ABSTRACT

Title of Thesis:	*SOIL ORGANIC CARBON IN MID-ATLANTIC REGION FOREST SOILS: STOCKS AND VERTICAL DISTRIBUTION*
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Soil contains the largest terrestrial pool of organic carbon (Boschi et al., 2018) and temperate forest soils have been a major sink for atmospheric carbon; however, determining the size of the soil organic carbon stock can be problematic. Sampling practices vary for sampling depth, and determining the density of the soil. The aforementioned standard practices need to be revised if the size of SOC stocks are to be accurately quantified, to establish a global SOC baseline.

A soil monitoring of 414 forested sites within 11 national parks in the National Capital Region (Schmit, 2014) was conducted over 10 years. Samples were collected from the leaf litter and each soil horizon to 1 meter depth. Soil bulk density (D_b) was determined by the core method for the A horizons, and proxy D_b values were investigated for the subsoil. The vertical distribution of SOC concentration and stocks were evaluated with respect to soil order, physiographic region/landform, drainage class and parent material.

SOIL ORGANIC CARBON IN MID-ATLANTIC REGION FOREST SOILS: STOCKS AND VERTICAL DISTRIBUTION

by

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Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Masters of Science
2019

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Preface

The motivation for conducting this research stemmed from my experience during the summers of 2015 and 2016 as an undergraduate field research intern in Dr. Weil's lab working for the National Park Service Inventory & Monitoring Program. In 2017 I served as the graduate student trainer for undergraduate field interns in the same program. As a graduate research assistant, I helped organize, harmonize, and interpret the soil carbon data collected over the life of the 10 year monitoring program.

Passion for researching SOC evolved with society's increasing interest in tackling anthropogenic accelerated climate change and offsetting carbon emissions. Soil organic matter is one of the most important, but least understood of the C pools affecting climate change. Among the aspects of SOC that need clarification are field sampling methods, differences in laboratory SOC and SOM analysis methods, and assumptions used in calculating C stocks. For this thesis I reviewed field sampling methods, bulk density sample collection, laboratory C analysis methods, rooting depths for different forest types, the relative importance of deep soil carbon, carbon sequestration and general temperate forest ecology. My research addresses the distribution of SOC in temperate forests using park sites in the National Capital Region Network (NCRN) of the US National Park Service (NPS). One of the innovations I tested was the use of NRCS/SURGO representative bulk density values in calculating carbon stocks. I also drew conclusions about SOC stocks in the NCRN and the depth of soil that should be considered in evaluating the size of SOC stocks in temperate forests.

Dedication

I dedicate my dissertation to my parents, Jeanne and Daniel Colopietro for supporting me throughout my graduate career. Not only did they provide monetary and moral support, they also assisted me out in the field, navigating through the woods of Prince William Forest Park, Antietam National Battlefield, and Greenbelt National Park to collect core samples.

I also dedicate my dissertation to Dr. Weil and Timothy Gerber, both of whom have provided me with my base of knowledge in the field of soil science and have mentored me through my undergraduate and graduate studies.

Acknowledgements

I would like to thank my advisors for their guidance and support throughout my graduate studies. I would also like to thank all the undergraduate interns and graduate student trainers who carried out the monitoring work in the field between 2007 and 2017. Financial and logistical support was provided by the US National Park Service, Inventory and Monitoring Program, task agreement P17AC01254.

I would also like to express my gratitude to the Harford County Running Club whom awarded me a $1000 scholarship. The scholarship assisted me in paying tuition.

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List of Acronyms

AESL - Agricultural and Environmental Services Laboratories

ANOVA - Analysis of Variance

C - Carbon

D_b - Bulk Density

ESM - Equivalent Soil Masses

FAO - Food and Agricultural Organization

GLM - Generalized Linear Model

GPS - Global Positioning System

GSOCmap - Global Soil Organic Carbon Map

GSP - Global Soil Partnership

GRTS - Generalized Random-Tessellation Stratified Survey

HWSD - Harmonized World Soil Database

IPCC - Intergovernmental Panel on Climate Change

LOI - Loss on Ignition

LSD - Least Significant Difference

LSM - Least Square Mean

ME - Mean Error

NCRN - National Capital Region Network

NPP - Net Primary productivity

NPS – National Park Service

NRCS - Natural Resources Conservation Service

OC - Organic Carbon

OM - Organic Matter

PM - Parent Material

PTF - Pedotransfer Functions

RMSE - Root Mean Square Error

SC - Soil Carbon

SDE - Standard Deviation of the Error

SOC - Soil Organic Carbon

SOM - Soil Organic Matter

SPW - Soil, Plant, And Water Lab

SSURGO - Soil Survey Geographic Database

TOC - Total Organic Carbon

USFS - United States Forest Service

WSS – Web Soil Survey

Chapter 1: Introduction to Forest Soil Carbon and Methods for its Sampling

Abstract

Soil comprises the largest terrestrial pool of organic carbon (OC) and temperate forest soils could act as carbon (C) sinks to offset anthropogenic emissions. However, determining the size of, and changes in, soil organic carbon (SOC) stocks can be problematic. A common practice is to sample soil to a depth of 20 cm (0.2 m); however, if roots contribute the most to the SOC pool, then sampling schemes that sample to a depth significantly less than the average rooting depth may miss an important proportion of the SOC stock present. Temperate deciduous and coniferous trees have an average rooting depth of 3.3 m (Foxx et al., 1982). Therefore, sampling to a depth of only 0.2 m may exclude 94% of the soil profile volume where C may be actively sequestered by roots. Another practice commonly used in the survey of SOC stocks is fixed-depth sampling. Fixed-depth sampling has numerous benefits for the researcher; however, soil horizons are fundamental to studies of pedogenesis. Also, it is thought that horizon-based soil sampling may reduce vertical and horizontal variability (Boone et al., 1999). A complication in calculating SOC stocks is collecting bulk density (D_b) cores. Collecting D_b cores can be a challenge, especially for subsurface horizons. Therefore, pedotransfer functions (PTFs) and equivalent soil mass (ESM) sampling schemes have been proposed in place of collecting core samples and determining D_b. For researchers to accurately estimate and map the size of SOC stocks, current standard sampling depth and use of PTFs should be improved.

Introduction

Carbon (C) is continuously exchanged among the atmospheric, oceanic, terrestrial and the geologic pools. The largest pool of C is the oceans with 39,000 Pg C, while the atmosphere has 750 Pg C and terrestrial systems have 2200 Pg C (Batjes, 1996). The terrestrial reservoir is subdivided into plant biomass and soil components, with the majority of the C stored in the soil (Lal, 2004). Global estimates of C vary, with the earliest estimate of global SOC being extrapolated from nine soils in the United States of America to 710 Pg C (Scharlemann et al., 2014). Scharlemann et al. (2014) calculated the median global SOC stock in the upper 1 m of soil across 27 different studies to be 1461 Pg C, with a range of 504–3000 Pg C. The SOC stock estimates vary due to differing sampling methods, inadvertently including some inorganic soil C in analyses, and/or varying procedures to account for levels of stone content in soil samples. Some studies fail to state specifically which forms of C were included or if correction were made for coarse fragments (Scharlemann et al., 2014). Notable differences in recent global SOC stock estimates were attributed to the differences in values used for the D_b of organic soils (Scharlemann et al., 2014). Such variability in global SOC stock estimates highlight the need for caution during data processing and suggest that data collection and sampling protocols still need to be standardized.

Forests ecosystems are important components of terrestrial C stock which continuously exchange CO_2 with the atmosphere. While they are young and accumulating biomass, forests generally sequester more C than they release. Recent research suggests that old growth forests may continue to act as C sinks. Luyssaert (2008) reported that forests between 15 and 800 years of age exhibited net positive ecosystem productivity (the net C balance in the forest ecosystem, including soils) which means such mature forests may continue to accumulate C, contrary to long-standing views that they are C neutral (Luyssaert, 2008; Lichstein et al., 2009; McGarvey et al., 2015; Craggs, 2016). Carbon sequestration in trees increases continuously because the overall leaf area increases as they grow, enabling larger and older trees to absorb more C from the atmosphere. Older and larger deciduous trees produce more new leaves, thus sequestrating more C from the atmosphere (Craggs, 2016). Net primary productivity (NPP) is expressed as mass of C per unit area per unit time (ex: g m^{-2} yr^{-1}). It is equal to all the C that was fixed during photosynthesis minus the C lost through respiration. Carbon is found in several different pools within forest ecosystems; aboveground biomass, coarse woody debris, leaf litter, belowground biomass and the soil. The largest of these terrestrial C pools is the soil C, which is 1.5 to 2.5 times as great as the vegetation C pool (Wang et al., 2002). Globally, the upper 1 m of soil contains three times as much C as does the atmospheric component (Lal & Lorenz, 2015). Current C stocks in the world's forests are estimated to be 861±66 Pg with 383±30 Pg C in the upper 1 m of soil and 43±3 Pg in the leaf litter. However, Estimates of C in leaf litter and soil are less certain than estimates for above ground biomass as there is much more data on the latter (Pan et al., 2011).

In order to understand and possibly mitigate climate change resulting from increased C in the atmosphere, there is growing interest in managing soil as a long-term C storage sink. As of 2010, fossil fuels provided 78.2% of the world's energy (Global Status Report, 2013). Even as renewable energy sources increase, fossil fuel burning is projected to remain substantial. From indirect data and analysis of ice cores, the pre-

Industrial atmospheric CO_2 concentrations were between 260–270 ppm (Wigley, 1983). As of April 2018, the concentration of atmospheric CO_2 surpassed 410 ppm for the first time in recorded history and is the highest concentration recorded in the past 800,000 years (Kahn, 2017). Over the past 250 years atmospheric CO_2 has increased by 140-150 ppm which equates to 0.56-0.6 ppm $year^{-1}$. This value exceeds all known natural rates of CO_2 change over the past 3 million years. Studying ice cores from the Antarctic ice sheets, J.R. Petit (1999) concluded that a 140-150 ppm shift is approximately equivalent to a glacial or interglacial cycle, which is a period of 100,000 years.

Soil Organic Carbon

Carbon is present in the soil in both inorganic and organic forms. Soil OC is a component of soil organic matter (SOM) and is a universal indicator of soil quality (Dumanski, 2004). Soil organic matter influences soil aggregation, which in turn affects soil aeration, erosion, and water infiltration, thus indirectly influencing surface and groundwater quality (Weil and Magdoff, 2004). In addition to these effects, an increase in SOM can enhance soil water storage capacity (Hudson, 1994). Increasing SOM also improves nutrient cycling, stimulates soil biological activity, and increases soil biodiversity (Dumanski, 2004). These effects, in turn, influence decomposition rate, nutrient turnover and soil fertility (Dumanski, 2004).

Soil organic matter is the solid component of soil that consists of animal and plant tissue in various stages of decomposition (Weil and Brady, 2016). Soil organic matter exists as four distinct fractions which vary in size, turnover time and composition in the soil; dissolved organic matter (OM), particulate OM, a complex mixture of protected biomolecules, and living biomass (Weil and Brady, 2016). Living biomass, dissolved OM, and a portion of the particulate OM are known as the liable (rapid) faction of the OM. Char and the complex mixture of protected biomolecules make up most of the protected faction of OM known as humus (Weil and Brady, 2016). Soil organic matter is composed of approximately 50% C and has traditionally been fractionated and quantified, after alkaline extraction from soils, as humin, humic acid, and fulvic acid (Weil and Brady, 2016). However, recent studies with in situ analysis techniques suggest that most SOC actually consists of microbial and plant tissue components partially decomposed and protected from further oxidation by soil structure, clays, and other conditions (Kleber and Johnson, 2010).

Historically, maintaining or increasing soil C levels has been associated with above-ground plant residues (Rasmussen et al., 1980), such as leaf litter and coarse woody debris in forests. The emphasis has been on the transformation of fresh aboveground plant tissues and composts in soils rather than on belowground biomass, i.e., plant roots. Nevertheless, many studies suggest that the relative contribution of plant roots to SOC stocks is larger than that of plant shoots (Persson, 2012; Rasse, et al., 2005; Broadbent and Nakashima, 1974). Long-term residue management studies suggest that above ground material has less impact on SOM levels than below ground biomass. Root systems and root-derived materials have a higher residence time in soils than shoot-derived materials (Gaudinski, et al., 2000; Rasse, et al., 2005). The total contribution of roots to particulate organic matter occluded within soil aggregates ranges between 1.2 and 6.1 times that of shoots (Rasse et al., 2005). Rasse et al. (2005) concluded that roots contribute most of the OC stored in soils in different ecosystems. Rasse et al. (2005) used a mechanistic model (TRAP) to assess the total root and shoot

C litter production in temperate forests. During 66 years of Scots pine growth in Belgium, more root C was returned to soils through root growth and turnover than the combined contributions of leaf, branch, and stem litter (Rasse et al., 2001). Another conclusion suggested by Rasse et al. (2001) was that the proportional contribution of C from root systems increases with soil depth. The 3-year study utilized TRAP, which is an mechanistic model developed for predicting the partitioning of photosynthates between fine and coarse roots of trees. It then determines the fate of those photosynthates as they are allocated to maintenance respiration, growth respiration, growth, C loss due to soil stress factors and litter production.

Currently, no internationally accepted definition exists to distinguish woody debris from forest floor (O horizons) in terms of particle size or diameter. Woldendorp and Keenan (2005) suggested a diameter threshold of 1 cm. Bastrup-Birk et al. (2007), on the other hand, suggested including woody debris up to the minimum dimensions for inventories of coarse woody debris, i.e. minimum diameter of 10 cm.

The term forest floor refers to all organic material resting on but not mixed with the mineral soil surface (Pritchett, 1979). The forest floor includes a litter layer (L) a partly decomposed and fragmented layer (F) and a humic layer (H) in well-drained conditions. Under poorly drained conditions, Green et al. (1993) classified the organic horizons (Oa) as poorly decomposed (Of), partially decomposed (Om), and well decomposed (Oh). Table 1 lists the classification of the forest floor, proposed by Green et al. (1993) and presented in Soil Taxonomy (USDA-NRCS 2012). The USDA-NRCS Soil Taxonomy designates organic horizons (O) as containing more than 20% TOC by dry weight. Based on degree of decomposition, organic soil materials can be further subdivided into fibric (Oi), hemic (Oe) and sapric (Oa), listed from least decomposed to most decomposed. The USDA-NRCS soil classification uses L for limnic soil material. In my thesis, I will use the following designation to refer to leaf litter, LL.

Table 1.1 Classification of forest floor organic materials according to Green et al., 1993 and the USDA-NRCS Soil Taxonomy (USDA/NRCS, 2012).

Forest Floor Classification	
Horizon	**Horizon Description**
Well-Drained Conditions	
L	Leaf Litter
F	Fragmented and Partly Decomposed; Fibric
H	Humic
Poorly-Drained Conditions	
O	Organic material influenced by the water table Of - Poorly decomposed Om - Partially decomposed Oh - Well decomposed

USDA-NRCS Soil Classification	
Horizon	**Horizon Description**
O	Organic Horizons >20% TOC Oi - Slightly decomposed (Fibric) Oe - Moderately decomposed (Hemic) Oa - Highly decomposed (Sapric)

When soil C pools are quantified, soils are typically sampled to relatively shallow depths to reduce study costs. Shallow soil sampling in research includes studies that estimate C and nutrient pools as well as studies assessing the response of terrestrial ecosystems to management treatments. The majority of studies reported sampling to a depth of 0.2 m or less. This depth is also termed the tillage zone, reflecting back to historically focus on croplands for soil fertility and nutrient cycling studies. The standard sampling depth considered by the Intergovernmental Panel on Climate Change (IPCC) is 0.3 m (Harper and Tibbett, 2013; Pierret et al., 2016). The IPCC (2006) recommends the sampling of the top 0.3-m depth of soil for SOC stock measurement or estimation since changes in SOC stock due to land-use change or management are primarily confined to the top 0.1- or 0.3-m depths in most soils. Furthermore, the IPCC states in the 2006 Guidelines for National Greenhouse Gas Inventories 4.2.3. that "a large proportion of input is from above-ground litter in forest soils so soil organic matter tends to concentrate in the upper soil horizons, with roughly half of the soil organic C in the upper 0.3 m layer." It is well documented that C accumulates well below 0.3 m in soils. Shallow sampling is often justified by assuming that deeper soil horizons are stable and do not significantly change over time. Studies (Jobbagy and Jackson, 2000; Grüneberg et al., 2010; Harrison et al., 2011; Wiesmeier et al., 2012; Harper and Tibett, 2013) do not support this long-standing assumption.

Shallow soil sampling can result in underestimates of the SOC present in the profile and inadequate evaluation of the impacts of specific land management (i.e., vegetation management, timber harvest, tree replanting) or other changes (i.e., global change and soil C sequestration) over time in ecosystem studies. Harrison et al. (2011) assessed the potential of shallow soil sampling to underestimate C in the soil profile. Their results showed that where soils were sampled to at least 0.8 m, 27-77% of mineral soil C was found below 0.2 m. Others suggest that globally 50% of the total soil C is stored below 0.2 m. (Jobbagy and Jackson, 2000, Wiesmeier et al.,2012). Grüneberg et al. (2010) found that more than 66% of the SOC in the soil groups (Luvisols, Cambisols, and Stagnosols) in their study area was stored in subsoil horizons. Harper and Tibett (2013) estimated that SOC stocks are two to five times greater than what would be reported using the standard IPCC sampling depth of 0.3 m. Data from Foxx et al. (1982) in Table 1 suggests that the average rooting depth for evergreen and deciduous trees is approximately 3.3 m. Table 1 shows the rooting depths for biomes from Canadell et al.

(1996), and the average rooting depth for temperate coniferous forests is 3.9 ± 0.4 m and for temperate deciduous forests the average is 2.9 ± 0.2 m. Schenk and Jackson (2002) quantified 475 root profiles for 209 geographic locations and estimated depths above which 50% of all roots (D_{50}) and 95% of all roots (D_{95}) were located in the soil based on biomes. The temperate zones D_{50} was 0.23 m and the D_{95} was 1.23 m (n=79) for woody species. Sampling just the top 0.2 or 0.3 m would exclude a significant portion of the root zone where OC may be actively sequestered. It is therefore important that soil sampling protocols for SOC stock estimation be modified to include as much of the root zone as possible. Sampling depths for C stock estimation should aim to capture approximately 95% of the root biomass zone for the biome and vegetation in question. For example, 1.23 m would include 95% of the root mass for temperate forests, based on Schenks and Jacksons (2002).

Table 1.2 Rooting depths in meters for trees and forested biomes. The biome(s) grasslands were included since the soil quality monitoring survey included Mollisols at six sites.

Rooting Depths				
		——m——		
	# Trees	**Maximum depth**	**Average root depth**	**Reference**
Deciduous Trees	107	30	3.32	
Evergreen Trees	40	60.9	3.36	Fox et al. (1982)
All Trees	147	60.9	3.34	
Rooting Depths by Global Biomes				
	n value	**Maximum depth**	**Average root depth (SE)**	**Reference**
Boreal Forest	6	3.3	2±0.3	
Temperate Coniferous Forest	17	7.5	3.9±0.4	
Temperate Deciduous Forest	19	4.4	2.9±0.2	Canadell et al. (1996)
Temperate Grassland	5	6.3	2.6±0.2	
Tropical Deciduous Forest	5	4.7	3.7±0.5	
Tropical Evergreen Forest	5	18	7.3±2.8	
Tropical Grassland/Savanna	15	68	15±5.4	

Soil Sampling Protocols

Soil sampling methods vary; however, they are primarily grouped under fixed-depth or horizon-based sampling. Fixed-depth soil sampling has numerous benefits over horizon-based sampling. A large number of samples can be collected quickly and easily with augers and it is cheaper. If sampling is done with multiple individuals and or groups, differences in horizon descriptions and subsequent analytical results could be attributed to a "lumper" versus "splitter" approach to describing the soil profile. However, horizon-based soil sampling would effectively reduce both vertical and horizontal variability. Furthermore, soil horizons are fundamental to studies of pedogenesis (Boone et al., 1999). In principle, the total SOC stocks obtained by sampling of soil horizons are identical to those found by the fixed-depth method. However, this holds true only if the total thickness of corresponding horizons are being sampled. If a soil horizon is homogeneous in terms of morphological, physical and chemical properties, SOC concentration and D_b obtained by genetic horizons could be transformed into fixed-depth values by weighted means. However, both fixed-depth or horizon-based samplings ability to detect changes in OC stocks vary. Temporal accumulation of soil C in mineral horizons was detected only by horizon-based sampling in a long-term monitoring of changes in forest soil C stocks in the UK (Benham et al., 2012). However, Grüneberg et al. (2010) demonstrated that changes in the soil profile may be detected much earlier by depth increments rather than by horizons. Palmer et al. (2002) also found a significant difference between SOC stocks determined by horizons and by fixed-depth intervals for the same forest soil. Horizon-based stocks being 22% lower in the top 0.2 m of mineral soil compared to stocks calculated by fixed-depth increments. According to Ellert et al. (2001), the differences in the calculated SOC stocks obtained by the two sampling methods are linked to pedoturbation, either natural or anthropogenic (Vanguelova et al., 2016). Nevertheless, Boone and his colleagues proposed a hierarchical sampling scheme, with fixed-depth sampling at the lowest intensity level and horizon sampling at the highest intensity level. Then a blend of approaches for the intermediate level. "The lowest level (I) provides the minimum amount of information acceptable for cross-site or long-term studies, while the highest level (III) is designed to capture at least 90% of the variation in a property at a site" (Boone et al., 1999). Level III is recommended as the goal for long-term research sites and for soil C stocks. All three sampling levels proposed provide soil data to a depth of 0.2 m as the standard. The depth, 0.2 m was chosen as a minimum standard because it extends below the plowing depth in most agricultural soils (Boone et al., 1999).

