MODELING LONG-TERM NITRATE BASE-FLOW LOADING FROM TWO AGRICULTURAL WATERSHEDS

Mohamed M. Hantush and Mingyu Wang*

ABSTRACT: Nitrate contamination of ground water from agricultural practices may be contributing to the eutrophication of the Chesapeake Bay, degrading water quality and aquatic habitats. Groundwater flow and nitrate transport and fate are modeled, using MODFLOW and MT3D computer models, in regional aquifers beneath two adjacent agricultural watersheds of the Chester River Basin, Maryland. Field evidence and geochemical analysis indicate the removal of nitrate by denitrification in a thin layer situated at the base of the surficial aquifer. The potential for denitrification in this layer may have impacted nitrate levels in the streams of the two watersheds, and is influenced by groundwater flow patterns, extent of the denitrifying layer below the watersheds, and the regional dip of the underlying strata. The groundwater flow model is calibrated and confirmed successfully. The lack of sufficient nitrate concentration and nitrogen input data, however, precluded a complete confirmation of the transport model. Model simulations predict a significant reduction in long-term nitrate loading from the two watersheds, due to denitrification in aquifer sediments and other riparian-instream nitrate removal processes. The results show the relative contribution of the different loss pathways on the potential reduction of long-term nitrate loading from each watershed. These findings may have implication on the management of nutrients in the two watersheds.
KEY TERMS: nitrate, groundwater, model, transport and fate, riparian zone, MODFLOW.

INTRODUCTION

Agricultural nitrate (NO_3^-) input to ground water has raised concerns about surface water quality and increased the public interest in the role of the environment in the removal of NO_3^- from ground water. Extensive research has shown that stream riparian zones (trees and vegetated strips located between streams or lakes and uplands) can substantially remove nitrate from ground water and regulate its' fluxes by denitrification, plant uptake, and dilution in ground waters flowing through these interfaces (*Hill*, 1996; *Devito et al*., 2000). Among these processes, denitrification (microbial reduction of nitrate to nitrogen gas under anaerobic condition) is the primary mechanism of NO_3^- removal, which occurs when groundwater flow carries NO_3^- into contact with reduced phases in an aquifer (organic carbon, sulfide, and other reduced Fe phases). Although most studies have focused on NO_3^- removal at shallow soil depths below the water table (e.g., *Peterjohn and Correll*, 1984), recent studies indicate that denitrification may occur at depth in aquifer sediments and within the saturated zone of riparian areas (e.g., *Böhlke and Denver*, 1995; *Devito et al*., 2000).

The Chesapeake Bay, the Nation's largest and most productive estuary is located in the Atlantic Coastal Plain. The stressed estuarine ecosystem in the bay has been linked to nutrient enrichment. Groundwater nitrogen accounts for approximately for 40 to 50 percent of the total nitrogen discharge to the bay from nontidal rivers and streams (e.g., *Bachman et al.,* 2002). This paper presents some results obtained from a three-dimensional groundwater flow and nitrate transport and fate numerical model developed to estimate nitrate discharge concentration and loading to the Chester River from two adjacent agricultural watersheds, the Morgan Creek and Chesterville Branch. Previous studies document the occurrence of denitrification in deep parts of the surficial aquifer, and that nitrate in ground waters that interact with these sediments is removed by denitrification before they are discharged to Morgan Creek and the Chesterville Branch (*Böhlke and Denver*, 1995, *Bachman et al*., 2002). Hydrogeology and subsurface stratigraphy appear to control the extent of NO_3^- removal by denitrification and its concentration in ground water discharging as stream base flow. The role of riparian zones along both creeks and instream processes on nitrate removal is not well understood. The model was calibrated and verified using hydrostratigraphic framework, hydrologic and geochemical data developed in a joint effort with the U.S. Geological Survey (IAG #DW14937941).

