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Technical Progress Report

**“Restoring Sustainable Forests on Appalachian Mined Lands for Wood Products,
Renewable Energy, Carbon Sequestration, and Other Ecosystem Services”**

Quarterly Report

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ABSTRACT

The overall purpose of this project is to evaluate the biological and economic feasibility of restoring high-quality forests on mined land, and to measure carbon sequestration and wood production benefits that would be achieved from forest restoration procedures. During this quarter we worked on methodologies for analyzing carbon in mine soils. A unique property of mine soils is the presence of coal and carboniferous rock particles that are present in mine soils in various sizes, quantities, and qualities. There is no existing method in the literature that may be of use for quantitative estimation of soil organic carbon (SOC) in mine soils that can successfully differentiate between pedogenic and geogenic carbon forms.

In this report we present a detailed description of a 16-step method for measuring SOC in mine soils designed for and tested on a total of 30 different mine soil mixtures representing a wide spectrum of mine soils in the hard-rock region of the Appalachian coalfield. The proposed method is a combination of chemical procedure for carbonates removal, a thermal procedure for pedogenic C removal, and elemental C analysis procedure at 900°C. Our methodology provides a means to correct for the carbon loss from the more volatile constituents of coal fragments in the mine soil samples and another correction factor for the protected organic matter that can also remain unoxidized following thermal pretreatment. The correction factors for coal and soil material-specific SOM were based on carbon content loss from coal and SOM determined by a parallel thermal oxidation analysis of pure ground coal fragments retrieved from the same mined site as the soil samples and of coal-free soil rock fragments of sandstone and siltstone origin.

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INTRODUCTION

Public Law 95-87 mandates that mined land be reclaimed in a fashion that renders the land at least as productive after mining as it was before (Torbert et al. 1995). Research has shown that restored forests on mined lands can be equally as or more productive than the native forests removed by mining (Burger and Zipper 2002). Given that most land surface-mined for coal in the Appalachians was originally forested, forestry is a logical land use for most of the reclaimed mined land in the region (Torbert and Burger 1990). However, since implementation of the SMCRA, fewer forests are being restored in the eastern and Midwestern coalfield regions (Burger et al. 1998). In several states, most notably Virginia, the majority of mined land is now being restored to forests. Over eighty percent of Virginia's mined land has been reclaimed to forested post-mining land uses since 1991. However, region-wide, the majority of mined land that was originally forested is not being reclaimed in a way that favors tree establishment, timber production, carbon sequestration, and long-term forest productivity (Torbert and Burger 1990).

We believe that these reclaimed mined lands are producing timber and sequestering carbon at rates far below their potential for reasons that include poor mine soil quality, inadequate stocking of trees, lack of reforestation incentives, and regulatory disincentives for planting trees on previously forested land (Boyce 1999, Burger and Maxey 1998). A number of these problems can be ameliorated simply through intensive silvicultural management. Through established site preparation techniques such as ripping, weed control, fertilizing, and liming, the quality of a given site can be improved. Other management and silvicultural techniques such as site-species matching, correct planting techniques, employing optimal planting densities, post-planting weed control, and thinning can also improve normal development of forest stands, and improve timber production and carbon sequestration.

Similar to the much-debated topic of converting agricultural land to forests, the conversion of reclaimed mined lands to forests carries with it many economic implications. The primary difference between converting agricultural lands to forests and converting reclaimed mined lands to forests is the absence of any obvious extrinsic opportunity cost in the latter scenario; this, of course, assumes that the reclaimed mined land has been abandoned and is not being utilized for any economically beneficial purpose.

A fair amount of research has been conducted regarding the amounts and values of timber produced on reclaimed mined lands. The effect that a carbon market may have on decisions pertaining to the reclamation of mined lands has also been researched. According to previous research, it appears that mined lands are capable of sequestering carbon and producing harvest volumes of equal or greater magnitude to similar non-mined lands. This fact alone, however, does not render afforestation of mined lands economically profitable or feasible in all cases. There is a lack of research pertaining specifically to the conversion of reclaimed mined lands from their current uses to forests and the economic implications of such a land use conversion. Furthermore, the potential for an incentive scheme aimed at promoting the conversion of reclaimed mined lands to forests has yet to be explored in depth.

This study ultimately addresses the potential for increasing carbon sequestration on surface-mined land. The overall research objective of this study is to determine the economic feasibility of carbon sequestration through converting reclaimed mined lands to forests using high-value tree species, and to demonstrate the economic and decision-making implications of an incentive scheme on such a land use conversion.

EXECUTIVE SUMMARY

The purpose of this project is to evaluate the biological and economic feasibility of restoring high-quality forests on abandoned mined land, and to measure carbon sequestration and wood production benefits that would be achieved from forest restoration procedures. The project is based on 14 afforested mined sites varying in age from 20 to 56 years located in a seven-state area of the eastern coalfields (Study 1) (Fig. 1), and a new field study, which is a 3 x 3 factorial in a random complete block design with three replications at each of three locations: Ohio (Fig. 1), West Virginia (Fig. 2), and Virginia (Study 2) (Fig. 2). For Study 2, which is the emphasis of this report, the treatments included three forest types (white pine, hybrid poplar, mixed hardwood) and three silvicultural regimes (competition control, competition control plus tillage, competition control plus tillage plus fertilization). Each individual treatment plot is 0.5 acres. Each block of nine plots is 4.5 acres, and the complete installation at each site is 13.5 acres.

Measuring carbon on mined land has additional challenges compared to measuring it on undisturbed soils. Soil carbon analysis is complicated by coal contamination, and mine soils are highly variable. In this report we present a detailed description of a 16-step method for measuring SOC in mine soils designed for and tested on a total of 30 different mine soil mixtures representing a wide spectrum of mine soils in the hard-rock region of the Appalachian coalfield. The proposed method is a combination of a chemical procedure for carbonates removal, a thermal procedure for pedogenic C removal, and an elemental C analysis procedure at 900°C. Our methodology provides a means to correct for the carbon loss from the more volatile constituents of coal fragments in the mine soil samples and another correction factor for the protected organic matter that can also remain unoxidized following thermal pretreatment. The correction factors for coal and soil material-specific SOM were based on carbon content loss from coal and SOM determined by a parallel thermal oxidation analysis of pure ground coal fragments retrieved from the same mined site as the soil samples and of coal-free soil rock fragments of sandstone and siltstone origin.

Study 1: Pre-SMCRA Mined Sites Study

Figure 1. Location and layout of experimental sites for Study 1 across a seven-state region.

Study 2: Post-SMCRA Mined Grasslands Study

Figure 2. Location and layout of experimental sites for Study 2 in Ohio, West Virginia, and Virginia.

TASK 1: Estimate forest productivity and carbon sequestration potential on mined lands supporting abandoned grasslands. (Burger et al.)

Executive Summary

A unique property of mine soils is the presence of coal and carboniferous rock particles that are present in mine soils in various sizes, quantities, and qualities. There is no existing method in the literature that may be of use for quantitative estimation of soil organic carbon (SOC) in mine soils that can successfully differentiate between pedogenic and geogenic carbon forms.

In this paper we present a detailed description of a 16-step method for measuring SOC in mine soils designed for and tested on a total of 30 different mine soil mixtures representing a wide spectrum of mine soils in the hard-rock region of the Appalachian coalfield. The proposed method is a combination of a chemical procedure for carbonates removal, a thermal procedure for pedogenic C removal, and an elemental C analysis procedure at 900°C. Our methodology provides a means to correct for the carbon loss from the more volatile constituents of coal fragments in the mine soil samples and another correction factor for the protected organic matter that can also remain unoxidized following thermal pretreatment. The correction factors for coal and soil material-specific SOM were based on carbon content loss from coal and SOM determined by a parallel thermal oxidation analysis of pure ground coal fragments retrieved from the same mined site as the soil samples and of coal-free soil rock fragments of sandstone and siltstone origin.

A total of 30 mine soil sample mixtures were constructed by adding six levels of ground coal material to five ground soil materials: sandstone, siltstone, 50:50 mixture of sandstone-siltstone, quartz sand, and Jefferson soil. These samples were used to evaluate the accuracy of the proposed 16-step soil organic carbon estimation method and the Walkley-Black method. The accuracy of the 16-step SOC estimation and Walkley-Black methods was calculated as the percent relative uncertainty from the true mean, PRUM (%), and was estimated for the individual C measurement replications made by the 16-step method (for a total of five replications) and for the Walkley-Black procedure (for a total of three replications), for the five materials and the six coal levels tested.

The results of this study indicated that the amount of carbonates can be significant in certain mine spoil materials. The C content from carbonates present in sandstone (SS) and siltstone (SiS) spoil materials was estimated at 60% of the SOC content present in the respective materials.

