

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

5
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15
16 **Abstract**

17 We developed a process model LM3-TAN to assess the combined effects of direct human
18 influences and climate change on Terrestrial and Aquatic Nitrogen (TAN) cycling. The model
19 was developed by expanding NOAA's Geophysical Fluid Dynamics Laboratory land model
20 LM3V-N of coupled terrestrial carbon and nitrogen (C-N) cycling and including new N
21 cycling processes and inputs such as a soil denitrification, point N sources to streams (i.e.
22 sewage), and stream transport and microbial processes. Because the model integrates
23 ecological, hydrological, and biogeochemical processes, it captures key controls of transport
24 and fate of N in the vegetation-soil-river system in a comprehensive and consistent
25 framework which is responsive to climatic variations and land use changes. We applied the
26 model at 1/8 degree resolution for a study of the Susquehanna River basin. We simulated with
27 LM3-TAN stream dissolved organic-N, ammonium-N, and nitrate-N loads throughout the
28 river network, and we evaluated the modeled loads for 1986-2005 using data from 16

1 monitoring stations as well as a reported budget for the entire basin. By accounting for inter-
2 annual hydrologic variability, the model was able to capture inter-annual variations of stream
3 N loadings. While the model was calibrated with the stream N loads only at the last
4 downstream Susquehanna River Basin Commission station Marietta (40.02' N, 76.32' W), it
5 captured the N loads well at multiple locations within the basin with different climate
6 regimes, land use types, and associated N sources and transformations in the sub-basins.
7 Furthermore, the calculated and previously reported N budgets agreed well at the level of the
8 whole Susquehanna watershed. Here we illustrate how point and non-point N sources
9 contributing to the various ecosystems are stored, lost, and exported via the river. Local
10 analysis for 6 sub-basins showed combined effects of land use and climate on soil
11 denitrification rates, with the highest rates in the Lower Susquehanna Sub-basin (extensive
12 agriculture; Atlantic coastal climate) and the lowest rates in the West Branch Susquehanna
13 Sub-basin (mostly forest; Great Lakes and Midwest climate). In the re-growing secondary
14 forests, most of the N from non-point sources was stored in the vegetation and soil, but in the
15 agricultural lands most N inputs were removed by soil denitrification indicating that
16 anthropogenic N applications could drive substantial increase of N_2O emission, an
17 intermediate of the denitrification process.

18

19 **1 Introduction**

20 Biologically available nitrogen (N) in terrestrial ecosystems has significantly increased via
21 anthropogenic nutrient inputs: artificial fertilizer, cultivation of N fixing crops, and fossil fuel
22 consumption (Galloway et al., 2004; 2008). This increase has caused acidification and N
23 saturation in some terrestrial and aquatic ecosystems (Henriksen and Brakke, 1988; Kelly et
24 al., 1990; Murdoch and Stoddard, 1992; Howarth, 2002). N-saturated soils and streams are
25 also major sources of nitrous oxide (N_2O) emissions, which is a potent greenhouse gas
26 (Albritton et al., 1994). Other concerns include severe water-quality problems associated with
27 cultural eutrophication, which results in harmful algal blooms and hypoxia in rivers, lakes,
28 estuaries, and coastal zone ecosystems (Smith, 2003; Smith et al., 2006). Climate change and
29 variability also affect water quality through the distribution of high and low flow extremes
30 (Scavia et al., 2002; Howarth et al., 2006). It is generally accepted that microbial processes
31 related to the N cycle are strongly influenced by abiotic factors, and warm or wet climate

1 provides favorable environments for certain groups of bacterial activities. Quantification and
2 management of the diverse and coupled effects of human activity and climate change on N
3 cycling requires a comprehensive model of the relevant coupled processes that can support
4 the design of optimal nutrient loading controls to maintain desirable water quality and
5 terrestrial ecosystem integrity.

6

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

17

18 There has been keen interest and progress in modeling the N cycle in terrestrial ecosystems.
19 However, in most models vegetation and land use type distribution are prescribed and do not
20 change in time. Modeling studies with EPIC, ANIMO, and CENTURY/DAYCENT typically
21 prescribe crop distribution and simulate crop production and related nutrient and carbon (C)
22 cycling (Sharpley and Williams, 1990; Parton et al., 1993; Williams et al., 1995; Kroes and
23 Roelsma, 1998; Del Grosso et al., 2009). Because these models do not simulate decadal-to-
24 century changes in vegetation structure (e.g. forest regrowth after harvesting) they are likely
25 to overlook changes in the storage of N in vegetation. Furthermore, during wood harvesting
26 and forest clearing for agriculture, biomass residue is an important additional input to the soil
27 organic C-N pools. Such additional N inputs lead to additional N inorganic loads. In addition,
28 many regional models (e.g. EPIC, ANIMO), which have been applied to far smaller basins
29 compared to the Susquehanna watershed, often use basin-specific parameters for
30 mineralization, nitrification, and denitrification, which complicates their application on a
31 global scale for decadal-to-century scale studies. LM3-TAN is capable of describing N
32 dynamics with a universal parameter set – the same parameters for all of the sub-basins within

1 an area of 71,220 km² and time periods for this simulation. LM3-TAN is among very few
2 modeling frameworks (e.g. CLM-CN: Thornton et al 2007; CLM4MOD: Thomas et al., 2013)
3 that can be used as a component of an ESM – that is it is capable to represent sub-diurnal
4 exchanges of moisture, energy, C and N species among land-atmosphere. Unlike
5 CLM4MOD, LM3-TAN simulates water quality in the rivers and nutrient loadings to the
6 coastal environment.

7

8 Contrary to the simulations of land models limited to the terrestrial component, most
9 watershed models do estimate stream N concentrations and loads, but they simplify or neglect
10 many key mechanisms describing terrestrial N dynamics (e.g., vegetation and land-use
11 dynamics, interactive C-N feedbacks on vegetation and soil microbial processes; phenological
12 leaf drop and its contribution to soil organic matter pools). INCA-N and SWAT are widely
13 used Geographic Information System-based watershed models (Wade et al., 2002; Schilling
14 and Wolter, 2009). However, when it comes to large scale applications, because these models
15 are semi-distributed, they are less capable of representing spatial variability, requiring users to
16 define the number and sizes of sub-basins, in which land use and all of the processes for each
17 land use are assumed to be homogeneous and needed to be defined individually. This limits
18 their ability to analyze complex land-use management scenarios. In this class of models,
19 RHESSys is one of a few models with an ecology component that can be used to investigate
20 interactions between ecosystems and hydrological processes according to climate variability
21 (Tague and Band, 2004; Beckers et al., 2009). However, like most models, because these
22 models do not simulate vegetation and land use type distribution, a specific parameter set that
23 describes typical soil, vegetation, and land use characteristics has to be developed using its
24 special module when a study site requires different vegetation or soil types from its default
25 application. This explains why RHESSys has only been applied to very small or sub sections
26 of catchments (Band et al., 2001; Tague and Band, 2004).

27

28 Given the current lack of models that link terrestrial C-N cycling, long-term vegetation and
29 land-use dynamics to N loads and concentrations in streams, accounting for different N
30 species, the goal of this research was to build a model to simulate stream N loads that is based
31 on a global-scale terrestrial and N-enabled land model, followed by its testing on a large and

1 complex watershed, for which many years of stream discharge and stream N data are
2 available. For this purpose and to assess the combined effects of direct human influences and
3 climate change on Terrestrial and Aquatic Nitrogen (TAN) cycling, we developed a process
4 model LM3-TAN. The new features include integrated effects of point and non-point sources
5 on river N loads, a soil denitrification module, and stream microbial processes.

6

7 We applied LM3-TAN to the Susquehanna River basin, the largest of the watersheds in the
8 northeastern U.S., draining an area of 71,220 square kilometers, at the resolution of 1/8
9 degree. The model was evaluated using 20 year (1986-2005) data of stream ammonium
10 (NH_4^+) and dissolved organic N loads as well as stream nitrate (NO_3^-) N loads from 16
11 monitoring stations. For each of 6 sub-basins, we conducted local analysis to assess combined
12 effects of land use and climate on the soil denitrification. We then built up a N budget and
13 compared it with the corresponding reported budget to better understand how point and non-
14 point N sources contributing to the various ecosystems are stored, lost, and exported via the
15 river at the level of the whole Susquehanna watershed. Although there are several parameters
16 that required calibration by fitting simulated to reported stream N loads, these parameters are
17 used universally for the entire basin where climate, soil, vegetation, and land use
18 characteristics vary. Efforts have been made in the development of this model to limit the
19 number of calibrated parameters.

20

21 **2 Model Description**

22 **2.1 Overview**

23 LM3V-TAN is an expansion of earlier GFDL land models, beginning with LM3V of
24 Shevliakova et al (2009), which describes vegetation and C dynamics. LM3-TAN was
25 expanded to include vegetation- and soil-N dynamics from LM3V-N (Gerber et al., 2010),
26 new soil physics and hydrology from LM3 (Milly et al, 2014), and N cycling processes
27 described here. LM3 was used as a component of the GFDL Earth System Models (Dunne et
28 al, 2012) and included several enhancements, such as vertically resolved soil physics and
29 hydrology and explicit river dynamics and physics. LM3-TAN includes soil denitrification
30 and transport and chemistry of N cycle in rivers. This version of model allows more complete

1 tracking of N through the soil-river continuum. In this section, we first summarize key
2 features of the model, and then we describe the newest N cycling features.

3

4 LM3V simulates distribution of five vegetation functional types (C3 and C4 grasses, and
5 temperate-deciduous, tropical, and cold-evergreen trees) on the basis of total biomass and
6 prevailing climate conditions. The model tracks hundreds of years of land use change using
7 global land use transition scenarios that were historically reconstructed by combining
8 satellite-based contemporary patterns of agriculture with historical data on agriculture and
9 population (Hurtt et al., 2006). The four land use types are natural vegetation (land
10 undisturbed by human activities), secondary vegetation (land formerly disturbed by human
11 activities), cropland, and pasture. The model is spatially distributed, and each grid cell
12 consists of up to 15 tiles: 1 natural vegetation, 1 cropland, 1 pasture, and 1 to 12 secondary
13 vegetation tiles representing unique disturbance histories (i.e. de/reforestation, agricultural
14 practice change). Exchanges of water, energy, and between land and atmosphere are
15 computed with a time step of 30 minutes. Atmospheric and terrestrial reservoirs include C
16 pools in vegetation (leaves, fine roots, sapwood, heartwood, and labile C storage), soil (fast
17 and slow), and anthropogenic storage. The C pools in the vegetation are updated on a daily
18 time step to account for vegetation growth and allocation, leaf drop and display, and natural
19 mortality and fire. The soil C, which is supplied by the vegetation both naturally and during
20 land-use conversion, is stored in two pools with different turnover times.

