  

Evaluation of Sorbed Polycyclic Aromatic Hydrocarbons on Biochar

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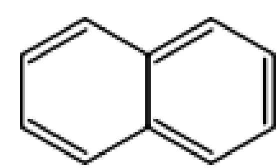
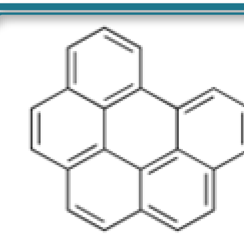
Tuesday – Biochar Characterization

PAH –Introduction

- Polycyclic aromatic hydrocarbons
  - Compose a large group of compounds (200+)
  - Characteristic of two or more fused aromatic carbon rings in the structure
  - Composed solely of carbon and hydrogen atoms
  - Simplest PAH is naphthalene



Naphthalene



Benzo(g,h,i)perylene

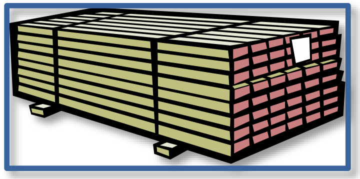
PAH occurrence

- PAHs are among the most common organic pollutants
  - **Ease of atmospheric transport**
  - **Universal environmental presence**
  - **US EPA lists 32 of these PAHs as priority pollutants**

Primary sources: Anthropogenic

- Largest stationary point source emissions in California:

  - Paper mills
  - Factories of various consumer wood products
  - Petroleum refining


(ARB, 1997)

PAH: Natural Sources

- Present in:
  - Fossil fuels
    - Crude oil
    - Shale oil
    - Coal
  - Coal tars

- Present in gases and ashes from:
  - Forest fires
  - Grassland fires
  - Volcanoes

- Biological Routes
  - Microbial degradation of black carbons
  - Microbial production during complex organic matter formation

(soil humic substances)

(HSDB, 1995)

Processes to form PAH compounds

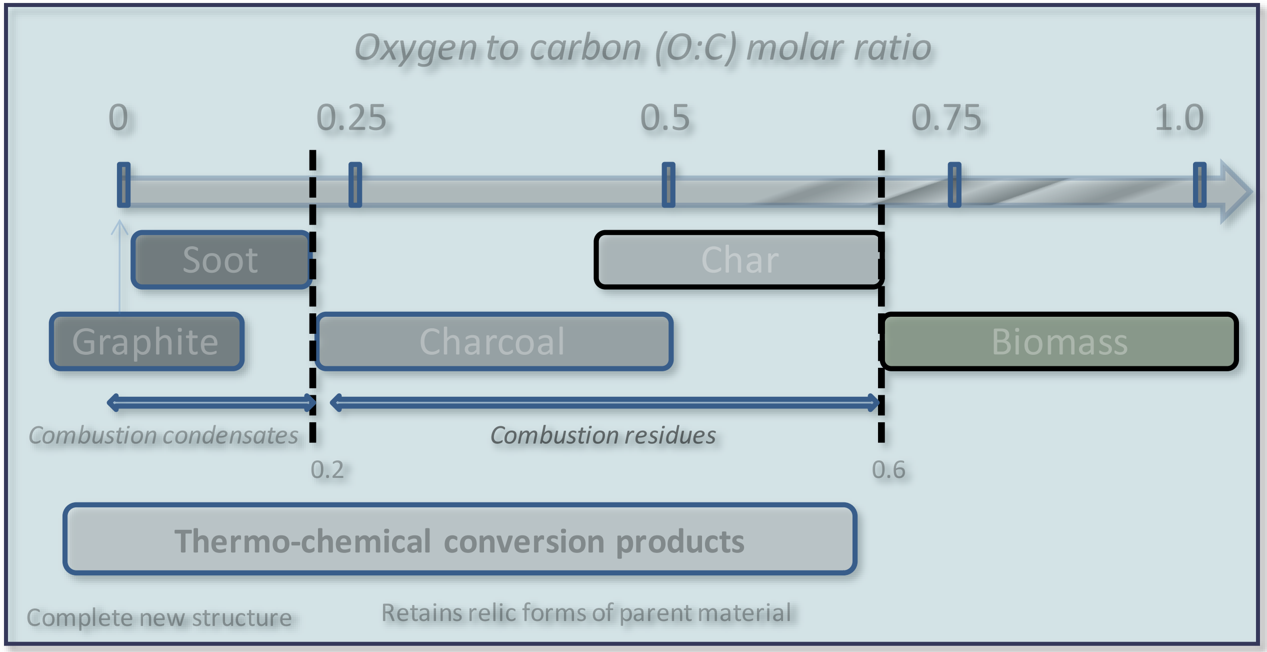
- Incomplete combustion
  - Burning of fossil fuels: coal, diesel, gasoline
    - Transportation sector
  - Burning of biomass (e.g. wood, tobacco, brush fires)
  - Cooking for meal preparation
- PAH production has also been confirmed during:
  - Production of charcoal by pyrolysis (e.g., Ré-Poppi and Santiago-Silva, 2002)
  - Present in bio-oil from biomass pyrolysis

PAH presence in various materials

Material	Σ USEPA PAH [µg g^{-1}]	Reference
Soils		
Urban soil (roadside)	0.04 to 13.5	(Ritschel, 2008)
Arable soil (farmland)	0.2 to 0.4	(Ritschel, 2008)
Terrestrial rocks	<0.1 to 45	(Mahajan et al., 2001)
Pine Needles	0.04 – 1.9	(Ratola et al., 2010; Navarro-Ortega et al., 2011)
Wood Chips	0.01 to 0.015	(Chinnici et al., 2007)
Sewage sludge	2.2 to 126	(Wild et al., 1990; Ritschel, 2008)
Composts		
Wood chips/leaves/grass clippings	16.0	(Grossi et al. 2011)
Fall leaves/twigs	14.4	(Grossi et al. 2011)
Wood chips/sewage sludge	20.8	(Grossi et al. 2011)