The mean PRUM (%) of SOC predictions made by a single replication of the 16-step method ranged from 13% to 148% for SS (compared to the true SOC, 0.082 C wt%), from 11% to 41% for SiS (with true SOC of 0.629 C wt%), from 5% to 84% for the 50:50 SS:SiS mixture (with true SOC of 0.382 C wt%), and from 9% to 103% for the Jefferson soil (with true SOC of 0.811 C wt%), across the spectrum of coal content levels tested. The mean PRUM (%) for the Walkley-Black predictions ranged from 17% to 1,003% for SS, from 2% to 122% for SiS, from 3% to 126% for the 50:50 SS:SiS mixture, and from 2% to 58% for Jefferson soil.

The means separation analysis for the 16-step method indicated that the 10% coal samples for SS and 50:50 SS:SiS mixtures were the only samples with significantly higher uncertainty compared to the remaining 28 mixtures tested. The uncertainties associated with the Walkley-Black procedure varied across materials and coal levels tested, with no trends observed.

We developed a linear regression model ($R^2 = 87\%$) intended to be used as a correction formula for Walkley-Black C estimates reported in previously published work for mined lands. The model is specific for soil material type and is only based on the Walkley-Black estimates of the soils of interest. The experimental design in this study can be used to develop site-specific and soil-specific regression models for Walkley-Black SOC correction that would produce SOC estimates much closer to the true SOC of the mine soils analyzed.

Experimental

Before now, mined land researchers have used standard soil organic matter measurement procedures, such as the Walkley-Black wet oxidation procedure (Walkley and Black 1934), for SOC analyses in mine soils with the assumption that coal and carboniferous rock particles are not as easily oxidized as organic matter (Rodrigue 2001). Although the latter could be true for some mine soils, the effect of the oxidizing agent used in the Walkley-Black procedure, potassium dichromate, could be significant depending on the size and quantity of geogenic carbon particles in the soil (Daniels and Amos 1982, Skjemstad and Taylor 1999).

Because of the uncertainties associated with SOC estimates determined by the Walkley-Black procedure, this method only provides a qualitative measure of SOC and is not recommended for quantitative SOC analysis in soils (Nelson and Sommers 1982, Skjemstad and Taylor 1999). Unfortunately, there is no existing method in the literature that may be of use for quantitative estimation of SOC that can successfully differentiate between pedogenic and geogenic carbon forms in mine soils.

The objectives of this report are: (1) to design a new technique for C content measurement on reclaimed mined land that will differentiate between pedogenic and geogenic C forms present in mine soils; (2) to evaluate and compare the performance (accuracy and precision) of the new C measurement method and the Walkley-Black procedure for C analysis on mine soils; and (3) to determine the effects of (i) spoil material type and (ii) coal content in mine soils on the accuracy and precision of the Walkley-Black procedure.

Subtask 1.1

After reviewing all previous work aimed at SOC measurement in soils, we realized that thermal oxidation pretreatment of mine soil samples can be used to fully eliminate all pedogenic carbon present in mine soils. We were also aware that the more volatile carbon constituents of geogenic origin in the mine soil samples will be oxidized to CO_2 leaving only the most resistant organic compounds in the sample unoxidized (Vorres 1998). Zoller et al. (1999) have determined these highly resistant organic residues to be carbon particles of highly aromatic chemical structure within individual coal fragments. The latter could be measured by elemental C analysis using automated carbon analyzer. However, one should also be aware that depending on the thermal temperature, some organic matter molecules can resist oxidation to CO_2 when they are protected by relatively high amount of clays present in the soil. The latter could easily be tested and determined with pure soil materials that are entirely free of coal fragments.

The most significant modification that we propose to the thermal oxidation methods described by Schmidt et al. (2001) and Kuhlbusch (1995) is that our methodology provides a means to correct for the carbon loss from the more volatile constituents of coal fragments in the mine soil samples and another correction factor for the protected organic matter that can also remain unoxidized following thermal pretreatment. The correction factors for coal and soil

material-specific SOM were based on carbon content loss from coal and SOM determined by a parallel thermal oxidation analysis of pure ground coal fragments retrieved from the same mined site as the soil samples and of coal-free soil rock fragments of sandstone and siltstone origin (Fig. 1-1). Based on our observations, coal fragments are commonly scattered on the soil surface and at various depths within the mine soil profile of the majority of mined sites, and retrieval of such site-specific coal fragments is expected to be effortless.

Figure 1-1. Proposed SOC estimation method designed to partition the total soil carbon to pedogenic and geogenic carbon fractions in mine soils.

Additionally, owing to the simplicity of the proposed SOC estimation and C fractionation method (Fig. 1-1) and its low costs of implementation, we believe that this technique will serve as a straightforward and cost-effective carbon sequestration accounting method for mine soils, given that it meets the accuracy and precision standards for a future carbon market. The following is a detailed description of a 16-step method for measuring SOC in mine soils designed for this project and tested on a total of 30 different soil mixtures representing a wide spectrum of mine soils in the hard-rock region of the Appalachian coalfield.

1. Collect mine soil samples from a desired depth or desired soil horizon.
2. Collect coal fragments detected during the soil sample collection process. If additional coal fragments are necessary, scout the site and collect additional coal fragments located at the surface of the mine site.
3. Remove the coarse fragments by sieving the mine soil samples through a 2-mm mesh sieve. Retain the separated coarse fragments for further analysis.
4. Grind approximately 15 g per sample of the fine mine soil material (<2 mm) using mortar and pestle until all ground material of the 15-g subsample is passed through sieve No. 60 (<250 μ m).
5. Grind approximately 15 g of the site-specific coal fragments until all ground coal material passes sieve No. 60 (250 μ m).
6. From both ground materials from Steps 4 and 5, place two replications of approximately 600 mg of the ground sample and two replications of approximately 100 mg of the ground coal on ceramic crucibles that can resist heating up to 1,000°C; record the crucible ID and sample weights to the nearest 0.0001 g. Use a separate aliquot of the ground sample and ground coal (about 5 g) to determine their moisture content, where:

$$\text{Moisture, \%} = [(\text{Air-Dry soil g}) - (\text{Oven-Dry}_{105^{\circ}\text{C}} \text{ soil g})] / (\text{Oven-Dry}_{105^{\circ}\text{C}} \text{ soil g}) * 100.$$

7. Add approximately 1 mL of distilled water to each 600-mg ground mine soil and to the 100-mg reference coal material to increase efficiency of carbonates removal by HCl acid fumigation (Harris et al. 2001).
8. Place between 20 and 30 samples in a vacuum desiccator (5 L) along with a beaker (150 mL) with 100 mL of concentrated HCl (12 M) to remove carbonates. Note that the desiccator is only used to confine the HCl vapors and no vacuum conditions are necessary for this pretreatment.

Repeat this step for the reference ground coal sample to assure consistency of the parallel analysis.

9. Allow all ground samples to be exposed to HCl vapor for a period of 24 hours.
10. After the HCl exposure, remove crucibles from the desiccator and put them in a drying oven at 60°C for 4 to 6 hours to remove residual moisture.

At this stage of the method, all ground mine soil samples will be carbonate-free, and if one is interested in measuring the amount of carbonates present in the samples, then duplicate soil samples should be used for elemental carbon analysis before and after the carbonates removal pretreatment, using a carbon auto-analyzer.

11. Use the first sample replication to measure the residual elemental carbon of each carbonate-free sample and reference coal sample using a carbon auto-analyzer with a preset combustion temperature of a minimum of 950°C.

Note that the C results reported by the auto-analyzer must be corrected for sample moisture content, as shown in Step 15 below.

12. Place the second sample replication into a muffle furnace preheated to 375°C to remove all pedogenic organic matter.

The 375°C temperature was the lowest of three chosen temperature settings, along with 550° and 650°C, which were tested to determine the optimal temperature for thermal pretreatment of mine soil samples at which detectable levels of soil organic carbon remained for elemental C analysis at Step 15. Note that the detection limit of the carbon auto-analyzer used in this study was 0.01% C by sample weight.

13. Allow samples to be exposed to thermal oxidation in the muffle furnace, preset to the chosen temperature, for a period of 24 hours.
14. Remove samples from muffle furnace and place them in a desiccator to allow cooling.
15. Without transferring to a different crucible, measure the residual elemental carbon of each soil sample and the reference coal sample using a carbon auto-analyzer with a preset combustion temperature of a minimum of 950°C.

Note that the C results reported by the auto-analyzer, reported_C%, must be corrected for sample moisture content as follows:

$$\text{Corrected C (wt\%)} = \text{reported_C\%} * (100 + \text{Moisture \%})/100$$

16. Soil organic carbon, SOC(wt%), is estimated by Equation 1 described later in the Results section of this task report.

