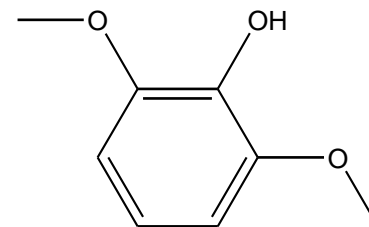
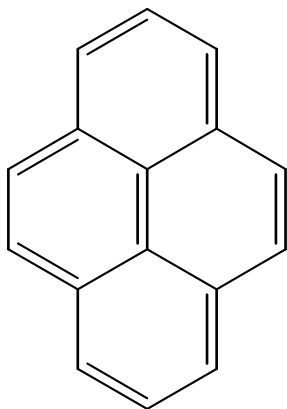
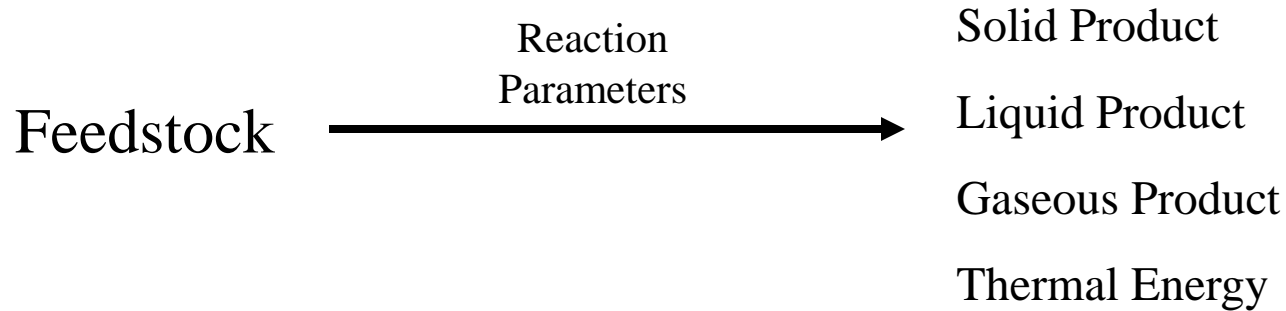


# Biochar Characterization Studies, PAH's and Phenols



John W Scott,  
ISTC Senior Analytical Chemist

# Thermochemical Conversion



Feedstock Factors + Reaction Factors = Product Characteristics

-Carbon, Nitrogen,  
Oxygen

-Halide (Cl, Br)

-Metals

-Moisture

-Particle Size

-Reaction System

-Operating Temperature

- Residence Time

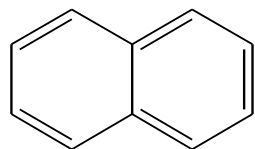
-Pressure/Gas Composition

-Planetary Alignment

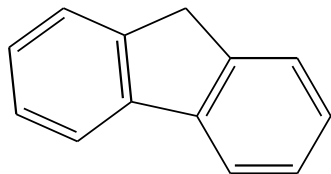
-Chemical Composition

-Phase Distribution

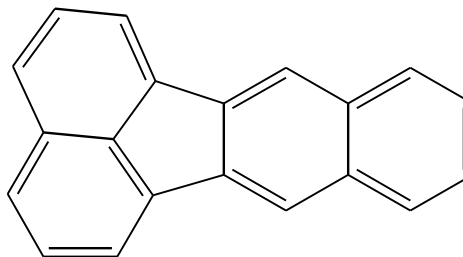
# Polynuclear Aromatic Hydrocarbons (PAHs)