21

22 **2.2 Coupled C-N dynamics in vegetation and soil**

23 The previous two soil C pools in LM3V were divided into four pools (fast and slow litter, and
24 slow and passive soil organic matter) in LM3V-N. Each C pool in the vegetation and soil was
25 paired with a respective N compartment using pool-specific C:N ratios. The decomposition
26 processes release biologically available forms of N ($\text{NO}_3^- - \text{N}$; $\text{NH}_4^+ - \text{N}$). This allows to
27 simulate N limitation on plant growth and biological N fixation as well as N feedbacks on
28 organic matter decomposition and stabilization. Inorganic N is removed by sorption to soil
29 particles, plant uptake, immobilization into long-lived organic compounds, and hydrological
30 leaching, while organic N is lost through fire, hydrological leaching, and mineralization. Loss

1 of nitrate N by soil denitrification was not differentiated from the hydrological nitrate-N
2 leaching in LM3V-N.

3

4 **2.3 Improved soil and river physics and hydrology**

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

13

14 **2.4 Synthesis and Extension of Earlier Developments**

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

22

23 **2.4.1 Merging lumped N model with distributed physical model**

24 To account for dependence of processes in the lumped soil C and N pools upon the vertically
25 resolved physical states of the soil (temperature and water content), the latter were vertically
26 averaged with an exponentially decaying weight function of depth (e-folding depth of 10 m).
27 Leaching of any mobile constituent was defined as the product of a concentration and the sum

1 of lateral and vertical discharge from the soil layer between the surface and a depth of 10 m.
2 The concentration of available N was calculated as dividing available N contents by the
3 effective soil depth which was approximated assuming C weight content 3.4% and average
4 soil density 1500 kg/m³. The available N refers to the N contents reduced by buffering
5 factors which represent processes such as sorption to soil particles. To compensate for many
6 processes that were not accounted for in the model, calibration factors for each N species
7 were introduced to slow down overall N movement from the soil to the stream. These factors
8 include impacts of soil microbes, which are able to take up and incorporate all N forms
9 ($\text{NO}_3^- - \text{N}$, $\text{NH}_4^+ - \text{N}$, DON) with a much greater capacity than plant uptake (Nordin et al.,
10 2004). The nitrate calibration factor also accounts for storage in groundwater since nitrate (the
11 primary form of N in ground water) can persist for decades at high levels with increasing N
12 applications. This is further explained by Bachman et al. (1998) which reported that 17 to 80
13 percent of the N delivered to streams of the Chesapeake Bay watershed was through ground
14 water. Furthermore, the lumped single-layer N sub-model bypasses most of the vertically
15 distributed hydrologic system, and the soil N leaching based on the average water drainage is
16 transferred directly from the N layer into the stream. These calibration factors were fit to
17 match inter-annual variations of reported and simulated stream N loads to make up for this
18 modeling approach as well as the unresolved processes that might cause inter-annual stream
19 N loads more sensitive to climate variability than those in reality. Considering its importance
20 in groundwater, a relatively larger size of the nitrate N factor is expected. The need to
21 incorporate these calibration factors, which are at the present basin specific, indicates that
22 future improvements to LM3-TAN should focus on resolving these processes (i.e. N cycle in
23 microbes, reservoirs, and vertically distributed soil layers). Dissolved organic, ammonium,
24 and nitrate N leaching from the soil are described as:

$$25 \quad L_{\text{DON}} = \frac{D_s}{\rho_w r_{\text{DOM}}} [N_{\text{DON},av}] = \frac{D_s}{\rho_w r_{\text{DOM}}} \left(\frac{f_{\text{LF}} N_{\text{LF}} + f_{\text{LS}} N_{\text{LS}} + f_{\text{SS}} N_{\text{SS}}}{b_{\text{DOM}} h_s} \right) \quad (1)$$

$$26 \quad L_{\text{NH}_4^+} = \frac{D_s}{\rho_w r_{\text{NH}_4^+}} [N_{\text{NH}_4^+,av}] = \frac{D_s}{\rho_w r_{\text{NH}_4^+}} \left(\frac{N_{\text{NH}_4^+}}{b_{\text{NH}_4^+} h_s} \right) \quad (2)$$

$$L_{NO_3^-} = \frac{D_s}{\rho_w r_{NO_3^-}} [N_{NO_3^-,av}] = \frac{D_s}{\rho_w r_{NO_3^-}} \left(\frac{N_{NO_3^-}}{b_{NO_3^-} h_s} \right) \quad (3)$$

$$h_s = \frac{C_{LF} + C_{LS} + C_{SS}}{r_c \rho_s} \quad (4)$$

3 where, L_{DON} , $L_{NH_4^+}$, and $L_{NO_3^-}$ are the dissolved organic, ammonium, and nitrate N leaching
 4 from the soil ($\text{kg}/\text{m}^2 \text{ s}$); D_s is the water drainage from the active soil layer ($\text{kg}/\text{m}^2 \text{ s}$); ρ_w is
 5 the water density ($1000 \text{ kg}/\text{m}^3$); r_{DOM} , $r_{NH_4^+}$, and $r_{NO_3^-}$ are dissolved organic matter,
 6 ammonium, and nitrate N calibration factors; $[N_{DON,av}]$, $[N_{NH_4^+,av}]$, and $[N_{NO_3^-,av}]$ are the
 7 concentration of available N in dissolved organic, ammonium, and nitrate N pools (kg/m^3);
 8 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} ,
 9 and f_{SS} are the fractions of soluble organic N in the fast litter, slow litter, and slow soil N
 10 pools; $N_{NH_4^+}$ and $N_{NO_3^-}$ are the soil ammonium and nitrate N contents (kg/m^2); b_{DOM} , $b_{NH_4^+}$,
 11 and $b_{NO_3^-}$ are dissolved organic matter, ammonium, and nitrate N buffering factors due to
 12 sorption to soil particles; h_s is the effective soil depth (m); r_c is the C weight content (3.4%);
 13 ρ_s is the average soil density ($1500 \text{ kg}/\text{m}^3$); C_{LF} , C_{LS} , and C_{SS} are the fast litter, slow litter,
 14 and slow soil C contents (kg/m^2).
 15

16 2.4.2 Denitrification in soil

17 Denitrification is a process that reduces nitrate or nitrite to gaseous forms (e.g., NO , N_2O , N_2)
 18 in anaerobic conditions, where the oxidized N species serve as a terminal electron acceptor in
 19 metabolism by soil denitrifying bacteria. The rate of denitrification generally depends on soil
 20 nitrate content or concentration, soil water content (a surrogate for oxygen content), and soil

1 temperature. Because soil nitrate contents are relatively low and limiting under natural
 2 conditions, we used a first-order loss function with respect to soil nitrate N content, with
 3 adjustments for the influence of soil water content and temperature to simulate soil
 4 denitrification rate:

$$5 \quad D_N = f_S f_T k_{denitr} N_{NO_3^-} \quad (5)$$

6 where, D_N is the soil denitrification rate ($\text{kg}/\text{m}^2 \text{ yr}$); f_S is a soil water content reduction
 7 function; f_T is a soil temperature reduction function; k_{denitr} is a first-order denitrification
 8 coefficient ($1/\text{yr}$); $N_{NO_3^-}$ is the soil nitrate N content (kg/m^2).

$$9 \quad f_T = Q_{10}^{(T-T_r)/T_p} \quad (6)$$

$$10 \quad f_S = \begin{cases} S_{min} & S < S_t \\ \left(\frac{S-S_t}{S_{max}-S_t}\right)^w & S_t \leq S \leq S_{max} \\ S_{max} & S_{max} < S \end{cases} \quad (7)$$

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

15

16 Heinen (2006) tabulates reported values of the various parameters introduced above. Figure 2
 17 shows the effects of the reduction functions on the soil denitrification rate that were applied in
 18 diverse models as well as LM3-TAN. Figure 2a shows how fast soil nitrate N content is
 19 reduced to half of the initial amount depending on the different first-order denitrification
 20 coefficients. As temperature increases the bacterial activities increase exponentially (Fig. 2b).
 21 Soil denitrification occurs and increases non-linearly only if soil water content exceeds a
 22 certain threshold point due to enhanced anaerobic bacterial activity (Fig. 2c). The soil water

1 content reduction function for other microbial processes (e.g., mineralization, nitrification)
2 used in LM3-TAN is also shown in Fig. 2d. Because k_{denitr} is by far the most widely used
3 parameter of these, with reported values ranging over three orders of magnitude, our strategy
4 was to fix the other parameters using reported values, and to calibrate the model by
5 determining k_{denitr} within the bounds reported in the literatures. Because soil denitrification
6 and nitrate-N leaching are competing sinks of nitrate N in the soil, soil denitrification
7 increases as soil nitrate-N leaching or stream nitrate-N load decreases; thus k_{denitr} was fit to
8 match reported and simulated stream nitrate-N loads.

9
10 The wide ranges of the functions discussed above are mostly driven by the dependencies of
11 the parameters on specific regions (with different soil properties, vegetation, land use, etc.).
12 Given a number of proposed individual functions, it seems that there is no universal process
13 module to simulate soil denitrification. Because such reduction functions display a diversity
14 of shapes as ecosystems are modeled over a range of climate patterns, vegetation type, and
15 land use practices, soil denitrification on a large scale cannot be modeled without proper
16 adjustments that compensate the site-specific properties. This explains why only a few studies
17 have applied models to watersheds larger than 1000 km² despite the diversity of existing
18 dynamic N models and why semi-distributed models often parameterize these individual
19 functions for each of sub-basins in large-scale applications. We hypothesize that LM3-TAN's
20 integrated modeling framework, which is capable of simulating long-term vegetation
21 functional type and land use change as a function of changes in CO₂, climate, and human
22 influences, allows us to use a universal parameter set to simulate soil denitrification for each
23 of the distinct sub-basins. Still, care has to be taken when applying the model to other
24 watersheds that may be very different in terms of soil and climate properties from the
25 Susquehanna watershed. Furthermore, because soil denitrification becomes zero-order in
26 extreme nitrate rich environment, instead of using the first-order loss function for all of the
27 land use types, using a Monod function for agricultural land use may help LM3-TAN's global
28 application where N loadings would vary widely.

29

1 2.4.3 Microbial processes in rivers

2 Despite its importance to water quality, processes that control N removal from water bodies
3 are rarely resolved in watershed scale models, due to both uncertainties in measurement
4 techniques and lack of measurements. To date, none of studies focusing on river
5 denitrification rate is based on measurements of an entire river network, but rather only on the
6 data from low order streams or individual catchments. Here we applied a non-linear
7 regression function based on the LINX (Lotic Intersite Nitrogen experiment; Mulholland et
8 al., 2008) reach-scale measurements that correlates river denitrification rate with nitrate-N
9 concentration and river depth to estimate the reaction rate constant of river denitrification for
10 each reach (Alexander et al., 2009). River denitrification happens mainly in the benthic and/or
11 hyporheic zones. Therefore, a river denitrification rate that is inversely proportional to the
12 river depth accounts for the ratio of water column to benthic area. The measured reaction rate
13 constants vary from 0.034 to 117 (1/day), and we chose the median value 0.53 (1/day) as the
14 minimum reaction rate constant of river denitrification. Equation 12 indicates that the reaction
15 rate constant decreases with increase in nitrate-N concentration and river depth, since both b_1
16 and b_2 are negative, and it increases with temperature. Reaction rate constants for river
17 mineralization and nitrification were calibrated to match stream N loads.