For the evaluation of the effectiveness of carbonates removal from each of the 30 mine soil mixtures, we estimated the difference of carbon content from two elemental carbon analyses before and after HCl fumigation (Harris et al. 2001, Hedges and Stern 1984, Yamamuro and Kayanne 1995). The two elemental carbon analyses necessary for estimation of the amount of removed carbonates-derived carbon (wt %) are depicted in Fig. 1-1, the [C2] and [C1] analyses of the proposed SOC estimation method. In the next paragraphs we describe the experiments used to evaluate the accuracy and precision of the above 16-step SOC measurement method.

Subtask 1.2

An experiment of 5 x 6 x 3 factorial design was set up to evaluate the effect of five soil materials, six levels of coal fragments content in mine soils, and three thermal oxidation temperature levels (see Step 12 in the description of the method). Five soil materials were chosen as follows: (1) weathered sandstone, (2) weathered siltstone, (3) a mixture of approximately 50 percent weathered sandstone and 50 percent weathered siltstone, (4) industrial grade quartz sand, and (5) standard laboratory soil, Ap horizon of a Jefferson soil.

The first two soil materials were collected from the Powell River Reclamation Research Project site in Wise County, Virginia. The chemical and physical properties of the spoil material from the Powell River Reclamation Research Project site are representative of most mined sites in the hard rock regions in the Appalachians (Daniels and Amos 1982). The weathered

sandstone and weathered siltstone materials were carefully chosen to be completely free of coal fragments.

All soil materials were ground to pass a No. 60 mesh sieve (<250 μm final particle size) in order to eliminate the effects of variable soil mineral and coal fragments particle size on the efficiency of SOC estimation by the proposed method, as coal fragments exist in mine spoils in a wide range of sizes (Daniels and Amos 1982). Grinding the entire sample to a standardized soil particle size of less than 250 μm was also considered to allow a more efficient means of removing all carbonates present in the sample (Harris et al. 2001). Note that the site-specific coal fragments were also ground to a final particle size of less than 250 μm with the purpose of producing an accurate correction factor for the carbon loss from the more volatile constituents of these fragments occurring during the parallel C analysis of the reference coal sample.

The six levels of coal fragment content were chosen similar to those used by Daniels and Amos (1982) in their experiment to evaluate the effect of coal fragments on the measured SOC in mine soils, using the Walkley-Black wet oxidation procedure. These levels were: 0%, 0.5%, 1.0%, 2.5%, 5.0%, and 10.0% of total soil weight.

A total of 30 mine soil sample mixtures were constructed by adding each of the six levels of ground coal material to each of the five ground soil materials previously mentioned. Following carbonates removal by HCl fumigation (Harris et al. 2001, Hedges and Stern 1984, Yamamuro and Kayanne 1995), the 30 soil mixtures were exposed to three thermal oxidation temperature levels: 375°C (adopted from Schmidt et al. 2001); 550°C (Bendfeldt et al. 2001, Schulten and Leinweber 1999), and 650°C (derived from Othman and Shamsuddin 2003 and Zoller et al. 1999), for a period of 24 hours to determine the effect of temperature on the efficacy of thermal transformation of C to CO₂ of pedogenic C and the more volatile geogenic C forms in each sample. All SOC measurements for the 30 soil mixtures were replicated five times for a total of 450 measurements using the 16-step SOC estimation method.

In a separate experiment with a 5x6 factorial design, each of the 30 soil mixtures were analyzed for their organic carbon content using the Walkley-Black procedure (Nelson and Sommers 1982, Walkley and Black 1934), as described below. All SOC measurements using the Walkley-Black procedure were replicated three times for a total of 90 measurements.

Walkley-Black wet oxidation procedure:

1. Collect mine soil samples from a desired depth or desired soil horizon.
2. Remove the coarse fragments by sieving the mine soil samples through a 2-mm mesh sieve. Retain the separated coarse fragments for further analysis.
3. Grind approximately 15 g per sample of the fine mine soil material (<2 mm) using a porcelain mortar and pestle until all ground material of the 15-g subsample is passed through sieve No. 60 (<250 μm). Note that using a metal mortar and pestle to grind the soil samples could introduce free Fe that could interfere with the Walkley-Black analysis.

Use a separate aliquot of the ground sample and ground coal (about 5 g) to determine their moisture content, where:

$$\text{Moisture, \%} = [(\text{Air-Dry soil g}) - (\text{Oven-Dry}_{105^\circ\text{C}} \text{ soil g})] / (\text{Oven-Dry}_{105^\circ\text{C}} \text{ soil g}) * 100.$$

4. Place approximately 0.5000 g air-dried soil (use greater amounts if necessary to assure at least 20 mg carbon present in the sample) into a 500-mL Erlenmeyer flask. Weigh soil to the nearest 0.0001 g.
5. Pipette exactly 10.00 mL of 1N $K_2Cr_2O_7$ onto the soil and swirl to mix. At this step, prepare two blank samples by adding 10.00 mL of 1N $K_2Cr_2O_7$ to two additional 500-mL Erlenmeyer flasks.
6. Under a hood, rapidly add approximately 20 mL of concentrated H_2SO_4 to each flask and swirl gently for 1 minute
7. Under a hood, allow the suspension to stand for 30 minutes on a wooden or plastic sheet.
8. Dilute the suspension with about 200 mL of distilled water.
9. Add 10 mL of concentrated (no less than 85%) H_3PO_4 to complex Fe^{2+} , which could interfere with the endpoint of the titration.
10. Add six drops of ferroin indicator (1,10-phenanthroline ferrous sulfate) and back-titrate with 0.5 N ferrous solution, $Fe(NH_4)_2SO_4$, to a brown endpoint.
11. The color sequence during titration is: (i) orange-yellow; (ii) pale green; (iii) blue-green; and (iv) brown. The brown endpoint occurs very rapidly and extra care is advised when the blue-green color is reached.
12. Organic carbon is estimated as:

$$C (\%) = [10 / (\text{Oven-Dry}_{105^\circ C} \text{ soil g})] * (1\text{-sample titer mL/blank titer mL}) * 0.395,$$
 assuming that approximately 58.8% of soil organic matter is C, and that 77% of the total soil organic matter is oxidized (Nelson and Sommers, 1982).

Note that the $\text{Oven-Dry}_{105^\circ C} (g) = \text{Air-dry} (g) * 100 / (100 + \text{Moisture}\%)$

Subtask 1.3

For the evaluation of the 16-step SOC estimation method, the dependent variable was the percent relative uncertainty from the mean, PRUM (%), which was the ratio between the absolute difference of the predicted and the true SOC of a soil sample, in the numerator, and the true SOC, in the denominator, $(\text{Abs}(\text{SOC}\%_{\text{measured}} - \text{SOC}\%_{\text{present}}) / \text{SOC}\%_{\text{present}}) * 100$, and multiplied by 100 to convert to percent. The $\text{SOC}\%_{\text{present}}$ is the soil organic carbon measurement of the sample with 0% coal addition, and $\text{SOC}\%_{\text{measured}}$ is the soil organic carbon of each constructed mine soil mixture. The three independent variables for this experiment were spoil material type, coal fragments content, and thermal oxidation temperature.

Similarly, for the evaluation of the Walkley-Black procedure, the dependent variable was PRUM(%), which was calculated as percent ratio between the absolute difference of the predicted and true SOC in the soil sample, in the numerator, and the true SOC, in the denominator, $(\text{Abs}(\text{WB-OC}\%_{\text{measured}} - \text{SOC}\%_{\text{present}}) / \text{SOC}\%_{\text{present}}) * 100$, where $\text{SOC}\%_{\text{present}}$ is the soil organic carbon measurement of the sample with 0% coal addition, and $\text{WB-OC}\%_{\text{measured}}$ is the soil organic carbon of each constructed mine soil mixture measured by the Walkley-Black method. The two independent variables for the evaluation of the Walkley-Black method were spoil material type and coal fragments content.

Analysis of variance (ANOVA) and means separation analysis were performed for both experiments using standard statistical procedures, PROC GLM, in the SAS® statistical software package. The degrees of freedom for each experiment were:

The Walkley-Black SOC measurements were further analyzed to attempt to determine any existing correlation between the Walkley-Black C estimates and the true SOC in the mine soil sample across the spectrum of spoil material type and coal contents analyzed. The established correlation was modeled to produce a regression model intended to be used as a correction formula for Walkley-Black C estimates reported in previously published work for mined lands, such as the soil organic carbon estimates reported by Rodrigue (2001).

The dependent and independent variables for the linear regression modeling task using regression analysis procedures (PROC REG) in SAS® statistical analysis software are:

Dependent	Regressors
SOC% _{present}	WB-OC% _{measured}
	Material Type
	Coal Content

Results and Discussion

Subtask 1.1

Carbonates removal. Because carbonates are resistant to thermal degradation, it is recommended that they are removed prior to elemental C analysis. Our results from two elemental carbon analyses, before and after carbonates removal using HCl fumigation, for the five pure material types used in this project indicated that the amount of carbonates can be significant in certain mine spoil materials (Fig. 1-2).

