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Insight into the weathering of the Marcellus Shale through Sulfur and Carbon Analysis

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Insight into the weathering of the Marcellus Shale through Sulfur and Carbon Analyses

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Abstract

The purpose of this paper is to study the interactions of sulfur and carbon within and around the soil profile, water table, and the Marcellus Formation of a sampling site that is located in Huntingdon, Pennsylvania. Through the use of total sulfur analysis, total organic carbon analysis, dissolved organic carbon analysis, carbonate (inorganic carbon) analysis, and sulfate analysis it will be possible to accomplish this goal. Results show that sulfur and carbon is actively transported between the soil, pore water, and parent rock settings. Sulfur and organic carbon is released from the Marcellus shale through weathering. Once released, the carbon and sulfur enter the soil profile and the pore waters within it. High concentrations of organic sulfur and carbon exist towards the top of the soil profile. By analyzing the pore water content of the soil, it was possible to distinguish modern organic carbon from old preserved organic carbon. It was found that new organic carbon is found at the top of the soil profile and is due to the decaying matter located on the forest floor. High concentrations of sulfur can be attributed to this reason as well. It was also found that old organic matter is found towards the soil-regolith interface. The modern organic matter found at the top of the soil profile is more labile than the old organic matter that is found at the bottom of the soil profile. The trend observed for sulfur is similar to that of carbon. Organic sulfur can be found at the top of the soil profile and is sourced from decaying organic matter on the forest floor. However, the high sulfur concentrations that exist near the bottom of the soil profile seem stem from different reasons other than organic matter. Here, high sulfur concentrations are attributed to the release of sulfur from within the Marcellus Formation, possibly sourced from pyrite.

Introduction

Overview of Black Shales

Black shale is a dark-colored very fine-grained mudrock that contains more than 1% total organic carbon (Stow et al. 2001). Black shales, found worldwide, extend over thousands of square kilometers. The basic mineralogic constituents of black shales include quartz (10-20%), feldspar (<10%), mica (5-30%), clay minerals (60%), organic matter (0.5-20%), and minor amounts of carbonate, phosphate, sulfides and other accessory minerals (Reon, 1983). However, black shales have been reported to contain metals such as Ag, Mo, Zn, Ni, Cu, Cr, V, Co, Se, U, Ba, Th, U, La, Zr, Sr, Nd, Sm, Tb, Tm, Yb, and Sc (Tourtelot, 1979; Abanda and Hannigan (2005)), often in accessory minerals, which can be hazardous when weathered. When these metals are released through weathering, waters can become toxic (Peng et al. 2004). Another constituent of black shales, organic carbon, is commonly found within the range of 2-10 wt. %, but some shales have been reported to have a carbon content up to 20% (Tourtelot, 1979). Typically, black shales are deposited in continental-shelf and deep-marine settings. In these areas, organisms thrive in the photic zone through the use of photosynthesis and the consumption of other, smaller organisms. As these biota die, the organic matter floats to the bottom of the sea floor and settles. At the bottom of the seafloor, organic matter accumulates faster than it decomposes. As the organic carbon falls to the bottom of the sea floor, it settles with clay-sized particles that are compacted into flat, sheet-like rock deposits with thin laminar bedding over millions of years (Kargbo et al. 2010). Overtime, this lithified rock was subjected to significant heat and pressure until hydrocarbons were developed.

The Marcellus Shale

The Marcellus Shale Formation is located in the Appalachian Basin of the northeastern United States. The Marcellus shale was deposited between 400mya-360mya during the middle Devonian in a shallow inland sea. Covering 95,000 square miles, the Marcellus Shale stretches from central New York, into Pennsylvania, across to eastern Ohio, and down to West Virginia (Arthur et al. 2008).

The Marcellus Shale has an estimated thickness of 50-200 feet and is generally buried at depths of 4,000-8,500 feet (Arthur et al. 2008). Arthur et al., also state that this formation tends to be thicker to the east and thinner to the west. It has been reported that shale rocks usually have a permeability on the order of 10^{-2}-10^{-5}mdarcies (Kargbo et al. 2010). For example, the permeability of a Marcellus core sample from Morgantown, West Virginia was determined to be 20 μd with a porosity of 10% (Soeder, 1988). However, porosity and permeability vary within the Marcellus. Soeder suggests that these variations in porosity and permeability are due to different organic contents, thermal maturities, natural fracturing spacing, and stratigraphic relationships between gray and black shale. It has been estimated that the organic content of the Marcellus Shale is 3-12% (Arthur et al. 2008).

Background

Sampling Sites

Pore water samples and soil samples were collected from a small ridge located near the outskirts of Huntingdon, Pennsylvania. This site is largely vegetated with pine and maple forests (Mathur et al., 2012). The location if this site is illustrated in Figure 1.

Figure 1 illustrates the location (A) of the site at which pore water samples and soil samples were collected. This site, located approximately 13 miles northeast of Huntingdon, Pennsylvania, is about twenty-three miles from State College, Pennsylvania. This image was accessed through GoogleMaps on April 26, 2012.

The location and samples have also been described by Mathur et al (2012) and Jin et al. (in prep.). At this site, lysimeters had been installed at the top of the ridge, at mid-slope, and at the valley bottom (referred to here as the valley floor). These lysimeters are categorized as porous cup tension lysimeters (soil water samplers) from SoilMoisture Equipment Corp (model number 1900 series). Installed in May of 2010, these lysimeters were installed in order to collect pore waters from different depths spaced at 10 cm intervals. Six lysimeters were emplaced at depths of 10, 20, 30, 40, 50, and 80 centimeters were installed at valley floor; eight lysimeters with depths of 10, 20, 30, 40, 50, 60, 80, and 100 centimeters were installed at mid-slope; and eight lysimeters were installed with depths of 10, 20, 30, 40, 50, 60, 70, and 80 centimeters at the top of the ridge. Pore water was extracted from these lysimeters in order to analyze them for their organic carbon content and sulfur content.

Soil samples were also collected at the Huntingdon field site from the top of the small ridge (RT1). A total of sixteen soil samples from different depth intervals were collected from this site. Soils were sampled in varying intervals from the O horizon of the soil surface to a depth of 119 centimeters (Table 3). The zero baseline level was defined as the interface between the mineral and organic soils. At these sites, soils were aurgered by hand until refusal (Mathur et al., 2012). It should be noted that sample #16 is a rock fragment that was recovered at the bottom of the augered hole. Through use of an online web soil survey, the soil in this region is classified as having a Berk-Weikert (BMF) association (Figure 2).

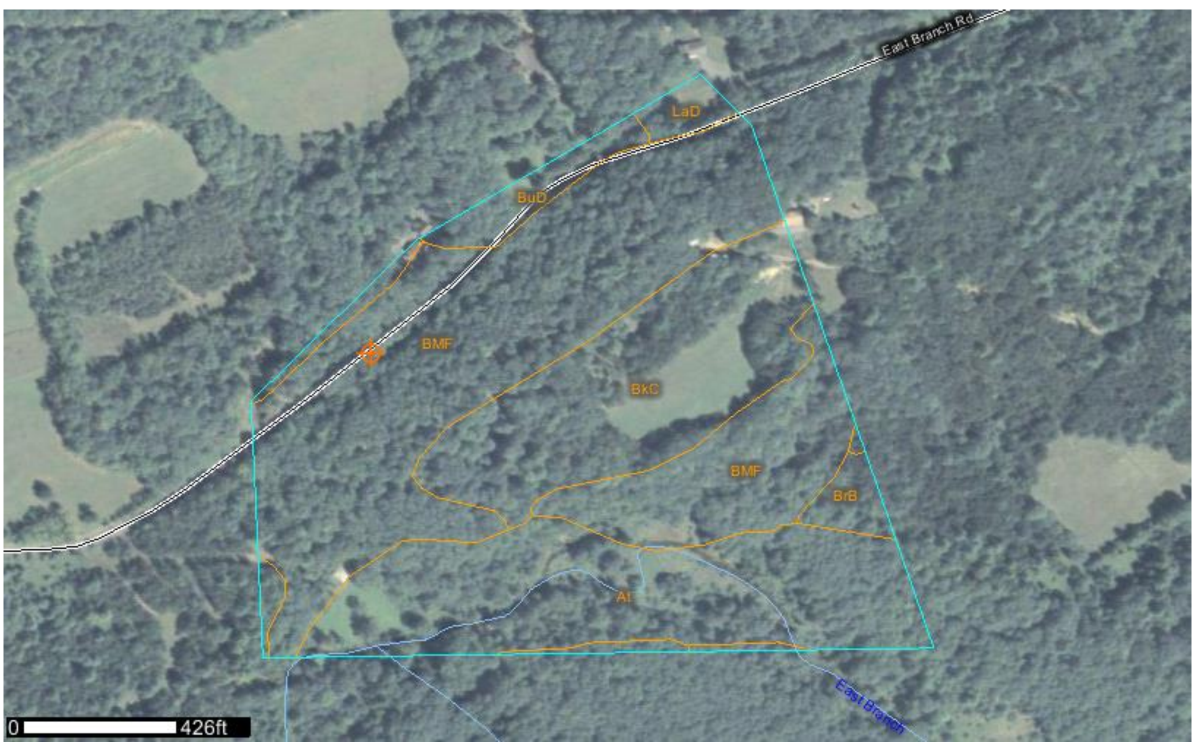


Figure 2. This figure illustrates the classification of soils within the region of the Huntingdon field site. On the shoulder of East Branch Rd, the symbol on the map of crosshairs with a circle indicates the approximate region where pore water and soil

sampling took place. This map was obtained from an online website (http://websoilsurvey.nrcs.usda.gov) soil survey website on April 18, 2012.

The Berks classification accounts for the ridges and valleys within the region and is characterized by channery silt within the top 20 centimeters of soil, very channery loam from a depth of 51cm to 86cm, and bedrock from a depth of 86cm and on. It was also suggested that within this classification, the depth of the paralithic bedrock is between 21cm and 102cm. The Weikert classification accounts for hills within the region and is characterized by channery silt loam within the top 15 cm of soil, very channery loam from a depth of 15cm to 38cm, and bedrock from a depth of 38cm and on. It was also suggested that within this classification, the depth of paralithic bedrock is between 25cm and 51cm. According to the web soil survey, this area is well drained and located on non-irrigated slopes with grades between 25 to 70 percent. It was also reported that the soil is residuum and weathered from shale and siltstone. Specifically, the soil of this site is underlain by the Marcellus Shale Formation (Mathur and Colleagues, 2012),

Ten Marcellus Shale samples of between the depths of 767ft and 923ft were collected for the characterization of parent composition. These samples were extracted from an area around Howard, Pennsylvania (41°01.906', -77°39.376'). Figure 3 illustrates the location of this site.

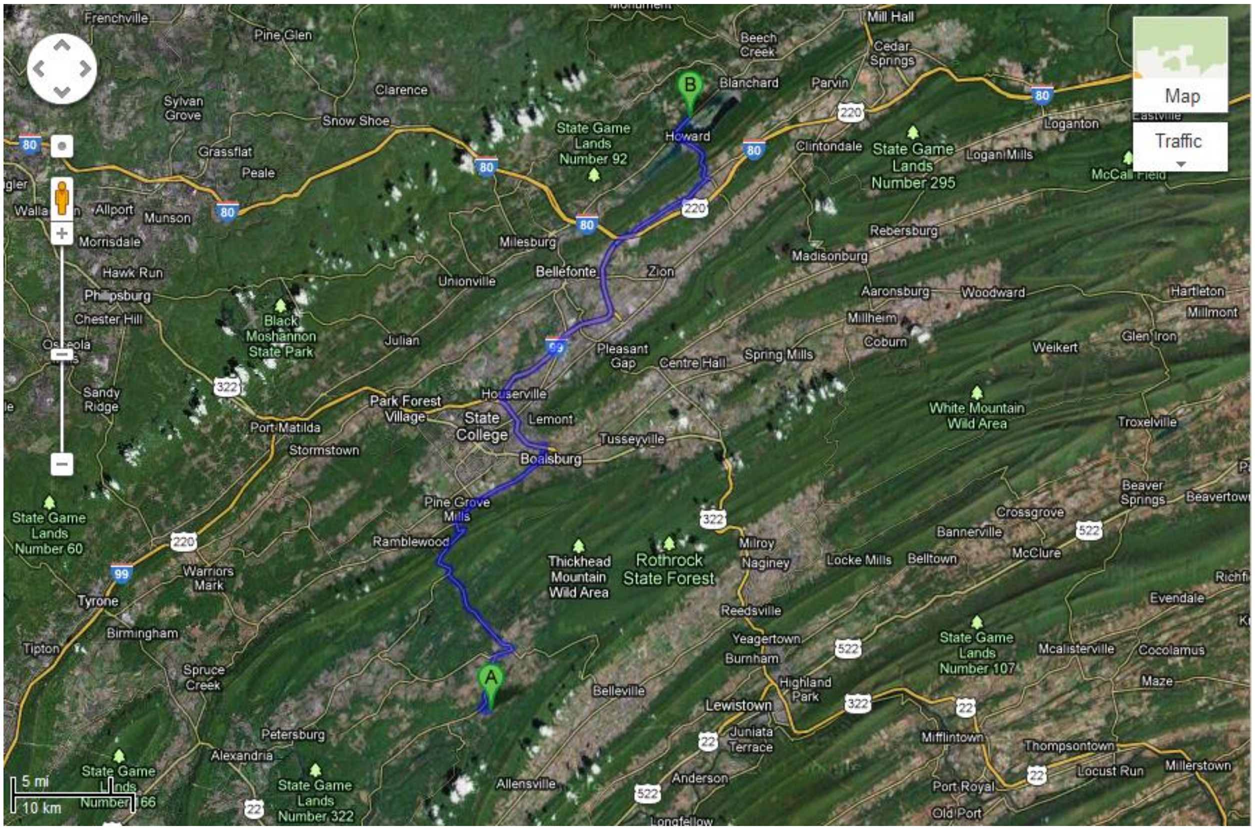


Figure 3. This figure illustrates the location of the pore water and soil sampling site (A) and the location of the core sampling site (B). Sample site B is about 30 miles from State College and about 50 miles from the site located in Huntingdon. This image was obtained from GoogleMaps on April 30, 2012.

The core samples were characterized by grey to dark black colors with the presence of pyrite and calcite veins. In this area, the Marcellus is located within the Hamilton Group. Within this group, the Marcellus is underlain by the Onondaga limestone beds and overlain by the Mahantango siltstone/shale (Boyce and Carr, 2009). The Marcellus itself can be divided into three members. These members, in stratigraphic order, include the: Union Springs Member, Purcell Member, and Otaka Creek Member (R. Slingerland pers. comm.). The Purcell Member was described to consist of fine-grained limestone that is distributed irregularly throughout the Marcellus region (Boyce and Carr, 2009). However, the Union Springs Member has been reported to consist of basal black shales and dark grey argillaceous limestones (Ver Straeten and colleagues, 1994). The Oatka Creek formation consists of organic carbon-rich black shales (Werne et al. 2002).

Hydrology of Central Pennsylvania

The Susquehanna River Basin (SRB) covers 27,510 square miles and drains portions of New York, Pennsylvania, and Maryland (Edwards, 1989). Edwards points out that the SRB consists of six subbasins-- the Chemung, Upper Susquehanna, Middle Susquehanna, West Branch Susquehanna (Figure 4), Juniata, and Lower Susquehanna. The West Branch of the Susquehanna watershed covers an area of 6,992 square miles. Counties within the Susquehanna watershed include Cambria, Northumberland, Clearfield, Elk, Cameron, Potter, Clinton, Centre, Tioga, Sullivan, Lycoming, Union, and Montour counties (Susquehanna Watershed Task Force, 2005). Specifically, within the region of study targeted for this paper, the mean annual precipitation was reported to be between 36 to 70 inches and the mean annual air temperature was reported to be 46 to 57 degrees Fahrenheit. Also, the elevation of this site was reported to be between 300 to 1,600 feet. The data described above that pertain to the characteristics of the field site were obtained from an online web soil survey that was accessed April 18, 2012.

