FOREST BIOMASS AND SOIL CARBON STOCK CHANGES

IN THE DELAWARE RIVER BASIN

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BASIN

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Dedicated to Fred Scatena

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ABSTRACT

FOREST BIOMASS AND SOIL CARBON STOCK CHANGES

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Bing Xu

Alain F. Plante

Forests play an important role in the global carbon cycle. Quantifying forest biomass and soil carbon stocks and their change over time and space is important to understand forest dynamics and their feedbacks with climate change. This dissertation investigates the forest biomass and soil carbon stocks and their controlling factors in the Delaware River Basin (DRB) using a combination of field measurements and modeling. In 2001-2003, 77 forest plots in three research sites were established and their biomass was measured. In 2012-2014, 61 of these plots were revisited and forest biomass was re-measured using the same protocols. Two soil sampling methods, the Forest Inventory Analysis standard soil core method and the quantitative soil pit method, were also used to collect soil samples. Based on the results of field measurements, a process-based ecosystem model (PnET-CN) was parameterized and used to simulate the spatial distribution of forest carbon pool and fluxes in the three sites. We found that the mean biomass carbon stock in the three sites was 166.5 Mg C ha⁻¹ and had increased by 2.35 Mg C ha⁻¹ yr⁻¹ and was thus a carbon sink over the past decade. The soil carbon stock to 40 cm depth was 76.6 Mg C ha⁻¹. The accuracy of the soil core sampling method was questioned because in the surface mineral soil layer, lower bulk density, lower coarse fragment content and greater carbon concentration were measured using the core method compared to the pit method. By parameterizing the wood turnover rate, maximum photosynthesis rate and disturbance year based on field measurements, the performance of the PnET-CN model was improved in capturing the spatial variation of forest carbon dynamics. The modified model was also used in experimental

scenarios, demonstrating 39% of forest carbon sequestered over the past decade could be attributed to the combined effects of elevated CO_2 and nitrogen deposition. Large uncertainties in forest carbon stocks at regional scales are associated with the spatial heterogeneity of the forest. A long-term forest monitoring system combined with modelling can greatly reduce the uncertainties and increase the accuracy of our estimates of forest carbon stocks.

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CHAPTER 1: Introduction

1.1 Forest carbon stocks and the global carbon cycle

Forests are a vital component of terrestrial ecosystems, covering $\sim 30\%$ of the world's land surface area (Bonan, 2008). Forests also play an important role in the global carbon cycle, accounting for ~45% of the carbon stored in the terrestrial biosphere (Dixon et al., 1994). Forest biomass and soil are the two largest carbon pools in the forested ecosystem. At the global scale, the estimated forest carbon stocks are 536 Pg C in biomass and 1104 Pg C in soil (Field and Raupach 2004). The annual change of carbon stock was 2941 Tg C yr⁻¹ in biomass and 456 Tg C yr⁻¹in soil during 2000-2007 (Pan et al., 2011a).

As the forest carbon stocks in biomass and soil have increased consistently in the past several decades, their potential to sequester atmospheric carbon dioxide (CO₂) is considered a mitigation strategy to reduce global warming (Luyssaert et al., 2007; Ciais et al., 2013). It was estimated that forest carbon stocks in the United States increased 239 Tg C yr⁻¹ in 2000-2007, which is equivalent to ~10 % of domestic carbon emissions (Turner et al., 1995; Birdsey et al., 2006). The forest in the Northeast region is a net carbon sink of 21.0 Tg C yr⁻¹, compensating for 7.6% of the region's fossil fuel emissions in 2001-2005 (Lu et al., 2013).

1.2 Forest biomass carbon stock and its controlling factors

Forest biomass is the most active carbon pool in the terrestrial system, with large spatial and temporal variations and considerable uncertainty. Various factors drive the change of forest biomass through different processes. Climate determines the geographical distribution of forest types at the global scale (Pan et al., 2013). Topography and soil type modify the effect of climate, and shape the growth curve of the forest (Clark and Clark, 2000). Natural and anthropogenic

disturbances (such as fire and harvest), and historical land use change determine the current stand age and succession stage of the forest, which could be the main drivers of biomass dynamics at the landscape scale (Caspersen et al., 2000; Pregitzer and Euskirchen, 2004).

During the process of forest succession following a large scale disturbance, living tree biomass accumulates and stem density decreases. This is the self-thinning process caused by competition for resources such as light and nutrient (Coomes and Allen, 2007). Changes in forest composition accompany this pattern as the species with different life strategies come to dominate the forest sequentially. At the later stages of succession, the forest reaches a steady state in which the accumulation of biomass saturates at large scale (Odum, 1969; Franklin et al., 2002; Walker et al., 2010; Yang and Luo, 2011). Most of the forests in the northeastern U.S. are secondary forests recovering from agricultural land use. However, carbon accumulation in some northern hardwood forests has been halted due to the impact of emerging stresses such as invasive pests and climate change (Ross et al., 2004; van Doorn et al., 2011; Gunn et al., 2014). This emphasizes the need to understand the linkage between tree demographic change and biomass carbon sequestration at multiple scales.

Forest biomass can also be affected by global environmental change induced by human activity. Global climate change can shift the distribution of different forest types (Gonzalez et al., 2010), extend growing seasons and stimulate both photosynthesis and respiration in plants (Menzel and Fabian, 1999; Walther et al., 2002). Climate change may also alter the frequency and severity of natural disturbance such as fire and drought (Dale et al., 2001), leading to a drastic change in forest biomass. Increasing atmospheric CO_2 concentration and atmospheric nitrogen deposition can fertilize the forest and promote carbon sequestration (Magnani et al., 2007; Bedison and Johnson, 2009; Allen et al., 2010a). Non-native insects and pathogens can have species-specific effects and tree mortality, and therefore change the species composition and structure of the

forest. These factors interact with each other, creating the complex mosaic of forest biomass distribution at the landscape scale (Anderson-Teixeira et al., 2013).

1.3 Forest soil carbon stock and its controlling factors

Soil properties are highly heterogeneous. At a given time and location, the size of the soil carbon pool reflects the balance between carbon input and loss, which are controlled by the major soil formation factors, including climate, vegetation, parent material, topography, human activity and time (Jenny, 1994; Amundson, 2001). The spatial variations of soil carbon at the pedon scale are mainly driven by plant-soil interactions (De Deyn et al., 2008). On one hand, soil properties determine the nutrient and water supply for forest growth, therefore are important factors controlling forest biomass dynamics. On the other hand, forest litter productivity and root turnover are the major inputs of soil carbon pool (Laganiere et al., 2013). The soil carbon cycle is also tightly coupled with nitrogen dynamics because of the latter's role as the primary limiting nutrient of plants in many terrestrial ecosystems (Manzoni and Porporato, 2009; Batjes, 2014). At the landscape scale, differences in soil carbon are likely determined by topography and climate (Allen et al., 2010b). Generally, in the northeastern U.S., soil carbon content is large in cooler and wetter conditions, at the bottom of slopes, and in older forests (Kulmatiski et al., 2004; Guo et al., 2006; Oueslati et al., 2013). Most of uncertainty in soil C and N cycling is associated with the difficulty in capturing the large spatial variation of soil properties in field measurements (Manzoni and Porporato, 2009). Plot design and sampling method are often the major source of errors in soil carbon and nitrogen studies (Peltoniemi et al., 2007). Comparing and optimizing the soil sampling methods are therefore essential steps to improving our understanding of soil C and N cycles.

1.4 Modeling forest carbon cycling at a regional scale

Ecological models have been widely used in studying forest carbon cycling and its feedback with climate change. Process-based models are a powerful approach to test our understanding of biogeochemical processes and to extrapolate ground survey data from limited plots to the landscape scale (Yan et al., 2011). In addition, the environmental changes stemming from human industrial and agriculture activities, such as climate change, nitrogen deposition, elevated atmospheric CO₂, increasing natural disturbances and land use change, interact with each other through a complex set of mechanisms and their long term effects on forest carbon cycling are difficult to test in controlled experiments (Ollinger et al., 2002). Process models provide a useful tool stimulating these effects on ecological process and analyzing the relative importance of each factor (Felzer, 2012).

The PnET-CN model (Aber and Federer, 1992; Aber and Driscoll, 1997) is a process-based ecosystem model that uses spatial information on vegetation, climate and soil to simulate the carbon, nitrogen and water dynamics of forest ecosystems in the northeastern United States. The model has been validated in various forest types (Goodale et al., 2002; Ollinger et al., 2002; Chen et al., 2004). Regional versions of the model based on geographic information systems (GIS) have been developed to extrapolate the simulation from the site to the regional level (Pan et al., 2004a; Pan et al., 2009). Applications of PnET models have provided important insights into the interactive effects of climate change, nitrogen deposition, increasing atmospheric CO_2 and ozone, and natural and anthropogenic disturbance (Ollinger et al., 1997; Chiang et al., 2008; Pan et al., 2009).

1.5 The Delaware River Basin (DRB) and the DRB Collaborative Environmental Monitoring and Research Initiative

The Delaware River Basin (DRB) is a ~33,000 km² watershed with tributaries in Pennsylvania, New Jersey, New York, Delaware, and Maryland. About 7.5 million people live in the DRB. An additional 8 million people in New York City and northern New Jersey rely on surface water diverted from the basin for their water supply (Fischer et al. 2004). A humid continental climate prevails throughout the DRB. The average annual temperature is 9-12 °C and the total average annual precipitation is 1143 mm (Kauffman et al. 2008). The DRB is located in the ecozone of deciduous forests and is ecologically diverse, with five physiographic provinces and multiple species assemblages that represent most of the major eastern forest type group (Murdoch et al., 2008). In the upper Appalachian Plateaus province the major forest type is Maple-beech-birch forest. In the lower part of Appalachian, valley and ridge, and piedmont provinces, the most prevalent forest type is Oak-hickory and Oak chestnut. Oak-pine forests are seen in New Jersey and south part of Delaware (Zhu and Evans, 1994). Coniferous forests intersperse in the upper Delaware Basin are residuals of historical landscape changes or the adaptation to local edaphic conditions.

The DRB Collaborative Environmental Monitoring and Research Initiative (CEMRI) was started in 1998 as a multi-agency project contributed by U.S. Forest Service (USFS), the U.S. Geological Survey (USGS), and the National Park Service (NPS). The major goal of this initiative was to augment existing monitoring systems with additional new measurements and develop interdisciplinarity to evaluate the health and sustainability of forest and freshwater aquatic systems in the DRB (Murdoch et al., 2008). Three areas in the DRB were selected as Intensive Monitoring and Research Areas (IMRA) for process-level studies in the forested landscapes. They are the Neversink River Basin (NS) in the northern, mostly forested region of the Appalachian Plateau province; the Delaware Water Gap Area (DEWA) with three small watersheds (Adams Creek, Dingman's Falls and Little Bushkill) lying in the central Appalachian Plateau Province, and the French Creek Watershed (FC) in the midbasin Piedmont province. The CEMRI project has produced a large amount of valuable data, which underpins this Ph.D. study.

1.6 General questions addressed in this dissertation

Utilizing the data collected during the DRB CEMRI and additional field investigations during 2012 to 2014, the research presented in this dissertation addresses the spatial and temporal trends in biomass and soil carbon stocks in the DRB forests. To define the scope and direction of the current work, the primary questions which correspond to the individual research chapters are:

Chapter 2:

Forest biomass carbon stocks were estimated based on field measurement campaigns in 2001-2003 and 2012-2013. The change of biomass carbon stock in the DRB forest during the recent decade was quantified by comparing the two measurements. The controlling factors of forest biomass carbon change were investigated and the impact of tree demographic change on biomass carbon change was examined.

Question 1: How did forest biomass carbon stocks in the DRB change in the past decade?

Question 2: Which factors drive spatial variation in forest biomass carbon stock change?

Chapter 3:

The standard Forest Inventory and Analysis (FIA) soil core method and a quantitative soil pit method were used to collect soil samples and estimate soil carbon and nitrogen stocks in the DRB forests. Soil properties measured by the two methods were compared and the contribution of variables to the spatial variation of soil carbon and nitrogen stocks were examined to evaluate the accuracy of the FIA soil core sampling method.

Question: Does the standard FIA soil core sampling protocol adequately quantify carbon content in the soils of the DRB?

Chapter 4:

The PnET-CN model was localized and improved by using field measured parameters, calibration by observed biomass data and incorporating disturbance history information. The model was used to generate maps of biomass and soil carbon stocks, and forest productivity in the three study sites in the DRB. The individual and combined effects of nitrogen deposition and CO_2 fertilization were evaluated by comparing model results using different scenarios.

Question 1: How are the forest carbon pools and fluxes spatially distributed in each sites?

Question 2: How do the forest carbon pools and fluxes response to nitrogen deposition and elevated atmospheric CO₂?

CHAPTER 2 Decadal Change of Forest Biomass Carbon Stocks and Tree Demography in the Delaware River Basin

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Xu B., Y. Pan, A.F. Plante, A.H. Johnson, J.A. Cole, and R.A. Birdsey. Decadal Change of Forest Biomass Carbon Stocks and Tree Demography in the Delaware River Basin. Forest Ecology and Management. *submitted*

Abstract

Quantifying forest biomass carbon(C) stock change is important to understand forest dynamics and their feedbacks with climate change. Forests in the northeastern U.S. have been a net carbon sink in recent decades, but C accumulation in some northern hardwood forests has been halted due to the impact of emerging stresses such as invasive pests, land use change and climate change. The Delaware River Basin (DRB), sited in the southern edge of the northern hardwood forest, features diverse forest types and land-use histories. These forests are sensitive to the controlling factors defining forest dynamics. In 2001-2003, the DRB Monitoring and Research Initiative established 61 forest plots in three research sites, using Forest Service inventory protocols and enhanced measurements. These plots were revisited and re-measured in 2012-2014. By comparing forest biomass C stocks in the two measurements, our results suggest that the biomass C stock of the DRB forest increased, and was thus a carbon sink over the past decade. The net biomass C stock change in the Neversink area in the north of the DRB was 1.94 Mg C ha⁻¹ yr⁻¹, smaller than the biomass C change in the French Creek area (2.52 Mg C ha⁻¹ yr⁻¹, southern DRB), and Delaware Water Gap Area (2.68 Mg C ha⁻¹ yr⁻¹, central DRB). An increase of dead biomass C accounted for 20% of the total biomass C change. The change of biomass C stocks did not correlate with any climatic or topographic factors, but decreased with increasing stand age, and with tree mortality rate. Mortality rates were highest in the smallest size class. In most of the major tree species, stem density decreased, but the loss of biomass from mortality was offset by recruitment and growth. The demographic changes differ dramatically among species. The living biomass of chestnut oak, white oak and black oak decreased because of the large mortality rate, while white pine, American beech and sweet birch increased in both biomass and stem density. Our results suggest that forests in the DRB could continue to be a carbon sink in the coming decades, because they are only at their middle successional stage. The linkage between tree demography and biomass C change underscore the effect of species-specific disturbance such as non-native insects and pathogens on forest dynamics.

2.1. Introduction

As global forest C stocks have increased consistently in the past several decades, their potential to sequester additional atmospheric carbon dioxide (CO₂) is considered a mitigation strategy to reduce global warming (Luyssaert et al., 2007; Pan et al., 2011; Ciais et al., 2013). Quantifying forest biomass C stock change and identifying the factors causing changes are important to understand forest dynamics and its feedback with climate change, and to successfully implement forest carbon management strategies (Hyvonen et al., 2007; Bonan, 2008). However large uncertainty still exists as forest biomass is highly heterogeneous (both spatially and temporally), and its dynamics are determined by different factors at different scales (Birdsey et al., 2006; Pan et al., 2013).

It is widely accepted that seasonal weather and climate regulate short-term fluctuations of carbon uptake, while disturbance history and management control C stock change on decadal time scales (Barford et al., 2001; Williams et al., 2012). Climatic, topographic and geologic factors determine forest dynamics across a broader range of environmental conditions, while stand age and gap dynamics control biomass accumulation at smaller spatial scales (Brandeis et al., 2009; Yi et al., 2010). Living tree biomass is one of the largest and most active C pools in forest ecosystems (Woodbury et al., 2007), and its dynamics are driven by the balance among three forest demographic changes: growth, recruitment and mortality (including harvesting). Each of these demographic changes can vary with age and species (Vanderwel et al., 2013a; Rozendaal and Chazdon, 2015). Long-term, periodic biometric measurements provide a unique opportunity to not only investigate forest biomass C dynamics at the regional scale, but also link biomass C stock with demographic change (Curtis et al., 2002; Xu et al., 2014).

Based on inventory data, forests in the northeastern U.S. are an overall net sink for atmospheric carbon in recent decades (Turner et al., 1995; Lu et al., 2013). However, C accumulation in some

northern hardwood forests has been halted due to the impact of emerging stresses such as invasive pests, land use change and climate change (Brooks, 2003; Siccama et al., 2007; Duarte et al., 2013). Small scale disturbances such as invasive pests, disease and selective harvesting may affect species differently, and increase C turnover at regional scales (Makana et al., 2011). The Delaware River Basin (DRB), situated in the southern edge of the northern hardwood forest, features diverse forest types and land-use histories. Most of the forests in the DRB are secondary forests recovering from agricultural land use, with stand ages around 80-100 years. Demographic change of different species composition in the DRB during the recovery process may reflect the impact of vegetation dynamics on forest biomass C change (Xu et al., 2012). These forests are sensitive to the controlling factors defining forest dynamics; thus, quantifying the biomass C stock in DRB forests acts as the basis for regional C cycle assessment and is essential for effective forest C management.