Study Area

The study area (Locust Grove) consists of the Morgan Creek and Chesterville Branch watersheds, located in central Kent County, Maryland, between the Chester and Sassafras Rivers (Figure 1). The two USGS gaging stations (site 01493500, Morgan Creek) and (site 01493112, Chesterville Branch) measures streamflow discharge rates and nutrients continuously. Agriculture is the dominant land use in the study area, accounting for about 90 percent of the watershed area. Most of the

* Respectively, Research Hydrologist, Land Remediation and Pollution Control Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 26 West Martin Luther King Dr., Cincinnati, OH 45268, Phone: (513) 569-7089, Fax: (513) 569-7105, E-mail: hantush.mohamed@epa.gov, Environmental Project Scientist, ManTech Environmental Research Services Corp., U.S. EPA R. S. Kerr Environmental Research Center, 919 Research Dr., P.O. Box 1198, Ada, OK 74820, Phone: (580) 436-8656, Fax: (580) 436-8718, E-mail: Wang.Mingyu@epa.gov.

cropland is in a rotation of corn, soybeans, and small grains. A significant part of the Chesterville Branch watershed is under cultivation for nursery stock. The remaining portions accounts for riparian wooded areas along both creeks, urban area (Kennedyville), a few confined animal-feeding operations and poultry houses, commercial establishments, and pasture land for dairy operations. The hydrologic setting of the study area has the potential to discharge large volumes of ground water to the streams. The surficial aquifer in the study area is composed of the deeply weathered sands and gravels of the Pensauken Formation (Columbia aquifer) and the underlying glauconitic sands of the upper Aquia Formation (Aquia aquifer). The Columbia-Aquia aquifer is underlain by the Aquia confining layer (silt-clay), which subcrops shallowly below (within 5 meters of the land surface) and roughly parallels Morgan Creek to the north of the creek in a band that strikes southwest to northeast across the northern edge of the study area (*Bachman et al*., 2002). Denitrification appears to occur in the sediment redox transition (primarily reduced glauconite and iron sulfide), identified in cores, situated at the base of the surficial Columbia-Aquia aquifer, at the top of the Aquia confining layer (upper 0.5-1 m). Effectively, the denitrifying layer underlies Chesterville Branch entirely, and underlies only portions of Morgan Creek, to the south and southeast of the Aquia confining layer subcrop. Because the coastal plain sediments dip gently to the southeast, the surficial aquifer dip and thicken to the southeast and the Aquia confining layer is generally shallower (within 5 meters) beneath Morgan Creek and deeper (about 22 meters) beneath the Chesterville Branch.

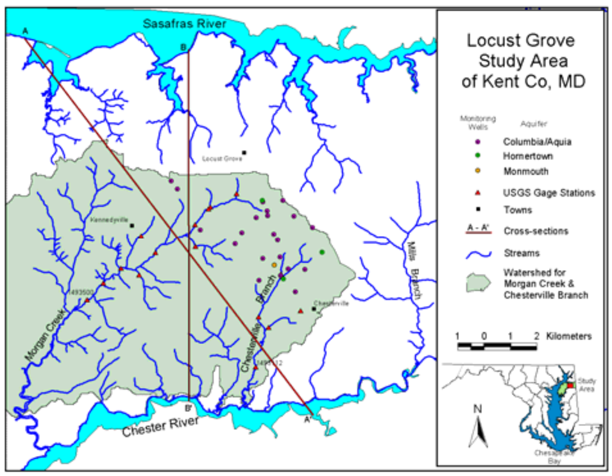

Figure 1. Overview and map of the Locust Grove study area

Numerical Model

The groundwater flow and nitrate transport and fate at the site are developed using the GMS modeling system which links the groundwater flow MODFLOW to the transport and fate MT3D computer package within user friendly Graphical User Interface (GUI). The layer of reducing sediments is inferred from core samples and reconstructed by interpolation and extrapolation over the entire domain using a GMS spatial estimation module. Three major aquifers are modeled, the surficial unconfined Columbia-Aquia, the confined Hornerstown aquifer, and the deeper confined Monmouth aquifer. Nitrate removal by denitrification in the redox transion zone, in wooded riparian areas along both creeks, and other reducing processes are modeled using first-order reaction rate parameters. Because of lack of nitrate measurements across riparian buffer strips, we were not able to resolve riparian nitrate removal rates from instream losses; therefore, first-order integrated riparian-instream loss parameter is considered for each creek. Nitrate concentrations in the streams are calculated from groundwater mass fluxes by a simple mass balance relationship, assuming complete mixing and steady state transport in each stream reach. All simulations are conducted during base-flow periods.

