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**LITHOLOGICAL CONTROLS ON SOIL PROPERTIES OF TEMPERATE FOREST
ECOSYSTEMS IN CENTRAL PENNSYLVANIA**

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Ecology

by

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ABSTRACT

Shale and sandstone are the most common lithologies of the forested ridges throughout the Appalachian Mountains. The overall goal of this thesis was to determine whether these two rock types impart distinct biogeochemical properties to soils and plants. The effects of rock type (lithology) on soil gas concentration, nutrient concentration and nutrient limitation were studied in the Ridge and Valley province of central Pennsylvania. To increase understanding of lithological controls on soil gases (Chapter 1), we monitored the depth distribution of soil CO₂ and O₂ concentrations in central Pennsylvania in two watersheds on different lithologies. We deployed gas monitoring instrumentation on two catena transects that included four topographical positions, one located on sandstone and the other on shale. As expected, with increasing soil depth O₂ concentrations decreased while pCO₂ increased. CO₂ and O₂ concentrations varied more with topographical position than with lithology, as the valley floor positions in both catenas had the highest pCO₂ for a given depth. Both manual sampling from gas access tubes throughout the soil profile and continuous sampling by buried sensors documented these patterns. Adjacent forests underlain by shale and sandstone lithologies are prevalent throughout the Appalachian Mountains and may have differences in nutrient concentrations and limitation due to the lithologies and subsequent weathering. Nutrient limitation in temperate forest ecosystems often regulates plant productivity, and contemporary conceptual models emphasize nitrogen (N) as the main limiting nutrient. However, with increased global fossil fuel emissions and subsequent deposition of nitrogen, this assumption may not hold. In ecosystems that are receiving high N inputs, the availability of phosphorus (P) and cations, such as calcium (Ca) and magnesium (Mg), may become a key determinant of plant growth. In many conceptual models, plant-soil interactions are depicted; however, lithology is often not incorporated. We use five sites located on shale lithology and five of sandstone lithology to investigate nutrient pools in the mineral soil and the foliage of two tree species (Chapter 2). Our results show that shale and sandstone weather to form different nutrient availability signatures, with higher availability of most rock-derived nutrients on shale. However, extractable P and inorganic N concentrations were higher in the sandstone-derived soils. Furthermore, trees grown on the sandstone sites had higher foliar P

concentrations and lower P resorption at senescence. These results suggest that relative to shale, soils developing on sandstone ridges have more P available in soil and less P limitation to plants, despite lower P concentrations in the underlying rock. We hypothesize that higher P availability on sandstone ridges is not from *in situ* weathering of sandstone, but rather, a possible result of periglacial loess deposits. In conclusion, our studies showed that 1) lower landscape positions have more soil CO₂ and could have higher carbonic acid weathering than other landscape positions and 2) sandstone-derived soils have greater concentrations of extractable N and P, which may be the result of higher deposition inputs (in the case of N) or historical loess (in the case of P), than the cation rich shale.

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LITHOLOGICAL CONTROLS ON SOIL PROPERTIES OF TEMPERATE FOREST ECOSYSTEMS IN CENTRAL PENNSYLVANIA

Contemporary models of forest nutrient cycles depict strong interactions among bedrock, soils, and plants. However, there is still much to learn about how bedrock, hereafter lithology, affects nutrient availability in soils. Lithology can affect nutrient cycles that connect soil and biota by directly providing soil nutrients via weathering (both nutrient concentration and rate of release) (Flinn et al. 2009; Hahm et al. 2014; Turrin et al. 2014). Lithology can also indirectly drive other soil properties (i.e. porosity and structure) as a parent material (Cline, 1977; Hartmink & Bockheim, 2013). The overarching goal of my research is to compare the nutrient availability in two rock types with field measurements of the soil and aboveground biota. Field studies like this will help to inform development of future nutrient cycling models.

Lithology has been popularly recognized as a factor of soil formation since Hans Jenny's *Factors of Soil Formation* was published in 1941; however, extensive measurements of bedrock chemistry did not begin until many years later (Jenny, 1994). The mineral composition of lithology affects soil nutrient pools as weathering releases chemical components and nutrients to the soil solution (Webber & Jellema, 1965; Neff et al. 2006; Morford, Houlton, & Dahlgren, 2011). Microbial and root activity accelerate weathering by producing CO₂ and organic acids, linking lithology, soils and microbiota (Welch & Ullman, 1993; Berner, 1997; Drever & Stillings, 1997; Hasenmueller et al. 2015). The connection between bedrock chemistry, soil nutrients, and microbiota is very explicit as the microbiota and macrobiota, along with physical and chemical reactions, weather bedrock to produce soil horizons (Goldich, 1938).

In this study, we focused on shale and sandstone lithologies. Shale is a finely stratified sedimentary rock that forms from consolidated mud or clay. In particular, our sites were located on Silurian Rose Hill Formation shale (Berg, Miles, & Kuchinski, 1980) that compositionally consists of quartz, illite, chlorite, vermiculitized chlorite, Fe oxides, and minor feldspar (Jin et al. 2010). Sandstone is

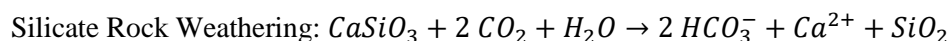
also a sedimentary rock, consisting of sand or quartz grains cemented together. Our sites were located on the Tuscarora Formation, which is nearly pure quartz sandstone with minor interbedded shales (Brantley et al. 2016). Rose Hill Shale and Tuscarora Sandstone differ greatly in their chemical composition (Table 1) as the shale lithology has a wide range of clay and silicate layers and the sandstone is mainly quartz. Both sandstone and shale have been compared to other lithology types in varying ecosystems (Skidmore et al. 2005; Flinn et al. 2009; Hahm et al. 2014; Turrin et al. 2014). However, this study will compare the lithology types in close proximity that experience a similar climate.

Table 1. Parent rock composition of the two lithologies used in this study. Rose Hill Shale data are from Jin et al., (2010), and represent the average of 12 samples at the Shale Hills catchment. Tuscarora Sandstone data are from Brantley et al. (2016), and represent the average of 5 samples from the soil pits in the Garner Run Catchment.

Lithology	P (%)	Ca (%)	K (%)	Mg (%)
Rose Hill Shale (Jin et al. 2010)	0.05	0.29	3.59	1.03
Tuscarora Sandstone (Brantley et al. 2016)	0.01	0.01	0.01	0.01

Strong connections also exist among lithology, soil and plant life (Searcy, Wilson, & Fownes, 2003; Pausas & Carreras, 2012). Lithological differences have been shown to change growth of particular plant species. For example, for Norway spruce, alkaline lithology leads to increased growth due to increased content of exchangeable calcium and magnesium compared to non-alkaline lithology (Vestin et al. 2013). Plants also play a role in weathering via roots exudates and symbiotic relationships with mycorrhizal fungi (Landeweert et al. 2001). Research also showed that lithological chemical composition, specifically basalt and arkose, produced drastically different soil nutrient pools and soil depths, promoting higher plant species diversity on basalt lithology than other lithologies, particularly sandstone (Searcy et al. 2003). Other research has used modeling to investigate temperature, moisture, and lithology as parameters to describe species richness, with lithology explaining most of the variation of the plant species in their model of forest ecosystems. This research was limited by the parameters taken into consideration when building their forest ecosystem (Pausas & Carreras, 2012). Even at the landscape

scale, lithology can affect tree canopy cover and primary production and therefore influence mountain ecosystems and landscape evolution (Hahm et al. 2014). Lithology has drastic impacts on many aspects of the ecosystem and may be important to include in conceptual and numerical models of nutrient cycles. The nutrient availability in the soil profile due to weathering arises from integrated effects of weathering during soil formation. One of the key weathering processes is acid weathering by soil CO₂, as shown in the reaction below:



This process exhibits the strong link between biota and soil formation. Biota produce CO₂ that generates carbonic acid in soil solutions. Acidic soil solutions weather minerals, liberating essential nutrients. Thus, measurements of soil pCO₂ coupled with soil pore water cation analyses can reveal weathering patterns that may help explain broader patterns of nutrient availability (Jin et al. 2010; Hasenmueller et al. 2015).

Nutrient Cycles and Limitations

One of the challenges of understanding mechanistic links between lithology and biota is that multiple nutrient cycles co-vary with lithology. That is, as you move from one lithology to the next, the availability of several elements may change. By investigating multiple nutrient cycles, such as nitrogen (N), phosphorus (P) and calcium (Ca), conceptual and mathematical models can be improved. Nitrogen limits primary and secondary productivity in most temperate forest ecosystems (Vitousek & Howarth, 1991; Elser et al. 2007; Tanner, Vitousek, & Cuevas, 2011) and the dominant N source is usually the atmosphere, not rock weathering. However, there are exceptions in locations where nitrogen-rich lithology can weather to form nutrient-rich soil (Morford et al. 2011). The P availability in soil can be strongly influenced by variability in P-containing minerals in rock, specifically apatite (Philpotts, 1967). Variation in apatite has also been linked to variation in plant and soil Ca availability in Northeastern forests (Yanai et al. 2005). When local rocks have low concentrations of P, or when rock-derived P is depleted by weathering, long-distance transport of P in dust may become an important source of P to biota

(Chadwick et al. 1999; Okin, et al. 2014). Soils in Pennsylvania have been impacted by these nutrient-rich dust inputs. The dominant ridges are sandstone lithology, with the side slope soils comprised of sandstone colluvium well mixed with eolian inputs. The lower elevation ridges are comprised of shale and limestone (Ciolkosz, et al. 1990; Simonson, 1995).

There can be tight coupling among nutrients that affect plant nutrient acquisition. For example, Ca has been shown to be coupled with other nutrient cycles, such as P and N (Perakis et al. 2006; Vadeboncoeur, 2010). In a sugar maple stand, researchers fertilized plots with base cations, such as Ca and Mg, and found that foliar P increased, along with overall plant growth and concentrations of all cations in soil and foliar tissue (Wilmot, Ellsworth, & Tyree, 1996). Ca has been shown to increase net primary productivity on soils affected by acid rain (Battles et al. 2013). However, in many fertilization studies, Ca is added with P, which can lead to a combined effect, making it difficult to determine if changes in plant growth are due to increased Ca or increased P (Vadeboncoeur, 2010). This project will examine the effects of calcium and phosphorus nutrient pools separately in the ecosystem.

There is no “gold standard” method for quantifying nutrient limitation to biota growing on soils derived from different lithology types. Experimental fertilization is often used to identify nutrient limitation. When a system is provided with a limiting nutrient, growth will increase and measurements can be taken to understand how the nutrient limits the system. However, fertilization studies also have constraints, including a need for a long-term approach to observe the nutrient limitations and issues with co-limitation and micronutrient over-fertilization. National programs, such as the US Forest Health Monitoring program, use similar measurements of soil chemistry to understand tree growth (Long et al. 2009). Given the logistical difficulties of using fertilizers and the challenging interpretation of the results, I will use a different approach that is based on a suite of assessments that investigate soil chemical and physical properties along with plant nutrient concentrations (Vitousek & Howarth, 1991; Vadeboncoeur, 2010; Sullivan et al. 2014).

Plant Interactions

One of the main goals of studying soil nutrient cycling is to use the information gained to understand plant growth dynamics. In most ecosystems, there is a tight relationship between the soil nutrient content and plant growth (Carmean, 1975). In temperate forests, such as Virginia, community type can be affected by the soil nutrition (Stephenson & Adams, 1989). Particularly in forest ecosystems, inter- and intra-specific competition can be affected by nutrient availability (Nambiar & Sands, 1993). Species respond differently to the increase of specific nutrients and there may be a shift in competitive advantage for species that are limited by the nutrient supply (Tilman, 1982). There is also a connection between plants and lithology, as tree roots and associated mycorrhizal fungi accelerate weathering via chemical reactions caused by the production of exudates and physical weathering by fracturing rocks with root growth (Landeweert et al. 2001; Blum et al. 2002; Calvaruso, Turpault, & Frey-Klett, 2006).

For this project the tree species red maple (*Acer rubrum*) and red oak (*Quercus rubra*) were selected because they are present on many lithologies through the northeastern United States and prior research has shown their distinct responses to nutrient fertilization. For instance, when exposed to increased N, both tree species grow faster (Aber et al. 1998), however they vary in their sensitivity to N fertilization. In long term additions over decades, red oak trees do not respond to nitrogen additions; however, over short time periods, such as growing seasons, red oaks can show increased basal area increment with nitrogen additions. Red maple tree species show an inverse relationship with nitrogen additions, as they do not respond strongly at the time scale of growing seasons, but will respond over decades (Finzi, 2009). Tree growth has also been assessed in the context of soil nutrition, such as calcium content, as tree species do differ in their interactions with cations (Long et al. 2009). Red oak trees can cycle high levels of cations, such as calcium and magnesium, through their foliage and may store more calcium in their tissues. In comparison, red maple trees can lose foliar cations due to acid rain (Schier, 1987; Hallett & Hornbeck, 1997; van Breemen, Finzi, & Canham, 1997).

Anthropogenic Impacts on Pennsylvania soils

In addition to the compositional contrasts between lithology as described above (Table 1), the soils in Pennsylvania have been affected by land use (farming, deforestation, and urban development) and anthropogenic changes to the atmosphere (N deposition, global warming and increased CO₂). Following Euro-American settlement, there was a decrease in land covered by forest ecosystems in PA, due to timber use and agriculture (Beck & Hooper, 1986). The switch from forested ecosystems to agricultural, highly disturbed ecosystems has led to changes in soil nutrient content, including decreased soil carbon (Murty et al. 2002). There was also a surge in nutrients to the soil and hydrologic systems with the loss of plant species (Hornbeck & Kropelin, 1982). Human development led to deforestation for agricultural land and to increased urbanization and use of fossil fuels. In PA, landform and physiology affected settlement and therefore changed the use of forested ecosystems (Abrams & Ruffner, 1995). With human settlement, there was also the development of pastures for livestock in central PA. Pasture land use may have affected soil nutrients, especially P or cations that we are interested in for this study (Fraterrigo et al. 2005). Other soil changes, such as lowering the soil pH can be tied to the increased use of fossil fuels and consequential acid deposition (Drohan & Sharpe, 1997). Many ecosystems across Pennsylvania have been affected by changes in soil chemistry due to atmospheric deposition (Drohan & Sharpe, 1997; Bailey, Horsley, & Long, 2005).

In recent years, forest composition shifted from oak dominance to more mesophytic tree species (Nowacki & Abrams, 2008). In experimental studies, maple trees begin to outcompete the other tree species when the soil is amended with lime to balance the pH (Long, Horsley, & Hall, 2011). The change of tree composition changes the nutrient composition of the soil and can have downstream effects of other components of the soil profile (Binkley & Giardina, 1998). However, as forests have been allowed to regrow after agricultural abandonment, reduced harvesting and fire suppression, there are effects on the carbon cycle. Some of the anthropogenic changes to the atmosphere, such as CO₂ fertilization, nitrogen deposition and climate change, enhanced tree regrowth. In addition, the history of agricultural use and abandonment has allowed forest to regrow and accumulate carbon (Caspersen et al. 2000). The other dominant land use history for Pennsylvania is oil and gas well exploration with wells installed across the

state and past iron furnaces and forges in Centre County (Abrams & Nowacki, 1992; Brantley et al. 2014). Land use has great impacts on soil properties (Drummond & Loveland, 2010) and by focusing on the location of central PA, we will be able to account for the age of the forest stand and taken into consideration the past land use practices.

Critical Zone Locations

In this study, I will be using two catchments based in the National Science Foundation funded Susquehanna Shale Hills Critical Zone Observatory (SSCZO) in central Pennsylvania. Shale Hills, the location underlain by Rose Hill Shale and Garner Run, the location underlain by Tuscarora sandstone will be used for the comparison of soil gas concentrations and for nutrient cycling measurements. The two catchments serve as our base locations and have distinct differences that could be tied to their lithologies. Many interactions control soil gas production and concentration, as well as nutrient cycling in an ecosystem. Therefore, major differences between the two catchments, including soil descriptions, are outlined in the tables below:

Table 2. Comparison of Shale Hills and Garner Run, the two locations of the Susquehanna-Shale Hills Critical Zone.

* Tree composition for Shale Hills is based on 2008 data for all trees greater than 20cm DBH and is a percent of total tree count.

**Tree composition of Garner Run is an average of the % basal area for the forest inventory transects completed at four topographical positions.

Data from (Brantley et al. 2016). & Data from (Smith, Eissenstat, & Kaye, 2016).

+ Data from (Lin, 2006). Depth to bedrock presented here may be shallower than other measurements.

Location	Shale Hills		Garner Run	
Lithology	Shale [Rose Hill] #		Sandstone [Tuscarora] #	
Main Soil Type	Weikert [Silt loam] #		Hazelton [Gravelly/sandy loam] #	
Tree Species Composition	Chestnut oak	30% * &	Sweet birch	22% ** #
	Hickory spp.	17%	Chestnut oak	21%
	Red oak	16%	Red maple	16%
	White oak	15%	Black gum	13%
	Virginia pine	5%	Red oak	9%
	Sugar maple	4%	Eastern white pine	4%
Slope (Note: planar midslopes were used)	North-facing Midslope	36% +	North-facing Midslope	25% #
	South-facing Midslope	18%	South-facing Midslope	27%
	Ridgetop	5%	Ridgetop	<2%
	Valley Floor	9%	Valley Floor	<1%
Depth to bedrock (meters)	North-facing Midslope	0.40 +	North-facing Midslope	1-1.5m #
	South-facing Midslope	0.40	South-facing Midslope	1-1.5m
	Ridgetop	0.30	Ridgetop	1-1.5m
	Valley Floor	1	Valley Floor	>1.5m
Elevation Range (meters)	251-319m +		300-600m #	
Hillslope Length (meters)	50-100m +		300-600m #	
Approximate Erosion Rates	20-30 m/My +		<10 m/My #	
Tree Biomass	290 gC /m ² &		n/a	
Litterfall	163.4 gC/m ² /year &		n/a	

Table 3. Soil descriptions of the soil pits located at the north facing midslope location.

Data from (Brantley et al. 2016). + Data from (Lin, 2006). \$ Data from (Takagi, 2009).

		Garner Run – North-facing Midslope #			Shale Hills – North-facing Midslope +				
Horizon Morphology		Depth (cm)	Clay (%)	Rock (%)	Depth (cm)	Clay (%)	Sand (%)	OM (%) ^{\$}	Rock (%)
A					5-15	13.08	43.89	11.13	0
AE					15-20				0
E		0-12	10	65					
B	Bhs	12-15	12	45					
	Bs	15-26	14	50					
	Bw1	26-50	18	20	20-30	15.13	41.51	4.39	0
	Bw2	50-72	20	30					
	Bt				30-53				0
C		72-145+	8	90					
C	2C				53-89	15.12	46.2	3.65	80
	3Cg				89-97				0
	4Cg				97-137				90
	5Cg				137-143				0
	6Cg				143-147+				90

Table 4. Soil descriptions of the soil pits located at the ridgetop location.

Data from (Brantley et al. 2016). + Data from (Lin, 2006). \$ Data from (Takagi, 2009).

		Garner Run – Ridgetop #			Shale Hills – Ridgetop +				
Horizon Morphology		Depth (cm)	Clay (%)	Rock (%)	Depth (cm)	Clay (%)	Sand (%)	OM (%) ^{\$}	Rock (%)
A					5-15	13.08	43.89	11.13	0
AE					15-20				0
E		0-10	10	60					
B	Bhs	10-14	12	45					
	Bs	14-20	15	15					
	Bw1	20-32	17	10	20-30	15.13	41.51	4.39	0
	Bw2	32-65+	28	10					
	Bt				30-53				0

C		72-145+	8	90					
C	2C				53-89	15.12	46.2	3.65	80
	3Cg				89-97				0
	4Cg				97-137				90
	5Cg				137-143				0
	6Cg				143-147+				90

Table 5. Soil descriptions of the soil pits located at the valley floor location.

Data from (Brantley et al. 2016). + Data from (Lin, 2006). \$ Data from (Takagi, 2009).

Horizon Morphology		Garner Run – Valley Floor #			Shale Hills – Valley Floor +				
		Depth (cm)	Clay (%)	Rock (%)	Depth (cm)	Clay (%)	Sand (%)	OM (%) ^{\$}	Rock (%)
A					5-15	18.05	38.74	11.8	0
AE					15-20		35		0
E		0-5	12	65					
B	Bhs	5-7	14	20					
	Bs	7-14	15	20					
	Bw1	14-33	26	20	20-30	24.11	31.99	4.6	0
	Bw2	33-60	32	32					
	Bt	60-95	24	50	30-53	33.2		4.1	0
BC		95-138	8	70					
C	2Cr	138-155+		Large sandstone blocks					
	2C				53-89	17.43	50.54	4.1	80
	3Cg				89-97				0
	4Cg				97-137				90
	5Cg				137-143				0
	6Cg				143-147+				90

Table 6. Soil descriptions of the soil pits located at the south facing midslope location.

Data from (Brantley et al. 2016). + Data from (Lin, 2006). \$ Data from (Takagi, 2009).

		Garner Run – Southfacing Midslope #			Shale Hills - Southfacing Midslope +				
Horizon Morphology		Depth (cm)	Clay (%)	Rock (%)	Depth (cm)	Clay (%)	Sand (%)	OM (%) ^{\$}	Rock (%)
A		0-6	12	65	5-12	13.08	43.02	11.13	0
AE		6-21	8	68			42		
B	Bw1	21-37	14	65	12-24	15.13	41.51	4.39	60
	Bw2	37-75	16	70					
	Bw3	75-95+	19	70					
C									
CR					24-37	15.12	38.66	3.65	90

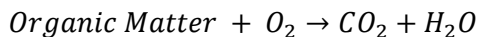
Objectives

In this project, I examined how the C, N, and other major nutrient cycles are impacted by the lithology on which the soil forms. I accomplished this by investigating interactions between lithology, soil nutrient availability, and soil pCO₂. The project was based in the NSF-Funded Susquehanna Shale Hills Critical Zone Observatory (SSCZO) in Pennsylvania, so that the project could benefit from field and data infrastructure at the site. The SSCZO has an interdisciplinary team working to comprehend weathering over multiple timescales. This project also continued the research of the CZO, increasing information about weathering and the concept of “rock meeting life” (2007). The CZO maintains two sites on shale and sandstone lithology. This project included five sandstone and five shale sites in the Ridge and Valley Region of Pennsylvania. Because these sites have been weathering for approximately the same amount of time and in the same climate with the same potential tree species, we expect differences among sites to be driven primarily by differences in lithology (in Jenny’s parlance, a lithosequence) (Jenny, 1994).