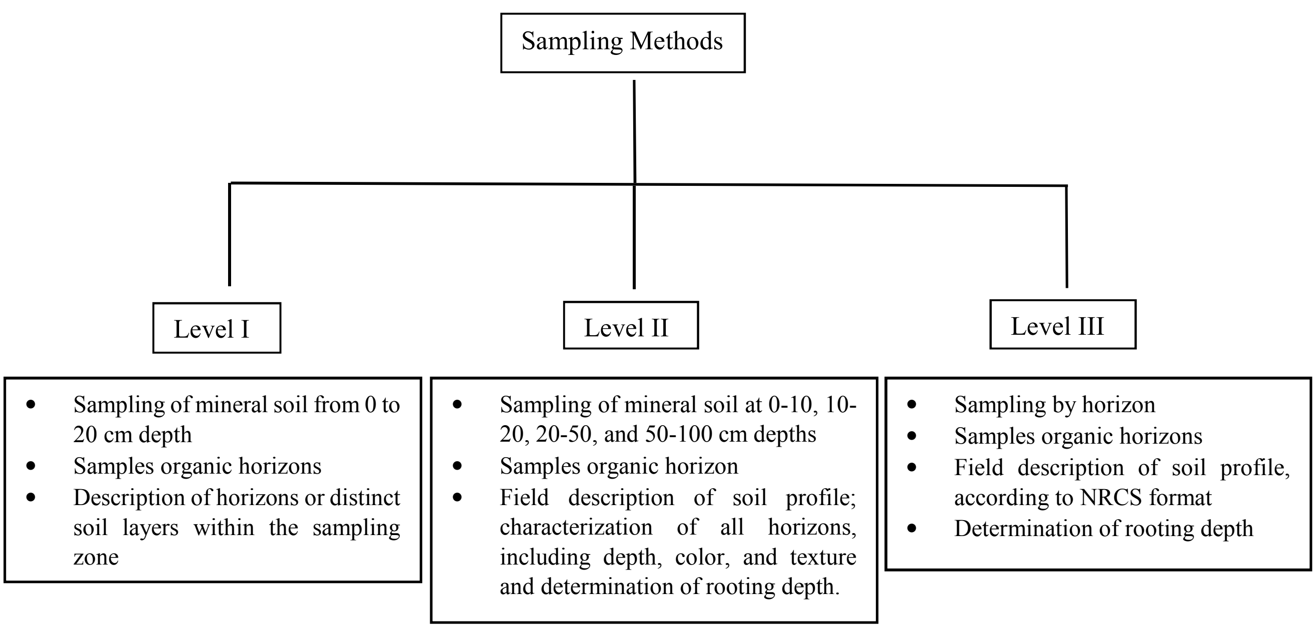

Figure 1.1 Hierarchical sampling scheme proposed by Boone et al. (1999). Level I is the lowest intensity and only samples the top 0.2 m of the soil profile. Level III is the highest intensity and samples throughout the entire soil profile, down to the rooting depth. The soil profile is also described using the NRCS format.

In order to convert mean SOC concentrations (g C kg^{-1} soil) into stocks (g C m^{-2} soil) D_b values (the dry mass of soil per unit volume) are necessary. Direct measurement of D_b is typically performed with the excavation, clod, or core methods (Blake and Hartge, 1986; Grossman and Reinsch, 2002). The excavation and clod methods involve extracting a sample in the field followed by mass determination by means of weighing. The volume is determined by filling in the void with a known volume of water, sand, or foam (excavation method) or coating the clod or extracted sample with a water repellent substance (paraffin wax) and determining the volume by displacement (Blake and Hartge, 1986). On the other hand, the core method involves weighing a known volume of soil extracted with a corer (Throop et al., 2012). The core method is favored by environmental scientists (Throop et al., 2012) over the excavation and clod methods because soil collected can be used for chemical analyses in the lab, a relatively small area is impacted compared to digging a soil pit and it does not require sophisticated equipment. There are also drawbacks with the core method, including that the small volume typically collected may not be representative of the site due to micro-spatial variability. Accurate measurements of D_b must also take into account coarse fragments. Coarse fragments are a major component of various soils and as the percentage of coarse fragments increases, a larger volume of soil for accurate assessment is required (Vincent and Chadwick, 1994). There is also reason to be concerned that as the corer is inserted into the soil it can cause compaction and give misleading estimates of soil volume (Page-Dumroese et al., 1999).

Methods for calculating D_b using the preferred core method vary considerably. Robertson and Paul (2000) suggest sieving to exclude the portion of the coarse fraction greater than 2 mm in diameter and using only the mass and volume of the fine earth fraction (<2 mm diameter) in calculations. This method is preferred in many soil survey programs (Grossman and Reinsch, 2002); however, other authors and researchers do not suggest separating out the coarse fraction from the fine earth fraction. Instead D_b is calculated using the mass of all material in the core volume (Blake and Hartge, 1986; Elliott et al., 1999). The method which removes the coarse fragments in the D_b calculations is the logical choice if soils contain very little to no coarse fragments, or when the question pertains to just the properties of the fine earth fraction. However, when the focus of the research is on quantifying soil C stocks, the focus goes beyond just the properties of the fine earth fraction to include the properties of the coarse fragments within a specific volume of material. An alternative hybrid method was proposed by Throop and Archer (2012) that calculates D_b using the mass of the fine earth component of the sample and the volume of the entire core.

To demonstrate the differences in calculated D_b among the three variations on the core method and how it can influence calculated C stocks, Throop and Archer (2012), present the following example; consider a soil in which 50% of a 100 cm^3 core volume is occupied by coarse fragments, and the masses of the fine earth and coarse fractions are 50 g and 130 g, respectively. A D_b of 1.8 g cm^{-3} is calculated if the coarse fraction volume and mass is included. When the coarse fraction volume and mass is removed, D_b is reduced by 44% to 1.0 g cm^{-3}, which in fact represents the density of the growing medium for roots. The proposed hybrid method which is obtained by excluding coarse fraction mass but including the entire core volume, yields an even lower value of 0.5 g cm^{-3}. Assuming SOC of 15 mg C g^{-1} fine earth and a soil depth of 20 cm, Throop and Archer obtain area-based values of 5400 g C m^{-2}, 3000 g C m^{-2}, and 1500 g C m^{-2} respectively. The calculation of SOC based on the method that excludes coarse fragments more than triples the amount of SOC calculated on an area basis, as it does not consider that greater than two thirds of the mass is in the coarse fraction. In this example, the 1500 g C m^{-2} obtained by the hybrid method represents the actual stock of C under a m^2 of land because the volume occupied by coarse rock fragments contains no OC.

Measuring D_b below the top 0.2 m is expensive and time-consuming, thus it is often excluded from ordinary soil analyses. Pedotransfer functions (PTF) have been proposed as an alternate solution to determine soil D_b from publicly available soil data. These functions relate D_b to other properties, such as soil texture and soil organic matter content, from field samples to create functions describing their statistical relationship. Pedotransfer functions to estimate soil D_b were introduced in 1970 by Jeffrey and used soil organic matter (Vos and Kobal, 2011). The term "pedotransfer" is further described by Bouma (1989) as "translate data we have to data we need". Essentially, these equations enable researchers to determine fundamental soil properties that are difficult to measure from other easily attainable soil data. Nevertheless, it has been shown that PTFs are site-specific equations with limitations to local soil data they were derived from and, therefore, their application in different environments might lead to misconceptions and inaccurate results (De Vos et al., 2005; Kaur et al., 2002; Martin et al., 2009; Suuster et al., 2011).

PTFs can be grouped into four types, physical-conceptual modeling approaches, simple linear or nonlinear regression equations, multiple regression methods and advanced mathematical modeling techniques (Al-Qinna & Jaber, 2013). Many studies have reported that D_b is negatively and nonlinearly related to organic matter, texture, and cation exchange capacity. However, only a few studies have been conducted to validate existing PTF's to D_b. Harrison and Bocok (2011) recommend that a specific function be created for each region rather than relying on published PTF's. Also, existing PTF relating SOM to Db are primarily limited to A horizons and the relationship is likely to be different when the change in SOM is associated with depth rather than texture and management of surface soil layers.

Due to the limitations of PTF's, the fixed-depth method as the product of soil D_b, depth and concentration is designated as 'good practice' by the IPCC (Wendt and Hauser, 2013; IPCC, 2003), thus it is used extensively in protocols of global importance to assess OC stocks if it is available and reported (Wendt and Hauser, 2013). However, the fixed-depth method has been shown to introduce substantial errors when soil D_b differs between treatments, land management, or when D_b has changed over a monitoring period (Ellert & Bettany, 1995; Ellert et al., 2002;). More accurate methods to quantify OC are necessary. Equivalent soil mass (ESM) is the reference soil mass per unit area chosen in a layer. ESM has been proposed by numerous authors to replace fixed-depth sampling. Equivalent soil mass corrections were demonstrated by Ellert and Bettany in 1995 (Lee et al., 2009) when comparing soil C stocks in genetic mineral horizons under different management practices. The equivalent C mass calculation is expected to reduce sampling errors in estimates of soil C due to differences in the amount and placement of organic material input throughout soil profiles under different management.

The depth to achieve a particular ESM varies with soil D_b, which can vary between treatments, sampling times and spatially within a plot (Wendt and Hauser, 2013). Equivalent soil mass procedures are best understood by visualizing soil profiles in terms of soil mass layers instead of soil depth layers (Figure 2). Soil mass layers such as, 0–1000, 1000–2000, 2000–3000 Mg ha^{-1} are similar to soil depth layers 0–10, 10–20, 20–30 cm (Wendt and Hauser, 2013). However, the mass of soil in a given depth layer will vary with D_b, whereas the mass of soil in a soil mass layer is fixed, and provides a consistent basis for comparing OC changes and differences. The mass of a soil sample depth corresponds directly to its soil mass (Wendt and Hauser, 2013).

To calculate the soil mass represented by a soil sample depth layer, divide the dry sample mass by the area sampled by the probe or auger, which is the cross-sectional area of its inside diameter, or $\pi(\frac{D}{2})^2$. Multiple soil cores can be combined to form one composite sample, $\pi\ (\frac{D}{2})^2 \times n$, where n is the number of cores sampled (Wendt and Hauser, 2013).

Mass of the soil for each layer:

$$M_{soil} = \frac{mass}{\pi(\frac{D^2}{2} * n)} * 1000$$

Mass of OC in the soil layer:

$$M_{SOC} = M_{soil} * C_{OC}$$

The total soil and OC masses are calculated by summing the respective depth layers. These equations come from Wendt and Hauser (2013) and are modified from the

ESM equations developed by Gifford and Roderick (2003), which uses cumulative soil and OC mass profiles to calculate OC contents in reference soil masses. Gifford and Roderick employed linear interpolation to calculate the OC mass in any reference soil mass from the soil surface, while, Wendt and Hauser Rather use a cubic spline function. Organic C stocks are then reported at the depth the ESM was achieved. This depth is referred to as the 'mass-equivalent depth', and has become the standard using ESM methods (Wendt and Hauser, 2013). It is essential to report the actual ESM layers in which OC stocks are calculated, rather than reporting the approximate depth. When the ESM layer is recorded and reported in this manner, it allows the possibility of returning to the same sampling site at a future date when monitoring changes in soil OC.

A hypothetical example to clarify the difference between fixed-depth sampling and ESM follows and highlights the bias associated with using D_b and fixed-depth sampling. A core is extracted at 10 cm and the C concentration is determined to be 20 g kg^{-1} of soil and the D_b is 1.4 g cm^{-3}. Now the plot of land is tilled to reduce the effects of compaction. A new core is taken and the C concentration is still 20 g kg^{-1} of soil; however, now the D_b is 1.1 g cm^{-3}. The hypothetical soils C stock is 2.8 kg C m^{-2} before tillage and 2.2 kg C m^{-2} after tillage. This is a 'loss' of 0.6 kg C m^{-2} which represents a 21% drop in the reported C stock to a given depth. However, the concentration of C stayed the same and the 'loss' is an artifact arising from the difference in the amount of soil collected in the core. This hypothetical example illustrates a possible bias introduced to C calculations when using D_b and fixed-depth sampling methods, especially when comparing soils that may be managed in such ways that change Db, as tillage or traffic compaction. On the other hand, important soil functions are more related to soil volume or depth than mass

Global SOC Estimates

Global Soil Partnership - GSOCmap

In 2012, the Food and Agricultural Organization (FAO) established the Global Soil Partnership (GSP) as a mechanism to improve soil management at regional and global levels. In 2016 the GSP instructed the Intergovernmental Technical Panel on Soils (ITPS) to develop the first-ever Global Soil Organic Carbon map (GSOCmap) (FAO and ITPS, 2018). On December 5th, 2017 (World Soil Day), FAO launched the GSOCmap, the most comprehensive global map to date. Soil organic carbon has long been used as an indicator of soil quality, SOC has received even more attention with the advent of the greenhouse gas reporting program of the IPCC in the mid-1990s. It was suggested that historic loss of SOC resulted in high potential for future carbon storage in degraded soils. The GSOCmap aims to provide C-stock baseline data at regional, national and global scales and support greenhouse gas reporting. The map data should also support estimates of soil respiration and illustrate the spatial variation of the potential of soils to sequestration C (e.g. through modeling) and the vulnerability of soil functions under climate change (FAO and ITPS, 2018). The GSOCmap is a compilation of SOC stock maps produced by the countries in accordance with the GSOCmap Guidelines (FAO and ITPS, 2018). A total of 1,002,562 soil profiles or sampling locations were used to create the global map. Sixty-seven countries submitted SOC maps as a contribution to the GSOCmap endeavor, 74 countries had maps produced using available data and 47 countries had maps created using soilgrids.org data (FAO and ITPS, 2018). To chemically analyze the soils for SOC 42% of the countries used wet oxidation, 14% used dry combustion, one country (Ethiopia) used Infrared radiation (IR) spectroscopy, and the remaining countries using mixed methods or did not report their methods (FAO and ITPS, 2018). Only 8% of the countries reported measured D_b data to estimate the SOC stocks. Twenty seven percent of countries submitted measured D_b values for some profiles, but used PTFs for others, while 28% of countries relied entirely on PTFs to obtain D_b estimates. External datasets such as soilgrids.org or the Harmonized World Soil Database were used for D_b estimates by 28% of all countries and 9% of the countries did not provide information about the source of their D_b data. According to the FAOs findings, more than 55% of the countries used PTFs; however, only 25% used locally fitted PTFs (FAO and ITPS, 2018). The PTFs used by the GSP are listed in Table 3.

Table 1.3 Pedotransfer functions used by the Global Soil Partnership for calculating soil organic carbon stocks when analytical D_b values are not available.

Function	**R^2**	**Db Method**	**Range of SOM contents in dataset[a]**	**Type of Ecosystem**	**Reference**
$D_b = 1.62 - 0.06OM$	NM[b]	NM	6.13*	NM	Saini, 1966 cited by Yigini Y. et al., 2018
$D_b = 1/(0.6268+0.036(OM)$	0.84	NM	2.5 – 60	Forest and Prairie soils	Drew, 1973 cited by Yigini Y. et al., 2018
$D_b = 1.482-0.6786\log(OM)$	0.79	Core	0.1 – 98.7	Various soils	Jeffrey, 1970 cited by Yigini Y. et al., 2018
$D_b = 0.669+0.941e^{(-0.06OM)}$	0.95	Irregular-Hole	0.2 – 16.6	Forest soils	Grigal et al., 1989 cited by Yigini Y. et al., 2018
$D_b = 1/(0.564+0.0556OM)$	0.95	Core	1.8 – 89.4	Forest soils	Honeysett and Ratkowsky, 1989 cited by Yigini Y. et al., 2018

[a] If soil organic carbon values were given, the values were converted to soil organic matter assuming SOM = 2*SOC.
[b]NM indicates not mentioned in the reference paper.
* SOC mean from the reference paper

The depth of sampling required for data input into the GSOCmap was 0-0.3 m for both mineral and peat soils. A second layer with SOC stocks between 0.3 m and down to 1 m depending on the depth of the peat is recommended (FAO and ITPS, 2018).

In the case of forests, the litter layer may be included if national data allows. There are two reporting options: 1) a separate model or map for the forest floor organic layer couls be produced and later added to the national SOC stocks 0-0.3 m or 2) the forest floor C stocks could be modelled jointly with the mineral SOC stocks 0-0.3 m (FAO and ITPS, 2018).

The global SOC stocks for the top 0.3 m calculated by the GSOC standards is 680 Pg. This estimate is nearly the same as the value for the HWSD (FAO and ITPS, 2018). The climatic zones used in the HWSD were classified based on monthly temperatures corrected to sea level. The climatic zones distinguished in GSOC are the following: tropics, subtropics (2 subtypes), temperate (3 subtypes), boreal (3 subtypes) and polar/arctic.

Harmonized World Soil Database Global SOC Estimates

The FAO and International Institute for Applied Systems Analysis have combined updated regional and national soil information with the information in the 1:5,000,000 scale FAO-UNESCO Digital Soil Map of the World (FAO 1971), to create a new comprehensive Harmonized World Soil Database (HWSD). In 2011 the HWSD released its findings for global SOC in the topsoil (0 - 0.3 m) and the subsoil (0.3 - 1.0 m) (Hiederer and Köchy, 2011). Where the soil depth was less than 1.0 m, the OC stocks were computed to that depth. The HWSD global SOC stock calculations used D_b values from either field measurements or PTFs that predicted D_b from data on SOC and/or texture. The initial D_b values for organic soils based on PTFs developed by Adams (1973) and modified by Vos et al (2005) were 0.244 to 0.311 g cm^{-3}, values far higher than most literature suggests for organic horizons (Hiederer and Köchy, 2011).

Ultimately the HWSD (Hiederer and Köchy, 2011) used SOC in a logarithmic relationship to predict much more realistic values of D_b for organic horizons and peat.

The global SOC stock estimate for the HWSD using the 30 arc second grid is 2,470 Pg OC (Hiederer and Köchy, 2011). The topsoil layer (0-0.3 m) estimated global C-stock was 967.3 Pg OC and the subsoil estimate (0.3-1.0 m) was 1,502.2 Pg OC (Hiederer and Köchy, 2011).

Carbon Sinks and Comparison of Global SOC Estimates

An area or system that exhibits a net C accumulation or net negative C emission is a "C sink" and one that exhibits a net release of C is a "C source." Most temperate forests are thought to contain less than their theoretical maximum C storage because of natural disturbances and timber harvesting practices (Dixon et al., 1994). Therefore, it should be possible for some temperate forests to act as C sinks. An area that is determined to be a C sink is considered to offset C emissions in accordance with local, state or federal goals and even international treaties. Terrestrial C sinks sequester approximately 40% of global anthropogenic CO_2 emissions (Malhi et al., 1999). The 1997 Kyoto Protocol committed signatories to reducing, before 2012, greenhouse gas emissions by 5.2% below their levels in 1990. This treaty includes terrestrial C sinks as one option for achieving this goal. Article 3 in the Protocol covers forest and cropland management and includes both above ground and below ground stocks of C. If temperate forests are properly managed, and areas that were previously degraded are reforested, they will be offsetting C emissions. However, measuring and verifying changes in C stocks is problematic. Verification of activities covered under article 3 in the protocol requires that for a given human-induced activity, there must be at least two independent methods for assessing the removal of emissions by a sink.

The IPCC special report outlines two methods which are used to measure losses or accumulations of C, direct measurement of C stocks and measuring the flux of C in and out of the system. In addition to the many challenges of measuring SOC stocks mentioned earlier, there is also the difficulty in determining changes in the SOC stocks. Due to the high spatial variability of soil, to obtain a mean with an acceptable standard error requires an intensive sampling design. Garten and Wullschleger (1999) determined that the minimum detectable difference in SOC for the top 40 cm is around 1 Mg C ha^{-1} which is 2-3% of the SOC stock and adequate statistical power was achieved only with greater than 100 samples. The minimum difference detected with a sample size of 16 samples per ha at 90% confidence was 5 Mg C ha^{-1} (Garten and Wullschleger, 1999).

Table 4 documents seven global estimates of SOC that vary drastically for both the top 1 m and top 0.3 m of soil. Differences in the top meter of soil are attributed mainly to differences in converting between C concentrations to C to stocks, partially due to unreliable D_b estimates. The GSP uses five different regional based PTF's and the HWSD uses different PTF's to estimate Db values.

Table 1.4 Compiled list of global soil organic carbon estimates in Pg OC.

	GSOCmap	**HWSD**	**HWSDa**	**NRCS**	**FAO2007**	**DSMW**	**Soilgrids 250m**
	-----------------	-----------------	-----------------	---Pg---	-----------------	-----------------	-----------------
Topsoil (0-0.3 m)	680	967	699	-	710	574	1267
Subsoil (0.3-1.0 m)	-	1502	718	-	746	632	-
Total (0-1.0 m)	680	2469	1417	1399	1459	1206	1267

HWSD - Harmonized World Soil Database
GSOCmap – Global Soil Organic Carbon map produced by the Global Soil Partnership
NRCS – National Resources Conservation Service
FAO – Food and Agriculture Organization of the United Nations
DSMW – Digital soil map of the world produced by the FAO

Conclusions

As mentioned in Section 1.2, it is highly likely that the 0.3 m sampling depth in the current guidelines has led to significant underestimates on global SOC stock by the GSOCmap. Furthermore, reporting global SOC stocks to a depth of 0.3 cm reinforces the outdated misconception that the majority of SOC is in the A horizon. The GSP should work toward obtaining data from the upper 1 to 2 m of soil so as to encompasses the zone in which 94% of the roots in a given biome occur.