The C content from carbonates present in sandstone (SS) and siltstone (SiS) spoil materials was estimated at 60% of the SOC concentration in the respective materials. In the spoil material comprised of approximately 50:50 SS:SiS material the carbonates-derived C content was 43% relative to the SOC concentration. These results further supported the recommendation for removing carbonates from mine soils before SOC analysis, as the failure to do so would result in 40% to 60% over-estimation of the organic carbon present in mine soils formed from SS and SiS overburden spoil material.

The carbonate contents of quartz sand and the Jefferson soil materials were estimated at 0% for the pure ground material. These results were as expected. The ground quartz sand was obtained from a commercially available source and was advertised to be approximately 100% silicon dioxide. The Jefferson soil was acquired from the Ap horizon of a site that has not been recorded to be limed in the past, and it was assumed that all carbonates that may have existed in the soil are now completely dissolved and leached out.

Our results also indicated that either (i) the presence of coal in the soil could inhibit carbonates removal by HCl fumigation, or (ii) the coal could promote an unspecified process of C addition to the sample from an external source, such as air, during the HCl fumigation treatment or during the sample drying prior to elemental C analysis (Fig. 1-2). The results for the quartz sand with added coal indicated that the total carbon of the sample significantly increased following HCl fumigation and sample drying at 60°C, prior to elemental C analysis, implying that carbon was added to these samples. The amount of added C increased as the

relative coal content (weight %) increased in the soil mixtures. One possible explanation of this phenomenon could be that CO₂ from air was incorporated in the soil mixtures via a chemical reaction promoted by the presence of coal either during HCl fumigation or during the 4- to 6-hr period of sample drying. In the case of the SiS and the 50:50 SS:SiS mixtures, the C addition appeared to negate the efficiency of the HCl fumigation technique to remove carbonates.

Although it is not clear what mechanisms are promoting the addition of air-CO₂ in the soil, if one assumes that carbonates removal efficiency is affected by the coal, then one could notice that there is an observable linear relationship between coal content present in the soil mixtures and the decrease in the efficiency of carbonates removal for the soil mixtures analyzed. The C addition to the soil mixtures was equivalent to a reduction of 6.5% and 4.6% of the efficiency of carbonates removal by HCl fumigation in the SiS and the 50:50 SS:SiS mixtures, respectively, for every 1 wt % of coal added to the soil (Fig. 1-2).

The latter indicates that additional work is needed in order to determine the exact causes and experimental conditions that may have led to C additions, most likely from air-CO₂, to mine soils analyzed for SOC content. For all SOC analyses in this project, we will assume that all carbonates were successfully removed by HCl fumigation from all soils analyzed and that the addition of air-CO₂ is insignificant relative to the SOC present in our soil samples.

Figure 1-2. Evaluation of the efficacy of carbonates removal using the HCl fumigation technique by (Harris et al. 2001) for mine soils of different spoil material type, ranging from pure sandstone and siltstone, to 50:50 sandstone-siltstone mixture, quartz sand, and standard laboratory soil (Jefferson soil), at six levels of sample coal content, expressed as percent by total sample weight. Vertical lines represent one standard error of the mean.

Equations for pedogenic and geogenic C estimation. One of the important steps in the proposed SOC estimation procedure was to determine the optimal temperature for thermal treatment of soil samples at which all pedogenic carbon would be released as CO₂ while measurable amounts of the more resistant carbon molecules from coal remained in the sample. Our results indicated that the optimal thermal treatment temperature should be somewhere between 375°C and 550°C (Fig. 1-3).

Although the range of thermal temperatures tested in this project was not sufficient to determine the exact temperature setting for thermal treatment of mine soil samples for SOC analysis, the results yielded sufficient evidence that at 375°C, organic matter molecules remained unoxidized during the 24-hr treatment period (Fig. 1-3). These organic matter compounds are most likely associated with clay soil minerals that protected them from the thermal degradation.

Because we were careful to suppress black carbon formation during the laboratory work by placing the samples directly in a 375°C heated oven, similar to the work by Kuhlbusch (1995) and Schmidt et al. (2001), we believe that the protected C in the SS- and SiS-containing soil mixtures is from the organic matter embedded in the SS and SiS rock sediments during ancient times, where they have been preserved and protected from microbial decomposition for millions of years. Similarly, we believe that all detectable organic carbon following 375°C thermal treatment of the Jefferson soil used in this study was protected by the clay and the silt-soil particles present in this soil (Fig. 1-3).

On the other hand, at temperatures equal to or greater than 550°C, all carbon forms, including the most resistant coal-derived C and protected organic matter, were oxidized to CO₂ and were released from the samples. Despite the relatively good detection limit (0.01 wt %) of the carbon auto-analyzer used in this project, there was no detectable amount of elemental carbon remaining in the samples for carbon analysis in all 550°C and 650°C samples analyzed in this experiment (Fig. 1-3).

Hence, the 16-step SOC estimation method for mine soils was developed solely from C results for the 0°C- and 375°C-samples. Note that the 0°C-sample C results, implying no thermal treatment, include all pedogenic and all geogenic carbon forms. In order to partition the total carbon in mine soils (after carbonates have been removed) to pedogenic and geogenic carbon, one needs to solve the following four simultaneous equations:

$$\begin{aligned} X1+Y1 &= C_0 \\ X2+Y2 &= C_{375} \\ X1/X2 &= A \\ Y1/Y2 &= B \end{aligned}$$

where:

X1 = pedogenic C concentration (wt %) in the 0°C-sample;
Y1 = coal-derived geogenic C concentration (wt %) in the 0°C-sample;
X2 = pedogenic C concentration (wt %) in the 375°C-sample;
Y2 = coal-derived geogenic C concentration (wt %) in the 375°C-sample;
A and B = ratios computed by dividing the pedogenic and geogenic C concentrations before thermal treatment by the respective C concentrations present in the sample after a 375°C thermal treatment. These ratios represent the relative C loss from

organic matter (X1/X2) and from coal (Y1/Y2) present in the soil due to the 24-hr exposure to 375°C.

C_0 = C concentration (wt%) measured from a soil sample with no thermal treatment; Note that this is the sum of all pedogenic and geogenic C in the soil;

C_{375} = C concentration (wt%) measured after thermal treatment for 24 hours at 375°C; Note that this includes a fraction of the pedogenic and geogenic C amounts in the soil.

Solving the above four equations for X1 and Y1 yields the following two equations, which will be used to determine the amount of pedogenic and geogenic C present in all 30 soil mixtures analyzed in this study:

$$\text{Pedogenic C (wt\%)} = \frac{A * (C_0 - B * C_{375})}{A - B}$$

$$\text{Geogenic C (wt\%)} = \frac{B * (A * C_{375} - C_0)}{A - B}$$

Because X1, X2, Y1, and Y2 are the C concentrations of distinctive components of a given soil sample which cannot be physically isolated for measurement, we assumed that the A ratio for pure materials (the 0%-coal soil mixtures) will stay the same when coal is added to these mixtures. This is to say that because of the relatively small amount of added coal, in grams, relative to the amount of the soil medium, in grams, in the soil mixtures, there will be no significant effect of coal on the properties of the soil medium.

For example, in all soil mixtures with 0.5 wt% coal content for each gram of coal in the mixture there were approximately 199 g of pure soil material. Similarly, there were approximately 99 g of soil for 1 g of coal in the 1.0% coal samples, approximately 39 g for 1 g of coal in the 2.5% coal samples, approximately 19 g for 1 g of coal in the 5.0% coal samples, and approximately 9 g for 1 g of coal in the 10% coal samples. Based on the relatively small amount of coal compared to the soil medium, the underlying assumption for computing the A ratio, per soil material, is that the effect of coal on the rate of C loss from soil organic matter in the soils analyzed is not significant.

Figure 1-3. Average C content (wt %) of 30 soil mixtures and of pure coal after a 24-hr thermal treatment at three experimental temperatures, 375°C, 550°C, and 650°C. Vertical lines represent the standard error of the average estimate. Depicted by the horizontal line on the bottom three graphs at 0.01% is the detection limit of the carbon fall to analyzer machine used in this study.

Depicted in Figure 1-4 are the data used to compute ratio A for mine soils derived from SS, SiS, 50:50 SS:SiS mixture, and the reference quartz sand and Jefferson soil materials. The following list depicts the estimates for ratio A used in Equations 1 and 2 for the five materials analyzed:

Material	A = X1/X2
Sandstone (1)	4.6835
Siltstone (2)	12.7343
50-50_SS-SiS (3)	11.6941
Quartz_sand (4)	7.5277
Jefferson_soil (5)	16.2548

Anchored in the abovementioned examples for the amount of coal relative to the amount of soil material present in the soil mixtures analyzed, and based on the assumption for computing ratio A, one should expect that the soil medium would have a significant effect on the rate of C loss from the coal present in the soil mixtures. That is, the rate of carbon loss from pure coal material could be significantly different than that from the same amount of coal “surrounded” by soil particles in a given soil medium.