CHAPTER 1

Soil CO₂ and O₂ concentrations in shale and sandstone catchments of central Pennsylvania

The terrestrial carbon cycle has and will continue to change with increased anthropogenic inputs of carbon dioxide (CO₂). Global carbon models have changed in response to the increased CO₂ to include other important carbon fluxes (Cox et al. 2000). However, there has been substantially less research on the distribution of CO₂ in soil profiles. The concentration of CO₂ in the soil often reaches thousands of parts per million (ppm), well above the current atmospheric concentration of 400 ppm (Lal, 2004; Hasenmueller et al. 2015). Soil CO₂ mainly comes from cellular respiration of roots and soil microorganisms. The concentration of oxygen (O₂) in soils is tightly coupled to that of CO₂ through these respiration reactions, seen in the aerobic respiration equation where organic matter could have a basic formula of CH₂O:



The purpose of this study is to quantify the effects of lithology on CO₂ and O₂ concentration throughout the soil profile. The concentrations of carbon dioxide and oxygen in the soil profile differ greatly due to their concentration gradients depicted in Figure 1-1. The figure illustrates that carbon dioxide concentration is greater in the soil due to respiration and CO₂ diffuses to the atmosphere, whereas oxygen diffuses in the opposite direction. However the concentrations of both gases have similar controls of soil moisture, texture, porosity and soil depth (Tang et al. 2003; Angert et al. 2015; Hasenmueller et al. 2015). Soil characteristics affect diffusion rates that control how quickly gases are lost to or gained from the atmosphere, and microbial activity controls the production and consumption of gases in situ. Previous research has shown that topography, due to its effects on soil characteristics (notably soil depth and soil moisture), is a major control on CO₂ and O₂ concentrations (Angert et al. 2015; Hasenmueller et al. 2015).

Topography is affected by the lithology of the landscape and lithology could affect the concentrations of these soil gases.

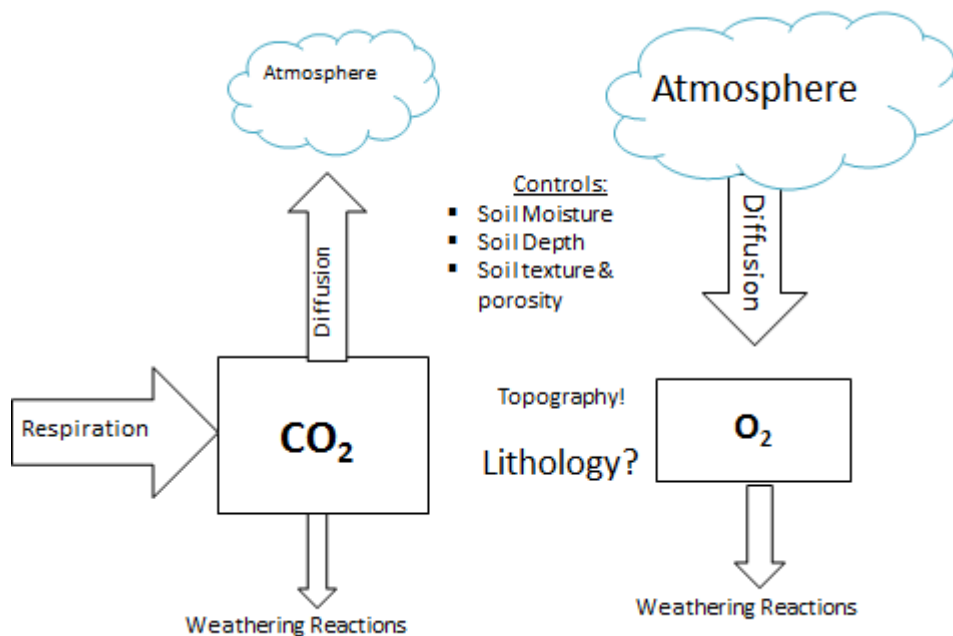


Figure 1-1. Depiction of CO₂ and O₂ diffusion between the atmosphere and the soil, respectively.

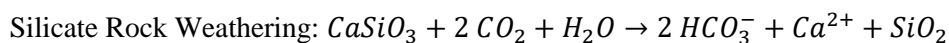
Lithology also has impacts on vegetation (Pausas & Carreras, 2012), soil properties (Webber & Jellema, 1965; Neff et al. 2006; Morford, Houlton, & Dahlgren, 2011) and microbial communities (Skidmore et al. 2005), thus leading to a possible effect on soil pCO₂ and O₂.

In the soil profile, biota respire and produce carbon dioxide, which has two main fates: it can dissolve in soil solution to form bicarbonate and carbonic acid or it can diffuse out of the profile to the atmosphere. The flux of CO₂ out of soil to the atmosphere is sensitive to climate (especially temperature and moisture), vegetation type, and soil properties (Janssens et al. 2001; Palmroth et al. 2005; Wang et al. 2016). However, heterotrophic respiration has further controls such as carbon and nitrogen content of litterfall and the size of the soil organic carbon pool (Wang et al. 2016). It is commonly assumed that soil CO₂ efflux, the gas that diffuses from the surface, is equal to soil respiration. Aside from calculating CO₂

concentration by measuring the partial pressure of CO₂ throughout the soil profile, others have used the relationship between oxygen concentration and carbon dioxide to measure soil respiration.

As outlined in other research (Angert & Sherer, 2011; Angert et al. 2015), CO₂ efflux may not be the best way to measure soil respiration, due to losses of CO₂ to soil pores, to weathering reactions and to soil water or the hydrologic system. The theoretical inverse relationship of oxygen consumption and carbon dioxide production during aerobic respiration (Angert et al. 2015; Kim, Stinchcomb & Brantley, *In Review*) allows researchers to evaluate the relative importance of differing metabolic processes on soil CO₂ concentrations. However, there are caveats with this method as well. Oxygen diffuses slowly as it moves deeper into the soil layers to the microorganisms; however, as the microorganisms continue to respire, the CO₂ concentration builds up as it diffuses slowly out of the soil profile and into the atmosphere. Therefore, as shown in Angert's work, the 1:1 ratio of O₂ and CO₂ does not always hold true (Angert et al. 2015). In cases where aerobic respiration and diffusion are the dominant processes controlling CO₂ and O₂ concentrations, a plot of CO₂ vs O₂ should have a slope of -1.32. Deviations from this predicted slope suggest that additional sources or sinks, including weathering reactions, hydrologic losses, or advection, are contributing to observed patterns in CO₂ and O₂ concentrations (Angert et al. 2015).

In this study, we used a combination of automated sensors and hand sampling techniques to account for spatial and depth differences in the concentrations of CO₂ and O₂. The automated sensors provided data points throughout the day for approximately a year at two depths: shallow for measurements of heterotrophic and autotrophic respiration from microbiota and roots, respectively and deep where biological activity may be lower and weathering reactions may have a greater impact on soil pore gas concentrations. The gas access tubes used for hand sampling were co-deployed with the automated sensors to compare the efficiency of the methods and then at additional depths and spatial locations. CO₂ and water react to form carbonic acid that dissolves primary minerals in weathering reactions (Berner, 1992). In silicate-containing lithologies, carbonic acid can weather away the calcium silicate from the composition, as shown in the reaction below:



The release of calcium (or other nutrient cations in the rock) can be a source of nutrients for the soil or biota, further linking the lithology-soil-biota interactions. Oxygen also participates in weathering reactions. Pyrite ($2FeS_2$) weathering, such as pyrite oxidation, has been documented in Shale Hills, where oxygen diffuses deep into the weathering front. Oxygen, water and pyrite react to form iron, sulfate and acids that continue to weather the bedrock (Brantley et al. 2013). This has also been documented in Puerto Rico, where oxygen diffuses into core stones and oxidizes ferrous minerals, weathering away primary minerals and creating more fractures in the lithology (Fletcher, Buss, & Brantley, 2006). The link between lithology-soil-biota is seen in both long and short timescales, with lithological effects to the weathering process and to vegetation respectively.

Lithology impacts soil formation and therefore has effects on soil pore size. For instance, the lithology that mudstones form on influence the pore size and permeability of the soil, due to the pore space of the rock (Yang & Aplin, 1998). Soil pore size changes the water movement and content of the soil, which has downstream effects on microbial activity and gas diffusion (Linn & Doran, 1984). Because lithology influences the rates and style of mechanical and chemical weathering processes, there are often strong lithologic contrasts in topography (Gilbert, 1877; Seibert, Stendahl, & Sørensen, 2007). Topography in turn changes water movement and nutrient availability, which can have effects on microbial activity and tree composition. Lithology also facilitates different microbial communities (Skidmore et al. 2005), that can lead to different gas production based on metabolism. While there are clearly strong potential interactions between soil pore gases, pore water and the lithology, we know of only one study (Kim, Stinchcomb & Brantley, *In Review*) that contrasted lithologies. Measurements of CO_2 have been taken at many lithologies (Palmroth et al. 2005; Angert et al. 2015; Hasenmueller et al. 2015), but no studies have compared varying lithologies of close proximity. Other studies have investigated how soil efflux and soil respiration are not equivalent (Angert et al. 2015; Kim, Stinchcomb & Brantley, *In Review*) and how topography affects respiration in the soil profile (Hasenmueller et al.

2015). We build on this prior work by investigating lithological effects in shale and sandstone lithologies that are close in proximity and have similar climate.

Research Objectives

Our objective was to quantify the effect of lithology on CO₂ and O₂ concentrations in soils. We measured CO₂ and O₂ concentration at varying topographical positions to take into account the significant effect of topography on soil gas concentration (Hasenmueller et al. 2015). We also measured the gas concentrations at varying depths, as we would expect to see greater CO₂ and less O₂ as we move deeper into the soil profile (Angert et al. 2015; Kim, Stinchcomb & Brantley, *In Review*). We co-located soil moisture measurements to account for the significant affect water has on gas concentration (Linn & Doran, 1984; Sexstone et al. 1985). We used a paired four site catena set up, as outlined in Brantley et al. (2015), to measure the gas concentrations. We focused on 3 main questions: 1) Do whole-profile soil CO₂ and O₂ differ in soils derived from shale and sandstone lithologies?, 2) Is the variation in gas concentration explained by lithology as large as well-documented effects of topographic position and soil moisture?, and 3) Do correlations between pCO₂ and pO₂ support the hypothesis that aerobic respiration the dominant process controlling CO₂ concentrations in soil profiles?

METHODS

Study Site

pO₂ and O₂ were measured within the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) in the Shaver's Creek watershed in central Pennsylvania (Figure 1-2). Samples were collected from two catchments with varying lithology, Shale Hills (Rose Hill shale) and Garner Run (Tuscarora sandstone). The two catchments have been detailed through publications from the SSHCZO (Lin, 2006; Jin et al. 2010; Andrews et al. 2011; Brantley et al. 2013; Hasenmueller et al. 2015; Herndon et al. 2015; Brantley et al. 2016).

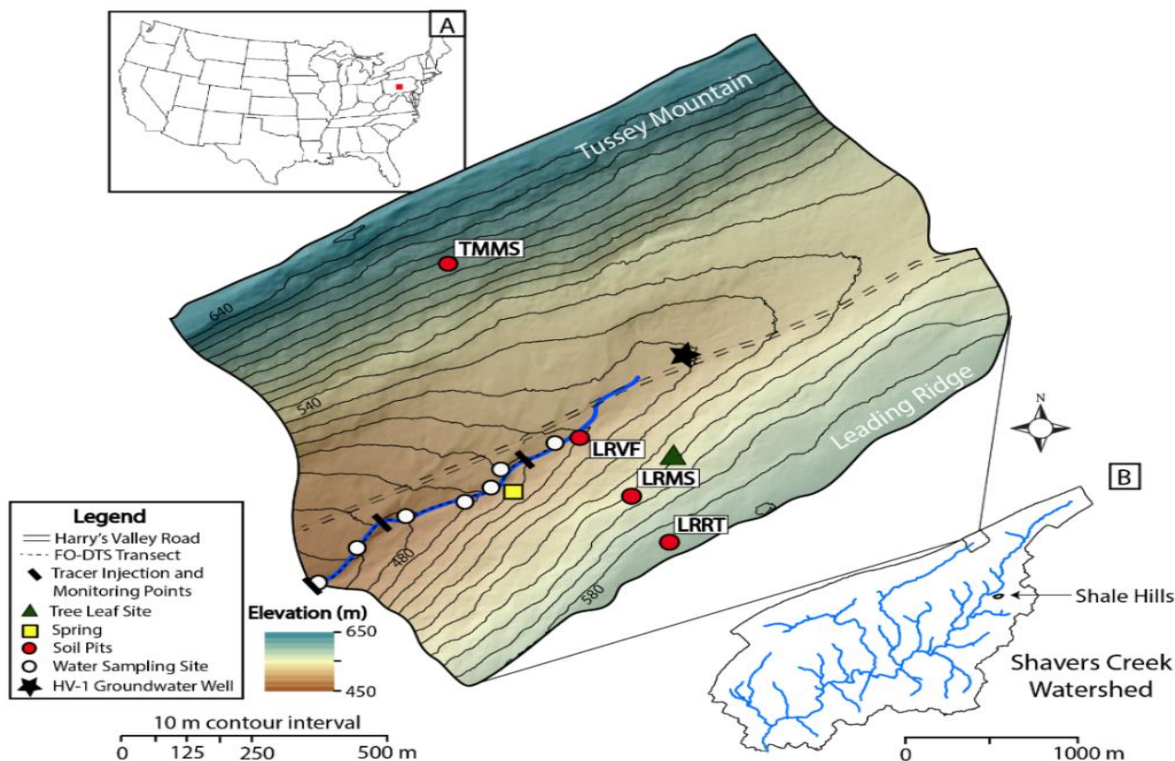


Figure 1-2. Sampling and instrumentation locations in Garner Run catchment. Background color indicates elevation (m). Red points represent soil pit locations. Inset maps show the location of Garner Run and Shale Hills within the USA (A) and in the greater Shaver's Creek watershed (B). Credited to Nell B. Hoagland.

Four plots are chosen in each catchment to measure slope, topographical and aspect effects: 1) a near-ridgetop plot located on a planar slope with north-facing aspect (i.e. LRRT, which is a south planar ridgetop), 2) a mid-slope plot (i.e. LRMS), 3) and a valley floor plot (i.e. LRVF) along the same planar slope as the near-ridgetop plot, and 4) another mid-slope plot on the opposite aspect (i.e.

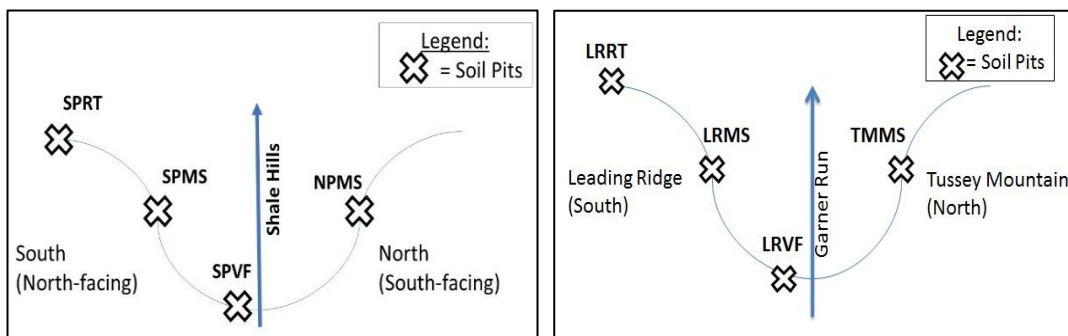


Figure 1-3. Depiction of Garner Run and Shale Hills catchment plots. The figure shows the location of the four pits in both catchments, displaying three pits on the south slope and one pit on the north slope.

TMMS) (Fig. 1-

3). At each plot, soil pits were dug to ~1 m using shovels, picks, breaker bars and in one pit (LRVF) a jackhammer. Equipment was installed and the pit was backfilled in attempt to recreate the soil profile. The Garner Run plots of Leading Ridge Valley Floor (LRVF), Leading Ridge Midslope, the north facing midslope (LRMS), Leading Ridge Ridgetop (LRRT) and Tussey Mountain Midslope (TMMS) were complete in October 2014. The Shale Hills plots of the south planer valley floor (SPVF), south planar midslope, the north facing midslope (SPMS), south planar ridgetop (SPRT) and north planar midslope (NPMS) were complete in May 2015. The soil descriptions of the soil pits at Garner Run are detailed in Brantley et al. (2016). Shale Hills soil profiles are described in Hasenmueller et al. (2015).

Sample Collection and Analysis

Field measurements were taken using a multi-sensor set-up, known as the GroundHOG (Brantley et al. 2016) that includes automated gas sensors and hand samplers for gas, soil water content and soil porewater. In the upslope wall of the soil pit, automated gas sensors, time domain reflectometry (TDR) wave guides, and gas access tubes were installed. Before installation, the automated O₂ sensors were fitted with PVC pipe and cap to cover the sensor and the automated CO₂ sensors were wrapped in Tyvek (DuPont, US). To deploy, an implement was used to create a hole for the equipment, a soil core for the automated sensors and a screwdriver for the gas access tubes. The sensors and gas tubes were deployed and backfilled with soil. The automated gas sensors were deployed at depths of 20 cm below soil surface and 20cm above the bottom of the pit. Gas access tubes and TDR wave guides were co-located with the automated sensors and at an additional depth of 40cm. Additionally, to measure spatial variation in gas concentrations, gas access tubes and TDR wave guides were also installed at the same depths into the face to the right and left of the uphill face. All sensors were installed into the pit face to limit the effect of disturbance. Soil from the soil pit was 2 mm sieved to ensure a good soil-air and porewater connection, before backfilling.

Gas access tubes for hand sampling were deployed following a modified USGS protocol (Schulz, 2006) described in Hasenmueller, et al. (2015). The samplers were constructed using stainless steel

tubing, stainless steel mesh, epoxy, and Swagelok caps (Hasenmueller, et al. 2015). A purge volume was calculated based on the volume of the tubing, with the volume of tubing multiplied by 2 and an additional 2mL added for the value and to ensure the purge volume was greater than the total volume of the gas tube plus syringe dead space (Appendix). Before each manual sample, a purge sample was taken and discarded. Manual samples were collected fortnightly during the growing season, from May to August. Samples were taken directly after purging the tube. Soil gas CO₂ concentrations were analyzed in the laboratory within 48 hours of field collection by an infrared gas analyzer (LI-7000, LI-COR Inc., Lincoln, NE). Samples were calibrated with standard curves made from multiple volumes of two CO₂ standards of 970 and 10,300ppm (Gas and Technology Services INC., Santa Maria, CA). Following Hasenmueller et al. (2015), we used the ideal gas law to calculate soil CO₂ concentration:

$$\text{Pressure} * \text{Volume} = n * R * \text{Temperature}$$

Where pressure was calculated from hillslope elevation (Kutz, 2006), volume is the volume (L) of gas injected into the IRGA in the lab, n is the moles of CO₂, R is the gas constant (L*atm/mol*K), and Temperature is the average soil temperature (K) across the growing season and across the two locations.

Gas access tubes were also used to measure oxygen concentration throughout the soil profile. After the CO₂ syringe sample was taken, percent (v/v) oxygen was measured using a Model 901 Headspace Oxygen Analyzer (Quantek Instruments, Graton, MA), calibrated with local air assuming a concentration of 20.95% O₂. The oxygen sensor is connected by tubing directly to the gas access tube and the sampler pumps a small volume of gas past the detector.

The aerobic respiration oxidation ratio was defined as the ratio of the concentration of CO₂ produced versus the concentration of O₂ used (Kim, Stinchcomb & Brantley, *In Review*). O₂ diffuses from the atmosphere into soil and is consumed as it moves down the soil profile. CO₂ is produced through the soil profile and diffuses upward through the soil profile to the atmosphere. Thus, if the only consumption process for O₂ is cellular respiration then the stoichiometry suggests that a regression of O₂ vs CO₂ concentrations should have a slope of negative one and a y intercept equal to the concentration of O₂ in the atmosphere (Angert et al. 2015). The oxidation ratio slopes were calculated from a general linear

model and the slope was corrected for the difference in diffusion; O₂ diffuses faster than CO₂. We used the following equation from Kim, Stinchcomb & Brantley (equation 1-1),

$$a^* = \frac{0.182}{0.138} a = 1.32a$$

Where a is the slope of the linear regression of pCO₂ vs O₂ and a^* is the corrected slope based on diffusion rates of O₂ and CO₂.

Automated sensors used for CO₂ measurements (Eosense, formally Forerunner Research, Nova Scotia, CA) were factory-calibrated for a range of 0 to 20,000ppm for all but the deepest sensors, which were calibrated over the range 0 to 40,000ppm. Automated sensors used for O₂ measurements (Apogee Instruments, Utah). The sensors are calibrated through an equation (equation 1-2):

$$\text{O}_2 (\%) = \text{calibration factor} * \text{signal} - \text{offset}$$

Where signal is the voltage output from the sensor. The calibration factor and offset were measured for each sensor before deployment, by measuring the voltage output using an oxygen-free N₂ tank and an ambient air measurement in the laboratory at The Pennsylvania State University. Sensors were wired to a CR1000 (Campbell Scientific, Logan, UT) to take and record measurements hourly, along with a daily average. Automated sensors were deployed at 20cm from the soil surface and at D-20. D-20 depth refers to the depth of each pit, which varies, up the soil profile 20cm to allow room to deploy the sensors. Automated gas measurements could not be statistically analyzed due to issues with sensors, leading to lack of replication.

