Title

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Permalink

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Journal

Transactions of the ASAE, 47(3)

ISSN

0001-2351

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Publication Date

2004-05-01

Peer reviewed

MODELING MINERAL NITROGEN EXPORT FROM A FOREST TERRESTRIAL ECOSYSTEM TO STREAMS

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ABSTRACT. *Terrestrial ecosystems are major sources of N pollution to aquatic ecosystems. Predicting N export to streams is a critical goal of nonpoint−source modeling. This study was conducted to assess the effect of terrestrial N cycling on stream N export using long−term monitoring data from Hubbard Brook Experimental Forest (HBEF) in New Hampshire. The field−scale DAYCENT model was used to quantify N pools and long−term annual streamflow and mineral N export for six subwatersheds at the HBEF. By combining DAYCENT with the Soil and Water Assessment Tool (SWAT) watershed model, mineral N export simulations were extended to the watershed scale. Our study indicated that only 13% of external N input was exported to streams during 1951−2000 at HBEF. As much as 4763 kg/ha of N was stored in forest litter, soil organic matter (SOM), and living plant biomass. Net N mineralization of SOM and forest litter contributed 93% of total available N for export within the HBEF ecosystem. The Nash−Sutcliffe coefficient (E_{ns}) evaluating model performance of DAYCENT at six subwatersheds ranged from 0.72 to 0.82 for simulating annual streamflow (1964−2000) and from 0.48 to 0.67 for annual mineral N export (1971−1995), indicating reasonable simulated values. DAYCENT successfully predicted the effect of ecosystem disturbance such as forest cut and insect invasion on stream mineral N export. The watershed−scale simulation suggested that soil spatial variability affects stream N export in addition to the accepted controls of land cover, external N input, climate, and ecosystem disturbance.*

Keywords. *Biogeochemical processes, Hardwood forest, Modeling, Nitrogen export, Nonpoint−source pollution, Soil organic matter, Terrestrial ecosystem, Water quality.*

Nitrogen (N) loading of terrestrial ecosystems is increasing worldwide as a result of human activities (Vitousek et al., 1997). As excess N exports from terrestrial ecosystems and moves with surface runoff and groundwater flow to streams, lakes, rivers, and coastal oceans, N loadings contribute to the nutrient enrichment of surface waters and the widespread international problem of aquatic eutrophication (Carpenter et al., 1998; Burkart and James, 1999). Nutrient exports from the terrestrial ecosystems to surface receiving waters and estuaries may be one causal factor contributing to the occurrence of harmful algal blooms and hypoxia in coastal waters (Burkart and James, 1999). In many estuaries, over−enrichment of N leads to eutrophication, presently the most widespread pollution problem in coastal marine waters of the U.S. (National Research Council, 2000). For instance, over 40% of the estuaries in the U.S. are degraded from eutrophication, with particularly severe problems in the New England, mid−Atlantic regions and the dead zone in the Gulf of Mexico (Bricker et

al., 1999; Mitsch et al., 2001). Nitrogen loadings in major U.S. rivers have increased during recent decades (Puckett, 1995; Jaworski et al., 1997). Most N delivered to coastal waters in the U.S. comes from nonpoint sources of the terrestrial ecosystems, with agricultural sources and atmospheric deposition being major contributors (Howarth et al., 1996; Goolsby et al., 1999; Castro et al., 2001). Quantitative estimate of N export from terrestrial ecosystems to streams is needed to develop nutrient management strategies.

The amounts of N fixed from natural and human activities have received much attention, but the fate and transport processes of this reactive N in terrestrial ecosystems are poorly understood. Terrestrial N cycling appears to be one of the greatest sources of uncertainty in quantitative estimates of stream N export (Krug and Winstanley, 2002). Recent studies concluded that only 20% to 60% of N inputs are exported in streamflow (Campbell et al., 2000; Dise et al., 1998; Castro et al., 2001; Howarth et al., 1996). In the forest−dominated watersheds of the northeastern U.S., riverine export of N represented only 11% to 40% of the total N inputs (Van Breemen et al., 2002). The N input in excess of riverine export has been termed the "missing nitrogen," highlighting the uncertainty in the scientific community of how to quantify the fate and transport of N in terrestrial ecosystems. The fraction of N "consumed" by the terrestrial ecosystems and not delivered to streamflow is partly stored within terrestrial ecosystems, with residence times exceeding decades to centuries, and partly returned to the pool of highly inert atmospheric N_2 by denitrification. The input N is not directly delivered to streams but rather enters soil pools and participates in the complex N cycling within terrestrial ecosystems. Approximately 90% of N in soil is contained in

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soil organic matter (SOM) (Stevenson, 1982). The identification of N biogeochemical processes associated with SOM dynamics in terrestrial ecosystems appears to be crucial for estimating stream N export using a deterministic model.

A variety of statistical and deterministic model methods have been used to estimate N export. Statistical approaches to modeling nitrogen flux have their origins in simple correlations of stream nitrogen measurements with watershed sources and landscape properties. These methods assume limited *a priori* knowledge of biogeochemical processes, but they provide empirical estimates of the aggregate supply and loss of nitrogen through the use of conventional stream monitoring data. Anthropogenic N sources constitute the principle predictor variables in these models. Some of the models (e.g., Howarth et al., 1996) make use of literature rates of N processing (crop N fixation, N removal in crops) to estimate agricultural source inputs. Recent examples include regressions of nitrogen export from watersheds on human population density (Peierls et al., 1991), net anthropogenic sources (Howarth et al., 1996), atmospheric deposition (Jaworski et al., 1997; Howarth et al., 1996), and measures of per capita energy consumption by humans (Meybeck, 1982). In contrast to complex deterministic models, these statistical methods have the advantage of being readily applied to large watersheds. Moreover, statistical approaches are capable of quantifying errors in model parameters and predictions. These simple correlative models are limited, however, in that they consider sources and sinks to be homogeneously distributed in space, they do not separate terrestrial from in–stream loss processes, and they cannot assess the effect of terrestrial N cycling on stream N export.

Export coefficient is a common statistical approach that has been used for more than 25 years to predict nutrient losses from the terrestrial landscape to surface receiving waters (Johnes, 1996). Export coefficients can be combined with information on land use and land cover to predict terrestrial N export, but precision is poor because the variability in export coefficients is large. There also are numerous sources of temporal and spatial variation (e.g., soil type, fertilizer type and amount, crop type, and land management practices) that cannot be fully incorporated into export coefficients. Uncertainties in export coefficients are a serious limitation to their use for estimating N export to surface receiving waters. Moreover, export coefficients and other empirically derived statistical models do not convey information about which terrestrial ecosystem processes are potentially important contributors to nonpoint–source N loading.

