incorporating the processes occurring over the entire watershed. As part of the restoration plan for Chesapeake Bay, predictions of N and P reductions in CREP buffers are substantial (USDA 2004) and may be based on the large reductions measured in past plot-scale research. There is no

watershed scale data that confirms restoration of riparian buffers improve stream water quality. Nutrient budgets reveal that on average, only 25% of the total N inputs to watersheds in northeastern United States are exported in river flow (Boyer et al. 2002). Watersheds may already be inherently efficient at reducing N and P through in-stream biological processes, denitrification in the soils and stream, and burial of particulates in the landscape and in stream sediments (Fig 1-6). Whether further nutrient reductions are possible by restoring riparian buffers has not been investigated sufficiently at the watershed scale.

My research focuses on two questions:

(1) Do restored riparian buffers reduce groundwater N at similar levels as established buffers?

(2) Does restoration of riparian buffers reduce stream water N and P at a watershed scale?

I approached the first question by performing plot scale research in buffers at two individual farms (Chapter 4). I monitored groundwater nutrients in transects through four types of buffers: a 7 year old CREP buffer, a 20 year old CRP buffer, a >100 year old established buffer, and a non-buffered field edge. This study differs from past studies by the addition of restored buffers to the groundwater monitoring. The other portion of my research focuses on stream water monitoring during baseflow and stormflow and GIS analysis of restored buffers in 30 sub-watersheds (Chapters 2 and 3). The widespread implementation of CREP in the Choptank watershed (1000 hectares) has given me the opportunity to investigate differences in stream water quality between sub-watersheds with varying amounts of CREP. The timing of previous monitoring at these

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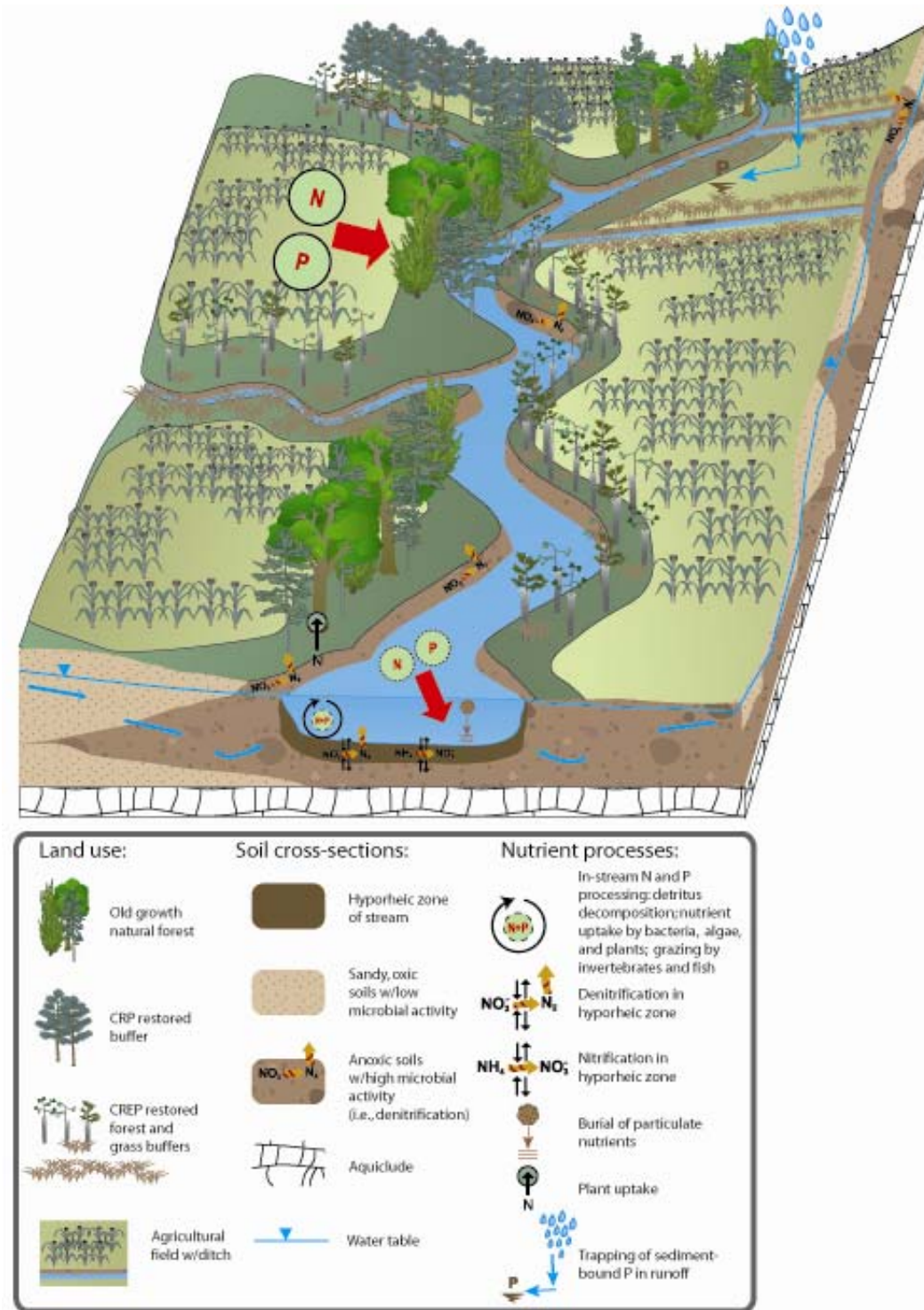
Figure 1-6. Nutrient processes at the watershed scale that interact with different land uses, soil types, and hydrology. Nutrients are reduced throughout the watershed by denitrification in anoxic soils, retained in riparian vegetation, cycled within the stream and hyporheic zone, and buried in the riparian buffers and stream sediments. Nutrient exported in the stream are typically 25% of nutrient inputs to the watershed.

same sites also allows me to compare stream water quality before any buffer restoration and current stream water quality after CREP implementation. More detailed water quality monitoring and application of BMPs in German Branch, a subbasin in the Choptank watershed, provides a case study of changes in stream water quality over time in relation to the restoration effort of recent years (Chapter 5). I seek to contribute a more complete understanding of the function of restored riparian buffers in managed agricultural landscapes at spatial scales directly relevant to nutrient reduction goals in Chesapeake Bay.

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Chapter 2

GROUNDWATER NUTRIENTS UNDER RESTORED AND ESTABLISHED FOREST BUFFERS IN THE OUTER COASTAL PLAIN OF MARYLAND

Abstract

Agriculture is a significant source of nutrients to Chesapeake Bay, and the effort to

reduce nutrient runoff and groundwater nitrate has led to restoration of riparian buffers

throughout the watershed. The Conservation Reserve Program (CRP) and Conservation

Reserve Enhancement Program (CREP) subsidize farmers to take stream-side land out of

agricultural production and plant riparian grasses and trees. I measured groundwater

nutrients in a >100 year old established riparian forest buffer, a 20 year old CRP pine

buffer, and a 7 year old CREP buffer on a farm in the fine-grained lowlands of the

Delmarva Peninsula. In general, nitrate (NO_3) decreases horizontally in the buffers from

the farm field to the stream and increases vertically with groundwater depth. In the

CREP buffer, dilution by infiltration of low nitrogen rainwater accounts for 56% of the

nitrate reduction, and denitrification accounts for 10 to 20 % of the nitrate reduction.

Denitrification was calculated by measuring excess nitrogen gas (N_2) in the groundwater

using the N_2/Ar technique, and even though there was excess N_2 throughout the buffer,

the low denitrification rate of 25 to 48 kg N ha^{-1} yr^{-1} measured in the CREP buffer may

due to N_2 loss in the groundwater through gas diffusion. The remaining NO_3 reduction

observed in the CREP buffer may be due to additional denitrification not captured by the

N_2/Ar method or by plant uptake in the riparian forest. Tidal creek and rainwater dilution

are substantial in all buffers and low groundwater discharge and long groundwater

retention times may contribute to the large NO_3 reductions. Comparison of low NO_3

concentrations in the restored buffers and higher NO_3 concentrations in a non-buffered

control site suggest that restoration of the buffers has been successful in filtering

groundwater nutrients and that groundwater discharged through the buffers is not

contributing a significant amount of NO_3 to the adjacent tidal creek.

Introduction

The restoration effort of Chesapeake Bay habitat and fisheries over the past two

decades has focused on reducing nutrient enrichment of water flowing into the bay.

Agriculture is the bay's largest source of nitrogen and phosphorus (Magnien et al. 1992)

and is often the center of nutrient reduction strategies and the resulting challenge to

preserve both farmers' livelihoods and the environment (Boesch et al. 2001, Staver and

Brinsfield 2001). One of the strategies is to provide financial incentives to farmers

implementing nutrient management and conservation practices. Progress has been made

in applying these Best Management Practices (BMPs) throughout the agricultural land in

the watershed, but the quantitative contribution that these practices will make to nutrient

reduction goals in Chesapeake Bay is not well understood.

Agriculture covers approximately one quarter of land use in the bay's 167 000

km^2 watershed and is more intensive in specific regions, such as diary farms in

southeastern Pennsylvania and poultry farms on the Delmarva Peninsula. Excess

nutrients from fertilizer applications and animal feeding operations have the potential to

flow from agricultural fields to adjacent streams in runoff during rain events (Beman

2005) or infiltrate into the surficial aquifer (Weil et al. 1990, Spalding and Exner 1993)

and gradually enrich streams over a long period of time.   Riparian zones may be the last

area of the landscape that runoff and subsurface groundwater flow through before entering the streams. Studies conducted in the early 1980s in agriculturally-dominated areas of the Atlantic coastal plain revealed that riparian forests reduced total nitrogen in surface runoff and subsurface groundwater by 67 to 89% (Lowrance et al. 1984, Peterjohn and Correll 1984, Jacobs and Gilliam 1985). Since then, numerous studies have investigated the nutrient filtering capability of riparian buffers.

Nutrient reduction occurs in riparian buffers through the following processes: soil trapping during overland flow, denitrification in subsurface groundwater, vegetative uptake, and rainwater dilution. Sedimentation occurs in grass and forest riparian buffers during runoff events, and sediment-bound nutrients may be reduced by over 50% as overland flow moves through the buffers (Peterjohn and Correll 1984, Magette et al. 1989). Soil particles deposit in riparian zones when vegetation encourages low-energy, sheet flow runoff and discourages the formation of high-energy, channelized flow from agricultural fields to adjacent streams (Naiman and Decamps 1997). The process often recognized as the primary mechanism of nitrate removal in riparian zones is denitrification, the microbial transformation of nitrate (NO_3) to nitrogen gas (N_2) in the presence of anoxic soils and a sufficient carbon source. Denitrification can be spatially and temporally variable and a standardized method to measure the process does not currently exist (Lowrance 1992, Hanson et al. 1994, Addy et al. 2002, Mookherji et al. 2003). Therefore, measurements in the literature vary but typically range from 30 to 40 kg N ha^{-1} yr^{-1} (Naiman and Decamps 1997). Vegetative uptake has been measured at similar rates but only 20 to 30% of the nutrient retention is permanently stored in the woody tissue of riparian forests (Peterjohn and Correll 1984, Fail et al. 1986). Finally, in

agricultural landscapes where groundwater is enriched in nitrogen, low nutrient rainwater that percolates through riparian soil may generate localized dilution within the buffer and has been shown to significantly contribute to nitrate reduction (Speiran et al. 1998, Spruill 2000, Maitre et al. 2003). This process is intensified in riparian buffers in the summer when evapotranspiration removes high-nutrient groundwater and the groundwater is recharged with low-nutrient rainwater. Considering this relatively short time span of intensive research, a large knowledge-base exists on the characteristics and function of mature, or established, riparian zones (Naiman et al. 2005).

Less understood is how these nutrient reduction processes perform in restored, or re-established, riparian buffers. Interest in restoring riparian zones as a management practice on farms gained momentum in the 1990s, and the US Department of Agriculture has helped support research in restored agricultural landscapes in Bear Creek watershed in central Iowa and in the headwaters of the Suwannee River watershed in southeastern Georgia. Studies in Bear Creek watershed suggest that restored grass buffers trap sediment and nutrients from surface runoff at similar amounts as observed in established riparian buffers. Six meter wide grass buffers removed 77% of the sediment in runoff and reduced total nitrogen and phosphorus by approximately 50% (Lee et al. 1998). Soil respiration at this site in re-established grass and forest riparian buffers was significantly higher than respiration rates in the adjacent agricultural fields, suggesting that these restored buffers are areas of high biological activity (Tufekcioglu et al. 2001). In the coastal plain of Georgia, an average denitrification rate of 68 kg N ha^{-1} yr^{-1} was measured in the subsurface groundwater under a restored riparian forest, which is comparable to rates in mature riparian forests (Lowrance et al. 1995). Research in the Georgia

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watershed has also revealed that a newly-restored buffer assimilated and removed significant amounts of nitrogen and phosphorus (Hubbard et al. 1998, Vellidis et al. 2003). The restored riparian forest, from year 1 to 8 after restoration, retained 66% of total phosphorus from the adjacent agricultural inputs and 59% of total nitrogen inputs, including 78% nitrate reduction attributed mostly to denitrification (Vellidis et al. 2003). These studies in demonstrations sites support the use of riparian grass and forest buffers as a nutrient management tool on farms.

Because of the realization that agriculture is contributing to nutrient enrichment of aquatic systems (Spalding and Exner 1993, Hamilton and Helsel 1995), restoration of riparian buffers on farms has become widespread in the US due to two conservation programs: the Conservation Reserve Program (CRP) and the Conservation Reserve Enhancement Program (CREP). CRP was introduced by the US Department of Agriculture in 1985 as a voluntary program that provides financial incentives for farmers to establish conservation practices on their agricultural land and originally focused on planting trees in highly erodible soils. In 1997, the program was expanded to the CREP and included financial incentives for taking land out of agricultural production and planting several kinds of riparian vegetation along ditches, streams, and rivers. Maryland was the first state to adopt a CREP and its specific goal is to protect water quality in Chesapeake Bay.

This chapter addresses the nutrient removal ability of two restored riparian forests implemented under the CRP and CREP in the coastal plain of Maryland. One field on the farm is buffered by a >100 year old established (or mature) forest, a 7 year old CREP forest buffer, and a 20 year old CRP forest buffer. I measured nutrients in the subsurface

groundwater in these buffers and also in a non-buffered control site on the farm. Substantial reductions, accounted for by estimates of denitrification and dilution, were observed in the restored buffers in comparison to the non-buffered site and at levels comparable to observations in established forests. This research suggests that nutrient reductions measured in established buffers and restoration demonstration sites may be applicable to the buffers restored under the CRP and CREP.

Methods

Study site

Radcliffe farm is located in the Maryland coastal plain of the Delmarva Peninsula on a tidal creek in the Little Choptank watershed (Fig 2-1). This low-lying region is underlain by the Kent Island Formation, an estuarine deposit of the middle-Wisconsin period, and the surficial sediments have the following hydrogeomorphic characteristics: fine-grained soils, shallow water table, and poor drainage (Owens and Denny 1979, Hamilton et al. 1993, Fig 2-2). The surficial aquifer in this region is often less than 5 meters thick (Owens and Denny 1979), and groundwater flow is likely to come into contact with the riparian zones near creeks and other discharge areas (Jordan et al. 1993, Lowrance et al. 1995). The upper soil profile of the agricultural fields on Radcliffe farm consists of moderately well to well drained soils of Mattapex and Matapeake series. The outer edges of the field where the established and restored riparian buffers are located have soils composed primarily of Keyport and Elkton silt loams (Table 2-1). Keyport silt loam is moderately well drained and not considered a hydric soil, whereas Elkton silt
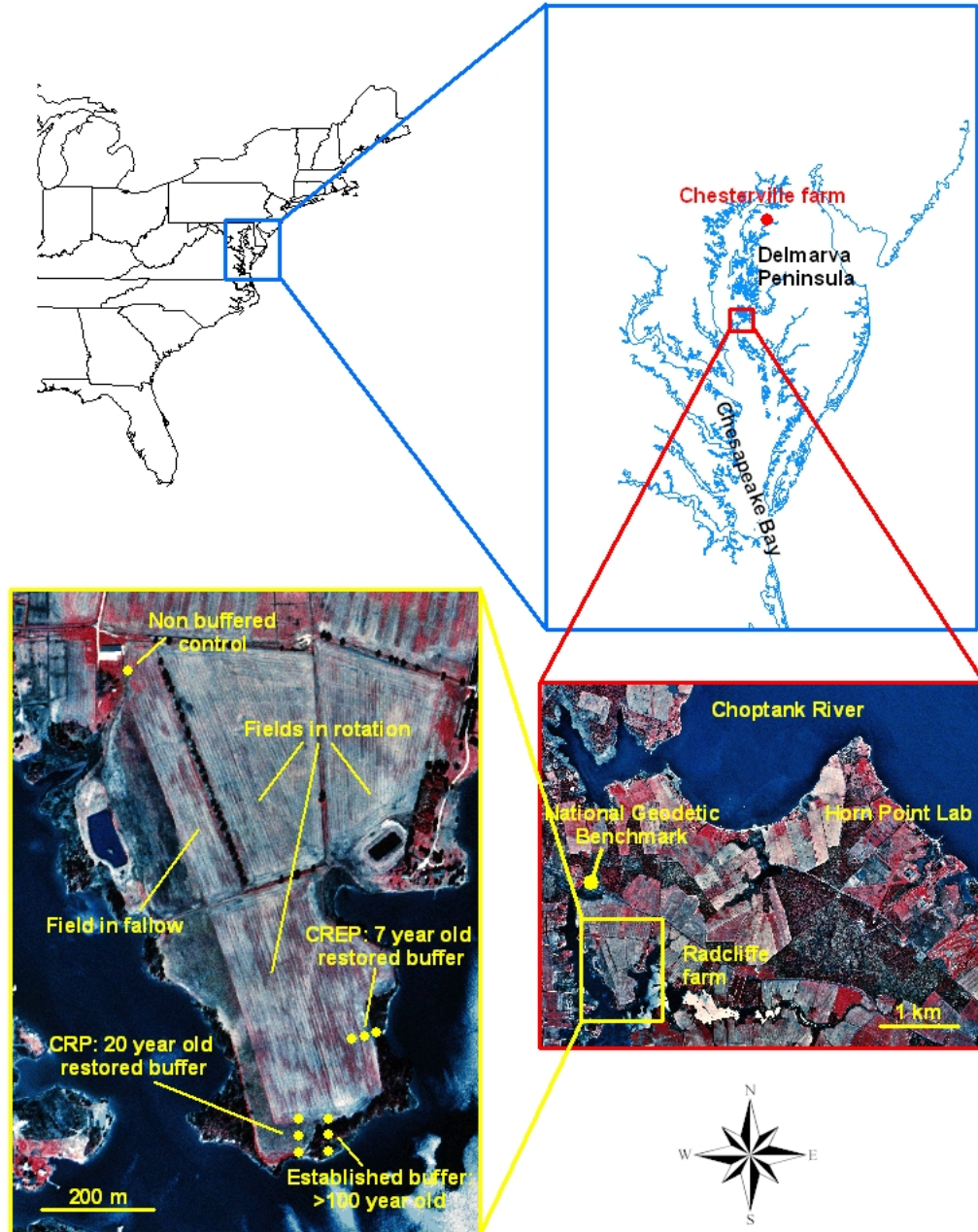
Fig 2-1. Location and DOQQ images of study sites, Radcliffe farm and Chesterville Branch farm, on Delmarva Peninsula. Radcliffe farm is approximately 3 km from Horn Point Lab and in the watershed of the Little Choptank River. The large DOQQ shows the CREP, CRP, and established forest buffers surrounding the southern farm field. The points are locations of the piezometer transects through each buffer. In the northwest portion of Radcliffe farm is the non-buffered control site.

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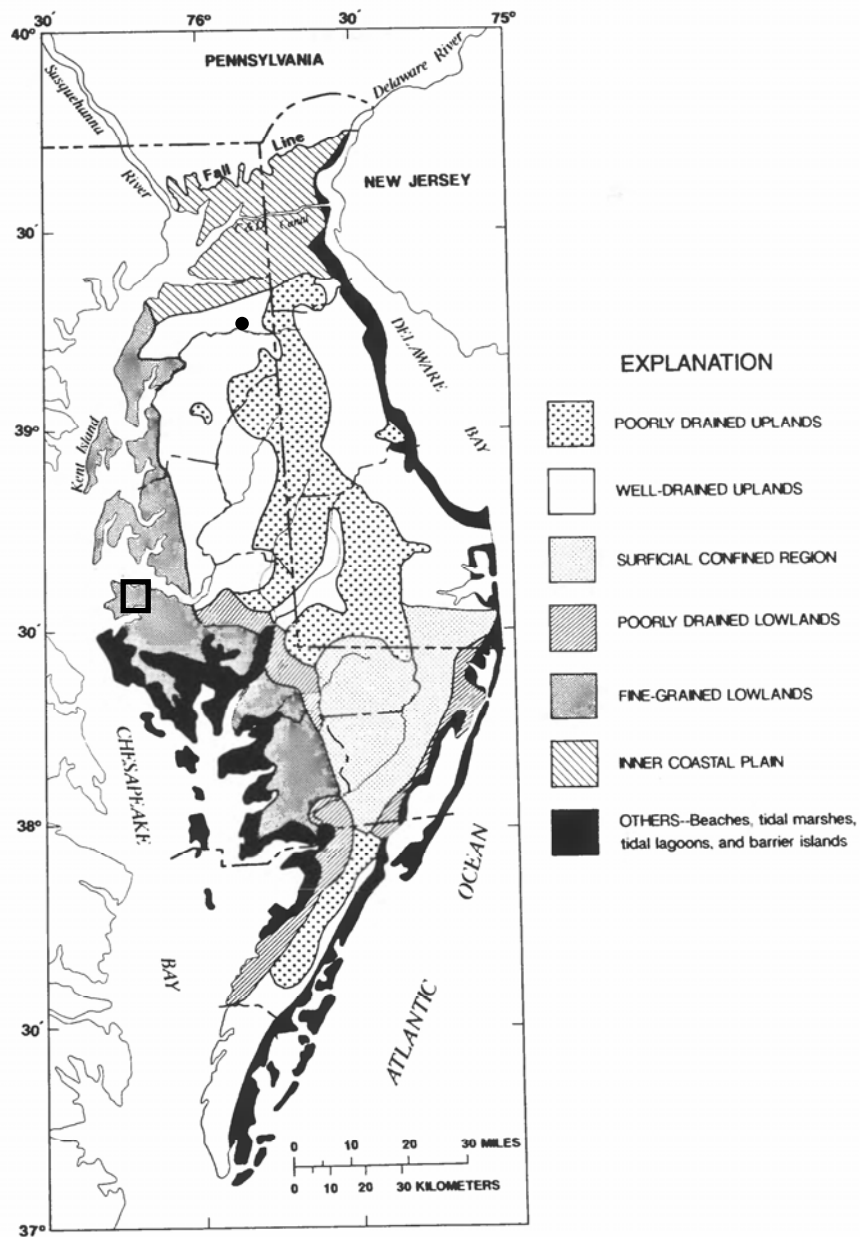
Fig 2-2. Hydrogeomorphic regions of the Delmarva Peninsula (from Hamilton et al. 1993). The box in the fine-grained lowland is the location of Radcliffe farm and the point is the Chesterville farm as seen in Fig 2-1.

Table 2-1. Background information for 4 riparian buffers involved in this study: restored CREP forest, established forest, restored CRP pine forest, and non buffered area of agricultural field used as a control. Buffer age and soil type was gathered from farm owner, George Radcliffe, and Dorchester County NRCS office. Buffer width and piezometer depth below ground were measured in the field and surveying equipment was used to measure ground elevation at each piezometer. K was calculated by slug tests in the deeper set of piezometers (see eq. 1).

| | | | | | | Background information | | | | |
Buffer	Buffer age, years	Soil type	Soil drainage	Hydric soils	Piezometer nest	Piezometer location	Buffer width, m	Depth, m	Ground elevation, m	K, 10^{-6} cm sec^{-1}
CREP	7	Keyport silt loam	moderately well	N	shallow	field edge	20.4	1.50	1.28	-
						mid-buffer		0.86	1.15	-
						stream edge		0.91	1.11	-
					deep	field edge 1		2.11	1.28	10.1
						field edge 2		2.39	1.32	7.3
						mid-buffer		2.23	1.15	-
						stream edge 1		1.93	1.11	147.0
						stream edge 2		2.04	1.09	198.0
Established forest	>100	Keyport silt loam	moderately well	N	shallow	field edge	24.5	0.80	0.91	-
						mid-buffer		0.67	0.82	-
						stream edge		1.14	0.58	-
					deep	field edge 1		2.43	0.91	2.9
						field edge 2		2.44	0.97	28.3
						mid-buffer		1.40	0.82	2.2
						stream edge 1		1.14	0.58	1.7
						stream edge 2		1.35	0.58	2.0
CRP	20	Elkton silt loam (Mattapex silt loam at field edge)	poor moderately well	Y N	shallow	field edge	50	1.40	1.27	-
						mid-buffer		1.35	1.14	-
						stream edge		1.54	1.11	-
					deep	field edge 1		3.72	1.27	5.7
						field edge 2		3.68	1.32	66.0
						mid-buffer		3.52	1.14	5.1
						stream edge 1		3.81	1.11	7.8
						stream edge 2		3.57	1.11	14.7
Non buffered control	Non buffered since 1800s	Keyport silt loam & Elkton silt loam	moderately well poor	N Y	shallow	stream edge	6.9	0.99	1.13	-
					deep	field edge		1.27	1.23	28.3
						stream edge		1.30	1.13	66.0

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loam is classified as poorly drained and hydric. In the middle of the agricultural field, the elevation is 2.5 meters above sea level and gradually decreases towards the edges and through the riparian buffers. Elevation gradients within the buffers are all positive from field edge to stream edge and range from practically zero at 0.1 cm m^{-1} from mid-CRP buffer to the CRP stream edge and up to 2 cm m^{-1} from mid-buffer in the established forest to the stream edge (Table 2-2).

Table 2-2. Topographic gradients through the transects in the riparian buffers at Radcliffe farm.

Buffer	Location in transect	Topographic gradient, cm m^{-1}
CREP	field edge to mid buffer	1.5
	mid buffer to stream edge	0.5
Established forest	field edge to mid buffer	1.0
	mid buffer to stream edge	1.9
CRP	field edge to mid buffer	0.6
	mid buffer to stream edge	0.1
Non-buffered control	field edge to stream edge	1.5

The 10.6 hectare farm field encircled by the CREP, CRP, and established forest buffers (Fig 2-1) is in a corn/soybean crop rotation typical of farmland in this area of the Delmarva Peninsula (Staver and Brinsfield 2001). Small grains are not grown in the winter; instead the fields are left undisturbed and used as wintering grounds by geese and other water fowl. Crop residue remains on the fields after harvest, and in the spring seed is planted directly into the soil without tillage. The crop was soybeans in the 2003 season, corn in 2004, and soybeans in 2005. Manure fertilizer from nearby poultry farms is applied to the fields at Radcliffe farm. Some seasons this is supplemented with inorganic fertilizer when a sufficient amount of manure can not be obtained from the nearby poultry farms. It is important to note here that the Radcliffe farm is a well

managed farm unique to this region. The farm has extensive buffers, practices no tillage

agriculture, has implemented wildlife conservation practices, and often does not apply

organic or inorganic fertilizer when soil tests reveal nutrient levels are already high. The

minimum recommended fertilizer applications in each year's Nutrient Management Plan

is strictly adhered to, whereas in Maryland only approximately a third of farmers file

Nutrient Management Plans and it is unknown how many actually follow the prescribed

fertilizer application (Mark Waggoner pers. com.). As part of the Nutrient Management

Plan for the farm in 2003, a soil analysis report was prepared by A and L Eastern

Agricultural Laboratories. The soil tests revealed a soil pH of 6.0, a medium rating of

organic matter in the soil and calcium (Ca) in the pore water (102 kg ha^{-1} and 23.2 mM,

respectively), a high rating for potassium (K) at 3.5 mM, and a very high rating for

phosphorus (P) and magnesium (Mg) (i.e., 3.7 mM and 6.9 mM, repetively). As a result

of these tests in 2003, a fertilizer application of 33.6 kg ha^{-1} of K and 784 kg ha^{-1} of

dolomitic lime was recommended in the Nutrient Management Plan. The agricultural

field adjacent to the non-buffered control site was last harvested in 2003 and has been

fallow throughout the study period. Considering the low hydraulic conductivity (Table 2-

1, to be presented below), the groundwater has the potential to move 15 m year^{-1}, and

agricultural contaminants are still likely to be present in the subsurface groundwater in

this fallow field.

The original study site was on a farm in the Chesterville Branch watershed

draining into the Chester River, approximately 80 km northeast of the Radcliffe farm (Fig

2-1). I was not able to develop a long term monitoring project at the Chesterville farm

but did sample groundwater under CRP and CREP buffers twice in the fall of 2003.

Similar to Radcliffe farm, the CRP and CREP buffers on the farm in the Chesterville Branch watershed surrounded an agricultural field which was in a corn/soybean rotation. However, this farm is located in a different hydrogeomorphic region and therefore, has different soils and groundwater hydrology. The Chesterville farm is located in the well-drained upland of the Delmarva Peninsula (Fig 2-2), which has lower water tables, well-drained soils in the uplands, and poorly-drained soils and sediments in the stream valleys (Owens and Denny 1979, Hamilton et al. 1993). The depth of the unconfined aquifer is thicker in the Chesterville Branch watershed and the confining layer varies from approximately 20 to 30 m below the surface (Böhlke and Denver 1995). The Chesterville farm has more topographic relief, approximately 20 m from farm field to stream. Types of soils range from deep, well-drained Sassafras soils on the farm field and the hill slopes where the buffers were located to poorly-drained soils of the Bibb series in the stream valley bottoms. Most of the data in this chapter refers exclusively to Radcliffe farm except where additional nitrate data in the subsurface groundwater at the Chesterville farm is presented later in Figure 2-15.

Piezometer transects

A conceptual diagram of piezometer transects on Radcliffe farm is shown in Figure 2-3. I drilled two piezometer transects in each buffer using a 5.7 cm diameter mud auger in the winter of 2003 and the summer of 2004. In the winter, the shallow piezometer transects consisted of one piezometer at the buffer/agricultural field edge, one midway through the buffer, and one at the buffer/creek edge, except at the non-buffered control site where only one stream edge piezometer was installed in the 7 m wide strip

between the field and the ditch. In the summer of 2004 when the water table was lower, I

drilled deeper holes. In most cases, I removed the shallow piezometer and installed two

nested piezometers at the field edge and the stream edge and one piezometer mid-buffer

(Fig 2-3). At the non-buffered control site, only one field edge and stream-edge (ditch in

this case) piezometers were installed. Piezometers consisted of schedule 80 5.1 cm inner
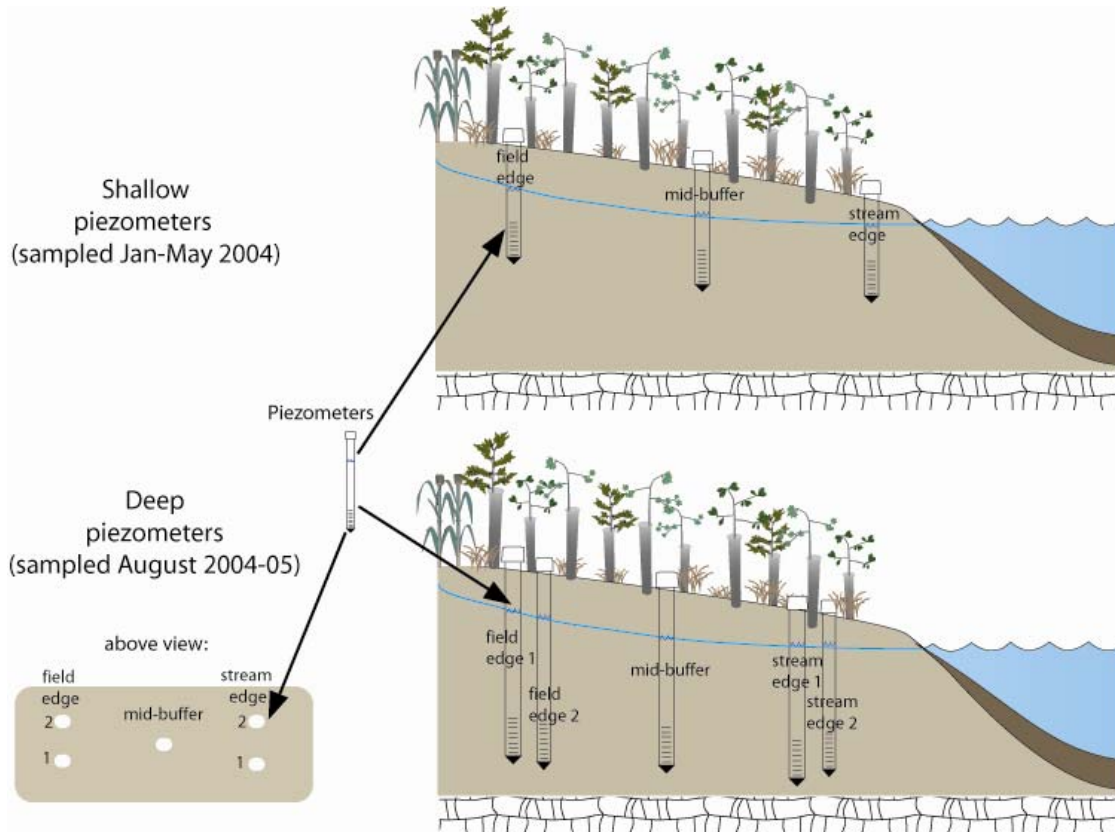
Fig 2-3. Conceptual diagram of piezometer installations at Radcliffe farm. This example
represents the CREP site as shown by the young tree saplings protected by plastic
casings. I installed one shallow piezometer at the field/buffer edge, one mid-buffer, and
one at the stream/buffer edge. I monitored groundwater in these piezometers for five
months in early 2004. In the spring of 2004, I installed deeper, nested piezometers and
monitored the groundwater for one year until August 2005. This installation was the
same for the CREP, CRP, and established forest buffers. For the non-buffered control
site, only one shallow piezometer was installed in early 2004 and the deep piezometer
installation included only one field edge and one stream (ditch) edge piezometer.
Piezometer depths are shown in Table 2-1.

diameter PVC pipe. Screens were either 23 or 36 cm long and slotted (0.20 mm) every

0.3 cm. Piezometer ends were fitted with a solid PVC point.

In the fall of 2004, I measured the elevation in the farm field and at each of the

piezometers. I used surveying equipment to measure elevation in relation to a benchmark

from the National Geodetic Survey located on Route 343 next to the farm; estimated

errors in elevation heights are ±15 cm. The elevation of the tidal creek adjacent to the

CRP buffer was measured and compared to tidal heights at two nearby tidal gauges in

McCready's Creek and at Cambridge, Maryland. There was a -15 cm bias in that

surveying measurement, which could reflect errors in surveying from the benchmark on

Route 343 or differences in the height of the water in the creek at Radcliffe farm and the

two tidal gauges in other creeks.

Hydrology

I estimated hydraulic characteristics of the subsurface groundwater using

measurements from the deep piezometer transects (Fig 2-3). The Hvorslev slug-test

method was used to determine the hydraulic conductivity (K) of the soils at each

piezomenter location (Fetter 2001). I measured hydraulic head before the test, pumped

the water completely from the piezometer, and measured water level during recharge.

The following formula was used to calculate K:

$$K = \frac{r^2 \ln(L/R)}{2LT_{37}}$$

(eq. 2-1)

where K is hydraulic conductivity, r is the inner radius of the piezometer casing, L is the

length of the piezometer screen, R is the inner radius of the piezometer screen, and T_{37} is

the time it takes for the water level to recharge 37% of the initial level (Fetter 2001). I

removed the water from the piezometers using a Solinst Model 410 Peristaltic Pump and measured water level at 10 minute intervals with a Solinst automated pressure transducer, Model 3001 Levelogger. Leveloggers were attached with a nylon line to the inside of a threaded PVC cap on the top of the piezometer and were lowered and placed on the bottom of the well. One Levelogger remained at Horn Point Laboratory recording barometric pressure in order to correct data from the field loggers for small pressure changes in the atmosphere.

I also used the same automated pressure transducers to measure groundwater response to a rain event in most of the deep piezometers. In this case, I installed Leveloggers prior to a storm and left them in the field for one to two weeks after the event recording hydraulic head and temperature every 30 minutes. Finally, water table level was measured with a Solinst Model 101 Water Level Meter each time I was in the field throughout the sampling period.

The application of lime, poultry manure, and inorganic fertilizers on Radcliffe farm has the potential to enrich the groundwater with conservative tracers such as chloride (Cl^-), magnesium (Mg^{+2}), and calcium (Ca^{+2}) (Böhlke and Denver 1995, Böhlke 2002) and makes it possible to examine whether piezometers are sampling the same groundwater flow path through each buffer. In January 2005, I collected samples from a field edge, mid-buffer, and a stream edge piezometer in each buffer and from both piezometers in the non-buffered control site. Samples were filtered and analyzed for major cations and anions on a Dionex ICS-2000 Ion Chromatography System. Samples were diluted by 10 or 100 to measure the high ion concentrations in the groundwater. Chloride (Cl^-) anion was measured with 1 to 100 ppm Cl^- standards. The cations

magnesium (Mg^{+2}), sodium (Na^+), calcium (Ca^{+2}), and potassium (K^+) were analyzed from undiluted samples with 1 to 50 ppm Mg^{+2} and Na^+ standards and 0.25 to 10 ppm Ca^{+2} and K^+ standards.

Nutrient sampling

I measured groundwater nutrient concentrations monthly in the shallow piezometers from January to May 2004 (5 samples) and approximately every month in the deeper piezometers (Fig 2-3) from August 2004 through August 2005 (11 samples). I pumped water completely from the piezometers and allowed fresh groundwater to recharge. Approximately 24 hours later, I collected a groundwater sample from each piezometer, measured temperature and electrical conductivity in the field with a portable Yokogawa SC82 conductivity meter (calibrated using a 100 $\mu S\ cm^{-1}$ conductivity standard), and brought a sample back to the lab for nutrient analysis. In the lab, I filtered original samples with GFF filters for automated colorimetric analysis of NO_3 in a Technicon AutoAnalyzer II in Horn Point's Analytical Services Lab. On average, nitrite (NO_2) was typically less than 5% of the NO_{3+2}, and I present the analysis of NO_{3+2} as solely nitrate (NO_3). Filtered samples were also autoclaved with the persulfate reagents of Valderama (1981) and subsequently analyzed for dissolved phosphate (PO_4) and nitrate (NO_3) in a Technicon AutoAnalyzer II to determine total dissolved phosphorus (TDP) and total dissolved nitrogen (TDN). I used manual colorimetric methods to measure ammonium (NH_4) and phosphate (PO_4) concentrations in the filtered groundwater samples (Strickland and Parsons 1972). The analytical precision estimated from replicates was typically 12% for NH_4, 10% for TDP, and 3% for PO_4.

Denitrification

The enrichment of nitrogen gas in groundwater relative to inert argon can be used to quantify denitrification (Blicher-Mathiesen et al. 1998, Mookherji et al. 2003). I measured nitrogen (N_2), oxygen (O_2), and argon (Ar) dissolved gases in groundwater samples from the deep piezometers in June and August of 2005. I pumped the piezometers dry and allowed the groundwater to recharge for approximately 24 hours. A plastic fishing float the same diameter of the piezometer inner diameter was placed in the piezometer to protect the recharging water from contact with the air. The following day the float was removed and I collected a groundwater sample by lowering a 700 mL, 4.8 cm outer diameter Norwell bailer to a few centimeters above the bottom of the piezometer. The one-way valves on both ends of the bailer allowed sampling of groundwater to the depth which the bailer was lowered and prevented loss of sample as the bailer was raised from the piezometer. The full bailer was then fitted with a stopcock to control the flow rate as the groundwater sample was dispensed into glass test tubes (4 replicates for each piezometer). The water flowed slowly from the bailer, through a Teflon tube, and into the bottom of a glass test tube. When the test tube as overflowing, I removed the Teflon tubing and inserted a glass stopper in the tube to seal the sample without trapping any air bubbles (methods adapted from Mookherji et al. 2003). Due to slow recharge in stream edge1 piezometer in the established forest buffer, I was never able to collect enough water sample for N_2/Ar analysis at this location.

Immediately after collecting samples, I analyzed N_2, O_2, and Ar on a Balzers 420 quadrupole mass spectrometer modified with a membrane inlet, also called a Dissolved Gas Analyzer (DGA, Kana et al. 1994). The resulting N_2 and Ar signals were corrected

for oxygen sensitivity (Kana and Weiss 2004), although O_2 concentrations measured in this study were very low (i.e., an average of 30 µM) and do not greatly affect the signals. I applied another correction if argon was lost along the transect by degassing, the process in which air bubbles escape and strip dissolved gases from the groundwater. If Ar concentrations decreased in the groundwater along a piezometer transect, I assumed that groundwater along the flow path was degassed and used the following correction for the amount of N_2 lost (Blicher-Mathiesen et al. 1998):

$$\Delta N = \alpha N_c \ln(A_2 / A_1) \tag{eq. 2-2}$$

where ΔN is the amount of N_2 degassed per liter in µM, α is the ratio of partition coefficients in water (N_2/Ar at 10^oC: $\alpha = 2.2$), N_c is the measured concentration of N_2 in the piezometer where degassing is occurring in µM, A_1 is the measured Ar concentration in µM before degassing occurring along the groundwater flow path, and A_2 is the measured Ar concentration in µM after degassing occurred. After these corrections, I used the measured N_2 in the groundwater samples to calculate the amount of NO_3 denitrified in each buffer using the following equation:

$$N_{excess} = N_{measured} - N_{equilibrium} \tag{eq. 2-3}$$

where N_{excess} is the excess N_2-N in the groundwater attributed to the amount of nitrate denitrified, $N_{measured}$ is the N_2-N concentration in the groundwater measured by analysis on the DGA, and $N_{equilibrium}$ is 577.5 µM. The N_2 concentration of groundwater during recharge when in equilibrium with the air was based on the solubility of N_2 gas at an average annual temperature of 15^oC.

Results

Hydrology

Soil types, buffer width, ground elevation at each piezometer, depth of

piezometers, and hydraulic conductivity (K) in the two restored buffers (CREP and CRP),

the established forest buffer, and the non-buffered control are shown in Table 2-1. The

range of piezometer depth varied during the shallow sampling in early 2004 from 0.7 to

1.5 m below ground and during the 2004 nested piezometer installation depth from 1.1 to

3.8 m below ground. The range of hydraulic conductivity measured was 1.7×10^{-6} to

2.0×10^{-4} cm sec^{-1} and indicated that soils in the buffers are a silty-clay mixture. This

measurement is consistent with soil profile observations noted during well drilling.

Figure 2-4 is an example of the recharge in a piezometer during a slug test. It took

approximately 15 hours for the piezometer to recharge to 37% of the original hydraulic
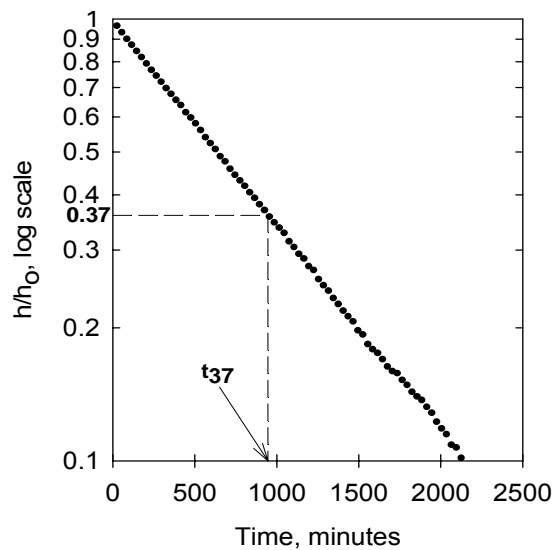
Fig 2-4. Example of the hydraulic head response over time during a Hvorslev slug-test. The y-axis (h/h$_o$) is the ratio of hydraulic head (h) to initial hydraulic head before piezometer was pumped dry (h$_o$) on a logarithmic scale. The time at 37% of piezometer recharge is T$_{37}$ in equation 2-1.

head. This time, 5.4×10^4 s, was T_{37} in equation 2-1 and along with the dimensions of the piezometer (r and R of 2.54 cm and L of 23 cm), K was calculated as 5.7×10^{-6} cm s^{-1}.

The presence of common agricultural contaminants in the groundwater under the CREP buffer is shown in the 2-D diagrams in Figure 2-5. Nitrate decreased horizontally in the groundwater from the agricultural field through the buffer towards the stream and vertically within the buffer as groundwater approached the surface. Chloride concentrations were consistent under the buffer (6.2 mM) until the stream edge
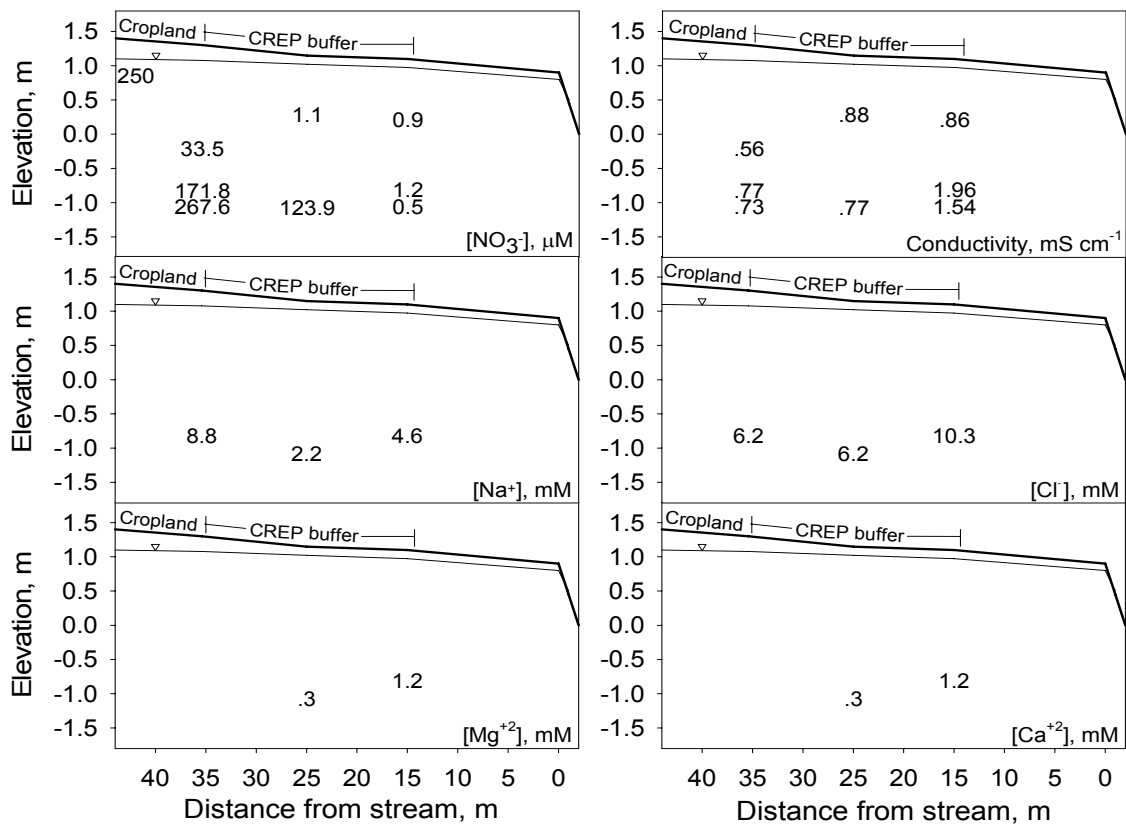
Fig 2-5. Cross-section of monitored groundwater in the CREP buffer. The ground surface is the solid line and annual average water table is the thin line below. Agricultural contaminant concentrations are shown in relation to the depth of groundwater sampled in each piezometer and distance from the stream. Nitrate and conductivity concentrations were the annual average of monthly measurements and the ions were from IC analysis of samples collected in January 2005. Note that nitrate (NO_3) concentrations are in μM, conductivity in mS cm^{-1}, and sodium (Na^+), magnesium (Mg^{+2}), chloride (Cl^-), and calcium (Ca^{+2}) are in mM.

piezometer (10.3 mM) where some salt may have intruded from the tidal creek. Salt ions

may have also influenced the high average conductivity measurement of 2 mS cm^{-1} at this

stream edge piezometer, which was approximately 3 times higher than near the crop

fields. Magnesium and calcium concentrations were high in the CREP buffer, but since

the field edge sample was not analyzed, I can not determine any trend. The decreasing

pattern of NO$_3$, salt water intrusion at the stream edge, and high Mg^{+2} and Ca^{+2}

concentrations throughout were also consistent in the CRP buffer (Table 2-3). The

established buffer however, is the lowest in elevation and had saltwater throughout. In

the mid-buffer and stream edge piezometers of the established forest, the salinity was 4

and 7, respectively, indicating considerable salt intrusion. There were no patterns in

agricultural contaminant concentrations between the groundwater at the field edge and 7

meters away at the edge of the ditch in the non-buffered control site.

