Collaborative Research: Quantifying Geologic and Temporal Controls on Water and Chemical Exchange between Groundwater and Surface Water in Coastal Estuarine Systems

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I. Scientific Problem

Coastal hydrologic systems are essential to the health of both human communities and nearshore marine ecosystems; aquifers are often the primary source of freshwater to residents, as well as a significant source of nutrients to coastal habitats. Human land and water use have led to problems such as saltwater intrusion and eutrophication of coastal surface waters due to elevated nutrient inputs from septic systems and agricultural activities (Howarth and Marino 2006). Among the most harmful impacts of eutrophication is mortality of clams and fish associated with decreased dissolved oxygen and loss of seagrass habitat as the ecosystem shifts to macroalgal and phytoplankton-dominated productivity (Short et al. 1996, Hauxwell et al. 2003). Direct discharge of fresh and saline groundwater into coastal surface waters, termed submarine groundwater discharge (SGD), is an important pathway for transport of these nutrients (e.g., Johannes, 1980; Moore, 1999; Burnett et al., 2006). Though formerly thought to be small in comparison to riverine inputs, combined fresh and saline SGD fluxes have been estimated to equal 40% or more of river flow in some areas (Moore, 1996). The combination of significant flow rates and high dissolved nutrient concentrations in SGD has led to adverse effects on coastal ecosystems in many areas of the world (e.g., Slomp and Van Cappellen, 2004; Kemp et al., 2005; Fisher et al., 2006).

Fresh groundwater flow to the sea is driven by regional head gradients and recharge, and saltwater circulates due to mechanisms such as tidal pumping and dispersion-induced density gradients. Though theory predicts a narrow zone of primarily fresh discharge near the coastline, studies have shown that discharge patterns can be complex (Michael et al., 2003; Smith and Zawadzki, 2003), and that significantly more saline than freshwater flux occurs in offshore waters (e.g., Taniguchi, et. al., 2002; Michael et al. 2005). Complex groundwater flowpaths imply a complex subsurface salinity distribution, which often results in inverted density gradients and more extensive mixing between fresh and saline water than predicted by theory. The freshwater-saltwater interface (zone of mixing or dispersion) also represents a zone of enhanced geochemical activity and reactions (e.g., Sanford and Konikow, 1989a, 1989b; Rezaei et. al., 2005). Both the flow pattern and salinity distribution in the subsurface are intimately linked to the local and regional geology of the aquifer system because geology controls the porosity and hydraulic conductivity distributions, which in turn affect the rates of flow and salt transport. Temporal forcing also affects flow and salt transport because it alters hydraulic gradients. The complex subsurface dynamics of fresh groundwater discharge, saltwater circulation, and mixing can greatly affect geochemical reactions, contaminant transport in groundwater, and chemical loading to estuaries.

The diffuse and heterogeneous nature of the exchange of water between coastal surface waters and aquifers presents challenges in measuring SGD and associated chemical loading (Burnett et al., 2006). Despite the challenges, our understanding of fluid and chemical fluxes associated with SGD has advanced substantially in the last decade. Investigations of temporal changes in groundwater discharge by direct measurements and modeling (e.g., Linderfelt and Turner, 2001; Michael, et al., 2005; Robinson et al., 2007a; 2007b; Trefry et al., 2007) and the use of geochemical tracers (e.g. Moore, 1997; Kelly and Moran, 2002; Chanton et al., 2003; Dulaiova et al., 2006; Charette, 2007) illustrate the temporal variability in fluid and chemical discharge. In addition to the conservative (nonreactive) changes in chemical loading that are proportional to changes in fluid flux, interaction between groundwater and surface water has been shown to result in geochemical transformations that lead to non-conservative solute transport (e.g., Charette and Sholkovitz, 2002; Spiteri et al., 2006; Beck et al., 2007; Kroeger and Charette, 2008).

A particularly important example of non-conservative behavior of solutes is the case of nitrogen. It has been observed that typically about 75% of the total nitrogen load to watersheds is lost through a variety of processes during transit through the watershed, so that only about 25% of that load actually reaches the land/sea margin (Valiela et al. 1997, Kroeger et al., 2006a). There is a substantial range, however, among estimated losses within different watersheds, from <50% to >90%. Watersheds exhibiting very large natural removal of nitrogen might require less intensive (less costly) management than portions that display relatively little natural remediation. In addition to losses in the freshwater aquifer, there is potential for further nitrogen removal near the point of discharge into the coastal ocean, where fresh and saline groundwater mix (Talbot et al., 2003; Kroeger and Charette, 2008).

Despite recent advances and the potential influence of physical flow processes on nitrogen loss, quantitative synthesis of physical and chemical understanding, including spatial geologic heterogeneity and temporally-variable forcing, at a single site is limited and rare; the detailed controls on subsurface flow patterns and resulting salinity distributions and geochemical transformations are largely unknown. This may be a reflection of the under-participation of hydrogeologists in SGD studies that was recently pointed out by Kazemi (2008). This study seeks to identify the physical processes that control flow and mixing in coastal aquifer systems, determine the relative influences of geology and temporal forcing, and quantify time-varying fluid and chemical fluxes across the aquifer-ocean boundary in a coastal system. This will be accomplished by a large-scale, multi-year field study using state-of-the art geophysical techniques, year-round monitoring, and geochemical analysis, complemented by numerical modeling designed to quantitatively simulate and evaluate physical controls and transient effects, synthesize data, and help estimate spatial and temporal distributions of fluxes.

The study site, Indian River Bay, Delaware (Figure 1) was chosen for several reasons. First, nitrogen loading through SGD was identified as a major contributor to the severe eutrophication problems in Indian River Bay by the Delaware Inland Bays Comprehensive Conservation and Management Plan (Roy F. Weston, Inc., 1994) as a result of work done by PI Andres. Efforts are being made to manage nutrient loading, but it is not well known how much nitrogen is removed in the Indian River Bay watershed by natural biogeochemical processes in groundwater during transit from the source to the shore. Second, several studies conducted from 2000-2004, produced geophysical, geochemical, and geologic data that provide a framework for the proposed investigation. Third, data show that the subsurface salinity distribution is complex, that it is controlled at least in part by geologic heterogeneity, and that both fresh and saline flow systems beneath the bay floor are active (Böhlke and Krantz, 2003; Bratton et al., 2004; Krantz et al., 2004; Manheim et al., 2004). Fourth, a quantitative variable-density hydrodynamic simulation model has never been developed for groundwater in this area. Our proposed development and application of this type of model will provide a means to integrate conceptual models with the various types of existing and new data and evaluate internal consistency among the different models and data sets. Lastly, Indian River Bay typifies estuarine systems throughout the eastern United States and other coastal-plain estuaries around the world that have similar hydrology, geology, and problems of eutrophication induced by human-enhanced nutrient loads and restricted circulation.

