Hydrological Control on Nitrate Delivery through the Groundwater-Surface Water Interface

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ABSTRACT

Near stream groundwater surface water interfaces (GSI) are considered to provide natural remediation for groundwater nitrate before it discharges into surface water bodies, largely through denitrification, but this function is not well understood based on the existing literature. The purpose of this study was to assess the combined influences of hydrological properties on groundwater nitrate delivery from terrestrial to aquatic systems. The study site, on the Eastern Shore of Virginia, is in the mid-Atlantic coastal plain of the Delmarva Peninsula.

 NO_3^- dynamics during both baseflow and bank storage (groundwater recharge by stream water) were examined in columns of undisturbed streambed sediments from the field. The laboratory experimental design incorporated two processes: groundwater discharge into the stream (forward flow) and groundwater recharge from the stream (reverse flow). The mean denitrification rate from the laboratory microcosm study was 361.3 mmol N m⁻² d⁻¹. The column experiments, combined with a numerical transport model, revealed that flow velocity and organic matter content are the most dominant factors contolling nitrate removal at the GSI.

The bank storage experiment showed that NO_3^- removal capacity persisted within the intact column during the discharge-recharge processes. The redox sequence was redeveloped through the column almost immediately after the reverse flow was reset to simulate the discharge condition. Hydrologic exchange induced by bank storage enables microbial communities to retain and utilize nitrate at the GSI that might otherwise be exported from the system. A field and numerical modeling study of riparian hydrology was conducted to investigate the NO_3^- flux and water table response occurring during bank flood events. Aquifer head responded relatively rapidly to changing stream stage during storm events. A variably saturated flow model specifically developed for this problem provided a reasonable match to the field observations. The reduced groundwater discharge due to the formation of a groundwater ridge within the stream bank was suggested by both field observations and model simulation. The increased residence time in the GSI favor microbial reactions such as denitrification, during which the stream NO_3^- loading is attenuated. This effect may not be important due to the limit bank storage in the field site with steep sloping banks and well-drained aquifer material.

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1 Introduction

1.1 Statement of the Problem:

The importance of groundwater as a contributor of nutrients from nonpoint sources to coastal and estuarine water is receiving increasing attention [*Lowrance, et al.*, 1997; *Paerl*, 1997; *Phillips, et al.*, 1993; *Reay, et al.*, 1992; *Weiskel and Howes*, 1991]. For shallow groundwater systems within the coastal plain region of Eastern Shore, Virginia, groundwater quality is vulnerable to contamination and strongly linked to land use because areal recharge is the dominant source of water. This increasing concern has emphasized the need for determining the nutrient-transport processes, especially for nitrogen, through the terrestrial-aquatic system and improving the methods of predicting nitrogen's fates in the landscape. Among all the forms of nitrogen, the transport and fate of NO₃⁻-N are particularly important because NO₃⁻ is a very soluble mobile anion that can readily be transported by groundwater [*Simmons, et al.*, 1992]. Attention is focused on NO₃⁻ transport from uplands in humid well-drained agricultural landscapes to streams and other receiving bodies of water.

The groundwater-stream interface (GSI) is an area of high biogeochemical reactivity and often acts to control fluxes of nitrogen from terrestrial to aquatic ecosystems by influencing controlling variables of nitrogen cycling, especially the hydrological residence time and redox conditions [*Duff and Triska*, 2000; *Hedin, et al.*, 1998; *Jonns and Mulholland*, 2000]. Coastal streams transport solutes derived from land to estuarine and marine environments, and riparian zones often function as buffers where

NO₃⁻ is removed from drainage water before it reaches the streams [*Haycock and Burt*, 1993; *Hill*, 1996a; *Jacobs and Gilliam*, 1985b]. However, in thick surficial aquifers with permeable materials beneath the upland, groundwater follows deeper longer flow paths toward the stream, bypassing the riparian zone and discharging upward to the streambed [*Bohlke and Denver*, 1995; *Hill*, 1996a]. In such a hydrogeological setting, the groundwater-stream water interface might be the final 'barrier' to the groundwater-derived contaminants instead of stream riparian zones [*Hedin, et al.*, 1998]. The ability of the groundwater-stream interface to control N-transport during baseflow condition may change during hydrological episodes, however. Transients in biogeochemical processes occurring on the time scale of these events may have very important implications for evaluating budgets at watershed scales [*Mills, et al.*, 1998]. Dahm et al. [1998] argue that disturbance of hydrological events has a strong impact on the time-averaged rates of biogeochemical transport, retention and transformation.

The objective of this study was to develop an understanding of the relationship between redox conditions in the groundwater-surface water interface and the potential for biological removal of nitrate during groundwater discharge, and how the biogeochemical fate of nitrate is influenced by hillslope-riparian hydrology. The study was based on field observations and laboratory transport experiments using intact cores from Cobb Mill Creek, a first-order coastal stream on the Eastern Shore of Virginia.

1.2 Introduction

1.2.1 Nitrate Contamination

Nitrate contamination of ground and surface water is of concern, because of nitrate's association with conditions such as eutrophication of surface waters and its

prevalence in many groundwater supplies [*Paerl*, 1997]. Discharge of nitrate-bearing groundwater to streams can be an important source of nitrogen to coastal marshes, lagoons and bays, and coastal waters, leading to accelerated eutrophication [*Reay, et al.*, 1992]. During eutrophication, high levels of NO_3^- cause excessive blooms of aquatic plants and algae. Death and decay of the enhanced production, in turn, decreases the amount of dissolved oxygen (DO) in the water, making conditions unfavorable for benthic and aquatic animal species including fish.

Under some conditions, NO_3^{-} in high concentrations can be a human health hazard. Groundwater from the unconfined aquifer is the source of drinking water for many rural residents the Eastern Shore of Virginia. Stomach microorganisms can reduce NO_3^- to NO_2^- , which combines with hemoglobin in the blood cells, rendering them unable to carry oxygen, resulting in a condition known as methemoglobinemia [Prasad and Power, 1995; Ward and Elliot, 1995]. Commonly referred to as "blue baby syndrome," this condition is linked to brain damage and asphyxiation in infants [*Prasad and Power*, 1995]. For this reason, the U.S.EPA has established a maximum level of 10 mg L^{-1} NO₃⁻¹ N in drinking water supplies (U.S.EPA 1995). Although proof is not conclusive, there is concern that NO_2 produced from NO_3 may react in the stomach to form carcinogenic, mutagenic and/or teratogenic nitrosamines in the body [Prasad and Power, 1995]. It has also been found that N₂O gas, a byproduct of denitrification contributes to the destruction of atmospheric ozone. Furthermore, N₂O accounts for 4% of the greenhouse warming effect [*WagnerRiddle, et al.*, 1996]. This information suggests the control of NO_3^{-1} in freshwater systems is important from both an environmental and health perspective.

Groundwater nitrate contamination is a major concern for the agricultural regions of the Eastern Shore of Virginia. Annual estimates of nitrogen loadings to shallow groundwater are on the order of 20 to 43 kg ha⁻¹ for dominanat row-crop land uses in the mid-Atlantic Coastal Plain [Peterjohn and Correll, 1984]. Septic tank nitrogen loading rates are on the order of 7 to 11 kg household⁻¹ yr⁻¹ [Stewart and Reneau, 1988]. Nitrate is widespread in the surficial aquifer, including parts of the aquifer used for drinking water. Concentrations of nitrate exceeded 10 mg/L in about one-third of 29 samples from wells in the part of the aquifer used for domestic water supply (median well depth 45 feet) [Denver, 2003]. Streams within the coastal watershed of the VA eastern shore exhibit significant interaction with surficial aquifers of the region making ground water a dominant source of water along the nontidal portion of these streams [Bohlke and Denver, 1995; Correll, et al., 1999; Jordan, et al., 1997]. Accordingly, stream water is vulnerable to groundwater contamination. Nitrate concentrations were greater than 3 mgL⁻¹ in about one-half of the headwater streams during base flow in the spring. Nitrate concentrations in streams generally increased with increasing agricultural intensity in upstream watersheds, particularly in areas with permeable, well-drained, and welloxygenated sediments [Denver, 2003]. Nitrogen transport through direct groundwater discharge has contributed to the nitrogen enrichment of surface water within the coastal watersheds and lagoons [Reay, et al., 1992; Staver and Brinsfield, 1996].

1.2.2 Nitrate removal by denitrification

Nitrogen processes are predominantly mediated by microorganisms in aquatic and terrestrial ecosystems [*Duff and Triska*, 2000]. A simplified diagram of the N cycle with a focus on the aquatic environments (without considering abiological atmospheric

processes) is shown in Figure 1.1. Theses processes are greatly influenced by the redox status of the system.



Figure 1-1 Simplified diagram of the N cycle highlighting the important microbially mediated processes. Figure ourtesy of Aaron Mills

Unlike ammonium that can bind to cation exchange sites on streambed sediments [*Triska, et al.*, 1994], nitrate is mobile and easily transported [*Duff and Triska*, 1990; *Holmes, et al.*, 1994; *Jones, et al.*, 1995; *Triska, et al.*, 1990]. Transformations of NO_3^- are mostly biochemically mediated [*Winter, et al.*, 1998]. Denitrification is the main process removing nitrogen entirely from the aquatic ecosystems by reducing NO_3^- into gaseous forms of nitrogen, which leaves the ecosystem by escaping to the atmosphere. Biological denitrification is the dissimilatory reduction of nitrogen oxides (NO_3^- and NO_2^-) to gaseous oxides (NO, N_2O) that may be further reduced to nitrogen gas (Figure 1.1) [*Knowles*, 1982]. Nitrate is used by facultative anaerobic microorganisms as electron acceptors in their respiratory chain [*Knowles*, 1982; *Tiedje, et al.*, 1989]. Nearly all respiratory denitrifiers prefer to use oxygen (O_2) as a terminal electron acceptor, and, in the presence of O_2 , synthesis and activity of denitrifying enzymes are repressed [*Tiedje, et al.*, 1989].

Denitrifying bacteria grow best in pH range of 6 to 8, and denitrification is negligible below a pH of 4 [*Paul and Clark*, 1996]. The amount of available carbon also controls denitrification because it is required for microbial growth. The range of temperature for denitrification is quite large, with a minimum at 5 °C and a maximum at 76 °C [*Paul and Clark*, 1996], with an optimal range from 30-35 °C [*Delwiche*, 1970].

Denitrification can thus occur if 1) anaerobic conditions are present, 2) there is a sizable denitrifying organism population, 3) there is a source of organic carbon and 4) if nitrate is available as electron acceptor. These factors are in turn influenced by soil topography, vegetation cover, local hydrology, and season. Presence of nitrate in the agricultural watershed is presumably not the limiting factor because of its usual abundance [*Denver*, 2003; *Mills*, 2002]. The limiting factors can thus be the existence of anaerobic conditions as well as the availability of organic carbon as a fuel. Most denitrification studies focus on the processes at the GSI, where anaerobic conditions are expected in the sediment at different depths, depending on the oxygen demand by the microbial biomass and the diffusive supply by overlying water [*Chen and Keeney*, 1974; *Galavotti*, 2004].

1.3 The terrestrial-aquatic interfaces as nitrate buffers

Two possible vectors that connect surface water and groundwater are (i) groundwater flow from the uplands through riparian zones to the active channel and (ii) surface water recharging groundwater along an upstream-downstream gradient. The later is also called in-stream or hyporheic process [Bencala and Walters, 1983; Holmes, et al., 1994; Jones, et al., 1995; Tiedje, et al., 1989; Triska, et al., 1990; Valett, et al., 1996; White, 1993]; The significance of this longitudinal exchange of groundwater and surface water depends on the hydrogeolgic and topographic settings. From the study of Shingobee River, Minnesota, Jackman [1997] concluded that hyporheic retention of stream-water ammonium and nitrate was minor because large groundwater pressure gradients limited exchange with subsurface sediments. In catchments with large groundwater pressure gradients, nitrogen retention and transformation are largely associated with processes in groundwater discharge, which corresponds to the first vector mentioned above and is based on the idea that groundwater-stream water interfaces that intercept terrestrially derived water are important control points for nutrient flux from uplands to streams. This perspective differs importantly from studies that consider nutrient transport in the opposite direction: from stream water into the "hyporheic zone" of steam sediments, during which additional biogeochemical transformations can occur [Bencala, 1993; Findlay, 1995; Grimm and Fisher, 1984; Harvey and Bencala, 1993; *Triska, et al.*, 1993a].

Lateral ground water flow underneath riparian zones has received a large amount of attention regarding its affect on watershed N chemistry [*Hedin, et al.*, 1998; *Hill*, 1990; , 1996a; *Hill, et al.*, 2000; *Lowrance, et al.*, 1984a; *Pinay, et al.*, 1993]. Jacobs and Gilliam [1985b] observed that up to 90% (10-55 kg ha⁻¹ y⁻¹) of nitrate removal took place in the first 10-15 m of a stream riparian zone when upland groundwater flows toward the stream in an agricultural area of North Carolina. Similar percentage reductions of nitrate concentrations have been reported in other areas of the southeast U.S. coastal plain [*Lowrance, et al.*, 1984b; *Peterjohn and Correll*, 1984]. Nitrate-N removal rates of 45 kg ha⁻¹ y⁻¹ and 60 kg ha⁻¹ y⁻¹ have been estimated in two Maryland riparian zones [*Peterjohn and Correll*, 1984]. Lowrance et al. [1984a] observed a removal rate of 31.5 kg ha⁻¹ y⁻¹ in a forest riparian zone receiving agricultural runoff in Georgia. Effective nitrate removal from groundwater by stream riparian zones has been reported in agricultural watersheds elsewhere in the U.S. and in southern England, southwest France and New Zealand [*Cooper*, 1990; *Haycock and Pinay*, 1993; *Pinay, et al.*, 1993].

Near-stream riparian zones often form a transition between upland soils and streams and though they may account for only a small percentage of watershed area, they may exert a disproportionately large role in regulating the flux of N to the stream [*Cirmo and McDonnell*, 1997; *Hill*, 1996a]. In riparian zones where groundwater flows in a shallow subsurface path toward the stream, a sequence of lateral zones dominated by redox reactions arrayed in thermodynamic order may occur between the upland perimeter and the stream [*Hedin, et al.*, 1998]. These zones attenuate groundwater N by biogeochemical processes.[*Hill*, 1991; , 1993; *Peterjohn and Correll*, 1984] Similar sequences of redox reactions can be associated with groundwater discharging upward into riparian sediments and streambeds [*Hedin, et al.*, 1998]. Vertical patterns of increased reduction and oxidation are also linked to water table fluctuations in riparian zones. Studies of riparian zones often point to the efficient removal of N at the ecotone

between upland groundwater and surface water [*Haycock and Burt*, 1993; *Jacobs and Gilliam*, 1985a; *Peterjohn and Correll*, 1984].

Nevertheless, there is no consensus as to the filter effect that riparian zones play in nitrate export in watersheds [*Hill*, 1996a]. In general, most of the studies that have identified near-stream wetlands and riparian zones as sinks for watershed N have been conducted in wetlands bordering agricultural uplands [Peterjohn and Correll, 1984]. Many similar studies conducted in forest-dominated watersheds have found little attenuation of N [Devito, et al., 1989; Hill, 1993; Warwick and Hill, 1988]. The hydrogeomorphology of an individual riparian zone can greatly affect its ability to remove or transform N. GSI can be an alternative filter for nitrate removal in some hydrogeological settings. Even though many studies of watershed nitrogen cycling have examined how stream-water chemistry is modified by the riparian zones, few [Hedin, et al., 1998] have studied the role of the GSI in regulating chemical fluxes from hillslope and/or riparian zone groundwater to streams. Uncertainty concerning hydrologic linkages between the GSI and the adjacent aquifer underscores the fact that stream chemistry is influenced by the interaction of hydrologic and biogeochemical processes at many locations within the catchment.

1.4 The importance of riparian hydrology

A common finding across field studies of riparian zones in diverse settings is the importance of hydrology in influencing the extent of nitrate removal from groundwater via denitrification [*Gilliam*, 1994; *Haycock and Burt*, 1993; *Hill*, 1990]. Riparian zone hydrology directly influences groundwater flow paths and therefore whether or not nitrate comes in contact with carbon-rich soils that support high rates of denitrification. Soil

denitrification potential is generally expected to be highest at the surface, where root density and organic matter are highest, and to decline rapidly with depth [Gold, et al., 2001]. In a study near a small stream in southern Ontario, Cey et al. [1999] observed decreases in nitrate concentrations beneath a break in slope, approximately 15 m from the stream. They attributed these decreases, in part, to downward flow of nitrate-laden groundwater induced by infiltration through an uncultivated buffer strip. The downward flowing, nitrate-laden water also experienced denitrification as it entered a reducing zone that coincides with a shallow clay layer. Maximum nitrate removal in riparian buffer zones has generally been found where there is a shallow, impermeable layer that causes groundwater to flow through high carbon zones [Hill, 1996a]. In contrast, water may be less affected by riparian-zone processes where subsurface water passes beneath the riparian zone, below the root zone and/or organic-rich surface soils, or in areas of hilly terrain, where small streams are commonly incised in steep valleys with minimal riparian zones [Bohlke and Denver, 1995; Burt, et al., 1999]. In such hydrogeological setting, the absence of NO₃ depletion has been noted [Bohlke and Denver, 1995; Phillips, et al., 1993; *Robertson, et al.*, 1991]. In aquifers without a shallow confining layer, it is critical to investigate the hydrology and biogeochemistry of the riparian and upland aquifer to understand the potential for a riparian zone to remove nitrate from the groundwater [*Puckett, et al.*, 2002].

The riparian hydrology affects residence time which influences the duration that denitification can act to change the nitrate concentration of a parcel of water. Schiff et al. [2002] found an order of magnitude difference in the NO_3^- export from two adjoining catchments and hypothesized that the high NO_3^- concentrations were due to the steep

hillslope gradients that expedited the movement of NO_3^- rich waters downslope. In four forested, glaciated, subcatchments in western New York, USA, Inamdar and Mitchell [2006] found steep slop gradients are the primary determinants of NO_3^- generation and delivery. Ocampo et al. [2006] suggested that dilution in the steep hillslope and denitrification in the flat hillslop are responsible for much of the observed $NO_3^$ attenuation in the riparian zones. They recommended the use of the Damkohler number, a simple dimensionless number that is a measure of the competition between transport and reaction processes, which allowed a favorable comparison of research findings for different geographical settings.

Precise analyses of riparian zone groundwater chemistry [*Cey, et al.*, 1999] and discrepancies between the results of laboratory simulations and field measurements [*Willems, et al.*, 1997] indicate that the funcitioning of a biogeochemical buffer strip may be hydrogeologically controlled. At the upland-stream valley boundary groundwater may be forced deep under the organic sediments of riparian strips and below plant root range. Thus, the shallow unpolluted water of the riparian strip may form a 'lens' fed mainly by rainwater and hydrologically do not bear relation to the water discharging from the adjacent uplands [*Cey, et al.*, 1999]. Vidon and Hill [2004] developed a conceptual model of the connection between landscape hydrogeologic characteristics and nitrate removal in the riparian zone based on eight stream riparian sites. They found that greater than 90% of nitrate removal occurred within the first 15 m of the riparian zone in sandy loam soils with shallow 1-2 m confining layers. In contrast, sites with sandy soils and confining layers at depths of 6 m had greater than 90% nitrate removal over 25-176 m.

From the above discussion, it would appear that the hydrogeological studies supported by an accurate site inspection and computer modeling that delineats groundwater flow pattern are essential for understanding of the riparian zone functioning and attenuation mechanisms in the stream-riparian systems.

1.5 Biogeochemical Significance of Groundwater-Surface Water Interface

There has been very little work on the fate of nitrogen advected directly through stream banks and sediments. Hedin et al. [1998] delineated groundwater flowpaths within a narrow zone at 20-40 cm depth adjacent to a first-order stream channel in Michigan and found that denitrification occurred primarily within this near-stream region, where upward flowing nitrate-rich water mixed with organic carbon-rich water from shallower flowpaths. McMahon and Bohlke [1996] reported that nitrate reduction in floodplain deposits and bed sediment beneath a Colorado stream was due to denitrification and mixing in the hyporheic zone. In the current study site, a small low-relief stream, Cobb Mill Creek, Virgninia, the stream NO_3^- concentrations of 1-2 mg NO_3 -N L⁻¹. It showed limited removal along the long flow path from the hillslope to the stream, but extraordinarily high removal of 84% when nitrate-rich groundwater passes through the GSI. The denitrification potential rates ranged 16.9-600 µmol N m⁻¹ h⁻¹ depending on the sampling seansons [*Galavotti*, 2004].

The groundwater-surface water interface is an ideal site for the development of biogeochemical activity by transporting limiting reactants to a substrate containing the remaining reactants [*McClain, et al.*, 2003]. Along the Boyne River in southern Ontario, Hill et al. [2000] found that groundwater transports NO_3^- into organic-rich river channel

deposits or peat, producing a zone of denitrification that is only a few meters wide. At the Cobb Mill Creek field site, the high activity in GSI is formed by the similar mechanism i.e. The presence of sediment layer on the bed and banks of stream affect the interchange flow between stream and adjacent aquifer. This layer is formed by the deposition of fine sediment particles on the stream banks and bed. This layer generally has two important properties, lower hydraulic conductivity compared to the surrounding aquifer material and high organic content originated from deposition and burial of particulate organic carbon in reworked sediment [Younger, et al., 1993]. The presence of a thin layer of finer grained bed sediment material along the stream bank has been documented in many streams [Schumm, 1960]. The layer is significant to N biogeochemical cycling in two ways: 1) It can reduce the saturated hydraulic conductivity (Ks) by several orders of magnitude, thereby reducing the groundwater discharge rate, and allowing a much longer residence time for microbial reactions to occur. And 2) High organic matter content of the layer can fuel the biogeochemical reactions that effect N removal by serving as carbon and energy sources.

Rates and pathways of nutrient cycling at the GSI are topics of growing interest [*Cirmo and McDonnell*, 1997; *Grimm and Fisher*, 1984; *Triska, et al.*, 1990]. Strong redox gradients commonly occur at this interface, and concentrations of many biogeochemically important solutes vary widely. A predictable sequence of microbial processes based upon thermodynamic energy yield would be expected along the groundwater flowpath. Groundwater containing dissolved O₂ supports aerobic metabolism if the necessary electron donors are present. When dissolved O₂ supplies are exhausted, alternative electron acceptors are used in organic matter catabolism. The

denitrifying bacteria are facultative anaerobes able to use a broad range of organic
substrates. The switch from oxic to anoxic conditions promotes synthesis of nitrate
reductase enzymes by a consortium of denitrifying microorganisms [*Payne*, 1973].
Denitrification yields the most free energy once dissolved oxygen is no longer available,
and this biogeochemical pathway is of great interest in GSI since it provides a permanent
sink for excess nitrate [*Groffman, et al.*, 1996; *Hill*, 1996a; *Pinay, et al.*, 1993].

1.6 Mechanisms of GW-SW Interaction

The runoff production from any particular hillslope may be dominated by a single mechanism or by a combination of several kinds of flow generation. Overland flow has been evaluated as an important contributor to the flood peak in arid areas [*Fetter*, 2001]. Rapid increase of stream stage contributed by Hortonian overland flow will reverse the groundwater flow by recharging stream water into adjacent aquifers (Figure 1.2B) in a process called bank storage [*Brunke and Gonser*, 1997]. In contrast, in humid regions the main direction of water flow is from the upland, vertically downward through the soil profile, horizontally (subsurface) across the riparian zone, and then upward into the stream channel [*Marti, et al.*, 2000] (Figure 1.2A). In the regions like coastal plains, upland soils are highly permeable, and overland flow occurs or antecedent dry condition when amount of rain exceeds soil infiltration rate. Thus, most of the water reaches the surface stream via subsurface flow path [*Fetter*, 2001; *Hill*, 1990; *Sklash and Farvolden*, 1979].



Figure 1-2 Contrasting routes of hydrologic linkage between riparian zone and stream. Curved arrows show routing of water (i.e., flowpaths). (a) A riparian-stream route characterizes stream-riparian linkage in humid zones under antecedent-wet condition, where storm water infiltrates soils before entering the riparian zone and then the stream. (b) In arid regions or in humid regions with antecedent-dry condition, water moves across the surface (overland flowpaths) from the riparian into the surface streams, where it then enters the riparian zone via subsurface flowpaths.

Besides surface runoff, the subsurface flow can also enter streams quickly enough to contribute to the event response. Such flow is called subsurface storm flow or interflow [*Sophocleous*, 2002]. One main concept used to account for rapid subsurface responses is groundwater ridging [*Sklash and Farvolden*, 1979], which describes the large and rapid increases in hydraulic head in groundwater during storms. Rapid changes in near-stream water-table levels are attributed to the conversion of a tension-saturated zone or capillary fringe overlying the pre-storm water table to a zone of positive potentials. Even a tiny amount of percolated water could immediately change the pressure of tension saturated water from negative to positive [*Gillham*, 1984]. This phenomenon thus produces a disproportionately large rise in the near-stream water table. Consequently, the net hydraulic gradient toward the stream and/or the size of the seepage face increases. The stream flow contribution induced thereby may greatly exceed the quantity of water input that induced it.

The hydrological exchange of groundwater-stream water (GW-SW) is controlled by 1) the distribution and magnitude of hydraulic conductivities, both within the channel and the associated alluvial-plain sediments; 2) the relation of stream stage to the adjacent groundwater level; and 3) the geometry and position of the stream channel within the alluvial plain [*Woessner*, 2000]. In coastal plains like Virginia's eastern shore, precipitation events rather than seasonal pattern are the main mechanism that alters the hydraulic head near streams and thereby induce changes in flow direction. Under low precipitation conditions, baseflow in many streams constitutes the discharge for most of the year. In contrast, under high precipitation condition, stream discharge gradually increase, leading to higher hydraulic pressures in the lower stream reaches, which cause the stream to infiltrate its banks and recharge the aquifer. The magnitude of bank storage depends on duration, height, and shape of the flood hydrograph, as well as on the transmissivity and storage capacity of the aquifer [*Sophocleous*, 2002].

The response of a stream/aquifer system to recharge that occurs uniformly over groundwater basin is shown schematically in Figure 1.3. As illustrated in Figs. 1.3 A and B, the total amount of recharge that arrives at the water table between start time t_s and end time t_e is equal to R (units of length). During recharge events, the groundwater head (shown in Fig.1.3 C) may rise by the amount Δh (=R/S_y, where S_y is specific yield), and groundwater discharge increases over ambient conditions (Fig.1.3D). After recharge ends at time t_e , the groundwater head and discharge rate gradually return to pre-recharge levels. The falling limb of the groundwater discharge graph is referred to as the groundwater recession curve (Fig.1.3C).

The response of a stream/aquifer system to a passing flood wave was described by Barlow and Moench [1998] as follows: Prior to the flood wave (time prior to t_s in Fig1.4), the hydraulic gradient is toward the gaining stream; thus, groundwater discharge is to the

stream. As the stream stage rises (Figs. 1.4 A and B), seepage occurs from the stream to the aquifer (Fig.1.4 C), and groundwater head near the stream increases (Fig. 1.4 D), i.e., bank storage. The total volume of bank storage held by the aquifer continues to increase until shortly after the time of the flood peak (t_p in Fig.1.4 E). After the flood wave passes and stream stage falls, bank stage water is discharged back to the stream and groundwater heads return to pre-flood wave conditions.



Figure 1-3 Response of stream/aquifer system to a gradual recharge event: (A) rise of water table; (B) recharge hydrograph; (C) groundwater head hydrograph; and (D) groundwater discharge hydrograph (ts, start of recharge; te, end of recharge; R, total recharge; Δh , maximum rise of water table). (Adapted from [*Barlow and Moench*, 1998]



Figure 1-4 Response of stream/aquifer system to flood wave: (A) rise of stream stage and seepage of streamflow into aquifer as bank storage; (B) stream-stage hydrograph; (C) seepage hydrograph; (D) groundwater head hydrograph; and (E) bank-storage-volume hydrograph (ts, start of flood wave; tp, time of flood peak). [*Barlow and Moench*, 1998]

1.7 Control on NO₃⁻ Retention by Hydrological Events

The NO₃⁻ retention capacity of GSI is largely determined by GW-SW interaction affected by hydrological episodes. The strength of lateral interactions between surface water and groundwater varies with hydrological stage. Groundwater flow paths are directed more perpendicular to the channel during high discharge, while longitudinal

interactions at the GSI along stream channels become increasingly dominant when stream discharge is low [*Wroblicky, et al.*, 1998]. The effect of lateral hydrological exchange on nitrogen retention has been investigated recently. Schnabel [1986] found that NO₃⁻ decreased by 40-70% along the lateral transit. However, the stream showed cycles of increased NO₃⁻ concentration that persisted for days after storm events. Schnabel [1986] suggested that this pattern may result from a rise in water table that flushes NO₃⁻ from surface soils, or alternatively that NO₃⁻ removal declines because of the reduced residence time of groundwater during high flows. Many concerns have been given to the "flushing" mechanism accounting for episodic response of stream nitrogen chemistry [*Creed and Band*, 1998; *Creed, et al.*, 1996], but less has been given to the effect of increased hydraulic gradient induced by storms on the N biogeochemical processes within riparian zones. The other often neglected characteristic of GSI is the bi-directional hydrological exchange; reversed flow induced by bank storage could also have an important effect on the nitrogen dynamics.

Hydrological events can produce nearly instantaneous shifts in state that alter nitrogen cycling pathways [*Dahm, et al.*, 1998]. The redox potential at a specific place and time in GSI is a function of groundwater residence time, the rates of metabolism within groundwater and mixing between groundwater with differing hydrological sources and chemical characteristics [*Dahm, et al.*, 1998]. The distribution and rates of N cycling processes within the GSI are tightly linked to the redox potentials regulated by hydrological conditions. Dahm et al. [1998] pointed out that locations within the GSI with variable hydrological conditions may have more temporally variable microbial processes, process rates, and chemical conditions. Hydrological conditions affect N- retention efficiency by controlling the duration of oxic and anoxic phases. Dissolved oxygen concentration strongly influences nitrogen transformations because biogeochemical processes involving nitrogen are sensitive to the redox status. Dissolved oxygen concentration in GSI is regulated by biological activities which are influenced by hydrologic residence time and delivery of dissolved oxygen by hydrological exchange [*Duff and Triska*, 2000]. A key factor affecting the temporal dynamics of N cycling at GSI is discharge/recharge. Nitrate retention is higher during low-flow condition due to longer hydrological retention [*Valett, et al.*, 1996]. When bank storage occurs, oxygenated surface stream water enters the subsurface as groundwater recharge, supplying oxygen to sediments, which shuts down denitrification process by switching from the existing anoxic conditions to oxic.

1.8 Knowledge Gaps and Research Objectives

Current uncertainties about NO₃⁻ retention within watersheds stem from inadequate attention to combine the flow processes and NO₃⁻ transport from groundwater, through near-stream GSI into streams [*Hedin, et al.*, 1998]. What is currently missing from our understanding of N cycling in aquatic environments is the link between N transport within watershed groundwater and N solute losses at the watershed outlet. This crucial link is the groundwater-surface water interface. To understand how biogeochemical cycling at the hillslope scale translates into patterns of N flux at the watershed outlet we require a better understanding of the flow patterns by which N is delivered to the stream and how transport under different biogeochemical conditions impacts the chemistry of water that reaches the stream. Based on the reviewed literature, the investigation of hydrological effects on N cycles at the GSI is unexplored, as little information is available on the prediction of nitrate load emergence with surface water, or on the rate and extent of biogeochemical processes affecting the fate of nitrate at this interface. Specific questions to be addressed to evaluate the effect of GW-SW interaction on the GSI and subsequent microbial process relating to transformation of nitrate can be posed in several areas. Does the storm induced varying flow affect nitrate retention in the GSI? Does dissolved oxygen in the surface water infiltrate into the top portion of the sediments control N cycle by influencing reduction potential of the sediments? Separate from physical interactions, do temporal and/or spatial changes in redox conditions at the GSI influence the transformation capacity of the GSI?

Additionally, many of previous studies have been conducted on sites located in forested landscapes with low NO_3^- inputs. Few studies have examined the NO_3^- dynamics of riparian zones along headwater streams that receive high groundwater NO_3^- inputs from thick extensive aquifers in agricultural landscapes. In these landscapes, the subsurface permeability of aquifer and the greater depth or absence of an aquitard are important factors that influence the flowpath and removal of NO_3^- -contaminated groundwater.

To address these knowledge gaps and proposed questions, we examined an experimental hillslope in a low-relief watershed drained by Cobb Mill Creek on the eastern shore of Virginia to evaluate hydrologic controls of N transport at GSI in a temperate agricultural watershed and to provide additional information on the controls of N cycling and transport within different landscapes. In the Cobb Mill Creek, the groundwater-dominated stream, with low surface NO_3^- , the groundwater-surface water interface may be removing N from groundwater discharge and thus serving as a nitrate sink.

The objectives of this research were (1) to determine the processes responsible for

nitrate transformations in the GSI of the Cobb Mill Creek and to quantify how fast these

processes are carried out, (2) to develop models to accurately describe the processes, and

(3) to infer the dynamic NO₃⁻N delivery pattern influenced by hydrological episodes

from numerical simulations.

By achieving the project objectives listed above, we will be able to provide some

new understanding to the kinetics of nitrogen transformations at the GSI at normal

baseflow conditions and at hydrological episodes conditions.

