Title: Hydrogeologic controls on groundwater discharge and nitrogen loads in a coastal watershed

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Coastal groundwater discharge and nitrogen loads

Abstract

Submarine groundwater discharge (SGD) is a small portion of the global water budget, but a potentially large contributor to coastal nutrient budgets due to high concentrations relative to stream discharge. A numerical groundwater flow model of the Inland Bays Watershed, Delaware, USA, was developed to identify the primary hydrogeologic factors that affect groundwater discharge rates and transit times to streams and bays. The distribution of groundwater discharge between streams and bays is sensitive to the depth of the water table below land surface. Higher recharge and reduced hydraulic conductivity raised the water table and increased discharge to streams relative to bays compared to the Reference case (in which 66% of recharge is discharged to streams). Increases to either factor decreased transit times for discharge to both streams and bays compared to the Reference case (in which mean transit times are 56.5 and 94.3 years, respectively), though sensitivity to recharge is greater. Groundwater-borne nitrogen loads were calculated from nitrogen concentrations measured in discharging fresh groundwater and modeled SGD rates. These loads combined with long SGD transit times suggest groundwater-borne nitrogen reductions and estuarine water quality improvements will lag decades behind implementation of efforts to manage nutrient sources. This work enhances understanding of the hydrogeologic controls on and uncertainties in absolute and relative rates and transit times of groundwater discharge to streams and bays in coastal watersheds.

1.   Introduction

Streamflow (Galloway et al., 2003; Knee and Jordan, 2013; Vitousek et al., 1997) and submarine groundwater discharge (SGD) (Johannes, 1980; Moore, 2010; Spiteri et al., 2008) are both important pathways for transport of nitrogen from land to sea (Slomp and Van Cappellen, 2004; Vitousek et al., 1997). These loads are linked to adverse ecosystem effects (Valiela et al., 1990; Whiting and Childers, 1989). Because nitrogen concentrations are often greater in SGD than in streams (Dubrovsky et al., 2010), it is not uncommon for SGD to be the primary vector for nitrogen to coastal waters (Johannes, 1980; Slomp and Van Cappellen, 2004). Furthermore, nitrogen loads to the environment have increased dramatically in the past half century as fertilizer use and atmospheric deposition increased (Lindsey et al., 2003; National Research Council, 2000; Vitousek et al., 1997). Due to the time lag between groundwater recharge and discharge, these effects may be felt for decades, even after reduction in nutrient loads to land (Sanford and Pope, 2013). It is therefore critical to understand the controls and uncertainties on absolute and relative rates and transit times of groundwater discharge to streams and bays in coastal watersheds.

The groundwater component of watershed budgets has been quantified in many studies. Modeling (Ahiablame et al., 2013; Winter, 1995) and field (Price, 2011; Smakhtin, 2001; Volk et al., 2006) techniques to quantify baseflow, the groundwater component of stream discharge, have been widely applied. Physical controls on baseflow have been well characterized (Farvolden, 1963; Price, 2011). These include hydraulic conductivity (K), recharge, and basin geometry, especially the relation between stream stage and water-table elevations. In coastal watersheds, fresh SGD rates have been estimated at the watershed scale with simple flow nets (Andres, 1987), water budgets (Kroeger et al., 2007), models (Robinson and Reay, 2002), and field measurements (Charette et al., 2001; Kroeger et al., 2007; Young et al., 2015). While these studies provide insights into groundwater discharge to streams and to estuaries independently, the controls on the relative rates of groundwater discharge to streams and bays in coastal watersheds have not been well explored.

The age distributions of groundwater discharging to streams and to estuaries (*transit times*) (Maloszewski and Zuber, 1982; McGuire and McDonnell, 2006) have been characterized

with numerical models (Konikow et al., 2008; Maloszewski and Zuber, 1982; Sanford, 2011) and passive environmental tracers (Bratton et al., 2004; Koh et al., 2006; McMahon et al., 2011). In coastal watersheds, transit times can average on the order of several decades for discharge to streams (Sanford, 2011; Sanford et al., 2012) and coastal waters (Robinson and Reay, 2002; Tait et al., 2014). Transit times of groundwater discharging to streams increases in the downstream direction (Modica et al., 1998, 1997), so it likely follows that SGD (which occurs downstream of the stream mouth) would tend to be older than groundwater discharging to streams. However, the distribution of transit times for groundwater discharge to streams compared to discharge to bays has not been investigated in the same watershed. Because these distributions are important for understanding the groundwater flow and contaminant processes in a watershed, as well as for informing management decisions and evaluating management outcomes, investigation of the hydrogeologic controls on transit time distributions is warranted.

This study uses a numerical model to examine the water budget and transit times associated with groundwater discharge to streams and bays in a coastal watershed. Sensitivity to recharge and horizontal and vertical hydraulic conductivity is analyzed to determine primary hydrogeologic controls on absolute and relative discharge rates and transit time distributions. Model-derived SGD rates are combined with nitrogen measurements near the points of discharge to estimate the nitrogen load contributed by direct discharge of fresh groundwater to the estuary.

2.   Study site

The 670 km^2 watershed draining to Indian River and Rehoboth Bays (collectively the *Inland Bays*) lies on the Atlantic edge of a southward-and-seaward-thickening wedge of Delaware's coastal plain sediments (Fig. 1) (e.g. Andres, 1986; see cross sections in Andres and Klingbeil, 2006). The aquifer-bearing units in this coastal area are heterogeneous clastic sedimentary deposits of interbedded and interfingering sandy and muddy units and are Miocene-aged and younger (Andres and Klingbeil, 2006; Andres, 2004; McLaughlin et al., 2008). These aquifer-bearing units are underlain by a thick, low-hydraulic conductivity (low-K) unit (the St. Marys Formation) that acts as a regional confining layer (Andres and Klingbeil, 2006). The maximum elevation within the watershed is 16.5 m along the western boundary. Bay depth is typically less than 3 m except at Indian River Inlet, the only inlet between this estuary and the ocean, which is scoured to a depth of about 21 m by strong tidal currents. One feature of

particular hydrogeologic interest in the watershed are low-K paleovalley features, which extend offshore of many of the marshes fringing the Inland Bays (Chrzastowski, 1986; Krantz et al., 2004). These organic-rich features act as a cap on the aquifer and have been shown to affect the distribution (Bratton et al., 2004; Russoniello et al., 2013) and chemistry (Böhlke and Krantz, 2003; Sawyer et al., 2014) of groundwater discharging to the Inland Bays.