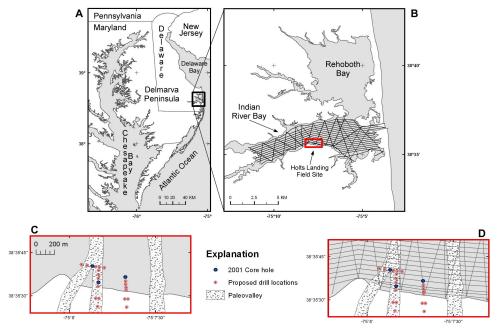


Figure 1. A) Location of Indian River Bay relative to mid-Atlantic states and other water bodies. B) Enlargement of Indian River Bay showing proposed geophysical survey grid and intensive study site at Holts Landing. C) Proposed piezometer sampling sites at Holts Landing and previous sampling sites and paleochannels locations from Krantz et al. (2004). D) Proposed high-resolution geophysical grid for the Holts Landing site.

Conceptual Model

Groundwater discharge into coastal surface waters is driven by physical forcing mechanisms, each of which is associated with a different zone of influence and timescale of fluctuation. Two primary mechanisms of steady forcing (in the sense that they force groundwater flow in the absence of temporal variation, though the forcing may vary in time) drive flow in coastal systems. Freshwater flow to the sea (process 1 in Figure 2A) is driven by upland (on-shore) hydraulic gradients that fluctuate due to changes in recharge and groundwater extraction. Dispersion along the interface between fresh and denser saline groundwater creates a density gradient that drives saltwater circulation (process 2 in Figure 2A; Cooper, 1959; Kohout, 1960). Transient changes also drive saltwater exchange. Seasonal changes in the upland water table drive alternating landward and seaward movement of the freshwater-saltwater interface that forces saltwater exchange (process 3 in Figure 2A; Michael et al., 2005). Tides and waves create two modes of saline exchange: nearshore circulation beneath the beachface caused by run-up and infiltration (process 4 in Figure 2A; Li and Barry, 2000; Michael et al., 2005; Robinson et al., 2007a), and 1D exchange offshore due to pressure changes in the water column (process 5 in Figure 2A; Riedl et al., 1972; Paulsen et al., 2004).

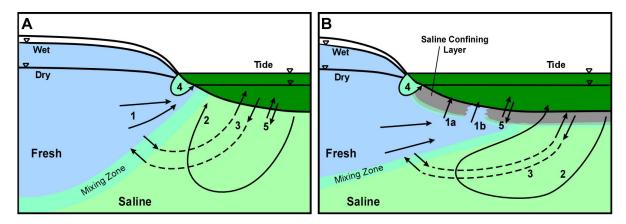


Figure 2. Conceptual model of groundwater-surface water interaction and salinity distribution in coastal aquifers. Process 1 is freshwater flow driven by the hydraulic gradient. Process 2 is dispersion-induced saltwater circulation. Process 3 is seasonal exchange. Process 4 is nearshore circulation due to tides and waves, and process 5 is offshore saline exchange driven by tides and waves. A) Theoretical cross-section with homogeneous hydraulic parameters. B) Hypothetical cross-section with a low-permeability layer at the sea floor. Diffuse and focused fresh discharge modes are depicted as processes 1a and 1b, respectively.

Though models predict a salinity distribution similar to that depicted in Figure 2A for aguifer systems with homogeneous hydraulic properties, measured salinity distributions are often considerably more complex. Onshore and offshore geophysical measurements indicate occurrence of freshened groundwater beneath shallower saline groundwater in a variety of geologic settings; examples are coastal systems in Waquoit Bay, MA (Belaval 2003), the Neuse River Estuary, NC (Cross et al. 2006), Dor Beach, Israel (Swarzenski et al., 2006), Corsica River Estuary, MD (Bratton et al., 2008), and our proposed study site, Indian River Bay, DE (Manheim et al., 2004). This unstable density configuration is likely caused by geologic heterogeneity such as shallow low-permeability confining units that force freshwater to discharge farther offshore (Figure 2B; Bratton, 2007) or paleochannels (Mulligan et al., 2007), and may result in complex hydrodynamically unstable salt fingering phenomena (Simmons et al., 2001). Factors such as temporal hydraulic forcing (processes 3-5 in Figure 2), or long-timescale changes in sea level (disequilibrium) may also produce such salinity distributions. Modes and locations of reducedsalinity SGD that may result are illustrated in Figure 3. The complex subsurface flow patterns, mixing of fresh and saline groundwater, spatial variations in SGD and saline exchange, and modes of low-salinity SGD (diffuse or focused discharge, processes 1a and 1b in Figure 2B; Figure 3) have not been well characterized, quantified, or simulated in 3D with variable-density flow models to date.

More complex submarine groundwater flow patterns, salinity distributions, and mixing zones than predicted by theory will produce more complex water quality variations. For example, nitrate, generally present in shallow fresh groundwater, is transported along flowpaths to the sea. Microbial denitrification

converts nitrate to N₂ as terrestrial groundwater encounters anoxic and organic-rich freshwater along shorelines associated with coastal wetlands, or as fresh groundwater mixes with anoxic saline groundwater containing organic carbon. Thus, mixing between fresh groundwater and saline groundwater can enhance denitrification, thereby reducing the ultimate nitrate load in SGD. Ammonium is generated by degradation of organic matter in seafloor sediments, and may be transported into and out of submarine aquifers by circulating saltwater. Increased circulation of saline submarine groundwater due to a more complex freshwater-saltwater interface (more dispersion-induced circulation) or greater temporal forcing may increase the flux of ammonium to the sea. Both nitrate and ammonium are (often limiting) nutrient sources for marine organisms, such as phytoplankton (Twomey et al., 2005) and macroalgae, the overabundance of which is harmful to coastal ecosystems. Quantification of N loading requires understanding of the full complexity of physical and chemical processes that produce subsurface salinity distributions, flowpaths, and fluxes of fresh and saline water between aquifers and coastal surface waters.



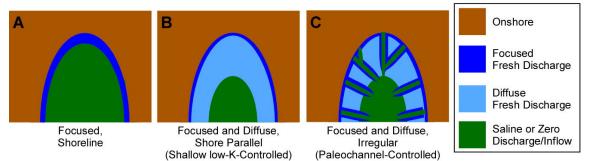


Figure 3. Schematic of low-salinity SGD modes and locations into an idealized bay. A) Focused discharge along the shoreline as predicted by theory. B) Focused nearshore discharge and diffuse offshore discharge parallel to shore. C) Combined discharge modes in an irregular pattern controlled by paleochannels

In many previous studies of discharge to estuaries, groundwater was assumed to discharge near shore, and microbial transformations of nitrogen species en route to discharge were assumed to be minor. The proposed investigation evaluates and refines these assumptions, placing the contribution of nutrients from land into a regional and temporal context. Estimates of groundwater-derived nutrient flux obtained as a result of this study will be compared to results from previous land-based studies (Andres et al., 1992) to develop a comprehensive understanding of nitrogen delivery across the land-sea interface. This work will better constrain the conceptual framework within which model estimates are made of groundwater discharge and nutrient flux to barrier-bounded estuaries in general (Valiela et al. 1992, Valiela et al. 1997; Bratton et al., in press). The information will also be useful for making management decisions about land use and zoning, water supply, wastewater disposal, and agricultural practices.