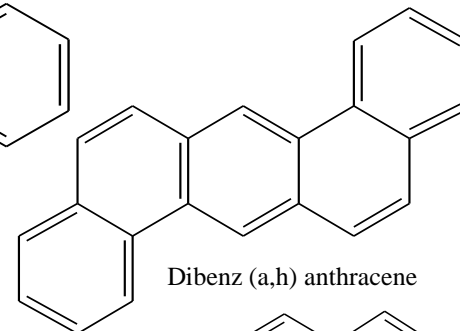
Naphthalene



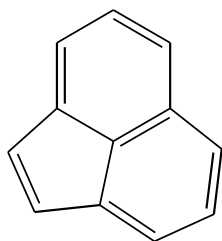
Fluorene



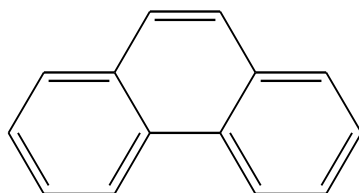
Benzo k fluoranthene



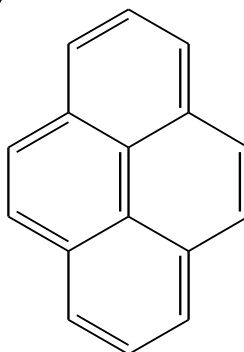
Dibenz (a,h) anthracene



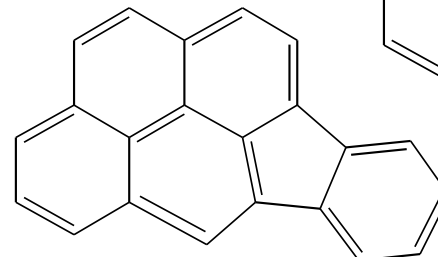
Acenaphthylene



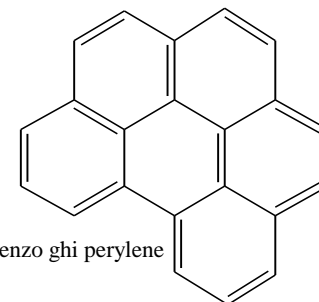
Phenanthrene



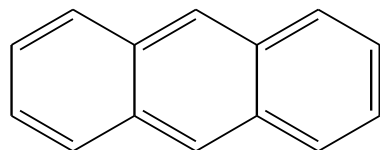
Pyrene



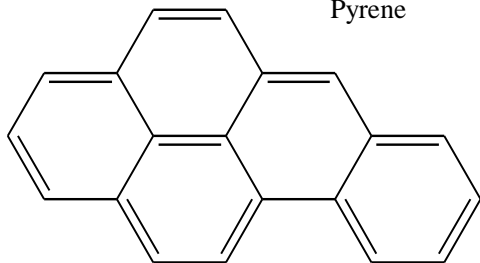
Indeno (1,2,3,c,d) perylene



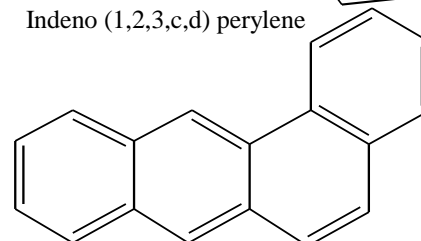
Benzo ghi perylene



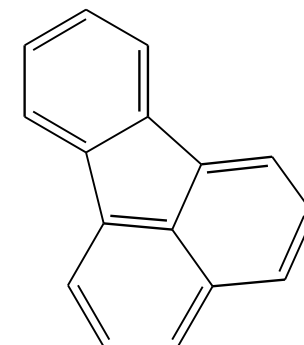
Anthracene



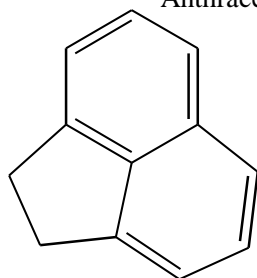
Benzo (a) pyrene



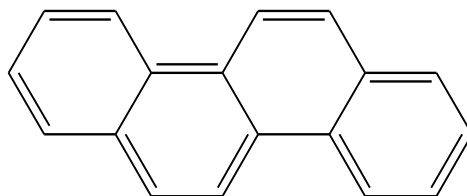
Benzo (a) anthracene



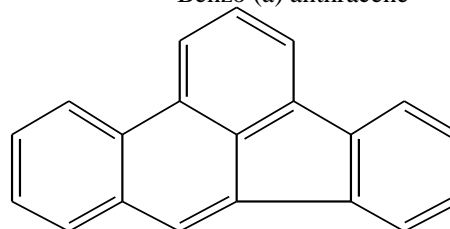
Fluoranthene



Acenaphthene



Chrysene



Benzo (b) fluoroanthene

# Extraction and Analysis



## ASE Extraction

### Dionex® ASE300 Parameters

- Solvent: Hexane-Acetone (1:1)
- Temperature: 100°C
- Pressure: 1500psi
- Static Time: 5 min
- Solvent to sample ratio:
  - Stover 20 ml/g
  - Stover BC 32 ml/g
  - Wood BC 8 ml/g



## Turovap Concentrate

### Turbovap Parameters

- Final Volume: 1.0 ml
- Temperature: 40°C
- Three Solvent Exchanges



## GC/MS Analysis

### Varian® GC/MS Parameters

- Detector: Saturn 2000 Ion Trap MS operated in selected ion mode
- Column: Restek® Rtx-5MS (30 m x 0.25 mm x 0.25 μ)
- Injection: 300°C, Split-less, 1 μl

-Oven:

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
45	0.0	1.00	1.00
130	43.0	0.00	2.98
180	12.0	0.00	7.14
240	7.0	0.00	15.71
320	12.0	10.00	32.38

# Biochar Feedstocks

## Corn Stover\*

- 7.2% Moisture
- 7.8% Ash
- 42% Carbon
- 0.87% Nitrogen
- 5 PAH's Detected
- Max Total PAH detected 0.064 mg/kg



(Most Likely Soil Contamination)

\* - Michael L. Machesky, Thomas R. Holm, and John W. Scott “Sorption of Polycyclic Aromatic Hydrocarbons (PAHs) to Biochar and Estimates of PAH Bioavailability”.

## Wood Chip Waste\*\*

- Urbana Landscape Recycling Center
- Dried to < 1% Moisture



\*\* - Wei Zheng and Zhewang “PAH formation under different slow-pyrolysis conditions”.