Soil volumetric water content was measured with the fortnightly gas samples using time domain reflectometry (TDR) waveguides and a TDR100 (Campbell Scientific, Logan, UT), as in Hasenmueller, et al (2015).

Statistical Analysis

Hand sampled CO₂ and O₂ measurements were averaged for each pit location (n=9) for each date. The three tubes for each depth were first averaged to account for spatial variance. I chose to analyze the

average of all depths for a given pit, because the patterns of CO₂ with depth are well-established; CO₂ increases as depth increases (Hasenmueller, et al. 2015). The measurements were analyzed using repeated-measures mixed-models (PROC MIXED SAS 9.4), with the fixed independent variables of lithology, topography, and time as fixed repeated-measures, and all interactions. CO₂ was natural log-transformed to fit a normal distribution. We generated a 3-way piecewise comparison to determine if there were significant differences between the time points for a given location (i.e. if mid-July 2015 was different than late-July 2015 at the valley floor location). We also used this comparison to determine if there were significant differences between locations for a specific time point (i.e. the valley floor vs the ridgetop in August 2015). The oxidation ratio (pCO₂ vs pO₂) was analyzed with an ANCOVA with lithology and topography as main effects (PROC ANCOVA SAS 9.4). pCO₂ and O₂ were log transformed to fit a normal distribution for the oxidation ratio ANCOVA.

RESULTS

Automated Gas Measurements

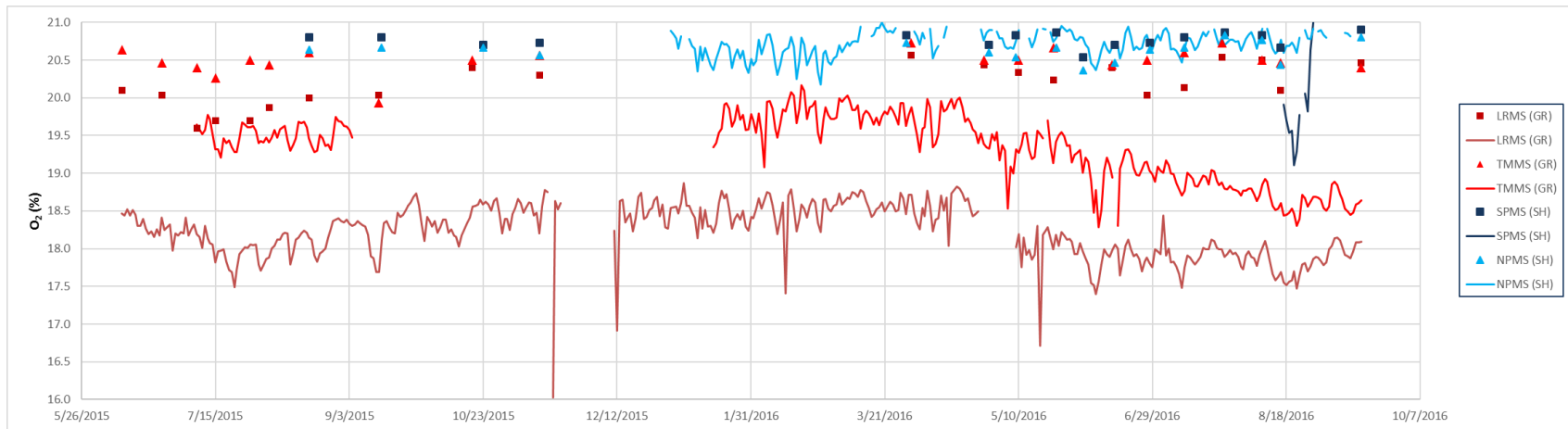


Figure 1-4. Concentration of O₂ (%; v/v) at 20cm depth at Shale Hills and Garner Run. The figure shows the automated data as a continuous line and the data points from the hand sampled dates. Site codes for Garner Run (red points and lines) data are: LRMS = leading ridge midslope and TMMS = tussey mountain midslope. Site codes for Shale Hills (blue points and lines) data are SPMS = south planar midslope and NPMS= north planar midslope.

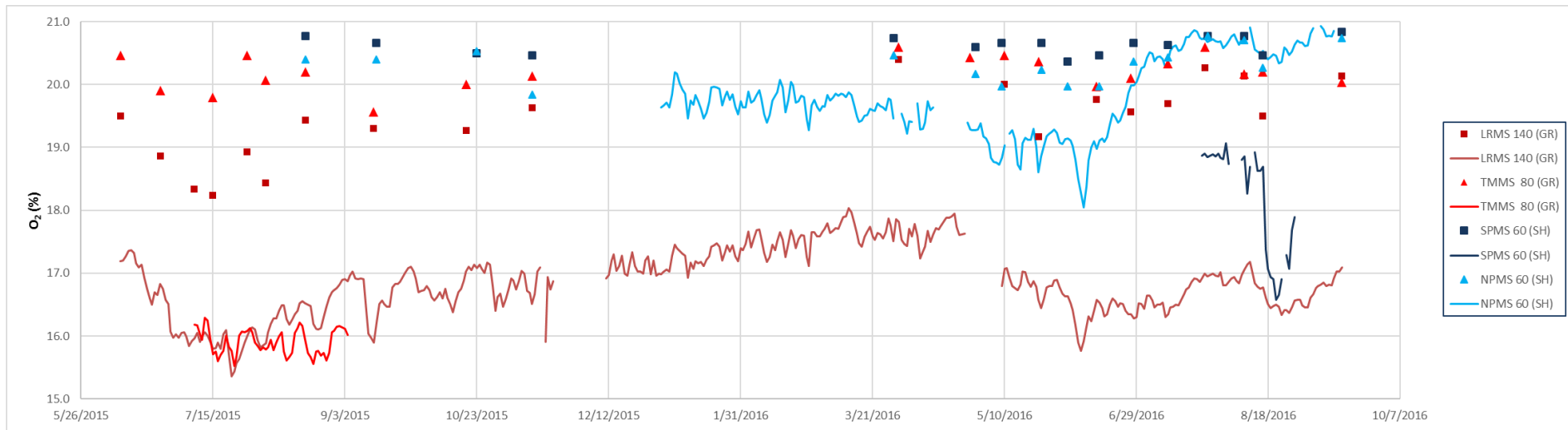


Figure 1-5. Concentration of O₂ (%; v/v) at the varying D-20 depths at Shale Hill and Garner Run. The figure shows the automated data as a continuous line and the data points from the hand sampled dates. Site codes for Garner Run (red points and lines) data are: LRMS = leading ridge midslope and TMMS = tussey mountain midslope. Site codes for Shale Hills (blue points and lines) data are SPMS = south planar midslope and NPMS= north planar midslope.

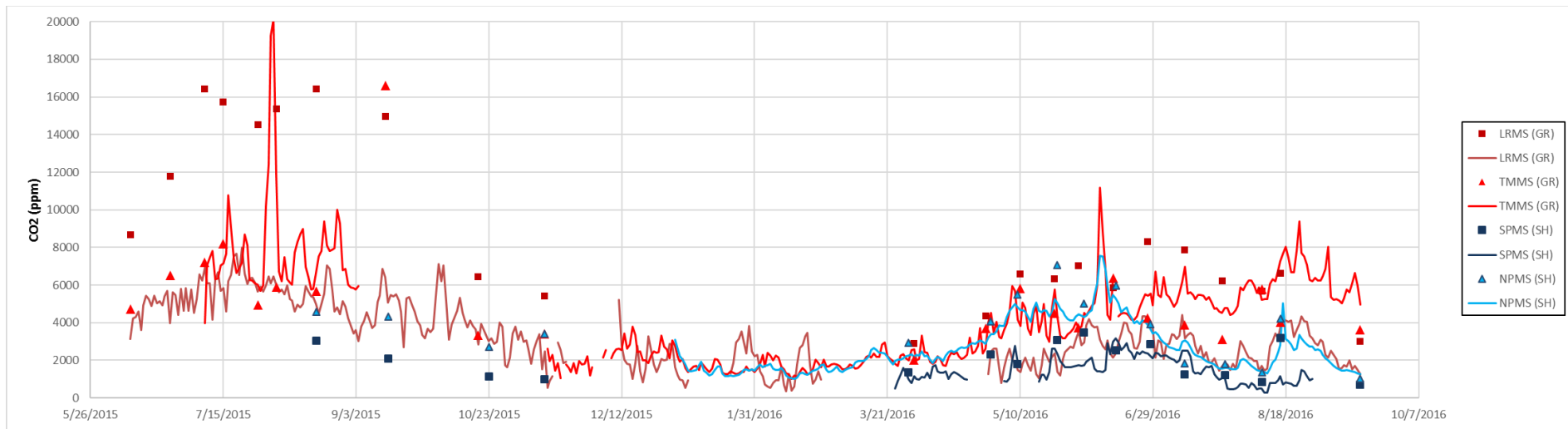


Figure 1-6. Concentration of soil CO₂ (ppm) at 20cm depth at Shale Hills and Garner Run. The figure shows the automated data as a continuous line and the data points from the hand sampled dates. Site codes for Garner Run (red points and lines) data are: LRMS = leading ridge midslope and TMMS = tussey mountain midslope. Site codes for Shale Hills (blue points and lines) data are SPMS = south planar midslope and NPMS= north planar midslope.

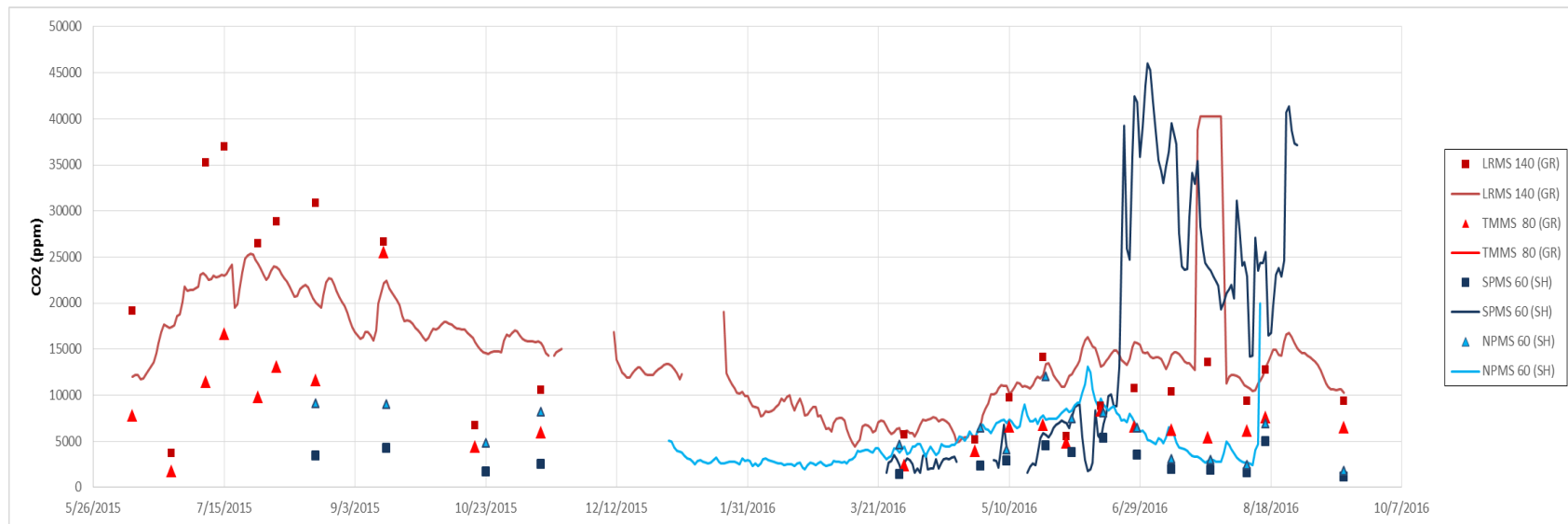


Figure 1-7. Concentration of soil CO₂ (ppm) at the varying D-20 depths at Shale Hills and Garner Run. The figure shows the automated data as a continuous line and the data points from the hand sampled dates. Site codes for Garner Run (red points and lines) data are: LRMS = leading ridge midslope and TMMS = tussey mountain midslope. Site codes for Shale Hills (blue points and lines) data are SPMS = south planar midslope and NPMS= north planar midslope.

Hand-sampled Measurements

For CO₂, there was a significant time effect and significant interactions for time * lithology type, time*topography and a three-way interaction between lithology type * topography *time (p<0.05). For topographic location, there were no significant differences between lithology type (p<0.05). At Garner Run's south facing midslope (TMMS), there was a significant increase in CO₂ concentration averaged across all depths from September to October in 2015. There were no other significant time * topography interactions in Garner Run. At Shale Hills' north facing midslope (SPMS), CO₂ increased about 3000 ppm averaged across all depths from early to mid-August and decreased about 3000 ppm mid-August to mid-September 2016. At SPRT, CO₂ increased about 3000 ppm from early-mid August and decreased about 3000 ppm mid-August to mid-September 2016. At NPMS, CO₂ increased about 4000 ppm from early-mid August and decreased about 4000ppm mid-August to mid-September 2016. At SPVF, CO₂ increased about 3000 ppm from November 2015 to March 2016.

For O₂, there was a significant topography and time effect with significant interactions between lithology type* time, topography*time and a three-way interaction between lithology type * topography *time (p<0.05). For topographic location, there were no significant differences between lithology type (p<0.05). At specific time points, there were significant changes in the O₂ concentration and significant differences between topographical positions. At TMMS, there was a significant increase about 0.3% in O₂ from Sept-October in 2015. At LRRT, there was a significant increase about 0.5% in O₂ from August to September 2016. At LRMS, there was a significant increase about 0.2% in O₂ from August to September 2015. At LRVF, O₂ significantly increased about 1% from September to October and about 0.5% from November 2015 to March 2016. It also significantly increased about 0.5% from mid-July to late-July and about 0.8% from August to September 2016. There was a significant difference between TMMS and LRVF in late-may and mid-July 2016, with greater O₂ in TMMS at both time points.

In Shale Hills, there were many time points when there were significant differences between topographical positions. There were also significant differences between time points at a specific topographical point. At SPVF, O₂ significantly increased about 1% from September to October, and about

1% from November 2015 to March 2016 and O₂ significantly decreased about 1% from October to November 2015.

There was a significant difference between the valley floor topographical position (SPVF) and NPMS in August and September 2015 and in mid-June 2016, with greater O₂ in NPMS for both time points. There was a significant difference between the valley floor topographical position (SPVF) and SPRT in August and September 2015 and in mid-June 2016, with greater O₂ in SPRT for both time points. There was a significant difference between the valley floor topographical position (SPVF) and SPMS in August, September, and November 2015 and in May, late-May and mid-June 2016, with greater O₂ in SPMS for all time points.

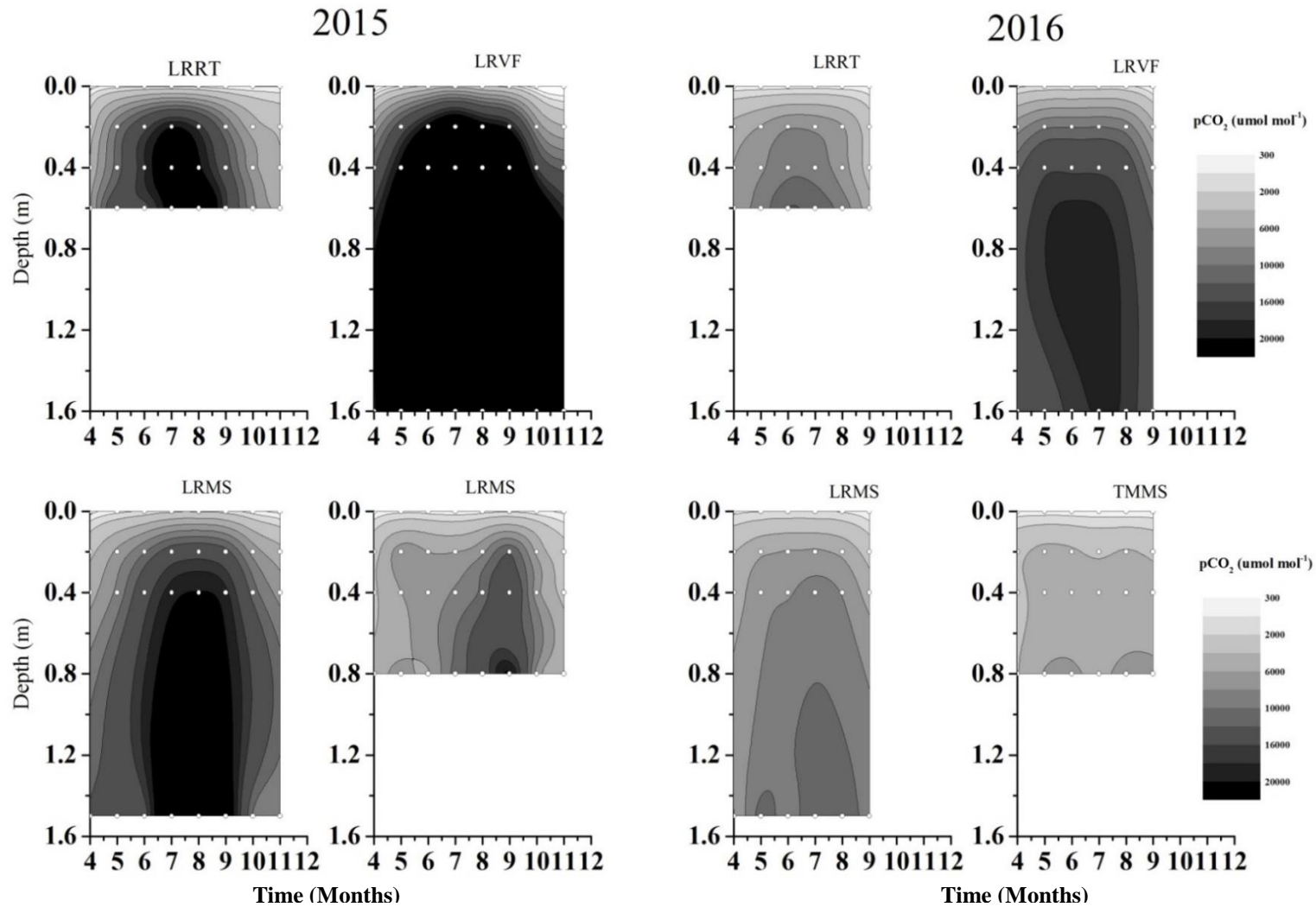


Figure 1-8. Contour plot of monthly soil pCO₂ (ppmv) as a function of soil depth (m) in Garner Run plots in 2015 and 2016. The figure shows the change in CO₂ concentration over time by the depths of ambient (0cm), 20cm, 40cm and the varying D-20cm depths. The values for each depth were averaged of the three gas tubes in each topographical position.

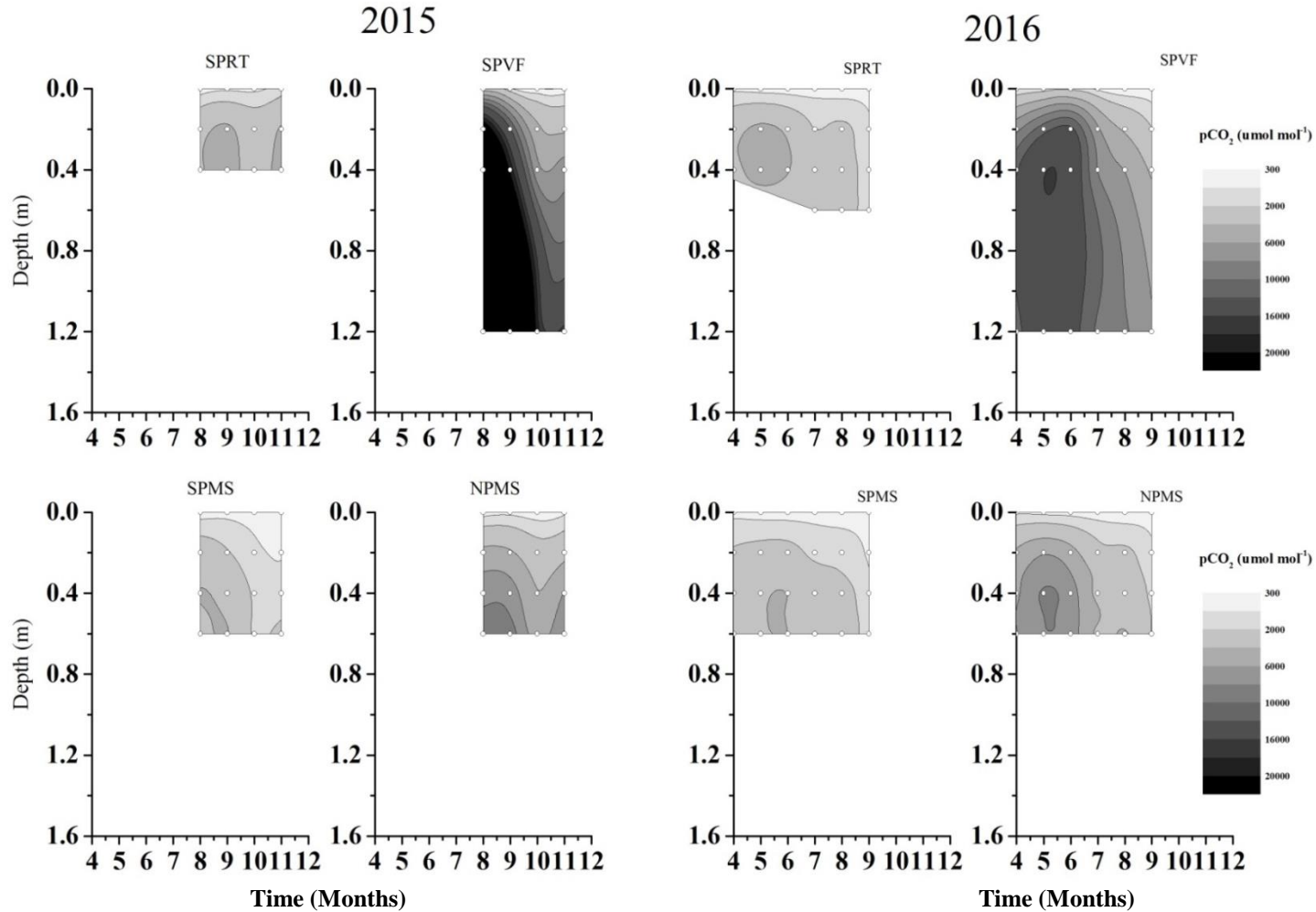


Figure 1-9. Contour plot of monthly soil pCO₂ (ppmv) as a function of soil depth (m) in Shale Hills plots in 2015 and 2016. The figure shows the change in CO₂ concentration over time by the depths of ambient (0cm), 20cm, 40cm and the varying D-20cm depths. The values for each depth were averaged of the three gas tubes in each topographical position.