Table 2-3. Concentration of common agricultural contaminants and conductivity measured in groundwater at Radcliffe farm in January 2005. High concentrations of Na$^+$ and Cl$^-$ and high conductivity measurements may also indicate saltwater intrusion.

Buffer	Piezometer location	NO$_3^-$	[Contaminant], mM				Conductivity, mS cm^{-1}	
			Na$^+$	Cl$^-$	Mg^{+2}	Ca^{+2}	Annual average	Standard error
CREP	field edge1	171.8	8.8	6.2	n.a.	n.a.	0.8	0.1
	mid-buffer	123.9	2.2	6.2	0.3	0.3	0.8	0.0
	stream edge1	1.2	4.6	10.3	1.2	1.2	2.0	0.8
Established forest	field edge1	0.7	25.4	60.0	6.3	7.3	4.7	0.3
	mid-buffer	0.1	73.5	107.2	10.0	12.3	10.7	0.4
	stream edge2	0.1	108.8	108.9	13.7	7.3	11.6	0.6
CRP	field edge1	184.8	2.9	11.7	0.8	0.5	0.4	0.0
	mid-buffer	34.6	4.0	9.6	1.2	1.1	0.7	0.1
	stream edge1	88.3	33.1	67.9	8.6	7.3	2.1	0.4
Non buffered field	field edge	84.0	12.8	14.1	4.1	4.0	1.7	0.2
	stream edge	99.3	3.5	13.9	3.1	4.7	1.7	0.1

During the sampling period, from January 2004 to August 2005, rainfall at Horn Point

Laboratory (3 miles from Radcliffe farm) was 10% less than the historical average (Table

2-4). Average monthly air temperature was comparable to historical averages through

most of the sampling period, although slightly cooler for some months (Table 2-4).

Average groundwater temperature in the deep piezometer transects through each buffer

exhibited a dampened seasonal pattern compared to air temperature (Fig 2-6). At the

warmest, groundwater temperature was almost as high as air temperature where sampled

groundwater was closest to the ground surface in the non-buffered control site and 7 $^{\circ}$C

less than air where groundwater was the deepest in the CRP buffer. During the coolest

time of year, groundwater temperature was 5.5 $^{\circ}$C warmer in the CRP buffer and 4 $^{\circ}$C

warmer in the other buffers where the sampled groundwater was shallower. The response

to air temperature was also delayed in groundwater (Fig 2-6). For example, the coolest

air temperature was measured in January, but the groundwater temperature was coolest

two months later in March.

Table 2-4. Total monthly rainfall and average monthly temperature at Horn Point Laboratory in Cambridge, MD during the sampling period and the historical averages of each. During the sampling period, total rainfall was 67 cm less and average temperature was 1 $^{\circ}$C cooler.

Month-Year	Rainfall, cm			Temperature, $^{\circ}$C		
	2004-2005	Historical average	Difference	2004-2005	Historical average	Difference
Jan-04	6.1	10.4	-4.3	-1	2	-3
Feb-04	5.2	8.0	-2.8	2	4	-2
Mar-04	6.2	11.3	-5.1	8	8	0
Apr-04	18.5	8.2	10.3	13	13	0
May-04	7.0	10.6	-3.6	21	19	2
Jun-04	4.5	8.2	-3.7	22	23	-1
Jul-04	17.5	11.0	6.6	25	26	-1
Aug-04	13.5	11.7	1.8	24	25	-1
Sep-04	7.6	9.8	-2.2	21	22	-1
Oct-04	1.2	7.8	-6.6	14	16	-2
Nov-04	10.8	8.7	2.1	10	10	0
Dec-04	6.6	9.3	-2.7	5	5	0
Jan-05	7.3	10.4	-3.2	2	2	0
Feb-05	5.1	8.0	-2.9	3	4	-1
Mar-05	11.3	11.3	0.0	5	8	-3
Apr-05	7.6	8.2	-0.6	13	13	0
May-05	12.3	10.6	1.8	15	19	-4
Jun-05	6.9	8.2	-1.3	23	23	0
Jul-05	6.6	11.0	-4.4	26	26	0
Aug-05	12.7	11.7	1.1	26	25	1
Total	174.5	194.1	-19.6	14	15	-1
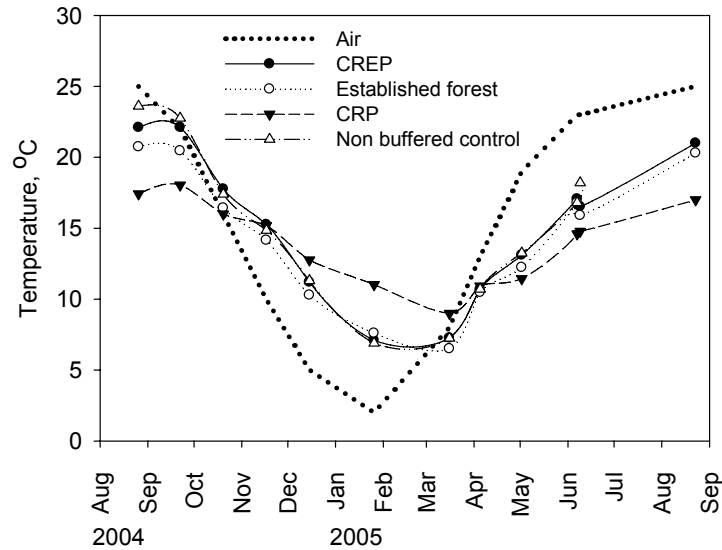
Fig 2-6. Air and groundwater temperature (^{o}C) during the study period from August 2004 through August 2005. Average monthly air temperature at Horn Point lab is shown by the large dotted line. I measured the groundwater temperature once a month in all piezometers and points are average temperature throughout the CREP buffer (closed circles), established forest (open circles), CRP (closed triangles), and non-buffered control site (open triangles).

I measured hydraulic head once a month and fluctuations over one year in each of the deep piezometers, shown in Figure 2-7. In most of the piezometers, hydraulic head did not fluctuate much during the year except in the summer when evapotranspiration was high, and in some cases, the water table fell below sea level (Fig 2-7). Unfortunately, measurements were lacking between the beginning of June and the end of August, and this pattern is dependent on one measurement at the end of August 2005 in the middle of a regional drought. If this pattern is real, the data from the end of September 2004 suggest the water table was high again by the fall. The CRP buffer was the one site where the seasonal recharge pattern was more apparent, in which hydraulic head was the highest from December through the end of May (Fig 2-7). The established forest was the buffer with the most salt water intrusion (Table 2-3), and hydraulic head
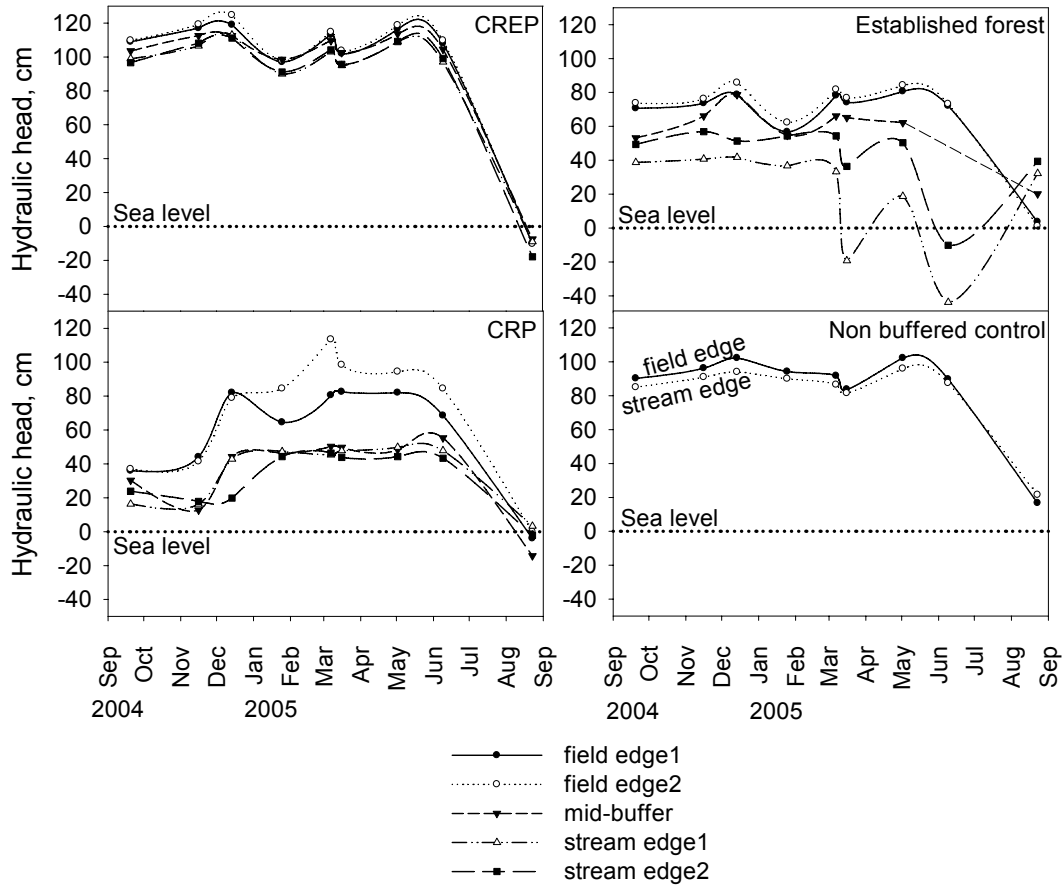
Fig 2-7. Hydraulic head in each of the buffers measured once a month during the study period in the deep piezometers (except for August and April 2004 when I did not measure water table). In the CREP, established forest, and CRP buffers, points represent the monthly measurement in the field edge1 piezometers (closed circles), field edge2 (open circles), mid-buffer (closed triangles), stream edge1 (open triangles), and stream edge2 (closed squares).

measurements in the streamside piezometers in the spring through summer were lower

than in the other buffers. When the water level in the stream edge piezometers was

below sea level, tidal creek water may inundate the fine-grained sediment at the edge of

the established forest buffer. The hydraulic gradient (difference in groundwater height

divided by distance) between the field edge piezometers and the stream edge piezometers

in the CREP, CRP, and non-buffered control site did not fluctuate seasonally to a large

extent, except between June and August 2005 when there was a reversal in gradient from

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stream edge to field edge (Fig 2-8). The established forest buffer exhibited a similar

pattern throughout most of the year, but in March through May 2005, the water table in

the stream edge piezometers were lower compared to the patterns in the other

piezometers (Fig 2-7) and resulted in higher hydraulic gradients (Fig 2-8).
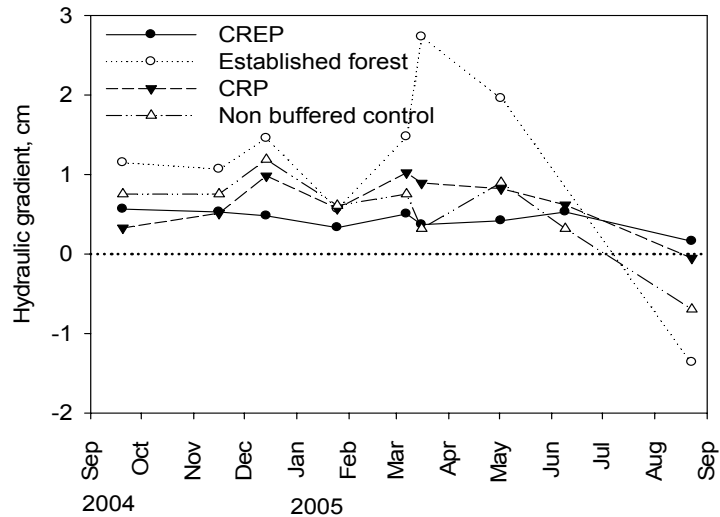
Fig 2-8. Horizontal hydraulic gradient in all buffers measured once a month during the study period in the deep piezometers (except for August and April 2004 when I did not measure water table). Hydraulic gradient was calculated by the average hydraulic head in field edge piezometers minus the average hydraulic head in stream edge piezometer and dividing by the buffer width ($\partial h/\partial l$). In June, hydraulic head was highest in the mid-buffer piezometer (see Fig 2-6), so two points were added for that measurement to represent the gradient from field edge to mid-buffer (negative) and mid-buffer to stream (positive).

Even though groundwater sampled through the transect in the established forest

buffer was salty, detailed water table measurements from the automated pressure

transducers show no signs of tidal fluctuations (Fig 2-9a). This detailed observation

period in October 2004 was 2 days after a rain event and the mid-buffer and stream edge

piezometer may have still been responding to rain water recharge, while hydraulic head

in the field edge piezometers was slowly decreasing after the rain event. No tidal

fluctuations were observed in this detailed data set, and the heavy clay soils with low
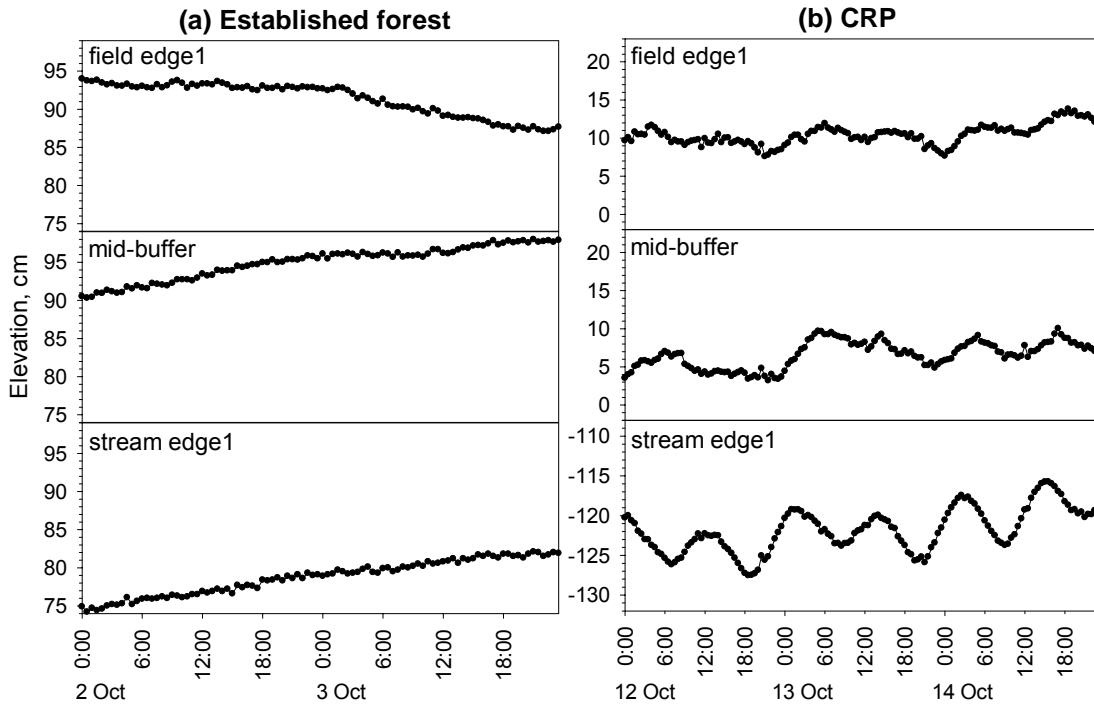
Fig 2-9. Detailed hydraulic head measurements in the field edge1, mid-buffer, and stream edge1 piezometers in the (a) established forest buffer and (b) CRP buffer. Piezometer depths were roughly equal within each buffer except field edge1 in the established forest was roughly a meter deeper than the mid-buffer and stream-edge piezometers (Table 2-1). Measurements were recorded by an automatic pressure transducer every 30 minutes from 2 to 3 October 2004 in the established forest buffer and 12 to 14 October 2004 in the CRP buffer and were not influenced by any rain events in that time period.

permeability in this buffer may prevent the movement of groundwater at tidal time scales. However, tidal fluctuations of 5 to 10 cm were observed in the stream edge of the CRP buffer and were dampened further inland where fluctuations were only 2 to 5 cm (Fig 2-9b). Even though salt water was not detected in the CRP field edge and mid buffer piezometers, the water table still fluctuated on a tidal cycle.

Groundwater discharge from the buffers is shown in Figure 2-10. Discharge was calculated using Darcy's Law:

$$Q = KA(\partial h/\partial l) \tag{eq. 2-4}$$

where Q is the discharge in m^3 m^{-1} day^{-1}, K is the average hydraulic conductivity in the

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buffer in m day^{-1}, A is the cross-sectional area of flow in m^3 m^{-2}, ∂h is the change in hydraulic head between the field edge and stream edge in m, and ∂l is the width of the buffer in m. I calculated cross-sectional area, A, by assuming a porosity typical of silt-clay soils (50% of the volume of soil per area of aquifer, Dunne and Leopold 1978, Novotny and Olem 1994) and assuming the depth of unconfined aquifer typical of fine-grained lowland of the Delmarva Peninsula (5 meters, Owens and Denny 1979, Lowrance et al. 1995). Therefore the cross-sectional area I used for discharge calculations was 2.5 m^3 m^{-2} and describes the volume of soil per area of the unconfined aquifer on Radcliffe farm. Hydraulic conductivity, K, was an average of measurements in each transect (Table 2-1). In general, groundwater discharge through the buffers was very low on Radcliffe farm (Fig 2-10). Discharge was highest in the CREP buffer and the non-buffered control site and fluctuated between 0.0005 and 0.001 m^3 m^{-1} day^{-1} through most of the year. Discharge was generally lower in the established forest and CRP buffers at less than 0.0005 m^3 m^{-1} day^{-1}. In the established forest, CRP buffer, and non-buffered control, groundwater flow was reversed in August (Fig 2-10). In this case, tidal creek water may have been infiltrating the streamside portions of the buffers.

These low discharge values are confirmed by a water balance calculation for the groundwater flowing into the buffers from the farm field. I calculated the groundwater discharge from the farm field into the buffers using the following equation:

$$Q_{ag} = P - (ET + OF + \Delta GWS) \qquad \text{(eq. 2-5)}$$

where Q_{ag} is the water available for groundwater discharge from the agricultural field, P is annual precipitation, ET is annual potential evapotranspiration, OF is annual overland flow, and ΔGWS is the change in groundwater storage (all units in cm). Annual
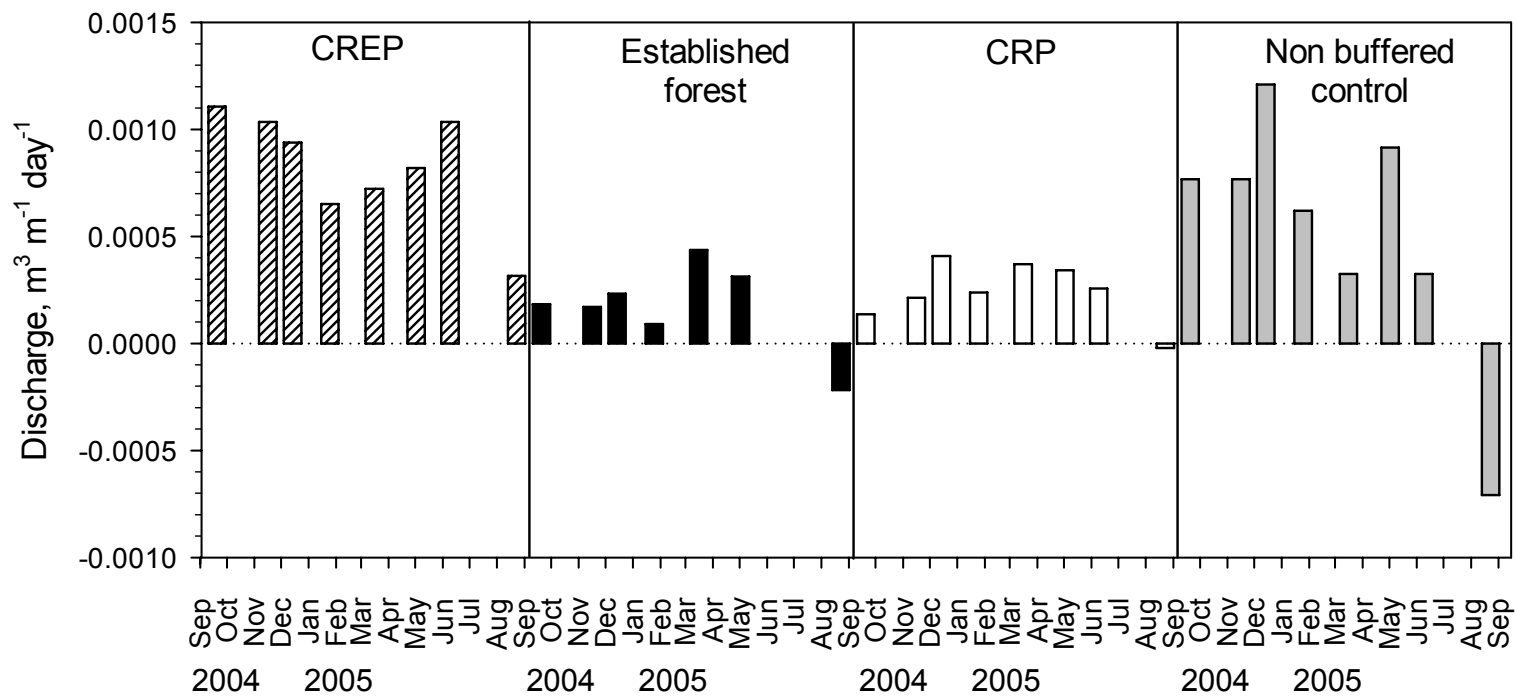
Fig 2-10. Groundwater discharge from each buffer during the study period using measurements from the deep piezometers. The discharge calculation (eq. 2-4) uses average K in each buffer (Table 2-1), cross-sectional area of the unconfined aquifer (2.5 m^3 m^{-2}), and hydraulic gradient (Fig 2-8).

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precipitation, P, is the total historical monthly precipitation at 115 cm for Horn Point

Laboratory in Cambridge, Maryland (Table 2-4). I calculated potential

evapotranspiration (ET) from the Thornthwaite method that uses monthly air temperature

as an index of energy available for evapotranspiration (Dunne and Leopold 1978).

Potential evapotranspiration accounted for 81 cm in the water balance per year. Overland

flow was estimated using runoff curve numbers developed by the National Resources and

Conservation Service (Figure 10-8 in Dunne and Leopold 1978). The curve number is

based on the hydrologic conditions on the farm field and used to predict the amount of

runoff per storm event. The curve number for Radcliffe farm was approximately 80

based on the moderately-well drained soils and the practice of straight row-cropping

(Tables 10-3 to 10-5 in Dunne and Leopold 1978). T.R. Fisher compiled rainfall data

from 1979 to 1990 from 9 weather stations on the Delmarva Peninsula and performed a

frequency distribution on the number of events per year for specified rainfall amounts. I

multiplied the runoff curve number for each rainfall amount by the average number of

events per year from this frequency distribution. Overland flow, OF, was then the sum of

the runoff for all the individual rain events, and this total runoff per year accounted for 27

cm of the water balance. Precipitation was high in 2003 at 151 cm and near normal in

2004 at 112 cm as measured at Horn Point Laboratory in Cambridge, Maryland. I

assume that this 35% difference in annual precipitation between 2003 and 2004 is also

the change in groundwater storage, ΔGWS.

The water remaining in the water balance was available for groundwater recharge

and eventual discharge into the established and restored buffers surrounding the field.

This was only 5 cm or 4% of the 115 cm annual precipitation. Based on the 2.5 m^3 m^{-2} of

unconfined aquifer, I estimated that 0.125 m^3 m^{-1} $year^{-1}$ or an average of 0.0003 m^3 m^{-1} day^{-1} of groundwater was discharged from the field to the buffers. This is comparable to the discharge measured out of the riparian buffers at Radcliffe farm (Fig 2-10) and suggests discharge into the buffers was roughly equal to discharge out of the buffers. Calculated by difference from the farm field discharge into the buffers, average discharge from the buffers measured over the sampling period from Figure 2-10 was approximately 0.0001 m^3 m^{-1} day^{-1} lower out of the established forest (>100 year old mixed forest) and CRP buffers (20 year old pine trees) than the estimated discharge from the field into the buffers. This suggests groundwater moving from the farm field was utilized within the buffer by the transpiration from large tree biomass. However, average discharge from the CREP buffer and non-buffered control was more than the groundwater input flowing into the buffers from the farm field, by 0.0005 and 0.0002 m^3 m^{-1} day^{-1} respectively. This suggests that not as much groundwater is being utilized in these two buffers, which have less vegetation than the CRP and established forests, and on average, groundwater is being recharged within the CREP and non-buffered control. It is also possible that these calculations are affected by groundwater flow paths that were not parallel to the piezometers where I measured buffer discharge or by imprecision of the water budget.

Finally, I also measured the groundwater response to two rain events in the CREP, established forest, and CRP buffers and one rain event in the non-buffered control site. Data was recorded by automated pressure transducers in the fall of 2004, but since there was no water table response to the little rainfall during the CRP site monitoring, another rain event was monitored in this buffer the following September 2005. In Table 2-5, water table increase was the difference in water table depth before the storm to the

highest water table measurement during or after the storm. Time of peak response was the time between the largest rainfall recorded at 30 minute time intervals at Horn Point Laboratory during each storm to the time when the highest hydraulic head was recorded in each piezometer. Hydraulic head increase and time to peak response varied between buffers and among the two rain events in each buffer (Table 2-5). Water table increase was as high as 80 cm during a 1.6 cm rainfall and the peak in hydraulic head occurred after 1.5 hours to 19.5 hours after peak rainfall (Table 2-5). These large increases in hydraulic head during a rain event are due to rainwater recharge and contribution from vadose zone moisture. The approximate porosity, or the percentage of soil volume with space available for groundwater, in the soils at Radcliffe farm is 50%. The voids in the soil can be filled by water with the potential to be stored (i.e., field capacity) and water

Table 2-5. Water table response to 7 separate rain events. Two events were measured in all buffers except the non buffered control where only 1 event was measured. Water table increase is the total rise in groundwater height from before the storm to the peak level after the storm. Time of peak response after rain is the amount of time it took for the groundwater to fully respond after the rainfall.

Buffer	Piezometer	Rain event 1 ‡		Rain event 2 §	
		Water table increase, cm	Time of peak response after rain, hrs:min	Water table increase, cm	Time of peak response after rain, hrs:min
CREP	field edge1	45.3	9:30	49.5	11:00
	field edge2	51.3	5:00	16.1	13:00
	mid-buffer	52.0	15:30	10.5	11:00
	stream edge1	80.3	4:30	42.6	11:30
	stream edge2	79.9	10:00	45.1	11:30
Established forest	field edge1	39.7	1:30	4.7	15:00
	field edge2	64.0	2:00	4.6	6:30
	mid-buffer	51.0	†	†	†
	stream edge1	15.2	15:00	23.7	4:30
	stream edge2	77.4	1:00	19.2	10:30
CRP	field edge1	21.3	19:30	47.9	2:30
	mid-buffer	21.5	19:00	9.0	12:00
	stream edge1	24.5	15:30	4.4	9:00
Non buffered control	field edge	49.2	7:30		
	stream edge	44.9	7:30		

Notes:
† Water table did not peak after rain event 1 in the following week of data records
‡ Rain event 1: The first rain event measured in the CREP buffer was 1.6 cm, 2.9 cm in the Established forest buffer, 6.5 cm in the CRP buffer, and 2.6 in the Non buffered control.
§ Rain event 2: The second rain event measured in the CREP buffer was 1.3 cm, 1.0 cm in the Established forest buffer, and 3.0 cm in the CRP buffer.
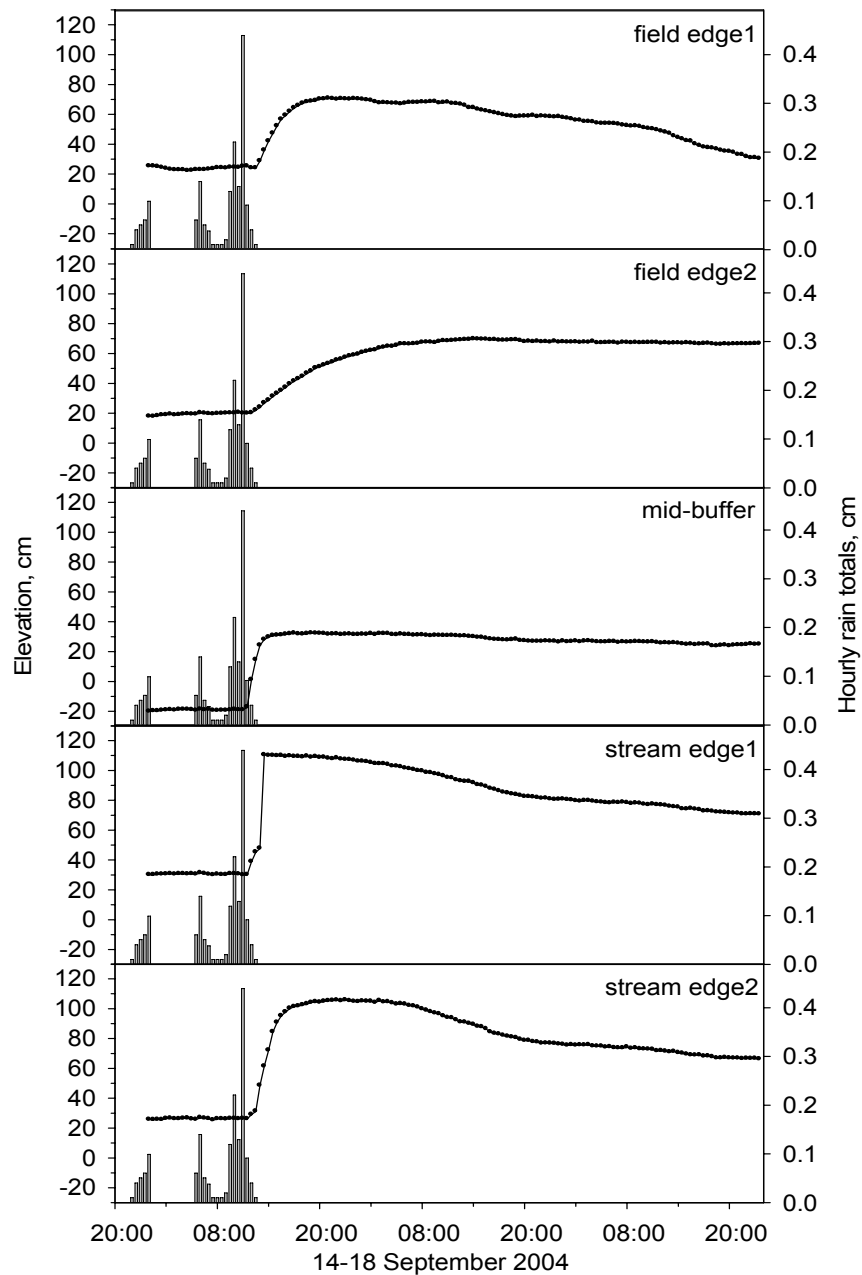
Fig 2-11. Example of groundwater response to a rain event in the CREP buffer. The bars are hourly rainfall totals and the duration of the 1.6 cm rain event was from the evening of September 14 through the morning of September 15. The points represent measurements of hydraulic head recorded by an automatic pressure transducer once every 30 minutes.

with the potential to flush out of the soil (i.e., specific yield). Silty soils have an

approximate specific yield of 18% (Fetter 2001) and the remaining 32% of aquifer

volume can move out of the vadose zone into the subsurface groundwater during a storm

and contribute to the measured increase in hydraulic head (Table 2-5).

An example of a full record of water table response to a rainfall is shown in

Figure 2-11, which is rain event 1 in the CREP buffer (Table 2-5) in September 2004.

Groundwater in the two stream edge piezometers reached approximately the same levels,

although stream edge1 reached the maximum level much faster than stream edge2 (Fig 2-

11). I found no obvious cause for the unusually rapid recharge in the stream edge 1

piezometer. I observed a similar pattern in the two field edge piezometers, and the rate of

decrease in hydraulic head after the storm was also faster in field edge1 in comparison to

field edge2. Before the rain event, the hydraulic head was slightly higher in the stream

edge piezometers than the rest of the buffer and was magnified during the rain event to an

average of 45 cm difference from stream to field edge (Fig 2-11). However, the

hydraulic gradient from field to stream was positive again by the monthly water table

measurement 5 days later (Fig 2-7).

Nutrients

Presented in Table 2-6 are average nutrient concentrations in the shallow

piezometers from January to May 2004 and in the deep nested piezometers from August

2004 to 2005. In August of 2005 I drilled temporary holes in the agricultural field

upslope of the CREP buffer and, since the CRP and established forest buffer are adjacent

to each other on the same side of the field, I drilled in an area upslope between these two

Table 2-6. Average nutrient concentrations and standard errors in subsurface groundwater in two sampling periods: January to May 2004 in shallow piezometers and August 2004 to August 2005 in deeper wells (see Table 2-1 for piezometer depths). In August 2005, subsurface groundwater was measured in the field and surface water from the stream was also measured.

Buffer	Piezometer nest	Piezometer location	Monthly sampling period	Average nutrients over sampling period, µM									
				NH_4	std error	NO_3	std error	TDN	std error	PO_4	std error	TDP	std error
CREP		in field	Aug 2005	1.77		249.5		514		0.170		0.170	
	shallow	field edge	Jan - May 2004	1.07	0.35	33.5	9.5	49.4	11.5	0.065	0.021	0.065	0.021
		mid-buffer	Jan - May 2004	0.69	0.23	1.1	0.4	15.1	6.5	0.024	0.015	0.330	0.172
		stream edge	Jan - May 2004	2.72	0.45	0.9	0.2	17.1	7.5	0.002	0.002	0.205	0.155
	deep	field edge1	Jan - May 2004	1.17	0.20	171.8	32.3	217.8	35.7	0.728	0.476	1.337	1.022
		field edge2	Aug 2004-2005	0.91	0.20	267.6	10.4	321.9	12.5	0.169	0.064	0.236	0.075
		mid-buffer	Aug 2004-2005	1.08	0.28	123.9	9.2	147.7	11.0	0.537	0.413	0.906	0.632
		stream edge1	Aug 2004-2005	7.49	1.61	1.2	0.3	30.1	4.5	0.217	0.065	0.340	0.098
		stream edge2	Aug 2004-2005	4.69	1.13	0.5	0.1	32.8	8.2	0.494	0.339	0.648	0.417
		stream	Aug 2005	0.54		0.7		21.3		0.350		0.960	
Established forest		in field	Aug 2005	3.64		153.0		185.0		0.110		0.110	
	shallow	field edge	Jan - May 2004	2.19	0.14	0.7	0.1	16.0	6.7	0.002	0.002	0.002	0.002
		mid-buffer	Jan - May 2004	5.59	0.42	0.7	0.1	17.0	7.7	0.000	0.003	0.035	0.031
		stream edge	Jan - May 2004	32.27	0.51	0.9	0.2	42.4	12.7	0.009	0.010	0.785	0.242
	deep	field edge1	Jan - May 2004	16.10	1.19	0.7	0.1	24.6	1.8	0.103	0.018	0.154	0.056
		field edge2	Aug 2004-2005	9.48	0.96	1.5	1.0	22.0	3.1	0.063	0.026	0.134	0.074
		mid-buffer	Aug 2004-2005	14.78	1.49	0.6	0.1	73.1	38.6	0.099	0.032	0.170	0.052
		stream edge1	Aug 2004-2005	34.02	1.33	0.5	0.1	37.5	5.0	0.094	0.023	0.142	0.045
		stream edge2	Aug 2004-2005	16.78	1.21	0.5	0.1	43.2	20.4	0.117	0.026	0.177	0.042
CRP		in field	Aug 2005	3.07		25.0		28.5		0.050		0.070	
	shallow	field edge	Jan - May 2004	0.05	0.05	1.4	0.4	10.2	4.2	0.016	0.018	0.018	0.018
		mid-buffer	Jan - May 2004	0.28	0.18	3.1	0.8	14.3	6.1	0.002	0.002	0.002	0.002
		stream edge	Jan - May 2004	0.49	0.31	0.6	0.1	10.6	4.5	0.016	0.018	0.374	0.303
	deep	field edge1	Jan - May 2004	2.90	0.37	184.8	29.9	217.0	31.4	1.329	0.930	1.363	0.927
		field edge2	Aug 2004-2005	3.78	0.71	218.6	51.0	263.0	59.6	0.125	0.051	1.037	0.912
		mid-buffer	Aug 2004-2005	1.10	0.16	34.6	9.4	51.5	10.0	0.049	0.020	0.111	0.038
		stream edge1	Aug 2004-2005	2.47	0.50	88.3	24.5	114.2	25.7	1.240	0.826	2.063	1.019
		stream edge2	Aug 2004-2005	0.47	0.23	140.2	32.1	169.9	34.4	1.653	0.741	1.819	0.780
		stream	Aug 2005	1.59		0.3		20.9		0.240		0.960	
Non buffered control	shallow	stream edge	Jan - May 2004	1.05	0.44	131.3	6.2	160.0	13.1	0.057	0.046	0.063	0.043
	deep	field edge	Aug 2004-2005	8.50	2.57	84.0	35.4	158.8	45.6	0.154	0.061	0.166	0.060
		stream edge	Aug 2004-2005	9.47	2.51	99.3	34.1	116.3	34.1	1.541	0.975	1.560	0.972

buffers. I drilled holes to approximately half a meter below the water table, pumped the temporary well dry, and retrieved a groundwater sample after allowing the well to recharge for approximately 3 hours. The same day I also collected surface water samples from the tidal creek below the CREP and CRP buffers. Nutrient analyses from these "in-field" and "tidal creek" samples are also shown in Table 2-6.

The measurements suggest that spatial and temporal patterns in nutrient concentrations may exist in some buffers. In the established forest buffer, ammonium concentrations were high in the deep nested piezometers throughout the year, ranging from 9.5 to 34 µM, but concentrations were approximately 60 to 90% less in the shallower piezometers (Table 2-6). Ammonium, nitrate, and total dissolved nitrogen concentrations were consistent throughout the sampling periods in the CREP buffer, except for a spike in NH_4 concentration in the stream edge piezometers in August 2005. However, I did observe seasonal patterns in nitrogen concentrations in the CRP buffer and non-buffered control site. Through most of the CRP transect, NH_4, NO_3, and total dissolved N were lowest in the winter (Fig 2-12a). The patterns in the non-buffered control site were similar (Fig 2-12b). However, peak NH_4 concentrations were 2 to 10 times higher than concentrations in the CRP buffer, peaked later in the spring, and remained high through the last sampling day in August. Groundwater in the stream edge piezometer had the highest NO_3 and total dissolved concentrations in the early spring, but the high concentrations did not appear in the field edge until late spring to summer (Fig 2-12b).
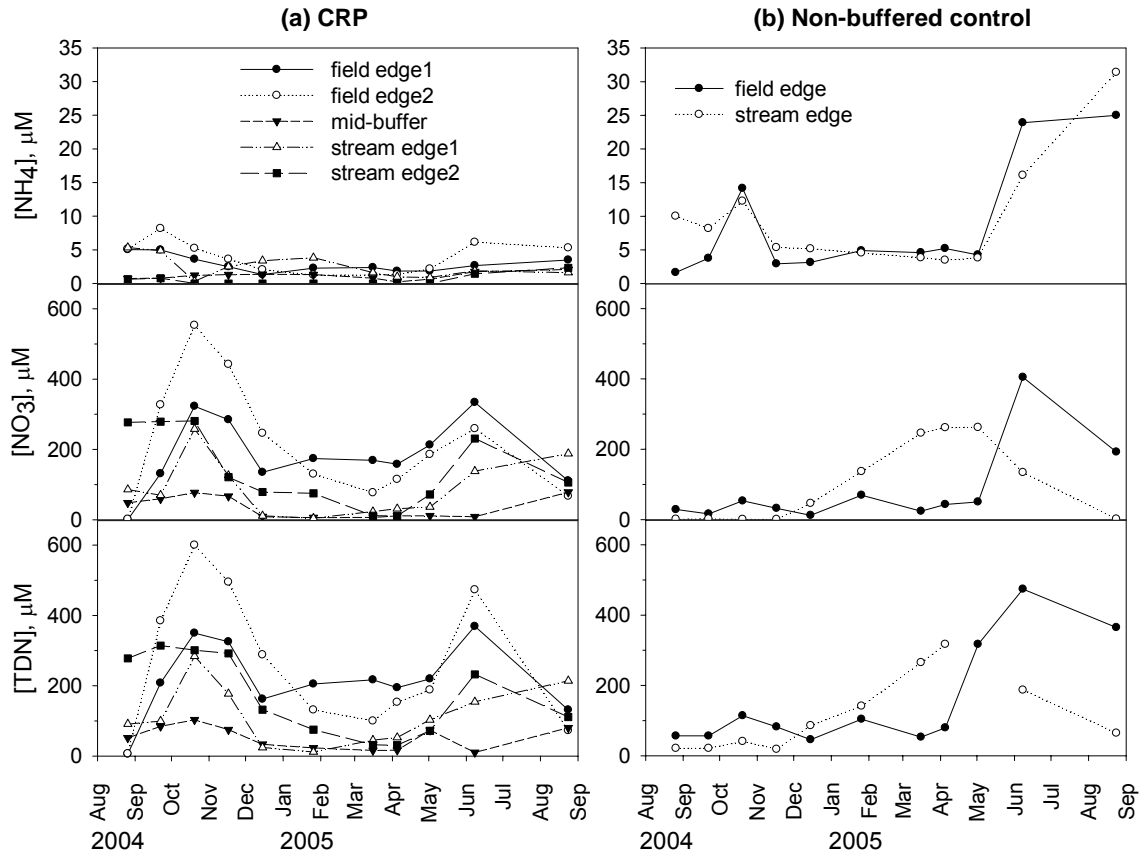
Fig 2-12. Monthly ammonium (NH$_4$), nitrate (NO$_3$), and total dissolved nitrogen (TDN) concentrations in the (a) CRP buffer and (b) non-buffered control from August 2004 through August 2005. Measurements, in µM, are shown for each piezometer: field edge1 (closed circles), field edge2 (open circles), mid-buffer (closed triangles), stream edge1 (open triangles), and stream edge2 (closed squares).

Phosphate and total dissolved phosphorus were consistently very low throughout the sampling period in most of the piezometers (Table 2-6). However, eight piezometers exhibited high total dissolved P concentrations in the late spring through fall (Table 2-7). Total dissolved P was composed entirely of PO$_4$ at low concentrations in the winter to early spring, but at warmer times of the year, PO$_4$ does not account for all of the total dissolved P (Table 2-7). In May through October, 0 to 84% of total dissolved P was PO$_4$ and, in this case, dissolved organic P may account for the remaining total dissolved P.

Oxygen concentration was also measured in June and August 2005 and was less than 100

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Table 2-7. Total dissolved P in 8 piezometers that showed high concentrations in the summer and fall. Phosphate accounts for most of the TDP during low concentrations, but in the summer, PO_4 accounts for less and more organic P could be contributing to high TDP concentrations. Dashes represent when P was less than analytical detection level.

		CREP			CRP				Non Buffered
	Piezometer	field edge1	mid-buffer	stream edge2	field edge1	field edge2	stream edge1	stream edge2	stream edge
[TDP], µM	January	0.141	0.089	0.018	0.063	---	---	0.037	0.089
	March	0.025	---	---	0.174	---	---	---	0.124
	April	0.060	---	---	0.234	---	---	0.184	0.234
	May	0.500	0.130	4.345	0.230	0.079	0.230	0.030	0.110
	June	0.615	0.630	0.530	0.260	0.320	0.170	0.150	5.500
	August	10.500	6.500	0.150	0.830	---	5.860	1.260	8.880
	September	0.787	1.123	0.470	9.626	8.316	6.676	5.846	0.292
	October	0.476	0.401	0.290	1.353	0.494	7.547	5.109	0.197
	November	0.224	0.071	0.607	0.633	0.122	0.148	5.071	0.122
	December	0.046	0.117	0.071	0.224	---	---	0.505	0.046
PO_4/TDP, %	January	100	100	100	100	---	---	100	100
	March	100	---	---	100	---	---	---	100
	April	100	---	---	100	---	---	100	100
	May	100	100	80	100	38	100	100	100
	June	100	100	72	31	13	18	13	100
	August	47	65	100	81	---	76	52	100
	September	53	4	41	100	4	0	84	83
	October	60	27	12	100	72	100	100	30
	November	100	100	100	100	100	100	100	100
	December	100	61	100	100	---	---	100	100
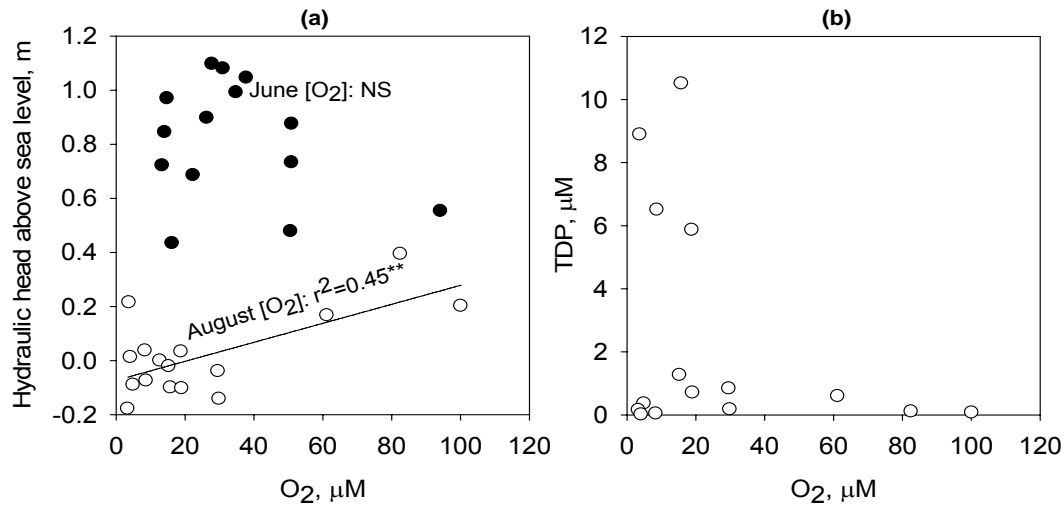
Fig 2-13. Dissolved oxygen concentrations in all piezometer (a) versus hydraulic head measurements in June (closed circles) and August (open circles, left panel) and (b) versus total dissolved phosphorus (TDP) in August (right panel).