[Approximate location Figure 1]

The hydrology and ecology of the watershed have been affected by historical conversion of forests to row-crop agriculture and, since the 1960s, seasonal and permanent population growth along the coast and enormous growth of the poultry production and processing industry (DNREC, 2001). These changes have led to ditching and canal building for agricultural drainage and transport, an increase in groundwater pumping for agriculture and residential use, and drastically increased nitrogen and phosphorous loads from septic and agricultural runoff (DNREC, 2008, 1998; U.S. EPA, 2002). The increased nitrogen loading, in particular, has severely increased eutrophication in the nitrogen-limited coastal waters (DNREC, 2001; Luther et al., 2004; Rozan et al., 2002) and led to strict regulations to control nitrogen (DNREC, 2008).

3.   Model development

3.1.   *Model setup*

Steady-state numerical simulations were performed using the finite-difference code MODFLOW (Harbaugh et al., 2000). This model was a simplified representation of the heterogeneous system in which three aquifers were represented by 7 layers ranging in thickness from 1 m to 25 m. The top surface of the model was assigned from a LiDAR-derived digital elevation model (unpublished Delaware Geological Survey data accessed 1/15/2011). Aquifer top and bottom elevations were assigned based on a three-dimensional stratigraphic model of the area (Andres and Klingbeil, 2006) with the model base coincident with the top of the St. Marys Formation. The numerical model contains 240,695 active cells in 7 layers, 233 columns, and 201 rows. Cells are 152.4 m on each side. A head-contour map of historical groundwater levels in the deep aquifers (DGS, 2011) and simulated hydraulic heads from the surface and lowest layers of a groundwater flow model of the entire Delmarva Peninsula (Sanford et al., 2012; Ward Sanford, personal communication 4/1/2011) were used to delineate groundwater flow divides. These were generally coincident with the surface watershed boundary (McKenna et al., 2007). This boundary

was taken as the model domain boundary, but extended to include Little Assawoman Bay to reduce boundary effects in this low-relief region (Fig. 1).

Flow boundaries were defined using MODFLOW packages. Recharge was applied to terrestrial cells in the top model layer. Spatially-variable recharge rates were based on a U.S. Geological Survey model of the Delmarva Peninsula (Sanford et al., 2012; Ward Sanford, personal communication 3/17/2011) and adjusted during calibration (see Section 3.3; Fig. S1). An equivalent freshwater head was assigned to bay and ocean cells using bathymetric data to account for the greater density of saline surface water (1025 kg/m^3) than fresh groundwater. This causes fresh discharge to occur close to shore as it would in a variable density model. Although this approach simplifies density effects on the flow system, we considered it to be an acceptable approximation considering our focus on watershed-scale fresh groundwater, the large computational cost associated with including density-dependent coupled flow and transport, and the uncertainty in hydraulic properties and boundary conditions. This simplification is consistent with prior work (Mack, 2008; Motz et al., 2009; Schubert, 1999). Although Little Assawoman Bay and the Atlantic Ocean are assigned as constant-head boundaries, only fluxes into areas representing Indian River and Rehoboth Bay were included when calculating discharge to bays.

Natural and manmade stream boundaries were represented using the stream flow routing package (SFR2) (Niswonger and Prudic, 2005) with vertical conductance calculated from the vertical K component (Kv) of the top model layer. Stream locations and lengths were assigned from the preexisting hydrography data (USGS, 2010) and stream segment elevations were extracted from a 2 m digital elevation model (unpublished Delaware Geological Survey data accessed 1/15/2011). The model was insensitive to the streambed conductance term, which includes the hydraulic conductivity and thickness of the streambed, channel width, and channel length in the model cell. A drain function (DRN package) was applied to all terrestrial cells to remove excess ponded water. This is consistent with the existence of manmade ditches in areas throughout the watershed. Except for simulations with raised water-table elevations (low-K or high-recharge cases), water only exited through drain cells located in stream valleys. Groundwater discharge to streams was calculated as the sum of modeled discharge to stream and drain boundaries.

Pumping well locations (accessed from Delaware Geological Survey WatSys Database 10/11/10) and an extract of the water-use database used by the Delaware Department of Natural

Resources (William Cocke, personal communication 2007) were used to establish estimates of pumping rates for industrial, public and irrigation wells. Wells were represented with the MNW2 package (Konikow et al., 2009). Records of the location, screen depth, and purpose of wells are largely complete in this study area, but water use records are incomplete because of minimal compliance with reporting requirements. To estimate pumping rates in wells with missing data, wells were grouped by size and purpose (industrial, public, or non-irrigation agricultural). An average pumping rate was calculated for each of these groups and assigned to all wells matching those criteria in the model. Irrigation water use was from an aerial-imagery-derived irrigated area dataset (James Adkins, personal communication 1/14/2011) and the average expected irrigation rate. This irrigation rate was calculated as the monthly deficit between average monthly precipitation (NOAA, 2010) and crop water requirements (3.6-25.2 cm/month) over the growing season (May to September; Ritter et al., 1985; Williams and Ritter, 1987) for corn and soybeans, the dominant irrigated crops in the study area (USDA, 2009). The calculated volume of water for each irrigated field was assigned to the nearest irrigation well. In all, 968 pumping wells were included in the model, pumping at an average combined rate of 0.91 m^3/s, equivalent to 14.5% of the total post-calibration recharge.

An analysis of the sensitivity of the flow system to hydraulic conductivity and recharge was conducted following model calibration (see Section 3.3). Horizontal and vertical K values (Kh and Kv, respectively) and recharge were each varied over two orders of magnitude. The K ranges are representative of coastal aquifers and the recharge range is representative of variations in climate, land cover, and seasonal variability in this and other watersheds (Johnston, 1973).

3.2. Transit time estimation

The flow paths and transit times of discharging groundwater were determined with particle tracking. Particles were tracked in reverse from each cell with groundwater discharge to a stream or bay (*discharge cells*) to terrestrial cells with recharge using MODPATH (Pollock, 2012). Each discharge cell was assigned a velocity-weighted average transit time calculated as the average transit time of each particle discharging to that cell (time between recharge and discharge), weighted by the velocity of that particle (particle path length ÷ particle transit time). To calculate an overall mean transit time for each simulation, the velocity-weighted average transit time of each discharge cell was then weighted by the amount of discharge from that cell,

yielding a domain-wide flux-and-velocity-weighted mean transit time. Hereafter, all transit times discussed are flux-and-velocity weighted unless otherwise specified.