During 2001 to 2003 a set of forested plots were established in the DRB, and their total biomass C stock was measured in a multi-agency program known as the Collaborative Environmental Monitoring and Research Initiative (CEMRI). Here we report the results of re-measuring these plots using the same measurement protocols in 2012-2013. By comparing forest biomass C in the two measurements, and carefully documenting the demographic changes, the major goals of this study are: (1) to quantify biomass C stock change in the DRB forest during the recent decade, (2) to investigate the controlling factors of forest biomass C stock change at the regional scale, and (3) to examine the impact of tree demographic change on biomass C change by comparing biomass C change in different size groups and tree species.

2.2. Methods

2.2.1 Research area

The Delaware River is one of the major rivers in the mid-Atlantic region of the United States, draining an area of about 33,000 km² in Pennsylvania, New Jersey, New York, Delaware, and Maryland. The Delaware River Basin is characterized by a humid continental climate, with mean annual temperature of 9-12 °C and mean annual precipitation of 1143 mm (Kauffman et al., 2008). The DRB is located in the eco-zone of deciduous forests and is ecologically diverse, comprised of five physiographic provinces and multiple species assemblages that represent most of the major eastern U.S. forest types (Murdoch et al., 2008).

Three areas in the DRB were selected as intensive monitoring and research sites for process-level studies in forested landscapes: the Neversink River Basin (NS) in the northern, mostly forested region of the Appalachian Plateau province; the Delaware Water Gap Area (DEWA) with three small watersheds (Adams Creek, Dingman's Falls and Little Bushkill) lying in the central Appalachian Plateau Province; and the French Creek Watershed (FC) in the midbasin Piedmont province (Fig 2.1).

During 2001-2003, 77 inventory plots were randomly located in the three sites. Within each plot, all trees with diameter at breast height (DBH) greater than 5 inches (12.7 cm) were measured and marked, and the specific locations of the plots were mapped. In 2012-2013, 61 forested plots of the 77 original plots were revisited and biomass parameters were re-measured using the same protocols. Between the two measurements some plots had been disturbed by human activities, such as clear-cut or land use change. Anthropogenic disturbance was recorded in the field and disturbed plots were not included in the following analyses, thus further reducing the number of usable plots from the original 77 to 55 plots.

2.2.2 Field measurements and biomass C calculations

The plot design and sampling method follow the forest inventory protocols in the two measurements, including additional variables that were specified for the intensive study sites (Fig 2.2; U.S. Department of Agriculture, 2014). Each plot has four round subplots, in total covering an area of 672.44 m². Live and dead trees, stumps and residue materials were measured in each subplot. DBH, total and bole height, tree species, and status change (e.g., live versus dead) of each tree were recorded. A laser rangefinder was used to measure the tree and bole heights. Each subplot has one microplot (area: 13.49 m²) and three transects (length: 7.92 m). Live and dead sapling (1 inch < DBH < 5 inch), seedling (DBH < 1 inch), shrub and herb coverage were measured in the microplots. Coarse woody debris and fine woody debris were measured along the transects. Within each plot, two trees close to the subplots that represent the dominant species and growing condition of the forest stand were selected as site trees. The age of the site trees was measured by counting rings in a tree core. The stand ages of plots were determined as the mean age of the two site trees.

Field measurement data from the original 2001-2003 inventory were acquired from a USFS database generated by the CEMRI project (http://www.fs.fed.us/ne/global/research/drb/summary.html). Data from the two inventories were compiled into a single database for biomass C calculations. Cole et al. (2013) provides a detailed description of the database, which contains CEMRI project data on tree biomass.

Biomass of live trees, dead trees, saplings, seedlings, shrubs, coarse woody debris, fine woody debris, and stumps were each calculated and summed for each of the two survey periods. Fine root biomass was the only pool not estimated in either survey in this study. As a result, we assumed that fine root biomass did not change between the two sampling periods. The species-specific allometric equations from Jenkins et al. (2004) were used to calculate above-ground tree

biomass, and the general equations were used to calculate coarse roots biomass. The total biomass of each tree was the sum of above-ground biomass and coarse roots. Dead tree biomass was multiplied by a reduction factor according to their decade classes and species groups (Waddell, 2002) to subtract the biomass loss from decomposition. Biomass of coarse woody debris and fine woody debris were calculated using standard equations (Woodall and Williams, 2005). Stump biomass was calculated as coarse root biomass multiplied by the reduction factor according to the decade classes. A conversion factor of 0.5 was used to convert biomass to C stock. The biomass C change of each component was calculated as the difference of biomass C in the two measurements divided by the number of years between the two measurements in each of the plot.

2.2.3 Data analysis

All data of topographic and climatic factors were extracted from spatial data layers based on the coordinated of each plots. The elevation data was derived from Global Land Cover Characterization datasets (https://lta.cr.usgs.gov/GLCC). Annual temperature and precipitation are 30-year means from 1981-2010 (Thornton et al., 2014). Wet deposition is inorganic nitrogen deposition from 1983-2007 (Grimm, 2008). The mean values of each site are shown in Table 2.1.

Biomass C stocks in each component and their changes between the two measurements were averaged by site and in all plots combined. In addition, all live trees were classified into size classes by their DBH using 5 cm intervals from 10 to 40 cm (size classes 1-6). Trees with DHB 40-50 cm were classified as size class 7 and trees DBH > 50 cm were classified to size class 8. The biomass C stocks of living tree were summed by each tree size class. Mortality rates (% yr⁻¹) of each size class were calculated as the number of trees that died between the two measurements divided by number of live trees in the first measurement, and divided by the number of years between the two measurements. The mortality rates and proportions of biomass C from each tree size class in the two measurements were compared to examine the structure change in each site.

Tree species richness (S), Shannon's diversity index (H), and evenness (E_H) were calculated for each plot using the live tree data in the second measurement to represent the species diversity at plot level. For each site, species importance values were determined as (relative live density + relative live basal area) \div 2 as described by (Forrester et al., 2003) for each species. The 15 most important species in each site were selected and their biomass C and density change was examined. Biomass C loss from mortality was calculated as the biomass C of trees that were live in the first measurement and died before the second measurement. Biomass C gain from recruitment was calculated as the biomass of new ingrowth trees in the second measurement. Biomass C gain from growth was calculated as the biomass increase for trees living in both of the two measurements.

Differences among the three sites in total biomass C and biomass C change were compared using one-way ANOVA. Type II (major axis) regression analysis was used to test correlations between biomass C stock changes and biotic (stand age, tree mortality rate, Shannon's biodiversity index) and abiotic (slope, elevation, temperature, precipitation, and wet nitrogen deposition) factors in all plots combined to detect regional patterns.

A non-metric multidimensional scaling (NMS) analysis was conducted using PC-ord (Version 6.08, MjM Software, Gleneden Beach, Oregon, U.S.A.) on the basis of live tree data to differentiate the species composition in the three sites. Species that were present in only one plot were removed from the database, after which one plot in FC had only 4 trees remaining and was thus also removed from the database. As a result, data for 60 plots and 28 species (Table 2.4) were used in the NMS analysis. NMS ordination was run using k=3 dimensions, as this leads to significantly lower stress. To test the difference of species composition among the three sites, one-way ANOVA was used to test the effect of sites on the first two axes and statistically significant differences between each pair of the sites were compared using the Wilcoxon method.

2.3. Results

2.3.1 Forest biomass C stock change and its components

Among the 61 plots that were revisited in 2012-2013, six plots had visible disturbances in the past decade. The biomass C loss in the disturbed plots was up to 9.72 Mg C ha⁻¹ yr⁻¹ (Fig 2.3). In the remaining 55 undisturbed plots, the total biomass C stocks were 146.7 Mg C ha⁻¹ in FC, 114.7 Mg C ha⁻¹ in DEWA, and 159.3 Mg C ha⁻¹ in NS in the first measurement during 2001-2003 (Table 2.2). In the second measurement during 2012-2014 of the same 55 undisturbed plots, the total biomass C stocks were 172.1 Mg C ha⁻¹ in FC, 142.2 Mg C ha⁻¹ in DEWA, and 185.1 Mg C ha⁻¹ in NS. The forests in the most northern site (NS), with higher elevation, and greater precipitation and nitrogen deposition, had larger biomass C pool than the other sites. The net biomass C stock change between the two measurements was 2.52 Mg C ha⁻¹ yr⁻¹ in FC, 2.68 Mg C ha⁻¹ yr⁻¹ in DEWA, and 1.94 Mg C ha⁻¹ yr⁻¹ in NS. The mean biomass C stock change in all plots was 2.45 Mg C ha⁻¹ yr⁻¹. The undisturbed forests in the DRB were therefore a net carbon sink over the recent decade (i.e., the mean of each site was above the zero line in Fig 2.3). The total biomass C change did not differ among the three sites (*p*=0.76).

Among all biomass components, live trees were the largest C pool and C sink over the past decade (Table 2.2). On average, live tree biomass contributed 76.9% of the total biomass C change. Dead biomass was also an important contributor to total biomass C change (20.1%). Dead trees and CWD were the two largest C pools in dead biomass. Variation in biomass C change among plots was large, especially in the dead biomass components (Table 2.2).

2.3.2 Controlling factors in biomass C change

For all undisturbed plots combined, the change in biomass C stock between the two measurements was poorly correlated with climatic and topographic factors, although demonstrating divided domains (Table 2.3, Fig 2.4). Stronger correlations were detected between biomass C change and biotic factors (Table 2.3, Fig 2.4). The change in biomass C increased significantly with total biomass in the second measurement (r = 0.505, p < 0.01), and with tree mortality rate between the two measurements (r = -0.403, p < 0.01). Biomass C change was negatively correlated with stand age (r = -0.232, p = 0.09). No significant correlation was detected between biomass C change and tree species diversity.

2.3.3 Forest demographic changes

Large trees (>35 cm DBH) made greater contributions to the living biomass, especially in FC where the largest size class (> 45 cm DBH) accounted for 37.8% of the total live tree biomass. Live tree biomass increased between the two measurements in all size classes, but the change in biomass was greater in large size classes than in small size classes (Fig 2.5a-c). Mortality rates were also greater in smaller size class (10-20 cm DBH, Fig 2.6d) compared to trees in the middle size class (20-35 cm DBH). High variability was observed in large size class mortality rates because there were few large trees (>35 cm DBH, Fig 2.5d).

Tree species composition of forests in NS was significantly different from FC and DEWA, but forests in FC and DEWA had more similar species composition. In results of NMS, all of the NS plots were in the lower-left quadrant, with only 4 plots from FC and DEWA (Fig 2.6). Site had significant effect on both of the NMS axes. The NS plots had significantly smaller scores on both of the axes comparing with FC and DEWA (axis 1: NS vs FC p < 0.01, NS vs. DEWA p < 0.01, axis 2: NS vs FC p < 0.01, NS vs. DEWA p < 0.01). However, the difference between FC and DEWA was not significant on both of the axes (axis 1: p = 0.73, axis 2: p = 0.59). Forests in NS were dominated by maple-beech-birch forest, while in FC and DEWA consisted of tree species typical of a southern deciduous type of oak-hickory forest. The DEWA site, located between the other two sites from north to south, appears to be more of a transition zone for tree species (Table 2.4).

Over the past decade, in spite of reduced stem density, the biomass C stock increased in the 15 most important species in the DRB forest (Fig 2.7). Growth of existing trees accounted for most of the biomass C increase, while recruitment contributed little to total biomass C change. Conversely, mortality played an important role in counterbalancing growth and recruitment. Because of the high mortality rate, the living biomass of chestnut oak, white oak and black oak decreased in FC and DEWA. White pine, red oak and sweet birch increased in both biomass and stem density in the oak-hickory forests in DEWA. In the maple-beech-birch forests in NS, the stem density of American beech, and biomass C stock of yellow birch and hemlock increased dramatically.

2.4. Discussion

2.4.1 The large biomass C sink in the DRB forests

The average biomass C stock in the DRB forest was smaller than previously reported for old grow forests in the region (Gunn et al., 2014; McGarvey et al., 2015), but comparable with the average biomass C stocks in deciduous forests of the northeast U.S. estimated by forest inventory data (Nunery and Keeton, 2010). The change of biomass C stocks over the past decade in the DRB forest was greater than other long-term biomass measurement in northern hardwood forests, such as the Adirondack Mountains (Bedison et al., 2007) and the Hubbard Brook Valley (van

Doorn et al., 2011). The change in biomass C stock was also greater than the national average of biomass C stock change during 2000-2007 (Pan et al., 2011).

Forest biomass C stocks differed significantly among the three sites (Table 2.2). Larger potential biomass C stocks in the maple-beech-birch forest and fewer disturbances at high elevation may be responsible for the larger biomass C stock in the NS (Turner et al., 1995). For the two sites dominated by oak-hickory forest (i.e., FC and DEWA), FC had a larger biomass C stock but smaller biomass C change, suggesting that the plots in FC were in a later successional stage compared to the plots in DEWA. The greater contribution of biomass C from the largest size classes and the high mortality rate in smaller size classes in the FC (Fig 2.5a and d) also indicated forest maturity. Although the average stand age in FC was younger than in DEWA (Table 2.1), it is likely that the warmer climate and greater atmospheric N deposition has allowed the forest in FC to accumulate more biomass C in a shorter period of time, and the growth rate of biomass C might have started to decline earlier (Odum, 1960; Anderson-Teixeira et al., 2013). In contrast, biomass C stocks increased at a greater rate in DEWA because the forests were in a relatively earlier successional stage and have greater potential to sequester more biomass C in the future.

Dead biomass was a substantial C pool in the DRB forests, but its change was also highly variable. The coefficients of variance ranged from 214% to 325% in the three sites (Table 2.2). Changes in dead biomass were negatively correlated with live biomass changes at the plot level (Fig 2.8), suggesting that biomass C lost from live biomass is transferred to, and can be preserved in, dead biomass for at least a decade. Dead biomass can thus function as a buffering C pool, reducing the C turnover rate at the ecosystem scale (Woods, 2014). McGarvey et al. (2015) also suggest that the importance of dead biomass C pools tend to increase as a forest ages.
2.4.2 Environmental versus biotic factors in determining biomass C change

The observed lack of correlation with climatic and topographic factors for biomass C change is likely because the plot variation in forest biomass is much larger than the spatial variation in environmental factors (as illustrated by scattering in a wide range vertically, but clustering in a small range horizontally in Fig 2.4a and b). The environmental factors were not adequate to explain the variation in biomass C change within each site, while biological factors such as tree mortality rate and stand age appeared to be more important in determining variation in biomass C stock changes. Our results suggest that forest biomass C change at the regional scale was mostly driven by internal community-level processes such as competition and natural succession, more so than external environmental factors. This is consistent with other research about the controlling factors of forest dynamics (Kardol et al., 2010; Nowacki and Abrams, 2015; Zhang et al., 2015).

To explain the lack of correlation between environmental factors and biomass C change, two points need to be mentioned. First, this result does not mean that forest biomass C is unaffected by climate change in the DRB. The total biomass C change we reported is a combination of natural growth and enhancement by climate change (Caspersen et al., 2000), whose effects cannot be easily separated because we have only two measurements and one-time interval. Second, environmental factors may determine demographic change and disturbance regime, and therefore may have indirect impacts on biomass C change (Vanderwel et al., 2013b; Baez et al., 2015). However, these effects are not strong enough to be detected at such small spatial scales compared to the more dominant influence of plot dynamics. Long term observations at more sites are needed to address the interactions between factors.

The observed negative correlation between stand age and biomass C change (Fig 2.4c) is consistent with the forest succession model, which predicts a decline in forest growth with increasing stand age (Williams et al., 2012). Our observed correlation was not particularly strong

because the range of stand ages in our DRB plots was relatively narrow, and the correlation was mostly driven by the three plots with the youngest stand ages. The observation that younger forests accumulated more biomass C than older forest over the past decade still indicated that most of the forests in the DRB had reached or passed the stage of maximum growth rate. While still accumulating C and thus acting as a sink, the rate at which C may be sequestered in the future may decrease as the age distribution shifts toward older stands in the DRB forest.

Although live biomass C loss from mortality could be preserved in the ecosystem as dead biomass for several decades, tree mortality rates still had a significant impact on biomass C change (Fig 2.4d). A larger proportion of the spatial variation in biomass C change can be explained by tree mortality rate, rather than the average tree growth rate (Table 2.3), indicating the importance of tree mortality in determining forest dynamics (Purves et al., 2008; Xu et al., 2012). It has been reported that tree mortality rates vary with climate, forest density, species and succession stage (Bell, 1997; Brown and Schroeder, 1999; Lutz and Halpern, 2006; Bond-Lamberty et al., 2014). In the following discussion, we therefore further examine tree mortality rates by size class and species, and their impacts on biomass C change.