18

19 Figure 1 shows structure of the river component. Each reach directly receives N from point
20 sources (e.g., sewage and waste water discharge) and indirectly receives N from non-point
21 sources (e.g., atmospheric deposition, fertilizer, manure, and legume applications) via soil
22 leaching. The N loads in a reach are routed downstream with the water as following.

$$23 \quad \frac{dR_{DON}}{dt} = F_{DON}^{in} - F_{DON}^{out} + L_{DON} + P_{DON} - f_T' k_{min}' R_{DON} \quad (8)$$

$$24 \quad \frac{dR_{NH_4^+}}{dt} = F_{NH_4^+}^{in} - F_{NH_4^+}^{out} + L_{NH_4^+} + P_{NH_4^+} + f_T' k_{min}' R_{DON} - f_T' k_{nitr}' R_{NH_4^+} \quad (9)$$

$$25 \quad \frac{dR_{NO_3^-}}{dt} = F_{NO_3^-}^{in} - F_{NO_3^-}^{out} + L_{NO_3^-} + P_{NO_3^-} + f_T' k_{nitr}' R_{NH_4^+} - f_T' k_{denitr}' R_{NO_3^-} \quad (10)$$

$$26 \quad f_T' = T_p^{(T-T_r')} \quad (11)$$

$$1 \quad k'_{denitr} = \max\{k'_{denitr,min}, C_{d,s}(b_0 C_{NO_3^-}{}^{b_1} H^{b_2} c^t)\} \quad (12)$$

2 where, i is DON , NH_4^+ , or NO_3^- ; R_i is the river N (kg/m^2); F_i^{in} and F_i^{out} is the inflow and
3 outflow of the river N ($kg/m^2 s$); L_i is the N leaching from the soil ($kg/m^2 s$); P_i is the N
4 point source ($kg/m^2 s$); f_T' is the stream temperature reduction function; T' is the water
5 temperature ($^{\circ}C$); T_r' is the reference water temperature ($^{\circ}C$); T_p' is a parameter; k'_{min} , k'_{nitr} ,
6 and k'_{denitr} are the reaction rate constants for river mineralization, nitrification, and
7 denitrification ($1/s$); $k'_{denitr,min}$ is the minimum reaction rate constant of river denitrification
8 ($1/s$); $C_{NO_3^-}$ is the nitrate N concentration ($\mu mol N/l$); H is the river depth (m); b_0 , b_1 , and b_2
9 are the constants; c^t is the log re-transform bias correction factor; $C_{d,s}$ is a unit-conversion
10 constant.

11

12 **3 Study site**

13 The Susquehanna River basin, where nearly four million people live, is the largest of the
14 watersheds in the northeastern U.S. and drains an area of 71,220 square kilometers,
15 contributing two-thirds of the annual N load to the Chesapeake Bay (Fig. 3). The basin
16 includes 2,293 lakes, reservoirs, and ponds ($322 km^2$) as well as 50,190 kilometers of rivers
17 and streams. The main stem of the Susquehanna River originates at Otsego Lake, N.Y., and
18 flows about 750 kilometers through New York, Pennsylvania, and Maryland to the
19 Chesapeake Bay at Havre de Grace, Md. The Susquehanna Large River Assessment Project
20 reported that only 6.9 percent of water quality values exceeded their standards, but the
21 majority of these exceedances were for nutrients (e.g. TN, TP) (Hoffman, 2009), explaining
22 why the Chesapeake Bay suffers from nutrient enrichment problems and hypoxia.

23

1 The reported 2000 land use is about 63 percent forest or wooded, 19 percent crop land, 7
2 percent pasture, 9 percent urban, and 2 percent water. The Upper Susquehanna River flows
3 through mostly forested and agricultural land with some small communities and one larger
4 population center, then confluences with the Chemung River at Sayre, Pa. The West Branch
5 Susquehanna Sub-basin is mostly woods and grasslands. The Middle Susquehanna River,
6 from the confluences with the Chemung River at Sayre, Pa. to the confluences with the West
7 Branch Susquehanna River at Sunbury, Pa., flows along very diverse land use. The Lower
8 Susquehanna Sub-basin contains extensive agriculture and several large population centers.
9 The other major urban areas are found within the Juniata Sub-basin (Hoffman, 2008).

10

11 The geology of the watershed is mainly clastic sedimentary rock of sandstone and shale.
12 Elevations vary from 30 meters at the Chesapeake Bay in Maryland to 955 meters in central
13 New York State (McGonigal, 2011). The Great Lakes and Midwest climate exert influence
14 over the Upper Susquehanna, Chemung, and West Branch Susquehanna Sub-basin, whereas
15 the Atlantic coastal climate affect on the other portions of the watershed. The basin has
16 experienced severe droughts about once every decade, and the worst droughts occurred in
17 1930, 1939 and 1964. The basin is also one of the most flood-prone watersheds in the nation
18 with frequent and localized flash floods every year. The worst recorded flooding in the basin
19 happened in 1972 as a result of tropical storm Agnes.

20

21 **4 Stream Sampling Description**

22 Stream discharge data are provided by the network of stream gauges operated by the U.S.
23 Geological Survey (USGS), which collects and summarizes time series data to derive annual,
24 monthly, and daily stream discharge and statistics (Fig. 3). mode were monitored by the
25 USGS and Susquehanna River Basin Commission (SRBC). One USGS and six SRBC long-
26 term nutrient monitoring sites monitored since 1985 and 9 newly introduced SRBC sites
27 monitored since either 2004 or 2005 to present (Table 3; Fig. 3; McGonigal, 2011; USGS,
28 2014) were chosen for model evaluation. The 16 sites vary in sub-basin area and land use.
29 Among the USGS and SRBC sites, the Conowingo and Marietta sites on the main channel of
30 the Susquehanna River have the largest sub-basin areas respectively (70,189 and 67,314
31 km^2). The sub-basin of the Conestoga site contains extensive agriculture (48%) and the most

1 populated urban land use with several large population centers (24%) within a very small area
2 (1,217 km²). The West Branch River flows mostly along woods and grasslands to the
3 Lewisburg site. The long-term sites have collected two samples per month. Additional
4 samplings are made during seasonal storm conditions. The collected water samples are
5 analyzed for various N species: dissolved N (**DN**), dissolved nitrite and nitrate (**DNO₂₃**),
6 dissolved ammonia (**DNH₃**), dissolved organic N (**DON**), and dissolved ammonia and organic
7 N (**DKN**) in milligrams per liter. In addition, annual, seasonal, and monthly loads are
8 computed by the Minimum Variance Unbiased Estimator (ESTIMATOR; SRBC, 2006;
9 USGS, 2014). River temperatures were reported when the samplings were collected for the
10 chemical analysis of stream waters.

11

12 **5 Anthropogenic N sources**

13 Anthropogenic N data over the two decades (1985-2005) were provided by the Chesapeake
14 Community Modeling Program (CCMP). Atmospheric deposition data were provided by the
15 county-based land segments. Fertilizer, manure, and legume applications as well as combined
16 sewer overflows (CSOs) were provided by the land-river segments of the GIS-based Phase
17 5.3 Community Watershed Model (USEPA, 2010a). The atmospheric deposition data were
18 calculated by the Chesapeake Bay Program (CBP) Airshed Model, which is a combination of
19 a regression model of wet deposition (Grimm and Lynch, 2005) and the Community
20 Multiscale Air Quality Model (CMAQ) that estimates dry deposition (Dennis et al., 2007;
21 Hameedi et al., 2007). The fertilizer, manure, and legume data were estimated for the years of
22 1985, 1987, 1992, 1997, 2002, and 2005 by the Scenario Builder Version 2.2, a process based
23 model that is designed to use agricultural censuses as a main input data (USEPA, 2010b). The
24 agricultural censuses were produced by the United States Department of Agriculture National
25 Agricultural Statistics Service (NASS) and include data of animal populations, farms,
26 agricultural land areas, and crop yields. The point sources were estimated by 42 CSO
27 communities within the Susquehanna basin, using either various versions of EPA's Storm
28 Water Management Model (SWMM) or spatial data collected as a result of a direct survey of
29 the communities (USEPA, 2010a). The detailed data description can be found in the Phase 5.3
30 Community Watershed Model documentation (USEPA, 2010a).

1

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

9

10 Figure 4 shows spatial distribution maps of the applied anthropogenic N sources, which were
11 calculated as a spatial resolution of 0.125° by 0.125° and a temporal resolution of one year.
12 For each grid cell, which consists of up to 15 land-use tiles, atmospheric depositions (nitrate-
13 N, ammonium-N, and organic-N) were applied to all of the land tiles, and fertilizer, manure,
14 and legume applications (nitrate-N, ammonium-N, and organic-N) were applied only to the
15 crop land tiles. Combined sewer overflows (nitrate-N, ammonium-N, and organic-N) were
16 directly applied to the river reaches. The 20-year (1986-2005) average non-point and point N
17 sources for the six sub-basins are summarized in the Table 4. The thick solid arrows in Fig. 1
18 depict fluxes of each of N species for the anthropogenic N sources to the corresponding
19 terrestrial and river pools respectively.

20

21 **6 Model forcing and simulations**

22 The model was implemented with a spatial resolution of 0.125° by 0.125° with time
23 increments of 30 minutes. The model was forced using reported hydrological data cycled over
24 a horizon of 61 years (1948-2008) to perform long-term simulations. The data include
25 precipitation, specific humidity, air temperature, surface pressure, wind speed, and short and
26 long wave downward radiation with a spatial resolution of 1° by 1° on timescales of 3 hours
27 (Sheffield et al., 2006). Land-use change was simulated from 1704 to 2005 using a scenario of
28 land use transitions (Hurtt et al., 2006). Preindustrial CO_2 concentration assumed as 286 ppm

1 was applied from 1704 to 1799, and changes in CO₂ concentrations were applied from 1800 to
2 2005 using reported data from NOAA's Earth System Research Laboratory. For 250 years
3 (1704-1953), the estimated preindustrial N deposition (Dentener and Crutzen, 1944; Green et
4 al., 2004; Gerber et al., 2010) was applied as a uniform annual rate. We then applied the
5 reported 1985's anthropogenic N data from 1954 to 1984, and reported annual anthropogenic
6 N data from 1985 to 2005.

