Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Terrestrial Sequestration

Development of a Rapid Assessment Method for Quantifying Carbon Sequestration on Reclaimed Coal Mine Sites

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May 8-11, 2006 • Hilton Alexandria Mark Center • Alexandria, Virginia

Introduction

- “New” carbon- organic matter added to soil through recent biological processes; plant root exudates and detrital matter

- “Old” carbon- organic matter in soil from fossilized plant matter, coal and inorganic carbonates

Introduction

- Projected global climate change from elevated CO_2 has given rise to various strategies to sequester carbon in terrestrial ecosystems

- Kyoto Protocol recognizes soil as a potential carbon sink, but soil organic carbon (SOC) accumulation must be verified by standard procedure

- Reclaimed coal mine sites represent one such sink to sequester carbon

Introduction

- Coal mining in US has disturbed ~ 2.4 million ha
- Lead to losses in soil quality, soil capability, function, and SOC
- Reclamation by reforestation can increase SOC over traditional reclamation techniques and restore the above parameters
- But standard procedure absent to quantify new SOC on reclaimed mine sites
- **WHY????**

Introduction

- Reclaimed coal mine sites can contain appreciable amounts of coal and carbonate particles
- Traditional soil analysis techniques do not accurately isolate and differentiate between three phases
- Present techniques expensive and availability limited

Objectives of Study

- Develop thermogravimetry (TG/DTG) as a potential cost-effective, rapid, and simple method to differentiate and quantify “new” SOC in mixed geological media
- Verify the thermogravimetry method in a field setting
- Determine “new” SOC sequestration rates on reclaimed coal mine sites

Thermogravimetry / Derivative Thermogravimetry (TG/DTG)

- TG- Mass changes with incremental temperature increases. As sample decomposes with heating, volatile material escapes causing a decrease in sample weight

- DTG- simultaneous subtle inflections from TG represented by discrete peaks

- Common uses- coal and carbonate rocks, oil shales, soil minerals, and organic matter fractions

TG/DTG- Weight Losses

- < 200 ^{o}C – dehydration reactions

(a) crystalline lattice water
(b) hygroscopic water in salts and organic matter

- 250 – 550 ^{o}C- organic matter – old and new

(a) Carbohydrates combustion
(b) Decarboxylation of acidic groups
(c) Aliphatic structure dehydration
(d) Phenolic hydroxyl groups splitting
(e) -C-C bond breaking

- > 600 ^{o}C – carbonate minerals

Method Development

Part 1

Materials - Samples

- Coal: Lewis Fork Mine - Perry Co., KY
- Grass Litter
- Limestone
- Cellulose (Sigma Aldrich)
- Lignin
- Apple Leaves (NIST)

Standard Materials (Coal, Grass Litter, Limestone, Cellulose)

Reference Materials (Cellulose, Lignin, Apple Leaves)

Initial C (total)

n=20

	C	N
Grass litter :	43.42% (0.14)	1.94% (0.02)
Coal:	71.60% (0.52)	1.52% (0.04)
Limestone:	13.74% (0.30)	0.29% (0.01)

- Mixture (35:45:20) – litter : coal : limestone

	C	N
Mixture	50.17% (0.34)	1.43% (0.03)

TG / DTG Results

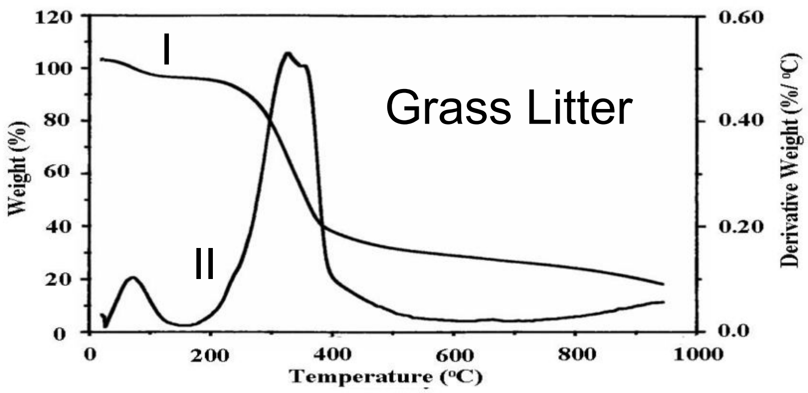
Optimum operating conditions for peak resolution, minimum baseline noise, and narrowest weight loss region:

(1) Sample weight: ~ 10mg (<1mm)

(1) Flow gas: Nitrogen

(2) Flow rate: 20 mL/min

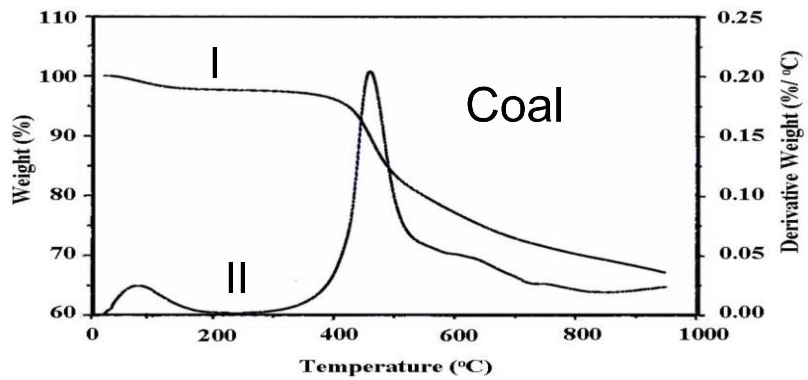
(3) Heating rate: 20 ^{o}C/min



Grass Litter (n=5)

