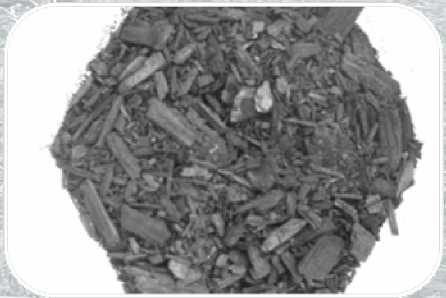
Impact of Biochar Field Exposure on Greenhouse Gas Production Potentials



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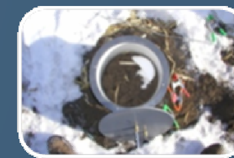
ASA/SSSA/CSSA Annual Meeting
Oct. 16-19, 2011 San Antonio, TX

Weathering



- Collective term for processes of:
  - Chemical transformations
    - Redox/reactions
  - Physical alterations
    - Freeze/thaw; desiccation; particle size reduction
- Interrelated action of factors:

  climate: water, wind, solar
  topography/geography,
  soil: protection in clods,
  time, and animals
- "Aging" or "Conditioning" are also used

Charcoal Weathering

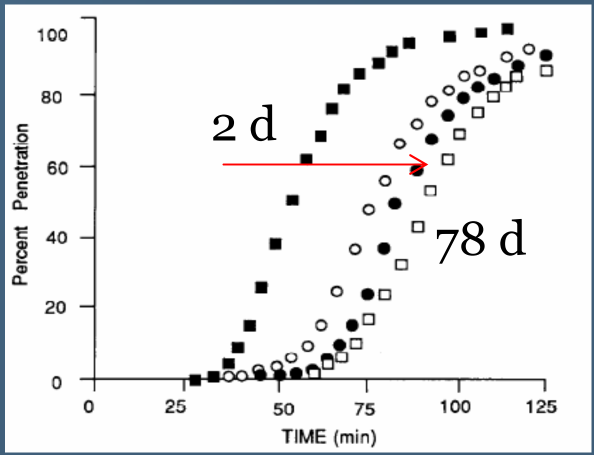



- Charcoal's adsorption behavior is a function of how charcoal is stored, treated and conditioned (activation)

(Rideal and Wright, 1925; Adams et al., 1988)

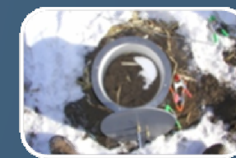
- Impact of the laboratory "aging" process is a function of adsorbent

  - Aged charcoals:
    - Increase polar molecule sorption
    - No change in non-polar sorption



Methanol breakthrough curves
(Adams et al., 1988)

Charcoal Weathering



➢Charcoal reacts with oxygen; classified as a "spontaneously combustible material" (49 CFR Ch. I 172.101)

➢Surface modification of charcoal occurs even under ambient conditions

➢3 fold increase in N_2 sorption, following 4 yr of laboratory storage (Sheldon, 1920)

180 *PHYSICS: H. H. SHELDON* Proc. N. A. S.

temperature. Above this we find deactivation, due to the breaking up of hydrocarbons at this high temperature which form an inactive carbon deposit on the active base.

In the case of U. S. Government 600 minute charcoal, no such deactivation at this high temperature was observed, but in this charcoal the hydrocarbons are supposedly all removed. It offers no contradiction therefore.

The outgassings were as indicated on the next page.

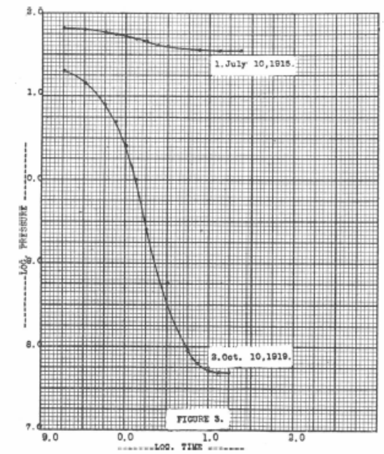


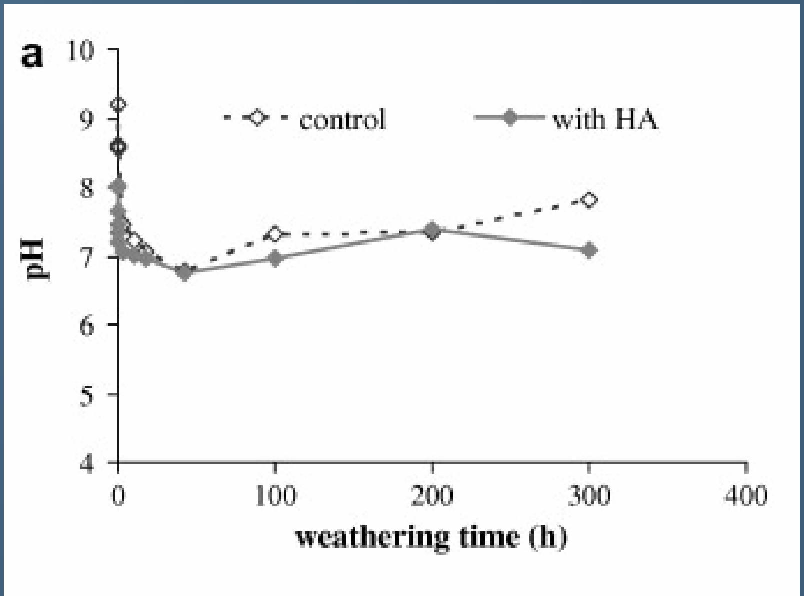
Figure 3 shows how charcoal may be activated by slow oxidation at room temperature. Curve 1 was taken July 10, 1915, and the sample was then put away and left undisturbed until Oct. 10, 1919, when curve 2 was taken.