Estimates of groundwater transit times were sensitive to the number of particles reverse-tracked from each cell and converged to a stable value when at least 125 particles were tracked from each cell. This is a much larger number of particles than is typically used in similar studies. There are few published effective porosity values for Atlantic Coastal Plain sediments. We therefore assigned a uniform value of 25%, which is within the range of values measured and assigned in other studies of Atlantic Coastal Plain unconfined sediments (25-30%; Achmad and Bolton, 2012; He and Andres, 2015; Spayd and Johnson, 2003). Because advective transit times scale inversely with porosity, errors in this estimate are reflected directly in calculated transit times. Please see Appendix A for additional information about particle tracking and transit time estimation.

3.3. Model calibration

A *Reference* model was calibrated to groundwater levels and measured baseflow in streams. Historical groundwater hydraulic head data was filtered to included only wells with more than 4 observations (n = 326 wells; Fig. S2). These time series were averaged for each well and each well was assigned a weight based on the number of observations, the number of years of record, and the proximity to other wells (weighting values ranged from 0.35 to 0.99). Baseflow values for 11 streams in the watershed were obtained from Ullman et al. (2002).

Calibration was performed by manually adjusting Kh, Kv, and recharge to reduce the residuals between simulated and observed hydraulic head in wells and the groundwater component of streamflow at gages. In initial calibration efforts, K values were adjusted within the 4 geologic units to match well head values. These manual and automated (Hill et al., 2000) calibration attempts failed to increase the goodness of fit relative to a homogeneous model when applying K values that were reasonable considering field measurements and geologic interpretations of the area (e.g. Andres and Klingbeil, 2006; Johnston, 1973). Therefore, in the interest of parsimony, a homogeneous model in which layering in these aquifers was represented as vertical anisotropy in K (Kh and Kv values = $2.2x10^{-4}$ m/s and $2.2x10^{-5}$ m/s, respectively) was applied to the Reference model. The homogeneous representation of hydraulic conductivity in the model may allow it to reproduce mean flow behavior but likely underrepresents variability (e.g. Cardenas et al., 2004). Because the primary goal of the study is to improve understanding of

broad system controls, a simple homogeneous model was used to avoid unnecessary complication in interpreting results.

The calibrated Kh value falls near the middle of the range of previously measured (Kasper et al., 2010; Johnston, 1973) and modeled (Achmad and Bolton, 2012; He and Andres, 2015; Sanford et al., 2012) K values ($8.8x10^{-5}$ to $4.2x10^{-4}$ m/s) of these aquifers in this and nearby watersheds. It also matches well with the mean value of 171 surficial aquifer wells ($2.2x10^{-4}$; accessed from Delaware Geological Survey WatSys Database 10/11/10). Assigning different K values to the individual geologic layers did not yield a better match between modeled and observed head and baseflow values.

The average calibrated recharge applied to the Reference model was 34.7 cm/yr (range = 18.9-41.0 cm/yr; Fig. S1), which is consistent with a water-budget-based recharge estimate for another Delmarva location of 33 cm/yr (Johnston, 1976). Sanford et al. (2012) prescribed drain boundaries at root depths associated with different land uses (0.6-1.8 m below land surface), whereas we prescribed drains at the land surface in the current study. They considered the additional water removed by prescribing drains below land surface to be evapotranspiration (*ET*), so the recharge they applied included this ET component. The current study applied a net recharge value that excluded the ET component, so the reduction to 75% of the value applied by Sanford et al. (2012) is reasonable. Average recharge applied to the calibrated Reference model is 43% of the 113 cm/yr mean annual precipitation recorded at the nearest NOAA rain gage (NOAA, 2010). This recharge value is within the range of those calculated for nearby Delmarva watersheds with water budget (36-40%; Johnston, 1976) and water-table fluctuation (52%; Rasmussen and Andreasen, 1959) methods. For the Reference model the sum of squares of weighted residuals for the 326 observation wells was 62.8 m^2 and the sum of squares of residuals for the 11 gaging stations was 0.027 (m^3/s). Please see Appendix A for additional information about Reference model calibration.

4. Field sampling methods

4.1. Nutrient sampling

SGD-borne nitrogen loads were calculated as the product of the quantity of fresh SGD and measured nitrogen concentrations. Nutrient measurements at Holts Landing State Park indicate that nitrate in fresh groundwater discharging beneath and around carbon-rich paleovalley cap features is removed prior to discharge, whereas nitrate concentrations in

groundwater discharging in the nearshore areas of sandy interfluves are elevated (Bratton et al., 2004; Fernandez, 2012; Sawyer et al., 2014). Groundwater discharge rates are also low in the paleovalleys and much higher and *focused* in the sandy interfluves (Russoniello et al., 2013; Sawyer et al., 2014). This pattern, where nitrate concentrations are elevated in areas of focused discharge, has also been observed elsewhere (Durand, 2014). Thus, while both SGD (Michael et al., 2003; Stieglitz et al., 2008) and groundwater nitrogen concentrations (Kroeger and Charette, 2008; Young et al., 2015) are spatially heterogeneous, we characterize the watershed nitrogen budget using groundwater samples collected in interfluve locations where much of the SGD occurs. Measured nitrate concentrations are spatially variable, but we did not discern any geographic trend to this variability among our distributed samples, so a single mean concentration was multiplied by modeled flux to bays to calculate N-loads.

Porewater samples were collected at 104 locations within the watershed between August 2011 and April 2013 to measure nitrogen concentrations in fresh groundwater discharge to the bay. Sampling was restricted to the Indian River Bay where surface water nitrogen concentrations are larger and pose a greater threat to ecosystem health than in Rehoboth Bay (DNREC, 1998). *Distributed* (n = 17) samples were collected with drive-point piezometers from sandy, interfluve bayfloor sediments to characterize bay-scale variability of nitrogen concentrations in areas of focused fresh SGD. Fresh or nearly fresh groundwater samples were collected as close as possible to the point of discharge to minimize errors resulting from nutrient transformations along flowpaths and mixing with saline surface water. Samples were collected within several meters of the shoreline and in sandy, permeable sediments at depths of 1-4 m (median 1.4 m) to avoid the influence of muddy, organic rich sediments that are more typical of areas with diffuse discharge. Additional groundwater samples were collected in an intensive study area at Holts Landing State Park (Fig. 1) where a paleovalley and interfluve were previously mapped in detail (Russoniello et al., 2013). *Paleovalley* samples were collected from the aquifer beneath low-K paleovalley-fill sediments (n = 53), and 'interfluve' samples were collected from high-K interfluve sediments (n = 34). The site-scale sampling was done for two reasons important to calculating a bay-wide nutrient load. First, to characterize smaller-scale variability of nitrogen concentrations in fresh groundwater discharge. Second, to confirm observations made at this (Russoniello et al., 2013; Sawyer et al., 2014) and other (Durand, 2014) sites that TDN and nitrate concentrations and associated fluxes are larger in sandy

sediments than in the neighboring paleovalley where the low-K cap inhibits focused groundwater discharge.