II. Hypotheses

Five primary hypotheses will be tested by the proposed research. Hypotheses H1 and H2 are designed to improve understanding of the physical processes that control subsurface flowpaths, salinity distributions, and fluid fluxes. Hypotheses H3 and H4 aim to tie the physical processes of H1 and H2 to geochemical processes that determine nitrogen species loading. Hypothesis H5 is designed to evaluate the use of numerical models as quantitative tools in complex coastal environments.

Physical Processes:

- H1. Geologic controls. Geological heterogeneity (hydrostratigraphy) is an important control (along with the upland hydraulic gradient, in turn affected by topography, recharge, and other factors) on (1) the subsurface salinity distribution, (2) the spatial distribution of submarine groundwater discharge, and (3) the fresh discharge mode (focused or diffuse).
- **H2. Temporal controls.** Temporally-variable forcing is an important control on the temporal fresh and saline discharge patterns, mixing of fresh and saline groundwater, and the saline exchange flux.

Geochemical Processes:

- **H3. Mixing decreases nitrate loading.** The extent of mixing between fresh and saline water in the subsurface, including the mode of fresh discharge (focused or diffuse) determines, in part, the extent of denitrification of freshwater-derived nitrates before discharge into the bay.
- **H4. Saline exchange increases ammonium loading.** The saline exchange flux determines, in part, the mobilization of ammonium derived from decay of organic matter in the bay floor sediments and subsequent transport into bay waters.

Modeling:

H5. Modeling can represent the complex flow system well. The complexities of this system can be quantitatively represented and integrated in a numerical, three-dimensional, variable-density, groundwater simulation model. Such a model can help to quantify fluid fluxes and mixing, as well as to understand and explain the observed variability in subsurface water quality and SGD.

III. Results of Prior Related Work

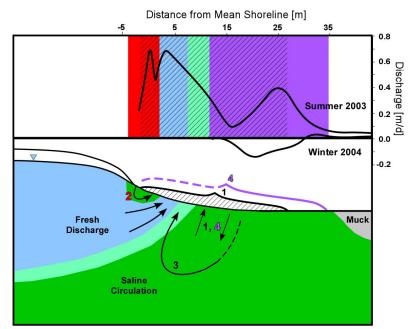
Submarine Groundwater Discharge Fluxes and Mechanism Identification

Field and numerical modeling methods were used by PI Michael and collaborators to quantify fresh and saline SGD into a coastal bay (Waquoit Bay, MA) and identify the forcing mechanisms driving particular components of discharge (Michael et al., 2003; Michael et al., 2005; Michael 2005). Lee-type (Lee, 1977) seepage meters were used to directly measure fresh and saline SGD into the bay during the summer. Hydraulic head and salinity measurements were obtained using onshore and offshore wells and piezometers during the summer and winter. Lastly, 2D variable-density numerical models were developed to test hypotheses, understand system sensitivity to geologic and hydrologic factors, and quantify fluid fluxes. The amount of SGD driven by individual forcing mechanisms and the (overlapping) spatial zones of influence were inferred from the data and numerical simulations. Results are summarized in Figure 4.

Although identification of discharge zones and quantification of fluxes was possible in Waquoit Bay, the work was limited to the nearshore zone only, which was tied directly to the shallow, unconfined aquifer. Offshore streaming resistivity (Belaval 2003) indicated the presence of freshened water at depth far offshore beneath the bay. Piezometer measurements in the offshore mucky sediments depicted in Figure 4 show a strong upward hydraulic gradient and fresh porewater, indicating upwelling of fresh

groundwater from a deeper flow system. This offshore flux has not been investigated to date, though it could comprise a substantial fluid and nutrient flux into the bay. Similar offshore fluid flux in Indian River Bay is the subject of the proposed research.

Figure 4. Interpretation of discharge zones for SGD driving mechanisms along a transect perpendicular to the shoreline in Waquoit Bay. Summer and winter discharge data are presented in the top panel. Color bars represent the approximate extent of each zone of discharge. Zone 1 (cross-hatching) represents tidal pumping. Zone 2 (red shading) represents nearshore circulation due to tides and waves. Dispersion-induced circulation discharges in zone 3 (blue-green shading). Zone 4 represents seasonal



exchange. The dotted line indicates zone where winter observations were not possible, but seasonal exchange likely exists. Adapted from Michael et al. (2005).

Variable-Density Numerical Groundwater Modeling

Numerical modeling capabilities have advanced in recent years due to development of modeling tools and improved computing capabilities. PI Konikow has developed widely-used, quantitative, numerical flow and solute transport modeling tools, including variable-density models, for groundwater systems (e.g., Konikow and Bredehoeft, 1978; Sanford and Konikow, 1985; Konikow et. al, 1996; Merrit and Konikow, 2000; Prudic et. al., 2004). Konikow has also published a review of seawater intrusion in coastal aquifers of the U.S., developed a laboratory and mathematical investigation of clay dispersion in coastal aquifers, and developed an accurate numerical solution to a variable-density benchmark problem.

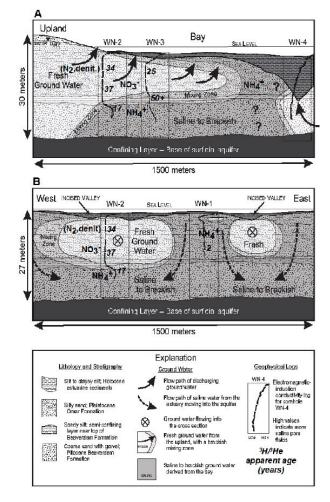
Indian River Bay Work

Indian River Bay, DE is located along the eastern shore of the Delmarva Peninsula (Figure 1). The bay and watersheds have been studied by numerous researchers who have produced digital representations of geology, hydrogeologic framework, water table elevation, and groundwater quality (Chrzastowski 1986; Andres, 1992; Andres, 2004; Andres and Klingbeil, 2006; Andres and Martin, 2006; Kasper and Strohmeier, 2007), defined watersheds (McKenna et al., 2007), located SGD using thermal imagery (Wang et al., 2008), and estimated fresh groundwater flow and nitrate flux to the Bay (Andres, 1987; Andres 1992). PIs Krantz and Bratton were part of a multi-disciplinary study of Indian River Bay geology, geochemistry, and hydrogeology conducted between 2000 and 2004 that greatly improved understanding of the submarine part of the system (Böhlke and Krantz, 2003; Bratton et al., 2004; Krantz et al., 2004).