2.4.3 Demographic changes in different size classes and species

Large trees played an important role in determining forest biomass C stock in the DRB forest. The largest 10% of trees accounted for 47% of the live tree biomass in FC, 41% in DEWA and 38% in NS. Between the two measurements, more biomass C was accumulated in the larger size classes than smaller size classes (Table 2.5), which is consistent with other studies (Fedrigo et al., 2014). Biomass C increases in large trees can be attributed to increased stem density of larger trees as a result of shifting forest age structure, and to large growth rate of large trees because they have better access to more resources such as light and water (Stephenson et al., 2014). The fact that large trees in the DRB forests are still growing rapidly indicated a large potential for biomass C increase in the future. In this study, most of the trees in the largest size class (50-70 cm DBH) are comparable to only the middle size class in the old-growth forest of the Mid-Atlantic (McGarvey et al., 2015). This comparison further suggests that the forests in the DRB are likely in a stage of middle succession, and could continue to be a carbon sink in the future, although C sequestration rate may decline.

The highest mortality rates were observed in the smallest tree size class (especially in FC, where the forest biomass largely consisted of the largest size class, Fig 2.5a and d), which can be explained by severe competition in the understory layer. Once individual tree height reaches the canopy height, growth is not limited by light and the mortality rate decreases (Bell, 1997; Miura et al., 2001). Our observations contrast with the pattern of mortality rate increasing with stem size as reported in an old-growth forest (Runkle, 2013). It is observed that as forests age, the peak of mortality biomass C loss shifts from young, small trees to large, dominant trees (Bond-Lamberty et al., 2014; Woods, 2014; Rozendaal and Chazdon, 2015). However, increased mortality rate in large trees was only present in DEWA, which has the largest sample size (number of trees = 953), and not in FC and NS, which both have a smaller number of trees in the largest size class.

Stem density decreased in most of the major species, probably due to the self-thinning process caused by resource competition during forest development (Coomes and Allen, 2007). Although tree density decreased, live tree biomass C stock in the DRB forest still increased because the loss of biomass C from mortality was offset by recruitment and growth in most of the dominant species. However, the balance between growth, recruitment and mortality varies dramatically among species. Even coexisting in a similar environment, different species can respond differently to the controlling factors of forest dynamics, especially with a changing disturbance

regime (Canham et al., 2006; Kardol et al., 2010). Our results reflect the importance of speciesspecific disturbances such as non-native insects and diseases, which may threaten a single species or genus of trees (Lovett et al., 2002; Flower et al., 2013). These disturbances are gradually changing the species composition in the DRB forest and may have profound impacts on biomass C stock change by altering the demographic change in different tree species (Hicke et al., 2012; Fahey et al., 2013).

For example, in the oak-hickory forests in FC and DEWA, oak species (e.g. chestnut oak and black oak in FC, white oak and chestnut oak in DEWA) are declining in both stem density and biomass C stock. The possible reasons for oak decline include regional selective harvesting and defoliation induced by gypsy moth outbreaks, or infestation of sudden oak death (Murdoch *et al.* 2008).

In the maple-beech-birch forests in NS, the most dominant species, American beech, was affected by infestations of beech bark disease (Griffin et al., 2003; Lovett et al., 2013), causing the largest biomass C loss from mortality (mostly from the largest size class) and the largest biomass C gain from recruitment among all the species and sites. These results implied that the forests in the NS are in the aftermath phase of the disease, in which the disease may stimulate regeneration and change the forest structure (Houston, 1994; Forrester et al., 2003).

Overall, it is difficult to predict the future dynamics of the forest because species composition is affected by various species-specific disturbances and the interactions among them, and other factors such as natural succession and climate change (Weed et al., 2013; Davalos et al., 2014). In general, disturbance-vulnerable species tend to be slowly replaced by other species that are tolerant to the disturbance or adapt to the changing environment. This process will have a dramatic impact on tree demography and biomass C stock change into the future.

2.4.4 Implications for regional C cycle and forest management.

In this study, periodic long-term field measurements of forest biomass allowed the quantification of total biomass C stock change, addressing controlling factors of biomass C change and examining the impact of tree demographic change in the DRB forest. Our results provided important information for understanding forest recovery processes in major forest types of the northeastern U.S., and for improving ecological modeling and forest management at the regional scale. Our results showed that forest biomass in the DRB was a relatively large carbon sink over the past decade compared with other sites and the national average. It is likely that the DRB forest will continue to be a carbon sink in the coming decades, because the forest is in its middle rather than a late successional steady state (Odum, 1969). These results underscore the potential of regional forest carbon management for climate mitigation and can serve as the baseline information for evaluating biomass C sequestration in the DRB forest.

We found that biomass C stock changes were driven by tree demographic change, which varied with tree size and species. This highlights the potential importance of species-specific disturbances such as insects and pathogens, and how the changing frequency and severity of these disturbances might impact forest biomass C sequestration. Forest management strategies must therefore pay close attention to the species that show declines in density and biomass over time, especially late successional species susceptible to biotic disturbances, to ensure sustainable forest development and a continuing biomass carbon sink.

Table 2.1 Environmental conditions in the three research sites in the Delaware River Basin. All data were extracted from geographic information layers, and mean values for each site are shown. The elevation data was derived from Global Land Cover Characterization datasets (https://lta.cr.usgs.gov/GLCC). Annual temperature and precipitation are 30-year means from 1981-2010 (Thornton et al., 2014). Wet deposition is inorganic nitrogen deposition from 1983-2007 (Grimm, 2008).

	Elevation (m)	Mean annual temperature (°C)	Mean annual precipitation (mm)	Wet deposition (kg N ha ⁻¹)	Average stand Age
French Creek (FC)	166	11.16	1171	6.55	85
Delaware Water Gap (DEWA)	360	8.53	1219	6.33	107
Neversink (NS)	773	5.75	1503	6.44	91

Table 2.2 Total biomass C stocks in the two measurements (unit: Mg C ha⁻¹) and biomass C stock change in different components (unit: g C m⁻² yr⁻¹) in each site and in all plots combined. Standard deviations among plots are given in the parentheses. P values show the statistical significance of differences among sites in a one-way ANOVA.

	FC (n=13)	DEWA (n=28)	NS (n=14)	Total (n=55)	P value			
Total Biomass C (Mg C ha ⁻¹)								
2001-2003	146.7 (50)	114.7 (39)	159.3 (37)	133.6 (45)	0.004**			
2012-2014	172.1 (56)	142.3 (51)	185.1 (45)	160.2 (53)	0.017*			
Biomass C c	Biomass C change (g C m ⁻² yr ⁻¹)							
Live Tree	216.0 (255)	204.8 (262)	131.1 (117)	188.7 (231)	0.56			
Dead Tree	57.3 (104)	20.2 (50)	-12.8 (113)	30.8 (106)	0.18			
Sapling	-6.0 (21)	-6.2 (28)	18.4 (40)	0.2 (31)	0.036*			
Seedling	1.2 (6)	10.2 (13)	2.1 (4)	6.0 (11)	0.010*			
CWD	5.8 (45)	18.0 (63)	36.0 (37)	19.7 (54)	0.34			
FWD	-15.5 (29)	5.5 (29)	1.2 (14)	-0.5 (27)	0.06			
Stump	-8.2 (33)	-5.0 (37)		-6.0 (36)	0.80			
Live Biomass	212.1 (262)	210.7 (258)	151.2 (108)	195.9 (228)	0.84			
Dead Biomass	40.2 (131)	57.0 (122)	42.6 (104)	49.3 (118)	0.49			
Total	252.3 (224)	267.7 (247)	193.9 (142)	245.2 (218)	0.76			

Variable	Slope	Intercept	\mathbf{R}^2	р
Slope (degree)	4.13	216	0.010	0.47
Elevation (m)	-0.18	320	0.037	0.16
Precipitation	-6.09	963	0.033	0.18
Temperature	18.48	92	0.030	0.21
Total Biomass (2012-2014)	0.0207	-87	0.255	<0.01**
Mortality Rate	-73.99	347	0.162	<0.01**
Stand Age	-2.13	454	0.054	0.09*
Shannon's diversity index	-92.91	368	0.032	0.19

 Table 2.3 Type II (major axis) correlations between biomass C change and environmental factors.

Common name	Latin name	NMS loading score			Importance		
		Axis 1	Axis 2	Axis 3	FC	DEWA	NS
Eastern red cedar	Juniperus virginiana	-0.463	0.301	0.164			0.023
Black spruce	Picea mariana	-0.262	-0.065	0.345		0.019	
Pitch pine	Pinus rigida	0.077	0.440	0.433		0.012	
White pine	Pinus strobus	-0.635	0.394	0.241	0.011	0.140	0.030
Hemlock	Tsuga canadensis	-0.579	-0.266	-0.046		0.042	0.152
Striped maple	Acer pensylvanicum	-0.253	-0.656	-0.869			0.007
Red maple	Acer rubrum	-0.028	-0.025	0.401	0.175	0.274	0.160
Sugar maple	Acer saccharum	-0.127	-0.665	-0.960		0.008	0.169
European alder	Alnus glutinosa	-0.507	-0.180	0.255			0.008
Eerviceberry spp.	Amelanchierchier	0.392	0.000	-0.010		0.006	
Yellow birch	Betula alleghaniensis	-0.462	-0.546	-0.161		0.015	0.179
Sweet birch	Betula lenta	0.506	0.235	-0.147	0.083	0.058	
Bitternut hickory	Carya cordiformis	0.308	0.438	-0.165	0.020	0.002	
Pignut hickory	Carya glabra	0.340	0.170	0.149	0.027	0.016	
Shagbark hickory	Carya ovata	0.530	0.040	-0.496	0.003	0.003	
Mockernut hickory	Carya tomentosa	0.380	0.202	0.135	0.009	0.023	
American beech	Fagus grandifolia	-0.172	-0.587	-0.720	0.068	0.001	0.189
White ash	Fraxinus americana	0.208	-0.219	0.315	0.005	0.045	0.006
Yellow poplar	Liriodendron	0.379	0.751	-0.434	0.252	0.002	
Black gum	Nyssa sylvatica	0.370	0.120	0.088	0.050	0.005	
Black cherry	Prunus serotina	-0.012	-0.419	-0.189	0.007	0.006	0.069
White oak	Quercus alba	0.270	0.154	0.339	0.044	0.107	
Scarlet oak	Quercus coccinea	0.166	0.352	0.418	0.009	0.031	
Chestnut oak	Quercus prinus	0.182	0.253	0.105	0.045	0.056	
Red oak	Quercus rubra	0.372	0.188	0.110	0.044	0.094	
Black oak	Quercus velutina	0.141	0.385	0.057	0.042	0.010	
Sassafras	Sassafras albidum	0.390	0.182	0.398	0.025	0.011	
Basswood	Tilia americana	0.741	-0.282	-0.168	0.003	0.004	

Table 2.4 The loading scores of species on the three axes in the NMS analysis and their importance in each site.

Table 2.5 Average DBH of the 10% largest trees and their contribution to total live tree biomass

 in each site and measurement.

	Measurement 1		Measurement 2		
	DBH	Biomass contribution	DBH	Biomass contribution	
FC	44.96	47.69%	50.55	47.93%	
DEWA	39.88	41.44%	42.67	40.54%	
NS	40.39	37.81%	45.72	37.96%	



Figure 2.1 The hydrological boundary of the Delaware River Basin and the main stream and tributaries of the Delaware River. The three research areas of the current study are shown in different shading color. The red dots represent the locations of forest biomass plots.



Figure 2.2 Plot design used for forest measurement (Revised from U.S. Department of Agriculture, Forest Service. (2002)). Trees within each subplot were measured. Sapling and seedlings were measured in microplots. Coarse and fine woody debris were measured on transects.



Figure 2.3 Biomass C stock changes in the three research sites and for all plots combined. Red dots represent the six disturbed plots. Boxes above the zero line represent increasing biomass C stock. Lines in the boxes show the median and the 25% and 75% quantiles, while bars outside the boxes show the 5% and 95% quantiles. Outliers are shown as black dots. FC: French Creek, DEWA: Delaware Water Gap, NS: Neversink.



Figure 2.4 Relationship between biomass C stock change and environmental (a and b) and biotic (c and d) factors among all the undisturbed plots. Plots in the three sites are shown in different colors and shapes.



Figure 2.5 Live tree biomass C and mortality rates in different tree size classes. Live tree biomass C in the two measurements in (a) French Creek, (b) Delaware Water Gap, and (c) Neversink. Mortality rates (d) of the three research sites between the two measurements. The three sites are shown in different shades.



Figure 2.6 Results from the NMS for live trees in the second measurement (2012-2014). Points represent individual plots sampled and sites are represented by different colors. Arrows represent species. See Table 2.4 for the loading score of species.



Figure 2.7 Stem density and biomass C change in the fifteen most important species in the tree sites in the DRB forests: (a) French Creek (b) Delaware Water Gap (c) Neversink. The lengths of the bars represent the biomass C gain from recruitment and growth and biomass C loss from mortality. Data points on the left side of the zero line represent decrease in stem density or biomass C stocks, and on the right side of the zero line represent increase in stem density or biomass C stocks. See Table 2.4 for species Latin names.



Figure 2.8 Correlation between change of live biomass and change of dead biomass. FC: French Creek, DEWA: Delaware Water Gap, NS: Neversink.

CHAPTER 3: Method comparison for forest soil carbon and nitrogen stocks in Delaware

River Basin

This chapter is in press as:

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Abstract:

The accuracy of forest soil carbon (C) and nitrogen (N) estimates is hampered by forest soils that are rocky, inaccessible and spatially heterogeneous. A composite coring technique is the standard method used in Forest Inventory Analysis (FIA), but its accuracy has been questioned. Quantitative soil pits provide direct measurement of rock content and soil mass from a larger, more representative volume. Here, the two sampling methods were used to estimate soil C and N stocks in forested plots in the Delaware River Basin. Mean stocks in the whole soil profile (organic and mineral layers, 0-40 cm, using pits) were 76.6 Mg C ha⁻¹ and 4.45 Mg N ha⁻¹. In the surface mineral layer (0-20 cm), lower bulk density (BD), lower coarse fragment (CF) content and greater C concentration (%C) were measured using the core method compared to the pit method. However, as the three variables are not independent and can be counterbalancing, soil C stocks did not differ between sampling methods. Spatial variation in C stocks was mainly driven by the variance of %C and BD in both methods, while the relative contribution of CF was greater in the soil pit method. Our results suggest that the physical problems associated with the core method and the ability of the core method to capture spatial variation in soil C and N stocks are questionable compared with quantitative soil pits. While variability and covariance among the contributing variables resulted in similar stock estimates from both sampling methods, they might

accumulate greater uncertainty in spatial extrapolation to regional estimates of forest soil C and N stocks.

3.1. Introduction

Soils represent the largest carbon pool and a highly dynamic component of the terrestrial carbon cycle (Batjes, 1996). Quantifying forest soil C and N stocks is critical to understanding the ecological responses of forests to changes in climate, land use and management, and to improve global change models (Smith et al., 2012; Dib et al., 2014). However, the accuracy of forest soil C and N estimates is hampered by the difficulty in characterizing forest soil properties because forest soils can be rocky, inaccessible and spatially heterogeneous (Qureshi et al., 2012; Lark et al., 2014). In addition to this inherent variability, there is large uncertainty in forest soil C and N estimates associated with the soil sampling methods used (Gifford and Roderick, 2003; Jandl et al., 2014).

Forest Inventory Analysis (FIA) provides a national database of forest soil C and N that has been broadly used in large-scale soil C and N estimations (Conkling et al., 2002; O'Neill et al., 2005). A composite coring technique is the standard soil sampling method in FIA, as well as in the national Forest Health Monitoring program (Conkling et al., 2002; Palmer et al., 2002). However, the accuracy of the soil core method has been questioned by several studies (e.g., Throop et al., 2012; Chimner et al., 2014). Several reports have compared sampling methods and found significant differences in measured variables (e.g., bulk density, soil C stocks, etc.) among them when used in forest soils, which are typically rocky and uneven with high spatial variation in soil development, horizon depth and rock content (Page-Dumroese et al., 1999; Harrison et al., 2003; Johnson et al., 2012).

In soil core method, soil C and N stocks are calculated using bulk density (BD), coarse fragment content (CF), soil C and N concentrations (%C) and soil depth. Several problems with the soil core method may result in underestimation or overestimation of these three variables, and therefore induce errors in soil C and N stock estimations (Table 3.1). First, when the core is punched into the soil, the soil inside and beneath the core can be compacted. If the compaction only happens inside the core, soil in the bottom of the core will have greater density and there will be an empty space in the top of the core. The values of BD, %C and CF will not be affected because we consider the volume of the whole core as the volume of the soil (Lichter and Costello, 1994). But if the soil beneath the core is compacted during sampling, part of the soil that should be sampled would be missed. This problem will lead to underestimation in BD and CF (Harrison et al., 2003). Because the missed soil is always deeper soil and %C typically decreases with depth, the soil sample will overemphasize the surface soil and the %C will be overestimated. Secondly, the soil core could be obstructed by rocks or coarse roots in the soil. If the coring stopped above the rock but there is still soil beneath the rock, the %C will be overestimated because subsoil is missed. CF will be overestimated, although the BD will not be affected. However, if the impact force of the core extruded the rocks and deep soil, leading to an overestimation of the soil volume (Levine et al., 2012), then the volume-based BD and CF will be underestimated (Page-Dumroese et al., 1999; Harrison et al., 2003). Thirdly, locations with fewer rocks within the sampling frame are more likely to be sampled in the core method. This will result in an underestimation of CF (Kulmatiski et al., 2003; Jandl et al., 2014). The problems identified above could combine together and lead to a large uncertainty of the soil C and N stock estimates, or may be counterbalancing, with no observable effect on the estimate. In spite of the limitations of this method, a literature survey has shown that the soil core is still the predominant method in soil C estimation (Throop et al., 2012).