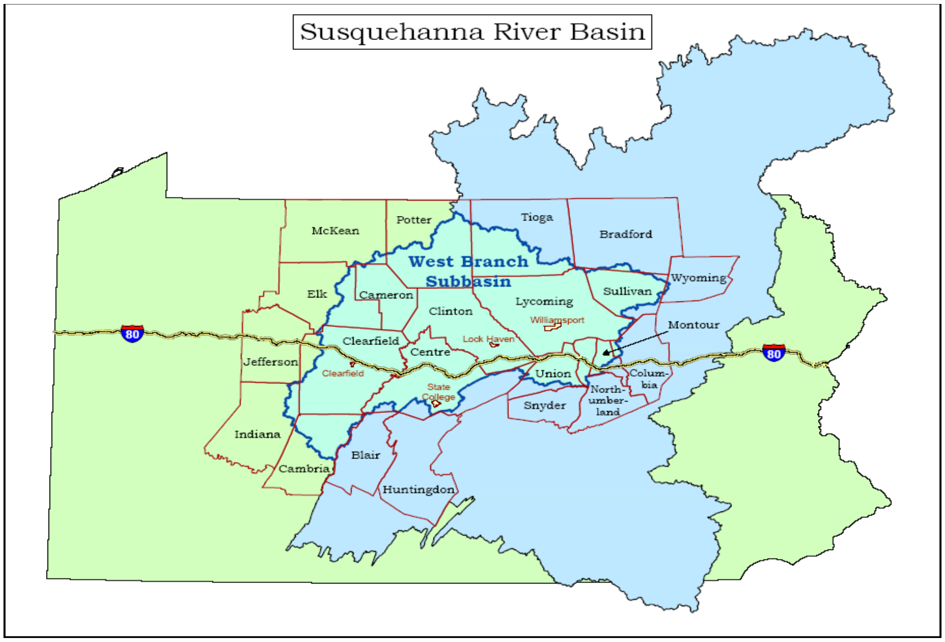


Figure 4 demonstrates the West Branch of the Susquehanna River Basin shown overlying a PA state map. Figure was reprinted from Susquehanna Task Force Report (2005) and was accessed online from the Susquehanna Task Force in the Fall of 2011.

The goal of this research is to take a small step forward in understanding the complex processes involved in the weathering of black shales. By understanding the complex processes of weathering, it will helpful to provide insight regarding a few of the many processes involved in the weathering of black shales in a world where weathering is not well understood for many lithologies. Also, through this research, it will be able to quantify sulfur and carbon concentrations that are natural to the environment. It is important to understand the "normal" conditions of the environment so it is possible to gauge human induced effects on the environment. For example, it is pretty well known that the Marcellus shale is a controversial subject to Pennsylvanians. A lot of this controversy stems from the impact that Marcellus drilling may have on our ecosystems and land. However, it would be hard to evaluate the "impact" or "lack there of" that drilling has on the surrounding environment if we do not even know how the environment and its corresponding ecosystem function in their natural state. Therefore, more of these studies need to be conducted in order to understand the natural conditions and the complex processes involved in weathering. Specifically, this paper will focus on the effect of organic carbon and sulfur during the weathering process of the Marcellus Shale. Through the use of various analyses, it will be possible to determine sulfur and carbon concentrations. By evaluation and comparing sulfur and carbon concentrations to each other and to other concentrations within different settings (soil, pore water, rock), it will be possible to provide insight into certain processes involved in weathering.

Methods

Sample Collection

Soil samples, pore water samples, and Marcellus Shale rock samples were collected in order to evaluate the weathering of the Marcellus Shale through sulfur and organic carbon analyses.

Soil samples were collected from the top of the ridge at the Huntingdon site at different intervals between 0-119 centimeters (Figure 3). These samples were collected by R. Mathur, L. Jin, and colleagues. A total of sixteen samples of soil from different depth intervals were collected from the top of the ridge. These samples were air-dried in an environment that contained a temperature of 80°C, pulverized with a porcelain mortar and pestle until the material could be passed through a 150 μm sieve, and then stored until analysis for their sulfur content and organic carbon content.

Table 1. List of Soil Samples

Sample Name	Depth (cm)
MSS-1	0-10

MSS-2	10-20
MSS-3	20-26
MSS-4	26-34
MSS-6	34-44
MSS-7	44-52
MSS-8	52-60
MSS-9	60-65
MSS-10	65-71
MSS-11	71-82
MSS-12	82-89
MSS-13	89-98
MSS-14	98-109
MSS-15	109-115
MSS-16	115-119
MSS-17	119

Table 1 illustrates a list of soil samples that were analyzed during this research. Each soil sample is labeled with "MSS#" where "MSS" represents "Marcellus Soil Sample". The samples used above were also analyzed by Mathur et al. (2012) in his paper pertaining to Cu isotopes but named using "RT_1-#". However, there are discrepancies regarding the sample depths reported in this paper and the depths reported in Mathur's paper. In this paper, it is reported that soil depths range from 0-119cm while according to Mathur, depths range from 0-134cm.

Pore water samples were collected from the low-tension suction lysimeters (1900 series; 48 mm in diameter) nested along a planar transects. One nest of lysimeters was located at each setting: ridge top, mid-slope, and the valley floor. These lysimeters were hand pumped at least 24 hours before the pore waters were sampled in order to create a vacuum of about -50 centibars pressure so that water from the soil pores could be sucked into the lysimeters (Mathur et al. in press). Each time water was collected from a lysimeter, it was portioned into three separate 30ml pre-cleaned high density polyethylene (HDPE) sampling bottles (A and B samples) and glass vials (DOC samples): A, B, and DOC. The "A" samples were acidified with 2-5 drops of concentrated nitric acid and refrigerated until tested for their cation contents, the "B" samples where refrigerated until analyzed for their anion contents, and the "DOC" samples were filtered, acidified with 1-2 drops of high purity hydrochloric acid (HCl) that was diluted by 50%, and then refrigerated until analysis for dissolved organic content. Samples were collected from the lysimeters nine different times resulting in a total of 175 “A” samples, 176 “B” samples, and 166 “DOC” samples. Each time samples were collected from each lysimeter, the volume and the pH values of the pore water was recorded using a model SP70P VWR SympHony pH meter and a VWR SympHony gel electrode calibrated with standard pH buffers (4 and 7). The volume of water was measured by continuously syringing out volumes of water until the lysimeter went dry. The syringe used was labeled in a way that made it possible to keep track of the volume of pore water being extracted. The volume and pH of each sample is represented in Table 5 of the Appendix. No attempt was made to filter soil pore waters, excluding DOC samples which were filtered through 0.45 μm filters once back at the lab, because the lysimeters are made from porous cups that filter out particles larger than 1.3 μm (Mathur et al, in press).

Rock samples from the Marcellus Shale were collected from the Devonian shale Bald Eagle core from the core lab managed by Rudy Slingerland, professor of geology in the Department of Earth and Mineral Sciences at The Pennsylvania State University. A total of ten rock samples were collected from this lab to be analyzed for bulk chemistry. Nine samples were collected from the Bald Eagle Formation, one sample was taken from the Onondaga Formation, seven samples were obtained from the Union Springs Member, and two samples from the Purcell Limestone Member (Table 4). The deepest sample was taken from 281m (923 ft) below the surface and the shallowest was taken from 234m (767ft) below the surface with intermediate samples approximately equidistant from each other.

Table 2. A List of Marcellus Shale Core Samples			
Sample Name	**Formation**	**Sample Depth (ft)**	**Sample Depth (m)**
BE-767	Purcell	767	234
BE-786	Purcell	786	240
BE-810	Union Springs	810	247
BE-832	Union Springs	832	254
BE-850	Union Springs	850	259
BE-874	Union Springs	874	266
BE-892	Union Springs	892	272
BE-896	Union Springs	896	273
BE-910	Union Springs	910	277
BE-923	Onondaga	923	281

Table 2 represents the core samples that were analyzed during this research. Core samples were named "BE-#" where "BE" stands for Bald Eagle and is followed by the depth of the sample in feet. Note that this table presents sample depths in feet and meters. However, results are presented only with units of meters.

The color of the core samples ranged from grey to dark black and contained a random scattering of white veins (possibly calcite) and pyrite nodules. All ten samples were then pulverized using a porcelain mortar and pestle and then sifted until particles less than 150μm could pass through the sieve. The samples were then stored until analysis for cation, anion, organic carbon, carbonate, and sulfur content.

ICP-AES Analysis

Pore water samples and Marcellus Shale core samples were analyzed by a Perkin-Elmer Optima 5300 Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) located in the Brantley Laboratory within the Earth and Mineral Sciences Department at Penn State in order to determine concentrations of potassium, aluminum, calcium, iron, magnesium, sodium, phosphorus, silicon, barium, manganese, strontium, and titanium in rock samples. ICP-AES was also used to determine concentrations of sulfur in pore water samples. A total of 176 samples of pore waters were portioned into plastic test tubes and inserted into the ICPAES along with standards at different concentrations. These dilutions range from 0.005 to 200.

In Fall 2011, cation content was measured for core samples during a Geoscience 413W class. In preparation for ICP-AES analysis, previously pulverized core samples were ashed. During ashing, the samples were heated to at least 900°C. Ashing releases entrained water, water of hydration, carbonates, and sulfur compounds and organic material (Gong, H., pers. comm.). Once ashed, an analytical balance was used in order to weigh out and mix together 100 milligrams of each sample and one gram lithium metaborate. Each sample was then placed in a graphite crucible. The graphite crucibles were then placed into a furnace at 900°C and heated for about ten minutes. In this way, solid samples were prepared so they can be analyzed by ICP-AES. After ten minutes, the molten lithium metaborate and sample mixture was poured into a five percent diluted nitric acid solution and stirred for thirty minutes. Once digested, each sample was then added to a test tube in order to be analyzed for major and minor cations. Therefore, each test tube was diluted to a ratio of one to nine (1% of sample to 9% of two percent nitric acid solution). This dilution was necessary so that the solute concentration was within the range of the calibration curve of the analysis. Standards for each element present in a reference rock sample were analyzed to calibrate the measurements. A calibration curve containing emission counts on the y-axis and concentration (mg/L) on the x-axis was constructed. By analyzing this curve, it was possible to assess the accuracy of the data and to determine the concentration of each element within the samples. Reference samples were also run and analyses were compared to published analyses to assess accuracy.

Sulfur Analysis

Both the collected soil samples and Marcellus Shale core samples were analyzed for their sulfur content through a LECO Sulfur Analyzer Coulometer located in the Brantley Laboratory within the Earth and Mineral Sciences Department at Penn State (Brantley, Holleran, and Jin, in review). This instrument works on titrimetric principles, volumetrically measuring the amount of reagent required to complete a chemical reaction with a analyte.

Approximately 100mg of sixteen soil samples were weighed using an analytical balance (Table 5). These soil samples, along with granular tin metals and iron chips supplied by the LECO Corporation, were added to ceramic crucibles and capped with ceramic lids. Tin and iron beads were added to the samples as combustion aids (Jones and Isaac, 1972). Replicates of these samples were made in order to increase the accuracy and precision of measurements. Each sample was inserted into the LECO Sulfur Analyzer and combusted within an oxygen atmosphere in order to release SO_2 gas (Brantley, Holleran, and Jin, in review).A standard was also run repeatedly during the analysis.

Once combustion had occurred, emissions traveled through a glass tube to be dissolved into a solution containing 2% HCl, dark blue colored starch, KI, and a small amount of KIO_3 according to reaction:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_3 + 3H_2O \qquad (1)$$

The blue color of the solution results from the interaction of the starch with I_2. When SO_2 is introduced into the solution, the reaction:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI \qquad (2)$$

Proceeds to the right and the starch loses its blue color due to the removal of I_2. To restore the blue color, a known concentration of KIO_3 solution is added (titrated) to the solution. The addition of KIO_3 drives reaction (1) back to the right, producing more I_2 which interacts with the starch, restoring the original blue color. The amount of KIO_3 needed to restore the starch solution back to its original shade of blue is proportional to the SO_2 evolved from the sample which, in turn, is proportional to the %S in the sample. From reactions (1) and (2), 1 mole of KIO_3 will neutralize the effects of 3 moles of SO_2 or 3 moles of original S. Since the molecular wt of KIO_3 is 214.001 gm and that of S is 32.064 gm, we can conclude that 214.001/32.064x3=2.2247 gms of KIO_3 is needed to neutralize 1 gm of S. If KIO_3 is dissolved in solution, the weight of KIO_3 added will be given by the equation:

$$m_{KIO3i} = C_{KIO3}\ (g/L) \times V_{KIO3}\ (L)$$

where V_{KIO3} is the number of liters of KIO_3 needed to neutralize the SO_2 evolved. Since 2.2247 gm of KIO_3 are needed to neutralize 1 gm of S, the weight of S is given by:

$$ms = \frac{\mathrm{CKIO3\ (g/L)\ \times\ VKIO3\ (L)}}{2.2247}$$

or expressed as:

$$wt.\%S = \frac{ms\ (mg)}{msample\ (mg)} \times 100\%$$

The overall formula will be:

$$\%S = \frac{C_{KIO_3}(g/L)*(b_{sample} - b_{blank})*0.005(L)}{0.001*\frac{M_{KIO_3}}{3M_S}} * \frac{1}{m_{sample}(mg)} *100\%$$

Here, C_{KIO3} represents the concentration of potassium iodide (g/L), b_{sample} and b_{blank} - the number of burette units of potassium iodide added to restore the color in liters, 0.005 is the volume of 1 burette unit in L, M_{KIO3} and M_s is molecular weight of KIO_3 and S, respectively; 3 – number of moles of SO_2 that needed to be neutralize1 mole of KIO3; 0.001 – conversion of g to mg and m_{sample} represents the mass of the sample in mg. Sulfur standards in the form of a 1,000 mg metal ring that contains 0.0288% sulfur and blank crucibles were also analyzed at the beginning and end of each run of sixteen samples in order to check the accuracy and precision of the LECO instrument. Such sulfur standards used were supplied by the LECO Corporation.

Core samples were also analyzed for sulfur content. Ten pulverized Marcellus Shale core samples were also prepared in duplicates, weighed by analytical balance, and analyzed for their sulfur content (Table 6). This analysis was conducted with the same method described above.

IC Analysis

Pore water samples were tested for their anion content using a Dionex ICS 2500 ion chromatograph (IC) located in the Brantley Laboratory within the Department of Earth and Mineral Sciences at Penn State. IC separates aqueous species to quantify their concentrations. An IonPac AS18 4×250mm Ion Chromatography column was used to separate the pore water samples. The peaks produced by this instrument were separated using an isocratic (same concentration of effluent) run method with 39mM

KOH as effluent. Such species analyzed during this analysis include Cl^-, F^-, Br^-, SO_4^{2-}, and NO_3^-.

A total of 175 pore water samples were analyzed during this analysis. At the beginning, middle, and end of each run, several standard solutions were run so that sample peaks could be identified and quantified. The standard solutions were prepared by making 1:2, 1:5, 1:10, and 1:20 dilutions of a concentrated mixed-standard stock solution. Six hundred microliters of each sample, standard, and blank were pipetted into vials, capped, and loaded into racks. These racks were then loaded into the auto sampler. Within the IC, ion exchange resigns are used to separate atomic or molecular ions based on their interaction with the resin. A retention time is determined by the attraction of an analyte to the ion-exchange resin that is located in the column. Different analytes travel at different speeds, allowing them to be distinguished. After samples were analyzed, retention times of the standards and samples were checked in order to assure accurate identification of the analytes. The instrument used has a detection limit of 4 parts per billion (EMSL 2012). Figure 1 in the Appendix illustrates a chromatograph that shows average retention times for pore water samples.