Weight loss range : 270–395 °C

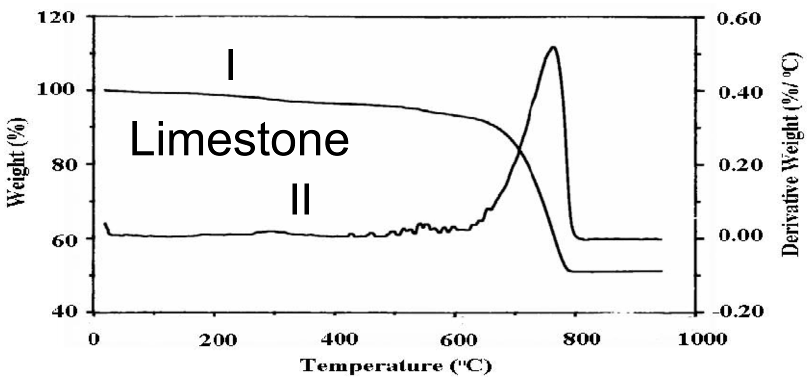
Weight loss = 58.6 ± 1.1%



Coal (n=5)

Weight loss range : 415–520 °C

Weight loss = 23.7 ± 0.1%

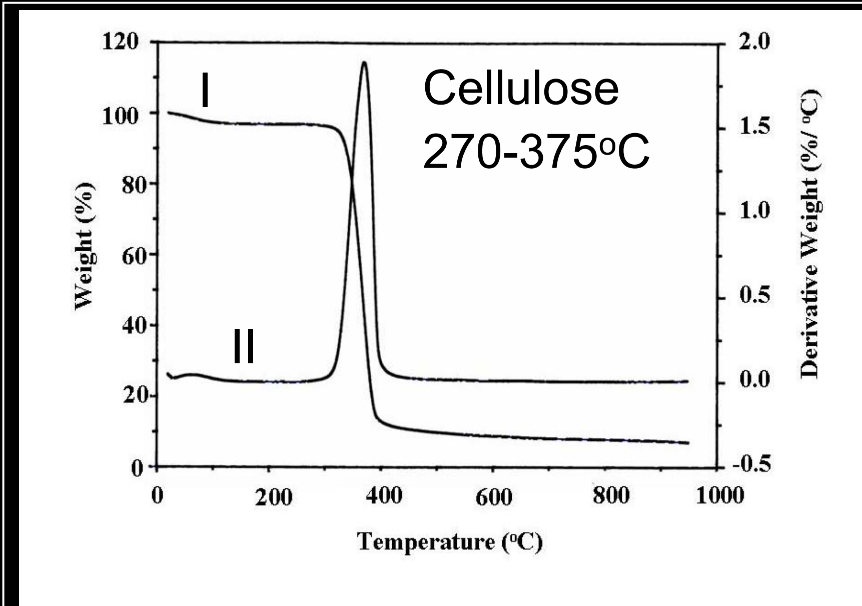


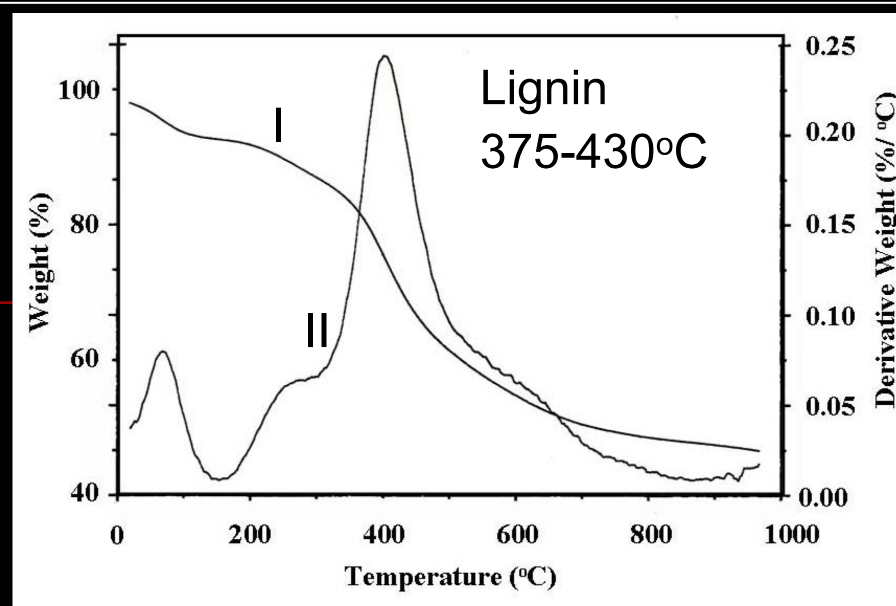
Limestone (n=5)