The quantitative soil pit method purportedly provides more accurate estimations of soil C and N stocks (Lyford, 1964). This method provides direct measurement of rock content and soil mass from a larger, more representative, volume of soil (Vadeboncoeur et al., 2012). There are fewer limitations for the location of a quantitative pit because it does not need to avoid the presence of rocks. In addition, deeper portions of the soil profile are more accessible in the pit method than the conventional coring method. Soil pit excavation was considered as the preferred soil sampling method in many studies evaluating methods in measurements of soil properties (e.g., Harrison et al., 2003; Kulmatiski et al., 2003; Levine et al., 2012). However, because the soil pit method is so labor-intensive, fewer pits than cores are likely to be sampled over the same landscape area and therefore spatial variability in soil properties may not be adequately characterized.

Estimation of soil C and N stocks requires resolving variables of BD, CF, soil C and N concentrations and soil depth. The choice of sampling method may bias each variable in different ways. In addition, variables may contribute differently to the spatial variation of soil C and N stocks in different sampling methods (Holmes et al., 2011; Schrumpf et al., 2011). Therefore, a comprehensive comparison between sampling methods, particularly the widely used soil core method and the standard quantitative soil pit method, considering all variables and their contributions to the spatial variation, is of fundamental importance for our prediction ability in estimating large-scale forest soil C and N stock changes.

The Delaware River is one of the major rivers in the mid-Atlantic region of United States, draining an area of about 33,000 km² in Pennsylvania, New Jersey, New York, Delaware, and Maryland. The Delaware River Basin (DRB) represents the major physiographic provinces, ecozones and soil types of the mid-Atlantic region. It contains several intensive monitoring and research sites maintained by U.S. Forest Service, with long-term research of ecological components and processes (Murdoch et al., 2008). The diverse geologic, topographic and ecological properties of the DRB and ongoing monitoring projects provided a good opportunity to explore the metrological uncertainty of soil C and N content at a regional scale.

In this study, the FIA standard soil core method and the quantitative soil pit method were used to estimate soil C and N stocks in three research sites in the DRB forest. The major goals of this study were to: 1) quantify soil C and N stocks to 20 cm using FIA soil core method, and to 40 cm using soil pit method in the DRB forest plots; 2) compare soil properties measured by soil core and soil pit methods in the 0-20 cm mineral soil layer; and, 3) compare the contribution of variables to the spatial variation of soil C and N stocks in the two sampling methods.

3.2. Methods

3.2.1. Study area and plot design

The Delaware River Basin is characterized by a humid continental climate, with mean annual temperature of 9-12 °C and mean annual precipitation of 1143 mm (Thornton et al., 2014). The DRB is located in the ecozone of deciduous forests and is ecologically diverse, comprised of five physiographic provinces and multiple species assemblages that represent most of the major eastern U.S. forest types (Murdoch et al., 2008).

Three sites in the DRB were selected as intensive research sites (Fig 3.1, Table 3.2). They are the Neversink River Basin (NS) in the northern, mostly forested region of the Appalachian Plateau province; the Delaware Water Gap Area (DEWA) with three small watersheds (Adams Creek, Dingman's Falls and Little Bushkill) lying in the central Appalachian Plateau Province; and the French Creek Watershed (FC) in the midbasin Piedmont province. The dominant soil suborders are Ochrepts in NS and DEWA, and Udults in FC (Soil Survey Staff, 2014).

In total, 60 forested plots were randomly located across the three research sites (14 in NS, 32 in DEWA and 14 in FC). The plots were established in 2001-2003 by the U.S. Forest Service and U.S. Geologic Survey, and designed according to FIA and Forest Health Management protocols (U.S. Department of Agriculture, 2004). Each plot had four round subplots, covering a total area of 672 m² (Fig 3.2). In each of the plots, three soil cores (0-20 cm) and one quantitative soil pit (0-40 cm) were sampled at systematically located positions as described below. If the locations for sampling landed on non-forested areas (e.g., road, water body, farmland, etc.), no sample was collected. All the soil samples in FC, DEWA and three plots in NS were collected in summer 2013, while the remaining eleven plots in NS were sampled in summer 2014.

3.2.2. Standard FIA soil core sampling method

The standard FIA soil core sampling protocol was used to collect soil core samples (U.S. Department of Agriculture, 2004). Core samples were collected 9.14 m away from the center of subplots 2, 3 and 4 (Fig 3.2). In 2001-2003, soil samples had been collected at the location of 'visit 1' in these DRB plots. So in this second measurement, the coring was located at 'visit 2' of each subplot, to avoid the disturbance of the previous survey. In the standard FIA protocol, only one mineral soil sample is collected at subplot 2, while in this study, mineral soil samples were collected in each of the 3 subplots (Fig 3.2) to get more representative samples (*i.e.*, larger area) to compare with the soil pit method.

The organic layers within the frame of a bicycle tire (30.5 cm in diameter) were cut by saw and collected into multiple sample bags. Mineral soils were sampled using an impact-driven soil corner (5 cm in diameter, 20 cm in length) with two internal steel liners (10 cm length each). The core was driven into the ground until the liner was even with the soil. The core was slowly rotated and carefully removed from the ground. The two liners were removed from the top of the core and soil in the liners was removed and collected into separate sample bags. If the soil core was

obstructed by a rock or large root, the actual depth of the two layers were recorded and the space beneath was assumed to be occupied by rocks. If the mineral soil horizons were shallower than 3 cm, no mineral soil sample was collected for that subplot, and samples from the remaining two subplots were used. Although they can be used to sample deeper soils, the coring was performed only to 20 cm to comply with FIA standard methods.

3.2.3. Quantitative soil pit sampling method

The middle point between the plot center and subplot 4 was selected as the location for the quantitative soil pit in each plot (Fig 3.2). If this location was not forested (e.g., located on agriculture land or on a road), or had a tree or rock outcrop within the sampling area, the same location in subplot 2 or subplot 3 was selected.

A 50 \times 50 cm square frame was secured to the ground by four nails on the outer edge to control the area of the pit. All living vegetation within the sampling area was removed. The entire layer of loose leaf litter (Oi horizon) and the underlying organic matter (Oe+Oa horizons) were removed and weighed separately in the field. A subsample of ~0.3 kg was collected and returned to the laboratory for subsequent analyses. The mineral soil was excavated to depths of 0-20 and 20-40 cm. For each of the soil layers, the actual depths were measured at the middle points of the four pit edges. Soil, rocks and roots were separated then weighed. A subsample of well mixed soil (~1 kg) from each layer was collected and returned to the laboratory for subsequent analyses. To measure the volume of the soil, known volumes of perlite (measured in a graduated cylinder) were poured into the pit until the pit was filled to the depth of the upper horizon. The density of perlite in the cylinder was found to be similar to its density when poured into the pit. All rocks and roots that had been excavated were placed back into the pit during this process, and submerged in the perlite. The volume of the perlite therefore represented the actual volume of the excavated soil. When the volume of rocks was too large, or there were too many small rocks in the pit, the portion of rocks that could not be submerged into the perlite was not placed back into the pit but was instead weighed. The volume of the rocks was then calculated using a standard rock density of 2.65 g cm⁻³ (Telford et al., 1990) and was subtracted from the volume of the perlite.

3.2.4. Soil C and N analyses and C and N stocks calculations

Organic layer samples were oven dried at 105 °C for more than 12 hours, then ground to < 2 mm. Mineral soil samples were air-dried and sieved through a 2-mm screen. Twenty mineral samples representing the two soil layers distributed among the three research sites and collected by both methods were oven dried, and a correction curve between air-dry and oven-dry soil weights was generated (oven-dry = $0.9845 \times air$ -dry, R²=0.999). Oven-dry weights of the mineral samples were estimated using this curve. An aliquot from each sample was ground by mortar and pestle to pass a 250-µm sieve to increase sample homogeneity. Ground samples (e.g., 15 mg for mineral soil and 5 mg for organic soil) were analyzed for total C and N concentrations (g kg⁻¹) using an ECS4010 Elemental Analyzer (Costech, Valencia, CA, USA). Approximately 11 % of the samples (n = 71) were measured twice to verify the precision of the C and N analyses. These analytical replicates showed a precision in line with instrumental error (*i.e.*, coefficient of variance of ~5 % for both C and N). Soil survey data for these regions indicates a lack of carbonates and soil pH values of 4.0 to 7.5 (Soil Survey Staff, 2014). We therefore equated total C concentrations to organic C. C/N ratios were calculated as the mass ratio between C and N concentrations.

For organic layers, soil masses were determined as the oven-dry weight divided by the sampling area. If all three subplots were sampled, the sampling areas were 731 cm² × 3 subplots for a total of 2193 cm² in the soil core method, and 2500 cm² in the soil pit method. C and N stocks (kg m⁻²) were calculated by multiplying the soil mass (kg m⁻²) by the C and N concentrations (g kg⁻¹).

For mineral soil layers, the soil bulk density (BD) was defined as the density of soil subtracting the weight and volume of rocks and roots. It was calculated by the oven-dry weight of 2-mm sieved soil divided by the volume of the soil. In the soil core method, the volume of the soil was taken as the volume of the core minus the volume of rocks collected through sieving (> 2 mm). In the soil pit method, the volume of the soil was taken as the volume measured by perlite minus the volume proportion of rocks measured in the sample during sieving. Because soil mass (kg m⁻²) can be measured directly using the quantitative pit method, the determination of soil BD is not strictly necessary. However, as noted below, we sought to compare how multiple variables such as BD contributed to the variability in both methods, and thus needed the values. By definition, the coarse fragment (CF) soil fraction was the volume percentage of rock and roots > 2 mm in diameter. It was equal to one minus the volume percentage of soil in the soil core or pit. In the soil pit method, the actual depths measured in the field were used to calculate the total volume. Because coarse roots accounted for very little volume in the soil, CF mainly consisted of the soil rock content. Using the BD, depth, CF and C and N concentration data for each mineral soil layer, the soil C stock was calculated using the following equation:

$$C \text{ stock} = BD \times Depth \times (1-CF) \times C \%$$
 (Equation 1)

N stocks were calculated using the same equation with N concentration.

As the major objective of the study was to compare estimates between the core and pit methods in the 0-20 cm depth increments, BD, CF, and %C for the two depth increments (0-10 cm and 10-20 cm) in the soil core method were combined using actual depth as their weighting. Soil mass and C and N stocks (0-20 cm, in units of g m^{-2}) were calculated as the sum of the two depth increments.

3.2.5. Data analysis

We performed three statistical tests on the experimental data. First, soil pit C stock (in Mg C ha⁻¹) and C/N ratio data for each layer (Oi, Oe+Oa, 0-20 cm, 20-40 cm, and total) were tested for differences among the three research sites (NS, DEWA, FC) using one-way ANOVA, followed by posthoc comparisons between sites when the main effect was found to be statistically significant using the nonparametric "Wilcoxon Each Pair" test in JMP Pro v12 (SAS Inc. Cary, NC). Second, to test for differences between the two sampling methods, BD, CF, soil mass, C and N concentration, C and N stock, and C/N ratio data for the calculated 0-20 cm layer from the three soil cores in each of the plots were averaged, and mean values were compared with the single pit values per plot. As the data was not normally distributed, the nonparametric Wilcoxon Signed-Rank Test was used to test the difference of the paired values of the two methods. Thirdly, Type II regression analysis was used to test for correlations among these soil properties measured using the two sampling methods.

To evaluate the spatial variability in assessment of soil C stock, an error propagation approach based on the linear Taylor series expansion (Goidts et al., 2009) was used to separate and quantify the contribution of variance from each input variable. In equation (1), soil C stock was calculated as the product of BD, depth, soil volume (1-CF) and C concentration (%C). Each of these variables has its own associated measurement error, as well as covariance since the variables are not necessarily independent from each other. Soil depth was fixed in this study so it will not be included as a source of error. The total variance of C stocks in the 0-20 cm mineral soil for each sampling method and research site can then be apportioned into the following terms including variances of single factors and covariances between factors:

$$Var(C \ stock) = (C \ stock)^2 \cdot \left[\frac{(\sigma_{BD})^2}{(BD)^2} + \frac{(\sigma_{C\%})^2}{(C\%)^2} + \frac{(\sigma_{(1-CF)})^2}{(1-CF)^2} + 2\frac{\sigma_{BD} \cdot C\%}{BD \cdot C\%} + 2\frac{\sigma_{BD} \cdot (1-CF)}{BD \cdot (1-CF)} + 2\frac{\sigma_{C\%} \cdot (1-CF)}{C\% \cdot (1-CF)} \right]$$
(Equation 2)

where σ_{BD} , $\sigma_{C\%}$ and $\sigma_{(1-CF)}$ are standard deviations of BD, %C and (1-CF). $\sigma_{BD-C\%}$, $\sigma_{BD\cdot(1-CF)}$ and $\sigma_{C\%\cdot(1-CF)}$ are their covariances, some of which could have negative values. The symbols in the denominators represent the means of the variables. Standard deviations and covariances were directly calculated from the measured data sets for each method, and for each site as well as all sites combined. To calculate the relative contribution of each variable, each term in the bracket was divided by the the sum of absolute values of each term in the brackets in equation (2) and expressed as a percentage. For instance, the relative contribution of BD is $\frac{(\sigma_{BD})^2}{(BD)^2}$ divided by $\left[\frac{(\sigma_{BD})^2}{(BD)^2} + \frac{(\sigma_{C\%})^2}{(C\%)^2} + \frac{1}{2} \frac{\sigma_{BD-C\%}}{BD-C\%}\right] + \left|2 \frac{\sigma_{BD-(1-CF)}}{BD-(1-CF)}\right| + \left|2 \frac{\sigma_{C\%}(1-CF)}{C\%\cdot(1-CF)}\right|\right]$. Positive values in the numerator result in positive relative contributions, while negative values in the numerator (e.g., covariance) result in negative relative contributions.

3.3. Results

3.3.1. Soil C and N content in different horizons

In the FIA standard soil core method, the mean C stock in the organic layer was 12.8 Mg C ha⁻¹ and the N stock was 0.52 Mg N ha⁻¹, and 40.8 Mg C ha⁻¹ and 2.28 Mg N ha⁻¹ in the 0-20 cm mineral layer (Table 3.3). In the quantitative soil pit method, the mean C stock in the organic layer across all plots was 14.6 Mg C ha⁻¹ and the mean N stock was 1.38 Mg N ha⁻¹. The C and N stocks in the 0-20 cm mineral layer were 44.7 Mg C ha⁻¹ and 2.59 Mg N ha⁻¹, and 17.3 Mg C ha⁻¹ and 1.26 Mg N ha⁻¹ in the 20-40 cm mineral layer (Table 3.3). Thus, the mean total (0-40 cm) C

and N stocks as measured by soil pits were 76.6 Mg C ha⁻¹ and 4.45 Mg N ha⁻¹. Mean C/N decreased from 31.1 in the surface Oi horizon to 14.0 in the deeper mineral horizon.

Among the three research sites, the NS site had the largest total C stock (99.8 Mg C ha⁻¹, p < 0.01) and N stocks (6.04 Mg N ha⁻¹, p < 0.01) based on the soil pit method (Table 3.3). The C stock in FC was the smallest, mainly because of a thinner Oe+Oa horizon. C/N in the organic layer was relatively constant among the three research sites. In DEWA, the C/N in the surface mineral soil was much greater than in the deeper mineral soil. However, in the NS site, the two mineral soil layers had very similar C/N.

3.3.2. Soil properties measured by the two sampling methods

Comparisons of the two sampling methods were focused on the surface mineral soil layer (0-20 cm) because the deeper (20-40 cm) layer was not sampled using the core method, and because CF is not a relevant issue in the organic layer. The results show that in the quantitative soil pit method the mean soil BD was 0.93 kg L⁻¹ in all the DRB plots combined. The mean BD measured from the FIA standard soil core method was 0.57 kg L⁻¹, a value approximately 40% smaller than the mean BD measured using the soil pit method (Table 3.4, Fig 3.3a). However, the volume percentage of CF measured by the soil core method was also significantly less than the CF measured by the soil pit method (Wilcoxon test, p < 0.01). Therefore the soil mass, which was calculated based on BD and CF, was still significantly greater in the soil pit method (p = 0.002). The difference in soil mass between the two methods was smaller than the difference in BD (Fig 3.3a and 3c). In some plots, C and N concentrations were very large in the soil core method, but not in the soil pit method (*i.e.*, cluster of data points above the 1:1 line in Fig 3.3d). The resulting soil C stock (0-20 cm) was estimated to be 40.8 ± 4 Mg C ha⁻¹ in the core methods was detected in C and N stocks (C stocks: p = 0.12, N stocks: p = 0.14), and the correlations between C and N

stocks measured by the two methods were not significant (C stock: r = 0.22, p = 0.096; N stocks: r = 0.39, p = 0.15). The C/N measured by the two methods were highly correlated (r = 0.72, p < 0.01) and the mean C/N in the soil core method was slightly greater than in the soil pit method (p = 0.047). Smaller BD but greater C and N concentrations and smaller CF content in the soil core method appear to have offset each other in this case, resulting in no significant differences in C and N stocks between sampling methods.