Deterministic nonpoint–source models, such as HSPF (Bicknell et al., 1997), SWAT (Arnold et al., 1993), and AGNPS (Young et al., 1995), describe transport and loss processes in detail by simulating nitrogen availability, transport, and attenuation processes according to mechanistic functions that include descriptions of the spatial and temporal variations in sources and sinks in watersheds. Although these models have been widely applied to nonpoint–source water quality prediction, they are rarely used to calculate stream N export and other N fluxes and pools within the terrestrial ecosystem. One of their limitations is that most have been developed for agricultural ecosystems. Nitrogen biogeochemical processes in forest and mixed ecosystems are not included or not adequately described in most common nonpoint–source models. Another problem is that the

association of N fluxes with SOM is not explicitly expressed. This limits their application to predicting N export and determining the model uncertainty from terrestrial ecosystems. On the other hand, the biogeochemistry models, such as CENTURY (Parton et al., 1988) typically link N biogeochemical processes with SOM dynamics and have been widely used for N cycling studies of different ecosystems. These models are spatially limited, however, because they were developed at the plot or site scale.

In this study, we incorporate detailed N biogeochemistry mechanisms into watershed modeling through coupling the daily version of CENTURY, DAYCENT biogeochemistry model (Parton et al., 1998; Del Grosso et al., 2002) with the SWAT watershed model. Our objectives are: (1) to investigate the importance of terrestrial N biogeochemistry to stream mineral N export, (2) to extend the simulation of stream mineral N export with detailed N biogeochemistry mechanisms to the watershed scale, and (3) to evaluate the feasibility and performance of this detailed modeling approach.

METHODS AND MATERIALS

Our modeling was conducted in three steps, each with a different focus. First, we used DAYCENT to investigate the detailed N pools and fluxes at the field scale within the Hubbard Brook Experimental Forest (HBEF) over decades. Next, we focused on the simulations of stream mineral N export and streamflow within each of the HBEF subwatersheds using DAYCENT. Finally, we extended the mineral N export simulation to the watershed scale by combining DAYCENT with the watershed model SWAT.

DESCRIPTION OF MODELS

The DAYCENT biogeochemistry model (Paustian et al., 1998; Kelly et al., 2000; Del Grosso et al., 2001) is the daily time step version of the CENTURY model (Parton et al., 1994), which operates at a monthly time step. DAYCENT and CENTURY both simulate the biogeochemical processes of carbon, nitrogen, phosphorus, and sulfur cycling associated with SOM dynamics for grasslands, agricultural lands, forests, and savannas. In addition to modeling decomposition, nutrient flows, soil water, and soil temperature on a finer time scale than CENTURY, DAYCENT has increased spatial resolution for soil layers. DAYCENT includes submodels for plant productivity, decomposition of dead plant material and SOM, soil water and temperature dynamics, and trace gas fluxes. Required inputs used to drive the model include daily maximum/minimum temperature and precipitation, site–specific soil properties, and current and historical land use. Disturbances and management practices such as fire, grazing, cultivation, timber harvest, irrigation, and organic matter or fertilizer additions can be simulated.

In DAYCENT, flows of C and nutrients are controlled by the amount of C in the various pools (e.g., SOM, plant biomass), the N and lignin concentrations of the pools, abiotic temperature/soil water factors, and soil physical properties related to texture. SOM is divided into three pools based on decomposition rates (Parton et al., 1993; Parton et al., 1994). Decomposition of SOM and external nutrient additions supply the nutrient pool that is available for plant growth and microbial processes. Plant growth is controlled

by a plant–specific maximum growth parameter, nutrient availability, and 0–1 multipliers that reflect shading, water, and temperature stress. Net primary productivity (NPP) is allocated among leafy, woody, and root compartments as a function of plant type, season, soil water content, and nutrient availability (Metherell et al., 1993). The land surface submodel of DAYCENT simulates water flow and evapotranspiration for the plant canopy, litter, and soil profile, as well as soil temperature throughout the profile (Parton et al., 1998; Eitzinger et al., 2000).

The nitrogen submodel mirrors that of the soil carbon submodel, which consists of eight compartments or pools: surface litter structural material, soil structural material, surface litter metabolic material, root litter structural and metabolic material, surface microbes, soil microbes, slow soil carbon, and passive soil carbon. Fluxes in and out of these pools are controlled by properties of each pool as well as empirically determined rate constants for soil organic matter decay (Parton et al., 1987). Organic nitrogen fluxes follow those of carbon at the C:N ratio of the pool receiving the flow of C and N. One feature of DAYCENT is its obvious improvement of the N cycling algorithms in CENTURY. For example, DAYCENT added the simulation of N_2O, NO, and N_2 gas emissions from soils resulting from nitrification and denitrification. The good performance for N cycling simulation and the improvement of related submodels, such as the land surface submodel, should enhance the stream N export simulation. The submodels used in DAYCENT are described in detail by Del Grosso et al. (2001).

SWAT (Arnold et al., 1993; Neitsch et al., 2001) is a spatially distributed watershed simulation model. It was developed to predict nutrient, sediment, and pesticide yields with reasonable accuracy at the watershed or basin scale. SWAT is the product of sequential modifications to earlier watershed models, starting from the field–scale model CREAMS, which was first extended to a watershed–scale model (SWRRB) and then combined with the ROTO model (Arnold et al., 1990) to form the more comprehensive model SWAT. The latter is integrated with GIS (GRASS GIS and ArcView) and a relational database to extract necessary input parameters and to implement an efficient routing capability. SWAT allows a watershed to be subdivided into hundreds or thousands of subwatersheds.

SWAT was used to delineate the HBEF watershed into a series of subwatersheds or hydrologic response units (HRUs). In each HRU, the streamflow and N fluxes were simulated using the DAYCENT model. We finally used the ArcView interface of SWAT to present the outputs at the watershed scale.

STUDY SITE

The simulation was conducted on the HBEF watershed because of the availability of high–quality, long–term monitoring data. The HBEF is a 3,160 ha reserve watershed in the White Mountain National Forest in central New Hampshire (fig. 1). The HBEF has hilly, occasionally steep topography; coarse, acidic, glacially derived soils; bedrock dominated by metamorphic rock of igneous and sedimentary origin; northern hardwood forests on lower slopes and spruce–fir on upper reaches; and continental climate of long, cold winters and mild to cool summers. Except for some of the experimental gauged subwatersheds, the HBEF is an unbroken forest of northern hardwood, with coniferous vegetation at higher elevations. The site is described in detail elsewhere (Bormann and Likens, 1979; Likens et al., 1995) and has been studied extensively since 1963.

Our detailed model outputs at the field scale were compared with the long–term monitoring data of subwatershed 6 (W6) of HBEF. W6 is the "biogeochemical reference" subwatershed for the HBEF. The forest in this subwatershed has not been manipulated since it was intensively logged during 1910–1917. Because it represents "untouched" 80–year–old second–growth forest, human access is limited to maintain its relatively undisturbed condition. However, W6 experienced some natural disturbances, including the hurricane of 1938 and the insect invasion during 1969–1973.