In order to effectively understand and verify changes in temperate forest C stocks, a standard field methodology of sampling needs to be determined which includes sampling depth, number of samples per unit area, and determining the mass of soil per unit volume.

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Chapter 2: Evaluation of Pedotransfer Functions for Estimating Bulk Density of Mid-Atlantic Region Forest Soils

Abstract

Lack of accurate values for soil bulk density (D_b) often limits the accuracy of SOC stock calculations. Measuring D_b directly can be difficult and expensive, especially for subsoil horizons and rocky soils. Thus, pedotransfer functions (PTFs) that relate D_b to SOM have been proposed as an alternative to actually collecting undisturbed cores in determining soil D_b in routine soil analyses and large spatial studies.

We evaluated the capability of 20 published PTFs to predict soil D_b in mid-Atlantic region forest soils using mean error, root mean squared error, and the coefficient of determination (R^2). The PTFs evaluated significantly overestimated $D_{b,}$ and had poor predictive capability for soil material low in organic matter (OM). We created a localized PTF that accounted for 86% of the variation between observed and predicted values when all horizons, including the O horizons, were included in the nonlinear regression model. We found that including organic soil materials (O horizons) increases the R^2 of the observed to predicted value and masks the very poor R^2 for the mineral horizons, especially subsoils. Representative D_b values listed by soil series in the NRCS/SSURGO database were also investigated as a possible proxy for measured D_b in mineral horizons. For A horizons there was no correlation between measured and NRCS/SSURGO D_b values by soil series. However, the NRCS/SSURGO representative D_b values for subsoil horizons of 10 soil series correlated well ($R^2 = 0.80$) with D_b values measured by the core method, suggesting their use has potential for C stocks calculations.

Introduction

Soil bulk density (D_b) is an important physical soil property investigated in many environmental studies. Values for D_b are also needed to calculate and monitor soil organic carbon (SOC) stocks (Kobal et al., 2011). Direct measurement of D_b is typically performed with the excavation, clod, or core methods (Blake and Hartge, 1986; Elliott et al., 1999; Grossman and Reinsch, 2002). The excavation and clod methods involve extracting a sample in the field followed by determination of the dry mass. The volume is determined by filling in the void with a known volume of water, sand, or foam (excavation method) or coating a carefully extracted clod with a water repellent substance (e.g. paraffin) and determining the volume by displacement (Blake and Hartge, 1986). The core method involves extracting an undisturbed cylindrical core of known volume with a specialized soil coring tool and then obtaining the dry mass of the soil in that core volume (Throop et al., 2012). The core method is favored by environmental scientists (Throop et al., 2012) over the excavation and clod methods because soil collected can be used for chemical analyses in the lab, a relatively small area is impacted compared to digging a soil pit and sophisticated equipment is not required. However, the excavation method, is generally considered the least biased soil sampling method (Gross and Harrison, 2018; Harrison et al., 2003; Xu et al., 2016). Yet, it is the least used soil sampling methods, as it tends to be the most cumbersome and labor-intensive (Harrison et al., 2003; Jandl et al., 2014).

The deeper the soil layer, the more difficult, expensive and time-consuming measuring D_b becomes by any of these methods. For this reason, D_b is often not measured in routine soil analyses and large spatial studies, especially for deeper soil layers. Pedotransfer functions (PTF) have been proposed as an alternative to actually collecting undisturbed cores in determining soil D_b. These mathematical functions are derived by regressing D_b against other, more commonly reported, soil properties, such as texture and soil organic matter (SOM) concentration.

The first pedotransfer function was developed by Briggs and McLane in 1907 to determine the wilting coefficient for certain crops (Landa and Nimmo, 2003). Pedotransfer functions using soil organic matter to estimate soil D_b were introduced by Jeffrey (1970). Bouma (1989) described PTFs as mathematical functions that "translate data we have to data we need." Essentially, these equations enable researchers to estimate soil properties that are difficult to measure from other more easily attainable soil data. Minasny and Hartemink (2011) suggested that pedotransfer functions should only be used when consistent with the principle that "nothing should be predicted if it is easier to be measured than its predictor". In digital maps of soil properties, D_b is increasingly predicted, rather than measured, using a combination of environmental data and/or selected soil related properties (Martin et al., 2009).

The overall purpose of this research was to evaluate and develop methods of predicting soil D_b for temperate forest soil profiles. The first objective was to evaluate the predictive capability of published PTFs to estimate soil D_b in forest soils using regressions of observed values against predicted values. The second objective was to develop a PTF using the SOC and SOM information collected from the 24 forest monitoring plots to estimate D_b using nonlinear modeling. The third objective was to evaluate the use of NRCS/SSURGO soil series 'representative" D_b values as a proxy for measuring bulk densities for calculating SOC stocks in A horizons and in subsoils horizons.

Materials & Methods

Types of Pedotransfer Function models in the literature

A literature review conducted within Google Scholar resulted in 20 pedotransfer functions. Key words and phrases used in the search included, “bulk density”, “pedotransfer function”, “organic matter”, “predicting bulk density”, “organic carbon”, and “forest soils”. This work expanded on the evaluation of published PTFs by Vos et al., 2005. The PTFs were evaluated by regressing their predicated values against D_b values measured using the core method in 24 forest monitoring plots in three US national parks. Vos et al. (2005) evaluated 12 pedotransfer functions in 2005 and concluded that including texture as a parameter in addition to SOM or SOC improved the models by less than 2%, resulting in no significant change in predictive ability. For this reason, and because our dataset did not include particle size analyses, PTFs which employed texture were excluded in this study. The 20 published PTFs selected for this review are summarized in Table 1. The required input parameters for these functions were SOC (% or g kg^{-1}) or SOM (% or g kg^{-1}) contents. Functions F6-F10 are used by the Food and Agricultural Organization (FAO) Global Soil Partnership (GSP) for estimating D_b if analytical D_b data are missing.

Table 2.1 Published pedotransfer functions considered in this study. R^2 values for observed versus predicted values, D_b method, and ecosystem/soil information are taken from the original papers.

No.	Function	R^2	D_b Method	Type of Ecosystem / Soils	Reference
F1	Db = -0.0071(OM) + 1.4649	0.27	Core	Upland soils	Byung-Koo Ahn et al., 2010
F2	Db = 1.449e^(-0.03OC)	0.68	NM	SSURGO Database	Abdelbaki, 2018
F3	Db = 0.5237OC^(0.3861)	0.64	Core	Alluvial soils	Jin Qian et al., 2017
F4	Db = -0.004OM + 1.44	0.36	Core	Various soils	Ghiberto et al., 2015
F5	Db = -0.04ln(OC) + 1.274	0.80	Core	Hydric soil	Manthan and Mankodi, 2018
F6*	Db = 1.62 - 0.06OM	NM	NM	NM	Saini, 1966 cited by Yigini Y. et al., 2018
F7*	Db = 1/(0.6268+0.036(OM)	0.84	NM	Forest and Prairie soils	Drew, 1973 cited by Yigini Y. et al., 2018
F8*	Db = 1.482-0.6786log(OM)	0.82	Core	Various soils	Jeffrey, 1970 cited by Yigini Y. et al., 2018
F9*	Db = 0.669+0.941e^(-0.06OM)	0.95	Irregular-Hole	Forest soils	Grigal et al., 1989 cited by Yigini Y. et al., 2018
F10*	Db = 1/(0.564+0.0556OM)	0.95	Core	Forest soils	Honeysett & Ratkowsky, 1989 cited by Yigini Y. et al., 2018
F11	Db = 1.51 – 0.113OC	0.36	NM	Forest soils	Manrique and Jones, 1991 cited by Boschi, 2018
F12	Db = 1.02 - 0.156ln(OM)	0.45	NM	NM	Hong et al., 2013 cited by Boschi, 2018
F13	$Db = -1.977 + 4.105(OM/100) – 1.229\ln[(OM/100)] – 0.103 \ln[(OM/100)]^2$	0.82	Core	Forest soils	Perie and Ouim, 2008 cited by Boschi, 2018
F14	$Db = -2.31 - 1.079\ln(OM) - 0.113\ln(OM)^2$	NM	Core	Forest soils	Federer, 1983
F15	$Db = -2.39 - 1.316\ln(OM) - 0.167\ln(OM)^2$	0.75	Excavation	Forest soils	Huntington, 1989
F16	$Db = 1.66 - 0.38OC^{(1/2)}$	0.46	Core & Clod	Upland and Alluvial soils	Alexander, 1980 cited by Boschi, 2018
F17	Db = 1.558 - 0.728 log10(OM)	0.81	Core	Topsoil	Harrison and Bocock, 1981 cited by Vos et al., 2005
F18	Db = 1.729 - 0.769 log10(OM)	0.58	Core	Subsoil	Harrison and Bocock, 1981 cited by Vos et al., 2005
F19	$Db = 1.565 - 0.2298(OM)^{1/2}$	0.61	Core	Forest soils	Tamminen and Starr, 1994 cited by Vos et al., 2005
F20	$Db = 1.775 - 0.173(OM)^{1/2}$	0.57	Core	Forest soils	Vos et al., 2005

D_b, bulk density soil, g cm-^{3}; ln, natural logarithm; OC, organic carbon, %; OM, organic matter, g kg^{-1}
NM = not mentioned in paper.
* PTF used by the GSP for the GSOCmap

Function Validation Methodology

The published PTFs ability to predict D_b was evaluated by comparing the difference between the predicted and observed values (deviations from the one to one line); the mean error (ME), the root mean square error (RMSE) and the coefficient of determination (R^2) using the soil cores collected from 24 sites between Antietam National Battlefield, Greenbelt National Park, and Prince William Forest Park. The mean error quantifies systematic errors and indicates tendencies to overestimate or underestimate. For best performing models, the ME should be close to zero. The root mean square error is the measure of the overall error in the prediction, with lower values indicating better model performance. It is the square root of the mean square error (MSE). The R^2 value represents the percent of the total variance that is explained by the model. All calculations were conducted in Microsoft Excel (2019).

$$\mathrm{ME} = \sum \frac{\mathrm{Dbo} - \mathrm{Dbp}}{\mathrm{N}} \qquad \text{Eq. 1}$$

$$\mathrm{RMSE} = \sqrt{\frac{(\mathrm{Dbo} - \mathrm{Dbp})^2}{\mathrm{N}}} \qquad \text{Eq. 2}$$

Study Area and Sampling Plots

This study took place in the National Capital Region Network (NCRN) of the US National Park System (US NPS), which is located within the eastern US deciduous forest ecosystem. The NCRN is composed of 11 national park units and the US NPS has been monitoring 425 plots (707 m^2) within these parks over a period of 10 years. In 2005 a 250 m^2 grid was established across each of the 11 parks in the network. Sampling plots were located using a generalized random-tessellation stratified survey (GRTS) (Stevens and Olsen, 2004). The GRTS approach was chosen over simple random sampling as GRTS creates a random sample that is spatially balanced so the points are not clumped in a single part of the study area. Potential monitoring plots were visited to determine suitability for forest vegetation monitoring. A location was removed if it did not contain forest vegetation, was located on a road, waterway, maintained field, etc., or was on a slope greater than 30°, or was otherwise hazardous (Schmit et al., 2014). The United States Forest Service criterion 1 was used to define the presence of forest, namely the land area must be at least 10% stocked by trees of any size. For this study on D_b analysis we sampled 24 plots within three parks, Antietam National Battlefield, Greenbelt National Park, and Prince William Forest Park. The location and characteristics of the sampled parks are given in Table 2.

Table 2.2 A summary of soils and forest types encountered at Antietam National Battlefield, Greenbelt National Park and Prince William Forest Park.

Park	**Park Coordinates**	**Forest Type**	**Soil Series Present[a]**	**Taxonomic Classification[b]**	**Parent Material[b]**
Antietam National Battlefield	39.47°N 77.74°W	Mixed oak/hickory Forest	Hagerstown	Fine, mixed, semiactive, mesic Typic Hapludalfs	Limestone Residuum
			Duffield	Fine-loamy, mixed, active, mesic Ultic Hapludalfs	Limestone Residuum
			Carbo	Very-fine, mixed, active, mesic Typic Hapludalfs	Limestone Residuum
Greenbelt National Park	38°59′21″N 76°53′54″W	Deciduous oak/poplar/ maple Forest	Christiana	Fine, kaolinitic, mesic Aquic Hapludults	Marine Sediments
Prince William Forest Park	38°35′07″N 77°22′47″W	Mixed coniferous-deciduous forest	Glenelg	Fine-loamy, mixed, semi active, mesic Typic Hapludults	Gneiss/Schist Residuum
			Meadowville	Fine-loamy, mixed, semi active, mesic Typic Hapludults	Alluvium
			Elsinboro	Fine-loamy, mixed, semiactive, mesic Typic Hapludults	Alluvium
			Ryder	Fine-loamy, mixed, semiactive,	Limestone Residuum

		mesic Ultic Hapludalfs	
	Buckhall	Fine, mixed, semiactive, mesic Typic Hapludults	Gneiss/Schist Residuum
	Hatboro	Fine-loamy, mixed, active, nonacid, mesic Fluvaquentic Endoaquepts	Alluvium

[a] Soil Survey Staff, NRCS, United States Department of Agriculture. Web Soil Survey and auger profile descriptions by NPS monitoring program.
[b] Soil Survey Staff, NRCS, United States Department of Agriculture. Official Soil Series Descriptions.

Field Plots and Sampling

At each sampling plot a permanently installed metal central point marker was located using GPS coordinates and a metal detector. This marker was considered the center of a circular plot 15 m in diameter. Organic horizon cores were taken at five locations randomly distributed throughout the entire 707 m^2 plot using a 4.76 cm diameter coring tool. Organic horizons were present at 18 of the 24 plots. At a single random location within 1 m of the center marker, an undisturbed soil core (10.16 cm long x 4.76 cm diameter) was extracted every 10.16 cm to a depth of 90 cm. Each soil core was sealed in a zip lock bag for transportation to the lab. The soil was analyzed to determine D_b, sand percentage, and total organic carbon (TOC).

Sample Preparation and Handling

Mineral soil cores were placed on a tared paper plate, weighed (fresh weight) and then allowed to air dry for a minimum of seven days. Subsamples were taken from each core, placed in a pre-weighed beaker, weighed and then oven dried at 105^{o} C for 24 hr in a forced-air oven, then weighed again to determine the air-dried water content of the soil. The weight of any coarse rock fragments was recorded.

Dried, ground and sieved subsamples from the oven-dried, fine earth fraction (<2.00 mm) were shipped to the University of Georgia Agricultural and Environmental Services Laboratories (AESL) Soil, Plant, and Water lab (SPW) for analysis of total organic carbon (TOC) by high temperature combustion using either Model Vario Max (Elementar, Langenselbold, Germany) and or Model TruMac (LECO, Saint Joseph, Michigan, USA).

Organic horizon cores were placed on a paper plate, weighed (fresh weight) and then allowed to air dry for a minimum of seven days. The organic cores were then oven dried in a Forced Air oven at 80° C for 6 hr and 100° C for 1 hr. The oven dry weights were then recorded. A subsample was collected and passed through a 2mm sieve. The material that passed the 2mm sieve was then ground and 1.0 g was weighed into a crucible to the nearest 0.0001 g and placed in a muffle furnace for 5 hr at 450° C to burn off the OM. After cooling in a desiccator, the samples were weighed and the difference of oven dry minus the ashed weight was calculated as loss on ignition and expressed as percent OM.

Soil Series Determination

The NRCS Web Soil Survey (WSS) (Soil Survey Staff, 2017) was used to determine the mapping unit in which each plot was located and the several soil series that comprised that mapping unit. The specific soil series present in the sample plot was determined by comparing an auger soil profile description made during the NPS monitoring program against the profile descriptions of the each of the soil series occurring in the mapping unit shown for the GPS coordinates of the sampling plot. A dry D_b value for each A and B master horizon was obtained from the NRCS SSURGO database as the dry D_b value listed as "representative" for that soil series and horizon. The SSURGO A horizon and B horizon representative D_b values for a specific soil series were compared to the mean D_b values measured by the core method for A horizons and B horizons in that soil series. We included in the analysis the 10 different soil series that were encountered at least twice in the 24 plots sampled. Linear regression was conducted in Microsoft Excel (2019) to determine the relationship (and R^2 value) between the soil series mean D_b values from cores measured in the field and the NRCS SSURGO representative D_b values for the same soil series, by A or B master horizon.

Results and Discussion

Function Validation Results

The performance of the 20 published PTFs in predicating the measured D_b in the current study (topsoil and subsoil) is recorded in Table 3. Most of the published functions, except F12, F14 and F15, overestimated D_b in these forested soils. The mean error ranged from +1.22 to -4.13 g cm^{-3}. Functions F1, F3 and F5 had mean errors below 0.1 g cm^{-3}. However, F1 and F3 in addition to F13, F14 and F15 predicated theoretically impossible D_b values ($D_b < 0 > 2.65$ g cm^{-3}) when SOM values were < 0.5.

Table 2.3 Mean error (ME), root mean squared error (RMSE), and the coefficient of determination (R^2) for the published pedotransfer functions (PTFs) evaluated using bulk density data for all mineral soil samples from the present study (with SOC ranging from 0.85 to 116.37 g C kg^{-1}) and the R^2 and range of SOM from the original publication.

PTF ID	Evaluative information from application to current study samples			Information from published report	
	ME	RMSE	R^2	R^2	Range of SOM included, %
F1	-0.08	0.25	0.420	0.27	27 – 33.1
F2	-0.24	0.32	0.304	0.68	NM
F3	-8.8E-4	0.71	0.299	0.64	15 – 37
F4	-0.13	0.25	0.294	0.36	5 – 40
F5	-0.08	0.25	0.247	0.80	0.13 – 3.56
F6	-0.26	0.34	0.294	NM	6.13*
F7	-0.21	0.30	0.320	0.84	2.5 - 60

F8	-0.18	0.34	0.247	0.79	0.1 – 98.7
F9	-0.28	0.35	0.319	0.95	0.2 – 16.6
F10	-0.40	1.18	0.317	0.95	1.8 – 87.9 (LOI) 2.4 – 89.4 (HTIL)
F11	-0.16	0.27	0.294	0.36	NM
F12	0.24	0.33	0.247	0.45	0.12 – 100
F13	-4.13	4.14	0.303	0.82	0.12 – 100
F14	1.10	1.12	0.319	NM	0.08 – 24.32
F15	1.22	1.26	0.027	0.75	NM
F16	-0.40	1.18	0.307	0.46	0.02 – 38.36
F17	-0.25	0.39	0.247	0.81	1.0 – 96.0
F18	-0.41	0.52	0.247	0.58	0.8 – 87.4
F19	-0.04	0.22	0.307	0.61	0.2 – 20.5
F20	-0.33	0.39	0.307	0.57	0.2 – 73.5

* = SOM mean from the paper.
NM = not mentioned in paper.
LOI = Low temperature LOI
HTIL = High temperature LOI

The PTF with the highest R^2 (0.42) was F1 (Byung-Koo Ahn et al., 2010), while F15 (Huntington, 1989) had the lowest R^2 (0.02). Figure 1 provides scatterplots of observed vs predicated D_b (g cm^{-3}) values for topsoil and subsoil using functions F1-F20 applied to the 95 mineral soil samples (including A, E, B and C horizons) from the current study. The scatterplots also show the 1:1 predication line. Function 13 is not scaled with the other scatterplots because it significantly overestimates D_b. A PTF that accurately predicts D_b would produce predicted values that fall very near the 1:1 line on the scatterplot. Predicted values below the 1:1 line indicate underestimation and those above the line indicate overestimation. Only F8 and F18 produced predicted values that tended to follow the 1:1 line, but with low R^2 values of only 0.25 and 0.32, respectively. Functions F12, F14 and F15 consistently underestimated D_b. Several of the published PTFs were based on soil sample sets with a very large range of SOM contents that included many organic soils (defined as > 20% OC or 40% OM). As can be seen in Table 3, the R^2 value for the regression of observed against predicted D_b tended to be greater where a such organic materials were included in the data from which the PTF was derived. Unfortunately, Table 3 also shows that when those PTFs were applied to a set of soil samples from mineral horizons with relatively low SOM or SOC contents, (e.g subsoil horizons), the functions exhibited only very weak predicative capabilities. Another issue that appears to limit the usefulness of several published PTFs is the inclusion of an intercept value. For example, F4, D_b = -0.004OM + 1.44 (Ghiberto et al., 2015), predicts the maximum D_b to be 1.44 g cm^{-3} when SOM is close to zero, although the measured D_b in many subsoil horizons is much higher than that limit. This effect is displayed strongly in Figure 1 panels for F2, F4, F5, F6, F7, F9, F15, F16 and F20 in which the data points cluster at a limiting D_b forming a trend that parallels the x-axis.

The performance of the 20 published PTFs in estimating D_b in forest soil A and B horizons, respectively, is documented in Table 4. Most of the published PTFs (except, F8, F13, F15, F16 and F17) consistently overestimated D_b in these forested mineral soil horizons. The average mean error ranged from 0.008 to 1.94 g cm^{-3}. For the functions that underestimated D_b, the average mean error ranged from -0.21 to -1.167 g cm^{-3}. Pedotransfer functions F1 and F8 exhibited average mean errors below 0.1 g cm^{-3}. Pedotransfer functions F3, F13, F14, F15 and F16 predicated theoretically impossible D_b values greater than the particle density of solid rock (D_b = 2.65 g cm^{-3}). Function 8, F12, F17, and F18 (Jeffrey, 1970 and Yigini Y. et al., 2018 and Hong et al., 2013 and Boschi, 2018) had the highest coefficient of determination when considering just the topsoil with 43.2% of the variation explained. Functions F4, F6 and F11 had the lowest coefficient of determinations, with 38.0% of the variation explained. Function F17 was the only function created specifically from topsoil cores.