3.3.3. Contributions to variation of soil carbon stock

The sources of variance in soil C stock propagated from different variables were plotted for each research site and sampling method (Fig 3.4). In the soil core method, the main source of variance in C stock was the soil %C, representing 43% of the total C stock variance. The contribution of %C was smaller in the soil pit method, where the contribution of %C was 36% in all plots combined, though in the FC site, BD and %C contributed equally (both 21%). CF accounted for only 3% of the variance in the soil core method and 12% of the variance in the soil pit method.

Part of the variance in %C, BD and CF was counterbalanced by covariance among these variables. The covariance between %C and BD contributed a greater proportion of the total variance of soil C stock in the soil core method (26%) compared to the soil pit method (20%). The covariance between %C and (1-CF) decreased the C stock variability by 12% in soil core method, and 15% in soil pit method. The covariance between BD and (1-CF) was positive in the soil core method, but negative in the soil pit method, except in the NS site. These largely negative covariance contributions demonstrate that the individual parameters are not independent, and may result in reducing potential discrepancies in soil C and N stocks between sampling methods.

3.4. Discussion

3.4.1. Sampling method comparison: soil pit versus soil core

The organic layer C and N stocks were similar between the two sampling methods in all three research sites. This may be attributable to the fact that sampling areas in the two methods were comparable: 2193 cm² (3 samples \times 731 cm² per samples) using a bicycle tire in the soil core method, versus 2500 cm² in the soil pit method. Comparable sampling areas are not the case in the mineral soil layers where the soil core method sampled 58.9 cm² (3 cores \times 19.6 cm² per core) versus 2500 cm² in the pit method.

The standard FIA soil core method samples only the surface 0-20 cm of the mineral soil. Conversely, the pit method more easily samples deeper surface layers. In this study, the deeper mineral layer (20-40 cm) accounted for 23 ± 10 % of the measured C stock and 28 ± 9 % of the measured N stock. The contribution of the deeper soil horizon varied among the three research sites ($29 \pm 8\%$ in NS, 19 ± 9 % in DEWA, and $23 \pm 12\%$ in FC). The FIA soil core method was therefore unable to capture large and variable C and N pools in the soil sampling process (Harrison et al., 2011; Jandl et al., 2014). In the soil pit method, C stocks in the deeper mineral layer were not correlated with the surface mineral soil in each site. This indicated the difficulty of predicting deeper soil C stocks on the basis of surface soil measurement. Therefore the ability of using FIA soil core data in regional soil C stock estimation is limited due to the inability to sample the deep soil horizon.

In the soil core method, the problems identified in Table 3.1 could combine together and lead to a large uncertainty of the soil C and N stock measurement. However, in previous studies only one or two of the possible problems of the core method were identified to explain the metrological divergence. For instance, Page-Dumroese et al. (1999) and Levine et al. (2012) separately

reported significantly lower rock fragment content in small diameter cores, which they attributed to the obstruction problem in rocky forest soils from Montana and California, Nevada, New York and New Hampshire. Soil compaction varying with soil texture was considered to be responsible for underestimation of BD and CF in a very gravelly sandy loam soil, but not in a loamy sand soil in Washington state (Harrison et al., 2003). In 18 forest plots in southern New England, the core method produced lower BD and CF compared with the pit method, such that C and N stocks in the two methods were nearly identical (Kulmatiski et al., 2003), but only the problem of location selection was considered to explain the difference between the methods.

In the current study, significantly smaller BD and CF, and greater %C were measured using the soil core method compared to the soil pit method (Table 3.4, Fig 3.3). This is consistent with the effect of soil compaction problems beneath the soil core. Assuming the BD measured by the soil pit method was accurate and constant within each plot, it can be used to calculate how much soil should be in the core. In all the completed cores with no obstruction problem, the result shows that ~32% of the soil was missed in the core method, comparing with the soil mass estimated by BD measured by soil pit method. Compaction could therefore be the most important problem of using the composite coring technique in the DRB forest soil. Obstruction and location selection also make some contribution to the difference between these sampling methods. In our case, only 71% of the soil cores reached the depth of 20 cm without being obstructed by rock.

In our study, %C, BD and CF and their covariances had errors in different directions (see below), and as a result, the soil C stock, which is the product of these variables, showed no significant differences between the soil core and soil pit methods. Although the Wilcoxon Signed-Rank Test indicated that the two methods generated the same C stocks (Table 3.4), results from the two methods were not well correlated due to high scatter (Fig 3.3e), negating the possibility of creating a robust regression curve to correct the values of one method using the other because of

the large error associated with the weak correlation. This outcome could be viewed as largely coincidental and not necessarily expected in all cases, but previous studies have observed relationships among the contributing variables, and thus an assessment of variability in soil C and N stocks requires a thorough examination of the sources of uncertainty, including potential covariance.

3.4.2. Source of uncertainty in soil carbon stocks in the two sampling method

The variation of soil C stocks in each research site and in all DRB plots combined was a combination of soil spatial variation, and of biases and uncertainty associated with the sampling methods. If both methods were assumed equally accurate, the variance of C stocks would represent only the spatial variation in each variable in equation (2) because spatial variation would not be method-dependent, and Fig 3.4a and 3.4b would have the same pattern. The observed patterns did indeed differ, and therefore methodological errors in each method are responsible for some of the variance in C stocks.

In the soil core method, variance in C stocks was mainly driven by the variance of %C (Fig 3.4b), which was consistent with previously reported results from multiple sites in Europe (Schrumpf et al., 2011), two grassland sites in Germany (Don et al., 2007), and five cropland sites in Australia (Holmes et al., 2011). The relative contribution of %C to total variance in our research sites was smaller than in the cited studies, which may be caused by the complexity of the temperate forest in the DRB and the larger distances among our sampling plots. The importance of %C in determining the variance of C stocks has been shown to decreases with increasing spatial scale (Goidts et al., 2009).

The relative contribution of %C to the variance of C stocks was smaller in the soil pit method than in the soil core method, while the contribution of BD and CF were larger. DRB soils had a

mean CF of 40%, larger than the stony soils assessed by Hoffman et al. (2014) where CF introduced the largest spatial variance in a mountainous boreal forest. CF therefore likely plays an important role in controlling the soil C stocks in the DRB. Unlike the pit method, the soil core method failed to properly detect the large spatial variation of CF representing conditions in the DRB study sites. CF tended to be underestimated in the soil core method because of the obstruction and location selection problems mentioned above.

The assessment of soil C stock variance can be improved by incorporating the covariance between input variables (Panda et al., 2008), as these variables are not independent. The covariance between BD and %C counterbalanced a portion of the C stock variance. Several studies have previously demonstrated a strong negative relationship between BD and %C (e.g., Federer et al., 1993; Périé and Ouimet, 2008; etc.), which result from a combination of the "lightening" of the heavier mineral soil by lighter organic matter and from increased aggregation and porosity because of the binding ability of organic matter. In addition, the covariance between BD and %C was greater in the soil core method than in the soil pit method. This was due, in part, to the compaction problem in the soil core method, which led to underestimating BD and overestimating %C at the same time, reflected in the negative covariance between BD and %C. The covariance between %C and soil volume (1-CF) was also found to be negative and counterbalanced a portion of C stock variance. A negative relationship between (1-CF) and %C is commonly observed (e.g., Johnson et al., 2012) and occurs because incoming organic matter is exposed to decreasing amounts of reactive soil mineral surfaces (i.e., silt and clay) as CF increases and thus becomes more concentrated. The covariance between BD and 1-CF was small and positive in the soil core method, reflecting greater CF associated with smaller BD. BD is typically greater in rocky soils (Mehler et al., 2014), but the obstruction problem is likely more severe in soils with greater rock content (Holmes et al., 2011), thus inducing a negative covariance between BD and CF in the core method, but not in the soil pit method.

Previous studies of the source of uncertainties in soil C stock were based on the soil core sampling method alone (Hoffmann et al., 2014). Our deconstruction of the sources of variance in both methods demonstrates that the importance of %C and its covariance with BD in determining the spatial variance of C stocks might have been overemphasized because of the limitations of the soil core method. By comparing the source of soil C stock variation in two sampling methods, we found that the soil pit method better estimated the spatial variance of BD, %C and CF and their covariance, and therefore the variance of soil C stock in the rocky soils of the DRB forest. The soil core method did not adequately estimate the magnitude of variance and direction of the covariance in these variables due to the physical limitations in the sampling method.

3.4.3. Soil C and N stocks in three sites of the DRB forest

Previous studies (e.g., Harrison et al., 2003; Vandeboncoeur et al., 2013; and references cited within) have concluded that the quantitative soil pit method has fewer sources of systematic errors in measuring soil C and N stocks relative to the soil core method, and as such should be the reference or standard method against which others are compared. Our results are consistent with this conclusion, which is especially important for the stony soils in the DRB. The pit method also provides a more complete C and N stock estimates by including a deeper mineral soil horizon compared with the FIA sampling method. Therefore, the following discussion is based on the soil pit sampling method only.

Soil C and N stocks within the DRB were greatest in NS site in the north and smallest in the FC site in the south, consistent with the climate gradient shown in Table 3.2. Warmer and drier climate tends to favor organic matter decomposition process more than the C input from productivity, resulting in less accumulation of soil organic matter in the southern area (Guo et al., 2006; Fissore et al., 2008). Other factors such as soil texture, topography, land use history and
forest type might also play an important role in determining the soil C and N stocks (Garten and Ashwood, 2002).

The soil C and N stocks measured in our three research sites were much smaller than the forested riparian zones in the DRB (100.3 Mg C ha⁻¹ and 5.6 Mg N ha⁻¹ in the 0-30 cm mineral soil) (Bedison et al., 2013). On the other hand, the upland forest plots in the Catskills region had smaller C and N stocks (19.0 Mg C ha⁻¹ and 1.96 Mg N ha⁻¹ in the 0-20 cm mineral soil) (Johnson, 2013) than our NS plots. Drainage condition can change soil C and N stocks dramatically, where soil organic matter stocks were up to a factor of ten smaller in the upland than in the riparian zones in small watersheds in NS (Ashby et al., 1998). Although our plots were randomly located in each research site, they were representative of the complex landscape, and our results adequately represent a regional mean of high C in the valleys and low C on the slopes.

The soil C and N stocks measured in our NS plots were comparable with other studies in the northern hardwood forest (Huntington et al., 1988; Finzi et al., 1998; Bedison and Johnson, 2009; Johnson et al., 2009), but the DEWA and FC sites had much smaller C and N stocks. The overall average soil C and N stocks in all our plots were therefore smaller than most studies in the northern hardwood forest. This large scale pattern was consistent with the C and N stocks within the DRB, which further emphasizes the climate control on soil C and N. The DRB lies in the transition area between northern hardwood, which is dominated by maple-beech-birch species group, and the mixed deciduous forest, which is dominated by oak-hickory (Table 3.2). Forest species composition and any temporal change in composition may be other factors affecting the accumulation of C and N in the soil (Laganiere et al., 2013).

3.4.4. Implication for regional estimates of soil C and N stocks

While other methods have previously been used (e.g., rotary core), the composite core is the most extensively used method and the quantitative pit method is the most labor-intensive approach used to estimate soil C and N stocks. The selection between the two methods depends on the aim of the study and the tradeoffs between accuracy and efficiency. Other studies have suggested that less effort was required using the soil core method to detect the same magnitude of change over time in soil C and N stocks (Kulmatiski et al., 2003; Gruneberg et al., 2010). However, to estimate the soil C and N stocks at the regional scale (such as the DRB in this study), the accuracy of the sampling method is of crucial importance to capture the heterogeneity of the forest soil.

Soil survey data, such as the FIA soil data, are normally used as a data source to assess C and N stocks at the regional scale, to map the spatial distribution of soil properties and to improve soil C and N simulation models (Meersmans et al., 2008; Ungar et al., 2010). However, the accuracy of soil data collected by the core method used in FIA and their ability to capture the spatial variation of soil C and N stocks are questionable compared with the quantitative soil pit method. The various errors associated with the various problems of the sampling method, some of which may cancel each other out while others might be additive depending on the situation, might be accumulated in spatial extrapolation and introduce larger uncertainty to the regional estimates of soil C and N stocks.

Table 3.1 Main problems associated with the soil core sampling method and their effect on soil properties. ("–", no effect; " \uparrow ", overestimate; " \downarrow ", underestimate; "?", uncertain)

Problem		BD	%C	CF	C Stock
Compaction	inside core	_	_	_	_
	beneath core	↓	Ť	\downarrow	?
Obstruction by rock	missing soil under rock	_	Ţ	↑	?
	compression by rock	Ļ	_	\downarrow	?
Plot selection		_	_	\downarrow	\downarrow

Table 3.2 Environmental conditions in the three research sites in the Delaware River Basin. All data were extracted from a GIS data base

 and mean values for each site are shown. Annual temperature and precipitation are 30-year means from 1981-2010 (Thornton et al., 2014).

 Wet deposition is inorganic nitrogen deposition from 1983-2007 (Grimm, 2008).

	Elevation (m)	Mean annual temperature (°C)	Mean annual precipitation (mm)	Wet deposition (kg N ha ⁻¹)	Dominant soil order	Dominant forest type
Neversink (NS)	773	5.7	1503	6.4	Inceptisols	Maple/beech/birch
Delaware Water Gap (DEWA)	360	8.5	1219	6.3	Inceptisols	Oak/hickory
French Creek (FC)	166	11.2	1172	6.6	Ultisols	Oak/hickory

Table 3.3 Soil C and N stocks and C/N sampled using soil core and soil pit methods in the three research sites in the Delaware River Basin. Sample size (n) represents number of plots sampled in each study site. In soil core method, organic layer was defined as a sum of Oi and Oe+Oa layers, and the C and N stocks measured in the two mineral layers (0-10 cm, and 10-20 cm) were summed together. Significant level of ANOVA testing for the effect of sites on C and C/N of each layer in the pit method are labeled as "*", p<0.1; "**", p<0.05. Significant differences (p< 0.05) among each pair of sites labeled by letter(s) next to the mean of each site.

	Method		Soil cores			Soil pits		
Site	Soil La	yer	N stock (Mg N ha ⁻¹)	C stock (Mg C ha ⁻¹)	C/N	N stock (Mg N ha ⁻¹)	C stock (Mg C ha ⁻¹)	C/N
6	Organic laver	Oi	0.53	12.8	26.5	0.86	2.61*	31.1
=26		Oe+Oa	0.55	12.0	20.5	0.52	12.0	23.0
L n	Minoral soil	0-20cm	2.28	40.8	18.9	2.59	44.7^{*}	18.4^{**}
AL J	willer at som	20-40cm				1.26	17.3**	14.0
7	Tota	1	2.80	53.6	20.2	4.45	76.6 ^{**}	18.0 *
	Organic laver	Oi	0.61	13.6	24.3	0.09	2.5^{ab}	30.6
=14	Organic layer	Oe+Oa				0.60	12.7	21.4
n=	Mineral soil	0-20cm	2.89	48.3	17.1	3.50	55.5 ^a	16.0 ^a
NS		20-40cm				1.85	29.1 ^a	15.9
	Tota	1	3.50	61.9	Ck C/N N stock (Mg N ha ⁻¹) C stock (Mg C ha ⁻¹) 8 26.5 0.86 2.61^* 8 26.5 0.86 2.61^* 8 18.9 2.59 44.7^* 1.26 17.3^{**} 6 20.2 4.45 76.6^{**} 6 20.2 4.45 76.6^{**} 0.09 2.5^{ab} 6 24.3 0.09 2.5^{ab} 0.60 12.7 3 17.1 3.50 55.5^a 1.85 29.1^a 9 18.1 6.04 99.8^a 0.55 13.4 3 20.6 2.21 41.8^b 1.01 13.6^b 3 22.1 3.85 71.2^b 0.32 6.9 3 7 26.4 0.11 3.3^b 6.9 3 16.7 2.56 41.1^b 1.32 15.9^b 0 13.0 67.2^b 67.2^b	16.9 ^a		
31	Organia lavor	Oi	0.46	12.0	27.5	0.08	2.4 ^a	31.1
n –	Organic layer	Oe+Oa	0.40	12.0	27.5	Soil pits N stock (Mg N ha ⁻¹) C stock (Mg C ha ⁻¹) 0.86 2.61* 0.52 12.0 2.59 44.7* 1.26 17.3** 4.45 76.6** 0.09 2.5 ^{ab} 0.60 12.7 3.50 55.5 ^a 1.85 29.1 ^a 6.04 99.8 ^a 0.08 2.4 ^a 0.55 13.4 2.21 41.8 ^b 1.01 13.6 ^b 3.85 71.2 ^b 0.11 3.3 ^b 0.32 6.9 2.56 41.1 ^b 1.32 15.9 ^b	23.6	
NA N	Minoral coil	0-20cm	1.95	38.3	20.6	2.21	41.8 ^b	20.1 ^b
EW	Mineral soli	20-40cm				1.01	13.6 ^b	13.9
D	Tota	1	2.41	50.3	22.1	3.85	71.2 ^b	19.3 ^b
	Organia lavor	Oi	0.55	127	26.4	0.11	3.3 ^b	31.6
:14	Organic layer	Oe+Oa	0.55	15.7		0.32	6.9	23.2
11	Minoral coil	0-20cm	2.43	39.3	16.7	2.56	41.1 ^b	16.9 ^a
FC		20-40cm				1.32	15.9 ^b	12.6
	Tota	1	2.99	53.0	18.0	4.30	67.2 ^b	16.1 ^a

Table 3.4 Comparison of soil core and soil pit sampling methods: means, standard deviations and results of Wilcoxon Signed-rank Test for all soil properties in surface mineral soil layers (0-20 cm depth). Paired data from 57 plots using both soil sampling methods were used for the Wilcoxon Signed-rank Test.