The model simulations of annual streamflow (1964–2000) and mineral N export (1971–1995) were compared with the measurements of experimental subwatersheds 1, 2, 3, 4, 5, and 6 (indicated as W1, W2, W3, W4, W5, and W6 in the following paragraphs). According to disturbance history of these subwatersheds, fire and insect invasion events were considered in the simulation. The events involved in the entire watershed included hurricane–force winds in 1815 and 1938, forest fire in 1885, and insect invasion during
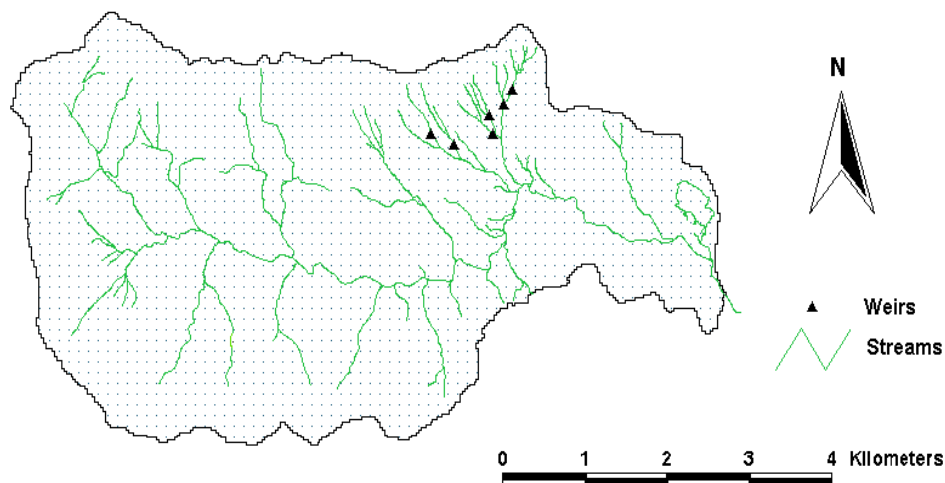

Figure 1. Hubbard Brook Experimental Forest watershed.
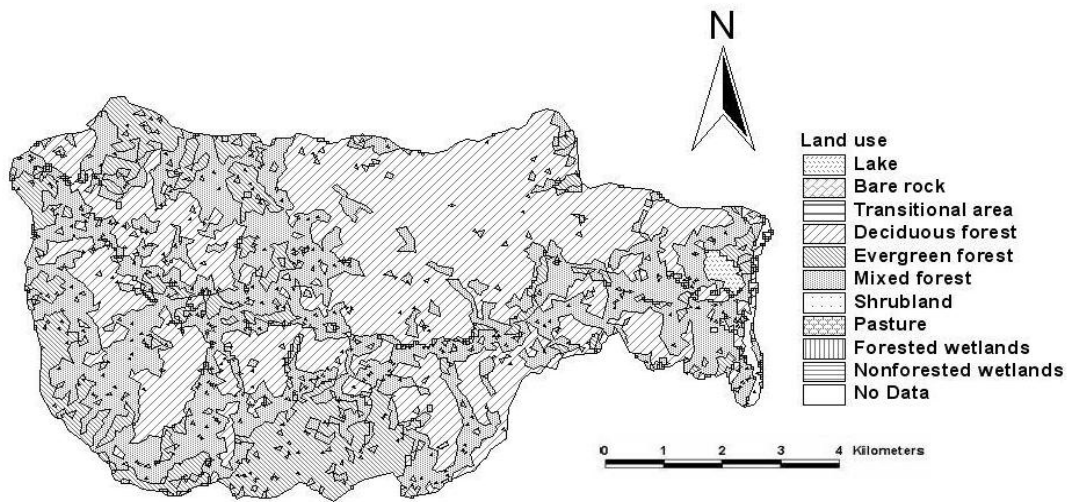
Figure 2. Land use of HBEF.

1969–1973 (Likens, 1985). W3 and W6 are untreated as reference experimental subwatersheds. The calcium fertilizer Wollastonite ($CaSiO_3$) was applied to W1 in 1999, and its impact on N cycling was ignored in the DAYCENT simulation. In 1965, all trees, shrubs, and woody vegetation were cut on W2, followed by herbicide application in 1966, and other chemical application for the next two summers. Vegetation was allowed to re–grow from 1969. In 1970, every third strip of trees was cut on W4. The second series of strips was cut in 1972, and the last set of strips was cut in 1974 (Hornbeck et al., 1987). On W5, all trees larger than 10 cm in diameter at breast height were harvested in 1983 and 1984 (Fahey et al., 1988).

INPUT DATA, MODEL PARAMETERIZATION, AND WATERSHED DELINEATION

The input data and their resolution used for this application are listed in table 1. The GIS layers of DEM, land use (fig. 2), and soil type (fig. 3) were used to delineate the watershed and to prepare SWAT input parameters. Weather data were obtained from eight weather stations at HBEF, including daily precipitation and maximum and minimum air temperatures. Other weather data, such as daily wind speed, solar radiation, and relative humidity, were generated by the

weather generator in SWAT. For HBEF, the N deposition data of 1979–2000 were obtained from EPA Clean Air Status Trends Network (dry deposition) and National Atmospheric Deposition Program (wet deposition). The N deposition data before 1979 were compiled from Aber et al. (1997). The long–term streamflow and stream chemistry data were used for comparisons with model outputs. Biomass, litter, soil biogeochemistry, and land disturbance data were used for model parameterization and for comparisons with model outputs.

SWAT was used to delineate the HBEF watershed into a series of subwatersheds following the procedures described in the user's guide of AVSWAT (ArcView Interface for SWAT2000; Diluzio et al., 2001). Digital Elevation Model (DEM) data were used for the delineation. The average area of actual experimental subwatersheds at HBEF is about 39.2 ha. Specifying an average area of 39.5 ha for the watershed delineation resulted in a network of 80 subwatersheds. In this case, each subwatershed includes one HRU. After watershed delineation, the land use and soil themes were imported and linked to the SWAT databases. The soil attribute data information were obtained from the more detailed Soil Survey Geographic (SSURGO) database. Because of SWAT input format requirements, the soil data had
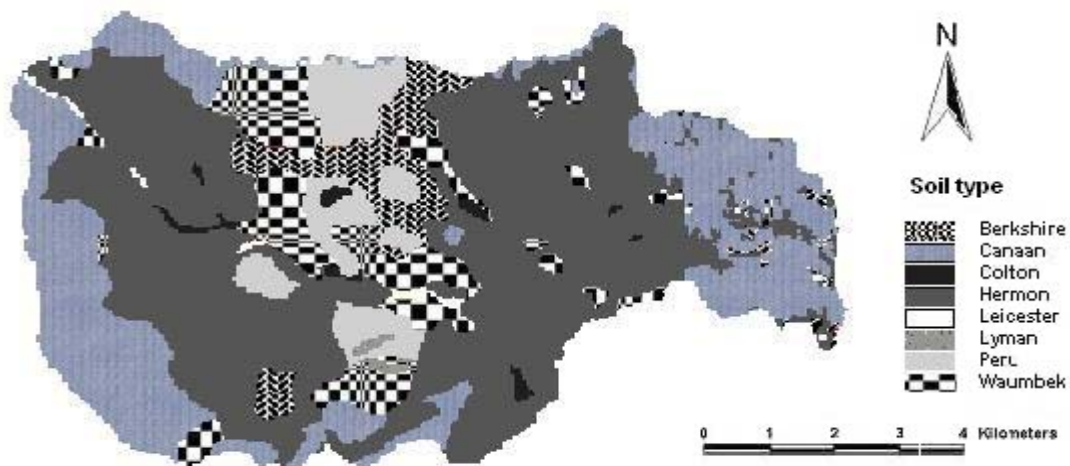

Figure 3. Soil distribution of HBEF.