Porewater samples were drawn with a peristaltic pump and field parameters were measured with a multiparameter sonde inserted into a flow-through cell (YSI-professional plus) following equilibration. Measured parameters included specific conductance, dissolved oxygen (DO), oxidation reduction potential (ORP), pH, and temperature. Dissolved nitrogen samples were filtered (0.2 or 0.45 µm) and chilled (4 °C) or frozen prior to analysis. Ammonium and nitrate + nitrite (here referred to as *nitrate*) concentrations were analyzed colorimetrically using the phenol-hypochlorite and cadmium reduction methods, respectively, on a Westco Smartchem 200 discrete sample autoanalyzer. Many of the groundwater samples contained large concentrations of dissolved iron. To reduce interference due to iron in nitrate analysis, EDTA in the buffer reagent was replaced with diethylenetriaminepentaacetic acid (DTPA) (Colman, 2010). Total dissolved nitrogen (TDN) concentrations were measured using high temperature catalytic oxidation and chemiluminescent detection of NO_x gas on an O/I Analytical 1030 TIC/TOC analyzer with TN module. Dissolved inorganic nitrogen (DIN) was calculated as nitrate + ammonium. Dissolved organic nitrogen (DON) was calculated as TDN – DIN. Negative DON values are not reported. For 10 of the 104 samples in which DIN exceeded TDN, DIN was substituted for TDN in calculations of TDN statistics

4.2. *Seepage meter measurements*

We compared our modeled fresh discharge to seepage meter measurements of fresh flux collected previously at Holts Landing State Park (Russoniello et al., 2013) and during this study (n=46) at the Bullseye Farm Site (Fig. 1). Please see Russoniello et al. (2013) for a thorough description of seepage meter measurement methods.

5. Results

5.1. *Reference model results*

The simulated water table in the Reference model averaged 2.29 m below land surface and was a muted expression of the surface topography (Fig. 2A) that cropped out at streams and other bodies of surface water. Simulated groundwater velocities were greater in the western half of the model where higher topographic relief supports higher hydraulic gradients (Fig. S3). Nearer the Atlantic coastline, where topographic relief is less, hydraulic gradients and groundwater flow velocities were smaller. Modeled groundwater discharge to the bays matches

well with seepage meter measurements of fresh flux at two field sites (Fig. 1) despite large differences in support scale between the model and measurements. At Holts Landing State Park modeled discharge (range = 1.1-1.6 cm/d across four cells) encompasses the average measured flux (mean =1.4 cm/d, n=299; Russoniello et al., 2013). Similarly, modeled discharge at the Bullseye Farm Site (range = 3.6-4.5 cm/d across three cells) is close to the measured fresh flux (mean = 5.3 cm/d, n=46; Table S1).

[Approximate location Figure 2]

Groundwater discharge to stream and bay cells in the Reference model accounted for 65.7% and 34.3% of groundwater discharge, respectively, and was spatially heterogeneous (Fig. 2B, C). Discharge through drains, 3.2% of groundwater discharge, is included within calculated groundwater discharge to streams. In total, groundwater discharged along 63.0% of the streambed length in the Reference model. Dry stream reaches were generally upland reaches (stream reaches further from the bay) because they are more likely to be above the water table where they cannot receive discharge from the aquifer, whereas lowland reaches (stream reaches nearer the bay) were more likely to receive groundwater discharge. Reaches with zero flux (shown in black in Fig. 2B) may recharge the aquifer during times when they receive overland runoff, or may capture discharge during periods of maximum water-table elevation, but this was not resolved in this steady-state model that was designed to capture average behavior. Most groundwater discharge to bays occurred along shorelines far inland from the ocean where neighboring topographic (and hydraulic) gradients were greatest (Fig. 2C) in agreement with previous work (Andres, 1987). The Indian River Bay and Rehoboth Bay sub-watersheds account for 77.9% and 22.1% of groundwater discharge to both streams and bays, respectively.

Simulated transit times of groundwater discharge to streams and bays in the Inland Bays Watershed varied spatially over a wide range (Figs. 2D, 3). Mean transit times and flow path lengths were shorter and varied less for groundwater discharge to streams than for groundwater discharge to bays. Mean transit times of all groundwater discharge, discharge to streams, and discharge to bays were 69.5 years, 56.5 years, and 94.3 years, respectively. Tenth to 90th percentile ranges were 14.3 to 106.0 years for stream discharge and 29.3 to 172.8 years for SGD. Velocity-weighted transit times of groundwater discharging to streams generally increased in a downstream direction (Fig. 2D).

[Approximate location Figure 3]

5.2. Model sensitivity analysis

The relative amounts of groundwater discharge to streams and bays were sensitive to the elevation of the water table. The water-table elevation increased in response to both lower K values and higher recharge rates, which resulted in an increase to the proportion of groundwater discharging to streams (Fig. 4A). This increase was due to an increase in the length of streambed intersected by the water table (Figs. 4B, S4), which increased the area through which groundwater discharges from the aquifer into stream channels. Kh had the greatest impact on the distribution between groundwater discharge to streams and bays, followed by recharge and Kv (Fig. 4A). The effect of changes in Kh on the length of streambed with discharge were similar in effect, but of much greater magnitude than that of Kv (Fig. 4B). Across the range of tested parameter values, groundwater discharge to bays varied between 9.2% and 81.6% of groundwater discharge. The model was relatively insensitive to streambed conductance values. Groundwater discharge to bays varied by just 5.2% (range = 38.6-33.4%) as conductance was varied over a range of one-tenth to five times the Reference value. This insensitivity is likely because groundwater discharge to streams is calculated as the combined flux through both stream and drain boundaries. A reduction to streambed conductance results in a decreased flux to stream boundaries that is nearly equivalent to the increased flux to drain boundaries.

[Approximate location Figure 4]

Groundwater transit time was most sensitive to recharge rate. Increased recharge rates raised the water table, increased the hydraulic gradient, and decreased mean transit times (Fig. 4C, D). Groundwater velocities were greater throughout the aquifer and flow paths were shorter (Fig. S6A, B), because the water recharging upland areas, which originally followed long flowpaths to the bay, discharged instead to upland streams closer to recharge areas (Figs. S4, S5). Mean groundwater transit times were less sensitive to changes in Kh and Kv. As Kh increased, flow paths lengthened and velocities increased (Fig. S6E, F) resulting in greater groundwater transit times (Fig. 4C, D). The net result of increased Kv was shorter flow paths and greater groundwater velocities for paths discharging to bays (Fig. S6A, E), and lengthened flow paths and reduced groundwater velocities for paths discharging to streams (Figs. 4C, D; S6B, F).