1.9 References

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2 Groundwater-Surface water interface: A flow-throughmicrocosm study from Cobb Mill Creek, VA

2.1 Introduction

The intensive use of nitrogen fertilizers has led to increased level of nitrates in the groundwater of the Atlantic Coastal Plain [*Lowrance, et al.*, 1997]. Near stream riparian areas are discharge areas for groundwater to nearby streams [*Cooper*, 1990; *Jacobs and Gilliam*, 1985b; *Peterjohn and Correll*, 1984; *Pinay, et al.*, 1993]. It has been documented that the riparian zone is able to reduce nitrate concentration in groundwater passing through the groundwater-surface water interface (GSI) [*Hedin, et al.*, 1998; *Lowrance, et al.*, 1997; *Triska, et al.*, 1993b]. High organic carbon contents in the GSI and permanently saturated conditions favor denitrification. Nitrate reduction to N₂ takes place at high rates in a narrow zone often localized at the GSI [*Galavotti*, 2004; *Hoffmann, et al.*, 2000]. The effects of soil properties and hydrology on NO₃⁻ removal processes are not fully understood, but it appears that the hydrology of near-stream zones is one of the most important factors governing NO₃⁻ removal [*Cirmo and McDonnell*, 1997; *Hill*, 1996a].

Uncertainties in biogeochemical reaction rates can result in significant error in predicting groundwater solute flux. Accurate model predictions of the nitrate delivery through GSI require appropriate reaction rate estimates. The hydrological flow has been shown to significantly affect biogeochemical reaction processes [*Langner, et al.*, 1998]. Estrella, et al. [1993] showed that degradation rate parameters determined under batch conditions were not suitable for predicting contaminant transport. In addition, results obtained by Kelsey and Alexander [1995] suggest a strong dependence of the degradation rate parameters on the solute flow regime. Thus, our ability to estimate chemical loads across a wide range of transport conditions using a single set of reaction rates is reduced significantly given that the reaction rates vary with the hydrological flow.

In summary, quantifying biogeochemical processes within the GSI in laboratory experiments requires accurate simulations of subsurface flow patterns. In the experiments described herein, we developed a flow-through sediment microcosm using intact cores of stream sediment that simulated hydrological flow and that were used to identify and quantify nitrate transformation rates in the GSI of a small coastal creek in the Mid-Atlantic region. Flow-through column experiments, using continuous flow sediment cores where water was pumped through the columns, showed that denitrification rates could be achieved in the laboratory that were comparable with denitrification rates measured in the field [*Galavotti*, 2004; *Sheibley, et al.*, 2003a]. The aims of this study were (i) to estimate denitrification rates using continuous flow through intact cores, (ii) to investigate spatial (vertical) distribution of denitrification in the GSI, as indicated by high resolution vertical profiles, (iii) to evaluate the effect of hydrological flow on bulk denitrification rates.

2.2 Materials and Methods

2.2.1 Field Site Description

Cobb Mill Creek is a sandy first-order tidal creek that drains into Oyster Harbor, located in Northhampton County, on the Eastern Shore of Virginia (Figure 2-1). Cobb Mill Creek is a groundwater-dominated stream, with groundwater entering as diffuse discharge and as bankside seeps. The magnitude of groundwater discharge into the creek has been examined by stream tracer experiments (Mills, et.al, unpublished data), seepage meter measurements (Flewelling, unpublished data), and vertical hydraulic gradients in the streambed (chapter 4). The study site is located along a non-tidal portion of Cobb Mill Creek. This part of reach is characterized by a sandy bottomed channel with a base-flow water depth of 20-40 cm, which allowed for easy access to the sediments. The watershed comprises approximately 496 hectares and drains to seaside lagoons through the harbor at Oyster, VA. Agriculture is substantial throughout the region; within this watershed it occupies approximately 34.2% of the land use while 62.3% of the watershed is forested [*Mills*, 2002]. Surface relief is low (the maximum elevation in the watershed is less than 10 m), with greater slopes along regions immediately adjacent to the streams. Upland soils are dominated by the Bojac sandy loam (Coarse-loamy, mixed, semiactive, thermic Typic Hapludults), a well-drained soil with high permeability in the subsoil and in the substratum. Molena loamy sand (Mixed, thermic Psammentic Hapludults) dominates along Cobb Mill Creek [Phillips, et al., 1993]. These permeable soils are underlain by the shallow, unconfined Columbia aquifer, which consists of an eastward thickening wedge of unconsolidated sand and gravel [Calver, 1968; Mixon, 1989]. The hydrogeological research conducted in a nearby lowland about 1 km away shows high hydraulic conductivity 5.53 x $10^{-3} \pm 1.56$ x 10^{-6} cm s⁻¹ [*Hubbard*, et al., 2001]. The higher values are close to those estimated for the upland part of the watershed studied here. The Columbia aquifer is underlain by the Yorktown-Eastover confined aquifer at a depth ranging from 8-20 meters below ground elevation [*Richardson*, 1992]. Groundwater nitrate concentrations are elevated in the aquifer due to fertilizer use in agricultural areas, and they often exceed the U.S. EPA primary drinking water standards of 10 mg-N L^{-1} .

The aquifer is aerobic (often saturated with O_2), resulting in little attenuation of nitrate concentrations during transport through groundwater.



Figure 2-1 Location of the experimental field site at Cobb Mill Creek on the Eastern Shore of Virginia near Oyster, VA. Cobb Mill Creek drains into Oyster Harbor, situated on the mainland inshore of the barrier island chain. An experimental hillslope was set up within a narrow stream riparian strip located at the non-tidal part of the creek. Figure courtesy of Aaron Mills

2.2.2 Field methods

A dense network of wells and piezometer nests was installed on the hillslope to monitor the spatial and temporal patterns of nitrate concentrations and hydrological conditions in the subsurface (Figure 2-2). To date, there have been 10 piezometer nests and 16 wells installed in the stream and hillslope. Wells and piezometers are constructed of 1 inch I.D. PVC well casing. Wells penetrate 1.5 to 5 m below the water table and are screened at least 1 m above the maximum water table. The piezometers open at different depths based on which the vertical hydraulic gradients could be derived (Figure 2-3). A single transect of six, shallow, partially penetrating wells and piezometer nests, S1, N1, N3, N7, N9, N11 straddled the hillslope, nearly perpendicular to the stream and generally parallel to the direction of the shallow groundwater flow (Figure 2-2). This hillslope transect is characterized by a relatively steep slope immediately adjacent to the deeply incised stream channel. The stream bank is eroded by the cutting effect of the stream channel curvature. As a result, there is a vertical stream bank of ~1.2 m. A stream bank well, N1, was equipped with a pressure transducer to continuously record groundwater levels at 10-min intervals. Another transducer was installed in a stilling well in the stream to record the stream stage at 10- min intervals.

The entire hillslope site was surveyed and related to mean sea level as datum, to establish the elevation of the monitoring wells (and thus the elevation of the hydraulic head), and a general topography of the site (Figure 2-2). Stream stage levels were also related to the ASL (above sea level) system to allow a correct estimate of the hydraulic head gradient between the shallow wells and the stream.



Figure 2-2 a) 3-D map of topography of the experimental slope; red open circles represent piezometer nests, b) plan view of topography of the hillslope with experimental transect highlighted by the black line. Red solid circles from top to bottom, represent the upstream, middle stream, and downstream intact core sampling locations, respectively.

The hydrochemical characteristics along shallow groundwater flowpaths were studied with data gathered over 4 years. Galavotti [2004] showed that although the stream water in Cobb Mill Creek comes almost exclusively from groundwater discharge, the chemical characteristics of the stream water are very different from those of groundwater (Figure 2-4), due to highly high biological activity located in the GSI adjacent to the stream channel [*Galavotti*, 2004]. These conditions are stable over time through the whole observation period (Figure 2-4). Owing to the large quantity of particular organic matter in these sediments, bacterial mineralization is fast and anaerobic reactions such as denitrification occur [*Galavotti*, 2004]. Nitrate removal across the GSI is largely attributed to denitrification process suggested by high denitrification potentials found in the sediments [*Galavotti*, 2004].



Figure 2-3 the multi-level piezometer nest. The hydraulic heads (ASL) were calculated by subtracting the distance between water level and top of stick-up from the elevation (ASL) of the stick-up. Figure courtesy of Aaron Mills.

In line with the field observations described above, we consider that the major removal of NO_3^- during groundwater discharge takes place in the last few tens of centimeters of flow path into the stream. In this small zone, the flow is saturated and

considered one-dimensional. There is abundant particulate organic matter present in the stream sediments (Galavotti, 2004). During mineralization of organic matter, electron acceptors O_2 and NO_3^- are used by bacteria to oxidize the organic carbon in order from O_2 to NO_3^- , in decreasing order of thermodynamic energy.



Figure 2-4 Temporal variation of NO_3^- concentrations in stream water and stream sediment pore water from streambed piezometers (data from Galavotti, 2004 and S. Flewelling, unpublished). S1B-upstream piezometer at 84.8 cm depth, S1A-upstream piezometer at 58.7 cm depth; S2B-middle stream piezometer at 73.2 cm depth; S2A-middle stream piezometer at 56.2 cm depth; SW1-Stream water.

2.2.3 Experiments with Intact Sediment Cores

2.2.3.1 Flow-through experiment

Columns of intact cores were obtained from the stream sediments of a 20-m long reach in the Cobb Mill Creek by driving sharpened 5-cm diameter PVC pipes (Schedule 40) vertically into the sediments. Once the expected depths were reached, the headspace of cores were filled with the stream water and sealed at the top with a rubber stop. Then

the cores were slowly extracted. Once the cores were out of sediment, the bottom of cores was sealed with another rubber stop rapidly to prevent pore water drainage. The cores were sealed at each end by goop and returned to the laboratory, where each column was cut to obtain a relatively undisturbed section with a length of 45 cm to 60 cm. Laboratory columns were mounted vertically on a rack and PVC end-caps fitted with 2.5-mm outlets were sealed to the columns at both ends. Artificial groundwater (AGW) was slowly pumped into the columns in an upflow direction and fully permeated the columns in $1 \sim 2$ days. In order to prevent any photosynthetic processes promoted by light penetration through the translucent end caps, the column tops were covered with aluminum foil. The AGW used in the experiment contained (per liter of deionized water): 60 mg MgSO₄ \cdot 7H₂O, 20 mg KNO₃, 36 mg NaHCO₃, 36 mg CaCl₂, 35 mg Ca(NO₃)₂ and 25 mg CaSO₄·2H₂O [*H.Bolster*, 2000]. Insertion of sampling ports along the length of the core after collection allowed incremental sampling. Sampling ports consisted of stainless steel hypodermic needles (Outer diameter 1.5 mm, Hamilton) that penetrated into the center of the column. Three-way stopcocks were installed at the luer end of the syringe needles. Sampling ports were positioned starting 5 cm from the column inlet with a vertical interval of 5 cm for the first 8 ports, 3cm for the next three, and 2 cm for the last one port. A schematic of the experimental setup is shown in Figure 2-5.

The columns were operated at ~24°C, upright, and under up-flow conditions. A peristaltic pump was used to deliver the influent to the column. The influent concentration of nitrate was 15 mg L⁻¹, the highest value of pore water nitrate concentration observed in stream piezometers (Figure 2-4). For oxic columns, the concentration of oxygen in the influent was set to ~8 mg L⁻¹. While other anoxic column



Figure 2-5 Schematic diagram of laboratory-column Setup. A peristaltic pump was used to pump AGW into the intact cores from the bottom. The pore water samples were collected through the sampling ports. An automatic fraction collector was used for continuous sampling of effluent.

runs were conducted by sparging the influent with N₂ gas for 20 minutes to investigate the effect of oxygen in the influent groundwater on the denitrificaiton rates. The outlet from the column was connected to an automatic fraction collector for continuous sampling measurement. Three intact cores were flushed by deionized water to removal background solute and were operated over 4 days (3~4 pore volume) to allow achievement of steady state. Then pore water samples were collected from intact sediment cores from each sampling port using a 3-mL syringe to determine initial concentration profiles. Pore water samples were centrifuged (with 704×g×10min) before analyzing. To investigate the effect of hydrodynamic flow on the nitrate attenuation process, several middle-stream cores were exposed to varying flow velocities. The flow rates of the solution varied between 0.3 and 5 cm h⁻¹, which are representative seepage rates under baseflow conditions (Figure 2-7). Transport parameters for each column were estimated by modeling breakthrough curves of Cl^{-} as a conservative tracer by a computer transport model CXTFIT2.0 [*Toride*, 1995].

2.2.3.2 Characterizing the Cores

After each flow-through column experiment was finished, the sediment core was cut open lengthwise and immediately sub-sampled at 5-cm intervals using a 10-mL syringe mini-corer The sub-samples were used to measure porosity, bulk density, and total organic matter content.

Determination of the porosity and density of the sediments was based on standard methods. The sub-samples were weighed to determine their wet mass, and oven dried at 105°C overnight. After drying, the sediment was re-weighed to determine the water loss which was equated with the pore volume. Total organic matter in the sediment was determined by weight loss on ignition of the dried samples at 500°C for at least 24 hours.

Falling head measurements were conducted to measure hydraulic conductivities of intact cores. Briefly, the cores were sealed on both ends by modified plunger and stopper fitted with outlets. CO_2 was purged through the cores to displace the air and for easier saturation to ensure no leakage from the column. Hydraulic conductivity (Ks) was calculated as:

$$Ks=(L/T)*ln(H1/H2)$$
 Equation 2-1

Where L was the column length; T is time taken for the head drop; H_1 is the initial head; H_2 is the final head.

2.2.3.3 Chemicals and Analytical Methods

Oxygen concentrations were measured with a DO meter. To conduct these measurements, a small flow-through system (unplugged syringe with the similar diameter of DO probe) was connected to the sampling port. Oxygen concentration was measured in situ while the pore water flowed through the port and filled the bottom of syringe (around 2 mL). Nitrate and chloride concentrations were determined using a Dionex Ion Chromatograph with a Dionex IonPac AS4A 4×250mm Analytical Column, which requires a sample volume of 1 mL. The eluent solution consisted of 1.44 mM Na₂CO₃ and 1.36 mM NaHCO₃ and was pumped at a flow rate of 2 mL min-1. The regenerant solution used was 0.028 N H₂SO₄. The eluent and regenerant were pressurized with helium gas with the valve pressure at approximately 70 psi.

2.2.4 Calculation of Denitrification Rate

The denitrification rate is derived from a steady state reactive transport equation in an incompressible porous medium by assuming dispersion is negligible:

$$v \frac{\partial N}{\partial x} = -R$$
 Equation 2-2

where *v* is the average linear pore velocity, N is nitrate concentration, and R is the denitrification rate. Integrating the equation from x=0 to x=L yields:

$$R = \frac{N_{in} - N_{out}}{L/v}$$
 Equation 2-3

in which N_{in} is nitrate concentration in inflow, N_{out} is the nitrate concentration in the outflow, *L* is column length, and *L/v* is the residence time.

2.3 Results

2.3.1 Field observation

The groundwater flow pattern derived from the measured hydraulic heads showed a lateral flow at the hill slope and upwelling of groundwater in the near-stream zone next to the channel. The flow pattern is shown as yellow arrows in Figure 2-6.



Figure 2-6 Cross-section view of NO_3^- distribution from the sampling event at Jan. 31, 2005 made by ordinary krigging method. Sampling points are represented by circles. The NO_3^- plume is detectable at the bottom left and right. This represents old NO_3^- -contaminated groundwater which flows deep as it discharges toward the stream. The low NO_3^- concentration observed in shallow groundwater might represent combined biological removal and dilution by young, uncontaminated groundwater from local recharge.

Nitrate concentrations decreased along the transect, mainly in the vertical direction in the upwelling area underneath the streambed (Figure 2-6). In contrast to the high NO₃⁻ concentration in deep groundwater, NO₃⁻ has decreased significantly at the discharging point. The concentration profiles in the aquifer showed only small variations with distance to the stream except near the banks. In fact, most of the chemical changes in the water were observed in the submerged superficial sediments of the stream. At the streambed piezometers, NO₃⁻ concentration was in the range of 9-13 mg L⁻¹ at 60 cm depth, but NO₃⁻ in the stream water was 2 mg L⁻¹. The distribution of NO₃⁻ suggests that a

deep flow path led to the stream that may have traveled beneath the hillslope from the adjacent agricultural fields. The deeper water contained higher nitrate concentrations than the water following a shallower flow path near the water table and that followed the ground-surface contours. This evidence suggested two distinct ground water flow domains along the experimental hillslope.

The groundwater seepage rates were estimated by Darcy's Law. Given a mean vertical saturated hydraulic conductivity of 1.7×10^{-3} cm s⁻¹ (from the intact cores), and a mean vertical hydraulic gradient of 0.18 from piezometer measurements in the field, the calculated pore water discharge rate was 3.24 cm h⁻¹. This value matches the value of 3.08 cm h⁻¹ from *in situ* mean seepage rates measured by seepage meters (Figure 2-7).

As expressed in Equation 2-3, the removal rate of nitrate, R, is a function of the flow rates and concentration gradients in the groundwater flow path. The sharpest concentration gradient along the flow path occurs at upwelling groundwater below the stream channel. Taking the upwelling area into account as a zone of enhanced denitrification activity, the removal rates of nitrate could be calculated from Equation 2-3. The measured nitrate concentration in the deep groundwater was about 10 mg L⁻¹, while stream water is about 2 mg L⁻¹ (Figure 2-4), given the averaged seepage rate of 3.08 cm h⁻¹, the calculated mean nitrate removal rate is 422.4 mmol N m⁻² d⁻¹.



Figure 2-7 Histogram of the groundwater seepage rate (cm h⁻¹) measured by seepage meters

2.3.2 Laboratory Experiments with Sediment Cores

2.3.2.1 Breakthrough curves

When Cl⁻ (the conservative tracer) was introduced into cores in the artificial groundwater, Cl⁻ reached a plateau concentration (C/C₀ = 1) in the outlet after about 2 pore volumes and remained constant the rest of the experiment. The breakthrough of NO_3^- yielded a sigmoid curve, which leveled off at maximum of 60% influent concentration after about 2 pore volumes. Only 60% of the influent NO_3^- was recovered as opposed to 100% of the conservative tracer, chloride. NO_3^- and Cl⁻ reached their plateau simultaneously, indicating that there was no significant retardation in NO_3^- transport. The breakthrough curves of chloride were fitted by CXTFIT 2.0 [*Toride*, 1995] to obtain the hydrodynamic parameters of the sediment cores for further modeling.



Figure 2-8 Breakthrough curves of chloride and nitrate. The dots are experimental data and the solid line is simulation by CXTFIT 2.0 [*Toride*, 1995]

2.3.2.2 Vertical profiles

The pore water profiles of nitrate and chloride from three flow-through columns were consistent with the profiles measured in the field by Galavotti [*Galavotti*, 2004]. Vertical profiles of chloride and nitrate during upflow through the sediment were similar in all three cores as shown in Figure 2-9, 2-10, and 2-11. Most of the nitrate reduction occurred in the top 30 cm and after flowing though the entire length of cores. However, nitrate gradients differed among the cores. About 59% of the nitrate in the influent was removed in the downstream core under a flow velocity of 2.81cm h⁻¹. The depthintegrated (bulk) nitrate removal rate calculated using Equation 2-3 was 0.39 mg NO₃-N $L^{-1}h^{-1}$ (Table 2-1), while the upstream core showed a maximum removal efficiency at 100%. The vertical profile of nitrate in the upstream core showed the nitrate was depleted 4 cm below the sediment surface. The bulk nitrate removal rate was as high as 0.55mg $NO_3^{-}-N L^{-1} h^{-1}$ (Table 2-1). In contrast to the high nitrate removal capacities shown in upstream and downstream cores, the core from the middle of the reach showed only 37% of the nitrate concentration was removed under a flow velocity of 2.34 cm h⁻¹ yielding a bulk removal rate of 0.23 mg NO₃-N L⁻¹ h⁻¹ (Table 2-1). The ranked organic matter content of the three cores was the same as the nitrate removal rate, i.e., upstream>downstream>middle stream.



Figure 2-9 Vertical profiles of chloride and nitrate for the middle stream core at flow velocity of 2.34 cm⁻¹ (Solid circle-Cl⁻, open circle-NO₃⁻).. Groundwater flow direction is upward.



Figure 2-10 Vertical profiles of chloride and nitrate for the downstream core at a flow velocity of 2.805 cm h^{-1} (Solid circle-Cl⁻, open circle-NO₃⁻). Groundwater flow direction is upward.



Figure 2-11 Vertical profiles of chloride and nitrate for the upstream core at flow velocity of 2.06 cm h⁻¹ (Solid circle-Cl⁻, open circle-NO₃⁻). Groundwater flow direction is upward.

Calculation of the specific nitrate removal rate at each of the measured depths showed that the nitrate removal rate tended to increase from the bottom to the top of the sediment Figure 2-12. In the three cores with sediment from depths of 40 to 60 cm, there was no denitrification in the horizons with a low organic matter content (<0.3%) (Figure 2-13). However, in the upper part of cores at depths above 30 cm, denitrification took place at comparatively high rates (>0.19 mg NO₃⁻-N L⁻¹ h⁻¹) with organic matter >0.5%. The denitrification rate reaches a maximum of 0.5~2.07 mg NO₃-N L⁻¹ h⁻¹ at the depth of 5~17cm, followed by a steep decrease due to depletion of NO₃⁻ (Figure 2-12).

Table 2-1 The bulk nitrate removal rates observed from three intact cores from different locations			
	Pore water	Depth averaged OM content	Bulk NO ₃ removal rate
	velocity (cm h ⁻¹)	(%)	$(\text{mg NO}_3^\text{N L}^{-1}\text{h}^{-1})$
upstream	2.06	4.26	0.55
middle stream	2.34	0.38	0.23
downstream	2.81	1.36	0.39



Figure 2-12 Vertical distributions of calculated nitrate removal rates in mg $NO_3^{-}N L^{-1}h^{-1}$ using vertical profiles of nitrate from three cores.



Figure 2-13 Vertical profiles of organic matter content from three cores.

2.3.2.3 The effect of flow rates

Nitrate removal efficiency (expressed as percentage removed) was greatly affected by changing flow rates. In general, effluent NO₃⁻ concentrations were greatest under the highest flow rate. The nitrate removal percentage, *r*, shows the negative relationship with pore water flow velocity, *v*. (Figure 2-14). The relationship between *r* and *v* showed that *r* is very large (>80%) when *v* <0.5cm h⁻¹, and decreases sharply at *v* < 1.5 cm h⁻¹, then remained relatively low at *v* > 3 cm h⁻¹ (r<20%) (Figure 2-12). To illustrate the observed relationship, a best-fit curve was included in (Figure 2-14) of the form:

$$r = a \times e^{bv}$$
 Equation 2-4

where a and b are fitted constants (a=107.18, b=-0.6729, R^2 =0.9359).



Figure 2-14 The relationship of pore water velocity and percentage nitrate removal

The bulk nitrate removal rate (R) of the column fed by the oxygenated influent showed a positive relationship with flow velocity (v) (Figure 2-15). R reached as high as 0.73 mg NO₃⁻-N L⁻¹ h⁻¹ and then flattened out when v > 4 cm h⁻¹. In contrast, the bulk nitrate removal rate showed a complicated relationship with pore water velocity. *R* increased sharply starting from 0.08 mg NO₃⁻-N L⁻¹ h⁻¹, reached the maximum rate at about 0.2 mg NO₃⁻-N L⁻¹h⁻¹ (0.343 mmol NO₃⁻-N L⁻¹ d⁻¹) when v was around 1.5-2 cm h⁻¹, then decreased with increasing flow velocity when v > 2 cm h⁻¹.



Figure 2-15 The relationship of porewater velocity and the bulk denitrification rates for the oxic colomn fed by anoxic influent.



Figure 2-16 The relationship of porewater velocity and bulk denitrification rates under oxic conditions.

2.4 Discussion

In this study, intact cores taken from the streambed were used to examine nitrogen cycling in the GSI. Use of sediment cores enables the inclusion of physical and hydrodynamic properties, such as convection, dispersion, and sorption while measuring N transformation processes. The biota in a core sample is undisturbed and stratigraphic locations of important microbial populations are preserved. Intact cores allow the study of a more complete system, and therefore provide a more thorough and realistic representation of *in situ* processes.

The intact-core experiments focus on a one-dimensional analog of the streambed where groundwater discharges into the surface water. The assumption of one dimension is valid only in areas of the stream that have large vertical hydraulic gradients that overwhelm any horizontal gradients imposed by the slope of the streambed, which is the case for our experimental part of the Cobb Mill Creek. Although the flow may be predominately vertical under these conditions, in general, the flow patterns are multidimensional in streambeds. Understanding of one-dimensional hyporheic nitrogen processing can be used as a foundation for further studies that can involve more complex flow patterns. The focus of this project is on the kinetics of hyporheic nitrogen processes, which are best studied using a simple, well-characterized, one-dimensional flow regime.

The comparison of vertical profiles of chloride and nitrate suggested a strong biological reactivity of nitrate (Figure 2-9,2-10,2-11). Although neither nitrate nor chloride is absorbed by soil particles, chloride does not undergo biological transformations, and, therefore, concentrations cannot be biologically controlled. The decrease in nitrate concentration in the vertical dimension in the shallow stream sediments did not correspond to a decrease in chloride, and NO₃⁻ was not retarded, suggesting that the nitrate loss results from a biological process.

2.4.1 Field flow and transport pattern

Nitrate in groundwater apparently flows conservatively through the Cobb Mill Creek aquifers until just before the ground water discharges into the stream through the GSI [*Callaghan*, 1999]. In the stream sediments, the discharging ground water encounters organic matter which stimulates heterotrophic microbial activity that first removes O_2 , and then the NO_3^- is denitrified to N_2 by bacteria that use it as an electron acceptor. Because N_2 is rapidly lost to the atmosphere, denitrification is a permanent sink for nitrate transported in streams.

The groundwater flow pattern characterized by lateral flow at the shallow aquifer and upwelling of groundwater in the zones adjacent to the stream has previously been reported by several investigators [*Hedin, et al.*, 1998; *Hoffmann, et al.*, 2000; *Spruill*, 2000]. The upward flow is fed by deeper water from the aquifer after traveling on the longest flow path. The high nitrate concentrations found in the pore water 60-80 cm beneath the streambed are similar to those found at depth upgradient, suggesting that that there is no significant biological nitrate removal along the deep groundwater flow path. 2.4.2 Spatial variability of nitrate loss rate

In calculating denitrification rates (Equation 2-3), plug flow was assumed, a condition in which advection dominates while molecular diffusion and hydrodynamic dispersion are insignificant. The magnitude of advection compared to dispersion can be evaluated from the Peclet number (P_e), defined as *vL/D* where *L* is the characteristic length, *v* is linear velocity, and *D* is the dispersion coefficient. With a mean linear

velocity *v* of 3 cm h⁻¹, column length of 50 cm, and a value of *D* of 8.0 cm² h⁻¹, P_e is 18.75. At this value, hydrodynamic dispersion is much smaller than advection, suggesting that the transport of NO_3^- is advection dominated.

Pore water sampling along the flow-through columns permitted obtaining highresolution nitrate profiles to examine the heterogeneity of biogeochemical activity close to the stream-sediment surface. Along the flow path from the approximately 60-cm depth to the sediment surface, the majority of the nitrate was lost in the top 30 cm. Furthermore, the nitrate removal rates (mass balance calculation) were greatest in the top 20 cm of the intact cores (Figure 2-12). The sediment conditions in this shallow zone were conducive to denitrification: organic matter was sufficient, the upwelling pore water was rich in NO_3^- , and reducing conditions became dominant as microbes oxidizing the organic matter first used up the oxygen before turning to the nitrate, evidenced by low platinum electrode potentials in the upper portion of sediment cores [*Galavotti*, 2004].

The chemical profiles in the flow-through columns in operation generally matched the profiles obtained by *in situ* measurements in both intact cores and in the stream sediments using mini drive samplers [*Galavotti*, 2004]. Unlike static batch experiments, the cores are relatively undisturbed and therefore maintain more natural chemical gradients and biomass distributions. In addition, unlike batch experiments, they allow for hydrologic characteristics such as diffusion, dispersion, and advection which influence biogeochemical process rates [*Sheibley, et al.*, 2003a]. Thus, the column experiments simulate the coupled hydrologic and biological processes, allowing estimates of nitrate delivery under quasi *in situ* conditions.

The high spatial variability of nitrate removal was shown by the more than 2-fold differences in cores distributed longitudinally by only several meters along the stream channel. This variability is presumably a result of differences in carbon availability and carbon content among the sediments (Figure 2-13). The narrow bands of deposited organic material may not be evenly distributed throughout the upwelling area, indeed visual examination of a number of dissected cores shows that they are not. The highest nitrate removal rate was found upstream near the stream curve, where fine-grained sediment accumulation and organic matter deposition and burial from nearby plants occurs to the maximum extent, indicated by organic matter content as high as 25% at the depth of 10cm in the upstream core (Figure 2-13). This is consistent to the previous finding that the highest organic matter content was found in sediments from the cross section of the stream curvature [Galavotti, 2004]. Compared to the upstream sediment, the sediment from the middle stream, where much less organic debris and foliage were found on the streambed visually, has much lower nitrate removal rate, and also has an order of magnitude less organic matter Table 2-1.

Differences in NO₃⁻-removal capacities among the depths were similarly the result of differences in microbial activity that, in turn, are correlated with organic matter (Figure 2-16). The results from the column experiment imply that denitrification in the deeper sediment is limited by carbon and the presence of oxygen. The lack of nitrate removal at these depths is concomitant with low organic matter content, while the (shallower) depths with significant denitrification activity also have a higher organic matter content (Figure 2-13). The capacity for the GSI to denitrify is dependent on the *in situ* denitrifier biomass and activity [*Tiedje*, 1982]. It was suggested that carbon is more important than oxygen in determining the denitrifying enzyme content of habitats although oxygen inhibits enzyme activity and represses synthesis of new denitrifying enzymes [Payne, 1973; Tiedje, et al., 1982]. Organic matter not only serves as electron donor for denitrification but also creates the hypoxic conditions necessary for denitrification to occur. The switch from oxic to anoxic conditions first eliminates oxygen inhibition, then releases the synthesis of additional denitrifying enzymes. In sediments from the Cobb Mill Creek, the content of DOC is apparently controlled by indigenous particulate organic carbon rather than stream-water-induced DOC since hyporheic exchange is very limited, as suggested by constant upward hydraulic gradients and results of a stream tracer experiment (data not shown). Laboratory flow-through microcosm studies without addition of DOC showed significant nitrate removal in intact cores. Long contact times allow the release of DOC from the buried organic matter and the subsequent development of reducing condition. There was a significant positive correlation between denitrification rates and total organic matter content (Figure 2-16). Several studies have also shown that denitrification in riparian wetland soils is highest in surface horizons and depends on organic matter content [Hoffmann, et al., 2000; Willems, et al., 1997].





In addition to the differences in organic matter content, it should also be noted that pore water velocities were different for each sediment layer in the intact cores, although the specific discharges (Darcy velocity, q) were the same. Pore water velocity, defined as the specific discharge divided by the porosity, was approximately two times lower in the surface loamy layer compared to the deep sandy layer. Low flow velocity increases the reaction rate by increasing residence time. In addition to high microbial activity (as a result of large amounts of organic matter), enhanced nitrate diffusion to sites of denitrification and long hydraulic residence times at low pore flow velocity increase denitrification rates in the surface carbon-rich layer.

The high variability of nitrate-loss rates observed in this study will induce variable nitrate loadings in groundwater discharge. The present study indicates that a large spatial variability of NO₃⁻ removal capacity is present in the GSI, where both nitrate free and nitrate rich seepage could occur. It is mainly induced by spatial variability of organic matter content. Additionally, the variable groundwater seepage rates would further contribute to the variability of nitrate flux from groundwater seepage. Some portions of the groundwater may flow fast by preferential flow or horizontal flow (bank discharge), and thus bypass the sites where denitrification takes place. The horizontal seepage (see Chapter 5). This difference in pore water velocities between the horizontal flow and upward flow certainly accounted for some of the large differences in denitrification rates and efficiency. Thus, stream water is a mixture of different inflow with different nitrate signatures.

2.4.3 The effects of flow on nitrate reduction rates

Nitrate removal efficiency was highly affected by pore water velocity (v)Figure 2-14). When v <0.4 cm h⁻¹ in oxic columns (columns fed by oxygenated influent), no NO_3^- breakthrough was observed. In other words, the residence time of beyond two days is long enough to allow complete nitrate removal, assuming the thickness of reaction zone of 20 cm. In contrast, 100% of nitrate breakthrough when v > 5 cm h⁻¹ (residence time of 4 hours). The residence time is too short to allow any biological reactions.

Bulk (depth integrated) nitrate removal rates were greatly affected by changing flow velocity (Figure 2-14). For NO_3^- transport process with O_2 involved, the flow velocity could affect denitrification activity mainly in two counteracting ways. The increased oxygen concentrations in the sediment could have a direct inhibitory effect, while the enhanced supply of nitrate could promote denitrification if the reaction kinetics is nitrate limiting. The net result depends on what is limiting denitrification in a sediment, nitrate availability or the extent of anoxic environment. The extent of anoxic environment seemed to limit denitrification in sediment cores within the higher range of flow velocities when cores were better aerated by increasing hydraulic loading. While within the lower range of flow velocities, increasing hydraulic loading enhance denitrification because of a better nitrate supply.

We might be able to understand this mechanism by comparing the denitrification rate response in anoxic columns with that in oxic columns. We observed that denitrification rates increased with increasing flow rates in the anoxic column (with deoxygenated eluent) (Figure 2-16), while denitrification rates initially increased with increasing flow rates and then decreased with further increasing flow rate in oxic columns (Figure 2-15). Williams et al. [1997] found a similar relationship between denitrification rates and flow rates as we found in oxic columns. The highest removal rate (0.2 mg NO₃⁻-N L⁻¹ h⁻¹) in these cores was observed in the flow velocity of 1.6c m h⁻¹. This rate was almost 3 times greater than the removal rate observed at either *v*=0.3 cm h⁻¹ and *v*=5 cm h⁻¹ (Figure 2-16). The increased bulk nitrate removal rate when *v* < 1.5cm h⁻¹ might be attributed to either the nitrate limiting condition or diffusion constraint or both.

nitrate ($K_N = 2 \text{ mg } L^{-1}$), the order of the denitrification reaction changes from zero-order (nitrate is not limiting) to 1st order (nitrate is limiting). The increasing flow rates result in an increased supply in NO₃⁻ per unit time. Nitrate removal rates increases with increasing flow velocity because the concentration of nitrate throughout the microcosms is higher and/or that increases the diffusion of nitrate into areas adjacent to preferential flow-paths. However, the initial increase in denitrification rate was always less than the increase in NO₃⁻ supply, resulting in an increased effluent NO₃- concentration (decreasing removal efficiency) (Figure 2-14).