Analysis of Organic Carbon

Pore water samples, soil samples, and Marcellus Shale core samples were all analyzed for their total organic carbon content. The pore water samples were analyzed for dissolved organic carbon (DOC) using a TOC-5000A Total Organic Carbon Analyzer at the Soil Research and Cluster Laboratory within the Department of Crop and Soil Sciences at Penn State while the soil samples and the Marcellus Shale core samples were all analyzed using an EA 110 CHNS-O Elemental Analyzer.

About 5 ml of pore water samples were pipetted into the glass vials and then loaded into the instrument to analyze the quantity of dissolved organic carbon. After loading, the pore water samples were combusted in an oxygen-rich environment resulting in the complete conversion of carbon to carbon dioxide (Drexler 2003). The instrument used has a detection limit of 4 parts per billion (EMSL 2012).

Twelve to eighteen milligrams of pulverized soil and core samples were weighed into tiny capsules and loaded into the instrument. Soil samples were weighed into tin capsules while core samples were weighed into silver capsules. Before core samples were added to the instrument, the samples were acidified with 2N hydrochloric acid in order to dissolve the carbonate within the rocks and dried at a temperature of 80° Celsius for approximately twenty-four hours. Triplicates were made of both soil and core samples. Once the samples were loaded into the instrument, they are combusted and sulfur is measured by several stages of thermal conductivity detectors (CHN ANALYSIS 2009-2012). The detection range of this instrument was estimated to be between 3.6 milligrams (CHN ANALYSIS 2009-2012).

Carbonate Analysis

Ten different Marcellus Shale core samples were analyzed for carbonate (CO_3). Approximately one gram of each sample was added to 120ml serum bottles, capped with rubber stoppers, and clamped. Five milliliters of 1N hydrochloric acid were injected into each serum vial using a needle syringe. After HCl reacted with the carbonates, CO_2 was released into the bottle headspace according to the reaction:

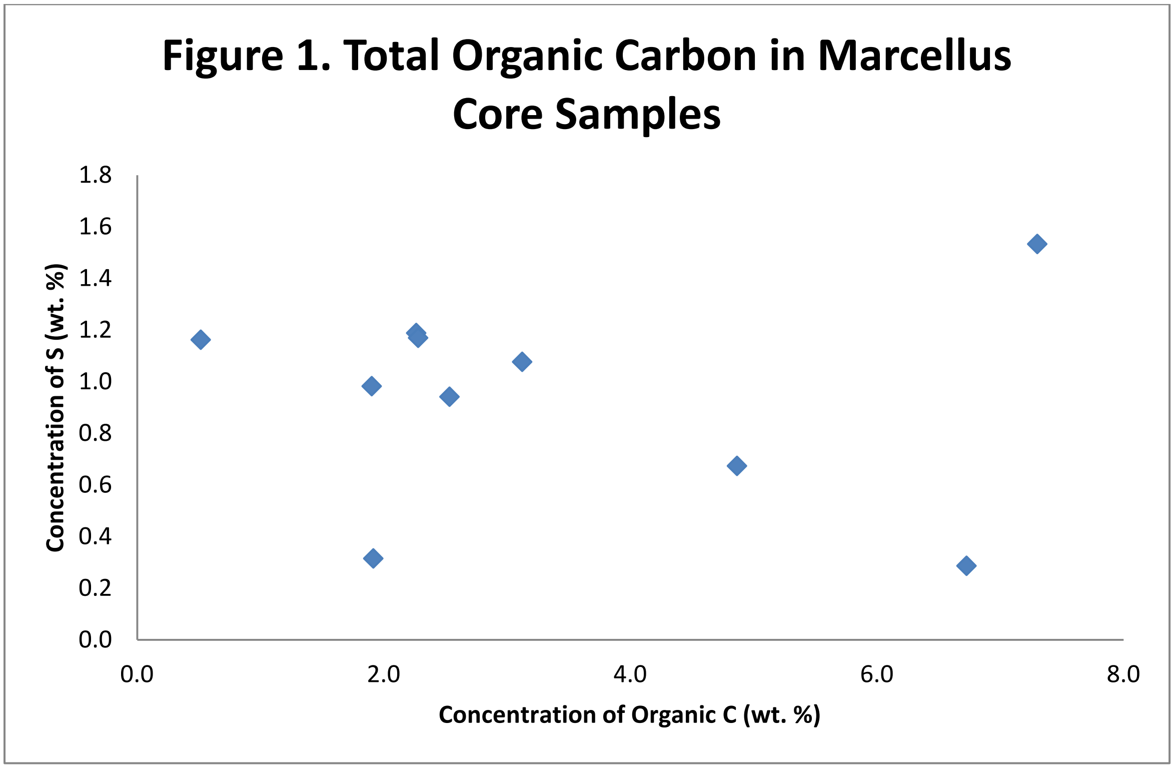
$$CaCO_3 + H^+ \rightarrow Ca^{2+} + CO_2 + H_2O.$$

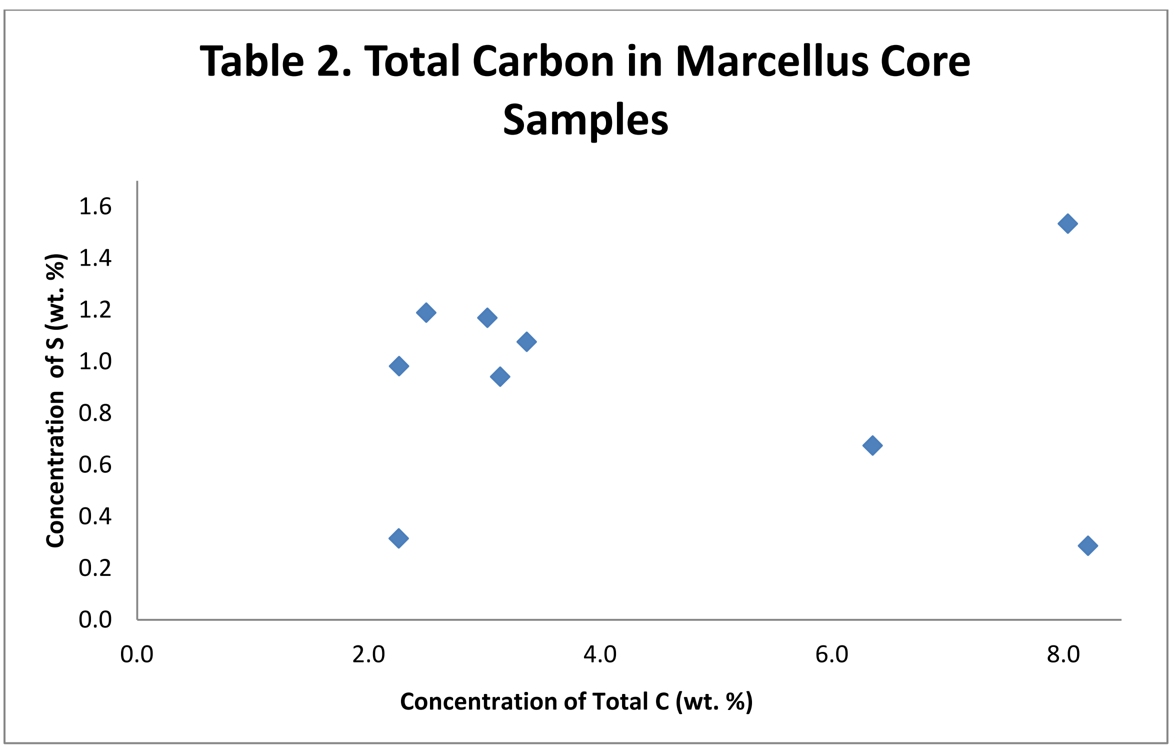
After twenty-four hours of shaking to ensure the reaction is complete, samples were analyzed by the LI-COR CO_2/H_2O Analyzer (LI-7000) at Professor Jason Kaye's Biogeochemistry Laboratory in the Department of Crop and Soil Sciences, Penn State. Three blanks containing only air and three blanks and there blanks injected with five milliliters of 1N HCl were also analyzed. About 0.5 milliliters of air was syringed from the headspace of each serum bottle and injected into the instrument. A calibration curve was created by injecting known amount of CO_2 into the instrument from 970 and 10,010ppm CO_2 gas tanks. The volumes of injected CO_2 gas were converted to moles of CO_2 using the gas law, and then gurther converted to mg of C. Carbon (in mg) was plotted versus peak areas recorded in the instrument to produce a calibration curve. The calibration curve was then used to calculate mg C in the samples. The known amount of gas (0.5 or 0.3ml) was sampled from the headspace of each sample bottle and injected into the instrument. The obtained concentrations were then recalculated for the total bottle headspace. The total headspace volume was determined as a difference between total bottle volume and the volume occupied by a sample and added HCl. Carbonate was not measured in soil samples because it was assumed that carbonate does not exist in soils with a pH less than 7.

Results and Discussion

Figures from sulfur analysis of soil and Marcellus Shale core samples, organic carbon analysis of pore water, soil, and Marcellus Shale core samples, cation analysis of pore water and Marcellus Shale core rock samples, anion analysis of pore water samples, and carbonate analysis of Marcellus Shale core samples are presented in Figures 1-12. The data tables for each figure can be found in the Appendix.

Core Samples





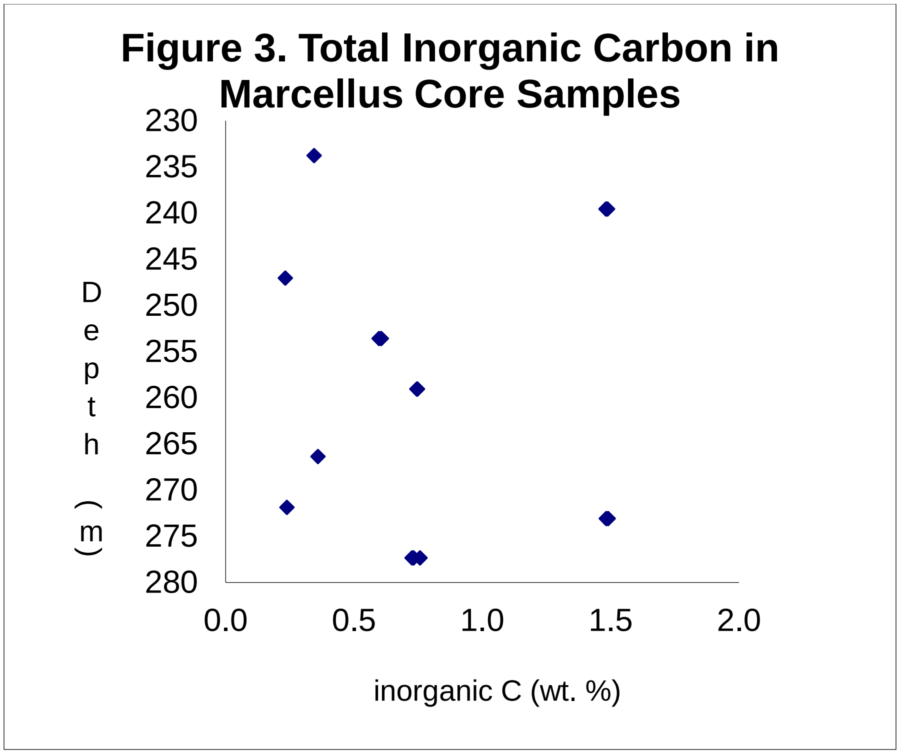


Figure 1, 2, & 3 and Table 1 (Appendix) summarizes the relationships between the total carbon, organic, and inorganic carbon content and the total sulfur content within nine different samples of the Bald Eagle core. Although total organic carbon was measured for sample BE-923, total inorganic carbon was not, causing difficulty in calculating accurate total carbon content. Therefore, this sample was left out of all three figures. Each sample was run three different times with the average shown in the figure for total organic carbon content. However, for inorganic carbon, only samples BE-896, BE-786, BE-832, and BE-850 were all run once and sample BE-910 was tested three different times. Regardless, the average value for each sample is presented in the figures representing total organic and inorganic carbon concentrations while the figure representing the total carbon content is a sum of the previous two graphs.
 Before analysis, each rock samples was treated with 2N hydrochloric acid in order to release inorganic carbon from each Marcellus Core sample. The data summarized in Figure 1, 2, & 3 are presented in weight percentages of organic carbon per 14.5-14.9 milligrams of pulverized Marcellus Shale rock.

By comparing all three graphs, it becomes apparent that the carbon within the Marcellus Formation is primarily organic. The concentration of inorganic carbon ranges from 0.2334-1.4907wt.% and is insignificant when compared to organic carbon concentrations, which range from 1.91-7.30wt.% (Figures 2 & 3).

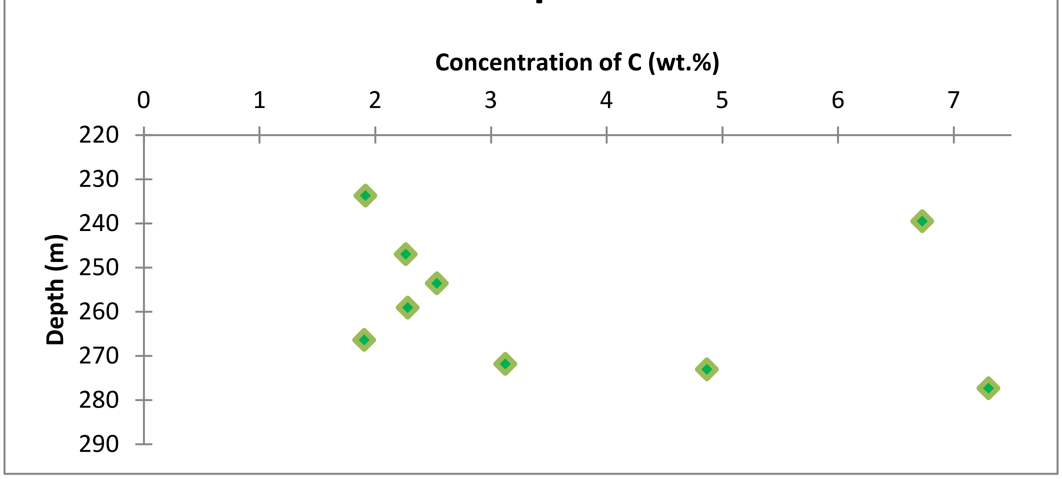


Figure 4. Total Carbon in Marcellus Core Samples

Figure 4 and Table 1 (Appendix) summarize the total carbon content within ten different samples of depths: 234m (767ft), 240m (786ft), 247m (810ft), 254m (832ft), 259m (850ft), 266m (874ft), 273m (896ft), and 277m (910ft). Each sample was run three different times. Data present in this figure, was produced by summing total inorganic concentrations and total organic concentrations. In addition, core sample BE-923 (281m) was not included in the figure due to the lack of inorganic carbon concentrations.

The concentration of organic carbon within the Marcellus shale varies with depth (Figure 4). It is possible to see that carbon increases from the depth of 234m to a depth of 240m then decreases from 240m to 247m in Figure 4. From 247m to 266m, concentrations of carbon slightly increase and then decrease. From 266m to 277m, organic carbon increases dramatically from 1.92wt.% of carbon to 7.30wt.%. Finally, at a depth of 281m, the percentage of carbon drops to 0.52wt.% from 7.30wt.%. These results are consistent with the previously proposed lithology of the Marcellus Shale. Specifically, the Union Springs Formation is vertically overlain by the Purcell Limestone, explaining the low concentrations of carbon at a depth of 234m. However, at 240m, the concentration of total carbon is rather high (6.7wt.%C) compared to the concentrations of carbon within the . This sample was taken from the Purcell member, which consists prominently of limestone. This sample may have been retrieved from interebedded shale that has been reported to exist within this member of the Marcellus Formation. This shale interbed seems to contain a significant amount of total carbon (~6.37wt.%) compared to other layers of shale within the Union Springs member that were analyzed during this analysis. Slightly higher weight percent values were measured for the Union Springs member (247m-277m) of the Marcellus Formation. At a depth of 277m, a high weight percent value (7.30wt.%) of total carbon was measured. This agrees with the perception of this depth being the "hot spot" of the Marcellus where efficient gas production is utilized (Slingerland, pers. comm.).