Detailed onshore work has characterized spatial distributions, hydraulic properties, and geochemistry of the highly transmissive Columbia aquifer and intervening confining units, and, through

analytic modeling by simplified box models, estimated the flux of groundwater and N across the shoreline. Offshore, airborne and satellite thermal infrared imagers identified focused and diffuse SGD. A small set of nutrient, isotope. dissolved gas, and age indicator measurements was obtained at a field site near Holts Landing (Figure 1) by extracting pore fluid from sediment cores and pumping water from temporary wells installed at three sites during the 2000-2004 study. Continuous resistivity profiling was used to obtain 2D images of the salinity distribution in the subsurface along shorelines and in several transects. These images were tied to the lithology, downhole geophysical logs, and measured salinity from vibradrilled core samples. Resistivity transects along the main tributary and across the bay indicate the presence of freshwater beneath a saline surface layer in some locations. The freshwater appears to be most evident landward: thickest beneath Indian River, and extending outward from both the north and south shores of the bay. In addition, a crossbay transect depicts a lens of fresh groundwater at a depth of about 10-20 m, which may indicate freshwater seepage from deeper aquifers.

Figure 5. Interpreted salinity distributions, chemical speciation, and flowpaths in two transects within Indian River Bay adjacent to Holts Landing. Groundwater ages are in italics. Nitrogen species are shown where measured. A) Perpendicular to shoreline. B) Parallel to shoreline. Figure from Böhlke and Krantz (2003).



The modern onshore topography, submarine paleo-topography, and lithology play an important role in the groundwater flow and affect the observed subsurface chemical profile. Changes from low to high onshore topography correspond with changes in offshore salinity of groundwater, as do the existence of submerged paleovalleys and sand ridges. The freshwater in these systems is likely moving, based on evidence such as narrow transition zones from fresh to saline water, the existence of oxygen and nitrate in fresh groundwater, and age dating indicating that groundwater in these areas is less than 50 years old. Surface salinity measurements suggest that freshwater discharges consistently in space and time at the shoreline, as expected, and up to 500 m offshore. The offshore saline flow system is similarly active. Saline groundwater was estimated to be younger than overlying fresh groundwater; at one location water at a depth of 21.6 m had an apparent age of only 2.2 years (Böhlke and Krantz, 2003).

The results of the geochemical sampling and analysis at Holts Landing provide evidence of subsurface N-species transformations. Fresh, oxic groundwater was shown to contain high levels of nitrate. Brackish zones were anoxic and contained excess nitrogen gas, indicating that denitrification occurred in mixing zones. Anoxic saline groundwater contained high levels of ammonium, consistent with the notion that saltwater flowing from the bay into the aquifer transports ammonium present in bayfloor sediments. A cross-sectional interpretation of the data collected at Indian River Bay is shown in Figure 5.

IV. Proposed Research

Though Indian River Bay and its watershed have been extensively studied and much has been learned about the system, a more quantitative characterization of the flow system and a better understanding of the relationship between physical and chemical processes are required to more accurately quantify nutrient loading into the bay. Though estimates of N loads have been computed, it is not possible to estimate the flux of particular N-species without an understanding of the subsurface flow patterns and mixing processes, which may be temporally controlled. More general insight, applicable to other types of coastal systems, can also be gained by identifying and testing the combinations of physical and chemical factors that control N and groundwater movement through the system.

The proposed research will move beyond previous work by adding:

- 1- **Physical flow processes.** Field and modeling methods will enable quantification of fluid fluxes and characterization of groundwater flowpaths and mixing, and provide a framework for analyzing hydrodynamically unstable displacement processes in coastal environments.
- 2- The temporal component. Previous field measurements of the submarine groundwater system beneath Indian River Bay were taken at a single point in time, yielding a fixed snapshot of conditions. The proposed work will include time-series measurements where possible, supplemented by snapshot field campaigns conducted quarterly over a two-year period. Numerical models will incorporate temporally-variable boundary conditions for transient simulations. This will enable evaluation of temporal controls on system dynamics and the sensitivity of the system to temporal changes.
- 3- Improved field methods. Continuous resistivity profiling (CRP) in marine settings was a new technology, first tested in the 2000-2004 study. The methods have been improved in subsequent years so that their new application will produce improved results, potentially a 3D representation of the subsurface resistivity distribution. CRP will also be used, for the first time, to study seasonal variations in subsurface resistivity.
- 4- Integration of information and incorporation of hydrology. The numerical model will integrate all geologic and hydrologic information and can be used to test system controls and sensitivity. A numerical model has not been developed previously for this site, and flow system controls have not been tested to the extent proposed here.
- 5- **The benefit of improved knowledge** of coastal groundwater systems in general (e.g., recent SCOR intercomparison experiments [Burnett et al., 2006]) and Indian River Bay in particular. This knowledge will guide the general approach as well as specific data collection.

Approach

To test our hypotheses, we will study the geology, hydrology, and geochemistry of the coastal groundwater flow system at Indian River Bay, Delaware. The overarching aim of the project is to

characterize the controls of geologic heterogeneity and temporally-variable hydraulic forcing on groundwater flow and fluid and chemical fluxes between aquifers and coastal surface water bodies. We seek to connect these controls to physical flow processes, to connect physical processes (flow rates, patterns, heterogeneity, and mixing) to geochemical transformations, and to combine these in order to better estimate fluxes of fluid and individual chemical species. The information obtained, though focused on a specific site, will improve the general understanding of freshwater-saltwater interaction and geochemistry of the subsurface, with implications for coastal systems worldwide.

Understanding of physical processes will be achieved, in large part, through development and application of a series of numerical models of variable-density groundwater flow and solute transport. Initially, a 3D model encompassing the area contributing groundwater to the bay will be constructed to understand the large-scale flow system and quantify (primarily fresh) groundwater fluxes into the bay. Geologic features will be added progressively so that an analysis of the effect of each feature on the salinity distribution and groundwater discharge can be conducted. Changing the geology will result in a change in the location and thickness of saltwater-freshwater interfaces and flow patterns, revealing large-scale geologic system controls. Temporal hydraulic controls will be investigated similarly: by progressively adding forcing mechanisms to the model in order to determine distinct and combined effects.

Both spatial and temporal variability present modeling challenges because of the computational intensity of solving the non-linear coupled equations of variable-density flow and transport. To improve spatial and temporal resolution, nested scales of models will be constructed. The large-scale structure will provide the framework for progressively more focused models, using finer discretization in space and time, to enable a more detailed understanding of fresh and saline groundwater interactions, quantification of mixing, and incorporation of smaller temporal scales of forcing (tides). A sensitivity analysis will also be conducted to determine how the models are affected by perturbing the unknowns: changing parameter values as well as the small-scale geometry of heterogeneity.

The field campaign is designed to connect the physical and geochemical aspects of the system, to understand geochemical transformations along flowpaths, and to characterize the physical controls on fluxes of particular nitrogen species. There will be one primary and one or two secondary field sites. The primary field site is Holts Landing (Figure 1), where subsurface properties and geochemistry were characterized in previous studies at a coarse scale. As described in Section III, complex but representative salinity distributions exist beneath the bay at this site, and age dating indicates that both fresh and saline flow systems are active. Though discharge has not been directly measured, data indicate that SGD is likely occurring at an observable rate, and both focused and diffuse discharge are likely taking place. The selection of secondary field site(s) will be directed in large part by the results of Phase I of the numerical modeling, and also by prior knowledge of the system. Results from the Holts Landing study site will be extended by limited distributed sampling around the bay shoreline.