When the regression included only data from topsoil (A horizon) samples which have relatively high SOC concentrations, the R^2 values were considerably higher for all of the PTFs (Table 4). Out of the 20 PTFs that were investigated in this study, only F18 was specifically based on data from mineral soil samples low in SOC (subsoil samples). When the regression included only data from subsoil (E, B, and C horizons) samples which have very SOC concentrations, the R^2 values were extremely low with all of the PTFs explaining less than 1.4% of the variation (Table 4).

Table 2.4 Mean error (ME), root mean squared error (RMSE), and the coefficient of determination (R^2) for the published pedotransfer functions (PTFs) evaluated using bulk density data separately for topsoil (A horizons) and subsoil (E, B and C horizon) cores.

	Topsoil			**Subsoil**		
PTF#	**ME**	**RMSE**	**R^2**	**ME**	**RMSE**	**R^2**
F1	-0.008	0.231	0.380	-0.102	0.252	0.008
F2	-0.369	0.394	0.393	-0.187	0.295	0.008
F3	-0.954	1.096	0.428	0.356	0.498	0.004
F4	-0.186	0.237	0.380	-0.109	0.253	0.008
F5	-0.241	0.288	0.432	-0.020	0.230	0.001
F6	-0.235	0.052	0.380	-0.269	0.353	0.008
F7	-0.192	0.237	0.426	-0.219	0.319	0.007
F8	0.021	0.138	0.432	-0.252	0.391	0.001
F9	-0.328	0.354	0.420	-0.265	0.350	0.007
F10	-0.132	0.207	0.430	-0.327	0.407	0.006
F11	-1.904	2.118	0.380	-0.162	0.281	0.008
F12	-0.148	0.237	0.432	0.238	0.344	0.001
F13	0.242	0.277	0.415	-4.210	4.218	0.007
F14	-3.905	3.908	0.422	1.076	1.101	0.014
F15	1.167	1.181	0.392	1.290	1.329	0.001
F16	1.027	1.041	0.423	0.166	0.496	0.004
F17	-0.001	0.142	0.432	-0.333	0.454	0.001
F18	-0.158	0.214	0.432	-0.507	0.598	0.001
F19	-0.006	0.139	0.423	-0.055	0.243	0.004
F20	-0.357	0.380	0.423	-0.320	0.395	0.004

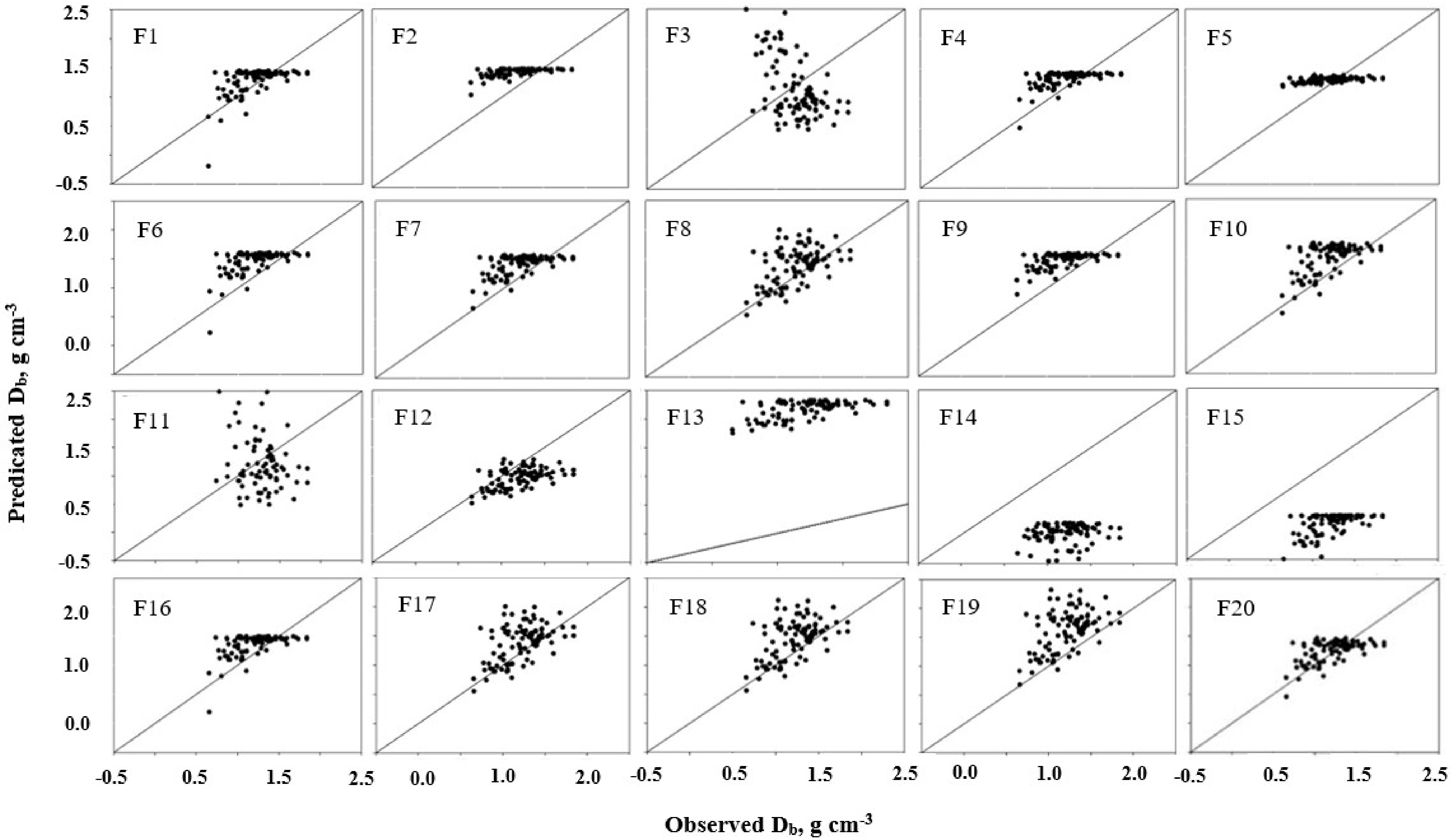

Figure 2.1 Observed versus predicted D_b values along with the 1:1 line for functions F1-F20. Only mineral soil core data was utilized in this figure.

Pedotransfer Functions Created from NCRN Forest Soil Cores

In order to create a locally applicable pedotransfer function that uses OM percent to predict D_b in temperate forest soils a total of 95 observations from mineral soil horizons (24 A horizons and 71 subsoil (E, B and C horizons) were used. The best fit logarithmic equation for the regression of organic matter versus D_b is shown in Figure 2. As organic matter increases, D_b decreases and approaches 0.8 g cm^{-3}. The calculated R^2 value was 0.25 (Figure 2), indicating that the equation offers low predictive capabilities. When percent sand was included in a multivariate regression the predictive capability did not significantly improve (data not shown).

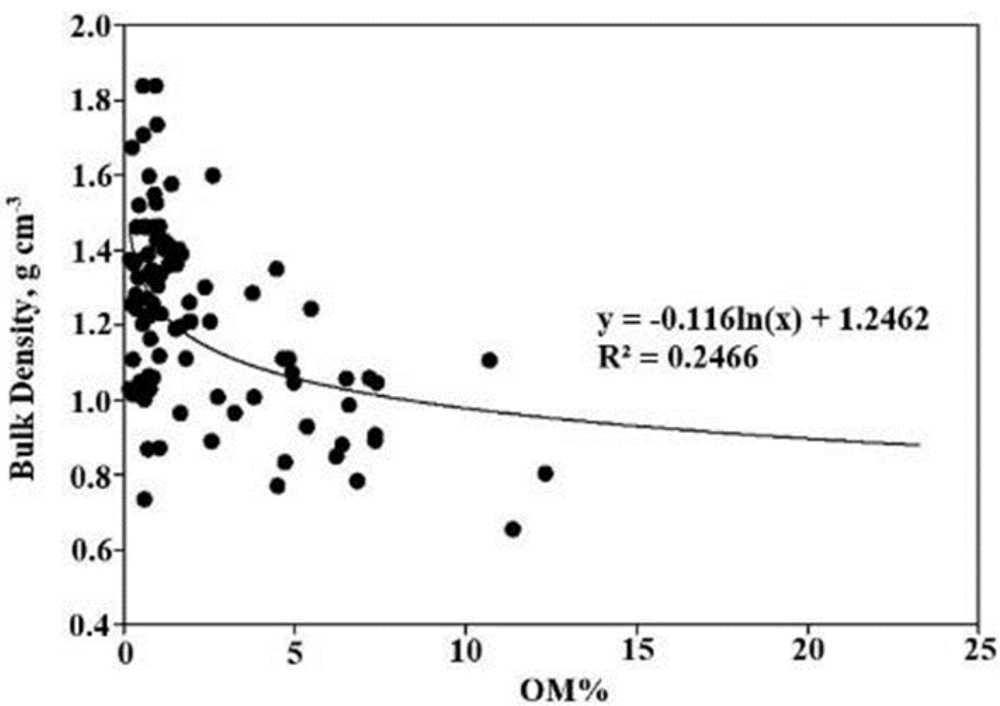

Figure 2.2 The logarithmic relationship between SOM and D_b for mineral soil horizons with less than 15% SOM in 24 forested study plots.

When data from the 90 organic cores (O horizons with >40% OM) collected in 2018-2019 (18 forest plots, 5 cores at each plot) were analyzed along with the data from the mineral horizon cores, the R^2 was 0.86, with D_b decreasing and approaching zero as organic matter increased. This high R^2 might suggest that reliable and accurate estimates of D_b values could be obtained using this PTF. However, as with the published PTFs reviewed, a high R^2 value (> 0.5) is exhibited only when the regression includes soils with SOM contents characteristic of O horizons and much higher than found in most A or B horizons. We find that applying such published PTFs to material low in OM, especially forested subsoils (E, B and C horizons) can be expected to poorly predict D_b and, on average, to significantly overestimate the true soil D_b.

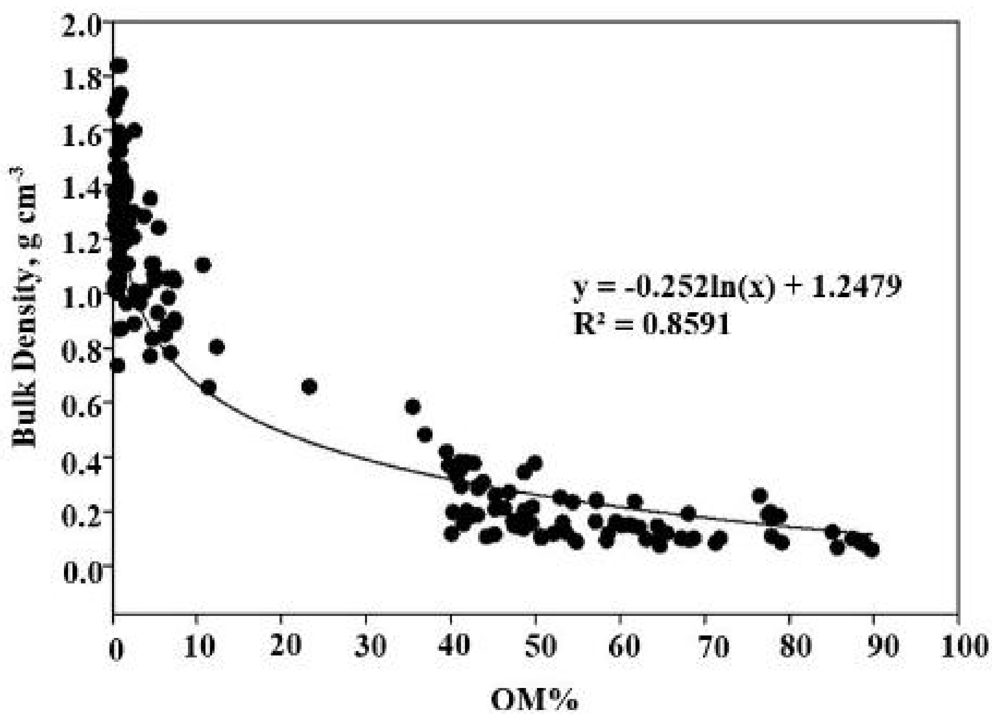

Figure 2.3 The logarithmic relationship between SOM and D_b across both mineral and organic soil horizons in 24 forested study plots.

Relationship between measured and SSURGO bulk density

Since all the PTFs reviewed in this study exhibited poor predictive ability for D_b of mineral soil horizons, we investigated the possible use of D_b values listed in the NRCS SSURGO database as representative of A or B horizons of identified soil series. The representative D_b values from the SSURGO database for subsoil horizons were strongly and linearly related (R^2=0.80) to the mean D_b values for 10 soil series determined from 24 cores (90 samples) collected in the field (Figure 4). In contrast, there was no significant relationship between the SSURGO database representative D_b values for A horizons with the mean measured A horizon D_b values for these 10 soil series (Figure 5).

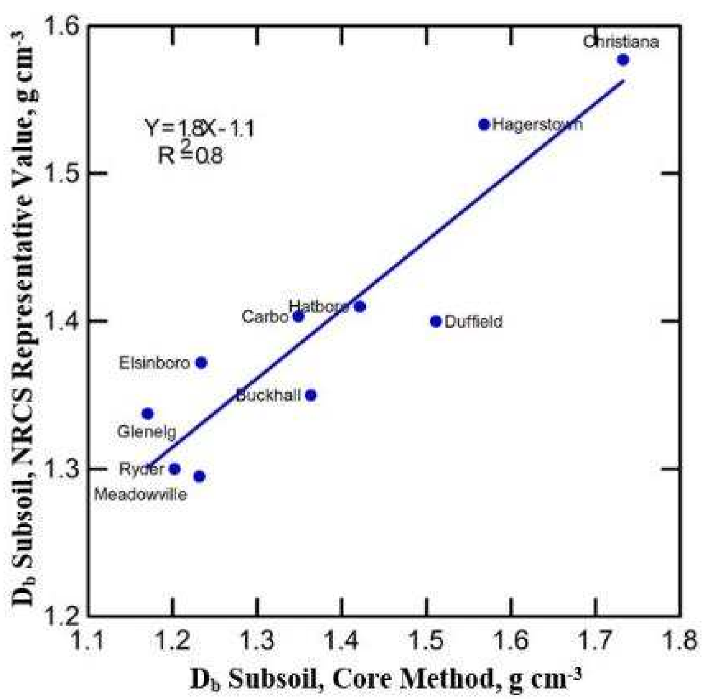

Figure 2.4 Relationship between SSURGO representative D_b values and mean D_b measured by core method for B horizons at 24 plots for the 10 soil series encountered at more than one sample point.

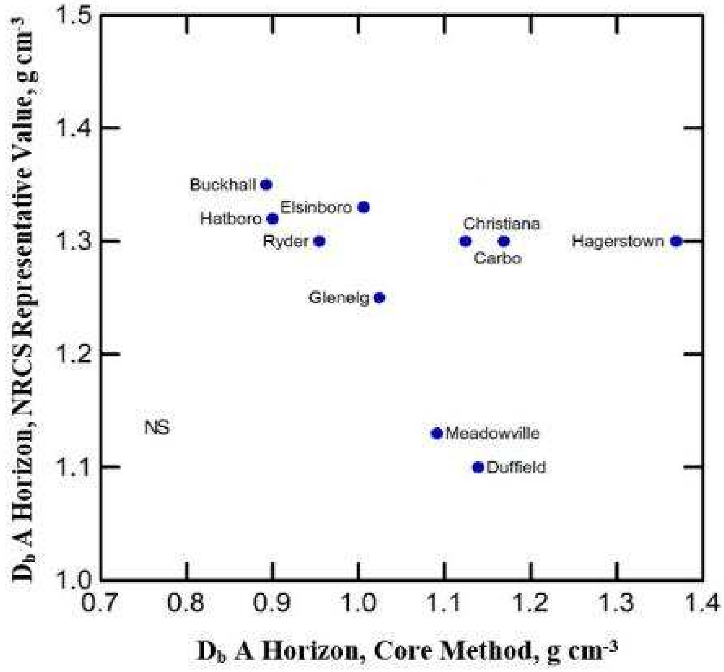

Figure 2.5 Relationship between SSURGO representative D_b values and mean D^b measured by core method for A horizons at 24 plots, total of 10 soil series. No significant relationship was found.

The lack of a significant relationship between the SSURGO representative D_b values for A horizons with the mean measured D_b for A horizons was not unexpected. The NRCS (and previous Soil Conservation Service) soil mapping and characterization efforts have historically focused primarily on agricultural lands. Since the Db of most agricultural lands has been impacted by trafficking and tillage, both of which tend to increase D_b in soils, it is not surprising that the SSURGO representative D_b values for the seven of the 10 soil series were significantly higher than the D_b values measured using undisturbed soil cores in our forested plots. Furthermore, the D_b of surface soils (A horizons) can be easily impacted by land management operations such as logging, plowing and trafficking, whether under forest or agricultural use, leading to greater variability and a lower likelihood that typical pedons characterized by NRSC soil mappers would correspond to other pedons of the same soil series under different land use conditions.

Fortunately, measuring D_b in A horizons is relatively easy and does not pose a challenge in most studies as compared to the difficulty of measuring Db in subsoil horizons. However, D_b values in subsoil horizons are much less likely to be influenced by farming (or silvicultural) operations than in A horizons. The SSURGO representative D_b values were quite closely correlated (R2=0.80) with the D_b values measured on undisturbed soil cores for the subsoils in this study. We therefore suggest that NRCS SSURGO representative D_b values can be used as proxies for Db if the soil series is identified.

Conclusion

The objectives of this study were to evaluate the performance of published PTFs in predicting soil D_b and to develop a new function applicable to mid-Atlantic temperate region forested soils. We determined that PTFs in the literature have limited predictive potential for D_b. The majority of PTFs in the literature significantly overestimated D_b and were unable to accurately predict D_b for most mineral soil horizons where a significant portion of forest ecosystem C stocks may be contained. Despite functions having a high R^2 values for the data set used to create them, little confidence can be had in the C stock calculation using such PTFs to estimate D_b in other soils, especially for mineral soil horizons. Our results support recent studies which recommend not using PTFs due to systematic biases, especially in forest soils (Schrumpf et al., 2011; Wiesmeier et al., 2012).

We therefore recommend that researchers attempting to calculate US regional or national soil C stocks identify the soil series and use SURGO representative D_b values for subsoil horizons while directly measuring D_b for A horizons. For estimates of global SOC stocks a similar approach may be useful where representative measured D_b values are available for specific soils from legacy data. The published PTFs currently used for this purpose are of little value in predicting the D_b of mineral soil horizons, especially those deeper in the profile and lower in SOC content than the A horizons. Therefore, we suggest that researchers not use such PTFs to predict D_b in mineral soil horizons, especially low SOM subsoil horizons.

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Chapter 3: Soil Organic Carbon in Mid-Atlantic Region Forest Soils: Stocks and Vertical Distribution

Abstract

Over a period of 10 years, 418 forested sites within the US National Capital Region Parks were monitored. Samples were collected from the O horizons, including loose leaf litter, and, using a hand auger, from each mineral horizon to 1 m depth. Soil carbon (C) concentration was determined by high temperature combustion and C stocks were then calculated for each master horizon as C concentration x corrected D_b. Soil bulk density (D_b) was determined by the core method for O and A horizons and corrected for coarse fragments. For deeper mineral horizons NRCS/SSURGO representative values for D_b were used. An average of 0.45 ± 0.02 kg C m^{-2} was contained in the loose leaf litter. For the sites with significant O horizons, the organic layer contained 3.19 ± 0.45 kg C m^{-2}. An average of 4.99 ± 0.23 kg C m^{-2} was stored in the A horizon to an average lower boundary of 19.8 cm. The mineral horizons below the A horizon averaged 8.42 kg C m^{-2}. In these forested soil profiles, 50.7% of the total OC in these forested soils is below the A horizon and 19.2% of the OC is in the organic horizons. The vertical distribution of SOC stocks was also evaluated with respect to soil order, physiographic region and parent material. The total OC in the top meter was significantly greater in Mollisols and Entisols and in the Blue Ridge region and floodplain land form. Parent material did not significantly affect C stocks.

Introduction

Temperate forests are located between 25°and 50° latitudes in both hemispheres and cover 10.4 million km^2 of land globally. Temperate forests are important globally as carbon sinks that fix more C as plant dry matter and soil organic matter than they give off by respiration (Lal, 2005; Luyssaert et al., 2008). The total carbon stocks in temperate forests have been estimated to comprise as much as 60% of the global SOC (Dixon et al., 1994).