μM in all piezometers (Fig 2-13a). In August, O_2-O concentration increased with height of hydraulic head ($r^2=0.45**$), although a rain event prior to the June sampling may have mixed the groundwater and obscured the relationship on that date. Also in August, the five piezometers that exhibited total dissolved P concentrations greater than 1 μM had O_2-O concentrations less than 20 μM (Fig 3-13b).

Vertical and horizontal gradients in average nitrate concentrations are shown in the cross-sectional diagrams in Figure 2-14. In the restored riparian buffers, nitrate decreases horizontally from the agricultural fields towards the tidal creek and vertically from deeper to shallow groundwater. An exception is the deep mid-buffer piezometer in the CRP buffer where nitrate concentration is 2.5 to 4 times lower than in the stream edge piezometers. Upslope of the established buffer nitrate concentration is 153 μM, but in the buffer, nitrate is less than 2 μM throughout the transect (Fig 2-14). The range of nitrate concentrations in the non-buffered control site were 84 to 131 μM and no reductions occurred from the agricultural field to the ditch. Using average groundwater

discharges from Fig 2-10 and annual average NO_3 in stream edge piezometers, I estimate that annual NO_3 discharges from each buffer are the following: 0.26 µmol NO_3-N m^{-1} yr^{-1} in the CREP buffer, 10 µmol NO_3-N m^{-1} yr^{-1} in the CRP buffer, 0.02 µmol NO_3-N m^{-1} yr^{-1} in the established forest buffer, and 19 µmol NO_3-N m^{-1} yr^{-1} in the non-buffered control site. Here I assumed that annual average NO_3 concentrations are low throughout the unconfined aquifer at the tidal creek edge. I sampled groundwater 1 to 4 m below ground at the tidal creek edge but am making estimates for the entire 5 m of unconfined aquifer. Future research at this site should include an attempt to install piezometers down to the confining layer.
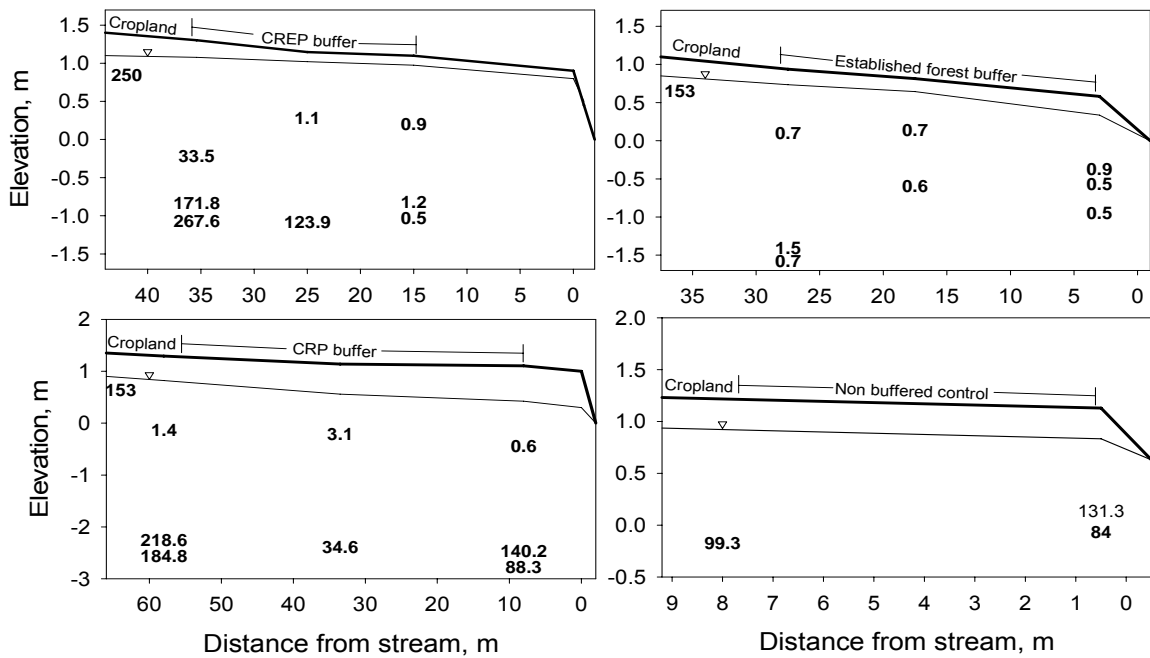
Fig 2-14. Cross-section of monitored groundwater in each buffer at Radcliffe farm and the vertical and horizontal gradients of nitrate concentrations. The ground surface is the solid line and annual average water table is the thin line below. Nitrate concentrations, µM, are shown in relation to the depth of groundwater sampled in each piezometer and distance from the stream.

The results of the two groundwater samples collected at the other site, Chesterville farm, in October 2003 are shown in Figure 2-15. Piezometer installation

was similar to the Radcliffe farm (Fig 2-3) except groundwater was collected from one

piezometer at the field edge in the CREP and CRP buffer, one piezometer at the stream

edge in the CREP buffer, two nested piezometers in the middle of both buffers, and three

nested piezometers at the stream edge of the CRP buffer (Fig 2-15). I did not survey the

land surface at this farm but estimated ground elevation from work done by Böhlke and
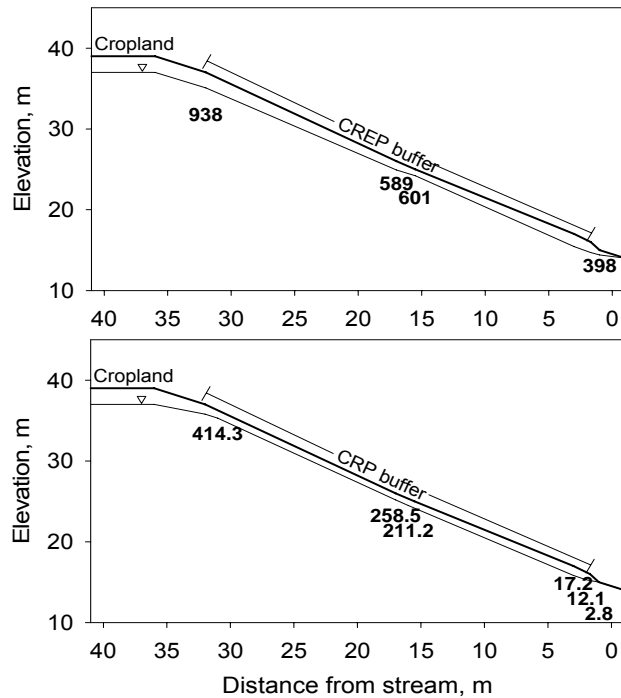
Fig 2-15. Cross-section of monitored groundwater in the CREP and CRP buffer at the
Chesterville Branch farm and the vertical and horizontal gradients of nitrate
concentrations. The estimated ground surface is the solid line and water table in October
2004 is the thin line below. Nitrate concentrations, µM, are shown in relation to the
depth of groundwater sampled in each piezometer and distance from the stream.

Denver (1995) in the same watershed of Chesterville Branch. The measurements

included piezometer depth below ground surface, depth below ground to hydraulic head,

and nitrate concentrations. Depth to hydraulic head varied from 2 m next to the farm

field to 20 cm next to the stream (Fig 2-15). Nitrate concentrations in groundwater

entering the buffers were approximately 2 to 4.5 times higher than in groundwater

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entering the CREP and CRP buffers at Radcliffe farm (Fig 2-14, Fig 2-15). I did detect a

horizontal gradient in nitrate concentrations, decreasing from field edge through the

buffers to the stream edge (Fig 2-15). Nitrate concentrations decreased in the CREP

buffer from 938 to 398 µM and from 414 to 3 µM in the CRP buffer. This is a 58 to 99%

reduction in NO_3 in groundwater under the restored buffers at the Chesterville farm,

although I have to assume that I was sampling along the same groundwater flow path

since I did not collect detailed hydraulic measurements at this site.

Denitrification

Dissolved gas analysis on the Membrane Inlet Mass Spectrometer revealed a

metabolically active environment in the groundwater at Radcliffe farm. Oxygen

concentrations were well below saturation (Fig 2-13), and excess N_2 was present in the

groundwater compared to concentrations expected in water at equilibrium with the

atmosphere (Table 2-8). Dissolved gas concentrations in water in equilibrium with the

atmosphere at average annual temperature (15^oC) are the following: 577.5 µM N_2-N,

311.3 µM O_2-O, and 15.3 µM Ar. In contrast, oxygen in groundwater varied from 13.4

to 94.3 µM in June and 3.4 to 100.2 µM in August (Table 2-8, Fig 2-13), and all

groundwater samples were suboxic or anoxic (as defined by Böhlke and Denver 1995).

Air temperature fluctuations over a year causes a variation of ±20% in saturated N_2

concentrations or, if assuming recent and local infiltration, a 18% increase in saturation

concentration in June (air temperature of 23^oC) and an 14% increase in saturation

concentration in August (air temperature of 25^oC). Average annual temperature has been

used by Mookherji et al. (2003) to calculate the concentration of nitrogen entering the

Table 2-8. Nitrogen (N_2), oxygen (O_2), and argon (Ar) measured in groundwater samples in June and August 2005 using the Dissolved Gas Analyzer of Kana et al. (1994). Excess N_2 is calculated assuming initial N_2 in water entering the groundwater is equilibrated with the air during recharge at 577.5 µM, based on solubility of N_2 gas at an average annual temperature of $15^{\circ}C$.

Buffer	Piezometer	Jun-05						Aug-05					
		measured on DGA, µM					calculated, µM	measured on DGA, µM					calculated, µM
		N_2-N	O_2-O	Ar	N_2-N/Ar	O_2-O/Ar	excess N_2	N_2-N	O_2-O	Ar	N_2-N/Ar	O_2-O/Ar	excess N_2
CREP	field edge1	706.6	31.1	16.5	42.8	1.9	129.1	668.0	15.9	16.0	41.6	1.0	90.5
	field edge2	708.0	27.9	16.5	42.9	1.7	130.5	677.9	19.1	16.3	41.5	1.2	100.4
	mid-buffer	722.4	37.9	16.1	44.8	2.3	144.9	688.9	8.7	16.4	42.1	0.5	111.4
	stream edge1	694.9	14.8	16.1	43.1	0.9	117.4	687.4	5.0	15.6	39.8	0.3	109.9
	stream edge2	690.9	34.9	16.1	43.0	2.2	113.4	677.6	3.4	15.6	39.4	0.2	100.1
Established forest	field edge1	732.1	13.4	17.0	43.2	0.8	154.6	683.3	8.5	16.3	41.8	0.5	105.8
	field edge2	663.7	51.0	16.3	40.7	3.1	86.2	676.5	4.2	16.3	41.6	0.3	99.0
	mid-buffer	676.5	48.5	16.5	41.0	2.9	99.0	577.8	100.2	15.0	38.6	6.7	0.3
	stream edge1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	stream edge2	712.0	21.8	15.6	45.6	1.4	134.5	530.9	82.6	13.7	38.6	6.0	-46.6
CRP	field edge1	765.9	22.4	16.1	47.4	1.4	188.4	753.6	29.6	16.5	45.7	1.8	176.1
	field edge2	706.4	14.2	15.7	44.9	0.9	128.9	749.4	12.8	16.7	44.8	0.8	171.9
	mid-buffer	667.5	94.3	16.5	40.4	5.7	90.0	741.6	30.0	16.1	43.2	1.9	164.1
	stream edge1	693.2	50.7	16.6	41.7	3.1	115.7	726.0	18.9	17.1	42.3	1.1	148.5
	stream edge2	751.2	16.3	17.1	44.0	1.0	173.7	762.0	15.4	17.9	42.5	0.9	184.5
Non buffered control	field edge	672.5	26.4	16.6	40.5	1.6	95.0	559.2	61.3	14.1	39.5	4.3	-18.3
	stream edge	656.7	51.0	16.6	39.6	3.1	79.2	622.3	3.8	14.8	42.1	0.3	44.8

groundwater at saturation and will also be used in the calculations here; however, it is important to note that most groundwater recharge in this area occurs during the winter when groundwater temperature is lower (Fig 2-6) and N_2 solubility is higher (Staver and Brinsfield 1998). The range of average N_2-N/Ar ratios was 39.6 to 47.4 in June and 38.6 to 45.7 in August (Table 2-8) in contrast to the expected N_2-N/Ar ratio of 37.9 based on an average groundwater recharge temperature and no denitrification. Elevated ratios suggest denitrification occurred along the groundwater flow path between recharge and sampling from the piezometers. Excess N_2 gas was present in all piezometers except two piezometers in August, and the excess N_2 measured in the field edge piezometers suggest that denitrification may be occurring under the farm field prior to entering the buffers (Table 2-8). The range of excess N_2 was 79.2 to 188.4 µM N_2-N in June and -46.6 to 184.5 µM in August (Table 2-8). The excess N_2 presented in Table 2-8 was the minimum NO_3 denitrified from the time of recharge in the agricultural field and along the groundwater flow paths before sampled from each piezometer. The two negative concentrations in August from the stream edge piezometer in the established forest buffer and the field edge piezometer in the non buffered stream suggest this groundwater may have recharged at a higher temperature, with less dissolved gas, than the annual average temperature of 15°C during recharge.

Since salt intrusion was likely in the established forest buffer and the stream edges of the CRP and CREP restored buffers (Table 2-3), excess N_2 can only be used to calculate denitrification of agriculturally-derived groundwater in the restored buffers from the field edge to the mid buffer piezometers. I must also account for degassing between the piezometers, the process in which air bubbles escape and strip dissolved

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gases from the groundwater. This may occur where hydrostatic pressure decreases

between piezometers (Mookherji et al. 2003) and where gas escapes from the

groundwater through spaces between the soil particles or macropores in the soil profile

(Blicher-Mathiesen et al. 1998). When this occurs, N_2 and Ar are stripped from the

groundwater at a predictable amount as a function of their partition coefficients (see eq.

2-2). In June, 39 μM N_2-N was estimated to have degassed between the field edge and

mid buffer piezometers in the CREP buffer using eq. 2-2, and in August, 45 μM N_2-N

was degassed between the same piezometers in the CRP buffer based on the decrease in

Ar concentrations. These corrections were applied to the data presented in Table 2-8.

In contrast to the pattern in the CREP buffer, N_2 in the CRP buffer decreases

between the field edge and mid-buffer piezometers more than can be accounted for by

decreases in Ar, even after I applied the correction to the N_2 concentrations for degassing

(see eq. 2-2). I could not detect denitrification along this transect in the CRP buffer since

measurements of N_2 were not increasing along the groundwater flow path. However,

excess N_2 was still present and may suggest that (1) denitrification is occurring under the

crop fields and the excess N_2 is lost in the buffer or (2) infiltrating water with similar

amounts of Ar but less N_2 dilutes the excess N_2 measurement.

However, N_2 does increase from the field edge to the middle of the CREP restored

buffer (Table 2-8). Excess N_2-N along this flow path increases between 11 and 21 μM

during the two sampling periods. I used these measurements of N_2 and average

measurements of hydraulic conductivity in the CREP buffer (7.8×10^{-2} m day^{-1}) and cross

sectional area (i.e., 5 m unconfined aquifer with 50% porosity) to calculate a

denitrification rate. Before accounting for the potential dilution of excess N_2 from

infiltrating groundwater (to be addressed in the next section), denitrification in the upper portion of the CREP buffer removed between 11 and 21 kg N ha^{-1} yr^{-1} in June and August.

<div align="center">Nitrate reduction processes</div>

Measurements of NO_3 concentrations, excess N_2, Cl$^-$ concentrations, and hydraulic conductivity (K) allowed me to estimate the relative contributions of denitrification and dilution to total nitrate reductions observed in the CREP buffer at Radcliffe farm. Monthly nitrate concentrations decreased from the agricultural field edge to the middle of the CREP buffer by 23 to 168 μM between August 2004 and August 2005 (i.e., based on the raw monthly data used to calculate annual averages in Table 2-6). When multiplied by cross-sectional area of the unconfined aquifer (A = 2.5 m^3 m^{-2}) and the time it takes for groundwater to flow from the field edge to mid buffer (i.e., 10 m/7.8x10^{-2} m day^{-1} = 128 days), this was a total reduction of 23 to 167 kg NO_3-N ha^{-1} yr^{-1}. Dilution from low-nitrate rainwater, denitrification in the anoxic groundwater, and plant uptake all contribute to this reduction in nitrate concentrations.

I estimated the relative contribution of dilution in the young restored buffer (CREP) by using the difference in Cl$^-$ concentrations between the non-buffered control site, where no dilution was occurring at the edge of the field, and the CREP site, where rainfall filtered through the buffer without contributing any agricultural contaminants to the subsurface groundwater (Spruill 2000). Chloride concentrations were 6.2 mM in the field and mid buffer piezometers of the CREP buffer and 14 mM in the non-buffered control (Table 2-3, Fig 2-16). This represented a 56% dilution in the CREP buffer in comparison

with the non-buffered control site. When applied to the Cl$^-$ concentrations in the CRP

buffer (Table 2-3), the comparison revealed a 24% dilution by rainfall from the field edge

to the middle of this buffer. These estimates were within the range of previous reports of

dilution in riparian buffers from 35 to 90% (Speiran 1996, Spruill 2000, Maitre et al.

2003).

Denitrification was also estimated using data collected with the N$_2$/Ar method in

June and August 2005 (calculated in the last section). However, since dilution of

rainwater was a dominant process in the CREP buffer that may have reduced 56% of the

nitrate in the groundwater, the rainwater with no excess N$_2$ also has the potential to

infiltrate the buffer and dilute 56% of the excess N$_2$ measurements made in June and

August. The measurements of 11 and 21 μM (Table 2-8) may reflect excess N$_2$-N

concentrations of 25 and 48 μM that were actually produced in the CREP buffer;

therefore, including potential dilution of excess N$_2$, denitrification may have accounted

for a reduction of at least 25 and 48 kg N ha^{-1} yr^{-1} in June and August. When the NO$_3$-N

decrease from the field edge to mid-buffer is 23 kg NO$_3$-N ha^{-1} yr^{-1}, denitrification may

be the dominant nitrate reduction process in the buffer. When the NO$_3$-N decrease is the

greatest, at 167 kg NO$_3$-N ha^{-1} yr^{-1}, denitrification may only account for 15 to 29% of this

NO$_3$-N decrease (Table 2-8, Fig 2-16).

After accounting for dilution and denitrification in the CREP buffer, the

remaining reduction at the maximum N loss was assumed to be plant uptake. The

difference of total reduction (167 kg N ha^{-1} yr^{-1}) and estimated dilution and denitrification

was a reduction of up to 13 kg NO$_3$-N ha^{-1} yr^{-1} attributed to plant uptake (Fig 2-16). This

is in the lower range of removal calculated in other coastal plain forests, 15 to 52 kg N

ha^{-1} yr^{-1}, as net incorporation of N into plant biomass (Peterjohn and Correll 1984, Lowrance et a. 1984).
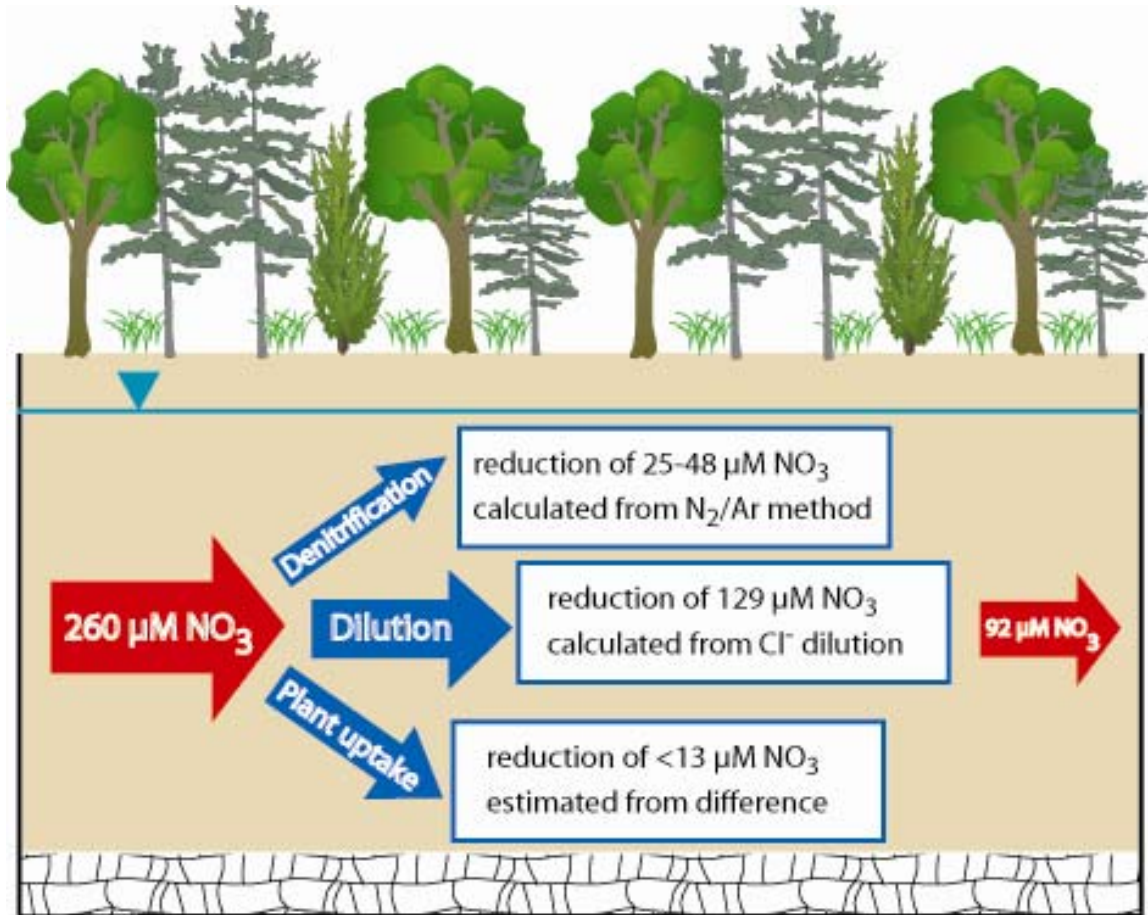
Fig 2-16. Conceptual diagram of groundwater cross-section at Radcliffe farm and the nutrient processes estimated when the difference in NO$_3$-N concentrations in the CREP site was at a maximum during the study.

Discussion

Hydraulic characteristics and connectivity

The ability of riparian forests to intercept agricultural nutrients depends greatly on the hydrogeologic conditions at each individual site (Phillips et al. 1993, Staver and

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Brinsfield 1996, Burt et al. 2002). Buffers have a limited ability to reduce groundwater nitrate if the biologically active riparian zone is not along the flow path of nitrate enriched groundwater. For this reason, this study on the effectiveness of restored riparian buffers to reduce groundwater nitrate included measurements of the hydraulic characteristics at Radcliffe farm.

Characterizing the hydrology on the farm and in the buffers required making some assumptions. First, due to the high water table and lack of equipment for drilling in very wet, unconsolidated soils, I was not able to drill down to the confining layer due to wall collapse. The deepest well was in the CRP buffer at 3.8 m below the ground surface (approximately 2 m below sea level). As a result, I was forced to assume that the unconfined aquifer at this farm is 5 m deep, similar to other areas in this hydrogeomorphic region (Owens and Denny 1979). Since the soils at Radcliffe farm are a mixture of silty clay loams, I assumed a porosity of 50% volume (Dunne and Leopold 1978, Novotny and Olem 1994); therefore, in calculations of aquifer volume I used a 2.5 m^3 water m^{-2} aquifer area. Porosity of the sand/clay mixture of soils at Radcliffe farm may vary between 45 to 55% volume. This 5% volume error would change the discharge calculations from eq. 2-4 and results in Figure 2-10 by ±10%. I also assumed that the groundwater flow path is parallel to the buffers along with the decreasing ground elevation (Table 2-1 and 2-2) and the positive hydraulic gradient from field edge to stream edge throughout most of the year (Fig 2-8).

Since Radcliffe farm is in a low-lying area next to a tidal creek, salt intrusion into the stream-side buffers is common. This contention is supported by three types of measurements during the study. First, conductivity measurements throughout the year

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and chloride measurements in January 2005 are high in the stream edge piezometers of the CREP and CRP buffers. This was also observed throughout the entire transect in the established forest buffer (Table 2-3), where salinity was as high as 7 and comparable to the salinity of local creeks. Secondly, I observed a reversal in hydraulic gradient in the non-buffered control, CRP, and established forest buffers in August (Fig 2-8). In the summer when evapotranspiration is high, the water table lowers in the buffers (Fig 2-7), and this may allow salt water from the adjacent tidal creek to inundate the edges of the forest buffers. Lastly, longer records of hydraulic head collected by automated pressure transducers show tidal fluctuations throughout the CRP buffer (Fig 2-9b). The fluctuations in hydraulic head were 5 to 10 cm in the stream edge piezometers and weakened to less than 5 cm in the field edge piezometers. I did not detect salt water from the tidal creek in the mid-buffer or field edge piezometers, but the tidal cycle in the adjacent creek may affect the hydraulic pressure in the groundwater in this buffer. However, I detected the highest salt concentrations in the established forest buffer (Table 2-3) but not any tidal fluctuations (Fig 2-9a). Hydraulic conductivity, K, is 2 to 7 times higher in the CRP buffer than in the established forest (Table 2-1). This low K in the established forest may prevent hydraulic pressure fluctuations in the groundwater at tidal time scales, whereas more permeable soils in the CRP buffer may allow faster responses to the changing tides.

Rainfall and tidal creek water have low nitrate concentrations and therefore dilute nitrate in the groundwater under the buffers. Tidal creek water may penetrate the soils in the streamside portion of the buffers (or the entire buffer in the case of the established forest) during high tides or in the summer when the hydraulic gradient is reversed (Fig. 2-

8). This may have influenced the very low annual average nitrate concentrations in the CREP stream edge and throughout the established forest buffer (Table 2-6, Fig 2-14). Low nitrate precipitation (38 µM, Rochelle-Newall submitted) falling on the buffers and infiltrating through the unfertilized soils may also dilute the upper portion of the saturated zone (Spruill 2000), which I observed from the lower nitrate concentrations in the shallow piezometers (Table 2-6, Fig 2-14). The lack of these nitrate and chloride patterns at the control site suggest dilution is not an important process where buffers do not exist and provide a benchmark to measure the importance of the dilution process in the established and restored buffers. Differences in Cl^- concentrations between the control site and the restored buffers suggest that groundwater is diluted by 56% in the CREP buffer and 24% in the CRP buffer. In these restored buffers, rain water may be contributing significantly to the NO_3 reductions observed along these flow paths (Fig 2-14). It is important to note that the Cl^- measurements were made in January, when the water table was high (Fig 2-8) at the time of year when evapotranspiration ceases and rainwater recharges the groundwater. Measurements in the summer may also reveal high dilution when evapotranspiration in the buffers removes high-nitrate groundwater, lowers the water table, and infiltrating rainwater reduces groundwater nitrate concentrations. The 57% less dilution estimated in the CRP buffer as opposed to the CREP buffer may be due to the 1 to 2 m deeper sampling depth (Table 2-1) or the greater tree biomass and more transpiration. Rainwater is likely to dilute the upper portions of the subsurface groundwater the most and have less effect with greater depth. The difference in dilution estimates may also depend on differences in transpiration between sites, where the 20 year old pine trees have more biomass and utilize more water from the subsurface

groundwater than the 7 year old trees in the CREP buffer.

Low groundwater nitrate concentrations at the stream edge of the buffers and low groundwater discharge through the buffers suggests nitrate from Radcliffe farm is not enriching the adjacent tidal creek. I estimate that nitrate discharge is lowest from the established forest buffer (0.02 μmol NO_3-N m^{-1} yr^{-1}) and highest from the non-buffered control (19 μmol NO_3-N m^{-1} yr^{-1}). The low hydraulic gradients, low hydraulic conductivities, and shallow unconfined aquifer result in very low groundwater discharges of less than 0.001 m^3 m^{-1} day^{-1} (eq. 2-3, Fig. 2-10). Net groundwater discharge per day was measured by Staver and Brinsfield (1996) along the Wye River, another tidal area on the Delmarva Peninsula, and they observed groundwater discharge much higher than the observations at Radcliffe farm. Discharge at the Wye River site was less than 0.1 m^3 m^{-1} day^{-1} in the summer and greater than 0.2 m^3 m^{-1} day^{-1} in the winter but fluctuated greatly on a daily basis depending on the tide (Staver and Brinsfield 1996). The discharge measurements at Radcliffe farm were based on one hydraulic head measurement per month and tidal fluctuations (especially in the CRP buffer, Fig 2-9b) may influence the discharge calculations at Radcliffe farm. The hydraulic conductivities (K) on Radcliffe farm (2 to 200×10^{-6} cm s^{-1}, Table 2-1) are also much lower than the K measured in the sandy sediments at the Wye River site of $10,000 \times 10^{-6}$ cm s^{-1} (Staver and Brinsfield 1996), and probably accounts for much of the difference between the two sites. Future studies at Radcliffe farm should include piezometers in the creek sediments adjacent to the riparian buffers similar to installations at Wye River (Staver and Brinsfield 1996). This may determine whether nitrate rich groundwater is bypassing the piezometers in the buffers and discharging into the tidal creek.

The low groundwater discharge reported here also may be underestimated due to macropores. Calculations of Darcian flow do not account for the potentially heterogeneous hydraulic characteristics of the soils along the groundwater flow paths or the potential for enhanced flow in macropores, which may cause an underestimation of discharge rates (Hubbard and Sheridan 1989). However, since a water balance for the farm field supported the low discharge measurements, I am confident the low groundwater discharge at Radcliffe farm is real. After accounting for potential evapotranspiration (70.5% of precipitation) and overland flow (23.5% of precipitation), only 6% of the annual average precipitation remained to infiltrate into the groundwater under the farm field (eq. 2-5). The groundwater input from the farm to the buffers was 0.0003 m^3 m^{-1} day^{-1}, comparable to the groundwater output from the buffers (Fig. 2-10). The slow groundwater discharge from Radcliffe farm into the tidal creek also suggests long retention times in the saturated soils and more opportunity for biological processing of nutrients in the buffers.

Nutrients and nitrate reductions

Nitrate is often the focus of groundwater research in agricultural landscapes. However, I observed some interesting patterns in other forms of nitrogen and organic forms of phosphorus in the groundwater at Radcliffe farm. In the established forest buffer, ammonium (NH_4) was consistently high, 9 to 34 μM, and nitrate (NO_3) was less than 1 μM in most of the piezometers throughout the year (Table 2-6). Other studies have also measured NH_4 concentrations of 10 to 40 μM in groundwater under riparian buffers (Jordan et al. 1993, Hedin et al. 1998, Spruill 2000, Maitre et al. 2003). In

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general, NH_4 is sorbed on soils or assimilated by the biological community in preference to NO_3, and consequently, NH_4 is usually low in groundwater. Maitre et al. (2003) proposes that the microbial process of dissimilatory NO_3 reduction to NH_4 may occur in groundwater, and in extremely reduced conditions of saturated soils, NH_4 accumulates from nitrogen reduction reactions (McBride 1994). Phosphorus is also very low in the established forest (less than 0.2 µM total dissolved P, Table 2-6) and may be a limiting nutrient to the vegetation in this mixed deciduous forest typical of the coastal plain. The plants may not be utilizing all available NH_4 as it is regenerated in the organic-rich soils and sediment.

Seasonal nutrient patterns exist in some of the buffers, but since I only sampled through one 4-season cycle, the observations may not be part of a repeating pattern. The peak in dissolved N concentrations in the fall and spring in the CRP buffer (Fig 2-12) and in the summer in the non-buffered control (Fig 2-13) may be a result of biological or physical processes during these seasons. Since groundwater movement is slow, spring fertilizer applications are not likely to be reflected immediately in the groundwater under the CRP buffer. However, 20 years ago the CRP buffer was planted because this portion of the farm had highly erodible soils. Hydraulic conductivity was low where I was sampling, approximately 3.5 m below the ground, but the erodible soils higher in the profile may be more sandy and permeable. If this is true, water moving through these soils may reflect spring fertilizer applications and diffuse into the deeper groundwater piezometers. However, it is more likely that the patterns in nitrogen concentrations in the CRP and non-buffered control (Fig 2-12) are a result of dilution during the winter and spring. The pattern of higher hydraulic head from December through May is apparent in

the CRP buffer (Fig 2-7) and may explain the lower nitrogen concentrations during this time period (Fig 2-12). In the winter when evapotranspiration is essentially zero, rainfall recharges the groundwater and the higher water tables dilute the nitrate-rich groundwater moving from the agricultural fields (Fig 2-17). Dilution may also be important in the summer when high evapotranspiration from warm temperatures and large tree biomass removes nitrate-rich water from the ground and is replaced by low-nitrate rainwater infiltrating into the soil during rain events (Fig 2-17). At this farm in particular,
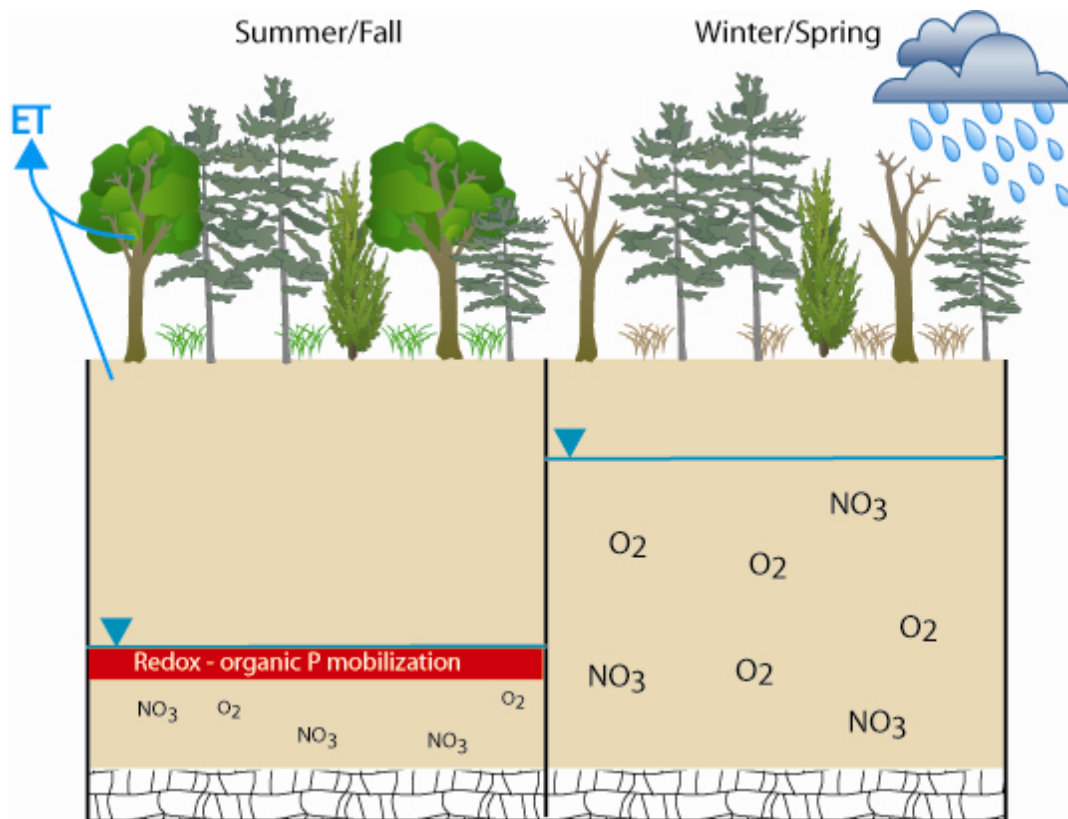
Fig 2-17. Conceptual diagram of groundwater cross-section at Radcliffe farm during the summer/fall and winter/spring. In the summer and fall when evapotranspiration is high and water table and dissolved oxygen concentrations are low, redox potential is high and organic phosphorus may be released from the soils. In the winter and spring when groundwater is recharging and water table is high, nitrate-rich groundwater is diluted when evapotranspiration shuts down during cold weather and when plants are inactive.

rainwater dilution may be more important to nitrate reductions than at other farms where the nutrients are not as well-managed. This farm has low groundwater nitrate concentrations in comparison to other farms on the Delmarva Peninsula (Hamilton et al. 1993), where rainwater may not dilute the high nitrate concentrations as much and denitrification may have a larger role in nitrate reductions. Large spikes in total dissolved P concentrations, up to 10.5 μM, were observed in many piezometers during the warm months of summer and fall (Table 2-7). Organic P, which is not detected at other times of the year, becomes a large fraction of the total dissolved P during this spike (Table 2-7) and may suggest mobilization and leaching of organic P in the warming soils (Russell 1973). In August, O_2 concentrations decrease as hydraulic head lowers (Fig 2-13a). In groundwater where hydraulic head is low and low O_2 concentrations lead to high redox potential, organic P may be released from the soils (Fig 2-13b and 2-17). Reduced conditions in riparian zones have been attributed to the desorption of dissolved phosphorus from iron and aluminum oxides and from soil particles, which allows mobilization in the subsurface groundwater (Mulholland 1992, Carlyle and Hill 2001). In general, NH_4 and total dissolved P are minor components of groundwater nutrients in most forest buffers and throughout most of the year, but considering the magnitude of some of the observed concentrations, these isolated spikes may represent important processes in the forest buffers studied here.

Groundwater nitrate concentrations measured in the buffers on Radcliffe farm were low in comparison to studies in other areas of the Delmarva Peninsula. Hamilton and Heisel (1995) collected groundwater samples from agricultural areas throughout the Delmarva Peninsula and found NO_3 as high as 48 mg L^{-1} (3400 μM) and a median of 8.2

mg L^{-1} (590 µM). In the restored buffers at the Chesterville Branch farm I observed NO$_3$

concentrations as high as 938 µM at the edge of the farm field (Fig 2-15), comparable to

those of Hamilton and Heisel (1995). Shallow groundwater under corn production at the

Wye Research and Education Center (WREC) in Queenstown, Maryland, also in the fine-

grained lowland of the coastal plain, had NO$_3$ concentrations of 10 to 20 mg L^{-1}, or 715

to 1430 µM respectively (Staver and Brinsfield 1998). It is likely that fertilizer

applications are similar at Radcliffe farm during corn production, but NO$_3$ concentrations

at two locations in the field were much lower (153 and 250 µM, Table 2-7) than at the

WREC site. This suggests that denitrification is occurring in groundwater under the farm

field or fertilizer input is more closely coupled to crop uptake. Parkin and Meisinger

(1989) measured denitrification potential under the crop rooting zone in a corn field at

WREC. Denitrification was insignificant and they concluded that the organic matter and

carbon levels in the soils were too low to support denitrification. Radcliffe farm does

have some of the same low organic matter, well-drained Matapeake silt loams as at the

WREC site. Although the mixture of other moderately well-drained and poorly drained

soils (Table 2-1) may have higher organic content and support some denitrification below

the farm field, which may have influenced the lower observed NO$_3$ concentrations.

 Excess N$_2$ in the piezometers throughout the riparian buffers suggests that

denitrification is occurring along the groundwater flow paths at Radcliffe farm (Table 2-

8). I measured a denitrification rate of 25 to 48 kg N ha^{-1} yr^{-1}, 15 to 29% of the NO$_3$

reduction, in the CREP restored buffer using the N$_2$/Ar method (Kana et a. 1994, Blicher-

Mathiesen 1998, Mookherji et al. 2003). This rate is lower than the 68 kg N ha^{-1} yr^{-1}

denitrification rate, or approximately 76% of the NO$_3$ reduction, measured in a restored

buffer by Lowrance et al. (1995) using the acetylene inhibition technique (Table 2-9). This study in the coastal plain of Georgia took place during the first 2 years of restoration of the riparian wetland buffer and liquid manure was being applied to the adjacent field. These higher denitrification rates may be the result of the manure application and very high NO_3 fluxes into the riparian wetland at this site (Lowrance et al. 1995) as opposed to potentially lower fertilizer application at Radcliffe farm. The denitrification rate measured at Radcliffe farm is also lower than rates typically measured in other aquatic environments (Table 2-9).

Table 2-9. Denitrification rates measured in riparian zones and various terrestrial and aquatic ecosystems. Denitrification rates from Greene 2005 are a compilation of data from a literature review. (see Greene, S.E. 2005. Measurements of denitrification in aquatic ecosystems: literature review and data report. University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, Maryland. 29 p.)

Ecosystem	Denitrification rate, kg ha^{-1} yr^{-1}	Source
Farm fields	2-25	Meisinger pers. com.
Restored riparian zones	68-125	Lowrance et al. 1995, this Ch.
Established riparian zones	1-295	Naiman et al. 2005
Freshwater streams/lakes	5-3500	Greene 2005
Salt marshes	2-900	Greene 2005
Estuaries/Coastal ocean	0-2700	Greene 2005

Low denitrification rates observed in the CREP restored buffer may also be a result of the technique used to measure excess N_2 production in the groundwater and due to the large influence of rainwater dilution at this farm. Not only did I measure very low rates in the CREP buffer, but I did not detect increasing excess N_2 along the groundwater flow paths in the CRP or established forest buffers (Table 2-8). The N_2/Ar method is affected by degassing, which has been corrected for in the results (eq. 2-2), but also by gas diffusion. Degassing will strip N_2 and Ar molecules from the groundwater at predictable amounts (eq. 2-2, Blicher-Mathiesen 1998). However, gas diffusion will decrease N_2 concentrations in the groundwater but not Ar. Gas diffusion is a very slow

process, and Blicher-Mathiesen (1998) did not attribute any N_2 losses from this process in a Danish riparian wetland. Considering the slow discharge rates (Fig 2-10), high water tables (Fig 2-14), and long groundwater retention times at Radcliffe farm, N_2 loss from the groundwater by diffusion may be a significant process. Other methods to account for diffusional losses of excess N_2 from groundwater should be used at this farm in the future. In addition to N_2 diffusion, rainwater dilution which lowers nitrate concentrations in the summer (Fig 2-12) may also dilute the N_2/Ar signal in the subsurface groundwater. The amount that dilution, denitrification, and plant uptake contribute to nitrate reduction depends on where these processes occur along the flow path from the farm field and through the buffer. In order to quantify this dilution effect and separate it from the measurement of denitrification, vertically stratified sampling for excess N_2 could be used to separate NO_3 reduction from rainwater dilution close to the surface from NO_3 reduction from denitrification throughout the unconfined aquifer.

Conclusion

Subsurface groundwater from Radcliffe farm is contributing very little nitrate to the adjacent tidal creek which eventually flows into the Little Choptank River and Chesapeake Bay. Groundwater NO_3 concentrations entering the buffers from the field are low in comparison with other similar crop fields, which suggests that NO_3 reductions are occurring before entering the buffers on the edge of the farm fields. Additional groundwater NO_3 reductions also occur in the extensive system of established and restored forest buffers around the farm field, and calculations suggest that rainwater dilution and denitrification influence groundwater NO_3 concentrations. These processes

are likely to be magnified by the slow groundwater discharge rates from the farm field through the riparian buffers. The non-buffered control site on Radcliffe farm is essentially the only area not restored within the last 20 years. The lack of NO_3 reduction in this control site provides insight into the higher NO_3 input into the tidal creek prior to the beginning of restoration at the farm 20 years ago.

This research is an example of measured nutrient reductions in restored riparian buffers in the coastal plain of Maryland. Nutrient reduction goals attributed to restoration of riparian buffers in programs such as CRP and CREP should consider reductions likely in different hydrogeomorphic regions (i.e., Lowrance et al. 1995). It is likely that the very low nitrate fluxes from Radcliffe farm into the adjacent tidal creek are due to low hydraulic conductivity of the soils, high water tables, and slow groundwater discharge from the farm. Riparian buffer restoration in saturated, poorly-drained soils may be important to mitigation of agricultural supply of nutrients to adjacent waterways by providing a constant carbon source to the soils (i.e., decomposing plant material) and enhance denitrification potential. However, nutrient reductions may not be as high in other regions with large topographic relief, well-drained soils, and lower water tables. In these areas, nutrient management may be more successful if buffer restoration was coupled with BMPs such as cover crops, which reduce nutrient leaching from the field. Similar research should be carried out in restored buffers in other hydrogeomorphic regions, which would help to set nutrient reduction goals for the extensive CREP effort implemented in Chesapeake Bay watershed.

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Chapter 3

WATERSHED-SCALE ASSESSMENT OF CREP RIPARIAN BUFFERS AND
WATER QUALITY

Abstract

Restoration of riparian buffers has been an important component of nutrient reduction

strategies in the Chesapeake Bay watershed. Maryland was the first state to adopt a

Conservation Reserve Enhancement Program (CREP), which provides financial

incentives to farmers to take agricultural land out of production and plant streamside

vegetation. Between 1998 and 2004, 1 to 30% of the streamline, or a total of 1120 ha,

was restored in 15 small, agriculturally-dominated subbasins in the Choptank River

watershed. However, I did not detect differences in nutrient concentrations between the

subbasins based on the area of restored buffer, the percentage of streamline restored, or

the percentage of total riparian buffer in the subbasins ($p > 0.05$). Even though the CREP

increased the total buffered streamline in these subbasins from an average of 33% to

44%, nitrate and total nitrogen concentrations have continued to increase in many streams

since past monitoring at these sampling sites almost 20 years ago. I propose that nitrogen

reductions in these subbasins have not occurred because (1) in addition to the length of

streamline buffered, buffer age, width, and connectivity between buffers are also

important to nutrient reductions, (2) agricultural nutrient sources and the

hydrogeomorphic characteristics within the subbasins dominate the stream water

chemistry, and (3) riparian buffer restoration is not extensive enough to have measurable

affects on the stream water quality in these subbasins.

Introduction

  The productivity of agriculture in the US has been a great success, although it has come at the expense of impaired water quality in many agriculturally-intensive regions. The green revolution in the 1960s led to the control of crops through genetics and chemical fertilizers and pesticides, has maximized crop yields, and has been successful in feeding a large population while keeping prices low (Evenson and Gollin 2003). Since this time, modern agriculture has been "decoupled" from the ecosystems supporting it through subsidies encouraging overproduction, externalization of environmental costs, pressure to minimize environmental regulations, and the public's desire for inexpensive food (Robertson and Swinton 2005). However, the overwhelming evidence is that excess nutrients from agricultural sources are contributing to the degradation of downstream aquatic ecosystems (Magnien et al. 1992, Malakoff 1998, Beman et al. 2005). Recognition of this has led to an effort to manage agricultural landscapes for food production and ecosystem health, and quantifying the success of these potential solutions on buffering the environmental impacts of agriculture is a critical research need in the United States. This research also has the potential to influence adoption of similar agricultural management in developing countries, where projected increases in human population may lead to an increase in fertilizer application worldwide by 2 to 3 times, an increase in land conversion to agriculture, and the worldwide expansion of eutrophied waters (Frink et al. 1999, Tilman 1999, Tilman et al. 2001). Adoption, monitoring, and adjustments of agricultural management practices may improve ecosystem health in the US and prevent ecosystem degradation in other areas of the world.