High-resolution marine seismic surveys will be conducted to map geologic features. Hydrologic and geochemical field work will characterize the flow system and geochemical profiles in both space and time. Where possible, dataloggers will record instrument measurements continuously over tidal, monthly, and annual cycles. In addition, sampling campaigns will be conducted four times per year for two years in order to obtain data-intensive snapshots in time. The hydrogeologic properties of the subsurface at particular field sites and at distributed locations around and within the bay will be characterized by obtaining sediment samples and with *in situ* hydraulic tests. Direct measurements of groundwater discharge and inflow, will be obtained to assess the hydrology in spatial and temporal detail.

The subsurface salinity distribution will be mapped by piezometer porewater profiling at representative intensive study sites and individual distributed shoreline sites, and by regional continuous resistivity profiling (described below) in order to determine fluid density changes and locations and thicknesses of freshwater-saltwater interfaces. These measurements will provide information on the physical flow field and changes in it over time. Geochemical analyses of groundwater will include 1) field parameters (conductivity, pH, temperature, dissolved oxygen, oxidation-reduction potential), and 2) nitrogen species (nitrate, ammonium, organic nitrogen, N₂ and N₂O gas) and isotopic values. This will constrain important chemical properties of the groundwater and the concentrations and transformations of dissolved nitrogen in the shallow subsurface prior to discharge.

Work Plan and Methods

Details of research plans, methodologies, and technologies are presented in this section, which is divided into four activities: modeling, geology, hydrogeology, and geochemistry. These designations

roughly correspond to the expertise of individual PIs, though there is some overlap. The PIs principally responsible for the work outlined in each section are indicated; where there are more than one, PIs will work closely together to complete it. Michael, as lead PI, is responsible for coordination of all aspects of the project so that information is transferred between investigators and tasks are completed on schedule. Adhering to a schedule is vital to project success because some activities, in particular the modeling, are directly dependent on collection and analysis of field data.

1. Modeling (Michael and Konikow)

We propose to use the finite-element model, SUTRA, developed by the US Geological Survey (USGS; Voss, 1984; Voss and Provost, 2002), which has the ability to capture the complicated densitydependent flow dynamics of coastal systems and has been used extensively in coastal groundwater applications (e.g., Voss and Souza, 1987; Emekli, et. al., 1996; Ataie-Ashtiani, et. al., 2001). Simmons et al., (1999; 2001) demonstrated that SUTRA can successfully simulate unstable displacement processes.

A 3D groundwater flow model of the entire Delmarva Peninsula (Figure 1) is currently under development by Ward Sanford as part of the USGS Chesapeake Bay Program. Though the focus is estimation of groundwater flow and nitrate loading into Chesapeake Bay, the model encompasses Indian River Bay and its watersheds. The model is being developed using MODFLOW (Harbaugh et al., 2000), a model that does not incorporate variable-density effects, so it cannot be used directly for our purposes to model the Indian River Bay system. However, Dr. Sanford, as indicated in the attached letter of support, will provide data used in the model (e.g., topographic and geologic data), and will allow use of the model for establishing boundary conditions for a 3D variable-density model of the Indian River Bay system.

Two phases of model development are proposed. Phase I will be constructed before, or concurrent with collection of field data, and will guide field site selection and data collection. Phase II will incorporate the new field data to develop more accurate site-specific models. Throughout the modeling effort, some general questions will be addressed. Among them, along with the relevant hypotheses, are:

- What controls the location of the freshwater-saltwater interface (mixing zone)? (H1)
- What controls the width of the freshwater-saltwater interface (size of the mixing zone)? (H2)
- What controls the magnitude of freshwater flux? (H1)
- What controls the mode of freshwater discharge? (H1)
- What controls the magnitude of saltwater exchange? (H2)
- Can knowledge of the subsurface salinity distribution provide knowledge of (1) geology, (2) flow directions, or (3) flow rates? (H1 and H2)

The modeling will also address questions specific to the Indian River Bay system, including:

- What type of geologic heterogeneity must exist in order to produce the observed hydraulic and salinity data? (H1 and H2)
- Can observed transient hydraulic forcing produce the observed data (in particular the size of the mixing zone)? (H2)
- Can observed and modeled forcing explain the observed fluid fluxes? (H1 and H2)
- Can modeled fluxes, flowpaths, and mixing explain geochemical observations? (H3 and H4)

The extent to which the model results reproduce observed data and supply answers to the above questions directly addresses hypothesis H5.

Phase I: Initial modeling

Task 1.1. 3D model development

A 3D variable-density model of groundwater flow and salt transport within the region contributing groundwater to Indian River Bay (based on the Sanford model) will be developed using SUTRA. The model parameters will be estimated initially based on previous work and understanding of the system. Recently produced digital models of hydrogeologic and geochemical conditions will allow rapid incorporation of existing conceptual models into the experimental design. Geologic features will be progressively added as heterogeneity in permeability becomes better defined. Features may be discrete, such as mapped paleochannels, or they may be generated stochastically using geostatistical methods and assumptions about spatial correlations, as may be done for bayfloor sediment heterogeneity. Beginning from the initial, homogeneous model, temporal variability will be added. In the largest-scale 3D model, only seasonal changes may be computationally possible. Combination of temporal variability and

geologic heterogeneity will be subsequently simulated. In each stage, the effect of the change in the model on fresh and saline water fluxes and the subsurface salinity distribution will be assessed.

Task 1.2. Small-scale models

A set of smaller and more highly discretized in space and time 2D and 3D models will be developed. The methodology of Task 1.1 will be repeated in the smaller-scale models, with the potential for incorporation of smaller-scale heterogeneity, fingering phenomena, and shorter-timescale temporal variability (e.g., tides). Small-scale models may be site-specific, or may represent idealized single processes for particular study.

Phase II: Data incorporation

Task 1.3. 3D model improvement

The geologic and hydrologic data collected in Tasks 2 and 3 will be incorporated into the models developed in Phase I. Measurements of fluid pressure, salinity, and density, as well as flux data, will be used to calibrate the model and improve parameter estimation. Estimates of hydraulic parameters obtained from tests in Task 3.2 will be incorporated in conjunction with geologic information (where lithologies are known, particular parameter values can be assigned). Modification of the conceptual model, boundary conditions, and parameter values will be made both to improve the accuracy of the model and to test alternative hypotheses about how the system works (physical and temporal controls).

Task 1.4. Small-scale model improvement

The set of small-scale models will be modified to represent specific field sites more accurately. As in task 1.2, data will be used to better estimate parameters and specific geologic features will be incorporated. Modifications to the conceptual model, boundary conditions, and parameters will be made based on the data, and hypotheses H1 and H2 will be tested.

