INTERACTIONS BETWEEN NITROGEN AND HYDROLOGICAL CYCLES: IMPLICATIONS FOR RIVER NITROGEN RESPONSES TO CLIMATE AND LAND USE WITH THE MODEL LM3-TAN

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Abstract

Human activities, such as legume/rice cultivation and fossil fuel combustion, have dramatically increased reactive nitrogen (Nr), and its movement through ecosystems and environmental reservoirs. The substantial magnitude of this ‘new’ Nr production is problematic, as excess Nr can be extremely detrimental to the functioning of the various ecosystems. Inarguably, tracking the anthropogenic Nr movement is necessarily, but also challenging because of the complex nitrogen (N) cycle. A central contribution of this research is the development of a new process model LM3-TAN. The model captures key controls of the transport and fate of N in the vegetation-soil-river system in a comprehensive and consistent framework that is responsive to climate change and land-use and land-cover changes (LULCC). This dissertation is focused on investigating interactions between hydrological and N cycles in terrestrial and aquatic ecosystems, which have large implications for responses of river N and coastal eutrophication to changes in climate and land use, using novel applications of LM3-TAN.

The N supply via large rivers controls water quality in many of the world’s estuaries or coasts, where N limits biological productivity. Evidence has mounted that climate change is associated with more frequent and intense extreme weather events. This research reveals the critical role of increasing climatic variability and extremes, interacting with N storage, on Susquehanna River N loads which contribute about half of annual N loads to the largest estuary in the U. S., Chesapeake Bay. It was found that after 1-4 year dry spells, the likelihood to exceed a threshold N load increases by 31-86%, which is explained by flushing of accumulated soil N and by stimulated soil microbial processes. This memory effect is amplified when longer dry spells are followed by extreme precipitation. This research also quantifies downstream N-removal benefits with respect to ecosystem components (e.g., climate, basin location, land use) to prioritize
sites for land-use management. In a case study for the Korean Peninsula, it was found that the greatest N-removal opportunities are given for sub-basins, with low precipitation, close to coasts, and with substantialNr production. This result provides important implications for effective mitigation strategies to reduce coastal eutrophication.
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To my parents and sister.
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Chapter 1

Introduction

1.1 Nitrogen

Nitrogen (N) is vital to life because it is an essential element for plant and animal tissues. Most of the N on the Earth is diatomic nitrogen (N\textsubscript{2}), which is not useable by most organisms because of the extremely strong triple bond in the elemental nitrogen (N \equiv N). In natural ecosystems, the inert N\textsubscript{2} in the atmosphere is converted into reactive nitrogen (Nr) by biological N\textsubscript{2}-fixation (BNF) as well as by lightning. These mechanisms provide nutrients for plants and animals, which cannot fix the atmospheric N\textsubscript{2}. Hence, increases in Nr, such as inorganic reduced (e.g., ammonium: NH\textsubscript{4}\textsuperscript{+}) and oxidized (e.g., nitrate: NO\textsubscript{3}\textsuperscript{-}) forms of N, can enhance ecosystem productivity through fertilization.

Over the past 100 years, human activities, mainly in order to increase food and energy production, have greatly altered natural rates of N-fixation [101] by over a factor of ten compared to the late 19\textsuperscript{th} century [37]; that is, both legume/rice cultivation and fossil fuel combustion have dramatically increased Nr and its movement through ecosystems and environmental reservoirs [37]. The substantial magnitude of this ‘new’
Nr production is problematic, as excess Nr can be extremely detrimental to the functioning of the atmosphere, terrestrial ecosystems, and freshwater and marine aquatic ecosystems [2, 49, 52, 53, 61, 75, 102, 103, 104]. Inarguably, tracking the anthropogenic Nr movement is necessarily, but also challenging because of the complex N cycle compared to those of other major elements.

A central contribution of this research was the development of a new process model LM3-TAN [65] by extending NOAA’s Geophysical Fluid Dynamics Laboratory (GFDL) land model LM3V-N [40] of coupled terrestrial carbon and nitrogen (C-N) cycling, and including new N cycling processes and inputs, such as a soil denitrification, point N sources to streams (i.e., sewage), and stream transport and microbial processes. Because the model integrates hydrological [71], ecological, and biogeochemical processes [40, 65, 100], it captures key controls of the transport and fate of N in the vegetation-soil-river system in a comprehensive and consistent framework which is responsive to climate change and land-use and land-cover changes (LULCC) [55]. Thus, this model allowed the complementary study contained in this dissertation to illustrate how point and non-point anthropogenic N sources contributing to the various ecosystems are stored, lost, and exported via rivers and to investigate the combined effects of direct human influences and climate conditions on terrestrial and aquatic nitrogen (TAN) cycling [65].

The harmful effects attributed to the excess Nr on the environment and on people can occur in sequence, which is referred to as the ‘nitrogen cascade’ [36]; for example, higher Nr in the atmosphere (e.g., ozone, O₃), in turn, increases air pollution-related illness, causes N saturation in forests, promotes production of greenhouse gas (GHG) (e.g., nitrous oxide, N₂O), alters forest productivity, acidifies surface waters, and
decreases species diversity. This dissertation is focused on investigating interactions between hydrological and N cycles in terrestrial and aquatic ecosystems, which have large implications for responses of river N and coastal eutrophication to changes in climate and land use, using novel applications of the model LM3-TAN, for studies of the Susquehanna River Basin and Korean Peninsula.

1.1.1 Nitrogen in Aquatic Ecosystems

In stream and rivers, there are two N species which are pollutants themselves. One is ammonia gas (NH₃). This unionized form of ammonia is toxic to living organisms like fish. The other is NO₃⁻. Its high concentrations in drinking water can occasionally lead to fatal effects in infants. Some of N species are also major causes of important environmental problems. For example, by nitrification, ammonia is oxidized to nitrite (NO₂⁻), and then to NO₃⁻. This process consumes oxygen, and thus, in turn, can result in serious oxygen depletion in water columns, increase benthic mortality, and amplifies risk of fisheries decline.

In many estuaries or coastal marine ecosystems, N limits biological productivity [114]. Thus, excessive N supply is one of the major causes of over-stimulating plant growth and eutrophication (nutrient over-enrichment), the primary environmental problem in the aquatic ecosystems worldwide. The eutrophication process is especially accelerated in densely populated urban or agricultural regions, where point N sources discharged from sewage-treatment plants supplement high levels of non-point N sources produced from vehicles or fertilizer/manure applications. The amplified eutrophication by human activity is sometimes called ‘cultural’ eutrophication [104]. Eutrophication has
many undesirable side effects [102, 103, 104]. For example, it can result in direct water-quality problems, such as taste/odor problems in water supplies and filter clogging problems at water treatment facilities. It can also affect pH and oxygen levels in waters, and thus lead to indirect water-quality [27, 104] or ecological [23, 119] problems, such as hypoxia, algal blooms, reductions in species diversity, and declines in coral reef health. Furthermore, it can cause considerable economic costs [90].

The N supply via large rivers to estuaries and coastal waters is substantial. Thus, reducing downstream N loads of the large rivers has become of particular concern for many of the world’s estuaries and coastal marine ecosystems, due to the water-quality and ecological problems associated with ‘cultural’ eutrophication. For example, frequently observed “Red tides” in coastal waters around the Korean Peninsula indicate serious N pollution provided by the rivers in South Korea. Implementing basin-wide management practices is an expensive enterprise. Nonetheless, there is little modelling study that indentifies sites where the potential for reducing downstream N loads is high. One of the important applications of this research is to quantify downstream N-removal benefits with respect to ecosystem components (e.g., climate, land use, subbasin location) to prioritize sites for N-loading controls in the Han River Basin, the largest river basin in South Korea.

1.1.2 Nitrogen and Climate Change

Despite three decades of basin-wide N waste-reduction efforts, the largest estuary in the U. S., Chesapeake Bay still suffers from eutrophication, and its hypoxic (“dead”) zone is persistent. A possible mechanism could be substantial ecosystem (i.e., vegetation, soil,
groundwater) nutrient storage, which has been accumulated over multiple decades [92]. At the same time, previous observational studies linked individual water-quality issues (e.g., high N load/concentration, chlorophyll-a; hypoxia) to hurricanes [70, 85], droughts [14, 34, 60, 73], or inter-annual river flow variability [1, 44]. Thus, current water-quality problems appear to be a combination of the slow response to legacy effects of long-term (~ multi-decades) anthropogenic N perturbations and the fast response to short-term (~ years) climatic perturbations.

Evidence has mounted that climate change is associated with more frequent and intense extreme weather events, and related adverse risks to ecosystems and humans are expected to increase [9, 21, 41, 57, 87]. Nonetheless, the mechanisms, by which the changing climate influences the delivery of anthropogenic N inputs into receiving waters, remain unclear. The other important application of this research is to reveal the critical role of increasing climatic variability and extremes, interacting with N storage, on Susquehanna River N loads which contribute about half of annual N loads to the Chesapeake Bay. This research improves our understating of how changes in inter-annual climatic variability can lead to high river N-load anomalies, and thus amplify risk of eutrophication.

1.2 Nitrogen, Phosphorus, and Algae

Just as N is a vital element for life, so is phosphorus (P). It plays a critical role in genetic systems, as soluble reactive phosphorus (SRP), such as phosphate (PO$_4^{3-}$), is a component of DNA, RNA, and ATP. In natural waters, P is usually in short of supply due to three primary reasons: first, it is not abundant in the earth’s crust; second, it does not have a gas
phase; and third, it tends to be quickly adsorbed onto fine-grained particles [16]. However, since the early 20th century, the supply of P into natural waters has been substantially enhanced from use of fertilizer and detergent as well as enhanced soil erosion by human activity. This has significantly accelerated the eutrophication process in P-vulnerable ecosystems. Many studies have identified P as the primary limiting nutrient in freshwaters, while biological productivity in coastal marine ecosystems tends to be more N limited [96, 103]. Hence, managing both N and P is crucial to maintaining desirable water quality in most of the aquatic ecosystems.

From a water-quality perspective, algae are as important as nutrients, since not only its amount is a direct index of the extent of eutrophication (and sometimes of turbidity) but also they are the dominant component of the primary producers in some aquatic ecosystems like lakes and estuaries [11]. In addition, algal photosynthesis, respiration, and decay are closely linked with nutrient dynamics via nutrient uptake and recycling. Thus, modeling algal dynamics can help water-quality models to obtain better simulations.

The dry-weight composition of algae and other biological constituents vary, but can be idealized as the following representation of the photosynthesis/respiration process (16, 109). The well known mass ratios of carbon (C) to N to P can be determined as 40:7.2:1, using this formula.

\[106CO_2 + 16NH_4^+ + HPO_4^{2-} + 108H_2O\]

\[\leftrightarrow C_{106}H_{263}O_{110}N_{16}P_1 + 107O_2 + 14H^+\]

"Algae" (1.1)
This research also designs a riverine/estuarine biogeochemistry model that couples nutrient (i.e., N, P) and algal dynamics, based on this stoichiometric ratio as well as a dynamic regulatory model that predicts chlorophyll a-to-carbon ratios [39]. Future work will be the development of this model which could serve as a medium of biogeochemical bonding between land and ocean components of the GFDL Earth System Model.

1.3 Overview of Chapters

The development of the model LM3-TAN, its applications and scientific implications, and the design of the riverine/estuarine biogeochemistry model are presented in this dissertation.

Chapter 2 is the development of the model LM3-TAN and its application for the study of the Susquehanna River Basin. This study reviewed previous modeling studies, and described structure and equations of LM3-TAN. This study also simulated stream and river dissolved organic-N, ammonium-N, and nitrate-N loads throughout the river network in the Susquehanna River Basin, and evaluated the simulated N loads using data from 16 monitoring stations for the period 1986–2005 and a reported N budget for the period 1988-1992. The findings are discussed in the context of the combined effects of human and climatic influences on terrestrial and aquatic N (TAN) cycling, by comparing reported and/or simulated soil denitrification and river N loads in different sub-basins which vary in land use and climatic conditions.

Chapter 3 is the scientific implication of the Susquehanna River Basin study.
This study analyzed long-term reported and simulated river flow and N-load data to investigate the effects of changing climate on river N loads. This study also analyzed model results to understand mechanisms that influence anthropogenic N transformations and transport into rivers. In addition, this study ran 549 experiments using LM3-TAN, and produced 9 river N-load distributions in response to different histories of hydrologic preconditioning for risk analysis of eutrophication. This study emphasizes the importance of accounting for changes in inter-annual climatic variability for the design of effective mitigation strategies.

Chapter 4 is the model application for the study of the Korean Peninsula and its scientific implication. This study simulated river flows and N loads throughout the entire drainage networks in South Korea and evaluated the modeled flows and N loads respectively at 11 flow and 11 nutrient monitoring stations in five river basins for the period 1999-2010. A key objective of this study is to provide forecasts of N loads using various anthropogenic N-reduction scenarios with and without inter-annual climatic variability observed during the past 63 years (1948-2010). Based on these model results, this study discusses about the roles of various ecosystem components (i.e., N storage, inter-annual climatic variability, precipitation, anthropogenic N inputs, and basin location) on reducing downstream N loads.

Chapter 5 is the design of the riverine/estuarine biogeochemistry model. This chapter describes the model structure and equations that will be developed in future research.
1.4 Publications

The research in this dissertation has contributed to three first-author publications that have been published or in preparation.


Materials from this dissertation have been also previously presented publicly at the 2011 and 2013 American Geophysical Union Fall Meetings, the 2012 Chesapeake Community Modeling Program (CCMP) Chesapeake Modeling Symposium, and the 2012 and 2014 Energy and Environment Corporate Affiliates (Effiliates) Annual Meetings.
Chapter 2

Capturing Interactions between Nitrogen and Hydrological Cycles under Historical Climate and Land Use: Susquehanna Watershed Analysis with the GFDL Land Model LM3-TAN

2.1 Introduction

Biologically available nitrogen (N) in terrestrial ecosystems has significantly increased via anthropogenic nutrient inputs: artificial fertilizer, cultivation of N-fixing crops, and fossil fuel consumption [37, 38]. This increase has caused acidification and N saturation in some terrestrial and aquatic ecosystems [49, 53, 61, 75]. N-saturated soils and streams
are also major sources of nitrous oxide (N$_2$O) emissions, which is a potent greenhouse gas [2]. Other concerns include severe water-quality problems associated with cultural eutrophication, which results in harmful algal blooms and hypoxia in rivers, lakes, estuaries, and coastal zone ecosystems [102, 103]. Climate change and variability also affect water quality through the distribution of high and low flow extremes [54, 93]. It is generally accepted that microbial processes related to the N cycle are strongly influenced by abiotic factors, and a warm or wet climate provides favorable environments for certain groups of bacterial activities. Quantification and management of the diverse and coupled effects of human activity and climate change on N cycling requires a comprehensive model of the relevant coupled processes that can support the design of optimal nutrient loading controls to maintain desirable water quality and terrestrial ecosystem integrity.

To characterize implications of human- and climate-driven perturbations in the earth’s N cycling and its implication for water and air quality, the next generation of N cycling models need to (1) account for regional and local changes in terrestrial and aquatic ecosystem structure and functioning, (2) represent in a consistent manner emissions and transformation of N to air, rivers, and coasts, and (3) be global in extent and integrated with climate and earth system models. Previously, none of the existing models addressed the above three challenges. Here we present a novel modeling framework capable of addressing these challenges and, prior to its global application, we evaluate this modeling framework in the Susquehanna River Basin whose sub-basins vary in climate, land use, and associated N sources and transformations, with a detailed data set of observations.

There has been keen interest and progress in modeling the N cycle in terrestrial ecosystems. However, in most models vegetation and land-use type distribution are
prescribed and do not change with time. Modeling studies with EPIC, ANIMO, and CENTURY/DAYCENT typically prescribe crop distribution and simulate crop production and related nutrient and carbon (C) cycling [24, 63, 88, 98, 122]. Because these models do not simulate decadal-to-century changes in vegetation structure (e.g., forest regrowth after harvesting), they are likely to overlook changes in the storage of N in vegetation. Furthermore, during wood harvesting and forest clearing for agriculture, biomass residue is an important additional input to the soil organic C-N pools. Such additional N inputs lead to additional N inorganic loads. In addition, many regional models (e.g., EPIC, ANIMO), which have been applied to far smaller basins compared to the Susquehanna watershed, often use basin-specific parameters for mineralization, nitrification, and denitrification, which complicates their global scale application for studies on the decadal-to-century scale.

LM3-TAN is capable of describing N dynamics with a universal parameter set – the same parameters for all of the sub-basins within an area of 71 220 km² and time periods for this simulation. LM3-TAN is among very few modeling frameworks (e.g., CLM-CN: [112]; CLM4MOD: [111]) that can be used as a component of an Earth System Model – that is, it is capable of representing sub-diurnal exchanges of moisture, energy, and C and N species within the land–atmosphere interface. Unlike CLM4MOD, LM3-TAN simulates water quality in the rivers and nutrient loadings to the coastal environment.

Contrary to the simulations of land models limited to the terrestrial component, most watershed models do estimate stream N concentrations and loads, but they simplify or neglect many key mechanisms describing terrestrial N dynamics (e.g., vegetation and land-use dynamics, interactive C-N feedbacks on vegetation and soil microbial processes;
phenological leaf drop and its contribution to soil organic matter pools). INCA-N and SWAT are widely used geographic information system (GIS)-based watershed models [95, 120]. However, when it comes to large-scale applications, because these models are semi-distributed, they are less capable of representing spatial variability, requiring users to define the number and sizes of sub-basins, in which land use and all of the processes for each land use are assumed to be homogeneous and needed to be defined individually. This limits their ability to analyze complex land-use management scenarios. In this class of models, RHESSys is one of a few models with an ecology component that can be used to investigate interactions between ecosystems and hydrological processes according to climate variability [7, 110]. However, like most models, because these models do not simulate vegetation and land-use-type distribution, a specific parameter set that describes typical soil, vegetation, and land-use characteristics has to be developed using its special module when a study site requires different vegetation or soil types from its default application. This explains why RHESSys has only been applied to very small or subsections of catchments [6, 110].

Given the current lack of models that link terrestrial C-N cycling, long-term vegetation, and land-use dynamics to N loads and concentrations in streams, accounting for different N species, the goal of this research was to build a model to simulate stream N loads that is based on a global-scale terrestrial and N-enabled land model, followed by its testing on a large and complex watershed, for which many years of stream discharge and stream N data are available. For this purpose and to assess the combined effects of direct human influences and climate change on terrestrial and aquatic nitrogen (TAN) cycling, we developed a process model LM3-TAN. The new features include integrated effects of point and non-point sources on river N loads, a soil denitrification module, and stream microbial processes.
We applied LM3-TAN to the Susquehanna River Basin, the largest of the watersheds in the northeastern US, draining an area of 71 220 km$^2$, at the resolution of $1/8^\circ$. The model was evaluated using 20 year (1986–2005) data of stream ammonium ($\text{NH}_4^+$) and dissolved organic N loads as well as stream nitrate ($\text{NO}_3^-$) N loads from 16 monitoring stations. For each six sub-basins, we conducted local analysis to assess combined effects of land use and climate on the soil denitrification. We then built up an N budget and compared it with the corresponding reported budget to better understand how point and non-point N sources contributing to the various ecosystems are stored, lost, and exported via the river at the level of the whole Susquehanna watershed. Although there are several parameters that required calibration by fitting simulated to reported stream N loads, these parameters are used universally for the entire basin where climate, soil, vegetation, and land-use characteristics vary. Efforts have been made in the development of this model to limit the number of calibrated parameters.