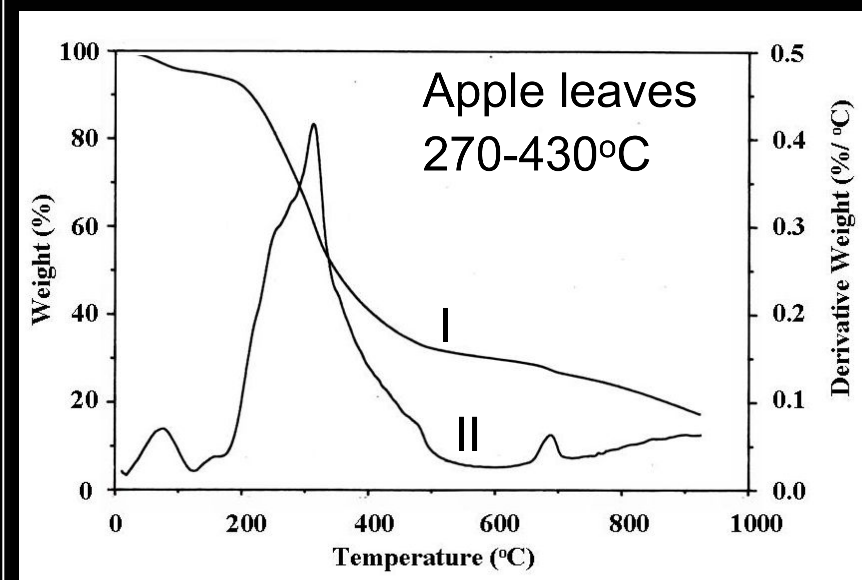
Weight loss range : 700–785 °C

Weight loss = 39.8 ± 0.7%

I : TG II: DTG





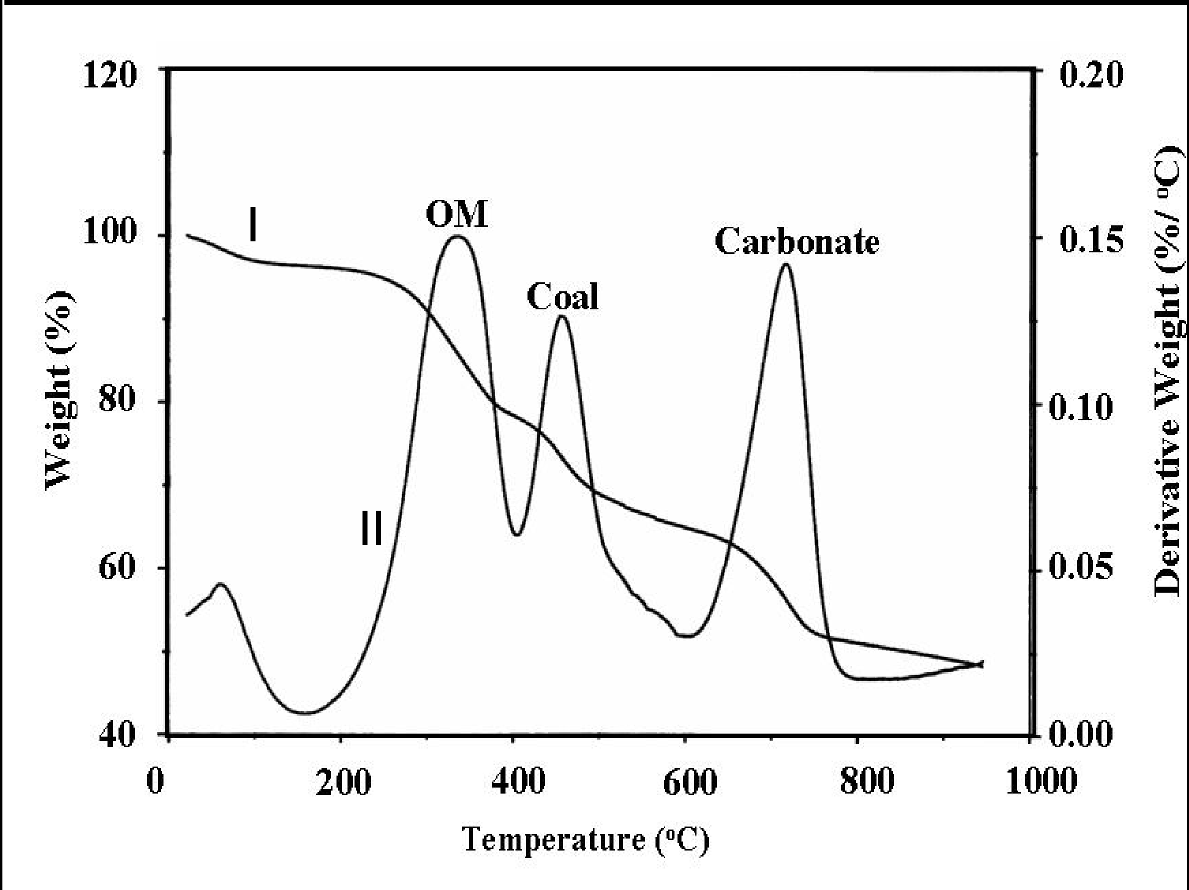


- Sample References

(1) Cellulose and lignin pyrolysis peaks approximate that of grass litter (270 – 395 °C)

(2) Apple leaves pyrolysis peak is a combination of those seen for cellulose and lignin

Representative TG / DTG for Mixture



Recoveries of C:

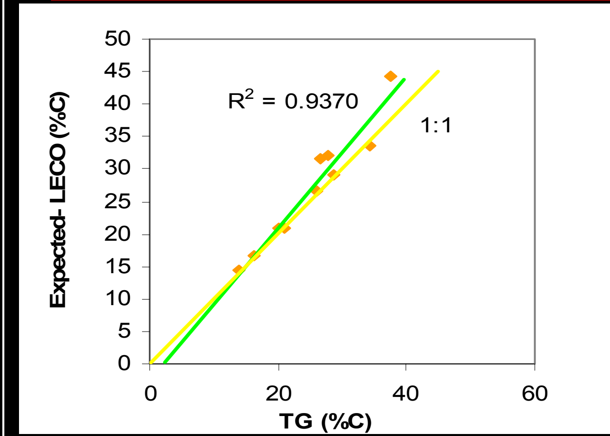
Litter: 94.2 ± 2.1%

Coal: 93.9 ± 4.2%

Limestone: 108.9 ± 2.9%

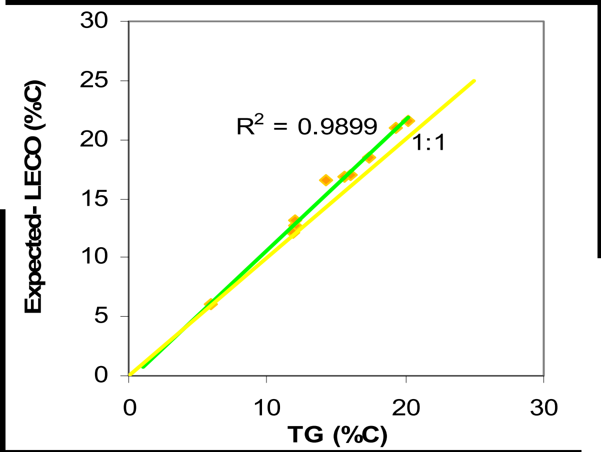
n=10

Expected C (%) versus TG %

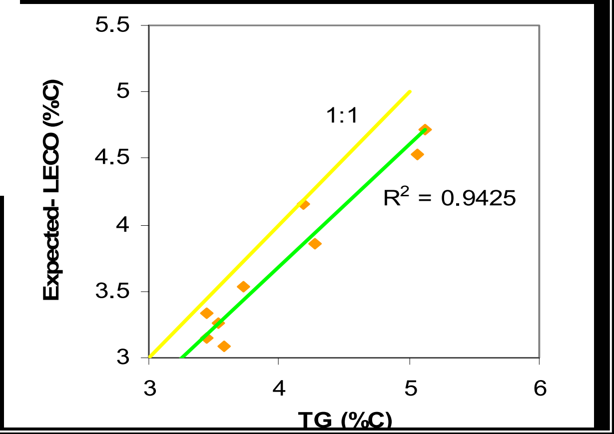


Grass Litter

Coal



Limestone



No significant differences between experimental data and 1: 1 model at $\alpha = 0.05$; n=10

Potential Interferences- Overlapping Peaks

- High mineral content - pyrite- 400-550 ^{o}C; goethite- 300-400 ^{o}C; kaolinite- 400-600 ^{o}C
- Different decomposition temperatures for carbonates- siderite, magnesite, and calcite
- Elemental analyses and X-ray diffraction (XRD) data may help to account for such interferences

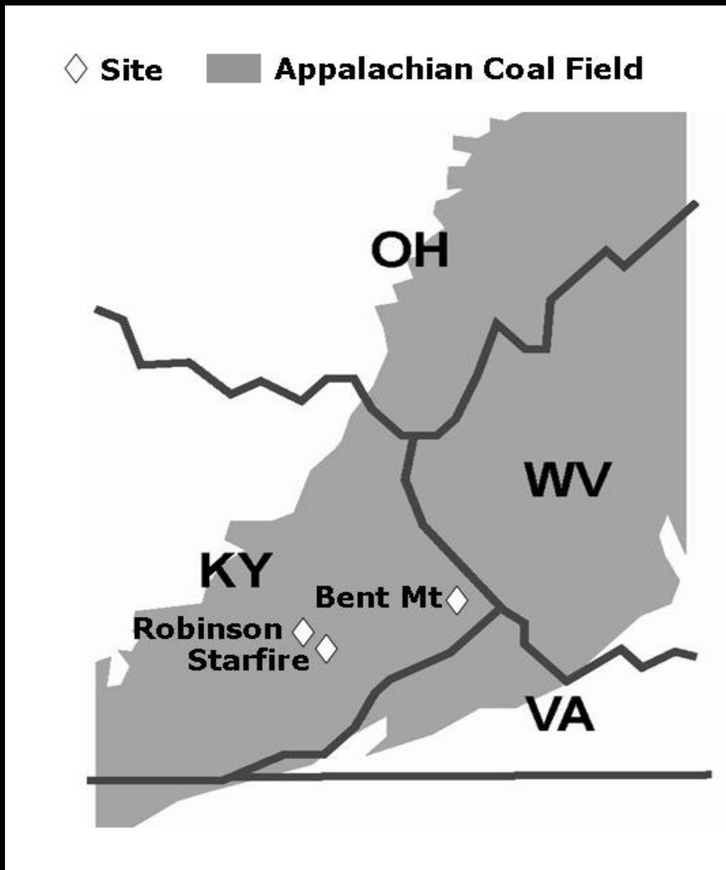
Potential Interferences- Overlapping Peaks

- Larger sample weights (> 15 mg) and larger particle size (> 1 mm) may also limit reproducibility of thermal curves
- Potential overlapping weight-loss temperature regions may be minimized and resolution enhanced by manipulating procedural conditions (carrier gases, flow rates, and temperature ramps)