Agricultural nutrient management has been an important part of the goals of abating eutrophic and hypoxic waters and restoring ecosystem health in Chesapeake Bay (EPA 2000, Staver and Brinsfield 2001, Boesch et al 2001). Many Best Management Practices (BMPs) have been implemented on farmland in the Chesapeake Bay watershed; BMPs include conservation tillage, winter cover crops, and grass and forest riparian buffers. In this paper, I focus on one program that has supported the restoration of riparian buffers throughout the watershed, especially in Maryland, the Conservation Reserve Enhancement Program (CREP). This program operates under the current provisions of a program introduced by the US Department of Agriculture (USDA) in 1985, the Conservation Reserve Program (CRP), which focused on planting trees in highly erodible soils on agricultural fields. The CREP was introduced in 1998 as a joint federal and state program that provides financial incentives to farmers to take stream-side agricultural land out of production and plant riparian vegetation. In addition to buffers restored under the CRP, 100 000 more acres (or 40 500 ha) of grass and forest buffers can be restored in states where a CREP has been adopted. The objectives for the program differ throughout the US, but in Maryland, the goal is to restore the 40 500 ha of riparian buffers to protect the water quality of Chesapeake Bay (Smith 2000, USDA 2004). The Chesapeake Bay Program has embraced the restoration of riparian buffers and has expanded its goal of 3230 km of restored streamlines in the watershed by 2010 to the current goal of 16 100 km by 2010 (EPA 2000, EPA 2003). The long term goal is to have 70% of the streams in the Chesapeake Bay watershed buffered by riparian forests (EPA 2003).

Predictions of restored buffers' ability to reduce nutrient inputs to Chesapeake Bay are based on plot-scale research in established, or mature, forest buffers. This research has shown that riparian forests have the potential to remove 67 to 89% of the nitrogen in subsurface groundwater (Lowrance et al. 1984, Peterjohn and Correll 1984, Jacobs and Gilliam 1985) and over 50% of the sediment and particulate phosphorus in surface runoff (Peterjohn and Correll 1984, Magette et al. 1989). Riparian buffers reduce and remove nitrogen from agriculturally-derived groundwater through denitrification, plant uptake, and dilution by rainwater infiltration through unfertilized buffers and trap sediment and phosphorus in erosion of agricultural soils during overland flow events (Fennessy and Cronk 1997, Naiman and Decamps 1997, Naiman et al. 2005). Considering this scientific understanding, the applicability of riparian buffers as a management practice in the Chesapeake Bay watershed was addressed by Lowrance et al. (1995). They highlighted the potential for riparian buffers to reduce agricultural nutrients in certain hydrogeomorphic regions of the watershed but stressed the importance of integrating research at scales appropriate to the restoration efforts.

However, research on the ability of restored riparian buffers to reduce nutrients at a watershed-scale in the agricultural landscape is lacking. Maryland CREP has ambitious goals for nutrient reductions in the restored buffers: 5.2 million kg of nitrogen and 0.5 million kg of phosphorus (USDA 2004). This is 31% of the total nitrogen reduction goal and 38% of the phosphorus reduction goal for the state of Maryland, which means that approximately one-third of the nutrient reductions goals are dependent on one restoration initiative. These goals are reasonable based on the reductions measured in established forests, but the degree and processes of nutrient reduction may be different in newly

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established riparian buffers with young trees. Furthermore, at the watershed-scale other ecosystem processes become important. For instance, Philips et al. (1993) found that on the Delmarva Peninsula, nitrate concentrations at the watershed scale do not depend solely on the amount of established forested wetlands but also the hydrogeomorphic characteristics within the watershed. Lee et al. (2001) also found that watershed nitrate export decreased as hydric soils in the watershed increased. There have been watershed-scale assessments of management practices such as the impact of fertilizer reduction on baseflow nitrogen concentrations (Tomer and Burkart 2003) and sediment-control BMPs on stormflow phosphorus concentrations (Bishop et al. 2005), but there has been no confirmation that restoration of riparian buffers has the ability to improve water quality at the watershed scale.

However, plot-scale studies and modeling of restored riparian buffers are emerging research topics. A few studies have documented nutrient reductions in surface runoff and groundwater through individual restored buffers at similar rates as plot-scale studies in established forest buffers (Clausen et al. 2000, Vellidis et al. 2003, see Ch. 2). Others have focused on gaining insight into effects of restoration efforts at the watershed-scale by modeling watershed-scale effects on nutrient concentrations based on the hydraulic characteristics and extent of restored buffers (i.e., Riparian Ecosystem Management Model, REMM, Stone et al. 2001) and by modeling the potential erosion control of CRP grass buffers in the western US (Das et al. 2004). In these cases, modeling may be an effective tool where large-scale restoration of buffers does not exist or obtaining information on the buffer locations in the watersheds is difficult.

The lack of watershed monitoring of restoration efforts is not unique to restored riparian buffers or to the Chesapeake Bay region. Only 6% of river restoration projects in the Chesapeake Bay watershed have been monitored, slightly lower than the national average of 10% (Bernhardt et al. 2005). In general, the potential for large restoration projects to serve as landscape-scale experiments is underutilized by the academic community. In a literature review, Holl et al. (2003) found that 32% of articles mentioning landscape restoration emphasized the importance of large-scale restoration but did not offer any specific methodologies to evaluate the restoration. Furthermore, 17% of the articles noted the need for restoration but offered no guidance for the effort. The Holl et al. (2003) review highlights the disconnect between management efforts applied in the field and the evaluation of the resulting effects on the ecosystems. Without this exchange of ideas and recommendations, adapting restoration efforts to take advantage of the full potential of water quality benefits is not likely to occur.

In this chapter, I discuss the water quality effect of riparian buffer restoration in 30 subbasins throughout two tributaries of Chesapeake Bay. I compared differences in amounts of restored buffers and stream water nutrient concentrations among the subbasins, in a comparative watershed study. I hypothesize that after correcting for differences in amount of agricultural land between subbasins, nitrogen concentrations will decrease as CREP increases in the subbasins. Riparian buffer restoration through the CRP and CREP has been substantial, especially in the Choptank watershed, and here I evaluate the effects of this restoration on water quality of baseflow in non-tidal streams.

Methods

Study sites

The Choptank and Chester River watersheds are located in the Atlantic coastal plain on the eastern side of Chesapeake Bay (Fig 3-1). In general, land use in these watersheds is dominated by agriculture (~50 to 55%), mostly a soybean and corn crop rotation which is widely used on the Delmarva Peninsula (Staver and Brinsfield 2001). Forests are the next most prominent land use, and 42% of the total forest is established riparian forest (Norton and Fisher 2000). Urban and developed areas make up less than 5% of the land use in this rural area, although there is evidence that urbanization is increasing (Benitez and Fisher unpubl). On average, rainfall is 110 cm per year in the Choptank and Chester watersheds, and stream water yields have generally been 35 cm yr^{-1} in the outer coastal plain of the Chesapeake Bay watershed (Jordan et al. 1997).

Descriptions of regions by hydrological and geological characteristics are useful in characterizing groundwater flow and water quality patterns (Hamilton et al. 1993, Philips et al. 1993, Bachman and Philips 1997). Most of the 30 subbasins sampled in this study (Fig 3-1) are located in the well-drained upland of the Delmarva Peninsula. Typically, the water table in this region is 3 to 10 m below ground and has well-drained soils which provide good soil conditions for agriculture. However, in the upper portions of the Choptank River watershed, some of the subbasins lie in the poorly drained uplands. This area has lower topographic relief, shorter groundwater flow paths, and lower-gradient stream valleys than the well-drained upland. The soils are permeable but are poorly-drained because the water table is generally 0 to 3 m below the ground.
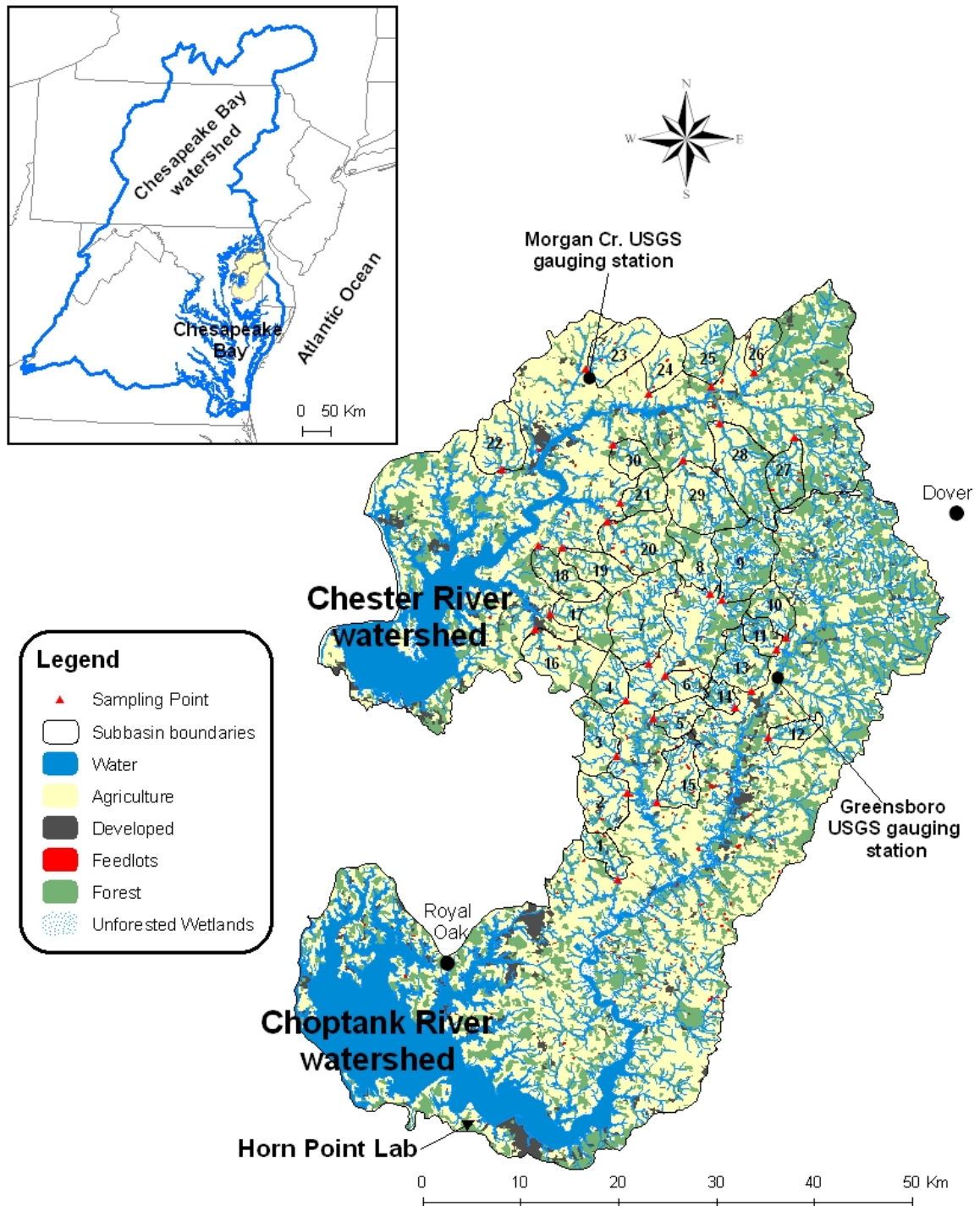
Figure 3-1. Location and land use of study sites in the Chesapeake Bay watershed on the Atlantic coastal plain. I sampled 15 subbasins in the Chester River watershed and 15 subbasins in the Choptank River watershed.

Figure 3-2 shows the extent of hydric, or water-saturated, soils in these Choptank subbasins. The poorly-drained uplands are located in the northeastern portion of the study area where there is an increase in hydric soils.
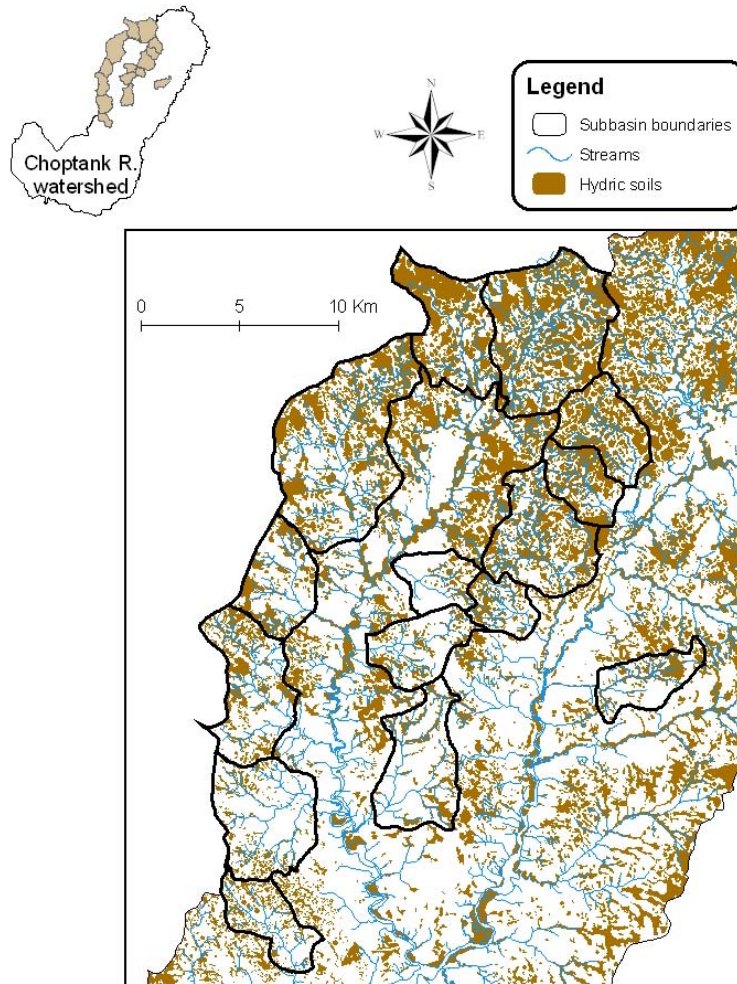
Figure 3-2. Location of hydric soils in the 15 Choptank subbasins.

This study focused on 15 subbasins in the Choptank and 15 subbasins in the Chester River watershed (Fig 3-1), and their individual size, land uses, and soil types are shown in Table 3-1. The sampling point for each subbasin is at or above the head of tide, and all non-tidal streams have been sampled in the past (1986 in the Choptank and 1992 to 1993 in the Chester, Fisher et al. 1998, Norton and Fisher 2000). Agriculture in these

Table 3-1. Land area, land use, soil types, and hydric soils in 15 Choptank River and 15 Chester River subbasins. Fisher et al. (1998) deriverd land use from Digital Orthophoto Quarter-Quadrangles (DOQQs) in 1990. Norton and Fisher (2000) derived soil type and hydric soils from digitized soil maps of the region.

Watershed	Subbasin	ID # (Fig 3-1)	Area, km^2	Land use, % of subbasin area				Soils, % of subbasin area				
				Agriculture	Developed	Feedlots	Forest	A	B	C	D	Hydric
Choptank River	Kittys Corner	1	13.5	64.3	2.0	0.9	32.1	46.2	22.1	23.3	2.5	26.0
	Cordova	2	26.5	75.1	4.0	1.3	18.4	53.8	22.4	16.9	1.2	14.6
	Norwich Creek	3	24.5	69.5	1.8	0.4	23.1	11.7	35.7	21.7	26.5	32.6
	Blockston Branch	4	17.0	63.3	0.0	0.3	28.3	2.3	39.5	20.1	38.0	34.3
	Piney Branch	5	14.7	78.0	3.6	1.6	16.2	57.9	13.6	23.3	0.8	24.1
	Oakland	6	10.0	83.8	4.4	1.3	9.6	74.2	5.9	15.9	0.9	16.8
	German Branch	7	51.4	67.8	0.2	0.9	26.8	0.7	36.6	11.7	51.0	45.2
	Beaverdam Ditch	8	23.3	62.3	0.8	0.0	32.2	0.7	27.9	5.3	66.1	64.1
	Long Marsh Ditch	9	40.5	54.1	0.4	0.5	40.8	13.7	22.3	9.5	54.5	63.7
	Broadway Branch	10	16.2	61.5	2.3	0.7	35.1	29.0	12.5	16.9	41.6	58.4
	Oldtown Branch	11	11.6	54.3	8.4	1.2	32.3	29.5	9.6	27.5	32.3	59.9
	Spring Branch	12	12.2	74.3	0.3	0.3	21.6	59.4	8.3	26.8	5.2	32.0
	North Forge Branch	13	25.0	59.6	2.1	0.2	30.7	31.0	16.8	29.8	21.0	51.2
	South Forge Branch	14	8.5	62.9	5.3	1.4	28.2	45.7	11.7	34.3	3.9	38.2
	Downes	15	23.4	76.8	5.1	1.7	15.6	66.6	11.9	19.0	0.4	19.4
	Average		21.2	67.2	2.7	0.8	26.1	34.8	19.8	20.1	23.1	38.7
Chester River	Mill Stream Branch	16	35.0	71.0	2.3	0.3	26.0	0.5	50.4	24.2	21.3	20.8
	Three Bridges Branch	17	22.2	65.0	1.7	0.3	32.6	0.0	41.6	22.6	30.2	30.1
	Island Creek	18	21.1	56.1	3.7	0.3	38.7	0.3	36.7	15.8	41.6	41.0
	Granney Finley Branch	19	20.6	64.9	1.1	0.5	31.6	0.2	53.6	4.8	35.3	35.3
	Southeast Creek	20	39.3	67.0	1.5	1.6	29.0	0.1	54.5	7.5	34.2	33.4
	Browns Branch	21	16.3	58.3	1.4	0.0	39.1	0.7	57.1	5.3	28.9	28.9
	East Langford Branch	22	29.1	82.3	1.3	0.3	13.9	0.0	61.3	34.7	1.9	4.4
	Morgan	23	31.2	88.9	1.3	0.9	8.2	1.5	35.4	57.0	0.1	1.1
	Chesterville Branch	24	17.3	91.9	0.0	1.0	6.7	0.0	78.2	16.0	5.2	8.9
	Mills Branch	25	26.3	64.5	0.4	0.3	33.7	0.3	14.3	58.2	26.5	28.6
	Wallace	26	12.7	77.4	0.2	1.2	20.5	2.6	57.0	21.7	18.3	16.3
	Peters Corners	27	19.7	50.2	0.8	1.7	46.9	4.1	39.7	1.5	53.5	53.5
	Unicorn Branch	28	44.3	63.2	1.8	0.3	33.9	3.6	53.3	2.7	39.7	39.6
	Dudley Corners	29	42.5	72.4	2.2	0.3	24.3	0.2	49.5	4.5	42.5	42.3
	Foreman Branch	30	13.4	64.7	1.7	0.0	33.1	0.9	66.3	0.9	27.7	27.7
	Average		26.1	69.2	1.4	0.6	27.9	1.0	49.9	18.5	27.1	27.5

subbasins varies from 50% to 92% of subbasin area, with 10 to 30% forest, and the

average land uses are similar between the Choptank and Chester subbasins. However,

soils differ between watersheds, and the subbasins in the poorly-drained uplands (i.e.,

German Branch, Beaverdam Ditch, Long Marsh Ditch, Broadway Branch, and Oldtown

Branch) have more hydric soils and D class (low permeable) soils than the other

subbasins located in the well-drained uplands (Table 3-1, Fig 3-2).

Location of CREP sites

Since riparian buffers provide wildlife habitats, especially for waterfowl, the

organization Ducks Unlimited provided partial funding for Maryland's CREP. They

compiled location, area, and type (grass, forest, or wetland) of each CREP buffer

implemented between 1998 and 2001 in Kent, Queen Annes, Talbot, Dorchester and

Caroline Counties into a geographic information system (GIS) database (Fig 3-3). I also

gathered data from the local Farm Service Agency (FSA) office in Kent County,

Delaware to develop a complete set for the Choptank and Chester watersheds (Fig 3-3).

However, the 30 subbasins in this study were only located in Kent, Queen Annes, Talbot,

and Caroline counties in Maryland.

Since the data set supplied by Ducks Unlimited only provided the locations of

farms with CREP sites (Fig 3-3) and not actual shape, I estimated the percentage of

streamline buffered by each CREP site in the 30 subbasins. At the time of analysis, a

polygon coverage of CREP location and shape was available for Talbot County. The

average width of CREP sites in Talbot County was 47 m, which officials at the local

USDA county offices agreed was a valid width estimate, and most CREP sites buffered

only one side of the stream. I used this width estimate and the area of each CREP site in the 2001 data to estimate total streamlength buffered in each subbasin:

$$\%L_b = \frac{(A/W)}{L_t \times 2} \times 100 \qquad \text{(eq. 3-1)}$$

where $\%L_b$ is the percentage of streamline buffered by CREP, A is the area of each CREP site, W is the average width of each CREP site (47 m), and L_t is the total streamlength in each subbasin, which includes both sides of the streams when multiplied by 2.
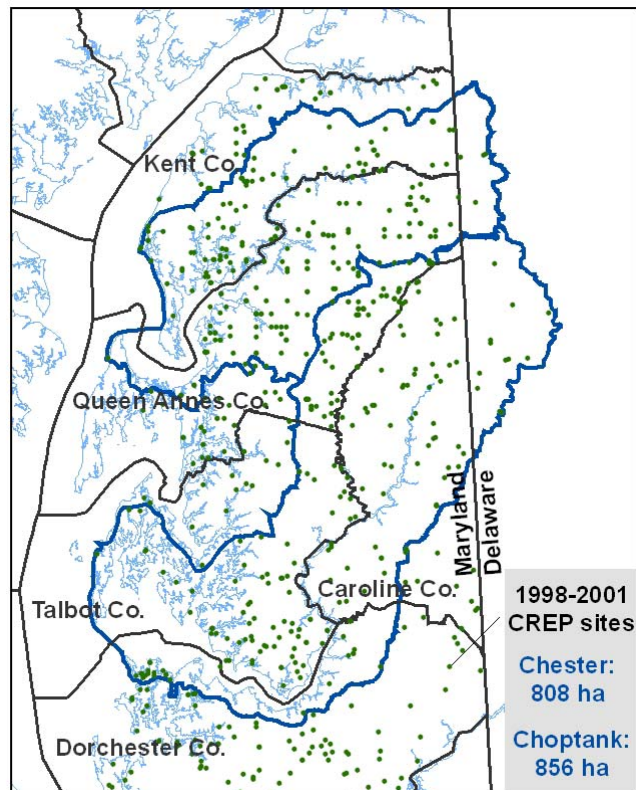
Figure 3-3. Location of CREP restored buffers which were partially funded by Ducks Unlimited and implemented between 1998 and 2001. Data source: Ducks Unlimited.

In 2004 T.R. Fisher and I began a collaborative project with USDA in the Choptank watershed. Through this cooperative project, we were able to gain more

detailed information on CREP buffers from local FSA offices. At the FSA offices, managers marked aerial photographs with outlines of CRP and CREP sites. I digitized these photos using ArcMapV9 and developed a GIS database of the location, size, and type of CREP buffers in all 15 subbasins of the Choptank watershed derived from copies of these aerial photographs. This coverage included buffers restored through the 2004 sign-up period.

Nutrient analyses

I sampled stream water during baseflow conditions from each of the 30 subbasins on a monthly basis from January 2003 through December 2004. All sampling locations were located at road crossings, and a sampling bucket was lowered from a culvert or bridge to collect water from the middle of the flowing stream. I measured temperature and electrical conductivity in the field with a portable Yokogawa SC82 conductivity meter (calibrated using a 100 μS cm^{-1} conductivity standard), and brought a sample back to the lab for nutrient analysis. In the lab, unfiltered samples were autoclaved with the persulfate reagents of Valderama (1981) and subsequently analyzed for dissolved phosphate (PO_4) with manual colorimetric methods (Strickland and Parsons 1972) to determine total phosphorus (TP). Nitrate (NO_3) in the autoclaved samples was analyzed separately in a Technicon AutoAnalyzer II in Horn Point's Analytical Services Lab to determine total nitrogen (TN). I also filtered original samples with GFF filters for automated colorimetric analysis of nitrate + nitrite in the Technicon AutoAnalyzer II. On average, nitrite (NO_2) was less than 1% of the nitrate + nitrite, and hereafter I present the analysis of nitrate + nitrite as nitrate (NO_3). Finally, I used manual colorimetric methods

for analysis of ammonium (NH_4) and phosphate (PO_4) concentrations in the filtered

samples (Strickland and Parsons 1972). The analytical precision estimated from

replicates was typically 12% for NH_4, 10% for TP, and 3% for PO_4.

Statistics

Statistical tests were performed using SigmaPlotV9 with SigmaStatV3.2

integration. The symbols *, **, and *** indicate statistical significance at the $p < 0.05$,

0.01, and 0.001 probability levels, respectively; "NS" is used for $p > 0.05$.

Results

CREP

There are many types of riparian buffers restored under the CREP. These include

grass filter strips, forest buffers, permanent wildlife habitat, and wetlands. Grass filter

strips are established with permanent herbaceous vegetation including a mixture of

grasses, legumes, or other forbs. Forested buffers are planted with a mixture of at least 4

tree species, and at least 80% of the total planting must be hardwood species. The

mixture of grass and/or trees in permanent wildlife habitats and wetlands is situation-

specific depending on the wildlife species of interest or location of the wetland. Since

documentation of the types of riparian buffers was not complete or consistent in the data

sets I compiled for this study, I do not differentiate between grass and forest riparian

buffers. Sabater et al. (2003) found that nitrogen removal rates in groundwater flowing

through herbaceous and forested buffers were similar, 4.4% and 4.2% N removed m^{-1},

respectively. Research from separate studies suggests that nitrogen and phosphorus

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reductions are also similar in surface runoff through grass (50% N and P, Magette et al. 1989) and forest buffers (75% N and 70% P, Peterjohn and Correll 1984). If data sets including the types of CREP sites exist in the future, the efficiency of nutrient reduction in restored grass versus restored forest buffers can be investigated, but for this study, that option was not available.

The CREP data set compiled by Ducks Unlimited included most buffers restored from 1998 through 2001 (Fig 3-3). During this time period, 394 ha of riparian buffers were restored in the 15 Choptank subbasins, and 267 ha were restored in the Chester subbasins. Within individual subbasins, there was from 0 to 105 ha of restored riparian grass and forest buffers (Table 3-2). Of the total streamline, CREP sites buffered an estimated 0 to 11%, whereas natural buffers represented 10 to 96%.

In 2005, I developed a GIS database of CREP sites in the 15 Choptank subbasins implemented from 1998 through 2004. These included not only location but also shape of each restored buffer, enabling more accurate evaluation of the length of stream buffers via GIS techniques. The resulting data set includes both CRP and CREP sites. When I discuss these restored buffers I usually only mention CREP sites because most of the restored grass and forest buffers in this region have been implemented under the CREP program. However, the analyses also include CRP sites.

After digitizing, I placed each buffer into one of the following categories: CREP buffering both sides of the stream, CREP buffering one side of the stream, and CREP added to an existing riparian buffer (Fig 3-4). In the calculation of total percentage of restored streamline in each subbasin, the length of CREP sites that buffered both sides of a stream were doubled to account for the streamline on both sides (Fig 3-4a). Some

Table 3-2. Amount of CREP sites in Choptank and Chester River subbasins from 2 different data sets. The 2001 data set is from Ducks Unlimited and streamline estimate is explained in eq. 1. The 2004 data set was derived from areal photographs marked with location of CREP sites by US Department of Agriculture employees from local Farm Service Agency offices. Streamline estimate for 2005 data set is shown in more detail in Table 3-3. Established riparian buffer was calculated by Norton and Fisher (2000). Unbuffered streamline was the remaining streamline after restored and established buffer.

| | | 2001 data set | | | | | 2004 data set | | | | |
| | | | % streamline | | | | | % streamline | | | |
Watershed	Subbasin	CREP area, ha	CREP	Established riparian	Total buffered	Unbuffered	CREP area, ha	CREP	Established riparian	Total buffered	Unbuffered
Choptank River	Kittys Corner	0.0	0.0	47.7	47.7	52.3	9.5	2.0	47.7	49.7	50.3
	Cordova	5.8	0.7	44.1	44.8	55.2	29.5	4.3	44.1	48.4	51.6
	Norwich Creek	55.5	6.2	32.4	38.5	61.5	127.8	12.7	32.4	45.1	54.9
	Blockston Branch	1.6	0.3	42.0	42.3	57.7	138.4	18.7	42.0	60.7	39.3
	Piney Branch	6.1	1.2	27.6	28.7	71.3	8.1	5.0	27.6	32.6	67.4
	Oakland	2.8	1.0	10.2	11.2	88.8	2.3	1.4	10.2	11.6	88.4
	German Branch	102.4	5.3	61.8	67.2	32.8	218.4	10.3	61.8	72.1	27.9
	Beaverdam Ditch	68.9	10.5	16.6	27.1	72.9	108.3	30.3	16.6	46.9	53.1
	Long Marsh Ditch	105.0	5.1	24.1	29.2	70.8	168.5	13.5	24.1	37.6	62.4
	Broadway Branch	9.9	1.9	26.1	28.0	72.0	5.9	1.1	26.1	27.2	72.8
	Oldtown Branch	0.0	0.0	26.3	26.3	73.7	42.5	8.3	26.3	34.5	65.5
	Spring Branch	10.8	2.1	37.2	39.3	60.7	42.3	5.9	37.2	43.1	56.9
	North Forge Branch	20.7	1.8	26.3	28.1	71.9	185.0	29.4	26.3	55.7	44.3
	South Forge Branch	4.5	1.0	40.4	41.4	58.6	18.4	19.0	40.4	59.4	40.6
	Downes	0.0	0.0	34.4	34.4	65.6	18.5	3.9	34.4	38.4	61.6
Chester River	Mill Stream Branch	9.4	1.8	76.4	78.2	21.8					
	Three Bridges Branch	6.1	1.4	74.2	75.6	24.4					
	Island Creek	12.4	3.6	87.6	91.2	8.8					
	Granney Finley Branch	34.4	8.7	81.4	90.1	9.9					
	Southeast Creek	26.5	3.2	65.2	68.4	31.6					
	Browns Branch	18.2	4.3	95.7	100.0	0					
	East Langford Branch	61.6	10.5	60.2	70.7	29.3					
	Morgan	3.0	0.4	52.1	52.5	47.5					
	Chesterville Branch	2.4	1.3	65.6	67.0	33.0					
	Mills Branch	11.2	1.7	51.1	52.8	47.2					
	Wallace	9.7	4.6	60.8	65.4	34.6					
	Peters Corners	7.2	1.2	67.9	69.1	30.9					
	Unicorn Branch	40.2	3.5	68.0	71.4	28.6					
	Dudley Corners	18.3	2.3	51.2	53.5	46.5					
	Foreman Branch	6.1	2.9	78.0	80.9	19.1					
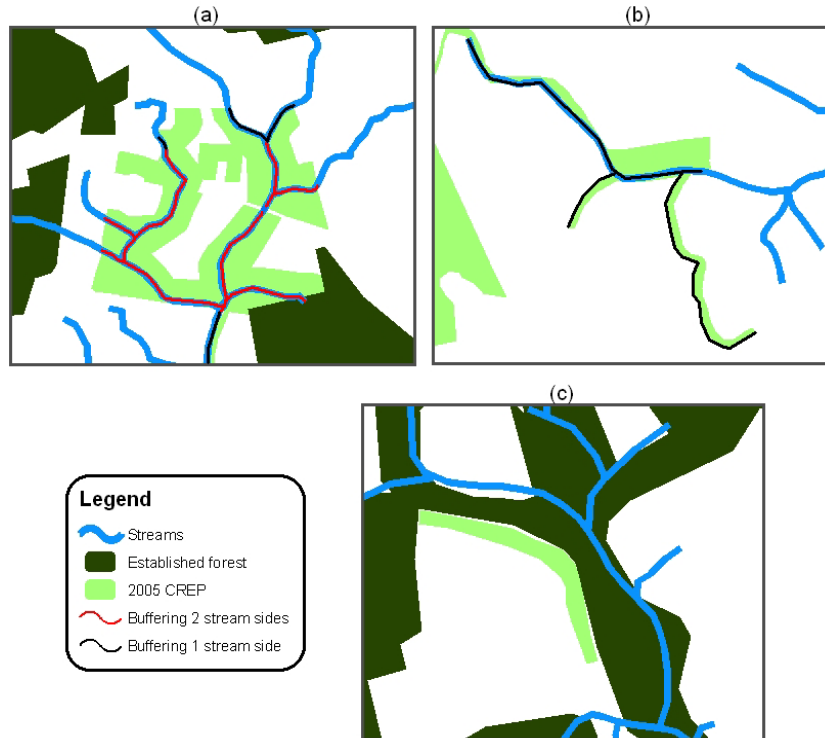
Figure 3-4. Examples of 3 categories of CREP buffers from 1998 through 2004 data set in the Choptank subbasins. (a) Streamline was doubled for CREP sites bordering both sides of the stream. (b) CREP bordering one side of the stream also includes CREP sites which I assume are bordering an agricultural ditch which is not included in the stream database. (c) CREP adjacent to an existing riparian buffer was not included in totals summarized in Table 3-2.

CREP sites were not adjacent to a blue-line stream on US Geological Survey 7.4 min maps (Fig 3-4b). Our stream file was derived from perennial and intermittent streams located on US Geological Survey (USGS) 7.5 min maps, but these maps do not always include agricultural ditches. I assumed the CREP sites that did not fall along a stream were located on one side of a ditch. However, maps with locations of ditches in this region do not exist and the length of ditches could not be incorporated into estimates of total streamline in each subbasin. There is a current effort at USDA to compile the location of ditches and add this information to the stream databases, but it is not yet available. Many CREP buffers were also located adjacent to an established riparian

Table 3-3. CREP buffered streamlength in the Choptank River subbasins from the 2004 data set. All CREP included the length of all restored buffer regardless of location. CREP adjacent to stream only includes CREP sites which directly border a stream or which are likely to border a ditch (Fig 3-4b). CREP adjacent to forest are the CREP sites installed adjacent to an established riparian forest (Fig 3-4c) and are not included in CREP streamline in Table 3-2.

	% of subbasin streamline	% of all CREP streamline	
Choptank River subbasins	all CREP streamline	CREP adjacent to stream	CREP adjacent to forest
Kittys Corner	8.7	22.4	77.6
Cordova	9.6	44.9	55.1
Norwich Creek	16.6	63.6	33.6
Blockston Branch	37.3	56.0	25.3
Piney Branch	5.0	100.0	0.0
Oakland	2.4	59.8	40.2
German Branch	19.7	52.4	47.6
Beaverdam Ditch	41.9	72.4	27.6
Long Marsh Ditch	16.0	84.2	15.8
Broadway Branch	1.5	73.9	26.1
Oldtown Branch	9.3	88.3	11.7
Spring Branch	10.9	54.5	45.5
North Forge Branch	29.9	98.5	1.5
South Forge Branch	20.1	94.4	5.6
Downes	5.2	75.6	24.4

buffer (Fig 3-4c). This category of buffers made up a large portion of the CREP buffered streamline, in some subbasins over 50% (Table 3-3). Since our focus in this paper is streamline buffered and not necessarily buffer width, these CREP sites were excluded from the streamline estimates presented in Table 3-2; they were also excluded in comparisons of buffered streamline and stream water quality later in the analysis.

The total area of riparian buffers restored in the Choptank watershed under CREP between 1998 and 2004 was 1123 ha (Table 3-2). Total subbasin streamline buffered by CREP varied from approximately 1% in Oakland and Broadway to 30% in Beaverdam Ditch and North Forge Branch. This is as much as 3 times the total CREP amount from the 2001 data set. Unfortunately, I did not have the updated and more detailed information in the Chester as I had in the Choptank watershed. However, there was a consistent increase in CREP area (slope=1.8, r^2=0.33*) and buffered streamline (slope=1.5, r^2=0.58**) in the Choptank subbasins from the 1998 to 2001 data to the 1998 to 2004 data set (Fig 3-5). This suggests the CREP sites implemented between 2001 and
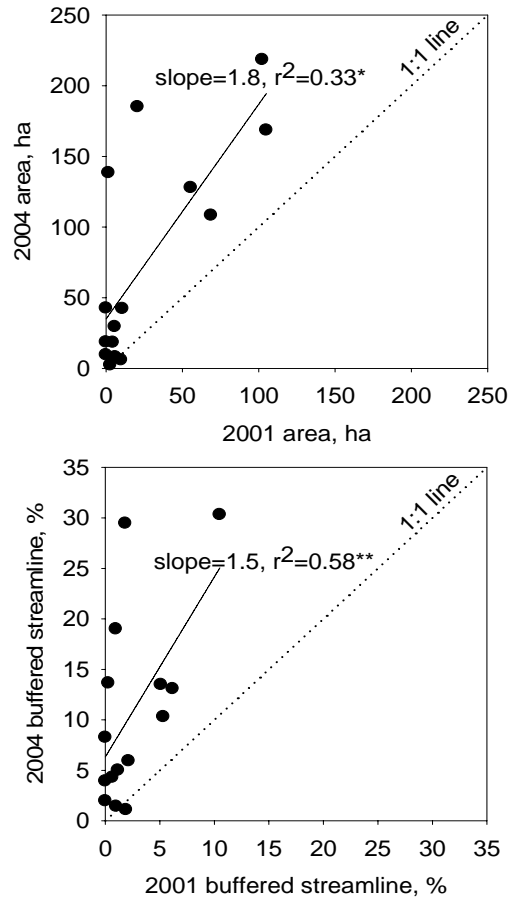
Figure 3-5. 1998 to 2001 data set versus 1998 to 2004 data set in the Choptank watershed. CREP area and streamline increase 1.5 and 1.8 times, respectively, from 2001 to 2004.

2004 in the Choptank increased relative to the amount at the beginning of the program, and therefore, the 2001 Chester data set may be useful in comparisons of relative amounts of CREP between the subbasins. The CREP coordinates from the Choptank 2001 data set were recorded on the farms that have a CREP and not necessarily where the CREP was located; however, the locations were relatively similar (Fig 3-6). The change apparent in Figure 3-6 for Beaverdam Branch basin was the increase from 69 to 108 ha of restored buffers between 2001 and 2004.

The final method to assess the amount of CREP sites in the Choptank and Chester watersheds is from the FSA annual summaries of CREP sites implemented within 11-digit Hydrologic Unit Areas (HUAs). Unfortunately, these watersheds are larger than the 30 14-digit HUA subbasins used in this study, but the FSA summaries can be used to confirm the accuracy of the 1998 to 2001 data set for the entire Choptank and Chester watersheds. The FSA summaries reported that 1490 ha of buffers in the Choptank watershed and 1640 ha in the Chester watershed were restored under the CREP from 1998 through 2001. However, the data set compiled by Ducks Unlimited only reported 856 ha in the Choptank and 808 ha in the Chester watersheds (Fig 3-3). Ducks Unlimited did not contribute financial support to all CREP sites in these watersheds, which may account for the under estimates of CREP in the watersheds. As a result, the 2001 data set for the Chester used in this study may be 50% under-reported.
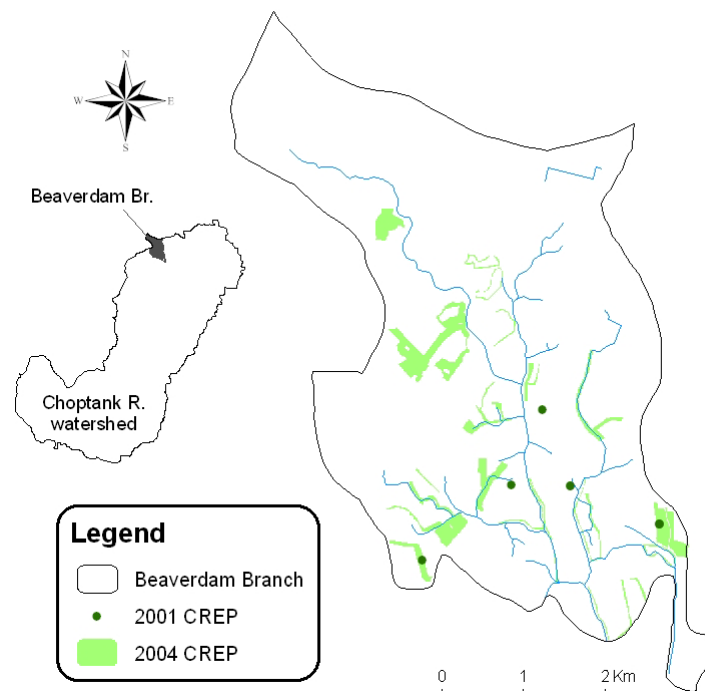
Figure 3-6. Location of CREP sites from the 2001 and 2004 data sets in Beaverdam Branch subbasin in the Choptank watershed. The 2001 data set from Ducks Unlimited are the black dots and the 2004 data set are the green polygons.

Seasonal nutrient patterns

In general, nutrient concentrations in baseflow were relatively stable throughout the year, except in two subbasins. For the remaining subbasins, the monthly variation in nutrient concentrations were similar to those shown in Figure 3-7a for Spring Branch in the Choptank watershed. Total nitrogen (TN) and nitrate (NO_3-N) concentrations fluctuated between 2.5 and 7 mg L^{-1} with no obvious seasonal pattern, and ammonium (NH_4-N) was always less than 0.15 mg L^{-1} in Spring Branch (Fig 3-7a). Total phosphorus (TP) and phosphate (PO_4-P) showed large variations in early 2003 during months of frequent rainfall when baseflow was difficult to sample (2003 was a regional record-breaking year for rainfall). The concentrations during the remainder of the sampling were less than 0.05 mg L^{-1} (Fig 3-7a). These variations were typical among the other 12 similar streams not included in Figure 3-7, and no seasonal patterns were apparent.

However, I observed seasonal patterns in two subbasins, Oakland in the Choptank watershed and East Langford in the Chester watershed. In Oakland subbasin, ammonium (NH_4) and organic N increased dramatically in the winter of 2003 and 2004 (Fig 3-7b), and I also measured organic P and phosphate (PO_4) spikes during these time periods. Nitrate (NO_3) did not fluctuate much during the two year sampling period, although NO_3 concentrations in the stream have almost doubled since prior sampling in 1986 by Norton and Fisher (2000) (Fig 3-8, total N increase is similar but not shown). There should not be analytical bias between the two time periods because samples collected in 1986 were also analyzed in Horn Point Analytical Services lab. Even though average NO_3 concentration increased in 11 of the 15 streams, the increase in Oakland was especially
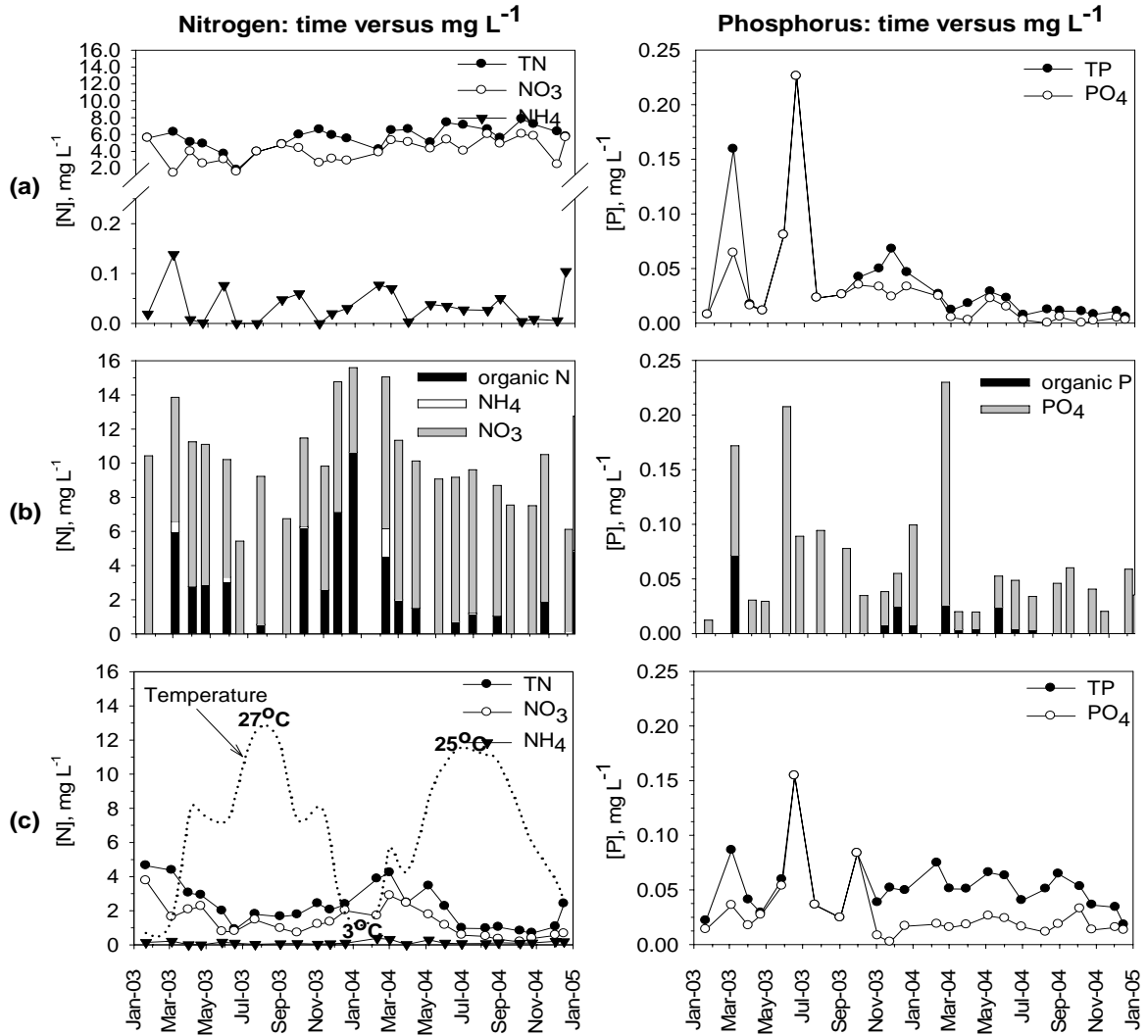
Figure 3-7. Three examples of monthly nutrient concentrations over the 2003 to 2004 sampling period. Nitrogen concentrations (left panel) and phosphorus concentrations (right panel) are in mg L^{-1}. (a) Example of the typical fluctuations in nutrient concentrations over the monitoring period. Measurements of total nitrogen (TN), nitrate (NO_3), ammonium (NH_4), phosphate (PO_4), and total phosphorus (TP) concentrations are shown for Spring Branch. (b) Organic N and organic P spikes during winter sampling in Oakland Branch. (c) Summer minimum in NO_3 and TN concentrations in East Langford Branch where low stream flow and tidal influences may enhance in-stream processing of N. The dotted line is stream temperature in ^{o}C and the summer peak and winter minimum temperatures are shown on the figure.