With a further increase in flow rate, the denitrification rates started to drop in oxic columns (Figure 2-16) because oxygen inhibition effect surpassed the effect of nitrate availability. The flow rate at which denitrification rates started to drop was dependent upon the denitrification capacity of the core which was related to sediment properties. The decrease started at higher flow rates in the cores with the organic-matter rich sediments compared to those with sediments having less organic matters. A flow velocity of 1.6 cm h^{-1} was the turning point in the cores used herein, comparable to 1.36 cm h^{-1} in as reported by Willems et al. [1997]. These authors [*Willems, et al.*, 1997] proposed that at the higher flow rates, denitrification may be limited by the rate of NO₃ diffusion to the sites of denitrification, resulting in lower denitrification rate. In the present case, it is proposed that the decreasing nitrate removal rate at flow velocities higher than 1.6 cm h^{-1} is probably due to a shorter nitrate-reduction zone induced by oxygen propagation upward to the shallower region. That is, rapid flow does not allow adequate time for complete removal of oxygen early in the transfer of water upward through the organicrich sediment layer. A zero order reaction would indicate a relatively constant removal

rate response to the velocity when nitrate serves as the single electron acceptor, which was suggested by rates flattening out in the O_2 free column (Figure 2-14). However, when oxygen consumption confounds nitrate removal, the increased flow velocity can lead to the propagation of redox front higher in the profile (chapter 3), in other words, the length of denitrification zone is reduced in response to the upward displacement of the oxygen front, given the fixed length of the reactive domain. As a result, observed bulk nitrate removal rates would decrease with increasing flow velocity. The detailed mechanisms involved would be investigated using the computer model presented in Chapter 3.

The reaction rate is highly influenced by hydrodynamic flow conditions. The measurements under different flow velocities would lead to different bulk reaction rates. Seepage measurements show the great variability in groundwater seepage rates (Figure 2-7). This variability makes the estimation of chemical fluxes implausible with a single reaction rate under different flow conditions. The lack of a constant bulk reaction rate under varying flow conditions might be overcome by the mathematic modeling of coupled multi-species reactive and transport processes, as will be demonstrated in Chapter3.

2.4.4 Denitrification rates

The denitrification rates obtained in this intact core study range from 68.6 to 490.3 mmol N m⁻² d⁻¹ (Rates were converted from mg N L⁻¹ h⁻¹ to mmol N m⁻² d⁻¹ using the ratio of sediment volume to cross-sectional area). These rates are among the highest reported. Other studies have shown denitrification rates in the range of 3.6 to 52.9 mmol N m⁻² d⁻¹ [*Cooper*, 1990; *Haycock and Burt*, 1993; *Pinay, et al.*, 1993]. Nitrate reduction rates were found, depending on nitrate load, to be up to 643 to 715 mmol N m⁻² d⁻¹, with a

nitrate reduction efficiency of 100 and 84%, for a riparian site and a rye-grass site, respectively [*Haycock and Pinay*, 1993]. Denitrification rates in the range of 359 to 599 mmol N m⁻²d⁻¹ were found in the waterlogged soil of a minerotrophic fen [*Hoffmann, et al.*, 2000]. Furthermore, Schipper et al. [1993] found high denitrification rates (80mmol N m⁻²d⁻¹) in an organic riparian soil receiving groundwater from a spray site irrigated with sewage. The reason for the much higher rates in present study in comparison to other environments is the biogeochemical status of the GSI. The zones not only receive a continuous supply of NO₃⁻ by drainage from upslope, but they are also kept predominantly anoxic to support such high rates of denitrification. This suggests that incoming O₂ is consumed rapidly. Our spatial pore water profiles indicate that the transition from O₂ respiration to NO₃⁻ to a dominantly anaerobic and organic carbon rich environment creates a high selection pressure in favor of denitrifiers [*Schipper, et al.*, 1993].

The mean denitrification rate from oxic columns (361.3 mmol N m⁻² d⁻¹) is slightly lower than mean field observed denitrification rates (422.4 mmol N m⁻² d⁻¹). This might be attributed to higher dissolved oxygen level in column influent than *in situ* condition. The well-oxygenated influent might not represent *in situ* hyoxic conditions. Oxygen levels of pore water in the laboratory column are an important factor in controlling the laboratory determined denitrification rate. Denitrification rates obtained from the anaerobic laboratory microcosm study showed denitrification rates as high as 592.0 mmol N m⁻² d⁻¹ at a flow velocity of 2.8 cm h⁻¹ and 748.4 mmol N m⁻² d⁻¹ at a flow velocity of 4cm h⁻¹ (Figure 2-15). This suggests an anoxic or hypoxic condition in groundwater 60~80 cm beneath the streambed. This intact-core microcosm study suggests that hypoxic conditions might prevail in upwelling groundwater even before reaching the surface sediment. Higher oxygen condition in the laboratory aerobic columns than the *in situ* levels in the sediments would largely underestimate the dentrification rates. It is also noted that several conditions are different in the laboratory and field sites. Firstly, groundwater temperature at the study site is about 15 °C compared to 24 °C in the laboratory. Thus laboratory-derived field denitrification rates could be slightly overestimated. Secondly, the groundwater flowing beneath the stream sediments contained between 9 and14mg NO₃-N L⁻¹ (Figure 2-4), while the nitrate concentration in laboratory influent was 15-20mg NO₃-N L⁻¹. Depending on the denitrification kinetics, the denitrification rates could vary with input concentration of NO₃⁻ (i.e. 1st-order or Monod kinetics).

The high denitrification rate measured in both laboratory and field in the present study show the capacity for nitrogen removal in the investigated GSI. The riparian area, especially the narrow zone comprising the groundwater surface water interface, is often the optimal location for nitrate transformations [*Cooper*, 1990; *Lowrance, et al.*, 1984b; *Peterjohn and Correll*, 1984; *Triska, et al.*, 1993a]. The results in the current study correspond to those findings, approximately 95% of the nitrate was removed and the highest denitrification rate was found at the GSI at Cobb Mill Creek, given that even in the absence of a riparian wetland along the study creek. Hoffman et al. [2000] observed the highest denitrification rates at 0~69cm depth of minerotrophic fen. Hedin et al. [1998] found that denitrification was restricted to a narrow zone at 20-40 cm deep near a stream bank where a lateral flow of pore water with high DOC from organic surface sediment

interacted with the vertical upwelling of nitrate-rich groundwater. The results of the Cobb Mill Creek study support a similar but slightly different conclusion, that denitrification occurs in the shallow streambed, where upwelling of nitrate-rich groundwater seeps through the carbon-rich surface sediment.

2.5 Conclusion

The NO₃⁻ flowing vertically upward through the soil column is reduced to N₂ by denitrifying bacteria in the sediment near the surface, reducing the NO₃⁻ concentration before it reaches the stream. This implies that the groundwater surface interface, even at high NO₃⁻ loading, will have the capacity to remove NO₃⁻ before it is discharged into the stream. A simple input-output mass balance calculation from the field observations shows a nitrate removal rate of 422.4 mmol N m⁻² d⁻¹. The mean denitrification rate from the laboratory microcosm study was 361.3 mmol N m⁻² d⁻¹. Anaerobic column results indicated that the smaller denitrifying capacity observed in laboratory experiments was probably attributed to more oxic condition than that in the field. Generally, the present study confirms that groundwater surface water interface represent active sites of nitrogen removal, and our direct laboratory experiments further support that NO₃⁻ removal occurs at top 20 cm surface layer and NO₃⁻ loss rate decrease with depth, which also corresponded well to sediment organic matter content.

Flow velocity highly influenced nitrate removal at the GSI. Nitrate removal efficiency was reduced with increasing flow rates. While bulk nitrate removal rate increased at low flow rates and decreased at high flow rate. Nitrate reduction was enhanced initially by increasing nitrate flux within the lower range of flow rates. Higher flow rates most likely limit diffusion of NO_3^- to the sites of denitrification, and reduce the

denitrification zone by expansion of the oxygen consumption zone, resulting in reduced NO_3^- removal. Therefore, a limitation of denitrification by both nitrate availability and the extent of anoxic environment was very probable in the sediment cores. Thus, local hydrology may be another determinant factor for nitrate removal besides the organic matter. Further insight into the local hydrology combined with spatial information about organic matter is required for the development of appropriate estimate of nitrate buffering effect of GSI. A mathematical modeling considering coupled reaction and transport processes of multi-species would be a promising tool to study the dynamics of denitrification influenced by hydrology, and will be explored in subsequent chapters.

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3 Nitrate Attenuation Process at GW-SW Interface--Balanced by Transport and Reaction

3.1 Introduction

The importance of groundwater as a contributor of nutrients from nonpoint sources to coastal and estuarine water is receiving increasing attention [*Bencala, et al.*, 1984; *Hedin, et al.*, 1998; *Weiskel and Howes*, 1991]. Eutrophication of marine and estuary environments is a problem caused mainly by the increased transport of dissolved nitrogen compounds from coastal groundwater [*Denver*, 2003; *Lowrance, et al.*, 1997; *Phillips, et al.*, 1993]. The groundwater surface water interface (GSI) has been identified as an area of high biogeochemical activity, often acting to control fluxes of nitrogen from terrestrial to aquatic ecosystems [*Bencala, et al.*, 1984; *Galavotti*, 2004; *Hedin, et al.*, 1998; *Jonns and Mulholland*, 2000; *Weiskel and Howes*, 1991]. It was found that the groundwater seepage rate has a profound impact on microbial processes through the GSI, since it controls the transport of electron acceptors and nutrients in saturated sediments [*Stepanauskas, et al.*, 1996; *Willems, et al.*, 1997]. Despite these findings, a quantitative estimate of linkage between hydrology and biogeochemistry in the GSI remains largely unmeasured [*Bencala, et al.*, 1984; *Hedin, et al.*, 1998; *Weiskel and Howes*, 1991].

There has been limited work on the fate of nitrogen advected directly through stream GSI [*Galavotti*, 2004; *Hedin, et al.*, 1998; *R.L.Chen and D.R.Keeney*, 1974]. The nitrate delivery through the GSI at the Cobb Mill Creek, Virginia, was investigated experimentally in Chapter 2. The flow-through column experiments were used to simulate groundwater discharge processes. It was found that intact cores taken from the stream sediment could successfully remove nitrate from the higher-NO₃⁻ artifical groundwater.

A useful theory for the reactive transport of NO_3^- , as well as for the transport of other redox-sensitive contaminants, relies on the ability to quantify the kinetics of these interacting microbial processes under conditions of advective-dispersive pore-water flow. Mathematical models that quantify coupled advective-dispersive transport and oxidation-reduction are available [*Chen, et al.*, 1992; *Kindred and Celia*, 1989; *Kinzelbach, et al.*, 1991; *Molz, et al.*, 1986; *Widdowson, et al.*, 1988]. Lensing et al. [1994] presented a model for transport and biodegradation in an aquifer including thermodynamic equilibrium modeling and four different species of bacteria. Kim et al. [2004] used a dual biofilm model to describe overlapping zones of aerobic respiration and denitrification observed in laboratory packed sandy columns. However, with few exceptions, these models are yet to be evaluated against experimental data using intact cores and/or field observation. Consequently, identifying of the mechanism that controls the dynamics of redox reactions remains uncertain.

The present study intends to contribute in the effort to fill these gaps in existing knowledge. In this study, intact core experiments were conducted to study biogeochemical processes of NO_3^- . Compared to traditional packed sediment columns, the experimental approach adopted here preserved the porous structure of the natural sediments and provided experimental systems that mimicked the solid-solution ratio, flow regime, distribution of microbes, and exposure of reactive solid surfaces found in the natural sediment. To interpret the experimental observations, we developed a new macroscopic model using multiple Monod kinetics for the transport and fate of redox-sensitive species. The model is able to describe the utilization of different electron acceptors in redox transition zones, and it was tested against laboratory data on the

movement of NO_3^- through the intact cores. A field application of the model to an experimental site in the Cobb Mill Creek, Virginia is then described. This work sheds further light on the physical and chemical processes that contribute to NO_3^- transport and transformation in the hyporheic zone. The transport model will be further used to investigate the biogeochemical processes of NO_3^- under varying hydrological stresses.

A transport model used to predict NO_3^- loading requires values of many input parameters, i.e.maximum uptake rate, half saturation constant, etc. that are not known with certainty. In an attempt to overcome these difficulties, a regionalized sensitivity analysis is performed first. It indicates the relative sensitivity of the parameters, identifies the important parameters and its associated range defining the model response. And then the automatic parameter calibration can be efficiently performed and the global optimal solution is more likely to be reached.

The overall aim of this study is to investigate the dynamic relation between transport and reduction of nitrate, and the resulting nitrate reduction rate variation during varying flow.

3.2 Methods

3.2.1 Field Site Description

The Cobb Mill Creek catchment, located in the eastern shore, Virginia, drains former agricultural fields (Figure 2-1). The creek is a groundwater dominated stream. Detailed field site situation has been described in Chapter2.

3.2.2 Laboratory Intact Sediment Cores Experiment

Detailed laboratory column setup and chemicals analytical methods have been described in Chapter2.

3.2.3 Model development

3.2.3.1 Transport Equation

In order to model the biological reactions that occur within the groundwater flow through the GW-SW interface, a one-dimensional advection-dispersion model was chosen as the mathematical formula for modeling the column experiments.

$$Ri\frac{\partial Ci}{\partial t} = D\frac{\partial^2 Ci}{\partial x^2} - v\frac{\partial Ci}{\partial x} + Bi$$
(3-1)

Where Ci is the concentration of the *ith* solute (ML⁻³), Ri is the retardation factor for the *ith* solute, D is the dispersion coefficient (L^2T^{-1}) given by $D=\alpha_Lv+D_d$ (α_L is the longitudinal dispersivity (L), D_d is the molecular dispersion coefficient), v is the linear velocity (LT⁻¹), and Bi is the biodegradation reaction rate term (ML⁻³T⁻¹) representing the total uptake of the *ith* solute due to all active biodegradation processes. The physical parameters (v and D) of the cores were obtained by fitting CXTFIT2.0 (Toride et al. 1995) to the observed BTCs of CI⁻.

3.2.3.2 Reaction Terms

3.2.3.2.1 Uptake Inhibition

The rate of nutrient utilization may be influenced by the presence of inhibiting compounds. The inhibition effect could be classified into three types [*Kindred and Celia*, 1989]: a) noncompetitive inhibition, b) competitive inhibition, c) biomass inhibition. Noncompetitive inhibition is usually used to describe the case in which electron acceptors with a higher thermodynamic sequence inhibit the enzyme for electron acceptors with lower thermodynamic sequence. Competitive inhibition is used to represent the inhibition of uptake of a secondary substrate when the primary substrate is still present. Biomass inhibition is an empirical means for limiting biomass growth.

The general way for modeling uptake inhibition involves defining an inhibition factor, which is mathematically defined by Segel (1975) as

$$I=1+Qs/Ks \tag{3-2}$$

Where I is the inhibition factor, Qs (ML⁻³) is concentration of inhibiting substance and Ks (M/L^3) is the inhibition constant. If Qs is much smaller than Ks, then I \approx 1.0 and the inhibitory substrate does not affect uptake. If Qs is much greater than Ks, I is very large and uptake may be inhibited considerably.

3.2.3.2.2 Multiple Monod Kinetics

The biological reaction is commonly described by the kinetic models, including the following: a) zero-and first-order reaction kinetics; b) instantaneous reaction kinetics; and c) Monod or Michaelis-Menten kinetics. The instantaneous reaction model assumes that the reaction between the organic matter and the electron acceptor mediated by the microorganisms is fast or almost instantaneous (Border et al., 1984). Therefore, the application of instantaneous reaction kinetics is limited to highly degradable compounds with large Damkohler numbers (Rifai and Bedient, 1990). Compared to zero- and firstorder kinetics, the Monod model is a more general reaction term, which contains firstorder, mixed-order, and zero-order regions, to describe the biological reactions. The multiple Monod expression is commonly used when it is unknown which of the species (i.e., substrate, electron acceptor, or nutrient such as assimilatory N, or all three simultaneously) is rate-limiting to avoid unnecessary analysis in the numerical solution to find the limiting species. In this study, the multiple Monod formulation [Molz, et al., 1986] was adopted, which assumes that the biodegradation reaction is limited by the concentration of each of the substances involved in the reaction.

$$B = \frac{dS}{dt} = \frac{\mu_{\text{max}}}{I_{nc}} \left(\frac{Cs}{Ks + Cs}\right) \left(\frac{C_{EA}}{K_{EA} + C_{EA}}\right) \frac{X}{Y}$$
(3-3)

Where B is the biological reaction rate for substrate, μ_{max} is the maximum specific growth rate (T⁻¹) of the microbe, K_s & K_{EA} are half-saturation constants (ML⁻³), The subscripts s and EA designate substrate and electron acceptor, respectively. I_{nc} is a noncompetitive inhibition factor, X is the biomass concentration (ML⁻³) of the microbial guild responsible for the biodegradation process. Y is yield coefficient (M bacteria/M substrate).

If
$$\frac{\mu_{\text{max}}}{Y}$$
 is replaced by V_{max}, the Monod expression reverts to:

$$B = \frac{v_{\text{max}}}{I_{nc}} \left(\frac{Cs}{Ks + Cs}\right) \left(\frac{C_{EA}}{K_{EA} + C_{EA}}\right) X$$
(3-4)

 V_{max} is the maximum substrate uptake rate. (T⁻¹)

3.2.3.2.3 <u>Reaction processes</u>

The biological reactions modeled in the flow-through column included aerobic respiration of dissolved organic matter followed by denitrification. The compositions of substrate were not well characterized, and were represented here with the simplified chemical formula CH₂O. The entire fraction of DOC, excluding any sorbed mass, was assumed to be labile and available to heterotrophic biomass.

3.2.3.2.3.1 Aerobic Respiration

Oxygen is often present in uncontaminated subsurface regions where organic compounds are scarce. However, in regions with abundant organic matter, the oxygen can be quickly depleted, so that aerobic metabolism will no longer dominate. The aerobic metabolism could be described by follow:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{3-5}$$

3.2.3.2.3.2 Nitrate Reduction

Some aerobic bacteria are capable of metabolism by nitrate-reduction. If the oxygen concentration is zero or minimal and nitrate is present, these bacteria switch to enzyme systems which use nitrate instead of molecular oxygen as the terminal electron acceptor. These nitrate reducing enzyme systems generally function only under anaerobic conditions. When oxidized nitrogen compounds are reduced to molecular nitrogen, the process is termed denitrification.

$$5(CH_2O) + 4NO_3^- \rightarrow 2N_2 + 5HCO_3^- + H^+ + 2H_2O$$
 (3-6)

3.2.3.2.3.3 POC Dissolution

Different sizes of organic matter (OM) rich layers exist in the intact cores from the field site. An important point is that the solid organic matter can not be used by microorganisms. Hydrolysis and solubilization of these compounds are necessary steps of latter energy or growth use. Those OM rich layers must act as a source of labile DOC. Carmichael (1994) and Robertson and Cherry [*Robertson and Cherry*, 1995] present data showing that the release of DOC from denitrification layer amended with wood chips or sawdust is a kinetic process, indicating that the effluent DOC is a function of residence time in the layer. Based on the DOC adsorption studies of [*Jardine, et al.*, 1992], a kinetic dissolution model is used to simulate the release of DOC from organic matter rich sediments. The model has the following form

$$\frac{dPOC}{dt} = \alpha \times (k_d \times DOC - POC)$$
(3-7)

Where POC is the mass of solid organic carbon per unit mass of solids (MM^{-1} solids), α is a first-order mass transfer coefficient (1/T), K_d is a linear distribution coefficient for the layer (L^3 water/M solids), and DOC is the dissolved organic carbon concentration (ML^{-3} water). The experimental results suggest that an organic matter bearing layer containing 2~10% by mass of particulate organic carbon is appropriate for the initial POC concentration used in the simulations.

3.2.3.2.3.4 Microbial Growth

It is reasonable to assume that the system is in steady state and that as a result, biomass is constant. Other investigators used one-way ANOVA tests to show that 11 out of 12 intact stream sediment samples showed no significant difference in microbial biomass between PRE and POST incubation conditions [*Battin, et al.*, 2003; *Sheibley, et al.*, 2003a]. Thus, there was no perceived need to model microbial growth kinetics in the present study. The amount of labile carbon present in the sediment was not modified during perfusion experiments. It is not expected that the steady state experienced during perfusion experiments is any different than *in situ* because no organic substrate was added.

In many column studies of nitrogen cycling, changes of the effluent of soil cores have been used to determine steady state conditions. Fluctuations in outlet concentrations of NO_3^- (Elrick et al., 1966) and NH_4^+ (Misra et al., 1974b) have been attributed to a changing microbial population within the column. If one observes a steady effluent concentration for the substrate of interest, it is safe to assume that the populations within the columns have achieved a steady state (McLaren, 1969). We constantly observed the plateau of NO_3^- BTC throughout the experiments (see the Results section). This is evidence that the denitrifying population may have reached a constant level.

In this scenario, we assume biomass is constant for any given depth in the cores. The reactions are only up to electron donors and acceptors. The lumped parameter v_{max} , will replace v_{max} in (3-4)

$$B = v_{\max}'(\frac{C_s}{K_s + C_s})(\frac{C_{EA}}{K_{EA} + C_{EA}})$$
(3-8)

3.2.3.3 Governing Equations

The biological reaction involved in the flow-through column included aerobic respiration of dissolved organic matter followed by denitrification. Monod type kinetics is assigned to those two reactions. Noncompetitive inhibition was used to suppress denitrification while dissolved oxygen was present. First-order dissolution rate of solid organic matter is used to describe the source of electron donor. The one-dimensional transport equation terms for the different species are given below:

Oxygen:

$$\frac{\partial O_2}{\partial t} = D \frac{\partial^2 O_2}{\partial x^2} - V \frac{\partial O_2}{\partial x} - V_O X_O \beta_O \left(\frac{DOC}{K_C + DOC}\right) \left(\frac{O_2}{K_O + O_2}\right)$$
(3-9)

Nitrate:

$$\frac{\partial NO_3^-}{\partial t} = D \frac{\partial^2 NO_3^-}{\partial x^2} - V \frac{\partial NO_3^-}{\partial x} - V_N X_N \beta_N \frac{1}{I_n} (\frac{DOC}{K_C + DOC}) (\frac{NO_3^-}{K_N + NO_3^-})$$
(3-10)

DOC:

$$\frac{\partial DOC}{\partial t} = D \frac{\partial^2 DOC}{\partial x^2} - V \frac{\partial DOC}{\partial x} + \alpha \times (POC - k_d \times DOQ - V_0 X_0 (\frac{DOC}{K_c + DOC}) (\frac{O_2}{K_o + O_2}) - V_0 X_0 (\frac{DOC}{K_c + DOC}) (\frac{NO_3^-}{K_c + DOC}) (\frac{NO_3^-}{K_c + DOC})$$
(3-11)

POC:

$$\frac{dPOC}{dt} = \alpha \times (k_d \times DOC - POC)$$
(3-12)

Where, V is linear velocity $[LT^{-1}]$,

D is dispersion coefficient $[L^2T^1]$,

 V_O and V_{N_-} is the maximum specific uptake rate of the substrate for aerobic respiration and denitrification, respectively [T¹],

 K_{O} , K_{N-} and K_{C} is the half-saturation constant for O₂, NO₃⁻ and DOC, respectively [ML⁻³], X is the biomass concentration of microbial population for the very biodegradation process [ML⁻³],

I_n is noncompetitive factor, given by I=1+Qs/Ks, where Qs is the concentration of the inhibiting substance s [ML⁻³], and Ks is the inhibition constant for that substance [ML⁻³], β is the uptake coefficient of the very solute for biodegradation process,

 K_d is the distribution coefficient [L³M⁻¹],

 α is first-order mass transfer coefficient [T⁻¹]

The overall dynamics discussed here are described by 4 coupled equations, three for each dissolved species (oxygen, nitrate, DOC), one for solid species (POC).

The microbiological modeling is based on microbiological reactions as "macroscopic", which is in contrast to the pore-scale modeling approaches including describing the biomass as a continuous biofilm [*Rittmann and McCarty*, 1981; *Taylor*

and Jaffe, 1990a], or as microcolonies [*Molz, et al.*, 1986; *Widdowson, et al.*, 1988]. Both approaches are based on the assumption that most of the biomass in the subsurface is attached to the surface of the solid phase of the porous media. The models separate the biological phase and the aqueous phase and assume that there is a mass transfer limitation between them. One simplification that can be made is that the mass transfer limitation between the biofilm and the aqueous phase can be neglected. If values of the mass transfer coefficient are very large, the "mobile-biophase" model can be reduced to a single aqueous phase model, or so called macroscopic model. Macroscopic modeling approaches describe biodegradation without considering the distribution of the biomass within the pore space, and biomass is usually included as a lumped parameter in the reaction terms of the governing equations. The advantage of this formulation is that it does not require assumptions that lack the ability to be verified by direct observations. The macroscopic approach has been used widely in simulating reactive transport processes [*Wood, et al.*, 1994].

The basic assumptions made in deriving the reactive transport model can be summarized as follows:

• A macroscopic approach has been used to represent biodegradation (Essaid&Bekins,1997).

- Multiple Monod kinetics (Bekins, et. al., 1997)
- Biomass growth and transport is not considered (i.e, biomass is at steady-state and attached to the solid particles)

• The dissolution of POC and the re-sorption of DOC is described by reversible first-order kinetics (Jardine,1992).

3.2.3.4 Numerical Solution

The Galerkin finite element technique was selected for a numerical solution. The finite-element method provides approximations of much higher order than does finitedifference methodology. The whole modeling domain can be subdivided into irregular elements as dictated by the physical geometry of the problem. Heterogeneity and anisotropy are easily accommodated with the finite element method.

Equations 3-9 to 3-11 can be generalized as:

$$(\mathbf{L}_{\mathbf{x}}-\mathbf{L}_{\lambda})\mathbf{S} = \frac{S^{n+1} - S^{n}}{\Delta t}$$
(3-13)

where L_x is a transport operator, and L_λ represents the dual-Monod operator The time derivative has been replaced by a finite-difference approximation, with n indicating the time level and $\Delta t = t^{n+1}-t^n$.

The domain can be subdivided into elements. The straight-line approximation for an element can be written in terms of general "basis function", $\xi(x)$, defined for each element. The basis functions are written explicitly as functions of x as follows (Hornberger and Wiberger , 2005):

$$\xi_{i} = \frac{x_{i+1} - x}{x_{i+1} - x_{i}}, \text{ for } x_{i} \le x \le x_{i+1}$$
(3-14)

$$\xi \mathbf{i} = \frac{x - x_{i-1}}{x_i - x_{i-1}}, \text{ for } x_{i-1} \le x \le x_i$$
(3-15)

The functions ξ are suitable as weighting functions for the spatial derivatives in the x direction. The trial function is of the form:

$$\mathbf{S} = \sum_{j=1}^{N} S_j \boldsymbol{\xi}_j \tag{3-16}$$

where S_j is the nodal unknown at node j, ξ_i is one-dimensional basis functions. Application of the weighted residual finite-element method to equation (3-13) along with the appropriate weighting functions leads to:

$$\int_{\Omega} \xi((L_t - L_\lambda)S - \frac{S^{n+1} - S^n}{\Delta t})dx = 0$$
(3-17)

where Ω is the domain over which the integration is carried out. After substituting the differential terms and integrating the second-derivative terms by parts (Hornberger and Wiberg, 2005), the trial function is substituted into equation (3-17). The time derivative term is replaced with an implicit finite difference approximation. The part of the approximation containing the unknown concentrations at time t^j is placed on the right hand side of the equation. The part of the approximation containing the unknown concentration containing the unknown concentrations at time t^{j+1} is added to the left of the equation. The element matrices for the left and right sides are the same because of the sign change when the knowns are moved to the right-hand side. The resulting sets of algebraic equations can be written in matrix form as:

$$([R]+[\lambda]+[Q])\{C\}^{n+1/2}=[Q]\{C\}^{n}+\{F\}^{n}$$
(3-18)

where [R] are the tridiagonal coefficient matrices for transport term, $[\lambda]$ is the multiple Monod decay matrices,[Q] is the element matrix for time derivative term. {F} is a specific flux vector introduced by non-diffusion boundary condition.

The elemental contribution to the coefficient matrix for the equation is of the form

$$[\mathbf{R}] = \left(\frac{D}{2\Delta x} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \frac{\nu}{2} \begin{bmatrix} -1 & 1 \\ -1 & 1 \end{bmatrix}\right)$$
(3-19)

where Δx is the length of element . The quantities D and v are elemental quantities. For the decay matrix $[\lambda]$ the elemental contributions are

$$[\lambda] = \left(\left(\frac{XK}{K_s + S} \right) \left(\frac{A}{K_A + A} \right) \left(\frac{\Delta x}{2} \right) \left[\frac{1}{3} \frac{1}{6} \frac{1}{6} \right] \right)$$
(3-20)

where K, K_S , and K_A are constant over an element. The terms involving X, S, and A in equations (3-20) are nodal quantities and not elemental as implied. It is only for notational brevity that they are shown outside the coefficient matrix.

The elemental contribution to the mass storage matrices [Q] in equation (3-18) is of the form:

$$[Q] = \left(\frac{\Delta x}{\Delta t}\right) \begin{bmatrix} \frac{1}{3} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{3} \end{bmatrix}$$
(3-21)

Equation (3-18) represents a system of nonlinear algebraic equations because the decay matrices $[\lambda]$ at the current solution time depend on the unknown S, at this time. This nonlinearity could be handled by predictor-corrector method proposed by Douglas and Jones (1963). The Douglas-Jones approximation uses two equations. One is the predictor, and the other is the corrector. Each equation advances the solution one-half of a time increment.

$$([R]^{n} + [\lambda]^{n} + 2[Q]^{n}) \{C\}^{n+1/2} = 2[Q]^{n} \{C\}^{n} + \{F\}^{n}$$
(3-22)

is followed by the corrector

$$([R]^{n} + [\lambda]^{n+1/2} + [Q]^{n}) \{C\}^{n+1} = [Q]^{n} \{C\}^{n} + \{F\}^{n+1/2}$$
(3-23)

An advantage of using the predictor-corrector approximation is that it gives rise to systems of linear-equations with a tridiagonal coefficient matrix. In equation (3-22) the unknowns occur at the n+1/2 time level and have a linear occurrence. In equation (3-23) the unknowns occur at the n+1 time level, and the equations are again linear. Equations (3-22 and 3-23) are unconditionally stable, and the truncation error is $0[(\Delta x)2+(\Delta t)3/2]$. Both systems of equations are tridiagonal and thus are easy to solve by the Gaussian elimination method.

In order to control numerical dispersion, the spacing of nodes and the size of a time step is determined by applying the Courant and Peclet criteria. These criteria are given by

$$C = v \frac{\Delta t}{\Delta x} \le 1 \tag{3-24}$$

$$P = v \frac{\Delta x}{D} \le 2 \tag{3-25}$$

Where C is the Courant number, P is the Peclet number and Δx is the average nodal spacing.

3.2.3.5 Initial conditions and Boundary Conditions:

The initial condition for NO_3 - was $OmgL^{-1}$ throughout the column. The preliminary results have shown a steady state was achieved quickly due to indigenous bacteria. Those steady-state profiles could further serve as initial conditions for later

transient simulations. Initial particulate organic carbon contents were derived according to the laboratory observed vertical profiles of POC (Figure 3-1).



Figure 3-1. Mean POC measured along sediment profiles from 31 intact cores extracted from the stream bottom (Galavotti, 2004).

Microbial biomass was set at each depth based on the results of Mills et al (2003) and Battistelli (unpublished data). As biomass needs to be set to the same unit as all other concentrations as expressed as an aqueous concentration in Monod kinetics, the total biomass can be calculated as an aqueous concentration, mgL⁻¹ of pore water, by using the results of MPN counts and a bacterial weight of 10^{-12} grams per cell, given a known porosity and bulk sediment density (Bouwer et.al, 1984). The absolute quantity of biomass need not be exactly determined because it could be included in lumped parameter $v_{max}' = v_{max}*X$ in eqn (3-8), which could be calibrated later by adjusting v_{max} . Given that v_{max} is constant, spatial distribution pattern of biomass, X, need to be estimated to account for heterogeneous reaction capacity in the columns and to reproduce the spatial profiles of constituents of interest.



Figure 3-2. Abundance of sediment denitrifiers measured by molecular MPN analysis in 8 intact cores extracted from the stream bottom (J Battistelli. unpublished data).

The specified concentration (Dirichlet condition) was used to represent a solute source area. Thus, the specified concentration boundary in this case would be that of the influent. In this model application, the rate at which solute mass leaves the column outlet by dispersive transport is very small and thus is neglected in the calculation. As a result, the third-type Cauchy boundary condition was applied to represent the dominant advective flux condition.

 $C_{DO}(0,t) = C_{DO}^{0}$ $C_{NO3-}(0,t) = C_{NO3-}^{0},$ $C_{POC}(0,t) = C_{POC}^{0},$ $C_{DOC}(0,t) = C_{DOC}^{0},$ $\frac{\partial^{2} C(L,t)}{\partial x^{2}} = 0, \text{ when } t \ge 0$

 C_{DO}^{0} , C_{NO3-}^{0} , C_{POC}^{0} , and C_{DOC}^{0} are solute concentrations in the influent.