The above and below ground C pools include aboveground plant biomass, coarse woody debris, leaf litter, belowground root biomass and soil organic carbon (SOC). The largest of these C pools is the SOC which is 1.5 to 2.5 times as large as the above ground vegetation pool (Wang et al., 2002). Carbon is stored in the soil in both inorganic and organic forms. Soil organic carbon is a component of soil organic matter and its quantity is an important indicator of soil quality (Dumanski, 2004). Global estimates of SOC vary, with the earliest estimate of global SOC being extrapolated from nine soils in the United States of America to 710 Pg C (Bohn, 1976: Scharlemann et al., 2014). Scharlemann et al. (2014) calculated the median global SOC the upper m of soil across 27 different studies to be 1461 Pg C with a range of 504–3000 Pg C. Published estimates of global soil C stocks vary due to varying sampling methods, inconsistent inclusion of inorganic C, and varying levels of coarse mineral fragments in the samples. Some studies do not state specifically which forms of C were included or if calculations were corrected for coarse fragments (Scharlemann et al., 2014). Notable differences in recent global SOC stock estimates were attributed to the values used for the D_b of in the calculation of stocks in organic soils (Scharlemann et al., 2014). Such differences in global SOC stock estimates highlight the need for standardization of data collection and sampling and calculation methods.

The majority of published studies that quantify C stocks in forest soils used relatively shallow sampling depths. The standard sampling depth recommended by and used by the Intergovernmental Panel on Climate Change (IPCC) is 0.3 m (Harper and

Tibbett, 2013). The Global Soil Partnership (GSP) Global Soil Organic Carbon Map (GSOC map) uses the IPCC standard depth of 0.3 m and the majority of ecosystem studies sample to a depth of just 0.2 m (IPCC, 2006; Janssens et al., 2005; Wiesmeier et al., 2012). The IPCC (2006) recommends sampling the top 0.3 m depth of soil for SOC stock measurements since changes in SOC stocks due to land-use change or management are primarily confined to the top 0.1 or 0.3 m depths in most soils. Furthermore, the IPCC states in the 2006 Guidelines for National Greenhouse Gas Inventories 4.2.3. that "a large proportion of input is from above-ground litter in forest soils so soil organic matter tends to concentrate in the upper soil horizons, with roughly half of the soil organic C in the upper 0.3 m layer." However, C accumulates well below this depth in soils. Studies suggest that the relative contribution of plant roots to SOC is larger than that of plant shoots (Broadbent and Nakashima, 1974; Persson, 2012; Rasse, et al., 2005). If the contribution of roots to SOC is greater than shoots, then sampling to estimate total C stocks should occur as deep as the bulk of the root system and not just the top 0.3 m. The average rooting depths for evergreen and deciduous trees reported from Foxx et al. (1982) was approximately 3.3 m. Canadell et al., (1996) concludes that the average rooting depth for temperate coniferous forests is 3.9 ± 0.4 m and for temperate deciduous forests the average is 2.9 ± 0.2 m. In 2002, Schenk and Jackson quantified 475 root profiles for 209 geographic locations and estimated depths above which 50% of all roots (D_{50}) and 95% of all roots (D_{95}) were located in the soil based on biomes. For the temperate zones D_{50} was 0.23 m and the D_{95} was 1.23 m (n=79) for woody species. Jobbagy and Jackson (2000) found that globally, 50% of the total soil C is stored below 0.2 m. Sampling just the top 0.2 m would miss a significant portion of the root zone and underestimate soil C stocks.

The purpose of this research was to investigate the stocks of SOC in Mid-Atlantic region forest soils, as represented in 11 US National Parks in the National Capital Region Network (NCRN). The first objective was to determine the stocks of SOC at each site. The second objective was to determine the vertical distribution of SOC by master pedogenic horizon, especially the proportion of C present below the typically sampled A horizon. The third objective was to analyze how the stocks of SOC varied by soil order, parent material (PM) type, soil drainage class, physiographic region and rock type within the study areas.

Materials and Methods

National Capital Region Network of forest parks

This study took place in the NCRN of the US National Park System, which is located within the eastern US deciduous forest ecosystem. The parks are all within 200 km of Washington, DC and are subject to varying degrees of urban influences. Besides some areas of marsh and managed turfgrass, forests are the dominant vegetation of the parks, making up approximately 75% of land cover (National Park Service, 2018; https://www.nps.gov/im/ncrn/index.htm). The parks span three states: Maryland, Virginia and West Virginia and four physiographic regions: the Coastal Plain, the Piedmont, the Blue Ridge and the Ridge and Valley (Figure 1).

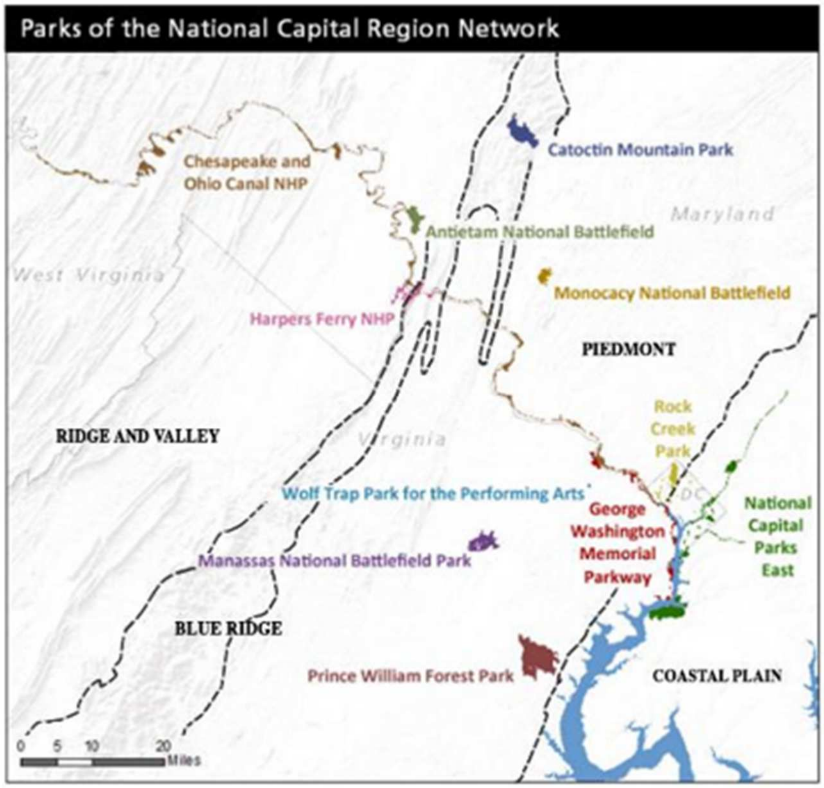


Figure 3.1 Map of sampled parks (colored shapes) and physiographic provinces (dashed lines) within the National Capital Region Network and (Modified from the National Park Service, 2018)

The NPS developed a program to inventory and monitor the quality of resources in their parks system, beginning with the vegetation and birdlife, but in 2007 expanding to include soils (Schmit et al., 2014). In 2005 the program established a 250 m grid across each of the 11 parks in the system. Sampling locations were selected by using generalized random-tessellation stratified survey (GRTS) (Stevens and Olsen, 2004). The GRTS approach was chosen over simple random sampling as GRTS creates a random sample that is spatially balanced, the locations are not clumped in a single part of the study area. Prior to plot setup, potential monitoring locations were visited to determine suitability for forest vegetation monitoring. A location was removed from consideration if it did not contain forest vegetation, was located on a road, waterway, maintained field, etc., or was on a slope greater than 30°, or was otherwise hazardous (Schmit et al., 2014). United States Forest

Service (USFS) criterion 1 was used to define the presence of forest. Criterion 1 states that the land area must be at least 10% stocked by trees of any size. Soil monitoring and sampling for our study was conducted on 418 of the established sampling sites during the summers of 2007, 2009-2012, and 2015-2017.

Field Plots and Sampling

Once a sampling site's central point marker was located using GPS coordinates and a metal detector, three 15 m long transects were established that radiated out from the central point at 120, 240, and 360 degrees (Figure 2). Wire stem flags were placed at the plot center point and at 4, 8 and 12 m along each of the three transects (total of 10 flags).

At a random location within 1 m of the center flag, a 1 m deep x 7.5 cm diameter bucket auger boring was made and the augered 10 cm soil increments laid carefully out in order and to scale on a plastic strip so that the horizons could be described and sampled. The horizons were delineated and described. Field descriptions included textural class and estimated percent clay (Thien, 1979) for each horizon. A Munsell color book was used to determine the hue, value and chroma for each horizon and identify redoximorphic features. Soil was collected (100 to 500 cm^3) from each horizon, placed in a labeled zip lock bag, returned to the lab, air-dried and sieved (< 2 mm) and stored for analysis. Later, soil C data on these samples was used to confirm appropriate delineation of O and A horizons, using 20% SOC content as the criteria distinguishing O from A horizons (Keys to Soil Taxonomy, 2014). Using this criterion, 15 samples originally designated as O horizons in the field were designated as A horizons because of too little C and three were redesignated from A horizon to O horizon because of greater than 20% SOC content.

Along each transect, at a random location within 1 m of each of the three 8 m transect flags, a cylinder (10 cm diameter x 15 cm long) made of a section of polyvinylchloride (PVC) pipe sharpened on one edge was hammered with a mallet into the top soil through the O horizon. The loose leaf litter was collected from inside each of these three cylinders, and composited together, placed in zip lock bags and returned to the lab for analysis. At a second random location within 1 m of the same three flags, the O horizon was carefully removed and a metal cylinder (7.5 cm diameter x 7.5 cm long) was pounded into the A horizon, using a second cylinder as a tool to receive the mallet blows until the upper edge of the first cylinder was just flush with the mineral soil surface. The cylinder was then excavated and the soil trimmed flush with a knife at both ends. The soil in the cylinder was then placed into a zip lock bag and transported back to the lab for determination of D_b.

At five random locations within the 707 m^2 plot, a metal cylinder (7.5 cm diameter x 7.5 cm long) was carefully pounded into the O horizon with a rubber mallet until it was flush with the organic material. The cylinder was then carefully excavated and any mineral material was carefully removed. The height of the organic material in the cylinder was measured and then the material was placed in a zip lock bag and transported to the lab for determination of D_b.

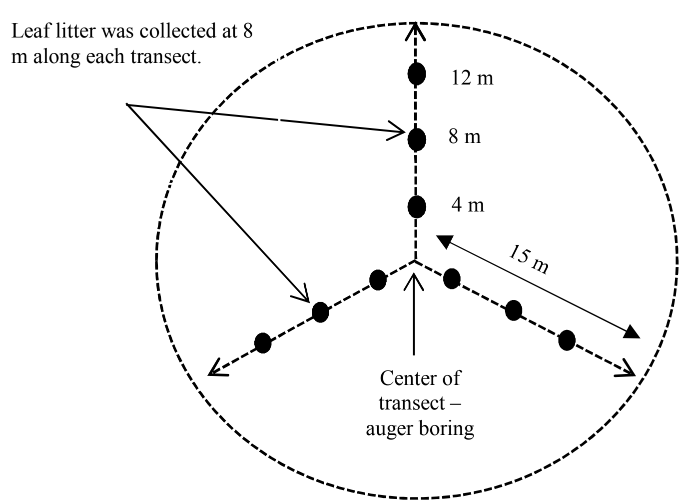


Figure 3.2 Layout of field plots. Five bulk density samples for the organic horizon were collected at random locations throughout the 707 m^2 circular plot at each site. Bulk density samples for the mineral horizons were collected along each transect at 4m, 8m and 12m from the center point.

Sample Handling and Preparation

Leaf litter samples were placed on a paper plate, the fresh weight recorded, and then air-dry for a minimum of seven days. After seven days, the sample air dry weigh was recorded before the soil was ground and passed through a 2mm sieve. The dried, ground and sieved samples were shipped to the University of Georgia Agricultural and Environmental Services Laboratories (AESL) Soil, Plant, and Water lab (SPW) for analysis of total organic carbon (TOC) by high temperature combustion using Combustion Analyzers, either Model Vario Max (Elementar, Langenselbold, Germany) and or Model TruMac (LECO, Saint Joseph, Michigan, USA).

Bulk density cores were placed on a paper plate, weighed (fresh weight) and then allowed to air dry for a minimum of seven days. Subsamples were taken from each core sample, placed in a pre-weighed beaker, weighed and then oven dried at 105^{o} C for 24 hr in a forced air oven. The subsamples were again weighed after being in the oven 24 hours and air-dried water content of the soil calculated. The weight of any coarse rock fragments was recorded.

Each mineral horizon sample was placed on a paper plate, weighed and then allowed to air dry for a minimum of seven days. Subsamples were taken from each soil horizon sample, as just described for D_b samples. The air-dried samples were then ground and sieved through a 2mm sieve. The dried, ground and sieved samples were shipped to the University of Georgia SPW lab for analysis of TOC as described above.

Carbon Calculations

The weighted average concentration (g C kg^{-1} soil) of C for each master horizon (O, A, B and C) was calculated. If sub-horizons were present, data for sub-horizons were merged to make 1 master horizon to allow for comparison between sites. Thus, Bt1, Bt2, Bt3 and BC horizon data for a given site would be merged into a single master B horizon value. For example, an 11 cm thick A horizon with 3.60% C from 0-11 cm depth and a 10 cm thick Ap horizon with 0.77% C from 11 – 21 cm depth, would be merged together into a master A horizon with a weighted average C concentration 2.26%:

$$\left(3.62\ x\ \frac{11}{21}\right) + \left(0.77\ x\ \frac{10}{21}\right) = 2.26\%\ C$$

These weighted average concentrations were used to characterize C stocks and concentrations by master horizon.

$$\text{Carbon stocks in a master horizon} = \frac{\text{mass C (g)}}{\text{mass soil (g)}} \text{x } D_b \frac{1x10^6 \text{ cm}^3}{\text{m}^3} \text{x thickness (m)} = \frac{\text{g C}}{\text{m}^2} \qquad \text{Eq. 1}$$

The soil series present at each site by comparing the auger soil profile description against the profile descriptions for the soil series listed in the mapping unit shown on Web Soil Survey (Soil Survey Staff, 2017). The "representative value" for the dry D_b value (in g cm^{-3}) for the B and C master horizons for that soil series listed in the NRCS SSURGO database was used for C stocks calculations. For calculating C stocks in all O horizons we used the mean D_b value (0.19 g cm^{-3}, standard deviation = 0.105, range = 0.058 to 0.583) measured for the organic horizons from 18 sites across Prince William Forest Park, and Greenbelt National Park.

Statistical Analysis

The design of this observational study was considered to be a completely randomized design with unequal replication. We tested the significance of the effect of soil order, physiographic region, parent material type, soil drainage class and rock type categories on the SOC stock (g m^{-2}) in the top meter of soil as the dependent variable using the generalized linear model (GLM) procedure in SigmaPlot (SigmaPlot, 2018). A similar unbalanced GLM was used to detect differences among soil master horizons for the C stocks in each horizon. When the F test for an effect was significant, means were separated using a post-hoc comparison with a pooled Fishers LSD. Categories with fewer than 2% of the sites (N< 9) were excluded from statistical comparisons. One site (CATO-0316) was considered to be an outlier and was removed from the GLM analysis because the mean SOC stock for this site was 10 standard deviations above the mean for all sites.

Results and Discussion

SOC Stocks and Distribution among Master Horizons

The weighted average concentrations of SOC in the O (excluding loose leaf litter), A, E, B and C master horizons were 296.9, 37.3, 10.7, 7.9 and 2.09 g C kg^{-1}, respectively (Table 1). The leaf litter (LL) had an average concentration of 406.4 g C kg^{-1} and the average amount of C per unit area is 0.45 ± 0.02 (SE unless otherwise noted) kg C m^{-2}. The mean total C in the upper 1 m in this study was 16.6 kg m^2.

Table 3.1 Mean soil organic carbon concentrations and stocks for each master horizon in the upper 1 m of soil sampled at 11 US National Park forests.

Horizon	Number of profiles (N)	Mean thickness	Weighted average C concentration (±SE)	Soil organic C stocks (±SE)	Mean percent of total soil profile C stocks
		m	g kg^{-1}	kg m^{-2}	%
O[a]	32	0.06	296.9 ± 16.56	3.19 ± 0.452	19.2
A	352	0.20	37.3 ± 1.67	4.99 ± 0.231	30.1
E	33	0.17	10.7 ± 1.06	2.09 ± 0.180	12.6
B	388	0.54	7.90 ± 0.49	4.75 ± 0.236	28.6
C	43	0.28	4.55 ±1.10	1.58 ± 0.333	9.5
Sum for 1 m total	848	1		16.6	100

[a] Excludes loose leaf litter.

In these forested soil profiles, 50.7% of the total OC in these forested soils is below the A horizon and 19.2% of the OC is in the organic horizons. The average thickness of the sampled portion of the C horizon is 0.28 m; however, it should be noted that many C horizons extended below the sampled 1 m of the soil profile. Furthermore, horizons which were described in the field to be buried A horizons were included with the B horizons. When researchers only sample the top 0.2 to 0.3 m they are severely underestimating the amount of OC stored in the soil. On average the B horizon was encountered at a depth of 0.37 m and it contained 4.75 ± 0.236 kg C m^{-2}. Our result of 50.7% of the total OC below the A horizon supports the findings of Batjes (1996), Harrison et al. (2011) and Jobbagy and Jackson (2000). If the average rooting depth for temperate evergreen and deciduous trees is 3.3 m (Canadell et al., 1996; Fox et al., 1982) then sampling just in the A horizon misses approximately 90% of the root zone, and according to our results, approximately half of the SOC in the top meter of soil.

By summing the SOC in all the horizons (Table 1), we calculate the mean SOC stock in the top meter of soil in our study area to be 16.6 kg C m^{-2}. A literature search found five published SOC stock estimates for temperate forest soils (Table 2) varying from 8.2 to 17.4 kg C m^{-2}. The mean value for the present study therefore falls near the higher end of the published estimates.

Table 3.2 Published estimates of temperature forest soils C densities and global stocks. Global C stocks for temperate forests calculated assuming 1.04E+13 m^{-2} of global land in temperate forests.

Carbon stocks, 0-1m	Global Temperate Forest Soil Carbon stocks, 0-1m	Reference
kg C m^{-2}	Pg C	
8.23	85.6	Pregitzer and Euskirchen, 2004
9.6	99.8	Dixon et al., 1994
12.2	127	Lal, 2005; cited Prentice, 2001
14.5[a]	151	Jobbagy and Jackson, 2000
16.6	173	This study
17.4[b]	181	Jobbagy and Jackson, 2000
13.1	136	Mean of six studies

[a] Temperate evergreen forest
[b] Temperate deciduous forest

Table 2 also lists estimates of global stocks of SOC in temperate forests as calculated by multiplying the SOC stock by the global land area of 10.4 million km^2 covered by temperate forests (Global Forest Atlas, 2019).

The calculated average global stock of SOC in the top meter of soil (136 Pg C) exceeds estimate (100 Pg C) published by Dixon et al. (1994) which is a commonly cited value in the literature (IPCC, 2000; Lal, 2005; Lal, 2004). Using the OC stock value determined in this study, the calculated global stock of SOC in temperate forests would be 173 Pg C. Given the variability encountered in our study within a limited geographic area covered mainly by deciduous forest, the 95% confidence interval for SOC was 16.0 to 17.2 kg m^{-2}. Therefore the 95% confidence interval for global temperate forest SOC stocks in the upper 1 m of soil based solely on the values determined in our study would range from 167 to 179 Pg C. This range is very similar to the value estimated by Jobbagy and Jackson (2000) for temperate deciduous forest (Table 2).

Comparison of SOC among Soil Orders

Out of the 418 sites, the number of sites with soils in the Inceptisols, Mollisols, Ultisols, Alfisols and Entisols soil order were 68, 6, 249, 90 and 3, respectively. Of these soil orders, only Mollisols are defined in term of soil organic carbon. That is, a mollic epipedon, which is a surface diagnostic horizon characteristic of the order, is by definition dark colored and contains at least 0.6% SOC. The occurrence of soils in the order Mollisols was not expected as they are typically formed in semi-arid to humid grasslands, not forested areas. The six sites that were determined to have Mollisols were located along the Chesapeake and Ohio Canal National Park and the soils belonged to families within the Fluventic Hapludolls subgroup, meaning they were simple humid region Mollisols associated with river sediments. The six sites were also located in forest clearings with few trees within the plot.

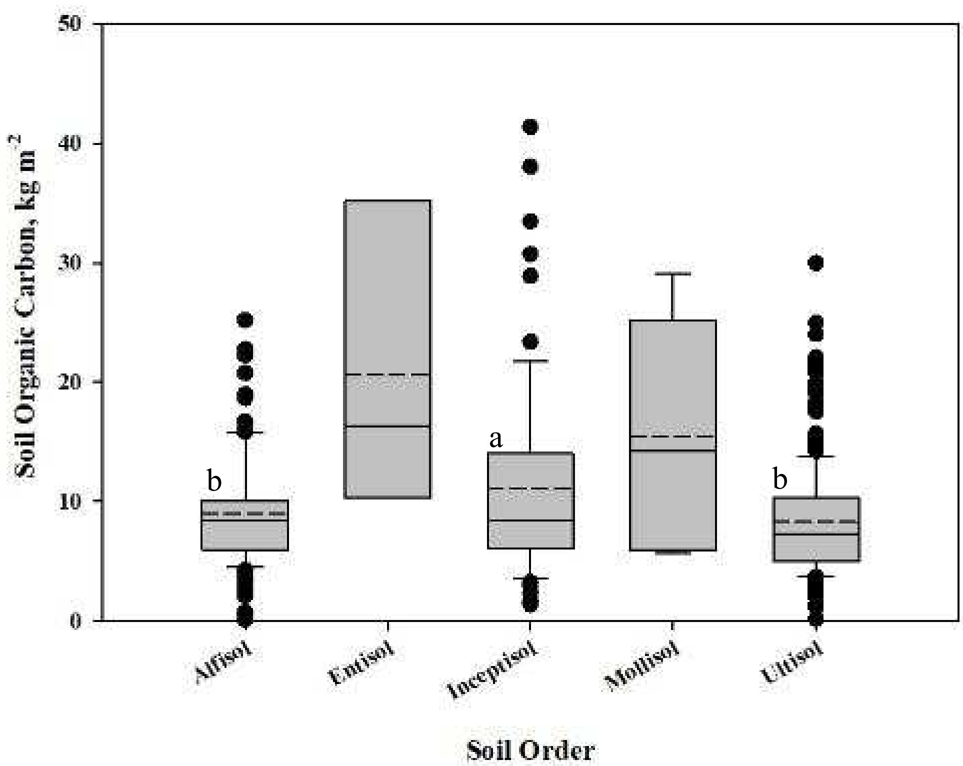


Figure 3.3 Box and whisker plots of SOC stocks in the top meter of soil by soil order. The box contains 50% of the values (the 2nd and 3rd quartiles). The dashed line inside the box indicates the LS mean. Fishers LSD was conducted to determine differences among groups Values with the same lower-case letter do not differ at P>0.05. Entisols (N=3) and Mollisols (N=6) were excluded from statistical comparison because they comprised < 2% of the sites.