7

8 **7 Result and Discussion**

9 **7.1 Evaluation of stream waters and N loads**

10 We simulated with LM3-TAN stream dissolved organic-N, ammonium-N, and nitrate-N loads
11 throughout the river network. The model was calibrated by comparing the modeled stream N
12 loads with the corresponding reported N loads at the last downstream SRBC station Marietta,
13 in which contributions of the entire watershed to the stream flows and N loads can be
14 assessed. Thus, temporal evaluation of the stream discharges and N loads for the period 1987-
15 2005 was focused on at the Marietta station. River data from the 16 monitoring stations
16 (1986-2005) were also used to evaluate spatial stream discharges and N loads.

17

18 Using global hydrological data and a universal parameter set for the entire watershed, the
19 model produced reasonable temporal patterns of annual stream discharge. The simulated
20 stream discharges were in a good agreement with the reported values in dry years and periods
21 (July to September), but under-estimated stream discharges in wet years and periods (March
22 to May). Overall, although the 19-year average simulated discharge was about 28% lower
23 than the corresponding reported value, their linear and rank correlations were significantly
24 high (Table 5), implying that the bias was systemic and accounted for in the calibration of the
25 N species.

26

27 Due to their complex physical and biogeochemical interactions with soil particles and soil
28 organic matter, simulating reactive transport of ammonium and dissolved organic N is far
29 more challenging than simulating nitrate N transport. For example, the correlation at Marietta

1 between stream discharge and nitrate N load ($R^2 = 0.98$) was significantly higher than that
2 for dissolved organic N ($R^2 = 0.48$) or for ammonium N ($R^2 = 0.85$) loads, implying that in
3 addition to the hydrological processes governing soil N transport to rivers, terrestrial physical
4 and microbial processes (e.g., sorption to soil particles, organic matter decomposition and
5 stabilization) have to be accounted for when estimating stream ammonium and dissolved
6 organic N loads. This, plus the fact that the highest component in the overall stream N load is
7 nitrate N, explains why existing watershed models have focused on stream nitrate N loads,
8 and neglected ammonium and dissolved organic N loads. Within the LM3-TAN's integrated
9 modeling framework, we estimated all of the N species for the entire drainage network.

10

11 At Marietta, 19 year average simulated stream dissolved-N (-0.5%), nitrate-N (-0.2%),
12 ammonium-N (+4.7%), and dissolved organic-N (-2.6%) loads were close to the
13 corresponding reported values. Both of the simulated and monitored dissolved-N loads
14 consisted of predominantly nitrate N (79%), followed by dissolved organic-N (18%), and
15 ammonium-N (3%). The model also produced reasonable temporal patterns of annual
16 dissolved-N ($r = 0.7$), nitrate-N ($r = 0.6$), ammonium-N ($r = 0.7$), and dissolved organic-N ($r =$
17 0.6) loads (Fig. 5; Table 5). At Conowingo, 20 year average simulated nitrate-N load agreed
18 well with the corresponding reported value (-3.7%), but the model, which doesn't have lakes
19 or reservoirs, fails to capture inter-annual variations of the loads ($r = 0.2$), which are affected
20 by the reservoir system between the Marietta and Conowingo monitoring sites (Fig. 5).

21

22 Simulated and reported dissolved -N loads were graphed in different units: **millions of kg/yr**
23 and **kg/km² yr** (normalized by its sub-basin area summarized in Table 3). Among the 6 long-
24 term monitoring sites, the highest and lowest amount of river N loads were reported and
25 simulated at the Marietta and Conestoga sites respectively (Fig. 6a). This finding is consistent
26 with the general view that the amount of stream N loads is proportional to size of the basin
27 area. A very high N flux was reported at the Conestoga site (Fig. 6b), which can be explained
28 by its sub-basin's extensive agriculture and urban land use. Because the West Branch
29 Susquehanna is dominated mostly by woods and grasslands, the Lewisburg site had the lowest

1 N flux. The model also captured the stream N loads at the 15 monitoring sites well (Fig. 6c
2 and 6d). These results attest to the model ability to correctly simulate the stream N loads for
3 the entire basin based on the climate as well as land use and the corresponding N sources and
4 transformations in the sub-basins.

5

6 **7.2 Spatial distribution of stream N load and soil denitrification rate**

7 Observation of the spatial distribution of the river N load (Fig. 7) and soil denitrification rate
8 (Fig. 8d) helps to identify the extent of the terrestrial and aquatic N pollution across the basin.
9 A large amount of N is exported via the main stem of the Susquehanna River as well as its
10 three major tributaries, where many small-order streams converge. The N loads in the streams
11 increase gradually from the headwaters to the watershed outlet, implying that the N loads to
12 the rivers exceed N removal mechanisms within the rivers. Although stream N loads are in
13 general higher in the larger rivers, at the Lower Susquehanna sub-basin, high N loads are
14 present even in small-order streams due to the extensive agricultural land use.

15

16 Figure 8 presents 20 year average (1986-2005) simulated soil water content, temperature,
17 nitrate-N content, and denitrification rate, and these for each of 6 sub-basins as well as the
18 corresponding sub-basin area, non-point and point N sources are summarized in Table 4. An
19 analysis for the 6 sub-basins shows that the combined effects of land use and climate on the
20 soil denitrification rate, which were the highest in the Lower Susquehanna Sub-basin
21 (extensive agriculture; Atlantic coastal climate) and the lowest in the West Branch
22 Susquehanna Sub-basin (mostly forest; Great Lakes and Midwest climate). These results
23 show that the most significant soil denitrification is associated with extensive agricultural land
24 use (non-point sources). The calculated R^2 statistic between the monthly soil denitrification
25 rate and soil water content ($R^2 = 0.51$) was significantly higher than that for soil temperature
26 or soil nitrate N content, implying that the soil water content played the greatest role in the
27 soil denitrification process among the three factors. This is because the soil denitrification
28 occurred and increased non-linearly only when the soil water content exceeded the threshold
29 point ($S_t = 0.577$). The significant effect of the soil water content on the soil denitrification is

1 further illustrated in the upper east side of the Upper Susquehanna Sub-basin, where
2 extremely low soil water content (Fig. 8a) impeded the overall soil denitrification process
3 (Fig. 8d).

4

5 **7.3 N budget**

6 As a further means of evaluating the model output, we compared the simulated N budget for
7 the period 1988-1992 to the budget constructed by Boyer et al. (2002), Seitzinger et al.,
8 (2002), and Van Breemen et al., (2002) for the same period (Fig. 9). Overall, reasonable
9 agreements were found between these two budgets. Total N inputs to the whole basin were
10 reported as 4,774 ($\text{kg}/\text{km}^2 \text{ yr}$; atmospheric deposition + fertilizer + forest and agricultural N
11 fixation + net N import in feed and food), while we applied 4,443 of N ($\text{kg}/\text{km}^2 \text{ yr}$;
12 atmospheric deposition + fertilizer + manure + legume + sewage) using the data sources
13 provided by CCMP (USEPA 2010a). The simulated soil denitrification (-4%), harvest rates
14 (+7%), river export (-1%), and river denitrification (-5%) agreed well with the corresponding
15 reported values. To investigate the importance of N removal within rivers, we ran an
16 experiment in which the reaction rate constant for river denitrification was set to zero. We
17 then compared N loads within the rivers with and without river denitrification. Figure 10
18 shows a spatial map of the difference in N loads between these simulations, which represents
19 the river N removal. A large amount of N was removed along the main stem of the
20 Susquehanna River as well as its three major tributaries, implying that the N removal
21 increases gradually as distance from the headwaters increases. About 28 percent of the N that
22 enters to the rivers was removed by river denitrification.

23

24 For the entire basin, we divided the simulated land use into either agricultural land (cropland
25 and pasture) or secondary forest (land formerly disturbed by human activities). We then
26 graphed simplified N budgets for each land use (Fig. 9c). The reported agricultural land use
27 was 29 percent (Fig. 9a), whereas the model simulated 24 percent of cropland and pasture
28 (Fig. 9b). In the secondary forest land, most of the applied N (43%) was stored in the
29 terrestrial system (vegetation and soil pools), whereas the highest proportion of the applied N
30 was removed by soil denitrification (44%) in the agricultural land. These results imply that

1 applications of artificial N to agricultural lands can result in considerable soil denitrification
2 rates, and thus significant increase of N_2O production. This is evident when comparing maps
3 of the applied fertilizer, manure, and legume N applications (Fig. 4c and 4d) and the
4 simulated soil denitrification (Figure 8d) that corresponds well, especially in the Lower
5 Susquehanna Sub-basin with extensive agricultural land use. Even if there are some
6 discrepancies between these two budgets, we can conclude that the reactive transport of N
7 from the terrestrial to aquatic ecosystems was appropriately simulated by the model,
8 providing suitable descriptive information for the entire drainage network.

9

10 **8 Conclusions**

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

- 13 • On a sub-basin scale with different climate and land-use regimes, the LM3-TAN properly
14 simulates terrestrial N cycling, including effects of long-term vegetation dynamics, land-
15 use changes, and hydrological cycles. The interaction among those three processes allow
16 LM3-TAN to capture soil C-N organic matter and mineral N transformations as well as
17 soil emissions of nitrate-N and leaching of dissolved organic, ammonium, and nitrate N.
- 18 • The ability to capture N soil budget and losses then enables LM3-TAN to consistently
19 characterize trends and variability in riverine N inputs and exports of ammonium,
20 dissolved organic, and nitrate N with explicit representation of their transformations and
21 transport in rivers.
- 22 • In the re-growing secondary forests, a large fraction of the N from atmospheric
23 deposition has been stored in the vegetation and soil, but in the agricultural lands most N
24 inputs were removed by soil denitrification indicating that anthropogenic N inputs could
25 drive substantial increase of N_2O emission, an intermediate of the denitrification process.
- 26 • LM3-TAN captures effects of long-term trends and variability of hydrological cycles
27 (e.g., precipitation, soil water content, stream discharge) on N cycling in vegetation-soil-
28 river system, and thus resolves inter-annual variations of stream N loadings caused by
29 climate variability.

- 1 • The model results suggest that the soil denitrification is most sensitive to soil water
2 variations.
- 3 • Among the 6 sub-basins, the soil denitrification rate was the highest in the Lower
4 Susquehanna Sub-basin with the most intensive land-use non-point N sources as well as
5 with the warmest and wettest soils, attributed to the Atlantic coastal climate.
- 6 • Even though the N denitrification and riverine biogeochemistry N modules were
7 calibrated only at the last downstream station Marietta, application of the universal
8 parameters at the entire watershed produced simulations which compared well at other
9 observational stations. The applicability of the universal parameters in other watersheds
10 is a subject of the future research.
- 11 • This study shows that linking terrestrial N and C cycling, long-term land-use and
12 vegetation dynamics, and hydro-climate variations to N loads and concentrations in
13 streams, provides an effective and consistent framework for analysis of the surface water
14 N processes and water quality for large watersheds and basins.