2.2 Model Description

2.2.1 Overview

LM3-TAN is an expansion of earlier Geophysical Fluid Dynamics Laboratory (GFDL) land models, beginning with LM3V of Shevliakova et al. (2009) [100], which describes vegetation and C dynamics. LM3-TAN was expanded to include vegetation- and soil-N dynamics from LM3V-N [40], new soil physics and hydrology from LM3 [71], and N cycling processes described here. LM3 was used as a component of the GFDL Earth System Models [29] and included several enhancements, such as vertically resolved soil physics and hydrology and explicit river dynamics and physics. LM3-TAN includes soil
denitrification and transport and chemistry of N cycle in rivers. This version of the model allows more complete tracking of N through the soil–river continuum. In this section, we first summarize key features of the model, and then we describe the newest N cycling features.

LM3V simulates distribution of five vegetation functional types (C3 and C4 grasses, and temperate-deciduous, tropical, and cold evergreen trees) on the basis of total biomass and prevailing climate conditions. The model tracks hundreds of years of land-use change using global land-use transition scenarios that were historically reconstructed by combining satellite-based contemporary patterns of agriculture with historical data on agriculture and population [55]. The four land-use types are natural vegetation (land undisturbed by human activities), secondary vegetation (land formerly disturbed by human activities), cropland, and pasture. The model is spatially distributed, and each grid cell consists of up to 15 tiles: 1 natural vegetation, 1 cropland, 1 pasture, and 1 to 12 secondary vegetation tiles representing unique disturbance histories (i.e., de/reforestation, agricultural practice change). Exchanges of water, energy, and between land and atmosphere are computed with a timestep of 30 min. Atmospheric and terrestrial reservoirs include C pools in vegetation (leaves, fine roots, sapwood, heartwood, and labile C storage), soil (fast and slow), and anthropogenic storage. The C pools in the vegetation are updated on a daily timestep to account for vegetation growth and allocation, leaf drop and display, and natural mortality and fire. The soil C, which is supplied by the vegetation both naturally and during landuse conversion, is stored in two pools with different turnover times.
2.2.2 Coupled C-N Dynamics in Vegetation and Soil

The previous two soil C pools in LM3V were divided into four pools (fast and slow litter, and slow and passive soil organic matter) in LM3V-N. Each C pool in the vegetation and soil was paired with a respective N compartment using pool-specific C:N ratios. The decomposition processes release biologically available forms of N ($\text{NO}_3^-$, $\text{NH}_4^+$). This allows the simulation of N limitation on plant growth and biological N fixation as well as N feedbacks on organic matter decomposition and stabilization. Inorganic N is removed by sorption to soil particles, plant uptake, immobilization into long-lived organic compounds, and hydrological leaching, while organic N is lost through fire, hydrological leaching, and mineralization. Loss of nitrate N by soil denitrification was not differentiated from the hydrological nitrate-N leaching in LM3V-N.

2.2.3 Improved Soil and River Physics and Hydrology

LM3 introduced vertically distributed soil–water, soil–ice and temperature profiles extending many meters below the surface, but with high resolution (thinnest layer 0.02 m) near the surface. Water (potentially) discharges laterally from each soil layer to the local river reach. Each horizontal grid cell of the model contains only one river reach, and each reach discharges to another reach in the downstream grid cell, following a network that ultimately discharges to the ocean; the sub-grid-scale stream network is ignored. Relations among discharge, storage, velocity, width, and depth in each reach are specified according to Leopold and Maddock (1953) [66].
2.2.4 Synthesis and Extension of Earlier Developments

For this study, we first combined the lumped N model LM3V-N with the distributed physics of LM3. To complete the N mass balance, we next added a soil denitrification module. Finally, we added stream transport and microbial processes to track the fate of soil N leaching and resolve N dynamics in the aquatic ecosystem. Each of these steps is described below. Figure 2.1 shows stores and fluxes of N in the resultant model, along with relevant processes. Newly introduced or adjusted parameters from the earlier developments are summarized in Table 1 and variables are listed in Table 2.

2.2.4.1 Merging Lumped N Model with Distributed Physical Model

To account for dependence of processes in the lumped soil C and N pools upon the vertically resolved physical states of the soil (temperature and water content), the latter were vertically averaged with an exponentially decaying weight function of depth (e-folding depth of 10 m). Leaching of any mobile constituent was defined as the product of a concentration and the sum of lateral and vertical discharge from the soil layer between the surface and a depth of 10 m. The concentration of available N was calculated as dividing available N contents by the effective soil depth, which was approximated assuming C weight content 3.4% and average soil density 1500 kgm$^{-3}$. The available N refers to the N contents reduced by buffering factors which represent processes such as sorption to soil particles.
Figure 2.1: Structure of LM3-TAN.
Two thick boxes show the incorporated denitrification module in the terrestrial component and stream microbial processes in the river component. The river systems are a series of continuously stirred tank reactors (CSTR) that simulate stream mineralization, nitrification, and denitrification. The other boxes show major C and N pools in vegetation (leaves, fine roots, labile, sapwood, heartwood, and N buffer storage), soil (fast and slow little, slow and passive soil, mineral N), and river (organic and mineral N). The arrows depict fluxes of anthropogenic N sources (thick solid), C-N organic compounds and mineral N (thin solid) with associated processes (italic), and C and N lost to the atmosphere or anthropogenic pool (dashed).
Table 2.1: Newly Introduced or Adjusted Parameters from the Earlier Developments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
<th>Reference or Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_{\text{DOM}}, b_{\text{NH}<em>4^+}, b</em>{\text{NO}_3^-} )</td>
<td>buffering factors for DOM, ammonium-N, nitrate-N</td>
<td>3, 5, 1</td>
<td>unitless</td>
<td>Leadly et al., 1997; Neff and Asner, 2001</td>
</tr>
<tr>
<td>( f_{\text{DOM}} )</td>
<td>fraction of litter soil decomposition that becomes potential DOM (Gerber et al., 2010)</td>
<td>0.034</td>
<td>unitless</td>
<td>calibrated to match stream DON loads; Gerber et al., 2010</td>
</tr>
<tr>
<td>( k_{\text{dinitr}} )</td>
<td>first-order denitrification coefficient</td>
<td>6.5</td>
<td>1/yr</td>
<td>Heinen, 2006</td>
</tr>
<tr>
<td>( r_{\text{DOM}}, r_{\text{NH}<em>4^+}, r</em>{\text{NO}_3^-} )</td>
<td>calibration factors for DOM, ammonium-N, nitrate-N</td>
<td>10, 20, 100</td>
<td>unitless</td>
<td>calibrated to match interannual variations of stream N loads</td>
</tr>
<tr>
<td>( q_{\text{max}} )</td>
<td>transfer fractions form slow litter to slow soil (Gerber et al., 2010)</td>
<td>0.6</td>
<td>unitless</td>
<td>Parton et al., 1993; Bolker et al., 1998; Gerber et al., 2010</td>
</tr>
<tr>
<td>( q_{\text{SP}} )</td>
<td>transfer fractions form slow litter to passive soil (Gerber et al., 2010)</td>
<td>0.004</td>
<td>unitless</td>
<td>Parton et al., 1993; Bolker et al., 1998; Gerber et al., 2010</td>
</tr>
<tr>
<td>( S_{\text{min}} )</td>
<td>minimum soil water content</td>
<td>0</td>
<td>unitless</td>
<td>Bril et al., 1994; Heinen, 2006</td>
</tr>
<tr>
<td>( S_{\text{max}} )</td>
<td>maximum soil water content</td>
<td>1</td>
<td>unitless</td>
<td>Bril et al., 1994; Heinen, 2006</td>
</tr>
<tr>
<td>( S_t )</td>
<td>threshold soil water content</td>
<td>0.577</td>
<td>unitless</td>
<td>Bril et al., 1994; Heinen, 2006</td>
</tr>
<tr>
<td>( w )</td>
<td>empirical constant</td>
<td>2</td>
<td>unitless</td>
<td>Bril et al., 1994; Heinen, 2006</td>
</tr>
<tr>
<td>( T_p )</td>
<td>parameter</td>
<td>10</td>
<td>unitless</td>
<td>Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006</td>
</tr>
<tr>
<td>( T_r )</td>
<td>reference temperature</td>
<td>15</td>
<td>°C</td>
<td>Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006</td>
</tr>
<tr>
<td>( Q_{10} )</td>
<td>factor change in rate with a 10 degree change in temperature</td>
<td>2</td>
<td>unitless</td>
<td>Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
<th>Reference or Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0, b_1, b_2 )</td>
<td>constants</td>
<td>0.559, -0.478, -0.612</td>
<td>unitless</td>
<td>Alexander et al., 2009</td>
</tr>
<tr>
<td>( c^\top )</td>
<td>log re-transform bias correction factor</td>
<td>1.90</td>
<td>unitless</td>
<td>Alexander et al., 2009</td>
</tr>
<tr>
<td>( k_{\text{dinitr,min}} )</td>
<td>minimum reaction rate constant of river denitrification</td>
<td>0.53/86400</td>
<td>1/s</td>
<td>Alexander et al., 2009</td>
</tr>
<tr>
<td>( C_{\text{d,s}} )</td>
<td>unit-conversion constant</td>
<td>1/86400</td>
<td>day/s</td>
<td>conversion from 1/day to 1/s</td>
</tr>
<tr>
<td>( k_{\text{min}}, k_{\text{nitr}} )</td>
<td>reaction rate constants for river mineralization, nitrification</td>
<td>0.11/86400, 0.51/86400</td>
<td>1/s</td>
<td>calibrated to match stream N loads</td>
</tr>
<tr>
<td>( T_p' )</td>
<td>parameter</td>
<td>1.047</td>
<td>unitless</td>
<td>Wade et al., 2002</td>
</tr>
<tr>
<td>( T_r' )</td>
<td>reference water temperature</td>
<td>20</td>
<td>°C</td>
<td>Wade et al., 2002</td>
</tr>
</tbody>
</table>
Table 2.2: Definition of Prognostic (PV) and Diagnostic (DV) Variables and Inputs/Forcings (IF) Used in the Equations

<table>
<thead>
<tr>
<th>Vegetation and Soil Equations</th>
<th></th>
<th>River Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{LF}$, $C_{LS}$, $C_{SS}$</td>
<td>PV</td>
<td>$C_{NO_3^-}$</td>
</tr>
<tr>
<td>$D_N$</td>
<td>DV</td>
<td>$f_T'$</td>
</tr>
<tr>
<td>$D_S$</td>
<td>DV</td>
<td>$F_{DON}^{in}$, $F_{NH_4^+}^{in}$, $F_{NO_3^-}^{in}$</td>
</tr>
<tr>
<td>$f_{LS}$, $f_{SS}$</td>
<td>PV</td>
<td>$F_{DON}^{out}$, $F_{NH_4^+}^{out}$, $F_{NO_3^-}^{out}$</td>
</tr>
<tr>
<td>$f_S$</td>
<td>PV</td>
<td>$H$</td>
</tr>
<tr>
<td>$h_S$</td>
<td>PV</td>
<td>$k_{denitr}$</td>
</tr>
<tr>
<td>$L_{DON}$, $L_{NH_4^+}$, $L_{NO_3^-}$</td>
<td>PV</td>
<td>$P_{DON}$, $P_{NH_4^+}$, $P_{NO_3^-}$</td>
</tr>
<tr>
<td>$N_{NH_4^+}$, $N_{NO_3^-}$</td>
<td>PV</td>
<td>$R_{DON}$, $R_{NH_4^+}$, $R_{NO_3^-}$</td>
</tr>
<tr>
<td>$N_{LF}$, $N_{LS}$, $N_{SS}$</td>
<td>PV</td>
<td>$T'$</td>
</tr>
<tr>
<td>$S$</td>
<td>PV</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>PV</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To compensate for many processes that were not accounted for in the model, calibration factors for each N species were introduced to slow down overall N movement from the soil to the stream. These factors include impacts of soil microbes, which are able to take up and incorporate all N forms (NO$_3^-$ – N, NH$_4^+$ – N, DON) with a much greater capacity than plant uptake [82]. The nitrate calibration factor also accounts for storage in groundwater since nitrate (the primary form of N in groundwater) can persist for decades at high levels with increasing N applications. This is further explained by Bachman et al. (1998) [5] which reported that 17–80% of the N delivered to streams of the Chesapeake Bay watershed was through groundwater. Furthermore, the lumped single-layer N sub-model bypasses most of the vertically distributed hydrologic system, and the soil N leaching based on the average water drainage is transferred directly from the N layer into the stream. These calibration factors were fit to match interannual variations of reported and simulated stream N loads to make up for this modeling approach as well as the unresolved processes that might cause interannual stream N loads to be more sensitive to climate variability than those in reality.

Considering its importance in groundwater, a relatively larger size of the nitrate N factor is expected. The need to incorporate these calibration factors, which are at the present basin specific, indicates that future improvements to LM3-TAN should focus on resolving these processes (i.e., N cycle in microbes, reservoirs, and vertically distributed soil layers). Dissolved organic, ammonium, and nitrate N leaching from the soil are described as:

\[
L_{DON} = \frac{D_S}{\rho_w R_{DOM}} [N_{DON,av}] = \frac{D_S}{\rho_w R_{DOM}} \left( \frac{f_{LFNLF} + f_{LSNLS} + f_{SSNSS}}{b_{DOM} h_s} \right) \tag{2.1}
\]

\[
L_{NH_4^+} = \frac{D_S}{\rho_w R_{NH_4^+}} [N_{NH_4^+,av}] = \frac{D_S}{\rho_w R_{NH_4^+}} \left( \frac{N_{NH_4^+}}{b_{NH_4^+} h_s} \right) \tag{2.2}
\]
\[ L_{NO_3^-} = \frac{D_s}{\rho_w r_{NO_3^-}} N_{NO_3^-av} = \frac{D_s}{\rho_w r_{NO_3^-}} \left( \frac{N_{NO_3^-}}{\rho_{NO_3^- h_s}} \right) \]  

(2.3)

\[ h_s = \frac{CLF + CLS + CSS}{r_c \rho_s} \]  

(2.4)

where, \( L_{DON} \), \( L_{NH_4^+} \), and \( L_{NO_3^-} \) are the dissolved organic, ammonium, and nitrate N leaching from the soil (kg/(m\(^2\) s)); \( D_s \) is the water drainage from the active soil layer (kg/(m\(^2\) s)); \( \rho_w \) is the water density (1000 kg/m\(^3\)); \( r_{DOM} \), \( r_{NH_4^+} \), and \( r_{NO_3^-} \) are dissolved organic matter, ammonium, and nitrate N calibration factors; \( [N_{DON,av}] \), \( [N_{NH_4^+,av}] \), and \( [N_{NO_3^-,av}] \) are the concentration of available N in dissolved organic, ammonium, and nitrate N pools (kg/m\(^3\)); \( N_{LF} \), \( N_{LS} \), and \( N_{SS} \) are the fast litter, slow litter, and slow soil N contents (kg/m\(^2\)); \( f_{LF} \), \( f_{LS} \), and \( f_{SS} \) are the fractions of soluble organic N in the fast litter, slow litter, and slow soil N pools; \( N_{NH_4^+,SS} \) and \( N_{NO_3^-,SS} \) are the soil ammonium and nitrate N contents (kg/m\(^2\)); \( b_{DOM} \), \( b_{NH_4^+} \), and \( b_{NO_3^-} \) are dissolved organic matter, ammonium, and nitrate N buffering factors due to sorption to soil particles; \( h_s \) is the effective soil depth (m); \( r_c \) is the C weight content (3.4%); \( \rho_s \) is the average soil density (1500 kg/m\(^3\)); \( C_{LF} \), \( C_{LS} \), and \( C_{SS} \) are the fast litter, slow litter, and slow soil C contents (kg/m\(^2\)).

### 2.2.4.2 Denitrification in Soil

Denitrification is a process that reduces nitrate or nitrite to gaseous forms (e.g., NO, N\(_2\)O, N\(_2\)) in anaerobic conditions, where the oxidized N species serve as a terminal electron acceptor in metabolism by soil-denitrifying bacteria. The rate of denitrification generally depends on soil nitrate content or concentration, soil water content (a surrogate for oxygen content), and soil temperature. Because soil nitrate contents are relatively low and
limiting under natural conditions, we used a first-order loss function with respect to soil nitrate N content, with adjustments for the influence of soil water content and temperature to simulate soil denitrification rate:

\[ D_N = f_S f_T k_{denitr} N_{\text{NO}_3^-} \]  

where, \( D_N \) is the soil denitrification rate (kg/(m² yr)); \( f_S \) is a soil water content reduction function; \( f_T \) is a soil temperature reduction function; \( k_{denitr} \) is a first-order denitrification coefficient (1/yr); \( N_{\text{NO}_3^-} \) is the soil nitrate N content (kg/m²).

\[ f_T = Q_{10}^{(T-T_r)/T_p} \]  

\[ f_S = \begin{cases} 
S_{min} & S < S_t \\
\left( \frac{S-S_t}{S_{max}-S_t} \right)^w & S_t \leq S \leq S_{max} \\
S_{max} & S_{max} < S 
\end{cases} \]  

where, \( T \) is the soil temperature (°C); \( T_r \) is a reference temperature (°C); \( T_p \) is a parameter; \( Q_{10} \) is a factor change in rate with a 10 degree change in temperature; \( S \) is the soil water content; \( S_t \) is a threshold soil water content; \( S_{max} \) is the maximum soil water content; \( S_{min} \) is the minimum soil water content; \( w \) is an empirical constant.

Heinen (2006) [48] tabulates reported values of the various parameters introduced above. Figure 2.2 shows the effects of the reduction functions on the soil denitrification rate that were applied in diverse models as well as LM3-TAN. Figure 2.2a shows how fast soil nitrate N content is reduced to half of the initial amount depending on the different first-order denitrification coefficients. As temperature increases the
bacterial activities increase exponentially (Figure 2.2b). Soil denitrification occurs and increases nonlinearly only if soil water content exceeds a certain threshold point due to enhanced anaerobic bacterial activity (Figure 2.2c). The soil water content reduction function for other microbial processes (e.g., mineralization, nitrification) used in LM3-TAN is also shown in Figure 2.2d. Because $k_{denitr}$ is by far the most widely used parameter of these, with reported values ranging over 3 orders of magnitude, our strategy was to fix the other parameters using reported values and to calibrate the model by

Figure 2.2: Overview of the Denitrification Module.
Effects of first-order denitrification coefficient (a), soil temperature reduction function (b), soil water content reduction function (c) on soil denitrification rate; soil water content reduction function for mineralization and nitrification (d). The curves were produced using the Table 3, 6, and 7 in Heinen (2006) [48].
determining $k_{\text{denitr}}$ within the bounds reported in the literature. Because soil denitrification and nitrate-N leaching are competing sinks of nitrate N in the soil, soil denitrification increases as soil nitrate-N leaching or stream nitrate-N load decreases; thus $k_{\text{denitr}}$ was fit to match reported and simulated stream nitrate-N loads.