3.2.3.6 Parameter Estimation

Reactive transport experiments involve the interaction of a series of dynamic processes. To obtain the starting values for the parameters in the model, values were obtained from the literature (i.e., half saturation constant) or data collected from the site (e.g., POC content) were used. A wide range of parameter values was explored because of significant uncertainty and variation in the reaction kinetics and physical parameters, which are likely to differ among the systems. The regionalized sensitivity analysis uses the observed data to infer the reaction parameters by systematically minimizing the least square mean to arrive at a set of parameters that best describe the observed data.

3.2.3.7 Generation and Sampling of Parameter Distribution

The first step for the parameter estimation is the generation of multiple realizations (or samples) of input parameters that are considered to be random variables. Generally, several hundred or more realizations may be required for Monte Carlo analysis if the sampling is done randomly. Because a single simulation run can take a significant amount of computer time, several hundred simulation runs may not be computationally feasible. However, techniques have been developed to permit constrained sampling, generally leading to significant reduction in the number of realizations needed for Monte Carlo analysis. One such technique that has been widely used is called Latin Hypercube Sampling [*McKay, et al.*, 1979].

Latin hypercube sampling (LHS), a stratified-random procedure, provides an efficient way of sampling variables from their distributions [*IMAN and Conover*, 1980]. The LHS involves sampling values from the prescribed distribution of each of k variables X_1, X_2, \dots, X_k . The cumulative distribution for each variable is divided into N equiprobable

intervals. A value is selected randomly from each interval. The *N* values obtained for each variable are paired randomly with the other variables. Unlike simple random sampling, this method ensures a full coverage of the range of each variable with significantly fewer samples. The number of necessary model runs can be largely reduced. The authors demonstrated that Latin hypercube sampling requires only 10% of the runs necessary using random sampling to produce similar uncertainty bounds [*Lahkim, et al.*, 1999; *Yu, et al.*, 2001].

The LHS can be summarized as:

• divide the cumulative distribution of each variable into *N* equiprobable invervals;

• from each interval select a value randomly, for the *i*th interval, the sampled cumulative probability can be written as:

$$Prob_{i} = (1/N) r_{u} + (i-1)/N$$
(3-26)

[Wyss and Jorgensens, 1998] where r_u is uniformly distributed random number ranging from 0 to 1;

• transform the probability values sampled into the value x using the inverse of the distribution function F^{-1} :

$$x = F^{-1}(\text{Prob});$$
 (3-27)

• the *N* values obtained for each variable *x* are paired randomly (equally likely combinations) with the *ns* values of the other variables.

The method is based on the assumption that the variables are independent of each other, but in reality most of the input variables are correlated to some extent. Random

pairing of correlated variables could result in impossible combinations; furthermore independent variables tend to bias the uncertainty.

3.2.4 Regionalized Sensitivity Analysis

The optimization algorithm adjusts the parameter vector starting from the initial guess until no more refinement is possible. Because of the large number of reaction parameters involved (11 in the present work), the objective function could be a complex surface with local minima in the n-dimensional space. Sensitivity analysis was used to limit the number of parameters that were optimized without compromising the quality of the solution. Parameters were first eliminated that were not expected to change significantly (porosity, bulk density, etc.). For the rest of parameters, the regionalized sensitivity analysis (RSA) developed by Hornberger and Spear [*Hornberger and Spear*, 1981] was employed to determine the relative importance of the parameters in the simulation model.

The RSA procedure involves Monte Carlo simulations by randomly selecting a set of parameter values form within the designated ranges and running the transport model using this particular set of values. Each simulation run is then classified either as producing acceptable results (i.e., simulated nitrate breakthrough concentration) or as not producing acceptable results. This procedure is repeated many times to give an accumulation of values of the parameters for which results are acceptable and another for which results are unacceptable. The key idea is then to identify the subset of meaningful parameters that appear to account for the acceptability of the results. The distribution of the parameter values associated with acceptable results is compared with the distribution of parameter values associated with unacceptable results. If the two distributions are not

statistically different, the paramter is unimportant for simulating the designated acceptable behavior; if the two distributions differ significantly, the parameter is important [*Hornberger, et al.*, 1986].

Briefly, The RSA procedure utilizes the following steps:

- Select the parameters for sensitivity analysis.
- Determine the ranges of the parameters from the related literature or from experience.
- Generate parameter distribution within the ranges by a Latin Hypercubic Sampling method.
- In each simulation, the coefficient of efficiency, which was proposed by Nash and Sutcliffe (1970), is calculated to evaluate the model performance. This coefficient is expressed as

$$R = \frac{\sum_{i=1}^{n} (\bar{y} - y_i)^2 - \sum_{i=1}^{n} (\hat{y} - y_i)^2}{\sum_{i=1}^{n} (\bar{y} - y_i)^2}$$
(3.28)

where n is the number of time steps in the simulation, \hat{y} and y_i are the computed and observed values, respectively, and \overline{y} is the average of the observed values. In this study, the breakthrough curve of nitrate was used as the criterion of model performance. If the R value obtained from the simulation is greater than a subjective R value then the result is acceptable, otherwise the result is unacceptable.

 A criterion of acceptance is chosen and compared to the coefficient of efficiency. Then the ranges of acceptable and unacceptable values are determined for each parameter. In this study, the value of the acceptance criterion was chosen as 0.9 and simulations resulting in EFF>0.9 are acceptable. For each parameter, the cumulative distribution of the parameter values associated with the acceptable cases, A(x), is compared to the CD of the unacceptable cases, U(x). The Kolmogorov-Smirnov(K-S) test, at a specified significance level, α=0.05, is used to test if the two continuous cumulative distribution functions are identical. The hypotheses tested by KSTWO are

$$H_0 ||A(x) = U(x)$$
 (3-29)

$$H_1 || A(x) \neq U(x)$$
 (3-30)

The largest absolute value, D, of the positive and negative maximum differences between the CDF of A(x) and of U(x) is ranked by decreasing value representing deceasing sensitivity.

3.2.4.1 Automatic Parameter Calibration:

See Figure 3.3

- Only the sensitive parameters identified by the RSA method or a subset thereof can be included. The parsimony of parameters is advisable because an increase in the number of parameters does not necessarily imply better results due to the inherent nonlinearities in the model structure and the increased likelihood of finding multiple local optima of the objective function surface.
- Give an initial guess for each parameter considered. The initial guess could be obtained from the literature or from experience. Initial values are used in the simulations in order to avoid getting a locally optimal solution.
- Define the objective function. The R value given in Equation 3-28 is used as the objective function. The objective is then to maximize the R value. The R value is calculated immediately after each simulation.

• Optimize each parameter in sequence. In this study, an unconstrained nonlinear optimization using the simplex search method [*Lagarias, et al.*, 1998] is used to find the parameter value giving the maximum R value. After all parameters are optimized, an optimization cycle is complete. The value of the objective function (R) is stored at the end of each cycle.

Return to step 4 and repeat the optimization cycle until the R value does not increase by more than a small amount, for example, 0.001.

3.2.7 Model verification:

In order to verify that the formulations discussed above are correctly implemented, model results are compared to analytical solutions.

Parlange et al. [*Parlange, et al.*, 1984] presented an analytical solution to equation (3-1) for the case of Monod degradation with no dispersion and no decay:

$$x = \frac{v}{V_{\text{max}}} \left[K \ln(\frac{C_0}{C}) + C_0 - C \right]$$
(3-31)

with boundary conditions:

$$C=C_0 \text{ at } x=0,$$
 (3-32)

and

$$\frac{\partial C}{\partial x} = 0$$
 at x=L. (3-33)

This solution may be used to calculate the distance x corresponding to a given concentration C(x). To evaluate the full Monod calculation in equations 3-9 to 3-11, this analytical solution was compared to the numerical solution obtained using the parameters given in table 3-1. The analytical and numerical solutions agreed well (Figure 3-4).



Figure 3-3. Flow chart of the automatic parameter calibration method.

			2					
	L	Δx	V	\mathbf{C}_0	\mathbf{V}_{\max}	Κ	Х	Т
	(cm)	(cm)	$(\operatorname{cm}\operatorname{hr}^{-1})$	(mgL^{-1})	(h^{-1})	$(mg L^{-1})$	$(mg L^{-1})$	(hr)
Monod Kinetics	50	1	2.1	15	1.5	8	1	100

 Table 3-1 Parameters used in steady-state Monod kinetics simulation



Figure 3-4 Comparison of analytical (line) and numerical (points) solutions for steady-state Monod kinetics. For the numerical solution, only the values at the even numbered nodes are shown.

3.3 Results

3.3.1 Application of the RSA to the transport model

Both microbial kinetic parameters and physical parameters were selected independently from uniform distributions over the physically meaningful range of the parameter in Table 3-2. If the parameter is one whose values can range over several orders of magnitude, the logarithm of the parameter was chosen from a uniform distribution [*Hornberger, et al.*, 1985]. It was shown by preliminary model runs that convergence of statistical measures of model output was achieved if number of model runs exceeds ten times the number of varied parameters. Thus, 200 Monte-Carlo simulations were run for either of two separate experiments. First, physical parameters were fixed at known values, and only the kinetic parameters were selected at random (case I). Second, both the physical parameters and kinetic parameters were selected at random (case II).

Parameter	Value
A. Non Random Parameters	
Column length (L)	50cm
Bulk density (ρ)	1.65gcm ⁻³
Porosity (n)	0.35
B. Derived Random Parameters	
Pore water velocity (v)	$0.1-10 \text{ cmh}^{-1}$
Dispersivity (d)	0.5-5cm
Maximum uptake coefficient of aerobic respiration	$0.3-3 h^{-1}$
(Vo)	
Maximum uptake coefficient of denitrification	0.15-1.5 h ⁻¹
(V _N)	
Non competitive Inhibition constant of O ₂ (K _{nc})	$0.005-0.5 \text{mgL}^{-1}$
Mass transfer coefficient (α)	$5 \times 10^{-6} - 5 \times 10^{-4}$
Distribution coefficient (Kd)	5-500
Monod half-saturation constant for $O_2(K_0)$	$0.02-2 \text{ mgL}^{-1}$
Monod half-saturation constant for $CH_2O(K_c)$	$0.1-10 \text{ mgL}^{-1}$
Monod half-saturation constant for $NO_3^-(K_N)$	$0.09-9 \text{ mgL}^{-1}$
Depth averaged particulate organic carbon (%w/w)	0.3-3

Table 3-2 Random basic parameters for RSA analysis

The parameter values from the Monte Carlo simulations were subjected to a statistical analysis to elucidate sensitivity characteristics of the model over the full range of parameter values. The sensitivity of parameters can be judged by a comparison of the cumulative frequency distributions (CDF) of the accepted and rejected cases Figure 3-5. It is necessary to have a significant number of accepted events for good comparison of the CDF about both cases. A few trials suggested that adjustment of some parameters can significantly increase the number of accepted cases. The adjusted ranges of parameter

values are listed in Table 3-2. The RSA was performed using the range of parameter values in Table 3-2. The results of the Kolmogoro-Smirnov two-sample test for the accepted and rejected cases are summarized in Table 3-3. The p value is defined as the smallest level of significance that would lead to the rejection of the null hypothesis [Hornberger and Spear, 1981]. The null hypothesis is that the distributions of the parameter values corresponding to the satisfactory and unsatisfactory cases are not significantly different, i.e. the parameter is insensitive. A small value of p indicates a sensitive parameter.

Parameter	symbol		case I		case II		
		\mathbf{H}^{1}	Р	dm,n ²	Н	Р	dm,n
Maximum uptake coefficient of aerobic respiration	Vo	1	$1.83 imes 10^{-14}$	0.57	0	0.06	0.19
Maximum uptake coefficient of denitrification	$V_{\rm N}$	1	2.32×10^{-15}	0.59	1	1.63×10^{-5}	0.35
Inhibition constant of O ₂	K _{nc}	0	0.12	0.17	0	0.16	0.16
Monod half-saturation constant for O ₂	Ko	0	0.13	0.17	0	0.18	0.16
Monod half-saturation constant for NO ₃ -	K_N	0	0.74	0.10	0	0.60	0.11
Monod half-saturation constant for substrate	K _C	0	0.43	0.12	0	0.70	0.10
Mass transfer coefficient	α	0	0.43	0.12	0	0.48	0.12
Distribution coefficient	K_d	0	0.30	0.14	0	0.97	0.07
Pore water velocity	v	N/A	N/A	N/A	1	3.30×10^{-18}	0.648
dispersivity	d	N/A	N/A	N/A	0	0.48	0.12
Mean POC content (%)	POC	N/A	N/A	N/A	0	0.67	0.10
Dissolved Oxygen in influent (mgL ⁻¹)	DO	N/A	N/A	N/A	0	0.12	0.19

Table 3-3.	Results c	of K-S test	(p values)) for the tran	sport model

 1 H=1 indicates parameter is sensitive (p<0.05), H=0 indicates parameter is insensitive

² dm,n is value of maximum distance in the Kolmogorov-Smirnov test

The parameter sensitivity is indicated by if there is significant difference between the cumulative distributions of parameters corresponding to accepted and unaccepted cases. For both cases, the model output was sensitive to several parameters (p<0.05). For case I, V_O and V_N are the most sensitive parameter with K_O and K_N moderately sensitive (Table 3-3). This is consistent with the expectation that not only denitrification but also aerobic respiration affects the fate of nitrate. The insensitivity of two DOC-related

parameters, α and K_d , indicates the system is not be DOC limiting when POC content is at or above 2.1%.

For case II, pore water velocity (v), is the most critical of the 12 parameters. In case II, only V_N is considered as sensitive instead of both V_O and V_N as in case I, because v is so much more sensitive here than any of the other parameters. The pore water velocity and dispersivity are picked to be the only parameters accounting for hydrodynamic characteristic of the system, because the hydraulic conductivity, porosity, and pore water velocity are highly correlated.

Sensitivity analysis of initial model including microbial growth showed that all parameters related to the microbial growth kinetics terms were insensitive (results not shown). Neglecting microbial growth in the model structure is justified based on results of the analysis.

The values of all of the insensitive parameters were fixed at the median value of the ranges chosen as physically meaningful for the Monte Carlo simulations, and optimization by the automatic calibration method described previously was done on the three parameters identified as important (*i.e.*, V_0 , V_N , and K_N) in the RSA. The final completed parameter sets used in the column simulation are shown in Table 3-4.

3.3.2 O_2 and NO_3 profiles

Before beginning the kinetic modeling, it was necessary to determine a representative dispersivity for the column setup. Using chloride as a tracer, an effective dispersivity was found by fitting Cl⁻ breakthrough data to a 1D non-reactive transport model CXTFIT 2.0(Toride,1995). The assumption of a constant dispersivity throughout the columns was not expected to affect the modeling results because these sediments appear to be an advection-dominated system; the Peclet number observed in the columns

(the ratio of advective to dispersive flow) ranged from 9 to 98, indicating that advection dominated the flow in these sediments.



Figure 3-5. Cumulative distributions of eight microbial kinetic parameters. The blue solid lines represented accepted cases and the red dot lines represented unaccepted cases.



Figure 3-6. Cumulative distributions of three physical parameters: linear velocity, dispersivity, averaged POC content, and input oxygen concentration. The blue lines represented accepted cases and the red lines represented unaccepted cases. Note that sharp difference of cumulative distribution functions between accepted and unaccepted cases for linear velocity.

Table 3-4 Input Parameters for Laboratory C	Column#1	Simulation
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	O_2	NO_3^-
Maximum specific growth rate, V _{max}	1.9 h^{-1*}	$1.6h^{-1*}$
Half-saturation constant of electron acceptors	0. 2 mg L ⁻¹	2 mg L^{-1}
Half-saturation constant of electron donor	1 mg L ⁻¹	1 mg L ⁻¹
Yield Coefficient	2	2
mass transfer coefficient of POC	5×10^{-4}	
distribution coefficient of DOC	50	
Inhibition constant	0.01 mg L ⁻¹	
Longitudinal grid spacing	1 cm	
column length	0.5 m	
effective porosity	0.28	
Longitudinal dispersivity	2 cm	
Linear velocity	2.0 cm h^{-1}	
Simulation time	340 h	
Time step size	0.2 h	
O_2 for x=0	8 mg L^{-1}	
NO_3 for x=0	15 mg L^{-1}	
DOC for x=0	0 mg L^{-1}	

*calibrated by automatic parameter calibration

Error! Reference source not found. Error! Reference source not found.Figure 3-8. Steady-state profiles of O_2 and NO_3^- in column #2 with depth averaged 2% POC content at $v = 1.2 \text{ cm h}^{-1}$



Figure 3-7 NO₃⁻ transient profiles during the step input for column#1 with 1.1% POC content at $v=2 \text{ cm h}^{-1}$. Initial NO₃⁻ concentrations was zero through the column. Flow direction is upward



Figure 3-8 Breakthrough curve of NO₃⁻ in column#1 with 1.1% POC content at v=2cmh⁻¹

The normalized effluent nitrate concentrations observed and simulated during continuous flow under varying flow rates are shown in Figure 3-11 and Figure 3-10. It appears that nitrate effluent shows an almost synchronized pattern as flow velocity. Increasing the flow rate resulted in increasing effluent concentrations, which flattened out during maintained flow. Likewise, decreasing the flow resulted in decreasing effluent concentrations and followed by a steady state plateau. This indicated that a new level of equilibrium between nitrate transport and reduction was reached at each new flow rate applied.

From the overall good agreement between the observed and simulated concentrations, it shows that the calibrated transport model provides a reasonable approximation to the highly variable nitrate fluxes observed during different flow rates with the columns. The reduction rates applied to fit the data were unique and consistent for each column. The ability of the model to reproduce the nitrate transport data shows that nitrate reduction in columns largely followed the reaction kinetics described by the model.

3.3.3 Aerobic and Anaerobic

Observed and simulated NO_3^- profiles under aerobic and anaerobic (N-sparged eleuent) conditions are shown in **Figure 3-11**. Nitrate reduction starts significantly earlier (~15cm) under anaerobic condition than under aerobic condition. It can be inferred that adding oxygen to the system delayed (spatially) the onset of the nitrate reduction process. Numerical experiments demonstrated that the pattern of establishment of NO_3^- -reducing conditions was not be described by a simple pseudo-first-order or zero-order kinetic. Therefore the concentration profiles of NO_3^- can be divided into an inhibitory part, a zero-, and a first-order reaction zone, which could be described best by the Monod kinetics.



Figure 3-9 Measured and simulated effluent nitrate breakthrough in response to applied stepwise increased flow rates for the column#1.



Figure 3-10 Measured and simulated effluent nitrate breakthrough in response to applied stepwise decreased flow rates for the column#1.



Figure 3-11. Profiles of NO₃⁻ with aerobic vs. anaerobic eluent delivered at 3cmh⁻¹

3.3.4 Effect of flow rate

Numerical simulation shows the concentration profiles of oxygen and nitrate during the migration of O_2 consumption and NO_3^- -reduction fronts from one steady state to another, with the oxygen and nitrate concentration front moving slowly towards the column outlet as the flow velocity increased (**Figure 3-12**). Nitrate reduction zone started at the depth of 35cm when v = 0.5 cm h⁻¹ in contrast to the depth of 15 cm when v = 4 cm h⁻¹.


Figure 3-12. Concentration profiles of O_2 and NO_3^- at flow velocities of 0.5 cm h⁻¹, 1 cm h⁻¹, 2 cmh⁻¹, and 4 cm h⁻¹

3.3.5 Field Application

The model was examined to determine if it could successfully simulate observations made on the stream sediments of the experimental site (Galavotti,H., 2004), and reproduce the features of the NO_3^- consumption found under baseflow conditions. To

this end, most parameters were estimated from previous laboratory microcosm experiments. The lower boundary was also a constant concentration boundary set at the measured or interpolated concentration at 50 cm deep. The upper boundary was represented by advective flux condition. The simulation was conducted under psuedosteady-state conditions, which means the flux of seepage water out of the stream sediments was constant throughout the simulation period.

The simulation reproduced the on-site finding (Figure 3-13): nitrate was gradually consumed during passing by the organic matter rich zone at top 20~30 cm. The starting point of the NO_3^- reduction zone differed from core to core and ranged between 10-25cm of depth.

3.4 Discussion:

3.4.1 Transport model

The transport model developed here has been approved capable of simulating the transient state and steady state utilization of multiple electron acceptors (O_2 and NO_3) during the groundwater seepage. The method, which is more simplified and efficient than previous models [*Chen, et al.*, 1992; *Doussan, et al.*, 1997; *Essaid, et al.*, 1995; *Widdowson, et al.*, 1988; *Zysset, et al.*, 1994], is attractive for simulating the nonlinear problem of multi-species transport and uncertainty analysis of modeling performance. The model equations are believed to provide a realistic description of the interaction of the substrate and electron acceptors (oxygen and nitrate). This was demonstrated by the favorable agreement with data obtained from both the laboratory column experiments and the field observations. Using the aforementioned kinetic dissolution model to represent



Figure 3-13. Nitrate concentration in sediment pore water from a) core #5 in August 6, b) core #4 in Oct 26, c) core #6 in Oct 26, d) core #6 in August 26 2003 (seepage velocity = 3cm/h.

DOC release from particulate organic carbon indicated that enough DOC may be leached to create anaerobic conditions in favor of denitrification processes further downgradient. Equations accounting for pore scale mass transfer and microbial growth may not be necessary to simulate the NO_3^- removal in the sediments. Also, it may be possible to neglect indigenous bacterial mobility so that the computation effort can be reduced because the number of advection-dispersion equations is largely reduced.

The joint strategy of regionalized sensitivity analysis and automatic parameter calibration technique for parameter estimation succeeds in classifying the parameters as sensitive or insensitive and reduces the number of model simulations for the calibration. It gives more confidence in the uniqueness of estimation parameter values and improves the likelihood of obtaining a global optimum parameter set. Two parameters appear to be of primary importance for the evolution of the NO_3^- in discharging water: the seepage velocity of the water through the stream sediments and denitrification rate constant, which is highly associated with organic matter content in these sediments.

3.4.2 Localization of O_2 and NO_3^- consuming processes

Modeling of biological processes can provide insight into the functioning of ecotone at groundwater surface water interface. A one-dimensional advection dispersion equation was used to simulate depth profiles of NO_3^- for determining the reaction rate kinetics for both aerobic respiration and denitrification in undisturbed cores. Modeling of intact cores was separated into two distinct regions. The bottom region of the sediment was aerobic; oxygen was present due to the lack of substrate and, therefore, microbial biomass. The upper region of the sediment, near the surface, was an anaerobic zone where nitrate reduction was developed.

There is a transition zone between these areas where oxygen depletion by microbial respiration of organic matter occurs. Dissolved oxygen concentrations of

8mgL⁻¹ in the artificial groundwater decreased to $<1mg L^{-1}$ within mean flow distance of 30cm (Error! Reference source not found.), and no breakthrough of O₂ occurred at any time during the experiments. In stream sediments, mean groundwater seepage rates are often below 1md⁻¹ (chapter2). According to the results of this study, the high concentrations of organic matter cause O₂ to be constantly consumed within the GSI when groundwater flows through yielding a permanent anaerobic region in the sediment. The resulting persistent anaerobic conditions favor continual denitrification at the GSI under baseflow conditions. This is consistent with many findings at field sites [*Grimm and Fisher*, 1984; *Pusch*, 1996]. Most GSIs have an aerobic/anerobic interface, with the prevailing microbial processes highly dependent on the local redox level [*Jones, et al.*, 1995]. The redox conditions observed in the flow-through column study here are consistent to the profiles of platinum electrode potential measured in *in situ* cores [*Galavotti*, 2004].

As expected, NO_3^- is utilized by microbes as the electron acceptor as soon as O_2 is depleted. A common feature of stream-bed sediments is intense microbial denitrification, if concentrations of organic matter and nitrate are high and oxygen concentration is low [*Duff and Triska*, 1990; *Holmes, et al.*, 1994; *Triska, et al.*, 1993b]. Facultative anaerobes that can switch to nitrate as terminal electron acceptor as dissolved oxygen is depleted dominate in such systems [*Triska, et al.*, 1993b] and are abundant in the sediments of Cobb Mill Creek (Mills et al. 2003, Battistelli, unpublished data). The low NH_4^+ concentrations in the column effluent and pore water (<0.1 mg L⁻¹) suggest that obligate anaerobic microorganisms known to use dissimilatory reduction of NO_3^- to NH_4^+ for respiration were of little importance. In summary, this means that denitrifying mineralization was the major NO_3^- consuming process, which is consistent with the observed high denitrification potentials [*Galavotti*, 2004].

3.4.3 Denitrification kinetics

Aerobic respiration and denitrification were modeled in sediment intact cores using a Monod kinetic model. The half saturation constant of nitrate in denitrification calibrated in the model were 2 mg N L⁻¹, comparable to the published values of 3.06mg N L⁻¹[*Messer and Brezonik*, 1984], 2.1 mg N L⁻¹ [*Schipper, et al.*, 1993],and 1.25 mg N L⁻¹ [*Maag, et al.*, 1997]. The two magnitude higher K_N than that found in pure culture studies has been attributed to NO₃⁻ ion diffusion constraints in soil [*Phillips*, 1978]. Published half saturation constant of nitrate (K_N) in denitrification in soil and sediment studies ranged from 0.21-4.06 mg N L⁻¹, with most values reported between 1 and 4 mg N L⁻¹ [*Esteves, et al.*, 1986; *Murray, et al.*, 1989; *Oremland, et al.*, 1984]. The nitrate concentrations in the intact cores (1~15 mg NO₃-N L⁻¹) were in the same magnitude as K_N. Thus, our use of Monod kinetics for denitrification is justified.

Few studies have estimated the maximum substrate uptake rate for denitrification (V_N) . Our study shows a mean V_N value of 1.1 mg N L⁻¹ h⁻¹, similar to the value of 1.51 mg N L⁻¹ h⁻¹ found in the upper horizon in the wet meadow soil [*Maag, et al.*, 1997], 0.46 mg N L⁻¹ h⁻¹ in riparian soils [*Schipper, et al.*, 1993], 1.8 mg N L⁻¹ h⁻¹ in agricultural soils and a pond sediment [*Murray, et al.*, 1989], and 1.26 mg N L⁻¹ h⁻¹ measured in a lake sediment at 35.5°C [*Messer and Brezonik*, 1984]. [*Sheibley, et al.*, 2003b] observed a mean 1st order rate coefficient for denitrification of 1.5 h⁻¹, converted to 3 mg N L⁻¹ h⁻¹ h⁻¹ (Assuming a half saturation constant of 2 mg N L⁻¹), which is comparable to that in the present study. However, the V_N value is several magnitudes higher than those V_{NO3}-

values converted from 1st order rate coefficients for denitrification reported in several studies from soil systems (Starr JL, et.al, 1974). The relatively high reaction rates in this study may typify streambed environments with continually renewed substrates and nitrate.

3.4.4 O₂ inhibition of denitrification

Denitrification is generally strongly inhibited by dissolved oxygen because oxygen is the preferred electron acceptor in facultative anaerobes. For facultatively denitrifying microorganisms, the O_2 concentration is the dominant regulator for the expression of enzymes for the reduction of NO_3^- , NO_2^- and N_2O in the respiratory chain [*Payne*, 1973]. Most of these microbes synthesize the denitrifying enzymes only when O_2 concentrations are below 0.2-0.67 mg $O_2 L^{-1}$ [*Tiedje*, 1988], and this concentration range is frequently regarded as the O_2 threshold for denitrification [*Tiedje*, 1988]. In this study, denitrifying processes were observed in the presence of mean O₂ concentrations around 0.2-1mg L^{-1} , consistent with reported O₂ threshold. The comparison of denitrification in aerobic and anaerobic systems suggested that the present of oxygen reduced the thickness of the active NO_3^- reduction zone (Figure 3-11), consequently lessening the NO_3^- removal capacity of the columns. The NO₃-removal rate is 2-3 times higher in anoxic columns (with oxygen-free eluent) than that in oxic columns (with oxygenated eluent) (see chapter 2). It could be further illustrated by the simulated relationship of depth-integrated nitrate removal rates and flow velocities in Figure 3-14. At low flow rates, the removal rates of oxic and anoxic columns were similar because long residence time allows anaerobic condition developed prior to the nitrate reduction zone in oxic columns. The difference of NO_3^{-1} removal rate between anoxic and oxic columns was enlarged to more than one

magnitude with increasing flow velocities when the propagation of oxygen front was enhanced by increasing pore water transport in oxic columns (Figure 3-14).



Figure 3-14. The simulated relationship of depth-integrated nitrate removal rate and pore water velocity. The solid line represents the anoxic column and the dotted line represents oxic column.

3.4.5 Pore water velocity

The dependence of NO_3^- reduction on flow rate demonstrates that the redox reaction is kinetically controlled; or, in other words, the time-scale for NO_3^- reduction is on the order of the time-scale for advective transport. Clearly, an increase in pore-water velocity decreases the thickness of the anaerobic zone and, consequently, lowers nitrate removal capacity (Figure 3-14). Given the fact that necessary bacteria are present in the GSI (Mills et al., 2003, Battistelli, unpublished data), the flow rate of seepage water may strongly influence the chemical evolution of the discharging water, particularly with

respect to the behavior of nitrate. When water velocity increases, it allows oxygen to penetrate more deeply in the sediment, which attenuates the reducing conditions, thereby decreasing the amount of nitrate reduced (Figure 3-12)

The relationships of depth-integrated nitrate removal rates and pore water velocities simulated by the transport model (Figure 3-14) are consistent with previous experimental results in chapter 2. Initially both oxic and anoxic columns showed an incline trend with flow velocities. And then nitrate removal rates in the anoxic column kept increasing until flattening out at v> 4.4 cm h⁻¹, while nitrate removal rates in the oxic column declined with flow velocity at v >1.2 cm h⁻¹. The mechanisms accounting for these patterns could be viewed in deep by denitrification rate profiles simulated by the transport model (Figure 3-16, Figure 3-17).

The depth-integrated denitrification rates in the anoxic column represented by areas of dot lines increased with increasing flow rates, and then kept nearly constant when v>4.4 cm h⁻¹ (Figure 3-16), which correspond to that denitrification rates flattened out at v>4.4 cm h⁻¹ in anoxic column (Figure 3-14).

While in the oxic column, the depth-integrated denitrification rates represented by areas of dot lines increase between 0.6 cm h⁻¹ and 1.2 cm h⁻¹, and then decrease when v >1.2 cmh⁻¹ because of shortened nitrate reduction zone induced by propagation of oxygen consumption zone. This result is also consistent to the declining denitrification rate at v>1.2 cm h⁻¹ in Figure 3-14.

The nitrate reduction showed a first order reaction kinetics due to the limiting supply of nitrate at low flow rates. When flow velocity was further increased, nitrate reduction reaction showed zero order reaction kinetics given the fact that the nitrate is not limiting at high flow rates. As a result, the nitrate reduction rate is independent to the nitrate flux, which is shown in anoxic column at v> 4.4 cm h⁻¹ (Figure 3-14). This switch from 1st order to 0 order is plausible given that the half saturation constant of nitrate (K_N) is as high as 2 mg L⁻¹, comparable to ambient nitrate concentration. In contrast, the relationship of denitrification rates and flow velocities showed a single decline trend when K_N is one magnitude lower (0.2 mg L⁻¹), well below the ambient nitrate concentration (Figure 3-15).



Figure 3-15. The simulated relationship of depth-integrated nitrate removal rate and pore water velocity for oxic columns at two different half saturation constants of NO_3^- . Solid line- $K_N=2 \text{ mg } L^{-1}$; dash line- $K_N=0.2 \text{ mg } L^{-1}$.



Figure 3-16. Denitrification rates variation in the anoix column at different flow velocities: 0.6 cm h^{-1} , 0.9 cm h^{-1} , 1.2 cm h^{-1} , 2.0 cm h^{-1} , 2.8 cm h^{-1} , 3.6 cm h^{-1} , 4.4 cm h^{-1} , and 5.2 cm h^{-1} .



Figure 3-17. Denitrification rates variation in the oxic column at different flow velocities: 0.6cm h^{-1} , 0.9cm h^{-1} , 1.2cm h^{-1} , 2.0 cm h^{-1} , 2.8cm h^{-1} , 3.6 cm h^{-1} .

Besides the shrinkage of the nitrate reduction zone, the other factor may contribute to the observed relationship between pore water velocity and the NO₃⁻ removal rate. Increases in v may result in lower concentrations of organic substrate important for both oxygen respiration and denitrification. The slow dissolution of POC as the only source of the DOC that is required for denitrification may be inadequate when v exceeds the characteristic dissolution rate (Figure 3-18). . As shown in Figure 3-18, the maximum DOC was 4 times higher at v= 0.6 cm h⁻¹ than that at v=2 cm h⁻¹.



Figure 3-18. Simulated DOC profiles under different flow velocities.

3.4.6 The role of microbial activity and organic carbon

Schlieker et al. [*Schlieker, et al.*, 2001] suggested that the rates of redox reactions catalysed by bacteria increase with increasing supplies of respective dissolved species, leading to a higher bacterial population density. Due to the high availability of acetate in the columns used in their study, the redox zones did not move when the flow velocities were changed. In systems such as those used in the resent study, microbial growth will

be limited due to the lack of labile organic carbon. The turnover rates of particulate organic carbon may be limited at higher flow velocities (Figure 3-18). An increasing flow velocity leads to a spreading of the redox sequence. This means that dissolved species taking part in redox reactions are transported further down the flow path. This is due to relatively constant microbial reaction rates. Doussan et al. [*Doussan, et al.*, 1997] observed spreading of redox zones in a sediment that was rich in particulate organic matter due to an increased flow velocity (from 0.05-0.20m/day).