Soil order significantly ($p \leq 0.001$) influenced the stocks of SOC in that the average amount of SOC in the upper m of soil was significantly greater for Inceptisols (N = 68, 11.08 ± 1.02 kg C m^{-2}) compared to the other two soil orders analyzed in the study (Alfisols N = 91, 8.97 ± 0.50 kg C m^{-2}; Ultisols N = 249, 8.30 ± 0.30 kg C m^{-2}) (Figure 3).

Comparison of SOC among Physiographic Provinces

Four physiographic provinces were encountered in this study: the Coastal Plain, the Piedmont, the Blue Ridge and the Ridge and Valley. The Coastal Plain is an area of low relief that is underlain by layers of clayey, silty, sandy and gravelly sediments in a wedge that increases in thickness toward the coast. The Piedmont is composed of hard, crystalline igneous and metamorphic rocks and extends from the inner edge of the Coastal Plain westward to Catoctin Mountain, the eastern boundary of the Blue Ridge province. The Blue Ridge exposes some of the oldest rocks in the region, with granitic gneiss over a billion years old (Southworth et al., 2000). The Ridge and Valley consists of folded Paleozoic sedimentary rock. Of the study sites, 70, 195, 57 and 36 were located in the Coastal Plain, Piedmont, Blue Ridge, and Ridge and Valley province, respectively. Alluvial soils on floodplains (N=58) were not considered to be in any of the physiographic provinces.

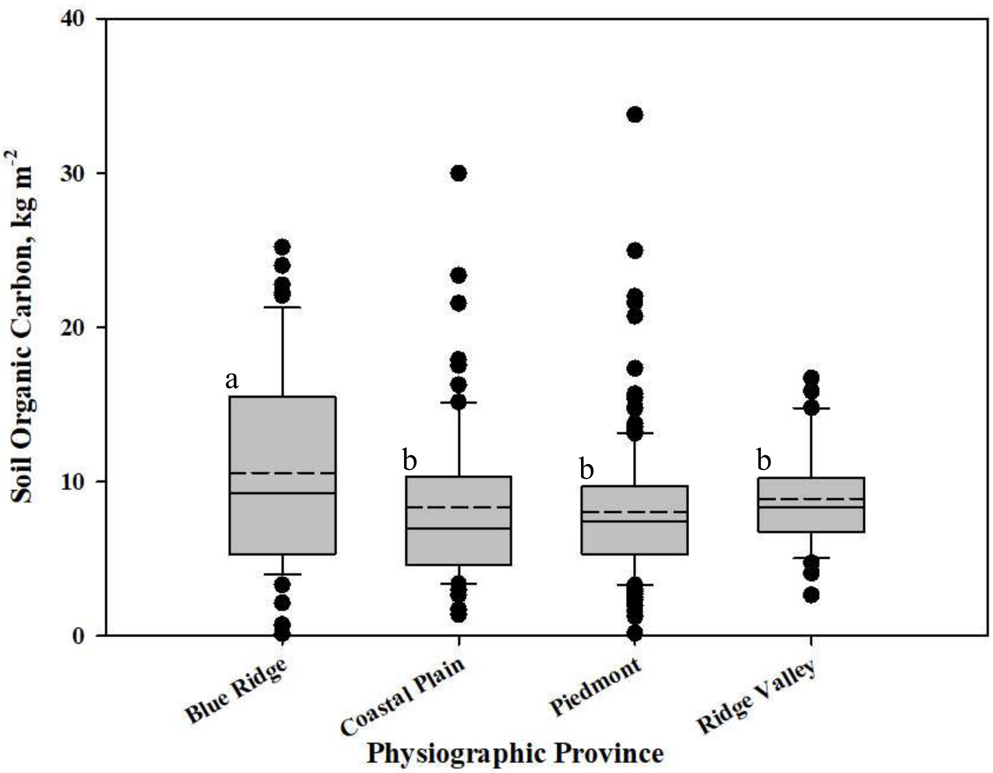
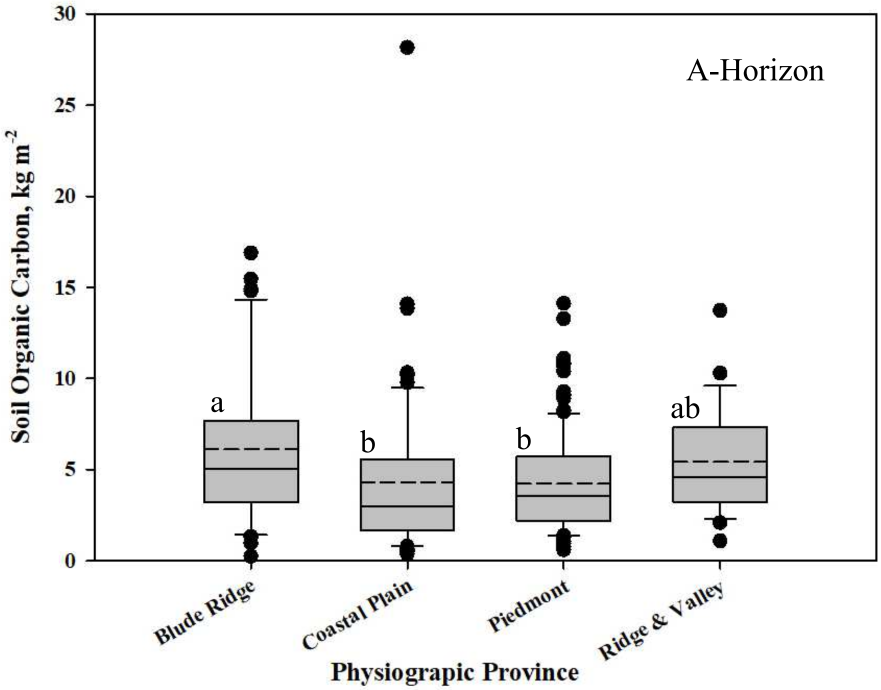


Figure 3.4 Box and whisker plots of SOC stocks in the top meter of soil for each physiographic province or land type in the study. The box contains 50% of the values (the 2nd and 3rd quartiles). The dashed line inside the box indicates the mean. Fishers LSD was conducted to determine differences among groups Values with the same lower-case letter do not differ at P>0.05.

The physiographic province significantly influenced the stocks of SOC in the upper meter of soil ($p \leq 0.001$). The Blue Ridge sites had significantly greater SOC than all the other regions in this study (10.55 ± 0.880 kg C m^{-2}) (Figure 4). Organic C stocks in the Ridge and Valley, Piedmont and Coastal Plain did not statistically differ.

The average depth of the auger boring in the Blue Ridge sites was only 0.43 m because many soils were too rocky to auger more deeply. At only three of the 58 Blue Ridge site was it possible to sample with the bucket auger to 1 m. Since an unknown amount of SOC may have been stored in the soil between rocky fragments, our estimate of SOC stocks for the upper 1 m in the Blue Ridge is probably an under-estimate. When just the A master horizons were considered, the results were less variable and the stocks of SOC in the Blue Ridge, floodplain, Ridge and Valley were significantly greater than the rest of the regions sampled. When the B master horizons were considered, the stock of SOC in the Blue Ridge and floodplain were significantly greater than the rest of the regions sampled. The average thickness of the A and B horizons in the Blue Ridge was 0.14 m and 0.36 m, respectively.

The differences in SOC stocks between the provinces could be related to the age of the forests. In the NCRN, nearly all land was cleared of forests and farmed within the past 200 years.



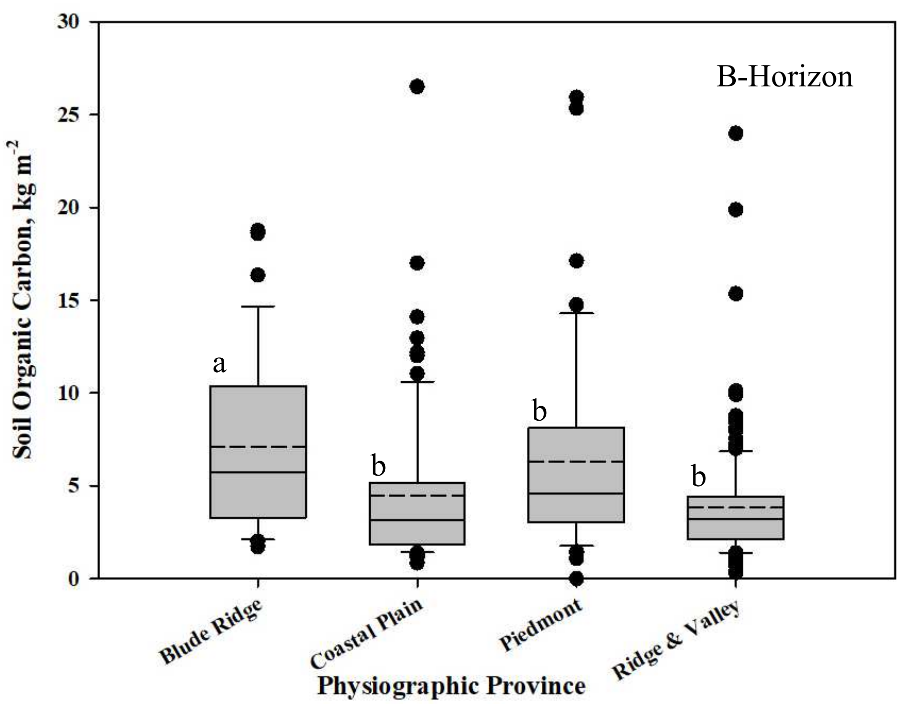


Figure 3.5 Box and whisker plots of SOC stocks by physiographic province or land type in (upper) the A horizons and (lower) the B horizons. The box contains 50% of the values (the 2nd and 3rd quartiles). The dash line inside the box indicates the mean. Fishers LSD was conducted to determine differences among groups.

Comparison of SOC among Soils Formed from Different Parent Material Types

In this study, four different PM types were encountered; alluvium, colluvium, residuum, and marine sediment. Alluvium is loose, unconsolidated soil or sediment that has been eroded and redeposited by water in a non-marine setting. There was a total of 140 sites in which the soils developed from alluvial material. Colluvium is loose, unconsolidated sediments that have been deposited at the base of hillslopes through mass wasting (falls, slides, creeps and flows) and 36 sites had soils developed from colluvial material. Residuum is material that forms (weathers) in place and 172 sites that were visited in this study had soil parent material formed in place. For statistical analysis, residuum was further divided and grouped by mafic and felsic rocks, 45 and 127 respectively. Marine sediment is ocean deposited material and 65 sites (all in the Coastal Plain region) had soils developed from ocean deposited material. Parent material did not have a significant effect (p = 0.682) on SOC stocks (Figure 6).

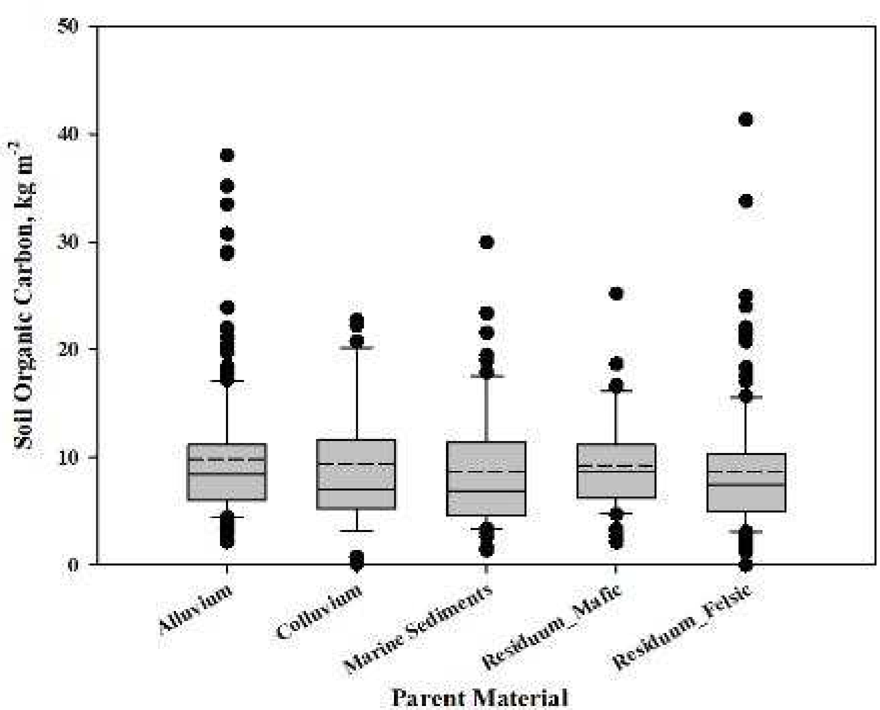


Figure 3.6 Box and whisker plots of SOC stocks in the upper meter by soil parent material type. The box contains 50% of the values (the 2nd and 3rd quartiles). The dashed line inside the box indicates the mean. Fishers LSD was conducted to determine differences among groups. No significant difference among parent material types were found by ANOVA.

Since PM did not have a significant effect on the distribution and storage of OC in these forested parks, then PM type may not need to be taken into consideration when calculating regional SOC estimates in the Mid-Atlantic region.

Comparison of SOC among Soil Drainage Classes

In this study, seven soil drainage classes were encountered, ranging from excessively drained to very poorly drained. Drainage classes refer to the frequency and duration of wet periods during soil formation (Soil Survey Staff, 1993). Of the study sites, 9, 5, 256, 84, 7, 54 and 2 were excessively drained, somewhat excessively drained, well drained, moderately well drained, somewhat poorly drained, poorly drained and very poorly drained, respectively. Due to the following drainage classes having low n values; excessively well drained, somewhat excessively drained, very poorly drained and somewhat poorly drained, statistical analysis was conducted with three drainage classes, well drained, moderately well drained and poorly drained. The “well drained” class was composed of excessively well drained, somewhat excessively drained and well drained, n = 266. The “poorly drained” class was composed of somewhat poorly drained, poorly drained and very poorly drained. n = 54.

A typical mineral soil generally consists of 50% solids, 25% water and 25% air. As the soil becomes increasingly saturated, the pore space occupied with oxygen decreases and oxygen diffusion is approximately 10000x slower through water. Under anaerobic conditions, OM decomposition slows down, and SOM tends to increase. Thus, we expect SOC in the top meter of soil to be higher in poorly drained, and very poorly drained soils.

The soil drainage class did significantly influence the stocks of SOC in the upper meter of soil ($p < 0.001$). Poorly drained soils contained significantly more SOC in the top meter of soil (12.14 ± 0.92) (Figure 7). Well drained and moderately well drained soils did not differ at $P > 0.05$, 8.87 ± 0.32 and 7.68 ± 0.46, respectively.

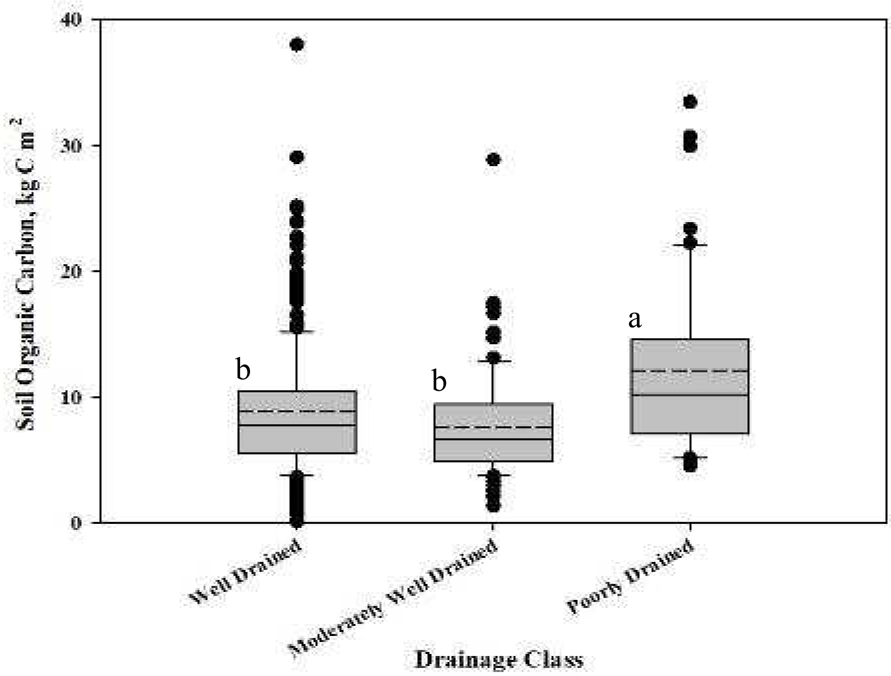


Figure 3.7 Box and whisker plots of SOC stocks in the upper meter by soil drainage class. The box contains 50% of the values (the 2nd and 3rd quartiles). The dashed line inside the box indicates the mean. Fishers LSD was conducted to determine differences among groups. Values with the same lower-case letter do not differ at P>0.05.

Comparison of SOC among Soils Formed form Different Rock Types

In this study, 5 different rocks or combinations of rocks were encountered. Rocks which formed by the cooling and consolidation of magma (igneous rocks) include basalt, and granite. Rocks which formed by the accumulation of sediments derived from the weathering of previous existing rocks (sedimentary rocks) include sandstone, shale, limestone and conglomerate. Metamorphic rocks, which have changed from their original igneous, sedimentary, or earlier metamorphic forms due to high heat and pressure, include quartzite, slate, gneiss, schist, greenstone and phyllite.

The stocks of SOC in the upper 1 m was significantly affected by rock material type ($p \leq 0.001$). Figure 8 shows that the mean SOC in g m^{-2} for soils formed from schist (8.10 ± 0.38 kg C m^{-2}) was significantly lower than gneiss (13.970 ± 6.877 kg C m^{-2}), and shale, siltstone, sandstone, and slate (11.645 ± 0.908 kg C m^{-2}). When the rocks were grouped into igneous, sedimentary and metamorphic, no difference in SOC stocks in the top meter of soil among these three rock types were detected ($p = 0.47$, table 3).

Table 3.3 There were no significant differences among mean by rock type for SOC stocks in the upper 1 meter of the soil profile.

Rock Type	Mean	SE	n
Igneous	13182a	5309	3
Metamorphic	11427a	610	227
Sedimentary	12834a	997	85

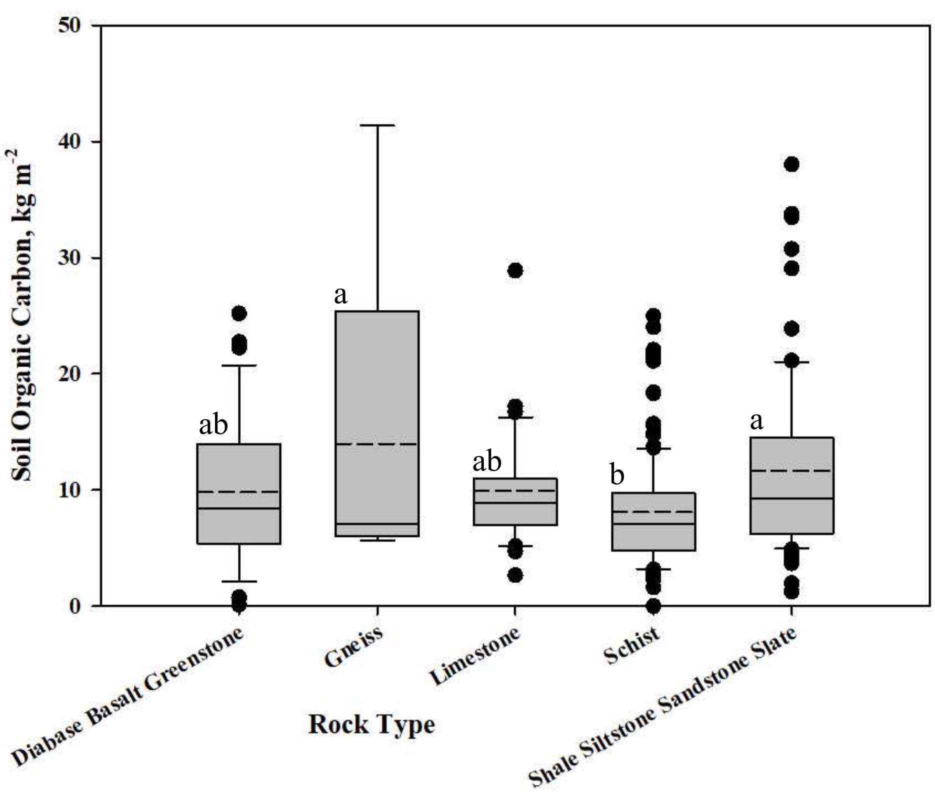


Figure 3.8 Mean mass of SOC per unit area for each parent material rock type. The dashed line inside the box indicates the mean. Fishers LSD was conducted to determine differences among groups. Values with the same lower-case letter do not differ at P>0.05.