5.3. Nutrient measurements

Concentrations of nitrogen species were similar in high-K interfluve sediments and in the baywide distributed samples, but both of these datasets were distinct from the paleovalley

samples. Average ammonium concentrations in interfluve (32.1 µM) and distributed (3.4 µM) samples were both relatively small, while average paleovalley sample concentrations were much greater (89.8 µM). The average nitrate concentration of interfluve samples (198.4 µM) was only slightly larger than that of distributed samples (163.2 µM) (Table 1, Fig. S7). Both were an order of magnitude greater than in paleovalley samples (21.9 µM). Nitrogen as nitrate comprised the majority of TDN, so TDN concentrations were larger in the distributed and interfluve samples than in paleovalley samples. Nutrient analyses are summarized in Table 1 and Fig. 5 and the complete dataset is presented in Table S2.

[Approximate location Table 1 and Figure 5]

Average annual TDN and nitrate fluxes to the Inland Bays were estimated as the product of the rate of fresh discharge to the bays (estimated with the Reference model) and mean measured nitrogen concentration in discharging groundwater (Table 1). All distributed samples except two had salinities below 2 practical salinity units (PSU) (mean = 1.01 PSU; median = 0.45 PSU). The resulting annual nitrate load of 1.1×10^5 kg/yr is in agreement with the range of 9.81×10^4 to 1.98×10^5 kg/yr calculated by combining a simple watershed water budget and fluxes based on a flow net with measurements of nitrate concentrations in well water at wells distributed throughout the watershed (Andres, 1992). Nitrate accounts for the majority of TDN, so TDN loads (1.3×10^5 kg/yr) are only slightly larger than nitrate loads (Table 1). While ammonium was also measured in this study, a bay-wide flux was not calculated because much of the ammonium load likely comes from decomposition of organic matter and saltwater exchange within sub-bayfloor sediments rather than fresh groundwater discharge (Sawyer et al., 2014).

6.   Discussion

6.1.   Geometric controls on groundwater discharge

Differences between the Rehoboth and Indian River Bay Watersheds illustrate the influence of watershed size and character on groundwater flow and discharge. The watershed of the Indian River Bay has a greater length of streams than that of the Rehoboth Bay watershed (264 and 51 km, respectively), a higher stream density (stream length to watershed area = 0.34 and 0.66 km/km^2, respectively), and a bay that covers less of the overall watershed area (10% and 20%, respectively; McKenna et al., 2007). As a result, groundwater discharge to streams in the IRB watershed (70.7% of groundwater discharge) is greater than that to the bay, whereas in the Rehoboth Bay Watershed groundwater discharge is more evenly divided between streams

(52.6% of groundwater discharge) and the bay. Mean transit times of discharge in the Indian River Bay Watershed are slightly longer than those in the Rehoboth Bay Watershed: 58.3 and 50.8 years for discharge to streams and 97.8 and 88.8 years for discharge to the bays, for the respective sub-watersheds. This likely reflects the larger size and longer flow path lengths of the Indian River Bay Watershed.

6.2.   *Effects of model boundary definition*

The manner in which boundaries are defined and treated can have significant impacts on the description of groundwater fluxes. The distinction between bay and river is not clear in most systems, so results are sensitive to where this break is placed. The amount of discharge to the upper *streamlike* reaches of the Inland Bays, which we define as areas where the bay boundary is consistently one cell in width, includes 58.7% of all groundwater discharge to bays. If these narrow bay areas were instead considered as streams, only 14.7% of groundwater discharge would directly enter the bays. Thus, slight changes in model boundaries, discretization, and rules by which stream and bay boundaries are defined can have large effects on the model-calculated rates of, and the balance between, groundwater discharge to bays and streams.

The definition of water budget components and nearshore boundary conditions also affect relative discharge rate calculations. A regional modeling study by Sanford et al. (2012) that includes the Inland Bays Watershed found that just 1% of recharge discharged directly to coastal waters, much less than estimated in this study. The discrepancy may be due to the inclusion of evapotranspiration in the total recharge rate in Sanford et al. (2012). Drains (prescribed 0.6-1.8 m below land surface in all terrestrial model cells) were used to simulate and to remove the evapotranspiration component of recharge. Along the coastline, these subsurface drains were prescribed below sea level and likely intercepted groundwater flow. This likely removed water just landward of surface water bodies, resulting in less calculated discharge to coastal waters. Because understanding groundwater discharge to coastal waters was our primary objective, we represented the bays and streams explicitly in our model. Thus, the two studies give different, but not inconsistent, results.

The steady-state model used in this analysis yields a time-averaged estimate of the distribution of groundwater discharge to streams and bays, but does not account for effects of temporally-variable boundaries. While short timescale perturbations (e.g. tides) would likely have little effect, longer timescale transience, such as seasonal and annual recharge variations,

could potentially cause variations to flowpaths and transit times. A water-budget analysis of long-term temperature and climate data (NOAA, 2010) generated with the Thornthwaite Monthly Water Balance Program (McCabe and Markstrom, 2007) indicates that monthly potential recharge rates (precipitation less ET) vary between 0 and twice the annual average. The modeling sensitivity analysis showed that doubling total recharge has a large effect on groundwater flow paths, transit times, and discharge locations (Figs. 4, S4, S5). Thus, it follows that rates and spatial distributions of groundwater discharge vary seasonally as has been observed previously (Michael et al., 2005; Robinson et al., 1998). Overland runoff and rainfall to riparian zones during storm events are also important components of aquifer recharge, which are at temporal scales inherently neglected in a steady-state model, resulting in reaches of streambed that are simulated as dry (Fig. 2B), despite flowing intermittently. The range of recharge values applied in the sensitivity analysis likely brackets such variability of groundwater flow and discharge at the storm-event and seasonal timescales – at least at the spatial scale of this model. Hydrologic fluctuations at seasonal and storm scales likely also impact the transit time of groundwater along short flow paths, though these effects are averaged out over long timescales. Similarly, interannual or decadal climatic changes should be expected to affect flow and transit times along all flow paths.