The wide ranges of the functions discussed above are mostly driven by the dependencies of the parameters on specific regions (with different soil properties, vegetation, land use, etc.). Given a number of proposed individual functions, it seems that there is no universal process module to simulate soil denitrification. Because such reduction functions display a diversity of shapes as ecosystems are modeled over a range of climate patterns, vegetation type, and landuse practices, soil denitrification on a large scale cannot be modeled without proper adjustments that compensate for the site-specific properties. This explains why only a few studies have applied models to watersheds larger than 1000 km$^2$ despite the diversity of existing dynamic N models and why semi-distributed models often parameterize these individual functions for each of the sub-basins in large-scale applications.

We hypothesize that LM3-TAN’s integrated modeling framework, which is capable of simulating long-term vegetation functional type and land-use change as a function of changes in CO$_2$, climate, and human influences, allows us to use a universal parameter set to simulate soil denitrification for each of the distinct sub-basins. Still, care has to be taken when applying the model to other watersheds that may be very different in terms of soil and climate properties from the Susquehanna watershed. Furthermore, because soil denitrification becomes zero-order in extreme nitrate-rich environment, instead of using the first-order loss function for all of the land-use types, using a Monod function for agricultural land use may help LM3-TAN’s global application where N
loadings would vary widely.

### 2.2.4.3 Microbial Processes in Rivers

Despite its importance to water quality, processes that control N removal from water bodies are rarely resolved in watershed-scale models, due to both uncertainties in measurement techniques and lack of measurements. To date, none of studies focusing on river denitrification rate is based on measurements of an entire river network, but rather only on the data from low-order streams or individual catchments. Here we applied a nonlinear regression function based on the LINX (Lotic Intersite Nitrogen experiment) [74] reach-scale measurements that correlates river denitrification rate with nitrate-N concentration and river depth to estimate the reaction rate constant of river denitrification for each reach [3]. River denitrification happens mainly in the benthic and/or hyporheic zones. Therefore, a river denitrification rate that is inversely proportional to the river depth accounts for the ratio of water column to benthic area. The measured reaction rate constants vary from 0.034 to 117 (1 day\(^{-1}\)), and we chose the median value 0.53 (1 day\(^{-1}\)) as the minimum reaction rate constant of river denitrification. Equation (2.12) indicates that the reaction rate constant decreases with an increase in nitrate-N concentration and river depth since both \(b_1\) and \(b_2\) are negative, and it increases with temperature. Reaction rate constants for river mineralization and nitrification were calibrated to match stream N loads.

Figure 2.1 shows structure of the river component. Each reach directly receives N from point sources (e.g., sewage and waste-water discharge) and indirectly receives N from non-point sources (e.g., atmospheric deposition, fertilizer, manure, and legume
applications) via soil leaching. The N loads in a reach are routed downstream with the water as following.

\[
\frac{dR_{DON}}{dt} = F_{in}^{DON} - F_{out}^{DON} + L_{DON} + P_{DON} - f_T^{'} k_{min}^{'} R_{DON} \tag{2.8}
\]

\[
\frac{dR_{NH_4^+}}{dt} = F_{in}^{NH_4^+} - F_{out}^{NH_4^+} + L_{NH_4^+} + P_{NH_4^+} + f_T^{'} k_{min}^{'} R_{DON} - f_T^{'} k_{nitr}^{'} R_{NH_4^+} \tag{2.9}
\]

\[
\frac{dR_{NO_3^-}}{dt} = F_{in}^{NO_3^-} - F_{out}^{NO_3^-} + L_{NO_3^-} + P_{NO_3^-} + f_T^{'} k_{nitr}^{'} R_{NH_4^+} - f_T^{'} k_{denitr}^{'} R_{NO_3^-} \tag{2.10}
\]

\[
f_T^{'} = T_{p}^{(T^{'} - T_r^{')}} \tag{2.11}
\]

\[
k_{denitr}^{'} = \max\{k_{denitr,min}^{'}, C_{d,s} (b_0 C_{NO_3^-}^{b_1 H^{b_2 c^{t}}})\} \tag{2.12}
\]

where, \(i\) is \(DON\), \(NH_4^+\), or \(NO_3^-\); \(R_i\) is the river N (kg/m²); \(F_i^{in}\) and \(F_i^{out}\) is the inflow and outflow of the river N (kg/(m² s)); \(L_i\) is the N leaching from the soil (kg/(m² s)); \(P_i\) is the N point source (kg/(m² s)); \(f_T^{'}\) is the stream temperature reduction function; \(T^{'}\) is the water temperature (°C); \(T_r^{'}\) is the reference water temperature (°C); \(T_p^{'}\) is a parameter; \(k_{min}^{'}\), \(k_{nitr}^{'}\), and \(k_{denitr}^{'}\) are the reaction rate constants for river mineralization, nitrification, and denitrification (1/s); \(k_{denitr,min}^{'}\) is the minimum reaction rate constant of river denitrification (1/s); \(C_{NO_3^-}\) is the nitrate N concentration (µmol N/l); \(H\) is the river depth (m); \(b_0\), \(b_1\), and \(b_2\) are the constants; \(c^{t}\) is the log re-transform bias correction factor; \(C_{d,s}\) is a unit-conversion constant.
Figure 2.3: Map of the Susquehanna Watershed.
The map shows six major sub-basins, main stem of the Susquehanna River, major tributaries (Chemung, West Branch Susquehanna, and Juniata River), streams, and the location of USGS stream gauges and USGS and SRBC nutrient monitoring sites.
2.3 Study Site

The Susquehanna River Basin, where nearly 4 million people live, is the largest of the watersheds in the northeastern US and drains an area of 71,220 square kilometers, contributing two-thirds of the annual N load to the Chesapeake Bay (Figure 2.3). The basin includes 2,293 lakes, reservoirs, and ponds (322 km$^2$) as well as 50,190 km of rivers and streams. The main stem of the Susquehanna River originates at Otsego Lake, New York (NY), and flows about 750 kilometers through NY, Pennsylvania (PA), and Maryland (MD) to the Chesapeake Bay at Havre de Grace, MD. The Susquehanna Large River Assessment Project reported that only 6.9% of water-quality values exceeded their standards, but the majority of these exceedances were for nutrients (e.g., TN, TP) [51], explaining why the Chesapeake Bay suffers from nutrient enrichment problems and hypoxia.

The reported year 2000 land use was about 63% forest or wooded, 19% cropland, 7% pasture, 9% urban, and 2% water. The Upper Susquehanna River flows through mostly forested and agricultural land, with some small communities and one larger population center, then confluences with the Chemung River at Sayeare, PA. The West Branch Susquehanna Sub-Basin is mostly woods and grasslands. The Middle Susquehanna River, from the confluences with the Chemung River at Sayeare, PA, to the confluences with the West Branch Susquehanna River at Sunbury, PA, flows along very diverse land use. The Lower Susquehanna Sub-Basin contains extensive agriculture and several large population centers. The other major urban areas are found within the Juniata Sub-Basin [50].

The geology of the watershed is mainly clastic sedimentary rock of sandstone
and shale. Elevations vary from 30 meters at the Chesapeake Bay in Maryland to 955 meters in central New York State [68]. The Great Lakes and Midwest climate exert influence over the Upper Susquehanna, Chemung, and West Branch Susquehanna Sub-Basin, whereas the Atlantic coastal climate affect on the other portions of the watershed. The basin has experienced severe droughts about once every decade, and the worst droughts occurred in 1930, 1939 and 1964. The basin is also one of the most flood-prone watersheds in the nation with frequent and localized flash floods every year. The worst recorded flooding in the basin happened in 1972 as a result of Tropical Storm Agnes.

2.4 Study Sampling Description

Stream discharge data are provided by the network of stream gauges operated by the US Geological Survey (USGS), which collects and summarizes time series data to derive annual, monthly, and daily stream discharge and statistics (Figure 2.3). Chemical constituents of the basin’s water were monitored by the USGS and Susquehanna River Basin Commission (SRBC). One USGS and six SRBC long-term nutrient monitoring sites monitored since 1985 and nine newly introduced SRBC sites monitored since either 2004 or 2005 to the present (Table 2.3; Figure 2.3) [68, 117] were chosen for model evaluation. The 16 sites vary in sub-basin area and land use. Among the USGS and SRBC sites, the Conowingo and Marietta sites on the main channel of the Susquehanna River have the largest sub-basin areas, respectively, 70 189 and 67 314 km². The sub-basin of the Conestoga site contains extensive agriculture (48 %) and the most populated urban land use with several large population centers (24 %) within a very small area (1217 km²). The West Branch River flows mostly along woods and grasslands to the Lewisburg site.
The long-term sites collect two samples per month. Additional samplings are made during seasonal storm conditions. The collected water samples are analyzed for various N species: dissolved N (DN), dissolved nitrite and nitrate (DNO$_{23}$), dissolved ammonia (DNH$_3$), dissolved organic N (DON), and dissolved ammonia and organic N (DKN) in milligrams L$^{-1}$. In addition, annual, seasonal, and monthly loads are computed by the minimum variance unbiased estimator (ESTIMATOR) [105, 112]. River temperatures were reported when the samplings were collected for the chemical analysis of stream waters.

2.5 Anthropogenic N Sources

Anthropogenic N data over two decades (1985–2005) were provided by the Chesapeake Community Modeling Program (CCMP). Atmospheric deposition data were provided by the county-based land segments. Fertilizer, manure, and legume applications as well as combined sewer overflows (CSOs) were provided by the land–river segments of the GIS-based Phase 5.3 Community Watershed Model [115]. The atmospheric deposition data were calculated by the Chesapeake Bay Program (CBP) Airshed Model, which is a combination of a regression model of wet deposition [43] and the Community Multiscale Air Quality Model (CMAQ) that estimates dry deposition [25, 46]. The fertilizer, manure, and legume data were estimated for the years of 1985, 1987, 1992, 1997, 2002, and 2005 by the Scenario Builder Version 2.2, a process-based model that is designed to use agricultural censuses as a main input data [116]. The agricultural censuses were produced by the United States Department of Agriculture National Agricultural Statistics Service (NASS) and include data of animal populations, farms, agricultural land areas, and crop yields. The point sources were estimated by 42 CSO communities within the
Susquehanna basin, using either various versions of EPA’s Storm Water Management Model (SWMM) or spatial data collected as a result of a direct survey of the communities [115]. The detailed data description can be found in the Phase 5.3 Community Watershed Model documentation [115].

Table 2.3: Susquehanna River Basin Geographic Statistics for the USGS and SRBC Nutrient Monitoring Sites [68, 117]

<table>
<thead>
<tr>
<th>Site Location</th>
<th>Waterbody</th>
<th>Subbasin Area, km²</th>
<th>2000 Land Use Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Water/Wetland</td>
</tr>
<tr>
<td>Towanda, 1989~</td>
<td>Susquehanna</td>
<td>20,194</td>
<td>2</td>
</tr>
<tr>
<td>Danville, 1985~</td>
<td>Susquehanna</td>
<td>29,060</td>
<td>2</td>
</tr>
<tr>
<td>Lewisburg, 1985~</td>
<td>W B Susque</td>
<td>17,734</td>
<td>1</td>
</tr>
<tr>
<td>Newport, 1985~</td>
<td>Juniata</td>
<td>8,687</td>
<td>1</td>
</tr>
<tr>
<td>Marietta, 1987~</td>
<td>Susquehanna</td>
<td>67,314</td>
<td>2</td>
</tr>
<tr>
<td>Conestoga, 1985~</td>
<td>Conestoga</td>
<td>1,217</td>
<td>1</td>
</tr>
<tr>
<td>Conowingo, 1985~</td>
<td>Susquehanna</td>
<td>70,189</td>
<td>2</td>
</tr>
<tr>
<td><strong>7 Long-term Sites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conklin, 2005~</td>
<td>Susquehanna</td>
<td>5,778</td>
<td>3</td>
</tr>
<tr>
<td>Smithboro, 2004~</td>
<td>Susquehanna</td>
<td>11,989</td>
<td>3</td>
</tr>
<tr>
<td>Campbell, 2005~</td>
<td>Cohocton</td>
<td>1,217</td>
<td>3</td>
</tr>
<tr>
<td>Chemung, 2004~</td>
<td>Chemung</td>
<td>6,488</td>
<td>2</td>
</tr>
<tr>
<td>Wilkes-Barre, 2004~</td>
<td>Susquehanna</td>
<td>25,785</td>
<td>2</td>
</tr>
<tr>
<td>Karthaus, 2004~</td>
<td>W B Susque</td>
<td>3,785</td>
<td>1</td>
</tr>
<tr>
<td>Castanea, 2004~</td>
<td>Bald Eagle</td>
<td>1,087</td>
<td>1</td>
</tr>
<tr>
<td>Saxton, 2004~</td>
<td>Raystown B Juni</td>
<td>1,957</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Manchester, 2004~</td>
<td>W Conewago</td>
<td>1,320</td>
<td>2</td>
</tr>
<tr>
<td><strong>9 Newly Introduced Sites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.4. Sub-basin Area, 20 Year (1986-2005) Average Applied Non-point and Point N Sources, and Simulated Soil Water Content, Temperature, Nitrate-N Content, and Denitrification Rate (% of the Non-point N Sources) for Each of 6 Sub-basins

<table>
<thead>
<tr>
<th>6 Sub-basins</th>
<th>Basin Area, km²</th>
<th>Non-point N Sources kg/(km² yr)</th>
<th>Point N Sources kg/(km² yr)</th>
<th>Soil Water Content</th>
<th>Soil Temp. C</th>
<th>Soil Nitr. N kg/km²</th>
<th>Soil Denitr. Rate (% of the N Sources)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Susquehanna</td>
<td>14,126</td>
<td>3,315</td>
<td>40</td>
<td>0.439</td>
<td>8.65</td>
<td>12,713</td>
<td>1,213 (37%)</td>
</tr>
<tr>
<td>Chemung</td>
<td>6,731</td>
<td>2,962</td>
<td>76</td>
<td>0.454</td>
<td>8.60</td>
<td>9,888</td>
<td>916 (31%)</td>
</tr>
<tr>
<td>Middle Susquehanna</td>
<td>9,847</td>
<td>3165</td>
<td>331</td>
<td>0.459</td>
<td>9.39</td>
<td>11,599</td>
<td>1,142 (36%)</td>
</tr>
<tr>
<td>West Branch Susquehanna</td>
<td>18,447</td>
<td>3,163</td>
<td>70</td>
<td>0.458</td>
<td>9.24</td>
<td>11,746</td>
<td>959 (30%)</td>
</tr>
<tr>
<td>Juniata</td>
<td>8,686</td>
<td>4,553</td>
<td>41</td>
<td>0.480</td>
<td>10.58</td>
<td>17,002</td>
<td>1,538 (34%)</td>
</tr>
<tr>
<td>Lower Susquehanna</td>
<td>16,070</td>
<td>6,098</td>
<td>163</td>
<td>0.463</td>
<td>10.27</td>
<td>27,358</td>
<td>2,717 (45%)</td>
</tr>
</tbody>
</table>

Over the two decades, the total N sources decreased by about 20%. The atmospheric deposition was predominantly nitrate-N, accounting for about 69%; ammonium-N 27%; organic-N 4%. The sum of the fertilizer, manure, and legume applications consisted of 49% ammonium-N, followed by 37% organic-N, and 14% nitrate-N. In particular, the ammonium-N and organic-N loads had considerable variability across the spatial domain because they were strongly influenced by local emissions from the extensive agricultural areas.

Figure 2.4 shows spatial distribution maps of the applied anthropogenic N sources, which were calculated as a spatial resolution of 0.125° by 0.125° and a temporal resolution of 1 year. For each grid cell, which consists of up to 15 land-use tiles, atmospheric depositions (nitrate-N, ammonium-N, and organic-N) were applied to all of the land tiles, and fertilizer, manure, and legume applications (nitrate-N, ammonium-N,
and organic-N) were applied only to the cropland tiles. Combined sewer overflows (nitrate-N, ammonium-N, and organic-N) were directly applied to the river reaches. The 20 year (1986–2005) average non-point and point N sources for the six sub-basins are summarized in Table 2.4. The thick solid arrows in Figure 2.1 depict fluxes of each of N species for the anthropogenic N sources to the corresponding terrestrial and river pools, respectively.

![Spatial Distribution Maps](image)

Figure 2.4: Spatial Distribution Maps of the Applied 20 Year (1986-2005) Average Anthropogenic N Sources: atmospheric deposition (kg/(km² yr)) (a), combined sewer overflow (kg/(km² yr)) (b), and fertilizer, manure, and legume applications (kg/(km² yr)) (c) and (kg/(crop land km² yr)) (d).

### 2.6 Model Forcing and Simulations

The model was implemented with a spatial resolution of 0.125° by 0.125° with time increments of 30 minutes. The model was forced using reported hydrological data cycled
over a horizon of 61 years (1948–2008) to perform long-term simulations. The data include precipitation, specific humidity, air temperature, surface pressure, wind speed, and short- and long-wave downward radiation with a spatial resolution of 1° by 1° on timescales of 3 hours [99]. Land-use change was simulated from 1704 to 2005 using a scenario of land-use transitions [55]. Preindustrial CO2 concentration assumed as 286 ppm was applied from 1704–1799, and changes in CO2 concentrations were applied from 1800–2005 using reported data from NOAA’s Earth System Research Laboratory. For 250 years (1704–1953), the estimated preindustrial N deposition [26, 40, 42] was applied as a uniform annual rate. We then applied the 1985 reported anthropogenic N data from 1954 to 1984, and reported annual anthropogenic N data from 1985–2005.

2.7 Result and Discussion

2.7.1 Evaluation of Stream Waters and N loads

We simulated with LM3-TAN stream dissolved organic-N, ammonium-N, and nitrate-N loads throughout the river network. The model was calibrated by comparing the modeled stream N loads with the corresponding reported N loads at the last downstream SRBC station Marietta, in which contributions of the entire watershed to the stream flows and N loads can be assessed. Thus, temporal evaluation of the stream discharges and N loads for the period 1987–2005 was focused on at the Marietta station. River data from the 16 monitoring stations (1986–2005) were also used to evaluate spatial stream discharges and N loads.
Using global hydrological data and a universal parameter set for the entire watershed, the model produced reasonable temporal patterns of annual stream discharge. The simulated stream discharges were in good agreement with the reported values in dry years and periods (July to September), but the model underestimated stream discharges in wet years and periods (March to May). Overall, although the 19 year average simulated discharge was about 28% lower than the corresponding reported value, their linear and rank correlations were significantly high (Table 2.5), implying that the bias was systemic and accounted for in the calibration of the N species.