The ease with which the charcoal could be deactivated for nitrogen compared to deactivation for hydrogen, suggested that a sample might be put into such a condition that it would adsorb hydrogen more readily than nitrogen. Results of this sort are shown in figure 4; curves 1 and 2 are nitrogen and hydrogen, respectively, before treatment, and curves

Synthetic Biochar Weathering

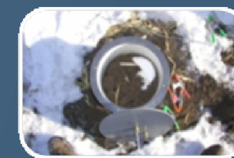
(Yao et al., 2010)

- Accelerated geologic weathering (Soxhlet reactor)
- Formation of carbonyl and carboxylic functional groups
- Very rapid pH decrease
- Loss of Ca ≫ Mg ~ K



(Yao et al., 2010)


Biochar Weathering (continued)

- Indication of alteration as a function of temperature of aging: oxygenated group formation

(Chen et al. 2009)

- Aging of 2 different biochars in field [Australia]

(Joseph et al. 2010)

Alteration of surface oxygen groups (carboxylic acids)
(O:C ratio from 0.2 to >0.7)


Field Plots

- USDA-ARS Rosemount, MN Field Biochar Plots

  - Replicated plots currently examining the impact of 7 different biochars
    - Fast pyrolysis hardwood sawdust
    - Slow pyrolysis green waste
    - Fast pyrolysis macadamia nut
    - Slow pyrolysis hardwood
    - Slow pyrolysis wheat middlings (wheat midds)
    - Slow pyrolysis pine chips
    - Slow pyrolysis wood pellets
    - Non-carbonized biomass comparisons

[application rate = 22,400 kg/ha]

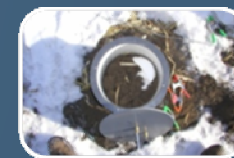



Field Plots

- Minnesota Climate

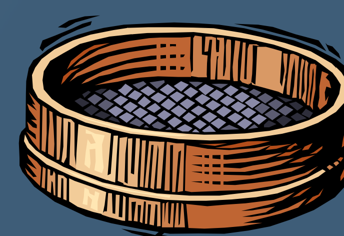
- Annual Average Temperature 7.4 C
- Average Annual Precipitation 750 mm
- Minimum annual air temperature - 35 C
- Maximum annual air temperature + 39 C



Biochar Retrieval

- Surface soil samples (0-5 cm) from plots selected due to larger particle size of biochar (1 year of weathering)
- Manually sieved: hand sorting pieces of biochar
- Biochar rinsed with deionized water

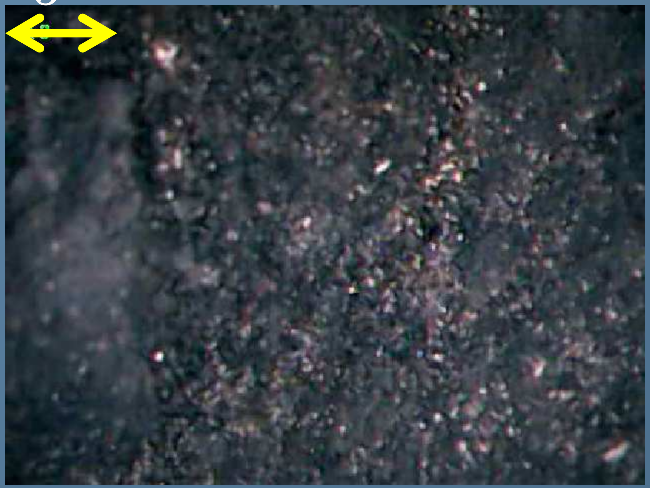


- Exception: Hardwood sawdust aged on soil surface (3-5 cm thick layer)

Visible Microscope




0.5 mm



Wood pellets
Slow pyrolysis

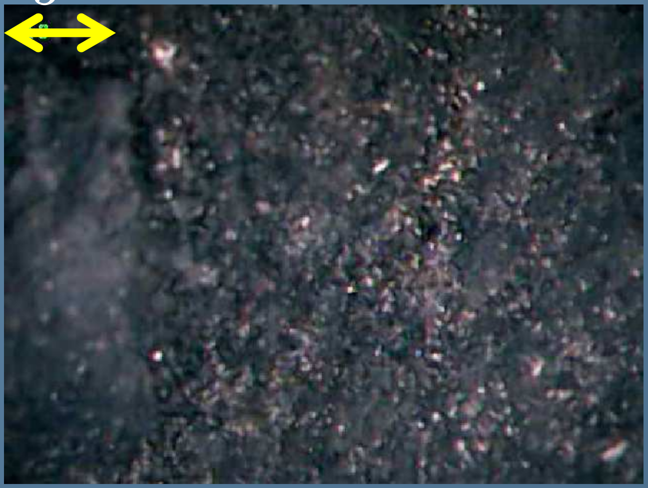
Hardwood
Slow pyrolysis

“Fresh”