Conclusion

This study adds to a growing body of research that demonstrates the importance of sampling soils deeper than the 0.3 m currently used by the IPCC and GSP in calculating global SOC stocks. Although in our study we sampled to 1 m depth, we suggest that the standard depth for SOC studies in mineral soils be based on the biome so as to include 90% of the mean natural vegetation rooting depth. For example, temperate forest soils would be sampled to 1.2 m.

Future studies in the NCRN should resample the permanent forest plots used in this study to determine rates of change in the stocks of SOC. It may also be useful for future studies to include samples from 1 to 2 m deep where possible to evaluate the contribution of even deeper soil layers to forest soil C stocks. Furthermore, it would be useful for future research to couple SOC stock data with data on forest growth and aboveground biomass. It is important that SOC stocks be accurately determined if temperate forests are too be managed as C sinks and changes in SOC stock are to be used to offset anthropogenic C emissions.

Appendix A

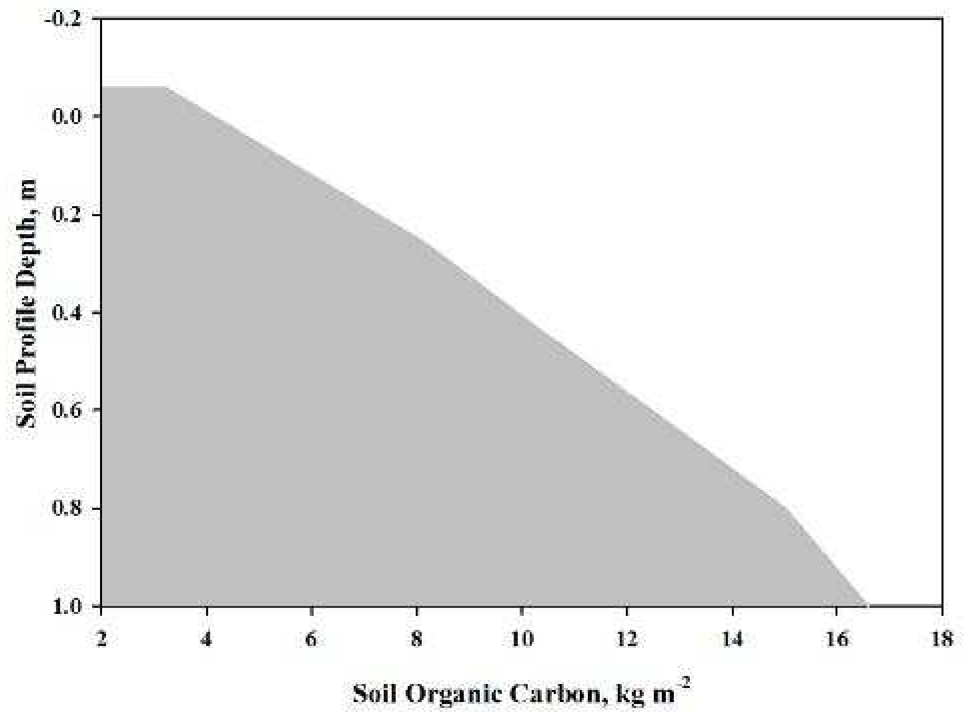


Figure S1 Cumulative soil organic carbon stocks (kg m^{-2}) versus depth (m) in the soil profile.

Table S1 Park units with the number of sites visited each year.

Park	PRWI	ROCR	GRBE	CATO	CHOH	GWMP	HAFE	MANA	MONO	NACE	WOTR	ANTI
Years	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**	**#Sites**
2007	12	2	4	6	9	9	2	6	0	10	0	2
2009	11	5	0	0	5	4	0	2	1	4	0	0
2010	16	0	3	7	9	1	2	6	2	5	1	2
2011	17	0	2	7	2	3	0	0	4	5	3	1
2012	16	6	1	5	15	9	12	5	3	2	0	1
2015	10	3	5	3	5	1	2	0	3	11	2	3
2016	4	3	1	5	11	1	3	1	4	5	0	2
2017	21	0	3	10	6	0	1	0	1	8	0	2
Total	145	19	19	43	62	28	22	18	15	50	6	13

PRWI - Prince William Forest Park
ROCR - Rock Creek National Park
GRBE - Greenbelt National Park
CATO - Catoctin Mountain Park
CHOH - Chesapeake & Ohio Canal National Historical Park
GWMP - George Washington Memorial Parkway
HAFE - Harpers Ferry National Historical Park
MANA - Manassas National Battlefield Park
MONO - Monocacy National Battlefield
NACE - National Capital Parks – East
WOTR - Wolf Trap
ANTI - Antietam National Battlefield

Table S2 ANOVA results, LS mean table and the SigmaPlot output for matrix pairwise comparisons and Fishers LSD test for soil order and average total OC in the upper 1 meter of the soil profile.

Source	**Sum-of-Squares**	**df**	**Mean-Square**	**F-ratio**	**P**
Soil Order	414.889	2	207.444	6.915	0.001
Error	12150.091	405	30.000		

Soil Order	**LS Mean**	**SE**	**n**
Alfisol (1)	8.973	0.501	91
Entisol	20.597	7.487	3
Inceptisol (2)	11.081	1.019	68
Mollisol	15.492	4.110	6
Ultisol (3)	8.296	0.295	249

Matrix of pairwise mean differences			
	1	**2**	**3**
1	0		
2	2.108	0	
3	-0.677	-2.785	0

Fisher's Least-Significant-Difference Test			
	1	**2**	**3**
1	1		
2	0.017	1	
3	0.314	<0.001	1

Table S3 ANOVA results, LS mean table and the SigmaPlot output for matrix pairwise comparisons and Fishers LSD test for physiographic provinces and average total OC in the upper 1 meter of the soil profile.

Source	Sum-of-Squares	df	Mean-Square	F-ratio	P
Province	288.350	3	96.117	4.071	0.007
Error	8380.755	355	23.608		

Province	LS Mean	SE	n
Blue Ridge	10.553	0.880	57
Coastal Plain	8.333	0.632	70
Piedmont	8.064	0.305	195
Ridge & Valley	8.876	0.581	36

Matrix of pairwise mean differences

	1	2	3	4
1	0			
2	-2.22	0		
3	-2.489	-0.269	0	
4	-1.677	0.543	0.812	0

Fisher's Least-Significant-Difference Test

	1	2	3	4
1	1			
2	0.011	1		
3	<0.001	0.655	1	
4	0.106	0.587	0.338	1

Table S4 ANOVA results, LS mean table for parent material and average total OC in the upper 1 meter of the soil profile from SigmaPlot.

Source	**Sum-of-Squares**	**df**	**Mean-Square**	**F-ratio**	**P**
Parent Material	98.203	4	24.551	0.690	0.599
Error	14665.767	412	35.597		

Parent Material	**LS Mean**	**SE**	**n**
Alluvium	9.79	0.542	140
Colluvium	9.394	1.018	36
Marine Sediment	8.650	0.679	69
Residuum_Mafic	9.306	0.674	45
Residuum_Felsic	8.740	0.535	45

Table S5 ANOVA results, LS mean table and the SigmaPlot output for matrix pairwise comparisons and Fishers LSD test for soil drainage class and average total OC in the upper 1 meter of the soil profile.

Source	**Sum-of-Squares**	**df**	**Mean-Square**	**F-ratio**	**P**
Soil Drainage Class	681.373	2	340.686	12.258	<0.001
Error	11145.002	401	27.79		

Drainage Class	**LS Mean**	**SE**	**n**
Well Drained	8.870	0.321	266
Moderately Well Drained	7.679	0.457	84
Poorly Drained	12.138	0.924	54

Matrix of pairwise mean differences

	1	**2**	**3**
1	0		
2	-1.297	0	
3	1.547	1.808	0

Fisher's Least-Significant-Difference Test

	1	**2**	**3**
1	1		
2	0.072	1	
3	<0.001	<0.001	1

Table S6 ANOVA results, LS mean table and the SigmaPlot output for matrix pairwise comparisons and Fishers LSD test for rock material and average total OC in the upper 1 meter of the soil profile.

Source	**Sum-of-Squares**	**df**	**Mean-Square**	**F-ratio**	**P**
Rock Material	728.149	4	182.037	4.996	<0.001
Error	10602.660	291	36.435		

Rock Material	**LS Mean**	**SE**	**n**
Diabase Basalt Greenstone	9.812	1.038	39
Gneiss	13.970	6.877	5
Limestone	9.929	0.843	34
Schist	8.098	0.380	146
Shale, Siltstone, Sandstone, Slate	11.645	0.908	72

Matrix of pairwise mean differences

	1	**2**	**3**	**4**	**5**
1	0				
2	4.158	0			
3	0.117	-4.041	0		
4	-1.714	-5.872	-1.831	0	
5	1.833	-2.325	1.716	3.547	0

Fisher's Least-Significant-Difference Test

	1	**2**	**3**	**4**	**5**
1	1				
2	0.148	1			
3	0.934	0.163	1		
4	0.116	0.033	0.112	1	
5	0.128	0.406	0.173	<0.001	1

Soil Profiles

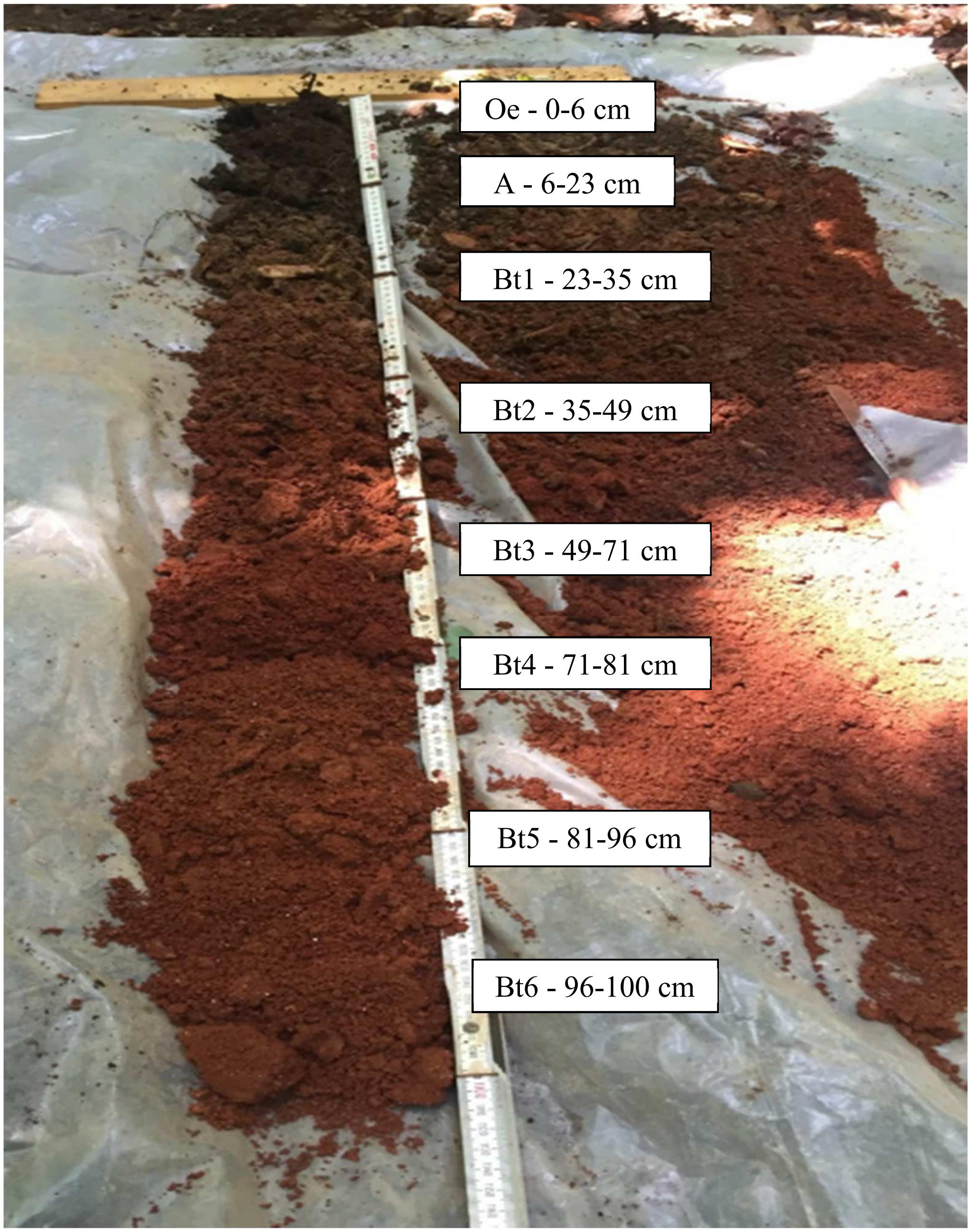


Figure S2 NPS Site GWMP-0062 profile, soil order: Ultisol, soil series: Brinklow. Taken 6-16-2015

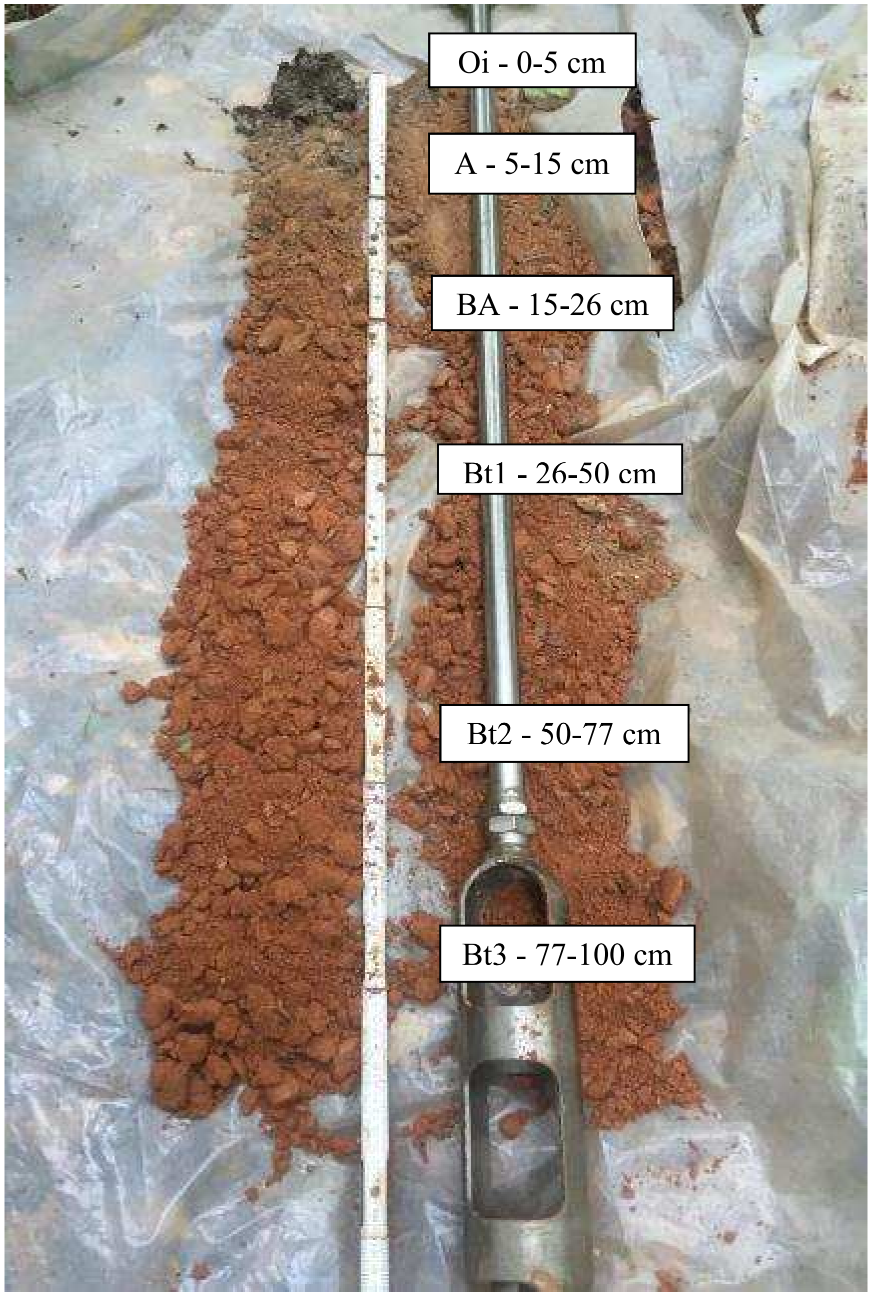


Figure S3 NPS Site PRWI-0463 profile, soil order: Ultisol, soil series: Glenelg. Taken 6-19-2015

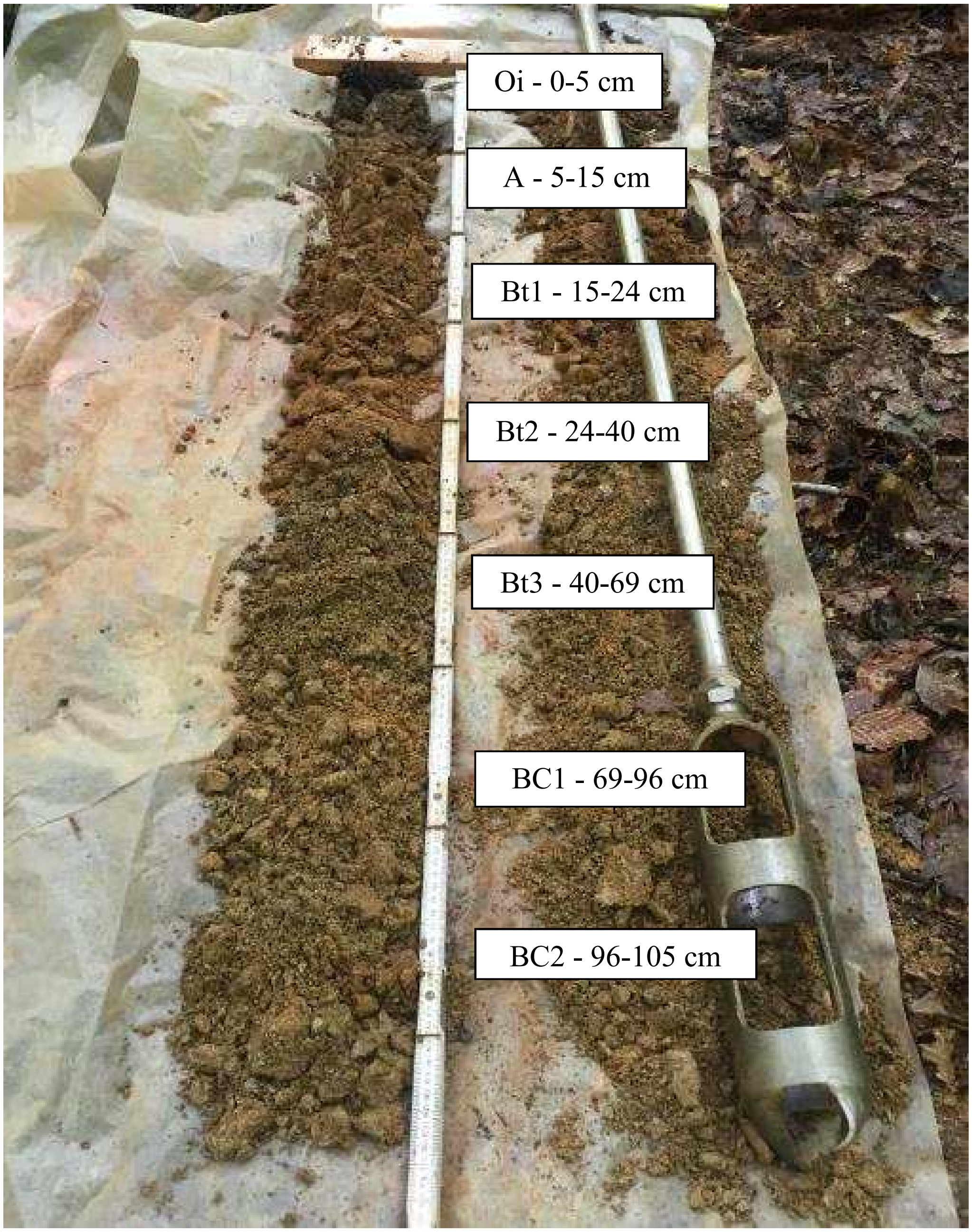


Figure S4 NPS Site PRWI-0435 profile, soil order: Ultisol, soil series: Meadowville. Taken 7-7-2015