15

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20

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27

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31

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24

1 Table 1. Newly introduced or adjusted parameters from the earlier developments.

Parameter	Description	Value	Unit	Reference or Rationale
Parameters in the Land Component Equations				
b_{DOM} , $b_{NH_4^+}$, $b_{NO_3^-}$	buffering factors for DOM, ammonium-N, nitrate-N	3, 5, 1	unitless	Leadly et al., 1997; Neff and Asner, 2001
f_{DOM}	fraction of litter soil decomposition that becomes potential DOM (Gerber et al., 2010)	0.034	unitless	calibrated to match stream DON loads; Gerber et al., 2010
k_{denitr}	first-order denitrification coefficient	6.5	1/yr	Heinen, 2006
r_{DOM} , $r_{NH_4^+}$, $r_{NO_3^-}$	calibration factors for DOM, ammonium-N, nitrate-N	10, 20, 100	unitless	calibrated to match inter-annual variations of stream N loads
q_{max}	transfer fractions from slow litter to slow soil (Gerber et al., 2010)	0.6	unitless	Parton et al., 1993; Bolker et al., 1998; Gerber et al., 2010
q_{SP}	transfer fractions from slow litter to passive soil (Gerber et al., 2010)	0.004	unitless	Parton et al., 1993; Bolker et al., 1998; Gerber et al., 2010
S_{min}	minimum soil water content	0	unitless	Bril et al., 1994; Heinen, 2006
S_{max}	maximum soil water content	1	unitless	Bril et al., 1994; Heinen, 2006
S_t	threshold soil water content	0.577	unitless	Bril et al., 1994; Heinen, 2006
w	empirical constant	2	unitless	Bril et al., 1994; Heinen, 2006
T_p	parameter	10	unitless	Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006
T_r	reference temperature	15	°C	Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006

Q_{10}	factor change in rate with a 10 degree change in temperature	2	unitless	Sogn and Abrahamsen, 1997; Johnsson et al., 1987; Heinen, 2006
Parameters in the River Component Equations				
b_0, b_1, b_2	constants	0.559, -0.478, -0.612	unitless	Alexander et al., 2009
c^t	log re-transform bias correction factor	1.90	unitless	Alexander et al., 2009
$k'_{denitr,min}$	minimum reaction rate constant of river denitrification	0.53/86400	1/s	Alexander et al., 2009
$C_{d,s}$	unit-conversion constant	1/86400	day/s	conversion from 1/day to 1/s
k'_{min}, k'_{nitr}	reaction rate constants for river mineralization, nitrification	0.11/86400, 0.51/86400	1/s	calibrated to match stream N loads
T'_p	parameter	1.047	unitless	Wade et al., 2002
T'_r	reference water temperature	20	°C	Wade et al., 2002

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- 1 Table 2. Definition of prognostic (PV) and diagnostic (DV) variables and inputs/forcings (IF)
 2 used in the equations.

Vegetation and Soil Equations			
C_{LF}, C_{LS}, C_{SS}	PV	fast litter, slow litter, slow soil C contents	kg/m ²
D_N	DV	soil denitrification rate	kg/m ² yr
D_s	DV	water drainage from active soil layer	kg/m ² s
f_{LF}, f_{LS}, f_{SS}	PV	fractions of soluble organic N in the fast litter, slow litter, slow soil N pools (Gerber et al., 2010)	unitless
f_S	PV	soil water content reduction function	unitless
f_T	PV	soil temperature reduction function	unitless
h_s	PV	effective soil depth	m
$L_{DON}, L_{NH_4^+}, L_{NO_3^-}$	PV	soil leaching for DON, ammonium-N, nitrate-N	kg/m ² s
$[N_{DON,av}], [N_{NH_4^+,av}], [N_{NO_3^-,av}]$	PV	concentration of available N in DOM, ammonium-N, nitrate-N pools	kg/m ³
N_{LF}, N_{LS}, N_{SS}	PV	fast litter, slow litter, slow soil N contents	kg/m ²
$N_{NH_4^+}, N_{NO_3^-}$	PV	soil ammonium-N, nitrate-N contents	kg/m ²
S	PV	soil water content	unitless
T	PV	soil temperature	°C
River Equations			
$C_{NO_3^-}$	PV	nitrate-N concentration	μmol N/l
f'_T	PV	stream temperature reduction function	unitless
$F_{DON}^{in}, F_{NH_4^+}^{in}, F_{NO_3^-}^{in}$	DV	river inflow of DON, ammonium-N, nitrate-N	kg/m ² s

$F_{DON}^{out}, F_{NH_4^+}^{out}, F_{NO_3^-}^{out}$	DV	river outflow of the DON, ammonium-N, nitrate-N	$\text{kg/m}^2 \text{ s}$
H	IF	river depth	m
k'_{denitr}	PV	reaction rate constant for river denitrification	1/s
$P_{DON}, P_{NH_4^+}, P_{NO_3^-}$	IF	point sources of DIN, ammonium-N, nitrate-N	$\text{kg/m}^2 \text{ s}$
$R_{DON}, R_{NH_4^+}, R_{NO_3^-}$	DV	DON, ammonium-N, nitrate-N in rivers	kg/m^2
T'	PV	water temperature	°C

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1 Table 3. Susquehanna River Basin Geographic Statistics for the USGS and SRBC nutrient
 2 monitoring sites (McGonigal, 2011; USGS, 2014).

Site Location	Waterbody	Sub basin Area, km ²	2000 Land Use Percentages					
			Water/ Wetland	Urban	Agricultural		Forest	Other
					Cropland	Pasture		
7 Long-term Sites								
Towanda, 1989~	Susquehanna	20,194	2	5	17	5	71	0
Danville, 1985~	Susquehanna	29,060	2	6	16	5	70	1
Lewisburg, 1985~	W B Susque	17,734	1	5	8	2	84	0
Newport, 1985~	Juniata	8,687	1	6	14	4	74	1
Marietta, 1987~	Susquehanna	67,314	2	7	14	5	72	0
Conestoga, 1985~	Conestoga	1,217	1	24	12	36	26	1
Conowingo, 1985~	Susquehanna	70,189	2	9	7	19	63	0
9 Newly Introduced Sites								
Conklin, 2005~	Susquehanna	5,778	3	3	18	4	71	1
Smithboro, 2004~	Susquehanna	11,989	3	5	17	5	70	0
Campbell, 2005~	Cohocton	1,217	3	4	13	6	74	0
Chemung, 2004~	Chemung	6,488	2	5	15	5	73	0
Wilkes-Barre, 2004~	Susquehanna	25,785	2	6	16	5	71	0
Karthaus, 2004~	W B Susque	3,785	1	6	11	1	80	1
Castanea, 2004~	Bald Eagle	1,087	1	8	11	3	76	1
Saxton, 2004~	Raystown B Juni	1,957	<0.5	6	18	5	71	0
Manchester, 2004~	W Conewago	1,320	2	13	12	36	36	1

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1 Table 4. Sub-basin area, 20 year (1986-2005) average applied non-point and point N sources,
 2 and simulated soil water content, temperature, nitrate-N content, and denitrification rate (% of
 3 the non-point N sources) for each of 6 sub-basins.

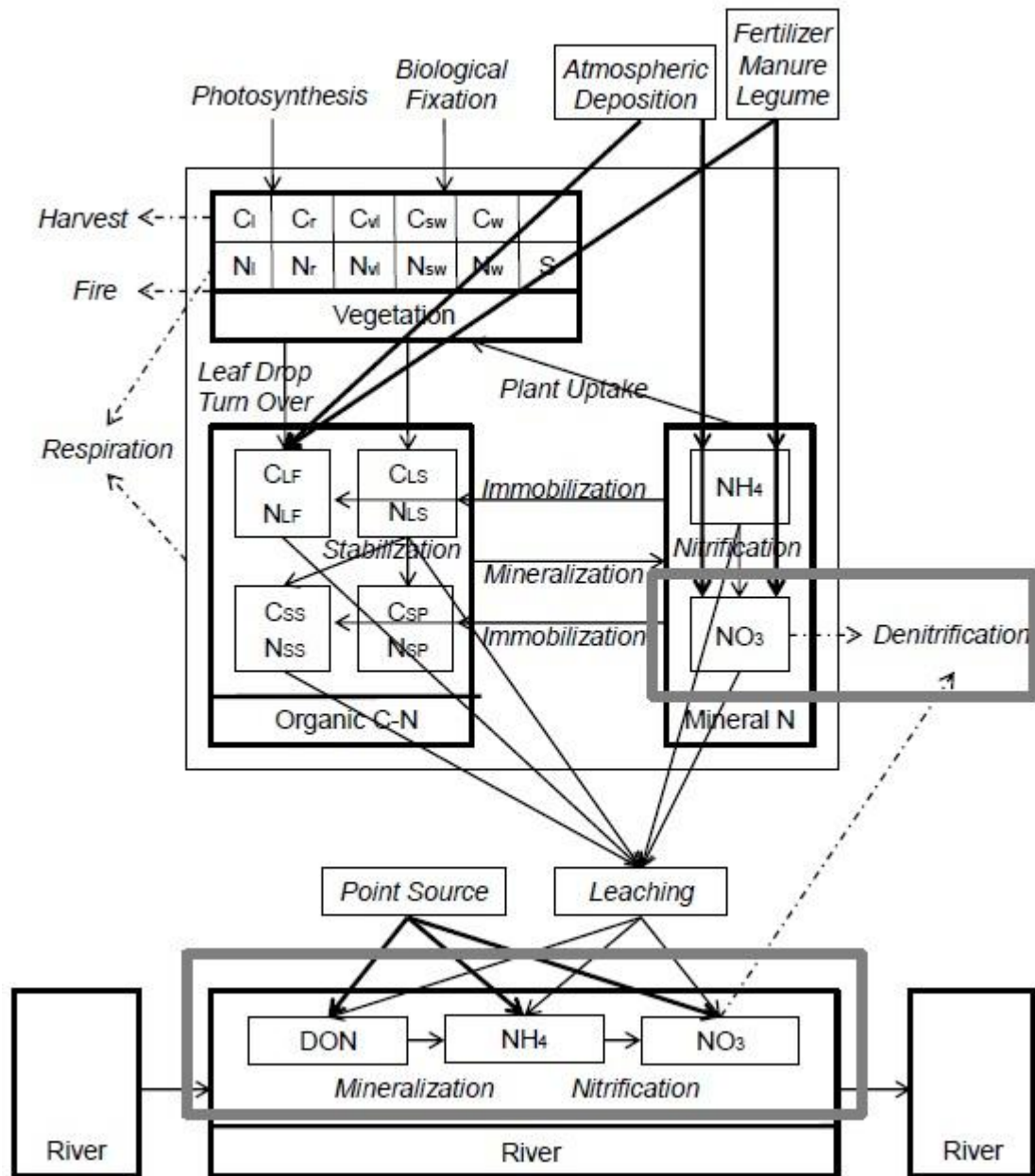
6 Sub-basins	Basin Area, km ²	Non-point N Sources kg/km ² yr	Point N Sources kg/km ² yr	Soil Water Content	Soil Temp. C	Soil Nitr. N kg/km ²	Soil Denitr. kg/km ² yr
Upper Susquehanna	14,126	3,315	40	0.439	8.65	12,713	1,213 (37%)
Chemung	6,731	2,962	76	0.454	8.60	9,888	916 (31%)
Middle Susquehanna	9,847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

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1 Table 5. Temporal evaluation of the annual stream discharges and N loads for the period
 2 1987-2005 at Marietta. If a p-value is smaller than 0.05, the correlation between the modeled
 3 and reported data is significantly different from zero.