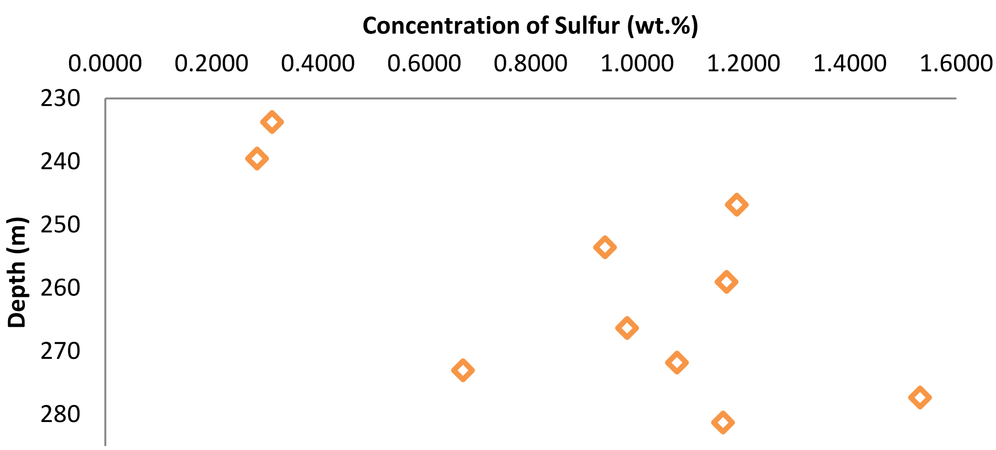


Figure 5. Total Sulfur in Marcellus Shale Core Samples

Figure 5 and Table 1 (Appendix) summarize the average composition of sulfur in all ten of Marcellus shale core samples. The data is presented with units of wt. percentage. Before and after each run, 1-2 standards where measured along with 2-3 blanks. The average blanks used to calculate % sulfur for Run 1 and Run 2 where 11.7 and 8.0. The check standards used contain a composition of 0.0288% sulfur and were run in order to check accuracy and precision. Each sample weighs about one gram and was run two separate times. The average of these runs is summarized in the Figure 5.

The sulfur content within the Purcell Limestone (234m and 240mt) is rather low (Figure 2). Within the Union springs Member of the Marcellus Shale, from the depth of 247m to a depth of 923m sulfur oscillates between 0.67wt.% and 1.19wt.% organic carbon. The Union Springs member tended to have higher sulfur concentrations than the Purcell limestone but of similar values to the Onondaga limestone. Differences in these concentrations can be attributed to the depositional environment of each member.

Soil Samples

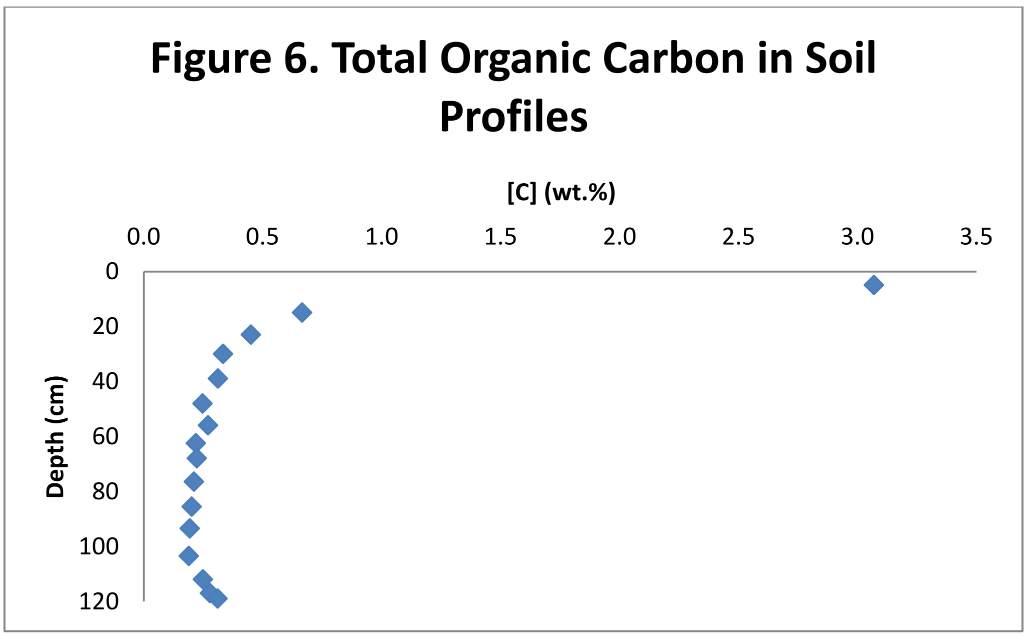
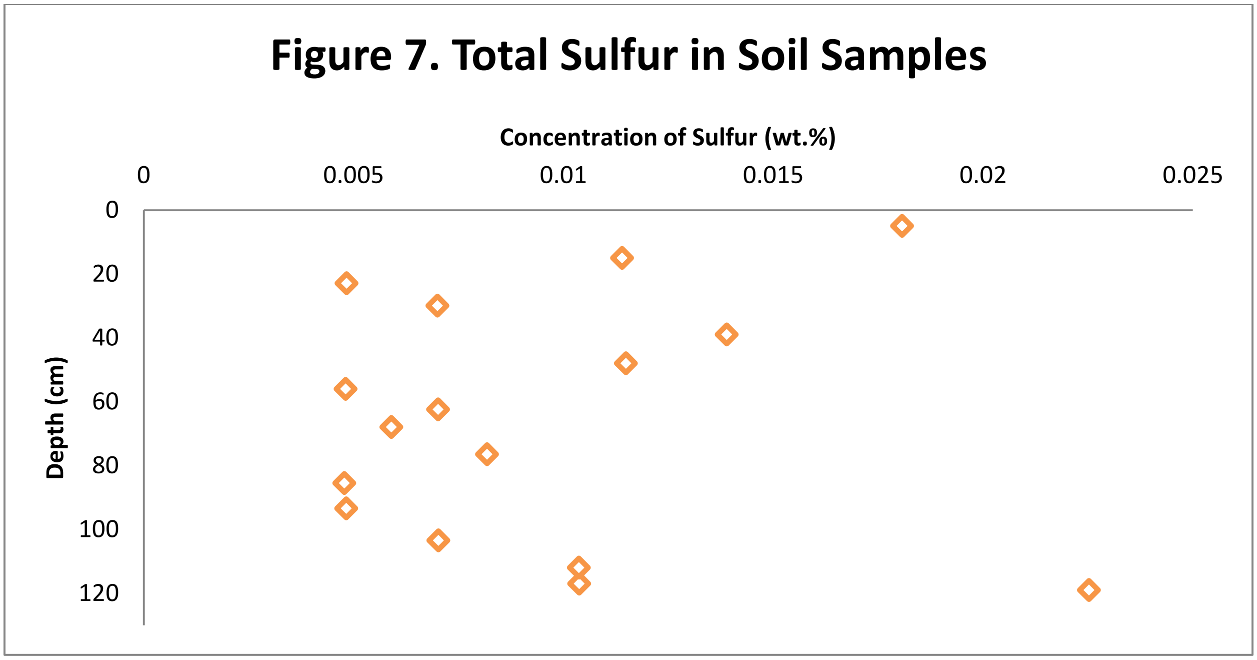


Figure 6 and Table 2 (Appendix) summarize the total organic content of sixteen different soil samples that were collected from Huntingdon, PA in mid-June of 2008. Soil samples were collected from a small ridge in Huntingdon from depth intervals of 0-10cm, 10-20cm, 20-26cm, 26-34cm, 34-44cm, 44-52cm, 52-60cm, 60-65cm, 65-71cm, 71-82cm, 82-89cm, 89-98cm, 98-109cm, 109-115cm, 115-119cm. The averages of these intervals are plotted against corresponding concentrations of total organic carbon. Samples at depth intervals of 0-10cm, 34-44cm, 60-65cm, 71-82cm, and 109-115cm were ran twice. Therefore, the average of these runs was plotted on the figure above. Total organic carbon concentrations are reported in weight percentages per 14.3-15.2 milligrams of soil samples.

Organic carbon within the soil of the Huntingdon site is of higher concentrations towards the top and bottom of the soil layers (Figure 2). Within the first 52 cm of soil, organic carbon decreases with depth. Between 52 cm and 109 cm, organic carbon remains relatively constant (0.2-0.3 wt. % of organic carbon). From 109 cm to 119cm, the weight percent of organic carbon increases with depth. The higher concentrations of organic carbon around the top and bottom layers of soil are due to separate reasons. The slightly higher concentrations of organic carbon near the bottom of the soil profile are attributed to decaying organic matter within the soil profile and also the weathering of the underlying Marcellus Shale resulting in the release of previously preserved organic carbon into the surrounding soil. However, the higher concentrations of organic carbon within the surface layer of the soil profile can most likely be associated to only the "O" horizon within the soil profile where loose sediment consists of partially decaying organic matter.

Figure 7 and Table 2 (Appendix) summarize the composition of sulfur in all sixteen samples of soil. This data is presented in weight percentages. Before and after each run, 1-2 standards where measured along with 2-3 blanks. The average of the blanks used to calculate percent of sulfur per samples for Run 1 and Run 2 were measured to be 8.3 and 9.5. The standards used contain a composition of 0.0288% sulfur and were ran before and after each run in order to ensure accurate results. Each sample weighed around 99.3-102.8 milligrams and was tested for its sulfur concentration a two different times. Therefore, the averages of these runs are illustrated in Figure 7.



Within the soil profile of the Huntingdon site, sulfur concentrations are higher at the top and bottom of the soil profile compared to the middle depths. Sulfur decreases from the surface of the soil profile to a depth of about 23 centimeters. However, from 23cm to 94cm, sulfur concentrations vary between the averages of 0.0048wt.%S and 0.014wt.%S. Then from 94cm to 119cm, sulfur percentages increase from an average of 0.0048wt.% to 0.023wt.% of total sulfur. Sample number 16 (119cm) was a rock sample from the bottom of the augured hole it was extracted from and, therefore, can represent the regolith of the sampling area. Similar to total carbon, the high concentrations of sulfur towards the shallow layers of the soil profile can be attributed to the existence of an organic-rich S-containing "O" horizon while the high concentrations of sulfur towards the deep layers of the soil profile can be attributed to the existence of organic matter throughout the soil profile and to the release of total sulfur through the weathering of the underlying Marcellus Shale.

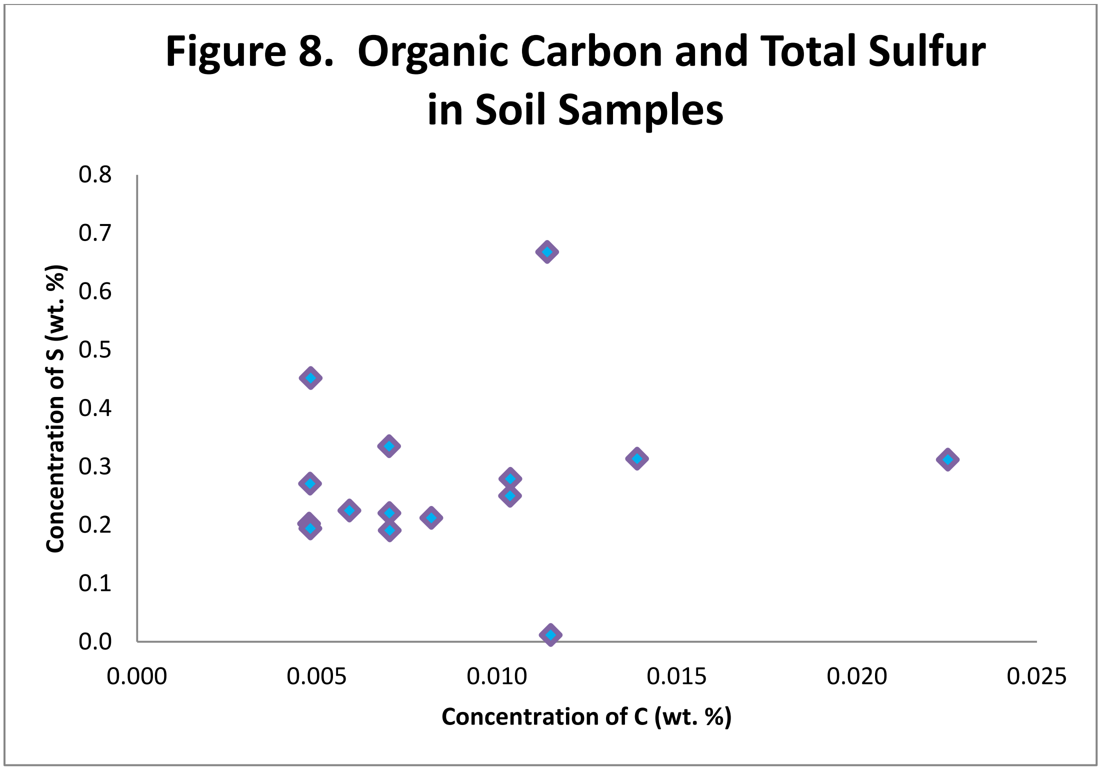
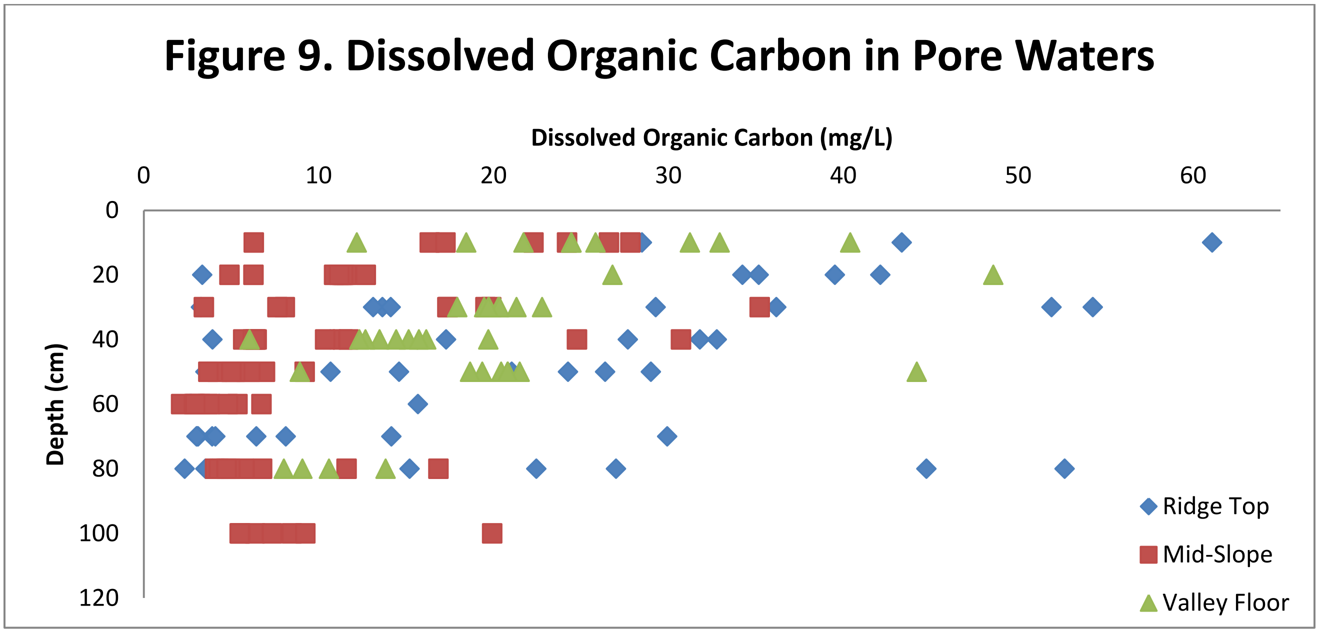


Figure 8 and Table 2 (Appendix) represents the relationship between total sulfur and total organic carbon in soil samples. The concentration of sulfur and organic carbon for the soil sample augured at the surface of the soil profile (0-10cm) was excluded from the above graph because it had much higher concentrations compared to other values. The data for this excluded point and all other points are included in Table *** of the Appendix. Both sulfur and organic carbon concentrations are presented in units of weight percent.