2. Geology

Task 2.1. Drilling (Andres, Michael, and Bratton)

Onshore and offshore drilling is proposed to install permanent and semi-permanent wells for geologic characterization, and for monitoring and sampling. Proposed drilling locations for the Holts Landing site will be a subset of the piezometer locations shown in Figure 1. Offshore, semi-permanent PVC wells will be installed via barge-based drilling using contractor and/or Delaware DNREC equipment. Onshore, permanent PVC wells will be installed with Delaware Geological Survey (DGS) equipment. Where possible, cores will be collected during drilling. Wells will be logged with DGS downhole geophysical equipment, at multiple times during the year.

Task 2.1. Marine seismic surveys (Krantz)

The offshore hydrostratigraphic setting for the study area will be constructed in three dimensions from a high-resolution marine seismic survey of central Indian River Bay. The two primary targets are the shallow Holocene system and the deeper regional aquifers. An EdgeTech swept-frequency (chirp) seismic system with both a lower-frequency SB512i and higher-frequency SB216 towfish will be used. The shallow seismics used to map the pre-Holocene drainage network and the Holocene transgressive infill sequence will be correlated with the extensive database of vibracores collected previously (John 1977; Chrzastowski 1986). Similarly, the deeper hydrostratigraphic units will be correlated with the DGS archive of well logs and scattered coreholes in the area.

The seismic survey will generally follow the marine resistivity survey grid, but with lower-density spacing of the east-west lines. More detailed seismic surveys will be completed at focus sites, with the goal of mapping the pre-Holocene stream valleys and the continuity of any shallow confining layers.

Previous seismic surveys of IRB for the University of Delaware CISNet project conducted in 2001, including that reported by Krantz et al. (2004), employed chirp and boomer seismic systems with good results: the chirp seismics penetrated 5 to 8m and had excellent resolution of bedding; the boomer system imaged strata well to 40-50m, with some coherent reflections as deep as 75m. The proposed surveys have finer grids than the previous surveys and will provide more refined details. The previously collected profiles are available and will be incorporated into the final hydrostratigraphic interpretation.

3. Hydrogeology (Michael and Andres)

Task 3.1. Hydrogeologic framework

Our approach to investigation of hydrogeologic framework has two primary aspects. First, we will refine the spatial distributions of the onshore Columbia aquifer and intervening confining beds from

Andres (2004) and Andres and Klingbeil (2006) using data from the proposed drilling, downhole geophysical logging and interpretation of offshore geophysical surveys. Secondly, we will investigate the spatial distribution and hydraulic properties of near sub-bottom sediments offshore by collecting bottom sediment grab samples and cores, and through laboratory grain-size analyses.

Task 3.2. Hydraulic properties

Hydrogeological site characterization will be done intensively at the field sites (Holts Landing and secondary site(s)), and at other locations within the bay and surrounding upland areas. Characterization will be accomplished with in-situ slug and pump tests to estimate subsurface hydraulic conductivity (K). Porosity and K will also be measured by laboratory analyses of sediment core samples, focusing on heterogeneity in hydraulic properties and the nature of the bay bottom sediments, which control the connection between the groundwater and surface water. Effort will be made to tie hydraulic properties to lithologies so that geologic mapping can be used to establish parameters for the numerical model.

Task 3.3. Hydraulic heads and pressures

Hydraulic head and pressure measurements will be made in order to calibrate the numerical model, establish hydraulic gradients, and characterize the nature of hydraulic variability in time. At each site, semi-permanent PVC piezometers will be installed onshore and offshore in transects perpendicular to the coastline (Figure 1C), and at several depths in each location. In addition, temporary hand-driven piezometers will be installed during a subset of the eight sampling campaigns. Pressure transducers with dataloggers will be used to record water pressures in both the subsurface and the bay. Those installed in semi-permanent wells will collect continuous data over long time periods, and those in temporary wells will provide single measurements. Porewater salinity will be measured in each piezometer so that fluid density can be tied to pressure measurements, in order to identify the locations of freshwater-saltwater interfaces, and so that continuous resistivity profiling data can be tied to point measurements (see also Section 4). Combined pressure and fluid conductivity instruments will be used in locations where fluid salinity varies over time. Hydraulic head and salinity will also be measured at various locations around the bay and within the watershed using temporary hand-driven piezometers and existing wells.

Task 3.4 Groundwater discharge

Seepage meters (Lee, 1977) will be used to measure water flux across the groundwater-surface water interface at the field sites. Discharge or inflow flux is measured over the time period of deployment (usually 1 to 3 hours, depending on the flow rate), and multiple measurements are made over tidal cycles. Seepage meters will be arranged in transects similar to those shown in Figure 1C, as well as in other locations of interest (e.g., suspected areas of focused discharge). Sample density will be sufficient to capture spatial variability and trends. Measurements over tidal cycles will allow assessment of the sensitivity of discharge to tidal changes as well as estimation of an average daily flow rate. Vertical pressure measurements may also be used to determine flow direction and temporal variability in conjunction with the seepage meters or in locations or times when seepage meters cannot be used. Effort will be taken to locate sites of both diffuse and focused SGD.

4. Geochemistry and electrical resistivity (Bratton)

We propose to use continuous resistivity profiling to image differences in porewater salinity beneath Indian River Bay. To obtain a detailed characterization of groundwater salinity and chemistry, we will use hand-driven piezometers and semi-permanent wells to collect submarine groundwater samples. Sample characterization will include examination of biogeochemical conditions, nitrogen speciation (chemical form), and nitrogen transformations including denitrification (removal or loss of biologicallyavailable nitrogen by microbial conversion to N₂ gas) within the coastal groundwater prior to discharge.

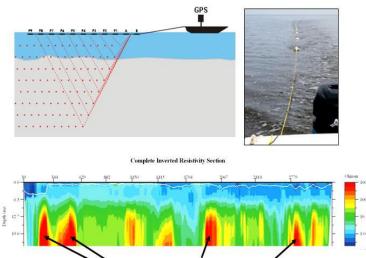
Continuous Resistivity Profiling

This geophysical method takes advantage of the differences in electrical properties of sediments saturated with salty groundwater (high electrical conductivity, low resistivity) versus fresh groundwater (low conductivity, high resistivity). Continuous resistivity profiling (CRP) surveys of shallow estuaries can produce tens of kilometers of resistivity data per day that can be converted into resistivity profiles showing areas of salinity anomalies consistent with underflow by fresh groundwater and submarine discharge offshore (Figure 6). Since performing the first such study in Indian River Bay in 2000 (Manheim et al. 2004), USGS-Woods Hole has carried out additional resistivity studies in coastal bays and estuaries in MD, VA, NC, NY, RI, and MA (e.g., Cross et al., 2006; 2008), and has developed 2D and 3D views of the freshwater-saltwater interface in groundwater beneath these water bodies (Figure 7).

Figure 6. Continuous resistivity profiling is performed by towing a streamer with multiple electrodes behind a boat (upper panels), and using inversion software to convert measurements of the apparent electrical resistivity of the watersediment system into resistivity profiles (lower panel). Higher resistivity values (red) indicate low-salinity groundwater.