6.3.   *Nitrogen flux estimate uncertainty*

There are many sources of uncertainty in the nutrient term of the load estimate. First, geochemical transformations along flowpaths can alter solute concentrations prior to discharge (Charette, 2007; Modica et al., 1998; Sawyer et al., 2014). Sawyer et al. (2014) demonstrated that nitrogen attenuation is limited along flowpaths in zones of focused fresh discharge where the majority of fresh groundwater discharges to the Inland Bays (Russoniello et al., 2013). Thus, we sampled porewater chemistry in interfluve sediments, which were presumably areas of focused fresh discharge. We also sampled at the shallowest depth where fresh porewater could be collected at the coastline in order to minimize the potential for transformation between the points of sampling and discharge. Another source of uncertainty is considerable variation of the concentrations of nitrogen species in both bay-scale and site-scale datasets, as evidenced by standard deviations exceeding the mean value of distributed nitrogen species concentrations (Table 1). A larger distributed dataset could reduce the uncertainty associated with final nitrogen

load estimates. However, agreement with earlier estimates (Andres, 1992) increases confidence in the calculated value.

The nitrate flux estimate presented here may be considered an upper bound on the nitrate flux associated with the discharge of fresh, terrestrial groundwater directly to the bays due to differences in discharge between interfluves and paleovalleys. The assumption that the entirety of fresh groundwater discharges to the bays through interfluves is inherent to this estimate because distributed samples were collected only at interfluve locations. Because nitrate concentrations in paleovalley samples are lower than in interfluve samples (Table 1; Fig. S7), we are overestimating that portion of the load, which propagates through to load estimates. However, we believe that this overestimation is small because diffuse discharge rates around paleovalleys are much lower than in interfluves: average measured fresh SGD rates were 3.8 cm/d in interfluve locations compared to 0.1 cm/d around paleovalleys (Russoniello et al., 2013).

6.4. *Implications for management*

Groundwater-borne TDN loads are a large fraction of the total TDN load reaching the bay from all sources. A recent regulatory effort established a baseline estimate of the total TDN load (sum of TDN from point discharge, combined contributions from surface and ground water, and atmospheric deposition) to the Inland Bays (DNREC, 2008) based on field observations collected between 1998 and 2000 (Ullman et al., 2002). This regulatory effort also established a new statute for allowable maximum TDN load (4.54×10^5 kg/yr), which was about one-half of the baseline value. Our modeled TDN load associated with groundwater discharge to the bays is 13% of the measured baseline value and 29% of the allowable value established by the regulatory effort.

The estimated TDN load associated with SGD for this 550 km^2 watershed is consistent with loads established for other watersheds. The watershed-area-normalized groundwater-borne TDN load of 1.68×10^4 mol/yr/km^2 to the Inland Bays is consistent with loads previously calculated for Tampa Bay, FL (1.1×10^4 to 2.7×10^4 mol/yr/km^2) (Kroeger et al., 2007) and bays on Cape Cod, MA (1.3×10^4 to 1.2×10^5 mol/yr/km^2) (Kroeger et al., 2006). The water budget approach used for the Cape Cod sites resulted in an estimate of total freshwater discharge from the watersheds, so to directly compare our results would require addition of stream TDN loads to our groundwater TDN estimates. Thus, it is no surprise that our estimate lies within, but at the low end of the range of estimated Cape Cod TDN loads.

The modeled range of groundwater transit times implies that the beneficial results of management efforts will not be fully felt for decades following implementation. Although nutrient management efforts and new TDN limits have been enacted during the past several decades (DNREC, 2008; IBEP, 1995), the long transit times reported here suggest that the Inland Bays will continue to receive large inputs of nitrogen applied prior to management efforts of the last several decades. Comparison with a previous study of stream baseflow nitrogen concentrations in this watershed shows that statistical aggregates of groundwater discharge to streams and bays are similar (Ullman et al., 2002), so both groundwater pathways carry large nitrogen loads. Furthermore, groundwater discharge to streams and bays is about three times that of surface runoff (Johnston, 1976), so groundwater accounts for the majority of total water and nutrient budgets. While groundwater mean transit times are long, a large portion of groundwater is much younger (Fig. 3), so reductions to terrestrial application will have a more immediate impact on nutrient loads than suggested by mean transit times alone. Nevertheless, nutrient load reductions that lag behind reductions in application rates should be expected for management efforts in this and other similar watersheds, consistent with previous work. This lag is of concern in this watershed as we estimate groundwater-borne TDN loads are responsible for a large portion (29%) of maximum total TDN load allowed from all sources.

7. Conclusions

This analysis employed numerical models to estimate rates and transit times of groundwater discharging to bays and streams, examined the sensitivity of these measurements to hydrogeologic characteristics, and combined groundwater flux with field nutrient measurements to estimate nutrient loads carried by groundwater to the bays. Results indicate that in this coastal estuarine watershed, groundwater discharge to streams is about twice that to the bays, accounting for 65.7% and 34.3% of groundwater discharge from the watershed, respectively. Mean groundwater transit times are shorter for groundwater discharge to streams (56.5 years) than to bays (94.3 years). The sensitivity analysis showed a link between the elevation of the water table and the relative distribution of groundwater discharge to streams and bays. Increases to the water table elevation (higher recharge, lower K) cause increased discharge to streams relative to bays because the water table intersects longer lengths of streambed. Dry streambeds do not receive groundwater discharge, so the water table elevation also affects the distance between groundwater recharge and discharge locations and thus transit times of discharge to streams and

bays. Mean transit times are most sensitive to recharge because higher recharge both increases groundwater flow velocities and shortens flow paths.

Field measurements of nutrient concentrations in fresh groundwater discharge to bays combined with modeled discharge rates yield a groundwater-borne TDN load directly to the Inland Bays of 1.3×10^5 kg/yr, which is 29% of the total permitted TDN load of this watershed. This load combined with long transit times of groundwater discharging to the bays indicates that watershed management decisions will not be fully felt within this watershed for decades. Furthermore, the consistency of our area-normalized TDN loads with those of other watersheds underscores the widespread nature of this problem. The delay between terrestrial application of solutes and discharge to these coastal waters highlights the importance of making timely management decisions when considering contaminants that are likely to enter groundwater. The demonstrated sensitivity of groundwater discharge and transit times combined with large TDN loads prevalent in many coastal systems highlight the importance of characterizing the groundwater system to effectively manage coastal watersheds. However, the groundwater transit time distributions indicate the need for patience and a long-term perspective in measuring full benefits of management actions.

Supplementary Material

Supplementary text, figures, and tables of data associated with this article can be found in the online version, in appendices A, B, and C, respectively, at doi:10.1016/j.jhydrol.xxxx.xx.xxx

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Table 1: Measured nutrient concentrations and calculated nitrogen (N) fluxes to the Inland Bays. Nitrogen species include mean nitrate (NO_3^-), ammonium (NH_4^+), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), and total dissolved nitrogen (TDN). Both distributed samples and samples collected at Holts Landing State Park (HLSP) are reported. Coefficients of variation (CV) are calculated by dividing standard deviation (stdev) by the mean. Loads of NO_3 and TDN were calculated as the product of discharge to bays in the reference model and the mean concentration of that nitrogen species.