Field Validation

Part 2

Field Samples Site Location



Bent Mountain: 0- and 2-year reforested

Starfire Mine: 3- and 8-year reforested

Reference; Robinson Forest: 80-year non-mined mature forest

Samples - upper 10 cm

White Oak

0-year

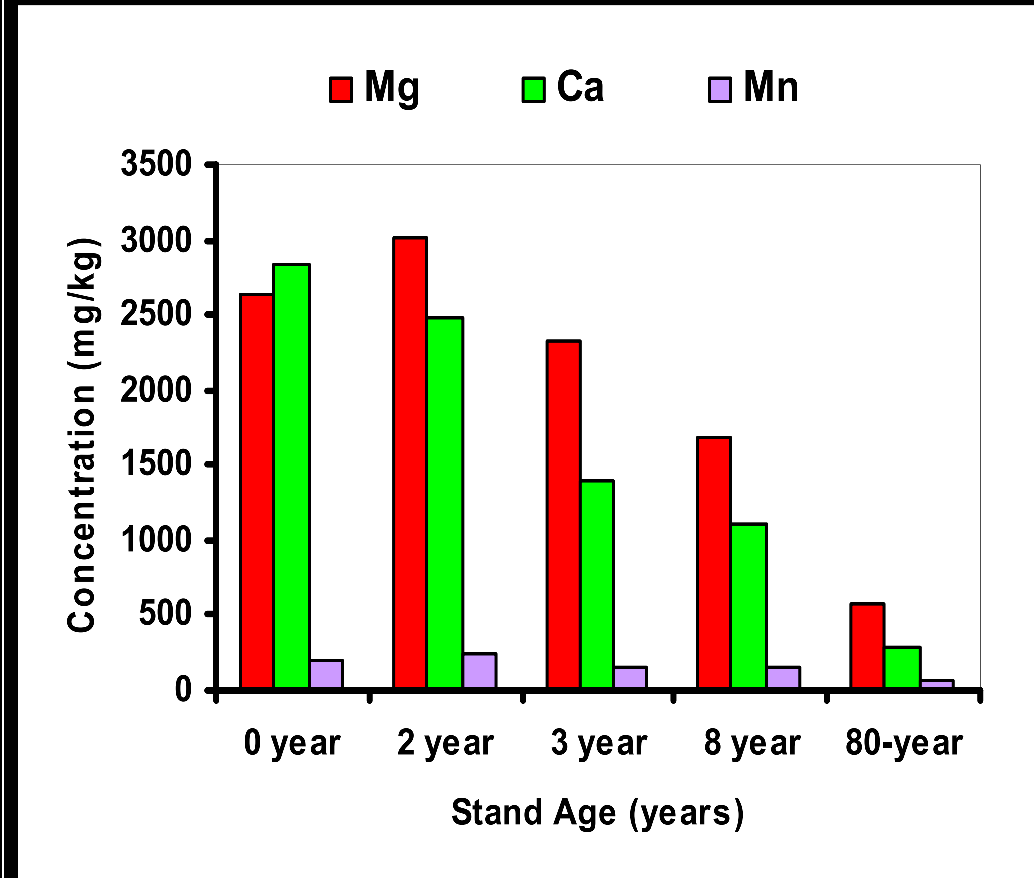
2-year- 60cm

3-year- 176 cm

8-year- 600 cm

80-year

Elemental Variations over Time



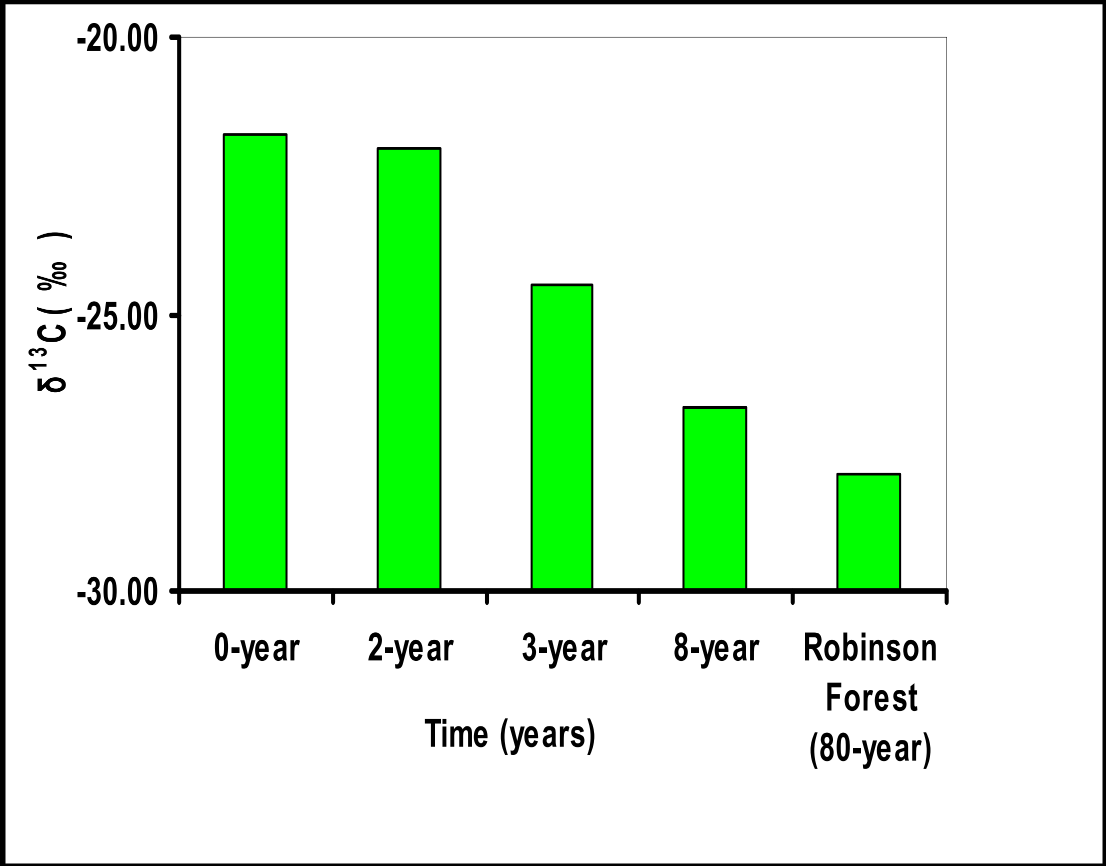
- Decrease of each element over time
- As trees grow