While total sulfur concentrations were measured to be between 0.1-0.75wt%, organic concentrations were measured to be between 0.005-0.01wt.% (Figure 8). Therefore, in the soil profile, higher concentrations of total sulfur are apparent compared to total organic carbon concentrations.

Pore Water Samples

Figure 9 and Table 3 (Appendix) summarizes the total organic carbon content within 186 pore water samples that were collected nine different times from a small ridge located in Huntingdon, PA from the month of September to early December. At the Huntingdon site, pore water samples were collected from the valley floor, mid-slope, and the top of the small ridge. Data in these illustrations is presented in units of mg/L. In an attempt to clean-up Figure 9, a sample from a ridge top lysimeter at a depth of 20cm was excluded from the Figure 3. Having an unusually large concentration of dissolved organic carbon (89.97 mg/L), it is very likely that a decaying leaf could have been at the bottom of this lysimeter during this particular time of sampling.



When focus turns to the organic carbon content of pore waters within the soil, three settings were considered: the valley floor, mid-slope, and top of a ridge. Dissolved organic carbon concentrations at the valley floor setting of the ridge generally decreases with depth (Figure 9). Now, recall that in the soil profiles previously talked about that organic carbon was high in organic carbon concentrations at the top and bottom of the soil profile. If, in fact, new organic is the cause of high concentrations at the top of the soil profile and the preserved “old” organic carbon concentrations where the cause of high concentrations, then this figure illustrates that the “new” organic seems to be more labile than the "older" organic carbon that was once preserved in the Marcellus Formation.

The presence of a trend starts to disappear as elevation on the ridge increases. Notice that the organic carbon concentrations at the mid-slope setting increase then eventually decrease with depth. The organic carbon concentrations at the ridge top setting vary greatly and are not characteristic of any kind of trend at all. This variation at the ridge top and valley floor settings may be due to the position of each setting on the ridge and the fact that the soil in this area is considered to be well-drained. For example, water percolates and flows through the soil or soil surface faster at a ridge top setting as opposed to a valley floor setting where water is allowed to react with the soil it percolates and flows through.

Variations in trends of each setting may also be due to the amount of precipitation that fell prior to sampling. By analyzing the total and average amount of water content that was collected from the lysimeters for each sampling day, it is possible to obtain an understanding of the amount of precipitation throughout the sampling period. Table 3 illustrates variation in rainfall from September to December. It is apparent that through the months of September to December, precipitation values vary.

Table 3. Water Content of Lysimeters

Date	Total (ml)	Average (ml)
9/28/2011	4,220	211.0
10/6/2011	2,245	102.0
10/11/2011	991	66.1
10/18/2011	2,149	107.5
10/29/2011	1,730	86.5
11/2/2011	2,045	107.6
11/18/2011	3,720	186.0

11/22/2011	1,787	85.1
12/2/2011	2,778	126.3

Table 3 illustrates the total and average amount of pore water that was extracted from September to December during each time pore water was collected from the sampling site.

The variability of precipitation may have affected the concentrations of dissolved organic carbon by diluting the pore water within the soil by diluting soil samples.

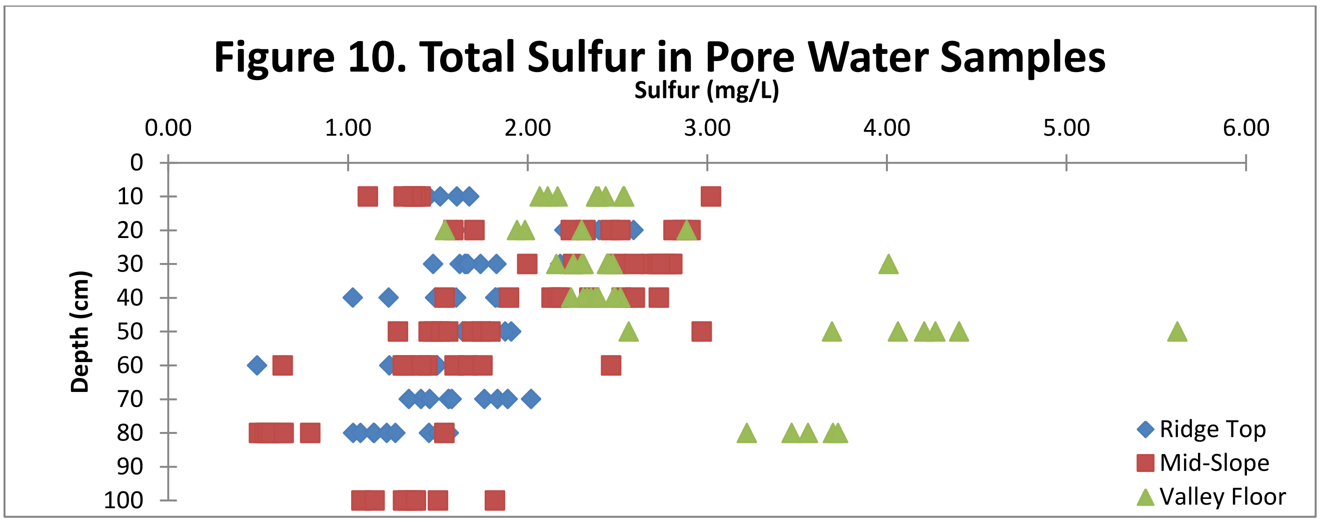


Figure 10 and Table 3 (Appendix) summarize the total sulfur content of pore water samples that were collected during nine different times from a small ridge located in Huntingdon, PA between the months of September and early December. At the Huntingdon site, pore water samples were collected from the valley floor, mid-slope, and the top of the small ridge. Sulfur concentrations are presented in units of mg/L. This data was collected through ICP-AES cation analysis, where the detection limit for Sulfur 180.669 was 200ppm.

Sulfur concentrations within the pore waters of the soil typically range between 1-3 mg/L (Figure 6). Sulfur throughout the pore water profile is sourced from its surrounding environment, soil and rock. A general trend of decreasing sulfur concentrations with depth is apparent. Higher concentrations of sulfur may exist towards the top of the pore water profile compared to the bottom profile because it may be easier for the sulfur to leach from sulfur-rich organic matter than shale rock that has been subjected to great deals of heat and pressure in its lifetime. As the sulfur concentrations decrease, concentrations seem to vary throughout the water column within the soil profile. This variation may, again, be due to position on the ridge and the amount of rainfall prior to sampling events, which is described in more detail above.

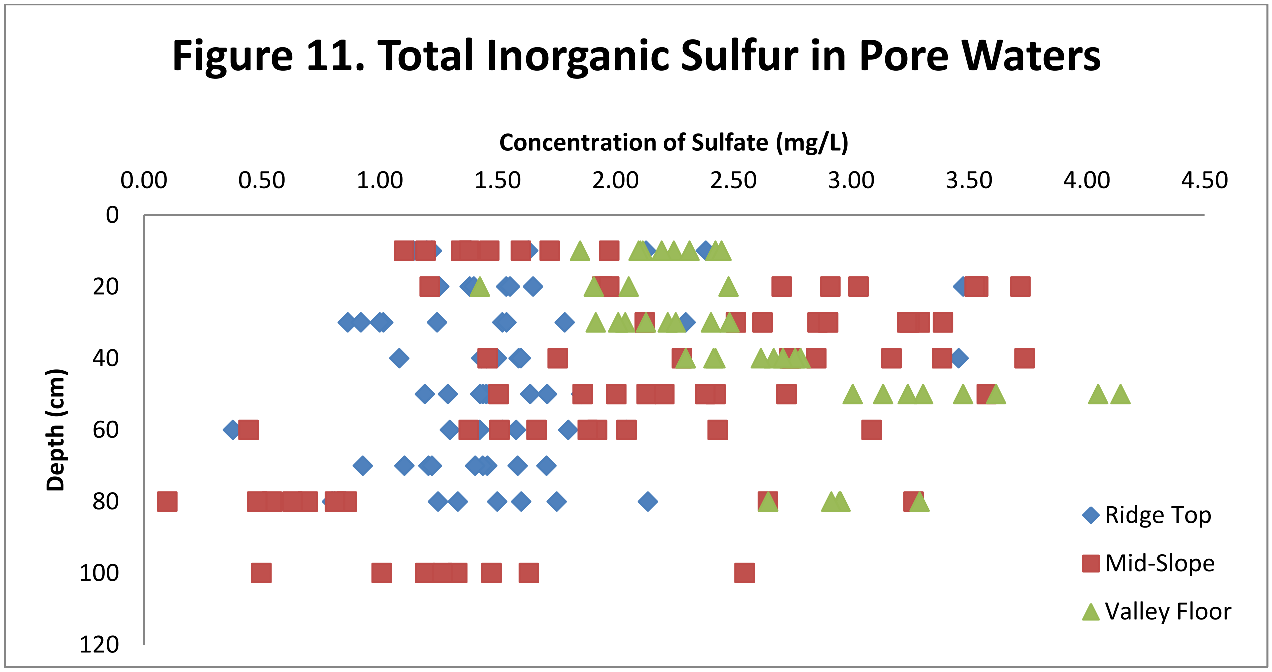


Figure 11 represents the concentration of sulfate measured within the pore water samples. This data is also reported in Table 3 of the Appendix. This data was measured through Ion Chromatography.

In summary, carbon and sulfur is exchanged between the rock, water, and soil settings within the subsurface of the Huntingdon site. In the rock samples, sulfur and carbon vary with depth, revealing higher concentrations of total carbon and sulfur where black shale is present. In the soil profile, total carbon and sulfur share similar trends. Both are of high concentrations towards the top and bottom of the soil profile. High concentrations of sulfur and carbon at the top of the soil profile can be attributed to high amounts of organic matter within the “O” horizon of the soil profile. Therefore, the carbon found in this surface layer is most likely sourced from the organic matter on the forest floor of the sampling site. High concentrations at the bottom of the soil profile can be attributed to the release of sulfur and carbon from the parent rock of shale due to weathering. Specifically, this presence of sulfur may be due to the existence of pyrite within the Marcellus Formation (Figure 12). Because total inorganic carbon analysis revealed that organic carbon is more abundant than inorganic carbon (carbonate) in the parent rock, the high concentration of carbon at the bottom of the profile can be attributed not to the presence of organic matter in the soil but to the release of preserved organic carbon from within the Marcellus Formation. Because the total inorganic sulfur analysis revealed that inorganic sulfur increases with depth in pore water samples, it is possible that the high concentration of sulfur found at the bottom of the soil profile is sourced from preserved inorganic sulfur that had been released from the parent rock (Figure 11). In addition, by looking at the dissolved organic carbon and total sulfur in pore waters, it is possible to determine the nature of dissolution of both elements. Organic carbon decreases with depth, suggesting that organic carbon sourced from modern organic matter is more labile in the water table within the soil profile than old organic matter that was once preserved in the parent rock. Sulfur seems to mimic the same trend as inorganic carbon but to a lesser degree, suggesting that modern organic sulfur is more labile than older organic sulfur. The reason that modern organic sulfur and carbon are more labile than old organic carbon or sulfur may be due to significant amounts of heat and pressure that were applied to the parent shale rock during formation causing easily combusted organic sulfur to be released, only leaving behind more resistant sulfur which is recalcitrant.

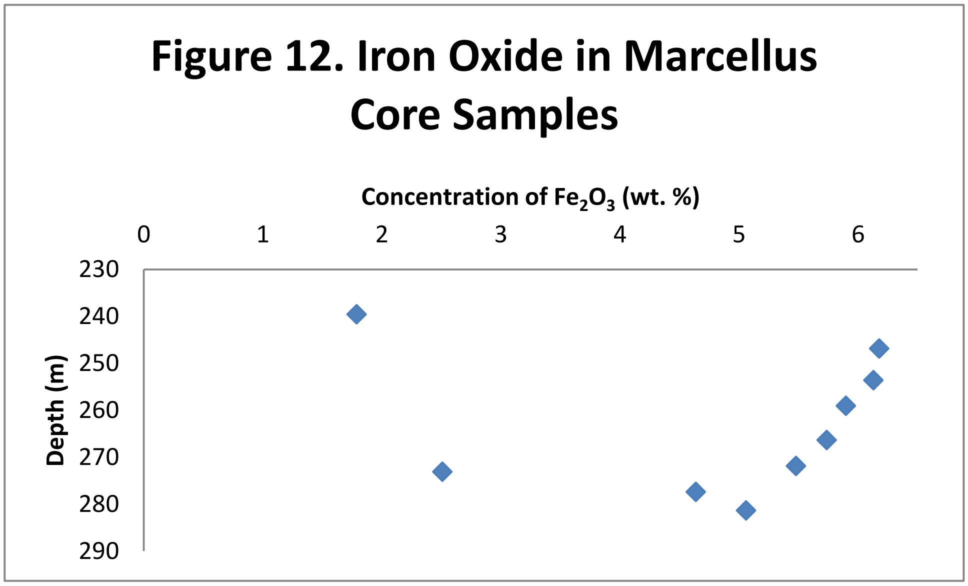


Figure 12 represents the concentration of iron oxide within the Marcellus Formation. Concentrations are represented in units of weight percent. Because there the Marcellus shale can contain high concentrations of iron, it is possible that this iron is in the form of pyrite. Complete data pertaining to this table is represented in Table 4 (Appendix). This data was measured through ICP-AES analysis when bulk chemistry of the core samples was measured.

Uncertainties

Naturally, many uncertainties arose during this research. Many experimental errors may have sourced from imprecise weighing of samples, inaccurate volumes of solutions when a solution needed to be made, miscalculations, and instrumental errors are only some areas where uncertainties could have occurred. Tables ***-*** represent instrumental accuracies, standard deviation, and relative error. Accuracies were determined by subtracting the "true" value from the measured value. Standard deviation was calculated through the use of an excel spreadsheet and relative error was calculated by used the following equation:

$$Rel. Error = \frac{Avg. Observed\ Value - "True"\ Value}{\text{"True"}\ Value}$$

Table 4. Uncertainties for Sulfur Analysis		
Name	**Wt. % S**	**Accuracy**
Standard 1	0.0222	-0.0066
Standard 2	0.0195	-0.0093
Standard 3	0.0222	-0.0066
Standard 4	0.0168	-0.012
Standard 5	0.0242	-0.0046
Standard 1	0.0239	-0.0049
Standard 2	0.023	-0.0058
Standard 3	0.0248	-0.004
Standard 4	0.0208	-0.008
Standard 5	0.023	-0.0058
Standard 6	0.0255	-0.0033
Average	0.0224	-0.0064
Rel. Error (%)	-22.3801	
Std. Dev.	0.0025	

Table 4 illustrates accuracy, relative error, and standard deviation values for sulfur analysis. The true value of these standards is 0.0288 wt. % of Sulfur. Standards used for both soil and core analysis are present in the table above.