			NO_3^-	NH_4^+	DIN	DON	TDN
Distributed	Concentration (µM)	Count	17	17	17	13	17
		Min	0.00	0.00	1.63	5.30	13.01
		Max	574.3	18.86	575.4	53.37	574.3
		Mean	134.6	3.58	138.2	23.42	155.3
		Median	61.42	1.35	62.64	17.10	79.74
		Stdev	198.8	5.40	198.1	14.05	187.2
		CV	1.48	1.51	1.43	0.60	1.21
Interfluve HLSP	Concentration (µM)	Count	34	34	34	27	34
		Min	0.00	0.00	14.78	1.37	38.25
		Max	749.9	498.2	749.9	253.3	753.1
		Mean	198.4	32.15	230.6	53.52	272.4
		Median	153.8	0.07	159.5	29.26	220.9
		Stdev	203.1	88.85	190.3	69.97	202.1
		CV	1.02	2.76	0.83	1.31	0.74
Paleovalley HLSP	Concentration (µM)	Count	53	53	53	47	53
		Min	0.00	0.00	0.25	2.83	5.02
		Max	86.00	938.4	939.0	318.2	1169
		Mean	21.89	89.78	111.7	35.37	139.6
		Median	2.40	9.08	62.60	16.32	69.90
		Stdev	30.10	184.1	176.0	55.8	191.5
		CV	1.38	2.05	1.58	1.58	1.37
Estuary N Loads	kg N/yr		1.12E+05	-	-	-	1.30E+05
	mol N/yr		8.02E+06	-	-	-	9.26E+06
	mol N/yr/km^2		1.46E+04	-	-	-	1.68E+04

Figure Captions

Figure 1. Site map of the Delaware Inland Bays. (A) Regional setting. (B) Groundwater model domain and boundary conditions, stream gage locations, and site locations of Holts Landing State Park and Bullseye Farm.

Figure 2. Simulation results for the Reference model. (A) Hydraulic head in the top model layer and location of stream and constant-head boundaries considered in analyses (black). (B) Boundary type and direction of flux in the Reference model. (C) Magnitude of recharge (positive values) and discharge (negative values) for bay and stream boundaries. (D) Velocity-weighted-mean transit time of groundwater discharging to bay and stream boundaries. In panels B and C, black indicates the location of a stream or bay boundary with no flux. In panel D, black cells indicate boundaries where there is no discharge from the aquifer.

Figure 3. Distribution of the transit times of groundwater discharge to streams and bays in the Reference model based on flux-and-velocity-weighted particle tracking. The percentage of flux within each transit time range is plotted as a probability distribution function (PDF) and the percentage of flux younger than a given transit time is plotted as a cumulative distribution function (CDF).

Figure 4: Sensitivity to the value of selected parameters (parameter multiplier is factor relative to that of the Reference model) for (A) groundwater discharge to bays (SGD) as percentage of total groundwater discharge in model, (B) total length of streambed through which groundwater discharges, and transit times of groundwater discharge to (C) bays and (D) streams. Simulation results are not shown where recharge was similar to or greater than pumping rates (recharge parameter multiplier < 0.5).