Table 1 Model input data sources for HBEF.

Data Type	Scale	Source	Data Description
DEM	1:24,000	USGS	SDTS DEM data
Soil	1:6,700	HBEF	Soil properties
Land use	1:24,000	USEPA/USGS	National land cover data (1997)
Weather	8 stations	HBEF	Daily precipitation and temperature
N deposition	1 station	USEPA	CASTNet dry deposition, Site No. HBR183
	1 station	NADP	Wet deposition, Site No. NH02
Stream	W1 to W6 weirs	HBEF	Streamflow and stream chemistry
Biomass, litter		HBEF	

to be converted into State Soil Geographic (STATSGO) database format. The details of input soil data required by SWAT can be found in the SWAT manual (Neitsch et al., 2001). The soil data were converted with the method described by Buland et al. (2002). One or more unique land cover/soil combinations (hydrologic response units or HRUs) can be created for each subwatershed using the overlay tool of AVSWAT.

DAYCENT is of intermediate complexity; important processes are represented mechanistically, but the model makes use of empirically derived equations, and the required input parameters are often available for many regions. Both site definition and forest characterization parameters are important input to DAYCENT for simulating a forest ecosystem. Site parameters include site identification, soil layers, external N input, and initial values for soil carbon mass, SOM C/N ratio, biomass, mineral N content, and soil water content. Forest parameters include maximum production, temperature response parameter, biomass chemistry, biomass and net primary production, production allocation pattern, and biomass turnover rate constants. The W6 site and hardwood forest parameter values are listed in tables 2 and 3.

Table 2. Site parameters required to run DAYCENT model for subwatershed 6 of HBEF.[a]

Name	Description	Value
Site and soil variables		
sitlat	Site latitude (degrees)	43.9440
nlaypg	Soil layers available for plant growth	3
nlayer	Total soil layers in solum	4
External N input		
epnfa(1)	Average annual dry N deposition (g N/m^2/yr)	0.18
epnfa(2)	Slope for determining the effect of annual precipitation on atmospheric N deposition	0.0068
Initial soil carbon pools		
som1ci(1,1)	Initial value for C in surface organic matter with fast turnover (g C/m^2)	372
som1ci(2,1)	Initial value for C in SOM with fast turnover (g C/m^2)	270
som2ci(1)	Initial value for C in SOM with intermediate turnover (g C/m^2)	5075
som3ci(1)	Initial value for C in SOM with slow turnover (g C/m^2)	1950
clittr(1,1)	Initial value for C in plant residue (g C/m^2)	1333
Initial SOM C/N		
rces1(1,1)	Initial C:N ratio in surface organic matter with fast turnover (active SOM)	11.5
rces1(2,1)	Initial C:N ratio in SOM with fast turnover (active SOM)	15.4
rces2(1)	Initial C:N ratio in SOM with intermediate turnover (slow SOM)	29.7
rces3(1)	Initial C:N ratio in SOM with slow turnover (passive SOM)	15.4
rcelit(1,3)	Initial C:N ratio for surface litter	69.0
rcelit(2,3)	Initial C:N ratio for soil litter	40.6
Initial Biomass		
rlvcis(1)	Initial value for C in forest system leaf component (g C/m^2)	157.5
rleave(1)	Initial value for N in a forest system leaf component (g N/m^2)	4.8195
fbrcis(1)	Initial value for C in forest system fine branch component (g C/m^2)	18.0
fbrche(1)	Initial value for N in a forest system fine branch component (g N/m^2)	0.5760
rlwcis(1)	Initial value for C in forest system large wood component (g C/m^2)	6310.0
rlwode(1)	Initial value for N in a forest system large wood component (g N/m^2)	50.48
frtcis(1)	Initial value for C in forest system fine root component (g C/m^2)	235.5
froote(1)	Initial value for N in a forest system fine root component (g N/m^2)	4.8042
crtcis(1)	Initial value for C in forest system coarse root component (g C/m^2)	1102.5
croote(1)	Initial value for N in a forest system coarse root component (g N/m^2)	16.3170
wd1cis(1)	Initial C values for forest system dead fine branch material (g/m^2)	108.45
wd2cis(1)	Initial C values for forest system dead large wood material (g/m^2)	1262.0
wd3cis(1)	Initial C values for forest system dead coarse root material (g/m^2)	300.0
clittr(2)	Initial C values for forest system dead fine root material (g/m^2)	38.4

[a] Data sources for site parameters are: Homer (1999), Aber and Driscoll (1997), Huntington et al. (1988), Whittaker et al. (1974), Whittaker et al. (1979), Fahey et al. (1988), Fahey and Arthur (1994), Gosz et al. (1972), Gosz et al. (1976), Metherell et al. (1993), U.S. EPA (2002), and National Atmospheric Deposition Program (2002).

Table 3. Tree parameters required to run DAYCENT model for hardwood forest of HBEF.[a]

Name	Description	Value
Forest production and control		
prdx(2)	Maximum net forest production (g C/m^2/month)	300.0
ppdf(1)	Optimum temperature for production (°C)	22.0
ppdf(2)	Maximum temperature for production (°C)	42.0
ppdf(3)	Left curve shape for parameterization of a Poisson density function curve	1.0
ppdf(4)	Right curve shape for parameterization of a Poisson density function curve	3.5
kmrsp(2)	Fraction of net primary production going to the maintenance respiration storage pool for trees	0.3
fkmrspmx(1)	Maximum fraction of live leaf C that goes to maintenance respiration for trees	0.004
fkmrspmx(2)	Maximum fraction of live fine root C that goes to maintenance respiration for trees	0.004
fkmrspmx(3)	Maximum fraction of live fine branch C that goes to maintenance respiration for trees	0.004
fkmrspmx(4)	Maximum fraction of live large wood C that goes to maintenance respiration for trees	0.004
fkmrspmx(5)	Maximum fraction of live coarse root C that goes to maintenance respiration for trees	0.004
Biomass chemistry		
cerfor(3,1,1)	Initial C/N for leaf	20.4
cerfor(3,2,1)	Initial C/N for fine root	65.5
cerfor(3,3,1)	Initial C/N for fine branch	133.0
cerfor(3,4,1)	Initial C/N for large wood	516.5
cerfor(3,5,1)	Initial C/N for coarse root	319.5
Production allocation pattern		
fcfrac(1,1)	C allocation fraction of new production for leaf	0.2470
fcfrac(2,1)	C allocation fraction of new production for fine root	0.2055
fcfrac(3,1)	C allocation fraction of new production for fine branch	0.0274
fcfrac(4,1)	C allocation fraction of new production for large wood	0.2470
fcfrac(5,1)	C allocation fraction of new production for coarse root	0.1133
Biomass turnover rates		
wooddr(1)	Monthly death rate fraction for leaf	0.0100
wooddr(2)	Monthly death rate fraction for fine root	0.0449
wooddr(3)	Monthly death rate fraction for fine branch	0.0606
wooddr(4)	Monthly death rate fraction for large wood	0.0143
wooddr(5)	Monthly death rate fraction for coarse root	0.0143
btolai	Biomass to leaf area index (LAI) conversion factor for trees (m^2/g)	0.0110
klai	Large wood mass at which half of theoretical maximum leaf area is achieved (g C/m^2)	1.00
maxlai	Theoretical maximum leaf area index achieved in a mature forest	20.00
Lignin fraction of tree components		
wdlig(1)	Lignin fraction for forest leaf	0.15
wdlig(2)	Lignin fraction for forest fine root	0.20
wdlig(3)	Lignin fraction for forest fine branch	0.22
wdlig(4)	Lignin fraction for forest large wood	0.25
wdlig(5)	Lignin fraction for forest coarse root	0.22

[a] Data sources for tree parameters are: Metherell et al. (1993), Whittaker et al. (1974), Whittaker et al. (1979), Gosz et al. (1972), Gosz et al. (1976), Fahey et al. (1988), and Fahey and Arthur (1994).