# Slow Pyrolysis Reaction Conditions

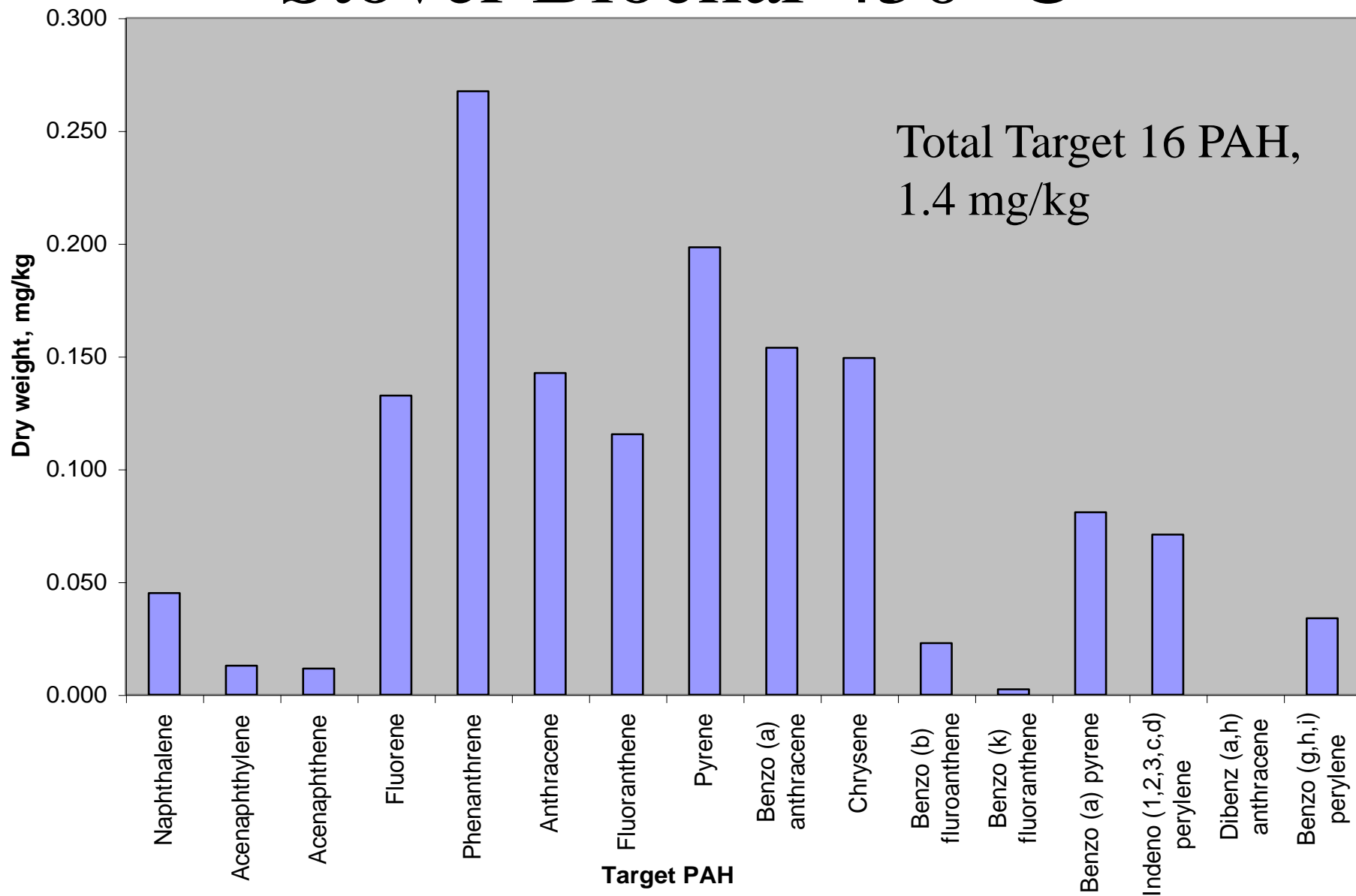
## Corn Stover

- Temperature 450 °C
- Residence Time: 30 minutes
- Gas Composition: N<sub>2</sub>
- Storage -20 °C
- Extracted within 3 days of production