	Soil Core		Soil P	Pits	Wilcox	Wilcoxon Signed-Rank Test		
	Mean	SD	Mean	SD	W	z-ratio	р	
Bulk density (kg L ⁻¹)	0.57	0.25	0.93	0.29	1549	6.15	<0.01**	
Coarse fragment (%)	21.4	17.5	39.5	18.0	1167	4.63	< 0.01**	
Soil mass (kg m ⁻²)	92.2	46.4	112	45.7	793	3.15	< 0.01**	
C concentration (g kg ⁻¹)	74.2	60.3	45.2	22.9	-969	-3.85	< 0.01**	
N concentration (g kg ⁻¹)	3.83	2.93	2.55	1.4	-937	-3.72	< 0.01**	
C stock (Mg C ha ⁻¹)	40.8	17.1	44.7	16.1	393	1.56	0.12	
N stock (Mg N ha ⁻¹)	2.3	1.02	2.6	1.16	369	1.46	0.14	
C/N	19.1	4.0	18.3	4.5	-501	-1.99	0.046*	

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Figure 3.1 The hydrological boundary of the Delaware River Basin and the main stream and tributaries of the Delaware River. The three research areas are shown in different shading color. The red dots represent the locations of soil sampling plots labeled by their plot ID.



Figure 3.2 Plot design of forest measurement and soil sampling (revised from U.S. Department of Agriculture, 2002). The red star represents the location of the quantitative soil pit. The FIA protocol uses 'visit 1', 'visit 2' (represent by blue dots) as the sampling locations in each of the sublot. The survey in 2012-2013 was the second measurement of these plots, so the 'visit 2' location of each subplot was selected for the soil core.



Figure 3.3 Correlations of (a) bulk density, (b) coarse fragment, (c) soil mass, (d) C concentration, (e) C stock, and (f) C/N mass ratio, measured by the soil core and soil pit methods. The 1:1 line and Type II (major axis) linear regression are shown, where slopes statistically different from 1 are denoted by \dagger . The three sites are represented by different symbols (Neversink, \blacksquare ; Delaware Water Gap, \bullet ; French Creek, \blacktriangledown). Vertical error bars represent the standard error among the cores (n = 3), versus only one pit (*i.e.*, no horizontal error bars).



Figure 3.4 Relative contributions of variance and covariance of bulk density (BD), carbon concentration (%C), and soil volume (1-CF) to the variance of soil carbon stocks for the Neversink (NS), Delaware Water Gap (DEWA) and French Creek (FC) research sites, using the soil pit method (a) and the soil core method (b).

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CHAPTER 4 Modeling forest carbon and nitrogen cycles based on long term carbon stock field measurement in the Delaware River Basin

Chapter to be submitted for publication as:

Bing Xu, Yude Pan, Alain F. Plante, Kevin McCullough, and Rich Birdsey Modeling forest carbon and nitrogen cycles based on long term carbon stock field measurement in the Delaware River Basin. *Ecosphere*.

Abstract:

Process-based models are a powerful approach to test our understanding of biogeochemical processes, to extrapolate ground survey data from limited plots to the landscape scale, and to simulate the effects of climate change, nitrogen deposition, elevated atmospheric CO₂, increasing natural disturbances and land use change on ecological processes. However, in most studies, the models are calibrated using ground measurements from only a few sites, though they may be extrapolated to much larger areas. Estimation accuracy can be improved if the models are parameterized using long-term carbon (C) stock data from multiple sites representative of the simulated region. In this study, forest biomass C stocks measured in 61 forested plots located in three research sites in the Delaware River Basin (DRB) were used to modify the PnET-CN model in three manners: (1) field measured mortality rates in each forest type were used to parameterize

the wood turnover rate; (2) a numerical approach method was used to calibrate the relationship between foliage N and maximum photosynthesis rate; (3) stand age was incorporated into the model as a input variable, which determines the year of the last disturbance. Model validation results showed that, these model modifications improved model performance in capturing the spatial variation of forest C dynamics in the DRB forests. The spatial distribution of forest C pools and fluxes in three sites were mapped using the modified model. The modified model was also used in experimental scenarios that demonstrated that 39% of forest C sequestered over the past decade can be attributed to the combined effects of elevated CO_2 and N deposition. This study present an effective method for using long-term biometric measurements of forest biomass C stocks to improve a process model at the regional scale. Further research should target on the parameters which are sensitive to the spatial variation of forest C dynamics.

4.1. Introduction

Process-based ecosystem models are a powerful approach to test our understanding of biogeochemical processes, to extrapolate ground survey data from limited plots to the landscape scale, and to simulate the effects of climate change, N deposition, elevated atmospheric CO₂, increasing natural disturbances and land use change on ecological processes (Campbell et al., 2009; Felzer, 2012). They can also be used for projecting future ecosystem changes and dynamics based on our current knowledge, which is important for future resource management and actions for climate change adaptation (Chen et al., 2000; Mickler et al., 2002; Hudiburg et al., 2013).

In most modeling studies of forest C cycles, models are parameterized or calibrated using ground measurements from eddy covariance techniques (Carvalhais et al., 2010; Liu et al., 2015). The eddy covariance data sets consist of fine time resolution (hourly observation), but very low spatial resolution (few sites covering a large area). Therefore, the parameters associated with rapid processes such as photosynthesis are well constrained, but the parameters associated with long-term processes such as the turnover rates of biomass and soil C are poorly constrained (Braswell et al., 2005; Richardson et al., 2010). Moreover, the ability of the model to capture the heterogeneity of the forest C and N cycles over complex landscapes is difficult to evaluate using eddy covariance data because the footprint area of each flux tower is normally smaller than 100 km², and a limited number of flux towers are used to represent large areas of forests (Owen et al., 2007).

Over the past decade, a large number of long-term biometric measurements have accumulated data for forest biomass and soil C stocks (Xu et al., 2014). Forest Inventory Analysis (FIA) and remote sensing techniques have provided useful information on the spatial distribution on forest

C stock changes (Mickler et al., 2002; Woodbury et al., 2007). The performance of a processbased simulation model could be improved if it can be parameterized using better data sources using long-term biometric C stock data from multiple sites representative of the simulated region (Carvalhais et al., 2010; Molina-Herrera et al., 2015).

The PnET model (Aber and Federer, 1992) design was based on general principles of ecophysiology and biogeochemistry, and has been validated in various vegetation types (Goodale et al., 2002; Chen et al., 2004; Thorn et al., 2015). Different from most of extant process-based ecosystem models and Dynamic Global Vegetation Models (DGVMs), PnET-CN uses finer vegetation classes down to forest type groups rather than coarse plant functional types (Pan et al., 2013), which gives the model some edge, making it more suitable for forest ecosystem studies at a regional scale. Regional versions of the models based on geographic information systems have been developed to extrapolate the simulation from the site to the regional level (Ollinger et al. 1998, Pan et al. 2009). Applications of PnET models have provided important insights into the interactive effects of climate change, N deposition, increasing atmospheric CO_2 and ozone, and natural and anthropogenic disturbance on forest CN cycles (Ollinger et al. 1997, Pan et al. 2004).

The PnET model was originally developed for site simulations in the northern hardwood forests in Northeast U.S.(Aber and Federer, 1992). The Delaware River Basin (DRB), situated in the southern edge of the northern hardwood forest, features diverse forest types and land-use histories, representing a transition zone from typical north hardwood forests to Mid-Atlantic oak dominated deciduous forests. To use the PnET model effectively in the DRB forest, the model needs to be localized. A multi-agency program known as the Collaborative Environmental Monitoring and Research Initiative has collected long-term biometric measurement of forest C stocks in the DRB (Murdoch et al., 2008). A recent reanalysis (Xu et al., 2016) has provided a good opportunity to examine the model performance outside its original range in landscapes along a gradient (Fig 4.1), and explore approaches for parameterizing and improving the model using long-term field measurements from multiple sites.

In this study, forest biomass C stocks and their change over the recent decade, measured in 61 plots from three sites, were used to modify the PnET-CN model for the DRB forests. The major objectives of this study were (1) exploring multiple parameterization approaches for improving the model performances using long-term biometric measurements; (2) validating the model specifically improved for our study sites and comparing the model performances between the original and newly modified model; and (3) applying the modified model to simulate the spatial distribution of C fluxes and pools in the DRB forests, and (4) investigating the effects of environmental changes such as N deposition and elevated atmospheric CO₂ concentration on the spatial distributions and temporal changes of forest C cycle. The newly adapted model for DRB is expected to provide more accurate modeling results which are useful to our understanding of regional forest C dynamics and forest management.

4.2 Methods

4.2.1 Model description

The PnET-CN model (Aber and Federer 1992, Aber et al. 1997) is a process-based ecosystem model that uses information on vegetation, climate and soil to simulate the carbon, nitrogen and water dynamics of forest ecosystems in the northeastern United States. After years of development, three versions of the model have formed a nested sequence in the PnET family of models. They are PnET-Day, a daily time step model of forest canopy C balance (Aber et al.,

1996); PnET-II, a monthly time step model which incorporates soil respiration and full water balance (Aber et al., 1995); and PnET-CN, which includes closed carbon and nitrogen cycles and the effects of elevated atmospheric CO_2 and ozone (Aber et al., 1997). The PnET-CN model contains a set of modules to simulate major processes of forest carbon, nitrogen and water cycles. The input data include climate variables (temperature, precipitation, radiation, etc.), site parameters (latitude, elevation, soil water holding capacity (WHC), etc.), and vegetation parameters (forest type, canopy trait, C allocation, N content, etc.). The major outputs include above- and belowground biomass, soil C content, net primary productivity (NPP), net ecosystem productivity (NEP), N leaching and water yield.

The PnET-CN model was built on the principal that the maximum photosynthetic rate (Amax) is a function of foliar N concentration. This represents the interaction between C and N cycles, and links leaf traits with physical processes at the ecosystem level. Photosynthesis is further constrained by temperature and water availability, and its production is then allocated to living C pools (foliage, wood, and fine root) and respiration. Living biomass is transferred to dead C pools (e.g., woody debris and soil organic matter) through leaf, root, and wood turnover, and disturbance. The model also incorporates the effect of atmospheric N deposition, which will increase the available soil N pool, and elevated CO_2 concentration, which will increase the potential photosynthesis rate and decrease stomatal water conductance.

The PnET-CN model was originally developed at the plot scale and included parameters for four vegetation types (northern hardwood, spruce - fir, red oak - red maple, and pine forests). A spatially explicit (i.e., GIS) version of the model has been developed to automatically run the model in multiple plots. A new forest type (mixed forests) has been created by numerically combining the results of red oak - red maple and pine forest types to represent the mixed forest in

the mid-Atlantic region (Pan et al., 2004c; Pan et al., 2009). More details about the model structure and processes have been described elsewhere (Aber and Driscoll, 1997; Ollinger et al., 2002; Pan et al., 2004a).

4.2.2 Study sites and field measurement

The Delaware River is one of the major rivers in the mid-Atlantic region of United States, draining an area of about 33,000 km² in Pennsylvania, New Jersey, New York, Delaware, and Maryland. The Delaware River Basin (DRB) is characterized by a humid continental climate, with mean annual temperature of 9-12 °C and mean annual precipitation of 1143 mm (Kauffman et al., 2008). The DRB is located in the eco-zone of deciduous forests and is ecologically diverse, comprised of five physiographic provinces and multiple species assemblages that represent most of the major eastern U.S. forest types (Murdoch et al., 2008). Three areas in the DRB were selected as intensive monitoring and research sites for process-level studies in forested landscapes: the Neversink River Basin (NS) in the northern, mostly forested region of the Appalachian Plateau province; the Delaware Water Gap Area (DEWA) with three small watersheds (Adams Creek, Dingman's Falls and Little Bushkill) lying in the central Appalachian Plateau Province; and the French Creek Watershed (FC) in the midbasin Piedmont province (Table 4.1; Fig 4.1).

During 2001-2003, 61 intensive inventory plots were randomly located in the three sites. In each plot, all trees with diameter at breast height (DBH) greater than 5 inches (12.7 cm) were measured and marked, and the specific locations of the plots were mapped. In 2012-2013, these plots were revisited and biomass parameters were re-measured using the same protocols.

The plot design and sampling method follow the FIA protocols in the two measurements (Fig 4.2; U.S. Department of Agriculture, 2014). Each plot has four round subplots, in total covering an area of 672.44 m². Live and dead trees were measured in each subplot. DBH, total and bole height, tree species, and status change of each tree were recorded. Each subplot also has one microplot (area: 13.49 m²). Live and dead sapling (1 inch < DBH < 5 inch), seedling (DBH < 1 inch) were measured in the microplots. Within each plot, two trees close to the subplots that represent the dominant species and growing condition of the forest stand were selected as site trees. The age of the site trees was measured by counting rings in a tree core. The stand ages of plots were determined as the mean age of the two site trees.

Field measurement data from the two measurements were compiled into a single database for biomass C and biomass C change calculations (Cole et al., 2013). Species-specific allometric equations (Jenkins et al., 2004) were used to calculate above-ground tree biomass and the general equations were used to calculate coarse roots biomass. To compare with model output, each plot was assigned to a vegetation type. The total biomass of living trees, saplings and seedlings were summed to calculate the observed live biomass in the two measurements. A conversion factor of 0.5 was used to convert biomass to C stock.

4.2.3 Model input data

To run the GIS version of the PnET-CN model, the required model input data include elevation, vegetation type and soil water holding capacity (WHC) for each pixel, and monthly maximum and minimum air temperature, precipitation, photosynthetically active radiation (PAR), wet NH_4 and NO_3 deposition, atmospheric CO_2 and ozone concentrations for the entire simulation period. The climatic data used include monthly averages and historical data. The historical data of

precipitation, maximum and minimum air temperature for each pixel and each month were extracted from the database developed by Prism Climate Group (http://www.prism.oregonstate.edu/). The monthly historical data was available from 1895 to 2010. PAR data was derived from Daymet data (http://daymet.ornl.gov/) which was available from 1980 to 2010. The climate data from 1980 to 2010 were used to calculate the 30 year monthly averages, and the monthly average data were used in the years when the historical data was not available. The ozone data layer was developed by Teague Prichard and US Forest Service based on the SUM60 data from May to September monitored by EPA (personal communication). The historical data is available from 1993 to 2010. The monthly average ozone deposition was calculated based on all the historical data, and then used when historical data was not available. Ammonium (NH_4) and nitrate (NO_3) wet deposition data from December 1982 to November 2007 was created by Jeff Grimm (NRS06, NGCRP) based on NADP/NTN-standardized precipitation grids (Grimm and Lynch, 2004). We assumed that N deposition before 1931 was approximately 20% of the average deposition from 1993 to 2007, and the deposition rate increased linearly from 1931 to 1993, and after 2007. This linear relationship was interpolated for each pixel.

In this study, the vegetation type data were reclassified from USFS forest type groups (http://data.fs.usda.gov/geodata/rastergateway/forest_type/conus_forest_type_group_metadata.ph p). Based on the map of forest type groups, the NS area is dominated by northern hardwood forest; FC area is dominated by red oak-red maple forest; DEWA is located at a transition area of these two vegetation types, with a small proportion of the area covered by mixed forest. Soil WHC data was derived from STATSGO soil database (http://websoilsurvey.nrcs.usda.gov/) (Soil Survey Staff, 1995). To run the GIS version model with a standardized pixel size, all the data layers of different spatial resolution were adjusted to 1×1 km.