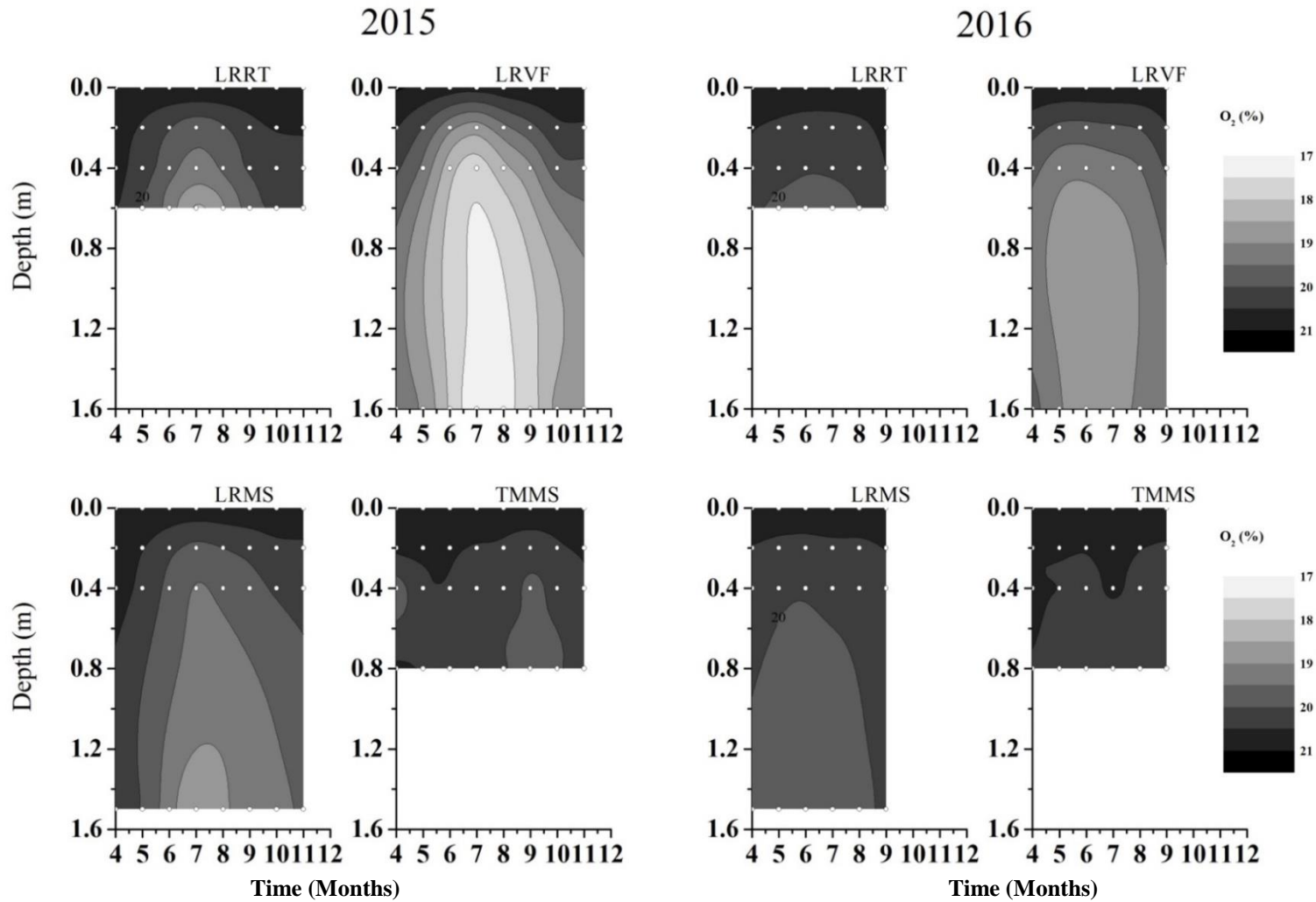


Figure 1-10. Contour plot of monthly soil O_2 as a function of soil depth (m) in Garner Run plots in 2015 and 2016. The figure shows the change in O_2 concentration over time by the depths of 20cm, 40cm and the varying D-20cm depths. The values for each depth were averaged of the three gas tubes in each topographical position.

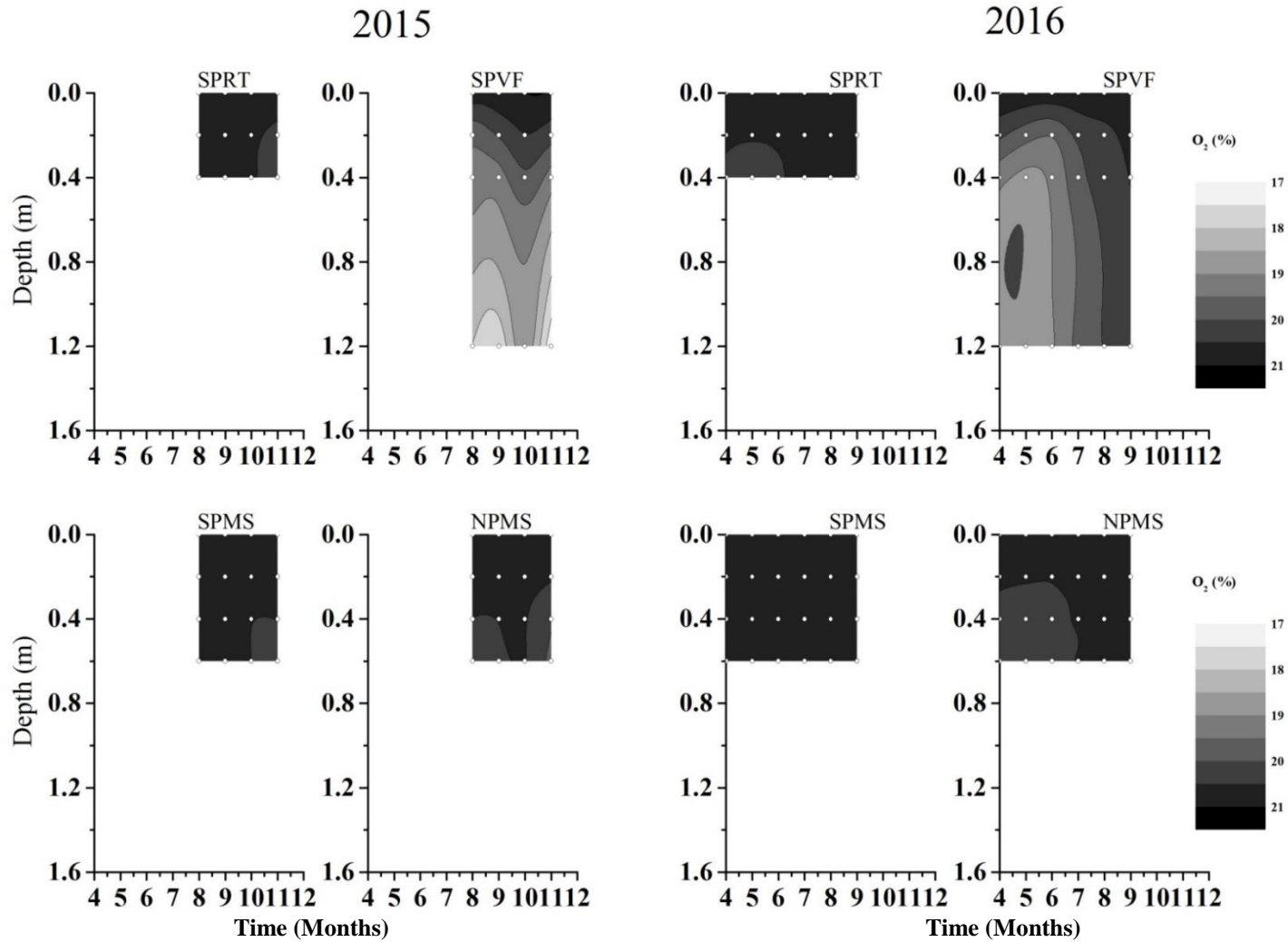


Figure 1-11. Contour plot of monthly soil O₂ as a function of soil depth (m) in Shale Hills plots in 2015 and 2016. The figure shows the change in O₂ concentration over time by the depths of 20cm, 40cm and the varying D-20cm depths. The values for each depth were averaged of the three gas tubes in each topographical position.

Table 7. Summary table of CO₂ and O₂ statistical analysis. The table indicates the degrees of freedom, the F value and p-value for each effect and interaction measured in the mixed model analysis. P < 0.05 is statistically significant.

Effect	CO ₂			O ₂		
	dF	F	P	dF	F	P
Lithology Type	1	1.02	0.3224	1	5.66	0.031
Topography	3	0.58	0.6323	3	15.17	<0.0001
Time	15	21.31	<0.0001	14	35.67	<0.0001
LithoxTopo	3	0.18	0.91	3	1.19	0.3462
LithoxTime	15	7.36	<0.0001	14	10.36	<0.0001
TopoxTime	45	2.22	<0.0001	42	6.93	<0.0001
LithoxTopoxTime	45	1.93	0.0006	42	3.18	<0.0001

Oxidation Ratio

pCO₂ and pO₂ have strong linear relationships with each other at the four topographical positions (Figs. 1-12 to 1-15). Table 8 shows the slopes, corrected slopes and y-intercepts for the oxidation ratios for each topographical position for both lithologies. The oxidation ratio slopes were corrected for the diffusivity differences of CO₂ and O₂ with equation 1 from Kim, Stinchcomb & Brantley (*In Review*). Topography affected the oxidation ratio, as the valley floor positions were significantly different from both midslopes and the ridgetop (p < 0.05). However, lithology was not statistically significant.

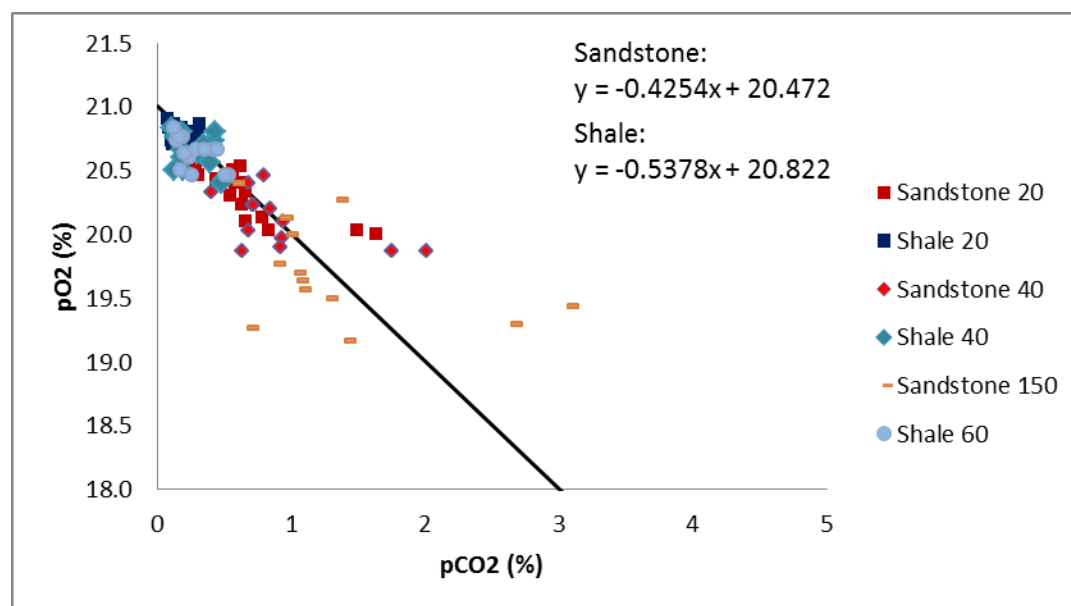


Figure 1-12. Oxidation ratio for the north-facing midslopes of Shale Hills and Garner Run. The figure depicts the

average CO₂ and O₂ of the three gas tubes for each time point at each depth of the two locations falls in relation to the theoretical -1:1 line. There was a significant topography effect on the oxidation ratio ($p < 0.05$). The R² values for the linear regression are 0.4288 for sandstone and 0.2774 for shale.

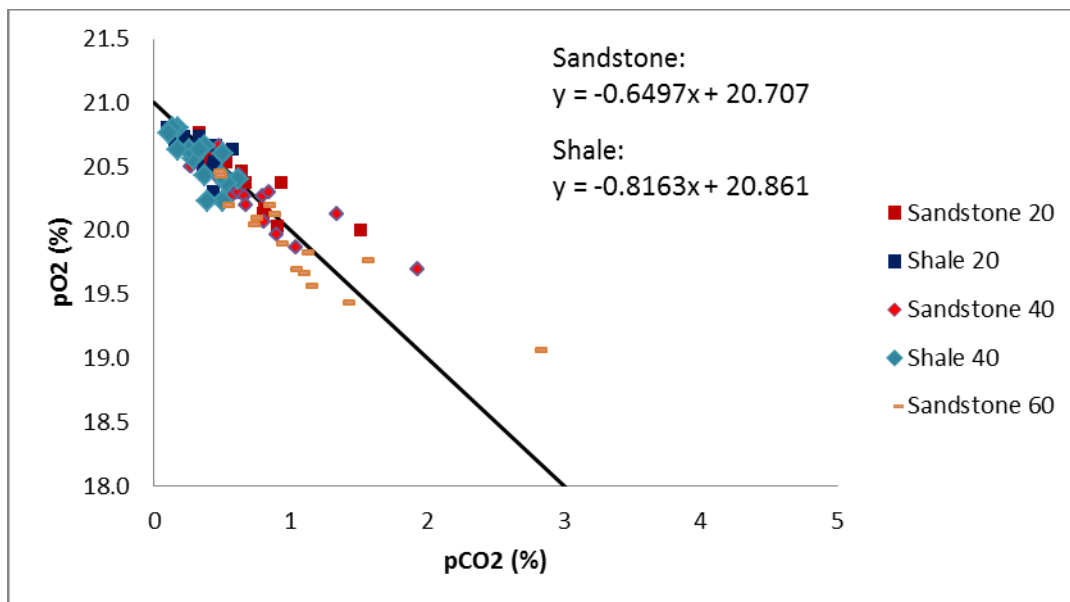


Figure 1-13. Oxidation ratio for the ridgetops of Shale Hills and Garner Run. The figure depicts the average CO₂ and O₂ of the three gas tubes for each time point at each depth of the two locations falls in relation to the theoretical -1:1 line. There was a significant topography effect on the oxidation ratio ($p < 0.05$). The R² values for the linear regression are 0.7346 for sandstone and 0.5217 for shale.

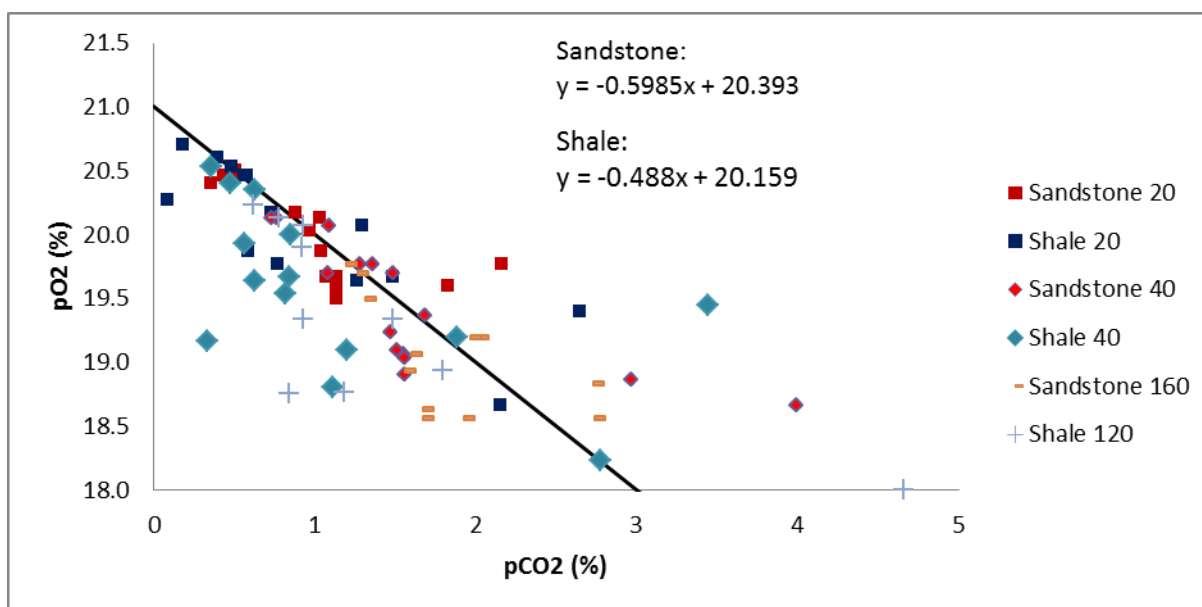


Figure 1-14. Oxidation ratio for the valley floor of Shale Hills and Garner Run. The figure depicts the average CO₂ and O₂ of the three gas tubes for each time point at each depth of the two locations falls in relation to the theoretical -1:1 line. There was a significant topography effect on the oxidation ratio ($p < 0.05$). The R² values for the linear regression are 0.7354 for sandstone and 0.4184 for shale.

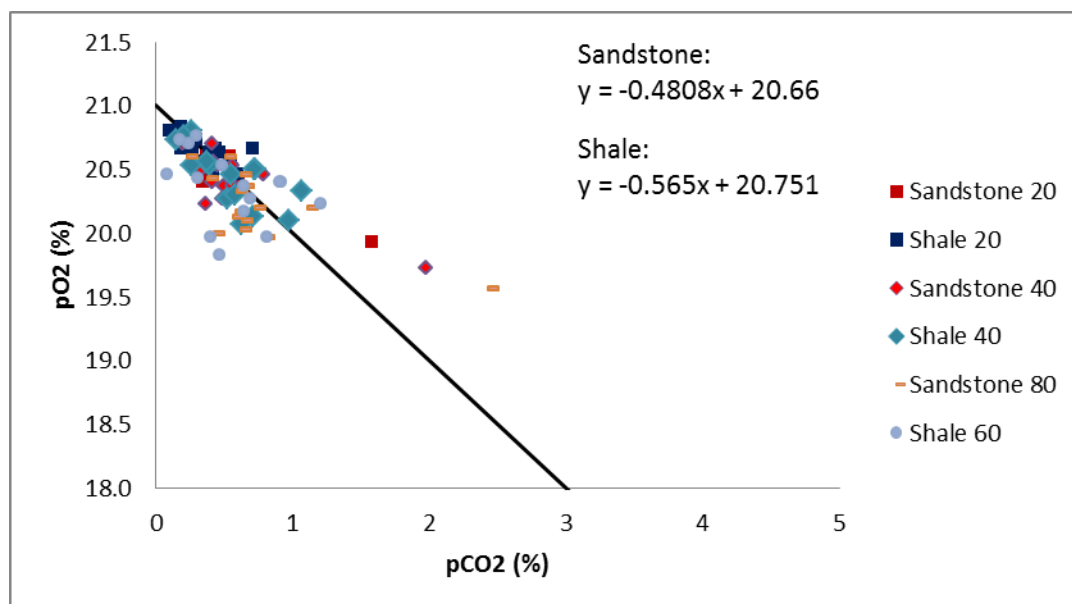


Figure 1-15. Oxidation ratio for the south-facing midslopes of Shale Hills and Garner Run. The figure depicts the average CO₂ and O₂ of the three gas tubes for each time point at each depth of the two locations falls in relation to the theoretical -1:1 line. There was a significant topography effect on the oxidation ratio ($p < 0.05$). The R² values for the linear regression are 0.6207 for sandstone and 0.3675 for shale.

Table 8. Oxidation Ratio Slopes, Corrected Slopes and Y-Intercepts. The table shows the slope from the pO₂ vs pCO₂ data, corrected slope using equation 1 and y intercept for each topographical point on the two lithologies.