(a) root production increases

(b) water infiltration increases

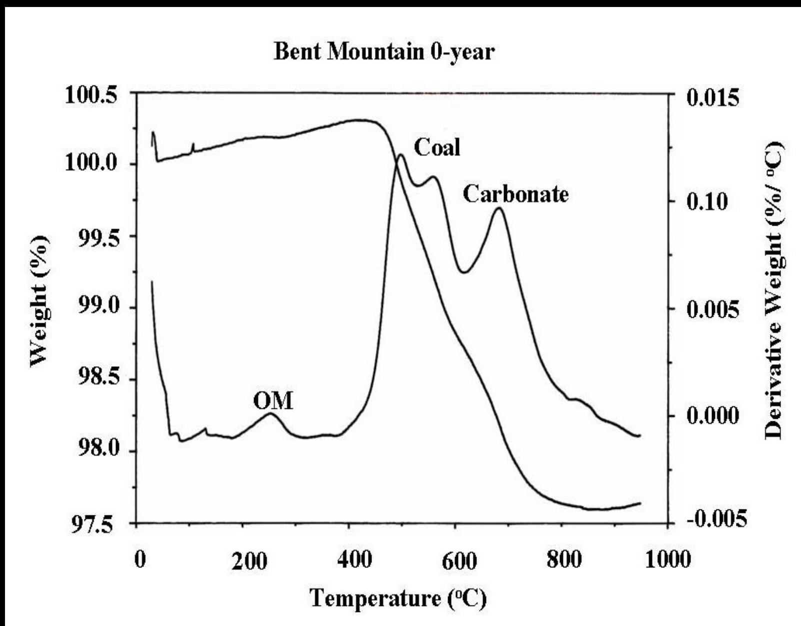
(c) physical weathering of parent material increases

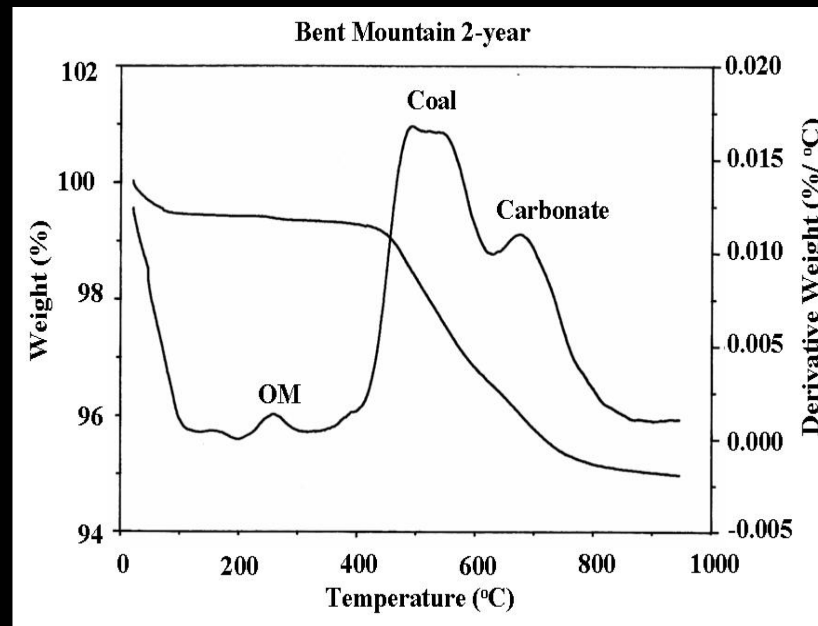
$\delta^{13}C$ Variation with Time



- 0-year: enriched $\delta^{13}C$
- $\delta^{13}C$ - Depletion over time
- More C_3 contribution over time
- More negative $\delta^{13}C$ could indicate more humic material as decomposition increases over time