4.2.4 Model modification

To apply the PnET-CN model to the DRB forests, we modified the model in three ways:

Parameterization

The wood turnover rate (Woodtrn) is a parameter representing the rate of biomass loss from mortality. It controls what proportion of live wood biomass can be transferred to dead biomass on a yearly basis, and was set to 0.025 for all the vegetation types in the original model. The wood turnover rate can also be calculated using the field measured biomass data for each vegetation type. Biomass mortality rate between the two measurements was calculated as the biomass of trees that were live in the first measurement and died before the second measurement, divided by the total live tree biomass. The relationship between the mortality rate between measurements and the yearly wood turnover rate can be expressed as:

$$(1 - Woodtrn)^n = 1 - M \tag{1}$$

where n is the number of years between the two measurements, and M is the measured biomass mortality rate between the two measurements. The average number of years and biomass mortality rate were calculated for each vegetation type separately, and wood turnover rates were determined algebraically using Equation (1).

Calibration

PnET model results are sensitive to the parameters AmaxA and AmaxB, which are the intercept and slope of the linear relationship between maximum photosynthesis rate and foliage N concentration. However, this relationship can vary with forest conditions such as species composition and nutrient availability (Schulze et al., 1994; Reich et al., 1995). In this study, a numerical approximation process was used to find the best AmaxA and AmaxB for each plot. The model ran multiple times with self-adjusted AmaxA and AmaxB on a step of 0.02. The best sets of parameters were reported when the biomass in the last year (2010) matched with the observed value in the second measurement (within a range of \pm 200 g m⁻²). The optimized parameters of each vegetation type were calculated as the mean of the best fitted AmaxA and AmaxB of all the plots. In total, 11 northern hardwood forest type plots and 38 red oak- red maple forest type plots passed the approximation process, and their best AmaxA and AmaxB values were used to calculate the optimized parameters. We had few plots representing the spruce-fir forest type and the pine forest type in the DRB sites, and as a result the AmaxA and AmaxB values for these two vegetation types were not calibrated.

Modification of input data

In the original settings of the PnET-CN model, it is assumed that no disturbance occurred over the past 210 years, and as a result, modeled forest ages are over 200 years. However, forest plots in the DRB have very diverse land use history and the age of the forest could be different among plots. The PnET-CN model has a harvesting section in the scenario module, in which a constant proportion of biomass can be removed at the harvest year. To improve the model, we created a new input variable as stand ages, and use it to calculate the year of the last disturbance. At that year 80% of the biomass was disturbed and 50% of the disturbed biomass was removed from the biomass C pool (Ollinger et al., 2008). Therefore the modified PnET-CN model was able to reflect forest recovery processes after disturbances, and better represent the different successional stages of each plot. Field measured stand age for each plot was used for the model calibration and validation process. To run the GIS version of the model in the three sites, the stand age for each pixel was derived from a national stand age map based on FIA plot measurement (Pan et al., 2011b).

4.2.5 Validation

While live biomass data from the second measurement (2012-2014) were used for calibration of the modified PnET model, the live biomass data from the first field measurement (2001-2003) were used to validate the model. Since the time interval between the two measurements was not ten years in most plots, the biomass data from the first measurement were standardized by using the actual number of years between the two measurements to calculate yearly biomass growth rates. As a result, the live biomass ten years before the second measurement was estimated for each plot, and compared with the model-simulated biomass in 2000.

The normalized root mean square error (NRMSE) was used to evaluate the overall model performance. The NRMSE assesses the difference between predicted (P) and observed (O) variables and can be expressed as:

NRMSE =
$$(0_{\text{max}} - 0_{\text{min}})^{-1} \sqrt{\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n}} \cdot 100\%$$
 (2)

where O_{max} and O_{min} are the maximum and minimum observed values, respectively; i is the ith observation plot; and n is the total number of plots. A NRMSE value close to 0 indicates perfect agreement, while a value of 100% indicates poor agreement. The NRMSE for the original PnET model and the modified model were compared to test if the modification processes improved model performance.

4.2.6 Simulations

The original and modified models were used to simulate the C cycles in forested areas in each of the three sites. The input data at 1×1 km resolution were used to run the model for 210 years (from 1801 to 2010). From the model output, four variables were mapped and compared among the original and modified PnET models. Vegetation biomass (VegM) and soil mass (SoilM) represent the major C pools, and NPP and NEP represent the major C fluxes in the forest C cycle. The NPP and NEP of the last ten years (2001-2010) were averaged and reported.

To evaluate the effect of N deposition and elevated CO₂, and their combined effects, four model scenarios were created using the modified PnET model (Table 4.2). The full scenario represented the combined effects of elevated CO_2 and N deposition by ramping atmospheric CO_2 concentrations according to the Mauna Loa record and using historic or ramping data for local N deposition. In the combined CO_2+N removal scenarios, the atmospheric CO_2 concentration was set to a fixed value (280 ppm) and the N input from N deposition was set to 0 g m⁻². Two additional scenarios were designed by removing only one of elevated CO_2 or N deposition at a time. NPP over the past 100 years in each of the scenarios was plotted for each site (e.g., NS, DEWA and FC) to illustrate the effects of elevated CO₂ and N deposition over time.

4.3. Results

4.3.1 Model performance

The wood turnover rate calculated using field measurement was 0.037 yr⁻¹ in northern hardwood forest, 0.0194 yr⁻¹ in red oak-red maple forest, and 0.012 yr⁻¹ in Pine forest (Table 4.3). For all forest types, the measured wood turnover rate was smaller than the value (0.025 yr⁻¹) used in the original PnET-CN model. The average best-fit AmaxA value was -48.4 µmol CO₂ m⁻² leaf sec⁻¹

and AmaxB was and 70.0 μ mol CO₂ m⁻² leaf sec⁻¹ in the northern hardwood forest, both close to the values used in the original model. In red oak-red maple forest, the average best-fit AmaxA value was -53.8 μ mol CO₂ m⁻² leaf sec⁻¹ and AmaxB was 64.1 μ mol CO₂ m⁻² leaf sec⁻¹, smaller than the original values (Table 4.3).

Compared with the observed live biomass in the two measurements, the original model overestimated the mean biomass in FC and DEWA (above the 1:1 line in Fig 4.2a), but underestimated the mean biomass in NS (below the 1:1 line in Fig 4.2a), for both 2000 and 2010. The model-predicted biomass in 2000 did not match well with the observed values in the validation plots (the blue dots apart from 1:1 line in Fig 4.2a). The original model was not able to simulate well spatial variations of biomass on the landscapes and resulted in a narrow range of predicted biomass values, with the SD of spatial variations about 70% smaller than the observed SD in each site (Table 4.4). The modified model improved the prediction of the mean biomass largely with the NMRSE reduced from -41% to 12%, and also increased the range of spatial variations although still smaller than the observed value. In particular, the modified model predicted accurately for the mean biomass in 2000, which was not affected by the calibration procedure, but matched very well with the observed values for model validation (the blue dots falling on the 1:1 line in Fig 4.2b). The model-predicted and observed biomass in 2010 was comparable in FC and DEWA. While in NS, the model underestimated biomass, mostly because some plots in this area that contain a small amount of conifer trees such as hemlocks (Tsuga *canadensis*) tend to have larger biomass. Because of their low amount, the parameters used in the conifer vegetation type which were originally derived from the data of red pine forests were not modified in this study.

The NMRSE was used to measure average errors in model predictions based on the errors in all individual plots. Although the modified model significantly improved the predictions of mean biomass, it is not necessary it could reduce prediction error for each plot. This is because most of spatial heterogenetic factors such as soils and microclimate causing variations in tree growths could not be picked up even by the modified model because the spatial input data used to run the model were derived from the coarse resolution datasets. The modified model slightly reduced NMRSE for FC and DEWA, but slightly increased for NS (Table 4.4). The overall NMRSE of predictions for all plots in three sites by the modified model remains about the same, only with a reduction of 0.6%.

4.3.2 C pools and fluxes in DRB

After the modification process, model-predicted vegetation biomass was greater in some pixels but smaller in other pixels in each of the three sites (Fig 4.3a, 4.3b, 4.4a, 4.4b, 4.5a and 4.5b), with obviously increased spatial variations due to the parameter modifications in mortality rate, maximum photosynthesis rate and stand age. The mean vegetation biomass in FC and DEWA was smaller in the modified model compared to the original model, but slightly greater in NS (Table 4.5). The soil C was smaller in the modified model in all the sites. The model modification process also resulted in a smaller NPP in all pixels, although NEP could either greater or smaller in different pixels comparing to the original model (Fig 4.3g, 4.3h, 4.4g, 4.4h, 4.5g and 4.5h). On average, the NEP predicted by the modified model was greater than the NEP predicted by the original model in all three sites.

Compared to the original model, the modified model performed better in capturing the spatial complexity of the C pools and fluxes in each site (Fig 4.3, 4.4 and 4.5). The SD of spatial

variations among all the pixels was larger in the modified model, especially for NEP, which is the net C sink of the ecosystem (Table 4.5).

The results of the modified model showed that, among the three sites, NS had the largest biomass C pool (153 Mg C ha⁻¹), while DEWA had the largest soil C pool (37 Mg C ha⁻¹) (Table 4.5). NPP was largest in the NS (3.1 Mg C ha⁻¹ yr⁻¹). The NEP in NS was 0.5 Mg C ha⁻¹ yr⁻¹, which is larger than in the other two sites. As predicted by the modified model, large C pools could be observed in the northern part of the FC (Fig 4.3b and 4.3d), northern-central part of the DEWA (Fig 4.4b and 4.4d), and in the northern part of the NS (Fig 4.5b and 4.5d). Large C sinks could be observed at southeast part of FC (Fig 4.3h), center part of DEWA (Fig 4.4h), and center and east part of NS (Fig 4.5h).

4.3.3 Effects of environmental changes

In the modified model scenarios, NPP values have dramatically changed over time (Fig 4.6). NPP decreased substantially in the year of major disturbances and increased gradually in the following years. Removing N deposition (N removed scenario) led to a decrease in NPP over last 100 years of modeling. Setting the atmospheric CO₂ concentration to a fixed value (CO₂ removed scenario) resulted in even smaller modeled NPP in DEWA and NS. Removing both N deposition and elevated CO₂ (CO₂+N removal scenario) led to the smallest NPP in all sites. In figure 6, the difference between the CO₂ removed curves to the CO₂+N removed curves represented the effect of N deposition. The difference between the N removed curves to the CO₂+N removed curves represented the effect of elevated CO₂. The combined effect of N deposition and elevated CO₂ was shown as the difference between the full scenario curves and the CO₂+N removed curves. The effect of N deposition appeared to be greater than the effect of elevated CO₂ during 1970-

1990 in FC, and during 1970-1980 in the DEWA and NS (Fig 6, blue curve lower than green curve). However, the effect of elevated CO_2 was greater than the effect of N deposition after 1990 in DEWA and NS (Fig 6, green curve lower than blue curve). The combined effect of N deposition and elevated CO_2 was stronger than sum of the two effects separately. The difference between the full scenario and other scenarios also increased continuously over time, especially in the last 30 years of the model simulations (Fig 4.6).

The forest biomass predicted by the modified model under the CO_2+N removed scenario was 17 to 20% smaller than the biomass predicted in the full scenario, indicating that elevated CO_2 and N deposition increased forest biomass C stocks in all three sites (Table 4.5). The removal of both elevated CO_2 and N deposition decreased NPP in the last ten years by 18 to 22% and decreased NEP by 29 to 48% compared to the full scenario.

4.4. Discussion

To improve the performance of a process-based model at the regional scale, model calibration or parameterization should target the parameters that the major output variables are sensitive to, and represent the spatial variation of forest C dynamics (Thorn et al., 2015). In this study, we modified the wood turnover rate, the maximum photosynthesis rate and the disturbance years in the PnET-CN model. The main objective of these modifications was not only to improve the accuracy of the model prediction compared to field observation, but also to increase the ability of the model to capture the spatial complexity of forest C cycling at the landscape scale.

Mortality is a key driver of the spatial distribution of forest biomass and also affects soil C pools and sink. A better estimation of mortality rate can strongly improve modelling of biomass and its spatial variations (Delbart et al., 2010). Comparisons among multiple process-based

models often resulted divergent predictions in C sink, which was rather caused by different formulations for turnover rates (Friend et al., 2013). In this study the wood turnover rates calculated from the observed mortality rate were directly used in the modified model. The smaller observed wood turnover rates in all the three vegetation types is very likely because the forests in the DRB are generally in their mid-ages, and subject to smaller mortality rates (Coomes and Allen, 2007). Our results showed that smaller wood turnover rates resulted in larger C accumulation in the live biomass C pool, but reduced the C stocks in soil. Increasing autotrophic respiration from larger biomass leads to a decreasing NPP. However, heterotrophic respiration is likely to be limited by the smaller C input to the soil C pool. As the balance between NPP and heterotrophic respiration, NEP did not have a consistent trend in its response to a smaller wood turnover rates. The effect of modified wood turnover can be detected in northern part of NS, where Amax did not change substantially and the forests are relatively older with more accumulative effect in biomass from a low mortality (Fig 4.5).

Lower optimized AmaxA and AmaxB values for the red oak-red maple forest type, but not for the northern hardwood forest type, indicated that the original model parameters (which were developed in the northern hardwood forests in the New England area) could be used in the northern hardwood forests in the DRB, but may substantially overestimate forest biomass and productivity in other forest types because to adapt their climate conditions northern hardwood trees usually muster higher photosynthetic rates with typically higher foliage N concentration in relatively shorter growing season (Pan et al., 2006). When the same growth rates were used in the southern type oak-dominated deciduous forests, it would cause overestimates in NPP and biomass. Because AmaxA and AmaxB are the parameters of a linear function of foliage N concentration, it could be also due to relatively lower foliage N concentration in southern

deciduous trees as they may have lower labile N storage to initialize new leaves as the northern types with a necessary higher stock for winter hardening. Therefore, a smaller photosynthesis rate under the same foliage N level better simulates the observed forest biomass changes. In the red oak- red maple forest, the smaller AmaxA and AmaxB values used in the modified model led to smaller living biomass and soil C pools, and smaller NPP and NEP. The difference between original and modified model results in the northern part of FC reflected the effect of smaller Amax.

As mentioned above, the relationship between maximum photosynthesis rate and foliage N concentration is one of the key principles in the PnET model that links the C and N cycles and determines forest productivity on a monthly basis (Aber and Federer, 1992). However, few studies have measured this relationship in different forest types, and the spatial variations of the parameters are not well constrained. In fact, the lack of information on these parameters is a major source of uncertainty in using the PnET model in different vegetation types (Thorn et al., 2015). The numerical approaching process we used in model calibration provided an effective method to quantify this relationship and to test the variability of these parameters over different forest compositions, ages and environmental conditions.

Successional stage is a critical factor determining forest C dynamics. Many process models have been used to simulate the effect of forest harvesting and forest regrowth processes (Chiang et al., 2008; Potter et al., 2008; Wang et al., 2014a). In the PnET model, after a destructive disturbance and losses of C stocks, forest biomass and soil C pools will increase during recovery of forest, and NPP and NEP will increase in earlier development years or decades and then decrease after canopy is closed and with increasing respirations (Wang et al., 2014b). As a result, younger forests are expected to have smaller C pools and larger productivity compared to older forests approaching an equilibrium stage. This trend has been tested and verified by long-term field measurements and chronosequence studies (Law et al., 2003; Pregitzer and Euskirchen, 2004). Our results show that incorporating stand age data (Pan et al., 2011b) into the PnET model can dramatically change the simulated distribution of C pool and fluxes in the DRB forests (Fig 4.3, 4.4 and 4.5). For example, the center area of DEWA experienced a clear cut in the late 1960s, but the impact of this disturbance cannot be detected by the original model. But in the results of the modified PnET model, this area had relatively smaller biomass and soil C stocks, and became a hotspot of C sequestration with the largest NEP.

The modification process generally improved the performance of the PnET-CN model in the DRB forests. The observed and predicted mean biomass in each site matched very well in the model validation. Our modifications also largely increase the SD of all the model outputs (error bar in Fig 4.2, SD in Table 4.4 and 4.5), which means the model can better capture the spatial variation in these small regions. However, the model still predicted SD much smaller than the observed SD, partly because the calibrated photosynthetic rates had to average for certain forest types although the calibrations were processed for individual plots. As the result, we lost some spatial variations again, which is similar for using averaged mortality rates, an inevitable limit in application of a spatially-explicit process model. The highly scattered data points in Fig 4.2b highlight the difficulty of simulating the heterogeneity of forest C dynamics.

Although the modified model significantly improved the mean values of predicted biomass, when examining prediction errors based on simulations in the sampling plots using NRMSE index, it was not always reducing much of the errors, and could even increase error such as in NS. As mentioned earlier, the spatial heterogenic nature reflected in biomass values observed in plots was the result of complex biotic and abiotic factors. Even after the modification of a few key parameters, the model still cannot realize the most effect of diverse factors when the model has to use the averaged parameters and driving climate/soil data derived from coarse resolution datasets. In NS, the low elevation areas are commonly patched by hemlock trees, which tend to have larger growth rates, and hence can accumulate more biomass C stock at young stand ages. However, the model-predicted biomass in the low elevation areas was limited by the observed young stand age. Although the modified model could be improved by better observed stand age here, in this case, it could cause even greater NRMSE from the observed high biomass in hemlock forests. This situation reflects uncertainty in modifying a handful of parameters in a model, which could worsen the effect of other unmodified parameters, if not always. This case also indicated the potential for further model improvement by calibrating additional forest types and better accounting for the effect of species composition (Porte and Bartelink, 2002).