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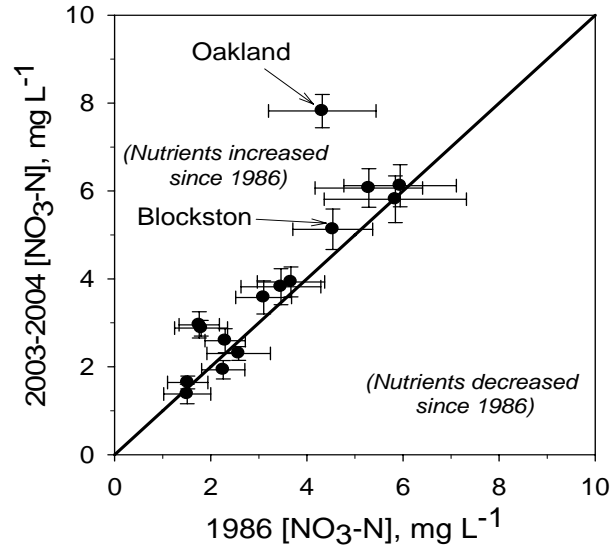
Figure 3-8. Nitrate (NO_3) concentrations in the 15 Choptank subbasins during this study and during a previous monitoring period in 1986.

large. As part of a collaborative project in the Choptank watershed and an effort to

update the 1990 land use data set, QuickBird satellite imagery (2 m spatial resolution)

was taken in the spring of 2005 over some of the Choptank subbasins, including Oakland.

Previously, 1990 aerial photographs were used by Fisher et al. (1998) to compile 1990

land use, and these showed only 3 animal feeding operations (AFOs) in Oakland subbasin

(Fig 3-9; AFOs A, B, and C). The 2005 land use in A was visually interpreted as a

developed area and not a feedlot as it was classified in the 1990 land use data set (Fig 3-

9). This was either digitized incorrectly in 1990 or has changed land uses since then.

The 2005 satellite imagery also shows another AFO approximately 1 km upstream of the

sampling point (Fig 3-9, D), and this has been confirmed by ground observation. This

AFO may be an additional source of nutrients to Oakland subbasin as suggested by the

large spikes in NH_4, organic N and P, and the large increase in NO_3 since 1986.

However, the AFO's presence is not evidence for the nutrient increases, since the manure

may not be spread on local farm fields but transported outside of the watershed.

Figure 3-9. Quickbird satellite imagery of Oakland subbasin in April 2005. A, B, and C were categorized as animal feeding operations (AFOs) in the 1990 land use database. B and C were still AFOs in 2005 but land use of A may now be a developed area. D is a AFO 1 km upstream of the stream sampling point that was not in the 1990 land use database.

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The other subbasin where nutrient concentrations were not consistent over an annual cycle was East Langford in the Chester watershed. I observed decreases in NO_3 and TN during the low flow months of summer and fall (Fig 3-7c). Originally, I also sampled in West Langford stream, a subbasin adjacent to East Langford, but I discontinued sampling there after I observed tidal fluctuations at the stream sampling point. The sampling point at East Langford may also be affected by tides in months of low baseflow as tidal influences move further upstream in warmer months due to seasonally higher sea levels (approximately 10 cm) in summer resulting from thermal expansion of the upper mixed layer of the ocean (Pickard 1979). In this case, in-stream nutrient processing may occur when the stream water is not flowing downstream and has longer retention times, which may explain the lower nitrogen concentrations observed during these low flow months.

Volume-weighted nutrient concentrations

The first sampling year, 2003, was a very wet year compared to the historical average. Precipitation at Horn Point Laboratory, located on the Choptank River (Fig 3-1), was 150 cm in 2003 and 112 cm in 2004. Total stream discharges at the USGS gauging stations in the Choptank and Chester River watersheds were also higher in 2003. The USGS station #01491000 in the Choptank River near Greensboro, Maryland has been a continuously gauged site since 1948 and drains a 293 km^2 subbasin, and the USGS station #01493500 in Morgan Creek near Kennedyville, Maryland has been gauged since 1951 and drains a 31 km^2 subbasin (Fig 3-1). Total discharge at Greensboro in 2003 was

2.7×10^8 m^3 and 1.1×10^8 m^3 in 2004. Difference in annual discharge between years was less at Morgan Creek from 1.7×10^7 m^3 in 2003 to 1.4×10^7 m^3 in 2004.

Even though I sampled during baseflow when there had not been a rain event for several days, the volume of baseflow contribution to the stream may differ between periods of rainfall and seasonal evapotranspiration (Jordan et al. 1997). A paired t-test revealed average total N concentrations in the Choptank and Chester subbasins were not significantly different ($p > 0.05$) between the two years (Fig 3-10). The supply of nitrate-enriched groundwater may not have varied enough between years to exhibit measurable differences between the two sampling years. However, the difference in average total P between the two years was significantly different in the Choptank (2003 > 2004, ΔTP = 0.041, $p < 0.001$) and was near the statistical level of significance in the Chester (ΔTP = 0.015, $p = 0.06$, Fig 3-10). This suggests that the storms during the wetter year (2003) may have supplied more P in overland flow events to enhance the baseflow P that I sampled between storm events.

Since there were different precipitation amounts between the two sampling years, I calculated volume-weighted nutrient concentrations using flow data from the USGS stream gauging stations in the Choptank and Chester watersheds. Discharge of streams on the Delmarva Peninsula is related to the size of the watershed, and Figure 3-11 shows the monthly water yield at Greensboro, Maryland for 3 years versus the monthly water yield at 7 smaller watersheds within 30 km of Greensboro. The monthly discharges at the smaller streams were adjusted for their watershed sizes in comparison to Greensboro, and the resulting water yields (cm month^{-1}) fell about the 1:1 ratio (Fig 3-11, $r^2=0.80$***). The slope was not significantly different from 1

(p < 0.001), and the intercept was not significantly different from 0 (p = 0.02).

Therefore, I estimated the area-weighted monthly discharge from each of the 15

Choptank subbasins based on the gauged discharge at Greensboro and used the gauged
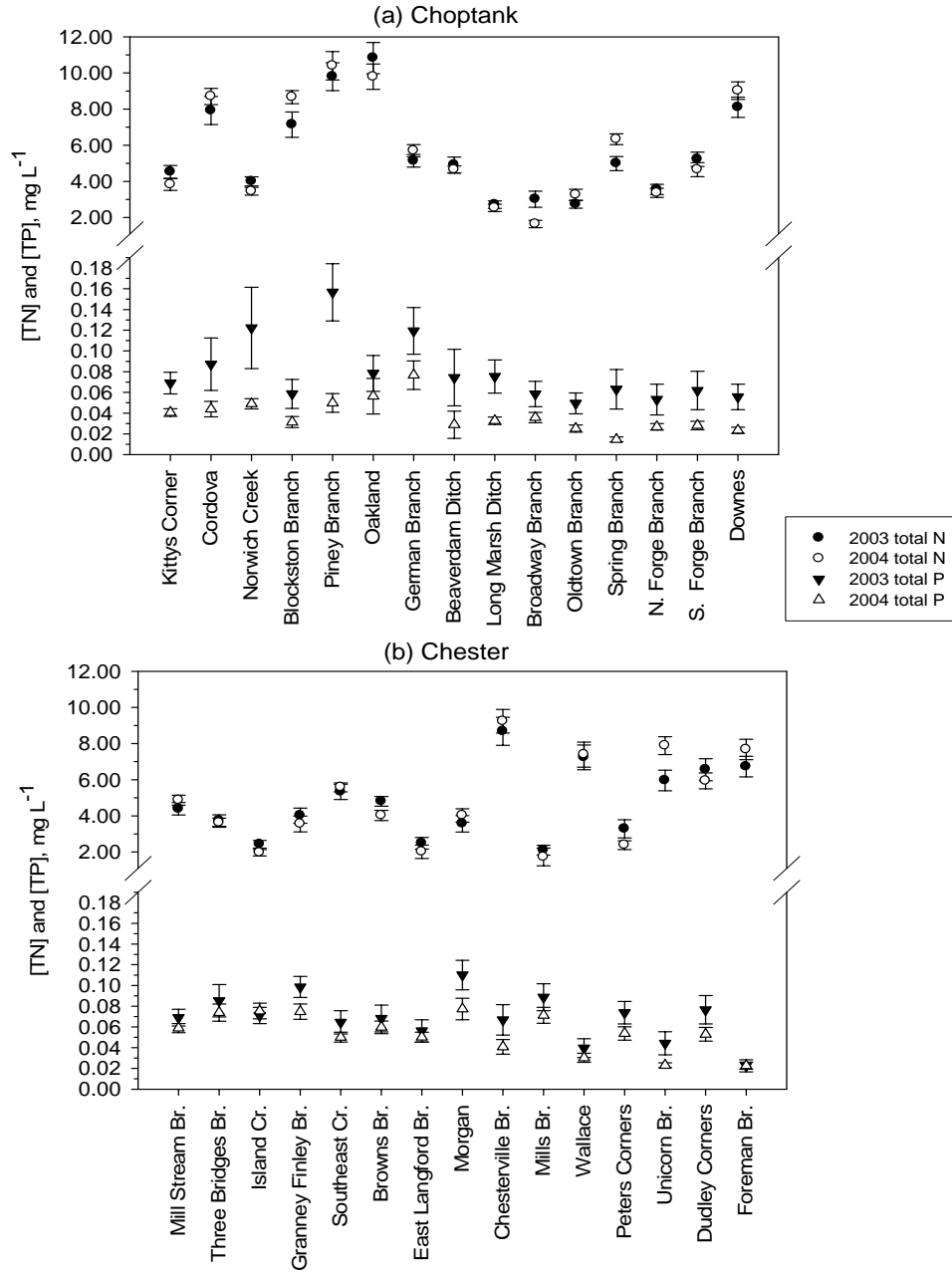
Figure 3-10. Average 2003 and 2004 nutrient concentrations in (a) the15 Choptank subbasins and (b) the 15 Chester subbasins. 2003 data are the closed symbols, 2004 data are the open circles, the circles are annual average total nitrogen in each subbasin, and the triangles are annual average total phosphorus in each subbasin.

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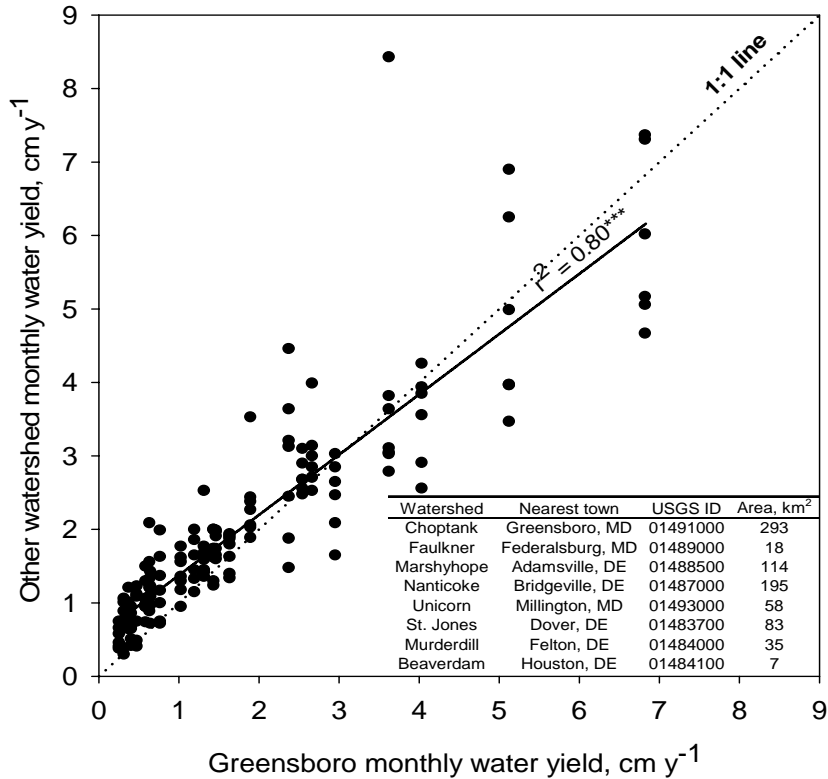
Figure 3-11. Monthly mean discharges at the continuously gauged USGS station at Greensboro, Maryland versus 7 other smaller watersheds (Faulkner, Marshyhope, Nanticoke, Unicorn, St. Jones, Murderkill, and Mispillion) on the Delmarva Peninsula in 1984 to 1986. The discharges for the 7 smaller watersheds were area-weighted (i.e., [subbasin area/Greensboro area]*Q). Data source: T.R. Fisher.

discharge at Morgan Creek to estimate the area-weighted monthly discharge at the other

14 Chester subbasins. I used the following equations to calculate volume-weighted

nutrient concentrations and standard error for measurements in each basin:

$$C_{vw} = \frac{\sum (C_i * Q_i)}{\sum Q_i}$$ (eq. 3-2)

$$SE_{vw} = \frac{\sqrt{\sum (C_i - C_{vw})^2 / (n-1)}}{\sqrt{n}}$$ (eq. 3-3)

where C_{vw} = volume-weighted mean concentration for 2003 to 2004, C_i = average

Table 3-4. Average flow-weighted nutrient concentrations during the study period from January 2003 through December 2004. Monthly nutrient concentrations were flow-weighted for the Choptank subbasins using monthy discharge measurements at Greensboro (USGS gauging station #01491000) and for the Chester subbasins using montly discharge measurements at Morgan Creek (USGS gauging station #01493500).

Watershed	Subbasin	Average volume-weighted [nutrient] 2003 to 2004, mg L^{-1}									
		NH_4-N	Std error	NO_3-N	Std error	TN	Std error	PO_4-P	Std error	TP	Std error
Choptank River	Kittys Corner	0.12	0.03	2.9	0.2	4.4	0.3	0.042	0.007	0.054	0.007
	Cordova	0.10	0.02	6.1	0.5	8.1	0.6	0.054	0.014	0.071	0.016
	Norwich Creek	0.16	0.07	2.6	0.3	3.7	0.2	0.055	0.009	0.093	0.022
	Blockston Branch	0.05	0.01	5.1	0.5	7.7	0.5	0.032	0.007	0.050	0.010
	Piney Branch	0.11	0.02	5.8	0.5	10.0	0.8	0.084	0.016	0.113	0.018
	Oakland	0.16	0.09	7.8	0.4	10.7	0.8	0.059	0.015	0.069	0.017
	German Branch	0.10	0.03	3.6	0.4	5.4	0.3	0.081	0.019	0.093	0.019
	Beaverdam Ditch	0.04	0.01	3.0	0.3	4.8	0.3	0.043	0.019	0.058	0.020
	Long Marsh Ditch	0.05	0.01	1.6	0.1	2.7	0.2	0.044	0.009	0.061	0.010
	Broadway Branch	0.06	0.01	1.4	0.2	2.4	0.3	0.027	0.006	0.049	0.009
	Oldtown Branch	0.08	0.03	1.9	0.2	2.8	0.3	0.022	0.004	0.040	0.007
	Spring Branch	0.04	0.01	3.9	0.3	5.4	0.4	0.034	0.010	0.046	0.011
	North Forge Branch	0.08	0.02	2.3	0.2	3.6	0.3	0.025	0.005	0.046	0.009
	South Forge Branch	0.12	0.05	3.8	0.4	5.2	0.4	0.036	0.010	0.049	0.011
	Downes	0.04	0.01	6.1	0.4	8.5	0.5	0.031	0.007	0.038	0.008
Chester River	Mill Stream Branch	0.12	0.03	2.8	0.2	4.2	0.3	0.044	0.007	0.056	0.007
	Three Bridges Branch	0.08	0.02	6.2	0.5	8.3	0.6	0.055	0.014	0.070	0.016
	Island Creek	0.16	0.07	2.5	0.3	3.7	0.2	0.055	0.009	0.093	0.022
	Granney Finley Branch	0.05	0.01	5.4	0.4	7.7	0.5	0.031	0.007	0.047	0.010
	Southeast Creek	0.10	0.02	6.3	0.5	9.9	0.8	0.084	0.016	0.111	0.018
	Browns Branch	0.12	0.09	7.6	0.4	10.2	0.8	0.058	0.015	0.065	0.017
	East Langford Branch	0.09	0.03	3.9	0.4	5.3	0.3	0.095	0.019	0.105	0.019
	Morgan	0.04	0.01	3.1	0.3	4.7	0.3	0.044	0.019	0.058	0.020
	Chesterville Branch	0.05	0.01	1.7	0.1	2.6	0.2	0.044	0.009	0.058	0.010
	Mills Branch	0.05	0.01	1.2	0.2	2.2	0.3	0.028	0.006	0.049	0.009
	Wallace	0.06	0.03	2.1	0.2	3.0	0.3	0.021	0.004	0.040	0.007
	Peters Corners	0.03	0.01	4.1	0.3	5.7	0.3	0.032	0.010	0.044	0.011
	Unicorn Branch	0.07	0.02	2.3	0.2	3.5	0.3	0.025	0.005	0.044	0.009
	Dudley Corners	0.11	0.05	3.6	0.4	4.9	0.4	0.036	0.010	0.048	0.011
	Foreman Branch	0.03	0.01	6.1	0.4	8.4	0.5	0.031	0.007	0.039	0.008

monthly nutrient concentration in month i (observed each month from 2003 to 2004), Q_i = monthly discharge in month i (estimated from Greensboro and Morgan Creek discharge and subbasin area), i = month, SE_{vw} = volume-weighted standard error, and n = number of months sampled. Volume-weighted concentrations and standard errors for the 2 year sampling period are shown in Table 3-4.

Nutrients and CREP

Nitrogen concentrations in streams in the Choptank watershed are dominated by the amount of agriculture in the subbasins (Fisher et al. 1998). During our 2 year sampling period I observed high correlations between agriculture from 1990 land use data and volume-weighted NO_3 ($r^2=0.75***$) and total N concentrations ($r^2=0.72***$, Fig 3-12). I also observed a significant relationship between agriculture and volume-weighted
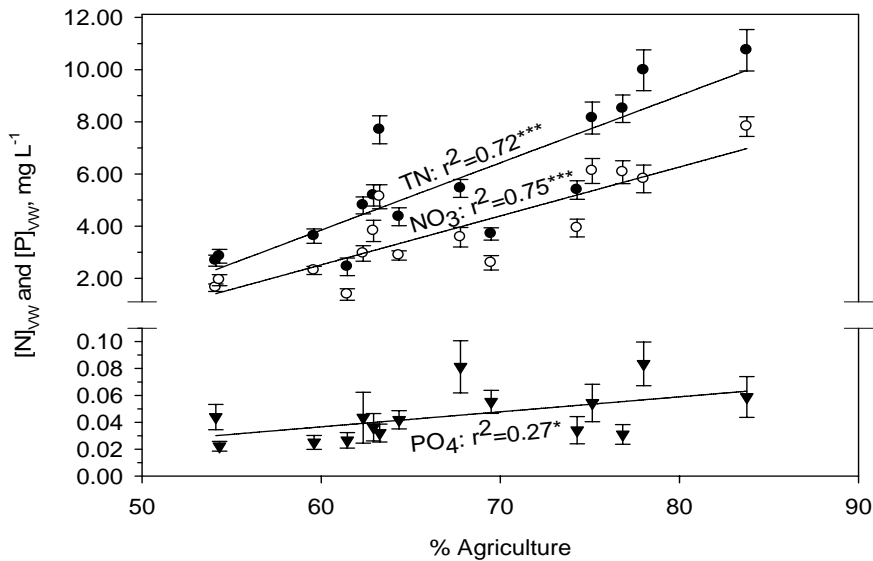
Figure 3-12. Relationship of total nitrogen (TN), nitrate (NO_3), and phosphate (PO_4) concentrations versus percent agriculture in the 15 Choptank subbasins. Closed circles: TN=0.26 * %agriculture - 11.6; open circles: NO_3=0.19 * %agriculture - 8.7; closed triangles: PO_4=0.001 * %agriculture - 0.030.

PO_4 concentrations (r^2=0.27*, Fig 3-12) but not total P or NH_4. Since stream nutrient

concentrations were primarily determined by the percentage of subbasin area in cropland,

I calculated the residual nutrient concentrations and plotted these as a function of

% CREP buffer (Fig 3-13). If restoration of riparian buffers reduced nutrient

concentrations in the subbasins, I would expect that as CREP increased in the subbasins
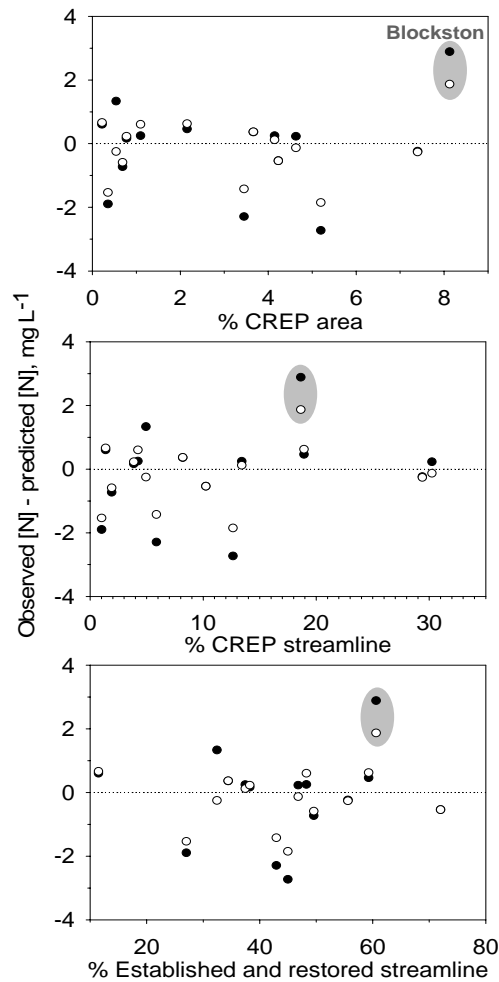
Figure 3-13. Residual total nitrogen (TN) and nitrate (NO_3) in the Choptank subbasins versus % subbasin are with CREP, % subbasin streamline with CREP, and % subbasin streamline with established riparian forest + streamline with CREP buffer. Residuals are predicted [N] based on the equations from Fig 3-12 minus the observed average volume-weighted concentrations measured from 2003 to 2004. Closed circles are TN and open circles are NO_3. Blockston Branch is highlighted by the gray oval.

the observed nutrient concentrations would be lower and the observed values would fall below the regression line. I did not observe any significant relationships between NO_3, total N, or PO_4 concentrations in relation to CREP area, CREP buffered streamline, or established plus restored buffered streamline in the Choptank subbasins.

Figure 3-13 shows the NO_3 and total N residual concentrations versus CREP area and percent streamline. Blockston Branch may be an outlier in this data set. Riparian buffers restored under the CREP between 2001 and 2004 were on average an additional 30 ha in each of the 15 Choptank subbasins (Table 3-2). However, 137 ha of riparian buffers were restored in Blockston Branch, 8% of the total subbasin area. Considering that most of the riparian buffers were restored 1 to 2 years before stream water sampling or even during sampling of 2003 to 2004, the nitrate and total N reductions assumed to be occurring in these CREP sites may not be reflected in the stream water chemistry over this short time period. North Forge Branch also had a large amount of area restored between 2001 and 2004: 164 ha or 6.6% of the subbasin area (Table 3-2). However, nitrate and total N concentrations in this stream were already relatively low, half of the N concentrations measured in Blockston Branch (Table 3-4). If Blockston Branch was in fact an outlier, the remaining 14 subbasins may have demonstrated the hypothesized relationship, although it is not statistically significant ($p > 0.05$, Fig 3-13). This could mean that concentrations at Blockston may fall in the future as the effectiveness of the newly established CREP sites increases. Therefore, Blockston may be considered an outlier in Figure 3-13, and this figure may be evidence that the other subbasins are responding to the amount of riparian buffers restored under the CREP.

In the Chester River watershed, it is likely that stream nutrient concentrations

were not as clearly dominated by agriculture as in the Choptank watershed. Norton and

Fisher (2000) concluded that the hydrologic pathways in the Chester watershed may be

the variable accounting for the differences in nutrient concentrations. They observed that

NO_3 and total N increased as the percentage of well-drained, fine-textured soils of types

A and B increased in the subbasins (Norton and Fisher 2000). I did not observe this

pattern in 2003 and 2004, perhaps because I sampled only half as many subbasins as in

the previous study. However, I did observe a general increase in total N concentrations

and a decrease in total P concentrations in most of the subbasins since the previous study

(Fig 3-14). I can not however, conclude that implementation of CREP buffers

significantly contributed to any changes in water quality during this time period.
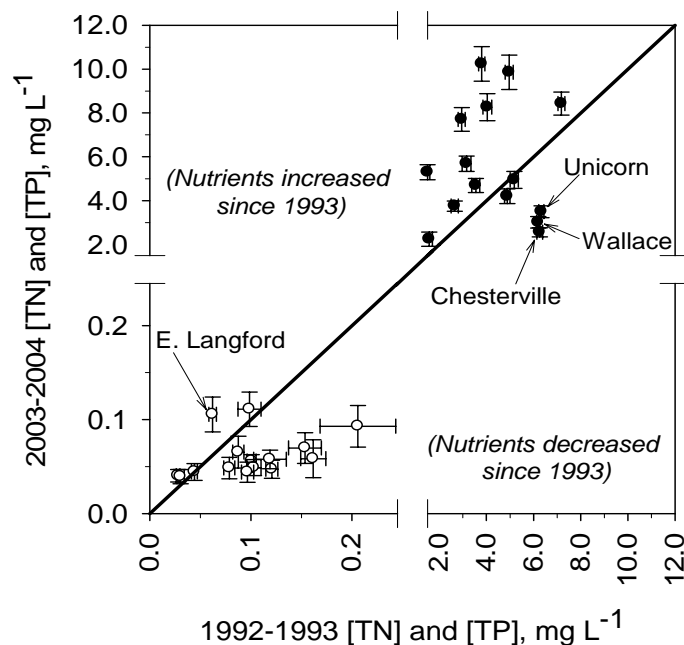
Figure 3-14. Total nitrogen (TN) and total phosphorus (TP) volume-weighted
concentrations in the Chester subbasins during this study and during a previous
monitoring period in 1992 and 1993. Closed circles are TN concentrations and open
circles are TP concentrations.

Discussion

Most research on Best Management Practices (BMPs) has been at the plot scale on individual farm fields (Staver and Brinsfield 1998, Vellidis et al. 2003) and has been extrapolated to the watershed scale by using models (Stone et al. 2001, Das et al. 2004). There are many possible explanations for the lack of watershed-scale research on BMPs including the following: few restoration projects concentrated at the watershed scale, difficulties in applying traditional experimental designs, difficulty in accounting for natural variability at large scales, and poor documentation of the restoration effort (O'Neill et al. 1997, Holl et al. 2003, Bernhardt et al. 2005). However, I propose that monitoring BMPs at the watershed scale is critical to assessing the impact of BMPs in the context of other processes operating beyond the plot scale (e.g., in-stream processing); this approach is also important to adaptive management strategies. The Conservation Reserve Enhancement Program (CREP) in Maryland has been a well-funded BMP with widespread support throughout the Chesapeake Bay management community, and provides a unique opportunity for managers and scientists to monitor the effects of a BMP at a watershed scale.

Restoration of riparian buffers beginning in 1998 through the CREP has been widespread in the Chester and Choptank River watersheds (Table 3-2, Fig 3-3). However, documentation of CREP was not fully available in the Chester subbasins. The data set I obtained from Ducks Unlimited included only CREP sites implemented between 1998 and 2001 that were partially funded by the organization. This included approximately half of the total area of restored CREP buffers in the Chester watershed. The data provided to the public by the Farm Service Agency are aggregated by 11-digit

HUAs which, in the Chester and Choptank watersheds, have tidal outputs and make it difficult to assess water quality effects from the land in those tidal areas. These 11-digit HUAs are much larger than the non-tidal subbasins I focused on in this study and the CREP statistics from them are too broad to use in the water-quality assessment. Since I had problems accessing information on CREP relevant to water quality monitoring in the Chester River, the ability to investigate restoration effects in this watershed is limited and highlights the importance of comprehensive data collection and sharing to monitoring successes and failures of restoration projects.

The processes controlling water quality in the Chester River watershed are also not as well understood as in the Choptank River watershed. Nitrogen concentrations are highly correlated with agricultural land use in the Choptank subbasins (Fig 3-12), however, water quality during two monitoring periods in 1992 to 1993 (Norton and Fisher 2000) and in 2003 to 2004 was not significantly correlated to land use, soil type, or amount of riparian buffers in the Chester subbasins. The Chester and Choptank watersheds have some different characteristics which may affect the relationships to water quality. Farmers in the Chester watershed use less organic fertilizer since transport of poultry manure is farther than to the farms in the Choptank watershed. Farmers in the Chester watershed also have slightly different management practices including the use of more conservation tillage than in the Choptank. There is greater topographic relief and depth to the water table is greater in the Chester as opposed to the Choptank watershed. The thinner, shallower unconfined aquifer in the Choptank may transport more nitrate-rich groundwater directly into the streams and lead to the correlation in agricultural land use and stream nitrogen concentrations. However, flow paths of nitrate-rich groundwater

in the Chester may be deeper and not be transported efficiently to the streams. These differences are important if considering extrapolating results from the Choptank watershed to the Chester watershed.

Participation on a larger project in the Choptank watershed has made it possible to obtain more complete data including all CRP and CREP sites implemented from 1998 to 2004 and each buffer's shape and size within the landscape (e.g. Fig 3-6). This, along with stream water monitoring, provided the ability to evaluate the effect of CREP on stream nutrient concentrations in this watershed. There was a strong effect of cropland in this data set (Fig 3-12), but I did not detect any effects of CREP on nutrient concentrations between the streams based on the amount of CREP buffers in the subbasins (e.g. Fig 3-13). Even if I assume that Blockston was an outlier in this data set due to the large and recent establishment of CREP sites, the effect is suggested but still not significant.

The focus in this portion of research was on baseflow nutrient concentrations. Even though I measured a significant relationship between baseflow phosphate concentration and % agriculture, particulate-bound phosphorus also moves to streams during short-term runoff events; therefore, the data reported here is not a complete representation of phosphorus loads to the Choptank streams. In Chapter 4 I present P concentrations during storm events sampled in Blockston Branch and Norwich Creek and can more accurately characterize P loads from these subbasins. In that research, stormflow P yields from Blockston and Norwich were correlated with the amount of streamline buffered in the two subbasins. Since baseflow is supplied by nitrogen-rich groundwater in these agriculturally-dominated watersheds, I also expected that

substantial restoration of riparian buffers, as much as 30% of streamline in the 15 subbasins, would reduce baseflow N concentrations in the stream. However, CREP implementation did not have any significant effects on nutrient concentrations, and I am forced to reject my hypothesis. I propose that no significant reductions in nitrogen concentrations were detected in the streams because (1) in addition to streamlength, riparian buffer age, width, and buffer connectivity are important to nutrient reductions, (2) agriculture and hydrogeomorphic characteristics dominate the water chemistry in this region, and (3) riparian buffer restoration is not extensive enough.

Many studies suggest that nitrate is rapidly retained and removed from subsurface groundwater under riparian buffers (Peterjohn and Correll 1984, Jacobs and Gilliam 1985, Lowrance et al. 1992, Jordan et al. 1993). The Chesapeake Bay Program has set their riparian buffer goals in terms of length of streamline restoration (i.e., goal of 70% riparian forests buffering streams in the Chesapeake Bay watershed, EPA 2003). Therefore, in this analysis I focused on the relationship between nitrogen concentrations and buffered streamline in each subbasin. For the 1998 to 2004 Choptank data set, I did not include in the % streamline analysis the CREP buffers that are located behind an existing riparian buffer, which is essentially increasing the width of the riparian buffer. If the existing riparian buffers are efficient in reducing nutrients in groundwater and overland flow, buffer restoration to widen the riparian zone may not be the most efficient use of resources. However, assuming additional width does not effect groundwater nitrogen reductions in buffers may not be valid for buffers with less than average nutrient reduction abilities (Weller et al. 1997). Studies have shown that most of the groundwater nitrogen reduction occurs within the first 20 to 30 meters of the buffer, but in buffers with

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insufficient denitrification and plant uptake for all nitrate removal, rainwater dilution in wide buffers may be important to reducing groundwater nitrate concentrations. Weller et al. (1997) also found it is likely that connectivity within riparian corridors is important to nutrient discharge. Small gaps in the corridor potentially allow surface runoff and groundwater to bypass the highly retentive riparian zone and discharge into the stream. Detailed analyses of CREP streamlength, width, and connectivity within each subbasin may help determine the parameters important for comparison at a watershed scale.

Research on the Delmarva Peninsula has shown that agriculture and hydrogeomorphic characteristics drive groundwater and stream water nutrient concentrations (Hamilton et al. 1993, Bachman and Philips 1996, Jordan et al. 1997, Norton and Fisher 2000, Lee et al. 2000). These factors are often related to one another since well-drained soils are likely to support more productive agricultural land. This is observed in the 15 Choptank subbasins, where agriculture increases as hydric, or water-saturated, soils decrease (r^2=0.73***, Fig 3-15). The characteristics of soils in the well-drained upland support more agriculture than other areas, yet may not have the anoxic, slower moving groundwater that supports denitrification as in poorly-drained soils.
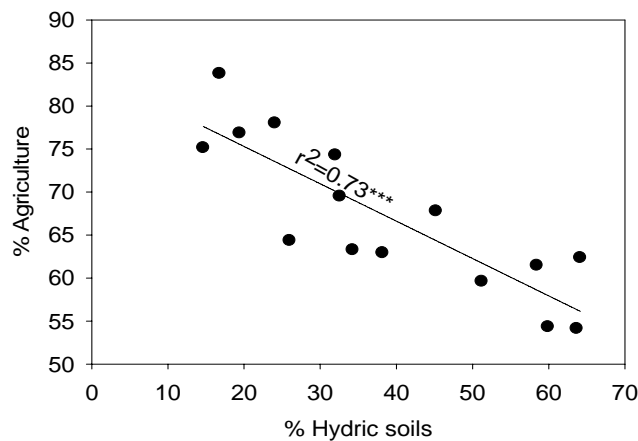
Figure 3-15. Percent agriculture versus percent hydric soils in the 15 Choptank subbasins. Data from Table 3-1.

As a result, the subsurface groundwater and streams in the well-drained upland, where most of the Choptank subbasins are located, tend to be enriched in nitrogen (Hamilton et al. 1993, Bachman and Philips 1996).

Considering that differences in agriculture between the subbasins explain 72 to 75% of the variance in baseflow nitrogen concentrations (Fig 3-12), determining the effects other factors have on the concentrations is likely to be difficult. These factors may include: weather variability, in-stream nutrient processing, nutrient retentive areas in the landscape (e.g., hydric soils and CREP buffers), and nutrient sources in the landscape that contribute an uneven amount of nutrients to the stream. For example, in Oakland, Piney Branch, and Blockston Branch, observed nitrogen concentrations are greater than the predicted nitrogen concentrations based on percent agriculture in the subbasin (Fig 3-8). These three subbasins also have animal feeding operations within 1 km of the stream sampling point, and the position of large nutrient sources in the landscape may contribute to the higher concentrations (e.g., feedlot D in Fig. 3-9). In these cases, nutrients have a shorter path from input to the sampling point and may have fewer opportunities for nutrient processing in the streams. Also, watersheds are inherently efficient in retaining nutrient inputs and only export from 25 to 50% of N in the stream flow (Peterson et al. 2001, Boyer et al. 2002, Ch. 5). Most of the N sink can not be accounted for by direct measurements and is assumed to be lost through denitrification within the landscape (Van Breemen et al. 2002). These other factors may explain the other 25% variance in nitrogen concentrations in the Choptank subbasins (Fig 3-12), but considering the

possible variability of these factors, determining the relative importance of each in such a narrow range may be difficult.

I assumed that the amount of buffers restored under the CREP was enough to detect nutrient reductions in the Choptank watershed streams. However, there may not be enough restored buffers to detect any changes above the other processes in the subbasins that may be reducing N inputs by 50 to 75%. Detailed monitoring in German Branch between 1991 and 1995 (Primrose et al. 1997, Jordan et al. 1997) allowed me to develop a nutrient budget for that subbasin (see Ch. 5) and test whether CREP restored buffers have the potential to reduce baseflow N concentrations (Table 3-5). I used average annual N inputs into the subbasin from 1991 to 1995, average annual baseflow discharge in German Branch from 1991 to 1995, and nitrogen reduction rates in riparian buffers to determine the relative impact CREP may have on water quality. I developed three scenarios: current CREP implementation as of 2004 (218 ha), an additional 3000 ha of CREP with 45 m width to restore all remaining unbuffered streams, and an additional 1330 ha of CREP with 20 m widths to restore all remaining unbuffered streams. In each scenario I calculated the N reduction based on a low removal rate from the literature (26 kg N ha^{-1} yr^{-1}, Lowrance et al. 1984) and based on the high removal rate observed in the groundwater of a CREP site in the Little Choptank watershed (124 kg N ha^{-1} yr^{-1}, Ch. 2). In applying these rates, I assumed that the groundwater from the upland farm fields will flow through the riparian zone of these buffers where the N-enriched water has the opportunity to be diluted, assimilated by vegetation, and denitrified.

At the current level of implementation, these estimates indicate that the restored riparian buffers in German Branch may have reduced the total N concentrations in

Table 3-5. Estimates of total nitrogen reductions in German Branch made by the current CREP sites and by potential CREP sites if all unbuffered streams were restored. I used a low riparian removal rate of 26 kg N ha^{-1} yr^{-1} from Lowrance et al. (1984) and high removal rate of 124 kg N ha^{-1} yr^{-1} from Chapter 5. Total input was the average yearly input into German Branch from 1991 to 1995 (3.6×10^5 kg yr^{-1}, Ch. 5). Average yearly baseflow was calculated from discharge measured by Jordan et al. (1997) from 1991 to 1995 (7.4×10^6 m^3 yr^{-1}). I estimated reductions by restored buffers for the current CREP sites (2004 CREP) and for the potential CREP sites if all unbuffered streamline was restored in German Branch (with 45 m and 20 m widths).

Total N reduction by CREP	2004 CREP		100% buffered streamline, 45 m width		100% buffered streamline, 20 m width	
	Low removal rate	High removal rate	Low removal rate	High removal rate	Low removal rate	High removal rate
kg N yr^{-1}	5.7E+03	2.7E+04	7.8E+04	3.7E+05	3.5E+04	1.6E+05
% of total inputs	1.6%	7.5%	21.7%	103.3%	9.6%	45.8%
Reduction in baseflow [TN], mg L^{-1}	0.8	3.7	10.5	50.3	4.7	22.3

baseflow by 0.8 to 3.7 mg L^{-1}; depending on the rate of N loss assumed (Table 3-5). In general, nitrate and total N are increasing in the Chester and Choptank watersheds (e.g., Figs 3-8 and 3-15), and even though total N concentration in German Branch is 1.5 mg L^{-1} higher than 20 years ago, it is realistic that restoration of riparian buffers may have reduced baseflow total N by 0.8 mg L^{-1}. However, it is not likely that restored buffers in German Branch have a high removal rate since a reduction in baseflow total N of 3.7 mg L^{-1} is unlikely. As of 2004 with the addition of CREP restored buffers, German Branch had over 70% of the streamline buffered (Table 3-2). This is the long term goal for the Chesapeake Bay watershed as a whole (EPA 2003), yet in this small, agriculturally-dominated subbasin, total nitrogen is still high with 72% riparian buffer. Also, the implementation of riparian buffers through the CREP is nearly finished in Maryland. As of June 2005, 70% of the 40 500 ha goal for the CREP in Maryland was achieved and unless the CREP is renewed, riparian buffer restoration under this program will end. This will leave, on average, 56% of the streams unbuffered in the 15 Choptank subbasins, which is still far from the Chesapeake Bay Program's goal.

Since 72% riparian buffer in German Branch has not significantly reduced total N concentrations, I can make some predictions for N reduction if the remaining 28% of the streams were restored (Table 3-5). Based on both N removal rates and assuming all restored buffers have a hydrologic connection with the subsurface groundwater, restoring the remaining streams with 45 m wide riparian buffer has the potential to remove all the nitrogen from the streams (Table 3-5), except for the background N concentration driven by natural sources in the forests and streams. Restoring the remaining streams with 20 m wide buffers has the potential to reduce baseflow N concentrations close to background

levels as well but requires the conversion of less farmland and may be a more efficient use of resources. However, these are estimates based on broad assumptions as to the nutrient removal efficiencies of restored buffers and are not management recommendations. They are meant to highlight the fact that detectable nutrient reductions in German Branch and other Choptank subbasins are not likely at the current level of CREP implementation, and considerably more restoration may be needed to achieve reductions based on this one best management practice.

Conclusion

There has been a large effort to restore riparian buffers in the agriculturally-dominated Choptank and Chester River watersheds. However, at the current level of restoration, these buffers have not had a detectable effect on stream nutrient concentrations in baseflow. Watershed-scale research introduces variability within the landscape including the uneven contribution of nutrient sources (e.g., locations of animal feeding operations and variations in nutrient management between farms and in seasons of extreme weather conditions) and nutrient retentive areas (e.g., denitrification in hydric soils) that are difficult to quantify. In this case, I also assume that restored riparian buffers have similar nutrient reduction abilities throughout the broad areas of the Chester and Choptank watersheds. Watershed-scale research is needed that quantifies some of the variability observed in nutrient inputs and exports (Boyer et al. 2002, Van Breman et al. 2002) and that quantifies the nutrient reduction ability of riparian buffers in basins with varying hydrologic conditions. This may help gain a better understanding of how

riparian buffer restoration can improve stream water quality and reduce nutrient inputs into Chesapeake Bay and other eutrophied waters.

However, nutrient reduction goals based on restoration of riparian buffers are based on the current level of knowledge. This research suggests that 6 years after the beginning of restoration under the Conservation Reserve Enhancement Program, restored riparian buffers have not had significant effects on stream nutrient concentrations. Over the past 15 to 20 years, nitrogen concentrations have continued to increase in many of the streams within the Chester and Choptank watersheds, suggesting that nitrogen-rich groundwater is still flowing into the streams or that more Best Management Practices are needed to have a measurable effect on stream nutrients. Phosphorus concentrations in the baseflow of streams in this time period have decreased and will be assessed further in Chapter 4.

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Chapter 4

STREAM NUTRIENTS DURING STORM EVENTS IN WATERSHEDS WITH
RESTORED BUFFERS

Abstract

The effort to improve water quality in Chesapeake Bay has focused on several nutrient

sources, including agricultural runoff within the 167 000 km^2 watershed. Agricultural

nitrogen and phosphorus are supplied to the bay through nitrate-rich groundwater and

sediment and particulate-bound phosphorus in overland flow during storm events. In this

study, I measured the nutrient concentrations during stormflow in two agriculturally-

dominated subbasins, Blockston Branch and Norwich Creek, in the Choptank River

watershed on the eastern side of Chesapeake Bay. Over the last 7 years, riparian buffer

restoration through the Conservation Reserve Enhancement Program (CREP) has been

significant, especially along Blockston Branch. In this subbasin, implementation of

CREP sites has increased the buffered streamline from 42 to 61%, and the restored

buffers are distributed evenly throughout the subbasin. In Blockston Branch, the

concentrations of nutrients that were the highest during stormflow (i.e., ammonium and

all forms of phosphorus) had lower peak concentrations than in the less buffered Norwich

Creek. Ammonium, phosphate, and total phosphorus yields during stormflow in 2004

were approximately 2 times higher from Norwich Creek than from Blockston Branch.

This research suggests that differences in nutrient export during stormflow may be a

result of different levels of riparian buffer restoration within the subbasins. Water quality

improvement in agricultural runoff may not be dependent on the total area of restored

riparian buffers but instead on the amount of continuous streamline buffered and the location of buffers in the subbasin.

Introduction

Export of nutrients from rivers have increased as anthropogenic land uses within watersheds have intensified. As human population increases around the world, so do the nitrogen concentrations in the adjacent rivers (Peierls et al. 1990). Increased nutrient inputs are particularly a problem where watersheds are intensively farmed such as in the basins of the Mississippi River and Chesapeake Bay (Turner and Rabalais 1991, Boynton et al. 1995). Excess nutrients in the Gulf of Mexico have resulted in extensive hypoxic waters (Malakoff 1998) and have also resulted in extensive algal blooms and loss of habitat throughout Chesapeake Bay (Carpenter et al. 1969, Orth and Moore 1983, Officer et al. 1984, Seliger et al. 1985, Fisher et al. 1988). Understanding the mechanisms of nutrient inputs into these eutrophied coastal waters is critical for the efforts to reduce nutrient loading from agricultural sources.

Rain falling on watersheds generates baseflow of streams via infiltration to groundwater and produces stormflow via overland flow. Phosphorus has a large particulate fraction and tends to move from the land into streams during overland flow events which transport soils and sediments from erosion. Jordan et al. (1997) found that total phosphorus concentrations correlated with the amount of suspended solids in 27 streams throughout the Chesapeake watershed. In another subbasin, Fisher et al. (1998) observed peaks in total phosphorus concentrations during rain events that follow the same patterns as stream discharge in the storm hydrographs. However, the same research in

these streams has shown that nitrogen concentrations are higher in baseflow than in stormflow during rain events (Jordan et al 1997, Fisher et al. 1998). Nitrate, largely derived from fertilizers in these agriculturally-dominated subbasins, is soluble and leaches from the croplands into the groundwater in high concentrations (Hamilton et al. 1993, Staver and Brinsfield 1998). Baseflow is the water supplied to the stream from groundwater flow in the watershed and is often enriched in nitrate in agricultural areas (Spalding and Exner 1993). This nitrate-rich baseflow is the main source of nitrogen to streams and is diluted during rain events (Jordan et al. 1997, Fisher et al. 1998).

Capturing the variability in nutrient export from anthropogenically-disturbed subbasins during large, rapid discharge events is challenging (Beaulac and Reckhow 1982). The contributions from stormflow vary with the duration and amount of rainfall and the conditions prior to rainfall such as the length of time since the last rainfall, soil moisture in the subbasin, and the season (Evans and Davies 1998, Chanat et al. 2002). Stream flows are also likely to differ between subbasins with various hydrologic and geomorphic conditions (Jordan et al. 1997). In addition to the land use in the subbasin, contribution of sediment-bound nutrients in overland flow is likely to depend on the geology of the soils (Grobler and Silberbauer 1985). Rainfall not only mobilizes suspended solids in overland flow but may contribute to the flushing of water out of the vadose zone beneath the ground surface. This may release nutrients stored in the unsaturated soils into the subsurface groundwater (Creed and Band 1998) and either percolate into deeper groundwater moving slowly to the stream or move more rapidly to surface waters in shallow subsurface flow. Nitrogen constituents available for transport in the vadose zone may include organic nitrogen, ammonium, and nitrate (Jordan et al.

1997). Since overland flow is a major pathway of phosphorus transport to streams, most research has focused on sediment-bound phosphorus. However, dissolved phosphorus from surface runoff and shallow subsurface flow may be important to total phosphorus export from streams. In groundwater, reduced conditions have been attributed to the desorption of dissolved phosphorus from soil and sediment particles and mobilization in the subsurface groundwater (Richardson 1985, Carlyle and Hill 2001). More research is needed to understand nutrient fluxes from agriculturally-dominated watersheds into downstream waters such as Chesapeake Bay.