Biogeochemical Methods

Biogeochemical transformations of nitrogen prior to discharge have the potential to profoundly alter the magnitude and chemical form of nitrogen exported from the watershed to Indian River Bay. In similar watersheds, the proportion of nitrogen loads carried by discharging fresh groundwater



submarine freshened ground water

that is composed of nitrate can range from ~1% to almost 100%, with the remainder composed of ammonium and organic nitrogen (Kroeger et al. 2006b, Kroeger et al. 2007). It is critical to include examination of biogeochemical conditions and all forms of nitrogen in this investigation, because all forms are capable of stimulating algal growth, yet their reactivity and mobility are often distinct in both the coastal aquifer and in receiving water.

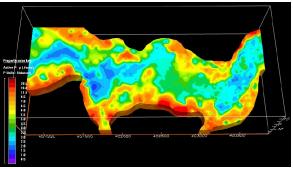
Samples from all wells and piezometers will be analyzed for dissolved nitrate, ammonium, and total dissolved nitrogen by nutrient autoanalyzer (Lachat). A subset of these samples will be analyzed for dissolved organic nitrogen by oxidation and analysis as nitrate, dissolved N₂ and N₂O by gas chromatography, $\delta^{15}N$ of N species by isotope-ratio mass spectrometry, and N₂:Ar ratios by membrane inlet mass spectrometry (MIMS; Kroeger et al., 2006b).

Task 4.1 Continuous resistivity profiling

Although CRP surveying has now been used in numerous coastal studies, none are known to have applied the method to studying seasonal variation in the position or sharpness of the fresh-saline interface beneath an estuary. The study proposed here will attempt to do this. A triangular grid covering the entire estuary (Figure 1B) will be surveyed under high water table (spring) and low water table (fall) conditions, using identical equipment and instrument settings, as well as continuous measurements of surface-water salinity, to allow for correction of associated resistivity influences due to seasonal or tidal variations in water column salinity. The regional CRP surveys will be conducted using an AGI SuperSting R8 marine logging system and a towed 50-m electrode cable, which typically allows for collection of data down to about 13 meters below the water surface. A higher-resolution grid using a 15-m streamer will be surveyed in the area of more intensive investigation around the piezometer, semi-permanent well and data logger study site adjacent to Holts Landing (Figure 1D). In addition, a stationary resistivity streamer (Swarzenski et al., 2006; Kroeger et al., 2007) will be deployed over a full tidal cycle at this site along shore-perpendicular piezometer transects (Figure 1C) during both the spring and fall CRP surveys to characterize movement of the fresh-saline interface at extremely high spatial and temporal resolution.

Figure 7. Horizontal slice of a 3D resistivity model obtained from a CRP survey.

An example of a 3D resistivity model sliced horizontally at 10 m below the water surface is shown in Figure 7, developed for a tributary of Chesapeake Bay, the Corsica River Estuary, based on a survey conducted in 2007. Red and orange colors indicate zones of lower-salinity (higher



resistivity) groundwater. Similar models will be developed for Indian River Bay from data collected on the same grid in spring and fall, and will be compared with the geometry of the submarine fresh-saline relationships determined by the proposed regional variable-density model and geologic framework data.

Resistivity transects also will be completed on land at the focus sites, both parallel and perpendicular to the bay shoreline to characterize the sediment and groundwater system where it is primarily fresh, and to identify landward extension of saline intrusion.

Task 4.2 Piezometer sampling and nitrogen biogeochemistry

We propose to examine denitrification in two primary zones: in the aguifer prior to arrival at the groundwater seepage face, and within the groundwater seepage face due to interactions with saline groundwater and with estuarine sediments (Portnoy et al. 1998, Nowicki et al. 1999). To quantify the extent of denitrification occurring within the aguifer prior to discharge, we will measure concentrations of N₂ gas and the noble gas, argon, using membrane inlet mass spectrometry (MIMS) (Kroeger et al., 2006b). In the absence of denitrification, the ratio of the concentrations of N_2 and Ar depends on the temperature at the time the groundwater enters the ground (is recharged). Any "excess" of measured N_2 concentrations would be indicative of removal of N from the water by denitrification. Complications in interpretation of dissolved gas concentrations in groundwater are: 1) uncertainty regarding water temperature at the time of recharge to the aquifer, which will determine the equilibrium concentrations of N₂ and Ar at recharge, and 2) the presence of "excess air" due to entrapment of air bubbles at the time of recharge or during sampling (Heaton and Vogel, 1981, Peeters et al. 2002). To estimate concentrations of excess N₂ (due to denitrification) and of dissolved gases due to bubble entrapment, and to constrain estimates of temperature at recharge, we will use graphical techniques, targeted measurements of additional noble cases (Peeters et al., 2002), and measurements of the temporal and spatial variability of groundwater temperatures. Isotopic measurements of N species will also be used to illuminate extents and locations of denitrification in submarine groundwater (Böhlke and Krantz, 2003; Bratton et al., 2004).

Submarine groundwater will be sampled with hand-driven Retract-A-Tip piezometers (Charette and Allen, 2006), multi-level (Martin et al., 2003) piezometers, or semi-permanent wells of larger diameter at the intensive study sites, and may be supplemented by barge-based sampling. Shore-perpendicular transects at multiple depths up to ~8 m will be performed, as well as shore-parallel transects that span previously identified paleochannels offshore (Figure 1C) (Krantz et al., 2004). Additional piezometer samples of low-salinity groundwater will be collected from approximately 20-30 sites around the rest of Indian River Bay (outside the Holts Landing study area) to extend geochemical results from this intensively-sampled site to the larger bay. Nutrient biogeochemical measurements, including dissolved gas and isotopic approaches for determining loss of nitrate prior to discharge as described above (see also Kroeger et al. 2007; Kroeger and Charette, 2008), will make it possible to further refine results of surveys and nitrogen budget estimates. Samples will be analyzed for field water quality parameters and nitrogen-argon ratios by USGS-Woods Hole and the Marine Biological Laboratory; nutrient and other chemical analyses will be performed by the University of Delaware, Woods Hole Oceanographic Institution, the USGS-Reston Chlorofluorocarbon Laboratory, or the USGS National Water Quality Laboratory (NWQL), and other contract laboratories.

5. Communication

Results of the proposed study will be submitted to academic journals, and data will be archived in the DGS database. Results will also be presented to local management and environmental agencies and groups, which have an interest in applying the results of the study.

Completion Schedule

The timeline of proposed activities is listed in Table 1. The beginning date is in the winter of year 1 so that CRP and seismic surveys can be conducted in early spring and drilling can begin in late spring or early summer. The project is divided into 3-month quarters for presentation in the timeline.