EVALUATION OF MODEL ACCURACY

Simulations with DAYCENT produce the following error function:

$$R^2 = \frac{1}{N} \sum_{i=1}^{n} (Q_{mi} - Q_{ci})^2 \qquad (1)$$

where R^2 is the coefficient of determination, Q_{mi} is the measured value, and Q_{ci} is predicted value. The R^2 value is an indicator of the strength of the relationship between the measured and predicted values. Nash and Sutcliffe (1970) modified the coefficient as:

$$E_{ns} = 1 - \frac{R^2}{V_{ar}(Q_{mi})} = 1 - \frac{\sum_{i=1}^{n} (Q_{mi} - Q_{ci})^2}{\sum_{i=1}^{n} (Q_{mi} - \overline{Q}_m)^2} \qquad (2)$$

where E_{ns} is the Nash–Sutcliffe coefficient, and the variation is:

$$V_{ar}(Q_{mi}) = \frac{1}{N} \sum_{i=1}^{n} (Q_{mi} - \overline{Q}_m)^2 \qquad (3)$$

where $\overline{Q}_m$ is the average measured value.

We used the Nash–Sutcliffe coefficient to evaluate model prediction. E_{ns} indicates how well the plot of measured versus predicted value fits the 1:1 line. E_{ns} varies from minus infinity to 1. The value of 1 indicates a perfect fit. While there is no absolute standard relating model performance to E_{ns} scores, this statistic allows comparison of model results with those from other studies. A value of 0.7 to 0.8 or above usually indicates a fairly good fit for streamflow simulation (Krysanova et al., 1998). A value above 0.5 indicates a good fit for stream nutrients export simulation (Rosenthal and Hoffman, 1999).
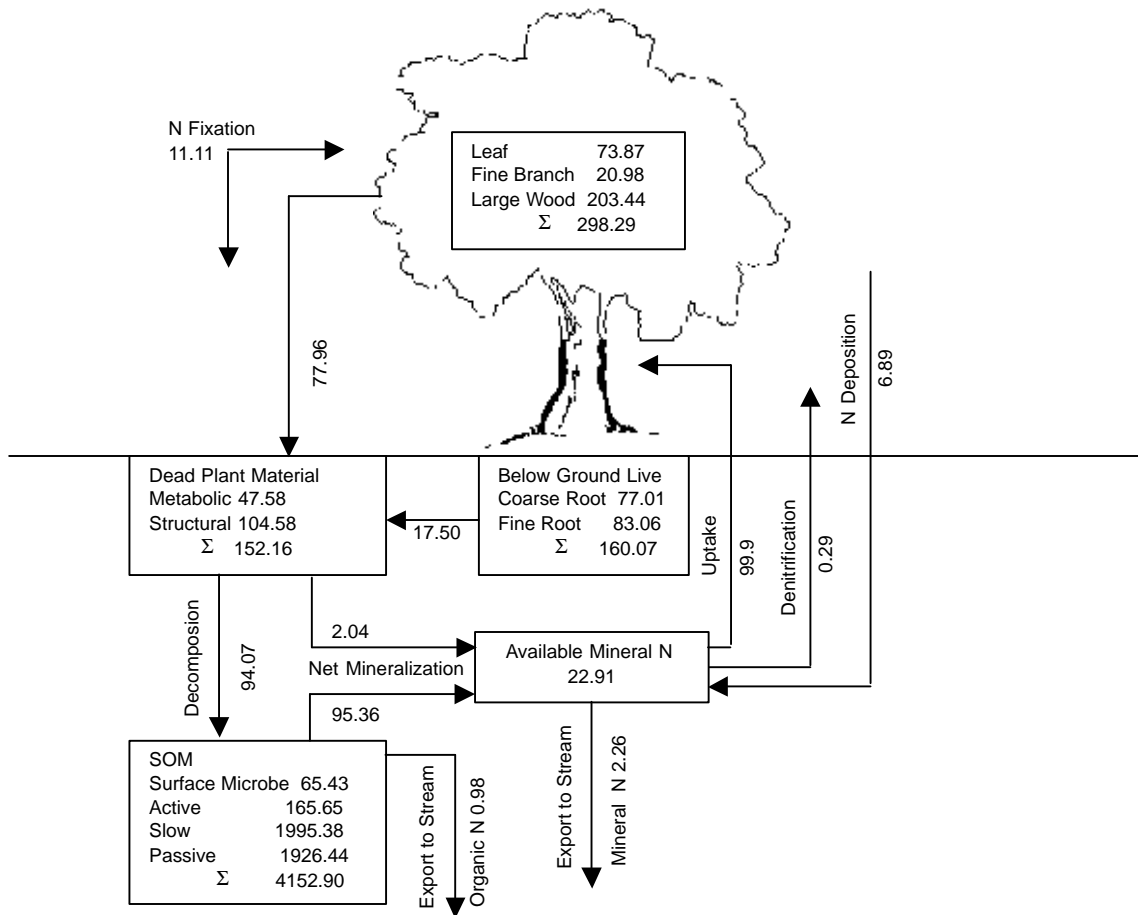
Figure 4. N pools and fluxes at HBEF. Simulated average annual N budget (1951–2000) for an undisturbed northeastern hardwood forest ecosystem at HBEF. The N pools (in boxes) are in kg N/ha. The N fluxes (in arrows) are in kg N/ha/yr.

RESULTS AND DISCUSSION

TERRESTRIAL N CYCLING AT HBEF

An annual N budget for the HBEF ecosystem was established through the calculation of N pools and fluxes by DAYCENT. The average annual N budget for 1951–2000 of experimental subwatershed 6 at HBEF is summarized in figure 4. At the undisturbed HBEF natural forest ecosystem, the main N input sources to the system are atmospheric deposition and N fixation. The measured annual atmospheric N deposition was 6.89 kg N/ha/yr, 1.80 kg N/ha/yr for dry deposition, and 5.09 kg N/ha/yr for wet deposition (U.S. EPA, 2002; National Atmospheric Deposition Program, 2002; Aber and Driscoll, 1997). N fixation of 11.11 kg N/ha/yr, which consisted of symbiotic biological N fixation and non−symbiotic N fixation, was assumed as the result of total input N minus atmospheric N deposition. The total N input data was obtained from the literature (Schlesinger, 1991). The total N atmospheric N fixation (N fixation plus dry N deposition) was 12.91 kg N/ha/yr.