Lithology	Topographical Position	Slope	Corrected Slope	Y-Intercept
Shale	Valley Floor	-0.488	-0.64416	20.159
Shale	South Facing Midslope	-0.565	-0.7458	20.751
Shale	Ridgetop	-0.8163	-1.0775	20.861
Shale	North Facing Midslope	-0.5378	-0.7098	20.822
Sandstone	Valley Floor	-0.5958	-0.7864	20.393
Sandstone	South Facing Midslope	-0.4808	-0.634656	20.66
Sandstone	Ridgetop	-0.6497	-0.8576	20.707
Sandstone	North Facing Midslope	-0.4254	-0.561528	20.472

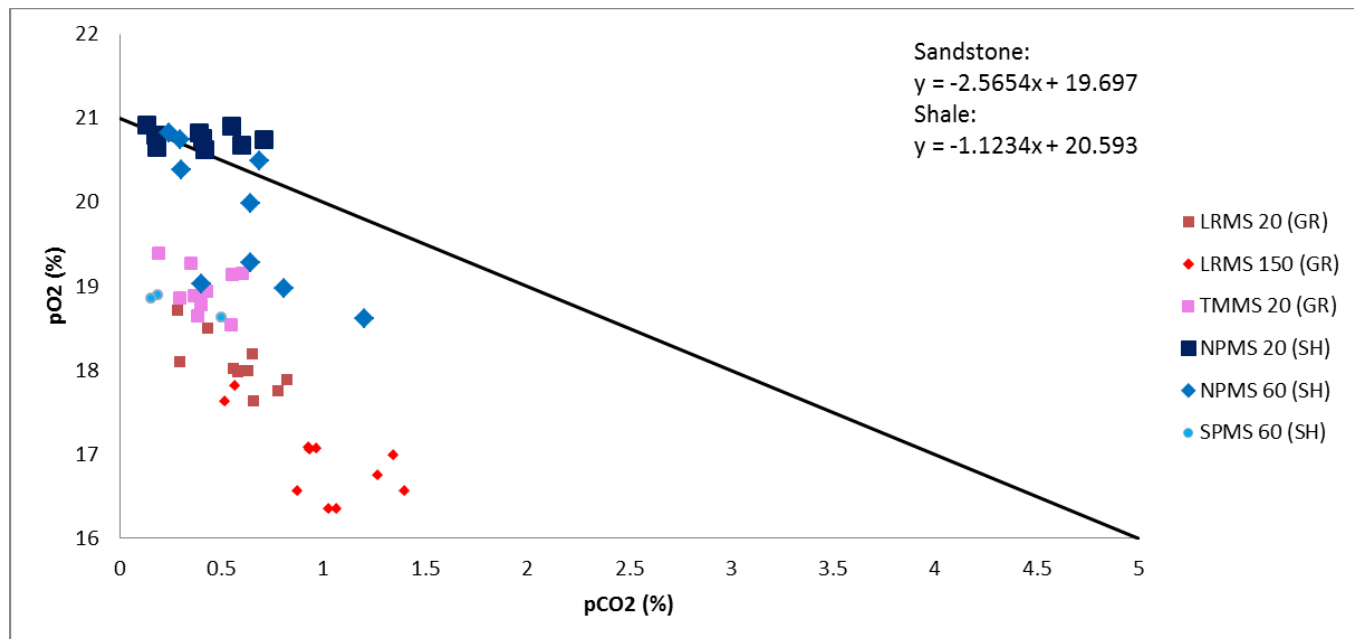


Figure 1-16. Oxidation ratio for Shale Hills and Garner Run using automated O₂ data from 2016. The figure depicts where each time point for the average CO₂ and O₂ for each lithology type falls in relation to the theoretical -1:1 line. The R² values for the linear regression are 0.7287 for sandstone and 0.1138 for shale.

Soil Moisture

Soil moisture was measured at corresponding depths with soil gas concentration (Figs. 1-17 and 1-18). Soil moisture was also averaged by spatial replicates.

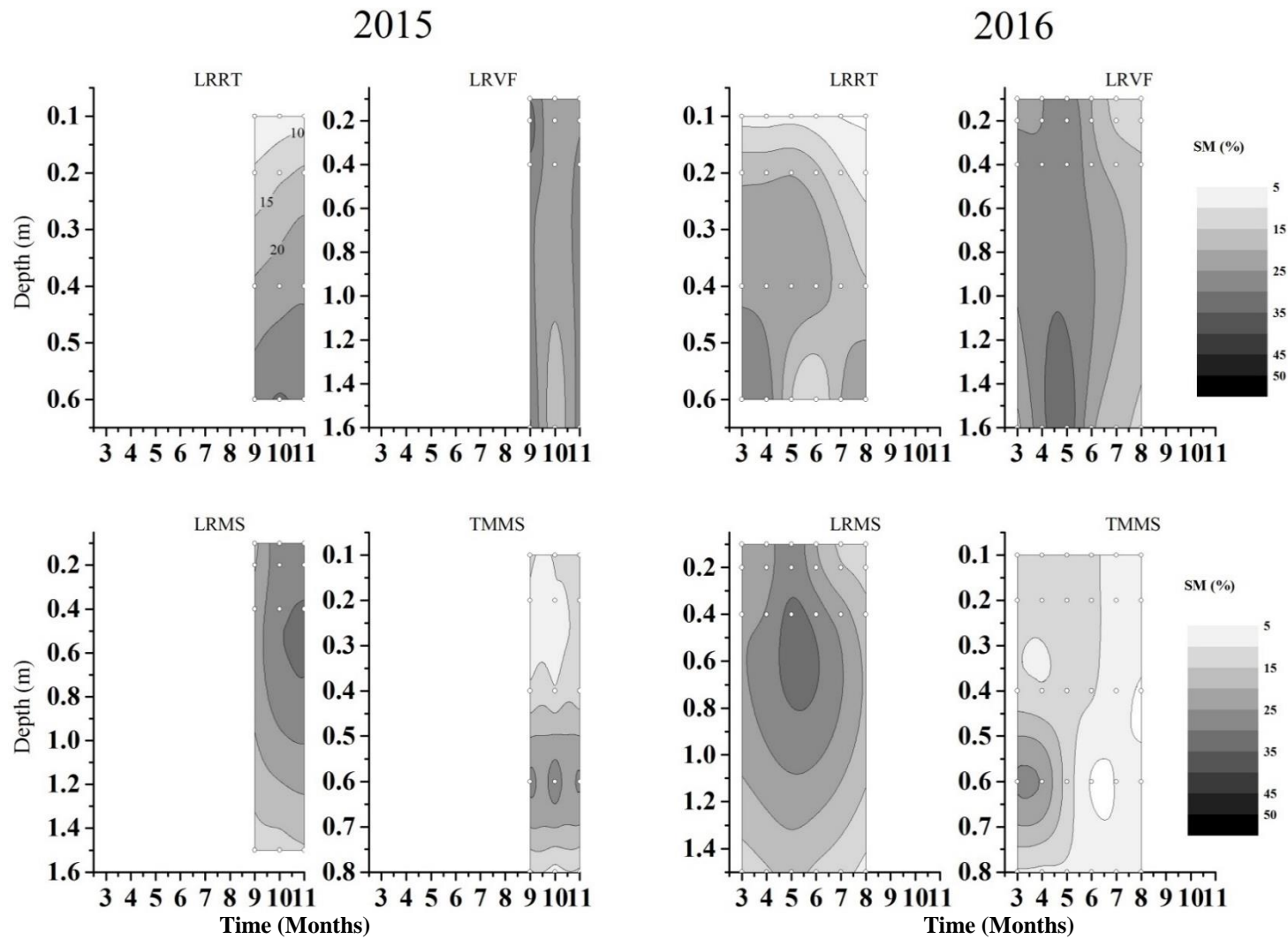


Figure 1-17. Contour plot of volumetric soil moisture (%) for Garner Run in 2015 and 2016. The figure shows the change in soil moisture over time by the depths of 20cm, 40cm and the varying D-20cm depths. The values are averages of the three TDR probes located at each depth in each topographical position.

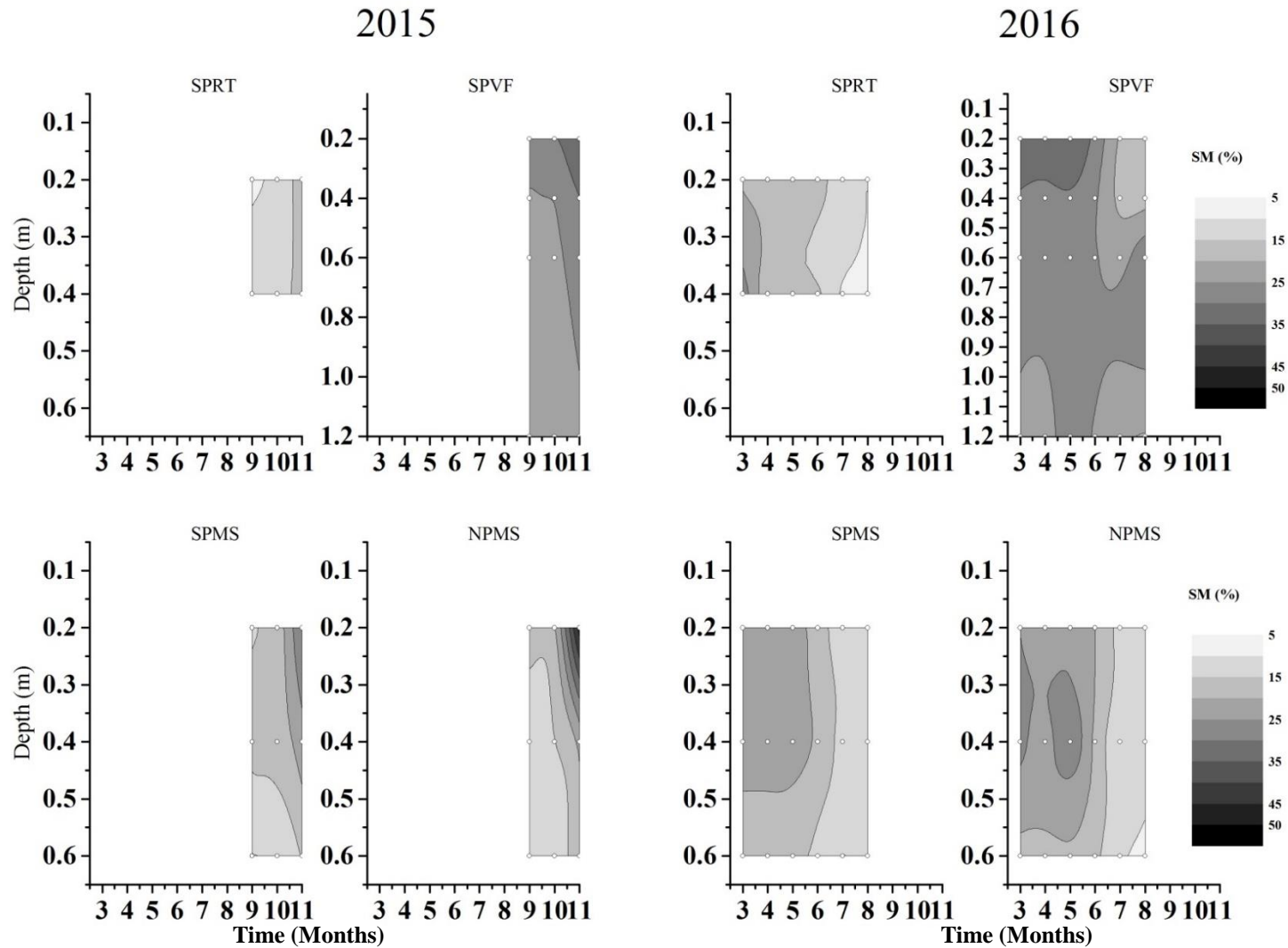


Figure 1-18. Contour plot of volumetric soil moisture (%) for Shale Hills in 2015 and 2016. The figure shows the change in soil moisture over time by the depths of 20cm, 40cm and the varying D-20cm depths. The values are averages of the three TDR probes located at each depth in each topographical position.

DISCUSSION

The primary objective of this project was to quantify CO₂ and O₂ concentrations and the oxidation ratio in different lithologies. This study examined three research questions: 1) Do soil CO₂ and O₂ differ in soils derived from shale and sandstone lithologies; 2) Is the variation in gas concentration that is explained by lithology as large as well-documented effects of topographic position and soil moisture; and 3) Do correlations between pCO₂ and pO₂ support the hypothesis that aerobic respiration the dominant process controlling CO₂ concentrations in soil profiles?

In this study, we focused on the patterns of topography and lithology on CO₂ concentrations. The patterns observed with depth are well-documented and I chose to analyze the average of all depths for a given pit. While this approach has some weaknesses, I do not think averaging across depths masked any major patterns in the dataset. First, contour plots show (Figs. 1-8 and 1-9) that the 20 and 40 cm depths for the sites do not differ between the shale and sandstone sites. Deeper locations do differ between shale and sandstone, but these differences are correlated with depth. This is because the deepest samples were collected 20 cm above the bottom of the pit and pit depth varied among sites. Lithology was not a main significant effect for the gas concentrations, due to the close interactions between topography and lithology. However, we observed differential drying patterns between the two lithologies, with soils derived from shale drying faster after the growing season than the soils derived from sandstone (Figs. 1-17 and 1-18). This difference in soil moisture also leads to an apparent pattern of less O₂ in the sandstone site at depth in all topographical positions. Thus, with more detailed observations, it is possible that lithology, through its effect on inundation and desiccation rates, may affect soil gas concentrations. Due to increased weathering reactions using carbon dioxide, we also expect there to be significant effect of lithology deeper in the soil profile, near the regolith-bedrock boundary (Kim, Stinchcomb & Brantley, *In Review*). Lithology may not be a significant control on CO₂ and O₂ in our locations, due to the similar climate and soil texture of the two sites (Table 2).

While lithology was not a significant main effect, the two-way interaction of lithology * time and the three-way interaction of lithology * time * topography was significant for both CO₂ and O₂

concentrations. Seasonality and topography have been documented to have significant impacts on soil gas concentration (Hasenmueller et al., 2015) and we were unable to separate lithological effects from soil moisture (seasonality) and topography. Topography and soil moisture are still the driving forces behind differences in soil gas concentrations. As our data show (Figs. 1-8 to 1-11, 1-17 and 1-18), the valley floor positions have the greatest water content and the highest $p\text{CO}_2$ concentrations and the lowest O_2 concentrations. The amplitude of temporal change is also greatest in the valley floor. The valley floors positions also have deeper soils and receive material deposits from higher in the catchment which may result in higher microbial activity and higher aerobic respiration.

If aerobic respiration was the dominant process controlling then our samples would fall around the -1:1 line, aside from correction for diffusivity differences. When the slope of -1 is corrected for the diffusion differences it is -1.32. Most of our points generate slopes that are not as negative as 1.32, we hypothesize that our slopes are driven by outliers that have decreased O_2 . Focusing on just the points during the growing season, the slopes from the valley floor and ridgetop positions for both sandstone and shale are not significantly different than the theoretical -1.32 line (Hill, Brantley and Kaye, 2016). However, the time points that deviate from the line at the valley floor positions are during August and May, when central PA may receive increased precipitation and the increased water may affect diffusivity, as both O_2 and CO_2 diffuse slowly through water filled soil macropores. For the other topographical positions, there was significantly higher CO_2 in August 2015, after a storm event (NOAA, 2016). The storm event led to increased water availability that may have increased root and microbial respiration, but it is unclear why O_2 did not decline proportionally. We suspect that weather is a larger factor than the parent material in the upper layers of the soil profile. In addition, we may not have been close enough to the sandstone regolith-soil boundary to detect the differences between shale and sandstone. Another hypothesis is that our sites may have also received dust additions that could have masked lithological differences (Ciolkosz, et al. 1990); (Chapter 2). Our oxidation ratio data may suggest that increased diffusivity is the driver in the differences between topographical positions. Under drier conditions when

higher diffusivity occurs, CO₂ may leave the soil faster than it is replaced by respiration, while O₂ may still be high, as it could be held in the water stored in the soil macropores (Neira et al. 2015).

Aside from lithology and topography, many soil characteristics drive the diffusion and concentrations of CO₂ and O₂ (Fig. 1-1). These characteristics include soil moisture, soil texture and porosity, soil depth and rooting depth. Soil moisture controls microbial activity and with temperature can control decomposition rates and CO₂ production. Soil moisture is related to soil texture, soil porosity and soil depth. In Garner Run the dominant soil texture is sandy loam (Brantley et al. 2016), whereas the dominant soil texture in Shale Hills is a silt loam (Lin, 2006). Both textures are comprised of 20% (by weight) or greater of sand particles and may behave similarly for gas diffusion. Soil texture affects the water holding capacity through its influence on soil porosity. Soil porosity is the pore space available in the soil profile and can affect the soil moisture and gas concentrations in the pore spaces (Law et al. 2001; Tang et al. 2003; Sullivan et al. 2008).

If topography and soil depth are dominant controls on soil gas concentrations, then the main imprint of lithology on soil gas may be through controls on soil thickness. These soil characteristics can be different throughout the soil profile and affect CO₂ concentration deeper in the soil profile. The deeper into the soil profile, CO₂ concentration increases, due to decreased diffusion (Hasenmueller et al. 2015). Soil depth or thickness can be significantly affected by lithology, and for our locations Garner Run has a greater soil depth than Shale Hills (Table 2).

Soil depth may also attribute to other differences between Shale Hills and Garner Run. As they also vary in their rooting distribution, as there is significantly more root biomass in the 20-40cm depth in Garner Run and significantly more root biomass in the first 20cm in Shale Hills (Orr, Szink, & Eissenstat, 2017). The rooting distribution differences can drive the concentration of carbon dioxide with an increase in root respiration and turnover (Tang et al. 2005). There is a feedback loop between rooting distribution and organic matter; as roots proliferate towards high nutrient concentration, such as organic matter, and with root die-off, organic matter is replenished (Gale & Grigal, 1987). The organic matter content of the

soils in Garner Run and Shale Hills varies as well. Garner Run has increased organic matter, possibly due differences in the tree species composition (Brantley et al. 2016) and understory growth.

In conclusion, topography had a greater effect on CO₂ concentration, O₂ concentration and oxidation ratio than lithology. Topography influences soil moisture, texture, porosity and depth; all of which influence on soil gases diffusing through the soil profile (Hasenmueller et al. 2015). Our results support prior work from the SSHCZO and others' research, that the drier soils in the ridgetop and planar mid-slopes have lower pCO₂ than their wetter counterparts in the swale and valley floor positions (Groffman & Tiedje, 1991; Hasenmueller et al. 2015). Dry soils have decreased pCO₂ due to increased diffusivity and decreased respiration. Our results show that O₂ is significantly converse to CO₂ concentrations, as the locations that have the highest CO₂ have the lowest O₂ concentrations. The oxidation ratio is changed by the differences in diffusivity and soil moisture which is a result of topographical position. The results of this study also help assist the call for greater topographical resolution for soil mapping to better predict soil carbon dynamics.

CHAPTER 2

Soil and leaf nutrient availability in shale and sandstone catchments of central Pennsylvania

Nutrients are compounds or elements essential to plant or microbial growth. Plant growth or production can be limited by low nutrient content, such as nitrogen (N) or phosphorus (P), other resources, such as water and light, or a combination (Canham et al. 1996). Measuring nutrient limitation and co-limitation to plants and microorganisms is key to understanding how nutrients cycle through an ecosystem and possibly leave, either via gaseous losses or water pathways. In deciduous forests of the Northeast, US, most studies of nutrient limitation have focused on N (Matson et al. 1999; Elser et al. 2007; LeBauer & Treseder, 2008) and perhaps because ecosystem N is derived from the atmosphere, these studies have not expanded our understanding of lithological controls on nutrient availability. Other nutrients have been investigated in fertilizations studies, such as liming to help increase tree growth (Long, Horsley, & Hall, 2011). The availability of other nutrients, such as P and cations may have strong lithological controls, and while N may be a common limiting nutrient, recent meta-analyses suggest that co-limitation by multiple nutrients is more common than previously thought (Elser et al. 2007; Harpole et al. 2011). The purpose of this study is to examine nutrient availability, to measure elements or compounds in the soil solution that can be absorbed readily into plants, that are present in forest soils developing on shale and sandstone lithology types that are commonly adjacent throughout the Appalachian Mountains.

Lithology has been documented to affect nutrient availability via fluxes of nutrients from the bedrock to soils through weathering. Soil nutrient composition is affected by the chemical composition of lithology, as parent material weathers to form soil layers and nutrients travel into soil nutrient pools (Cline, 1977; Jenny, 1994; Neff et al. 2006; Hartmink & Bockheim, 2013). In Massachusetts, lithology

affects soil nutrients pools, with higher pH and soil nutrients on basalt than arkose (sandstone), corresponding to higher plant species diversity (Searcy et al. 2003). Lithology significantly affects soil and foliar nutrient levels through weathering and topography. Topography affects temperature, slope, water movement and microclimate, leading to changes in microbial communities (Eimil-Fraga et al. 2014; Skidmore et al. 2005). Aside from nutrients, lithology can also affect the water holding capacity and impact water availability to plants (Witty et al. 2003). Due to the lithological effects on soil properties, nutrient cycles, microbial and plant communities, whole landscapes can be affected by lithology, including spatial variation in primary productivity (Hahm et al. 2014).

Nutrient or resource limitation has been widely studied through fertilization studies, but fertilization is often impractical and can change the ecosystem (Sullivan et al. 2014). Fertilization studies also require a long-term approach to observe nutrient limitations, and without expansive full-factorial designs fertilizations studies cannot detect co-limitation. One unintended result of fertilization is that sometimes the increased concentration of nutrients can lead to saturation and have negative impacts on the ecosystem (Aber et al. 1989). Due to these complications, ecologists have increasingly turned to alternative indicators of soil nutrient supply and organismal indicators of nutrient limitation (Sullivan et al. 2014). Nutrient limitation is best assessed with an array of methods focused on the distribution of the nutrients in multiple pools and how they move from one pool to the next. Therefore, we focused on measurements of soil and foliage nutrient concentration to quantify the two largest pools of nutrients and how nutrients cycle within tree species with a measure of nutrient resorption efficiency (Kozovits et al. 2007). Our suite of soil and tree analyses assessed whether and where different nutrients may limit plant activity, by measuring soil nutrient concentration, cation exchange capacity and percent base saturation, and live and dead leaf nutrient concentration.