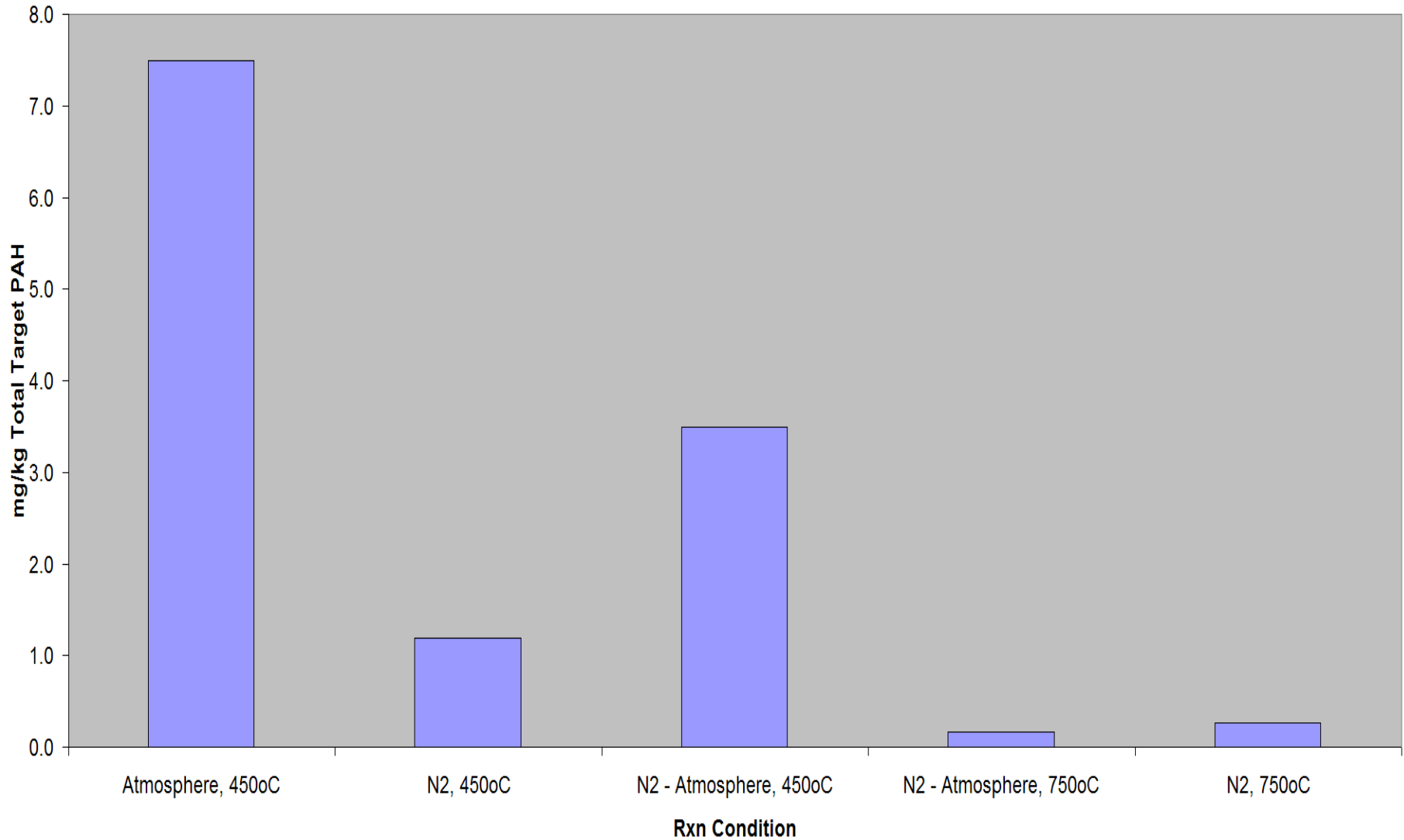
## Wood Chip Waste

- Temperature 450 °C and 750 °C
- Residence Time: 30 minutes
- Gas Composition: N<sub>2</sub>, N<sub>2</sub>-Atmosphere and Atmosphere
- Storage -20 °C
- Extracted six months after generation