Visible Microscope




0.5 mm



Wood pellets
Slow pyrolysis

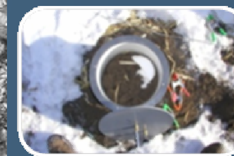
0.5 mm

Hardwood
Slow pyrolysis

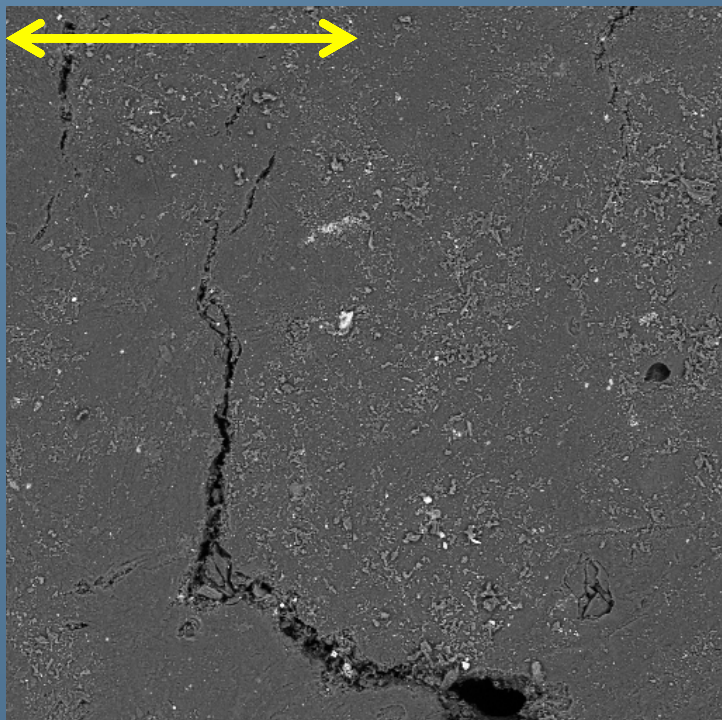
"Fresh"

"Weathered"

SEM-EDX

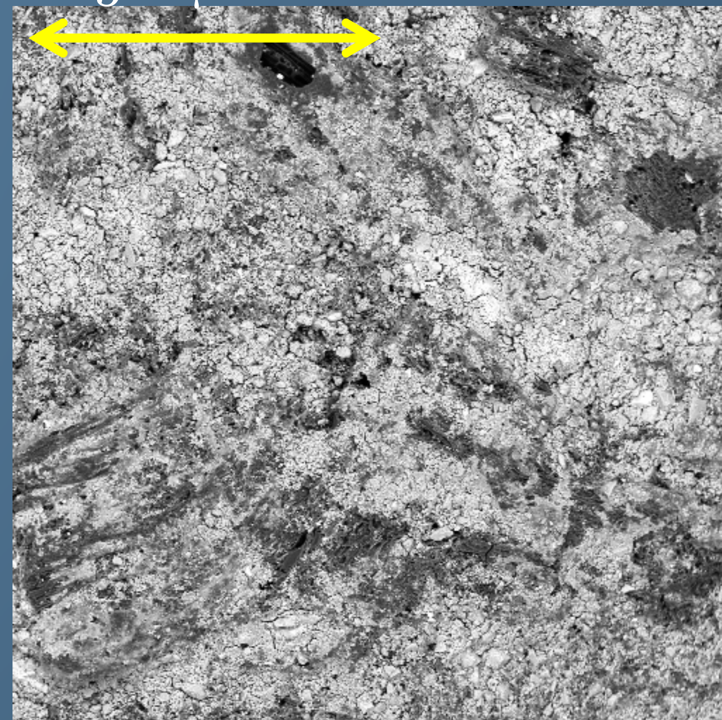


500 μm



“Fresh” wood pellet biochar

500 μm

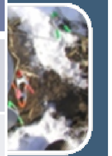


“Weathered” wood pellet biochar

Biochar	C	O	Al	Si	P	S	K	Ca
Wood Pellet (Slow Pyrolysis)								
Fresh	98.3	4	0	0	0.1	0	1.8	13.5
Weathered	26.5	51	4.0	10	0	0	3.8	0.9