Table 2.5: Temporal Evaluation of the Annual Stream Discharges and N Loads for the Period 1987-2005 at Marietta. If a p-value is smaller than 0.05, the correlation between the modeled and reported data is significantly different from zero.

<table>
<thead>
<tr>
<th></th>
<th>Discharge</th>
<th>DN</th>
<th>Nit. N</th>
<th>Amm. N</th>
<th>DON</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Pearson’s linear</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>(p-value)</td>
<td>(&lt; 0.0001)</td>
<td>(&lt; 0.0001)</td>
<td>(0.0044)</td>
<td>(&lt; 0.0001)</td>
<td>(0.0064)</td>
</tr>
<tr>
<td>Spearman’s rho</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>(p-value)</td>
<td>(0.0011)</td>
<td>(&lt; 0.0001)</td>
<td>(0.0056)</td>
<td>(0.0099)</td>
<td>(0.0160)</td>
</tr>
</tbody>
</table>

Due to their complex physical and biogeochemical interactions with soil particles and soil organic matter, simulating reactive transport of ammonium and dissolved organic N is far more challenging than simulating nitrate N transport. For example, the correlation at Marietta between stream discharge and nitrate N load ($R^2 = 0.98$) was significantly higher than that for dissolved organic N ($R^2 = 0.48$) or for ammonium N ($R^2 = 0.85$) loads, implying that in addition to the hydrological processes governing soil N transport to rivers, terrestrial physical and microbial processes (e.g., sorption to soil particles, organic matter decomposition and stabilization) have to be accounted for when estimating stream ammonium and dissolved organic N loads. This, plus the fact that the
highest component in the overall stream N load is nitrate N, explains why existing watershed models have focused on stream nitrate N loads, and neglected ammonium and dissolved organic N loads. Within the LM3-TAN’s integrated modeling framework, we estimated all of the N species for the entire drainage network.

![Figure 2.5: Simulated River Nitrate-N, Ammonium-M, and DON loads (Normalized by Sub-basin Areas) at the Marietta and Conowingo stations and the Corresponding Reported Data from SRBC and USGS for the Period 1986-2005.](image)

At Marietta, 19 year average simulated stream dissolved-N (−0.5 %), nitrate-N (−0.2 %), ammonium-N (+4.7 %), and dissolved organic-N (−2.6 %) loads were close to the corresponding reported values. Both of the simulated and monitored dissolved-N loads consisted of predominantly nitrate-N (79 %), followed by dissolved organic-N
(18 %), and ammonium-N (3 %). The model also produced reasonable temporal patterns of annual dissolved-N ($r = 0.7$), nitrate-N ($r = 0.6$), ammonium-N ($r = 0.7$), and dissolved organic-N ($r = 0.6$) loads (Figure 5; Table 5). At Conowingo, 20 year average simulated nitrate-N load agreed well with the corresponding reported value (−3.7 %), but the model, which does not have lakes or reservoirs, fails to capture interannual variations of the loads ($r = 0.2$), which are affected by the reservoir system between the Marietta and Conowingo monitoring sites (Figure 2.5).

Simulated and reported dissolved N loads were graphed in different units: millions of kg year$^{-1}$ and kg km$^{-2}$ year$^{-1}$ (normalized by its sub-basin area summarized in Table 2.3). Among the six long-term monitoring sites, the highest and lowest amount of river N loads were reported and simulated at the Marietta and Conestoga sites, respectively (Figure 2.6a). This finding is consistent with the general view that the amount of stream N loads is proportional to the size of the basin area. A very high N flux was reported at the Conestoga site (Figure 2.6b), which can be explained by extensive agriculture and urban land use in its sub-basin. Because the West Branch Susquehanna is dominated mostly by woods and grasslands, the Lewisburg site had the lowest N flux. The model also captured the stream N loads at the 15 monitoring sites well (Figure 2.6c and d). These results attest to the model’s ability to correctly simulate the stream N loads for the entire basin based on the climate as well as land use and the corresponding N sources and transformations in the sub-basins.
Figure 2.6: 17 Year (1989-2005) Average Simulated and Reported (SRBC) Stream N Loads at the 6 Long-term Monitoring Sites in (a) millions of kg/yr and (b) kg/(km² yr); Simulated and Reported Stream N Loads for the Year 2005 at the 15 Monitoring Sites in (c) millions of kg/yr and (d) kg/(km² yr).
2.7.2 Spatial Distribution of Stream N Load and Soil Denitrification Rate

Observation of the spatial distribution of the river N load (Figure 2.7) and soil denitrification rate (Figure 2.8d) helps to identify the extent of the terrestrial and aquatic N pollution across the basin. A large amount of N is exported via the main stem of the Susquehanna River as well as its three major tributaries, where many small-order streams converge. The N loads in the streams increase gradually from the headwaters to the watershed outlet, implying that the N loads to the rivers exceed N removal mechanisms within the rivers. Although stream N loads are in general higher in the larger rivers, at the Lower Susquehanna Sub-Basin, high N loads are present even in small-order streams due to extensive agricultural land use.

Figure 2.7: Spatial Distribution Maps of 20 Year (1986-2005) Average Simulated Stream N Loads: (a) dissolved-N, (b) dissolved nitrate-N, (c) dissolved ammonium-N, and (d) dissolved organic-N loads, log (kg/yr).
Figure 2.8 presents 20 year average (1986–2005) simulated soil water content, temperature, nitrate-N content, and denitrification rate, and these for each of six sub-basins as well as the corresponding sub-basin area, non-point and point N sources are summarized in Table 2.4. An analysis of the six sub-basins shows that the combined effects of land use and climate on the soil denitrification rate, which were the highest in the Lower Susquehanna Sub-Basin (extensive agriculture; Atlantic coastal climate) and the lowest in the West Branch Susquehanna Sub-Basin (mostly forest; Great Lakes and Midwest climate). These results show that the most significant soil denitrification is associated with extensive agricultural land use (non-point sources). The calculated $R^2$ statistic between the monthly soil denitrification rate and soil water content ($R^2 = 0.51$) was significantly higher than that for soil temperature or soil nitrate N content, implying that the soil water content played the greatest role in the soil denitrification process among the three factors. This is because the soil denitrification occurred and increased...
nonlinearly only when the soil water content exceeded the threshold point \( S_t = 0.577 \). The significant effect of the soil water content on the soil denitrification is further illustrated in the upper-east side of the Upper Susquehanna Sub-Basin, where extremely low soil water content (Figure 2.8a) impeded the overall soil denitrification process (Figure 2.8d).

### 2.7.3 N Budget

As a further means of evaluating the model output, we compared the simulated N budget for the period 1988–1992 to the budget constructed by Boyer et al. (2002), Seitzinger et al. (2002), and Van Breemen et al. (2002) [12, 97, 118] for the same period (Figure 2.9). Overall, reasonable agreements were found between these two budgets. Total N inputs to the whole basin were reported as 4774 kg km\(^{-2}\) year\(^{-1}\) (atmospheric deposition + fertilizer + forest and agricultural N fixation + net N import in feed and food), while we applied an N of 4443 kg km\(^{-2}\) year\(^{-1}\) (atmospheric deposition + fertilizer + manure + legume + sewage) using the data sources provided by CCMP [17]. The simulated soil denitrification (−4 %), harvest rates (+7 %), river export (−1 %), and river denitrification (−5 %) agreed well with the corresponding reported values.

To investigate the importance of N removal within rivers, we ran an experiment in which the reaction rate constant for river denitrification was set to zero. We then compared N loads within the rivers with and without river denitrification. Figure 2.10 shows a spatial map of the difference in N loads between these simulations, which represents the river N removal. A large amount of N was removed along the main stem of the Susquehanna River as well as its three major tributaries, implying that the N removal
increases gradually as distance from the headwaters increases. About 28% of the N that enters the rivers was removed by river denitrification.

For the entire basin, we divided the simulated land use into either agricultural land (cropland and pasture) or secondary forest (land formerly disturbed by human activities). We then graphed simplified N budgets for each land use (Figure 2.9c). The reported agricultural land use was 29% (Figure 2.9a), whereas the model simulated 24% of cropland and pasture (Figure 2.9b). In the secondary forest land, most of the applied N (43%) was stored in the terrestrial system (vegetation and soil pools), whereas the

Figure 2.9: Comparison between the Calculated and Reported Budgets: N sources, retention, lost, transport, and river export at the level of the whole Susquehanna Watershed for the period 1988 to 1992 [12, 97, 118].
highest proportion of the applied N was removed by soil denitrification (44 %) in the agricultural land. These results imply that applications of artificial N to agricultural lands can result in considerable soil denitrification rates, and thus significant increase of N2O production. This is evident when comparing maps of the applied fertilizer, manure, and legume N applications (Figure 2.4c and d) and the simulated soil denitrification (Figure 2.8d) that corresponds well, especially in the Lower Susquehanna Sub-Basin with extensive agricultural land use. Even if there are some discrepancies between these two budgets, we can conclude that the reactive transport of N from the terrestrial to aquatic ecosystems was appropriately simulated by the model, providing suitable descriptive information for the entire drainage network.

Figure 2.10: N Removal by River Denitrification (%): river N load with “$k_{denitr}^{'}=0$” – river N load with “estimated $k_{denitr}^{'}$”) / river N load with “$k_{denitr}^{'}=0$” × 100.
2.8 Conclusion

Results of our study show that LM3-TAN captures well the key mechanisms that control N dynamics in the climate–plant–soil–river system. Specifically, we demonstrate:

- On a sub-basin scale with different climate and land-use regimes, the LM3-TAN properly simulates terrestrial N cycling, including effects of long-term vegetation dynamics, land-use changes, and hydrological cycles. The interaction among those three processes allow LM3-TAN to capture soil C-N organic matter and mineral N transformations as well as soil emissions of nitrate-N and leaching of dissolved organic, ammonium, and nitrate N.

- The ability to capture N soil budget and losses then enables LM3-TAN to consistently characterize trends and variability in riverine N inputs and exports of ammonium, dissolved organic, and nitrate N with explicit representation of their transformations and transport in rivers.

- In the re-growing secondary forests, a large fraction of the N from atmospheric deposition has been stored in the vegetation and soil, but in the agricultural lands most N inputs were removed by soil denitrification, indicating that anthropogenic N inputs could drive substantial increase of N2O emission, an intermediate of the denitrification process.

- LM3-TAN captures the effects of long-term trends and variability of hydrological cycles (e.g., precipitation, soil water content, stream discharge) on N cycling in vegetation–soil–river system, and thus resolves interannual variations of stream N loadings caused by climate variability.

- The model results suggest that the soil denitrification is most sensitive to soil water variations.
Among the six sub-basins, the soil denitrification rate was the highest in the Lower Susquehanna Sub-Basin with the most intensive land-use non-point N sources as well as with the warmest and wettest soils, attributed to the Atlantic coastal climate.

Even though the N denitrification and riverine biogeochemistry N modules were calibrated only at the last downstream station Marietta, application of the universal parameters over the entire watershed produced simulations which compared well with other observational stations. The applicability of the universal parameters in other watersheds is a subject of future research.

This study shows that linking terrestrial N and C cycling, long-term land-use and vegetation dynamics, and hydro-climate variations to N loads and concentrations in streams provides an effective and consistent framework for analysis of the surface water N processes and water quality for large watersheds and basins.
Chapter 3

Increasing Climatic Variability and Extremes, Interacting with Nitrogen Storage, Amplify Eutrophication Risk

3.1 Introduction

Many ecological and water-quality problems, such as algal blooms and hypoxia, have been attributed to increasing eutrophication, which threatens freshwater and coastal marine ecosystems worldwide [23, 27, 102, 113]. Most mitigation policies have focused on reducing anthropogenic nutrients discharged from farming, industry, and sewage-treatment plants [30, 58, 67]. However, for large estuaries and near-shore environments (e.g., Chesapeake Bay, Baltic Sea), such nutrient reductions over decades have not achieved intended water-quality improvements [19, 20, 76]. For example, despite the ambitious Baltic Sea Action Plan to cut both phosphorus (P) and N inputs, the ‘dead zone’ (low oxygen area) in the Baltic Sea remains, with only small improvements of water quality and with expected recovery only after many decades [20]. A possible mechanism
could be substantial ecosystem (i.e., vegetation, soil, groundwater) nutrient storage, which has been accumulated over multiple decades [92]. At the same time, previous observational studies linked individual water-quality issues (e.g., high N load/concentration, chlorophyll-a; hypoxia) to hurricanes [70, 85], droughts [14, 34, 60, 73], or inter-annual river flow variability [1, 44]. Thus, current water-quality problems appear to be a combination of the slow response to legacy effects of long-term (~ multi-decades) anthropogenic N perturbations and the fast response to short-term (~ years) climatic perturbations.

Evidence has mounted that ongoing climate change is associated with more frequent and intense extreme weather events [9, 21, 41, 57], and related adverse risks to ecosystems and humans are expected to increase [87]. Nonetheless, the mechanisms by which the changing climate influences the delivery of anthropogenic N inputs into receiving waters remain unclear. These mechanisms are likely to be complex and nonlinear, and have not been explored because most previous modeling frameworks rely on empirical relationships that do not account for the legacy effects.

Prolonged absence or reduction of precipitation can decrease runoff and promote N stores in soil and groundwater, whereas tropical storms, hurricanes, or strong snowmelts can result in increased river flows (volume of water per time) [70, 85], elevated river N loads (mass of N per time) [85], and enhanced soil microbial processes (e.g., mineralization, nitrification) [60]. Here we focus on analysis of N loads in the Susquehanna River to understand implications of interactions between increasing climatic variability/extremes and N stores for water quality under N-pollution mitigation, using the process-based terrestrial-aquatic model LM3-TAN [65]. The Susquehanna River drains an area of 71,220 km², contributing about half of annual N loads to the
Chesapeake Bay, the largest estuary in the U. S. Despite three decades of basin-wide N waste-reduction efforts, the bay still suffers from eutrophication.

3.2 Materials and Methods

3.2.1 Reported River Flows and DN Loads

The reported seasonal and annual river flows and DN loads at the Marietta station (Figure 3.1-3.4) are provided by the U. S. Geological Survey (USGS) [117] and the Susquehanna River Basin Commission (SRBC) Sediment and Nutrient Assessment Program (SNAP) [105, 107]. Marietta is the last downstream SRBC station, and its sub-basin covers 95% (67,314 km²) of the Susquehanna Watershed. Thus, contributions of the entire watershed to the flows and DN loads can be assessed at this station. See chapter 2 for the watershed and station descriptions.

3.2.2 Deviations of Previous Flows and Subsequent DN Loads

In Figure 3.3b-e, ‘previous-four-season mean flow deviations’ are the four-season running mean flows (1987 spring to 2009 winter; 88 running means in total) minus the mean flow and ‘subsequent seasonal DN load deviations’ are the seasonal DN loads (1988 spring to 2009 winter) minus the corresponding DN loads for given flows by the all-season regression. The residual variance around the all-season regression increases as flows increase (Figure 3.3a). Thus, a log scale is used to bring out the variability in lower
flow conditions, which prevents the explained variance from being dominated by the high
flow conditions. In Figure 3.4, ‘previous-four-year mean flow deviations’ are the four-
year running mean flows (1983-2009; 23 running means in total) minus the mean flow
and ‘subsequent annual DN load deviations’ are the annual DN loads (1987-2009) minus
the corresponding DN loads for given flows by the regression between the annual flows

3.2.3 Model Simulations

In Chapter 2, LM3-TAN has been applied for the entire river network in the Susquehanna
Watershed and evaluated using long-term (1986-2005) reported data from 16 monitoring
sites [65]. The simulated annual river DN loads at Marietta agreed well with the
corresponding reported data ($r = 0.7$; Figure 3.1b).

Starting from the Lee et al., 2014 simulation (1704-2005; spin-up simulation)
[65], holding all the other inputs (e.g., anthropogenic N inputs) the same as in 2005, we
ran 4 simulations with various lengths of dry spells (4 drying segments: D1, D2, D3, D4;
(Table 3.1; Figure 3.5), 4 simulations with different histories of extreme high
precipitation (4 wetting segments: W1, W2, W3, W4), and 1 simulation with one normal
year (No). The gamma distribution was fitted to annual precipitation from the 1948-2008
forcing [99]. Its lower and upper percentiles are used as hydrological dry and wet indices
(Figure 3.5). For each of the above 9 simulations, we ran 61 annual simulations with
individual climate years from the 1948-2008 forcing. We then constructed 9 probability
density functions of DN load from the 549 experiments (Figure 3.7).
3.2.4 Distribution Fitting

The gamma distribution is fitted to (1) the reported 1932-2013 annual and seasonal river flows at the Marietta station (Figure 3.2a-e), (2) the 1948-2008 annual precipitation from the 61-year forcing [99] (Figure 3.5), and (3) the 9 groups of 61 simulated annual river DN loads at the Marietta Station. The parameters are estimated with Maximum Likelihood Estimation (MLE) using the R package fGarch. The goodness-of-fit of the distributions is evaluated by the one-sample Kolmogorov-Smirnov test (K–S test) using the R package stats.

Table 3.1: 9 Initialization Segments.

4 drying segments D1-D4, 4 wetting segments W1-W4, and 1 normal segment No are defined based on annual precipitation from the 1948-2008 forcing.