Obviously, not all external N input that entered the ecosystem was exported to the streams through surface runoff, subsurface and base flow, or emitted to the atmosphere through denitrification. Of the 18 kg N/ha/yr added to the ecosystem, only 13% of input N or 2.26 kg N/ha/yr was exported from the ecosystem through water flows to streams and 7% or 1.27 kg N/ha/yr was exported through gaseous emissions. If compared with wet N deposition, mineral N exports to stream accounted for 44%. A large proportion of N input was retained within the ecosystem. This estimate is similar to a previous study (Bormann et al., 1977). This fact suggests that the terrestrial ecosystem is important when stream mineral N export is investigated.

Of the biomass N, the turnover rate of aboveground N was 77.96 kg N/ha/yr, which accounted for 11% of N in total above ground biomass. The turnover rate of blow ground N was 17.50 kg N/ha/yr, which accounted for 26% of N in total blow ground biomass. Forest litter and soil stored large amounts of N, of which N storage in SOM pools accounted for 96% or 4152.90 kg N/ha/yr.
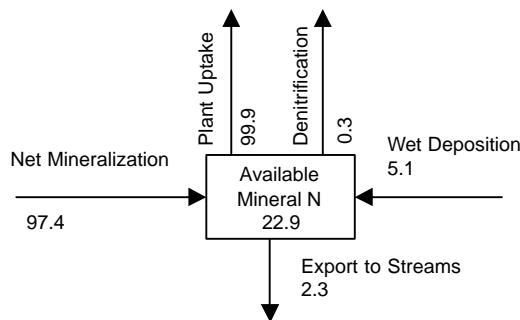

Figure 5. Simulated average annual N budget (1951–2000) for available mineral N pools and fluxes for an undisturbed hardwood forest ecosystem at HBEF. The N pools (in boxes) are in kg N/ha. The N fluxes (in arrows) are in kg N/ha/yr.

Table 4. Simulated and measured net primary production at HBEF.[a]

Years	Leaves		Wood		Total	
	Observation	DAYCENT	Observation	DAYCENT	Observation	DAYCENT
1956–1960	3739	3501	9214	8884	12385	12460
1961–1965	2938	3608	7612	8222	10550	11830
1968	3160	3647	––		––	
1969	2730	2814	––		––	
1974	2960	3375	––		––	

[a] Measured data are from Whittaker et al. (1974) and Covington and Aber (1980). All data in kg/ha/yr.

Table 5. Simulated and measured nitrogen contents and fluxes at HBEF.[a]

	Observation	DAYCENT
N in live biomass (kg N/ha)		
1965, Leaves	69.1	77.9
1965, Aboveground wood	263.5	229.3
1965, Root	180.7	174.7
1965, Total	513.3	481.9
Total N uptake (kg N/ha/yr)		
1956–1960	114.4	101.3
1961–1965	104.9	98.2
Net N mineralization (kg N/ha/yr)		
1974–1975	100	97.8
Stream mineral N export (kg N/ha/yr)		
1965–2000	2.4	2.3

[a] Measured data are from Whittaker et al. (1979), Gosz et al. (1972), and Melillo (1977).

Available mineral N pool is directly related to stream N export. The N influxes to the available mineral N pool are critical factors that determine stream N export flux. Net N mineralization of plant residue and SOM was the biggest source of N influx to the available mineral N pool, accounting for 93% of total influx N or 97.4 kg N/ha/yr (fig. 5). Thus, the accurate simulation of mineralization is essential to stream N export prediction in a deterministic process–based model. About 97% of efflux N or 99.9 kg N/ha/yr from the available mineral N pool entered the plant biomass through plant uptake at HBEF. The N influx through precipitation did not simply export entirely to streams through water flow. The stream N export only accounts for about 45% of the wet N deposition. This may indicate that complex competition exists among microbial immobilization, plant root uptake, denitrification, and leaching ability. A recent study on large forest–dominated watersheds in the northeastern U.S. also indicated that riverine N export represented only a fraction (11% to 40%) of the total N inputs of the ecosystems (Van Breemen et al., 2002). The N loss from denitrification from well–drained, upland forest soils at HBEF was very low (0.3 kg N/ha/yr). This agrees with experimental results (Groffman and Tiedje, 1989) in which lower denitrification

N loss (<1 kg N/ha/yr) was observed in a well–drained soil of north temperate forest. The simulated results of DAYCENT were compared with the measured net primary production (NPP) and N data of subwatershed 6 at HBEF (tables 4 and 5).

The simulated leaf NPP during 1961–1965 was higher than the measured values. The relative simulated errors varied from 3.1% to 22.8%. The effect of wet (during 1956–1960) and dry (during 1961–1965) climate change on leaf NPP was not captured by the model. During 1956–1960, DAYCENT had very good simulations in wood and total NPP. The differences with observations were only 3.6% and 0.6%, respectively. During 1961–1965, the relative differences were 8.0% and 12.1% for wood and total NPP simulations. The simulated error in dry years may have resulted from the inaccurate algorithm descriptions of water stress effect on NPP and/or respiration.

The simulations of N contents and fluxes generally agreed with the observations. For instance, the relative simulation errors for average annual total N uptake are 11.5% (1956–1960) and 6.4% (1961–1965), 2.2% for net N mineralization (1974–1975), and 4.2% for stream mineral N export (1965–2000). The differences between simulated and measured values for N content in different tree tissues and total N content in 1965 ranged from 3.3% to 13.0%. The simulated value in leaves is higher than measured value, and the simulated values in root and aboveground wood were lower than their measured values.

STREAMFLOW AND MINERAL N EXPORT AT HBEF

Observed annual streamflow (1964–2000) and mineral N export (1971–1995) were compared to those simulated by DAYCENT for W1 to W6 (fig. 6). The average observed and simulated annual streamflow and stream mineral N export fluxes are summarized in table 6. Overall, DAYCENT performed satisfactorily for both annual streamflow and mineral N export simulations. The E_{ns} values indicated that the simulation for streamflow was better than that of mineral N export, but the simulation for mineral N export was also acceptable. DAYCENT was able to capture the response of disturbance on mineral N export. For instance, the peak during

Table 6. Summary of average annual streamflow, stream mineral N export and subwatershed features of HBEF.