Calibration and Confirmation

The surficial Columbia-Aquia aquifer with an average thickness of 28 meters was divided into two layers (mostly unconsolidated sand and gravel for the upper layer and fine to medium sand for the lower layer situated above the redox transition zone) to add vertical resolution to the solutions, and the lower Aquia confining layer was divided into a lower tight confining layer associated with a peak in the gamma logs, and an upper more permeable redox transition zone associated with lower gamma activity (mostly glauconitic sand). Groundwater levels at the study site inferred from observation wells in the surficial aquifer were at quasi-steady during the period of November 1998 to April 1999. A steady state model is calibrated during this period for horizontal and vertical hydraulic conductivity, streambed conductance, and recharge rates in the riparian zones along Morgan Creek and the Chesterville Branch and in other portions of the watersheds. The calibration was achieved by trial and error. The calibration criteria were matching observed groundwater heads and stream flow discharge rates at the gage stations with estimated hydraulic heads and base-flow rates from the model. The calibrated recharge rate values during this period were 0.2 cm/d in the Chesterville Branch riparian zone, 0.21 cm/d in Morgan Creek, and varied from 0.02 to 0.115 cm/d in other areas. The calibrated streambed conductance (the hydraulic conductivity of the streambed divided by its thickness) for both creeks varied from 1.3 to 14 day^{-1}. Starting with a few locally measured hydraulic conductivities, the final calibrated horizontal and vertical conductivities in the two layers of the surficial aquifer, respectively, ranged from 6 to 12 m/d and 0.6 to 1.2 m/d. We used vertical conductivity of order of magnitude less than the horizontal value. Observed water table levels during the period of May 1998 to October 1998 indicated transient flow conditions. A transient flow model was used during this period and was calibrated for specific yield (value of 0.26) of the first layer in the surficial aquifer and the specific storativities of all other layers and aquifers (ranged from 10^{-5} to 10^{-4} m^{-1}). This transient period was divided into three two-month periods each with a uniform recharge rate. The calibrated recharge rates and recorded precipitation during the calibration period (May 1998 - April 1999) were used to roughly estimate the monthly recharge rates for years other than the calibration period. We used the period November 1998- October 1999 to confirm/verify the calibrated transient model. Figure 2a shows satisfactory confirmation (or verification) of simulated heads in the surficial aquifer at date 10/10/1999, with $R_N^2 = 0.89$, Nash-Sutcliffe coefficient (Loague & Freeze, 1985), as a measure of the model performance ($R_N^2 = 1$ means a perfect agreement). Figure 2b compares observed with computed base-flow rate at the major station 1493500 in Morgan creek with a satisfactory goodness of fit $R_N^2 = 0.94$.

Nitrate loading to the water table in the study area is obtained from *Böhlke* (personal communication, also, *Böhlke*, 2002). Application of fertilizers during the last four decades of the last century resulted in a dramatic increase in NO_3^- -N recharge concentration approximately from 2 to 17 mg/L as N. Nitrate at the recharge (i.e., source magnitude) is assumed to be uniform over the modeled area; seasonal variations therefore are ignored. Annually averaged recharge rates were used during the calibration and confirmation (or verification) of the nitrate transport model. The nitrogen transport model (MT3D) was calibrated manually by attempting to match measured nitrate-nitrite concentrations in ground water and at the two stream gaging stations with model estimates of concentrations in groundwater and those calculated based on simple mass balance in each stream reach. The calibrated parameters in the transport model were aquifer dispersivities in the longitudinal, lateral, and transverse vertical directions, varied from 0.1-10 meters, first-order reaction rate of 0.006 day^{-1} for denitrification in the redox transition zone (i.e., reducing sediments), first-order integrated riparian-instream removal/reduction rates of 0.017 day^{-1} and 0.006 day^{-1} at Morgan Creek and the Chesterville Branch, respectively. A constant porosity of 0.3 was used for the surficial aquifer obtained from literature related to the site. Bulk density of magnitude 1350 and 1600 Kg/m^3 were used for the aquifers during the calibration. Figure 2c shows computed versus observed NO_3^- in mg/L as N at the gaging station 1493112 in the Chesterville Branch, with $R_N^2 = -0.65$ (R_N^2 varies from $-\infty$ to 1).