The redox zonation is characterized by steep spatial gradients in the profiles of both rates and chemical concentrations. In the present system, transport of solutes is dominated by advection, while the biomass is attached to the immobile solid matrix. As a result, the biomass concentration of any given bacterial group at any given point along the flow path reflects the local reaction rate of the redox processes associated with this group. Such dynamics leads to a high spatial correlation between the distribution of the redox reaction rates and the concentration of the corresponding bacterial group. As a result, the identification of the redox stratification in the system would allow a quantification of the biomass of different functional groups in such a system. Transient effects, such as moving reaction fronts or changing boundary conditions, might affect the relationship between biomass concentrations and associated reaction rates. However, this effect depends on the relative magnitude of the time scale for microbial growth and decay compared to the time scale for transport process. A small time scale for transport combined with a large time scale for microbial growth lead to the observed constant biomass distribution. The good agreement between observed and simulated NO₃⁻ profiles

during transient flow conditions has justified our assumption of negligible biomass growth and transport.

DOC supply is an important factor for denitrification because DOC is the only energy source available for the microbes. In natural uncontaminated aquifers, the rate of biodegradation is usually limited by the availability of organic carbon [*Kindred and Celia*, 1989]. The high, but heterogeneous, DOC concentrations in the mobile pore water suggest that desorption or DOC release from the soil matrix is fast in this case (Figure 3-18). Further studies of redox sequences should include differential analysis of fate, degradation rate, and composition of the several organic carbon fractions. The excessive consumption of dissolved organic carbon released from the matrix can deplete the high reduction capacity of the subsurface flow path with time. But this depletion would not be significant until several months of flow-through column run indicating that there is a large organic carbon pool in the sediments that is not easily depleted by microbial degradation.

Supply of organic matter as the substrate may crucially influence the chemical evolution of NO₃⁻ in the discharging water. Bulk NO₃⁻-removal rates are positively correlated to the averaged POC content in the sediment. At low POC content, denitrification shows a first order kinetics in terms of DOC. When stream sediments contain >2% of POC, denitrification proceeds rapidly and achieve asymptotic plane Figure 3-19 capacity. In other word, POC content is not a limiting factor. Denitrification is likely permanent as the sedimentary organic carbon is continuously renewed by sedimentation in the stream and surficial mixing of the sediment layers. POC contents affect denitrification not only by supply of substrate, but also by directly changing

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Figure 3-19. Simulated relationship between bulk NO₃⁻ removal rate and depth averaged POC content.

3.5 Summary and Conclusions

Diffusive groundwater N input has been identified as an important contributor to the coastal eutrophication. It is therefore essential to know what biogeochemical processes may occur in the water during its transfer from the aquifer to the stream. Data were presented here on the effect of the groundwater surface water interface (GSI) at an experimental site located along a 1st-order sandy creek. The major feature of this site is the great difference in chemical composition of the water in the stream and in the aquifer, especially nitrate. It appears that here GSI induces very strong reducing conditions. The evolution of discharging groundwater water towards more reducing conditions is the result of intense bacterial activity involving organic carbon mineralization. The stream sediments, acting as an interface between stream water and groundwater, are preferred sites for this microbial activity. Laboratory intact flow-through column experiments show that many of the changes undergone by discharging water occur in the last 20-30 centimeters of flowpath into the stream water. The evolution of the water chemistry during the transfer through the sediments is represented by consumption/production electron acceptors (oxygen and nitrate) coupled with organic matter degradation. Bacteria play an essential role in these processes as they consume organic matter to produce energy and growth. More than 80% of NO_3^- removal occurred under the flow velocities similar to the field base flow rates, which is consistent with field observations.

A numerical model was developed to simulate the important biogeochemical changes during groundwater seepage with emphasis on NO_3^- . Two parameters appear to be of primary importance for the evolution of the NO_3^- in discharging water: the seepage velocity of the water through the stream sediments and organic matter content in these sediments. An increase in water velocity allows the oxygen propagate further downstream, diminished the extent of the anaerobic zone and attenuates the reducing conditions in the GSI, leading to a decrease in NO_3^- reduction capacity. The influence of sedimentary organic carbon on NO_3^- -removal capability depends on the amount initially present in the GSI and the exoenzymatic solubilization kinetics. In the case studied here, relatively low water velocity combined with high inputs of particulate organic carbon from deposition and surface mixing lead to strong NO_3^- reduction conditions in the GSI.

Optimal parameter estimation by RSA, coupled with multispecies reactive transport models, can be used to improve understanding of NO₃⁻ transport processes and microbial

reaction rates in the GSI. The approach presented in this paper could be modified to

estimate rates and examine processes for the field situation.

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4 NO₃ Delivery through Groundwater Surface water Interface under Laboratory Simulated Bank Storage Condition

4.1 Introduction

The groundwater-surface water interface (GSI) is an area of high biogeochemical activity, often acting to control fluxes of solutes including nitrate from terrestrial to aquatic ecosystems [*Dahm, et al.*, 1998; *Duff and Triska*, 1990; *Hedin, et al.*, 1998]. This critical transition zone plays a major role in determining the concentration of dissolved nutrients in stream waters. Due to the presence of organic deposits, anoxia is common where rates of metabolism are high and pore water is isolated from exchange with overlying oxygenated surface water. Respiration in these environments frequently uses alternate terminal electron acceptors, such as nitrate, after oxygen is depleted. The combination of slow transport of electron acceptors and high rates of metabolism may result in a sharp redox gradient within a few centimeters of the sediment water interface in sandy or muddy streambeds and processes such as denitrification can be concentrated very close to the streambed surface [*Hedin, et al.*, 1998].

Water flow dynamics influence contaminant transport directly due to changes in the volume and direction of water flux across the GSI. The direction of water flow and contaminant flux will respond to changes in water level in either the surface water or groundwater, or both. Changes in water level may originate from hydrological events such as rainfall. However, changes in water flow also exert an indirect effect by altering chemistry that can stimulate or quench biogeochemical reactions controlling the

chemicals. As an example, the inflow of oxygen by groundwater recharge may impact nitrate reduction at the GSI.

A clear understanding of the biogeochemistry of the GSI requires a basic knowledge of the system's hydrology. The impact of temporal gradients associated with hydrological events on the functioning of the groundwater-stream water system is largely unknown [Cirmo and McDonnell, 1997]. In locations with continual infiltration or exfiltration at a relatively steady rate, temporally stable chemical gradients and distribution of microbial processes tend to develop. Other locations within the GSI with variable hydrological conditions may have more temporally variable microbial processes, process rates, and chemical conditions [Dahm, et al., 1998]. With regard to hydrology, it must be understood that water flow across the transition zone may be bi-directional. When a flood wave passes down the stream, the rise in stream level and increasing hydraulic pressure is expected to temporarily impede groundwater input and interstitial water flowpaths may even reverse so that the shallow aquifers are recharged from the channel. At same time, shallow GSI regions immediately adjacent to the sediment surface are likely to be flushed and re-aerated by the increased area and strength of the downwelling zone [Hancock and Boulton, 2005]. This process is referred as bank storage. Bank storage could induce infiltration of oxygenated surface water into GSI. Whether subsurface biochemical processes are curtailed or their rates are altered because of the influx of surface water with radically different chemical composition remains unanswered. To address how biogeochemical processes in the groundwater-stream interface vary during bank storage events, a series of laboratory experiments were conducted in sediment cores collected from the streambed of Cobb Mill Creek, VA. In

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this study, laboratory-based flow-through intact cores were used to study the transport and transformation of nitrate. Bank storage events were simulated by the changing flow direction through the column and also the chemistry of the influent solution. The goals of this study were 1) to determine the physical and biogeochemical processes induced by bank storage, 2) to evaluate the temporal effects of hydrology on nitrate delivery to the stream water, and 3) to determine how the microbial processes affects the nitrate fate.

In line with the experimental evidence (Chapter 2), we consider that the major processes affecting nitrate during bank storage takes place in the first few tens of centimeters of downward infiltration into the submerged streambed sediments. The evolution of nitrate depends on redox process and hydrological flow rate. In this infiltration zone, the flow can be considered saturated and one-dimensional. A simplified diagram of the groundwater surface water interface is shown in. The graphic simplicity of this diagram is purposeful to emphasize the importance of processes involved including hydrologic and biogeochemical processes. Three components are identified within a hypothetical boundary encompassing the groundwater and surface water bodies that exchange water and the chemicals within that component. The three components include 1) the groundwater aquifer, 2) the groundwater surface water interface, and 3) the surface water body. Differences in the relative water level between stream and aquifer will dictate both the direction and magnitude of water flux across the GWI. The figure shows the groundwater recharge induced by the stream water level rise in response to rainfall. The oxygenated surface water is infiltrated into GSI and induces the changing redox condition that might regulate the nitrate attenuation processes. The final





Figure 4-1. Schematic illustration of groundwater surface water interaction induced by bank storage.

4.2 Materials and Methods

4.2.1 Field Site at Cobb Mill Creek

The Cobb Mill Creek is located near the town of Oyster on Virginia's eastern shore between the Chesapeake Bay and the Atlantic Ocean. This is an intensely cultivated sandy coastal plain where the surficial deposits are part of the late Pleistocene Columbia Aquifer and consist of medium-grained quartz sands with some gravelly layers and small amounts of clays and silts. The Cobb Mill Creek is underlain by sandy sediment interbedded by a thin silt layer that is rich in organic material. The field site has been extensively characterized for nitrate contamination and active biogeochemical conditions at the groundwater surface water interface, where natural organic matter have stimulated sufficient indigenous microbial activity to result in nitrate reduction process (Chapter2&5). The details of the field site condition have been recorded in Chapter 2.

4.2.2 Groundwater discharge and recharge rates

Cobb Mill Creek is a first order, groundwater-dominant tidal creek. Measurements of groundwater seepage rate consistently revealed upwelling of groundwater into the stream channel. Estimates of the groundwater velocities within the riverbed were adapted for the inflow rate of Artificial Ground Water used in laboratory column experiment. The mean groundwater gradient measured at 11 sites was 0.15. These gradients were determined by measuring the hydraulic head difference between the stream stage and the groundwater at a depth of about 60cm beneath the stream bottom. The Cobb Mill Creek data are consistent with vertical hydraulic gradient measurements in groundwater discharge zones reported by [Harvey and Bencala, 1993] (0.21 to 0.38), Valett (1993) (0.03 to 0.35) and [Cey, et al., 1999] (0 to 0.55). Groundwater flow rates and NO₃⁻-N loading in Cobb Mill Creek were strongly influenced by the textural composition of subsurface materials at the study sites. The streambed is made of clean, medium-grained sand with an organic material rich layer around 10-20cm deep. Low permeable organic sediment restricted flow and nitrate loading to the stream. The estimated vertical hydraulic conductivity of stream sediments is about 1×10^{-3} cm sec⁻¹ by the laboratory falling head measurement. The porosity was estimated as 0.35. Using these values, the average linear velocity is calculated to be about 3 cm h^{-1} , within the range of extensive seepage meter measurements conducted at streambed (Flewelling, unpublished data). At this rate, groundwater 1m beneath the streambed would take about 1~2 days to reach the stream.

The lack of long-term real-time water table data prevents any information about reversed flow during some large transient hydrological events (our 3-year biomonthly based water table measurement did not capture any reversed hydraulic gradient in the streambed piezometers). As a result, numerical groundwater flow model calibrated at the field site (chapter 5) was used to estimate stream water infiltration rate in response to flood wave. The groundwater downward pore water velocity is less than 0.05 m d⁻¹ (Figure 4-2b), converted to 0.2 cm h⁻¹, according to numerical model assuming a storm with maximum of 1.5 m stream stage rise within 7 days. This flow velocity is too low to allow significant infiltration of overlying stream water within reasonable experiment period. As a result, a velocity of 1.4 cm h⁻¹ was adapted for downwelling rate to exaggerate the extent of surface water infiltration so that a significant effect on solute transport could be investigated.

4.2.3 Experimental Scheme

The experiment was divided into three phases according to the differences in the imposed hydraulic regime (Figure 4-2a). In phase I (140hrs) the column was operated under upflow condition with artificial groundwater (AGW) (chapter 2) as the influent to simulate groundwater baseflow. In phase II (40hrs), the flow direction was reversed to simulate groundwater recharge from stream water induced by rising stream stage Figure 4-2Figure 4-3). The influent is changed into artificial stream water (ASW) simulating low NO₃⁻, high Cl⁻, well-oxygenated surface water. In phase III (150 hrs), the flow was changed to upward direction again to simulate the release of bank storage water after the flooding wave passed.

The intact core was flushed by AGW around 3 pore volumes so that the steady state condition was achieved, indicated by the plateau of breakthrough curve, before the bank storage manipulation. During the whole manipulation of transient flow, pore water samples were collected from intact sediment core from each sampling port using a 3mL syringe. A total of 6-8 concentration profiles were measured at 10-hr intervals. Although there was no direct replication of experiments in this study, comparable concentration profiles were observed in other column operation, suggesting that behavior is reproducible in the collected sediment sample. Pore water samples were centrifuged before analyzing. Nitrate and Chloride concentrations were determined using a Dionex Ion Chromatography with a Dionex IonPac AS4A 4×250mm Analytical Column. The details of column experiment operation could be found in Chapter 2.

4.2.4 Numerical Model

In order to model the biological reactions that occur within the groundwater flow through the GW-SW interface, a one-dimensional advection-dispersion model was chosen as the mathematical formula for modeling the column experiments.

$$Ri\frac{\partial Ci}{\partial t} = D\frac{\partial^2 Ci}{\partial x^2} - v\frac{\partial Ci}{\partial x} + Bi$$
(4-1)

Where Ci is the concentration of the *ith* solute (ML⁻³), Ri is the retardation factor for the *ith* solute, D is the dispersion coefficient (L^2T^{-1}) given by D= α Lv+Dd (α L is the longitudinal dispersivity (L), Dd is the molecular dispersion coefficient), v is the linear velocity (LT⁻¹), and Bi is the biodegradation reaction rate term (ML⁻³T⁻¹) representing the total uptake of the *ith* solute due to all active biodegradation processes. The detailed model development is described in Chapter 3. The physical parameters (v and D) of the cores were obtained by fitting CXTFIT2.0 (Toride et al. 1995) to the observed BTCs of



Figure 4-2. Schematic representation of the experimental setting for simulating bank storage event. a) flow rate and direction adapted in the column study; b) the modeled groundwater discharge/recharge during the bank storage in response to a stream stage rise of 1.5m with duration of 8 days.

Cl-. The constant concentration condition was applied to domain inlet, while nondispersive flux condition was applied to domain outlet. The variation of boundary condition is illustrated in Figure 4-3.



Figure 4-3. Schematic show of bank storage manipulation in the laboratory flow-through column experiment. The normal base flow condition on the left represents the pre-event condition with upward flow and oxygenated, high NO_3^- influent. The bank storage condition on the right represents the downward stream water infiltration with oxygenated low NO_3^- influent.

An important aspect of these simulations was to accurately predict the outlet concentration of NO_3^- from the columns. In a real sediment system this outlet concentration will represent the nitrate flux that enters the stream. If we can model these changes accurately then we have succeeded in showing the important role of the GSI in controlling the release of nitrate into the surface system.

4.3 Results

4.3.1 NO₃⁻ temporal variation during simulated stream water infiltration

The infiltration of oxygenated surface water had a dramatic effect on pore water NO_3^- chemistry. The evolution of NO_3^- concentration during the artificial stream water (ASW) infiltration is shown in Figure 4-4. Prior to the infiltration of surface water into

the sediment, nitrate concentration exhibited a sharp gradient from $\sim 15 \text{ mg L}^{-1}$ in the deep portion of the sediment to about 7 mg L^{-1} at <20cm below the sediment surface. Soon after flow was reversed, the porewater nitrate in the upper portion decreased and approached the nitrate concentration of the artificial surface water (ASW), while nitrate concentration in the undisturbed groundwater (bottom portion) remained high. The dilution front expanded toward the deeper part of the sediment along the time. After 40 hrs of surface water downwelling, the porewater nitrate profile was relatively uniform and did not differ significantly from the nitrate concentration in surface water except for the concentration dip around 15cm depth. Nitrate showed a decrease between 15cm~20cm depth indicating that production of nitrate through nitrification, even if it occurs, has only a minor effect on the observed nitrate profiles. Further, the upper 20cm of the sediment was a main site of inorganic nitrogen metabolism, especially for nitrate reduction. The changes in porewater NO_3^{-1} during the stream water infiltration reflect mixing processes between surface water and groundwater combined with biological activity (see discussion).



Figure 4-4. Transient vertical profiles of NO_3^- during artificial stream water penetration(downward). The reverse flow started at time=0hr.

4.3.2 Mixing Model Results

To distinct biological reduction from hydrodynamic mixing, the Cl⁻ profiles (Figure 4-6) were used to derive the extent of mixing of AGW and ASW. Mixing of surface and subsurface water masses was estimated by a two-end-member mixing analysis (EMMA) using Cl⁻ concentration observed in ASW and AGW. EMMA solves the equations:

$$[Cl]_{PW} = [Cl]_{SW} + [Cl]_{GW}(1-f)$$

where $[Cl^-]_{PW}$ is the porewater Cl^- concentration, $[Cl^-]_{SW}$ is the surface water Cl^- concentration, $[Cl^-]_{GW}$ is the groundwater Cl^- concentration, and f is the fraction of water

derived from surface water. EMMA assumes that Cl⁻ is chemically and biologically

conservative. This mixing model allowed for estimation of NO_3^- retention or production compared with dilution by low- NO_3^- surface water.

Measured NO_3^- concentrations at all depths were lower than predicted from mixing, indicating NO_3^- reduction. Observed NO_3^- concentration at 20hrs after manipulation was 10~82% lower than predicted by EMMA during the infiltration (Table 4-1,

 Table 4-1. Pore water NO₃- concentration 20hrs after ASW infiltration compared to the predicted values based on end member mixing analysis (EMMA)

Depth	% Surface	Predicted NO ₃ ⁻	Observed NO ₃ ⁻	$\% NO_3^-$
(cm)	water	(mg/L)	(mg/L)	retention
4	0.89	0.71	0.39	45.03
7	0.87	0.76	0.40	47.67
10	0.96	0.49	0.38	22.42
13.5	0.89	0.71	0.32	54.89
17.3	0.60	1.59	0.29	81.74
26.5	0.42	2.14	0.85	60.23
31.7	0.27	2.58	1.29	49.93
36.5	0.09	3.13	1.99	36.33
41.3	0.04	3.29	2.67	18.85
46.7	0.00	3.40	3.06	10.00



Figure 4-5. Comparison between observed nitrate concentration and nitrate concentration predicted by endmember mixing analysis (EMMA). Points above the mixing line indicate nitrate production while points below the line indicate nitrate retention.

4.3.3 Transport Modeling Results

Before modeling the profiles of NO_3^- within the columns, it was necessary to determine the hydrodynamic parameters for the columns. Chloride was used as a conservative tracer to estimate and calibrate the hydrodynamic parameters for the sediment columns.

4.3.3.1 <u>Cl⁻ concentration profiles</u>

Before the flow reversed, a pre-event steady state condition was achieved, indicated by a nearly constant spatial profile of Cl⁻ at 0 hr in Figure 4-6. The lack of Cl⁻ concentration gradient suggests that Cl⁻ is a conservative solute, in contrast to $NO_3^$ inFigure 4-4. When high Cl⁻ concentration was introduced via ASW input into the column, Cl⁻ concentration front started to migrate downward (Figure 4-6). The mixing process is the only mechanism involved in the infiltration process. Transport model was calibrated by transient profiles of Cl⁻ without considering biogeochemical reactions. The simulated Cl- profiles matches the observed Cl- profiles very well (Figure 4-6). The calibrated transport model including reaction terms is then applied to NO₃⁻.



Figure 4-6. Simulated (lines) and observed (points) Cl⁻ profiles during the ASW infiltration

4.3.3.2 <u>NO₃ concentration profiles</u>

We now examine if the previously developed model can give results coherent with observations made on the intact cores from the experimental site (concentration profiles), and reproduce the features of the bank-storage effect on the NO_3^- delivery. To this end, some parameters are estimated from laboratory experiments (i.e. Cl⁻ as conservative tracer), from literatures[*Chen, et al.*, 1992; *Hunt*, 1990; *Kindred and Celia*,

1989; *Kinzelbach, et al.*, 1991; *Taylor and Jaffe*, 1990a; 1990b], or from model calibration (chapter 3). The model parameters are listed in Table 4-2 and

Table 4-3. The simulation was run over 14-day period and a comparison between the calculated and observed data for transient state during ASW infiltration is shown in Figure 4-6. Generally, the transient nitrate profiles are well reproduced by the model.

	O_2	NO ₃
Maximum specific growth rate, u_{max} (d ⁻¹)	48	43.2
Half-saturation constant of electron acceptors (mgL ⁻¹)	1.4	2
Half-saturation constant of electron donor (mgL ⁻¹)	1	1
Microbial yield (mg microbial carbon/mg DOC)	0.25	0.2
α , mass transfer coefficient of POC (d ⁻¹) 5×10^{-5}		10-5
Kd, distribution coefficient of DOC	50	
Inhibition constant(mgL ⁻¹)	1.00×10^{-2}	

 Table 4-2 Microbiological parameters used in the simulation of column experiments

 Table 4-3 Physical parameters and boundary conditions used in the simulation of concentration profiles in intact cores of the experimental site

Longitudinal grid spacing	1cm
column length	0.51m
effective porosity	0.28
Longitudinal dispersivity	3cm
Linear velocity	1.4cmh ⁻¹
Simulation time	340h
Time step size	0.2h
O_2 for x=0	$8 mg L^{-1}$
NO_3^- for x=0	15mgL^{-1}
DOC for x=0	0mgL^{-1}

Simulated transient dissolved oxygen profiles are shown in Figure 4-8. Prior to the infiltration of surface water into the sediment, the lowest oxygen concentration was found above 10cm depth. Upon surface water infiltration, the oxygen concentration at the shallow pore water increased immediately response to oxygenated ASW (Figure 4-8). However, O_2 was rapidly consumed at top 10cm presumably by aerobic respiration

process. According to numerical simulation, dissolved oxygen disappeared at around 10cm depth at infiltration rate of 1.5cm/h. The inflow of oxygenated ASW switched the previous anaerobic zone (top 20cm) to aerobic zone, while previous aerobic zone to anaerobic zone (bottom 30cm). The transition of O_2 profiles induced the changing redox condition influencing sequentially microbial reaction with NO_3^- as the electron acceptor.

Nitrate concentration in the pore water increased dramatically just after the upward flow was recovered (Figure 4-9). The rapid migration of NO_3^- concentration front was induced by inflow of high NO_3^- artificial groundwater (AGW). The final steady state profile of NO_3^- was almost identical to pre-event profile of NO_3^- indicating the transient hydrological flow did not significantly affect the biogeochemical characteristics of the sediment.





Figure 4-7. Simulated (lines) and observed (points) NO₃- profiles during the ASW infiltration.

Figure 4-8. The evolution of vertical profiles of O₂ during the ASW infiltration.



Figure 4-9. Simulated (lines) vs.observed (points) NO₃⁻ profiles after upward flow recovered (start point time = 40hrs)

4.3.3.3 Temporal Export of NO3=

NO₃⁻ temporal evolution along the experimental manipulation was shown in Figure 4-10. There was not solute and flow export during the groundwater recharge process. However, the NO₃⁻ concentration at the discharge point was represented by stream water NO₃⁻ concentration for illustration. The NO₃⁻ concentration at outlet initially dropped to zero right after the upward flow reset. And later on, a breakthrough curve was observed and NO₃⁻ profile reached a steady state condition with essentially same NO₃⁻ in effluent as pre-event condition. The breakthrough curve of NO₃⁻ was well fitted by numerical model with unchanged microbial parameters (Figure 4-10). It indicated that microbially mediated reaction kinetics did not change in response to the manipulated disturbance.



Figure 4-10. Temporal variation of NO₃⁻ at the discharge point (simulation:-, observation:*)
4.4 Discussion

4.4.1 Chemical gradient during Streamwater Infiltration

This study is the first to explore the influence of a hydrological event on the solute delivery at GSI using an intact core from a coastal stream in temperate humid area. In the present study, the manipulation of the pore water velocity and the subsequent shift in the direction of the interstitial flow led to changes in porewater chemistry similar to previous findings (Hendricks, 1993; [*Pusch*, 1996]. Some transient changes in water quality were observed associated with the 6 days transient flow pulse. As compared with the original, upwelling steady-state base flow condition, downwelling of surface water led to lower concentrations of nitrate and to a concurrent increase in oxygen concentration immediate beneath the sediment surface. The observed changes in pore water chemistry suggest that during the simulated bank storage, the sediment pore water was successively replaced by infiltrating water from the surface.

Our microcosm system reproduced a clear vertical gradient from aerobic to anaerobic processes at a centimeter scale. Nitrate removal at the top 15 cm depth during stream water infiltration was negligible. At this depth, since O_2 could be preferentially used as an electron acceptor during the organic matter degradation, any large removal of NO_3^- by denitrification was not accomplished. The respiration in the top layer leaded to a rapid decrease of oxygen concentrations within short distance in the sediment, promoting the occurrence of anaerobic process downstream the flow path, i.e. denitrification.

4.1.2. Mechanisms of NO_3^- Transient Dynamics

Hydrological changes during bank storage had important biogeochemical consequences of NO_3^{-} . In the field scale, flash floods or spates can produce nearly

instantaneous shifts in state that alter nutrient cycling pathways [*Dahm, et al.*, 1998]. Likewise, in our laboratory setting, NO_3^- concentration in the pore water was significantly reduced. Nitrate concentrations at GSI declined after the stream water infiltration, implying the dilution by the low NO_3^- stream water. This was also documented in the study by Pinay et al.(1998), in which they attributed a large portion of the seasonal NO_3^- decrease only to dilution by NO_3^- poor river water. Our results show that this explanation is not necessarily the case. Although pore water contained a successively greater amount of surface water during ASW infiltration, observed $NO_3^$ concentrations were still 10~80% lower than those predicted from dilution alone (Table 1). Indeed, biologically mediated loss must not be discounted.

The microbial NO_3^- reduction during the ASW infiltration could be detected from the transient vertical profiles of NO_3^- (Figure 4-4). The mixing front of low- NO_3^- ASW and high- NO_3^- AGW penetrated downwardly during the infiltration of ASW. However, instead of single increasing trend of NO_3^- along the depth, we observed a concentration dip around 15 cm deep, corresponding to the location of POC-rich layer. We hypothesize that the strip of NO_3^- is related to the microbial activities within this layer.

We estimated substantial rates of denitrification despite of oxygenated inflow of ASW (Table 4-1,). Pinay et al.(1998) argued that groundwater denitrification at the GSI with significant hydrological exchange should be minimal because of the presence of dissolved oxygen. In contrast to this observation, while the bank storage flow caused an increase oxic zone of the GSI where nitrate reduction occurred, this was not complemented by subsequent quench of denitrification. The rate of oxygen replenishment from ASW lagged behind the rate of consumption of O_2 by oxidative degradation of

organic matter at the surface layer of the sediment and biogeochemical conditions favorable for denitrification were developed in the depth below the oxidizing surface layer. In this sense, redox zonation was just reversed during the reversed flow without affecting biogeochemical function of GSI.

This result was comparable with downwelling area in Speed River, Canada, where anaerobic condition and denitrification were observed at downwelling area [*Storey, et al.*, 2004]. An increase in dissolved oxygen from bank recharge influx was never observed in groundwater samples at Chena River, AK (Hinzman et al., 2000). This absence of dissolved oxygen was attributed to quick utilization by microorganisms in the sediment. Dissolved oxygen concentration was usually highest in the sediment surface [*Brugger, et al.*, 2001] and decreased with increasing depth in the slow filtration columns [*Mermillod-Blondin, et al.*, 2005]. [*Hancock and Boulton*, 2005] observed same nitrate decline as we found in the Hunter River, Australia and attributed it to flushing of interstitial nitrate from the sediments by the increased flow and enhanced microbially facilitated denitrification.

The observed active nitrate reduction in infiltrated stream water in this study is in contrast to most previous studies [*Jones, et al.*, 1995; *Wondzell and Swanson*, 1996]. In most of these studies, dissolved oxygen (DO) remained relatively high through the GSI and nitrate increased along subsurface flow paths. In Cobb Mill Creek sediment, however, nitrate and DO both decreased to low levels along the infiltration flow path. This is due to a number of factors. First, because interstitial flow velocities were 2-3 magnitudes lower than the other studies described here (0.126-4.5mh⁻¹,[*Jones, et al.*, 1995]; 0.01-0.02mh⁻¹ in this study), microbial activity at GSI had ample time to remove

oxygen from the inflowing water. Second, respiration rates and denitrification rates were higher probably because POM was higher in Cobb Mill Creek sediments than at most other sites, causing rapid oxygen uptake and nitrate reduction.

Nitrification was likely of minor importance during the bank storage. The most likely reason is that the high amount of POM in the top portion of the sediment allowed heterotrophs to outcompete nitrifiers for oxygen [*Storey, et al.*, 2004]. The other reason is probably relatively low concentrations of ammonium brought in by groundwater and surface water. The relative importance of nitrification as a source of nitrate was further decreased by the moderately high concentration of nitrate in inflowing surface water. In contrast, denitrification was of major importance because of this moderately high nitrate concentration.

The NO₃⁻ profile of pre-event condition was recovered very rapidly right after the upward flow was reset with initial AGW influent. Most denitrifying bacteria are facultative anaerobes, allowing them to exploit environments that alternate between oxic and anoxic conditions. Since bank storage induce alternating oxic and reduced conditions in the top layer of sediments, a significant change occurs in nitrate dynamics in the sediments, as was observed in this study. Although it has been argued that the alteration of redox condition would have a negative effect on the removal of nitrate through denitrification process, Reddy and Patrick (1975) observed that nitrogen losses in soil slurries increased with the frequency of alternating aerobic and anaerobic conditions. In our experimental setting, NO₃⁻ removal efficiency of the stream sediment was neither strengthened nor weakened in this study. It indicated microbial community could adapt

the transient variation of redox condition occurring in the time scale of hydrological events, i.e. days.

4.4.1 Reaction Rates

The spatial distribution of aerobic respiration and denitrification rates under both upflow and downflow condition indicates the active reaction zone of up 20cm (Figure 4-11~14). The redox zonation did not move but was reversed by changing flow direction.



Figure 4-11. Microbial reaction rates distribution at pre-event steady state condition.



Figure 4-12. Microbial reaction rates distribution during the ASW infiltration

The respiration rates measured in the surface layer of the sediment indicated an aerobic respiration of $1.7 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$. This is about one magnitude lower than respiration rates measured with a flow through system filled with natural hyporheic sediments (126-864µg O₂h⁻¹) measured in several stream sediments (Kaplan and Bott, 1983; [*Pusch*, 1996]. The discrepancy is probably due to the different system. Most of those studies applied artificial labile substrate i.e. acetate in the influent as the electron donor supply. In contrast, the only carbon source is from POC enzymatic hydrolysis in our system. The NO₃⁻ consumption rate was estimated to 0.38 mg NO₃⁻ -N L⁻¹h⁻¹ at the 17 cm depth. This process rate was close to the denitrification rates (14.25 mg NO₃⁻-N L⁻¹h⁻¹) measured by Sheibley et al. [*Sheibley, et al.*, 2003a] in sediment perfusion cores simulating a sandy hyporheic zone. Our estimations of NO₃⁻ consumptions were consistent with studies performed in different sediment types (see Table 5 in [*Sheibley, et al.*, 2003a]. These comparisons of rate of biogeochemical processes demonstrated that

our intact core properly simulated hydrologic characteristics and function occurring in natural stream sediment.

During the ASW infiltration, while aerobic respiration rate kept almost unchanged, denitrification appeared to be limited by nitrate (Figure 4-11, Figure 4-12), which occurred at much lower rate ($0.4 \text{ mg NO}_3^-\text{-N L}^{-1} \text{ h}^{-1}$ at maximum) than in the upward flow conditions ($1.9 \text{ mg NO}_3^-\text{-N L}^{-1} \text{ h}^{-1}$ at maximum). Hill et al. [1998]reported that denitrification rates in another N-rich agricultural stream similarly were limited by the rate of nitrate supply. The higher denitrification rates were observed in upwelling flow due to the higher nitrate concentrations in the upwelling flow, as the denitrification was strongly correlated with nitrate concentration. Organic carbon, which appeared to be responsible for raising the denitrification rate, did not seem to be an important factor during the whole processes because POM content kept unchanged and the replenishment of DOC from the dissolution of POM was essentially same given the similar pore water velocity of the downward and upward flow.

In our experiment setting, DOC was not included in ASW since it was assumed the intact core was not carbon limited. However, DOC is present in natural stream water, which could be another factor to the denitrification process in carbon-limit area. Storm and associated increased in discharge lead to an increase in DOC concentration by two to as much as five to tenfold in nearly all streams and rivers (McDowell and Likens, 1988; Mulholland and Hill, 1997;Wehr et al., 1997). Organic carbon in stream water was found to be responsible for raising the denitrification rate of the downwelling zone above that of the upwelling zone in an Arizona desert stream [*Holmes, et al.*, 1996].

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4.5 Implication

The bank storage could induce the groundwater recharge by stream waters [*Sophocleous*, 2002]. While this process caused aeration of GSI, this was not complemented by subsequent deterioration of nitrate reduction capacity as would be expected if denitrification was inhibited by oxygen. This experimental result is consistent to our field observation, where the absence of a temporary pulse in stream nitrate concentration were found during storms.

Change in water chemistry after floods will depend on hydrologic residence time, and rates and types of biochemical processes in the GSI [*Triska, et al.*, 1993b]Longer interaction time with GSI zone and biota will be allowed when stream water enters the adjacent aquifer. The parafluvial functioning re-established immediately after the flood receded in a desert stream, Sycamore Creek, in AZ [*Holmes, et al.*, 1994]). In our simplified experimental setting, for a hypothetical storm, concentration of NO₃⁻ in seepage water returned to pre-event values almost immediately after "flood". Some of the stream water entering the GSI zone during the bank storage slowly seeps back into the surface stream during the interflood period as hydraulic gradients reverse. Due to biological removal of NO₃⁻ in the storage water, returning water dilute stream water with respect to NO₃⁻, but gradually enriched NO₃⁻ after high NO₃⁻ deep groundwater replace the storage water until a post-event steady state was built.