<table>
<thead>
<tr>
<th>D4</th>
<th>D3</th>
<th>D2</th>
<th>D1</th>
<th>N</th>
<th>W1</th>
<th>W2</th>
<th>W3</th>
<th>W4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 normal yr + 4-yr long dry spell</td>
<td>3-yr long dry spell</td>
<td>2-yr long dry spell</td>
<td>1 dry yr (lowest precip.)</td>
<td>1 normal yr (avg. precip.)</td>
<td>1 normal + 1 drier + 1 wet + 2 normal yrs</td>
<td>1 wet + 2 normal yrs</td>
<td>1 wet + 1 normal yrs</td>
<td>1 wet yr (intense precip., Hurricane Agnes)</td>
</tr>
</tbody>
</table>
3.3 Results and Discussion

3.3.1 Influences of Anthropogenic N Inputs and River Flows on River N Loads

Fertilizer and manure applications, municipal and industrial wastewaters, and emissions of oxidized reactive nitrogen (NOx) in the Chesapeake Bay were controlled by adoption of agreements among participating jurisdictions and government agencies to meet nutrient reduction goals during 1983-2008 [19, 76]. As a result, reported annual atmospheric N deposition, fertilizer- and manure-N applications, and point N sources (e.g., sewage, industrial wastewaters) imply an overall 17 percent decrease of anthropogenic N inputs to the Susquehanna Watershed from 1984 to 2005 (Figure 3.1a). However, this N-input reduction does not appear to be manifested in reported (1987-2009) or simulated (by LM3-TAN) (1987-2005) annual river dissolved nitrogen (DN) loads at the Marietta station (40.02' N, 76.32'W) (Figure 3.1b), whose sub-basin covers 95% of the Susquehanna Watershed. This indicates that mechanisms determining N-input transformation and transport to rivers can significantly modulate the relationship between anthropogenic N inputs to watersheds and N loads in rivers. Also, the high correlation between reported 1987-2005 annual DN loads and flows (R²=0.986) suggests that on annual-to-decadal time scales the influence of hydroclimatic conditions and resultant river flows on the DN loads outweighs the influence of the decreasing anthropogenic N inputs. Furthermore, this analysis suggests that it may require multiple decades to see effects of N-mitigation policies on freshwater N loads and associated water-quality trends.
Figure 3.1: Influences of River Flows and Anthropogenic N inputs on River N Loads.
a, reported (1984-2005) annual atmospheric N deposition (squares), fertilizer (circles) and manure (asterisks) N applications, and point N sources (i.e., sewage, industrial wastewaters) (diamonds) [17].

b, reported (1987-2009) and simulated (1987-2005) [65] (bold line) annual river DN loads at the Marietta station. c-f, reported (1987-2009) seasonal DN loads for winter (c), spring (d), summer (e), and fall (f). The line styles represent regressions (black solid) and averages (black dotted). The markers represent the seasonal flows during which historical crests (filled circles) and extreme weather events (squares) (Table 3.2) happened.
3.3.2 Seasonal Hydroclimatic Variability and N-load Anomalies

The Susquehanna Watershed is characterized by a strong seasonal hydrological cycle (Figure 3.2b-e), with extreme dry-wet transitions in river flow from summer to fall and winter and wet-dry transitions from winter and spring to summer. Regressions between reported 1987-2009 seasonal river flows and DN loads at the Marietta station (Figure 3.3a; Figure 3.1c-f) show strong correlations between the flows and DN loads. We find that fall and winter runoff brings higher DN loads than those for given flows by the all-season regression (black solid line in Figure 3.3a); this is due to N accumulation during the dry periods (summer) and enhanced microbial processes in the following wetter periods (fall and winter) [14, 34, 60, 73]. In contrast, spring and summer DN loads per unit flow are lower than those given by the all-season regression, and this is consistent with observations that Chesapeake Bay primary production is often limited by N in summers [62]. This result is consistent with the hypothesis that high disparities in hydroclimatic conditions in successive seasons amplify river N-load anomalies due to interactions between N stores and runoff variability. More broadly, it is indicative of a critical role of hydroclimatic variability in riverine and estuarine eutrophication.

3.3.3 Interannual Hydroclimatic Variability and N-load Anomalies

Analysis of long-term (1932-2013) reported annual river flows at the Marietta station (Figure 3.2a) reveals complex patterns of hydroclimatic extremes and variability over the
Figure 3.2: Increased Hydroclimatic Variability and Extremes.
a-e, reported 1932-2013 annual and seasonal total river flows (F) at the Marietta station; regressions (black solid), averages (black dotted), lower (red dotted)/upper (blue dotted) 15th percentiles, historical crests (filled circles), extreme weather events (squares) (Table 3.2). f-j, 20-year moving variances of de-trended flows (MF); regressions (black solid).
The colors represent spring (green), summer (red), fall (yellow), and winter (blue). a, Regressions between reported 1987-2009 seasonal river flows and DN loads at the Marietta station; winter ($R^2=0.993$), spring ($R^2=0.978$), summer ($R^2=0.997$), fall ($R^2=0.997$), and all seasons ($R^2=0.976$). b-e, Regressions between previous-four-season mean flow deviations from the flow mean and subsequent seasonal DN-load deviations from the all-season regression (log-scale), with Pearson’s correlations ($r$) and p-values ($p$). For each season, the markers show if the seasonal DN loads are lower (circles) or higher (squares) than the seasonal DN-load means.

entire watershed: (1) dry spells in the 1960s (1965, 1963, 1969, 1966; lower 15\textsuperscript{th} percentile of the flow distribution; See the Methods), (2) prolonged wet periods in the 1970s (1972, 1975, 1977, 1979; upper 15\textsuperscript{th} percentile), and (3) severe variability in the 1990s (lower/upper 15\textsuperscript{th} percentiles; 1995, 1999, 1991/1996, 1994, 1993). Twenty-year moving variances of de-trended flows also show that inter-annual (Figure 3.2f) and -
seasonal (Figure 3.2g-j) hydroclimatic variability generally increased over the last eight decades.

The historical crest (highest river levels above a flood stage) data with ranks (1\textsuperscript{st} ~ 36\textsuperscript{th}) at the Marietta station since the late 19\textsuperscript{th} century (Figure 3.2b-e; Table 3.2) are provided by the NOAA National Weather Service. Lower ranks of the crests indicate more severe crests. During the 1930-40s, 1950-60s, and 1970-80s, the historical crests occurred seven times respectively, but the frequency increased to eleven times during the 1990-2000s. Sum of the ranks of the seven crests are much lower in the 1970-80s, compared to those in the 1930-40s and 1950-60s. These data imply that hydroclimatic extremes in the watershed became more frequent since the 1930s and more intense since the 1970s, perhaps as a result not only of climatic variability, but also of land use.

In addition, many of the highest recorded crests were caused by hurricanes (1\textsuperscript{st}, Agnes in 1972; 4\textsuperscript{th}, Irene in 2011; 6\textsuperscript{th}, Ivan in 2004; 7\textsuperscript{th}, Eloise in 1975) or a Nor’easter (5\textsuperscript{th}, in 1996) (Figure 3.2b-e; Table S1). The data also suggest that many severe summer hypoxic (DO < 0.2 mg l\textsuperscript{-1}) volumes in the Chesapeake Bay during 1950-2001 [44] and volumes of Chesapeake Bay’s summer ‘dead zone’ during 1985-2013 [18] are associated with winter or spring crests. River flows are in general well correlated with river N loads, and inferred N distributions are related to hypoxia, algal blooms or chlorophyll a in estuarine or coastal waters [1, 44, 70, 94]. Thus, these analyses demonstrate the influences of extreme weather events on crests, and in turn, on eutrophication-associated water-quality problems.

Unlike flow data, basin-wide observations of aqueous chemical constituents are seldom available for long-term periods to analyze impacts of changing climate and its
Table 3.2: Increased Hydroclimatic Extremes’ Frequency and Intensity.

<table>
<thead>
<tr>
<th>Historical Crests at Marietta</th>
<th>Flood Stage (14.9352 m)</th>
<th>Extreme Weather Events which Affected the Entire Susquehanna Watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Stage (m)</td>
<td>Rank</td>
</tr>
<tr>
<td>1889 6/2</td>
<td>17.7698</td>
<td>3</td>
</tr>
<tr>
<td>1933 8/25</td>
<td>15.0693</td>
<td>34</td>
</tr>
<tr>
<td>1936 3/19</td>
<td>18.5105</td>
<td>2</td>
</tr>
<tr>
<td>1940 4/2</td>
<td>16.255</td>
<td>11</td>
</tr>
<tr>
<td>1942 5/24</td>
<td>15.1272</td>
<td>31</td>
</tr>
<tr>
<td>1943 1/1</td>
<td>16.2154</td>
<td>14</td>
</tr>
<tr>
<td>1946 5/29</td>
<td>16.7335</td>
<td>8</td>
</tr>
<tr>
<td>1948 4/16</td>
<td>15.1394</td>
<td>30</td>
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</tbody>
</table>

1930 and 1940s
Frequency: 7; Sum. of Ranks: 130

<table>
<thead>
<tr>
<th>Date</th>
<th>Stage (m)</th>
<th>Rank</th>
<th>Extreme Weather Events which Affected the Entire Susquehanna Watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950 11/27</td>
<td>16.1422</td>
<td>15</td>
<td>Great Northeast Snowstorm, 2/3-4</td>
</tr>
<tr>
<td>1950 3/30</td>
<td>15.0236</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>1952 3/13</td>
<td>15.3406</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>1956 3/10</td>
<td>15.3162</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>1960 4/2</td>
<td>15.6393</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>1961 2/27</td>
<td>15.7947</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>1964 3/12</td>
<td>16.4683</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

1950 and 1960s
Frequency: 7; Sum. of Ranks: 150

<table>
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<th>Date</th>
<th>Stage (m)</th>
<th>Rank</th>
<th>Extreme Weather Events which Affected the Entire Susquehanna Watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 4/4</td>
<td>15.3833</td>
<td>24</td>
<td>Hurricane Agnes, 6/14-23</td>
</tr>
<tr>
<td>1972 6/23</td>
<td>19.6718</td>
<td>1</td>
<td>Hurricane Eloise, 9/13-24</td>
</tr>
<tr>
<td>1975 9/27</td>
<td>16.9865</td>
<td>7</td>
<td>President’s Day Snowstorm #1, 2/19</td>
</tr>
<tr>
<td>1979 3/7</td>
<td>16.2184</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>1981 2/24</td>
<td>15.1059</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>1984 2/16</td>
<td>16.3038</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1986 3/16</td>
<td>15.7033</td>
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1970 and 1980s
Frequency: 7; Sum. of Ranks: 107

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</tr>
</thead>
<tbody>
<tr>
<td>1993 4/12</td>
<td>15.0754</td>
<td>33</td>
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</tr>
<tr>
<td>1994 3/26</td>
<td>15.5478</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>1996 1/21</td>
<td>17.3126</td>
<td>5</td>
<td>Nor’easter, 1/6-13</td>
</tr>
<tr>
<td>1996 1/28</td>
<td>15.1729</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>1998 1/10</td>
<td>15.301</td>
<td>28</td>
<td>Ice Storm, 1/4-10</td>
</tr>
<tr>
<td>2004 9/19</td>
<td>17.1511</td>
<td>6</td>
<td>Hurricane Ivan, 9/2-24</td>
</tr>
<tr>
<td>2005 4/4</td>
<td>15.7612</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>2005 3/30</td>
<td>15.3162</td>
<td>26</td>
<td>Nor’easter, 1/5-12</td>
</tr>
<tr>
<td>2006 6/29</td>
<td>16.0111</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

1990 and 2000s
Frequency: 11; Sum. of Ranks: 234

<table>
<thead>
<tr>
<th>Date</th>
<th>Stage (m)</th>
<th>Rank</th>
<th>Extreme Weather Events which Affected the Entire Susquehanna Watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011 9/9</td>
<td>17.7272</td>
<td>4</td>
<td>Hurricane Irene, 8/21-30</td>
</tr>
<tr>
<td>2011 3/12</td>
<td>16.1117</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2011 4/29</td>
<td>15.5905</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

Summer Volume (%)

- 1970: 27.5%
- 1972: 26.5%
- 1975: 30%
- 1979: 28%
- 1981: 21.9%
- 1984: 24%
- 1986: 24%
- 1993: 27.5%
- 1994: 26.5%
- 1996: 28%
- 1998: 28%
- 2004: 28%
- 2005: 28%
- 2006: 28%
- 2011: 27.5%
interannual variability and extremes on water quality. Mechanistic models provide a means of exploring these mechanisms, which have large implications for optimal nutrient loading controls, as additional data is collected. Unlike most previous models, which focused on either terrestrial [40] or aquatic [95] N cycling, LM3-TAN captures key mechanisms describing N dynamics across the vegetation-soil-river system [65]. Specifically, LM3-TAN is capable of capturing decadal-to-century changes in nutrient stores (e.g., vegetation, soil) in response to climate change and land-use and land-cover changes (LULCC) [55]. Thus, it allows us to investigate legacy effects of long-term anthropogenic N perturbations as well as the influence of climatic variability on water quality (e.g. river N-loading variability).

We find negative relationships between previous-four-season mean flow deviations and subsequent seasonal DN-load deviations (Figure 3.3b-e; See the Methods). These suggest that lower previous-four-season flows are likely to result in higher DN loads in following seasons (i.e., one-year memory effects on seasonal DN loads). These relationships, however, are not statistically significant for winter or spring and would require more data for validation. We also find that both reported (1987-2009) and simulated (1987-2005) annual DN-load deviations have significant negative relationships with reported previous-four-year mean flow deviations (Figure 3.4; See the Methods), which demonstrates that higher (lower) annual DN loads can arise from multi-year dry (wet) spells (i.e., multi-year memory effects on annual DN loads). This result shows LM3-TAN’s capability to capture the DN-load responses to interannual hydroclimatic variability, although the model has somewhat stronger sensitivity of the DN loads to previous-year flows than in the real world.
3.3.4 Interaction between Climatic Variability and N Storage

Here we analyze 9 groups of numerical experiments with LM3-TAN to explore implications that hydrologic preconditioning by climatic variability and extremes has for river N-loads. Starting from a common spin-up simulation, we run 4 simulations with dry
spells ranging from 1-4 years (4 drying segments: D1, D2, D3, D4), 4 simulations with different histories of extreme high precipitation (4 wetting segments: W1, W2, W3, W4), and 1 simulation with one hydrological normal year (No) (Table 3.1; Figure 3.5; see the Methods). For each of the above 9 simulations, we then run 61 annual simulations with individual climate years taken from the 1948-2008 forcing [99] (549 experiments in total). The drying segment D1 corresponds to the driest year (1963) in the 61-year forcing. For the wetting segment W4, we use climate from 1972 – a year with the most intense summer precipitation event (from hurricane Agnes) and the second wettest annual precipitation amount in the forcing.

![Figure 3.5: Annual Precipitation.](image)

The gamma distribution is fitted to the 61 year annual precipitation from the 1948-2008 forcing [99]. Its lower and upper 5th, 10th, and 15th percentiles are used as hydroclimatic dry and wet indices. This analysis reveals complex patterns of hydroclimatic extremes and variability over the entire Susquehanna Watershed: (1) a dry spell in the 1960s, (2) prolonged wet periods in the 1970s, and (3) severe hydroclimatic variability in the 1990s.
Simulated annual mean river DN load in the W4 experiment is 83 percent higher than in the D1 experiment (Figure 3.6a) due to enhanced soil DN leaching (+ 109%; Figure 3.6b) and stimulated soil microbial processes, such as mineralization (+ 22%; Figure 3.6c) and nitrification (+ 21%; Figure 3.6d). Furthermore, elevated soil denitrification in W4 (+ 471%; Figure 3.6e) indicates that the extreme wet condition results in substantial N losses from the soil nitrate-N store. In contrast, in D1, vegetation and soil lose less N during the extreme dry condition. For example, simulated annual mean soil nitrate-N content in W4 is 14% less than in D1 (Figure 3.6h). The high annual mean soil denitrification in W4 is caused by higher soil water content (+ 32%; Figure 3.6f), rather than soil temperature (no significant difference; Figure 3.6g) or soil nitrate-N content (- 14%; Figure 3.6h). This result suggests that lower soil nitrate-N storage in an extreme wet year is not sufficient to attenuate soil denitrification, while increased soil water content promotes denitrification sufficiently, so the overall outcome is enhanced denitrification.

To characterize river DN-load responses to interactions between N storage and climatic variability, we constructed 9 probability density functions of DN load, using the 61 corresponding experiments for each of the 9 initialization segments (Figure 3.7; see the Methods). The DN-load distribution following the one driest year (D1) has higher mean (+ 12%), standard deviation (+ 16%), and extremes (i.e. lower/upper 5th percentiles, + 12% / + 13%) than the distribution following the normal year (No) (Figure 3.8). The longer the antecedent dry spells (D2, D3, D4) are, the higher are means, standard deviations, and extremes in the obtained DN-load distributions. After the 4-year dry spell, which happened in 1962-1965 (D4), the distribution has 44% and 51% higher mean and standard deviation compared to the distribution for No. In contrast, after the extremely wet condition (W1), the distribution has lower mean (- 15%), standard deviation (- 13%),
Figure 3.6: Interaction between N Stores and Climatic Perturbations.
Model simulations in the drying segment D1 and the wetting segment W4 are compared by \( \frac{(W4 - D1)}{W4} \times 100 \), % for annual mean river DN loads (a), soil-DN leaching (b), soil mineralization (c), soil nitrification (d), soil denitrification (e), soil water contents (f), and soil-nitrate N contents (h) and by W4 – D1 for annual mean soil temperature (g).
and extremes (i.e. lower/upper 5th percentiles, -16% / -15%) compared to that for No. Even after precipitation in subsequent 1-2 years returns to normal states, the extreme N-flushing effect is still evident in the subsequent years, that is, the distribution for W2 (i.e., after 1 extremely wet and 1 normal year) and W3 (i.e., after 1 extremely wet and 2 normal years) have very similar shapes to that for W1 (i.e., after just 1 extremely wet year). However, a drier year (e.g. 1971 with 22% lower precipitation than the normal year) before the one extremely wet year reduces the N-flushing effect, resulting in only 6% and 4% lower mean and standard deviation of the distribution for W4 compared to No.

Our analysis suggests that dry preconditioning of the watershed appears to have stronger impacts on river N-load deviations than wet preconditioning. In addition, because both means and standard deviations of the distributions increase with the length of antecedent dry spells, the risks of extreme N loads and resultant eutrophication also increase. For example, after the 4-year dry spell, the likelihood to exceed threshold DN loads of 56 and 68 millions of kg yr\(^{-1}\) (reported 1998 and 1993 values at the Marietta station when Chesapeake Bay’s summer ‘dead zone’ volumes were much higher than the 1985-2013 average) increases by 86% and 44% (Insert in Figure 3.7). As we have seen (Figure 3.3), wet years result in high DN loads. When this fact is combined with the sensitivity to dry preconditioning discussed above, we can make the generalization that increasing hydroclimatic variability and extremes (both dry and wet) act to increase N loads above what they would otherwise be.
Figure 3.7: River N-load Responses to Interaction between N Storage and Climatic Variability/Extremes.

9 distributions of DN load following the segments D4 (red dotted), D3 (red dashed), D2 (red long dashed), D1 (red solid), No (green solid), W4 (blue solid), W3 (blue dotted), W2 (blue dashed), and W1 (blue long solid). The hydroclimatic variability in the distributions following the drying (wetting) segments increases in the right (left) direction. The subplot shows right-hand side percentages of the thresholds 56 and 68 (millions of kg yr$^{-1}$) for each distribution. The likelihood to exceed the thresholds increases from the wettest (following W1) to driest (following D4) distributions.
This study illuminates the combined effects of short-term (~ years) climatic and long-term (~ multi-decades) anthropogenic N perturbations, and the resultant soil N stores, on N releases into freshwaters. Model simulations (Figure 3.8) show that: substantial organic N had been accumulated for multiple decades; although climate-stimulated soil microbial processes transformed only a small portion of organic N to mobile inorganic N, promoted

### 3.4 Conclusion

...
inorganic nitrate-N storage led to fast responses of river nitrate-N loads that account for about 70% of DN loads in the river [65].