# Table 1: Target PAH's for Corn Stover Biochar 450 °C

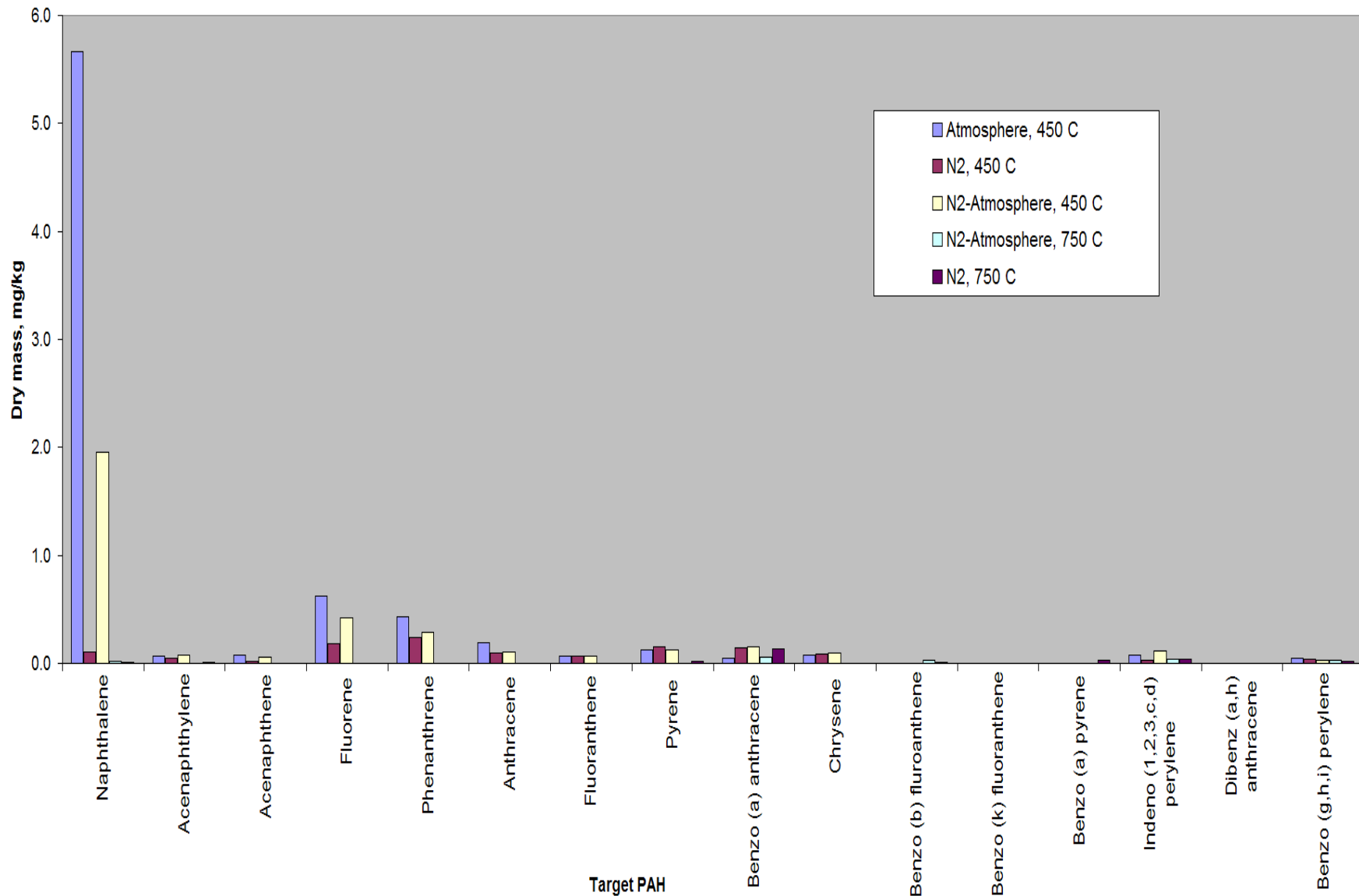


# Table 2 Total Target PAH's for Woody Waste Biochar under Different Reaction Conditions

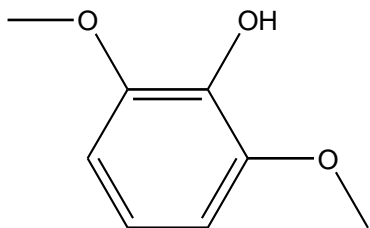




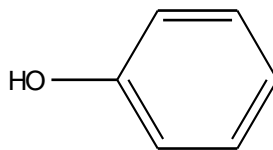
# Table 3 PAH profile for Woody Waste Biochar