In order to analyze the effect of soil material on the thermal properties of coal in the soil mixtures, we performed an analysis of variance (ANOVA) of our data where the dependent variable was Y2, and material type and coal content were the two independent variables. Y2 was computed as the difference $[C_{375 \text{ for } Z\% \text{ coal}} - C_{375 \text{ for } 0\% \text{ coal}}]$, where Z% represents the coal content level in each sample from the data in Fig. 1-3. The results from the ANOVA analysis (N = 123 observations for five levels of material type and five levels of coal content [0.5, 1, 2.5, 5, and 10]) showed that material type ($P = 0.0133$), coal content ($P < 0.0001$), and the interaction between material type and coal content ($P = 0.0003$) were significantly affecting the magnitude of Y2. Results from a similar ANOVA analysis for Y1 as the dependent variable and material type and coal content as the two independent variables showed that material type ($P = 0.0065$) and coal content ($P < 0.0001$) were significantly affecting the magnitude of Y1. The effect of the interaction between material type and coal content ($P = 0.2857$) on the magnitude of Y1 was not significant. The dependent variable Y1 was computed as the difference $[C_{0 \text{ for } Z\% \text{ coal}} - C_{0 \text{ for } 0\% \text{ coal}}]$, where Z% represents the coal content level in each sample from the data in Fig. 1-3. The above analyses of variances for Y1 and Y2 indicated that material-specific ratios, $B = Y1/Y2$, were necessary for each of the five soil materials tested.

Because the thermal properties of the coal were significantly affected by the content of the coal in our sample, we performed regression analyses (PROC REG in SAS® statistical software) to model the Y2 of each sample as a function of the Y2 of a pure coal, 0.22636 wt% C (from Fig. 1-3). Prior to the modeling task, the latter was adjusted to the coal content level of the sample analyzed. For example, Y2 of the pure coal was multiplied by a factor of 0.5/100 to match all soil samples with 0.5wt% coal content. Similarly, the Y1 of each sample was modeled as a function of the Y1 of a pure coal, 82.87406 wt% C (Fig. 1-3). Y1 was also adjusted to the coal content level of the sample analyzed prior to modeling.

Figure 1-4. Average C concentration estimates for six pure mine soil materials (sandstone, siltstone, 50:50-mixture of sandstone and siltstone, quartz sand, Jefferson soil, and coal) for three thermal treatment temperatures (375°C, 550°C, and 650°C). Vertical lines represent the standard error of the average estimate. The horizontal line depicts the detection limit (0.01 wt %) of the carbon auto-analyzer machine used for this analysis.

In order to stabilize the variance of the residuals from the regression analyses and to meet the normality assumption of the dependent variable, the latter was transformed using the square root transformation, i.e., $Y1' = \text{SQRT}(Y1)$ and $Y2' = \text{SQRT}(Y2)$. The Cp model selection procedure in SAS® was used to determine the most appropriate model that would characterize $Y1'$ and $Y2'$, respectively, as a function of the adjusted $Y1$ and $Y2$ of pure coal. For all models, the intercept was forced to 0 because extremely small levels of coal content in a sample would result in a very small surface area of the soil coal, hence the effect of the soil medium on the coal would be infinitely small. Table 1-1 depicts the regression models that were developed to describe $Y1$ and $Y2$ of the sample as a function of the adjusted $Y1$ and $Y2$ of pure coal.

The regression models used to describe $Y1$ and $Y2$ as a function of $Y1$ and $Y2$ of pure coal, respectively, were developed from the five replicated measurements of C_0 and C_{375} for each of the 5 levels of coal content, 0.5, 1, 2.5, 5, and 10 wt%, for each of the five soil materials, resulting in total of 25 measurements per material type. All 25 measurements were used in the models for all materials with the exception of quartz sand and SiS. One outlier was removed from the SiS and quartz data sets for this modeling task (Table 1-1).

Table 1-1. Regression models used to describe sample $Y1$ and $Y2$ as a function of the $Y1$ and $Y2$ of pure coal. Ratio B was used to calculate pedogenic C (wt%) and geogenic C (wt%) in Eq. 1 and Eq. 2, respectively.

Material type	Dependent Variable	a	n	R^2	Adj.- R^2	@ B = $Y1/Y2$
Sandstone (1)	^{\$} SQRT($Y1$)	0.99535	25	99.99	99.99	0.70359 * F
	SQRT($Y2$)	1.18663	20	88.14	87.52	
Siltstone (2)	SQRT($Y1$)	1.00605	24	99.99	99.99	0.22158 * F
	SQRT($Y2$)	2.13724	24	94.36	94.11	
50-50_SS-SiS (3)	SQRT($Y1$)	0.99613	25	99.98	99.98	0.41394 * F
	SQRT($Y2$)	1.54827	25	91.13	90.76	
Quartz_sand (4)	SQRT($Y1$)	0.99952	24	99.97	99.97	0.37108 * F
	SQRT($Y2$)	1.64081	23	91.48	91.10	
Jefferson_soil (5)	SQRT($Y1$)	0.99519	25	99.99	99.99	0.53876 * F
	SQRT($Y2$)	1.35584	18	52.76	49.98	

^{\$} Regression model $\text{SQRT}(Y_i) = a * \text{SQRT}(Y_i \text{ of pure coal})$, where $i=1, 2$

@ F is computed as the ratio $Y1/Y2$ of pure coal

Subtask 1.2

Estimates for soil organic carbon content (weight %), also referred to in this text as pedogenic C (wt %) and $\text{SOC}\%_{\text{predicted}}$, for each of the 30 soil mixtures were computed using Equation 1. The Walkley-Black organic carbon estimates were measured as described in the Methods section of this task report.

In order to evaluate the accuracy of the 16-step SOC estimation and Walkley-Black methods, the percent relative uncertainty from the mean, PRUM (%), was estimated for the individual C measurement replications made by the 16-step method (five replications) and for the Walkley-Black procedure (three replications). Additionally, $\text{PRUM}_{5\text{reps}}$ (%) was evaluated for the $\text{SOC}\%_{\text{predicted}}$ by the 16-step method, where C_0 and C_{375} (see their use in Eq. 1) were computed as the average of five replicated C_0 and C_{375} measurements for the 30 soil mixtures. The latter was done to determine whether a larger number of replicated measurements for C_0 and C_{375} will increase the accuracy of $\text{SOC}\%_{\text{predicted}}$. Although in most cases increasing the number of measurements usually leads to a better final estimate of a given soil property, one may have to make a decision whether the relative gain in accuracy of this estimate is worth the additional costs associated with carrying out additional measurements.

The precision of any method describes the repeatability of the end results. In order to determine the precision of the two methods, the standard error of PRUM (%), which is a measure of the relative accuracy of the results, was estimated (Tables 1-2 and 1-3). Using the standard error of PRUM (%), one can determine the confidence limits of the accuracy of $\text{SOC}\%_{\text{predicted}}$ by the 16-step SOC estimation method (Table 1-2) and by the Walkley-Black procedure (Table 1-3), for any probability level, e.g., 80%, 90%, and 95%, using the corresponding student's t values from a statistical t -table for 4 degrees of freedom for the 16-step method, and for 2 degrees of freedom for the Walkley-Black procedure. Note that there is no standard error estimated for the mean $\text{PRUM}_{5\text{reps}}$ (%) in Table 1-2, as these values were computed from the average C_0 and C_{375} of five replicated measurements, as opposed to the mean PRUM (%), which were estimated as the average of the PRUM (%) of five individual measurement (Table 1-2).

Due to the design of the Walkley-Black procedure, each individual measurement, a total of three measurement replications, was analyzed separately from the rest and was associated with a unique PRUM (%) estimate. For all parameters other than the blank, there was no valid way to combine the replicated measurements done in a Walkley-Black procedure, such as the volume of the sample titrate which is specific for the amount of oven-dried soil used for this one replication, to calculate a better average estimate that can then be used in the equation to produce a better Walkley-Black organic C estimate (see the Methods section) (Table 1-3).

Table 1-2. Percent relative uncertainty from the mean, PRUM (%), of the 16-step SOC estimation method for 30 mine soil mixtures constructed from five soil materials at six levels of coal content (wt%). Five replicated organic carbon measurements were made for each mixture. The right-most column depicts the PRUM_{5reps} (%) described in the text.