Figure 3.9: Soil N Storage and Microbial Processes.
LM3-TAN simulates six soil N stores with different turnover times (fast and slow litter, slow and passive soil, nitrate and ammonium) [40, 100]. Model simulations show that substantial organic N had been accumulated for multiple decades; although climate-stimulated soil microbial processes transformed only a small portion of organic N to mobile inorganic N, promoted inorganic nitrate-N storage led to fast responses of river nitrate-N loads that account for about 70% of DN loads in the river [65].

In conclusion, river N loads and subsequent water-quality problems in large ecosystems such as the Susquehanna Watershed respond strongly to climatic variability
and extremes that interact with different N stores, but only slowly to year-to-decadal changes in anthropogenic N inputs. This contrast could explain recent extensive hypoxia in the Chesapeake Bay [44] under increased climatic variability and extremes, despite the basin-wide nutrient waste-reduction efforts over decades. If long dry spells as well as hurricane-strength precipitation were to become more prevalent, the risks of extreme N loads and eutrophication events would increase. Thus, effective mitigation strategies must account not just for anthropogenic N inputs and climatic trends but also for changes in climatic variability and extremes.
Chapter 4

Dynamic Modeling to Explore River Basin Management Strategies for Reducing Coastal Eutrophication: Korean Peninsula Case Study

4.1 Introduction

Human activities, such as legume/rice cultivation and fossil fuel combustion, have dramatically increased reactive nitrogen (Nr), such as inorganic reduced (e.g., ammonium: \( \text{NH}_4^+ \)) and oxidized (e.g., nitrate: \( \text{NO}_3^- \)) forms of nitrogen (N), and its movement through ecosystems and environmental reservoirs [37, 38, 101]. The substantial magnitude of this ‘new’ Nr production is problematic, as excess Nr can be extremely detrimental to the functioning of the various ecosystems [36]. For example, eutrophication (‘excessive plant growth due to nutrient enrichment’) is the primary environmental issue facing surface waters worldwide [52, 102, 103, 104], because not only it results in many undesirable
ecological (e.g. species [23, 119]) and water-quality (e.g., algal blooms, hypoxia or dead zone [27; 104]) problems but also it causes economic costs [90]. The eutrophication process is accelerated by human activity in densely populated urban or agricultural regions, where point N sources discharged from sewage-treatment plants supplement high levels of non-point N sources produced from vehicles or fertilization [53], which sometimes called ‘cultural’ eutrophication [104].

In many of the world’s estuaries and coastal marine ecosystems, N limits biological productivity [114], and thus the substantial N supply via large rivers is a major cause of over-stimulating plant growth in the ecosystems. Previous studies related large rivers’ N loads to problems associated with eutrophication in estuarine or coastal waters, such as algal blooms [1, 70, 85, 86, 113] and hypoxia or dead zone [44, 62, 85, 94]. Inarguably, elevated downstream N loads of the large rivers have received considerable scientific and political attention [53].

Stream restoration strategies for reducing river N loads have been documented [22]; for example, the greatest N-removal opportunities are given for small-order streams, which include considerable N loads, during low to moderate flows [3, 89, 31], with enhanced in-stream carbon availability [8, 45, 121] or enhanced connections between streams and adjacent terrestrial environments [33, 60]. However, until more is known about how much N could be removed by stream restoration alone, it should be a complement to land-based best management practices [22]. Implementing basin-wide management practices is an expensive enterprise. Dynamic modeling with mechanistic models provides a mean of exploring appropriate sites for land-use management, as potential approaches are tested in various landscape contexts for effective nutrient loading controls. Nonetheless, there is little modelling study that indentifies sites where
the potential for reducing downstream N loads is high. Here we quantify downstream N-removal benefits with respect to ecosystem components (e.g., climate, land use, sub-basin location) to prioritize sites for N-loading controls, using a novel application of the mechanistic model LM3-TAN (Terrestrial and Aquatic Nitrogen) [65]. LM3-TAN’s comprehensive modeling framework is, unlike previous models, capable of capturing decadal-to-century key N dynamics in the vegetation-soil-river in response to changes in land use [55] as well as climatic trends and variability.

Despite decades of countrywide N waste-reduction efforts, frequently observed “Red tides” in estuarine and coastal waters around the Korean Peninsula indicate severe land-originated N pollution. In this study, we simulated stream and river flows and N loads throughout the entire drainage networks in South Korea at a 1/8° resolution. We then evaluate the modeled flows and nitrate-N loads using data from 11 flow and 11 nutrient monitoring sites in five river basins for the period 1999-2010. In addition, we provide forecasts of N loads using various N reduction scenarios with and without inter-annual climatic variability observed during the past 63 years (1948-2010) [99]. Finally, we use these model results to critically assess, under N-pollution mitigation, the roles of various ecosystem components on downstream N loads based on calculated N-removal efficiency ratios.
4.2 Methods and Materials

4.2.1 Study Site

South Korea is located on the southern part of the Korean Peninsula. The country is surrounded by the sea on three sides: Sea of Japan (east), Yellow Sea (west), and Korea Strait (south) and is composed of five river basins: Han, Nakdong, Gum, Sumjin, and Youngsan River Basins (Figure 4.1; Table 4.1). A humid continental climate exerts influence over much of the Korean Peninsula and a humid subtropical climate affects on areas along the coast. The reported land use for the year 2006 was about 63.8% forest or other wooded land, 19.0% arable and permanent crop land, 0.5% permanent grass land, and 16.7% other areas [84].

Table 4.1: Basin area, Basin-wide Mean Anthropogenic N-input Rates in 2010, and Basin-wide Means of Annual Precipitation from 2010 Climatic Forcing Data [99] for the 11 MOLIT Flow and 11 NIER Nutrient Monitoring Sites.

<table>
<thead>
<tr>
<th>Station Number</th>
<th>River Basin</th>
<th>Flow Station</th>
<th>Water Quality Station</th>
<th>Basin Area km²</th>
<th>N-input Rate kg km⁻² yr⁻¹</th>
<th>Precipitation mm yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Han</td>
<td>Hangangdaegyo</td>
<td>Yeongdeungpo</td>
<td>25,232</td>
<td>2,924</td>
<td>1,475</td>
</tr>
<tr>
<td>2</td>
<td>Han</td>
<td>Yeongwol</td>
<td>Yeongwol1</td>
<td>2,448</td>
<td>2,488</td>
<td>1,364</td>
</tr>
<tr>
<td>3</td>
<td>Han</td>
<td>Yeongwol1</td>
<td>Pyeongchanggang3</td>
<td>1,773</td>
<td>2,524</td>
<td>1,364</td>
</tr>
<tr>
<td>4</td>
<td>Nakdong</td>
<td>Samrangjin</td>
<td>Samrangjin</td>
<td>22,892</td>
<td>3,131</td>
<td>1,444</td>
</tr>
<tr>
<td>5</td>
<td>Nakdong</td>
<td>Andong Dam</td>
<td>Dosan</td>
<td>1,584</td>
<td>2,219</td>
<td>1,209</td>
</tr>
<tr>
<td>6</td>
<td>Nakdong</td>
<td>Hapcheon Dam</td>
<td>Hwanggang1</td>
<td>925</td>
<td>3,316</td>
<td>1,679</td>
</tr>
<tr>
<td>7</td>
<td>Geum</td>
<td>Gongju</td>
<td>Gongju1</td>
<td>7,150</td>
<td>3,345</td>
<td>1,536</td>
</tr>
<tr>
<td>8</td>
<td>Seomjin</td>
<td>Gurye2</td>
<td>Gurye</td>
<td>3,810</td>
<td>3,891</td>
<td>1,759</td>
</tr>
<tr>
<td>9</td>
<td>Seomjin</td>
<td>Seomjingang Dam</td>
<td>Unam</td>
<td>763</td>
<td>3,423</td>
<td>1,730</td>
</tr>
<tr>
<td>10</td>
<td>Yeongsan</td>
<td>Yeongsanpo</td>
<td>Yeongsanpo</td>
<td>2,142</td>
<td>5,995</td>
<td>1,626</td>
</tr>
<tr>
<td>11</td>
<td>Yeongsan</td>
<td>Mareuk</td>
<td>Gwangju2</td>
<td>684</td>
<td>5,901</td>
<td>1,524</td>
</tr>
</tbody>
</table>
Among the OECD countries, South Korea displays one of the highest rates of economic growth and the highest population density [84] in an area of 100,210 km² (2014 estimates: 51 millions in total, 509 inhabitants km⁻²). While the economy and population grew substantially, strong pressures on water and energy resources led to many fresh and coastal water-quality problems [83, 84]. In 2004, only about one third of 194 river sections met their quality targets [84]. By enacting rigorous legislation for river-basin management, progress was made to the extent; for example, the Green Vision 21 target was reached a few years early for the country’s four main water supply reservoirs [83, 84]. However, challenges still remain, concerning nutrient pollution in air, rivers, and coastal zones, which is mainly resulted from high emissions of oxidized reactive nitrogen (NOₓ) by a rapid increase in the number of vehicles [84].

### 4.2.2 Monitoring Sites

Twenty two monitoring stations were chosen to evaluate the model results for the period 1999-2010: 11 flow monitoring stations, operated by the Ministry of Land, Infrastructure and Transport (MOLIT) [72]; 11 nutrient monitoring stations, operated by the National Institute of Environmental Research (NEIR) [78] (Figure 4.1; Table 4.1). The Hangangdaegyo/Yeongdeungpo, Samrangjin, Gongju/Gongju1, Gurye2/Gurye, and Yeongsanpo stations are respectively on the main channel of the five rivers: Han, Nakdong, Geum, Seomjin, and Yeongsan Rivers, and have the largest basin areas among the chosen stations. Thus, contributions of the most or many parts of the basins to the river flows and N loads can be assessed in these stations.
Figure 4.1: Map of the Five River Basins in South Korea. The map shows main stem of the five rivers, their major tributaries, and the locations of the 11 MOLIT flow and 11 NIER nutrient monitoring sites.
The water samples were analyzed for total nitrogen (TN), dissolved nitrogen (DN), dissolved nitrite (NO$_2^-$) and nitrate (NO$_3^-$) nitrogen (DNO$_{23}$-N), and dissolved ammonium (NH$_4^+$) nitrogen (DNH$_4$-N) in mg L$^{-1}$. The data show that the sums of the DNO$_{23}$-N and DNH$_4$-N from some stations are higher than the DN. Because nitrate is not likely to be attached to soil particles, DNO$_{23}$-N should not be very different from total nitrite (NO$_2^-$) and nitrate (NO$_3^-$) nitrogen (TNO$_{23}$-N). However, if the water samples were not filtered or coarse filters were used, it may have resulted in overestimation of DNH$_4$-N. Thus, here we only use DNO$_{23}$-N data for model evaluation. We refer to DNO$_{23}$-N as nitrate-N from here on.

### 4.2.3 Model Forcing and Simulations

The model was implemented with a 1/8° resolution and 30-minute timescale. The model’s hydrological component was forced by reported global climatic data [99], which include precipitation, specific humidity, air temperature, surface pressure, wind speed, and short- and long-wave downward radiation with a 1° resolution and 3-hour timescale. The data were cycled over a horizon of 63 years (1948-2010) to perform long-term simulations from 1381 to 2010. A scenario of land-use transitions [55] was used to simulate land-use changes from 1700 to 2005. Preindustrial CO$_2$ concentration assumed as 286 ppm was applied from 1704 to 1799, and annual CO$_2$ concentrations were applied from 1800 to 2005 using reported data from the NOAA’s Earth System Research Laboratory. Estimated preindustrial atmospheric deposition N inputs were applied as a uniform annual rate from 1381 to 1950 [26, 40, 42], and annual 1999-2010 anthropogenic N-inputs were cycled to perform simulations from 1951 to 2010. The anthropogenic N-input database was provided by NEIR [79].
The database includes 9 N-input datasets: three anthropogenic N sources of atmospheric deposition, agriculture (fertilizer + manure + legume), and sewage discharge, and each of the N sources have three N species (nitrate-N, ammonium-N, organic-N). The N inputs in this database were somewhat underestimated, because the data were produced without accounting for some anthropogenic N sources in/to the basins, such as partially treated municipal wastewaters during the time with very high precipitation and imported N for feed and food from outside the basins. For each grid cell, which consists of up to 15 land-use tiles, atmospheric deposition N inputs were applied to all of the land tiles, whereas agricultural N inputs were applied only to the cropland tiles. Sewage discharge N inputs were directly applied to the river reaches. Each of the N species for the three N sources was applied to the corresponding terrestrial and river pools respectively. See Lee et al. [65] for detailed model structure and N movement description.

4.2.4 Anthropogenic N-input Reduction Scenarios

After the evaluation period 1999-2010, the model was run from 2011 to 2073 using the 2010 climatic forcing [99] cycled for the next 63 years (that is, without inter-annual climatic variability) and different anthropogenic N inputs. The input data were modified by multiplying the following constant percentages, compared to the averages in 1999-2010, to the N-input rates (kg km\(^{-2}\) yr\(^{-1}\)) in each of the 9 input datasets.

- **Scenario 1**: Use the N inputs as in 2010; that is an increase of 3%
- **Scenario 2**: Reduce the N-input rates in a single step by 6%, 23%, and 39%
- **Scenario 3**: Reduce the atmospheric deposition N-input rates in a single step by 23% and use the other N inputs as in 2010
Scenario 4: Reduce the agricultural N-input rates in a single step by 23% of and use the other N inputs as in 2010.

Scenario 5: Gradually reduce the N-input rates by 0.10% yr\(^{-1}\), 0.36% yr\(^{-1}\%), and 0.62% yr\(^{-1}\) (6%, 23%, and 39% by 2073).

To account for the effect of inter-annual climatic variability, the model was also run from 2011 to 2073 using the 63 year (1948-2010) climatic forcing [99] and the different N inputs described above. In addition, the model was run, for each of 6 different grouped sub-basins in the Yeongdeungpo station’s basin (Figure 4.2; Table 4.2), using 23% reduced atmospheric deposition N-input rates and the other N inputs as in 2010 without inter-annual climatic variability.

Table 4.2: Sub-basin Area, Distance from the Yeongdeungpo Station to the Grouped Sub-basins, and Basin-wide Mean atmospheric N-input Rates and Total N inputs in 2010 for the Grouped Sub-basins within the Yeongdeungpo Station’s Basin.

<table>
<thead>
<tr>
<th>Group</th>
<th>Subbasins</th>
<th>SubBasin Area km(^2)</th>
<th>Distance from Yeongdeungpo m</th>
<th>N-input Rate, kg km(^{-2}) yr(^{-1})</th>
<th>N Input millions of kg yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 2</td>
<td>4,221</td>
<td>204,004</td>
<td>2,543</td>
<td>10.74</td>
</tr>
<tr>
<td>2</td>
<td>3, 4</td>
<td>4,098</td>
<td>132,852</td>
<td>2,795</td>
<td>11.46</td>
</tr>
<tr>
<td>3</td>
<td>4, 5, 6</td>
<td>3,630</td>
<td>97,310</td>
<td>3,072</td>
<td>11.15</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>2,073</td>
<td>61,814</td>
<td>5,497</td>
<td>11.39</td>
</tr>
<tr>
<td>5</td>
<td>9, 10, 12</td>
<td>4,371</td>
<td>128,871</td>
<td>2,601</td>
<td>11.37</td>
</tr>
<tr>
<td>6</td>
<td>13, 14, 15</td>
<td>3,048</td>
<td>61,814</td>
<td>3,340</td>
<td>10.18</td>
</tr>
</tbody>
</table>
Figure 4.2: Map of the Yeongdeungpo Station’s Basin. The map shows the 16 sub-basins, main stem of the Han River and its two major tributaries (NHR and SHR), and the location of the Yeongdeungpo Station.
4.3 Results and Discussion

4.3.1 River Flow and Nitrate-N Load Evaluation

Stream and river flows and N loads throughout the entire drainage networks in South Korea were simulated by LM3-TAN for the period 1999-2010. Although the model’s biogeochemical component was adjusted to account for the underestimated anthropogenic N inputs by comparing the simulated nitrate-N loads to reported data at the Yeongdeungpo station (126°96’E, 37°51’N), the same parameters were used for the entire country, which is composed of five river basins with varying climate and land use. The Yeongdeungpo station is the Han River’s last downstream station and its basin covers 96% of the Han River Basin (26,219 km²), the largest river basin in South Korea. The adjusted 7 parameters from Lee et al. (2014) [65] are listed in Table 4.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
<th>Reference or Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{DOM}$, $r_{NH_4-}$, $r_{NO_3-}$</td>
<td>calibration factors for DOM, ammonium-N, nitrate-N</td>
<td>1, 2, 3</td>
<td>unitless</td>
<td>calibrated to match inter-annual variations of stream N loads</td>
</tr>
<tr>
<td>$k_{LF}$, $k_{LS}$, $k_{SS}$</td>
<td>Decomposition rates of fast litter/soil and slow soil (Gerber et al., 2010)</td>
<td>18.5, 4.8, 0.2</td>
<td>1/year</td>
<td>Parton et al., 1993; Bolker et al., 1998; Gerber et al., 2010</td>
</tr>
<tr>
<td>$k_{denitr.min}$</td>
<td>minimum reaction rate constant of river denitrification</td>
<td>0.11/86400</td>
<td>1/s</td>
<td>Alexander et al., 2009</td>
</tr>
</tbody>
</table>

Using global climatic forcing data [99], the model’s hydrological component [71] simulates river flows well (Figure 4.3); that is, 12-year average flows at all of the stations, except at the Gurye2 station on the Gum River (+54%), are in good agreement with the
corresponding reported values (-25% ~ +11%). The model also simulates the temporal patterns of annual flows at the 11 monitoring stations well (Spearman’s correlation, \( r_s = 0.61 ~ 0.96, p < 0.04 \)) (Figure 4.3).

The model’s integrated components simulate river nitrate-N loads reasonably well (Figure 4.4-6). Twelve-year average nitrate-N loads are compared well with the corresponding reported values at all of the stations (-39% ~ +18%), except at the Gurye station (+126%) (Figure 4.4-5). In general, river N loads are closely linked to river flows [47]. Thus, the underestimated flows at Gurye2 appear to have contributed to the lower
Figure 4.4: Spatial Distribution Map of the Simulated 12 Year (1999-2010) Average Stream and River Nitrate-N Loads, log(kg yr$^{-1}$).

nitrate-N loads in the river. The result also shows that both the simulated and reported
nitrate-N loads at most of the stations are proportional to the size of their basins. However, this linear relationship is not shown at some stations and their basins; for example, the nitrate-N loads at the Gwangju2 station (its basin area: 684 km$^2$) is much higher than those at the Dosan station with a larger basin area (1,584 km$^2$), which is explained by very high anthropogenic N-input rate (5,901 kg km$^{-2}$ yr$^{-1}$) and precipitation (1,524 mm yr$^{-1}$) in the Gwangju2 station’s basin, compared to those in the Dosan station’s basin (anthropogenic N-input rates: 2,219 kg km$^{-2}$ yr$^{-1}$ precipitation: 1,209 mm yr$^{-1}$) (Table 4.1).