Table 5. Uncertainties for TOC Analysis		
Name	**OC (mg/L)**	**Accuracy**
BBOT 1	71.86	-0.67
BBOT 2	71.41	-1.12
BBOT 3	71.79	-0.74
BBOT 4	72.02	-0.51
BBOT 5	71.90	-0.63
BBOT 6	71.17	-1.36
BBOT 7	72.05	-0.48
BBOT 8	74.19	1.66
BBOT 9	77.81	5.28
BBOT 10	71.13	-1.40
BBOT 11	77.95	5.42
Average	73.02	0.49
Rel. Error (%)	0.68	

Std. Dev.	2.53	

Table 5 illustrates the accuracy, relative error, and standard deviation values for total organic carbon analysis. “BBOTs” are samples used in order to check the instrument method. The true value of BBOT’s is 72.53 wt. %. Standards from soil and core analysis are included in this above table.

Table 6. Uncertainties of IC

Dilution True Value	1:2 25 ppm	Accuracy	1:5 10 ppm	Accuracy	1:10 5 ppm	Accuracy	1:20 2.5 ppm	Accuracy
Observed Value	22.4239	-2.5761	9.2546	-0.7454	3.8724	-1.1276	2.1945	-0.3055
	26.5655	1.5655	8.3228	-1.6772	4.8908	-0.1092	2.2011	-0.2989
	26.4513	1.4513	9.1948	-0.8052	4.466	-0.534	2.5009	0.0009
	26.6886	1.6886	9.2788	-0.7212	5.045	0.045	n.a.	n.a
Average	25.5323	0.5323	9.0128	-0.9873	4.5686	-0.4315	2.2988	-0.2012
Rel.Error (%)	2.1293		-9.8725		-8.6290		-8.0467	
Std. Dev.	2.0745		0.4613		0.5247		0.1750	

Table 6 represents the accuracy, relative error, and standard deviation for sulfate concentrations that where produced through Ion Chromatography. Note that for the dilution of 1:2 (2.5ppm), there is only three values instead of four. This is because the value produced for this standard looked questionable so was discarded.

Table 7. Uncertainties for DOC Analysis

Name	(mg/L)
Standard 1	8.522
Standard 2	8.593
Standard 3	8.325
Standard 4	8.228
Standard 5	8.391
Standard 6	8.226
Standard 7	8.126
Standard 8	8.165
Standard 9	8.368
Standard 10	8.424
Standard 11	8.843
Standard 12	8.491
Standard 13	8.789
Standard 14	8.76
Standard 15	8.36
Standard 16	8.855

Standard 17	8.684
Standard 18	8.356
Standard 19	8.438
Standard 20	8.736
Standard 21	9.102
Average	8.513
Std. Dev.	0.261

Table 7 represents only the standard deviation values of the dissolved organic carbon analysis. Accuracy could not be determined because the samples were not replicated or spiked. However, this instrument has been reported to have an accuracy of 97.56% in recent studies. Also the "True" value (8.513) was determined from averaging the measured values. Therefore, if standard error was calculated, it would be 100% which may not exactly be true.

Table 8. Uncertainties of ICP-AES in [Fe2O3]

Name	Fe2O3T (wt.%)	Accuracy
W-2	11.14	0.31
W-2	11.10	0.27
W-2	11.15	0.32
Average	11.13	0.3
Rel. Error (%)	0.0277	[redacted]
Std. Dev.	0.0265	[redacted]

Table 8 represents the accuracy, relative error, and standard deviation values of iron oxide determined through ICP-AES analysis.W-2 is USGS diabase standard that has a "true" value of 10.83.

Table 9. Uncertainties of Carbonate Analysis

Sample Name	Integral	C (wt.%)	Std. Dev.
Blank1 (HCl)	209.9	0.0293	0.00040
Blank1 (HCl)	209.5	0.0293	0.00044
Blank2 (HCl)	208.1	0.0291	0.00061
Blank3 (HCl)	208.2	0.0291	0.00060
Blank1 (air)	214.8	0.0299	-0.00020
Blank (air)	213.8	0.0298	-0.00007
Blank4 (HCl)	206.7	0.0289	0.00078
Average		0.0294	0.00037

Table 9 represents the standard deviation values produced during carbonate analysis. The accuracy of instrument is 99.9%, which was determined by calibration using the company's internal standards.

Conclusion

Sulfur concentrations are variable in the shales (0.6 to 1.6%wt) and do not show much trend with depth. This variability most likely reflects the natural deposition of the layers within the Marcellus Formtaion, causing each layer to have slightly different composition. However, shale sulfur concentration are significantly high than the overlying Purcell limestone formation (~0.3%) due to the presence of pyrite. It was also found that total organic carbon concentrations are much higher than inorganic carbon (carbonates). Also, total carbon concentrations are higher in the Union Springs and Onondaga member than the Purcell member of the Marcellus Shale.

In soils, modern organic carbon located at the top of the soil profile is more labile than the old organic carbon located towards the bottom of the soil profile. High organic carbon concentrations exist at the top and bottom of the soil profile. High concentrations towards the top of the soil profile are due to the presence of organic matter within the "O" horizon at the top of the soil profile while the high organic carbon concentrations towards the bottom of the profile is due to the dissolution of the underlying Marcellus Formation.

In pore waters, dissolved organic carbon generally decreases from the top to the bottom of the soil profile at valley floor setting and somewhat at the mid-slope setting suggesting that modern organic carbon is more labile than old organic carbon. However, at the ridge top setting, do not show any trend. This is most likely due to the water flow pattern which affects the residence time of water and also the amount of rainfall prior to the each sampling event. Sulfur variations may also be due to the characteristics just described.

Acknowledgements

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Appendix

Tables that Pertain to the Figures referred to the paper:

Table 1. Carbon and Sulfur in Core Samples

Sample Name	Total Organic C (wt. %)	Total Inorganic Carbon (wt. %)	Total Carbon (wt. %)	Total Sulfur (wt. %)
BE-923	0.5200	-	-	1.1621
BE-786	6.7299	1.4856	8.2156	0.2860
BE-767	1.9176	0.3450	2.2626	0.3140
BE-896	4.8687	1.4874	6.3562	0.6733
BE-810	2.2674	0.2334	2.5008	1.1879
BE-892	3.1269	0.2400	3.3669	1.076
BE-832	2.5361	0.6030	3.1391	0.941
BE-874	1.9058	0.3598	2.2656	0.9817
BE-910	7.3025	0.7390	8.0415	1.5326
BE-850	2.2823	0.7454	3.0277	1.1685

Table 1 summarizes the total carbon content, the total inorganic and organic content, and the total sulfur content within ten different samples of depths234m (767ft), 240m (786ft), 247m (810ft), 254m (832ft), 259m (850ft), 266m (874ft), 273m (896ft), and 277m (910ft). The data above is presented in weight percent. Each sample was ran three different times during total organic carbon analysis. Before organic carbon analysis, each rock samples was treated with 2N hydrochloric acid in order to eliminate inorganic carbon. The organic carbon data summarized above is the average of three separate runs for each element. Two reference samples of soil were ran in the beginning of the run while BBOT samples were ran every eleventh analyte in order t monitor the accuracy and precision of the instrument used. However, BBOT and Reference samples were excluded from the graph and this table. Before and after each sulfur analysis run, 1-2 standards where measured along with 2-3 blanks. The average blanks used to calculate % sulfur for Run 1 and Run 2 where 11.7 and 8.0. The check standards used contained a composition of 0.0288% sulfur and were ran in order to ensure accurate results. Each sample weighed about one gram and was run two separate times. The average total sulfur value of these samples is summarized in the above table.

Table 2. Organic Carbon and Total Sulfur in Soil Samples				
Sample Name	**Sample Depth (cm)**	**Average Sample Depth (cm)**	**Average S (wt. %)**	**Average C (wt. %)**
MSS-1	0-10	5	0.01808	3.07081
MSS-2	10-20	15	0.01141	0.66724
MSS-3	20-26	23	0.00484	0.45137
MSS-4	26-34	30	0.00701	0.33459
MSS-5	34-44	39	0.01390	0.31351
MSS-6	44-52	48	0.01150	0.24765
MSS-7	52-60	56	0.00482	0.27059
MSS-8	60-65	62.5	0.00702	0.22005
MSS-9	65-71	68	0.00591	0.22451
MSS-10	71-82	76.5	0.00818	0.21207
MSS-11	82-89	85.5	0.00479	0.21207
MSS-12	89-98	93.5	0.00483	0.19407
MSS-13	98-109	103.5	0.00703	0.19070
MSS-14	109-115	112	0.01037	0.25002
MSS-15	115-119	117	0.01038	0.27876
MSS-16	119	119	0.02253	0.31174

Table 2 summarizes the total organic carbon and sulfur content of sixteen different soil samples that were collected from Huntingdon, PA in mid-June of 2008. Soil samples were collected from a small ridge in Huntingdon from depth intervals of 0-10cm, 10-20cm, 20-26cm, 26-34cm, 34-44cm, 44-52cm, 52-60cm, 60-65cm, 65-71cm, 71-82cm, 82-89cm, 89-98cm, 98-109cm, 109-115cm, 115-119cm. The data summarized above in Table 13 is presented in weight percentages. Two reference samples of soil were ran in the beginning of the run while BBOT samples were ran every eleventh analyte during total organic carbon content in order to monitor the accuracy of the results obtained. Before and after each sulfur analysis run, 1-2 standards where measured along with 2-3 blanks. The average of the blanks used to calculate percent of sulfur per samples for Run 1 and Run 2 were measured to be 8.3 and 9.5. The standards used contain a composition of 0.0288% sulfur and were run before and after each run in order to ensure accurate and precise results. Each sample weighed around 99.3-102.8 milligrams and was measured three times. The average of these total sulfur runs is presented in the table above.

Table 3. Organic Carbon and Total Sulfur in Pore Waters

Sample Name	Position	Depth (cm)	Total S (mg/L)	Inorganic S (mg/L)	Total Dissolved Organic Carbon (mg/L)
SB11-0006	VF	10	2.11	2.106	40.42
SB11-0007	VF	20	1.94	1.910	48.6
SB11-0008	VF	30	2.30	2.407	22.79
SB11-0009	VF	40	2.35	2.426	16.17
SB11-0010	VF	50	5.62	4.049	44.22
SB11-0013	MS	10	1.37	1.104	27.85
SB11-0014	MS	20	1.71	1.945	12.71
SB11-0015	MS	30	2.00	2.126	35.23
SB11-0016	MS	40	1.90	2.283	11.4
SB11-0017	MS	50	1.28	1.862	9.223
SB11-0018	MS	60	1.32	1.380	5.372
SB11-0019	MS	80	0.79	0.099	6.787
SB11-0020	MS	100	1.08	1.009	6.373
SB11-0021	RT	10	1.43	1.201	-
SB11-0023	RT	30	2.18	1.651	51.92
SB11-0024	RT	40	1.03	0.866	17.3
SB11-0025	RT	50	1.55	1.454	29.01
SB11-0027	RT	70	1.41	1.105	3.924
SB11-0028	RT	80	1.03	0.798	8.862
SB11-0029	VF	40	2.33	2.418	15.17
SB11-0030	VF	80	3.22	2.951	10.6
SB11-0031	VF	50	3.70	3.008	20.45
SB11-0032	VF	30	2.26	2.043	19.48
SB11-0033	VF	20	1.54	1.426	-
SB11-0034	VF	10	2.07	1.852	32.94
SB11-0035	MS	10	1.41	1.601	22.3
SB11-0036	MS	40	2.13	2.854	6.392
SB11-0037	MS	50	1.48	2.133	6.952
SB11-0038	MS	60	1.31	1.509	3.671
SB11-0039	MS	80	0.51	0.544	5.776
SB11-0040	MS	20	2.24	2.707	11.34
SB11-0041	MS	100	1.15	1.329	7.353
SB11-0042	MS	30	2.26	2.626	24.78

SB11-0043	RT	70	1.46	1.457	4.328
SB11-0044	RT	80	1.07	0.810	4.116
SB11-0045	RT	60	0.50	0.378	-
SB11-0046	RT	50	1.69	1.453	15.21
SB11-0047	RT	40	1.23	1.085	14.61
SB11-0048	RT	30	1.62	1.522	32.79
SB11-0049	RT	20	1.60	1.538	54.28
SB11-0050	RT	10	1.39	1.388	34.24
SB11-0051	VF	10	2.53	2.426	12.2
SB11-0052	VF	40	2.31	2.673	19.72
SB11-0053	VF	30	2.44	2.485	20.29
SB11-0054	VF	50	4.27	3.617	20.84
SB11-0055	MS	30	2.68	2.859	8.081
SB11-0056	MS	40	2.17	2.739	11.72
SB11-0057	MS	20	2.32	2.914	11.47
SB11-0058	MS	50	1.45	2.004	5.01
SB11-0059	MS	80	0.63	0.861	4.093
SB11-0060	MS	60	1.44	1.667	2.144
SB11-0061	RT	70	1.56	1.208	28.5
SB11-0062	RT	30	1.65	1.539	14.18
SB11-0063	RT	40	1.60	1.432	13.66
SB11-0064	RT	50	1.64	1.440	3.945
SB11-0065	RT	80	1.14	0.856	26.39
SB11-0066	VF	10	2.54	2.249	18.45
SB11-0067	VF	20	2.89	2.481	-
SB11-0068	VF	30	2.46	2.224	17.95
SB11-0069	VF	50	-	-	8.944
SB11-0070	VF	80	3.47	3.306	13.84
SB11-0071	VF	40	2.38	2.649	6.072
SB11-0072	MS	40	2.19	2.300	30.73
SB11-0073	MS	10	1.38	2.512	6.302
SB11-0074	MS	50	1.52	1.459	4.221
SB11-0075	MS	60	1.41	1.975	6.737
SB11-0076	MS	80	0.56	1.506	11.62
SB11-0077	MS	20	2.46	0.445	4.918
SB11-0078	MS	100	1.33	2.648	19.94
SB11-0079	MS	30	2.50	1.213	3.448
SB11-0080	RT	80	1.15	2.549	2.345
SB11-0081	RT	70	1.45	1.174	3.945

SB11-0082	RT	60	1.23	0.930	8.142
SB11-0083	RT	50	1.65	1.299	15.69
SB11-0084	RT	40	1.49	1.291	24.28
SB11-0085	RT	30	1.65	1.499	31.82
SB11-0086	VF	40	2.39	2.299	15.74
SB11-0087	VF	50	4.21	3.477	19.37
SB11-0088	VF	30	2.47	2.132	19.75
SB11-0089	VF	20	2.30	0.000	24.46
SB11-0090	VF	10	2.44	2.316	26.61
SB11-0092	MS	40	2.35	1.346	6.479
SB11-0093	MS	50	1.56	2.747	5.869
SB11-0094	MS	60	1.60	2.209	3.252
SB11-0095	MS	80	0.54	1.923	4.69
SB11-0096	MS	20	2.52	0.481	11.62
SB11-0097	MS	100	1.36	3.033	8.483
SB11-0098	MS	30	2.60	1.194	19.89
SB11-0099	RT	20	2.35	2.903	89.97
SB11-0100	RT	10	1.45	1.857	47.52
SB11-0101	RT	30	1.66	1.425	43.36
SB11-0102	RT	50	1.69	1.438	14.14
SB11-0103	RT	60	1.37	1.500	3.535
SB11-0104	RT	70	1.58	1.145	2.639
SB11-0105	RT	80	1.22	1.254	3.128
SB11-0106	VF	40	2.56	0.922	14.44
SB11-0107	VF	50	4.01	2.619	21.52
SB11-0108	VF	30	2.38	3.242	20.36
SB11-0109	VF	10	2.24	2.012	25.85
SB11-0110	MS	30	2.78	2.117	19.56
SB11-0111	MS	20	2.86	3.266	11.41
SB11-0112	MS	60	1.67	3.293	3.784
SB11-0113	MS	50	1.69	1.975	6.098
SB11-0114	MS	40	2.52	3.088	5.708
SB11-0115	MS	10	1.36	3.577	16.37
SB11-0116	MS	100	1.31	1.757	5.539
SB11-0117	MS	80	0.55	1.381	4.311
SB11-0118	RT	10	1.61	0.499	
SB11-0119	RT	20	2.40	1.712	44.76
SB11-0120	RT	30	1.74	2.047	39.54
SB11-0121	RT	50	1.91	1.587	13.13