Chemical Composition: EDX



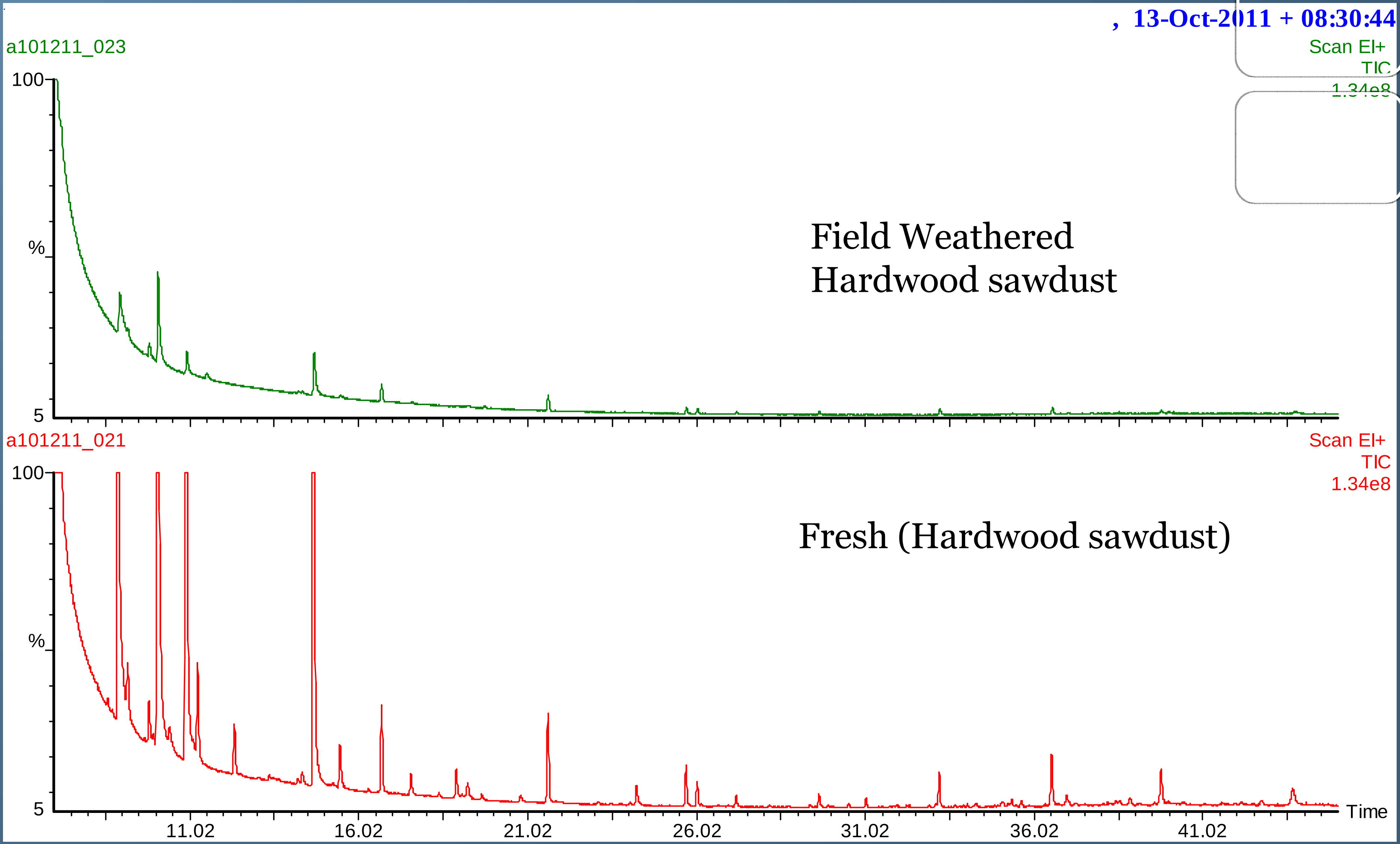
Biochar	C	O	Al	Si	P	S	K	Ca
Hardwood Sawdust (Fast Pyrolysis)								
Fresh	88.7	8.9	0	0	0	0	1.7	0.5
Weathered	80.7	13.0	0	2.0	0	0	0.5	0.1
Hardwood (Slow Pyrolysis)								
Fresh	78.6	11	0.5	0.5	0.1	0.1	2.3	4.4
Weathered	84.3	10	0.9	1.9	0	0	1.7	0.4
Wood Pellet (Slow Pyrolysis)								
Fresh	78.3	4.0	0	0	0.1	0	1.8	13.5
Weathered	26.5	51	0.2	10	0	0	3.8	0.9
Macadamia nut shell (Fast Pyrolysis)								
Fresh	60.2	36	0.0	0.1	0.4	0.1	1.9	0.4
Weathered	22.6	58	3.9	6.9	0.2	0.2	3.2	0.8

Chemical Composition: Ultimate /Proximate Analysis (% dry basis)

Biochar	Ash	C	H	N	O	VM	Fixed C	pH
Hardwood Sawdust (fast pyrolysis)								
Fresh	21.1	63.9	3.0	0.2	11.8	26.1	52.8	7.9
Weathered	22.2	62.9	2.8	0.3	11.8	29.1	48.7	6.5
Hardwood (slow pyrolysis)								
Fresh	2.5	90.1	1.5	0.2	8.2	12.5	85.0	7.4
Weathered	3.0	89	2.5	0.2	5.7	14.8	82.2	6.4
Wood Pellet (slow pyrolysis)								
Fresh	6.4	73.4	1.3	0.2	18.8	12.4	81.3	10.1
Weathered	8.8	76.9	2.1	0.2	11.9	23.5	67.6	5.7
Macadamia Nut Shell (fast pyrolysis)								
Fresh	1.9	93.2	2.6	0.6	1.7	16.8	81.2	7.5
Weathered	4.8	84.3	2.8	0.7	7.3	21.0	74.0	5.4