Figure 4.6: Temporal Patterns of the Simulated 12 Year (1999–2010) Annual River Nitrate-N Loads at the 11 Nutrient Monitoring Stations Compared with the Corresponding Reported Data with Spearman’s Correlations (rs).
Although the model failed to capture temporal patterns of annual nitrate-N loads at some stations, such as the Gongju1, Gurye, and Yousanpo stations ($r_s = 0.10 \sim 0.28$), which is perhaps affected by unmodeled processes (e.g., by reservoirs or construction), the simulated and reported loads are correlated well at other stations, such as the Yeongdeungpo, Pyeongchanggang3, Dosan, and Gwangju2 stations ($r_s = 0.55 \sim 0.83$, $p < 0.07$) (Figure 4.6). These results attest to the model’s capability to simulate the stream and river nitrate-N loads as well as flows for the entire country in response not only to different land-use practices and associated anthropogenic N sources but also to climatic trends and variability.

### 4.3.2 The Role of Ecosystem N Storage

After the evaluation period 1999-2010, stream and river N loads were forecasted using the N-input reduction scenarios and the 2010 forcing cycled for the next 63 years (See Section 4.2.4). This experimental analysis allows us to investigate, under various N-pollution mitigation scenarios, how ecosystem N storage and relevant N transformation and transport mechanisms affect river water quality, without considering the influence of inter-annual climatic variability.

The model results illustrate that after immediate decreases in the N inputs (Scenarios 1-4), it takes about 25-48 years to reach new equilibriums for river nitrate-N loads at the 11 stations; for example, the nitrate-N loads at the Yeongdeungpo station reach steady states 40 years after the N-input decreases (Figure 4.7). The model results also illustrate that the nitrate-N loads do not respond linearly to the N-input changes; that is, the nitrate-N loads at the Yeongdeungpo station average 45 kt yr$^{-1}$ in 1999-2010, and
then, for the N-input changes to the basin of +3%, -6%, -23%, and -39% (Scenarios 1-2), the nitrate-N loads in the river respectively increase or decrease to averages of 47 (+5%), 38 (-15%), 29 (-35%), and 21 (-54%) kt yr\(^{-1}\) in 2062-2073 (Figure 4.7). In addition, when the N inputs are presumed to continuously decrease by 0.62% yr\(^{-1}\) (39% decrease by 2073; Scenario 5), the nitrate-N loads decrease up to 50% compared to the average in 1999-2010 (Insert in Figure 4.7 and Figure 4.7). These results demonstrate that if there is a considerable excess in anthropogenic N sources to basins, a decrease in the N sources will lead to a larger N-pollution reduction effect in rivers. It appears that only a certain range of the N sources can be used for ecosystem processes, such as plant uptake, sorption to soil particles, and soil microbial processes, and this make the overall mechanism, which influences the delivery of anthropogenic N into receiving waters, nonlinear.

In addition, holding all the other N inputs the same as in 2010, the immediate 23% reduction in the atmospheric deposition N-input rates (Scenario 3) and agricultural N-input rates (Scenario 4) respectively leads to a 31% decrease and a 1% increase in averages of river nitrate-N loads at the Yeongdeungpo station in 2062-2073 compared to the average in 1999-2010 (Figure 4.7). The 1% increase is attributed to the higher atmospheric deposition N inputs in 2010 than the averages in 1999-2010. This finding is consistent with observations that TN at 118 sites in the Han River Basin has a significant positive relationship with urban land use, but it has a negative relationship with agricultural land use, although the negative relationship is not significant [15]. The reduced use of nitrogenous chemical fertilisers by 29% during 1997-2003 [84] can also explain this finding. This result highlights the present and future vulnerability of this ecosystem to atmospheric N pollution, and suggests that mitigation efforts should be focused on urban land-use management to reduce NO\(_X\) from the transport sector.
The Role of Climatic Variability

After the evaluation period 1999-2010, stream and river N loads were forecasted using the N-input reduction scenarios and the 1948-2010 forcing for the next 63 years (See Section 4.2.4). This experimental analysis allows us to illustrate the range of nitrate-N loads without inter-annual climatic variability (See section 4.2.4).

Figure 4.7: Forecasted River Nitrate-N Loads Using the N-input Reduction Scenarios without Inter-annual Climatic Variability (See section 4.2.4).

4.3.3 The Role of Climatic Variability

After the evaluation period 1999-2010, stream and river N loads were forecasted using the N-input reduction scenarios and the 1948-2010 forcing for the next 63 years (See Section 4.2.4). This experimental analysis allows us to illustrate the range of nitrate-N
loads that is expected, for each of the scenarios, given inter-annual climatic variability observed during the past 63 years (1948-2010).

Figure 4.8: Forecasted River Nitrate-N loads Using the N-input Reduction Scenarios without and with Inter-annual Climatic Variability (See section 4.2.4).

Comparison between the results using the 2010 forcing and the 1948-2010 forcing (Figure 4.8) demonstrates that short-term inter-annual climatic variability can significantly mask the effects of reduced N inputs to basins on N loads in rivers. The model simulates nitrate-N loads of 34-66 kt yr\(^{-1}\) in 1999-2010, the lowest loads in 2000, 2009, and 2005 and the highest loads in 2003 and 2010. The 0.62% yr\(^{-1}\) N-input rate reduction (39% decrease by 2073; Scenario 5) without inter-annual climatic variability
leads to nitrate-N loads of 28-51, 23-27, and 21-23 kt yr\(^{-1}\) respectively in the three 12-year time periods of 2011-2022, 2023-2034, and 2035-2046 (Figure 4.7), whereas the same N-input reduction with the inter-annual climatic variability leads to nitrate-N loads of 50-66, 40-48, and 33-39 kt yr\(^{-1}\). Specifically, the highest loads in each of the three time periods are respectively 31\%, 77\%, and 71\% higher in the simulations with inter-annual climatic variability than in those without inter-annual climatic variability. These results suggest that policy makers should consider setting goals based on not only long-term climatic trends but also short-term inter-annual climatic variability which could significantly diminish N reduction effects on reducing river N pollution.

### 4.3.4 The Role of Climate

The 11 sites vary in anthropogenic N-input rate and precipitation (Figure 4.1; Table 4.1). The Youngsanpo station’s basin has the highest basin-wide mean N-input rates in 2010 (5,995 kg km\(^{-2}\) yr\(^{-1}\)) among the 11 sites, due to its extensive agricultural lands (28\%), whereas the Dosan station’s basin has the lowest rates (2,219 kg km\(^{-1}\) yr\(^{-1}\)), as it contains mostly forest or other wooded lands. The 11 basin-wide means of annual precipitation from the 2010 forcing vary from 1,209 mm yr\(^{-1}\) in the Dosan station’s basin to 1,759 mm yr\(^{-1}\) in the Gurye station’s basin.

We use the model results with the 23\% reduced N-input rates (Scenario 2) without inter-annual climatic variability to calculate, for each of the 11 stations and their basins, an efficiency ratio as a percentage decrease of river nitrate-N loads at the station after it reaches a new equilibrium divided by a percentage decrease of the N inputs to the station’s basin. We find that the basin-wide mean annual precipitation has a strong
negative relationship with the efficiency ratios ($r = -0.82, p = 0.002$; Figure 4.9), but there is no significant relationship between the N-input rates and efficiency ratios ($r = -0.04, p = 0.92$). This result supports the hypothesis that as precipitation and resultant runoff increase, N-removal efficiency decreases. In addition, on annual-to-decadal time scales, the influence of climatic conditions on N removal effectively outweighs the influence of land use and associated N sources in the five river basins in South Korea.

Figure 4.9: The Relationship between the Basin-wide Means of Annual Precipitation and Efficiency Ratios for the 11 Stations and Their Basins, with Pearson’s Correlations ($r$) and $p$-values ($p$). The numbers identify the 11 stations in Table 4.1.
4.3.5 The Role of Land-use and Sub-basin Location

To minimize the influence of climatic conditions and explore implications that land use and basin location have for reducing downstream N loads, we focus here on the Yeongdeungpo station and its basin. This station is near to the outlet of the Han River, the largest river in South Korea. Han River is of special concern for its severe N enrichment problems [15], as it is the primary water source for drinking, irrigation, and industrial use for about 24 million people (about half of the country’s population), who live in the densely populated Seoul-Incheon metropolitan and surrounding area. The river also contributes eutrophication in the Han River estuary, resulting in undesirable ecological changes in the ecosystem [56].

Table 4.10: The Relationships of the Efficiency Ratios with (a) the 6 Grouped Sub-basin-wide Means of N-input Rates and (b) Distances from the Yeongdeungpo Station to the 6 Grouped Subbains, with Pearson’s Correlations (r) and p-values (p). See Table 4.2.
The Yeongdeungpo station’s basin consists of 16 sub-basins with varying land use and associated N-input rates. The basin includes Han River’s two major tributaries: South Han River (SHR) and North Han River (NHR) (Figure 4.2). The SHR flows along extensive agricultural land and relatively larger residential districts (sub-basins 1-7), whereas the NHR flows through mostly forested land, with a few small residential districts (sub-basins 9-15). The main stem of the Han River originates at the confluence of the SHR and NHR, and flows through the Seoul metropolis (sub-basins 8, 15, and 16) to the Yellow Sea. We divided the 16 sub-basins into 6 groups by combining 1 to 3 sub-basins (Table 4.2). We attempted for each of the groups to have similar amounts of total atmospheric deposition N inputs (10.18-11.46 kt yr\(^{-1}\)), but with varying areal atmospheric N deposition rates (2543-5497 kg km\(^{-2}\) yr\(^{-1}\)). We focus on the deposition because, as we have seen (Section 4.3.2), it is the primary source of N pollution in this basin, and which is expected to increase due to continuously growing population and traffic.

We analyze 6 simulations, which were run, for each of the 6 different grouped sub-basins, using 23% reduced atmospheric deposition N-input rates without inter-annual climatic variability. For each simulation, we calculate an efficiency ratio as a percentage decrease of river nitrate-N loads at the Yeongdeungpo station after it reaches a new equilibrium divided by a percentage decrease of the N inputs to the station’s basin. This experimental analysis allows us, under N-pollution mitigation, to investigate the effects of basin location as well as land use and associated anthropogenic N sources on reducing downstream N loads near to river outlets (or coasts).

We find that the efficiency ratios have a strong positive relationship with the N-input rates (r = +0.85, p = 0.06; Figure 4.10a), while they have a strong negative relationship with the distances from the sub-basins to the Yeongdeungpo station (r = -0.79,
p = 0.03; Figure 4.10b; Table 4.2). The sub-basin 7 has the highest N-removal efficiency, which can be explained by its extremely high N inputs per unit area as well as its close location to the station. In contrast, the group 1 (sub-basins 9, 10, 12) and the group 5 (sub-basins 1, 2) have the lowest efficiencies for the opposite reasons compared to the sub-basin 7. Specifically, if 5% of the N inputs to the entire basin are reduced within the sub-basin 7, it would effectively reduce 11% of river nitrate-N loads (difference of the efficiencies: 1.37-1.26 = 0.11, that is, 264,000 kg yr\(^{-1}\)) more than reducing the same amount of the N inputs in the group 1 (sub-basins 9, 10, 12). Such high N-removal efficiencies for sub-basins near to river outlets can be explained by relatively insufficient travel time that is given for N-removal processes (e.g., denitrification) and by generally decreasing N removal rates toward downstream due to increasing river depth (or size) [3, 4]. This result supports the hypothesis that downstream N-removal efficiency increases, as human land-use increases and distances from sub-basins, where N-pollution mitigation is applied, to river outlets decrease.

## 4.4 Conclusion

In this study, we show that dynamic modelling with the mechanistic model LM3-TAN allows us to critically assess the roles of various ecosystem components on potentially altered anthropogenic N perturbations and their affects on river N pollution, given climatic variability and trends observed during the past 63 years (1948-2010). Specifically, we demonstrate:

- By adjusting only 7 parameters from the Susquehanna River Basin study [65] to account for the underestimated anthropogenic N inputs and by using the same
parameters for the entire country (100,210 km²), which is composed of five river basins with varying climate and land use, the model simulated spatial (11 sites) and temporal (1999-2010) patterns of flows and nitrate-N loads well. Main uncertainties are inherent in the database due to the unaccounted N sources in/to the basins, such as partially treated municipal wastewaters and imported N for feed and food from outside the basins.

- During basin-wide N waste-reduction efforts over decades, the substantial ecosystem (i.e., vegetation, soil, river) N storage can significantly modulate the relationship between decreased anthropogenic N sources to basins and resultant N loads in rivers. It appears that a certain range of the N sources can be used for ecosystem processes (e.g., plant uptake), and this makes the overall mechanism, which influences N transformations in basins and its transport into rivers, non-linear. This indicates that if there is a considerable excess in anthropogenic N sources to basins, a decrease in the excess N sources will lead to a larger N-pollution reduction effect in rivers. However, this also indicates that an increase in the excess N sources will result in severe N pollution not only in rivers but also other ecosystems; for example, in forested lands, most of N tends to be stored in the vegetation and soil, but in agricultural lands provided with a large amount of artificial fertilizers, most of N tends to be removed by runoff and soil denitrification, indicating that substantial anthropogenic N sources could promote N₂O production, an intermediate of the denitrification process [65, 118].

- Effective river basin management strategies should account for the roles of various ecosystem components on reducing N loads via large rivers discharged to estuarine and coastal waters, and thus on reducing coastal eutrophication: (1) major anthropogenic N sources should be identified (e.g., atmospheric N deposition in the Han River Basin), (2) goals in reducing N sources should be set
on basis not only of long-term climatic trends but also of short-term inter-annual climatic variability since the variability can significantly mask the effects of the reduced N on river N loads, and (3) sub-basins for land-use management should be prioritized based on their potential to effectively reduce downstream N loads; for example, the greatest N-reduction effects on downstream N loads discharged to coasts are given for sub-basins with low precipitation, close to the coasts, and with much human land use.
Chapter 5

Design of a Riverine/Estuarine Biogeochemistry Model: Coupled Nutrient and Algal Dynamics

5.1 Model Structure and Equations

In the Chapter 1, the roles of nutrient (i.e., N, P) and algae on aquatic ecosystems and how they are associated with water-quality problems (e.g., eutrophication) were discussed. Because nutrient cycles are closely linked with algal photosynthesis, respiration, and decay, modeling their dynamics together will help to obtain better simulations. This chapter designs a simple modeling framework that couples N, P, and algal dynamics, which could serve as a medium of biogeochemical bonding between land and ocean components of Earth System Models. In particular, along with a dynamic regulatory model [39] that predicts net growth rates of algae with respect to irradiance, water temperature, and nutrient availability, the framework will be expanded to include N and P
cycles. Bowie et al. (1985) [11], Chapra (1997) [16], and Geider et al. (1997) [39] are used as primary references for the design of model structure and equations.

Figure 5.1: Riverine/Estuarine Biogeochemistry Model Structure.
This figure shows a conceptual outline of the model formulation. The boxes represent N, P, C, and chlorophyll a in algae, sediment, particulate/dissolved organic nutrient and dissolved inorganic nutrient pools. The arrows depict fluxes of the N, P, C, and chlorophyll a with associated processes. The capital letters (N, C, P, A) represent elements or compounds and the small letters (a, s, p, d, (i,a), (i,n), and (i,o)) represent pools.
5.1.1 Algae

Algal dynamics are governed by net growth (i.e., gross growth – respiration and excretion) and mortality (i.e., non-predatory mortality + grazing + settling) (Figure 5.1). For a batch system, a mass balance is written for algae as:

\[
\frac{dN_a}{dt} = \mu(I, T, N, P) \cdot N_a - m(T)
\]  

(5.1)

where, \(N_a\) is a algae N concentration \((\frac{g\ N}{m^3})\); \(\mu(I, T, N, P)\) is an algae net growth rate \((\frac{1}{s})\) as a function of irradiance \(I\), temperature \(T\), nitrogen \(N\), and phosphorus \(P\); \(m(T)\) is an algae mortality \((\frac{g\ N}{m^3\ s})\) as a function of \(T\).