Differences in lithology interact with forest tree composition. Tree species can affect soil nutrient pools through atmospheric deposition, nitrogen fixation, mineral weathering by roots exudates, carbon outputs, and increase of soil microbiota (Binkley & Giardina, 1998). In this study, we focus on the effect that lithology (possible parent material) has on nutrient cycling between two specific tree species and the

soil supporting them. Due to specific nutrient use and requirements, we focused on two common tree species, *Quercus rubra* (red oak) and *Acer rubrum* (red maple). Red oak and red maple trees are located in the canopy of all 10 of our study sites. Prior research has shown that these species present different responses to nutrients. Both tree species have been shown to be N limited; however red oak are not as sensitive to low soil N as red maple (Aber et al. 1998; Schneider & Allen, 2012). Red oak trees may cycle high levels of cations, such as calcium and magnesium, through their foliage (Hallett & Hornbeck, 1997). In comparison, red maple trees may lose foliar cations due to acid rain (Schier, 1987; van Breemen et al. 1997). Red maple and red oak vary in their root production. Both red oak and red maple have a concentrated peak in root production in late May; however, the peak is more distinct for red oak than red maple. In McCormack's work, there was also more interannual variation for red oak than red maple. Overall, they observed that red maple trees produced more roots than red oak trees, but red oak trees have a greater turnover rate than red maple trees (McCormack et al. 2014).

The interaction between tree species and soil nutrient pools is very pronounced in nutrient cycles, as trees affect the distribution and transformation of nutrients across a landscape (Johnson, Verburg, & Arnone, 2016). Throughout PA, increased acidity has led to a decline in foliar and soil cations which results in reduced growth and increased mortality in red oak (Demchik & Sharpe, 2000). Tree species can also affect soil acidity and indirectly mineral weathering with the exchange of N and Ca in the root system (Mueller et al. 2012). In forested catchments, nutrient pulses from harvesting change the nutrient cycling in the catchment (Hornbeck & Kropelin, 1982). In temperate forests, trees drop their leaves and can reuse the nutrients from the litterfall as it decomposes in the soil. However, nutrient resorption of foliar cations before leaf senescence can help mitigate the effects of low soil nutrient pools and decrease plant dependence on soil nutrient pools (Covelo, Durán, & Gallardo, 2008). There are many documented ways to measure nutrient use; for this study we focused on nutrient use efficiency as reflected in foliar nutrient concentrations and resorption rates (Boerner, 1984; Kobe, Lepczyk, & Iyer, 2005; Vergutz et al. 2012).

Nitrogen (N) has been studied extensively as a limiting nutrient (Matson et al. 1999; Baribault et al. 2010), as a pollutant from over fertilization (Kaiser, 2001) and more recently as a co-limiting nutrient with phosphorus (P) and calcium (Ca). Nitrogen deposition due anthropogenic use of N has resulted in a growth increase but then a detrimental effect to the overall ecosystem, through gaseous and leaching losses. Many ecosystems are exhibiting large N pulses from the ecosystem to the stream water, similar to the pulse when a forest is clear cut (Johnson, 1995). Therefore, the paradigm of N limitation is shifting to co-limitation by N and other nutrients (Harpole et al. 2011). Phosphorus is often studied with N, as a shift in N limitation to P limitation may occur over long time scales as P is depleted from soils (Walker & Syers, 1976). Phosphorus inputs to an ecosystem are normally rock derived or atmospherically deposited. Phosphorus limitation can occur when the rock-derived P is depleted, especially since many lithologies are low in phosphorus; or when P in the soil binds with soil minerals (Vitousek et al. 2010). Phosphorus additions have shown to improve biotic growth; however, most phosphorus fertilizers also included calcium. Therefore, in prior studies with P fertilizer additions, ecosystem changes following fertilization may reflect responses to both the P and Ca inputs (Sullivan et al. 2014). Calcium is an essential macronutrient for plants (White & Broadley, 2003) and is a recognized biogeochemical factor that can influence ecosystem function and structure (Dauer & Perakis, 2014). However, Ca pools are being depleted due to increased acid deposition and forests can decline in growth when soil Ca pools are depleted (Battles et al. 2013; Johnson et al. 2014). Ca is exchanged in soil via cation exchange and can easily be lost through the hydrologic cycle by leaching (Johnson et al. 1988; Federer et al. 1989; Bailey et al. 1996). When Ca is depleted the main effect on plants may not be direct limitation by Ca, but rather changes in the abundance of toxic metals (Al and Mn) on exchange sites and soil solutions (Chapin III, Matson, & Vitousek, 2011).

The two lithologies we focused on are the Rose Hill shale formation and the Tuscarora sandstone formation. Both are located in the Ridge and Valley province of central PA and they (or similar shales and sandstones) are common throughout the Appalachian Mountains. The mineral composition of the two lithologies strongly contrast: the Rose Hill Shale consists of quartz, illite, chlorite, vermiculitized chlorite,

Fe oxides, and minor feldspar (Jin et al. 2010; Hasenmueller et al. 2015); the Tuscarora Sandstone is predominately quartz (Brantley et al. 2016). In this study, we focused on measurements of nutrients in four pools: soil solution or pore water, leaf nutrient concentration in both live and senesced leaves, bulk mineral soil, and organic horizon soil. By focusing on two trees species, we are accounting for the tree species-specific nutrient use.

We focused on nitrogen, phosphorus and calcium due to their importance in plant growth, exchange of the nutrients and reported limitation in forest ecosystems (Vitousek & Farrington, 1997; Matson et al. 1999; Baribault, Kobe, & Rothstein, 2010; Vitousek et al. 2010; Sullivan et al. 2014). By investigating the magnitude of these nutrient pools, we sought to learn how nutrient limitation may be affected by the specific mineralogy and chemical composition of the lithologies. Based on the elemental concentrations of P and Ca in parent rocks (Table 1), we hypothesize that there would be large differences in the nutrient pools in the soil and biota and nutrient availability would be lower in soils derived from sandstone than soils derived from shale.

METHODS

Site Description

Soil chemistry and leaf chemistry were measured in the Ridge and Valley Region of Pennsylvania at five sandstone and five shale sites that include the two locations of the SSCZO, Garner Run and Shale Hills (Fig. 2-1). The five sandstone sites are all located on Tuscarora sandstone with Hazleton or Hazleton association soil series and the five shale sites are located on Rose Hill shale with Berks or Berks association soil series (Lin, 2006; Brantley et al. 2016). We focused on north-facing midslope positions, as the ridgetop normally has shallow soil and the valley floor can be affected by sediment deposition (Frissell et al. 1986; Dere et al. 2013).

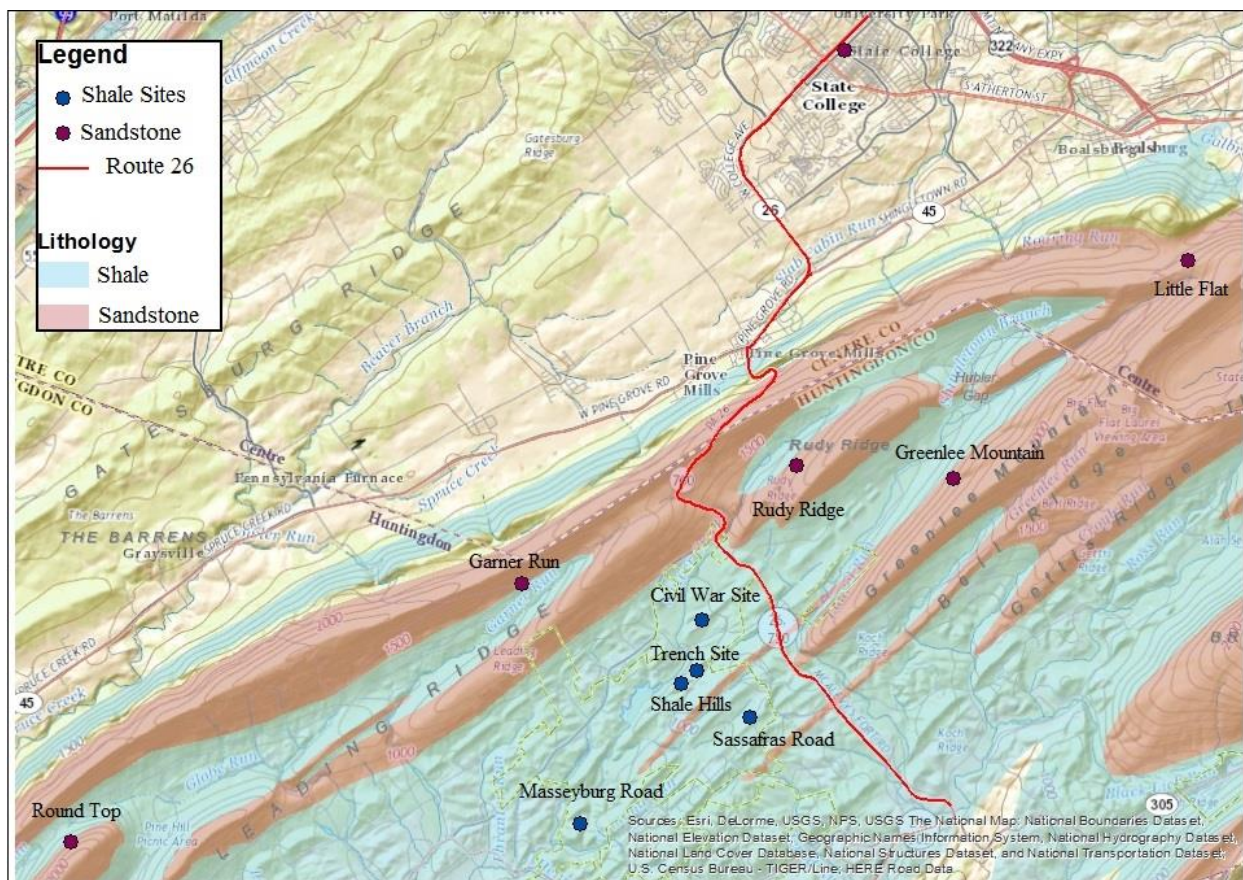


Figure 2-1. Ten locations of shale and sandstone lithologies in central PA. Background color indicates lithology and color coded points indicates lithology and study sites.

Table 9. Latitude and longitude of the ten locations in central PA.

Location	Latitude	Longitude
Garner Run	40.6949	-77.9199
Shale Hills	40.66402	-77.90642
Trench Site	40.66944	-77.89907
Sassafras Road	40.66013	-77.88484
Masseyburg Road	40.63858	-77.93030
Civil War Site	40.67970	-77.89741
Round Top	40.63490	-78.06433
Little Flat	40.75130	-77.76883
Rudy Ridge	40.71056	-77.87569
Greenlee Mountain	40.71110	-77.83975

Soil Collection and Chemistry

Mineral soils were collected from five subsampling locations within all 10 sites at two depths, 0-20 cm and 20-40 cm, using slide hammer manual soil corer (D= 5 cm). Organic horizon samples were

also taken near the mineral soils samples using a PVC Ring (D = 25 cm). Bulk elemental concentrations for each soil horizon were analyzed in the laboratory. Mineral and organic soil samples were homogenized for each subsample. A 20 g aliquot of each subsample was extracted the day of collection using 2M potassium chloride and filtered using a Whatman #1 filter paper for inorganic nitrogen analysis. The remaining subsample was wet-sieved using a 2mm sieve to obtain the rock weight. The extracts were measured for inorganic nitrogen via a spectrophotometer microplate reader. Nitrate plus nitrite ($\mu\text{g N/g}$ soil) was measured using the vanadium chloride protocol (Doane & Horwath, 2003). We assume nitrite was negligible in these samples and refer to these data as nitrate concentrations. Ammonium ($\mu\text{g N/g}$ soil) was measured using the salicylate, citrate and hypochlorite method (Baethgen & Alley, 1989). Gravimetric water content was measured within 48 hours of sample collection, using a 5 g aliquot of soil. Rocks in the gravimetric water content aliquot were also weighed using a wet-sieving method with a 2 mm sieve. The remaining mineral and organic soil samples were air-dried to a constant weight. Organic samples were ground using a Wiley-Mill 4. Samples were then analyzed for total carbon and nitrogen content using CHNS/O Elemental Analyzer (CE Instruments Elemental Analyzer EA 1110, Thermo Fisher Scientific, U.S.). The soil samples were also extracted, using the Mehlich-3 solution, for cations and phosphorus by the Agricultural Analytical Services at Pennsylvania State University and analyzed on the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Optima 7300 DV, PerkinElmer). The soil samples were analyzed for pH and acidity in soil-water solution, cation exchange capacity (CEC) through the summation method (Sims & Wolf, 1995) and percent of CEC for calcium, magnesium and potassium by the Agricultural Analytical Services at Pennsylvania State University.

Soil Solution – Porewater Samples

Soil water samplers (Soilmoisture Equipment Corp., Santa Barbara, CA) were installed in the Shale Hills catchment in September 2006 (Jin et al. 2011). In the growing season, a vacuum of -50 kPa was pulled fortnightly and the samplers were left overnight. A peristaltic pump is used to pump the water out of the samplers and into collection bottles for further analysis in the laboratory. Soil water samples

(Prenart Equipment ApS, Frederiksberg, Denmark) were deployed in the Garner Run catchment with the GroundHOG in October 2014. Polyethylene collection bottles were attached to the Prenart soil water samplers and a vacuum of -50 kPa was pulled and left overnight. The porewater samples were transported back to the laboratory and analyzed for major cations using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and inorganic nitrogen using a microplate colorimetric analysis. Nitrate (mg N/ L) was measured using the vanadium chloride protocol (Doane & Horwath, 2003). Ammonium (mg N/ L) was measured using the salicylate, citrate and hypochlorite method (Baethgen & Alley, 1989).

Leaf Resorption Analysis

In 2015, one *Acer rubrum* and one *Quercus rubra* canopy tree were selected on the north-facing midslope of the ten sites. In July 2015, live sun leaves (leaves high in the canopy that receive the most radiation) were shot down using a Winchester 1300 Pump Action Shotgun and approximately 100 leaves were collected. At the end of the growing season, recently (within 1 week of falling) senesced leaf litter was collected in litter traps (approximately 1ft x 0.5ft x 1.5ft) at the base of each tree. Leaf samples were oven dried at 60 degrees C for at least 48 hours. Leaves were ground using a Wiley Mill #4 and a small pore filter (5mm). Twigs and debris, larger than 8cm long and 2cm wide, were removed from the sample before grinding. Ground samples were tin rolled and measured for total carbon and nitrogen content using a CHNS/O Elemental Analyzer. Other elements were determined by the Agricultural Analytical Services at the Pennsylvania State University, using an ICP-AES after nitric acid digestion of the ground leaf material. By investigating the nutrient concentration of the live leaves and leaf litter, the relative resorption (e.g. ratio of N resorption to P resorption) was calculated and used to infer relative nutrient limitation (Kozovits et al. 2007; Sullivan et al. 2014). In 2016, two additional *Acer rubrum* and *Quercus rubra* trees were selected at the Garner Run and Shale Hills sites to account for tree to tree variation. Live sun leaves and senesced leaves were collected and analyzed in the same fashion. Nutrient resorption calculations were based on the following equation (Boerner, 1984; Kobe et al. 2005; Vergutz et al. 2012):

$$\frac{\text{Nutrient Content (Green)} - \text{Nutrient Content (Sen.)}}{\text{Nutrient Content (Green)}} * 100\%$$

Statistical Analysis

We used a nested ANOVA (PROC GLM, SAS 9.4) to analyze the effects of lithological type and location nested within lithological type on soil chemical concentration data. Phosphorus (Pppm), magnesium (Mgppm), Sulfur (Sppm), Copper (Cuppm), Zinc (Znppm), and Calcium (Cappm), and pH, % saturation of CEC for Ca and Mg were log transformed to fit a normal distribution. Acidity and CEC were square root-transformed to fit a normal distribution. All other chemistry variables were normally distributed. Soil total inorganic nitrogen, nitrate and ammonium were analyzed with a mixed model analysis with location as a random effect (Fig. 4). Total nitrogen, nitrate and ammonium abundance +1 were log transformed for the analyses.

Leaf chemistry was analyzed with a mixed model with the fixed effects of tree species, lithology type and year; location was included as a random effect. Tree to tree variation was measured in Shale Hills and Garner Run in 2016 by adding two additional trees of each species. Within-site tree variation was greater than the lithology type effect (Table 11) ($p < 0.05$). However, across all sites there were significant effects of lithology type, species and year. Nutrient resorption efficiency was analyzed with two-way fixed ANOVA (PROC GLM, SAS 9.4). The relative nutrient resorption efficiencies between P: N were statistically analyzed using linear regressions. Resorption efficiencies between 2015 and 2016 will be analyzed for relative nutrient resorption efficiency and correlation to green leaf nutrient status (Kobe et al. 2005).

RESULTS

Soil Chemistry

Concentrations of all nutrients showed a location effect ($p < 0.05$) implying high site to site variability (Table 9). Magnesium, calcium, sulfur and potassium were higher in shale derived soils

($p < 0.05$). Phosphorus was higher in sandstone derived soils ($p < 0.05$) (Fig. 2-2). Copper and Zinc were not significantly different between rock types (Fig. 2-2).

All acidity measurements were significantly different for main effects of location and lithology ($p < 0.05$) (Fig. 2-3 to 2-5). The interaction between lithology and depth was significant for pH ($p < 0.05$). pH was significantly lower in sandstone derived soils than shale (Fig. 2-3). Acidity and CEC were significantly different for lithology and depth (Figs. 2-3 and 2-4). Acidity was significantly higher in sandstone derived soils ($p < 0.05$), whereas CEC was only higher in sandstone in shallow (0-20cm) soils. The percent CEC occupied by K and Mg didn't differ among lithologies, but calcium was more abundant on the CEC in shale soils than in sandstone soils ($p < 0.05$) (Fig. 2-5). There was a significant lithology type effect and lithology type* depth interaction for total nitrogen and ammonium ($p < 0.05$). There was greater ammonium in sandstone derived soils than shale, but only in shallow soils. There was no significance difference for nitrate (Fig. 2-6).

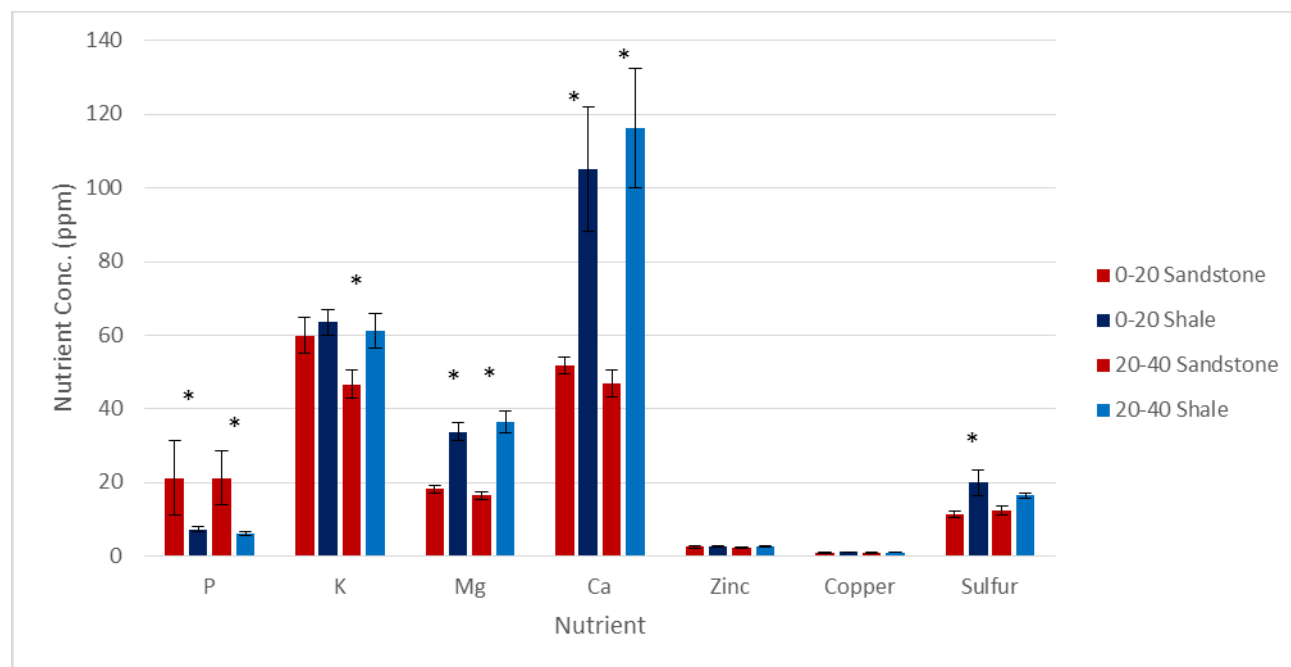


Figure 2-2. Nutrient concentrations in 0-20cm and 20-40cm depths of sandstone and shale sites. Bars are means (n

= 5) and one standard error. An asterisk indicates statistically significant differences between shale and sandstone for a given nutrient ($p < 0.05$).

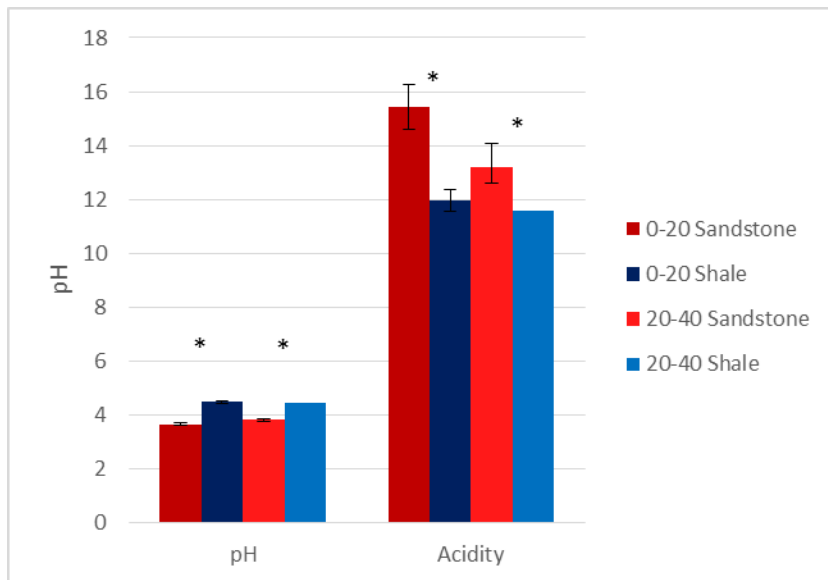


Figure 2-3. pH and Acidity for the in 0-20cm and 20-40cm depths of sandstone and shale sites. Bars are means ($n = 5$) and one standard error. An asterisk indicates statistically significant differences between shale and sandstone for pH and Acidity ($p < 0.05$).