Task	Description	Hypotheses	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Modeling														
1.1	Phase I Large-scale	H1, H5	х	х	х									
1.2	Phase I Small-scale	H1, H2, H5		х	х	х								
1.3	Phase II Large-scale	H1, H2, H5					х	х	х	х	х			
1.4	Phase II Small-scale	H1, H2, H5								х	х	х	х	
Geology														
2.1	Drilling	H1		х										
2.2	Marine Seismic Surveys	H1	х		х									
Hydrogeology														
3.1	Hydrogeologic Framewor	rk H1	х	х	х	х								
3.2	Hydrologic Properties	H1	х	х	х	х	х	х						
3.3	Heads & Pressures	H1, H2, H5			х	х	х	х	х	х	х	х		
3.4	SGD H	H1, H2, H3, H4, H5		х	х	х	х	х	х	х	х	х		
Geochemistry and Resistivity														
4.1	CRP H	H1, H2, H3, H4, H5	х		х		х							
4.2	Biogeochemistry	H3, H4			х	х	х	х	х	х	х	х		
5.	Write-up											х	х	х

 Table 1. Timeline of proposed activities (2/1/10-1/31/13). Tasks, descriptions, and hypotheses addressed are listed.

 The quarter in which they will be performed is marked with an x.

V. Intellectual Merit and Broader Impact

Intellectual Merit

The intellectual merit of this multi-disciplinary project lies primarily in the integration and advancement of the understanding of physical and chemical processes, which is critical to evaluation of the role of submarine groundwater discharge in nitrogen loading to coastal waters and has not been fully achieved previously. Individual components of the complex natural system that result in nitrogen loading to bays have been considered. Numerical groundwater models have been used to estimate fresh aroundwater discharge to the sea and associated N loads assuming conservative transport and steadystate flow, small-scale geochemical investigations have demonstrated reactivity of N species near the coast, and spatial and temporal variability of fresh and saline groundwater fluxes have been measured in coastal waters. No studies, however, have integrated all of these aspects quantitatively. The proposed research will use 3D numerical modeling to understand the role of large- and small-scale spatial and temporal heterogeneity in controlling fresh and saline groundwater flowpaths and subsurface salinity distributions. Hydrogeologic, geochemical, and geophysical field measurements will constrain the sitespecific models in order to understand how system physics can produce observed patterns and to estimate rates and modes of discharge fluxes. The role of physical flow and mixing in controlling chemical transformations and loading rates will be assessed, thus fully synthesizing physics and chemistry in a coastal groundwater system. This basic understanding will be applicable to coastal systems worldwide, and may greatly improve our ability to manage nutrient loading and eutrophication in coastal ecosystems.

The proposed research will add to the large body of geologic, hydrologic, geophysical, and geochemical work performed in and around Indian River Bay by the Delaware Geological Survey, the U.S. Geological Survey (USGS), University of Delaware students and faculty, the Delaware Department of Natural Resources and Environmental Control, and many others. This will make Indian River Bay one of the best studied estuarine systems in the world, in which geologic and hydrologic interactions are quantitatively described and their relation to water-quality variations in the subsurface and in the estuary are explained. This will provide a basis for development of conceptual understanding that can be applied to coastal systems that do not have the benefit of tens of years of investigation, as well as establishing a solid framework for future use of this site as a coastal hydrogeological observatory by other investigators.

NSF has invested in the critical zone observatories because processes occurring at and near the Earth's surface are interdependent, and the extent to which they are coupled, and at what temporal and spatial scales, remains largely unknown. In 2001, the NRC Water Science and Technology Board stated, "What is needed for understanding water resources is a more holistic conceptual framework that encompasses regional hydrologic systems, land-atmosphere interactions, and biogeochemical cycles that control contaminant transport." Our proposed research will encompass exactly this. It is relevant to the

NSF investment in the Critical Zone because it seeks to understand the coupling and interaction of processes at Earth's surface across scientific disciplines.

Broader Impact: Management, Research, and Education

Eutrophication is one of the most common and most severe problems facing coastal bays in populated and agricultural areas. Unnaturally high quantities of nutrients enter fresh groundwater and surface water as a result of human activities. These nutrients contribute to the overpopulation of phytoplankton and macroalgae in coastal surface waters, which results in deterioration of water quality and animal habitat. This is a particular problem in the Delmarva region, where poultry farms, agricultural activity, and growing human populations have contributed to rapidly-declining populations of blue crabs, striped bass, and many other species which live and breed in estuarine waters. The economic value of these species has, in part, prompted political action and efforts to manage nutrient inputs to groundwater and surface water, the primary pathways for nutrient loading to coastal waters. Despite significant reductions, coastal water quality has largely remained poor. A better understanding of the processes that moderate nutrient loading to coastal waters, particularly via groundwater, which is much more difficult to monitor than surface water inputs, is essential for improved management methods that will result in healthy coastal ecosystems. This project will improve understanding of where nutrients are coming from and how loading may be reduced, and may aid in identification of activities that exacerbate negative impacts. For example, understanding of the effects of seafloor confining units can help to identify potential impacts of human activities such as installation of dock and bulkhead pilings (Stieglitz et al., 2008) and channel dredging, which can open discharge conduits for focused nitrate-rich SGD and create pathways for saltwater intrusion into fresh groundwater resources (Foyle et al., 2002). The new understanding and predictive capabilities developed from this project will provide insight and tools that can be used by managers and policy-makers who allocate public resources for restoration, and who develop regulations to reduce nitrogen loading to Indian River Bay and other coastal systems (see letter of support from Christopher Bason, Science and Technical Coordinator for the Center for the Inland Bays).

The research project also has an important educational component. The PIs are affiliated with multiple institutions with distinct educational missions. The science produced by USGS (Bratton, Konikow) and DGS (Andres) serves to educate the public, assess the state of natural resources (including water), and produce scientific results that can be used by water managers and policy-makers to guide decisions. Both agencies support student research projects, and the USGS-Woods Hole geochemistry group does regular outreach through the Woods Hole Science and Technology Education Partnership and other groups. Bratton also teaches at Stonehill College, Bridgewater State College, and Au Sable Institute of Environmental Studies (MI). Konikow has taught at Stanford University, and Andres is an adjunct faculty member at the University of Delaware. Michael and Krantz are full-time faculty at the University of Delaware and the University of Toledo, respectively; each teach and advise both graduate and undergraduate students.

This project will be a learning opportunity for the graduate and undergraduate students involved. The students and Michael, who is very early in her career, will benefit from the mentoring of the other PIs, all of whom are in more advanced stages of their careers. Moreover, the equipment obtained with this funding and the graduate student supported at the University of Delaware would help to build Michael's research lab, which, if successful, will provide a foundation for education of undergraduate and graduate students as well as advancement of scientific knowledge for many years at the University of Delaware. All of the PIs will also benefit from interaction with each other: the range of complementary expertise will broaden their understanding of different aspects (hydrologic, geochemical, geologic, and computational) of environmental problems, which will benefit future projects. The collaborative partnerships formed between the University of Delaware, the University of Toledo, USGS, and DGS enable pooling of resources to further mutual scientific interests, and provides a rich environment for students and researchers to pursue multi-disciplinary research in water and earth sciences.

VI. Results from Prior NSF Support

None of the PIs have received NSF support within the last 5 years.