Limited scientific understanding of the mechanisms of nutrient input into Chesapeake Bay has not prevented the application of nutrient reduction strategies. One of the Best Management Practices (BMPs) applied on farmland in the Chesapeake Bay watershed is restoration of streamside vegetation. The Conservation Reserve Program (CRP) was established by the US Department of Agriculture in 1985 and was expanded in 1998 as the Conservation Reserve Enhancement Program (CREP). These programs provide financial incentives to farmers who take streamside land out of agricultural production and plant trees or grasses. Previous studies have shown that riparian buffers reduce groundwater nitrogen through denitrification, rainwater dilution, and plant uptake (Peterjohn and Correll 1984, Lowrance et al. 1992, Speiran et al. 1998). However, the initial interest in this BMP was in preventing erosion and trapping sediments (i.e., CRP). Early studies confirmed that grass and forested riparian buffers trap eroded soil and remove particle-bound phosphorus from surface runoff (Peterjohn and Correll 1984, Lowrance et al. 1984, Cooper et al. 1987, Magette et al. 1989, Dillaha et al. 1988). The low elevation gradients in flood plains where riparian zones are located and the riparian

vegetation tend to dissipate the energy of surface flows. This allows suspended particles and sediment-bound contaminants to deposit in the buffers prior to entering ditches or streams. Percentages of phosphorus removal in overland flow through grass and forest buffers have varied from approximately 50 to 70% of the upland input (Peterjohn and Correll 1984, Cooper et al. 1987, Dillaha et al. 1988). Studies also suggest that riparian buffers may have a capacity for long-term sediment removal since eroded soils and sediments were deposited only within the first few meters of the buffers (Peterjohn and Correll 1984, Lowrance et al. 1986).

All the measurements in the studies mentioned above were taken at the scale of individual buffers, yet not many measurements have been made at the watershed scale where nutrient reduction goals are set. Bishop et al. (2005) measured phosphorus reductions in a small watershed where extensive sediment-control BMPs were implemented, including a manure storage lagoon, grass buffers, fencing to exclude livestock from the streams, and contour strip cropping. After BMP implementation, total dissolved phosphorus loads during rain events decreased by 43% and particulate phosphorus decreased by 29% from initial loads pre-BMP implementation (Bishop et al. 2005). However, Owens et al. (1991) found no differences in baseflow and stormflow nutrient export between watersheds dominated by pasture and forested land as opposed to a watershed dominated by fertilized agricultural land. They did not take into account the extensive riparian buffers in the agricultural watershed and concluded that more work needed to be done in this area.

In this chapter, I assess the nutrient concentrations in two streams in the Chesapeake Bay watershed, Blockston Branch and Norwich Creek on the Delmarva

Peninsula, during several rain events in the context of riparian buffer restoration in the watersheds. Both baseflow and stormflow in these agriculturally-dominated streams are important to nitrogen and phosphorus fluxes. In Chapter 3, I compared the baseflow nitrogen concentrations between subbasins with varying amounts of restored riparian buffers. However, phosphorus transport in this coastal plain region tends to be correlated with suspended sediment fluxes (Jordan et al. 1997) and stream discharge (Fisher et al. 1998). Therefore, baseflow does not capture most of the phosphorus flux, and in this chapter I discuss stormflow sampling in order to evaluate the amount of phosphorus exported from these two subbasins. Both subbasins have similar land uses but varying amounts of riparian buffers, and I hypothesize that total phosphorus fluxes will be lower in the subbasin with more restored riparian buffers.

Methods

Study site

Blockston Branch and Norwich Creek are located in the Choptank River watershed on the eastern side of Chesapeake Bay (Fig 4-1). They were chosen as study sites because of their close proximity and the large differences in CREP sites between the two watersheds. The initial CREP data set collected in 2001 showed a larger restoration effort in Norwich Branch of 55.5 ha of CREP area than in Blockston Branch with only 1.6 ha. However, based on 1990 land use data, both subbasins were similar in size, land use, and soil types (Table 4-1). However, Norwich (24 km^2) is 31% larger than Blockston (17 km^2) and has some low-density housing developments which Blockston lacks. Percentages of agriculture and forest vary by only 5 to 6% between basins, and

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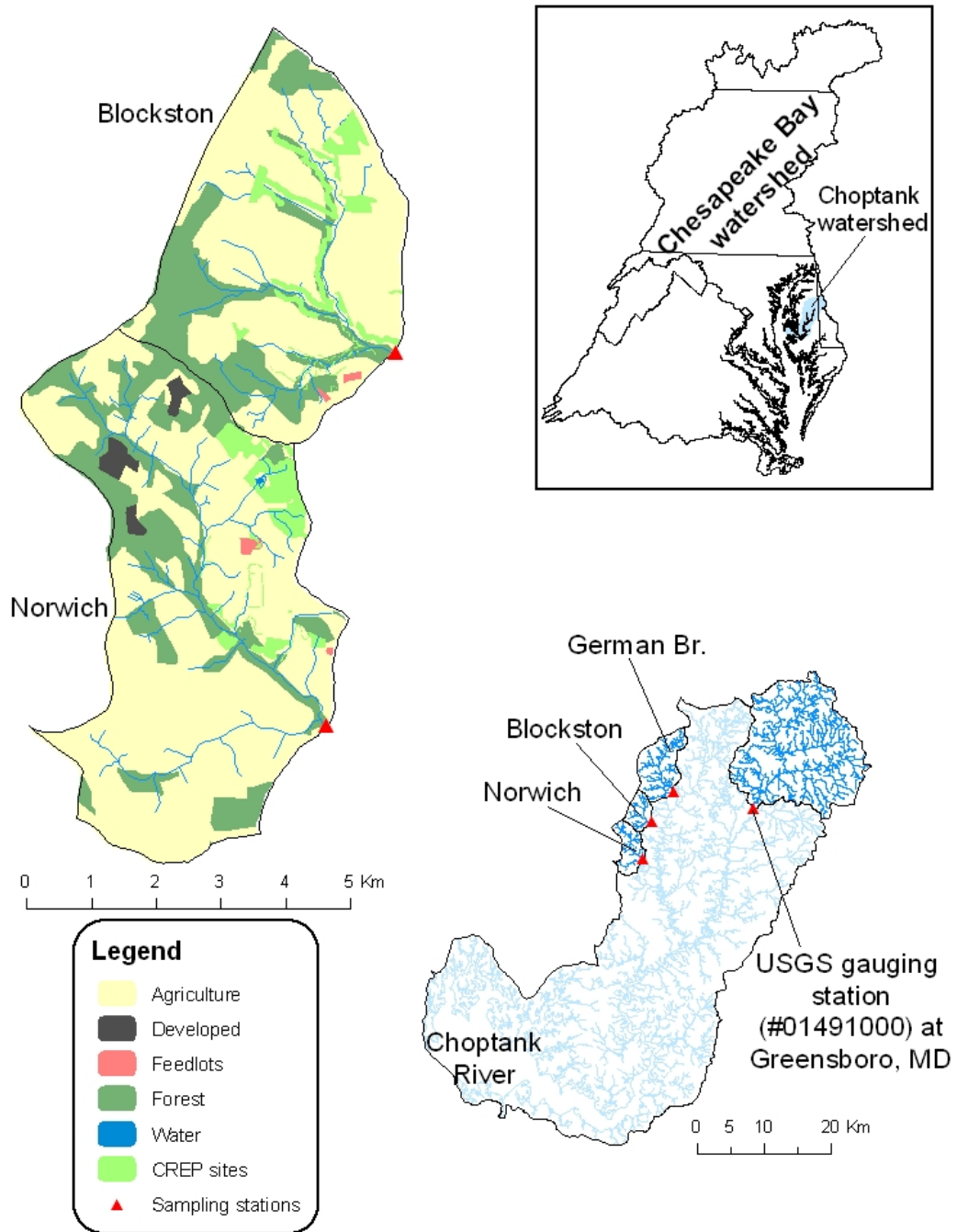
Fig 4-1. Location of the sampling sites, Blockston Branch and Norwich Creek, in the Choptank River watershed. Land use and riparian buffer restoration (CREP) is also shown for the two subbasins. Stream discharges measured in German Branch and Greensboro were used to estimate baseflow and stormflow in Blockston and Norwich.

Table 4-1. Land area, land use, soil types, and hydric soils in Blockston, Norwich, and the watershed draining to the USGS gauging station (#01491000) at Greensboro, Maryland. Fisher et al. (1998) derived land use from Digital Orthophoto Quarter-Quadrangles (DOQQs) in 1990. Norton and Fisher (2000) derived soil type and hydric soils from digitized soil maps of the region.

Subbasin	Area, km^2	Land use, % of subbasin area				Soils, % of subbasin area				
		Agriculture	Developed	Feedlots	Forest	A	B	C	D	Hydric
Blockston Branch	17.0	63.3	0.0	0.3	28.3	2.3	39.5	20.1	38.0	34.3
Norwich Creek	24.5	69.5	1.8	0.4	23.1	11.7	35.7	21.7	26.5	32.6
Greensboro	293.0	45.7	4.6	0.4	45.7	15.4	12.4	13.0	59.2	63.2

both subbasins have two animal feeding operations each. Soils vary more substantially; Norwich had more permeable soils (i.e., A drainage class), and Blockston has more poorly drained soils (i.e., D drainage class), although the percentages of hydric soils were similar (Table 4-1). Volume-weighted baseflow concentrations of nutrients at Blockston Branch and Norwich Creek in 2004 are shown in Table 4-2 (see Ch. 3). In general, phosphate (PO_4-P) and total phosphorus (TP) concentrations were slightly higher in Norwich baseflow, and nitrate (NO_3-N) and total nitrogen (TN) were 2 to 2.5 times higher in Blockston baseflow during the monitoring period in 2004.

Table 4-2. Flow-weighted nutrient concentrations from baseflow sampling January 2004 through December 2004. Monthly nutrient concentrations were flow-weighted for Blockston and Norwich using monthy water yields at Greensboro, Maryland (USGS gauging station #01491000, see Ch. 3)

Volume-weighted nutrient, mg L^{-1}	Blockston	Norwich
[NH_4-N]	0.06 ±0.01	0.07 ±0.01
[NO_3-N]	5.9 ±0.4	2.7 ±0.2
[TN]	8.6 ±0.4	3.4 ±0.2
[PO_4-P]	0.023 ±0.004	0.037 ±0.005
[TP]	0.042 ±0.004	0.051 ±0.005

CREP sites

Location of CRP and CREP restored buffers were recorded by Farm Service Agency (FSA) or Natural Resources Conservation Service (NRCS) personnel on printed aerial photographs in local county FSA offices. Copies of these photographs were obtained from the FSA, and I digitized each CREP site in Blockston and Norwich to create GIS databases using ArcGISV9. The resulting shapefile included buffers restored through the 2004 sign-up period. There is a current effort at the US Department of Agriculture's research laboratories in Beltsville, Maryland to add updated land use, including cropland, established forest, animal feeding operations, and developed areas, to these GIS databases with the digitized CRP and CREP buffers. In this chapter, when I discuss these restored buffers I usually only mention CREP sites because most of the restored grass and forest buffers in this region have been implemented under the CREP program. However, the analyses also include CRP sites.

Stormflow sampling

Both stream sampling sites (Fig 4-1) were equipped for automated recording of stream stage (water depth) and automated sampling of stream water. A cinderblock was installed in each stream to protect an automated pressure transducer, Solinst Model 3001 Levelogger, that was attached to the block with wire ties. At Norwich, I attached the cinderblock to a cement bridge pillar with chain to ensure that the block would not move during high stormflows. At Blockston, the cinderblock was attached to an earth-anchor driven approximately 1 meter into the streambank. I removed the Levelogger after each storm to download the stream stage data, and an additional Levelogger remained at Horn

Point Laboratory recording barometric pressure in order to correct data from the field loggers for atmospheric pressure changes. Hourly rain totals are also collected at Horn Point Laboratory, approximately 40 km southwest of Norwich subbasin, and I used rain data to characterize the sampled storm events.

Stream samples were collected automatically every hour during a storm event by ISCO 3700 portable samplers that remained in the field at each site from April through November 2004. In the field, we chained the samplers to an earth anchor and ran Tygon suction line from the samplers, underground, and into the stream where we attached the tube to the top of the cinderblock housing the stage loggers. Prior to a rain event, the samplers were programmed to purge air and water from the suction line and take a 500 mL sample every hour throughout the rain event and at least a day following the event. Every 24 hours, I replaced the full bottles with empty ones and brought the samples back to the lab for analysis.

Nutrient analyses

In the lab, I filtered the samples with GFF filters for automated colorimetric analysis of nitrite plus nitrate (hereafter, nitrate or NO_3) in the Technicon AutoAnalyzer II. I also used manual colorimetric methods to measure ammonium (NH_4) and phosphate (PO_4) concentrations in the filtered samples (Strickland and Parsons 1972). Filtered samples were also autoclaved with the persulfate reagents of Valderama (1981) and subsequently analyzed for dissolved phosphate (PO_4) using manual colorimetric methods (Strickland and Parsons 1972) to determine total dissolved phosphorus (TDP) and analyzed for nitrate (NO_3) in a Technicon AutoAnalyzer II in Horn Point's Analytical

Services Lab to determine total dissolved nitrogen (TDN). The analytical precision estimated from replicates during the manual techniques was typically 12% for NH_4, 10% for TDP, and 3% for PO_4.

Prior to filtering the samples for the nutrient analyses above, I pre-weighed GFF filters. I filtered a known volume of samples through 2 filters, and saved the filters for duplicate weighed measurements of total suspended solids. One of these filters was subsequently used for particulate carbon and nitrogen analyses, and the other for particulate phosphorus analysis. I measured total suspended solids (TSS) by weighing dry filters on the pre-weighed GFF filters and calculating the difference. Particulate carbon (POC) and nitrogen (PN) were measured in an elemental analyzer and particulate phosphorus (PP) was measured using the Andersen ignition method (Andersen 1976). In the PP method, the filter was ashed in a muffle furnace, boiled in HCl, and orthophosphate was determined by the molybdate-ascorbic acid method of Strickland and Parsons (1972). During filtering of the original samples, I recorded the volume of each sample filtered to calculate TSS and particulate nutrient concentrations.

Statistics

Statistical tests were performed using SigmaPlotV9 with SigmaStatV3.2 integration. The symbols *, **, and *** indicate statistical significance at the 0.05, 0.01, and 0.001 probability levels, respectively; "NS" is used for $p > 0.05$.

Results

CREP

Riparian buffers have been partially restored under the Conservation Reserve

Enhancement Program (CREP) in Blockston and Norwich subbasins (Fig 4-1). The total

area of CREP sites in each subbasin is approximately the same (i.e., 1.4 km^2 or 140

hectares); however, since Blockston is a smaller subbasin, the percentage of total

subbasin area restored is greater than in Norwich (Table 4-3). Since this stormflow study

Table 4-3. Total area of all CREP in each subbasin and the average length and width of CREP sites adjacent to streams that already had established riparian forest and CREP sites directly adjacent to streams (1 in Fig 4-2) and ditches that were previously unbuffered (2 in Fig 4-2).

| | | | CREP adjacent to establ. riparian forest | | | | CREP directly adjacent to stream/ditch | | | |
| | Total area of all CREP | | Length, m | | Width, m | | Length, m | | Width, m | |
Subbasin	km^2	% Subbasin	mean	se	mean	se	mean	se	mean	se
Blockston	1.4	8.1	669.2	103.6	55.5	9.5	851.2	27.1	164.2	23.1
Norwich	1.3	5.2	400.3	75.8	95.0	31.6	690.6	55.7	188.0	25.8

included only 2 subbasins, I evaluated the size and location of CREP sites in more detail

than in Chapter 3 where I was evaluating CREP sites in 30 separate subbasins. I divided

the CREP sites into two classes: (1) CREP sites adjacent to an established riparian forest

and (2) CREP sites directly adjacent to a stream or ditch (Fig 4-2). The amount of land

restored between an existing riparian buffer and an agricultural field (1 in Fig 4-2) was

less than the amount of unbuffered streamline restored (2 in Fig 4-2), but this widening of

existing riparian buffers was still a large fraction of the CREP buffered streamline (i.e.,

25% in Blockston and 34% in Norwich, calculated in Ch. 3). The width of CREP sites

that were added to an existing buffer was an average of 100 m less than the width of

CREP sites on previously unbuffered streams (Table 4-3). In 1990, 32% of the total

streamline in Norwich had established riparian buffers and in 2004 the buffered

streamline had increased to 45% as a result of the CREP (Table 4-4). A slightly larger

increase was observed in Blockston subbasin, from 42% in 1990 to 61% in 2004 (Table

4-4).
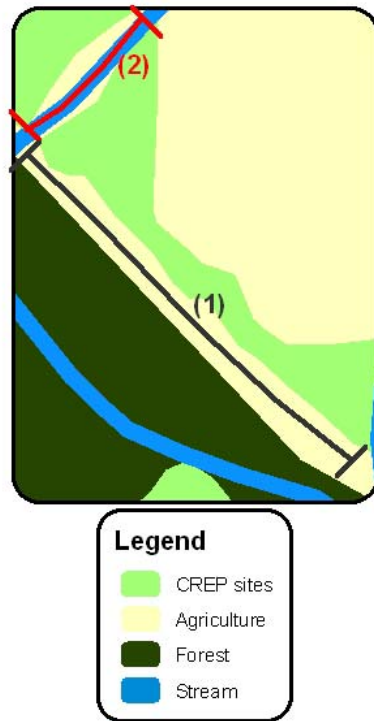
Fig 4-2. Example of CREP length measurement for (1) a CREP site implemented behind an established riparian buffer and (2) a CREP site implemented directly adjacent to a stream or ditch. The space between the CREP sites and the established forest or stream is the result of digitizing the 1990 land use at different scales compared to the 2005 CREP digitizing. Current land use in these subbasins is being added to the 2005 CREP shapefile and will correct these errors.

Table 4-4. Total streamline with riparian buffers in Blockston and Norwich watersheds before and after restoration. Streamline calculation includes both sides of the streams.

Subbasin	Total streamline, km	Buffered streams before CREP		Buffered streams after CREP	
		Streamline, km	% streamline	Streamline, km	% streamline
Blockston	51.9	21.8	42.0	31.5	60.7
Norwich	81.6	26.4	32.4	36.8	45.1

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I also evaluated the location of CREP sites in the subbasins according to stream order (Fig 4-3). An intermittent stream (zero order) is a stream that does not flow year-round. Most of the streams in these small subbasins are intermittent, headwater (or 1st order), and 2nd order streams (Fig 4-3). In Blockston, 73% of the intermittent streams were buffered by established forest, whereas only 48% of the intermittent streams in Norwich had established riparian buffers (Fig 4-3). In both subbasins, half the headwater streams were unbuffered, and the remainder was buffered by equal amounts of CREP sites and established forest (Fig 4-3). Restored buffers were distributed most differently along the 2nd order streams in the two subbasins. Thirty-eight percent of the 2nd order streams in Blockston were restored, whereas only 4% were restored and most remained unbuffered in Norwich (Fig 4-3). And lastly, the majority of 3rd order streams had established riparian forests in both subbasins.
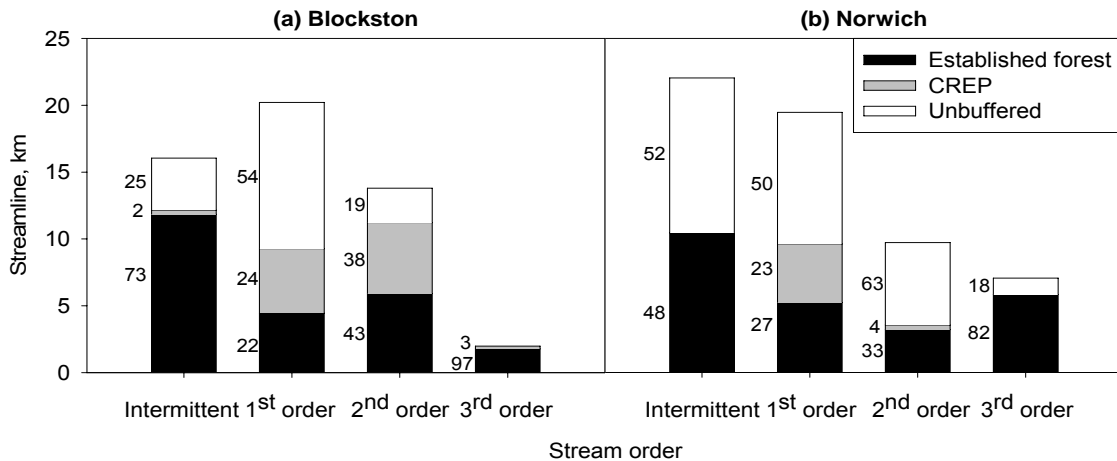
Fig 4-3. Type and total length of riparian buffers around the intermittent, 1st order, 2nd order, and 3rd order streams in Blockston and Norwich subbasins. Black bars are total established forest streamlength, light gray bars are total CREP streamlength, and white bars are total unbuffered streamlength. The percentage of buffer types in the different stream orders is shown beside the bars.

Storm hydrographs and nutrients

In order to characterize nutrient export as a result of overland flow from storm events, I measured the response to 4 rainfalls in Blockston Branch and Norwich Creek, 2 in spring 2004 and 2 in fall 2004. The first sampled rain event lasted 6 hours during the evening of April 26 for a total of approximately 2 cm, after 11 days of no rainfall (top panels in Fig 4-4). The next storm event in the spring was over a 24-hour period, from the night of May 2nd throughout the next day. This 2 cm rainfall did not have a distinctive peak period of rain, as the previous 6 hour rainfall, but was a prolonged rain with several periods of varying rainfall intensities. As a result, there were several peaks in stream stage, and stream samples were not collected throughout the full storm hydrograph since the streams did not lower to baseflow levels until 4 days after the storm began. The first sampled rainfall in the fall totaled almost 3 cm, most of the rain was over an 8 hour period on the night of September 28, and there had been no rainfall for 10 days prior (top panels in Fig 4-5). The last rain event was sampled the 4th of November after over 2 weeks of no rain. This rain event lasted approximately 6 hours during the afternoon and totaled 2.6 cm. I performed nutrient analyses on the stream samples collected during the rain events in April, September, and November, and I will present the data from these three storms throughout the rest of the chapter.

Hydrographs can be used to evaluate some of the relationships in nutrients and stormflow between the two subbasins. All nutrient concentrations are presented for a spring example (26 April rain, Fig 4-4) and a fall example (28 September rain, Fig 4-5). In Norwich, peak total phosphorus and phosphate concentrations occurred at peak stream stage and total nitrogen and nitrate concentrations either did not change (Fig 4-4b) or
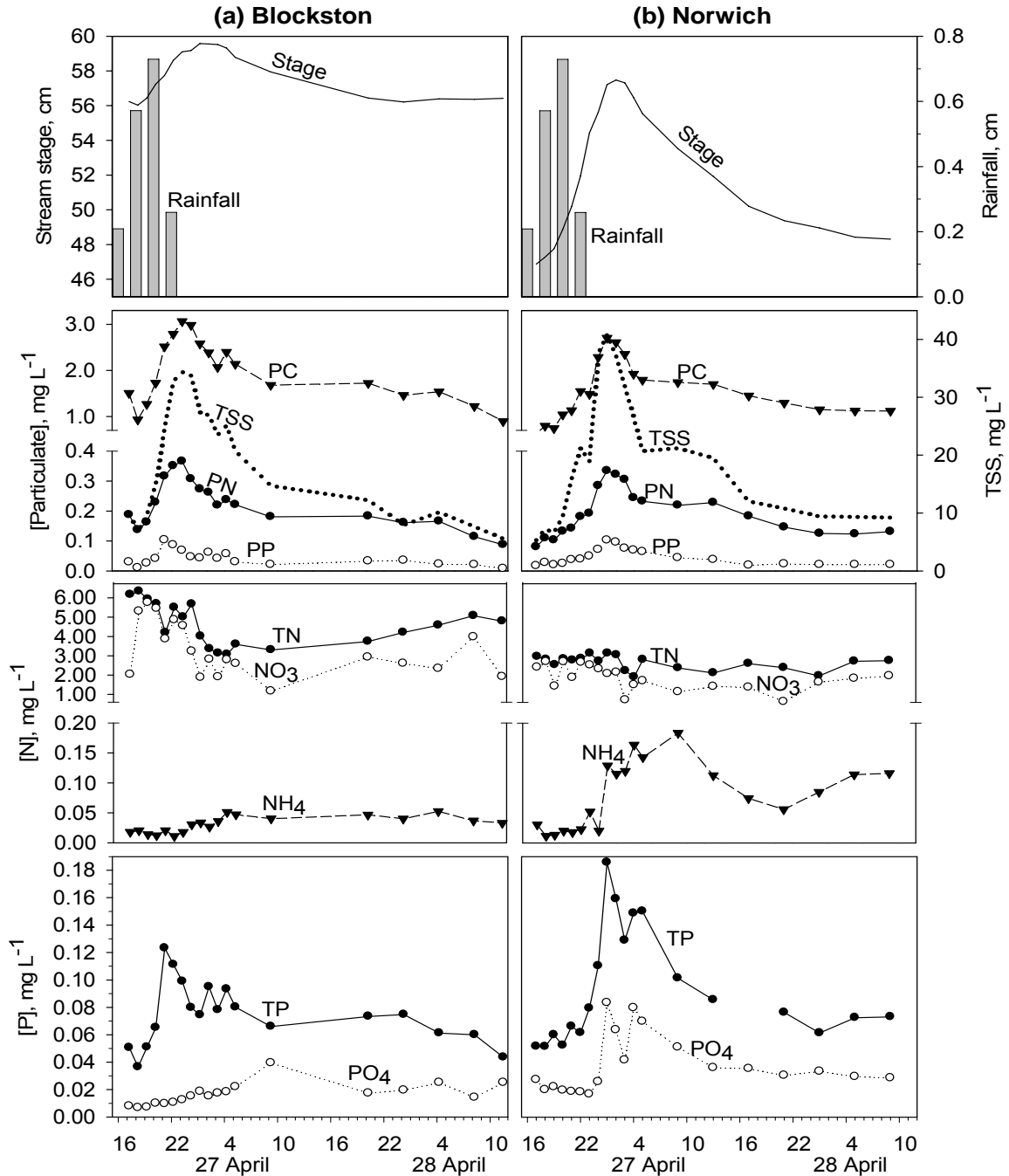
Fig 4-4. Rainfall, stream stage, total suspended solids (TSS), particulate carbon, nitrogen and phosphorus (PC, PN, and PP), total nitrogen (TN), nitrate (NO_3), ammonium (NH_4), total phosphorus (TP), and phosphate (PO_4) concentrations as response to the 26 April 2004 storm in (a) Blockston and (b) Norwich. The x and y axes are the same in (a) and (b) in order to compare nutrient response between subbasins.
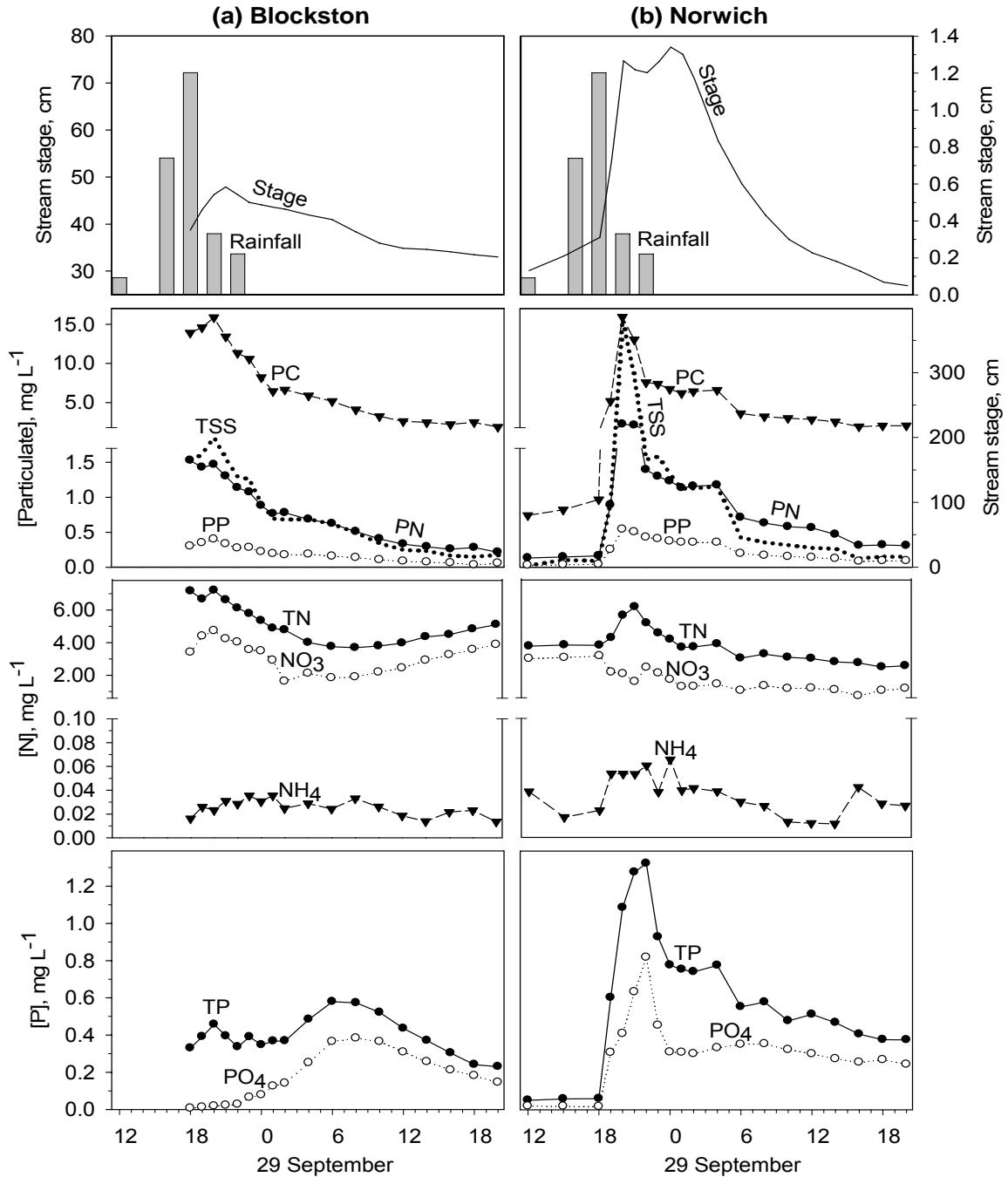
Fig 4-5. Rainfall, stream stage, total suspended solids (TSS), particulate carbon, nitrogen and phosphorus (PC, PN, and PP), total nitrogen (TN), nitrate (NO_3), ammonium (NH_4), total phosphorus (TP), and phosphate (PO_4) concentrations as response to the 28 September 2004 storm in (a) Blockston and (b) Norwich. The x and y axes are the same in (a) and (b) in order to compare nutrient response between subbasins.

increased slightly at the beginning of the storm and then became diluted by the time the rain was ending (Fig 4-5b). In Blockston, however, the peak in PO_4 concentrations and time of the most diluted total N and NO_3 concentrations were approximately 12 hours after peak stream stage during most of the storms. In the fall Blockston had a double peak in total P concentrations (Fig 4-5a). There was an initial peak in particulate P (PP) that followed the rise in stream stage and caused the initial increase in total P. As the stage was declining 12 hours after the rain event, there was a second peak in dissolved P. This is not as pronounced in Norwich Creek where there was a peak in concentrations for all forms of P at peak stream stage, and then a slow recovery to baseflow concentrations as the stream height came down after the storm (Fig 4-5b). The exception was during the September storm when there was a small second peak in PO_4 as the stream stage was declining (Fig 4-5b). In both storms, peak TP and PO_4 concentrations in Norwich were twice as high as peak concentrations in Blockston; furthermore, NO_3 dilution was 1.5 to 2 times more pronounced in Blockston compared to dilution in Norwich. The total suspended solids and particulate nutrients did not lag behind the stream stage in either subbasin (2nd set of panels in Fig 4-4 and 4-5). The concentrations of total suspended solids, particulate C, particulate N, and particulate P increase rapidly along with the stage, were highest when stream stage peaked, and decreased slowly as the height of the stream declined (Fig 4-4 and 4-5).

There were some differences in the stream responses between spring (Fig 4-4) and fall storms (Fig 4-5). Ammonium concentrations were higher during the April storm as opposed to the September storm. I measured a large spike in NH_4 concentration of 0.18 mg L^{-1} in Norwich Creek during the spring rain (Fig 4-4b), which was 2.5 times the

highest concentrations measured in the September event (Fig 4-5b). In Blockston, NH_4

concentrations in the spring were only 0.01 mg L^{-1} higher than in the fall. Phosphorus

exhibited the opposite pattern: higher concentrations during the fall rain events as

opposed to the spring event (Fig 4-6). Peak total P concentrations in Norwich during the

two fall events were 2.5 to 7 times higher than in the spring, whereas in Blockston total P

concentrations were only 3 to 4 times higher. Total P and total suspended solid

concentrations were the highest during the September rain event (Fig 4-5). In Norwich
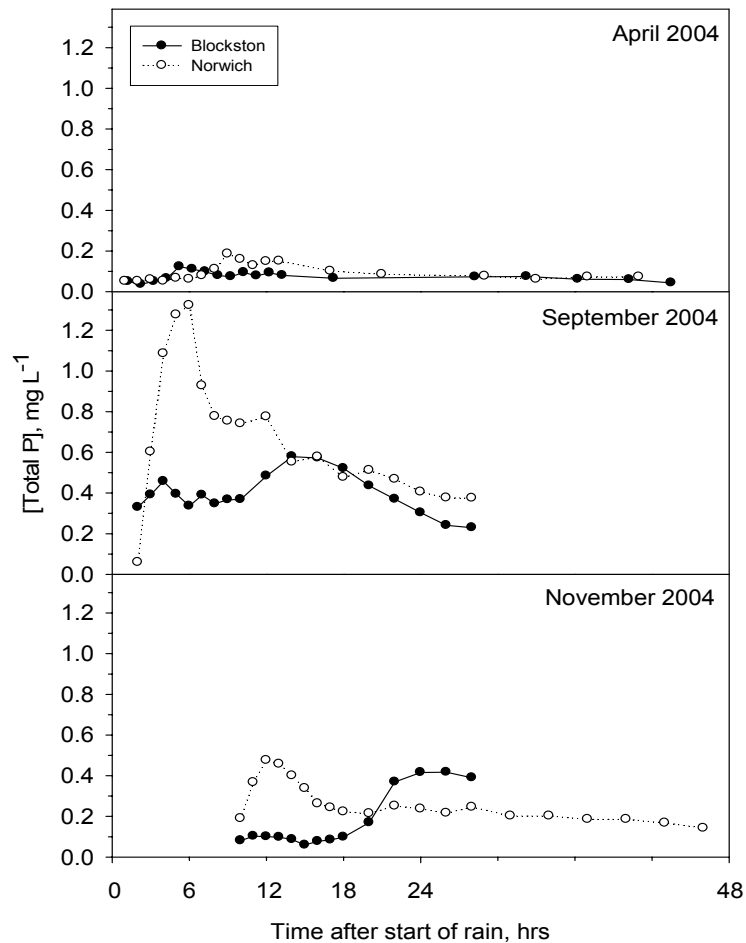
Fig 4-6. Total phosphorus (TP) concentrations in Blockston (closed circles) and Norwich (open circles) during all three measured storm events.

Branch, TSS concentrations during the September event were 9 times the concentrations during the spring, and concentrations in Blockston Branch were 6 times higher in September than in the spring.

A summary of the nutrient responses in Blockston Branch and Norwich Creek to the 3 storm events in 2004 is shown in Table 4-5. Presented are the stream stage, total suspended solids (TSS), and particulate and dissolved nutrients before the storm and at the peak response to each rain event. The peak response was not necessarily when the

Table 4-5. Summary of stream stage and nutrient response to three rain events in Blockston and Norwich subbasins. Presented are the pre-storm values, peak values during or after the storm, and the difference (Δ = peak minus pre-storm values). Peak is either the largest value, or in the case of nutrient dilution, the lowest value.

Storm	Parameter	Blockston			Norwich		
		Pre-storm	Peak response	Δ	Pre-storm	Peak response	Δ
26-Apr-04	Stage, cm	56.0	59.6	3.6	46.9	57.5	10.6
1.8 cm rain	TSS, mg L^{-1}	6.7	34.3	27.6	5.3	40.8	35.5
	particulate C mg L^{-1}	1.3	3.1	1.8	0.6	2.7	2.1
	particulate N, mg L^{-1}	0.14	0.37	0.23	0.08	0.33	0.25
	particulate P, mg L^{-1}	0.029	0.103	0.074	0.017	0.102	0.085
	NH_4-N, mg L^{-1}	0.02	0.05	0.03	0.02	0.18	0.16
	NO_3-N, mg L^{-1}	5.3	1.9	-3.4	2.4	0.7	-1.7
	TDN, mg L^{-1}	6.0	2.8	-3.2	2.9	1.7	-1.2
	PO_4-P, mg L^{-1}	0.007	0.039	0.032	0.027	0.083	0.056
	TDP, mg L^{-1}	0.021	0.050	0.029	0.035	0.086	0.051
28-Sep-04	Stage, cm	38.7	47.9	9.2	30.1	77.6	47.5
2.6 cm rain	TSS, mg L^{-1}	163.1	200.4	37.3	2.5	381.7	379.2
	particulate C mg L^{-1}	1.8	15.9	14.1	0.7	22.9	22.2
	particulate N, mg L^{-1}	0.22	1.53	1.31	3.80	6.20	2.40
	particulate P, mg L^{-1}	0.057	0.400	0.343	0.028	0.542	0.514
	NH_4-N, mg L^{-1}	0.02	0.04	0.02	0.04	0.07	0.03
	NO_3-N, mg L^{-1}	3.4	1.6	-1.8	3.0	0.7	-2.3
	TDN, mg L^{-1}	5.6	3.1	-2.5	3.6	2.2	-1.4
	PO_4-P, mg L^{-1}	0.006	0.383	0.377	0.019	0.818	0.799
	TDP, mg L^{-1}	0.029	0.437	0.408	0.022	0.896	0.874
4-Nov-04	Stage, cm	39.2	43.0	3.8	46.7	70.2	23.5
2.6 cm rain	TSS, mg L^{-1}	15.2	27.1	11.9	11.9	30.9	19.0
	particulate C mg L^{-1}	2.3	3.1	0.8	2.5	4.2	1.7
	particulate N, mg L^{-1}	0.34	0.42	0.08	0.36	0.64	0.28
	particulate P, mg L^{-1}	0.065	0.076	0.011	0.100	0.178	0.078
	NH_4-N, mg L^{-1}	0.04	0.01	-0.03	0.04	0.01	-0.03
	NO_3-N, mg L^{-1}	3.7	1.3	-2.4	1.1	0.7	-0.4
	TDN, mg L^{-1}	5.1	3.1	-2.0	2.1	2.1	0.0
	PO_4-P, mg L^{-1}	0.012	0.345	0.333	0.064	0.298	0.234
	TDP, mg L^{-1}	0.016	0.347	0.331	0.090	0.298	0.208

stream was at the highest stage, but when the nutrient was at the highest (or lowest if stormflow diluted the nutrient, as in NO_3). In some cases this occurred during the peak stormflow (e.g., TP in Norwich, Fig 4-5b) and in some cases this occurred after a slight lag behind the peak stormflow (e.g., TP in Blockston, Fig 4-5a). During all 3 rain events, the response in stream stage was higher in Norwich Creek than Blockston Branch (Table 4-5). Norwich subbasin is only 31% larger in area, yet increases in stream stage were 3 to 6 times the stage increase in Blockston. In general, TSS, particulates, NH_4, and dissolved P concentrations all increased during the storm events; in contrast, NO_3 and total dissolved nitrogen concentrations were diluted (Table 4-5). Nitrate and total dissolved N tended to be higher in Blockston, and NH_4 and dissolved P tended to be higher in Norwich, both in stormflow during the 3 storm events in 2004 (Table 4-5) as well as in baseflow during the 2004 sampling (Table 4-2).

Stormflow discharge and nutrient yields

Annual volume-weighted nutrient concentrations in baseflow were calculated using the monthly flow data from Greensboro (Table 4-2, see Ch. 3). The relationship between area-weighted discharges at Greensboro (water yields) compared to other subbasins on the Delmarva Peninsula becomes less significant at time scales less than a month; therefore, this approach can not be used for hourly stormflow measurements. In lieu of actual discharge measurements during low and high flows currently being collected at Blockston and Norwich, I used an adjusted rating curve from the subbasin north of Blockston, German Branch (Fig 4-1), which was calibrated by Jordan et al. (1997). Baseflow discharge was measured in Blockston and Norwich in June 2005 and

related to the stage data collected by the automated pressure transducers that were

installed in the streams prior to the 2004 stormflow sampling. The rating curve for

German Branch was adjusted for stage datum and area differences assuming that

rectangular bridge structures at these sites will result in similarly shaped rating curves for

German Branch, Blockston, and Norwich (e.g., Blockston in Fig 4-7). I used the

resulting relationships between stage depth and discharge to predict the stormflow from

the stage measurements during the storm events:

$$Q_B = -1.05 + 0.74e^{(0.978 \times d)} \qquad \text{(eq 4-1)}$$

$$Q_N = -2.28 + 1.91e^{(0.699 \times d)} \qquad \text{(eq 4-2)}$$

where Q_B was discharge in Blockston (m^3 s^{-1}), Q_N was discharge in Norwich (m^3 s^{-1}), and

d was the stream stage data measured by the loggers.
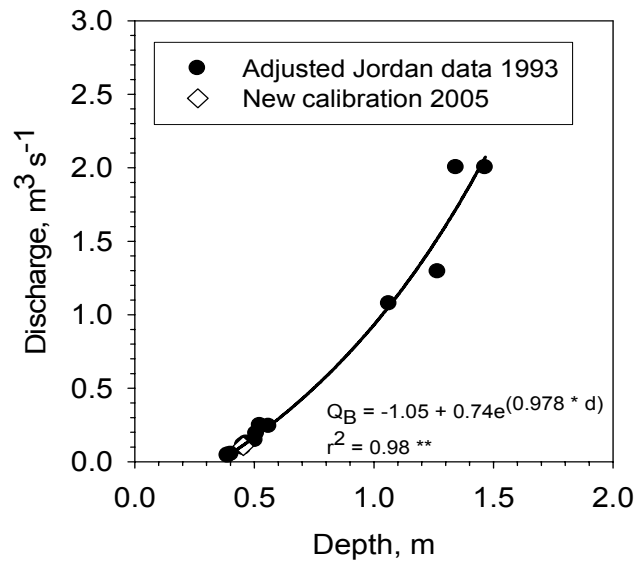
Fig 4-7. The area-corrected rating curve for Blockston Branch. The depth versus
discharge relationship for German Branch (Jordan et al. 1997) was adjusted for the
smaller area of Blockston and adjusted to fit the calibration point of measured baseflow
in June 2005. The same procedure was used for Norwich Creek and the resulting
relationships are shown in eq. 4-1 and 4-2. Q_B is the stormflow discharge in Blockston
(m^3 s^{-1}) and d is the stream depth (m) throughout the storm.

I used the resulting stormflow discharges to evaluate the relationships between nutrient concentrations and discharge. Examples of these C-Q plots during the April and September 2004 rain events are shown in Fig 4-8. An example of a positive relationship with discharge was the concentration of total suspended solids in both subbasins during the two storms (Fig 4-8a&b, and the only significant negative relationship during the storms was total dissolved N in April (Fig 4-8a). Total dissolved nitrogen concentrations
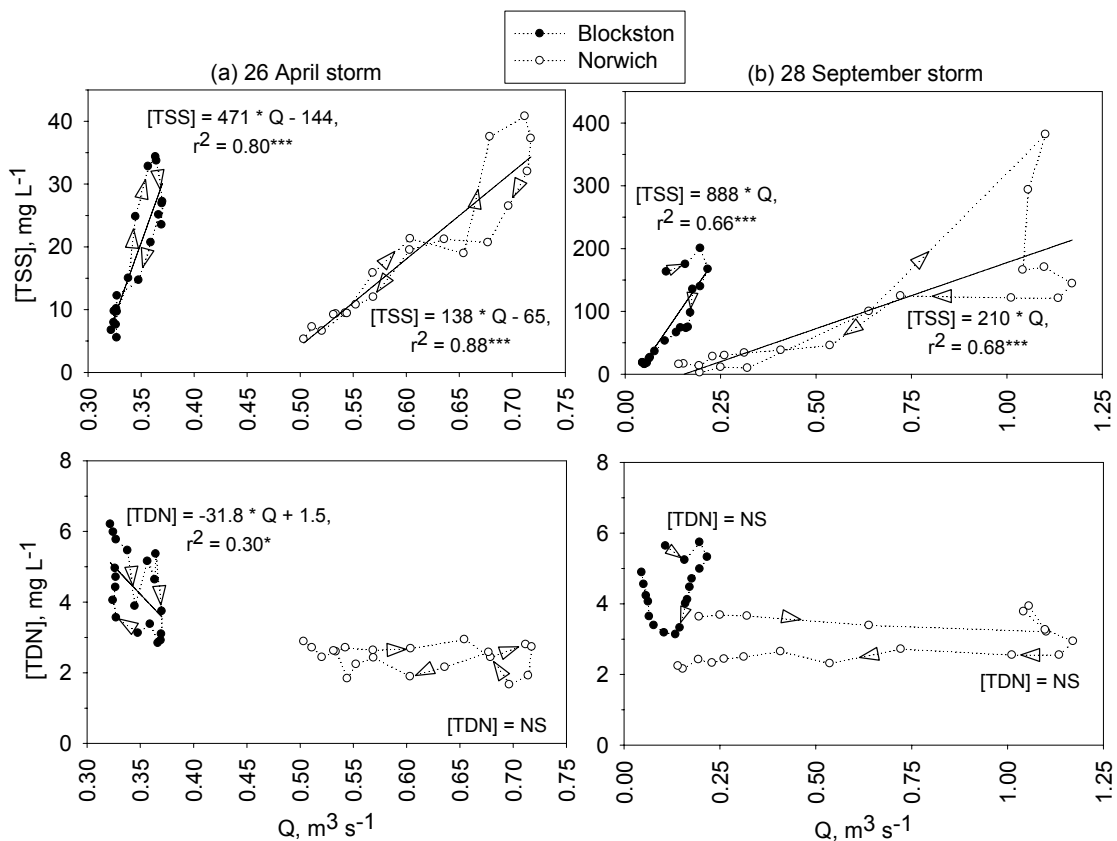
Fig 4-8. Examples of C-Q plots for Blockston Branch and Norwich Creek during the (a) 26 April and (b) 28 September storms. Total suspended solids (TSS) are the top panels and total dissolved nitrogen (TDN) on the bottom. The lines are significant linear regressions between discharge (Q) and nutrient concentrations, and formulas are shown. Dotted lines show hysteresis during the rising and falling stream stage, and the arrows show the time sequence of increasing TSS during the storms and decreasing TDN during the storms. Note the slight difference in x axes between the two storms and the order of magnitude difference between TSS from the spring to the fall storm. The results for all nutrients during the April and September events are shown in Table 4-6.

Table 4-6. A spring and fall example in each subbasin of concentration-discharge relationships during the storms. Discharge (Q) during the storms was calculated using equations 4-1 and 4-2 and is in $m^3 s^{-1}$. If the y-intercept was not significantly different from zero ($p>0.05$), it was removed from the equations below. NS is not significant.