SB11-0122	RT	60	1.48	1.752	3.644
SB11-0123	RT	70	1.76	2.384	2.720
SB11-0124	RT	80	1.27	1.383	3.059
SB11-0125	VF	10	2.40	1.001	31.24
SB11-0126	VF	40	2.49	2.198	13.50
SB11-0127	MS	10	1.31	2.787	24.22
SB11-0128	MS	40	2.60	1.466	6.252
SB11-0129	MS	50	1.75	3.172	5.239
SB11-0130	MS	60	2.47	2.425	2.885
SB11-0131	MS	20	2.81	1.885	10.9
SB11-0132	MS	30	2.81	3.540	17.42
SB11-0133	MS	100	1.38	3.390	9.246
SB11-0134	MS	80	0.57	1.634	4.966
SB11-0135	RT	10	1.52	0.811	27.02
SB11-0136	RT	20	2.21	1.590	61.11
SB11-0137	RT	30	1.67	1.640	35.18
SB11-0138	RT	40	1.84	1.521	36.18
SB11-0139	RT	50	1.81	1.708	11.25
SB11-0140	RT	60	1.49	1.602	3.634
SB11-0141	RT	70	2.02	1.222	2.716
SB11-0142	RT	80	1.56	1.553	3.039
SB11-0144	VF	80	3.56	1.223	-
SB11-0145	VF	10	2.38	2.957	21.74
SB11-0146	VF	30	2.31	2.451	19.72
SB11-0147	VF	40	2.52	2.257	12.69
SB11-0148	VF	50	4.06	2.764	18.67
SB11-0149	VF	80	3.70	3.137	9.086
SB11-0150	MS	10	1.54	2.918	-
SB11-0151	MS	30	3.02	1.723	17.38
SB11-0152	MS	40	2.73	3.249	6.393
SB11-0153	MS	100	1.54	3.388	5.496
SB11-0154	MS	50	1.82	1.476	5.022
SB11-0155	MS	20	2.97	2.382	11.19
SB11-0156	MS	60	1.59	3.526	2.952
SB11-0157	MS	80	0.64	2.048	5.645
SB11-0158	RT	10	1.68	0.696	-
SB11-0159	RT	20	2.59	1.786	52.68
SB11-0160	RT	70	1.83	2.139	3.358
SB11-0161	RT	30	1.83	1.601	29.95

SB11-0162	RT	80	1.45	1.801	3.282
SB11-0163	RT	40	1.82	1.193	22.47
SB11-0164	RT	60	1.50	1.631	-
SB11-0165	RT	50	1.79	1.248	10.68
SB11-0166	VF	10	2.17	1.401	24.48
SB11-0167	VF	20	1.99	2.100	26.82
SB11-0168	VF	40	2.48	2.058	12.35
SB11-0169	VF	80	3.73	2.713	8.030
SB11-0170	VF	30	2.16	3.291	21.32
SB11-0171	VF	50	4.40	1.918	20.81
SB11-0172	MS	10	1.11	4.145	16.86
SB11-0173	MS	30	2.78	2.217	17.27
SB11-0174	MS	40	2.73	3.738	7.662
SB11-0175	MS	20	2.91	3.719	10.39
SB11-0176	MS	50	1.79	2.728	6.284
SB11-0177	MS	60	1.75	2.435	3.716
SB11-0178	MS	80	0.64	0.630	4.828
SB11-0179	MS	100	1.50	1.268	4.759
SB11-0180	RT	10	1.40	1.580	21.05
SB11-0181	RT	80	1.50	1.245	3.551
SB11-0182	RT	20	2.40	3.458	42.14
SB11-0183	RT	60	1.45	1.428	4.353
SB11-0184	RT	30	1.48	1.406	29.28
SB11-0185	RT	40	1.82	1.718	27.7
SB11-0186	RT	50	1.88	1.618	10.7
SB11-0187	RT	70	1.89	1.556	6.456

Table 3 summarizes the total sulfur and dissolved organic carbon content of pore water samples that were collected during nine different times from a small ridge located in Huntingdon, PA between the months of August and early December. At the Huntingdon site, pore water samples were collected from different depths (10-100cm) at the valley floor (VF), mid-slope (MS), and the top of the small ridge (RT). All samples were run at once along with standards of different dilutions at the begging, middle, and end of the run. The data in the table above is represented in units of mg/L and summarizes the concentration of sulfur and organic carbon at different depths and positions on a small ridge. The wavelength used to measure the sulfur content was 180.67. Each sulfur sample and standard were measured three times by the instrument and then averaged. Only the average is presented here. When samples were run to measure dissolved organic carbon, every tenth analyte was a standard in order to monitor the accuracy of and extrapolate the results. During analysis, the samples that are highlighted in blue in Table 3 contained organic carbon values that were greater than the values of our calibration curve (>40 mg/L). These samples were diluted to ratios of 1:2, 1:3, or 1:5 and re-ran in order to assure accurate results.

Table 4. Concentration of Rock Sample Analytes (wt. %)

Sample Name	Al2O3 (wt.%)	BaO (wt.%)	CaO (wt.%)	Fe2O3T (wt.%)	K2O (wt.%)	MgO (wt.%)	MnO (wt.%)	Na2O (wt.%)	P2O5 (wt.%)	SiO2 (wt.%)	SrO (wt.%)	TiO2 (wt.%)	LOI (wt.%)	**Total**
BE 767	17.70	0.12	1.96	7.13	3.94	1.76	0.03	0.66	0.09	56.14	0.02	0.80	9.55	99.89
BE 786	4.41	0.10	40.66	1.79	0.89	1.37	0.10	0.17	0.10	14.67	0.04	0.22	33.92	98.43
BE 810.5	16.44	0.15	1.47	6.18	3.68	1.41	0.02	0.67	0.09	58.36	0.02	0.80	9.31	98.60
BE 832	15.70	0.13	3.71	6.13	3.36	1.67	0.03	0.65	0.10	57.71	0.02	0.78	10.24	100.23
BE 850	15.86	0.13	5.55	5.90	3.42	1.52	0.03	0.63	0.13	54.79	0.03	0.77	11.35	100.12
BE 874	15.60	0.12	2.42	5.74	3.53	1.41	0.03	0.72	0.11	60.91	0.02	0.76	8.62	99.99
BE 892	15.64	0.12	1.58	5.48	3.74	1.40	0.02	0.67	0.10	59.49	0.02	0.71	10.04	99.01
BE 896	4.91	0.12	36.43	2.51	1.08	0.65	0.07	0.24	0.05	23.83	0.03	0.23	29.99	100.14
BE 910	7.69	0.07	5.10	4.64	1.60	1.28	0.01	0.37	0.12	63.69	0.02	0.34	15.48	100.40
BE 923	22.67	0.20	0.47	5.06	4.13	2.36	0.01	0.94	0.18	51.02	0.03	0.39	10.60	98.05
Reference	15.45	0.02	10.86	10.83	0.63	6.37	0.17	2.20	0.14	52.68	0.02	1.06	-	-

Table 4 summarizes the cation content within all ten Marcellus Shale core samples. However, concentrations of Fe_2O_3 (blue values) are the only cations referred to in this paper. All samples were named "BE", referring to the Bald Eagle location of the Marcellus Shale, with a corresponding depth (in feet) for the sample. "LOI" refers to the weight percent of the sample that was lost on emission during ashing. For some samples, the total % oxides did not add up to 100% even after the "LOI" percentages were taken into account. This may be because an element within the composition of the sampled rock was not tested in the ICP-AES analysis. Sometimes elements can become trapped in other adjacent molecules, prohibiting such elements to be measured accurately. For example, sulfur, which exists in the form of pyrite in sections of the Union Spring Member, can combine with calcium during the ashing process. Therefore, when the samples were ashed, small amounts of sulfur were retained in the sample and not included in LOI values. For this reason, Sulfur was analyzed separately as described in methods and LOI was corrected to include sulfur so that the weight percent totals would approach 100% as shown in Table 4.

Figure 1. Chromatograph for Sample SB11-00010

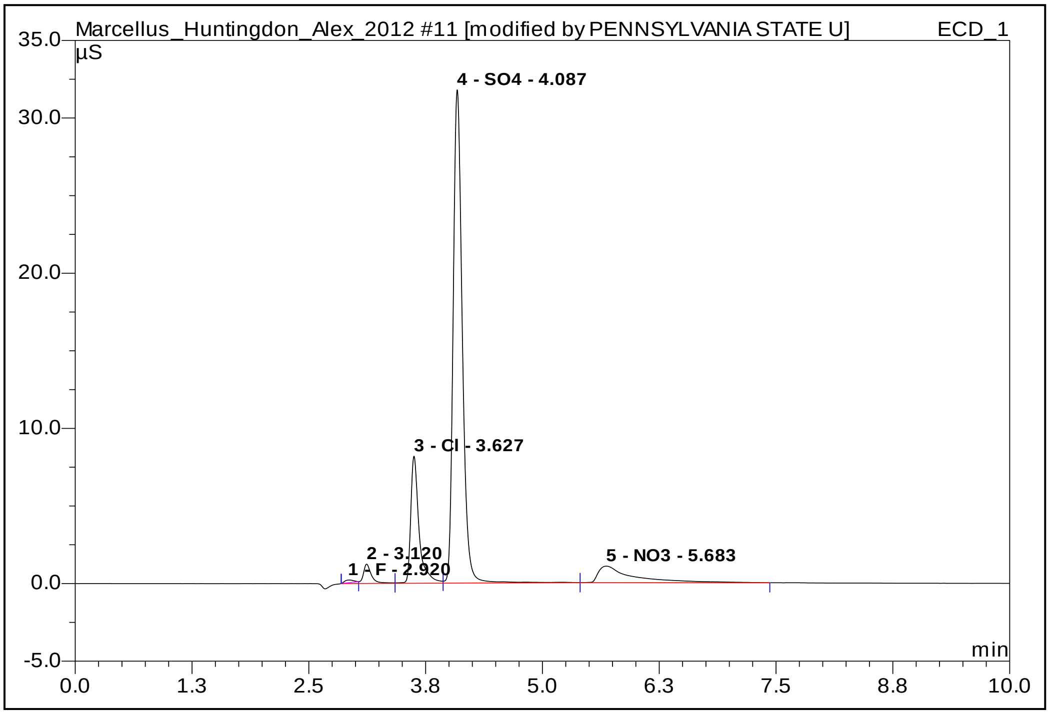

Figure 1 represents the retention times of pore water sample SB11-00010. As you can see, within these samples bromide, chloride, sulfate and nitrate were all identified in this sample. However, one peak (peak 2) could not be identified. This particular sample was picked because it was a good representation of all the samples as a whole.

Raw Data

Table 5. Raw Data for Pore Water Samples

Date	Sample #	Sample Name	Position	Depth (cm)	Volume (mL)	pH
9/28/2011	SB11-00006	MVF-1	VF	10	150	4.52
	SB11-00007	MVF-2	VF	20	65	4.46
	SB11-00008	MVF-3	VF	30	95	4.75
	SB11-00009	MVF-4	VF	40	115	4.57
	SB11-00010	MVF-5	VF	50	40	5.36

	SB11-00011	MVF-6	VF	60	10	6.80
	SB11-00012	MVF-8	VF	80	na	na
	SB11-00013	MMS-1	MS	10	130	4.43
	SB11-00014	MMS-2	MS	20	215	4.37
	SB11-00015	MMS-3	MS	30	180	4.18
	SB11-00016	MMS-4	MS	40	275	4.44
	SB11-00017	MMS-5	MS	50	375	4.56
	SB11-00018	MMS-6	MS	60	115	4.97
	SB11-00019	MMS-8	MS	80	60	5.07
	SB11-00020	MMS-10	MS	100	160	4.78
	SB11-00021	MRT-1	RT	10	30	4.48
	SB11-00022	MRT-2	RT	20	na	na
	SB11-00023	MRT-3	RT	30	70	4.78
	SB11-00024	MRT-4	RT	40	180	4.89
	SB11-00025	MRT-5	RT	50	330	4.62
	SB11-00026	MRT-6	RT	60	na	na
	SB11-00027	MRT-7	RT	70	1035	5.14
	SB11-00028	MRT-8	RT	80	590	4.96
10/6/2011	SB11-00029	MVF-4	VF	40	123	4.70
	SB11-00030	MVF-8	VF	80	67	5.16
	SB11-00031	MVF-5	VF	50	36	5.66
	SB11-00032	MFV-3	VF	30	68	4.89
	SB11-00033	MVF-2	VF	20	27	4.72
	SB11-00034	MVF-1	VF	10	100	4.65

	SB11-00035	MMS-1	MS	10	67	4.55
	SB11-00036	MMS-4	MS	40	91	4.49
	SB11-00037	MMS-5	MS	50	167	4.61
	SB11-00038	MMS-6	MS	60	91	5.00
	SB11-00039	MMS-8	MS	80	96	5.15
	SB11-00040	MMS-2	MS	20	78	4.45
	SB11-00041	MMS-10	MS	100	222	4.86
	SB11-00042	MMS-3	MS	30	147	4.2
	SB11-00043	MRT-7	RT	70	266	5.20
	SB11-00044	MRT-8	RT	80	195	5.27
	SB11-00045	MRT-6	RT	60	19	5.38
	SB11-00046	MRT-5	RT	50	87	4.91
	SB11-00047	MRT-4	RT	40	137	5.07
	SB11-00048	MRT-3	RT	30	92	4.69
	SB11-00049	MRT-2	RT	20	46	4.60
	SB11-00050	MRT-1	RT	10	23	4.61
10/11/2011	SB11-00051	MVF-1	VF	10	43	4.55
	SB11-00052	MVF-4	VF	40	96	5.34
	SB11-00053	MVF-3	VF	30	33	4.49
	SB11-00054	MVF-5	VF	50	28	5.43
	SB11-00055	MMS-3	MS	30	70	4.19
	SB11-00056	MMS-4	MS	40	108	4.44
	SB11-00057	MMS-2	MS	20	105	4.39
	SB11-00058	MMS-5	MS	50	122	4.56

	SB11-00059	MMS-8	MS	80	80	4.99
	SB11-00060	MMS-6	MS	60	110	4.94
	SB11-00061	MRT-7	RT	70	42	5.17
	SB11-00062	MRT-3	RT	30	25	4.51
	SB11-00063	MRT-4	RT	40	30	4.91
	SB11-00064	MRT-5	RT	50	40	4.89
	SB11-00065	MRT-8	RT	80	59	5.30
10/18/2011	SB11-00066	MVF-1	VF	10	145	5.79
	SB11-00067	MVF-2	VF	20	15	4.41
	SB11-00068	MVF-3	VF	30	60	4.63
	SB11-00069	MVF-5	VF	50	38	5.16
	SB11-00070	MVF-8	VF	80	37	4.96
	SB11-00071	MVF-4	VF	40	140	4.29
	SB11-00072	MMS-4	MS	40	120	4.39
	SB11-00073	MMS-1	MS	10	40	4.35
	SB11-00074	MMS-5	MS	50	175	4.48
	SB11-00075	MMS-6	MS	60	145	4.78
	SB11-00076	MMS-8	MS	80	105	4.99
	SB11-00077	MMS-2	MS	20	143	4.30
	SB11-00078	MMS-10	MS	100	175	4.74
	SB11-00079	MMS-3	MS	30	120	4.05
	SB11-00080	MRT-8	RT	80	163	5.24
	SB11-00081	MRT-7	RT	70	170	5.04
	SB11-00082	MRT-6	RT	60	137	5.11