Increase in ash content, decrease in fixed C and pH, and an increase in VM

Sorbed VOC's



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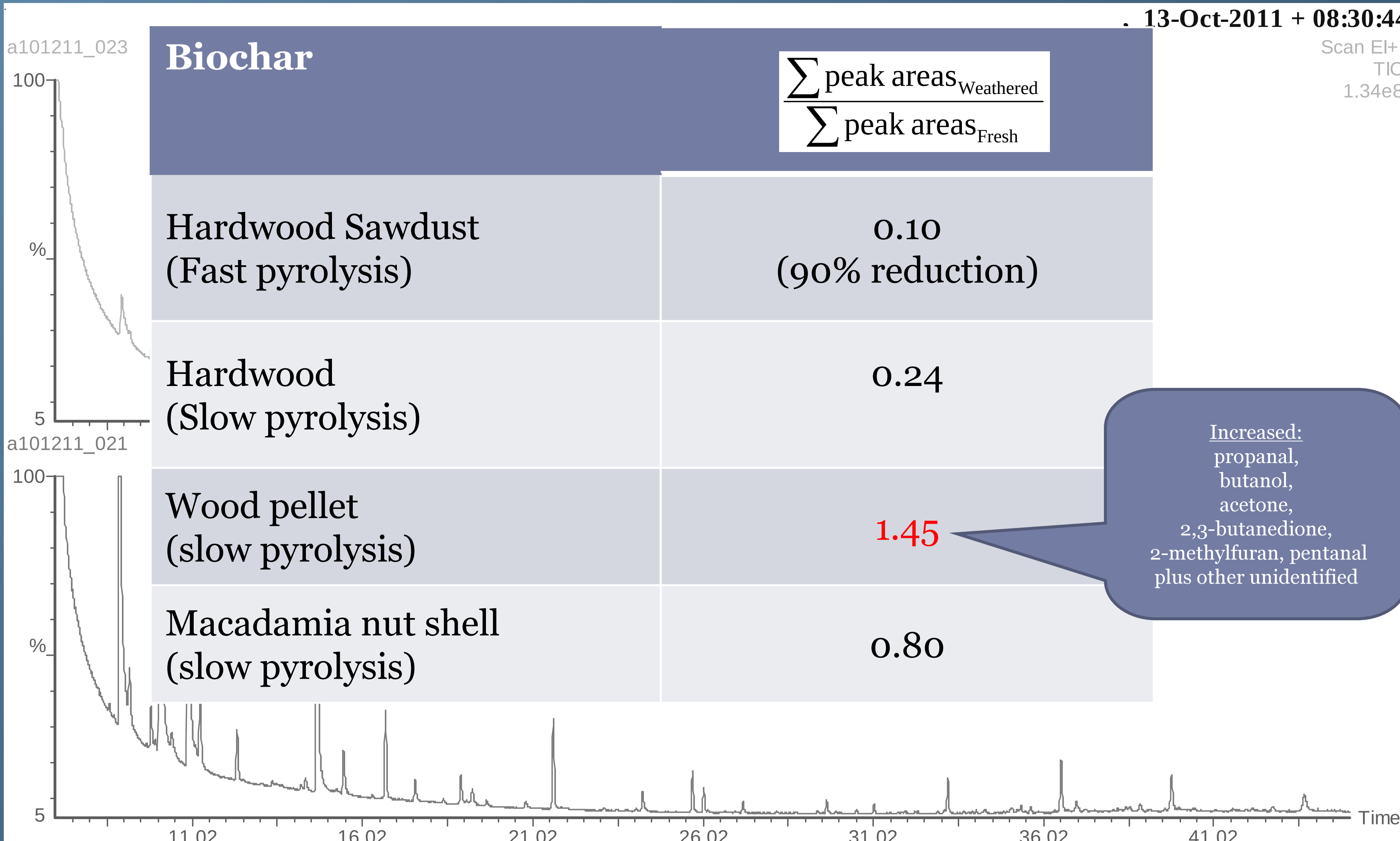
a101211_023
Scan EI+
TIC
1.34e8
100
%
5
Field Weathered
Hardwood sawdust
a101211_021
Scan EI+
TIC
1.34e8
100
%
5
Fresh (Hardwood sawdust)
11.02
16.02
21.02
26.02
31.02
36.02
41.02
Time

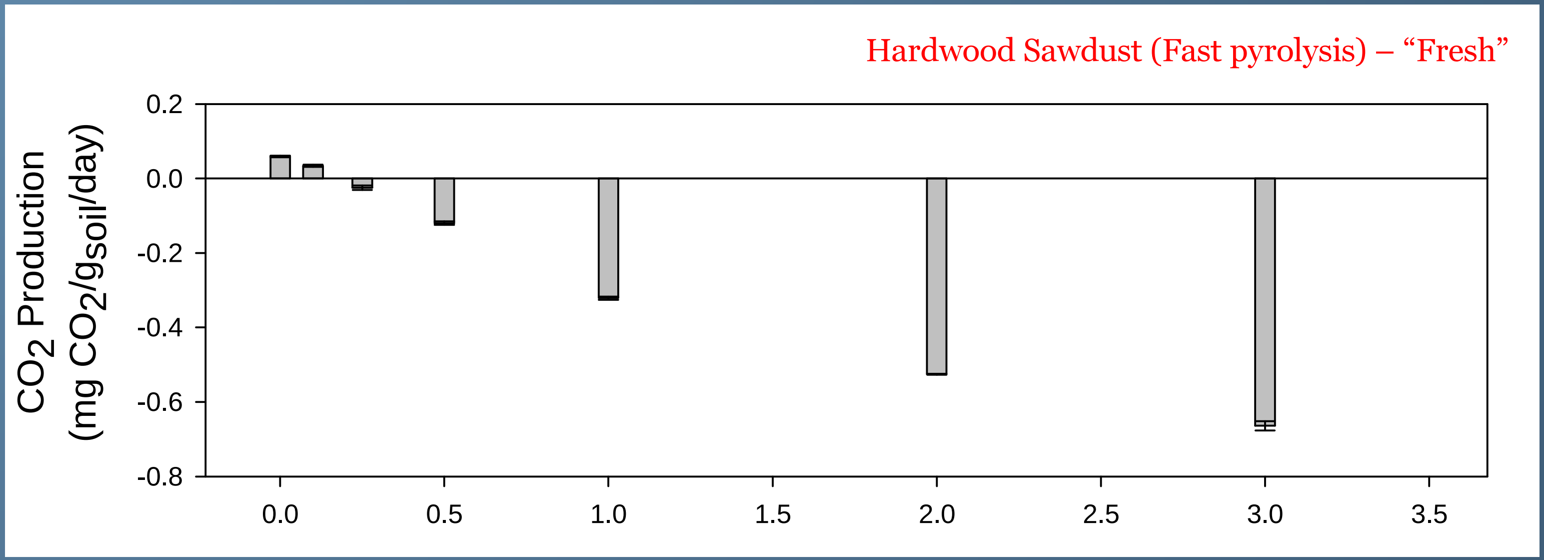
Sorbed VOC's



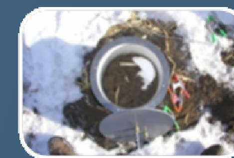
Biochar	$\frac{\sum \text{peak areas}_{\text{Weathered}}}{\sum \text{peak areas}_{\text{Fresh}}}$
Hardwood Sawdust (Fast pyrolysis)	0.10 (90% reduction)
Hardwood (Slow pyrolysis)	0.24
Wood pellet (slow pyrolysis)	1.45
Macadamia nut shell (slow pyrolysis)	0.80