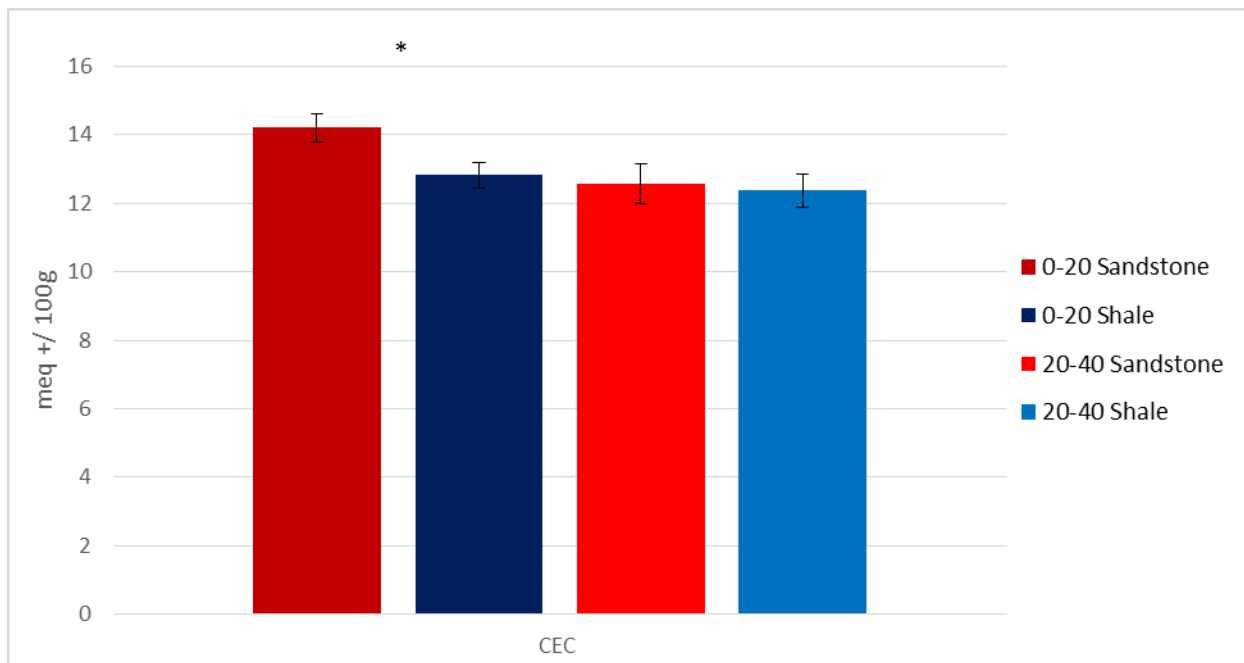


Figure 2-4. CEC for 0-20cm and 20-40cm depths of sandstone and shale sites. Bars are means ($n = 5$) and one standard error. An asterisk indicates statistically significant differences between shale and sandstone for CEC ($p < 0.05$).

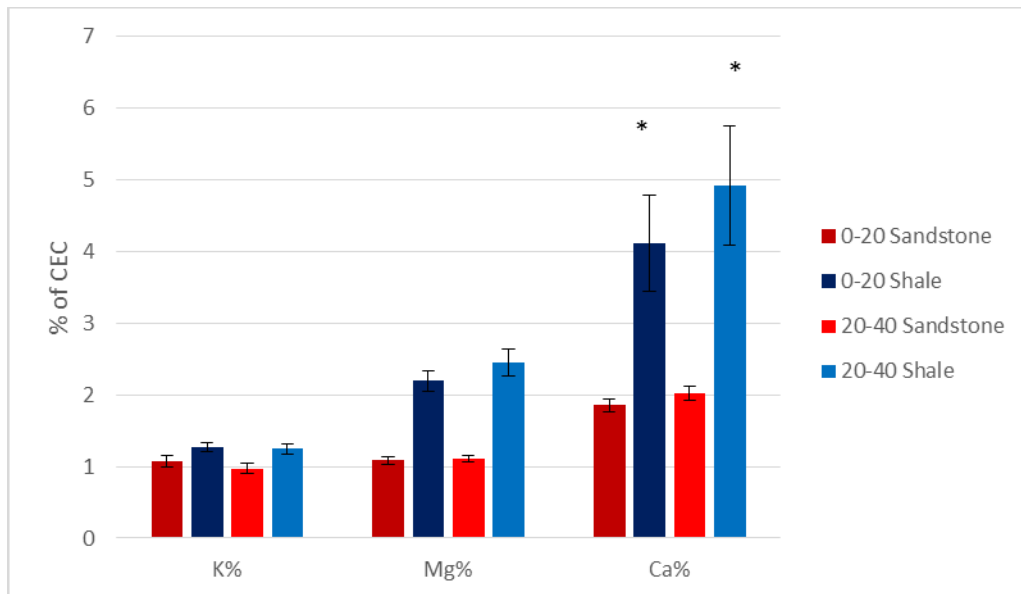


Figure 2-5. Percent of CEC for 0-20cm and 20-40cm depths of sandstone and shale sites. Bars are means ($n = 5$) and one standard error. An asterisk indicates statistically significant differences between shale and sandstone for Ca % of CEC ($p < 0.05$).

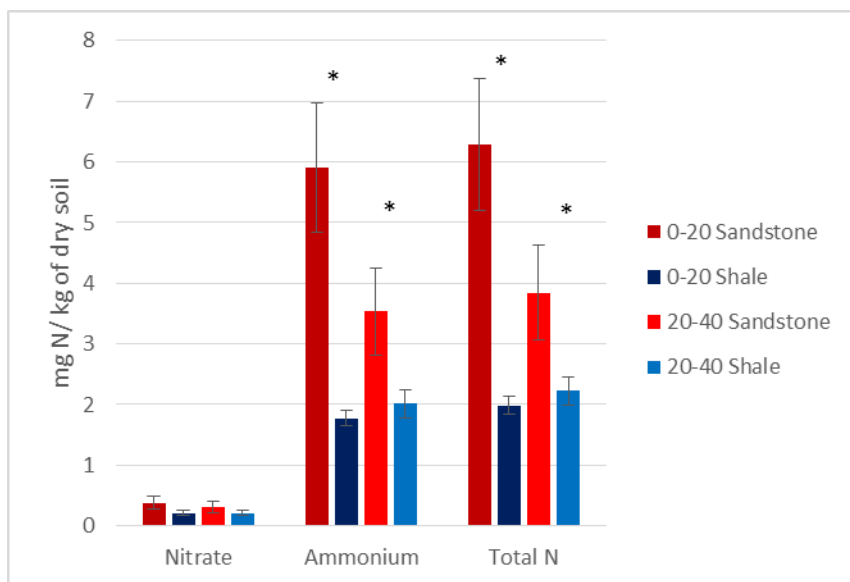


Figure 2-6. Inorganic N in mineral soils from shale and sandstone sites. Bars are means ($n = 5$) and one standard error. An asterisk indicates statistically significant differences between shale and sandstone for ammonium and total inorganic N ($p < 0.05$).

Table 10. Summary table of soil chemistry ANOVAs.

Effect	dF	P (ppm)		K (ppm)		Mg (ppm)		Ca (ppm)		Zn (ppm)		Cu (ppm)		S (ppm)	
		F	P	F	p	F	P	F	P	F	p	F	p	F	p
Lithology	1	6.48	0.0339	2.01	0.193	14.38	0.0051	9.13	0.016	1.1	0.3227	1.56	0.2469	6.84	0.0301
Location (Litho)	8	8.22	<0.0001	4.9	<0.0001	8.18	<0.0001	6.18	<0.0001	3	0.0057	13.15	<0.0001	6.11	<0.0001
Depth	1	0.06	0.8098	5.46	0.022	0.75	0.3892	0	0.9707	1.16	0.2848	1.46	0.2312	0.04	0.8451
Litho*depth	1	2.27	0.1358	3.05	0.0848	2.17	0.1447	1.64	0.2049	0.08	0.7786	1.35	0.2485	0.7	0.4057

Soil Pore Water

Pore-water analyzed for nutrient content of inorganic N, cations and anions (Figs. 2-7 and 2-8). Unfortunately, due the lack of replication for any site, we could not run a statistical analysis on the data. The averages for Garner Run and Shale Hills are presented below. Data from 2015 for the sandstone sites were previously published in Hoagland, et al. (*In Review*).

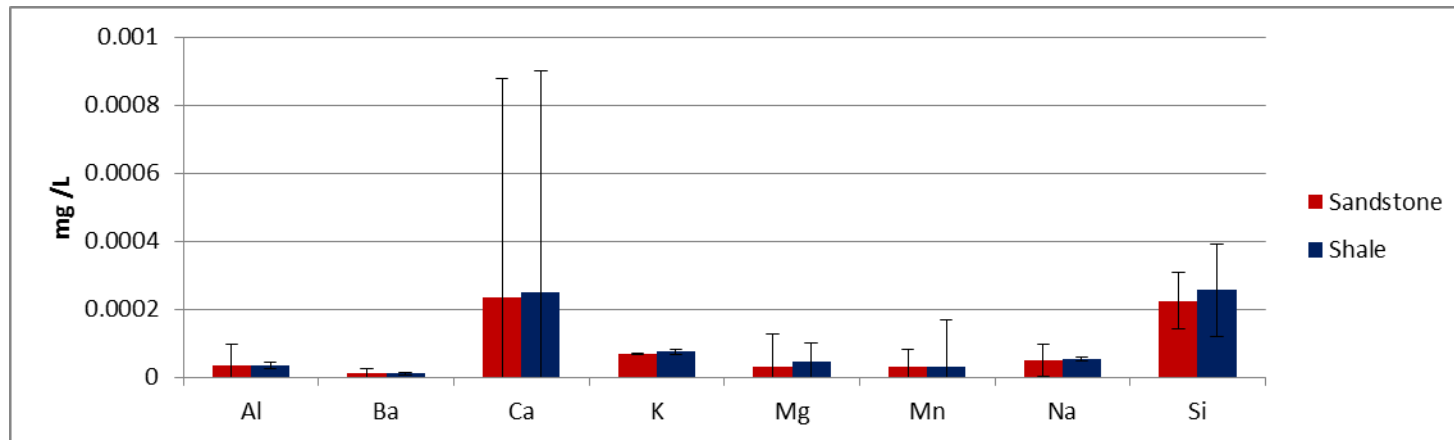


Figure 2-7. Porewater nutrient concentrations in sandstone and shale locations. Bars are means (n=13;n=15) of the samples from the Garner Run and Shale Hills, respectively.

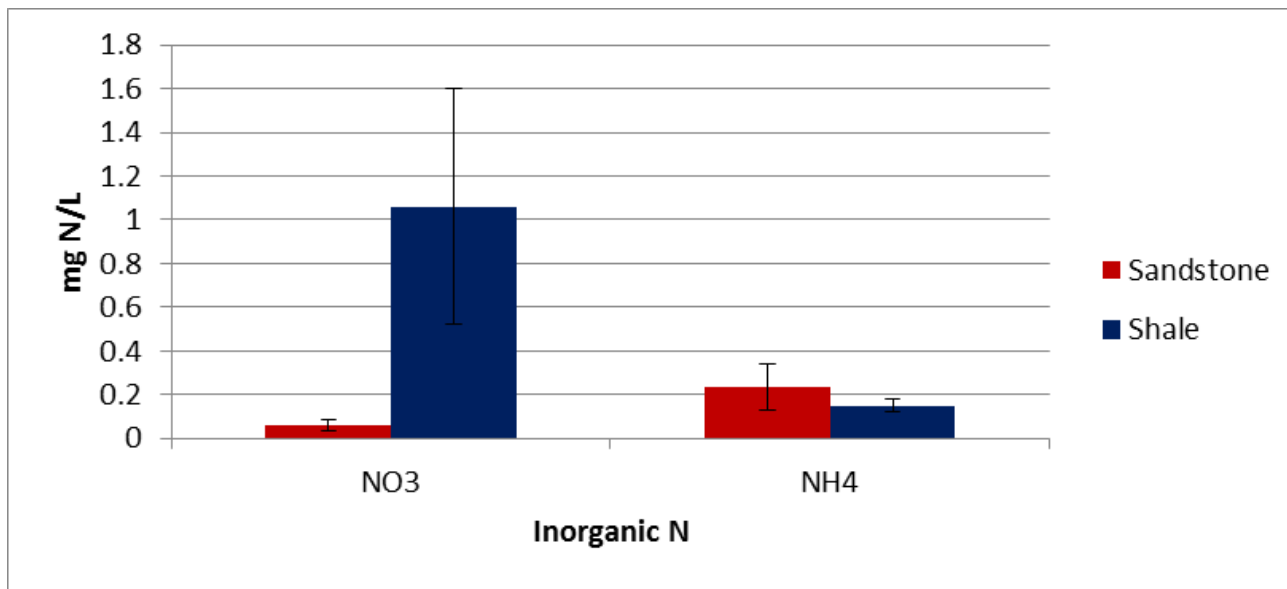


Figure 2-8. Inorganic N concentrations in porewater in sandstone and shale locations. Bars are means (n=13; n=15) of the samples from the sandstone site, Garner Run (vary in depth from 20cm to 160cm) and the shale site, Shale Hills (vary in depth from 20 to 160cm), respectively. Samples were collected throughout the year, with the most samples coming from the growing season.

Leaf Chemistry

Total carbon concentration had a significant year effect and lithology type * year interaction (Table 12) because live leaf C % was higher in the shale and sandstone sites in 2016 than 2015 (48.899, 48.471% C in 2016 and 45.448, 46.199% C in 2015; shale and sandstone respectively). Total nitrogen had a significant year and tree species effect and there was a higher live leaf concentration of N in red maple trees ($p < 0.05$) (Fig. 2-10). Phosphorus concentrations in live leaves of trees growing on sandstone derived soils were higher than on shale derived soil (Fig. 2-9) ($p < 0.05$). Calcium had significant lithology and tree species effect, with greater calcium in the foliage of trees grown on shale-derived soils (0.49% Ca in sandstone and 0.77% Ca in trees grown on shale) ($p < 0.05$). Magnesium showed the same patterns as Ca. Zinc had a significant lithology type effect and a significant lithology type * tree species interaction (Fig. 2-9) with greater zinc in red maple trees growing in shale derived soils. There was greater copper in foliage of trees grown on shale derived soils (Fig. 2-9) ($p < 0.05$).

Live leaf total nitrogen had a significant tree species and year effect (Fig. 2-10) with more nitrogen in red maple trees ($p < 0.05$). Red oak trees had greater magnesium and calcium than red maple trees (Fig. 2-10) ($p < 0.05$). Aluminum had significant tree species and year effects and a significant lithology type * tree species interaction (Figs. 2-9 and 2-10). Boron had a significant tree species effect, lithology type * tree species and tree species * year interaction, with more boron in red maple trees ($p < 0.05$). Iron and manganese had a significant tree species effects (Fig. 2-10). Manganese was greater in red maple trees than red oak ($p < 0.05$).

At the time this thesis was submitted, senescent leaf chemistry was only available from 2015 (Fig. 2-11). With 2015 data, there was significantly higher phosphorus resorption for red oak growing on the shale lithology (57% for shale and 28% for sandstone) (Fig. 2-12) ($p < 0.05$). N: P resorption ratio was significantly greater for the red oak on sandstone sites than red maple on sandstone or either tree species on shale ($p > 0.05$) (Fig. 2-13).

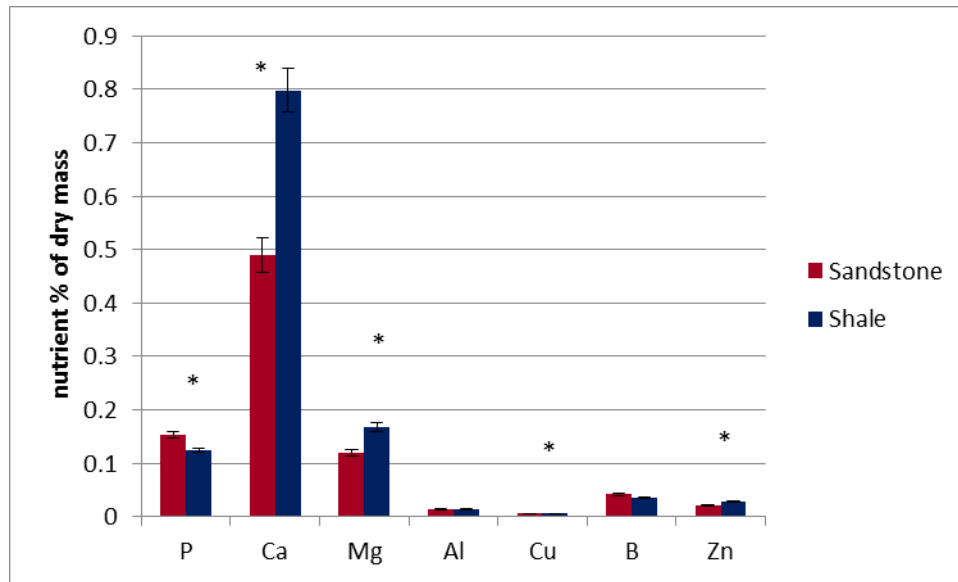


Figure 2-9. Live leaf nutrient concentrations averaged from 2015 and 2016 from sandstone and shale. The leaves were collected in mid-July from red maple and red oak trees located on north facing midslopes and were averaged for lithology. Bars are means (n=14). An asterisk indicates statistically significant differences between sandstone and shale for a given nutrient ($p < 0.05$).

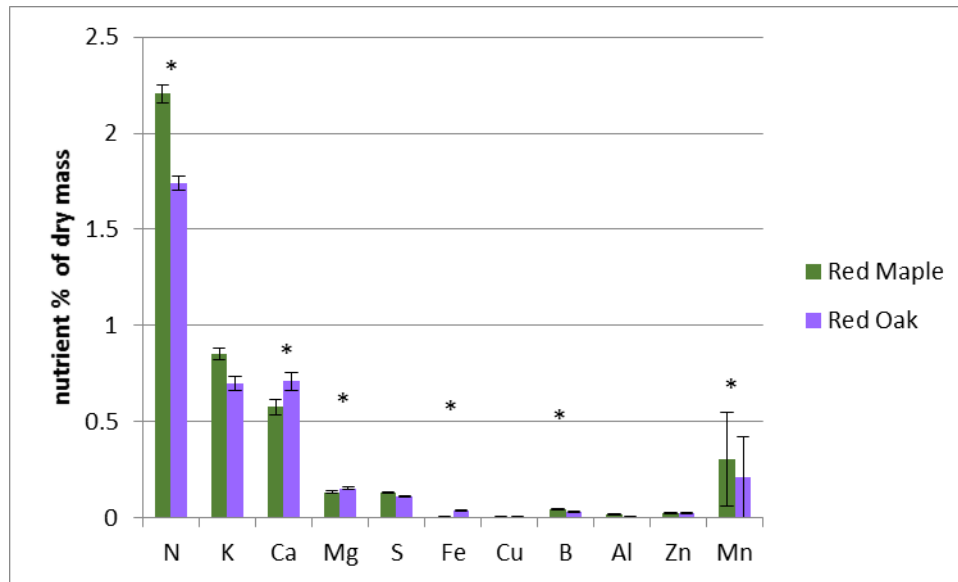


Figure 2-10. Live leaf nutrient concentrations averaged from 2015 and 2016 in red maple and red oak trees. Bars are means (n=14).

An asterisk indicates statistically significant differences between red oak and red maple for a given nutrient ($p < 0.05$).

Table 11. Summary table for live leaf chemistry ANOVAs of the ten sandstone and shale site.

Effect	dF	C%		N%		P%		K%		Ca%		Mg%		S%	
		F	p	F	P	F	P	F	P	F	p	F	p	F	P
Lithology	1,33	0.35	0.5577	0.32	0.5735	15.4 4	0.0004	0.7	0.4084	16.0 6	0.000 3	19.9 2	<0.000 1	0.15	0.699
Tree Species	1,33	0.14	0.7094	75.1	<0.0001	0.28	0.6	25.3	<0.000 1	12.2 9	0.001 3	5.05	0.0315	31.7 6	<0.000 1
Year	1,33	113.85	<0.0001	5.8	0.0218	2.24	0.1438	36.3 6	<0.000 1	0.93	0.342 6	3.76	0.0611	16.6 3	0.0003
LithoxTree	1,33	2.82	0.1025	0.9	0.3505	1.01	0.3223	0.01	0.9269	0.43	0.514 4	0.27	0.6039	2.18	0.1496

LithoxYear	1,33	4.43	0.0431	1.22	0.2764	0.93	0.3412	1.43	0.2407	1.82	0.1861	1.21	0.2792	1.11	0.2996
TreexYear	1,33	0.04	0.8341	1.53	0.2255	0.87	0.3582	1.3	0.2621	0.21	0.6518	0.01	0.9034	0.56	0.4582
		Mn		Fe		Cu		B		Al		Zn		Na	
Effect	dF	F	p	F	P	F	P	F	P	F	p	F	p	F	P
Lithology	1,33	1.76	0.1937	0.03	0.8679	5.02	0.032	6.51	0.0156	0.01	0.9365	24.83	<.0001	6.4	0.0164
Tree Species	1,33	18.32	0.0002	4.59	0.0397	11.96	0.0015	97.05	<.0001	166.2	<.0001	0.01	0.9105	1.83	0.1848
Year	1,33	0.66	0.4209	0.05	0.8217	1.59	0.2162	0.13	0.7173	29.24	<.0001	0.59	0.4468	72.81	<.0001
LithoxTree	1,33	0.01	0.9088	0.08	0.7743	0.08	0.7802	48.5	<.0001	5.98	0.02	5.17	0.0297	0.98	0.33
LithoxYear	1,33	1.53	0.2249	0.13	0.7171	1.3	0.2621	2.23	0.1446	0.27	0.6093	0.11	0.7479	8.63	0.006
TreexYear	1,33	0.16	0.6953	0.02	0.8979	4.13	0.0503	5.21	0.029	1.37	0.2509	0.01	0.944	1.83	0.1848
Covariance Estimates	Location	0.084													
	Residual	0.806													

Table 12. Within site tree to tree variation t-test summary.