	SB11-00083	MRT-5	RT	50	55	4.90
	SB11-00084	MRT-4	RT	40	90	4.86
	SB11-00085	MRT-3	RT	30	76	4.53
10/29/2011	SB11-00086	MVF-4	VF	40	115	5.38
	SB11-00087	MVF-5	VF	50	40	5.34
	SB11-00088	MVF-3	VF	30	55	4.40
	SB11-00089	MVF-2	VF	20	10	4.39
	SB11-00090	MVF-1	VF	10	125	4.43
	SB11-00091	MMS-1	MS	10	55	4.53
	SB11-00092	MMS-4	MS	40	115	4.65
	SB11-00093	MMS-5	MS	50	140	4.56
	SB11-00094	MMS-6	MS	60	105	4.88
	SB11-00095	MMS-8	MS	80	85	5.13
	SB11-00096	MMS-2	MS	20	110	4.36
	SB11-00097	MMS-10	MS	100	50	5.06
	SB11-00098	MMS-3	MS	30	105	4.15
	SB11-00099	MRT-2	RT	20	75	4.73
	SB11-00100	MRT-1	RT	10	40	4.36
	SB11-00101	MRT-3	RT	30	70	4.58
	SB11-00102	MRT-5	RT	50	55	4.85
	SB11-00103	MRT-6	RT	60	85	5.11
	SB11-00104	MRT-7	RT	70	160	5.23
	SB11-00105	MRT-8	RT	80	135	5.24
11/2/2011	SB11-00106	MVF-4	VF	40	145	5.25

	SB11-00107	MVF-5	VF	50	35	5.37
	SB11-00108	MVF-3	VF	30	65	4.60
	SB11-00109	MVF-1	VF	10	55	4.39
	SB11-00110	MMS-3	MS	30	135	4.17
	SB11-00111	MMS-2	MS	20	135	4.30
	SB11-00112	MMS-6	MS	60	110	4.81
	SB11-00113	MMS-5	MS	50	140	4.52
	SB11-00114	MMS-4	MS	40	125	4.40
	SB11-00115	MMS-1	MS	10	45	4.48
	SB11-00116	MMS-10	MS	100	220	4.80
	SB11-00117	MMS-8	MS	80	85	5.08
	SB11-00118	MRT-1	RT	10	20	4.37
	SB11-00119	MRT-2	RT	20	65	4.64
	SB11-00120	MRT-3	RT	30	50	4.49
	SB11-00121	MRT-5	RT	50	100	4.75
	SB11-00122	MRT-6	RT	60	80	5.11
	SB11-00123	MRT-7	RT	70	340	5.17
	SB11-00124	MRT-8	RT	80	95	5.20
11/18/2011	SB11-00125	MVF-1	VF	10	170	5.23
	SB11-00126	MVF-4	VF	40	140	4.55
	SB11-00127	MMS-1	MS	10	95	4.57
	SB11-00128	MMS-4	MS	40	215	4.43
	SB11-00129	MMS-5	MS	50	200	4.55
	SB11-00130	MMS-6	MS	60	120	4.95

	SB11-00131	MMS-2	MS	20	170	4.43
	SB11-00132	MMS-3	MS	30	145	4.17
	SB11-00133	MMS-10	MS	100	90	4.79
	SB11-00134	MMS-8	MS	80	120	5.02
	SB11-00135	MRT-1	RT	10	25	4.41
	SB11-00136	MRT-2	RT	20	105	4.76
	SB11-00137	MRT-3	RT	30	135	4.47
	SB11-00138	MRT-4	RT	40	45	4.77
	SB11-00139	MRT-5	RT	50	65	4.93
	SB11-00140	MRT-6	RT	60	195	5.16
	SB11-00141	MRT-7	RT	70	1055	5.05
	SB11-00142	MRT-8	RT	80	600	5.10
	SB11-00143	MVF-2	VF	20	10	na
	SB11-00144	MVF-8	VF	80	20	4.97
11/22/2011	SB11-00145	MVF-1	VF	10	90	5.48
	SB11-00146	MVF-3	VF	30	60	3.71
	SB11-00147	MVF-4	VF	40	60	4.28
	SB11-00148	MVF-5	VF	50	55	4.91
	SB11-00149	MVF-8	VF	80	60	4.94
	SB11-00150	MMS-1	MS	10	22	4.40
	SB11-00151	MMS-3	MS	30	125	4.18
	SB11-00152	MMS-4	MS	40	107	4.41
	SB11-00153	MMS-10	MS	100	220	4.81
	SB11-00154	MMS-5	MS	50	162	4.53

	SB11-00155	MMS-2	MS	20	130	4.02
	SB11-00156	MMS-6	MS	60	185	4.78
	SB11-00157	MMS-8	MS	80	65	5.03
	SB11-00158	MRT-1	RT	10	15	4.54
	SB11-00159	MRT-2	RT	20	53	4.76
	SB11-00160	MRT-7	RT	70	110	5.27
	SB11-00161	MRT-3	RT	30	37	4.63
	SB11-00162	MRT-8	RT	80	90	5.32
	SB11-00163	MRT-4	RT	40	46	4.49
	SB11-00164	MRT-6	RT	60	30	5.57
	SB11-00165	MRT-5	RT	50	65	5.02
12/2/2011	SB11-00166	MVF-1	VF	10	135	6.04
	SB11-00167	MVF-2	VF	20	20	4.73
	SB11-00168	MVF-4	VF	40	160	4.47
	SB11-00169	MVF-8	VF	80	80	4.87
	SB11-00170	MVF-3	VF	30	73	4.76
	SB11-00171	MVF-5	VF	50	60	4.23
	SB11-00172	MMS-1	MS	10	90	4.53
	SB11-00173	MMS-3	MS	30	200	4.18
	SB11-00174	MMS-4	MS	40	110	4.43
	SB11-00175	MMS-2	MS	20	160	4.25
	SB11-00176	MMS-5	MS	50	190	4.96
	SB11-00177	MMS-6	MS	60	255	4.82
	SB11-00178	MMS-8	MS	80	160	4.04

	SB11-00179	MMS-10	MS	100	220	4.85
	SB11-00180	MRT-1	RT	10	25	4.46
	SB11-00181	MRT-8	RT	80	240	5.09
	SB11-00182	MRT-2	RT	20	90	3.09
	SB11-00183	MRT-6	RT	60	170	5.40
	SB11-00184	MRT-3	RT	30	120	4.59
	SB11-00185	MRT-4	RT	40	90	4.9
	SB11-00186	MRT-5	RT	50	90	4.99
	SB11-00187	MRT-7	RT	70	40	5.08

Table 5 represents the ph and volume of pore water and its corresponding position and depth that was measured from each lysimeter during field work. The data was collected nine separate dates, which are also presented in the graph. In this figure, RT represents ridge top, MS represents mid-slope, and VF represents valley floor.

Table 6.Total Sulfur in Marcellus Shale Core Samples

Trial #	Sample Name	Weight (mg)	KIO3	Wt. % S	Average wt. % S
1	Standard 1	1000.0	118.0	0.0239	
	Standard 2	1000.0	114	0.0230	
	BE-767	100.8	129	0.2616	0.3140
	BE-786	100.6	142	0.2912	0.2860
	BE-810	100.2	648	1.4272	1.1879
	BE-832	100.7	555	1.2126	0.941
	BE-850	100.7	561	1.2260	1.1685
	BE-874	100.9	490	1.0654	0.9817
	BE-892	100.3	575	1.2622	1.076
	BE-896	100.7	342	0.7372	0.6733
	BE-910	100.3	696	1.5334	1.5326
	BE-923	100.7	454	0.9872	1.1621
	Standard 3	1000.0	122	0.0248	
2	Standard 4	1000.0	104.0	0.021	
	Standard 5	1000.0	114	0.023	
	767	100.8	176	0.366	
	786	100.3	137	0.281	
	810	100.3	435	0.949	
	832	100.3	310	0.668	
	850	100.6	509	1.111	
	874	100.2	412	0.898	
	892	100.2	408	0.889	
	896	100.8	285	0.609	
	910	100.4	696	1.532	
	923	100.4	609	1.337	
	Standard 6	1000.0	125	0.025	

Table 6 illustrates the raw data collected during sulfur analysis in core samples. Each sample was ran twice.

Table 7.Total Sulfur in Soil Samples

Trial #	Sample Name	Depth Interval (cm)	Depth (cm)	Weight (mg)	KIO3	Wt. %S	Average wt. % S
1	Standard 1			1000.0	107.0	0.02217	
	MSS-6	44-52	48	100.2	14	0.01271	0.01150
		44-52	48	102.0	13	0.01028	
	MSS-5	34-44	39	99.3	17	0.01961	0.01390
		34-44	39	100.7	12	0.00818	
	MSS-2	10-20	15	101.1	12	0.00815	0.01141
		10-20	15	102.2	15	0.01466	
	MSS-10	71-82	76.5	101.3	12	0.00813	0.00818
		71-82	76.5	100.1	12	0.00823	
	MSS-4	26-34	30	100.8	11	0.00595	0.00701
		26-34	30	102.1	12	0.00807	
	MSS-11	82-89	85.5	101.4	11	0.00591	0.00479
		82-89	85.5	102.1	10	0.00367	
	MSS-8	60-65	62.5	101.6	12	0.00811	0.00702
		60-65	62.5	101.2	11	0.00592	
	MSS-15	115-119	117	101.0	13	0.01038	0.01038
		115-119	117	101.0	13	0.01038	
	Standard 2			1000.0	95	0.01948	
2	Standard 3			1000.0	107.0	0.02217	
	MSS-14	109-115	112	100.4	13	0.01045	0.01037
		109-115	112	101.8	13	0.01030	
	MSS-12	89-98	93.5	100.8	10	0.00372	0.00483
		89-98	93.5	100.9	11	0.00594	
	MSS-3	20-26	23	100.6	10	0.00372	0.00484
		20-26	23	100.7	11	0.00595	
	MSS-7	52-60	56	101.1	11	0.00593	0.00482
		52-60	56	101.1	10	0.00370	
	MSS-9	65-71	68	101.1	10	0.00370	0.00591
		65-71	68	101.6	12	0.00811	
	MSS-13	98-109	103.5	101.0	11	0.00593	0.00703
		98-109	103.5	101.5	12	0.00812	
	MSS-1	0-10	5	100.1	16	0.01721	0.01808
		0-10	5	102.8	17	0.01895	
	MSS-16	119	119	100.9	20	0.02599	0.02253
		119	119	102.1	17	0.01908	
	Standard 4			1000.0	83	0.0168	
	Standard 5			1000.0	116	0.0242	

Table 8. Total Organic Carbon in Marcellus Core Samples

Depth of Sample (ft)	wt. % of N	wt. % of C
923	0.368	0.314
923	0.365	0.308
923	0.354	0.278
Average	**0.362**	**0.300**
786	0.069	7.419
786	0.074	5.617
786	0.066	7.154
Average	**0.070**	**6.730**
767	0.178	1.831
767	0.180	2.004
767	0.150	1.662
Average	**0.169**	**1.832**
896	0.074	5.166
896	0.067	4.575
896	0.072	4.865
Average	**0.071**	**4.869**
892	0.173	2.455
892	0.216	3.983
892	0.166	2.942
Average	**0.185**	**3.127**
832	0.165	2.760
832	0.166	2.404
832	0.175	2.444
Average	**0.169**	**2.536**
874	0.176	2.032
874	0.159	1.817
874	0.177	1.869
Average	**0.171**	**1.906**
810.5	0.185	2.105
810.5	0.207	2.347
810.5	0.175	2.351
Average	**0.189**	**2.267**
910	0.248	7.253
910	0.183	5.926
910	0.260	8.729
Average	**0.230**	**7.303**
923	0.382	1.572
923	0.359	0.336
923	0.355	0.312

Table 9. Total Organic Carbon in Soil Samples				
Depth Interval (cm)	**Average Depth (cm)**	**Sample Name**	**Carbon (wt. %)**	**Average Carbon (wt%)**
		BBOT 1	71.8612	
		BBOT 2	71.4079	
0-10	5	MSS-1	3.0708	
115-119	117	MSS-15	0.2788	
60-65	62.5	MSS-8	0.2184	0.2201
60-65	62.5	MSS-8	0.2217	
82-89	85.5	MSS-11	0.2023	
26-34	30	MSS-4	0.3346	
34-44	39	MSS-5	0.3090	0.3135
34-44	39	MSS-5	0.3180	
65-71	68	MSS-9	0.2245	
		BBOT 3	71.7863	
119	119	MSS-16	0.3117	
71-82	76.5	MSS-10	0.2018	0.2121
71-82	76.5	MSS-10	0.2223	
52-60	56	MSS-7	0.2706	
20-26	23	MSS-3	0.4514	
109-115	112	MSS-14	0.2503	0.2500
109-115	112	MSS-14	0.2498	
98-109	103.5	MSS-13	0.1907	
89-98	93.5	MSS-12	0.1941	
		BBOT 4	72.0177	
10-20	15	MSS-2	0.6456	0.6672
10-20	15	MSS-2	0.6889	
44-52	48	MSS-6	0.2476	
		BBOT 5	71.8987	

Table 10. Total Carbonate in Marcellus Core Samples						
Sample Name	**Sample Depth (m)**	**Sample Weight (g)**	**Integral**	**mg C/kg sample**	**mg CaCO3/kg sample**	**Wt. % Carbonate in sample**
BE-874	266	1	5000	3598.226	29987.216	2.999
BE-767	234	1	4794	3449.750	28749.836	2.875
BE-810	247	1	3246	2334.020	19451.461	1.945
BE-892	272	1	3338	2400.329	20004.078	2.000
BE-896	273	1	20600	14842.023	123691.764	12.369
BE-896		1	20690	14906.891	124232.367	12.423
BE-786	240	1	20580	14827.608	123571.630	12.357
BE-786		1	20660	14885.268	124052.166	12.405
BE-832	254	1	8430	6070.420	50590.203	5.059
BE-832		1	8317	5988.975	49911.446	4.991
BE-850	259	1	10390	7483.102	62363.339	6.236
BE-850		1	10350	7454.272	62123.071	6.212
BE-910	277	1	10520	7576.800	63144.210	6.314
BE-910		1	60700	7266.260	60556.200	6.056
BE-910		1	61200	7326.323	61056.758	6.106

Note: Table 10 is missing a total carbonate concentration at a depth of 281 meters.

Table 11. Carbonate Analysis for Core Samples

Sample Name	Sample Weight (g)	Integral	mg C/kg Core	mg Carbonat/kg Core	Carbonate (wt. %)	Depth (ft)	Depth (m)	C (wt.%)
874	1	5000	3598.226	29987.216	2.999	874	266.40	0.3598
767	1	4794	3449.750	28749.836	2.875	767	233.78	0.3450
810	1	3246	2334.020	19451.461	1.945	810.5	247.04	0.2334
892	1	3338	2400.329	20004.078	2.000	892	271.88	0.2400
896	1	20600	14842.023	123691.764	12.369	896	273.10	1.4842
896	1	20690	14906.891	124232.367	12.423	896	273.10	1.4907
786	1	20580	14827.608	123571.630	12.357	786	239.57	1.4828
786	1	20660	14885.268	124052.166	12.405	786	239.57	1.4885
832	1	8430	6070.420	50590.203	5.059	832	253.59	0.6070
832	1	8317	5988.975	49911.446	4.991	832	253.59	0.5989
850	1	10390	7483.102	62363.339	6.236	850	259.08	0.7483
850	1	10350	7454.272	62123.071	6.212	850	259.08	0.7454
910	1	10520	7576.800	63144.210	6.314	910	277.37	0.7577
910	1	60700	7266.260	60556.200	6.056	910	277.37	0.7266
910	1	61200	7326.323	61056.758	6.106	910	277.37	0.7326