Storm	Parameter	Blockston		Norwich	
		equation	r^2	equation	r^2
26-Apr-04	TSS, mg L^{-1}	[TSS]=471*Q-144	0.80***	[TSS]=138*Q-65	0.88***
1.8 cm rain	particulate C mg L^{-1}	[PC]=29.9*Q-8.4	0.71***	[PC]=7.6*Q-3.1	0.89***
	particulate N, mg L^{-1}	[PN]=3.0*Q-0.8	0.53***	[PN]=1.0*Q-0.4	0.91***
	particulate P, mg L^{-1}	[PP]=0.72*Q-0.21	0.30*	[PP]=0.33*Q-0.16	0.88***
	NH_4-N, mg L^{-1}	NS		[NH4]=0.39*Q	0.29*
	NO_3-N, mg L^{-1}	NS		NS	
	TDN, mg L^{-1}	[TDN]=-31.8*Q+1.5	0.30*	NS	
	PO_4-P, mg L^{-1}	NS		[PO4]=0.19*Q-0.08	0.48***
	TDP, mg L^{-1}	NS		[TDP]=0.15*Q	0.37**
28-Sep-04	TSS, mg L^{-1}	[TSS]=888*Q	0.66***	[TSS]=210*Q	0.68***
2.6 cm rain	particulate C mg L^{-1}	[PC]=66.4*Q	0.62***	[PC]=12.1*Q	0.67***
	particulate N, mg L^{-1}	[PN]=6.3*Q	0.63***	[PN]=1.40*Q	0.73***
	particulate P, mg L^{-1}	[PP]=1.69*Q	0.73***	[PP]=0.39*Q	0.88***
	NH_4-N, mg L^{-1}	[NH4]=0.78*Q+0.015	0.43**	[NH4]=0.39*Q	0.29*
	NO_3-N, mg L^{-1}	NS		NS	
	TDN, mg L^{-1}	NS		NS	
	PO_4-P, mg L^{-1}	[PO4]=0.34*Q-1.37	0.35**	[PO4]=0.29*Q+0.14	0.37**
	TDP, mg L^{-1}	[TDP]=0.37*Q-1.32	0.30*	[TDP]=0.36*Q+0.15	0.45**

in Norwich during the April storm and in both subbasins during the fall storm were not

significantly related to discharge (Fig 4-8). These relationships also show signs of

hystersis. During the rising limb of the hydrograph, total suspended solids concentrations

were higher than the concentrations during the falling limb of the hydrograph. This is

similar for total dissolved nitrogen; however, total suspended solid concentrations peaked

when stream discharge was the highest and total dissolved N concentrations peaked when

stream discharge was the lowest. Nitrate was not significantly related to stormflow

discharge during the April or September events (Fig 4-8c and Table 4-6). Comparison

between subbasins shows that TSS concentrations in Blockston Branch respond more

rapidly to stream discharge; however, TSS concentrations reach higher levels in

Norwich (Fig 4-8).   Total dissolved nitrogen concentrations in Blockston Branch also

respond more rapidly to stream discharge than in Norwich Creek (Fig 4-8). Table 4-6 is

a summary of C-Q relationships during the April and September events. In general, TSS,

particulate nutrients, NH_4, and phosphorus were positively correlated to stormflow

discharge. The exception to this is during the spring storm in Blockston where NH_4, total

dissolved P, and PO_4 were not significant (Table 4-6). The slopes of the equations, or

rate of concentration increase as discharge increased, presented in Table 4-6 tended to be

higher in Blockston compared to Norwich and during the September storm compared to

the April storm.

Stormflow discharges were also used to calculate volume-weighted nutrient

concentrations during the 3 measured storms in 2004:

$$C_{vw} = \frac{\sum (C_i * Q_i)}{\sum Q_i} \qquad\qquad\qquad\qquad \text{(eq. 4-3)}$$

$$SE_{vw} = \frac{\sqrt{\sum_{i=1}^{n} (C_i - C_{vw})^2 \Big/ (n-1)}}{\sqrt{n}} \qquad\qquad\qquad \text{(eq.4-4)}$$

where C_{vw} was the volume-weighted mean concentration during the storm, C_i was the

nutrient concentration at time i during the storm, and Q_i was the estimated discharge at

time i during the storm. The resulting average volume-weighted nutrient concentrations

during each storm are shown in Table 4-7. In general, TSS, particulate nutrients, NH_4,

and P volume-weighted concentrations are significantly higher in Norwich, and NO_3 and

total dissolved N are significantly higher in Blockston (Table 4-7).

I also calculated the nutrient export from Blockston and Norwich from 2004 data.

In order to calculate nutrient fluxes in baseflow and stormflow throughout the year,

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measurements of volume-weighted nutrient concentrations and estimates of flow were

needed. I evaluated baseflow nutrient concentrations in Blockston Branch and Norwich

Creek in Chapter 3. To estimate annual stormflow nutrients, I am assuming the April

storm is representative of storms during half the year and an average of the fall storms is

representative of the storms during the other half of the year. Stream discharge in

Blockston and Norwich has not been measured in the past; therefore, I used monthly

water yields from the US Geological Survey stream gauging site (#01491000) in the

Choptank River at Greensboro, Maryland (Fig 4-1) and basin areas of Blockston and

Table 4-7. Average volume-weighted (V-W) nutrient concentrations and standard errors during the three rain events in Blockston Branch and Norwich Creek (from equations 4-3 and 4-4). Also shown are the differences in the subbasins (Δ = Norwich minus Blockston) and whether the volume-weighted concentrations are significantly different between the subbasins.

Storm	Parameter	Blockston		Norwich		Norwich-Blockston	
		V-W mean	se	V-W mean	se	Δ	Significance
26-Apr-04	TSS, mg L^{-1}	18.8	0.608	19.8	0.576	1.0	NS
1.8 cm rain	particulate C mg L^{-1}	2.0	0.041	1.6	0.031	-0.4	***
	particulate N, mg L^{-1}	0.22	0.004	0.20	0.004	-0.02	***
	particulate P, mg L^{-1}	0.042	0.001	0.047	0.001	0.005	*
	NH_4-N, mg L^{-1}	0.03	0.004	0.08	0.003	0.05	***
	NO_3-N, mg L^{-1}	3.2	0.086	1.8	0.032	-1.4	***
	TDN, mg L^{-1}	4.3	0.108	2.4	0.019	-1.9	***
	PO_4-P, mg L^{-1}	0.016	0.002	0.039	0.001	0.023	***
	TDP, mg L^{-1}	0.034	0.002	0.057	0.002	0.023	***
28-Sep-04	TSS, mg L^{-1}	107.7	3.743	146.2	5.920	38.6	***
2.6 cm rain	particulate C mg L^{-1}	8.8	0.300	9.6	0.342	0.8	NS
	particulate N, mg L^{-1}	0.93	0.027	1.22	0.038	0.29	***
	particulate P, mg L^{-1}	0.230	0.007	0.333	0.010	0.103	***
	NH_4-N, mg L^{-1}	0.03	0.000	0.04	0.001	0.02	***
	NO_3-N, mg L^{-1}	3.3	0.055	1.7	0.038	-1.5	***
	TDN, mg L^{-1}	4.5	0.048	3.0	0.031	-1.5	***
	PO_4-P, mg L^{-1}	0.132	0.008	0.387	0.010	0.255	***
	TDP, mg L^{-1}	0.174	0.008	0.464	0.012	0.290	***
4-Nov-04	TSS, mg L^{-1}	14.3	0.438	18.1	0.349	3.8	***
2.6 cm rain	particulate C mg L^{-1}	2.2	0.029	2.9	0.040	0.7	***
	particulate N, mg L^{-1}	0.35	0.004	0.47	0.006	0.12	***
	particulate P, mg L^{-1}	0.067	0.001	0.135	0.002	0.068	***
	NH_4-N, mg L^{-1}	0.02	0.001	0.01	0.000	0.00	***
	NO_3-N, mg L^{-1}	3.5	0.087	1.8	0.022	-1.7	***
	TDN, mg L^{-1}	4.8	0.076	2.9	0.040	-1.9	***
	PO_4-P, mg L^{-1}	0.088	0.011	0.137	0.003	0.049	***
	TDP, mg L^{-1}	0.096	0.011	0.147	0.003	0.051	***

Norwich to calculate total streamflow from these basins in 2004. Stream water yields

have generally been 35 cm yr^{-1} in the outer coastal plain of the Chesapeake Bay

watershed (Jordan et al. 1997), and when adjusted for subbasin area, discharges between

watersheds on the Delmarva Peninsula over a 2-year period were also correlated

(r^2=0.80***, see Ch. 3). I used annual discharge data from Greensboro to calculate total

discharge from Blockston and Norwich in 2004:

$$Q_x = Q_G \times (\frac{A_x}{A_G}) \qquad\qquad \text{(eq 4-5)}$$

where Q_x is the total 2004 discharge in Norwich or Blockston in m^3 yr^{-1}, Q_G is the sum of

the monthly mean discharge in 2004 at Greensboro in m^3 yr^{-1}, A_x is the area of Norwich

or Blockston, and A_G is the area of Greensboro. Based on this approach, 2004 discharges

from Norwich Creek and Blockston were 9.3x10^6 m^3 yr^{-1} and 6.5x10^6 m^3 yr^{-1},

respectively.

Finally, the last estimate needed to calculate total nutrient fluxes during the

different flows was the relative importance of baseflow and stormflow to the total 2004

flows (i.e., 6.5x10^6 m^3 yr^{-1} in Blockston and 9.3x10^6 m^3 yr^{-1} in Norwich). Lee et al.

(2000) calculated the relative contribution of baseflow and stormflow over a 10-year

period at Greensboro using USGS PART software. The decadal average baseflow

contribution was 71% of total annual flow, and stormflow was 29% of total annual flow.

I am assuming here that the relative contributions of baseflow and stormflow are similar

between the long-term mean for Greensboro and the two subbasins in this study.

Since I only sampled storms in the spring and fall, I must assume that stormflow nutrient

concentrations during half the year was similar to the measured April event and the

concentrations during the other half of the year was an average of the measured September and November events. I calculated nutrient flux in baseflow and stormflow in 2004 using the following equations for each subbasin:

$$F_{baseflow} = C_{VWbaseflow} \times Q_{baseflow} \qquad \text{(eq 4-6)}$$

$$F_{stormflow} = \left(C_{VWAprstorm} \times Q_{stormflow}\right) + \left(\frac{C_{VWSepstorm} + C_{VWNovstorm}}{2} \times Q_{stormflow}\right)$$

$$\text{(eq 4-7)}$$

where $F_{baseflow}$ was the nutrient flux during baseflow in kg yr^{-1}, $C_{VWbaseflow}$ was the annual volume-weighted nutrient concentration during baseflow in kg m^{-3} (Table 4-2), $Q_{baseflow}$ was the baseflow discharge in m^3 yr^{-1} (71% of estimated annual flow), $F_{stormflow}$ was the nutrient flux during stormflow in kg yr^{-1}, $C_{VWAprstorm}$ was the average volume-weighted nutrient concentration during the April storm in kg m^{-3} (Table 4-7), $Q_{stormflow}$ was the stormflow discharge in m^3 yr^{-1} (29% of estimated annual flow), $C_{VWSepstorm}$ was the average volume-weighted nutrient concentration during the September storm in kg m^{-3} (Table 4-7), and $C_{VWNovstorm}$ was the average volume-weighted nutrient concentration during the November storm in kg m^{-3} (Table 4-7).

In order to compare nutrient fluxes between Blockston and Norwich, I normalized the fluxes (described above in eq. 4-6 and 4-7) by the area of each subbasin. This converts nutrient fluxes (kg y^{-1}) into nutrient yields (kg ha^{-1} yr^{-1}) which can be used to contrast baseflow and stormflow nutrients in the two basins (Table 4-8). In general, nitrogen moved primarily with baseflow (i.e., 70 to 85%), whereas phosphorus moved primarily during short periods of stormflow (i.e., 55 to 70%, Table 4-8). In comparisons between subbasins, total N yield from Blockston during baseflow (22.8 kg N ha^{-1} yr^{-1})

Table 4-8. Nutrient yields from Blockston and Norwich subbasins during baseflow and stormflow in 2004. Since discharge has not been measured yet at Blockston and Norwich, estimates of total baseflow and stormflow were based on the area-weighted relationship in discharge to the USGS gauging station at Greensboro, Maryland (see Ch. 3). Along with these flow estimates, I used average volume-weighted nutrient concentrations (Tables 4-2 and 4-6) to calculate total flux during baseflow and stormflow. Also presented is the % total flux in baseflow and stormflow within each subbasin.

	Blockston				Norwich			
	Baseflow, 4.9×10^6 m^3 year^{-1}		Stormflow, 1.5×10^6 m^3 year^{-1}		Baseflow, 7.1×10^6 m^3 year^{-1}		Stormflow, 2.2×10^6 m^3 year^{-1}	
Nutrient	Yield, kg ha^{-1} year^{-1}	% of 2004 yield	Yield, kg ha^{-1} year^{-1}	% of 2004 yield	Yield, kg ha^{-1} year^{-1}	% of 2004 yield	Yield, kg ha^{-1} year^{-1}	% of 2004 yield
NH_4	0.17	85%	0.03	15%	0.19	75%	0.06	25%
NO_3	15.6	81%	3.7	19%	7.3	79%	2.0	21%
TN	22.8	81%	5.5	19%	9.2	72%	3.6	28%
PO_4	0.06	46%	0.07	54%	0.10	38%	0.17	62%
TP	0.11	36%	0.20	64%	0.14	28%	0.35	72%

was 2.5 times higher than from Norwich during baseflow (9.2 kg N ha^{-1} yr^{-1}), and total P yield from Norwich during stormflow (0.35 kg P ha^{-1} yr^{-1}) was almost 2 times higher than the total P yield from Blockston during stormflow (0.20 ha^{-1} yr^{-1}). This is consistent with the patterns in peak nutrient responses (Table 4-5) and volume-weighted nutrient concentrations integrated throughout each storm (Table 4-7).

Discussion

CREP and nutrients

Riparian buffer restoration in Blockston and Norwich subbasins may explain some of the differences in the streams' nutrient responses during the monitored rain events. Both subbasins have the same area that has been restored through CREP (Table 4-3), yet the restored sites in Blockston subbasin buffer more streamline and are more evenly distributed throughout the subbasin than in Norwich (Fig 4-1). The lengths of restored buffers along the streams and ditches tend to be longer in Blockston (Table 4-3), and as a result, more of the streamline is buffered than in Norwich. Only 45% of the streams in Norwich are buffered, including both established forests and restored grass and forest buffers, and the remaining streams flow through agricultural land without any grass or forest buffer (Table 4-4). However, 61% of the streams in Blockston subbasin have riparian buffers, either established or CREP. The Chesapeake Bay Program has a goal of restoring 70% of the streamline in the entire Chesapeake Bay watershed (EPA 2003), and monitoring the water quality in streams such as Blockston Branch which are approaching this goal may be a valuable case study to predict how other basins will respond to the 70% goal.

Buffers have also been restored along a greater variety of streams in Blockston Branch. CREP sites in Norwich are almost exclusively around headwater streams (Fig 4-1 and 4-3). Headwater, or 1st order, streams have been shown to control a disproportionately large amount of the nitrogen uptake and transformation as compared to higher order streams (Peterson et al. 2001). These streams may be important areas to target riparian buffer restoration to enhance nitrogen uptake by denitrification, plant uptake, and dilution in the buffers. Therefore, the headwater streams buffered in Norwich may be areas of large nutrient reductions. However, just as much of the headwater streams in Blockston are buffered by CREP sites, and in addition, 38% of the 2nd order streams are restored, as well as a small amount of intermittent and 3rd order streams (Fig 4-1 and 4-3). Other than the CREP sites along headwater streams, Norwich does not have much more buffer restoration in the subbasin. In general, Blockston Branch has 15% more streamline buffered by established and restored buffers, and the buffers are distributed along mostly 1st and 2nd order streams throughout the subbasin.

The more extensive riparian buffer network in Blockston may be the cause of the nutrient differences among the two subbasins. There is approximately a 12 hour lag time from peak stream height to peak response of all nutrients, except particulate-bound nutrients, in Blockston Branch (Fig 4-4a and 4-5a). CREP sites are evenly distributed throughout the subbasin, including the lower portion of the stream network (Fig 4-1 and 4-3). Riparian buffers may trap much of the nutrients during runoff events, and nutrient sources from unbuffered portions of the upper subbasin may take longer to flow downstream after the rain event. The particulate-bound nutrients that respond immediately to the stream hydrograph may primarily be material from the stream bottom

or banks that is resuspended or eroded during high stormflows. In Norwich there are more unbuffered streams, especially higher order streams further downstream (Fig 4-3), which may be a rapid source of nutrients during runoff events.

Ammonium and all forms of phosphorus tend to reach the highest concentrations during storm events in Blockston and Norwich as compared to baseflow concentrations measured in 2004 (Tables 4-2 and 4-7). These stormflow nutrient concentrations are consistently higher in Norwich, even when the concentrations are volume-weighted to take into consideration the larger subbasin and greater flow from Norwich Creek (Table 4-7). These lower stormflow concentrations of NH_4, PO_4, and total P in Blockston Branch may be another result of the extensive buffered streamline, where more areas in the landscape potentially trap sediments and nutrients. However, slight differences in land use between the two subbasins may also drive the nutrient differences. Norwich has 0.4 km^2 of low-density housing developments that may contribute extra nutrient sources to the creek. CREP sites are implemented on agricultural land and not on developed land, but the housing developments in Norwich are mostly located in established forests which may already buffer their effects from the nearby streams. The two animal feeding operations in each subbasins (Fig 4-1) may also supply an uneven amount of nutrients during storm events depending on the nutrient management at the farms (i.e., manure storage, timing of manure applications, and runoff control practices). This would be difficult to evaluate without access to the Nutrient Management Plans or stream sampling directly downstream of the farms. Even though the effect of these other factors on stormflow nutrients is not fully understood, this research suggests that the lower concentrations of sediment and phosphorus during stormflows in Blockston Branch

compared to Norwich Creek may be a result of the more extensive system of riparian buffers created by the significant addition of CREP sites in Blockston subbasin. In addition to the spring and fall storms measured in Blockston and Norwich during this study, stormflow sampling is currently being conducted through all 4 seasons in 4 subbasins (including Blockston and Norwich) in the Choptank watershed. This ongoing research will continue to investigate the relationships observed in Blockston and Norwich during this study.

Nutrient characteristics during stormflow

Regardless of the effects of CREP sites in Blockston and Norwich, this study has revealed some important characteristics of stormflow from these subbasins and has implications for future research in the Choptank watershed. In general, Norwich has flashier storm hydrographs, which may be a result of more runoff in the watershed versus infiltration into the subsurface groundwater. However, the stream stages did not rise and fall as fast in Blockston Branch and suggests there is more infiltration of rainwater into the soils and less overland flow during storm events. Storm runoff is likely to be lower in nitrate and higher in phosphorus than the baseflow stream concentrations. This may explain why Norwich had higher phosphorus concentrations during the storms and Blockson had higher nitrogen concentrations during baseflow and stormflow (Figs 4-4 and 4-5).

Another difference between the storm responses in the two streams was the immediate nutrient response as stream stage rises in Norwich Creek versus the lag time in nutrient response in Blockston Branch. This may be a result of a greater buffering effect

of riparian vegetation in Blockston subbasin. However, this difference could partly be caused by hydrologic differences in overland flow versus subsurface groundwater flow between the two subbasins. The movement of sediment and particulate-bound nutrients to streams in overland flow was expected, but I also measured high dissolved nutrient concentrations during the storms. Considerable nutrient concentrations have been found in the vadose zone of cropland and riparian buffers. Staver and Brinsfield (1998) measured high nitrate concentrations under the root zone in agricultural fields near the two subbasins sampled in this study. This nitrate may flush into the shallow groundwater during rainwater infiltration and move to the stream quickly in unbuffered areas. High phosphorus concentrations have also been measured in the shallow groundwater in riparian zones (Carlyle and Hill 2001), which may also be a potential source to streams when rainwater infiltration speeds the flux of shallow groundwater into streams, especially in riparian buffers where groundwater moves relatively short distances to the streams.

I also observed large differences in stream responses to rain events between the two seasons of monitoring. The large ammonium concentrations in Norwich Creek during the storm at the end of April 2004 (Fig 4-4b) may be an indication of runoff from agricultural fields with recent fertilizer or manure applications or runoff from the animal feeding operations. This may be a process specific to Norwich, since spring NH_4 concentrations were only elevated 0.01 mg L^{-1} during the stream response in Blockston. In the fall, all forms of phosphorus were higher in concentration than during the spring event. The source of phosphorus may be from the decomposition of plant material remaining on recently harvested fields and leaching of soluble P into overland flow

and/or the shallow groundwater (Staver and Brinsfield 1994). This may occur after the fall harvest on agricultural fields where conservation tillage is practiced and plant residue is left on the field surface. The release of dissolved P from the plant material in the fall may explain the increase in total dissolved P concentrations of 3 to 12 times during the fall storms over the spring storm (Table 4-6). This may be validation at the watershed scale of phosphate leaching from individual fields in the fall measured by Staver and Brinsfield (1994).

Finally, nutrient yield calculations are important to understanding the nutrient export from these agriculturally-dominated subbasins into downstream rivers and estuaries. Unfortunately, intensive discharge monitoring such as the gauge at Greensboro, Maryland maintained by the US Geological Survey is not a widespread practice. Stage data can help predict the stream response during a rain event, but discharge data takes into account the flow based on the morphology of the streambed and the velocity of the water movement. There is currently an effort to monitor the discharge at 15 subbasins in the Choptank watershed, including Blockston and Norwich, and stage data is being collected at each stream. However, a stage-discharge relationship has only been completed in German Branch (Jordan et al. 1997). At the present time, the remaining streams have only one baseflow discharge measurement which was used to estimate discharge at higher flows based on the rating curve at German Branch (Fig 4-7), as described above. Blockston and Norwich may not respond to higher flows in the same way as German Branch, but I used the flow estimates here to make reasonable calculations of nutrient flux. Rating curves for both basins will be available in 2006 and will be used when this chapter is published in the formal scientific literature.

Calculations based on these discharge estimates suggest that nutrient export from Blockston and Norwich is dominated by baseflow nitrogen and stormflow phosphorus; however, nitrogen export is 2.5 times higher from Blockston and phosphorus export is almost 2 times higher from Norwich. The difference in phosphorus yields may be explained by the differences in riparian buffered streamline in the two subbasins as described in this study, but the higher baseflow nitrogen yields and concentrations from Blockston were not expected. The small differences in land use between the basins would not be expected to cause the large nitrogen differences, and the more D class and hydric soils in Blockston suggest this subbasin should have more sites supporting denitrification, which would decrease nitrogen concentrations relative to Norwich (Table 4-1). The same variance in volume-weighted nitrogen concentrations between the subbasins was also observed during previous monitoring in 1985 to 1986 (Norton and Fisher 2000); therefore, this may be a consistent pattern in Blockston and Norwich.

Measuring discharge and nutrient fluxes from streams in the Choptank watershed will help scientists better understand the effect that best management practices, including CREP, may have on water quality downstream in Chesapeake Bay. Characterizing these relationships could also contribute to the adoption of nutrient management practices at the subbasin level. Examples from this study may include (1) encouraging the implementation of cover crops in Blockston subbasin to prevent nitrate from leaching into the groundwater and elevating baseflow concentrations and (2) encouraging the implementation of buffers on 1st and 2nd order streams in Norwich subbasin to decrease sediment and particulate-bound phosphorus in runoff.

Conclusion

Between 1998 and 2004, 20 km of riparian buffers were restored under the Conservation Reserve Enhancement Program (CREP) in Blockston Branch and Norwich Creek basins. This restoration may have affected nutrient fluxes from the agricultural land in these watersheds during runoff events. The subbasin draining into Blockston Branch has 15% more total streamline buffered, and the riparian buffers are more evenly distributed throughout Blockston compared to Norwich. This extensive system of buffers appears to have resulted in lower phosphorus yields from Blockston and may represent a success of buffer restoration through CREP. However, the unexpectedly high N yields of Blockston indicate that better N controls are needed in this basin.

This research suggests that the distribution of CREP sites may also be important, in addition to the total buffer area and streamlength buffered. Long, continuous restored buffers along streamlines throughout the subbasin may be more effective in reducing nutrient runoff than taking entire farm fields out of production. The CREP is a voluntary program on private lands, and specific land can not easily be targeted for buffer restoration. However, managers may take information such as this and encourage farmers to restore more continuous buffers along streams and ditches. This may be particularly important for trapping sediment in runoff and reducing the flux of particulate-bound nutrients, ammonium, and phosphorus which tend to move rapidly downstream during stormflows.

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Chapter 5

TWENTY YEARS OF NUTRIENT MANAGEMENT AND WATER QUALITY
MONITORING IN AN AGRICULTURAL WATERSHED

Abstract

One of the strategies to improve Chesapeake Bay's degraded biological health focuses on

reducing losses of sediments and nutrients from agricultural areas. At the plot scale, a

series of studies suggested that Best Management Practices (BMPs) reduce nutrients and

sediment losses, and managers have been supporting farmers to use a variety of BMPs

throughout the bay's watershed. In particular, German Branch, also known as Jarmin

Branch, is a site in the bay watershed that had BMPs on all farms in the early 1990s,

including Nutrient Management Plans, conservation tillage, riparian buffers, and cover

crops; stream water quality was monitored before, during, and after implementation. In

the 1990s, managers estimated that the sediment and erosion control BMPs reduced soil

erosion in the watershed by 33%. In fact, at the watershed level there was a 33%

decrease in total phosphorus concentrations in baseflow of the stream after BMP

implementation, from an average of 0.13 mg L^{-1} in the 1990s to 0.090 mg L^{-1} during the

2003 to 2005 sampling, but there was insufficient data to evaluate stormflow conditions.

There were no significant changes in nitrate or total nitrogen concentrations from the

1990s to current sampling; however, the significant rate of increase at approximately 0.14

mg N L^{-1} yr^{-1} from 1986 to the 1990s did not continue to present day baseflow

conditions. The results suggest that BMPs may have suppressed the rate of increase in

nitrogen which was observed earlier in German Branch and documented in other

agriculturally dominated watersheds in this region. A nutrient budget for German Branch

revealed that only 50% of the nitrogen input and 10% of the phosphorus input was exported from the watershed in crop harvest and streamflow between 1991 and 1995. This suggests that in addition to phosphorus retention by sediment control practices during this time period, German Branch is inherently efficient at retaining nutrients within the watershed. Increases in fertilizer applications due to double-cropping and natural processes such as denitrification and in-stream processing at the watershed scale may obscure nitrogen reductions made by BMPs. While these results are somewhat encouraging, future research on water quality effects of BMPs must be long-term and focus on ecological interactions at the watershed scale in areas dominated by agriculture.

Introduction

Nutrient enrichment of coastal ecosystems is a global phenomenon. The amount of nutrients in coastal rivers are increased by dense human populations and agriculture associated with supporting these populations (Peirls 1991, Jordan and Weller 1996, Vitousek et al. 1997, Beman et al. 2005). Nutrient enrichment and eutrophication, an increase in the rate of supply of organic matter (Nixon 1995), have received much attention in Chesapeake Bay due to the resulting extensive algal blooms, oxygen depletion in bottom waters, increased turbidity, loss of submerged aquatic vegetation, and loss of habitat (Carpenter et al. 1969, Orth and Moore 1983, Officer et al. 1984, Seliger et al. 1985, Fisher et al. 1988). Concerns for the bay's biological health and protection of the productive natural resources led to the formation of the Chesapeake Bay Program and its current large-scale restoration effort (CBP 2000).

Chesapeake Bay is the largest estuary in the United States, and its 167 000 km^2 watershed is home to nearly 16 million people (Fig 5-1). This shallow aquatic system is weakly flushed by tides and has a ratio of watershed area to water volume which is on average 5 times larger than other coastal water bodies; therefore, water quality in Chesapeake Bay is particularly susceptible to intensive land uses which leak nitrogen and phosphorus into waterways (Horton 2003). Agriculture covers 30% of the watershed and is the dominant source of nitrogen (N) and phosphorus (P) to the bay (www.chesapeakebay.net). The Chesapeake Bay Program considers reducing N and P loads to be the most critical element in improving water quality and restoration of natural resources, and substantial reduction goals were described in the Chesapeake Bay Agreement 2000. Because of the importance of agriculture as a source of nutrients, much of the resulting management strategies have focused on reducing agricultural nutrient losses.

The bay management community has embraced many different Best Management Practices (BMPs) as tools to reduce agricultural nutrient loads. In this paper, I will focus on some BMPs determined in a recent analysis of nutrient reduction strategies for the bay to be the most cost effective and widely applicable for the Chesapeake Bay region (CBC 2004). These practices include, but are not limited to: conservation tillage, riparian buffers, cover crops, and the Nutrient Management Plans that include practices to prevent fertilizer loss from agricultural fields. Many farmers in the Chesapeake Bay region are now required to file Nutrient Management Plans with local Maryland Department of Agriculture (MDA) offices. The plans involve managing the amount, timing, and placement of fertilizer to minimize nutrient loss to surface and groundwater while
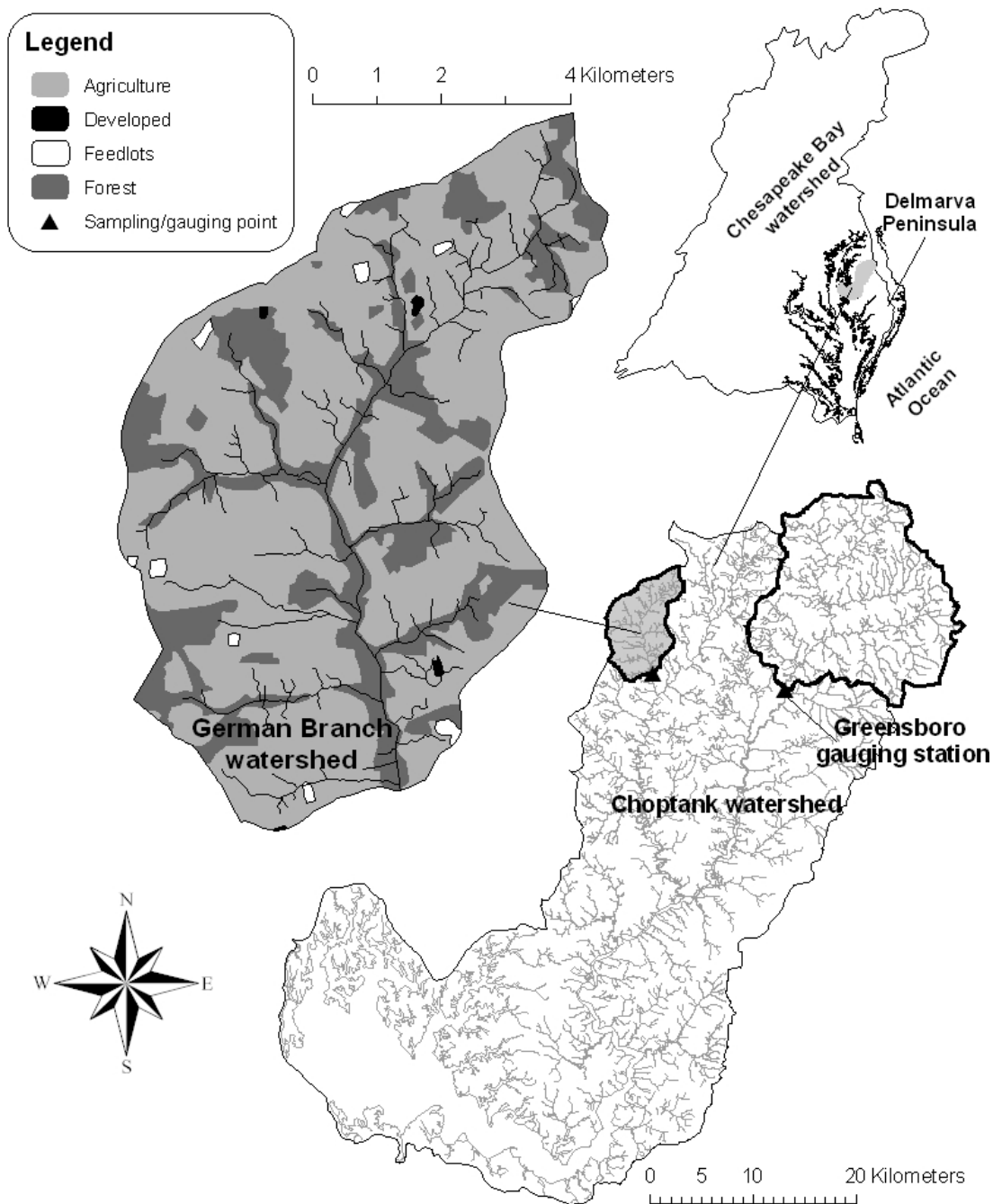
Figure 5-1. Schematic of Chesapeake Bay watershed in the Mid-Atlantic region of the
United States and location of the Choptank River. Located in the Choptank watershed is
the study site, German Branch, and the US Geological Survey gauging station
(#01491000) at Greensboro, Maryland. The enlarged version of German Branch shows
the sampling site for all monitoring periods and land use in the watershed, including
agriculture, low-density development, animal feeding operations, and forests.

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maintaining desired crop yields. Throughout the watershed most farmers also use

conservation tillage, which is a broad range of soil tillage practices that leave at least 30

percent of soil surface covered with plant residue after planting to reduce erosion and

increase soil organic matter. Continuous no-till, in which crop residue is maintained on

the soil surface year round, is the most common in Chesapeake Bay (CBC 2004). On

many farms, land is under production up to the edge of streams and ditches. However,

farmers and managers are restoring streamside, or riparian, grass and forest buffers to

create shade and lower stream water temperature, provide large woody debris essential

for healthy aquatic habitats, intercept nutrients and sediment in overland flow and

subsurface groundwater, and provide wildlife habitat. Finally, instead of fertilizing and

harvesting winter grain crops, USDA local offices have programs encouraging farmers to

plant an unfertilized cover crop and till it into the soil in the spring. One of the goals is to

prevent residual nitrate from leaching into the groundwater in the winter during

groundwater recharge (Staver and Brinsfield 1998). More detailed BMP information can

be found at the NRCS Technical References web page:

http://www.nrcs.usda.gov/technical.

Scientists in the bay region have evaluated the effects of several conservation

practices on stream and groundwater quality at field-plot scales. Among these are

conservation tillage (Staver and Brinsfield 1994, Butler and Coale 2005), grass and forest

riparian buffers (Phillips et al. 1993, Jordan et al. 1997, Lowrance et al. 1997), and cover

crops (Clark et al. 1997, Staver and Brinsfield 1998). These practices have been shown

to reduce losses of agricultural nutrients at the field or plot scale, and are currently being

implemented throughout the bay watershed at varying levels. Because implementation of

some BMPs has occurred at relatively low rates, the management community proposes to increase application of the practices in the future (CBC 2004). For example, the Chesapeake Bay Program's goal for restoring 3230 km (2010 miles) of riparian buffers by the year 2010 was met by 1996, and their current goal is now 16 100 km. Scientists and local stakeholders are also involved in long term programs monitoring water quality which track the successes and failures in meeting nutrient reduction goals. These monitoring programs in streams and the estuary include: Maryland Department of Natural Resources [MD DNR] Stream Corridor Assessment Survey (http://www.dnr.state.md.us/streams/stream_corridor.html), Creekwatchers (http://www.talbotrivers.org/creekwatchers.html), and MD DNR Chesapeake Bay Monitoring Program (http://www.dnr.state.md.us/bay/monitoring/water/index.html).

In 1989, German Branch (also referred to as Jarmin Branch) was selected by the State of Maryland as an agricultural watershed to initiate BMPs on all farms and monitor the resulting stream water quality as part of a Targeted Watershed Project. Previous monitoring in this watershed indicated relatively high nutrient loads compared to other subbasins in the upper Choptank watershed on the Delmarva Peninsula and was therefore targeted for large-scale restoration (Primrose et al. 1997). Due to the scale and complexity of activities during this project, MD DNR and many other federal, state, and local agencies worked together in order to manage the restoration and monitoring program and to assist farmers in BMP implementation. The goal of the Targeted Watershed Project was to implement nutrient management and BMPs throughout the entire watershed and monitor the effect on nutrient loading to German Branch. Managers hoped this assessment of BMPs at a large scale would support widespread use of these

practices in other agriculturally dominated watersheds and help achieve the nutrient reduction goals stated in Chesapeake Bay Agreement 2000.

In this paper I discuss water quality in German Branch watershed over the last two decades in relation to implementation of BMPs throughout this time period. Because German Branch has a rich monitoring history and has been the focus of intensive BMP implementation through the Targeted Watershed Project, it is an ideal case study to evaluate the effects of watershed management. Below I show that BMP implementation in German Branch watershed was effective at reducing P but not N concentrations in baseflow of this non-tidal stream. Insufficient data were available to assess N and P concentrations in stormflow.

Methods

Study site

German Branch is a third order stream located in the Choptank River watershed on the Delmarva Peninsula (Fig 5-1). Two associations of soil groups dominate cropland in this coastal plain region: well drained Sassafras-Woodstown soils and poorly drained Elkton-Othello soils. Soil classes C and D with slow infiltration rates dominate the watershed (A = 0.6%, B = 33.0%, C = 13.3%, D = 53.1%) and a large proportion (45.2%) is hydric (Norton and Fisher 2000). Lee et al. (2001) have shown that the low oxygen conditions in hydric soils result in low transfer of groundwater nitrate to baseflow of streams, presumably due to denitrification.

With a total watershed area of 52 km^2 and a human population in year 2000 of approximately 680, land use in German Branch watershed is 72% agriculture, 27% forest,

and 1% low-density development and animal feeding operations. Almost 50% of the streams have riparian forests that have regrown since channelization in the 1930s and 1940s (Primrose et al. 1997). Of the agricultural land, intensive row crops of grains, soybeans, and corn predominate. Much of the row crops on Delmarva, including those of German Branch, support the large poultry industry centered in the lower region of the peninsula (Staver and Brinsfield 2001).

Monitoring

Many investigators were involved in measuring water quality in German Branch during three time periods of the past twenty years (1985-1986, 1991-1995, 2003-2005). Data collected during these three time periods were obtained using somewhat different approaches, and below I characterize the methods of each time period in order to provide information that enables us to separate the effects of different methods from true temporal changes.

In 1985 to 1986 Norton and Fisher (2000) obtained grab samples from German Branch 5-6 times per month for 15 months, largely under baseflow conditions. Temperature and electrical conductivity were measured in the field with portable meters, and samples were kept cold until nutrient analyses, usually within a few days. In the lab, unfiltered samples were autoclaved with the persulfate reagents of Valderama (1981) and subsequently analyzed for dissolved phosphate (PO_4) and nitrate (NO_3) in a Technicon AutoAnalyzer II to determine Total P (TP) and Total N (TN). Aliquots of the original samples were also filtered with GFF filters for automated colorimetric analysis of NO_3 in a Technicon AutoAnalyzer II.

During the Targeted Watershed Project of 1991 through 1995, Jordan et al. (1997) collected weekly composited samples. Automated samplers continuously monitored stream flow and pumped a fixed volume of sample from the stream after a specified volume of flow had passed (i.e., samples were pumped more frequently at higher flow rates). Samples were composited in a single sample bottle on a weekly basis and include both base and storm flows. Jordan et al. (1997) describe the flow-weighting method in more detail. Sample bottles initially contained sulfuric acid as a preservative and were collected ~monthly for nutrient analyses. Jordan et al. (1997) used perchloric acid digestion and colorimetric analysis of PO_4 to measure TP. Total N was measured by Kjeldahl N digestion followed by Nesslerization of the NH_4 in the digestate, and NO_3 was reduced to nitrite and measured by colormetric analysis with sulfanilamide (see Jordan et al. 1997 for details). Previous comparisons of TN measured using Kjeldahl N digestion + nitrate (US Geological Survey, USGS) and TN measured using persulfate digestion (Fisher et al. 1998) revealed similar TN concentrations using these different methods. Samples from Greensboro, MD, a USGS gauging station (#01491000), taken on the same day by USGS and Fisher et al. (1998) resulted in TN values with differences <10%.

From January 2003 through December 2004, I collected monthly baseflow grab samples from German Branch, and continuation of sampling in 2005 is currently being carried out as part of a project in the Choptank watershed with the US Department of Agriculture Environmental Quality Lab (USDA EQL). These samples were largely processed as described above for 1985 to 1986. Samples were exclusively collected at baseflow, when there had been no rain for 3 days. In the lab, TN, TP, and NO_{3+2} were

processed as described above. On average, nitrite (NO_2) was 80% of the NO_{3+2}, and I

present the analysis of NO_{3+2} as solely nitrate (NO_3).The two analytical services labs

involved in water chemistry analyses between 1985 and 2005 (HPL, SERC, and USDA

EQL) follow strict QA/QC procedures and have repeatedly analyzed split samples to

correct interlab bias.

Statistics

Statistical tests were performed using SigmaPlot v9 with SigmaStat v3.2

integration. The symbols *, **, and *** indicate statistical significance at the $p < 0.05$,

0.01, and 0.001 probability levels, respectively; "NS" is used for $p > 0.05$.

Results

Over the past two decades, German Branch has undergone many changes in

nutrient management practices (Table 5-1). Before the Targeted Watershed Project,

conservation tillage was the only BMP implemented at a wide scale, applied on

approximately 50% of the cropland in the watershed (Mark Waggoner pers. com.).

During the Targeted Watershed Project between 1990 and 1995, various federal and state

agencies supported implementation of several BMPs for all of the farms in the watershed.

There were Soil Conservation and Water Quality Plans on 99% of the watershed (Table

5-1), and the plans contained various combinations of the following BMPs: conservation

crop rotation, grassed and lined waterways, roof runoff management, grade stabilization

structures, various animal waste management practices, and pest management (USDA

1996). Most of the conservation efforts focused on soil erosion and include the following

BMPs implemented within the entire watershed from 1991 through 1995: a total of 8

Table 5-1. Best management practices in German Branch watershed during three water quality monitoring periods.

Year	Soil Conservation and Water Quality Plans/ Nutrient Management Plans % watershed	Conservation Tillage % agricultural land	Riparian Buffers % streamlength buffered	Cover Crops % agricultural land	Source
1985-1989	25 †	50	62	0	M. Waggoner pers. com.
1990-1995	99	65	62	4.2	USDA 1996
1996-2005	100	60-90 ‡	72 §	2 ¶	various, see notes

Notes:
† USDA 1996
‡ estimate from Natural Resources Conservation Service 1999
§ USDA Environmental Quality Lab data 2005
¶ MD DNR data 2005

stabilization structures (installed where structures were needed for stabilizing the grade

and preventing gullies and erosion), 1.4 hectares of grassed waterways (perennial grasses

established in concentrated runoff areas), and 378 meters of lined waterways (concrete or

riprap waterway where a grass waterway is not sufficient or can not be established)

(USDA 1996). Managers estimated that these erosion control practices prevented the

loss of 1.4×10^7 kg of soil in German Branch during the Targeted Watershed Project

(USDA 1996). All farms had a Nutrient Management Plan included in the more

substantial Soil Conservation and Water Quality Plan. Also included were two other

BMPs that I discuss in this paper: conservation tillage and winter cover crops. Farmers

used conservation tillage on the majority of agricultural land (65%); however, cover

crops were implemented only on small portions of the watershed (4% of agricultural land,

Table 5-1).

After 1995, all farms in the basin have continued to file Nutrient Management

Plans, and in 1998 a new program began funding the restoration of grass and forest

buffers, the Conseration Reserve Enhancement Program (CREP). This program has

supported farmers to restore 102 hectares and 175 km of streamlines with riparian buffers

(each km of stream has 2 km of streamlines or edges), bringing the total streamlines

buffered in the watershed to 72% (including established forest buffers, Table 5-1). The

cover crop program has not been well funded, and this is reflected by the decrease of

cover crops planted in the 1990s during the Targeted Watershed Project from 155

hectares to 85 hectares during the 2004 to 2005 winter season (2% of agricultural land,

Table 5-1). New funding (i.e., Chesapeake Bay Recovery Act of 2005) may support

more cover crops in German Branch in the future.

The goal of this study was to measure the effect of the implementation of these

BMPs on water quality in German Branch over the last 20 years. I assembled the three

monitoring data sets described above, but sampling techniques differed among the

projects, particularly with regard to stream flow. Therefore, I needed to transform the

data to enable comparisons between monitoring periods. Nutrient concentrations are

often influenced by variations in stream flow, and this was accounted for in comparisons

between years with varying rainfall. German Branch is not a continuously gauged

stream, but flow was measured during the Targeted Watershed Project. To expand the

flow data to other years, I compared monthly discharge measured by Jordan et al. (1997)

from 1991 to 1995 in German Branch to monthly discharge at Greensboro, MD, a USGS

station gauging station (#01491000) in the Choptank watershed that has been monitored

continuously for flow since 1948 (Fig 5-1).   Although the magnitude of flow at

Greensboro was about five times larger than German Branch due to differences in basin

size (293 vs. 52 km^2, respectively), there was a strong relationship between monthly

water yields (flow normalized to basin area) measured by Jordan et al. (1997) at German

Branch and monthly water yields at Greensboro measured by USGS (Fig 5-2,

r^2=0.84***). The slope of the line is not significantly different from 1, and the intercept

is not significantly different from 0. Without adjusting for watershed area, the slope of
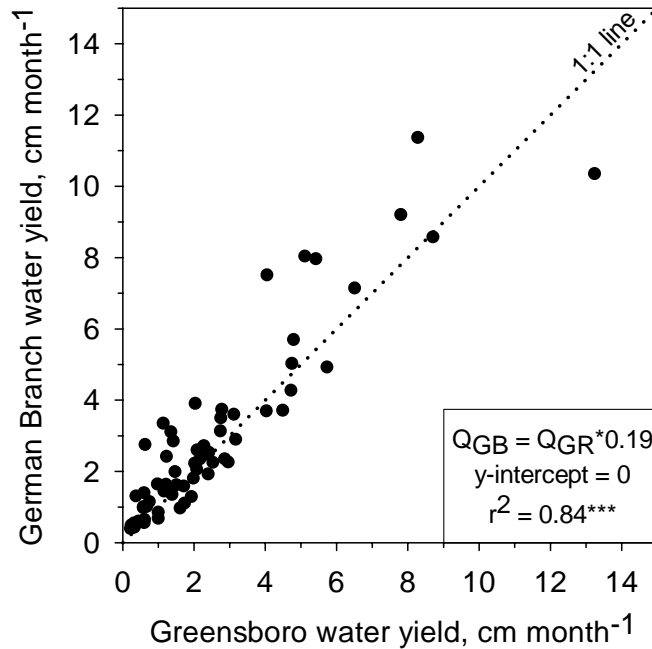
Figure 5-2. Monthly stream water yield from 1991 to 1995 in German Branch and Greensboro. The y intercept was not significantly different from zero and was forced through zero for the resulting 1:1 relationship (r^2=0.84*). This allows the development of an equation to predict German Branch discharge: $Q_{GB} = Q_{GR}$*0.19 (eq. 5-1), where Q_{GB} is monthly discharge in German Branch and Q_{GR} is monthly discharge at Greensboro.

German Branch discharge versus Greensboro discharge was 0.19, indicating that German Branch discharge is 19% of Greensboro discharge. I used the resulting relationship between the two subbasins, in which German Branch monthly discharge (Q_{GB}) is approximately one fifth of Greensboro monthly discharge (Q_{GR}), to estimate monthly German Branch discharge for 1986 and 2003 to 2005 using the Greensboro record from those time periods:

$$Q_{GB} = Q_{GR} \times 0.19 \qquad \text{(eq. 5-1)}$$

where Q_{GB} is the monthly discharge for German Branch and Q_{GR} is the discharge for Greensboro (m^3 month^{-1}).