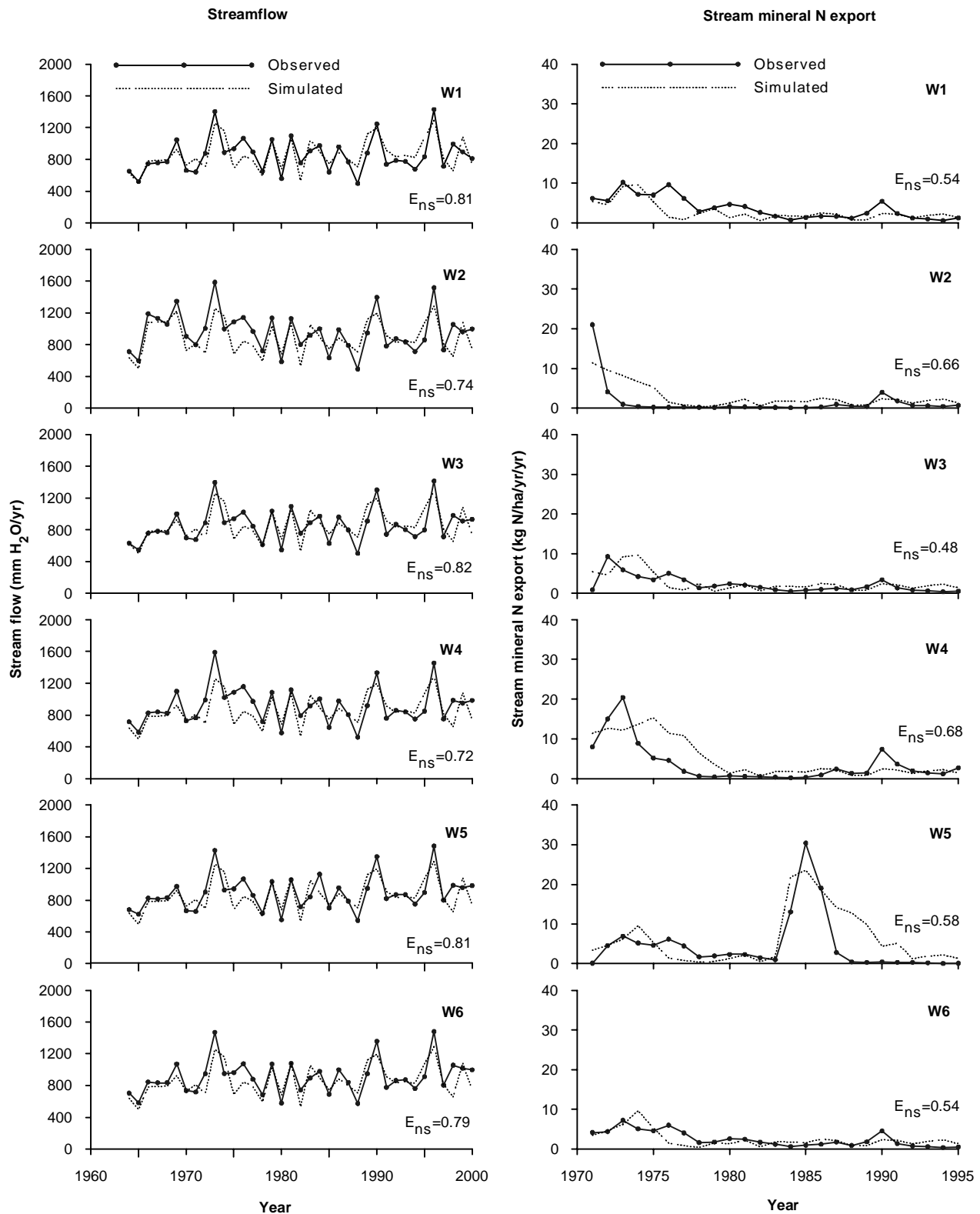| Subwatershed	Area (ha)	Slope (degrees)	Avg. Precipitation (mm/yr), 1964–2000	Avg. Streamflow (mm/yr), 1964–2000		Avg. Stream Mineral N Export (kg N/ha/yr), 1971–1995	
				Observed	Simulated	Observed	Simulated
W1	11.8	12.3	1359	851	834	3.71	2.78
W2	15.6	17.5	1372	956	891	1.59	2.86
W3	42.4	15.9	1365	857	834	2.21	2.66
W4	36.1	15.1	1417	913	842	3.66	4.98
W5	21.9	14.3	1403	890	840	4.44	6.22
W6	13.2	14.0	1407	907	851	2.49	2.42

Figure 6. Observed and simulated annual streamflow (left column, 1964–2000) and mineral N export (right column, 1971–1995) at HBEF.

1971–1973 represents the effect of insect invasion (right column of fig. 6). For the effect of the 1983–1984 forest cut in W5, the simulated values did not decline as steeply as the observed values. Peaks of simulated stream mineral N export were slightly lower than the observed values on W2, W4, and W5, but these effects lasted for a relatively longer period

(right column of fig. 6). The variability of streamflow contributed less to the large fluctuations of stream mineral N export than the insect and logging disturbances did.

However, streamflow was still an important controlling factor of mineral N export. During the periods without disturbances, the peaks of streamflow corresponded to those
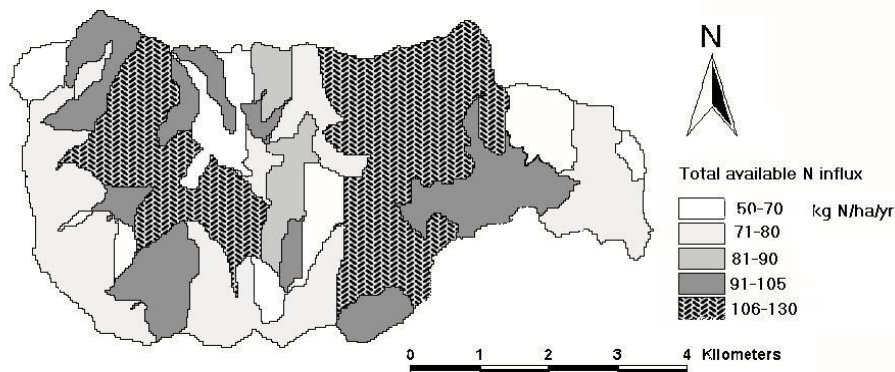
Figure 7. Simulated average annual total available N influx at HBEF during 1951–2000.

of mineral N export. This corresponding relationship can be found in two obvious examples. One is that the peaks of N export during 1973–1976 agreed with those of streamflow. Those peaks on W2, W4, and W5 may reflect the mixed effects of disturbance and streamflow. Another example is that the streamflow controlled mineral N export in 1990 on all subwatersheds except for W5. On W5 (right column of fig. 6), the observed value of mineral N export did not reflect the effect of peak streamflow in 1990, although the model did. We do not know why the N export did not agreed with some actual peak values of streamflow.

STREAM MINERAL N EXPORT AND TOTAL AVAILABLE N INFLUX AT HBEF WATERSHED

The distributions of total available N influx (net N mineralization plus atmospheric N deposition) to the available mineral N pool and stream mineral N export through the entire HBEF watershed were obtained from our simulation. Average annual values from 1951 to 2000 are shown in figures 7 and 8. The simulations were conducted by DAYCENT for each of HRUs and then merged into the entire watershed distribution through AVSWAT. The total available N influx ranged from 50 to 130 kg N/ha/yr, while the stream mineral N export was only 1.5 to 3.5 kg/ha/yr at HBEF. This may suggest there is a large potential source of available N in the terrestrial ecosystem for the stream N export. When the complex competition relations for the available N are disturbed by human activities and climate change in the terrestrial ecosystems, the relatively high total available N

influx would be another important factor that increases stream N export. Thus, it is essential to accurately describe the N biogeochemistry cycle in terrestrial ecosystem in a deterministic model in order to predict N export.