Material	Coal Content	Mean	Std.Error	MIN	MAX	n	MEAN 5reps
	wt %	----- % -----					%
Sandstone (1)	0	16.9	1.4	6.1	46.4	5	0.0
	0.5	14.6	1.1	12.0	19.2	5	2.3
	1	12.6	1.5	3.7	28.4	5	8.3
	2.5	13.0	1.6	2.3	29.6	5	8.9
	5	23.8	1.1	19.0	30.6	5	14.8
	10	148.0	1.3	76.6	337.2	5	60.1
Siltstone (2)	0	21.3	1.2	13.2	32.1	5	0.0
	0.5	10.9	2.1	0.6	25.2	5	18.3
	1	15.5	1.9	1.2	47.7	5	14.5
	2.5	33.2	1.6	5.5	90.7	5	31.5
	5	40.9	1.3	16.8	92.9	5	25.0
	10	15.8	1.5	5.1	44.6	5	16.4
50-50_SS-SiS (3)	0	10.4	1.7	1.7	36.3	5	0.0
	0.5	6.9	1.5	1.8	17.9	5	7.5
	1	8.6	2.1	0.7	46.0	5	19.0
	2.5	5.4	1.3	2.6	10.9	5	2.0
	5	34.4	1.2	19.7	54.8	5	36.5
	10	84.4	1.5	29.6	277.9	5	45.3
Quartz_sand (4)	0	21.2	1.3	8.9	32.6	5	0.0
	0.5	38.1	1.2	22.7	61.9	5	40.9
	1	84.8	1.3	39.6	152.7	5	35.9
	2.5	309.9	1.2	204.8	511.9	5	59.7
	5	302.2	1.3	114.7	485.2	5	38.8
	10	412.1	1.5	182.2	1839.9	5	199.1
Jefferson_soil (5)	0	20.1	1.2	13.5	30.8	5	0.0
	0.5	11.0	1.7	1.4	25.2	5	12.0
	1	8.8	1.2	4.1	14.7	5	7.8
	2.5	27.9	1.8	9.0	229.4	5	30.9
	5	103.4	1.7	19.4	535.8	5	172.6
	10	65.7	1.2	39.2	86.7	5	68.1

Table 1-3. Percent relative uncertainty from the mean, PRUM (%) of the Walkley-Black organic carbon measurements for 30 mine soil mixtures constructed from five soil materials at six levels of coal content (wt%). Three replicated organic carbon measurements were made for each mixture.

Material	Coal Content	Mean	Std.Error	MIN	MAX	n
	wt %	----- % -----				
Sandstone (1)	0	51.1	1.3	32.6	66.5	3
	0.5	17.3	1.3	12.1	29.3	3
	1	98.5	1.2	72.6	126.3	3
	2.5	203.3	1.3	125.9	343.1	3
	5	427.3	1.2	288.3	547.2	3
	10	1002.8	1.2	694.5	1412.3	3
Siltstone (2)	0	16.7	1.1	15.3	19.6	3
	0.5	22.3	2.3	8.7	117.6	3
	1	2.1	1.4	1.2	4.1	3
	2.5	30.6	1.4	17.0	45.8	3
	5	51.9	1.2	38.5	65.4	3
	10	122.1	1.1	105.9	139.4	3
50-50_SS-SiS (3)	0	15.6	1.7	6.2	41.0	3
	0.5	12.9	1.1	10.9	14.8	3
	1	3.3	1.4	2.0	5.8	3
	2.5	40.4	1.1	33.4	50.0	3
	5	63.6	1.4	35.8	102.0	3
	10	125.8	1.5	55.2	204.1	3
Quartz_sand (4)	0	5.3		5.3	5.3	3
	0.5	98.0	1.5	45.7	147.6	3
	1	279.1	1.1	227.8	356.8	3
	2.5	512.8	1.2	338.1	715.0	3
	5	1247.8	1.2	1019.2	1674.2	3
	10	2703.6	1.1	2402.1	2948.6	3
Jefferson_soil (5)	0	2.2	1.4	1.4	4.2	3
	0.5	2.7	1.6	1.3	7.0	3
	1	6.9	1.1	5.4	8.0	3
	2.5	20.0	1.4	13.0	41.7	3
	5	7.9	3.1	0.8	27.0	3
	10	57.8	1.1	47.4	66.1	3

The results for PRUM (%) of predicted SOC values from both methods (Tables 1-2 and 1-3, Fig. 1-5) indicated that neither method was suitable to predict SOC of quartz sand soil mixtures used in this study. The PRUM (%) for quartz sand samples with coal ranged from 38% to 412% for the 16-step method, and ranged from 98% to 2,704% indicating a colossal overestimation of the SOC present in these mixtures, 0.033 C wt% (Fig. 1-3). The main reason for this is attributed to the problem associated with handling quartz sand soil mixtures and specifically the electrostatic interactions between the soil mixture particles and the plastic storage bag. There was an underlying problem associated with handling the soil mixtures constructed from quartz sand. Because all samples were stored in plastic bags between measurements, there was a clearly observable electrostatic interaction between the coal particles and the bag, as well as between the individual quartz particles and the inside surface of the plastic bag. As a result, each time the soil mixture was measured, an unspecified amount of coal and sand were electrostatically removed from the sample and were adsorbed to the inside surface of the plastic bag. For the remainder of this task report, the results for quartz sand soil mixtures will not be further discussed.

The mean PRUM (%) of SOC predictions made by a single replication of the 16-step method ranged from 13% to 148% for SS (0.082 C wt%), from 11% to 41% for SiS (0.629 C wt%), from 5% to 84% for the 50:50 SS:SiS mixture (0.382 C wt%), and from 9% to 103% for the Jefferson soil (0.811 C wt%), across the spectrum of coal content levels tested (Table 1-2, Fig. 1-5). The corresponding PRUM (%) estimates of SOC predictions made by the Walkley-Black procedure were equal to or greater than those by the 16-step procedure for all materials tested except Jefferson soil. The mean PRUM (%) for the Walkley-Black predictions ranged from 17% to 1,003% for SS, from 2% to 122% for SiS, from 3% to 126% for the 50:50 SS:SiS mixture, and from 2% to 58% for the Jefferson soil (Table 1-3, Fig. 1-5).

The Walkley-Black procedure yielded better SOC predictions compared to the 16-step method for the Jefferson soil mixtures. The latter could be due to the fact that Walkley-Black was specifically calibrated for natural soils such as the Jefferson soil (Tables 1-2 and 1-3, Fig. 1-5). It is also of interest to point out that the increase of coal content in the Jefferson soil mixture did not result in a dramatic increase in the uncertainty of the SOC prediction made by Walkley-Black relative to all other materials tested (Table 1-3). However, for the rest of the materials, increase in soil coal content resulted in appreciable increase in the uncertainty associated with SOC predictions made by the Walkley-Black procedure.

The overall results indicated that the 16-step SOC estimation method yielded better results (with low PRUM %) than the Walkley-Black procedure for all soil mixtures constructed from SS, SiS, and the 50:50 SS:SiS material (Tables 1-2 and 1-3, Fig. 1-5). The latter are also the most likely soil medium for minelands in the hard-rock regions of the Appalachian coalfield. Therefore, it is expected that the 16-step SOC estimation method would be the preferred method of SOC estimation on mineland in this region.

For the three mine spoil materials, SS, SiS, and the 50:50 SS:SiS mixture, the accuracy of SOC predictions by the 16-step method was increased for SS by increasing the number of measurement replications, but was not appreciably improved for SiS and the 50:50 SS:SiS mixture (Table 1-2, Fig. 1-5). The latter indicated that predicting the SOC in mine soils derived from sandstone and siltstone materials was possible from a single measurement of C_0 and C_{375} (Eq. 1) and that additional replications may not improve the accuracy of these predictions.

Figure 1-5. Average percent relative uncertainty from the mean, PRUM (%), for SOC predictions made by the 16-step method (graphs a and b) and by the Walkley-Black procedure (graph c). Note that the grey area in graph c is equivalent to the full extent of graphs a and c.

Analysis of variance performed on the PRUM (%) of the SOC results from the 16-step method, as the dependent variable, indicated that the effects of coal content ($P < 0.0001$) and the interaction between material and coal content ($P = 0.0146$) were significant, but material type ($P = 0.1798$) was not significant. Note that only results for SS, SiS, and the 50:50 SS:SiS soil mixtures were used in the ANOVA for the 16-step method, as these materials were the targeted soil media for evaluation that could be used for projects on minelands.

Similar analysis for the results from the Walkley-Black procedure showed that the effects of material type ($P < 0.0001$), coal content ($P < 0.0001$), and their interaction ($P = 0.0008$) were significant. Results for all soil materials, excluding quartz sand, were used in the ANOVA for the Walkley-Black procedure.

