Appendix 1. Model Overview

1.1 PnET-FrAMES

To facilitate the simulation of aquatic ecosystem variables in the Upper Merrimack River Watershed (UMRW), we coupled terrestrial aquatic model that simulated forest processes and had regionally specific mechanisms for capturing the influence of developed land covers. We utilized the Photosynthesis and EvapoTranspiration-Carbon-Nitrogen (PnET-CN) for its proven ability to accurately simulate forest processes in New England (Aber and Driscoll 1997, Ollinger et al. 2002, Ollinger et al. 2008) and an aquatic process-based model, the Framework for Aquatic Modeling of the Earth System (FrAMES) for simulation of instream denitrification (Wollheim et al. 2008a, 2008b), routing of discharge and solute fluxes (Zuidema et al. In Prep), and instream temperature re-equilibration with the atmosphere (Stewart et al. 2013) at a daily time-step. The following sections provide detail on the functionality of each model component, and a description of specific parameterizations and linkages required for the coupling of the aquatic and terrestrial ecosystem models.

1.2 PnET

PnET-CN is a forest ecosystem model that combines algorithms for processes such as photosynthesis, evapotranspiration, litter production, decomposition, and N mineralization along with climate inputs to estimate complete fluxes of carbon (C), nitrogen (N), and forest water at a monthly time step (Aber and Driscoll 1997, Ollinger et al. 2002, Ollinger et al. 2008). PnET-CN is used to predict time varying net primary production (NPP), evapotranspiration, carbon storage, wood biomass, and nitrogen leaching losses associated with forest type, climate variability, atmospheric nitrogen deposition, and forest succession. The model was developed and validated in the Northeastern U.S. at both site and regional scales (Ollinger et al. 2002, 2008, Aber et al. 2005 and Zhou et al. In Prep). In this study, in order to be coupled with FrAMES, we revised the monthly model into a daily model that adds the role of impervious surfaces and lawns in urban areas to accommodate the coupling with the regional aquatic model (Zhou et al. In Prep). Several processes were revised, such as minor revision of photosynthesis and foliar growth due to non-linear relationship between photosynthesis and climate input. The rain/snow precipitation processes were also modified as precipitation in daily time step normally occurs as either rain or snow in winter. It is not appropriate to split it for rain and snow as in monthly version because monthly precipitation is the sum of rain and/or snow. This improved PnET prediction of snowpack and runoff in winter and early spring (Zhou et al. In Prep).

Reasonable physiological response of atmospheric CO_2 and acclimation of respiration are important for future projections of ecosystem functions in the changing environment. Previous version of PnET had a CO_2 effect on carbon assimilation using a Michalis-Menton equation fitted to normalized A-Ci (photosynthesis assimilation and the internal CO2 concentration) curves (scaled from 0 to 1 where 1 is CO_2 saturated carbon fixation) taken from a number of CO_2 exposure studies (Ollinger et al. 2002). More newly existing empirical data from CO_2 exposure studies were added to improve the regression. Especially the high end of CO_2 concentrations of over 2000 ppm showed much less increased effect in photosynthesis than expected (Franks et al. 2013). The revised response function suggested a lower photosynthetic CO_2 compensation point of 40 ppm compared to the Ollinger et al.'s 68 ppm. If, for example, a change in CO_2 from 350 to 1000 represents the high emission climate scenario, a 59% increase in photosynthesis will be predicted by the previous function and only 22% by the revised version. The two equations estimate similar relative change in photosynthesis between ambient and historical CO_2, implying the revision only impact future project.

Evidence suggests that respiration acclimation (RA) to temperature in plants can have a substantial influence on ecosystem carbon balance. Previous versions of PnET had not included explicit respiration acclimation in a future warming climate. This study incorporated temperature-sensitive Q10 and foliar respiration acclimation algorithms in the model (Wythers et al. 2013). e.g., at the temperature of 35 ^{o}C, the RA algorithms estimate a 37% reduction in foliar respiration relative to that using previous version. Wythers et al. (2013) reported that averaged across four boreal ecotone sites and three forest types at year 2100, the enhancement of NPP in response to the combination of rising CO_2 and warming was 9% greater when RA algorithms were used, relative to responses using fixed respiration parameters.

Biogeochemical monitoring for 50 years at the Hubbard Brook Experimental Forest in New Hampshire has revealed N export in stream water has steadily declined and is presently just a small fraction of atmospheric N input, despite negligible changes in aboveground biomass. It implies that the forested ecosystem has shifted to a net N sink (Yanai et al. 2013), which could not explained by the previous theory. The "missing" deposited N were thought to accumulate in the mineral soil, or be lost in gaseous form. Processes of N gas losses (i.e., N_2O, NO, and N_2) through nitrification and denitrification were added in PnET-CN to enhance its N cycling and to investigate the role of denitrification in the missing N sink (Zhou et al. In Prep). We used first order kinetics to estimate N gas losses and partitioned N_2O, NO, and N_2 based on soil water content. In this study, the parameter, denitrification constant was set to the averaged value of 0.03 (McCray et al. 2005) to represent a more general pattern for a large region, which could be potentially underestimate in mountainous areas.

1.3 FrAMES

FrAMES, the Framework for Aquatic Modeling in the Earth System, is a spatially distributed gridded river network model that has been applied extensively at various spatial scales (Wollheim et al. 2008a, 2008b and Stewart et al. 2011, Vörösmarty et al. 1998, Wisser et al. 2010, Stewart et al. 2013 and Zuidema et al. In Prep). FrAMES incorporates a number of dynamically linked modules that operate on a daily time step. These modules include the Water Balance Model (WBM), the Water Transport Model (WTM) (Vörösmarty et al. 1998; Wisser et al. 2010), suburban dissolved inorganic nitrogen (DIN) loading (Wollheim et al. 2008b), in-stream nitrogen removal (Stewart et al. 2011), the Non-point Thermal Loading Model or NTLM and the River Temperature Re-equilibrium Model (RTRM) (Stewart et al. 2013), the Thermoelectric Power and Thermal Pollution Model (TP2M) (Miara et al. 2013), and the Non-point Anthropogenic Chloride Loading (NACL) module (Zuidema et al. In Prep). Typically, FrAMES has a land surface hydrology component that operates independently of forest dynamics. In this study, FrAMES has been coupled with PnET to simulate the dynamic interactions among terrestrial and aquatic processes in the UMRW across a spectrum of land cover and climate projections for the region. Here, we substitute PnET-CN predictions of runoff and nitrogen to load material from forests to river networks.

In the PnET-FrAMES coupling, PnET-CN predicts runoff and DIN leaching from forests, whereas FrAMES simulates inputs of specific conductivity, thermal loads, and DIN loads from urban and agricultural areas. Water from the soil root zone in PnET as runoff is partitioned to surface and groundwater runoff generating pools in FrAMES, which introduce a lag in delivery to the stream network. PnET nitrogen leachate is applied to the daily runoff volume of the linked model. PnET does not consider riparian nitrogen removal, which is parameterized in FrAMES as a zero-order removal process that eliminates 75% of the forest leachate prior to entering the stream network. This value was determined by calibration to extensive headwater concentration data (Appendix 3) and deserves additional investigation. FrAMES propagates discharge and all solute loads downstream using a cascade routing method at a daily time step.