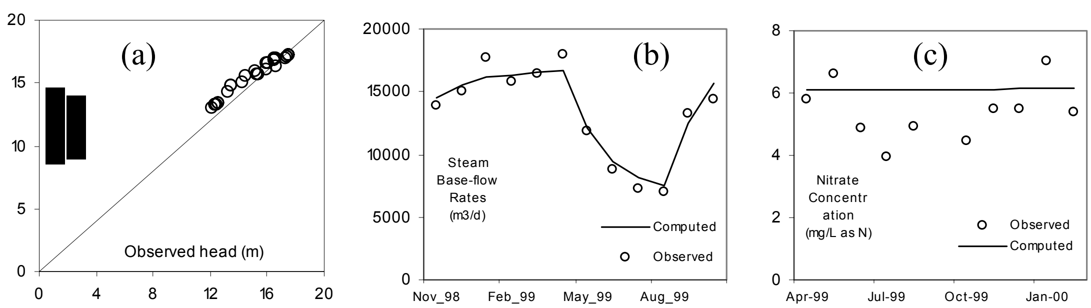

Figure 2. Computed versus observed (a) hydraulic heads (10/10/1999), (b) base-flow rates at gaging station 1493500 in Morgan Creek; and (c) base-flow nitrate concentrations in (mg/L as N) at gaging station 1493112 in the Chesterville Branch

Discussion

The computed uniform base-flow nitrate concentration at the Chesterville Branch gaging station in Fig. 2c (about 6 mg/L as N) is within order of magnitude and relatively close to measured values which displayed seasonal variations. This is expected as seasonal variations of the recharge and nitrate source loading were averaged out leading to quasi-steady simulated concentration during the period of April 1999 to February 2000. Also, the dynamics of nitrate transformation and the related spatial and seasonal variations are far too complex to be modeled accurately with a simplified first-order reaction rates. The simulated long-term loading of nitrate from Morgan Creek to the Chester River is more than twice the load from the Chesterville Branch, as figure 3 shows (compare at time year 2180). Because the drainage area of the former is about twice that for the latter, drainage from Morgan Creek is expected to be greater, thus, leading to a greater groundwater nitrate loading to the creek. Further, as indicated above, Morgan Creek is only partially underlain by the denitrifying zone at depth in the surficial aquifer; whereas the Chesterville Branch is entirely situated above this denitrifying zone. Therefore, there is less potential for nitrate removal from ground water in Morgan Creek watershed. At the local transect scale, however, *Hantush and Mariño* (2001), using an analytical lagrangian solution, estimated greater potential for nitrate reduction in groundwater discharge to Morgan Creek than to the Chesterville Branch, because of shallower redox transition layer beneath the Former. The difference in nitrate loading (Kg/d) between the hypothetical scenario of no denitrifying aquifer sediments and the actual one in figures 3a and 3b support the interpretation of greater potential for nitrate removal by denitrification in the denitrifying layer in the Chesterville Branch than in Morgan Creek. Although not shown in figures, total nitrate load reduction in the Chesterville Branch watershed is roughly estimated to be 54% by year 2180, and 64% in the Morgan Creek watershed. Denitrification in aquifer sediments would have accounted for 77% of total base-flow nitrate removal in the Chesterville Branch watershed (i.e., of the 54%), compared to 23% reduction for riparian-instream in the same watershed. For the Morgan Creek watershed, the latter two values, respectively, are 24% and 76% (of the 64% of total load reduction). This information may be used by regulators and resource managers to manage agricultural nutrients to reduce nitrate loads from the two watersheds.

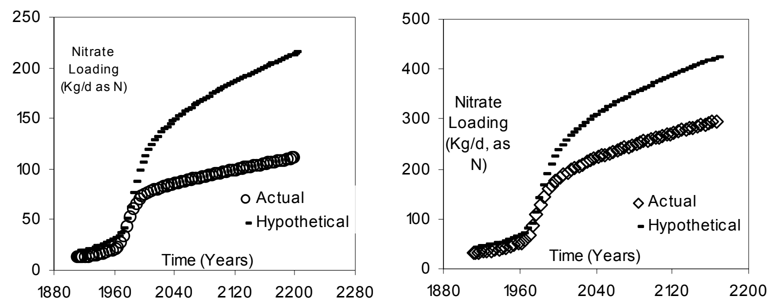

Figure 3. Simulated nitrate loading (Kg/d as N) to the Chester River from (a) Chesterville Branch, and (b) Morgan Creek, with the hypothetical scenario of no denitrification in aquifer sediments (i.e., only riparian-instream removal)

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