Because of the significant effect of the interaction between the independent variables for both methods, means separation analyses (PROC GLM in SAS®; multiple comparison of least squares means [adjustment used: Tukey]) were used to determine which means, by specific material type and by coal content level, were significantly different from the rest (Tables 1-4 and 1-5). For both analyses, the dependent variable was the log-transformed PRUM (%) and the independent variables were material type and coal content. Log-transformation, i.e. $\text{PRUM}'(\%) = \ln(\text{PRUM}[\%])$, was required to satisfy the normality and the equal variance assumptions needed for an ANOVA analysis.

The means separation analysis for the 16-step method indicated that the 10% coal samples for SS and 50:50 SS:SiS mixtures were the only samples with significantly higher percent relative uncertainty compared to the remaining 28 mixtures tested (Table 1-4). These results provide sufficient evidence to claim that the 16-step SOC estimation method produced consistent SOC predictions (with consistent relative uncertainty) for the three most common mine spoil materials tested, with coal contents ranging from 0 to 10 wt%, with the exception of the 10% coal level of SS and 50:50 SS:SiS samples.

However, the same could not be claimed for the Walkley-Black procedure. The means separation analysis results depicted in Table 1-5 indicate that the performance of the Walkley-Black procedure for SOC estimation varied across material type and across coal content level without any apparent trends. The latter further supported the claims by other researchers showing that SOC predictions made by the Walkley-Black procedure could be of appreciable uncertainty, depending on the properties of the soil (Daniels and Amos 1982, Skjemstad and Taylor 1999).

Table 1-4. Multiple comparison of least squares means the log-transformed PRUM (%) of SOC predictions from the 16-step method for three material types (SS, SiS, and 50:50 SS:SiS) and for six levels of coal content (0, 0.5, 1, 2.5, 5, and 10). Highlighted rows and columns are used to depict the means that are significantly different than the rest.

Material	Coal Content	LSMEAN Number	i/j	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
50-50 SS-SiS (3)	0	1	1				*						***								
	1	2																			
	5	3	2	1.000			**						***								
	10	4																			
	0.5	5	3	0.880	0.705																
Sandstone (1)	2.5	6	3																		
	0	7	4	0.085	0.037	0.991		**	***												
	1	8																			
	5	9	5	1.000	1.000	0.450	0.012						***								
	10	10																			
Siltstone (2)	0.5	11	6	1.000	1.000	0.223	0.003	1.000					***								
	2.5	12																			
	0	13	7	1.000	1.000	0.999	0.448	0.991	0.921				*								
	1	14	8	1.000	1.000	0.972	0.184	1.000	0.995	1.000			***								
	5	15																			
	10	16	9	0.996	0.967	1.000	0.828	0.846	0.601	1.000	1.000										
	0.5	17	10	0.006	0.002	0.625	1.000	0.001	0.000	0.062	0.015	0.239		**	**		*		*	***	
	2.5	18	11	1.000	1.000	0.994	0.299	0.999	0.976	1.000	1.000	1.000	0.032								
			12	1.000	1.000	0.978	0.202	1.000	0.993	1.000	1.000	1.000	0.018	1.000							
			13	0.999	0.989	1.000	0.718	0.922	0.727	1.000	1.000	1.000	0.161	1.000	1.000						
			14	1.000	1.000	0.997	0.357	0.997	0.959	1.000	1.000	1.000	0.042	1.000	1.000	1.000					
			15	0.723	0.505	1.000	0.999	0.275	0.118	0.992	0.895	1.000	0.809	0.964	0.912	1.000	0.979				
			16	1.000	1.000	0.998	0.378	0.996	0.951	1.000	1.000	1.000	0.046	1.000	1.000	1.000	1.000	0.983			
			17	1.000	1.000	0.909	0.103	1.000	1.000	1.000	1.000	0.998	0.007	1.000	1.000	1.000	1.000	0.770	1.000		
			18	0.903	0.742	1.000	0.986	0.489	0.250	1.000	1.000	1.000	0.585	0.996	0.985	1.000	0.999	1.000	0.928		

* significantly different at the 0.10 level
 ** significantly different at the 0.05 level
 *** significantly different at the 0.01 level

Table 1-5. Multiple comparison of least squares means the log-transformed PRUM (%) of SOC predictions from the Walkley-Black procedure for three material types (SS, SiS, and 50:50 SS:SiS) and for six levels of coal content (0, 0.5, 1, 2.5, 5, and 10).

Material	Coal Content	LSMEAN Number	ij	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
50-50 SS-SiS (3)	0	1	1				.											..	..					.			
	1	2	2	0.477		..	..	..				..			..	..	..	..	..	..			..	..		..	
	5	3	3	0.663	0.001				..	.		..						..				..					
	10	4	4	0.072	<.0001	1.000		..	..	..	..	..						.			.	..					
	0.5	5	5	1.000	0.712	0.434	0.029										.	..	..	..							
	2.5	6	6	1.000	0.987	0.009	1.000	0.320	..			..					.	..	..	..	..						
Jefferson soil (5)	0	7	7	0.125	1.000	<.0001	<.0001	0.256	0.001			..		..	..	..	..	..	.	..	.		..	..	..	..	..
	1	8	8	0.998	0.999	0.040	0.001	1.000	0.262	0.916		.				..	..	..	..	..			.	..			
	5	9	9	1.000	0.995	0.074	0.002	1.000	0.399	0.807	1.000					..	..	..	..	..	..			..			
	10	10	10	0.779	0.001	1.000	0.999	0.552	1.000	0.000	0.062	0.112	..					..				..					
	0.5	11	11	0.280	1.000	0.000	<.0001	0.488	1.000	0.003	0.990	0.957	0.000		..	..	..	..	..	..	..		..	..	.	..	
	2.5	12	12	1.000	0.222	0.910	0.198	1.000	1.000	0.041	0.981	0.991	0.959	0.110	..	..	..	..	..	..	..	..	..				
Sandstone (1)	0	13	13	0.890	0.890	0.002	1.000	1.000	0.000	0.107	0.182	1.000	0.001	0.989		..	.	..				..					
	1	14	14	0.196	<.0001	1.000	1.000	0.091	0.394	<.0001	0.004	0.009	1.000	<.0001	0.436	1.000		..				..					
	5	15	15	<.0001	<.0001	0.155	0.862	<.0001	0.020	<.0001	<.0001	<.0001	0.105	<.0001	0.000	0.061	0.593		..		..	..	..	.	..	..	..
	10	16	16	<.0001	<.0001	0.002	0.075	<.0001	0.000	<.0001	<.0001	<.0001	0.001	<.0001	<.0001	0.001	0.937	..	..		..	..	..	..	.	..	..
	0.5	17	17	1.000	0.356	0.789	0.113	1.000	0.997	0.080	0.992	0.999	0.877	0.193	<.0001	0.951	0.001	0.283	0.024	0.937	..	..	..	..			
	2.5	18	18	0.007	<.0001	0.908	1.000	0.002	0.412	<.0001	0.000	0.000	0.832	<.0001	0.024	0.700	1.000	1.000	0.435	<.0001	0.011	..	..	..	..	..	..
Siltstone (2)	0	19	19	1.000	0.397	0.748	0.096	1.000	0.395	0.094	0.995	1.000	0.222	<.0001	0.933	0.000	0.250	1.000	<.0001	<.0001	1.000	0.009	..	.			
	1	20	20	0.105	1.000	<.0001	<.0001	0.222	1.000	1.000	0.888	0.764	1.000	<.0001	0.034	1.000	0.000	<.0001	<.0001	0.067	1.000	0.067	0.079	..	..	..	..
	5	21	21	0.879	0.002	1.000	0.995	0.686	1.000	0.000	0.100	0.172	1.000	0.001	0.987	1.000	1.000	0.065	0.001	0.944	0.718	0.924	0.000	..			
	10	22	22	0.082	<.0001	1.000	0.034	0.340	1.000	<.0001	0.001	0.003	1.000	0.221	0.996	1.000	1.000	0.836	0.066	0.128	0.937	0.937	0.937	0.937	0.937	0.937	0.937
	0.5	23	23	1.000	0.147	0.963	0.290	1.000	1.000	0.024	0.905	0.963	0.987	1.000	0.068	0.998	0.570	1.000	0.001	1.000	0.041	1.000	0.020	0.997	0.997	0.997	0.997
	2.5	24	24	1.000	0.036	0.660	0.396	1.000	0.005	0.574	0.736	0.963	0.987	1.000	0.015	1.000	0.903	0.001	<.0001	1.000	0.161	1.000	0.004	1.000	0.696	1.000	1.000

. significantly different at the 0.10 level
 .. significantly different at the 0.05 level
 ... significantly different at the 0.01 level

Subtask 1.3

The third objective of this project was to determine the effect of material type and coal content on the accuracy of Walkley-Black SOC predictions for mine soils. Furthermore, if there was a significant correlation between the latter and material type and coal content, then we would develop a model that will allow SOC estimates for minelands measured by the Walkley-Black procedure in the past to be corrected for coal content- and material type-induced uncertainties associated with these SOC measurements.