Figure 5. Locations and measured total dissolved nitrogen (TDN) values for (A) distributed porewater samples, and (B) paleovalley and interfluve samples.
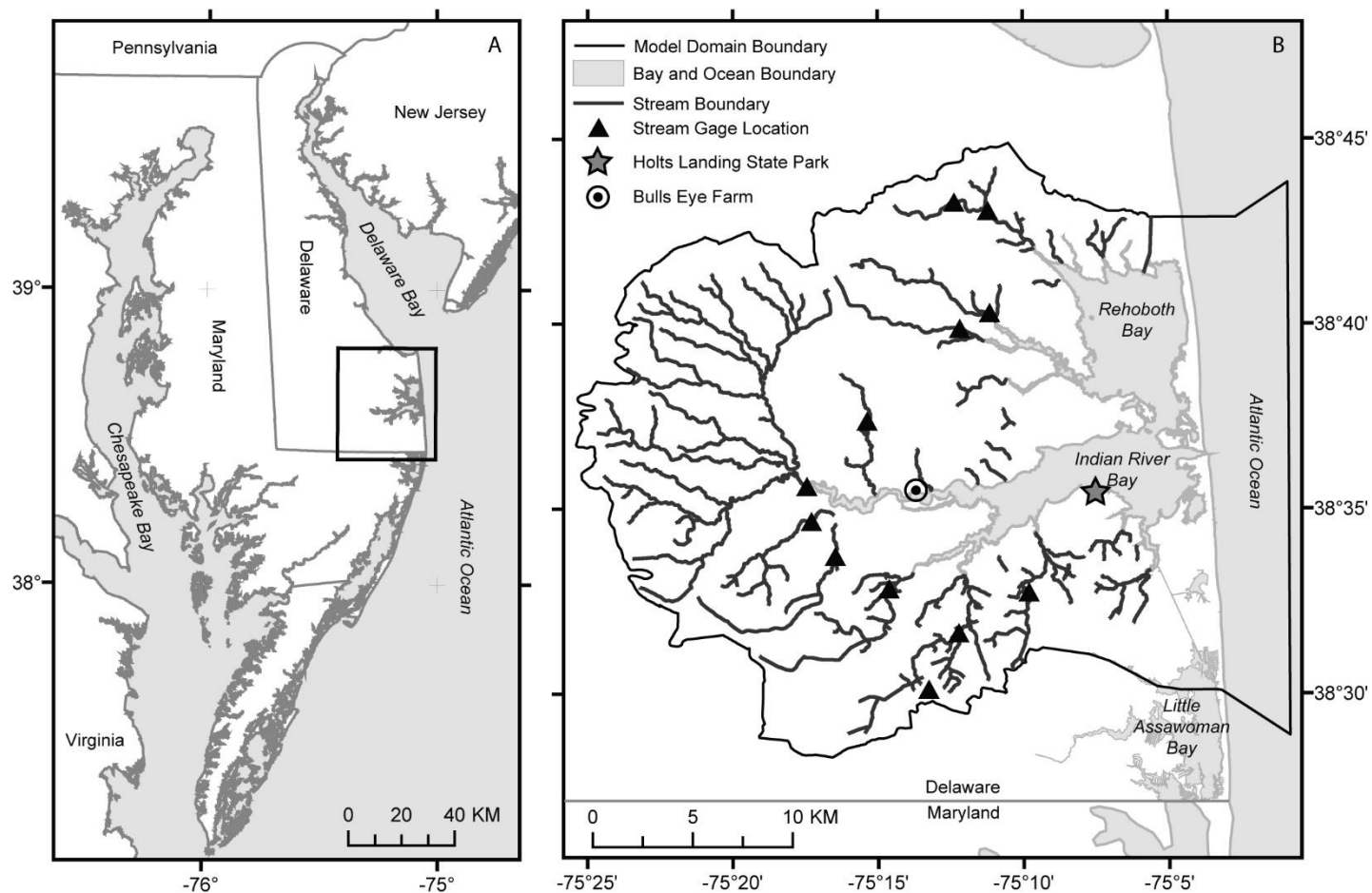
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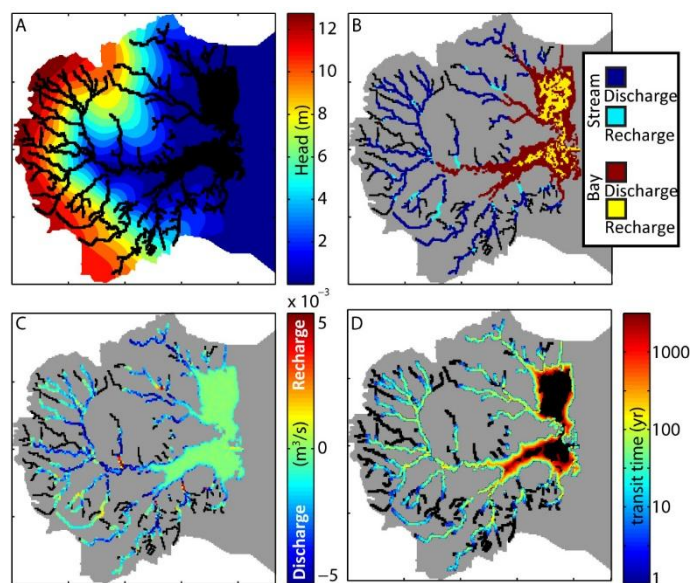
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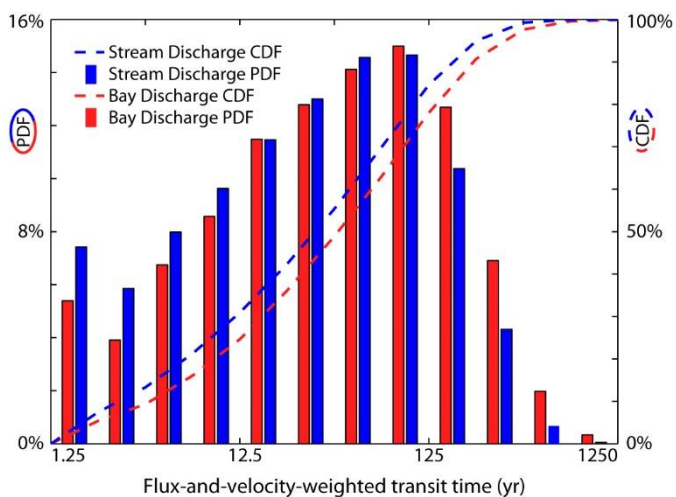
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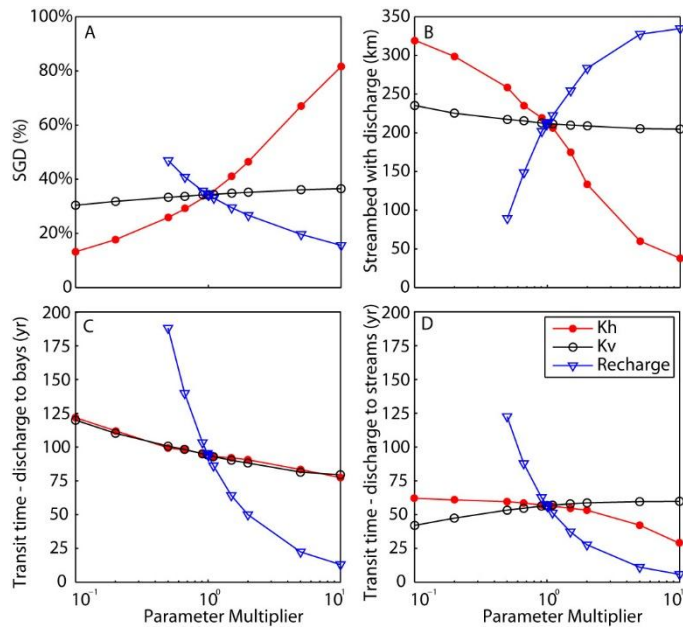
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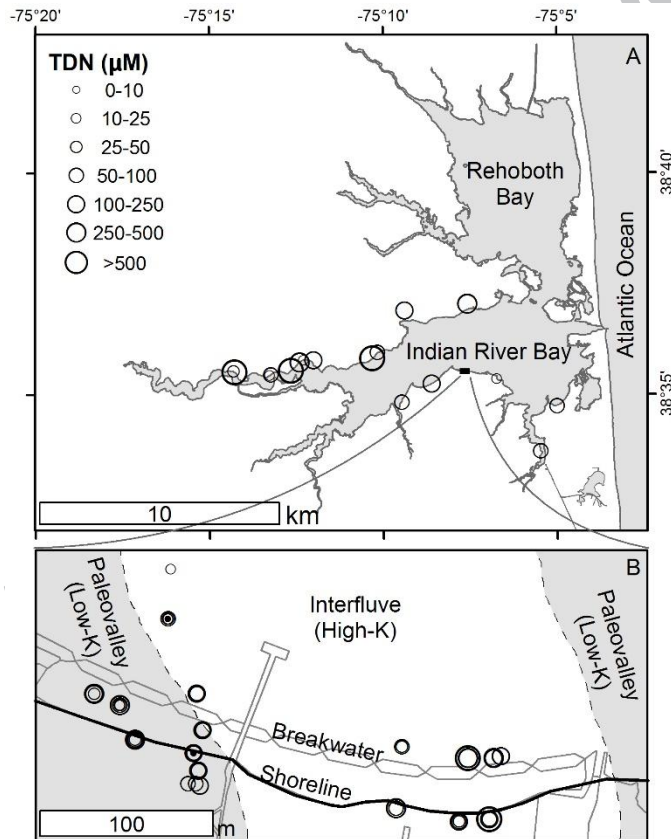

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Highlights

1. Hydrogeologic properties control relative groundwater discharge to streams & bays

2. Transit time more sensitive to recharge than to hydraulic conductivity variations

3. Groundwater discharge to bays carries 13 to 29% of total watershed nitrogen load

4. Long transit times delay arrival and mitigation of large nutrient loads by decades