The total available N influx and stream mineral N export for the main forest types and soil types at HBEF are presented in figure 8. Both total available N influx and mineral N export exhibited the same general pattern, their values always ranking from high to low as deciduous forest > mixed forest > evergreen forest for the same soil type. There are no statistically significant differences among different forest types for the same soil type or among different soil types for the same forest type. Nevertheless, some differences can be discerned visually. During 1951–2000, for example, the simulated annual total available N influx was 86 to 130 kg N/ha/yr for deciduous forest, 70 to 104 kg N/ha/yr for mixed forest, and 55 to 90 kg N/ha/yr for evergreen forest. The simulated annual total available N influx also varied under different soil types (fig. 9). The pattern of simulated stream mineral N export was similar to that of annual total available N influx. This may suggest that the input of soil information is necessary for N export simulation, especially for a watershed with high variability of soil hydraulic properties. The combination of forest and soil types also affects the variability of N influx and mineral N export. For instance, the N influx for Hermon or Leicester soils under mixed forest was higher than that of Canaan soil for deciduous forest. The stream mineral N export did not always follow the trend of N influx. The mineral N export was higher for a Peru soil than
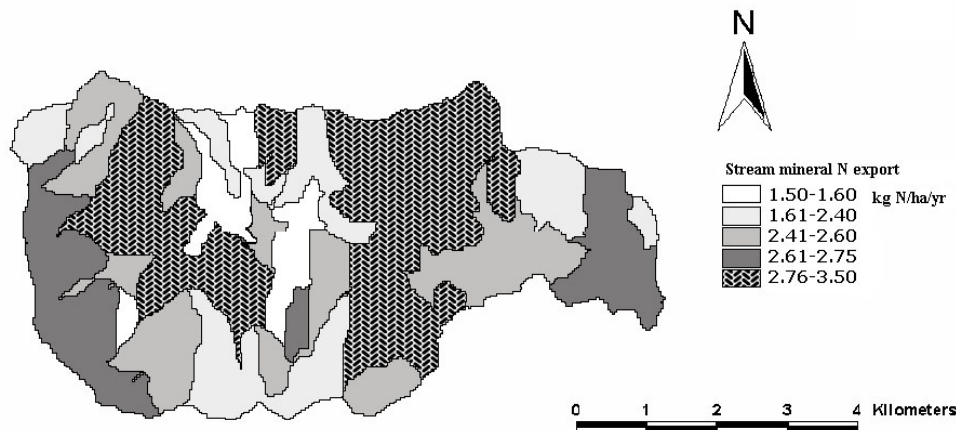

Figure 8. Simulated average annual stream mineral N export from HBEF during 1951–2000.
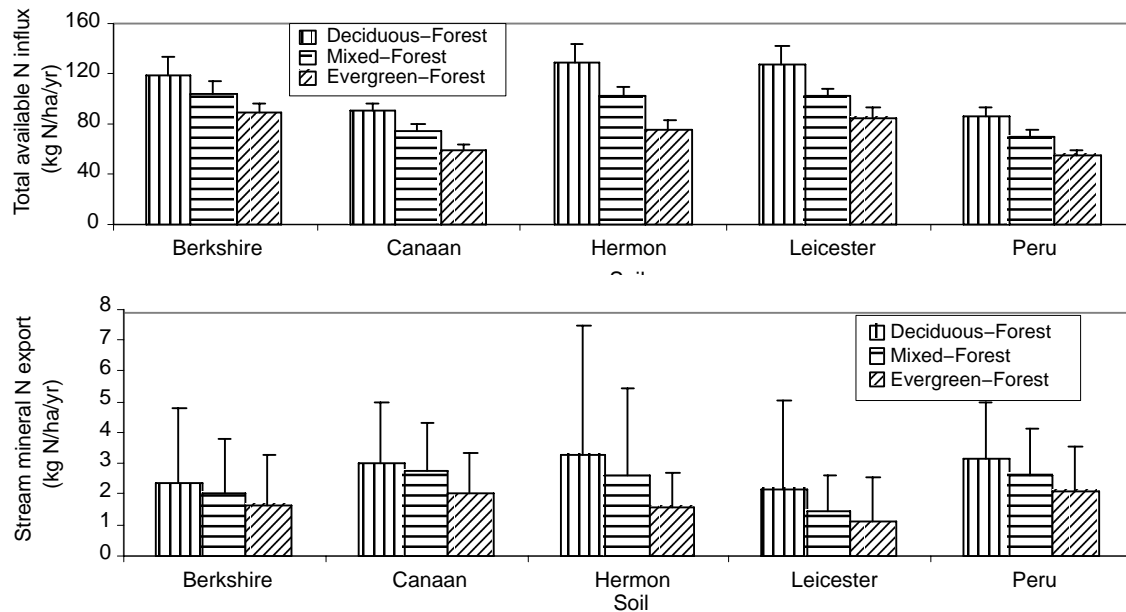
Figure 9. Simulated annual total available N influx and stream mineral N export during 1951–2000 under different land cover and soil type at HBEF.

that for a Leicester soil, but the N flux had an opposite relationship for these soils. One possible reason is that Peru soil has higher hydraulic conductivity than Leicester soil, but Leicester soil is more favorable in the consumption of available N by plant uptake, which causes less available N to stream export.

CONCLUSIONS

The field–scale DAYCENT model was used to simulate N pools and fluxes within a terrestrial forest ecosystem and to estimate long–term streamflow and stream mineral N export at HBEF. The simulations of annual N budget, streamflow, and mineral N export were validated by HBEF long–term monitoring data. Combining with the watershed–scale SWAT model, we extended the simulations of annual total available N influx and stream N export to the watershed scale. Setting up and running this coupled modeling system for the HBEF proved feasible. The total effort required to apply this technology to a new watershed should take 2 to 4 months, depending on the availability of required data.

For this application to HBEF, DAYCENT predicted that only 13% of input N was finally exported from terrestrial ecosystems to streams and that 7% was lost as gaseous flux. Most input N in the HBEF simulations remained in the terrestrial ecosystem and participated in N cycling within the system. Ninety–three percent of available N flux within the system was associated with N mineralization of SOM. These simulated results imply the importance of incorporating terrestrial N biogeochemical processes in an N export prediction model, particularly for forested catchments.

The comparisons of DAYCENT predictions with long–term monitoring data of six subwatersheds displayed satisfactory model performance on streamflow and mineral N export simulations. Overall, DAYCENT performed better on streamflow simulation than mineral N export. The model also successfully predicted the effect of ecosystem distur-

bances such as insect invasion and forest cut on stream mineral N export. The analyses of watershed simulation showed that the inputs of both soil and land cover data were necessary for predicting mineral N export at the watershed scale. This means that this advanced technology depends crucially on the availability and accuracy of these data. Our study indicated that the terrestrial N biogeochemical mechanisms are extremely important to a deterministic watershed water quality model applied to forested areas. The stream mineral N export at the watershed scale can be successfully predicted through coupling the existing biogeochemistry model and watershed model. We expect to test this coupling in future work in other watersheds with different land uses or different ecosystems. Ultimately, we hope that this or similar technology will lead to more efficient and effective management of watersheds to reduce nutrient impacts in rivers and streams.

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