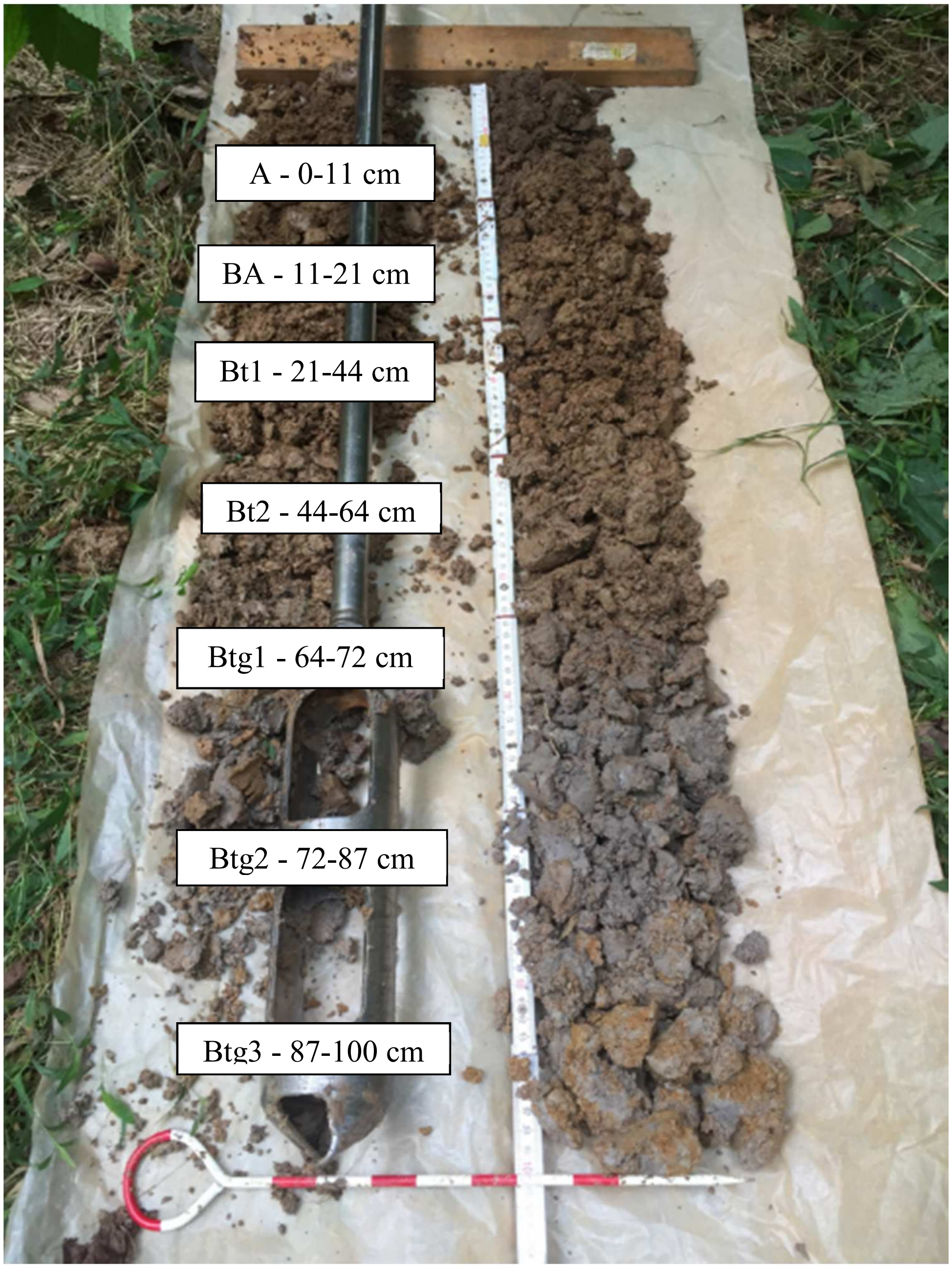


Figure S5 NPS Site NACE-0032 profile, soil order: Inceptisol, soil series: Hatboro. Taken 7-21-2015

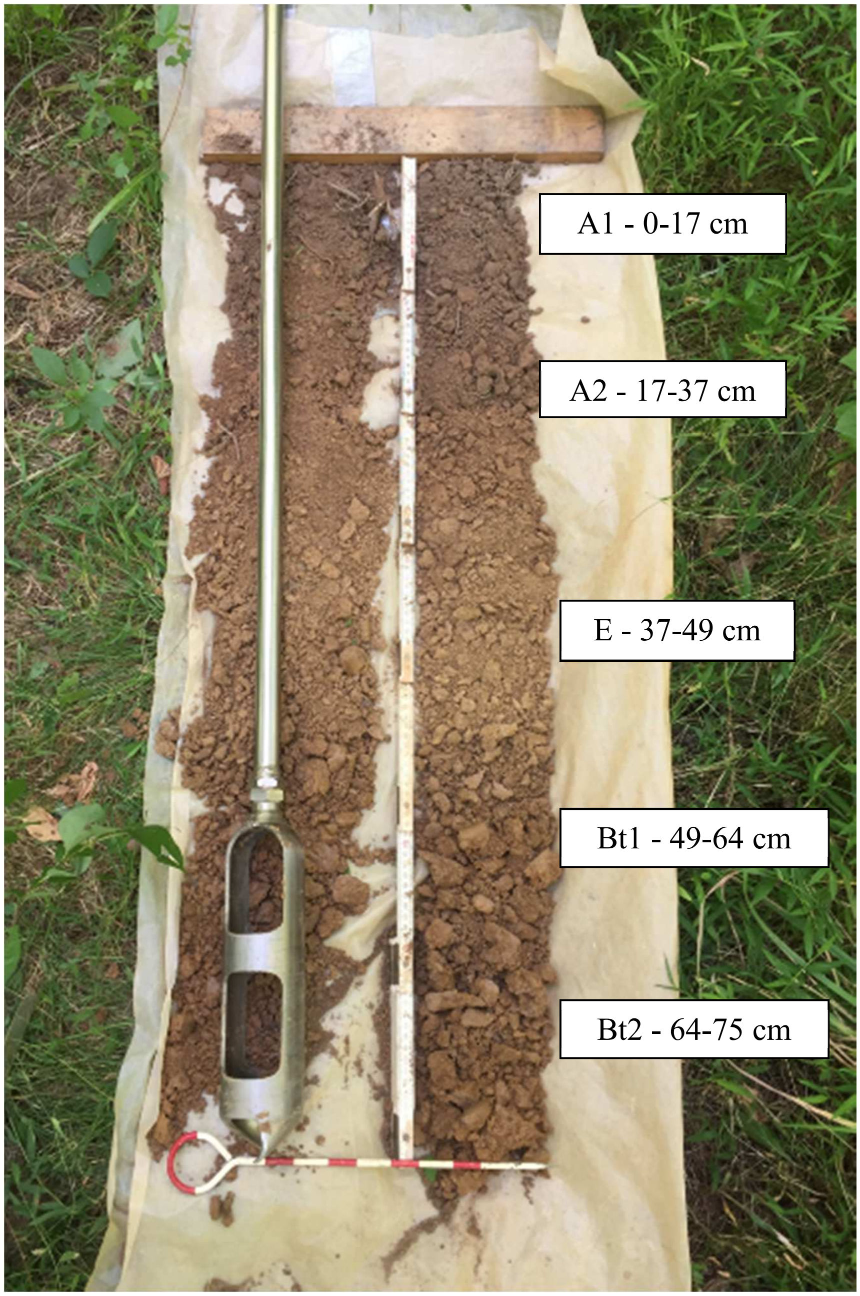


Figure S6 NPS Site CHOH-0015 profile, soil order: Ultisol, soil series: Bigpool. Taken 8-13-2015

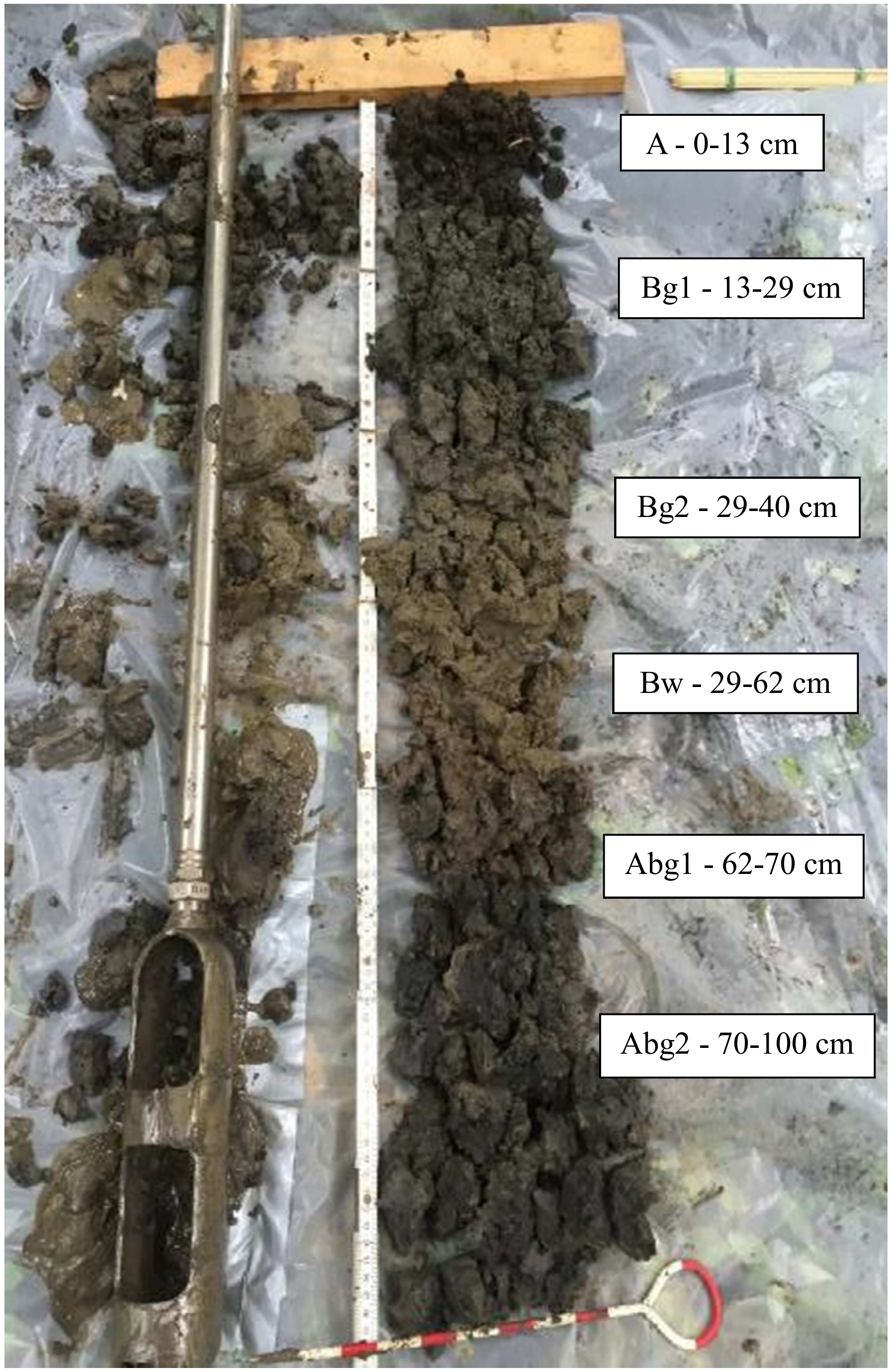


Figure S7 NPS Site ROCR-0079 profile, soil order: Inceptisol, soil series: Manor. Taken 6-3-2016

Figure S8 NPS Site CHOH-1063 profile, soil order: Inceptisol, soil series: Lindside. Taken 6-22-2016

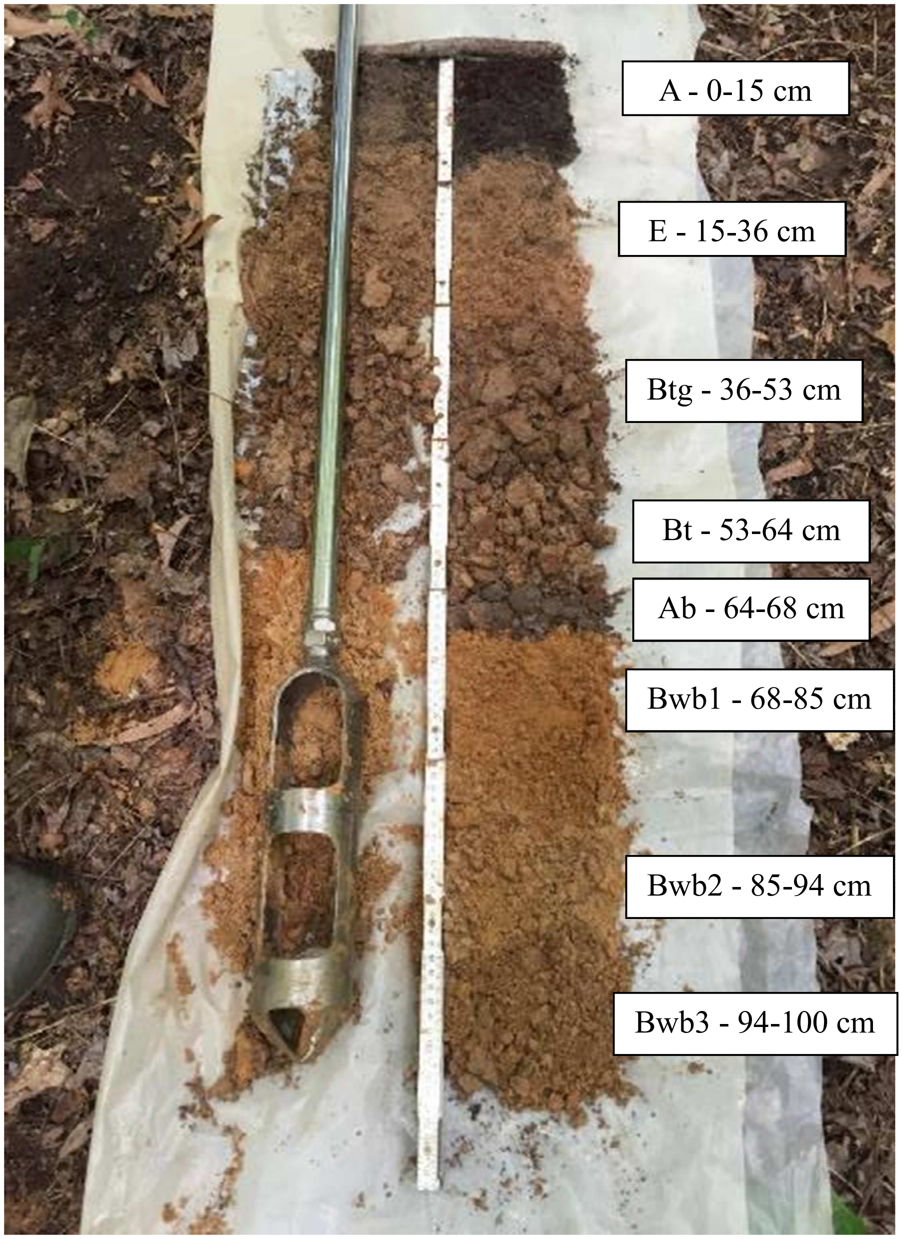


Figure S9 NPS Site NACE-0174 profile, soil order: Ultisol, soil series: Fallsington. Taken 7-1-2016

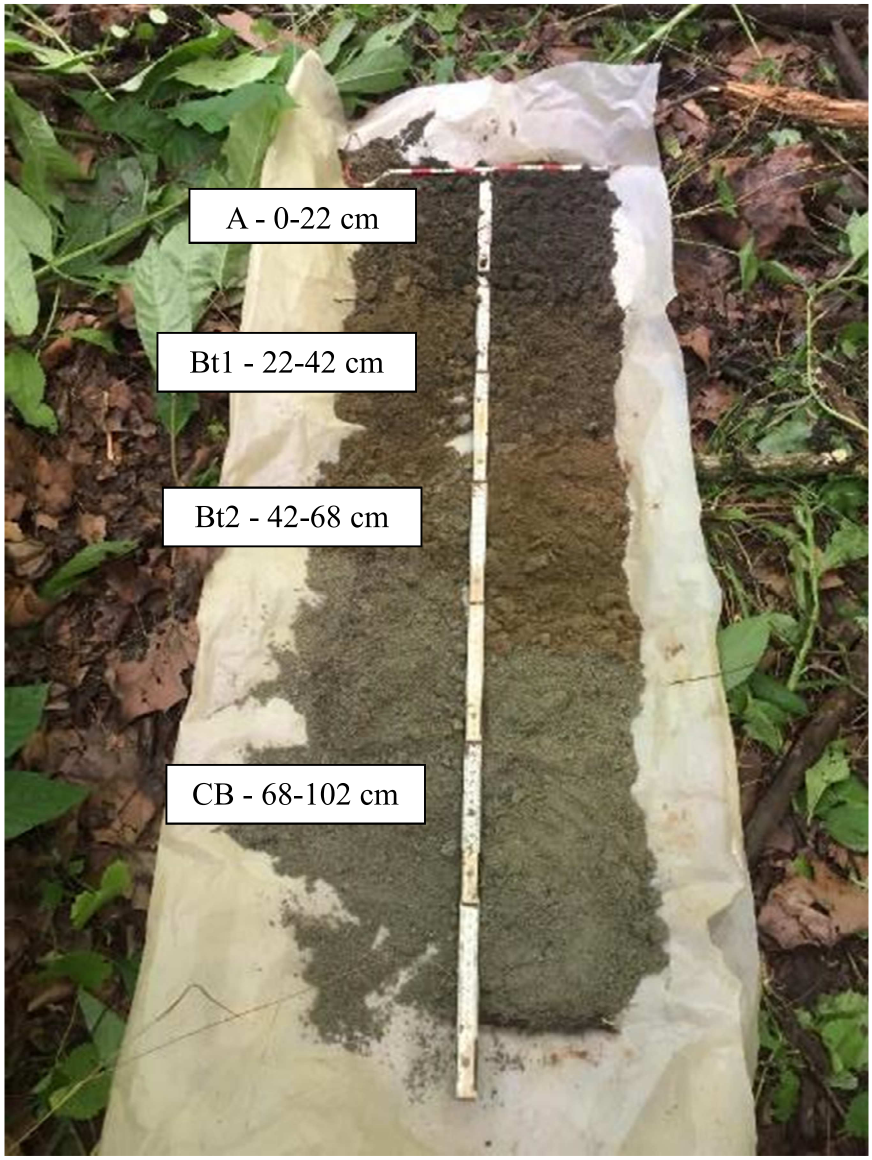


Figure S10 NPS Site CHOH-0262 profile, soil order: Alfisol, soil series: Ryder. Taken 8-2-2016

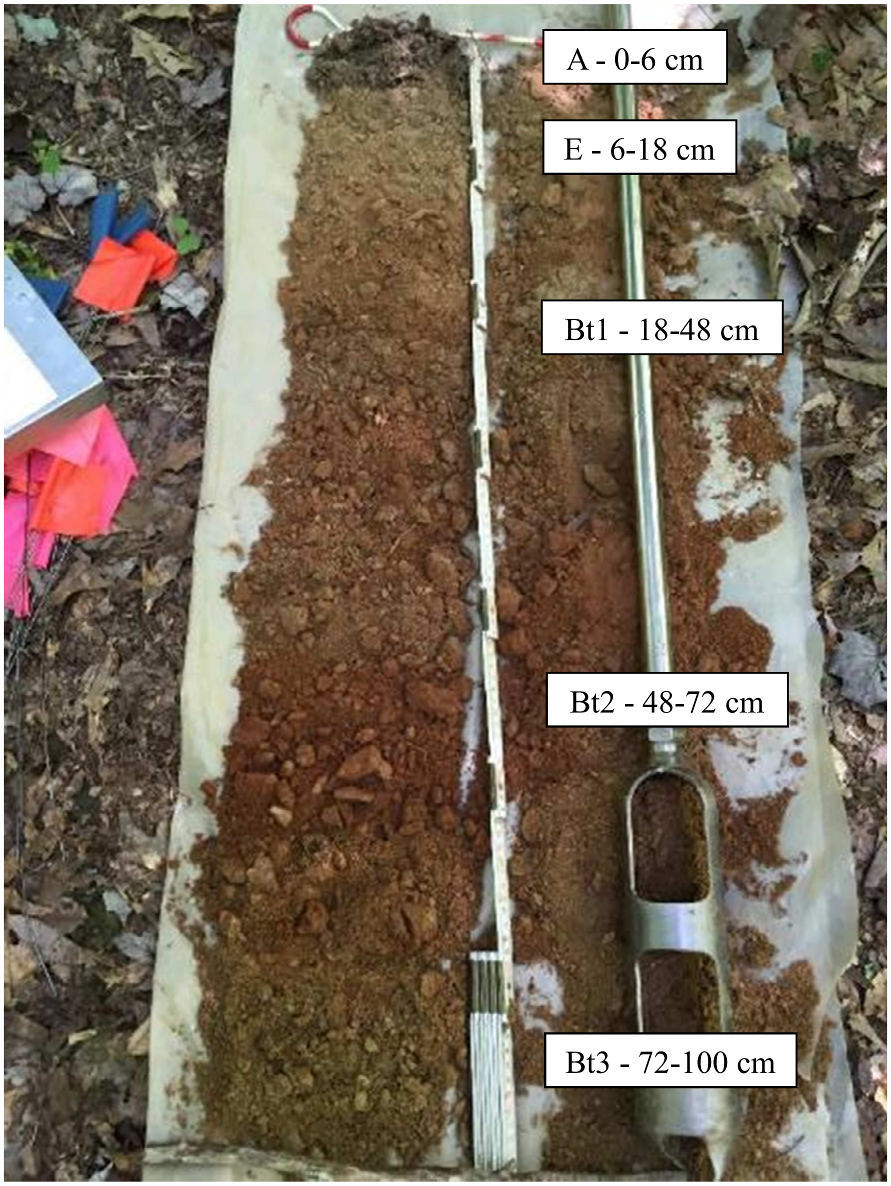


Figure S11 NPS Site PRWI-00494 profile, soil order: Ultisol, soil series: Elsinboro. Taken 8-11-2016

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