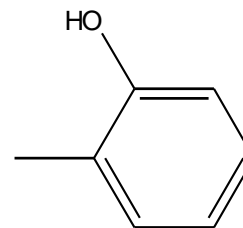
# Phenols



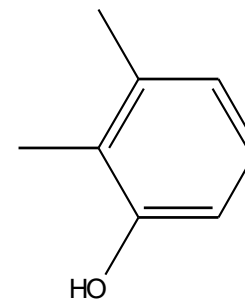
Syringol



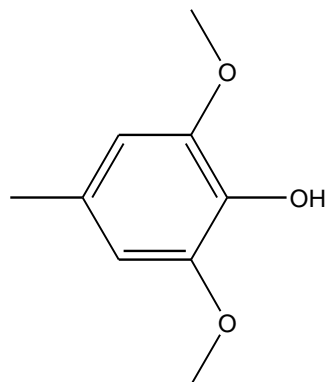
phenol



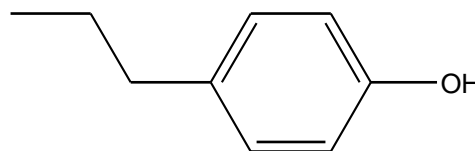
cresol



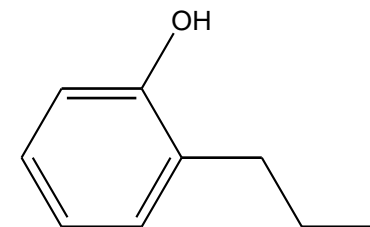
Dimethylphenol



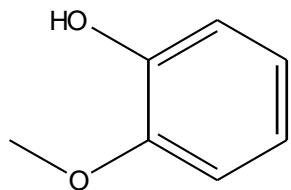
2,6-Dimethoxy-4-methylphenol



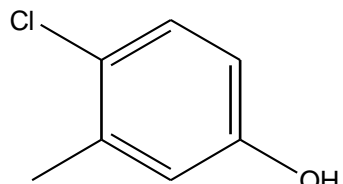
4-Propylphenol



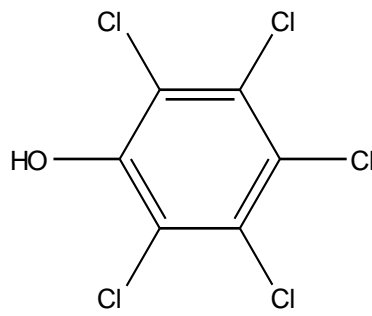
2-Propylphenol



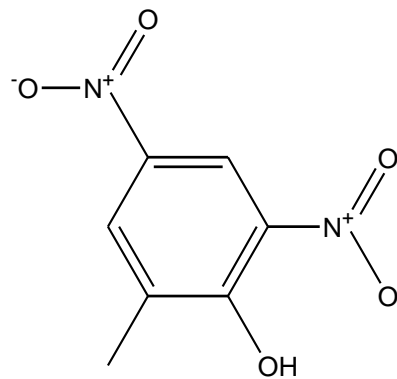
guaiacol



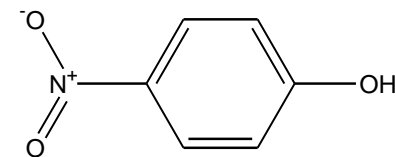
4chloro3methylphenol



pentachlorophenol

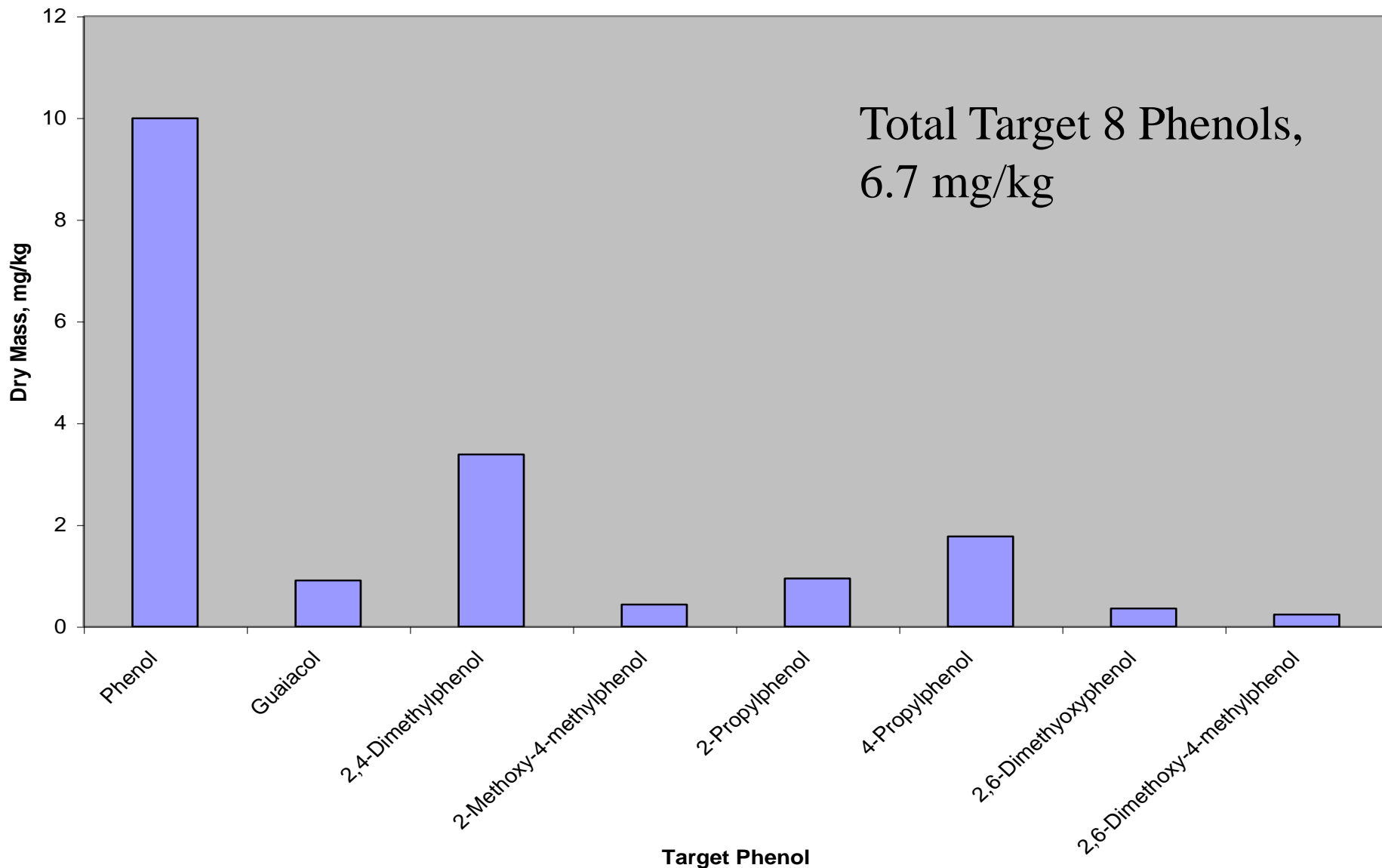


2-methyl-4,6-dinitrophenol

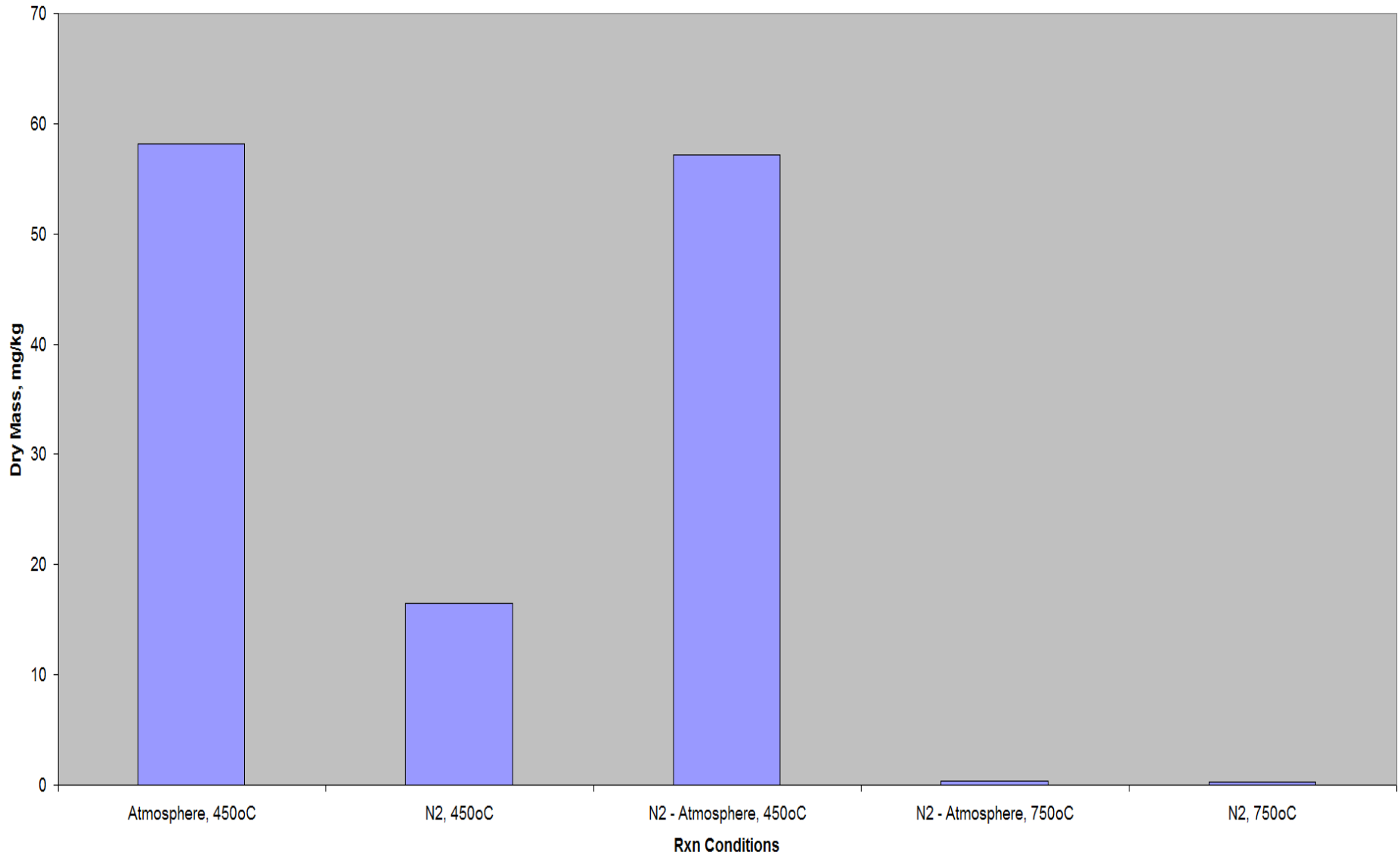


4nitrophenol

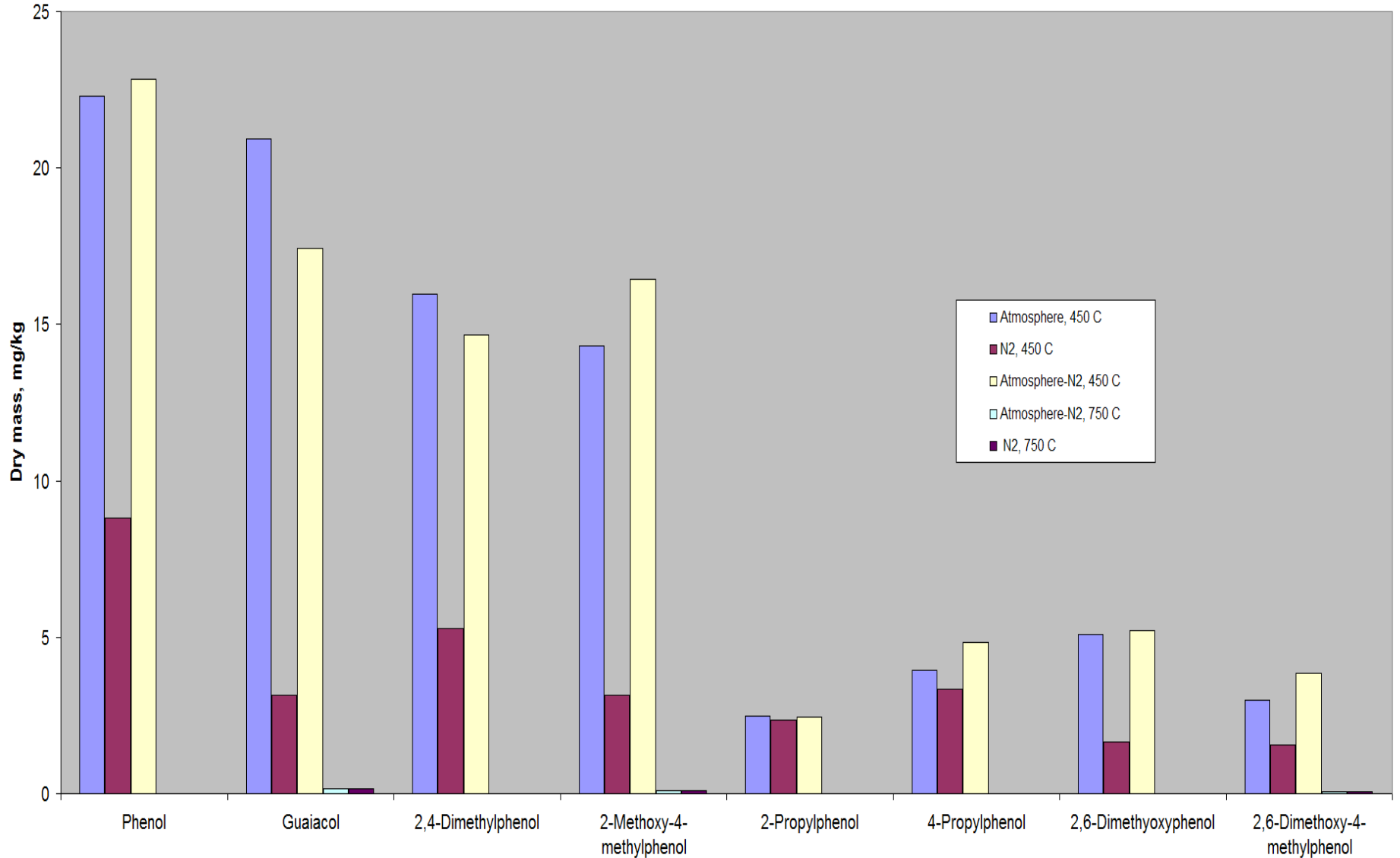