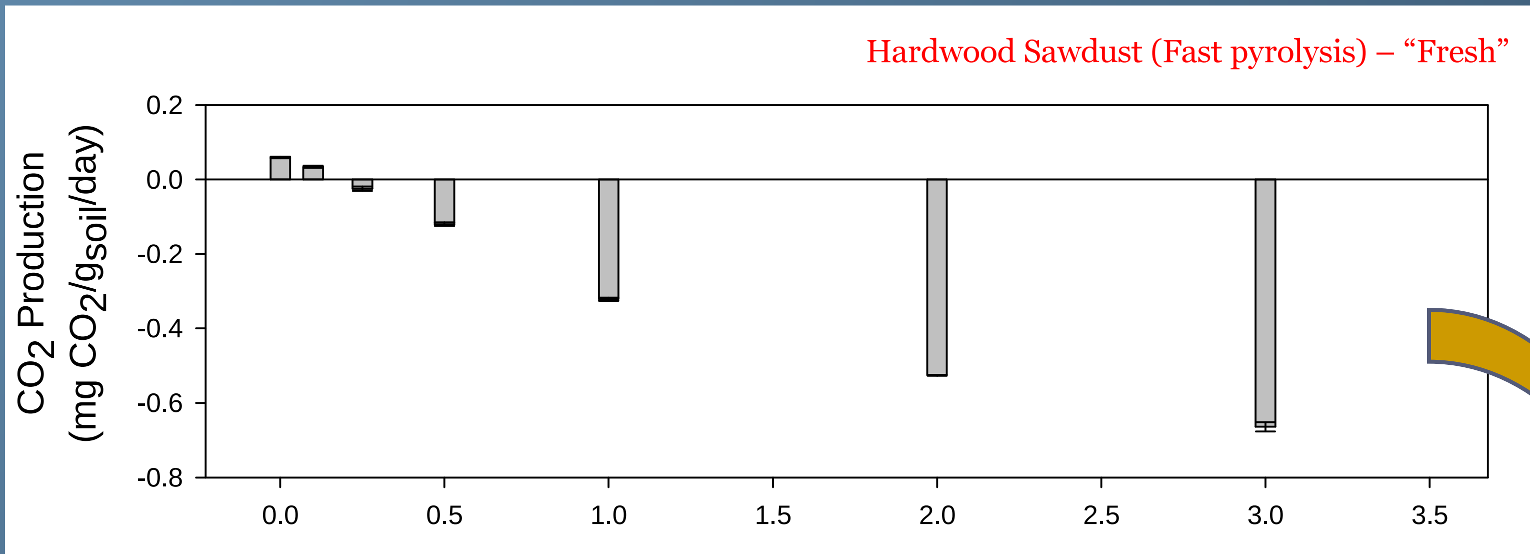
Increased:
propanal,
butanol,
acetone,
2,3-butanedione,
2-methylfuran, pentanal
plus other unidentified