The observation from laboratory simulation could be extrapolated to the catchment scale NO_3^- delivery dynamics during transient bank storage event. The biogeochemical reactions during the stream-aquifer interaction are often limited to the top layer of sediments (<60cm) [*Galavotti*, 2004; *Hill, et al.*, 1998; *Morrice, et al.*, 2000]. In

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consequence, studies at small scale (laboratory microcosm) are needed to finely quantify biogeochemical processes in near stream zone. The laboratory microcosm experiments using intact cores constitute a promising tool to measure biogeochemical rates in heterogeneous sediments and under realistic interstitial flow conditions (Mermillod-Blondin et al., 2000; [Mermillod-Blondin, et al., 2005; Sheibley, et al., 2003a].

The mitigation of nitrate in stream water during bank storage consists of two parts, temporal shut down of nitrate source from deep groundwater, and removal of infiltrated nitrate as nitrate sink. The long water residence time during bank storage meant that the cumulative effect was great. The extent of this attenuation largely depends on penetration depth. The penetration depth is the important indicator of the extent of exchange of groundwater and surface water. The numerical flow and transport simulation indicates that reduced nitrate flux is positively related to the penetration depth (Figure 4-13). In high order river with extensive floodplain area, the penetration depth of river water during bank storage could be as deep as 1-2 m below the river sediment [*Squillace*, 1996]. According the linear relationship shown in Figure 4-13 (same denitrification capacity assumed as the present study), the estimated flux reduction for this region would be $10\sim16.5$ g NO₃⁻-N m⁻². Given the large wetted perimeter and reach length of floodplain region, the total reduction of nitrate loading would be greatly significant.

Although only reversed flow was simulated in this study, the reduced discharge induced by stream stage rise has the same effect as bank storage. As a flood wave passes in the stream, hydraulic gradient drives stream water into the GSI or just reduced the groundwater discharge. Water resides there for different durations depending on rainfall intensity and patterns. During small events the water table rose by 0.1-0.3 cm and

residence time was in the order of 3-5 days. During larger bank-full events, the stream water level rose as high as 1-2 m and residence time was in the order of a couple weeks. When flood wave passed, the positive streamward gradient is re-established and then water eventually drains back to the stream. Conditions favorable for denitrification processes in GSI occur via two mechanisms as well as found at Coochin Creek, Australia [*Rassam, et al.*, 2006]: firstly, as base flow passes through the carbon-rich saturated GSI, and secondly, as stream water gets temporarily stored in GSI. In our experimental study, the relative importance of the second mechanism is likely to be low because the limited exchange of groundwater and surface water, and low nitrate in stream water compared to high nitrate delivery from deep groundwater.



Figure 4-13. The relationship between reduced NO_3^- load and stream water penetration depth under the current denitrification capacity found in the sediment of the Cobb Mill Creek

Attention should also be paid to the hydrology of bank storage water release.

Instead of gradually recovered baseflow, at the high order river with large floodplain, the bank storage water might release at a much higher discharge rate "release pulse" initially then gradually declines back to pre-event baseflow condition. Squillace [1996] observed that during the first three weeks of base flow bank storage caused groundwater discharge to the river to increase by a factor of five compared to the pre-event conditions. Furthermore, it took about five weeks for bank storage water to release until steady-state

discharge to the river was once again established. This might induce the relatively long-time transitional high NO_3^{-1} loading to the stream due to shortened residence time.

On a long-term basis, large floods recur, and NO_3^- delivery will be presumably affected by the disturbance regimes. By the numerical model tested in the laboratory microcosm experiments, we will be able to investigate the response of NO_3^- delivery to storm frequency, intensity, and duration. The key factor here is penetration depth, which determines the magnitude of bank storage zone and time scale of transient variation of chemical loading. Based on the knowledge obtained from theses numerical experiments and the field hydrograph, we can estimate to what extent the transient hydrological events could change the annual NO_3^- exports in the Cobb Mill Creek.

4.6 Conclusion

In summary, hydrologic exchange induced by bank storage enables microbial communities to retain and utilize nitrate at the GSI that might otherwise be exported from the system. The extent of hydrologic exchange has a significant effect on the GSI's ability to retain nitrate by increasing sediment surface in contact with stream water and increasing the amount of nitrate in contact with biologically and chemically active

sediment surfaces. The shift of redox condition induced by groundwater surface water exchange does not impact the nitrate attenuation function at GSI. In streams with high nitrogen loading and significant groundwater surface water interaction, hydrologic exchange has a significant impact on nitrogen loads as microbial reactions at the GSI serves as a natural filter of nitrate either from groundwater or from surface water.

The laboratory microcosm study presented here point to the need, at high order river with extensive floodplain areas, to monitor during base-flow conditions and during times when system hydrology is perturbed from base-flow, e.g., during a storm event. Observation of the response and recovery of the groundwater surface water transition zone to significant perturbation to the hydrologic system could provide useful insight into the system functionality. First, this type of study will provide a realistic assessment of the range in the magnitude and directionality of contaminant flux that can be anticipated for the stream-riparian system. In addition, this type of study presented here will delineate the dominant processes controlling nitrate loading into or out of the surface water. A complete understanding of the hydrology helps us construct sound conceptual models for nitrate removal at GSI. When this conceptualization is coupled with field-based estimates for denitrification rates, we can incorporate this knowledge into catchment scale models and hence have the ability to assess the role of GSI buffers in limiting nitrogen delivery to streams.

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5 Numerical modeling of stream-aquifer interaction and consequential NO₃⁻ delivery in a hillslope-riparian forest area at Cobb Mill Creek, VA

5.1 Introduction

Stream riparian areas represent zones of important ecological and hydrological processes that control the linkage between hillslope and channel domains in watersheds. In humid temperate environments, the riparian is of great significance to pathways and dynamics of contaminant transport [*Hill*, 1990; , 1996a]. Stream-aquifer interaction has important implications on stream chemical loading [Cirmo and McDonnell, 1997]. Despite considerable research on channel-aquifer interactions in the hyporheic zone [Dahm, et al., 1998; Stanford and Ward, 1993], very little has been published about the complex hydrological interactions between stream-riparian zone on a high-resolution event base. Such high-resolution transient dynamics are essential to an understanding of riparian hydrology and thereby its biogeochemical functions. For example, nitrogen cycling processes will be strongly dependent on hydrological "fluctuations" within the groundwater surface water interface (Chapter2). The hydrological interaction impacts flow paths, residence times, and the exchange of potential reactants. Hence, a better understanding of the dynamics of riparian hydrology is a key step toward the better water quality management in watershed scales.

In the absence of field data or a detailed conceptual model, suitably parameterized and validated numerical modeling would seem a useful methodology for initial studies, providing an indication of the location, scale, and intensity of surface-subsurface interaction zone [*Claxton*, 2003]. Recently, interest in the hyporheic zone has led to research into stream-subsurface interactions and limited use of numerical models to analyze and extend field data sets [*Wondzell and Swanson*, 1996; *Wroblicky, et al.*, 1998]. [*Wroblicky, et al.*, 1998] used the two-dimensional generalized groundwater scheme MODFLOW to simulate seasonal variation in the areal extent of the hyporheic zone in two first-order streams. The model was applied in the horizontal plane with a 3-day time step that did not resolve individual flow events themselves and used the hillslope fluxes to calibrate the hydraulic head predicted by the model.

Several limited modeling of groundwater piezometric heads and water table gradients have been undertaken with a view to quantifying bank storage and aquifer recharge. For example, [*Squillace*, 1996] used MODFLOW to simulate a 440-m lateral cross section of the floodplain of the Cedar River, Iowa. The model consisted of 660 cells 10 m wide and 1m deep and extended 15m below the ground surface. Groundwater movements during a 42-day period representing a small in-bank flood peak and subsequent recession were then simulated using a daily model time step. The model provided a reasonable match to the observed hydraulic head data and a sensible estimate of the daily bank storage flux.

Bates et al. [2000] combined field data with two-dimensional vertically aligned numerical modeling to study river-floodplain-hillslope interactions along a crossfloodplain transect for two over-bank events at the River Severn field site. The results showed that an extensive hyporheic zone and a groundwater ridge formed within the floodplain during over-bank flooding because, while the water table in the near-channel zone rose near-synchronously with the rising river stage, the water table at the base of the hillslope did not respond until much later in the event. The groundwater ridge temporarily "switching off" subsurface hillslope inputs to the channel, a condition that, depending on the event dynamics, can prevail for up to 10 days according to the results of [*Claxton*, 2003]. The two-dimensional model was found to perform well around the flood peak but was much less successful during the rising and recession limbs.

A combined modeling and field monitoring study of hydrological interactions within a hillslope field site will help to understand the hydrological control on NO₃⁻ transport and export in the catchment scale. Accordingly, we developed a generalized two-dimensional finite element model capable of representing variable saturated flow in vertically aligned cross section through the hillslope/channel continuum. Simulations were conducted to determine flow pathways and the magnitude of hydrological fluxes during several flood events. Further, we extend flow model to include an advectiondiffusion equation for conservative and nonconservative transport. This model is then applied to a hillslope-riparian site on the Cobb Mill Creek, VA, for which peizometric, precipitation, and stream stage measurements exist to parameterize and calibrate the model. Our aim was to use a suitably conditioned high-resolution numerical model to better understand hydrological processes and solute transport in hillslope scale during the transient storm events.

5.2 Field Site

Cobb Mill Creek drains a 4.96 km² low relief coastal plain catchment, located 19 miles north of the mouth of the Chesapeake Bay on the Eastern Shore of Virginia in the Anheuser-Busch Coastal Research Center (ABCRC) (Figure 2-1). Land use in the catchment is dominated by forested (62%) and agricultural (34%) areas, with the remaining 4% of land area in residential and other uses. Ground water discharging to

Cobb Mill Creek comes from the unconfined Columbia aquifer, composed of Pleistocene-aged unconsolidated sands (generally 8-30 m thick; [*Calver*, 1968; *Mixon*, 1989]) with high hydraulic conductivity previously determined from slug tests to be 5.53 x $10^{-5} \pm 1.56 \times 10^{-8} \text{ m s}^{-1}$ [*Hubbard, et al.*, 2001]

Cobb Mill Creek is a sandy first-order tidal creek that drains into Oyster Harbor. It is a groundwater-dominated stream surrounded by a riparian forest. Surface relief is generally low, with greater slopes along regions immediately adjacent to the streams. The majority of the length of Cobb Mill Creek is non-tidal freshwater. A hill slope along the non-tidal portion of the Creek, just upstream of the tidal zone was chosen as the focus of observational and experimental work (Figure 2-1, Figure 5-1).

This part of reach is characterized by sandy bottom of channel with a water depth of 20-40cm. Hillslope lengths are short, less than 50 m, with slopes of 5~15%.

5.3 Methods

5.3.1 Field methods

A network of wells and piezometer nests has been installed on the hill slope to monitor the spatial and temporal patterns of nitrate concentrations and hydrological conditions in the subsurface (Figure 5-1). To date, there have been 10 piezometer nests and 16 wells installed in the stream and hillslope. Wells and piezometers are constructed of 1 inch I.D. PVC well casing. Wells penetrate 1.5- to 5-m below the water table and are screened at least 1-m above the maximum water table. A single transect of six shallow, partially penetrating wells and piezometer nests, S1, N1, N3, N7, N9, N11 crossed the hillslope, nearly perpendicular to the stream and parallel to the direction of the shallow groundwater flow (Figure 5-1). This hillslope transect was characterized by a relatively steep slope immediately adjacent to the deep incised stream channel. The stream bank is eroded by the curvature of the stream. As a result, it has a deep stream bank of ~1.2m. A streambank well, N1, was equipped with a pressure transducer (Levellogger, Solinst – details) to continuously record groundwater levels at 10 min intervals. Another transducer was installed in a stilling well to record the stream stage at 10 min intervals.



Figure 5-1 Plan view of experimental hillslope showing piezometer locations and contours of hillslope surface topography.

The entire hillslope site was surveyed with mean sea level (MSL) as the datum to establish the elevation of the monitoring wells (and thus the elevation of the hydraulic head), and a general topography of the site. All measures, including stream stage, were expressed as ASL (above sea level). Storm-event sampling for the two storms was conducted using a stage-activated ISCO sampler. The automated ISCO sampler was triggered for event sampling when the stream stage rose above a threshold of 5 cm. The sampler was programmed to sample at one-hour intervals. All samples were collected within 24 hours of an event in 500 ml plastic bottles. Anion concentration analysis of nitrate and chloride was conducted on a Dionex ion chromatograph.

5.3.2 Model development

A numerical model capable of simulating the effects of stream-aquifer interactions on the fate and transport of nitrate in a near-stream zone was developed for use in this investigation. The numerical model comprised a saturated-unsaturated flow module and a contaminant fate and transport module.

Although the hydrodynamic processes in stream-aquifer system are threedimensional, the relevant processes can be approximated on a vertically oriented plane. The primary processes of concern in the aquifer are the transport of contaminants towards the stream and the interaction of stream water and the aquifer that can also be approximated on a vertical plane.

The general problem to be evaluated is shown in Figure 5-2. The setting is a stream channel situated at the right edge of the cross-section domain. The creek has sediments of low permeability around the channel. The underlying aquifer is part of Columbia aquifer and is fairy homogeneous [*Reay, et al.*, 1992]. The upper surface shown in the diagram is land surface, and the water table is allowed to move freely within the porous medium.



Figure 5-2. Schematic cross-section of the Experimental transect at Cobb Mill Creek Site. Each piezometer nest consists of a well and several piezometers with opening holes at different depths (not all piezometer nests along the transect are shown).

5.3.2.1 Groundwater flow model

Whiting and Pomeranets [1997] developed a specific model, WaTAB2D, for application to floodplain hydrology. Their model was thus based on an exact formulation for time-dependent, unconfined, saturated groundwater flow. They investigated channel/floodplain interactions to determine the effect of the release of bank storage water on river flow over periods of several months following an instantaneous drop in water level. The model applied only to saturated conditions and only idealized floodplains of varying width and hydraulic conductivity were simulated.

Problems that involve non-steady flow of groundwater with a free surface in the saturated zone are extremely difficult to solve by exact analytical methods. To simplify

the treatment of such problems, groundwater hydrologists have traditionally relied on the well-known Dupuit assumptions. Most widely known groundwater modeling packages designed to treat extensive regions (MODFLOW (McDonald and Harbaugh,1988); AQUIFEM (Townley and Wilson,1980)) make use of the simplifying Dupuit assumptions when dealing with a free surface (Anderson and Woessner,1992). These assumptions lead to the Boussinesqu equation, which has been extensively treated by Bear (1968) and others. Giesen and others (1994) found that, because the Boussinesq equation neglects vertical flow, the resulting solution overestimated seepage rates immediately after a sudden change in stream stage and underestimated seepage rates at later times. The analytical solutions, however, are limited to flow systems in which the boundaries are simple and geometric, the porous medium is relatively uniform, and the vertical gradients throughout are not too large.

In summary, previous numerical modeling of floodplain hydrology has ignored unsaturated flow or assumed Dupuit-Forcheimer condition that may not be appropriate in hillslope situations. A combined modeling horizontal and vertical variable saturated flow will overcome the limitations of previous research.

Most of the previous models dealing with variable saturated flow are based on the numerical solution of the well known Richards equation having either the pressure head (ψ) or the moisture content (θ) as a dependent variable [*Clement, et al.*, 1994; *Cooley*, 1983]. Numerical solutions of the ψ -based equations have been reported to produce significant mass balance errors in contrast to the θ -based equations [*Celia, et al.*, 1990]. The θ -based formulations, however, have the drawback that they are not suitable for saturated-unsaturated or near saturated flows. The θ -based equation is usually not used

for general groundwater hydrology problems because material discontinuities produce discontinuous θ profiles [*Celia, et al.*, 1990].

Celia et al. [1990] presented a mixed form of the Richards equation to overcome mass conservation problems while retaining the advantages of the ψ -based formulation. Rathfelder and Abriola [1994] worked in a 6-h infiltration simulation under constant surface ponding and showed that finite difference solutions of the ψ -based form of the Richards equation can produce excellent mass balance accuracy if the specific moisture capacity function is evaluated by a standard chord slope approximation. Babajimopoulous [2000] suggested that the ψ -based formulation is more accurate and faster than the mixed form, if the Douglas-Jones predictor-corrector method is used for its solution.

Consequently, we used an exact traditional model describing time-dependent unconfined (i.e. with a free surface) saturated-unsaturated groundwater flow (Bear, 1972). In notation used by Neuman and Witherspoon(1971), the model reads:

$$\frac{\partial}{\partial xi} (KrKi \frac{\partial h}{\partial xi}) = (SwSs + C(\psi)) \frac{\partial h}{\partial t}$$
(5-1)

where

xi = horizontal and vertical coordinate directions, L;

Ki = principal components of the hydraulic conductivity tensor, aligned collinear with the x and z direction, L/T;

Kr = relative permeability, assumed to be a scalar function of water saturation, L/T; S_w = water saturation, which varies between zero for dry conditions and 1 for saturated conditions, dimensionless;

Ss = specific storage, 1/L;

n = porosity, dimensionless;

h = hydraulic head, L;

C = specific moisture capacity, $= n \frac{dSw}{d\psi}$

 ψ = pressure head, equal to h-z, z is elevation head, L;

t = time, T.

Equation (5-1) contains two unknown parameters for which functional relationships need to be specified. Relationships between water saturation and pressure head and between water saturation and relative permeability are nonlinear. They also vary greatly for different types of soils and rocks. The homogeneity of soil texture observed at our site suggests a single relationship would suffice. The general characteristic curve from the literature could be used (Cooley and Westphal, 1974; Winter, 1983)

Normalized water saturation can be specified as (Cooley and Westphal, 1974)

$$S_{wD} = \frac{A}{\left(-\psi\right)^c + A} \tag{5-2}$$

where

$$S_{wD} = \frac{S_w - S_{wr}}{1 - S_{wr}}$$
(5-3)

 S_{wr} is residual, or nonmoving water saturation, and A and c are empirical parameters. Relative permeability is specified as (Cooley and Westphal, 1974)

$$Kr = S_{wD}^{d}$$
 (5-4)

where d is an empirical parameter. Because of the preliminary nature of this study, and for simplicity, hysteresis is neglected in (5-2) and (5-3).

Soil parameters were prescribed on the basis of regional slug tests (Hubbard et al. 2001) and laboratory falling head tests. These indicated an average saturated hydraulic conductivity of 5×10^{-3} cms⁻¹ [*Hubbard, et al.*, 2001] for the aquifer and 4×10^{-4} cm s⁻¹ for the stream channel materials (Chapter 2). For these simulations, spatially uniform material properties were used and represented by a Brooks and Corey soil water retention model. This approach was selected as run times were quicker and with fewer stability problems than with the van Genuchten model. The residual and saturated moisture contents and the Brooks and Corey parameters were mean values for a sandy soil. To develop an appreciation of the physical meaning of the empirical parameters A, c, and d, plots of the functions for a number of different values are given in Figure 5-4. The relationship of water saturation to pressure head is affected by the pore size distribution of the media [Brooks and Corey, 1966]. The relationship is shown in Figure 5-3a for five values of A at a value of c = 4. For example, if A = 1, the curve has an S shape characteristic of a relatively uniform sand. As progressively greater values of A are considered at the same c value of 4, the curves move upward, but their shapes do not change much; their S shape becomes slightly less sharp. Plots of this same relationship where A is constant (A=10) and values of c are varied are shown in Figure 5-3b. Variation in this parameter clearly has a significant effect on the sharpness of the S shape of the curves. The shapes of the curves in Figure 5-3b for progressively smaller values of c are characteristic of curves determined for progressively finer-grained and more poorly sorted media. For example, the curve for a c value of 2 is very much like those for silty loams and silty clay loams. A c value of 4 is used in this simulation to represent the medium grained sand. Concerning the relationship of relative permeability to water

saturation, the empirical approximation was developed in equation (5-4). The exponent in this approximation (d) is directly related to the pore size distribution of the porous media shown in Fig 5-3c. The exponent almost always is between 3 and 4 based laboratory analysis of porous media samples [*Brooks and Corey*, 1966].



Figure 5-3. Relationship of water saturation to pressure head and relative hydraulic conductivity for various values of the empirical parameters used to describe unsaturated water flow a) curves for different values of A with c constant (equation 2), b) Curves for different values of c with A constant (equation 2), c) Curves for different values of d (equation 3).



Figure 5-4 (cont.). Relationship of water saturation to pressure head and relative hydraulic conductivity for various values of the empirical parameters used to describe unsaturated water flow a) curves for different values of A with c constant (equation 2), b) Curves for different values of c with A constant (equation 2), c) Curves for different values of d (equation 3).

In addition to the functional relationships discussed above, equation (5-1) also contains several simplifications, as discussed by Cooley (1971); (1) The movement of air is considered passive, (2) the effects of total stress changes at a point caused by increasing or decreasing saturation are neglected. (3) the effects of variable formation compressibility caused by deformation and changing saturation are neglected. The latter appears in the specific storage (Ss) term.

5.3.2.2 Solute transport

The differential equation describing mass transport and dispersion of dissolved constituents in a saturated or partially-saturated porous medium can be written in two dimensions (Bear, 1972) as:

$$L(C) = \frac{\partial}{\partial x} \left(\theta Dxx \frac{\partial C}{\partial x} + \theta Dxy \frac{\partial C}{\partial y}\right) - qx \frac{\partial C}{\partial x} + \frac{\partial}{\partial y} \left(\theta Dyy \frac{\partial C}{\partial y} + \theta Dyx \frac{\partial C}{\partial x}\right) - qy \frac{\partial C}{\partial y} - R - \frac{\partial C}{\partial t} = 0 \quad (5-5)$$

in which C is concentration of solutes; D_{xx} , D_{xy} , D_{yy} , D_{yx} are hydrodynamic dispersion coefficients; q is specific discharge (Darcy velocity); θ is effective porosity; R is zero order reaction constant. This form of the equation includes the effects of advection, dispersion, zero-order reaction for the dissolved constituent.

A comprehensive discussion of the factors affecting the hydrodynamic dispersion coefficients is given by Bear (1972). Briefly, hydrodynamic dispersion includes two processes: mechanical dispersion and molecular diffusion. Mechanic dispersion depends on both the flow of the fluid and the pore system through which flow takes place whereas molecular diffusion results from variations in solute concentration within the liquid phase.

$$D_{ij} = D'_{ij} + D''_{ij}$$
 (5-6)

where D'_{ij} is coefficient of mechanic dispersion and D''_i is coefficient of molecular diffusion. For most situations, the contribution of D''_{ij} to hydrodynamic dispersion is negligible when compared to D'_{ij} . Hence, for all practical purposes we can assume that $D_{ij} \cong D'_{ij}$.

Since it is impractical to evaluate all the components of the mechanic dispersion tensor, it is generally assumed that the porous medium is isotropic with respect to dispersion. Using this assumption, Bear (1972) expressed the hydrodynamic dispersion coefficient as:

$$D_{xx} = \alpha_L v_x^2 / v + \alpha_T v_y^2 / v$$

$$D_{yy} = \alpha_L v_y^2 / v + \alpha_T v_x^2 / v$$

$$D_{xy} = D_{yx} = (\alpha_L - \alpha_T) v_x v_y / v$$
(5-7)

where α_L is longitudinal dispersivity of the porous medium (in the direction of flow); α_T is transverse dispersivity of the porous medium (normal to the direction of flow); v_i , v_j are components of the seepage velocity in the i- and j- directions, respectively; v is magnitude of the velocity.

In this analysis it has been assumed that the longitudinal and transverse dispersivities are related by

$$\alpha_{\rm T}=0.1*\alpha_{\rm L} \tag{5-8}$$

5.3.2.3 Numerical solution

Galerkin's finite-element method is used to determine approximate solutions to equ.5-1 and 5-5 under the appropriate initial and boundary conditions. If the time

derivative $\partial h/\partial t$ appearing in equation (5-1) is replaced by $\partial h^n/\partial t$ as is commonly done, Neuman (1973) found difficulty in obtaining numerical convergence. He obtained a more stable solution by defining the nodal values of the time derivatives as weighted averages over the entire flow region according to:

$$\frac{\partial h}{\partial t} = \frac{\sum_{e} \int_{\Omega^{e}} (S_{w}S_{s} + C) \frac{\partial h}{\partial t} Nidxdz}{\sum_{e} \int_{\Omega^{e}} (S_{w}S_{s} + C) Nidxdz}$$
(5-9)

A functional representation of the parameters K and C within an element can be assumed to vary linearly using the same set of spatial functions Ni in the form:

$$K=K1(\psi)N_1$$
, $S_w=S_w(\psi)N_1$, and $C=C_1(\psi)N_1$ (5-10)

The technique of using fuctional representations of system properties has been used by Neuman (1973) and Pinder et al. (1973).

The resulting set of finite-element equations for water flow can be written in matrix form as:

$$A\{h\} + B\{\frac{\partial h}{\partial t}\} + E = 0$$
(5-11)

where A and B are $n \times n$ matrices and E is a vector of length n. These are expressed:

$$A_{ij} = \sum_{e} \int_{\Omega^{e}} \left[K_{xxJ} N_{l} \frac{\partial Ni}{\partial x} \frac{\partial Nj}{\partial x} + K_{zJ} N_{l} \frac{\partial Ni}{\partial z} \frac{\partial Nj}{\partial z} \right] dx dz = \sum_{e} \frac{1}{12\Delta} \left[\left(\sum_{l=1}^{3} K_{xx,l} \right) b_{l} b_{j} + \left(\sum_{l=1}^{3} K_{zz,l} \right) c_{i} c_{j} \right]$$
(5-12)

$$B_{ij} = \sum_{e} \int_{\Omega^{e}} (Sw_{i}Ss + C_{i})N_{i}N_{i}dxdz = \sum_{e} \frac{\Delta}{12} [((\sum_{l=1}^{3} Sw_{l}) + Sw_{i})Ss + (\sum_{l=1}^{3} C_{l}) + Ci], \text{ for } i=j$$
(5-13)

$$B_{ij}=0, \text{ for } i\neq j$$
 (5-14)

and

$$Ei = \sum_{e} \left[\int_{\Gamma^{e}} qNid\Gamma + \int_{\Omega^{e}} K_{zz,l} N_{l} \frac{\partial Ni}{\partial z} dxdz - \int_{\Omega^{e}} QiNidxdz \right] = \sum_{e} \left[\frac{(q_{n}L_{e})_{i}}{2} + \left(\sum_{l=1}^{3} K_{zz,l} \right) \frac{c_{i}}{6} - \int_{\Omega^{e}} Q_{i}N_{i}dxdz \right]$$
(5-15)

where b_i,c_i are element dimensions, Δ are element areas and q_n is the normal flux across the side of length L_e of any element including nodal point i. A given flux Qi can be specified at any internal source or sink node and is zero at all other nodes. It should be noted that B_{ij} is a diagonal matrix as a result of the averaging process given by eq.19. The Darcy fluxes from eq.2 can be formulated as:

$$q_{x} = -\sum_{e} \left(K_{xx,l} N_{l} \frac{\partial N_{j}}{\partial x} h_{j} \right) = -\sum_{e} \frac{1}{6\Delta} \left[\left(\sum_{l=1}^{3} K_{xx,l} \right) b_{j} h_{j} \right) \right]$$
(5-16)

5.3.2.4 Transport equations

The resulting set of finite-element equations for solute transport can be written in matrix form as:

$$F{C}+G{\partial C}/\partial t+H=0$$
(5-17)

Where F and G are n by n matrices and H is a vector of length n. These are expressed:

$$Fij = \sum_{e} \int_{\Omega^{e}} \left[\theta_{l} N_{l} \left(D_{xx} \frac{\partial Ni}{\partial x} \frac{\partial Nj}{\partial x} + D_{xz} \frac{\partial Ni}{\partial x} \frac{\partial Nj}{\partial z} + D_{zx} \frac{\partial Ni}{\partial z} \frac{\partial Nj}{\partial x} + D_{zz} \frac{\partial Ni}{\partial z} \frac{\partial Nj}{\partial x} + D_{zz} \frac{\partial Ni}{\partial z} \frac{\partial Nj}{\partial z} \right] dx dz$$

$$= \sum_{e} \left[\frac{1}{12\Delta} \left(\sum_{l=1}^{3} \theta_{l} \right) (D_{xx} b_{l} b_{j} + D_{xz} b_{l} c_{j} + D_{zx} c_{l} b_{j} + D_{zz} c_{i} c_{j}) + q_{x} \frac{b_{j}}{6} + q_{z} \frac{c_{j}}{6} + \frac{R_{e} \gamma \Delta}{12} \right]$$

$$(5-18)$$

$$Gij = \sum_{e} \int_{\Omega^{e}} Nidxdz = \sum_{e} \frac{\lambda \Delta}{12}$$
(5-19)

$$\operatorname{Hi} = -\sum_{e} \left\{ \int_{\Gamma^{e}} Ni \left[\left(D_{xx} \frac{\partial Nj}{\partial z} + D_{xz} \frac{\partial Nj}{\partial z} \right) lx + \left(D_{zx} \frac{\partial Nj}{\partial z} + D_{zz} \frac{\partial Nj}{\partial z} \right) lz \right] C_{j} d\Gamma - \int_{\Omega^{e}} \left(Q\overline{C} \right)_{i} N_{i} dx dz \right\}$$
(5-20)

where γ is a constant equal to 2 if i=j and 1 if i≠j. A given solute flux (QC) can be specified to act at any internal source or sink node and is zero at all other nodes. G_{ij} is a diagonal matrix that results from the averaging process given by equation (5-9).

5.3.2.5 *Finite element discretization*

The cross-sectional representation of the saturated flow system is divided into an equivalent system of subregions, in this case, triangular elements. The general objective of this dicretization process is to divide the system into a suitable number and arrangement of elements so that the true solution can be adequately approximated.

For linear triangular elements the shape functions are given by the dimensionless triangular coordinates, each having the value of unity at one node, the value of zero at the others, and values varying linearly everywhere within the element. A full explanation of the relationship between the local triangular coordinate system and the global coordinate system of the cross section is given by [*Hornberger and Wiberg*, 2005]. The relationship between the global and triangular coordinates is given by:

$$\begin{bmatrix} 1 \\ x \\ y \end{bmatrix} = \begin{bmatrix} 111 \\ x_i x_j x_k \\ y_i y_j y_k \end{bmatrix} \begin{bmatrix} Ni \\ Nj \\ Nk \end{bmatrix}$$
(5-21)

hence

$$Ni = (a_i + b_i x + c_i y)/2\Delta$$
(5-22)

$$ai = x_i y_k - x_k y_i \tag{5-23}$$

and

$$bi=y_i-y_k \tag{5-24}$$

$$ci=x_k-x_i$$
 (5-25)

with the other coefficients obtained by a cyclic permutation of subscripts in the order i, j, and k. The area of the triangle Δ is given by

$$\Delta = \frac{1}{2} \begin{bmatrix} 1x_i y_i \\ 1x_j y_j \\ 1x_k y_k \end{bmatrix}$$
(5-26)

5.3.2.6 <u>Time Derivative</u>

The time-dependent nature of equation (5-1) and (5-5) can be accommodated by employing a finite-difference scheme to approximate the time derivatives. Neuman (1973) advises the use of a backward difference scheme rather than a time-centered scheme in the analysis of saturated-unsaturated flow systems. Also the backward difference scheme has been found by Pinder (1973) and Smith et al. (1973) to provide better results than a Crank-Nicholson centered in time approach for the time derivative of the solute-transport equations. Employing a fully implicit backward difference scheme in terms of h in equation 11. Yields:

$$\left(A_{ij}^{k} + \frac{1}{\Delta t^{k}}B_{ij}^{k}\right)h_{i}^{k+1} = \frac{1}{\Delta t^{k}}B_{ij}^{k}h_{i}^{k} - E_{i}^{k}$$
(5-27)

where k indicates the time t^k and $\Delta t^k = t^{k+1} - t^k$. The Douglas-Jones predictor-corrector method for the solution of Eq. (21) is described by the following equations:

Predictor equation
$$\left(A_{ij}^{k} + \frac{1}{\Delta t^{k}/2}B_{ij}^{k}\right)h_{i}^{k+1/2} = \frac{1}{\Delta t^{k}/2}B_{ij}^{k}h_{i}^{k} - E_{i}^{k}$$
 (5-28)

Corrector equation
$$\left(A_{ij}^{k+1/2} + \frac{1}{\Delta t^{k}}B_{ij}^{k+1/2}\right)h_{i}^{k+1} = \frac{1}{\Delta t^{k}}B_{ij}^{k+1/2}h_{i}^{k} - E_{i}^{k+1/2}$$
 (5-29)

5.3.3 Application to the field

After the preliminary tests had established a reasonable degree of confidence in the ability of the model to simulate flow and solute transport conditions, it was applied to the particular problem of water and solute transport in the transect at the Cobb Mill Creek hillslope. A schematic representation of a stream-aquifer system is shown in Figure 5-2. The finite-element discretization of the cross-section is shown in (**Error! Reference source not found.**). The distance between the stream and groundwater divide was chosen at 50m, the approximate distance from the flat upland to the creek. The mesh consists of 1652 elements and 886 nodes with element sizes varying from 0.2m at the stream channel to 2.5 m at the upland and base of aquifer. It represents a vertical cross section 16m by 50m through the riparian zone with hillslope on the left and stream channel on the right. The orientation of the mesh was chosen to be parallel to the dominant groundwater flowpath during the flood events.