		Discharge	DN	Nit. N	Amm. N	DON
R^2		0.6	0.5	0.4	0.5	0.4
Corr.	Pearson's linear	0.7	0.7	0.6	0.7	0.6
	(p-value)	(< 0.0001)	(< 0.0001)	(0.0044)	(< 0.0001)	(0.0064)
Coef.	Spearman's rho	0.7	0.7	0.6	0.6	0.6
	(p-value)	(0.0011)	(< 0.0001)	(0.0056)	(0.0099)	(0.0160)

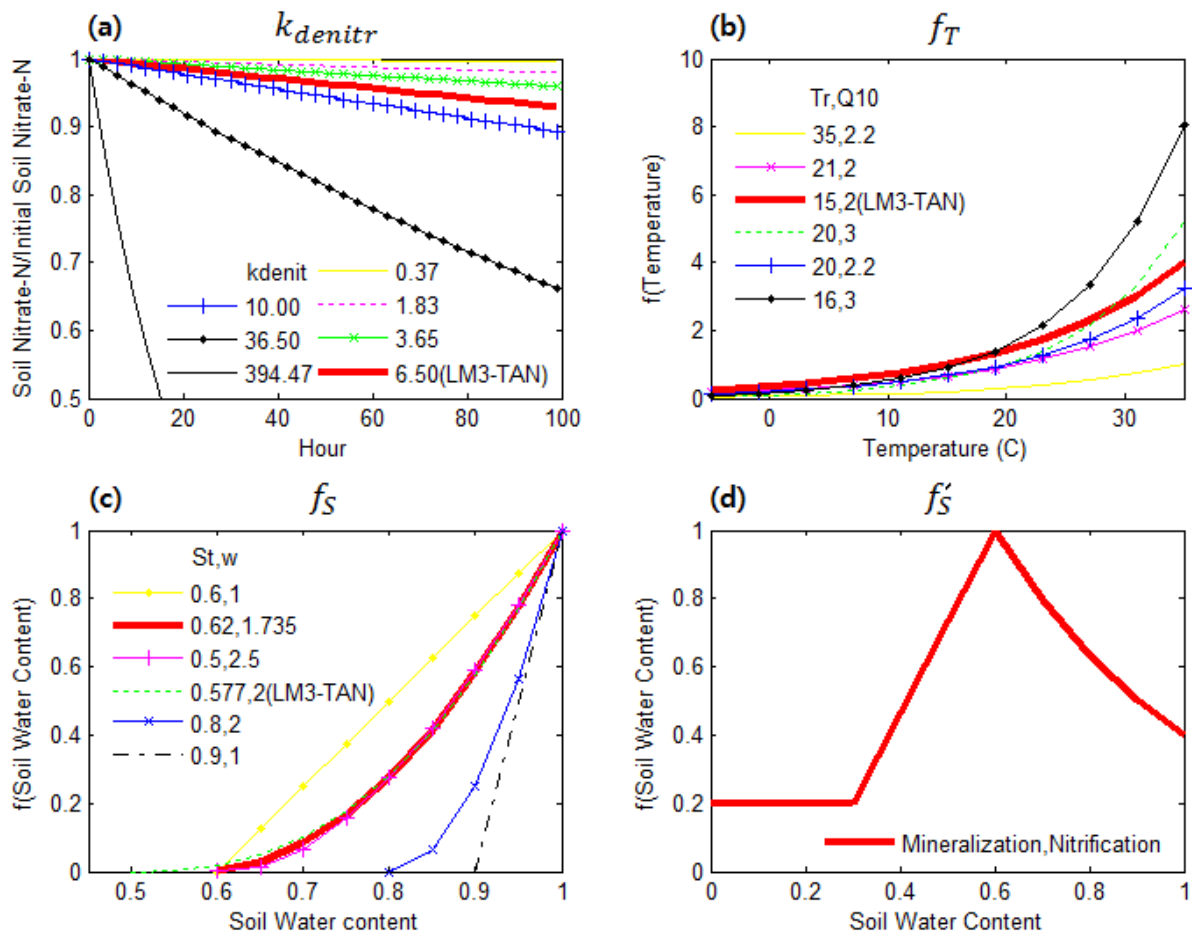
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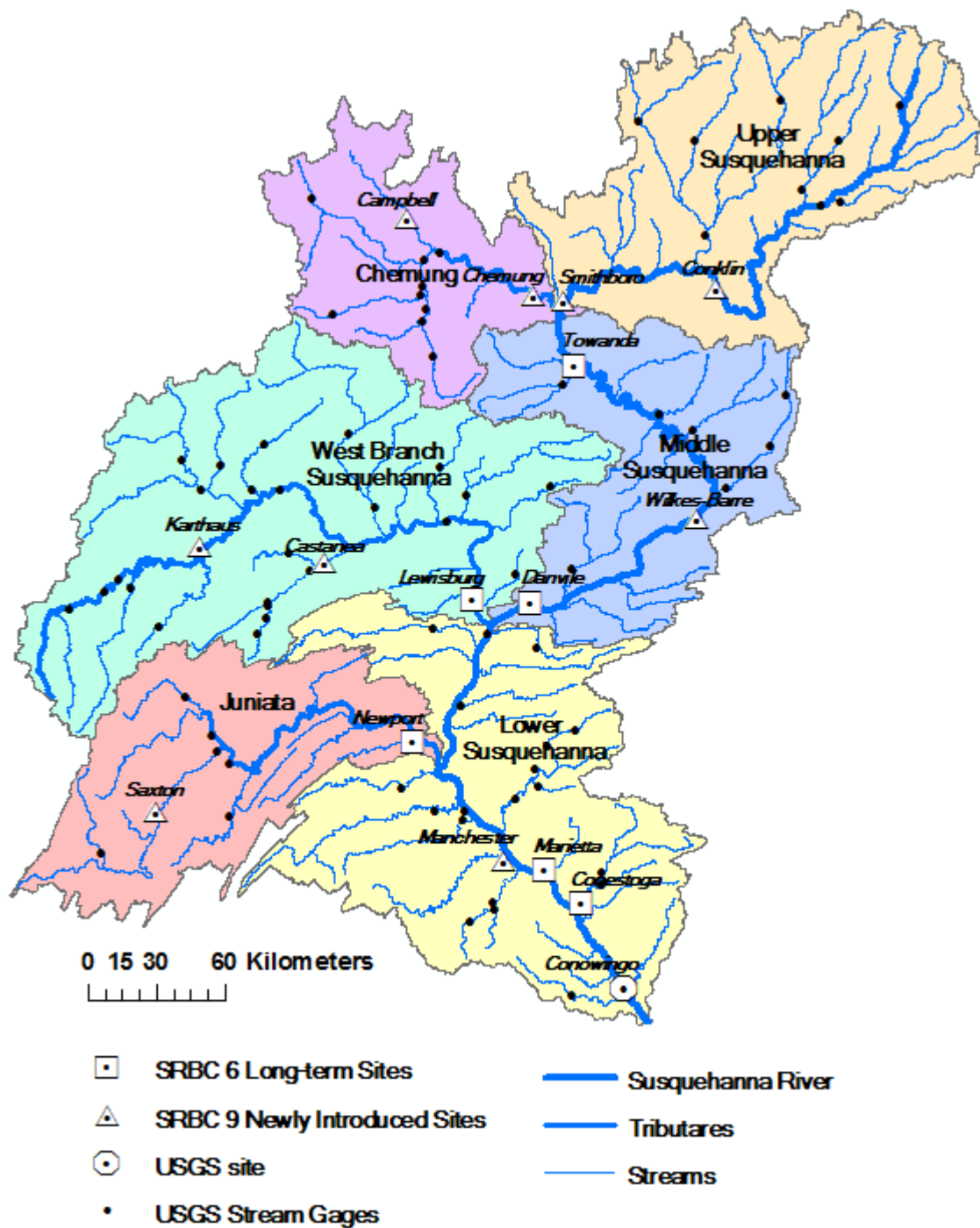
3 Figure 1. Structure of LM3-TAN. Two thick boxes show the incorporated denitrification
 4 module in the terrestrial component and stream microbial processes in the river component.
 5 The river systems are a series of continuously stirred tank reactors (CSTR) that simulate
 6 stream mineralization, nitrification, and denitrification. The other boxes show major C and N
 7 pools in vegetation (leaves, fine roots, labile, sapwood, heartwood, and N buffer storage), soil
 8 (fast and slow little, slow and passive soil, mineral N), and river (organic and mineral N). The
 9 arrows depict fluxes of anthropogenic N sources (thick solid), C-N organic compounds and