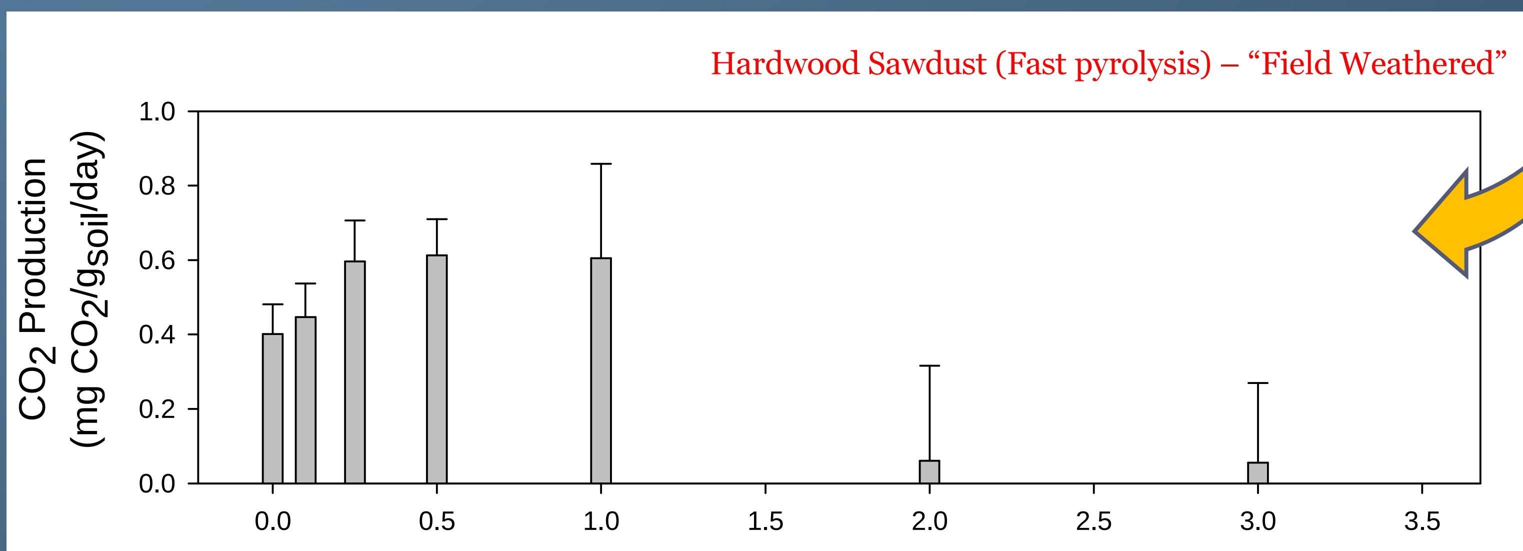
GHG Impacts: CO_2



GHG Impacts: CO_2





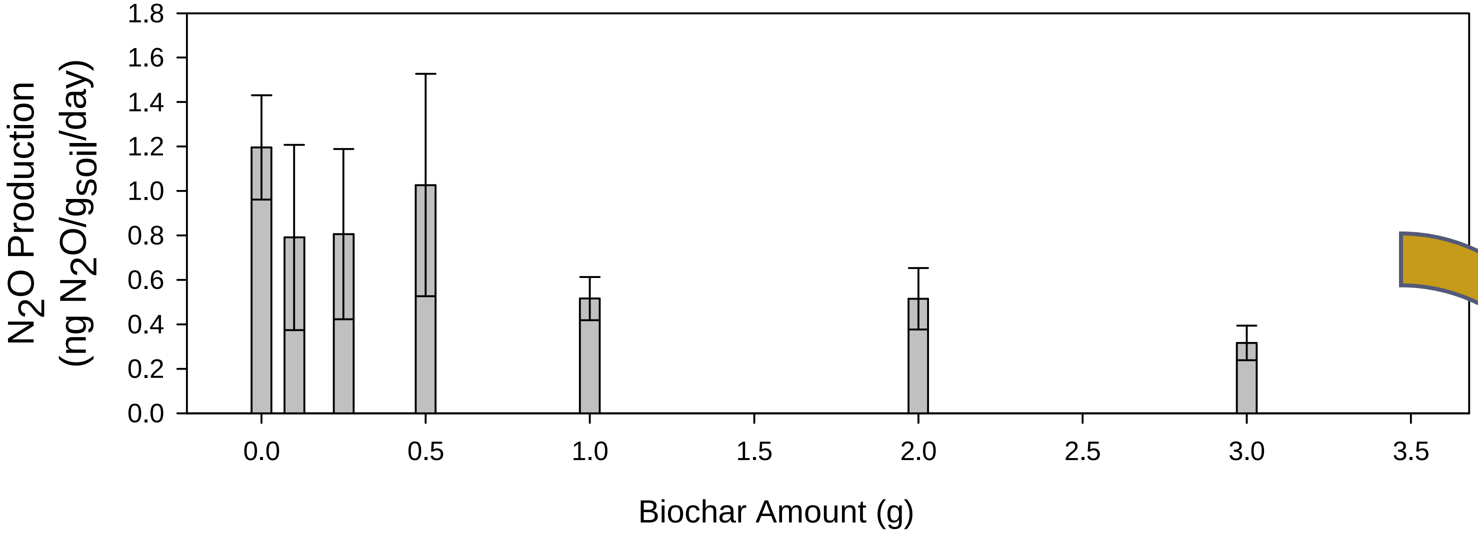


CO2 production corrected for BC abiotic production

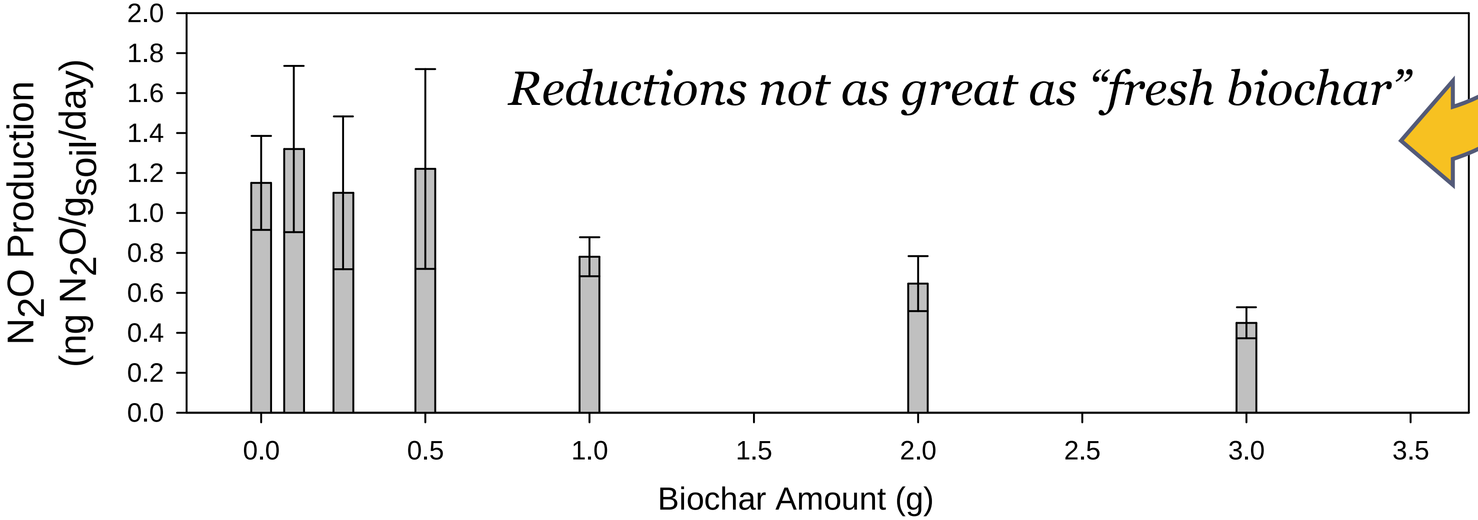
GHG Impacts: N_2O




Hardwood Sawdust (Fast pyrolysis) – "Fresh"