The model domain in the region of the stream represents half the channel width, with the vertical boundary at the center of the stream channel specified as a no-flow boundary. Choosing this geometry permits correct interpretation of water flow through both the channel bed and banks. The geological survey indicated the aquifer is about 10 m thick [*Hubbard, et al.*, 2001], hence, the domain has been extended down 16m below the surface where a no-flow boundary can reasonably be assumed. Although no hydraulic head data are available at upland boundary, hydraulic head recorded at the hilltop well (not within the studied transect) showed the upland water table is fairly stable during transient rainfall events (Figure 5-6), which indicated the constant head hillslope boundary is justified, at least at transient-event time scale. Thus, initially, the hilltop

hydraulic head was used to specify the hillslope boundary condition. Further model calibration indicated a constant head of 3.3 m at the hillslope boundary shows a good fit to the head observations. The stream stage was used to specify the boundary condition on the right-hand side of the mesh. The initial pressure-heads at each computational node for each flow simulation were established using a steady state solution with time-constant boundary conditions representing piezometric heads at the start of each event. The upper boundary was prescribed with a small inward flux appropriate to the rainfall conditions for that event. A seepage face was allowed to develop during falling limb along that part of the creek bank that was above the level of the stream stage if it was saturated at the previous time step. Seepage face nodes were assigned a pressure equal to atmospheric pressure (zero). The possible effects of evapotranspiration were ignored here to simplify the model formula. All boundary nodes on the creek bank above the stage and seepage face were therefore assigned no-flow boundary conditions.



Figure 5-5 Finite element meshes and boundary conditions constructed for the transect. It consists of 1068 nodes and 2004 linear triangular finite elements.

5.4 Results

5.4.1 Response of piezometers to stream stage

The time series of water table data are presented in **Figure 5-6**. The transducer data was filtered to remove those with the higher-than-daily frequency (e.g. diurnal signals). During the period of 08/20/05-12/20/05, the water table in N1 changed approximately in parallel with the stream stage (Figure 5-6B). In contrast to that in the stream bank, the water table in hillslope upland (**Figure 5-6** B) showed a steady, continuous decrease throughout the monitoring period indicating the slow drainage of previous large recharges, i.e., large storms. No response to single rainfall events was evident from the water table records. Storm events considered in this paper are labeled from A to C in chronological sequence. We consider all the three events as in-bank since maximum stream stage rise in all three events is no more than 30 cm Figure 5-6 indicating only relatively localized flooding occurred near the stream.

Stream stage in general showed a prompt rise to rainfall events accompanied by prompt response of near stream groundwater table (Figure 5-7), although at a lower rising rate. At N1 well, the water table level remains above the stream all of the time, and flow from the hillslope to the stream continues without interruption. But the discharge velocity decreased in response to the reduced hydraulic gradient toward the stream (Figure 5-8).

In hysteresis plots, the stream bank piezometers showed a synchronous and essentially identical behavior to stream stage since all data points aligned along the 1:1 line (Figure 5-9). The hysteresis plots for the three events were remarkably similar suggesting very little difference in the water table response between events (Figure 5-10).


Figure 5-6 Time series of hydrometric measurements during the period of 08/20/05-12/20/05. A) Precipitation, B) stream stages and hydraulic heads in N1 (note the data was filtered to removal those with higher-than-daily frequency (e.g. diurnal signal), and C) hydraulic head in the Hilltop well. Three events were selected as the studied cases of transient processes.

The narrow separation of the ascending and descending curves implies only minor differences in the water table response between the rising and recession limbs. The water table was a maximum of 2-3 cm higher during the recessions in comparison to the rising limbs for the same stream stage, and frequently much less. The shape of the hysteresis curves, in term of how open or closed they are, therefore approximates to how much water is stored temporarily within the streamband over the course of a flood event (i.e., the bank storage effect). There is, as expected, little retention capacity for flood water within the stream bank as shown by the closed hysteresis loops. The groundwater level was higher than the stream stage at all times, but still exhibited a trend following the river hydrograph, although with a lower rate of change than the stream stage.





Figure 5-7 Comparison of observed hydraulic heads at N1 well during event A, B, and C to predictions from the two-dimensional finite element model. The blue line is stream stage. The red solid line denotes model prediction, while the dashed line denotes the field observations.



Figure 5-8 Stream bank and stream sediment seepages predicted by the model for event A, B, and C.



Figure 5-9. Stream-stage-hydraulic head hysteresis plots for N1 well, providing insights into the response of the water table to stream stage. The solid line gives the 1:1 relationship (identical water table level). Data from event A, B, and C.



Figure 5-10. stream stage-hydraulic head hysteresis plots for N1 during the event sequence. The blue solid line gives the y=x relationship. Data from events A, B, and C are shown in chronological order from red to blue to green.

5.4.1 Numerical Simulation Results

5.4.1.1 Groundwater flow

5.4.1.1.1 Steady flow

The numerical simulation result of the flow showed that flow toward the stream is essentially horizontal, except when approaching the stream channel (Figure 5-11). The simulated groundwater seepage rate through the stream sediment is around 0.2 m d⁻¹. This values agree well with the field-determined upward seepage values of $0.12 \sim 0.31$ m d⁻¹.



Figure 5-11. Model simulated pre-flood steady state hydraulic head distribution. Approximate locations of the piezometers internal to the domain are also shown.



Figure 5-12 Calibrated fit between modeled and observed heads at all wells along the transect.

Simulation results from the modeling transects were compared with observed field data by trial-and-error method Figure 5-12. All the locations of observation data points are shown in Table 5-1. It shows that the model over-predicted the near stream hydraulic heads, while under-predicted upslope hydraulic heads. The maximum difference of simulated and observed data is 0.12m. All data points lie close to the 1:1 line, indicating that the model simulates heads accurately.

Nest	Piezometer	Elevation of	Distance from	Observed	Simulated
	ID	piezometer opening	the stream (m)	heads ASL (m)	heads ASL (m)
		(mASL)			
N1	А	0.903	1.5	1.239	1.345
	В	0.613		1.324	1.367
	С	0.266		1.374	1.410
	W			1.249	1.332
N3	А	0.971	2.5	1.393	1.443
	В	0.794		1.423	1.478
	С	0.626		1.411	1.498
	W			1.432	1.450
N7	А	1.090	7.1	2.159	2.078
	В	0.789		2.183	2.081
	W			2.131	2.072
N9	W	1.593	14.6	2.675	2.595
N11	W	1.414	23	2.894	2.832
S 1	A	0.291	0	1.253	1.323
	В	0.030		1.238	1.362

Table 5-1 Piezometer nest survey and hydraulic heads information

The average flux of groundwater, per unit area, through the stream bank was about four times larger than the average flux through the stream bottom largely because the horizontal hydraulic conductivity is similar magnitude greater than the vertical hydraulic conductivity due to the anisotropy. The calibrated model indicated that 80% of the total base flow as discharging laterally through the stream bank and remaining 20% as moving through the stream bottom by accounting for seepage area (A_{bank}:A_{sediment}=1:1 at this specific transect). However, the bottom discharge could account for more significant portion of the total discharge for the wide and shallow reach of the stream. The proportion of groundwater discharge is consistent to the observed stream water chemistry of chloride, which is presumably mixing of two end members, deep groundwater moving through stream sediment and shallow groundwater moving through stream bank.

5.4.1.1.2 Transient flow during the storms

The simulations were analyzed by comparing predicted and observed pressure heads at piezometers internal within the model domain (Figure 5-7). In general, the pressure heads were well modeled, except at the beginning and end of the event. Toward the end of event A, the model underpredicted the observed pressure head by ~0.05m (Figure 5-7). Reasons for this may be the model's failure to represent the impact of threedimensional hydrologic processes on the riparian subsurface pressure field. It indicates that for the majority of the flood event two-dimensional later process is reasonable simplification. This process representation seems to fail at the beginning and ending of each event when the downstream hydraulic gradient may become significant in determining the pressure field.

5.4.1.1.3 Darcy velocity vectors

For event A, before the stage rises, the flow velocities are highest just around the stream channel, especially at the intersection of stream bank and streambed, and most flow converges within 2 m of the creek (Figure 12 A). Flow velocities are low beneath the creek bottom compared to the flow through the bank, and decreases away from the creek (the horizontal vectors are longer than the vertical vectors). At 0.5 day into the simulation, when stream hydrograph peak occurs, there is an upward flux of water from the hillslope to the channel at stream bank area leading to a humped water table (Fig.12 b) (see the equipotential lines become flattened). Toward the end of the event this flux

returns to the previous status which is dominated by horizontal flow. Water movements are solely confined to the channel as an in-bank flow. In effect, a groundwater ridge forms and strong velocities develop in the near-stream area that are directed up toward to the bank unsaturated zone. Instead of a traditional groundwater ridge caused by the capillary fringe that results in a steepening of the hydraulic gradient to the channel, the ground ridge here is a pressure wave response from the stream and contributes to a reduced hydraulic gradient toward the stream. Due to the high hydraulic gradient from the hillslope to the stream, the groundwater ridge does not produce reversed flow, i.e., classic bank storage. This is in contrast to standard ideas concerning extensive bank storage applied to cross-sections with wide floodplain adjacent to the river channel.



Figure 5-13. Model predicted Darcy velocity vectors during the storm A with 0.30 m rise of stream stage and duration of 3 days. A) pre-event velocity vectors; B) the bend up velocity vectors at stream bank zone at 0.5 day when stream stage reached its peak. C)&D) During flood recession, the pre-event velocity vector is gradually re-established. Note the vector length represents the magnitude of velocity

5.4.1.2.1 Steady state NO₃⁻ distribution

The reactive transport modeling was run within a sub-domain in Figure 5-14. It represents a vertical cross section of 8m by 2m in near stream riparian zone. The reasons to focus on the near stream NO_3^- simulation are: 1) The main biological transformation of NO_3^- and mixing of water with a different NO_3^- signature only occurs at the near-stream area. 2) The observation data points are relatively more numerous for comparison of modeling results with the observed results. 3) To save the computational effort needed in the least interesting part of the aquifer.



Figure 5-14. The near stream channel sub-domain used for solute transport simulation. The red grids represent highly biologically active groundwater surface water interface

The observation of nitrate-poor stream water fed predominately by nitrate-rich groundwater suggests that nitrate is removed at the interface of the terrestrial-aquatic continuum. (Chapter 2). In order to determine the location and mechanism of NO_3^- removal along the ground water flow path, the water table profile, vertical head gradients, and NO_3^- concentrations were investigated by field measurement and numerical simulation.

Initially, the filed observation of the conservative solute, Cl⁻, was used to calibrate the transport model to see if flux-weighted Cl⁻ concentration integrated along the seepage face is consistent to the observed Cl- concentration in the stream water. We observed the concentrated Cl⁻ as high as 40 mg L⁻¹ close to the stream bank (Figure 5-15). Thus, a Cl⁻ source zone was applied in the stream bank area to simulate the potential evaportranspiration effect. Boundary conditions were specified as zero concentration gradient at each side of the model domain except for the left hand boundary and the bottom boundary. A constant concentration of 16 mg L⁻¹ was assigned at the left and bottom sides of the model domain. The agreement of measured and simulated Cl concentration in the transect was achieved by manual adjustment of the location of this source zone and the Cl⁻ production rate within the source zone. The comparison between simulated and measured Cl⁻ concentration is presented in Figure 5-15. The numerical model successfully reproduced the concentrated Cl⁻ concentration at stream bank area. And intuitively, the stream water Cl⁻ concentration would represent the mixing of two flow components with distinct Cl⁻ signature, the shallow groundwater with high Cl⁻ (30-45 mg L^{-1}), and the deep groundwater with low Cl⁻ (<20mg L^{-1}).

The specific discharge and seepage concentration of Cl⁻ along the creek bank and channel bottom is shown in Figure 5-16. The specific discharges and seepage concentrations of Cl⁻ decrease from the bank to the channel bottom. The maximum specific discharge is at the stream water table line. This finding is consistent to the other researches studied by [*Gardner*, 2005]. Since the area under each of these curves represents the total discharge, calculated discharge of stream bank for unit length of stream channel is 0.30 m² d⁻¹, is about 1.5 times higher than the stream sediment

discharge of 0.21 m² d⁻¹. The flux weighted seepage concentration of Cl⁻ is 30 mg L⁻¹, consistent to our field observed Cl⁻ concentration in the stream.



Figure 5-15. Cl⁻ distribution in the experimental cross-section. A) observed concentration; B) simulated concentration



Figure 5-16. Plot of specific discharge and seepage concentration of Cl⁻ versus distance along the stream channel from water table to the intersection of the bank and sediment, and thence to the center of channel bottom.

After calibrated and verified by Cl⁻ simulation, the model was applied to simulate NO_3^- distribution along the transect. Boundary conditions were specified as zero concentration gradient at each side of the model domain except for the left hand boundary and the bottom boundary. Left hand boundary was assigned a concentration gradient from 6 mg L⁻¹ to 15 mg L⁻¹ with increasing NO_3^- concentration along the depth to represent two different sources of groundwater, shallow low NO_3^- -bearing groundwater and deep high NO_3^- -bearing groundwater. One source zone at the right bottom boundary was assigned to represent deep groundwater with high NO_3^- concentrations. In this source zone, specific concentration boundary of 15 mg L⁻¹ was used to represent the NO_3^- source. The same evaportranspiration zone applied in Cl⁻ simulation was also applied in NO_3^- simulation as a sink zone to simulate plant uptake or denitrification. A NO_3^- sink zone around the stream channel indicated in Figure 5-13 was applied to represent the biologically reactive groundwater-surface water interface (GSI). The goal in the transport

simulation is to illustrate the effect of groundwater flow pathway on the NO_3^- spatial distribution, rather than to exactly reproduce the observed NO_3^- profiles. The observed and simulated concentration distributions of NO_3^- are shown in **Figure 5-17**. Comparison shows that the transport model with biologically reactive GSI (**Figure 5-17** C) is able to reproduce the general patterns of NO_3^- concentration plumes much better than the one without biologically reactive GSI (**Figure 5-17** D).

The ground water flow paths along the hillslope that deliver NO_3^- to the stream are illustrated in **Figure 5-17** A. The groundwater flows horizontally until it approaches the near-stream channel zone where the flow direction gradually begins to bend upward. Two main NO_3^- sources for the stream can be identified in the **Figure 5-17** B. One is upward discharging, old groundwater with a NO_3^- concentration >12 mg L⁻¹ after long and deep flow pathway. The other is relatively shallow (<2.5 m BGS) horizontal groundwater with a NO_3^- concentration of <6 mg L⁻¹. It might represent a young locally recharged groundwater with low NO_3^- signal. The steepest concentration gradient occurs right beneath the stream sediment (**Figure 5-17** B). Note the extremely shallow cross section in **Figure 5-17**due to the lack of available data points in the deep region.



Figure 5-17. NO_3^- distribution in the experimental cross-section. A) groundwater flow pattern B) observed concentration; C) simulated NO_3^- concentration with the biological reactive GSI; D) simulated NO_3^- concentration without the biological reactive GSI.

The specific discharge and seepage concentration of NO_3^- along the creek bank and channel bottom at steady state are shown in (Figure 5-18). Similar to Cl⁻, the seepage concentrations of NO_3^- decrease from the bank to the channel bottom. Seepage concentration of NO_3^- shows a maximum concentration as high as 3.7 mg L⁻¹ at stream bank about 0.2 m above the sediment surface. And generally much higher NO_3^- exports from the stream bank than that from the sediment. The calculated NO_3^- flux from the stream bank is 0.98 gm⁻¹ d⁻¹, is almost 4 times higher than NO_3^- flux coming out from the sediment (0.27 gm⁻¹ d⁻¹). The calculated flux-weighted NO_3^- concentration calculated is 2.44 mg L⁻¹ consistent to the observed NO_3^- concentration in the Cobb Mill Creek.



Figure 5-18. Plot of specific discharge and seepage concentration of NO₃- versus distance along the stream channel from water table to the intersection of the bank and sediment, and thence to the center of channel bottom.

5.4.1.2.2 Transient transport

Temporal evolution of NO_3^- and CI^- in stream water can be seen during a 20 mm precipitation event on April 22-25, 2005 (Figure 5-19). NO_3^- concentrations decreased on

the rising limb, reached a minimum at or slight after the discharge peak, while Clreached the minimum point about 4 hours earlier than NO_3 .and then both ion slowly recovered through hydrograph recession.

The groundwater flow and transport model calibrated in previous study was used to simulate the subsurface transport of NO_3^- during a hypothetic storm. A very similar pattern of NO_3^- evolution was found in the numerical simulation (Figure 5-21 C). The groundwater seepage rate decreased on the rising limb of the hydrograph (Figure 5-21 B), reached a minimum at the stream stage peak, and then slowly increased through hydrograph recession. After the flood wave passed, the seepage rate recovered to the preevent condition. Similarly, NO_3^- deceased in response to the reduced seepage rate (longer residence time), and reached a minimum slightly after the stream stage peak, then recovered in response to increasing seepage rate (shorter residence time) (Figure 5-21 C).

We attribute these two different patterns of $C\Gamma$ and NO_3^- to their different biological reactivities. In contrast to the NO_3^- concentration dip corresponding to the hydrograph peak, the residence time variation induced by subsurface flow cannot affect $C\Gamma$ concentration because $C\Gamma$ is conservative solute. The earlier concentration dip of $C\Gamma$ is probably due to the dilution effect by direct interception of rainfall with low $C\Gamma$ signature in the stream.



Figure 5-19. Temporal evolution of stream chemistry for Cl⁻ and NO₃⁻ during the storm event on 04/22/06-04/25/06



Figure 5-20. Temporal evolution of stream chemistry for Cl $^{\circ}$ and NO3 $^{\circ}$ during the storm event on 04/26/06-04/27/06



Figure 5-21 Numerical simulated temporal evolution of NO_3^- concentration at the discharging point in response to a 0.15 m rise of stream stage in 4 days. A) stream stage, B) specific discharge, C) NO_3^- concentration

The reduced nitrate load could be estimated from the flow and transport modeling results presented above. The results have shown extremely limited groundwater-surface water exchange at the Cobb Mill Creek site. The real time NO_3^- flux out of the column was calculated as the product of discharge rates and NO_3^- concentrations in seepage water. The total reduced NO_3^- flux was then estimated as the difference of groundwater nitrate flux across the GSI between baseflow condition and storm condition, by integrating the valley area below the base flow flux line. The calculation result shows a total reduction of nitrate flux of 3.84 g NO_3^- -N m⁻². If we assume a wetted perimeter of 1.5 m and lowland stream reach length of 200 m, we estimate about 1.15 kg NO_3^- -N less

loading during this bank storage event, which is insignificant in terms of annual nitrate loading.

5.5 Discussion

5.4.1Rapid water table response

The classical model of bank storage response during a flood has not been well demonstrated during these three events. After stream stage rises, the hydraulic head in near stream zone responses rapidly. Due to the steep hydraulic gradient, the upland water table, augmented by subsurface stormflow, remains higher than the stream all the time (Figure 5-7) and there is no sustained barrier to hillslope water draining into the stream except during the flood peak when hydraulic gradient reaches the minimum. Once stream stage falls, the pre-event hydraulic gradient from slope to stream is re-established, slowing the flood recession. In locations where sloping land borders a stream, the behavior of the water table within the riparian zone is largely determined by upslope conditions, and the influence of the adjacent river or stream on riparian soil hydrology will be limited. In the watershed where the riparian zone is flat, the water level in the river can largely influence riparian water table [Burt, et al., 2002]. However, in Cobb Mill Creek, where a steep slope directly borders the stream, the stream cannot significantly influence water table fluctuations in the riparian zone since there will rarely be a hydraulic gradient away from the stream towards the land. The slope is sufficient (>5%) that fluctuations in stream stage are not influential, except very close to the stream. The numerical simulation in this work shows negligible water table response >10 m away from the stream.

The rise of the stream induces a kinematic wave that operates by pushing "old" riparian water ahead and, hence, causes the stream bank water table to rise near-synchronously, although with lower rising rate. Because of decreasing hydraulic gradients, and hence decreasing fluxes toward the stream, the water table in riparian area will tend to rise as a result.

Kinematic wave processes can be triggered by a rapidly rising stream. There are several arguments that support the kinematic wave hypothesis here. The flux velocities associated with Darcian flow are in the range of 10^{-2} - 10^{-3} m h⁻¹ given a saturated hydraulic conductivity of 10^{-4} - 10^{-5} m s⁻¹ at the field site and maximum water table gradients of only a few percent. These velocities are at least two orders of magnitude too low to lead to mass transfer (i.e., movement of water) over the distances involved in the time available.

The rising water table at the stream bank is not caused by the groundwater ridge driving water into this zone, but results from the accumulation of hillslope water, which is "dammed" by the presence of the ridge. The development of a groundwater ridge has important implications since it temporarily prevents hillslope water from rapidly reaching the stream and thereby limits hillslope contributions to flood waves propagating downstream. The development of the ridge will depend on the stream stage and water table in adjacent aquifer. Its magnitude is therefore controlled by both stream stage and hillslope runoff conditions. This is, however, unlikely to occur for the hillslope riparian such as Cobb Mill Creek, since hillslope discharge will sustain high water tables. The typical base flow conditions associated with a weak hydraulic gradient toward the river will therefore tend to be maintained.

Jung et al. [2004] suggested a critical role for the anticedent soil moisture of the unsaturated zone and the capillary fringe in determining water table response on their study of recurring patterns of water table response in a lowland floodplain, U.K. Our relatively wet riparian zone, with high soil moisture content, is typical for east coast humid regions like the present site and may assist in generating a rapid water table rise with recurring characteristics, as is evident for all the observed storm events.

The pattern of transient response found in the Cobb Mill Creek riparian zone is in contrast to that modeled by [*Bates, et al.*, 2000] and described by [*Burt, et al.*, 2002] for the extensive floodplain of the River Severn in central England. Their work involves a reverse groundwater ridge that moves across the floodplain towards the slope during flood events. At our site, with a steep hydraulic gradient toward the stream, the groundwater ridge at the near stream area can not generate reversed flow, thus is not sufficient to interrupt the slope drainage and, the hydraulic gradient from slope to river is always existing. This finding is consistent with results of a stream tracer experiment (data not shown) showing that Cobb Mill Creek does not have significant hyporheic exchange. Although much less magnitude of bank storage (here the word "bank storage" refers to reduced groundwater discharge instead of reversed flow) observed at this site, the essential effects of these processes are identical in the sense that they both attenuate flood propagation, slow the flood recession, and help to sustain baseflow between flood events.

It is important to keep in mind that the hillslope cross section profile at this site is based on only six piezometer nests in one transect. More hillslope piezometers that are installed deeper into the ground water will be necessary to establish the ground water flow paths along the hillslope in a comprehensive manner. The vertical head gradients described in this work only encompass a very shallow lens of the ground water (approximately two meter deep) in the Cobb Mill Creek riparian zone. Multiple deep piezometers along the hillslope are needed to confirm the hypothesized deeper flow paths that connect the agricultural field with the stream and to relate them to the sources and sinks of nitrate along that flow path.

5.5.1 NO_3^- delivery through hillslope-riparian-stream continuum

5.5.1.1 <u>Steady state transport pattern</u>

Within the aquifer and the GSI transition zone, contaminant flux is dependend on water flow and contaminant distribution. The spatial and temporal distribution of the contaminant will depend on source location, the spatial distribution and velocity of water flow, and the abundance and biotic/abiotic reactivity of biogeochemical components along the flow water flow paths. The extent to which biogeochemical processes will influence contaminant transport will depend on the relative rates of water transport and chemical reactions (chapter 3). For example, contaminant transport will be relatively conservative for systems in which the timescale for water flow within a reactive zone is much shorter than the timeframe for significant reaction to take place. In contrast, significant attenuation/transformation will be observed for contaminants in systems where reactions occur rapidly relative to the timescale for fluid transport. The earlier situation might be the case for stream bank discharge, while the latter situation is commonly apply to streambed condition. The detailed site characterization is particularly important for GSI that may experience large variability in water flux and fluid velocities.

Several findings emerge from the detailed analysis of the proportions of seepage from stream bank and stream bottom. The higher pore water seepage from adjacent aquifer occurs along the stream bank area rather than along the streambed. The proportion of seepage water varies depending on surface areas of bank and sediment. In this transect with relatively large stream bank (0.4m high), bank seepage is about 1.5 times higher than sediment seepage. However, for most part of the reach in the Cobb Mill site, stream bank is generally small. Numerical simulation exposed that sediment seepage is about 1.5 times higher than that of stream bank given averaged 0.2 m high stream bank. From this, we may conclude the seepage from stream bank and streambed is in the same magnitude in the Cobb Mill Creek.

The contribution of pore water seepage from stream bank and streambed might play a significant role in solute flux through groundwater-surface water interface. Stream bank discharge in the transect accounts for nearly 79% of NO₃⁻ flux to the stream, although the source of bank discharge, shallow groundwater, has much lower NO_3^{-1} concentration of $\sim 6 \text{ mg } \text{L}^{-1}$ than the source of streambed discharge, which is deep groundwater with NO_3^- concentration greater than 12 mg L⁻¹. This is mostly attributed to the different residence time of groundwater in the stream bank and streambed. Due to the anisotropy of channel materials, the horizontal flow velocity of groundwater through stream bank is 3-4 times as high as that vertical flow through the stream sediment. The rapid horizontal bank discharge would not allow residence time long enough for microbial reduction, while there is significant microbial reduction of NO₃⁻ in streambed discharge (chapter 2& 3). The velocity for the horizontal discharge through the stream bank is generally >2.5 cm h^{-1} . It corresponds to less than 20% removal shown in Figure 3-4. The vertical pore water seepage through the streambed is about 0.8 cm h^{-1} , corresponding to >70% removal shown in Figure 3-4. Numerical model shows the stream

water NO_3^- concentration would be 8.16 mg L⁻¹ if no biological reduction effect occurs in stream sediment and no reduced hydraulic conductance caused by sediment materials. Thus, we estimate stream sediments play a much larger role in buffering NO_3^- export to the stream than stream banks in the Cobb Mill Creek Site.

The hydrologic and chemical data in the Cobb Mill Creek study suggest two distinct flow domains within the local flow system, which differ in NO_3^- concentration. High concentrations of NO_3^- leach from the upland agricultural field and flow through an oxidized, deeper ground water region generally greater than two meters below the water table and the NO_3^- discharges vertically to the stream. On the other hand, recently hillslope-recharged shallow groundwater flows receive less NO₃⁻ than deep groundwater flows that receive from the agricultural fertilizers in upland area. The NO_3^{-1} transported by these shallow flows is most likely discharged laterally into the stream at the stream bank and contributes to the open channel NO_3^{-1} concentration. This mixing process explained the slight discrepancy of the stream water with $2 \sim 3 \text{ mg L}^{-1} \text{ NO}_3^{-1}$ and sediment pore water at discharge points with <1mg L⁻¹ NO₃⁻ (Holly, 2004; Chapter 3). The ground water in the shallow bank side piezometers was found to have NO_3^{-1} concentrations of 4~6 mg L⁻¹ suggesting a shallower oxidized ground water flow path in which the NO₃⁻ most likely originates from natural decomposition and deposition processes. The final NO_3^{-1} concentration in stream water is determined by the mixing of shallow groundwater and deep groundwater. Our Cl⁻ concentration profiles give additional evidence of this mixing process of shallow and deep groundwater. About $16 \sim 20 \text{ mg } \text{L}^{-1} \text{ Cl}^{-1}$ is found in sediment pore water representing deep groundwater signature, while the CI concentration in stream water is about 32 mg L⁻¹. Cl⁻ concentration in stream bank is as high as 40 mg L⁻¹

probably due to the plant evaportranspiration. This bank-discharge water with concentrated Cl⁻ most probably accounts for the higher Cl- concentration in the stream water than that in the sediment pore water.

In hydrogelogical settings like the Cobb Mill Creek site, the relatively thick aquifers may contain discrete flow systems at several scales [*Toth*, 1963]. Riparian zones in the downstream areas of these watersheds may receive groundwater inputs from local systems which recharge on adjacent slopes, from intermediate systems that include at least one local flow system between their recharge and discharge points, and regional flow systems that begin at regional topographic divides. Riparian zones connected to thick aquifers receive large constant groundwater inputs. If permeable aquifer material present, groundwater may flow rapidly under the riparian zone and discharge directly to the stream channel.

The groundwater surface water interface is the most important area for reduction of NO₃- loading. Pure mixing of shallow and deep groundwater without considering microbial removal will produce a NO₃⁻ concentration of 11.32 mgL⁻¹ in the stream according to the numerical simulation (spatial pattern is shown in **Figure 5-17** D). The sharp NO₃⁻ concentration gradient only occurs near the groundwater-surface water interface surrounding the stream channel (**Figure 5-17**). The lack of significant horizontal concentration gradient indicates localized recharge flow. NO₃⁻ remained in the deep groundwater below the riparian zone and in ground water beneath the creek, meaning that the chemically reducing conditions present in shallow portions of the riparian zone were largely being bypassed. Puckett & Hughs (2005) found a limited NO₃⁻ removal effect within a riparian aquifer adjacent to a coastal stream, Cow Castle Creek, SC. They proposed that the coarser-grained sediments in surficial aquifer provide a preferential flow path that allows NO₃⁻ in groundwater to pass beneath the shallow reducing layer in the riparian zone and discharge directly into the streambed. However, they also found that significant denitrification in the upper 0.7 m of the streambed. The combined flow path with concentration profile in **Figure 5-17** suggests that the groundwater water NO₃⁻ is mainly removed at the ground water- surface water interface before the water reaches the open stream channel.

Based on the total discharge and NO_3^- reduction, we calculated that removal rate of NO_3^- is as much as 3.39 g m⁻²d⁻¹ (note that this rate only applies to the biogeochemically reactive zone around the channel). This removal rate is about twice as much as the rate of 1.8 g m⁻²d⁻¹ studied in the Smith Creek, Michigan [*Hedin, et al.*, 1998] and two orders of magnitude greater than other values in riparian zone study [*Lowrance*, 1992]. We conclude that with sufficient carbon source in the stream channel, groundwater surface water interface can possess a remarkable potential for NO_3^- removal from subsurface waters. In fact, removal rates were so rapid in our experimental transect that NO_3^- concentrations change from 12 mg L⁻¹ to as low as 0.1 mg L⁻¹ over as little as 30 cm of flow path.

The riparian-buffer effect for NO_3^- removal has been the research focus recently [*Cey, et al.*, 1999; *Cirmo and McDonnell*, 1997; *Hill*, 1996a; *Hill, et al.*, 2000]. However, less work has been done to assess mechanisms of combined hydrologic flow and biogeochemical processes regulating dynamics of NO_3^- delivery. Buffer-zone functions such as denitrification are most effective where there is sustained soil saturation and soil organic matter content. Results at some of the European NICOLAS sites suggest that

where slopes are directly coupled to the channel, soil moisture conditions are unlikely to favor processes such as denitrification since the water table is usually too deep [Burt, et al., 2002]. In contrast, there is significant denitrification observed at extensive floodplain or wetland areas with shallow water tables [Gilliam, 1994; Haycock and Burt, 1993]. It follows, therefore, that some buffer zone functions cannot work effectively in low-order (i.e. head water) tributaries where there is only a very narrow floodplain or none at all [Burt, et al., 2002]. In riparian area of low-order streams, small streams are commonly incised in steep valleys with minimal riparian zones, which reduced the effect of riparian areas on streams. However, previous results at the Cobb Mill Creek site suggested, given that even in the absence of a riparian wetland along the study reach, approximately 85% of the NO₃⁻ was removed and the highest denitrification potential was found at the ground water-stream sediment interface at Cobb Mill Creek (Galavottie, 2004, Chapter 2,3). This is because significant NO₃- removal processes could occur at the close-to-stream area around the stream channel where stream-bank water table is high enough to reach the organic-matter-rich suface soil horizon or tree-root zone for plant uptake, and where permanent saturated stream sediment is replenished by deposited organic matter from adjacent vegetation. [Hedin, et al., 1998] found that denitrification was restricted to a narrow zone at 20-40 cm deep near a stream bank where a lateral flow of pore water with high DOC from organic surface sediment (electron donor) interacted with the vertical upwelling of NO₃-rich ground water (electron acceptor). Our research applying flow path analysis suggests that the carbon source might not be from the DOC-rich shallow lateral flow. Instead, it is most probably from the organic matter deposit from surrounding vegetation. A high denitrification zones were also found at sites where groundwater flow

paths transport NO_3^- to supplies of available organic carbon, located at interfaces between sands and buried river channel deposits [*Hill, et al.*, 2000]. Furthermore, residence time determined by flow velocity is another important factor controlling NO_3^- removal besides the thermodynamic conditions.

The role of vegetation uptake as a removal process has been questioned from comparative studies of detailed spatial patterns of groundwater nitrate concentrations in riparian zones [*Vidon and Hill*, 2004]. It might not be reasonable to exclude the effect of plant uptake at the near-stream area, but the lack of significant concentration gradient along the shallow flow line suggests that plant uptake does not contribute greatly to the observed NO₃⁻ removal. The spatial distribution of NO₃⁻ combined with the groundwater flow path analysis suggests the only significant NO₃⁻ reduction is right beneath the stream sediment surface. The results of the Cobb Mill Creek study support that the highly biologically reactive, near-stream groundwater-surface water interface, rather than a broader riparian zone, accounts for the processes, based on the fact that the largest nitrate removal were found at the location of the intersection of nitrate-rich groundwater water with layers of organic matter near the sediment surface.

Our Cobb Mill Creek site study provide an example of groundwater-surface water interface that can influence, but not fully control, fluxes of NO_3^- across the terrestrial-aquatic interface. We propose that the effectiveness of denitrification as a mechanism for NO_3^- retention depends critically on whether there is adequate carbon source within groundwater-surface water interface with rapid throughput of terrestrially derived water. Such regions function within watershed as a controlling point that connects catchment processes and the surface water chemistry. The sustainability of groundwater-surface

water interface to remove NO_3^- via microbial denitrification is likely to depend on two main domain factors: 1) the residence time of the discharging groundwater associated within biologically reactive GSI, 2) the rate of supply of carbon from terrestrial environments to these active flow paths. It is the crucial combination of sufficient organic matter and long residence time in the streambed that produces the efficient attenuation for groundwater NO_3^- loads.