	C (%)		N (%)		P (%)		Ca (%)	
	T	p	t	P	T	p	T	p
Sandstone	0.58	0.5900	-5.70	0.0047	0.55	0.6114	1.71	0.1617
Shale	-1.18	0.3018	-1.63	0.1781	-2.25	0.0873	2.43	0.0718

Table 13. Total C and N (%) for both tree species for live leaves for 2015 and 2016 and senesced leaves for 2015.

Year	Lithology	Live/Dead	Species	C (%)	N (%)
2015	Sandstone	Live	Red Oak	45.98	2.09
2015	Sandstone	Live	Red Maple	46.42	1.68
2015	Sandstone	Dead	Red Oak	49.73	0.73
2015	Sandstone	Dead	Red Maple	49.25	0.83
2016	Sandstone	Live	Red Oak	48.35	2.37
2016	Sandstone	Live	Red Maple	48.59	1.79
2015	Shale	Live	Red Oak	45.71	2.09
2015	Shale	Live	Red Maple	45.18	1.72
2015	Shale	Dead	Red Oak	48.50	0.87
2015	Shale	Dead	Red Maple	48.18	0.70
2016	Shale	Live	Red Oak	49.18	2.20
2016	Shale	Live	Red Maple	48.62	1.75

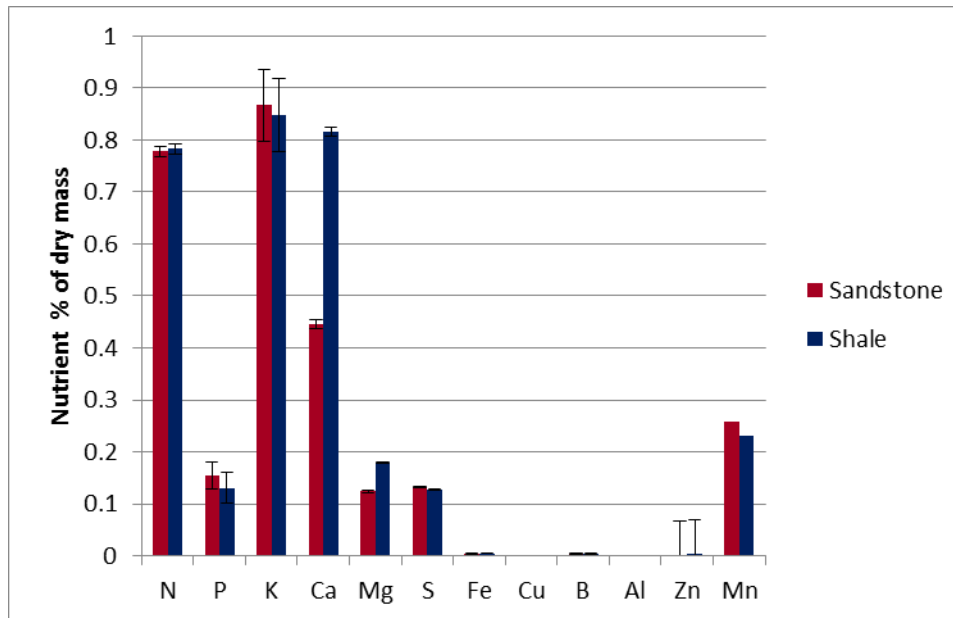


Figure 2-11. Nutrient concentrations in senesced leaves for red oak and red maple in 2015. Bars are means (n=5) of the senesced leaves from the sandstone and shale sites with one standard error.

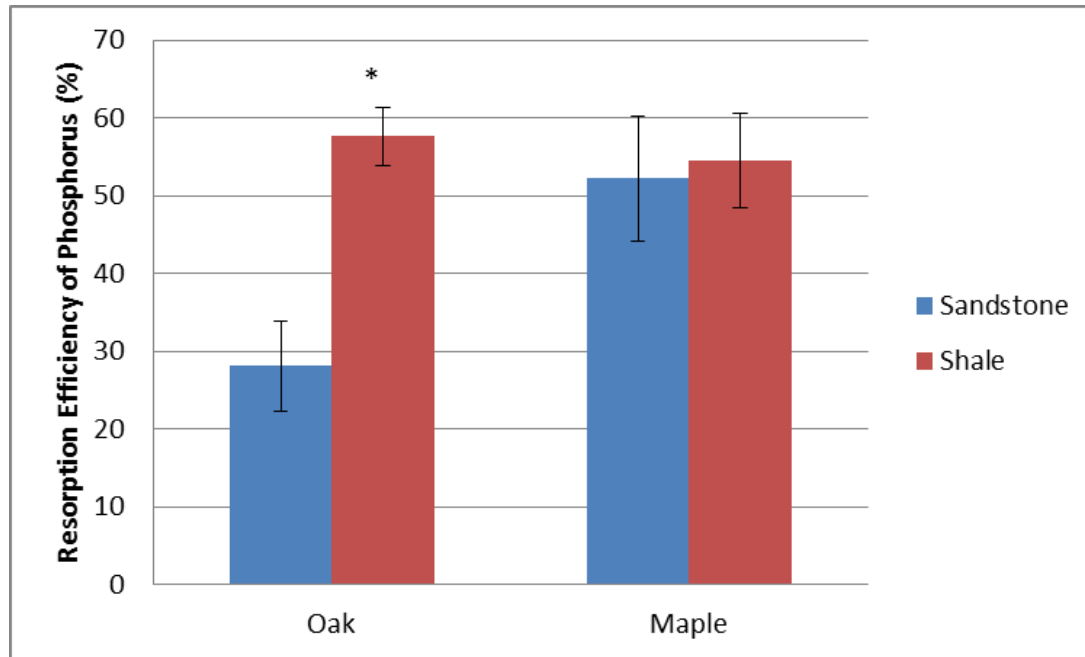


Figure 2-12. Resorption efficiency of P in sandstone and shale sites in 2015. Bars are means (n=5) with one standard error. An asterisk indicates statistically significant differences between sandstone and shale for the two tree species ($p < 0.05$).

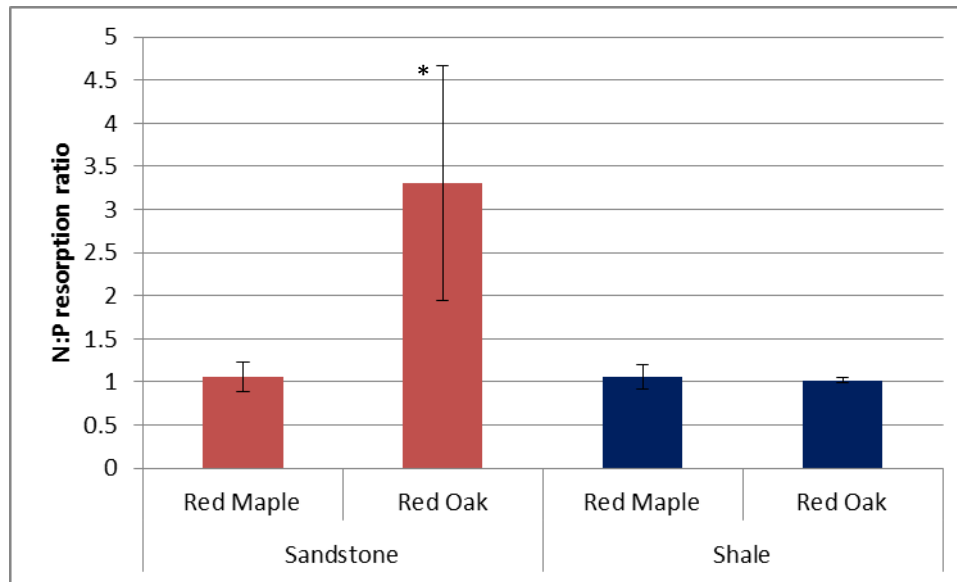


Figure 2-13. N: P resorption ratio in the sandstone and shale sites in 2015. Bars represent the average (n=5) of trees measured for each lithology. An asterisk indicates statistically significant difference between red oak on sandstone and red oak on shale or red maple on either lithology ($p < 0.05$).

Table 14. Summary table for nutrient resorption ANOVAs of the sandstone and shale sites.

Effect	dF	C%		N%		P%		K%		Ca%		Mg%	
		F	P	F	p	F	p	F	P	F	p	F	p
Lithology	1	0.49	0.4960	0.00	0.9585	6.81	0.0189	0.13	0.7269	0.01	0.9395	4.73	0.0449
Tree Species	1	0.50	0.4885	1.95	0.1821	2.97	0.1042	0.93	0.3503	1.47	0.2425	1.31	0.2689
LithoxTree	1	1.32	0.2672	1.40	0.2536	4.96	0.0407	0.39	0.5431	0.17	0.6868	1.72	0.2076

DISCUSSION

Shale and sandstone-derived soils can occur in close proximity as the lithologies are adjacent in forests throughout the Appalachians. The primary objective of this research was to investigate the nutrient pools present on two lithologies to determine the possible nutrient limitation to the aboveground biota. Our hypothesis was that the specific mineralogy of the bedrock would lead to differences in nutrient concentrations in the pools we measured and could affect tree nutrient limitation. As we hypothesized, soil nutrient pools were significantly different between sandstone and shale sites. The shale sites were rich in most rock-derived nutrients and maintain higher Ca on the CEC and higher soil pH. Cation exchange capacity has been measured in Garner Run (sandstone) and Shale Hills (shale) before using a different method, barium chloride exchange (BCE). In these studies, CEC was greater for the Shale Hills midslope position than the north and south-facing midslope positions at Garner Run. The results from Shale Hills and Garner Run using BCE differ from ours, as their results shows that the shale has a greater CEC, whereas our results show that our sandstone-derived soils have a greater CEC than the shale-derived soils (Jin et al. 2010; Hoagland et al. *In Review*). Our study also showed that the sandstone sites have greater P concentrations in soils and leaves and less P resorption for both tree species. Inorganic nitrogen was also greater in the sandstone sites than shale sites, due to variation in ammonium (nitrate did not vary with lithology).

Nutrient limitation assessed via resorption

We used variation in foliar nutrient concentrations and resorption to determine whether variation in soil nutrients may be affecting availability to plants. In general, the variation in base cations that we observed in soils was reflected in foliar element concentrations. Trees growing in soils derived from high-cation shale bedrock had greater Ca and Mg in foliage than trees growing on soils derived from low-cation sandstone bedrock. For P, bedrock concentrations cannot account for the variation in soils (see discussion below), but we still found that higher P concentrations in sandstone soils relative to shale soils was reflected in foliage; there was higher P in foliage of sandstone trees compared to shale trees. In

contrast, high N concentrations in soil extracts was not correlated with variation in foliar N concentrations. Soil extractable N from a single extraction date is probably not a good indicator of overall N availability at these sites, since it is one timepoint in the growing season and is not representative of the N cycle throughout the year. However, the data suggest that further research on the N cycle in these two rock types is warranted.

In addition to lithology, live foliar nutrient concentrations were affected by tree species. There were significantly greater concentrations of nitrogen, boron, aluminum and manganese in red oak than red maple. Tree species also differed in their internal nutrient cycling, leading to distinct differences in red maple and red oak resorption. Red oak and red maple differ in their response to N fertilization. Red oaks show increased basal area increment in short term additions, but do not respond over decades. Inversely, red maples do not respond in growing seasons, but will respond over decades (Finzi, 2009). Red oaks and red maples also differ in their interactions with cations. As red oak trees can cycle high levels of cations, such as calcium and magnesium, through their foliage and may store more calcium in their tissues, whereas red maples do not store calcium in high concentrations (Schier, 1987; Hallett & Hornbeck, 1997; van Breemen, Finzi, & Canham, 1997).

Retranslocation or the resorption of nutrients from senescing leaves is critical for nutrient retention. The nutrient resorption efficiency gives an insight into what may be a limiting nutrient for the tree, by quantifying the amount of nutrient retained by the tree. Trees on nutrient poor soils often increase nutrient resorption to increase the mean residence time of nutrients in the plant, thus increasing nutrient use efficiency (Chapin III, Matson, & Vitousek, 2011). The foliar stoichiometry differs in the two lithologies with a higher N: P resorption ratio in red oaks grown on sandstone-derived soils. The differences can be attributed to soil N and P variability (Reed et al. 2012). The nutrient resorption of leaves on red oak and red maple trees show similar nutrient use, except for phosphorus; for oak, there was greater P resorption on shale than sandstone. Relative nutrient sorption can be a stronger indicator of nutrient limitation than resorption alone (Reed et al. 2012; Sullivan et al. 2014) and we found that the ratio of N resorption to P resorption was substantially higher for oaks on shale than oaks on sandstone. This

corroborates our assertion low P availability on shale soils is impacting trees; oaks seem to be targeting resorption of P (relative to N) on P-poor soils. The stoichiometry differences will be further analyzed with the 2016 leaf litter data.

Surprisingly high P and N availability at sandstone sites

We hypothesized that the nutrient concentrations and availabilities would be driven by the specific mineralogy and chemical composition of the lithologies. Our hypothesis was supported by the cation data in the mineral soil, in live leaf concentrations and in leaf nutrient resorption. However, the P concentration in the sandstone did not match our expectations. With lower P in the bedrock, how did sandstone soils end up with greater extractable P in soils and greater P availability to plants than the shale sites? Our documented differences in phosphorus may come from other inputs, such as dust or loess deposits and organic matter in the soil profile; may be a relic of water stress in the system; or may be due to the differences in the tree composition in the catchments. Here we explore each of these alternative hypotheses.

High P in sandstone soils may be derived from P inputs from dust or loess. Loess with high concentrations of P (about 580 ppm of P as apatite) originated near North American glaciers (Yang et al. 2013), and is thought to have affected many soils in PA (Clark & Ciolkosz, 1988; Gardner et al. 1991; Harrison et al. 2001). Many ecosystems are dependent on atmospheric P inputs, such as loess deposits (Runge, Walker, & Howarth, 1974; Okin et al. 2004). While there may have been increased phosphorus deposition to the sandstone sites through loess from the last Glacial Maximum (Okin et al. 2004), it is unclear why loess did not similarly enrich our shale sites with P. It could be due to uneven loess or dust deposition, with a higher concentration on the high elevation sandstone ridges, or that the inputs were differentially eroded, with higher erosion rates on the shale sites. Along with loess depositions, dust deposits are shown to impact soils and eolian inputs can have large amounts of nutrients (Ciolkosz, et al. 1990; Simonson, 1995).

There are several other potential P inputs that could be explored to explain the high extractable P in the sandstone sites. The increased phosphorus may be tied to more local deposition from charcoal dust aerosols. In Pennsylvania, timber was used predominantly to maintain charcoal iron furnaces located through central Pennsylvania (Straka, 2014). The charcoal pits produced to smelt iron produced nutrient-rich aerosols that may have deposits in the Ridge and Valley province. However, the amount of biomass burned during this time would not distribute the amount of P and other nutrients through the smoke created (Harrison et al. 2001; Kohfeld & Harrison, 2001). It is also possible that that increased P in the sandstone-derived soil may be attributed to other parent materials weathering into the catchment, as there are shale layers in the sandstone lithology near our study sites (Berg, Miles, & Kuchinski, 1980; Brantley et al. 2016).

An alternative hypothesis for the increased phosphorus in the sites underlain by sandstone is that the differences are linked to water stress, especially for the leaf nutrient concentrations. Central PA received more rainfall in 2015 than the anticipated amount for 2016 (42.05 inches, 35.06 inches respectively) (NOAA, 2016). Red maple and red oak differ greatly in their response to drought and overall nutrient uptake is decreased in drought conditions. Resorption efficiency and timing of leaf drop is affected by soil moisture and water availability. Red maple trees and similar tree species may senesce their leaves earlier than red oak when there is lower water availability. However, the early senescence can lead to greater resorption of the nutrient, which is converse to our findings. Red maple would have greater phosphorus resorption with early senesce due to drought conditions (Schlesinger et al. 2016). Also, measurements of nutrient concentration in plants can also be affected by drought through biomass dilution. During periods of stress, tree species will store nutrients for future growth and therefore, may seem to have greater nutrient concentrations during this time. Whereas, other tree species may be using those nutrients to maintain growth (Chapin, 1980). In this study, we assume that biomass dilution does not account for the differences we see in P concentration in the leaves, because the phosphorus in plant tissues does not vary extensively through time (Vitousek et al. 2010).

Inputs of P may have been higher due to the higher elevation of the sandstone sites, since a higher elevation can lead to a better dust trap (Ciolkosz et al. 1990). This may also explain high ammonium availability at the sandstone sites. In forest ecosystems across North America, ammonium was a more common N input at high elevation sites, and canopy leaf uptake was a significant source of N to the forests (Lovett & Lindberg, 1993). Increased ammonium concentrations at higher elevation could be attributed to fog deposition (Lovett & Kinsman, 1990). Wet deposition increases at high elevation sites due to orographic effects on precipitation (Lovett & Kinsman, 1990). Thus, the higher N concentrations in sandstone soils may be due to higher atmospheric inputs. However, we would urge caution in interpreting our one-time N estimates as indicative of a general pattern of higher N in the sandstone sites. It is unclear whether loess (and associated P) is also deposited in greater amounts at higher elevations.

Another alternative hypothesis to explain the increased phosphorus and nitrogen in the sandstone sites is tied to distinct differences in tree species composition. There are substantial differences in tree species composition between Shale Hills and Garner Run (Introduction). Shale Hills has more chestnut oak, hickory and red oak, and less sweet birch, red maple and black gum than Garner Run (Table 1). If these results are generalizable across all shale and sandstone sites, then chestnut oaks may be a key species to study as they are present on both sites and may not be affected by the decreased P in the shale sites. There are large differences in the tree species composition that may drive the differences in nutrient cycling and limitation. Tree species differ in their internal cycling and in their storage physiology, which can affect nutrient replacement rates (Villar-Salvador, Uscola, & Jacobs, 2015).

A possible alternative hypothesis is that the increased N and P in the sandstone locations may also be attributed to organic matter (Berg & Matzner, 1997), as Garner Run has a great amount of organic matter than Shale Hills (Table 2 and 12). With the documented concentrations, our next steps could be to measure rates of microbial N cycling, as that can give insight into plant N availability (Kaye & Hart, 1997) and work to develop a way to measure P fluxes.

Conclusions

Many studies have taken lithology into consideration and focused on the effects of lithology on soil properties and biota (Searcy et al. 2003; Skidmore et al. 2005; Neff et al. 2006). In some cases, one rock type is barren but surrounded by healthy forest ecosystems on a different rock type. Our contrast is more subtle, but no less important as shale and sandstone lithologies underlie critically important ecosystems that provide an array of ecosystem services for the eastern third of North America. We started from the hypothesis that concentrations of nutrients in bedrock would be a good predictor of nutrient concentrations in soils and foliage. This initial hypothesis was not refuted for cations; shale sites have higher cation concentrations in rock, soils, and leaves than sandstone sites. However, we were surprised to find that the shale sites were not rich in phosphorus relative to sandstone sites despite higher concentrations of P in bedrock. Variation in N and P availability among these rock types is not due to large difference in substrate age as postulated by Walker & Syers (1976). We speculate either that 1) dust deposits added P to sandstone locations, and that these inputs were either lower to shale, weathered out of shales sites, or are bound to minerals in the shale sites (Ciolkosz et al. 1990), or 2) that inputs of P from rock layers that have weathered away but contributed P to the contemporary soils. Our measurements of soil solution, foliage concentrations and easily extractable soil nutrients would not measure these P pools and fluxes. Further research into the alternative hypothesis for the increased P and N in sites underlain by sandstone will help to close the gap in understanding and modeling lithology-soil-biota interactions.

Whatever the mechanism, the pattern of higher P availability on sandstone soils has broad implications for Appalachian forests. Chapin et al. (2011) suggest that tree species respond to nutrient supply by sorting themselves on the landscape according to competitive advantages and tolerance. Thus, species variation throughout the Appalachians may be correlated with nutrient supply on these two lithologies. The differences in nutrient level may also lead to the distinct differences in understory cover, as the shale locations have high understory cover and the sandstone locations have low cover. Our data suggest that adjacent forests throughout the Appalachians may have distinct nutrient signatures and the implications for this variation for community and ecosystem dynamics should be further explored.

APPENDIX: Purge Calculations for Gas Access Tubes

Purge calculations for the hand-sampled gas measurements were calculated based on: the actual length of the tube, which is equal to the desired depth +20cm to be above ground +10cm to bend into the pit face, and the volume of the stainless-steel tubing. We also included 2 mL to account for the volume of the valve at the top of the gas access tube.

To standardize sampling for others, we recommended a 5mL purge for 20 and 40cm depths and a 10mL purge for 60-160cm depths.

Desired Depth (cm)	Actual Length (cm)	Final Volume (mL)
20	50	3.83
40	70	4.56
60	90	5.29
80	110	6.03
120	150	7.49
150	180	8.59
160	190	8.95

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