Based on the results from the ANOVA analysis for PRUM (%) described in the previous section, it was evident that material type and coal content significantly affected the uncertainties associated with SOC estimates made by the Walkley-Black method (Table 1-5); hence, the SOC predictions were affected by material type and coal content. Because any potential regression models would only be used to correct SOC estimates for mine soils, only the data for SS, SiS, and 50:50 SS:SiS materials were analyzed. The “true” soil organic carbon content of these three materials (equal to $SOC\%_{\text{present}}$), as the dependent variable, was regressed (PROC REG in SAS®) against the SOC predictions made by the Walkley-Black method and material type, as the two independent variables. The general form of the model was $SOC\%_{\text{present}} = a * \{\text{material type}\} + b * \{\text{WB-OC}\}$.

In order to incorporate material type, which is a categorical variable, in the regression model, a “dummy” variable was created in our data set labeled *order* where *order* = 1 for SS, 2 for SiS, and 3 for 50:50 SS:SiS samples. Additionally, the intercept in the model was forced to 0, as noted in the general form above, because of the presence of the dummy variable *order*, which would become the value of the intercept after substituting 1 for *order* in the final SS correction model, 2 for the final SiS model, and 3 for 50:50 SS:SiS final model.

The following is the ANOVA output from the regression analysis completed in SAS® statistical software:

ANOVA table					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	8.57112	4.28556	172.57	<.0001
Error	52	1.29135	0.02483		
Uncorrected Total	54	9.86247			
Root MSE	0.15759	R-Square	0.8691		
Dependent Mean	0.36429	Adj R-Sq	0.864		
Coeff Var	43.25885				
Parameter Estimates					
Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > t
order	1	0.10647	0.01724	6.18	<.0001
MeanData	1	0.27496	0.05457	5.04	<.0001
Variable	DF	Standardized Estimate	Variance Inflation	95% Confidence Limits	
order	1	0.53821	3.01653	0.07188	0.1411
MeanData	1	0.43918	3.01653	0.16547	0.3845

The R^2 of the model indicated that 87% of the uncertainty associated with measuring the true SOC%_{present} was explained by material type, hence variable *order*, and by the WB-OC% data for the 54 samples analyzed (for a total of three replications of three materials at six coal content levels). The final regression model for correcting Walkley-Black carbon estimates was developed as follows:

$$\text{SOC (wt\%)} = 0.10647 + (\text{order}) + 0.27496 * (\text{WB} - \text{SOC, \%}) \quad \text{Eq. 3}$$

where:

order = 1 for SS;
 = 2 for SiS;
 = 3 for 50:50 SS-SiS.

By substituting 1, 2, and 3 for variable *order* in Eq. 3 for SS, SiS, and 50:50 SS:SiS materials, respectively, one would be able to use Walkley-Black SOC estimates measured in the past to produce a better approximation of the true soil organic carbon present in the samples for the respective study areas. For mine soils derived from spoil material of different ratios between SS and SiS than 50:50, separate analyses similar to the current study should be performed in order to develop valid models for Walkley-Black estimates correction.

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TASK 2: Develop classification and inventory criteria and procedures for mined land. (Galbraith et al.)

This task was completed in September, 2005; all work will be presented in the final report.

TASK 3: Develop reforestation methods and procedures for mined land. (Fox et al.)

This task was completed in September, 2005; all work will be presented in the final report.

TASK 4: Conduct economic analyses of reforestation and forest management activities for carbon sequestration and a variety of forest products and services. (Amacher and Sullivan)

This task was completed in September, 2005; all work will be presented in the final report.

TASK 5: Determine the potential of large-scale SMCRA grassland restoration to sequester carbon and create other societal benefits. (Zipper and McGrath)

Executive Summary

Six mine sites were sampled in OH, KY, and VA, and seven mines were sampled in WV during the summer and early fall. The 25 sites yielded 225 sample locations. The soil samples were split at the topsoil-subsoil interface (0-10 cm and 10-30 cm) for a total of 450 subsamples. During the 4th quarter of 2005, we initiated data compilation and laboratory analysis of mine soil samples collected during the summer and early fall of 2005 at 25 mine sites selected randomly from VA, WV, KY, and OH and herbaceous biomass assessment plots in VA.

Experimental

Soil analysis procedures discussed below were initiated during the reporting period and continued through subsequent reporting periods.

Field parameters include slope, aspect, herbaceous biomass cover (kg/ha), and rooting depth (Jones et al. 2005). Rooting depth was determined using a screw auger to penetrate the soil until refusal. Soils were sampled by excavation of a 30 x 30 x 30 cm volume (approximate dimensions), separated at 10-cm depth into surface and subsurface fractions. The volume of the excavated cavity was determined by filling the hole with small spheres and determining their volume upon retrieval. Soil samples were bagged and weighed, and a subsample of the soil-sized fraction was removed to determine moisture content. After air drying, samples were sieved at 2 mm and the coarse fragment content (>2 mm) was determined as a mass proportion of the total sample. Bulk density of the soil-sized fraction was determined as the dry mass-to-volume ratio, assuming a coarse fragment density of 2.4 g/cm³. Particle size distribution of the soil-sized fraction (% sand, % silt, % clay of the soil-sized fraction) was determined using the hydrometer method (Gee and Bauder, 1986). Percent composition of coarse fragments within each of the following classifications was estimated visually: shale, gray siltstone, brown siltstone, unweathered sandstone, weathered sandstone, and coal. Bulk density was determined on a whole-soil basis (0-30 cm), while coarse fragment content and composition were determined separately for 0-10 and 10-30cm depths. Particle size analysis was conducted on a composite sample (1/3 surface + 2/3 subsurface).

All soil chemical properties were determined separately for the surface and subsurface soil fractions. Soil nutrients (P, K, Ca, Mg, Zn, Mn, Cu, Fe, and B) were extracted with a Mehlich 1 solution using a 1:5 vol:vol soil to extractant ratio and analyzed on an ICP-AES instrument by Virginia Tech Soil Testing Laboratory. Soil pH was determined on a mixed suspension of 1:1 vol:vol ratio of soil material to distilled water (McLean, 1986), buffer pH was determined by using a similar procedure but replacing distilled water with a Mehlich 1 buffer solution, and soluble salts were determined using the method of Rhoades (1986) by measuring the electrical conductivity of a 1:2 vol:vol ratio of soil material to distilled water, also by the Virginia Tech Soil Testing Laboratory.

Sodium-bicarbonate extractable P was determined using the method of Olsen and Summers (1986). Exchangeable cations (Ca, Mg, K, Na) were extracted with 1M ammonium acetate (Thomas 1986). Exchangeable acidity was determined using the potassium chloride extraction technique (Thomas 1986). Effective cation exchange capacity (ECEC) was estimated by summing the charge associated with exchangeable acidity and exchangeable Ca, Mg, K, and Na. Base saturation was calculated as the proportion of the ECEC occupied by base cations (Thomas 1986). Soil organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1986).

Results

No analyses were completed during the reporting quarter.

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PROJECT TIMETABLE

		Planned				Completed						
Year:	2002	2003				2004				2005		
Quarter:	4th	1st	2nd	3rd	4 th	1st	2nd	3rd	4th	1st	2nd	3rd
Task 1												
Subtask 1.1	Baseline Carbon Sequestration Potential											
Subtask 1.2	Mine Soil Productivity											
Subtask 1.3						Carbon Sequestration by Forest Practice						
Subtask 1.4						Accounting Procedures						
Task 2												
Subtask 2.1	Classification Criteria											
Subtask 2.2				GIS Mapping								
Subtask 2.3				Test Remote Sensing								
Subtask 2.4						Experimental Plots						
Subtask 2.5							Soil Analyses					
Subtask 2.6											Validate classification criteria	
Task 3												
Subtask 3.1	Locate sites											
Subtask 3.2			Establish experiment									
Subtask 3.3			Silvicultural recommendations									
Subtask 3.4						Reforestation costs						
Subtask 3.5						Evaluate survival and growth						
Subtask 3.6						Estimate growth potential						
Subtask 3.7							Estimate timber & carbon value					
Task 4												
Subtask 4.1	Economic feasibility											
Subtask 4.2				Evaluation								
Subtask 4.3								Government policies				
Task 5												
Subtask 5.1			Identify SMCRA grassland									
Subtask 5.2				Use characteristics of permits								
Subtask 5.3							Soil properties by permit					
Subtask 5.4								Est. quantity grassland				
Subtask 5.5								Est. C sequ. by site quality class				
Subtask 5.6											Est. C seq. by policy scenario	