5.5.1.2 Transient effects of hydrological events

Most of the temporal variation in solute concentrations in the surface stream is associated with floods [Marti, et al., 2000]. [Butturini and Sabater, 2002] found that discharge explained 47% of the annual NO_3 -N concentration variance in their study in a small perennial Mediterranean catchment in Spanin. However, this percentage increased to 97% when single floods were analyzed. Floods not only represent a pulse of water, but also of solutes, to the near stream zone. During a single flood, 60% of the floodwater was retained in subsurface subsystems (the riparian and hyporheic zones) in Sycamore Creek, AZ [Marti, et al., 2000]. This movement of water represented a great amount of solute transfer as well, as high as 3 kg NO_3^- -N ha⁻¹ pulse moved from the stream to the adjacent subsystems [Marti, et al., 2000]. The flood-pulse concept (Junk et al., 1989) was first developed for large rivers and mainly focused on surface interactions between river and adjacent floodplain as water overflowed stream banks. The flood-pulse increases the area of "active zones" in the river ecosystem by connecting the main channel with the floodplain from which it is usually disconnected. Floods in Cobb Mill Creek act similarly, but because floods often do not overflow banks, the stream-riparian linkage occurs via subsurface flowpaths.

The variability of NO_3^- attenuation processes has been investigated over only limited ranges of spatial and temporal scales [*Cey, et al.*, 1999; *Hill, et al.*, 2000; *Vidon and Hill*, 2004]. The variability over shorter time scales and their relation to transport processes is less known. Most studies on riparian NO_3^- dynamics consider the biogeochemical transformations but not the transport of NO_3^- , and in particular, neglect the transient characteristics of runoff mechanisms and water pathway, which strongly affect that transport [*Cirmo and McDonnell*, 1997]. Prediction of catchment NO_3^- export will continue to be problematic until the relative importance, and interaction, of the primary controls are better understood.

Field measurement combined with numerical model could be very helpful tool for watershed hydrochemistry researches. In this study, it was not intended to exactly replicate the nitrate loads observed during and after floods, but rather to simulate the general behavior, which is observed in the field. The model was developed for its ability to handle time varying boundary conditions, to account for unsaturated/saturated flow behavior, which are important in describing the interaction between rising and falling stream levels and the adjacent groundwater. This is the first attempt to apply a combined flow and transport model with time vary boundary conditions to stream/aquifer interaction.

Temporal evolution of stream chemistry will depend largely on groundwater signature given that the storm flow is mainly supplied by pre-event subsurface flow in humid areas [*Sklash and Farvolden*, 1979]. Catchment runoff generation mechanism is prerequisite for understanding the watershed hydrochemical response to the storm. [*Inamdar and Mitchell*, 2006] proposed an model for NO₃⁻ where the occurrence of seeps and steep slope gradients are the primary determinants of NO₃⁻ generation and delivery, and the areal extent and the rate of expansion and contraction (wetting up and drawdown) of variation saturation area have a secondary role as loci for interception of NO₃⁻ contributions from throughfall. There is a similar topographic setting with relatively steep slopes within the Cobb Mill Creek catchment ranged from 5%~15% to the site in western New York [*Inamdar and Mitchell*, 2006]. Thus, we believe these steep gradients combined with well-drained soil expedited the movement of subsurface storm runoff carrying out NO₃⁻. As a result, the change in biologically reactive solute in stream during floods will be controlled by hydrological residence time, and rates and types of biochemical processes in the groundwater surface water interface [*Triska, et al.*, 1993b]. For the two floods studied here, concentrations of nitrate in stream water had a larger and later dilution dip than chloride concentration, suggesting that biological processes play an important role in nitrate concentration reduction.

In terms of flow domains and pathways implied by the model, examination of predicted velocity vectors and fluxes showed the formation of a groundwater ridge within the stream bank. This led to the reduced hydraulic gradient toward the stream. Burt, et al. [*Haycock and Burt*, 1993] emphasized the role of riparian buffer zones in headwater catchments. Results of groundwater flow simulation and observed movement of bankstorage water at Cedar River, Iowa indicate that a 2-m rise in river stage caused bankstorage water to move horizontally at least 30m into an alluvial aquifer and vertically about 4 m below the river bottom [*Squillace*, 1996]. However, unlike the extensive bank storage (with reversed flow) occurring in floodplain area [*Bates, et al.*, 2000; *Squillace*, 1996], the bank storage process may be limited in hillslope areas without floodplains or

riparian wetlands because of a much steeper hydraulic gradient toward the stream. In the present study, the effect of pseudo 'bank storage' is to retard the flow of hillslope water to the stream. Thus the residence time of hillslope water within the near-stream riparian zone is increased. This condition favors the biogeochemical reduction process (denitrification) that lowers NO_3^- concentrations (chapter 2).

From an ecosystem perspective, lateral linkage between stream and riparian zones during floods enhances the capacity of the riparian subsystem to retain the hillslope runoff and contaminant flux. Retention of water can include both bank storage by holding episodic stream water and reduced discharge by decreasing gradient. Retention of solute includes both storage *in situ* and losses to the atmosphere (e.g., via denitrification). Most research has examined how stream-water chemistry is modified by interaction with the hyporheic zone (in-stream transient storage) [Bencala and Walters, 1983; Triska, et al., 1990; , 1993b; Valett, et al., 1996], few, if any, have studied the role of the groundwater surface water interface in regulating chemical fluxes from riparian zone groundwater to streams. In this sense, riparian zones act as a large transient storage zone effectively retaining a fraction of storm flow and, therefore, decreasing the rapid downstream export of water and solutes. Cooper [1990] also concluded that the role of in-stream processes is considerably less important than the riparian zone in regulating baseflow nitrate flux in a small New Zealand pasture catchment. But the present study has shown that the nearstream riparian zone influences not only baseflow nitrate flux but also the storm-flow nitrate flux, although in this specific topographic and hydrogeologic setting, the latter is affected to a limited extent. This effect has been acknowledged in large rivers with

extensive floodplains [*Burt, et al.*, 1999; *Marti, et al.*, 2000]. But in headwater riparian area with limited or no floodplain, the effect has not been well recorded.

The general pattern of stream-aquifer interaction is limited in this hillslope riparian area due to the dominant hydraulic gradient towards the stream. However, the low-frequency, big storms, i.e., hurricanes, could lead to overland flooding and true bank storage process (with reversed flow) Figure 5-22. In this scenario, groundwater discharge is "shut off" by the reversed hydraulic gradient. The duration of this interruption of groundwater discharge depends on the storm magnitude. The NO₃-bearing, groundwater discharge is temporarily terminated. This attenuation effect on stream NO₃⁻ loading could last for several days or weeks depending on the storm duration, thus, might significantly change stream annual budget of NO_3^- export depends on storm frequency. However, at some point, severe floods may also erode banks and remove riparian vegetation, thereby decreasing both storage volume and retention capacity. Coastal storms can occasionally generate a storm surge up into Cobb Mill Creek that can overtop the banks, and the return frequency of these storms is about 3 years [*Mills, et al.*, 1998]. Hurricane landfall in this area is infrequent; storms large enough to cause 1962-class flooding (the most significant storm in recent history) occur once per 40 years [Mills, et al., 1998].

Further study should be conducted on the effect of water table rise at near stream unsaturated zone on nitrate delivery. The decline in nitrate in near-stream zone water may result from denitrificaiton and direct input of NO_3^- poor floodwater from the stream channel, but bank storage water released later may not be of the same constitute due to the other potentially important mechanisms. Rewetting of unsaturated stream bank may trigger leaching of NO_3^- (produced from nitrification) and increase rates of riparian
biological processes such as mineralization or nitrification. The relative importance of these processes may vary with flood magnitude and the flow path of recharge water. Thus, hydrochemical dynamics during the bank storage may be caused not just by direct solute delivery but also by indirect effects of increases in water table.



Figure 5-22. Model predicted Darcian velocity vectors for a hypothetic storm with 1.5 m rise of stage with duration of 2 days. A) pre-event velocity vectors; B) the reversed velocity vectors toward the hillslope at stream bank zone at 0.5 day when stream stage reached its peak. C) and D) During flood recession, the pre-event velocity vector is gradually re-established and the temporally stored water in unsaturated zone drains out.

5.6 Conclusion

Here is presented a field and numerical modeling study of riparian hydrology. For the first time, this has included the chemical flux and water table response occurring during bank flood events. Patterns of riparian water table fluctuations during transient hydrological events of the period Aug, 2005-Dec, 2005 within a non tidal reach of the Cobb Mill Creek, VA were identified and discussed. A conceptual model that incorporates a kinetic wave process due to rapidly rising stream water levels and impact of topography to the interaction of stream aquifer continuum is proposed. Simulations using a saturated-unsaturated flow model specifically developed for this problem provided a reasonable match to the pressure head field recorded at a number of piezometers located within to the computational domain. From this it was concluded that riparian hydrology is predominately a two-dimensional (lateral) process. In terms of flow pathways implied by the model, examination of predicted velocity vectors and fluxes showed the formation of a groundwater ridge within the stream bank. This led to the reduced hydraulic gradient toward the stream. This transient hydrological interaction might have important role on episodic NO_3 loading during the storms depend on the extent of the stream-aquifer interaction. In the Cobb Mill Creek site, the building up of a water table ridge at the near stream area prevents hillslope discharge water from flowing quickly to the stream; thus the residence time of hillslope water within the biologically reactive zone, groundwater-surface interface, is increased. Waterlogged conditions in this zone favor microbial reduction of NO_3^- to N_2 . This transient period could be several days, or weeks depending on the storm characteristics, during which the stream NO_3^- export is attenuated. This may not be important for long-term NO_3^- export in our field site, while might significantly change the NO_3^{-1} export for high order rivers with extensive flood plain area.

The processes identified in this paper will generally apply to stream-riparian system with steep sloping banks and well-drained aquifer material. The interactions

between hillslope runoff and the spatial response patterns in the riparian zone are

obviously site specific, controlled by local topography and hydrogeologic setting.

Nevertheless, the geomorphology of this study site is typical of many coastal streams in

east U.S.; the processes identified herein should be common for this class of system.

5.7 References

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6 Dissertation Synthesis

The difficulties in catchment biogeochemical researches arise from the complex interactions between hydrological processes and biogeochemical processes occurring over a wide-range of spatial and temporal scales. In contrast to the "catchment scale" approach looking into the hydrological controls on observed solute export through concentration-discharge relationships, the "field scale" approach focusing on internal processes involved in chemical cycling as well as attenuation or export studied by using laboratory and field experiments, is an essential part towards predictions at the catchment scale. In this dissertation, a process-oriented approach is taken to study the NO₃⁻ transport through a small hillslope field within an agricultural catchment at the costal plain, VA. This hillslope or sub-catchment is a spatial component or unit of catchment on the basis of it's hydrological and ecological functioning. As a result, a distributed approach is required to understand the differing functioning of different landscape components. We have taken the process-based approach of applying field and laboratory measurement and numerical models to the study of steady and episodic NO_3^- transport in this streamhillslope continuum. This study has made a significant contribution to our catchmentscale knowledge of NO_3^- transport on that it helped to generate improved N delivery model components that have been incorporated into lumped and/ or distributed, conceptual and/or physically based hydrological models of differing complexities.

Almost every process need to understand catchment hydrology and biogeochemistry occurs in the subsurface. The groundwater flow pathways and dynamics are the most crucial elements in the prediction or modeling of catchment N responses because they regulate the movement and fate of NO_3^- from the upland to the stream. Thus, combination of riparian hydrology and biogeochemistry is required to stream NO3loadings from adjacent terrestrial systems for different spatial and temporal scales.

Integrating the manuscript chapters provides a holistic understanding of nitrate delivery through this hillslope-stream continuum. Results from the column experiments and the one-dimensional numerical modeling provide some of the first estimates of kinetic parameters (Chapter 3) for denitrification in the GSI. By simulating groundwater and surface water interaction in the intact cores in chapter 4, we were able to trace the denitrification dynamics in reproducible laboratory conditions similar to the groundwater-stream interface of the Cobb Mill Creek. The hydrology of GSI will ultimately influence biological reactions through flow paths, supply of reactants, and residence time, etc. Thus, integrating hydrology and biogeochemistry in the intact cores and subsequent models has lead to a better understanding on how microbial kinetics in the GSI can influence NO_3^- -N delivery from groundwater into stream.

The field monitoring work combined with a 2D flow and transport simulation conducted in chapter 5 suggests that the hydrology of riparian zone has a significant effect on their capacity to remove NO_3^- via denitrification. The NO_3^- removal capacity of GSI is depend on firstly, groundwater flow paths that intercepts the carbon-rich matrix material, thus providing carbon source and anaerobic condition for denitrification, and secondly, sufficient residence time for nitrate to be denitrified. This minimum residence time is a function of intrinsic denitrification rate of the sediment material, which is highly determined by organic carbon content [*Galavotti*, 2004]. In summary, the flow velocity and organic carbon are two most important factors controlling the NO_3^- flux from the upland to the stream. In this sense, the Damkohler number (Da) (a ratio of reaction rate and rate of advective transport), analogy to the dimensionless ratios of hydrological and chemical timescales [*Hornberger, et al.*, 2001], will be a good indicator for nitrate removal efficiency in wide range of catchments. The present study has shown that more than 80% NO₃⁻ removal within the GSI for Da>2, in contrast to less than 50% NO₃⁻ removal for Da<1 in the riparian zone located in the steep hillslope, West Australia [*Ocampo, et al.*, 2006]. Da might also help to explain the 10-fold differences in NO₃⁻ export from two adjacent catchments [*Schiff, et al.*, 2002]. The same concept can be extrapolated to other catchments with different hydrogeomorphologic settings in terms of the first-order controls on NO₃⁻ removal, as it incorporates the balance between hydrological and biogeochemical processes occurring within riparian zones.

The biogeochemical reactions during the stream-aquifer interaction are often limited to the top layer of sediments (<50cm) (Chapter 2). In consequence, studies at small scale (laboratory flow-through columns) are needed to finely quantify biogeochemical processes in near stream zone. The observation from laboratory "bank storage" simulation could be extrapolated to the catchment scale NO₃⁻ delivery dynamics during transient bank storage event (Chapter 4). The numerical model combined with microbial reaction kinetics validated in "bank storage" simulation revealed that the reduced nitrate flux is positively related to the penetration depth. Accordingly, the total reduction of groundwater-derived contaminant loading would be significant in high order river with extensive floodplain area with a great extent of groundwater-surface water interaction. At the Cobb Mill Creek Site, groundwater flows deep and essentially bypasses the shallow carbon-rich soils, providing little opportunity for denitrification to effect nitrate concentrations prior to discharging to the stream. This process is similar to the findings of [*Bohlke and Denver*, 1995]. According to the results presented in chapter 5, riparian buffer can affect nitrate concentrations in two principal ways. First, riparian buffers can affect old groundwater discharging from long flow paths by increasing organic carbon buildup and debris on the streambed and creating a reducing environment through which deep groundwater must pass. Second, riparian buffers can dilute young groundwater discharging to streams through shallow flow paths in the upper saturated zone beneath the ground by locally recharge along the riparian area.

Riparian buffer areas allow recharge through undisturbed soil with no chemical applications (as opposed to cultivated upland soils), shallow groundwater moving beneath a wide vegetative buffer will normally be dilute in the upper portion of the saturated zone. Dilute recharge results in lower concentrations of several constituents, including nitrate and chloride, in shallow groundwater in riparian areas. This hypothetic mechanism is supported by lower NO₃⁻ concentrations observed in the shallow groundwater underneath the near-stream riparian area than those in the deep aquifer (chapter5), while invalidated by the lack of lower CI- concentration especially during summer, probably due to the evapotranspiration by the vegetation. However, the absence of simultaneously concentrated NO₃⁻ in shallow groundwater indicated by the decreased NO₃⁻/CI⁻ during summer might be attributed to denitrification. Thus, dilution alone cannot account for observed lower concentrations of nitrate nitrogen in shallow groundwater discharging into the stream, although the relative importance of dilution and

denitrification are difficult to measure. These results suggest that shallow groundwater moving near the water table just below the land surface in transmissive sandy aquifers through riparian buffer areas is probably denitrified because of DOC availability from surface organic matter rich horizon.

The organic carbon content of the streambed appears to exert a major effect on discharging groundwater chemistry. Nitrate loss rates were significantly correlated with organic matter content (Chapter 2 & 3). The origin of this organic material is vegetation and organic debris from streambank riparian areas and vegetation growing upstream within the watershed. The thickness of the organic streambed material varied but functional causing the observed spatial variability of nitrate removal rates (chapter 2). Streambed organic matter content could be artificially affected by management activities. The streams that are regularly dredged or have been channelized, as is common in agricultural areas, would have less capacity to reduce nitrate and could increase exported nutrients in groundwater. The finding of nitrate reduction in the GSI could be extrapolated to the other solutes transport in discharging from groundwater to streams. Conceptually, the GSI is an important consideration when attempting to model mass transport in a terrestrial-aquatic system, because the streambed sediment can significantly change the chemical quality of groundwater before it discharges to a stream by elevating concentrations of some chemical constituents (Fe^{2+} and Mn^{2+}) and reducing others (i.e. $O_2 \& NO_3$).

Apparently, one single transect in the present study cannot fully represent the hillslope-riparian conditions. In fact we might have chosen the least representative transect along the whole reach. This transect is characteristic of steep, convex near-

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stream topography, which favors deeper water tables and subsurface flow paths. While the most parts of reach are more like concave-shape which favors interactions between subsurface water and surface soil horizons where denitrification and root uptake are likely to occur. This is supported by the much lower NO_3^- concentration in downstream bank wells (N4 and N5), where a flatter near stream area present compared with the transect with N1, N3, and N7. Additionally, the flat near-stream area along the major reach might have more significant groundwater-stream interaction than the current steep transect according to chapter 5.

The following studies presented in Chapter 5 have revealed the transient patterns of groundwater-stream interaction and sequential NO₃⁻ delivery during the storms. Channel bed, banks, and hydrologically linked floodplains together attenuate flow volume, which would otherwise be routed downstream (Wilby and Gibert, 1996). However, the present study in catchments with high gaining reaches indicates that stream-water exchange is low because large groundwater pressure gradients limit surfacewater exchange and suggests that bank storage processes can reduce nitrogen loads entering the stream in groundwater discharge but to a limit extent (chapter 5). One question need to be further studied is the role of the flat riparian, a lowland area on the other side of the stream. Based on the understanding of the current study, there will be much more significant interaction of stream water with the adjacent lowland area than with the hillslope side during the flood. Consequently, much higher nitrate retention capacity would be expected in the lowland side induced by bank storage process than in the hillslope side. The groundwater ridge developed during the storm could have a benefit to nitrate reduction on that the water table may arise to reach the organic matter rich surface soil where denitrification could be facilitated. Because of vertical movement of water, the length of the saturated soil profiles varies and so does the effective denitrification rate, which increases as we approach the soil surface. Denitrification capacity is expected to be highest at the surface where organic matter is sufficiently supplied by above-ground plants. The groundwater level at stream bank rose as high as 20 cm and residence time was in the order of 2-4 days during the 4 months continuous monitoring. This may favor additional microbial reduction of nitrate during the storm period, and then filtered water drains back the stream after flood wave passes, helping to reduce the transient loading of nitrate. Similar processes was observed by [*Rassam, et al.*, 2006] in a floodplain area, Australia, where the bank storage is conducive to denitrification on filtering nitrogen load from groundwater.

The elongated residence time induced by the groundwater ridge at stream bank will also contribute to denitrification process during the storm. The subsurface flow rate declined by a factor of 2 in our three monitored storms, favorable to more denitification to remove appreciable amount of nitrate. The larger the discharge event, the higher the water level in the stream bank and the longer the period during which nitrate is interacting with the upper sediments containing the higher carbon resources that result in a higher denitrification removal.

The storm frequency also has important role on nitrate export. Repeated draining and filling potentially results in a greater flow of water through the shallow unsaturated zone than under the baseflow condition. The riparian buffer becomes more efficient in removing nitrate during intermittent events where the unsaturated stream bank fills up with nitrate-bearing water, denitrifies, discharge slows down or even stops, perched groundwater drains, then another event fills the stream bank again and so forth. Material exchange and retention are greatest when high stream flow events are of intermediate frequency [*Matrti*, 2000]. The riparian zone will still keep elevated water table from the event to the event.

The study proposed alternative mechanisms for NO_3^{-} transport in response to transient hydrological events. Most of catchment scale approaches are based on the merely hydrological processes as antecedent moisture condition, mechanisms of runoff generation, and multiple members mixing without considering nitrogen biogeochemical processes and dispersive transport [Correll, et al., 1999; Creed and Band, 1998; Creed, et al., 1996; Hill, et al., 2000; Inamdar and Mitchell, 2006]. In these studies, tracer-based separation has been generally used to derive the source zones contributing to streamflow generation. However, the normal assumed constant signature in flow components is invalid given the fact both transient advective transport and hydrodynamic mixing effects play a role [*Chanat and Hornberger*, 2003; *Jones, et al.*, 2006]. By using a dynamic and full integrated flow and transport model that explicitly accounts for dispersion processes, it was shown that hydrodynamic mixing processes can dramatically influence estimates of the tracer-based separation [Jones, et al., 2006]. In present study, we adapted a similar process-based approach as Jones, et al. did to understand the transient NO_3^- export affected by both hydrological transport and biological reactions during the storms (chapter 5). The solute transport model reproduced a very similar NO₃⁻ export pattern to the observed NO_3^- concentration variation during the storm. NO_3^- concentration dips

during the storm are hypothesized to be induced by reducing groundwater discharge or even temporarily storing the water in banks, rather than mixing of end members with different NO_3^- signatures.

In summary, the importance of groundwater surface water interface (adjacent zones to stream channels, i.e. stream bank and streambed) has been emphasized by the laboratory, field and modeling works with limited spatial and temporal scales. This study provides evidence that near stream riparian buffers affect old ground water that has bypassed the physical riparian buffer by supplying significant amount of organic matter to stream channels. The importance of riparian vegetation in providing a carbon source to streams for water quality management also has been noted by [Hill, 1996b]. Riparain vegetation appears to affect groundwater quality at the watershed scale by supplying carbon to stream sediments through which the old groundwater must pass. Riparian buffers also may affect shallow groundwater through simple dilution, a potentially important effect of buffers that is often overlooked. The extent of interaction between groundwater and surface water, and its sequential effect on NO_3^{-1} loads directly relates to the size and frequency of the storm event, and the site hydrogeology and geomorphology. The processes identified herein should be common for this class of system. A complete understanding of the riparian hydrology helps us construct sound conceptual models for denitrification in stream-riparian zones. When this conceptualization is coupled with field-based estimates for denitrification rates, we can incorporate this knowledge into catchment scale models and hence have the ability to assess the holistic role of riparian buffers in controlling nitrate delivery to streams. The processes and mechanisms exposed in the Cobb Mill Creek are obviously site specific, controlled by local topography and

hydrogeologic setting. Nevertheless, the hydrogeomorphology of this study site is typical

of many streams in the Coastal Plain, east U.S.

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Appendix A

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Table A Influents	and ettluent	s tor the	intact	tlow_fk	hrough	column ey	neriments
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		Linear velocity	Residence time	NO ₃ -influent	NO3 ⁻ effluent
Core	Influent	$(\operatorname{cm} \operatorname{h}^{-1})$	(hrs)	$(mg L^{-1})$	(mgL^{-1})
#3	anoxic	2.80	21.11	20.15	8.00
#3	anoxic	5.03	11.93	20.15	11.40
#3	anoxic	3.99	14.77	20.15	9.40
#3	anoxic	1.91	30.96	20.15	9.30
#3	anoxic	1.55	38.18	20.15	7.35
#3	anoxic	0.95	62.11	20.15	6.50
#3	oxic	3.22	18.33	20.00	18.50
#3	oxic	2.23	26.43	20.00	15.00
#3	oxic	1.70	34.72	20.00	13.50
#3	oxic	5.00	11.81	20.15	18.30
#3	oxic	5.00	11.81	15.61	14.80
#3	oxic	5.00	11.81	10.53	9.00
#3	oxic	1.24	47.72	20.00	11.00
#3	oxic	0.58	102.10	20.00	2.60
#3	oxic	0.92	64.17	20.00	6.50
#3	oxic	0.55	107.08	20.00	4.00
#3	oxic	1.08	54.76	20.43	11.10
#3	oxic	0.39	152.93	14.68	3.26
#4	oxic	1.09	50.85	14.68	1.67
#4	oxic	0.47	117.10	15.00	0.10
#4	oxic	0.83	67.15	15.60	7.25
#4	oxic	0.63	88.29	15.60	5.80
#4	oxic	0.29	190.70	15.50	0.00
Bank core	oxic	1.15	34.07	15.74	9.84
Bank core	oxic	0.69	56.85	15.60	10.70
Bank core	oxic	0.75	52.11	15.60	11.45
Bank core	oxic	0.48	81.22	15.54	11.02
#5 (Poor OM)	oxic	0.75	72.16	15.18	13.00
#6	oxic	0.51	98.13	15.00	1.14
#6	oxic	0.61	81.77	15.00	2.81
#6	oxic	0.90	55.75	15.00	5.72
#6	oxic	1.05	47.70	15.00	9.56
#6	oxic	0.51	98.13	15.00	0.67
#7	oxic	0.73	68.56	15.00	6.77
#7	oxic	1.09	45.82	15.88	9.76
#7	oxic	0.93	54.00	18.56	11.72
#7	oxic	0.75	66.66	20.45	11.51
#7	oxic	1.49	33.65	18.39	14.22
#7	oxic	1.07	46.66	17.26	11.39
#7	oxic	0.78	63.73	18.83	10.78
#8	oxic	0.64	78.05	15.15	6.77
#8	oxic	2.61	19.14	15.13	15.00
#8	oxic	2.90	17.23	15.08	15.00
#8	oxic	3.51	14.25	15.21	14.04
#8	oxic	3.90	12.81	15.03	14.11
#8	oxic	4.51	11.08	15.06	14.87

Appendix B

	eone	entration ey .	000000000)	
Time	Pore	Cl	NO ₃	Cľ	Cl	NO ₃ ⁻
(min)	volume	(mgL^{-1})	(mgL^{-1})	(C/C_0)	CXTFIT	(C/C_0)
0	0.00	0.00	0.00	0.00	0.00	0.00
540	0.26	0.00	0.26	0.00	0.00	0.02
900	0.44	0.00	0.26	0.00	0.00	0.02
1350	0.66	0.27	0.26	0.01	0.03	0.02
1530	0.75	1.64	0.58	0.07	0.09	0.04
1620	0.79	2.86	0.90	0.11	0.14	0.06
1710	0.84	4.71	1.66	0.19	0.20	0.11
1800	0.88	6.93	2.64	0.28	0.27	0.17
1890	0.92	8.85	3.63	0.35	0.35	0.23
2070	1.01	13.15	5.53	0.53	0.51	0.35
2160	1.06	15.40	6.63	0.62	0.58	0.42
2340	1.14	18.25	7.76	0.73	0.72	0.49
2430	1.19	18.77	8.18	0.75	0.77	0.52
2520	1.23	20.29	8.58	0.81	0.82	0.54
2700	1.32	21.91	9.20	0.88	0.89	0.58
3240	1.58	23.47	9.64	0.94	0.98	0.61
3600	1.76	23.95	9.68	0.96	0.99	0.61
4140	2.03	24.50	9.84	0.98	1.00	0.62
Influent		24.98	15.74	1.00	1.00	1.00

Table B The temporal Cl⁻ and NO₃⁻ concentrations in effluent compared to simulated Cl⁻ concentration by CXTFIT 2.0 (bank core #6 with v=1.14cmh⁻¹)

Appendix C

Spatial Interpolation

Potentiometric maps and spatial distribution maps of dissolved inorganic constituents were produced from head data and groundwater sampling data by kriging using geostatistical method (Davis, 2002).

For spatial data, a related function called the semivariance typically is used to characterize the spatial correlation. The theoretical semivariogram γ is defined as one-half of the variance of the differences in sample values between points separated by a distance h, the so-called "lag" (Davis, 2002). It provides a measure of spatial dependence between pairs of samples at a distance h. In practice, the semivariograms are constructed based on limited number of samples:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i + h) - Z(x_i)]^2$$

Where: Z(xi)=the observed value of the variable at sampling site xi;

N(h)=the number of pairs of samples separated by h

A semivariance model is typically fit to a semivariogram calculated from experimental data to provide a continuous description of the semivariance for use in interpolation methods such as kriging method. A linear semivariogram model was applied in this research and has the form (Davis, 2002):

 $\gamma_h = \alpha h$ for h < a

 $\gamma_h = var(z)$ for h > = a

In kriging, the semivariogram is used to determine the best weights to apply to the control points when performing spatial interpolation. Ordinary kriging was used as the interpolation method in this research. The mean of the variable to be interpolated is assumed to be constant over the region containing the points used to construct the semivariogram The MATLAB program following the mathematical formulation provide in Davis (2002) was used to make spatial interpolation of groundwater head and solute data (see the appendix CD).

Appendix D

Table D Vertical profiles of chemicals and organic matter content for four intact cores

Upstream v=2.06cmh ⁻¹			v=0.63cm	h⁻¹	Middle stream core	v=2.34cmh ⁻¹		
Depth(cm)	%OM	Cl ⁻ (mgL ⁻¹)	NO ₃ ⁻ (mgL ⁻¹)	NO ₃ ⁻ (mgL ⁻¹)	Depth(cm)	%OM	Cl ⁻ (mgL ⁻¹)	NO ₃ ⁻ (mgL ⁻¹)
0.00	N/A	8.64	0.00	N/A	0.00	0.16	8.50	8.80
2.00	0.12	N/A	N/A	0.44	4.00	1.88	8.20	9.22
4.00	0.10	7.90	0.14	0.12	9.00	0.36	7.81	11.39
6.00	0.17	N/A	N/A	0.00	15.00	0.19	N/A	N/A
9.00	25.00	7.88	2.78	0.00	20.00	0.65	8.18	11.83
12.00	22.83	N/A	N/A	5.99	25.00	0.31	N/A	N/A
15.00	6.07	N/A	N/A	12.79	30.00	0.24	8.36	13.42
20.00	0.27	8.55	13.84	15.38	35.00	0.20	N/A	N/A
25.00	0.17	N/A	N/A	15.14	40.00	0.24	8.47	13.82
30.00	0.23	8.50	13.80	15.11	45.00	0.09	N/A	N/A
35.00	0.15	N/A	N/A	15.60	50.00	0.14	8.25	13.74
40.00	0.15	8.67	14.00	15.22	54.00	0.10	N/A	N/A
45.00	0.08	N/A	N/A	15.43				
50.00	0.06	7.67	12.38	15.09				
Downstream core	v=2.8	81cmh⁻¹	v=0.5	5cmh⁻¹	Bank core		v=2.040	cmh⁻¹
Depth(cm)	%OM	Cl⁻(mgL⁻¹)	NO ₃ ⁻ (mgL ⁻¹)	NO ₃ ⁻ (mgL ⁻¹)	Depth(cm)	%OM	Cl⁻(mgL⁻¹)	NO3 ⁻ (mgL ⁻¹⁾
0.00	N/A	8.70	5.80	N/A	2.00	0.52	8.41	2.54
1.50	0.16	N/A	N/A	0.00	5.00	1.29	8.48	3.83
3.00	0.38	N/A	N/A	0.00	10.00	4.22	8.21	4.53
5.00	0.56	8.08	5.86	0.44	15.00	3.92	8.37	6.54
7.00	7.19	N/A	N/A	0.12	20.00	7.15	N/A	N/A
9.00	1.02	N/A	N/A	5.48	25.00	8.40	8.82	8.75
12.00	3.01	8.06	9.23	6.17	30.00	1.84	N/A	N/A
15.00	1.04	N/A	N/A	9.57	35.00	5.60	8.40	13.62
20.00	0.70	8.64	12.33	11.79	40.00	2.91	N/A	N/A
25.00	3.94	N/A	N/A	N/A	45.00	0.89	8.67	13.66
30.00	0.29	8.55	13.69	12.36	50.00	0.60	N/A	N/A
35.00	0.14	N/A	N/A	14.23	55.00	N/A	8.25	13.50
40.00	0.10	8.75	13.90	15.78				
45.00	0.19	N/A	N/A	13.55				
51.00	0.24	8.25	13.15	15.40				

Time(hrs)	pre-	event	10	hrs	20	hrs	30	hrs	40hrs	
	Cl	NO ₃								
Depth(cm)	(mgL^{-1})	(mgL^{-1})								
4	15.88	7.84	29.01	3.10	30.11	1.78	30.13	1.73	30.02	1.73
7	15.80	6.38	29.11	3.78	29.90	1.82	30.01	1.73	30.03	1.64
10	15.73	7.75	28.22	4.06	29.20	1.73	30.03	1.55	29.84	1.55
13.5	16.10	11.53	26.60	5.02	28.72	1.46	29.98	1.14	29.89	1.09
17.3	15.67	14.09	23.41	7.25	28.30	1.32	30.10	0.59	30.05	0.32
26.5	16.21	14.32	18.06	8.84	25.12	3.88	27.90	1.14	29.40	0.50
31.7	16.10	14.59	17.10	11.72	24.02	5.88	27.45	2.51	28.63	0.82
36.5	15.98	15.00	16.30	14.82	21.06	9.07	26.51	3.05	28.20	1.00
41.3	16.02	14.82	16.10	15.32	18.92	12.17	25.40	4.92	27.82	1.41
46.7	16.22	15.41	15.80	15.96	18.03	13.95	22.07	6.47	26.53	1.91

Table E Laboratory bank storage simulation by infiltration of artificial stream water (ASW)

Appendix E