I then calculated annual volume-weighted mean concentrations and standard errors for German Branch. The monthly averaged nutrient concentrations reported in the three studies described above and the estimated monthly discharges (Fig 5-2) were used in the following formulas:

$$C_{vw} = \frac{\sum_{i=1}^{n} C_i * Q_i}{\sum_{i=1}^{n} Q_i} \qquad \text{(eq. 5-2)}$$

$$SE_{vw} = \frac{\sqrt{\sum_{i=1}^{n} (C_i - C_{vw})^2 \Big/ (n-1)}}{\sqrt{n}} \qquad \text{(eq. 5-3)}$$

where C_{vw} = annual volume-weighted mean concentration, C_i = average monthly nutrient concentration in month i, Q_i = monthly discharge in month i, i = month, SE_{vw} = volume-weighted standard error, and n = sample size (number of months). Comparison of the annual average concentrations and the annual volume-weighted concentrations suggests that differences in general were small, <20%, even though the range of annual rainfall between years was 67 to 151 cm (Table 5-2). Annual volume-weighted concentrations appear in the remainder of Results and Discussion.

Table 5-2. Annual average concentrations of three nutrients in baseflow at German Branch. Standard errors (s.e.) are monthly fluctuations from annual means. Annual volume-weighted concentrations are adjusted for variations in discharge as described by eq. 1. Rainfall is an average of data from three surrounding stations: Royal Oak MD, Horn Point Lab in Cambridge MD, and Dover DE, except 2003 to 2005 which only from Horn Point.

Year	Rainfall cm	Annual average concentration, mg L^{-1}						Annual volume-weighted concentration, mg L^{-1}					
		[NO$_3$-N]	s.e.	[TN]	s.e.	[TP]	s.e.	[NO$_3$-N]	s.e.	[TN]	s.e.	[TP]	s.e.
1986	97	3.4	0.6	4.4	0.2	0.14	0.03	3.1	0.2	3.9	0.4	0.07	0.05
1991	120	3.5	0.1	4.4	0.1	0.20	0.02	3.5	0.1	4.4	0.1	0.20	0.02
1992	81	4.1	0.1	5.1	0.1	0.24	0.02	3.8	0.2	4.7	0.3	0.20	0.05
1993	67	4.2	0.2	5.0	0.2	0.20	0.02	3.5	0.3	4.5	0.3	0.19	0.05
1994	72	3.9	0.1	4.7	0.1	0.19	0.02	3.7	0.2	4.5	0.3	0.18	0.05
1995	85	4.3	0.2	5.2	0.2	0.20	0.02	3.9	0.4	4.7	0.4	0.17	0.04
2003	151	3.6	0.3	5.4	0.3	0.12	0.02	3.4	0.3	4.7	0.4	0.12	0.02
2004	112	4.4	0.4	5.7	0.4	0.08	0.01	3.7	0.4	5.9	0.3	0.06	0.02
2005 †	50	4.1	0.3	4.5	0.7	0.09	0.02	4.3	0.3	4.4	0.7	0.08	0.02

Notes:

† Monitoring year 2005 is only 6 months of data: January through June

In addition to annual rainfall and discharge variations, comparison of nutrient concentrations between the three monitoring periods is also affected by sampling during baseflow or stormflow conditions. The weekly, flow composited data collected from 1991 to 1995 by Jordan et al. (1997) includes analysis of stream water during rain events, whereas baseflow data collected in 1986 and 2003 to 2005 does not. In agriculturally dominated watersheds, N concentrations are inversely correlated and P concentrations are positively correlated with discharge during rain events (e.g., Fisher et al. 1998, Fisher et al. in press).   Nitrogen concentrations are highest during baseflow when stream flow is mostly supplied by groundwater enriched with agricultural nitrate. During a rain event, the fraction of stream flow supplied by groundwater is diluted as low N overland flow contributes to the total flow. In contrast, a large fraction of P is particle-bound and supplied to streams as particulate P in overland flow during rain events. In a nearby Choptank watershed dominated by agriculture, both total P and total N increased as the stream responded to a 3 cm rain event (Fig 5-3). As stream stage increased in response to a rain event on 28 to 29 September 2004, total P concentration (r^2=0.70) and total N concentration (r^2=0.35) increased. This behavior of N and P demonstrates changes in stream chemistry between baseflow and stormflow and highlights the importance of comparing data only between periods of similar sampling regimes. The data of Jordan et al. (1997) composited at weekly intervals includes these effects, but do not enable ready separation of stormflow effects on concentrations.

I separated the weekly baseflow and stormflow measurements in the 1991 to 1995 data of Jordan et al. (1997) using their reported discharge data (Fig 5-4). Weekly discharge varied during the five year monitoring period from $3.4x10^4$ m^3 to a maximum
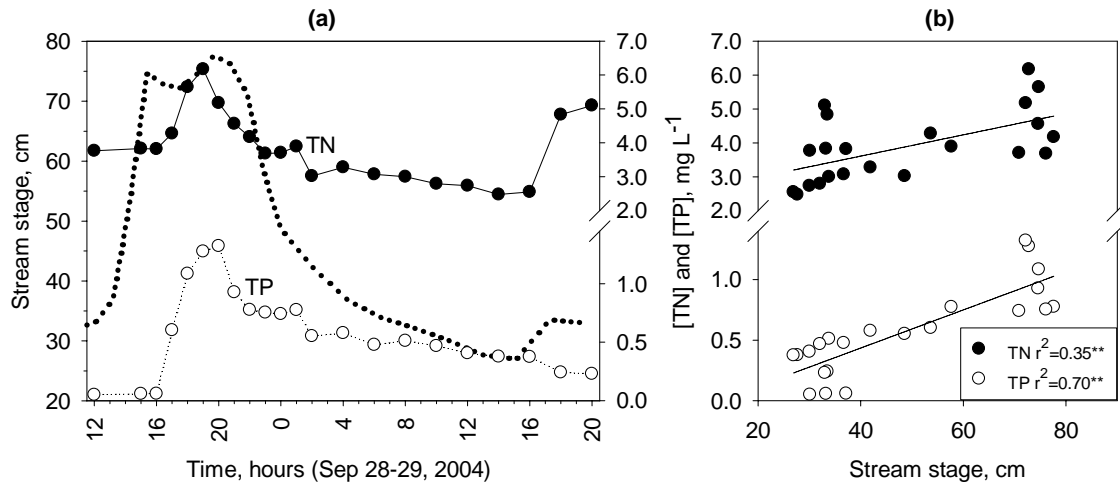
Figure 5-3. Stream stage and nutrient concentrations in Blockston Branch in the Choptank watershed during a rain event in September 2004 (rainfall = bars; stage = dotted line; [TN] = closed circles; [TP] = open circles). Panel (a) shows stream and nutrient response over time and (b) shows the relationship between stream stage and total N and total P concentrations. Rainfall was measured every 30 minutes by the Horn Point Laboratory weather station, and stream stage was measured every 30 minutes using a Solnist pressure gauge attached to the stream bottom. An ISCO automated sampler collected stream water every hour as stream height increased to peak discharge and through the next 24 hours as stream stage declined. Nutrient analyses were the same as baseflow sampling in 2003 to 2005 (see Methods). Blockston Branch is close in geographical location to German Branch, has a smaller watershed (17 km^2), but similar land use (71% agriculture, 28% forest, and 1% low-density development and animal feeding operations).

of 2.9×10^6 m^3 (Fig 5-4). The equation

$$y = y_o + a\sin(\frac{2\pi x}{b} + c) \qquad\qquad\qquad\qquad \text{(eq. 5-4)}$$

where x is the monitoring date, y is the weekly flow, and y_o is the weekly flow at the

initial starting date in July 1990, represents the annual baseflow fluctuations and was fit

to the lower discharge data in each month with $r^2 = 0.52$***. This annual sinusoidal

pattern in baseflow is the result from the seasonal variations in groundwater levels.

Although long-term average rainfall is relatively constant throughout the year in the Mid-

Atlantic region, there are large seasonal variations in evapotranspiration caused by
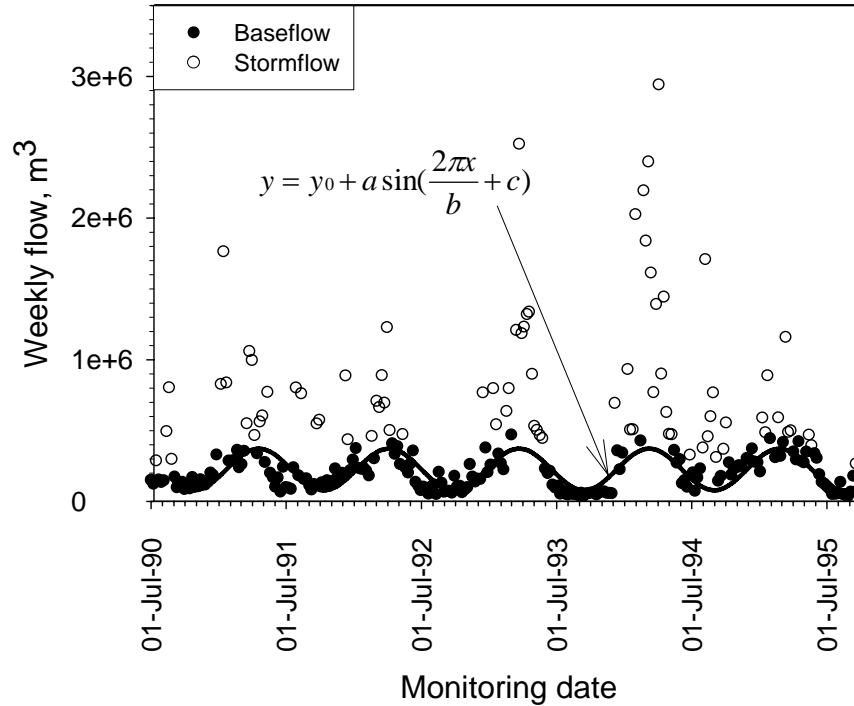
Figure 5-4. Weekly streamflow in German Branch during the Targeted Watershed Project from July 1990 to July 1995. The equation $y = y_{\circ} + a\sin(\dfrac{2\pi x}{b} + c)$ represents the annual baseflow fluctuations and was fit to the baseflow data with $r^2 = 0.52^{***}$, where y is the weekly streamflow, x is the monitoring date, $y_0=2.2\times10^5$, $a=1.5\times10^5$, $b=3.7\times10^2$, and c=-6.3. Baseflow data ($\pm1\times10^5$ m^3 of predicted weekly baseflow based on sinusoidal equation) are represented by closed circles and stormflow data ($>1\times10^5$ m^3 predicted weekly baseflow based on sinusoidal equation) are open circles.

temperature and vegetative growth. This results in low groundwater and baseflow at the

end of summer, and high groundwater, baseflow, and stormflow at the end of winter,

compounded by random variations in rainfall due to weather patterns. Most groundwater

recharge occurs in late fall through spring. High evapotranspiration rates in summer limit

groundwater recharge, but low temperatures and plant harvest or estivation result in high

infiltration in fall through spring (Staver 2001). Weekly composited samples of Jordan et

al. (1997) were classified as baseflow if the discharge was within 1×10^5 m^3 from the

predicted sinusoidal line (Fig 5-4). Using these well-described hydrologic patterns,

weekly discharges greater than this departure from the predicted value were assumed to be influenced by rain events during those weeks.

This weekly classification of base and storm flows in Fig 5-4 was used to estimate volume-weighted nutrient concentrations. Average total N concentration over the five-year monitoring period was 5.1 mg L^{-1} in baseflow and 4.3 mg L^{-1} in stormflow, and average total P concentration was 0.13 mg L^{-1} in baseflow and 0.28 mg L^{-1} in stormflow. Because of these differences between N and P concentrations and the large range in weekly flows from a low of 3.4×10^4 m^3 during baseflow and 2.9×10^6 m^3 during the largest stormflow (Fig 5-4), I included only baseflow nutrient concentrations from the 1991 to 1995 for comparison to baseflow sampling during the other monitoring periods. Insufficient stormflow data are available to test for interannual changes in concentrations during 1986 to 2005.

The annual volume-weighted nutrient concentrations revealed significant interannual trends in baseflow over the last two decades in German Branch. Nitrate and total N increased from 1986 to 1995 by 0.15 and 0.13 mg N L^{-1} yr^{-1}, respectively (r^2=0.76* for both, Fig 5-5, Table 5-3). This increasing trend did not continue through 2005, suggesting N concentrations are not changing or have stabilized after peak concentrations in the 1990s. The increasing trend in N observed earlier in German Branch has also been observed in the longer water quality records at Greensboro, the USGS gauging station in the Choptank watershed (Fig 5-1). Greensboro is a larger watershed (293 km^2) with less agriculture (49%) than German Branch, and NO$_3$ concentrations are lower but were increasing at a rate of 0.01 mg NO$_3$-N L^{-1} yr^{-1} from 1964 to 2003 ($r^2 = 0.35$***, Fig 5-6). This increasing trend in N observed continuously

through four decades at Greensboro and from 1986 through 1995 in German Branch

contrasts with the current monitoring data (2003 to 2005) at German Branch, which

shows no significant changes after the 1990s.
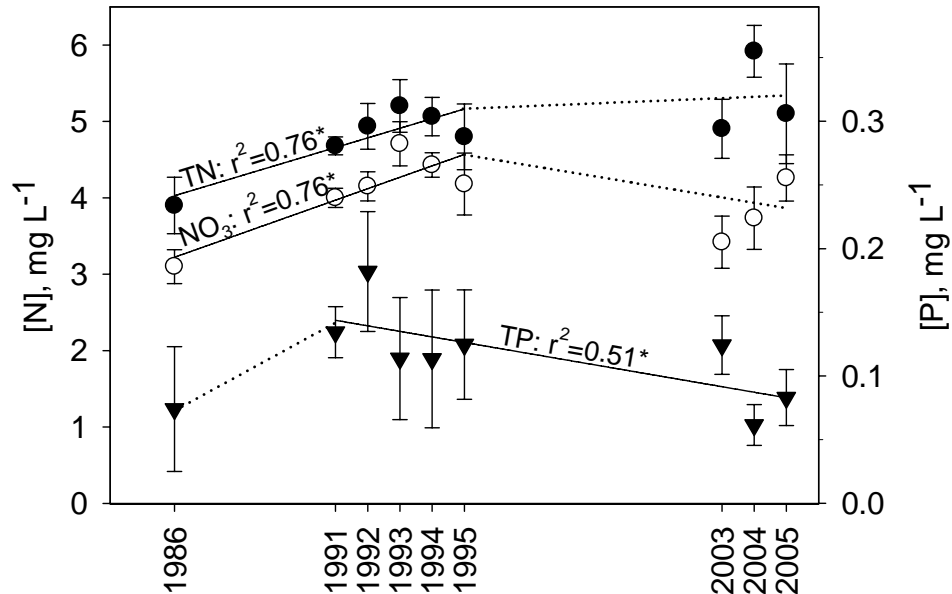
Figure 5-5. Annual volume-weighted nitrogen and phosphorus concentrations in German Branch during monitoring years ([TN] = closed circles; [NO$_3$] = open circles; [TP] = triangles). Solid lines are significant linear regressions; the slope of the dotted lines are not significant.

Table 5-3. Rate of change of annual volume-weighted nutrient concentrations in German Branch during the monitoring periods over 20 years. If symbol representing level of significance (*) is missing, rate of change is not significant.

Sampling periods	Rate of change, mg L^{-1} yr^{-1}		
	TN	NO$_3$-N	TP
1986 to 1990s	0.13*	0.15*	0.005
1990s to 2000s	0.03	-0.04	-0.004*

In contrast to N concentrations, total P concentrations significantly decreased after the Targeted Watershed Project in the 1990s (Fig 5-5). After an average of 0.134 mg TP L^{-1} during 1991 to 1995, I measured an average of 0.090 mg L^{-1} during 2003 to 2005, a decreasing trend of 0.004 mg P L^{-1} yr^{-1} ($r^2 = 0.51*$, Fig 5-5, Table 5-3). This trend again contrasts with nearby Greensboro basin where total P has increased by 0.001 mg P L^{-1} yr^{-1} from 1970 to 2003 ($r^2 = 0.14*$, Fig 5-6). Both the significant decrease in P observed at German Branch and the lack of change in N (Fig 5-5) may be viewed as a result of the BMPs implemented during the Targeted Watershed Project.
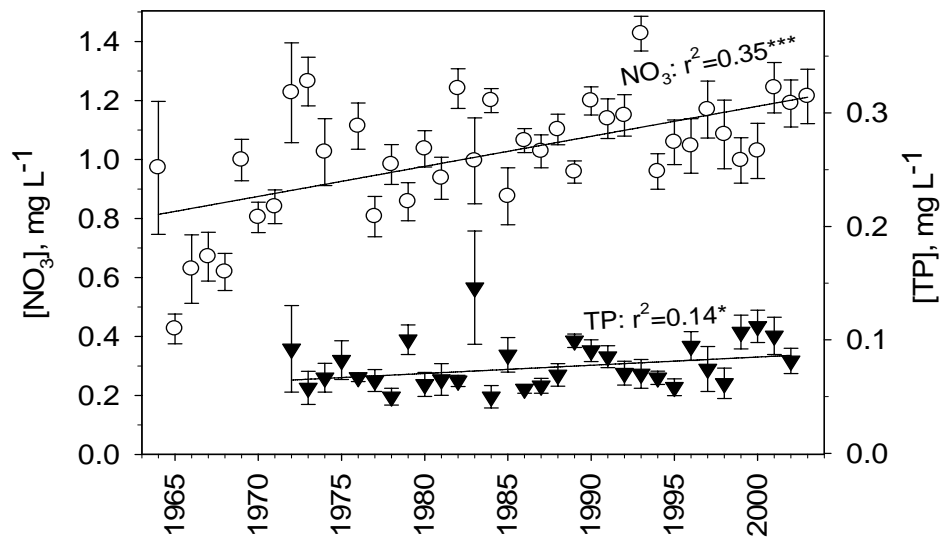
Figure 5-6. Annual volume-weighted nitrate and total phosphorus concentrations in the Choptank River at Greensboro from 1964 to 2003 ([NO_3-N] = open circles; [TP] = triangles). (Data sources: USGS, Fisher et al. 1998)

Discussion

Comparing long-term monitoring data collected under differing sampling regimes (described above in Methods) usually requires some data manipulation. Such comparisons are more complicated but unavoidable when long-term monitoring is

difficult for one university or agency to sustain. Although sampling techniques differed

between monitoring regimes, I am confident in the resulting N and P trends in baseflow

at German Branch. Seasonal and annual rainfall variability can create small

discrepancies in comparisons of annual average nutrient concentrations (Table 5-2).

Volume-weighting the monthly data takes discharge variability into account and allows

us to compare nutrient data between monitoring years. The P trend however, is more

susceptible to the different sampling techniques due to the higher P concentrations during

rain events (Fig 5-3). Since baseflow grab samples were collected in 1986, 2003, and

2004, I excluded the composited samples of Jordan et al. (1997) from the trend analysis if

collected during weeks of high flow in 1991 to 1995 (Fig 5-4). This removes data from

large rain events which are likely to contribute high P concentrations in rainwater runoff

to the weekly composited samples. Yet smaller storms may have occurred during weeks

of low flow and may be included in the comparison with 1986 and 2003 to 2005 data,

which do not include any storm events. It is possible that the potential inclusion of

smaller storm events in the 1990s data of Jordan et al. (1997) contributes to the

decreasing trend observed between the 1990s and 2003 to 2005 sampling (Fig 5-4);

however, I have attempted to exclude this as much as possible. Note that I have focused

only on trends in baseflow conditions; there are insufficient data available to estimate the

impacts of BMPs on storm flows. However, baseflow typically represents 71% of total

annual stormflow on Delmarva (Lee et al. 2000). Focusing on baseflow measurements

also ignores most of the particulate-bound P that dominates P transport through the

watershed and is not the ideal approach to monitoring P loads to the stream. Current

efforts to evaluate the P loads in German Branch during storm events will help in comparisons with the 1991 to 1995 data.

Even after considering the sampling differences between monitoring periods, the extensive erosion and sediment control BMPs implemented in German Branch from 1991 to 1995 may explain the decreasing trend in P concentration. The Targeted Watershed Project estimated that the sediment BMPs reduced soil erosion in the watershed by 33% (USDA 1996), and the analysis of the P data in Fig 5-5 in fact, shows a 33% reduction in stream P concentrations, from 0.134 mg L^{-1} in the 1990s to 0.090 mg L^{-1} during the current monitoring period at a rate of change of -0.004 mg L^{-1} yr^{-1} (Table 5-3). This suggests that the soil erosion BMPs may be responsible for the decrease. Although there is a possibility that sampling differences between the two time periods may be driving some of that reduction, reductions have not been observed at the USGS gauging station at Greensboro where extensive BMPs have not been implemented and total P has increased at a rate of 0.001 mg P L^{-1} yr^{-1} since 1970 (Fig 5-6).

In addition to erosion control practices, organic nutrient sources applied to cropland in the watershed also changed during the monitoring period. According to Primrose et al. (1997), sewage sludge was introduced in German Branch as an organic nutrient source to cropland in the 1980s and peaked in 1990 at applications on 12% of the cropland. Poultry manure also increased during this time period from 4% of the P imported into the watershed in 1986 to 13% in 1995 (Primrose et al. 1997). These agricultural and management actions may explain the increase in stream P concentrations between 1986 and the 1990s, and the implementation of erosion and sediment control BMPs may have contributed to the reduction in stream concentrations by 2003 to 2005.

Unlike nitrogen, phosphorus concentrations in streams are likely to respond faster to BMP implementation since a large fraction of P is particulate-bound and supplied to the stream by overland flow events.   Furthermore, extensive use of no-till agricultural practices tends to concentrate P rich plant material at the soil surface, increasing the leaching of soluble PO_4 from plant tissues (Staver and Brinsfield 1994), especially in the fall after plant harvest (e.g., Fig 5-3). The many erosion and sediment control practices may also have reduced P losses during rain events and may be another success of the Targeted Watershed Project; however, this hypothesis should be tested in future research.

Unlike total P, which decreased significantly 10 to 15 years after extensive BMP implementation, my assessment of monitoring data in German Branch did not detect significant decreases in total N. However, the data suggest that concentrations in the stream may be beginning to respond to agricultural nutrient management in the watershed (Fig 5-5). There was also an increase in German Branch from 1986 to the 1990s at a rate of 0.15 mg NO_3-N L^{-1} yr^{-1} and 0.13 mg TN L^{-1} yr^{-1} (Table 5-4), followed by no significant changes after 1995. In contrast, nitrate has been steadily increasing by 0.01 mg L^{-1} yr^{-1} at the Greensboro gauging station since 1964 (Fig 5-6). German Branch is a smaller watershed (17% of the size of Greensboro watershed) with 24% more watershed area of agricultural land use, which may explain the order of magnitude difference in the rate of increase. Regardless, this increasing N trend observed continuously at Greensboro and early in the monitoring period in German Branch did not continue at German Branch into 2003 to 2005 (Fig 5-5, Table 5-3). This suggests that the trend of increasing concentrations of nitrate and total N in the stream has disappeared, and that concentrations may be maintaining 1990s levels or potentially beginning to decrease.

There are three possible explanations for no significant decreases in N during 1990 to 2005. First, long retention times for groundwater in the surface unconfined aquifer may delay observation of reduced N in baseflow; (2) there may have been changes in farming practices which counterbalanced impacts of the BMPs, and (3) the BMPs may have been ineffective in significantly reducing N concentrations. With regards to the first possible explanation, K.W. Staver (pers. com.) has estimated groundwater retention time in German Branch watershed by calculating groundwater volume and recharge rate using a digital elevation model, field measurements of groundwater volumes in the unconfined surface aquifer, and groundwater recharge (Fig 5-7). The cumulative frequency distribution in Fig 5-7 is hyperbolic in form (r^2=0.99), with the oldest groundwater less than 80 years old and a median groundwater residence time of 10.7 years. Using these data, I estimate that during the Targeted Watershed Project from 1991-1995, <25% of groundwater was replaced under BMPs in the watershed, and it was not likely that decreases in baseflow N would be observed during this short time period. I did, however, expect N decreases by the 2003 to 2005 monitoring when almost 65% of the groundwater had been replaced in the watershed following the extensive BMP implementation in the 1990s. The data in Fig 5-5 show a small decrease in nitrate between the peak in 1994 and 2003 to 2005, but there are small, continuing increases in total N. This suggests that the groundwater retention time in the unconfined aquifer suppressed the nitrate response for several years, that the changes in nitrate were small, and that organic N or ammonium continued to increase.

Changes in farming practices during 1990 to 2005 may be a second possible explanation for the lack of a decreasing trend in N concentrations. For example, while
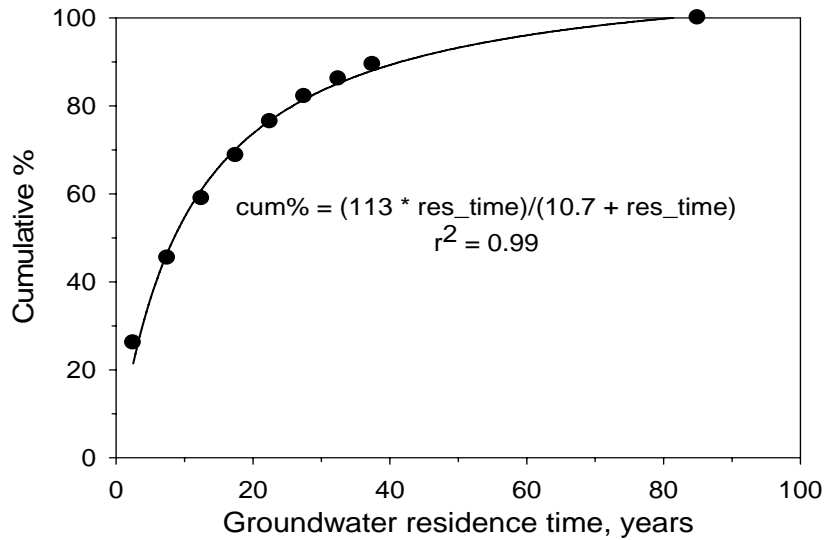
Figure 5-7. Groundwater residence time in German Branch represented by percentage of cumulative groundwater entering baseflow over time. A grid of groundwater residence times for German Branch watershed obtained from K.W. Staver (pers. com.) was used to generate the cumulative frequency distribution shown here. Groundwater residence time was estimated using recharge rates collected in the field and groundwater volume, which was calculated using a digital elevation model and field measurements of depth to aquiclude and water table.

areas in agricultural production stayed the same, the total area of harvested crops steadily increased from 4250 to over 4860 hectares (Fig 5-8) during the Targeted Watershed Project due to an increase in wheat and barley production and more soybean crop cycles on the same cropland per season (Primrose et al. 1997). Fertilizer applications are likely to have increased as well, as it was applied to more crops during this time period. Nutrient management on farms is voluntary, and changes in farming practices driven by economic and weather-related pressures may overwhelm any current nutrient reductions from BMPs. Changes in federal subsidies, crop prices, and technology (e.g. in this case, double-crop soybean production) can all lead to changes in amounts of fertilizer application (Primrose et al. 1997). Other external forces can also affect BMP implementation. For instance, the goal for area of farmland in winter cover crops was not

met during the Targeted Watershed Project due to a national shortage of seed in the early

1990s (USDA 1996). This variability in farming practices makes long term monitoring

essential to assessing the water quality effect of BMPs functioning in realistic farming

scenarios.
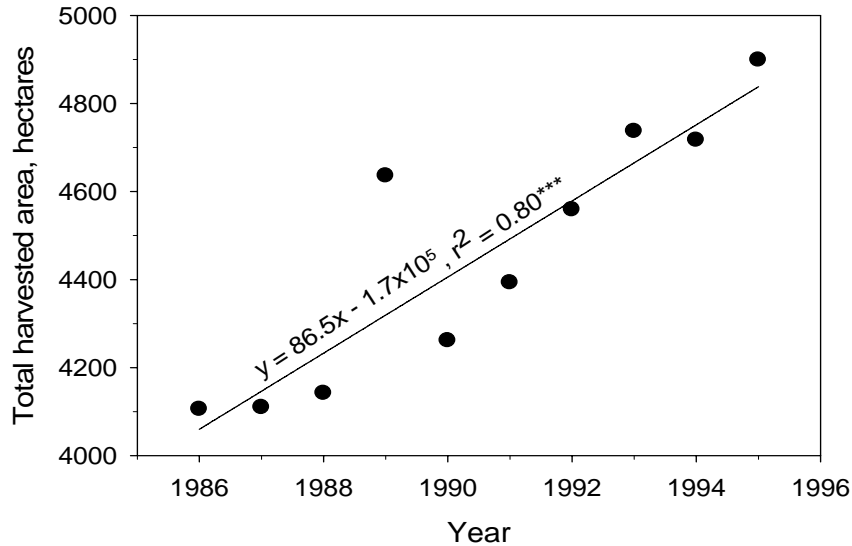
Figure 5-8. Amount of harvested cropland in German Branch from 1986 through 1995.
(Data source: Fig 5 in Primrose et al. 1997)

The third and final reason for the lack of N reductions may be that at the current

level of implementation, BMPs are ineffective at a large scale. The effects of

conservation tillage, riparian buffers, and cover crops on nutrient concentrations have

been measured primarialy at the plot scale, but not at the watershed scale. Watershed-

scale processes such as denitrification and in-stream nutrient processing may dominate

and obscure smaller nutrient reductions by BMPs, even when the practices are widely

implemented. In order to assess how much nutrients are being retained in the watershed,

I developed a nutrient budget for German Branch from 1991 to 1995 with estimates of N

and P inputs (atmospheric deposition, fertilizer, soybean N fixation, and human waste)

and compared these inputs to the amount of nutrients exported in the stream and grain harvests during this monitoring period (Table 5-4). Inputs and grain harvests were calculated from a variety of sources (see Table legend), and N and P export in baseflow and stormflow were calculated using discharge and nutrient data collected during the 1991 to 1995 monitoring period by Jordan et al. (1997). Fertilizer application was the largest nutrient input (87% of N inputs and 99% of P inputs), but crop removal accounts for only 27% of fertilizer N inputs and 8 % of P inputs. The unused fertilizer may have remained in the root zone of agricultural fields (primarily P), it may be flushed to the groundwater (primarily N) during infiltration events, or may be removed in overland flow moving towards the stream. However, the net nutrient export in stream flow was only 26% of the N inputs and 3% of the P inputs to the watershed (Table 5-4), which together with crop removal accounted for only ~50% of N inputs and 10% of P inputs. Therefore, 50% of N and 90% of P inputs were retained within German Branch watershed. Although N may be stored in groundwater for several decades (Fig 5-7), it is likely that denitrification and in-stream processing accounted for a large portion of the nutrient sink. The percentage of N exported as stream flow from German Branch (i.e., 26%) is similar to N export in other watersheds in the northeast US; Boyer et al. (2002) reported that 10 to 40% of N inputs were exported in stream flow in 16 watersheds. Much of the P in German Branch was likely sorbed to soil particles and contributed to reported increases in soil P levels on Delmarva (Sims et al. 1998). Erosion of P-enriched soil from German Branch may have been trapped by sediment control BMPs. The nitrogen not removed from the basin was probably consumed by non-crop vegetation, denitrified, or transformed within the stream corridors. These large natural sinks for N and P at the

Table 5-4. Nutrient budget for German Branch watershed 1990-1995. Atmospheric deposition was measured by Rochelle-Newall et al. (8 kg N ha^{-1} yr^{-1} and 0.1 kg P ha^{-1} yr^{-1}, unpubl.). Fertilizer application rates for soybean, corn, and grains were estimated by MD Cooperative Extension Service (Jim Newcomb, NRCS, pers. com.), and land area in each crop was obtained from Primrose et al. (1997). Soybean N fixation was derived from 1.11 kg N ha^{-1} yr^{-1} * harvested area (Meisinger and Randall 1991). Human population was based on 2000 census data, and waste production was estimated at 4.0 kg N person^{-1} yr^{-1} and 1.2 kg P person^{-1} yr^{-1} (Lee et al. 2001). We calculated baseflow and stormflow exports using nutrient data and discharge measurements as shown in Fig. 5-4. Removal of N and P in grain harvest was obtained from Primrose et al. (1997).

Parameters	Nutrient totals (kg)			
	Nitrogen	% of total input	Phosphorus	% of total input
Inputs:				
Atmospheric deposition	2.1E+05	11.5	2.6E+03	0.3
Fertilizer application	1.6E+06	87.3	8.4E+05	99.2
Soybean nitrogen fixation	7.8E+03	0.4	-------	-------
Human waste production	1.4E+04	0.8	4.1E+03	0.5
Total input	1.8E+06	100.0	8.5E+05	100.0
Outputs:				
Export in baseflow	1.9E+05	10.5%	6.7E+03	0.8%
Export in stormflow	2.8E+05	15.5%	1.8E+04	2.2%
Crop removal/harvest	4.3E+05	23.8%	6.3E+04	7.4%
Inputs accounted for in streamflow & harvest	9.0E+05	49.8%	8.8E+04	10.4%

watershed scale (i.e., 50% of N inputs, 90% of P inputs) could easily obscure the effects of small improvements due to applications of agricultural BMPs.

Of the nutrients that were exported from the watershed, 60% of N and 73% of P was exported during weeks of high flows associated with storm events. Only using baseflow concentrations in the nutrient analysis for German Branch may neglect the contributions of these nutrients from stormflow but does capture the changes in nutrient-rich groundwater and baseflow movement of nitrogen and phosphorus over long periods of time. Regardless, BMPs may reduce nutrients at a field plot scale (Staver and Brinsfield 1994, Butler and Coale 2005, Phillips et al. 1993, Jordan et al. 1997, Lowrance et al. 1997, Clark et al. 1997, Staver and Brinsfield 1998), but a nutrient budget reveals that when applied in watersheds with inherently efficient retention of nutrients (i.e.,

retention of 50% of N and 90% of P), BMPs may not always cause detectable changes in nutrient concentrations.

Many challenges exist facing the future of BMP implementation and meeting nutrient reduction goals in Chesapeake Bay. Farmers' economic concerns for the possibility of decreasing crop yields make it difficult to promote Nutrient Management Plans. In the Chesapeake Bay region in general, matching fertilizer application to crop needs is likely to require more transportation of manure from areas of animal feeding operations to areas without a nearby source of manure, proper storage facilities to allow spreading of manure only during growing seasons, more industrial processing of animal wastes, and widespread use of precision agricultural technologies. All these measures require substantial funds to implement because farmers gain little or nothing economically from these practices, and applying them represents a potentially large expense. Matching fertilizer applications with crop needs has the potential to reduce nutrient loads to Chesapeake Bay, but only when followed on farms throughout the watershed (CBC 2004). In Maryland, farmers are required to file Nutrient Management Plans, but in general only a third do, and the amount of farmers who actually follow the prescribed fertilizer application is unknown (Mark Waggoner pers. com.). Most managers agree that no more than 60% of Nutrient Management Plans are fully implemented (CBC 2004).

The reason conservation tillage is the most widely implemented BMP in German Branch (Table 5-1) may be because it is potentially cost efficient for farmers. Conservation tillage not only reduces erosion rates (Staver and Brinsfield 1994) but also directly benefits farmers by requiring fewer passes over fields to plant crops, which saves

time, fuel, and the use of different types of equipment. However, the effect of leaching

plant residue left on the field during conservation tillage can increase P loading to

streams (Staver and Brinsfield 1994). Plant residue remaining on the soil surface

potentially provides a large amount of P to streams during fall rain events, in some cases

several orders of magnitude above background P levels (e.g., Fig 5-3 and Fisher et al. in

press).

The management community embraced riparian buffers early in the Chesapeake

Bay restoration effort as an effective tool to reduce agricultural nutrient loading

(Lowrance et al. 1997). Managers expect restored riparian buffers, mostly through

CREP, to be responsible for approximately one-third of the total nitrogen and phosphorus

reduction goals in Maryland waters (USDA 2004). Funding for new CREP contracts is

coming to an end, and almost all buffers that can be restored under this widely used

program have been implemented (Mark Waggoner pers. com.). The challenge now is for

scientists to evaluate the actual water quality effects that young buffers have made and

the effects as they mature, as long as farmers do not return CREP sites to cropland after

initial contracts expire.

Finally, cover crops have been shown to be successful at reducing nitrate leaching

to groundwater (Staver and Brinsfield 1998) but have not been widely implemented (e.g.,

Table 5-1). New monetary sources may fund more farmers to use cover crops, but this

effort must be long term in order to evaluate potential nutrient reductions. In watersheds

similar to German Branch, the effects of management actions on nitrate concentrations in

streams are unlikely to be observed for five to ten years (Fig 5-5 and 5-7, Bohlke and

Denver 1995) after groundwater nitrate reductions occur under cropland with consecutive

plantings of cover crops. If managers, politicians, scientists, and stakeholders are fully

committed to Chesapeake Bay restoration through reducing agricultural nutrient loading,

they must be prepared for long-term funding, more extensive BMP implementation,

continuous water quality monitoring, and flexibility resulting from both successes and

failures.

Conclusion

The outcome of only six percent of river and stream restoration projects are

monitored or assessed in Chesapeake Bay watershed (Bernhardt et al. 2005). This makes

past studies as well as ongoing research at watersheds such as German Branch critical to

the understanding of the effectiveness of BMPs. The wide application of BMPs and a

long history of water quality monitoring make German Branch a good example of a

managed agricultural watershed. Although BMPs may have contributed to the 33%

reduction in TP concentrations, the lack of significant N reductions in the stream was not

the outcome predicted by the management community involved in the restoration in

German Branch watershed. More monitoring data in German Branch will be needed to

determine whether N concentrations have leveled off or are beginning to decrease.

However, I believe that the experience in German Branch has been a valuable

exercise in guiding future scientific research and management options in Chesapeake

Bay. This evaluation of historical data in German Branch suggests that at a watershed

scale, other factors such as denitrification and in-stream processing may compete with

detecting measurable nitrogen reductions. Furthermore, the current level of BMP

applications such as CREP and winter cover crops in the watershed is likely to be

insufficient to reduce nitrogen concentration. Best Management Practices will affect

water quality only if sufficiently implemented to be at least equivalent to other watershed

processes influencing nutrient reductions (e.g., denitrification and in-stream processing).

Managers have assumed that BMP nutrient reductions throughout the Chesapeake Bay

watershed would be similar to those measured in plot scale studies but are now

recognizing that at the current level of implementation, BMPs are not successful at the

bay-wide scale. Scientists must shift their research focus to a larger scale in order to

assess BMPs embedded with other processes in the environment to determine the level of

implementation needed to improve Chesapeake Bay water quality. The health of the bay

depends on a more complete understanding of ecological interactions in agricultural

landscapes, nutrient management programs, and BMPs that also include consideration of

the inherent variability in socioeconomic factors affecting farming practices.

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Chapter 6

SYNTHESIS

My research interests have been on how human activities on land affect downstream aquatic ecosystems. The scientific community's level of involvement in ecosystem restoration in Chesapeake Bay and the integration of applied and basic science provided the motivation to do my Ph.D. research in this region. The response to increasing nutrient loads to Chesapeake Bay has been extensive; however, there are some signs that improvements in ecosystem health have resulted from nutrient reductions (e.g., Potomac River, Kemp et al. 2005). My research focused on the effect of restored riparian buffers on nutrient reductions from agricultural land draining into Chesapeake Bay, one of the primary sources of N and P.

Past research on the nutrient reduction capabilities of riparian buffers has mostly been on established forest buffers and at a plot, or individual farm, scale. My research goals were to investigate the mechanisms of nutrient reductions in restored riparian buffers on two individual farms and also at the watershed scale in 30 subbasins of the Choptank and Chester River watersheds. An important component was to make these assessments where riparian buffers had been restored as part of the nutrient management strategies in the Chesapeake Bay watershed. I chose to study restored riparian buffers through the Conservation Reserve Enhancement Program (CREP) because of the widespread implementation on the outer coastal plain of Maryland and the program's goal to reduce nutrient inputs to the bay. I investigated nutrient reductions in groundwater under a CREP restored buffer and in baseflow and stormflow in 30 streams

in the Chester and Choptank River watershed. My hypotheses were (1) that nutrient reductions occur in young, CREP restored buffers, though not at the high levels observed in established riparian forests and (2) that baseflow and stormflow nutrient concentrations would be negatively correlated with the amount of CREP restored buffers in the 30 subbasins. Lastly, due to my interest in other Best Management Practices (BMPs) I assessed the nutrient reductions in German Branch, a subbasin in the Choptank watershed, after significant nutrient management strategies were implemented on the farmland in that basin.

At the Radcliffe farm in the Little Choptank River watershed and another farm in the Chester River watershed, I measured groundwater nutrient concentrations in young (<7 years old) restored buffers, older (~20 years old) restored buffers, an established forest buffer, and a non-buffered control site. The groundwater nitrate reductions were large in all forest buffers and resulted in very small groundwater nitrate contributions through these buffers into adjacent creeks. At the Radcliffe farm, where more detailed data were available, these reductions were dominated by the dilution of nitrate-rich groundwater from low-nitrate rainwater percolating through the riparian soils. I also detected nitrate reduction through the process of denitrification in all of the buffers; however, the method used to measure denitrification may not be the most ideal for this particular farm. Even though the three forest buffers surrounded the same field, the groundwater hydrology was different in all buffers. This makes it difficult to compare nutrient reductions between the buffers since creek water intrusion, transpiration through the riparian vegetation, and groundwater recharge varied between the buffers. However, it is apparent that the 7 year old CREP restored buffer on this farm has developed the

characteristics necessary to filter nutrients as efficiently as many established riparian forests.

I suspect that young CREP buffers in the coastal plain rapidly develop the abilities to reduce nitrate concentrations in groundwater. Vellidis et al. (2003) measured large nitrogen reductions in groundwater, mostly through denitrification of nitrate, immediately after a buffer was restored. At the Radcliffe farm, the nitrate reductions were mostly from taking that creek-side land out of agricultural production and no longer applying fertilizer in that area. Rainwater now infiltrates through the soil profile without any fertilizer-derived nitrogen leaching from the soil profile into the subsurface groundwater, diluting the upslope, high nitrate groundwater from the crop fields. This process may be important in other CREP sites on the outer coastal plain of the Chesapeake Bay watershed where there is low topographic relief and groundwater flow is slow through soils with low hydraulic conductivity. The nutrient reduction capabilities in restored buffers may not be developed as rapidly at CREP sites in other regions of the Chesapeake Bay watershed, and in order to characterize this, research on restored buffers should expand outside of the coastal plain.

Since I detected large nitrate reductions in a buffer restored through the CREP, I expected to detect reductions in baseflow nitrate concentrations at the watershed scale in this region. I put a considerable amount of effort into compiling the location of CREP sites in the Chester and Choptank River watersheds. Unfortunately, I was not successful in gathering a complete set of data on CREP areas and locations from the beginning of the CREP in 1998 through 2004 in the Chester watershed; therefore, my ability to evaluate water quality in relation to CREP implementation there is limited. The effects

of land use on nutrient inputs into the Chester River is not as well understood as in the Choptank River, and not as many working relationships between scientists and the farming community exist. Collaborative research is needed in the Chester River watershed. However, the CREP data I compiled for the 15 subbasins in the Choptank watershed is complete and reveals that the restored stream length varied from 1 to 30% of total subbasin stream length. This was not correlated with baseflow nitrate or total nitrogen concentrations in the subbasins, and in fact, nitrogen concentrations have largely increased since the last monitoring period in 1986, before any buffer restoration through the CREP. A nutrient budget for one of the subbasins, German Branch, revealed that it is not likely that the restored buffers have the high nitrogen reduction capabilities observed in the 7 year old CREP during the groundwater study (i.e., 124 kg N ha^{-1} yr^{-1}). The budget revealed that when this large nitrogen reduction was projected for all the CREP sites in the subbasin, the stream nitrogen concentrations would have decreased significantly to be detectable. It is more likely that, on average, the restored buffers in the 15 subbasins may exhibit lower reduction rates than those measured on the farm near Horn Point. If this is the case, at the current level of buffer restoration it may not be possible to detect measurable nutrient reductions in baseflow above other factors affecting the nutrient budgets such as variations in cropland between basins, changes in farming practices, seasonal weather variability, and large nitrogen reduction processes spread throughout the subbasin (i.e., denitrification in hydric soils and in-stream nutrient processing). More research on these nutrient processes in watersheds may be needed before BMP reductions at the watershed scale can be assessed.

As opposed to baseflow, stormflow phosphorus yields were related to buffer restoration in one of the Choptank subbasins. I performed a detailed comparison of size and location of CREP sites and measured stormflow nutrient concentrations in two of the subbasins, Blockston Branch and Norwich Creek. The restored buffers were widely distributed throughout Blockston, and the CREP sites increased the total buffered streamline from 42% in established forested buffers to a total of 61% buffered streamline in 2004, compared to a total of only 45% in Norwich. During the rain events, ammonium, total suspended solids, particulate nutrients, and phosphorus concentrations increased with stream discharge, and in most cases, the integrated volume-weighted concentrations of these nutrients were significantly higher in Norwich as opposed to Blockston. Calculations of streamflow in 2004 revealed that nutrients mainly supplied in stormflow (i.e., ammonium and phosphorus) had higher yields from Norwich, and nutrients mainly supplied in stormflow (i.e., nitrate) had higher yields from Blockston. Baseflow nitrate concentrations and nitrate yields were over 2 times higher in Blockston compared to Norwich, even though the two basins have similar land use and Blockston has more soils that can support denitrification (i.e., hydric and D class soils).

Measurements such as this may have important implications for the design of nutrient management practices at the watershed scale. The nutrient management in watersheds dominated by nitrate export may need to focus on implementing cover crops, while the focus may need to be on buffer restoration in watersheds dominated by sediment and phosphorus export. This study has started to define the nutrient responses in the two streams during storm events, but I can not be certain that restored buffers are

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driving the differences among the subbasins until the sample size of storms and subbasins sampled is increased and stream discharge measurements are complete.

Finally, the detailed history of nutrient management in German Branch and the resulting water quality changes 10 years after BMP implementation demonstrate a possible success of nutrient reduction strategies. During the early 1990s, when extensive soil and erosion control BMPs were implemented within the watershed, phosphorus reductions were not observed in the stream. However, by the 2003 to 2004 monitoring reported here, phosphorus concentrations in baseflow had decreased 33%, which was the same percentage of reduction that managers had expected from these BMPs. Even though I did not measure significant decreases in nitrogen concentrations, the significant rate of increase observed from the mid 1980s to the 1990s in German Branch and observed at other streams in this region was not detected from the 1990s to the current monitoring, indicating that the BMPs may have halted the nitrogen increases, but not reversed them. Also, a nutrient budget for German Branch from data collected in the early 1990s revealed that this subbasin exported only 50% of the nitrogen inputs and 10% of the phosphorus inputs. This has been observed in headwater streams throughout the US (Peterson et al. 2001), large watersheds in the northeastern US (Boyer et al. 2002), and from continents draining into the Atlantic Ocean (Howarth et al. 1996). This process is characteristic of ecosystems at many scales, but many of the processes taking place between nutrient input on land and nutrient export in streams, rivers, and oceans are not well understood. Quantifying denitrification of nitrate and soils sorption of phosphate at the watershed scale is much needed to understand these types of nutrient budgets. In landscapes that retain much of the nutrient inputs, presumably through denitrification,

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plant growth, and soils sorption, detecting BMP nutrient reductions above other nutrient reduction processes may be difficult at these scales.

There are many obstacles to a complete understanding of agricultural nutrient loading and possible reductions to Chesapeake Bay. The challenge of basic science is to understand the nutrient processes occurring between cropland and downstream aquatic systems within the agricultural landscape. One of the main challenges to applied science is to integrate this basic knowledge into studying the management efforts. It is difficult to balance farmer and science-based environmentalism, especially when farmers are balancing the quality of the environment and economic stability (Paolisso and Maloney 2000). However, the more scientists can quantify how these strategies are affecting the bay and the more these practices are implemented to maximize nutrient practices and crop yields, the closer we may get to striking that balance.

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