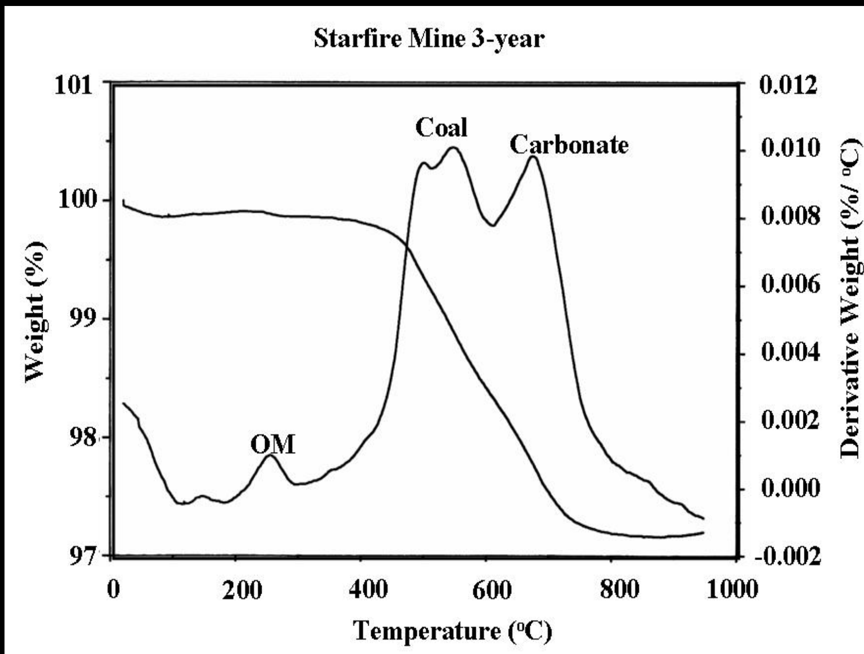
TG/DTG Results- Bent Mountain

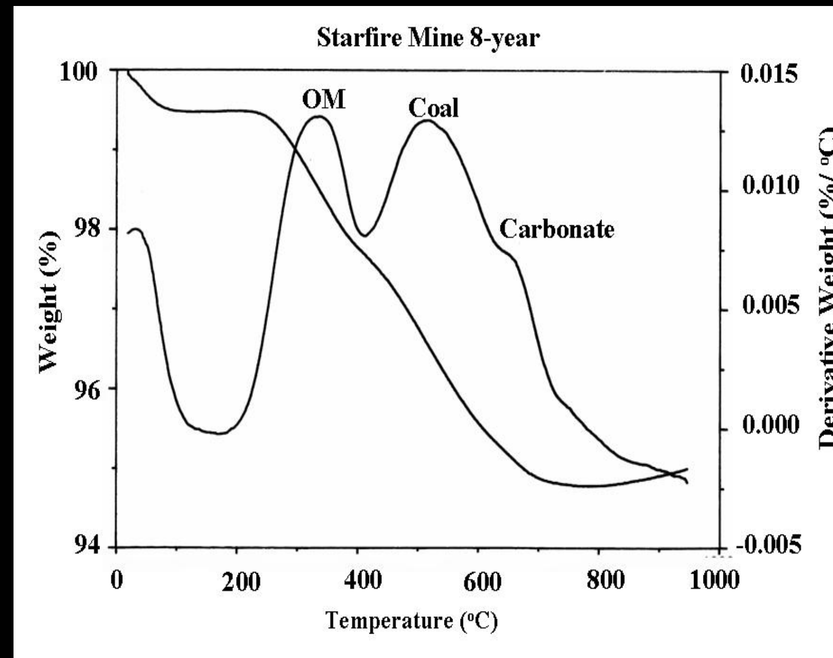




- OM fraction increased from 0.03 to 0.095%
- Variation in coal and carbonate peak