Algae N is converted to algae carbon \((C)\), \(P\), and chlorophyll \(a\) using stoichiometric ratios.

\[
Ca = Na \cdot c_{cn}
\]  

(5.2)

\[
Pa = Na \cdot c_{pn}
\]  

(5.3)

\[
Aa = Ca \cdot c_{ac}
\]  

(5.4)

where, \(Ca\) is an algae C concentration \((\frac{g\ C}{m^3})\); \(Pa\) is an algae P concentration \((\frac{g\ P}{m^3})\); \(Aa\) is an algae chlorophyll a concentration \((\frac{g\ chl}{m^3})\); \(c_{cn}\) is an algae carbon-to-nitrogen ratio \((\frac{g\ C}{g\ N})\); \(c_{pn}\) is an algae phosphorus-to-nitrogen ratio \((\frac{g\ P}{g\ N})\); \(c_{ac}\) is an algae chlorophyll a-to-carbon ratio \((\frac{g\ chl}{g\ C})\).
5.1.1.1 Algae Net Growth Rate

A dynamic regulatory model is used to predict the chlorophyll a-to-carbon ratio ($c_{ac}$) and net growth rate ($\mu$) with respect to irradiance, water temperature, and nutrient availability [39]. The model results suggested that imbalance between the rate of light absorption and the energy demands for photosynthesis and biosynthesis makes microalgal cells to adjust the $c_{ac}$ [39]. The $\mu$ is simulated by the difference between the photosynthesis and respiration/excretion rates. The effects of temperature and nutrient availability on the algae growth are combined to the carbon-specific light-saturated photosynthesis rate ($P_m^C$). A commonly used formulation, theta ($\theta$) model based on the Arrhenius or van’t Hoff equation, is applied to account for the effect of temperature ($\theta = 1.066$) [32]. To combine the limiting effects of nutrients, Liebig’s law of the minimum formulation is used. An ammonium preference factor is used to account for inhibition of nitrate uptake when ammonium concentrations are high compared to an ammonium half-saturation constant [35, 108]. The concept of Michaelis-Menten (1913) [69] is used for handling the P limiting effect.

$$\mu(I, T, N, P) = \frac{P_m^C}{1 + \zeta} \left[1 - \exp \left(\frac{-\alpha_{ch}l_{aw} c_{ac}}{P_m^C} \right) \right]$$

(5.5)

$$c_{ac} = \max \left[ c_{ac,\min}, \frac{c_{ac,\max}}{1 + (\frac{c_{ac,\max} a_{ch} l_{aw}}{2P_m^C})} \right]$$

(5.6)

$$P_m^C(T, N) = \frac{P_{max}}{\theta_{\mu,m}^{T-T_{ref}}} \cdot \min [(\lim_{Ni,n} + \lim_{Ni,a}), \lim_{Pi,o}]$$

(5.7)

$$\lim_{Ni,n} = \frac{Ni,n}{(k_{Ni,n} + Ni,n) + (1 + \frac{Ni,a}{k_{Ni,a}})}$$

(5.8)

$$\lim_{Ni,a} = \frac{Ni,a}{k_{Ni,a} + Ni,a}$$

(5.9)
\[ \text{lim}_{p_{i,o}} = \frac{p_{i,o}}{k_{p_{i,o}} + p_{i,o}} \] (5.10)

where, \( P^c_m \) is a carbon-specific, light-saturated photosynthesis rate \( \left( \frac{l}{s} \right) \); \( P^c_{\text{max}} \) is a carbon-specific, light-saturated photosynthesis rate at a reference temperature \( T_{\text{ref}} \) \(^\circ\text{C}\) under nutrient-repletion conditions \( \left( \frac{l}{s} \right) \); \( \zeta \) is a cost of biosynthesis; \( \alpha^\text{chl} \) is a chlorophyll a-specific initial slope of the photosynthesis-light curve \( \left( \frac{g \text{ C m}^2}{g \text{ chl \mu mol photons}} \right) \); \( I_{av} \) is a 24-hour integrated, euphotic zone averaged irradiance \( \left( \frac{\text{watts}}{\text{m}^2} \right) \); \( c_{\text{ac,min}} \) is a minimum algae chlorophyll a-to-carbon ratio \( \left( \frac{g \text{ chl}}{g \text{ C}} \right) \); \( c_{\text{ac,max}} \) is a maximum algae chlorophyll a-to-carbon ratio \( \left( \frac{g \text{ chl}}{g \text{ C}} \right) \); \( \theta_{\mu,m} \) is an algae growth and mortality rate temperature correction factor, 1.066; \( \text{lim}_{\text{Ni,n}} \) is a nitrate limitation; \( \text{lim}_{\text{Ni,a}} \) is an ammonium limitation; \( \text{lim}_{\text{Pi,o}} \) is an orthophosphate limitation; \( \text{Ni,n} \) is a dissolved inorganic ammonium N \( (N_{\text{NH}_4^+}) \) concentration, \( \left( \frac{g \text{ N}}{m^3} \right) \); \( \text{Ni,n} \) is a dissolved inorganic nitrate N \( (N_{\text{NO}_3^-}) \) concentration \( \left( \frac{g \text{ N}}{m^3} \right) \); \( \text{Pi,o} \) is a dissolved inorganic orthophosphate P \( (P_{\text{PO}_4^{3-}}) \) concentration \( \left( \frac{g \text{ P}}{m^3} \right) \); \( k_{\text{Ni,n}} \) is a nitrate half-saturation constant for algal growth \( \left( \frac{g \text{ N}}{m^3} \right) \); \( k_{\text{Ni,a}} \) is an ammonium half-saturation constant for algal growth \( \left( \frac{g \text{ N}}{m^3} \right) \); \( k_{\text{Pi,o}} \) is an orthophosphate half-saturation constant for algal growth \( \left( \frac{g \text{ P}}{m^3} \right) \).

The light attenuation with depth is modeled by the Beer-Lambert law using an extinction coefficient [11]. Because the river systems in LM3-TAN [65] consist of continuously stirred tank reactors (CSTR) in series, 24-hour integrated, euphotic zone (depth where light intensity falls to one percent of that at the surface) averaged light level \( (I_{av}) \) is used for each of the reactors. The extinction coefficient is estimated dynamically to account for seasonal variations in turbidity due to algae shading [91], light extinction due to particle-free water and color, and variations in nonvolatile suspended solids and
detritus (nonliving organic suspended solids) [28].

\[
I = \begin{cases} 
I_s e^{-k_e z} & z \leq z_{0.01} \\
I_s e^{-k_e z_{0.01}} & z > z_{0.01}
\end{cases}
\]  

(5.11)

\[
z_{0.01} = -\frac{\ln(0.01)}{k_e}
\]  

(5.12)

\[
I_{av} = \frac{I}{k_e z} \left(1 - e^{-k_e z}\right)
\]  

(5.13)

\[
k_e = k'_e + c_{s1} Aa_2 + c_{s2} Aa_2^{b_{s2}}
\]  

(5.14)

\[
k'_e = k_{ew} + 0.052S + 0.174D
\]  

(5.15)

\[
Aa_2 = 1000 \: Na \cdot c_{cn} \cdot c_{ac}
\]  

(5.16)

where, \( I \) is a 24-hour integrated irradiance \( \left(\text{watts/m}^2\right) \); \( I_s \) is a 24-hour integrated irradiance at the surface \( \left(\text{watts/m}^2\right) \); \( z \) is a river depth (m); \( z_{0.01} \) is a river depth where light intensity falls to one percent of that at the surface (m); \( k_e \) is a light extinction coefficient \( \left(\text{1/m}\right) \); \( k'_e \) is a light extinction due to factors other than algae \( \left(\text{1/m}\right) \); \( k_{ew} \) is a light extinction due to particle-free water and color \( \left(\text{1/m}\right) \); \( c_{s1} \) and \( c_{s2} \) are self-shading factors, 0.0088, 0.054; \( b_{s2} \) is an exponent of the equation relating algae concentrations to the light extinction coefficient, 2/3; \( S \) are nonvolatile suspended solids \( \left(\text{mg/l}\right) \); \( D \) is a detritus (nonliving organic suspended solids) \( \left(\text{mg/l}\right) \); \( Aa_2 \) is a algae chlorophyll a concentration \( \left(\text{mg chl/m}^3\right) \).
5.1.1.2 Algae Mortality Rate

The algae mortality is adjusted by factors of temperature and algae N concentration. The mortality is assumed to increase with algae concentration and predators, and the predators proportionally increase with algae concentration. Thus, the mortality increases with the square of algal N concentration. The theta (θ) model is applied to account for the effect of temperature (θ = 1.066) [32].

\[
m(T) = k_m \cdot \theta_{\mu,m}^{T-T_{ref}} \cdot Na^2
\]

(5.17)

where, \( k_m \) is an algae mortality rate \( \left( \frac{m^3}{g\cdot N\cdot s} \right) \) at a reference temperature \( T_{ref} \) (°C); \( \theta_{\mu,m} \) is an algae growth and mortality rate temperature correction factor, 1.066.

5.1.2 Organic Matter and Nutrients

Organic matter and nutrients are present in the following different forms in the model’s aquatic ecosystems:

1) Biotic (living) algae, (a) – nitrogen (Na), phosphorus (Pa), carbon (Ca), and chlorophyll a (Aa)
2) Particulate (nonliving) organic (detrital), (p) – nitrogen (Np) and phosphorus (Pp)
3) Sediment (nonliving) organic, (s) – nitrogen (Ns) and phosphorus (Ps)
4) Dissolved (nonliving) organic, (d) – nitrogen (Nd) and phosphorus (Pd)
5) Dissolved (nonliving) inorganic, (i) – ammonium-N (\( N_{NH_4} \), Ni,a), nitrate-N (\( N_{NO_3} \), Ni,n), and orthophosphate-P (\( P_{PO_4^{3-}} \), Pi,o)
The nonliving suspended organic matter is divided into the particulate and dissolved pools in order to distinguish between settleable and nonsettleable forms. The algal mortality is added to the particulate/dissolved organic pools and some of the dissolved inorganic pools. The dissolved inorganic nutrients are used for the algal growth.

The particulate organic matter is gained by the algal mortality and lost by mineralization and settling. The sediment organic matter is gained by the settling and lost by mineralization. The dissolved organic matter is gained by the algal mortality and lost by mineralization. The dissolved inorganic nutrients are gained by the algae mortality (i.e., Ni,a, Pi,o) and mineralization (i.e., Ni,a, Ni,n, Pi,o), nitrification (i.e., Ni,a), and denitrification (i.e., Ni,n) [3, 65]. The dissolved organic matter and inorganic nutrients are also directly gained from point sources (e.g., sewage, waste water discharge) and indirectly gained from non-point sources (e.g., atmospheric deposition, fertilizer, manure, and legume applications) via soil leaching. First-order kinetics is used to simulate some of the transformations between the abiotic compartments. The theta (θ) model based is used to describe the temperature-dependent effects of first-order rate coefficients.

5.1.2.1 Particulate Organic Matter

\[
\frac{dNp}{dt} = f_{m,Np}m(T) - \left(k_{Np,m}(T) + v_N \frac{1}{z}\right) \cdot Np \tag{5.18}
\]

\[
\frac{dPp}{dt} = c_{pn} \cdot f_{m,Np}m(T) - \left(k_{Pp,m}(T) + v_P \frac{1}{z}\right) \cdot Pp \tag{5.19}
\]

where, Np is particulate organic N concentration \(\frac{g_N}{m^3}\); Pp is a particulate organic P
concentration \( \left( \frac{g \text{ P}}{m^3} \right) \); \( f_{m,NP} \) is a fraction of algal mortality which is deposited to the particulate organic N pool; \( k_{NP,m} \) is a particulate organic N mineralization rate \( \left( \frac{1}{s} \right) \) as a function of temperature \( T \); \( k_{PP,m} \) is a particulate organic P mineralization rate \( \left( \frac{1}{s} \right) \) as a function of \( T \); \( v_n \) is a particulate organic N settling velocity \( \left( \frac{m}{s} \right) \); \( v_p \) is a particulate organic P settling velocity \( \left( \frac{m}{s} \right) \).

### 5.1.2.2 Sediment Organic Matter

\[
\frac{dNs}{dt} = k_{NS,m}(T)Ns + v_N \frac{1}{z}NP
\]  
\[
\frac{dPs}{dt} = k_{PS,m}(T)Ps + v_P \frac{1}{z}Pp
\]

where, \( Ns \) is a sediment organic N concentration \( \left( \frac{g \text{ N}}{m^3} \right) \); \( Ps \) is a sediment organic P concentration \( \left( \frac{g \text{ P}}{m^3} \right) \); \( k_{NS,m}(T) \) is a sediment organic N mineralization rate \( \left( \frac{1}{s} \right) \) as a function of temperature \( T \); \( k_{PS,m}(T) \) is a sediment organic P mineralization rate \( \left( \frac{1}{s} \right) \) as a function of \( T \).

### 5.1.2.3 Dissolved Organic Matter

\[
\frac{dNd}{dt} = f_{m,Nd}m(T) - k_{Nd,m}(T)Nd
\]  
\[
\frac{dPd}{dt} = c_{pn} \cdot f_{m,Nd}m(T) - k_{Pd,m}(T)Pd
\]
where, \( N_d \) is a dissolved organic N concentration \( (\text{g N m}^{-3}) \); \( P_d \) is a dissolved organic P concentration \( (\text{g P m}^{-3}) \); \( f_{m,Nd} \) is a fraction of algae mortality which is deposited to the dissolved organic N pool; \( k_{N_d,m}(T) \) is a dissolved organic N mineralization rate \( (\text{1 s}^{-1}) \) as a function of temperature \( T \); \( k_{P_d,m}(T) \) is a dissolved organic P mineralization rate \( (\text{1 s}^{-1}) \) as a function of \( T \).

### 5.1.2.4 Dissolved Inorganic Nutrients

\[
\frac{dN_{i,a}}{dt} = \left(1 - f_{m,Np} - f_{m,Nd}\right) \cdot m(T) + k_{N_p,m}(T)Np + k_{N_s,m}(T)Ns + k_{N_d,m}(T)Nd - k_{nitr}(T)Ni, a - f_{N_{i,a,up}} \cdot \mu(I,T,N,P) \cdot Na
\]

(5.24)

\[
\frac{dN_{i,n}}{dt} = k_{nitr}(T)Ni, n - k_{denitr}(T)Ni, n - \left(1 - f_{N_{i,a,up}}\right) \cdot \mu(I,T,N,P) \cdot Na
\]

(5.25)

\[
\frac{dP_{i,o}}{dt} = c_{pn} \cdot \left(1 - f_{m,Np} - f_{m,Nd}\right) \cdot m(T) + k_{P_p,m}(T)Pp + k_{P_s,d}(T)Ps + k_{P_d,m}(T)Pd - c_{pn} \cdot \mu(I,T,N,P) \cdot Na
\]

(5.26)

\[
f_{N_{i,a,up}} = \frac{\lim_{N_{i,a}}}{\lim_{N_{i,n}} + \lim_{N_{i,a}}}
\]

(5.27)

\[
k_{denit} = \max[k_{denit, min}, C_{d,s} (b_0 Ni, a_2^{b_1} H^{b_2} c^c)]
\]

(5.28)

where, \( N_{i,a} \) is a dissolved inorganic ammonium N concentration \( (\text{g N m}^{-3}) \); \( N_{i,a} \) is a
dissolved inorganic nitrate N concentration \(\left(\frac{\text{\(\mu\)mol } N}{\text{m}^3}\right)\); \(N_i\) is a dissolved inorganic nitrate N concentration \(\left(\frac{g\ N}{m^3}\right)\); \(P_i\) is a dissolved inorganic phosphorus concentration \(\left(\frac{g\ P}{m^3}\right)\); \(f_{N_i,a,up}\) is a fraction of dissolved inorganic ammonium uptake for algae growth; \(k_{nit}(T)\) is a nitrification rate as a function of temperature \(T\); \(k_{denit}(T)\) is a denitrification rate as a function of temperature \(T\); \(k_{denit,min}\) is a minimum denitrification rate; \(\lim_{N_i,ln}\) is a nitrate limitation; \(\lim_{N_i,a}\) is an ammonium limitation; \(C_{d,s}\) is an a unit-conversion constant \(\left(\frac{d}{s}\right)\); \(b_0\), \(b_1\), and \(b_2\) are constants; \(c^t\) is a log re-transform bias correction factor.
Chapter 6

Concluding Remarks

6.1 Conclusion

Using the mechanistic model LM3-TAN, the complementary studies in this dissertation provide novel quantitative insights into responses of river N and estuarine/coastal eutrophication to interactions between hydrological and N cycles in terrestrial and aquatic ecosystems, under anthropogenic N and/or climatic perturbations.

Chapter 2 developed the model LM3-TAN. Its comprehensive modeling framework, unlike previous models, captures key controls of the transport and fate of N in the vegetation-soil-river system that is responsive to climate change and land-use and land-cover changes (LULCC). By using the same parameters for the entire Susquehanna River Basin, which is composed of 6 sub-basins with varying climate and land use, the model simulated spatial (16 sites) and temporal (1986–2005) stream and river dissolved organic-N, ammonium-N, and nitrate-N loads throughout the river network well. The calculated terrestrial-aquatic N budget using model results also agreed well with the
reported budget, and which illustrates how point and non-point anthropogenic N sources applied to the various ecosystems are stored, lost, and exported via rivers at the level of the whole basin. In the forests, most of the applied N is stored in the vegetation and soil (43%), whereas, in the agricultural lands, most of the applied N is removed by soil denitrification (44%). This result indicates that increasing human land use and associated N sources could promote a potent greenhouse gas (N$_2$O, an intermediate of the denitrification process) production substantially. Furthermore, local analysis of the six sub-basins shows the combined effects of direct human influences and climatic conditions on soil denitrification, with the highest rates in the Lower Susquehanna Sub-basin (extensive agriculture; Atlantic coastal climate) and the lowest rates in the West Branch Susquehanna Sub-basin (mostly forest; Great Lakes and Midwest climate).

In Chapter 3, the novel application of LM3-TAN reveals the critical role of interaction between N storage and climatic variability on Susquehanna River N loads. By analyzing both reported and simulated long-term river flow and N-load data, this study demonstrates that high N-load anomalies arise after prolonged dry spells even if precipitation returns to normal states, explained by flushing of accumulated soil N and by stimulated soil microbial processes. This study also ran 549 experiments to produce 9 N-load distributions in response to different histories of hydrologic preconditioning, and illustrates that after 1-4 year dry spells, the likelihood to exceed a threshold N load increases by 31-86%. This memory effect is amplified when longer dry spells are followed by extreme precipitation. Thus, increasing climatic variability and extremes exacerbate risk of eutrophication. These results provide an important implication for the largest estuary in the U. S., Chesapeake Bay, where hypoxic (“dead”) zone is persistent, despite three decades of basin-wide N waste-reduction efforts and suggest that effective mitigation strategies must account not only for N waste reduction and climatic trends but
also for allowing policy adjustments based on changes in inter-annual climatic variability.

Chapter 4 explores river basin management strategies for reducing coastal eutrophication by applying LM3-TAN to the southern Korean Peninsula. This study quantified downstream N-removal benefits with respect to ecosystem components (e.g., climate, land use, sub-basin location) to prioritize sites for N-loading controls. Based on forecasted N loads (2011-2073) using various N-reduction scenarios without and with inter-annual climatic variability observed during the past 63 years (1948-2010), this study demonstrates that (1) if there is a considerable excess in anthropogenic N sources, a small increase in the N sources can result in severe river N pollution, as only a certain range of the N sources can be used for ecosystem processes (e.g., plant uptake), (2) goals in reducing N sources should account for inter-annual climatic variability, which can significantly mask the N-reduction effects on N loads, and (3) the greatest N-reduction effects on reducing downstream N loads discharged to coasts are given for sub-basins with low precipitation, close to the coasts, and with much human land use.

6.2 Future Work

The mechanistic model LM3-TAN developed here is a methodological advance that can be used to address a range of questions related to the effects of climate- and human-driven perturbations on the N cycle and their implications for soil, air, and water quality. One promising research opportunity is to develop a global riverine/estuarine biogeochemistry model, which could serve as a medium of biogeochemical bonding between land and ocean components of Earth System Models (ESMs). This research could be done by enhancing the LM3-TAN’s regional framework and expanding it by
including the coupled nutrient (i.e., N, P) and algal dynamics, designed in Chapter 5.

By coupling terrestrial and riverine N cycles, the research contained in this dissertation has addressed major limitations in current watershed modeling, which simplifies or neglects many key mechanisms in terrestrial ecosystems. As shown in Chapter 3, LM3-TAN is capable of capturing the nonlinear mechanism between climatic variability and N storage, and their effects on river N-loading variability. Thus, enhancement and expansion of LM3-TAN, and its global implementation would provide unique riverine/estuarine nutrient loading for ocean models, which currently rely on prescribed data largely based on empirical approaches. Furthermore, emphasizing the nonlinearity would resonate with assessing marine ecosystem tipping points and improve our ability to deal with future climate and land-use changes.

Currently, there are several parameters which were calibrated by fitting the simulated river N loads to reported data. Care has to be taken when applying the model to other watersheds very different in terms of soil properties and climatic conditions. For example, observational studies have described various biogeochemical processes (e.g., soil denitrification) with wide ranges of functions dependent on site-specific parameters. Thus, modeling such processes with respect to land-use type may be a way to move forward to the global level. The global framework could be evaluated and constrained using detailed reported datasets of riverine nutrient loads (e.g. Global NEWS Datasets).
Bibliography


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