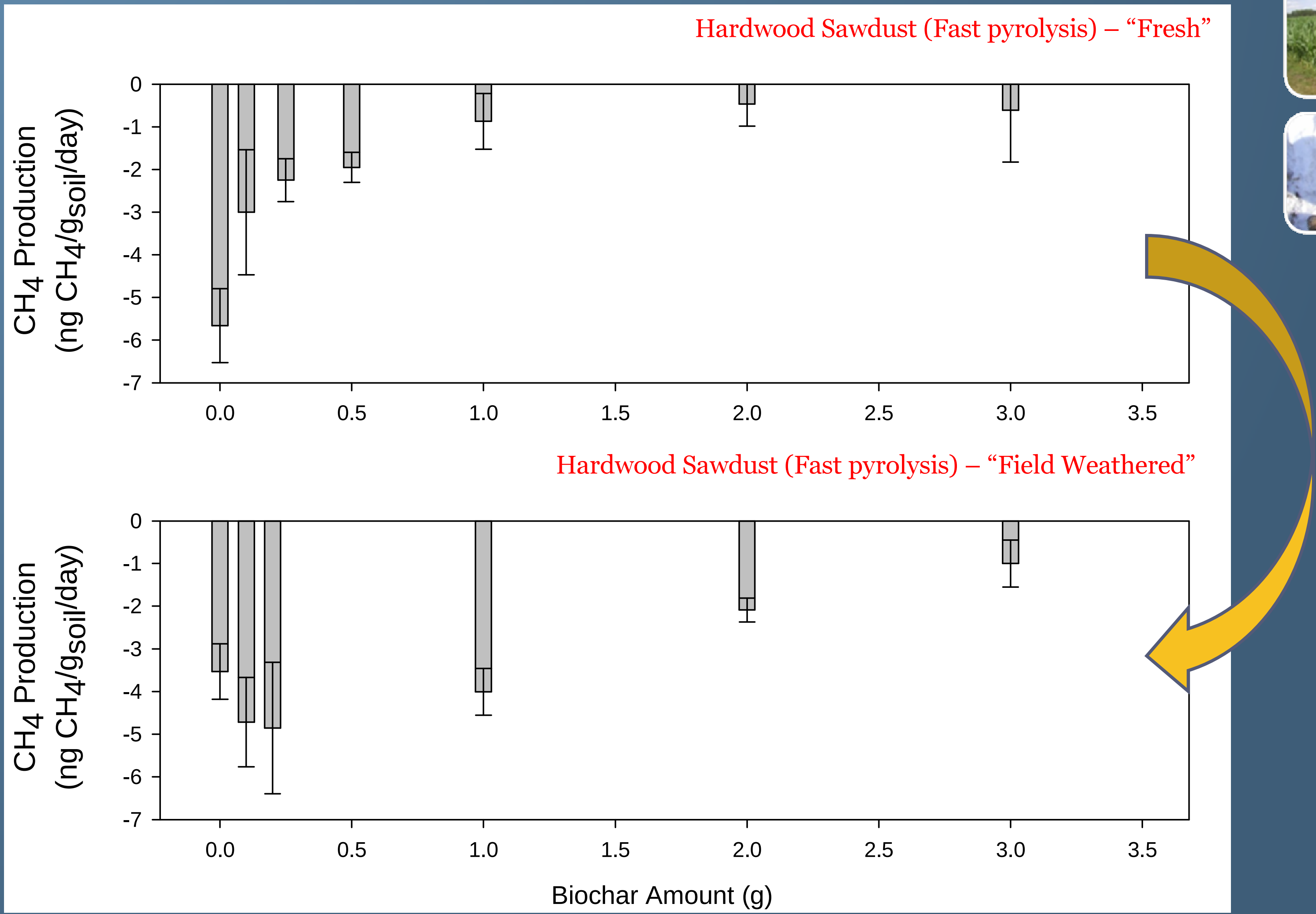


Hardwood Sawdust (Fast pyrolysis) – "Field Weathered"



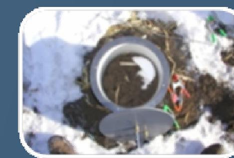
Reductions not as great as "fresh biochar"

GHG Impacts: CH4



GHG Impacts: Summary



Impacts of weathering on GHG production compared to fresh biochar

Biochar (10% w/w soil)	**CO2 (ug CO2 g_{soil}^{-1} d^{-1})**	**N2O (ng N2O g_{soil}^{-1} d^{-1})**	**CH4 (ng CH4 g_{soil}^{-1} d^{-1})**
Hardwood Sawdust (Fast pyrolysis)	**Increased**	**Lower degree of suppression**	**Stimulated oxidation activity**
Hardwood (Slow pyrolysis)	**Increased**	*No net change*	**Stimulated oxidation activity**
Wood pellet (slow pyrolysis)	**Increased**	**Stimulated N_2O**	**Stimulated oxidation activity**
Macadamia nut shell (slow pyrolysis)	*No net change*	**Lower degree of suppression**	Lower suppression

Conclusions




- Just like biochar is not a homogenous species; behavior of weathering is not universal

- Typically resulted in decreased fixed carbon + increased ash
  However, impact of the "soil filled pores" ?

- 3 of the 4 weathered biochars had increased CO_2 respiration activity – Increased potential BC mineralization?
  O:C ratios would indicate this

- Enhanced CH_4 oxidation activity in 3 out of 4; "fresh" biochar suppressed CH_4 oxidation in laboratory incubations

- In general, suppression of N_2O was reduced with weathering
  - One biochar even increased net N_2O production

- These weathering alterations will play a significant role in the assumed duration of observed initial short-term biochar impacts

Acknowledgements: Special thanks to all the companies that provided the biochar for the field experiments and Martin du Saire, Tia Phan, Amanda Bidwell, Eric Nooker, Edward Colosky, Michael Ottman, Lianne Endo, Kia Yang, and Lindsey Watson for their technical laboratory and field assistance.