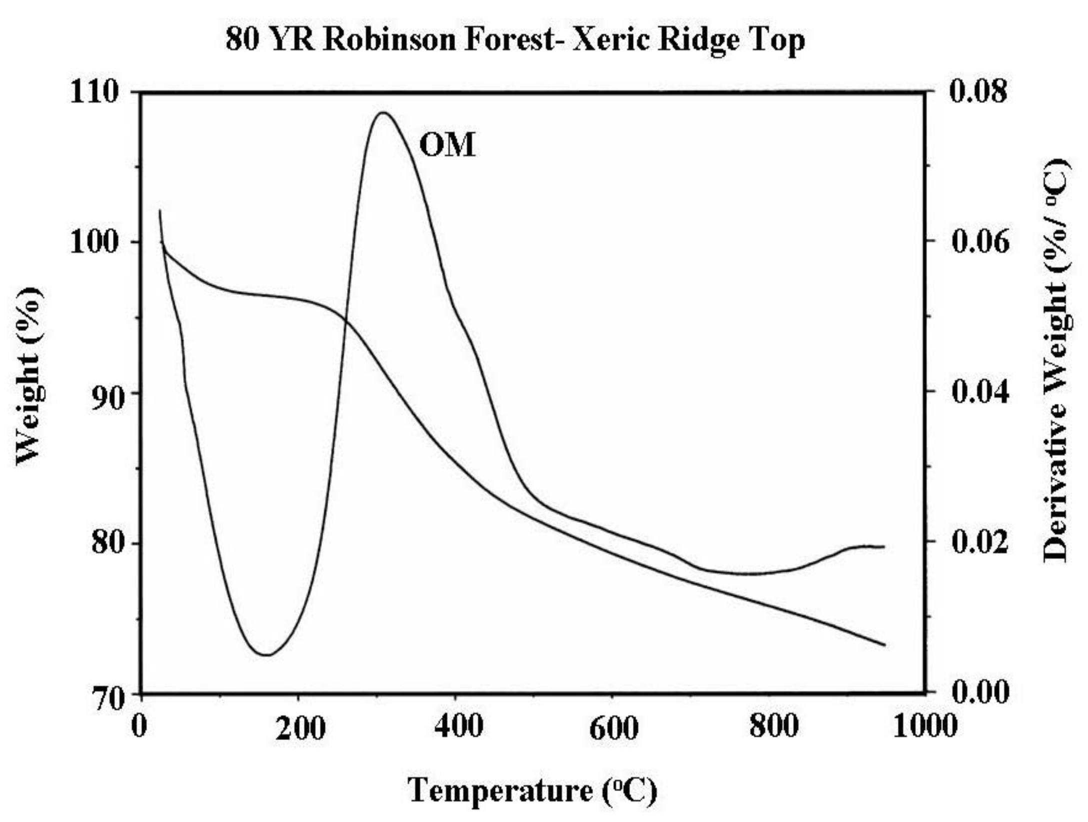
TG/DTG Results- Starfire Mine





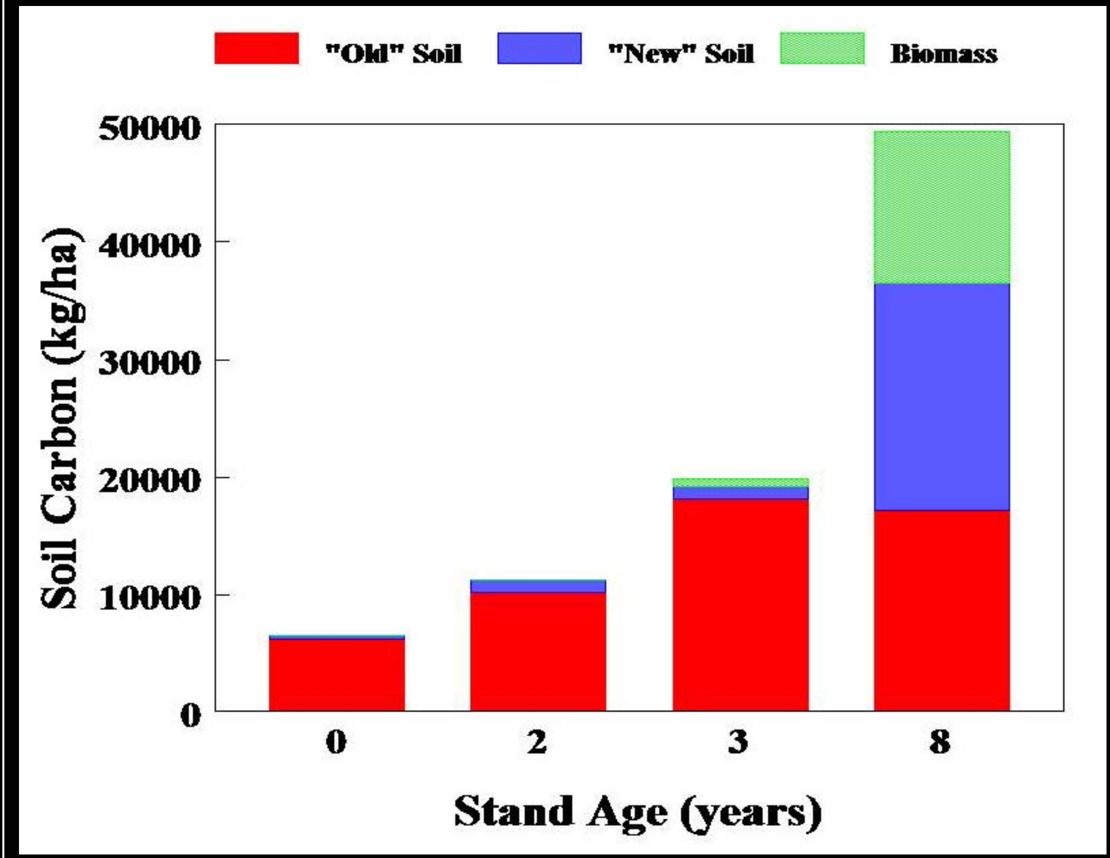
- OM fraction increased from 0.095 to 1.47%
- Decrease in carbonate fraction (~ 36%)

TG/DTG Results- Robinson Forest



- OM ~ 4.7%
- Shift to ~ 425 ^{o}C
- More humified material

Biomass Results



- Biomass increase of > 12,000 kg/ha over 5 year period (year 3 to year 8)
- "New" C increase of ~ 19,000 kg/ha over same time period

Conclusions

- C-fractions can be differentiated by TG/DTG, with;

(1) "new" OM - 270–395 ^{o}C

(2) "old" OM (coal) - 415–520 ^{o}C

(3) Inorganic C - 700–785 ^{o}C

- TG/DTG can potentially be used as metric for quantifying SOC changes in presence of coal and carbonate phases

Conclusions

- “New” OM is being accumulated at an average rate of 2.92 Mg ha^{-1} yr^{-1} on reclaimed coal mine sites in eastern KY
- TG/DTG may provide the standard procedure required by the Kyoto Protocol to monitor SOC changes
- TG/DTG has potential to be more cost-effective, simple and rapid over other methods

Acknowledgements

- U.S. Department of Energy
- Association of American Petroleum Geologists
- Dr. Christopher Barton
- Dr. A. D. Karathanasis, Dr. Susan Rimmer, Dr. Harry Rowe
- Yvonne Thompson and Jarrod Miller
- Mr. Henry Francis at the KGS
- ERTL staff and facility at the University of Kentucky
- Danielle Andrews

Questions???

Comments