In field measurements, the observed biomass C change is a combined effect of natural forest growth and growth enhancement due to environmental changes such as elevated CO_2 and N deposition (Caspersen 2000, Fang 2014). Process-based models provide a useful tool to quantify the contribution of these effects separately, which cannot be identified by observations (Ollinger et al., 2008; Pan et al., 2009). Results of model scenarios (Fig 4.6) demonstrated that elevated CO_2 and N deposition had a large impact on NPP in recent decades. The effect of N deposition was larger than elevated CO_2 before 1980. However, after 1980, the effect of elevated CO_2 was greater in two of the three sites. The effect of N deposition estimated in this study was smaller than the effect estimated by Pan et al. (2009). Possible reasons include the decreasing N deposition in the historical input data after 2000, and the continuously increasing atmospheric CO_2 concentration. The combined effect of the two factors was greater than the sum of the two separated effects. This result demonstrated a positive interaction between N deposition and

elevated CO_2 , and is consistent with the results from controlled experiments of CO_2 enrichment and N addition and with other model simulations (Nowak et al., 2003; Savage et al., 2013). By removing these factors from the modified PnET-CN model, we found that 19% of the current biomass C stock and 39% of the NEP was attributable to the effects of elevated CO_2 and N deposition, suggesting that environmental change has substantial changed the C dynamics in the DRB forest in recent decades. Because of the effects, forests remain vigorous with high productivity, otherwise they would be likely set off earlier with lower productivity (Fig 4.6).

The model simulation effectively extended our understanding of the forest C cycle spatially and temporally (from 61 plots to the area of three sites, from two measurements to 210 years time serial, from live biomass to multiple output variables). The modified model could be used to extrapolate the result of the field survey to the whole DRB forests. Moreover, the PnET-CN model integrated multiple controlling factors on forest C cycle. The experimental scenario simulation method described in this study can also be used to test the effect of other variable such as climate change and ozone and their interactions (Sun et al., 2000).

In this study, forest biomass C stock measurements were used as the key data in the model calibration and validation processes. Compared to C fluxes variables, which are frequently used in model calibrations based on eddy covariance data, forest biomass better represents the spatial variation of forest C cycling and comprehends more information about the long-term processes of forest dynamics since it is an accumulative variable (Miehle et al., 2006). Moreover, field measurement of biomass is feasible in all the forested area, whereas eddy covariance towers are much less numerous and cannot be installed in highly complex topographies. The FIA database has collected periodic measurements of forest biomass all over the country, and the structure of the database is similar to our observational data inform the three sites in the DRB forest (Potter et

al., 2008). The methods of model modification used in this study could be therefore easily used at a larger scale to improve model predictions of forest C and N cycling.

To further improve the PnET model, which is particularly important and necessary for a regional or local application, input data with higher resolution should be used and more long-term field measurement data is needed (Campbell et al., 2009). Based on our experiences through this study, the following changes could be examined. Foliage N concentration is an important and sensitive variable that determines maximum photosynthetic rates in the PnET model (Pan et al. 2004c). If field measurements of foliage N concentrations are available, they should be used to parameterize the model for each forest type. Soil water holding capacity is one of the most important input data and is the only soil property that is required in the PnET model. The Web Soil Survey, a new soil database with high spatial resolution has recently been published (Soil Survey Staff, 2014), and could be used to improve the model. Large areas of the northeastern U.S. are covered by mixed forests, and species composition can change over time. More accurate model predictions will result if the model applied to this region uses input data that retains fine resolution forest type variability, and with more forest types being parameterized in the model (Jenkins et al., 1999). Incorporating forest species dynamics in the model may also greatly improve the ability of the PnET model to capture spatial variability.

Table 4.1 Environmental conditions in the three research sites in the Delaware River Basin. All data were extracted from the model input GIS database and mean values for each site are shown. Annual temperature and precipitation are 30-year means from 1981-2010 (Thornton et al., 2014). Wet deposition is inorganic N deposition from 1983-2007 (Grimm, 2008).

	Number of plots	Elevation (m)	Mean annual temperature (°C)	Mean annual precipitation (mm)	Wet deposition (kg N ha ⁻¹)	Average stand age (years)	
French Creek	15	166	11.16	1171	6.55	85	
(FC)							
Delaware Water Gap	32	360	8 53	1219	6 33	107	
(DEWA)	52	500	0.55	1217	0.55	107	
Neversink	1/	773	5 75	1503	6 44	91	
(NS)	14	115	5.15	1505	0.44	91	

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Table 4.2 Settings and input data used in PnET model simulation scenarios to test the effects of N deposition and elevated atmospheric CO_2 concentrations.

Scenario	Wet N deposition	Atmospheric CO ₂ concentration		
Full commin	Historical data from 1982-2007,	Ramped based on Mauna Loa		
Full scenario	ramped data in other years	measurements (280-390 ppmv)		
CO memorie d	Historical data from 1982-2007,	Fixed, 280 ppmv		
CO_2 removed	ramped data in other years			
Namound	No N input $(0.0 \times m^{-2})$	Ramped based on Mauna Loa		
IN Ternoved	No N input (0.0 g in)	measurement (280-390 ppmv)		
CO ₂ +N removed	No N input (0.0 g m^{-2})	Fixed, 280 ppmv		

Table 4.3 Parameter values used in the original and modified PnET model for the three major vegetation types present in the three study

 sites of the Delaware River Basin.

Parameter	Description	Northern hardwood		Red oak - red maple		Pine	
T ut utiliteter		Original	Modified	Original	Modified	Original	Modified
Woodtrn	Wood turnover	0.025	0.0137	0.025	0.0194	0.025	0.012
	Intercept of relationship						
AmaxA	between maxim photosynthesis	-46	-48.4	-46	-53.8	5.3	5.3
	rate and foliage n concentration						
AmaxB	Slop of relationship between						
	maxim photosynthesis rate and	71.9	70.0	71.9	64.1	21.5	21.5
	foliage n concentration						
Number of	Number of harvest	0	1	0	1	0	1
harvest		Ŭ	1	Ŭ	1	Ŭ	1
Harvest year	Year of disturbance	1926	2010-age	1926	2010-age	1926	2010-age
Intense	Disturbance intensity	0	0.8	0	0.8	0	0.8
Remfrac	Biomass removal fraction	0	0.5	0	0.5	0	0.5
Table 4.4 Comparison of observed and model-predicted live forest biomass (Mg C ha⁻¹) in each site in 2000 and 2010. The mean, standard deviation (SD) of spatial variations, and normalized root mean square error (NRMSE) for estimating predicted errors by the original model and modified PnET-CN models are shown. The observed forest biomass data for 2000 were not used in the modification process, therefore could be considered as validation of model results.

	Site	Live E	Biomass (Mg	NRMSE (%)		
Year		Observed	Original model	Modified model	Original model	Modified model
	FC	130.8 ± 49	156.8 ± 14	130.5 ± 23	34.5%	26.0%
2000	DEWA	113.1 ± 63	122.4 ± 17	116.2 ± 15	13.0%	12.6%
2000	NS	134.5 ± 37	126.2 ± 11	132.5 ± 29	21.0%	28.5%
	Total	122.4 ± 55	131.7 ± 20	123.5 ± 22	12.8%	12.2%
	FC	146.3 ± 52	167.0 ± 15	144.6 ± 21	30.6%	26.6%
2010	DEWA	127.5 ± 64	131.7 ± 17	123.9 ± 12	15.5%	14.5%
2010	NS	154.6 ± 44	134.2 ± 11	143.6 ± 31	24.8%	29.3%
	Total	138.3 ± 58	141.0 ± 21	133.5 ± 22	15.1%	14.5%

Table 4.5 Model-predicted forest biomass (VegM, Mg C ha⁻¹), soil C (SoilM, Mg C ha⁻¹), net primary productivity (NPP, Mg C ha⁻¹ yr⁻¹) and net ecosystem productivity (NEP, Mg C ha⁻¹ yr⁻¹) in the three study sites of the Delaware River Basin, using the original model, modified model under full scenario, and modified model under CO₂+N removed scenario. The effects of elevated CO₂ and N deposition were calculated as the percentage change of each variable from the full scenario to the CO₂+N removed scenario using the modified model. Negative effect values indicate that elevated CO₂ and N deposition resulted in increased values of the variables in the full scenario.

C :40	V	Original		Modified		CO ₂ +N removed		
Sile	variables	Mean	SD	Mean	SD	Mean	SD	Effect
FC	VegM	139	17	128	14	102	12	-20%
	SoilM	41	5	32	3	27	3	-13%
	NPP	4.1	0.5	3.5	0.4	2.8	0.4	-22%
	NEP	0.42	0.12	0.45	0.12	0.23	0.11	-48%
DEWA	VegM	146	14	133	14	106	13	-20%
	SoilM	48	5	37	4	32	4	-11%
	NPP	4.2	0.4	3.8	0.4	3.0	0.3	-20%
	NEP	0.39	0.04	0.55	0.19	0.33	0.15	-39%
NS	VegM	163	9	153	16	127	15	-17%
	SoilM	60	5	35	4	33	4	-8%
	NPP	5.2	0.4	3.8	0.4	3.1	0.3	-18%
	NEP	0.53	0.08	0.71	0.19	0.50	0.16	-29%



Figure 4.1 The hydrological boundary of the Delaware River Basin and the main stream and tributaries of the Delaware River. The three research areas of the current study are shown in different shading color. The red dots represent the locations of forest biomass plots.



Figure 4.2 Comparison between model-predicted and observed live forest biomass for the original (a) and modified (b) PnET model.

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Figure 4.3 Spatial distributions of forest biomass, soil C, net primary productivity (NPP) and net ecosystem productivity (NEP) as simulated by the original and modified PnET models in the French Creek study site in the Delaware River Basin.



Figure 4.4 (Continued)



Figure 4.4 Spatial distributions of forest biomass, soil C, net primary productivity (NPP) and net ecosystem productivity (NEP) as simulated by the original and modified PnET models in the Delaware Water Gap study site in the Delaware River Basin.



Figure 4.5 Spatial distributions of forest biomass, soil C, net primary productivity (NPP) and net ecosystem productivity (NEP) as simulated by the original and modified PnET model in the Neversink study site of the Delaware River Basin.



Figure 4.6 Changes in average net primary productivity (NPP) from 1910 to 2010 in French Creek (a), Delaware Water Gap (b) and Neversink (c) under different model scenarios. Difference between curves showed the effect N deposition and elevated atmospheric CO₂.

CHAPTER 5: Conclusions

This dissertation quantified the biomass and soil C stocks in three sites of the DRB forest using field measurements and an ecosystem process model. Each chapter focused on the most important variables of carbon pools and fluxes and source of uncertainties in estimating biomass and soil C stocks and forest productivity, in an attempt to improve our understanding of key factors controlling the forest C dynamics and minimize uncertainties in our estimations. In this final chapter, the biomass and soil C stocks measured at the plot level were summed and compared with a regional scale model simulation. Here, I provide suggestions for potential directions and improvement in the future research to address some other uncertainties in measuring and estimating forest carbon variables which were not specifically addressed in this study.

5.1. The total C stock in the DRB forest

The field-measured total forest C stocks (i.e., aboveground biomass, coarse roots and soil C to 40 cm depth) in 2012-2014 were 239 ± 21 Mg C ha⁻¹ in FC, 213 ± 12 Mg C ha⁻¹ in DEWA, and 285 \pm 15 Mg C ha⁻¹ in NS (Table 5.1). The NS area was the largest in total C stocks, indicating that disturbance in the northern hardwood forests in the northern part of the DRB could have a large impact on the forest C pool in the DRB forests. The total C stock in the oak-hickory forests was smaller, but the biomass C stock increased substantially in the recent decade. So it is likely that the forests in the southern part of the DRB could be a larger C sink in the future compared to the northern hardwood forest.

The mean field measured total C stock of the three sites combined was 246 ± 15 Mg C ha⁻¹. Biomass accounted for 68% of the total C stock and soil accounted for 32%. The model-predicted mean biomass C stock in each site (Table 4.4, simulated by the modified model) was consistent with average live biomass estimated by field measurements in the sampling plots (Table 5.1). The total C stocks in our sites in the DRB were also comparable with other sites in the northeastern U.S. (Curtis et al., 2002). The contribution of soil C to the total forest stock was relatively small compared to the national average (Dixon et al., 1994), probably because soils in our sites, and in the DRB in general, are comparatively shallow and rocky.

This research represents an estimation of full C storage in the forest ecosystem. The only two C components that were not included are fine root biomass and soil layers deeper than 40 cm. The study provided a precise and well-documented set of methods to quantify forest C stocks. This is the first step in evaluating forest function and C dynamics at the regional scale. Long-term periodic measurements using the same methods are needed to provide more useful information for understanding changes and trends in the DRB forest ecosystems, which are critical to regional forest management and evaluating ecosystem services

In this dissertation, we found that most of the uncertainties in forest C stock estimates at regional scales are associated with the spatial heterogeneity of the forest over the landscape. Chapter 2 illustrated that most of the spatial variation in the biomass C stocks is driven by tree demographic changes (e.g. tree mortality, recruitment and growth rate etc.) in different species. Chapter 3 demonstrated that using the quantitative soil pit sampling method can reduce the uncertainties of estimating spatial variations of soil C content, compared to the FIA standard soil core method. Chapter 4 reported an approach to using field measurements to improve the performance of a process model in simulating the spatial distribution of forest C stocks and fluxes. A long-term

forest monitoring system using well validated methods with multiple sites and measurement times can greatly improve our understanding of the key processes controlling the spatial variation of forest, and increase the accuracy of our estimates of forest C stocks in regions similar to the DRB.

5.2. Future studies

The database and methods reported in this dissertation can be used to address many other questions about regional forest C cycling. Some of the most practical directions of futures studies built upon this work are:

1) Modeling the whole DRB forest

In Chapter 4, the PnET-CN model was parameterized and validated using the field measurements in the three study sites within the DRB. Because the three sites are representative of the environmental gradients and forest type transitions in the DRB area, this modified model could be used to simulate forest C cycles in the whole DRB to extrapolate the field measurements from a few sites to the larger area. Additional data from FIA plot measurements and Web Soil Survey could be used to validate the model results at a larger spatial scale. If spatialized information about projected future climate change is available, the modified model could also be used to predict the future change of the DRB forest under different environmental change scenarios.

2) Interactions between biomass and soil

The biomass and soil C stocks were analyzed separately in Chapter 2 and Chapter 3. Combining these two databases would provide a good opportunity to test the interactions between biomass and soil components. For example, preliminary analyses show that increasing soil N availability

may accelerate the spreading of red maple in the DRB forest; tree mortality rates are highly correlated with the change of soil drainage conditions. Is soil nitrogen content a limiting factor of forest growth at current succession stage in the DRB? How does soil C content response to the long-term forest composition change induced by the species-specific disturbance? These questions should be addressed in detail in future studies.

3) Carbon and water cycle

Since the hydrological boundaries of small watersheds were used as the boundaries of the research sites, our databases provide a good opportunity to examine how forest growth and land use change might affect the water balance and stream chemical properties in small watersheds. The forests in the DRB protect the drinking water source for more than 15 million people (Fischer et al., 2004). But if forest growth is enhanced by environmental change, it is likely that water consumption through evapotranspiration will also increase. The PnET-CN model is able to simulate the water yield of ecosystems, and the result could be compared with stream gage measurements. Therefore the water balance of each smaller watershed could be simulated using different environmental change scenarios to provide future predictions of reginal water resources. Moreover, the C and N losses through surface runoff and groundwater infiltration can also be simulated by the PnET-CN model. Lateral C transport can be estimated and verified by stream chemical data. The relationship between stream flow C and N content and forest biomass and soil C content and how this relationship are affected by land use strategy could be tested in the small watersheds. By combining field measurements with modeling results, a complete C budget of the watershed could be achieved.

Table 5.1 Biomass and soil C stocks, and the total C stock in each site and mean of the three sites. The biomass C stock was measurement during 2012-2014 and the soil C stock was measured in the quantitative soil pit method. Unit: Mg C ha⁻¹

	FC	DEWA	NS	Mean
Live tree	150.6	117.8	146.5	138.3
Dead tree	9.3	9.7	16.9	12.0
Sapling	1.8	3.1	7.5	4.1
Seedling	0.5	1.5	0.8	0.9
CWD	4.5	5.4	8.3	6.1
FWD	3.4	3.7	2.8	3.3
Stump	2.7	2.0	2.6	2.4
Live biomass	152.9	122.0	154.6	143.2
Dead biomass	19.2	20.2	30.4	23.3
Total biomass	172.1	142.2	185.1	166.5
Oi	3.2	2.4	2.5	2.7
Oe	6.9	13.4	12.7	11.0
M1 (0 - 20 cm)	41.1	41.8	55.5	46.1
M2 (20 - 40 cm)	15.9	13.6	29.1	19.5
Organic	10.2	15.7	15.3	13.7
Mineral soil	57.0	55.5	84.5	65.7
Total soil	67.2	71.2	99.8	79.4
Total	239.3	213.4	284.9	245.9

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