# Table 3: Target Phenols for Corn Stover Biochar 450 °C



# Table 4: Total Target Phenols for Woody Waste Biochar under Different Reaction Conditions



# Table 5: Target Phenols for Woody Waste Biochar



# Current Data Summary

## Corn Stover

- Biochar from corn stover produced by slow pyrolysis at 450 °C under a nitrogen blanket contains 1.4 mg/kg target PAH's
- The PAH profile for this material is dominated by three and four cyclic ring species
- Eight phenols were detected with a total concentration of 6.7 mg/kg

## Wood Chip Waste

- Biochar from wood chips processed by slow pyrolysis at 450 °C contains more target PAH's than wood chips processed at 750 °C
- PAH formation during slow pyrolysis at 450 °C is atmosphere dependent
- The PAH profile is atmosphere dependent
- Eight phenols were detected with a max total concentration of 58 mg/kg
- The phenol profile is also atmosphere dependent

# Future Studies

## Corn Stover

- Bioavailability studies by Michael Machesky and Thomas Holm at the Illinois State Water Survey
- Create biochar at 550 °C and 750 °C under same conditions and repeat experiments
- Continue to identify and quantify other chemical components of this material

## Wood Chip Waste

- Prepare a sample processed at 750 °C by slow pyrolysis with no nitrogen atmosphere
- Expand target phenol list and re-analyze extracts
- Continue to identify and quantify other chemical components of this material

# Acknowledgments

Nandakishore Rajagopalan for Technical Assistance and Discussions

Gerald Bargren “The Sample Prep Master!”

Wei Zheng for Initiating Biochar work and Collaboration

BK Sharma and Dheeptha Murali for Biochar Preparation

ISWS Collaborators Michael Machesky and Thomas Holm

Richard Larson and Karen Marley for Assistance with Phenol Analysis and Sharing of Reference Materials

USDA Kurt Spokas for Collaboration and Discussions