- 1 mineral N (thin solid) with associated processes (*italic*), and C and N lost to the atmosphere or
- 2 anthropogenic pool (dashed).
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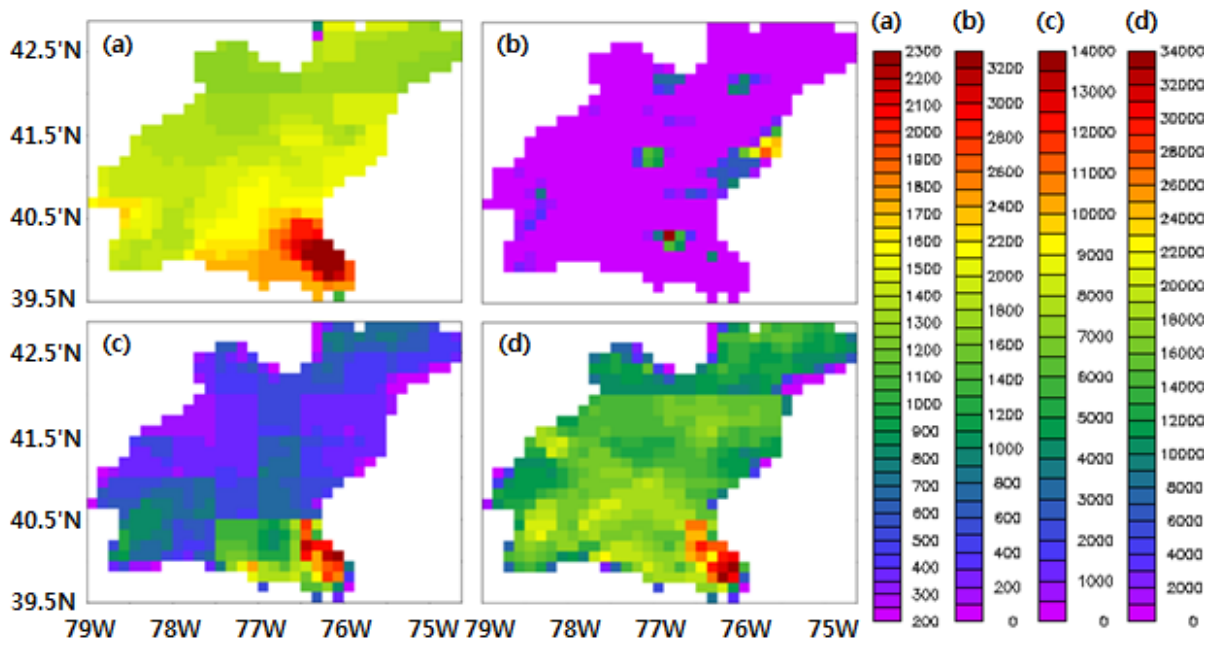
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Figure 2. Overview of the denitrification module. Effects of first-order denitrification coefficient (a), soil temperature reduction function (b), soil water content reduction function (c) on soil denitrification rate; soil water content reduction function for mineralization and nitrification (d). The curves were produced using the Table 3, 6, and 7 in Heinen (2006).



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Figure 3. Map of the Susquehanna watershed, showing 6 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.



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3 Figure 4. Spatial distribution maps of the applied 20 year (1986-2005) average anthropogenic
 4 N sources: atmospheric deposition ($\text{kg}/\text{km}^2 \text{ year}$) (a), combined sewer overflow
 5 ($\text{kg}/\text{km}^2 \text{ year}$) (b), and fertilizer, manure, and legume applications ($\text{kg}/\text{km}^2 \text{ year}$) (c) and
 6 ($\text{kg}/\text{crop land km}^2 \text{ year}$) (d).

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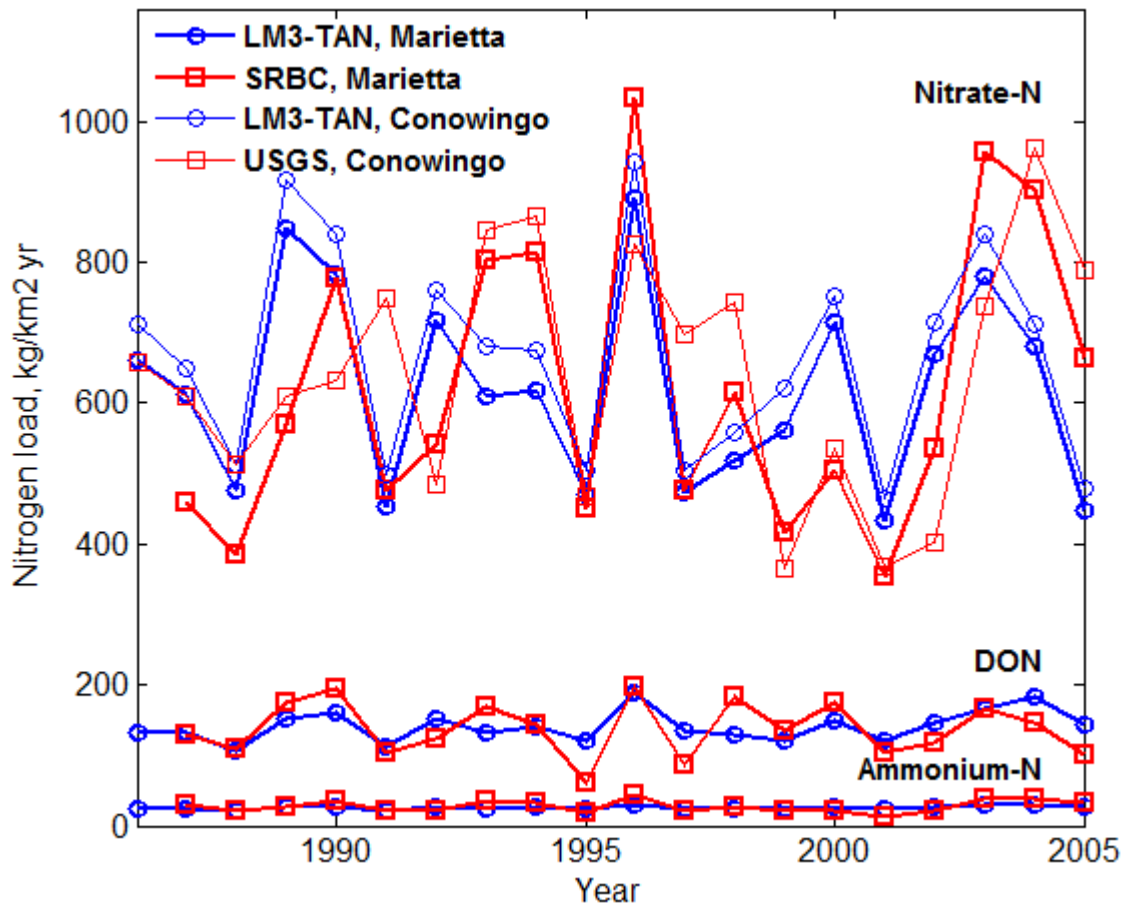
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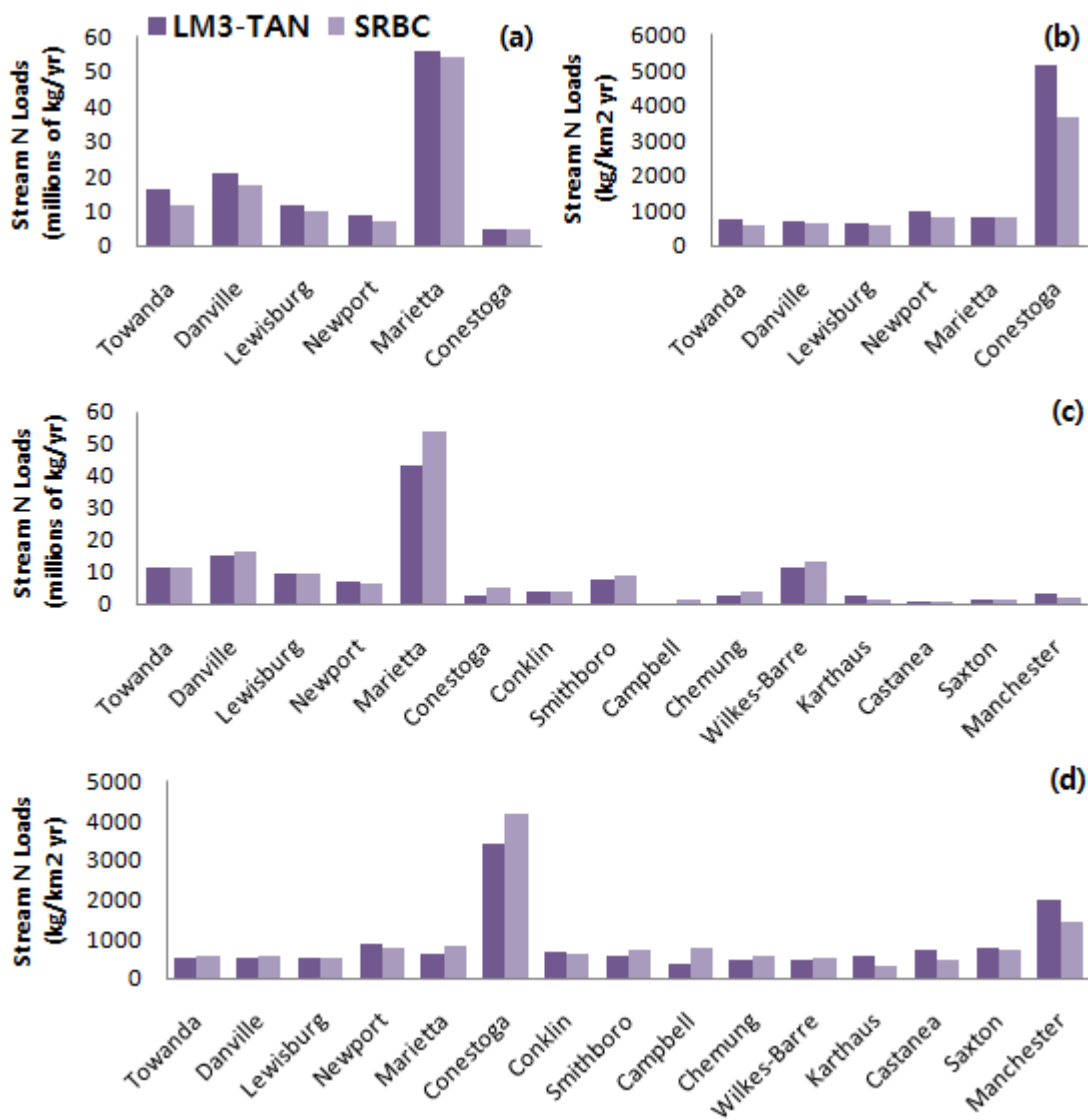
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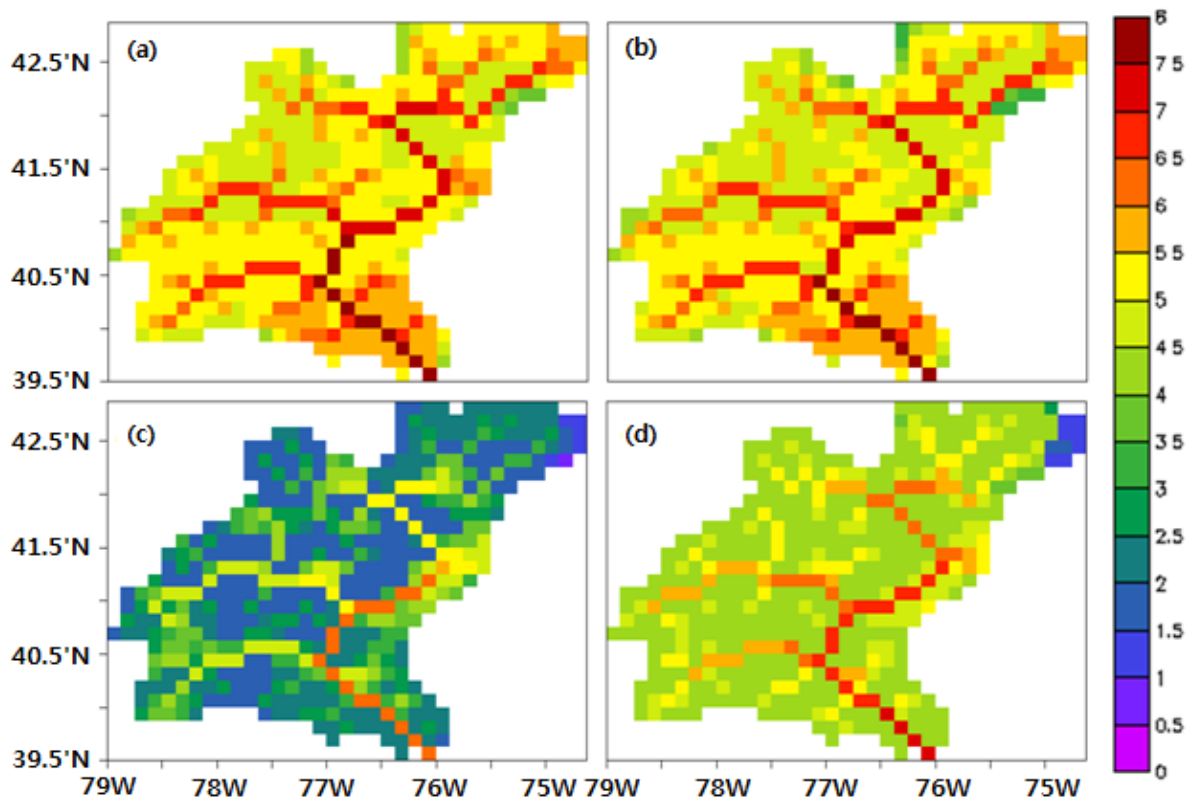
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Figure 5. 20 years (1986-2005) of the simulated stream N loads (normalized by sub-basin areas) at Marietta and Conowingo and the corresponding reported data from SRBC and USGS.



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Figure 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.



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3 Figure 7. Spatial distribution maps of 20 year (1986-2005) average simulated stream (a)
 4 dissolved N, (b) nitrate N, (c) ammonium N, and (d) dissolved organic N loads,
 5 log (kg/year).

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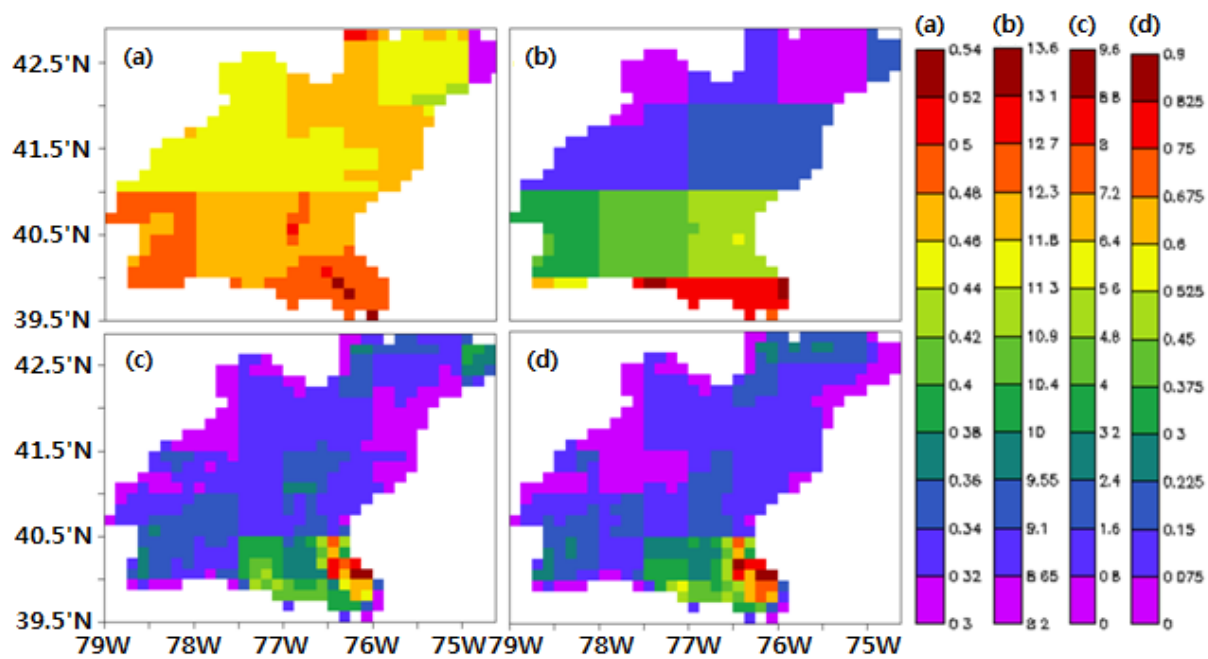
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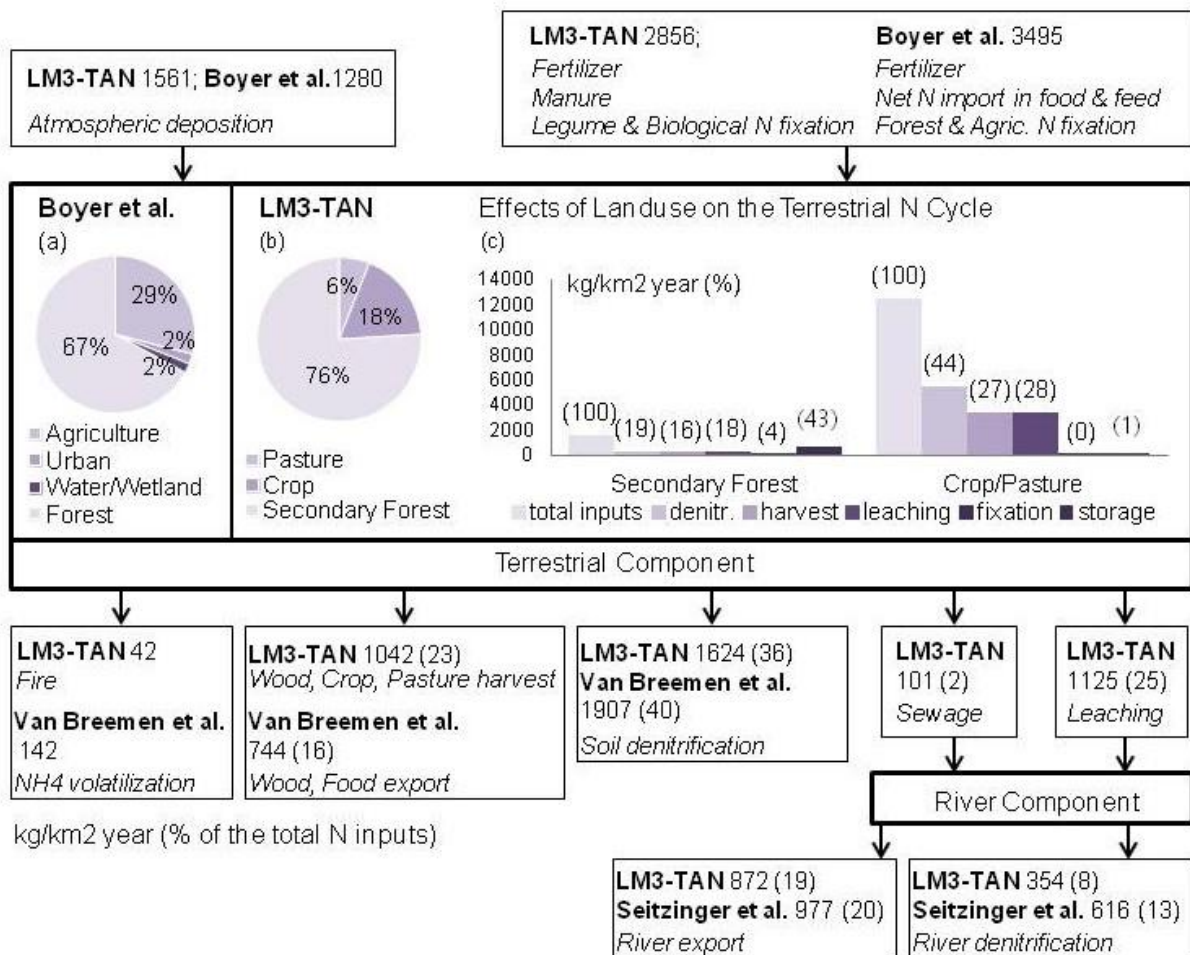
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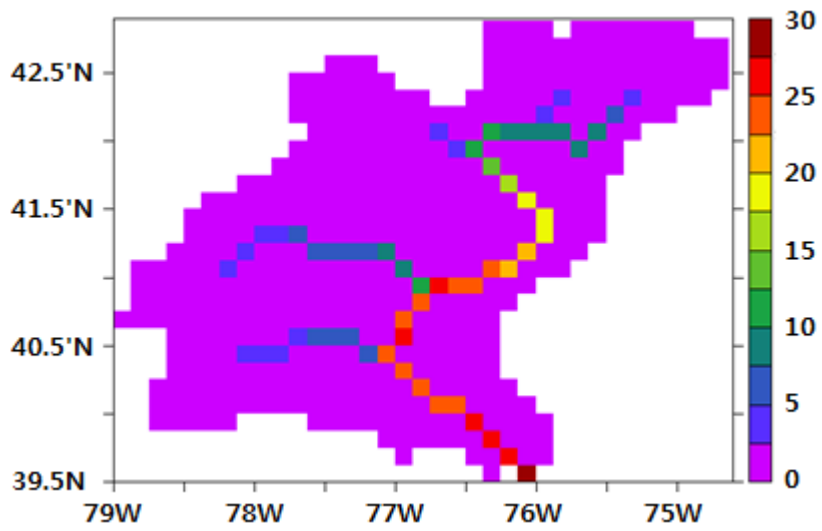
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Figure 8. Spatial distribution maps of 20 year average (1986-2005) (a) soil water content, (b) temperature ($^{\circ}\text{C}$), (c) nitrate N content ($10^2 \times \text{kg/m}^2 \text{ year}$), and (d) denitrification rate ($10^2 \times \text{kg/m}^2 \text{ year}$).



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Figure 9. Comparison between the calculated and reported budgets of N sources, retention, lost, transport, and river export at the level of the whole Susquehanna watershed for the period 1988 to 1992 (Boyer et al., 2002; Breemen et al., 2002; Seitzinger et al., 2002; USEPA, 2010a).



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3 Figure 10. N removal by river denitrification (%) = (river N load with “ $k'_{denitr}=0$ ” – river N

4 load with “estimated k'_{denitr} ”) / river N load with “ $k'_{denitr}=0$ ” $\times 100$.