Biochar is a form of black carbon

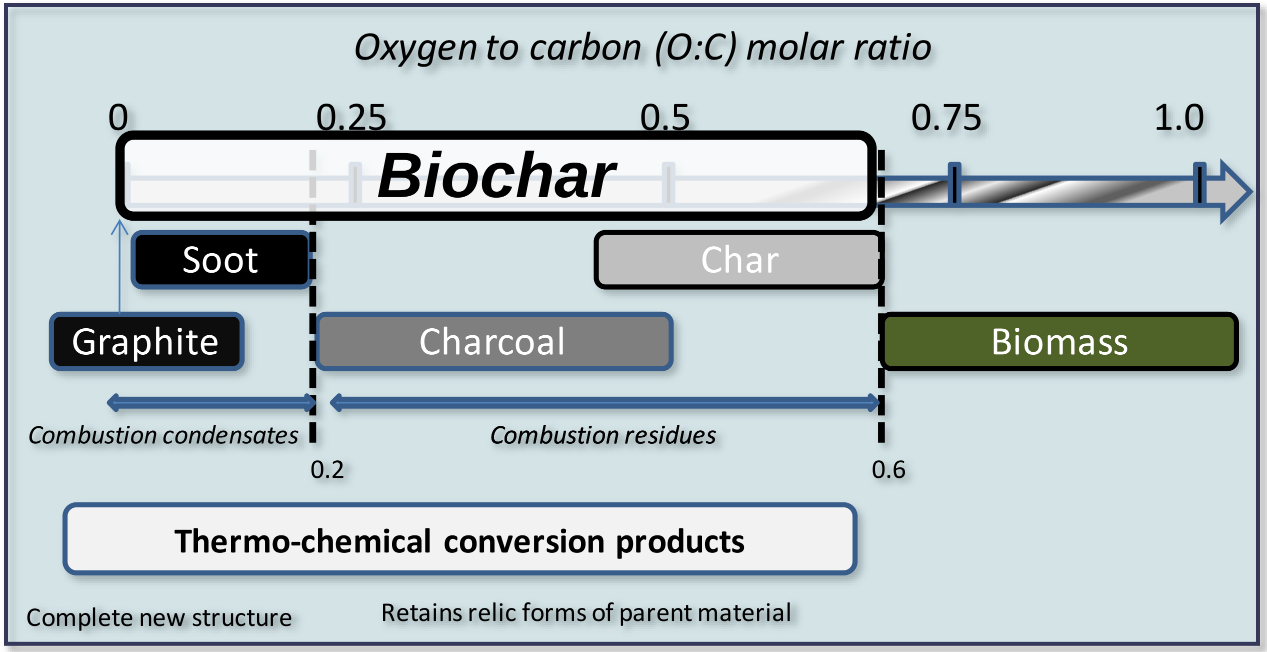
- Biochar : Name given to the production of black carbon for the purpose of soil carbon sequestration



Adapted from Hedges et al., 2000; Elmquist et al., 2006

Biochar is a form of black carbon

- Biochar : Name given to the production of black carbon for the purpose of soil carbon sequestration
- Biochar spans the entire spectrum of black carbons



Adapted from Hedges et al., 2000; Elmquist et al., 2006

PAH sorbed to black carbons

Material	Σ USEPA PAH [µg g⁻¹]	Reference
Black Carbons		
Coal	0.3 to 253	(Wang et al., 2010) (Laumann et al., 2011)
Slow Pyrolysis (wood)	<0.01	(Zhurinsh et al. 2005) (Singh et al., 2010)
Wood Ash (3.7% C content)	16.8	(Bundt et al., 2001)
Natural and synthetic charcoal	1.0 to 3.7	(Brown et al., 2006)
Coconut shell charcoal (CocoNara™)	2.9	(Sepetdjian et al., 2010)
Hardwood Lump Charcoal	0.5	(Sepetdjian et al., 2010)
Three Kings™ (waterpipe charcoal)	1.2	(Sepetdjian et al., 2010)
Biochar (11 biochars/5 feedstocks)	<0.5	(Singh et al., 2010a)
Biochar (50 biochars/majority from same production unit)	0.3 to 45	(Hale et al.. 2012)

Current observed biochar range: 0.01 to 45 µg g^{-1}

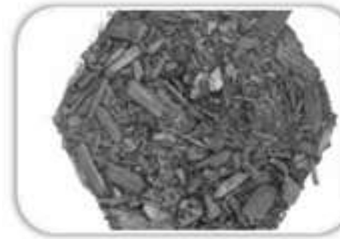
Incinerator/Gasifier Residues

Material	Σ USEPA PAH [μg g^{-1}]	Reference
Bottom/fly ash mixture (wood feedstock)	37 – 77	(Davies et al., 1976; Dugenest et al., 1999; Johansson and van Bavel, 2003a)
Coal Fly Ash	15 – 185	(Gohda et al., 1993)
Municipal solid waste incinerator – bottom ash	0.5 to 3.6	(Johansson and van Bavel, 2003b)

- Incineration and gasification residues contain higher amounts of PAH compounds (0.5 to 185 μg g^{-1})

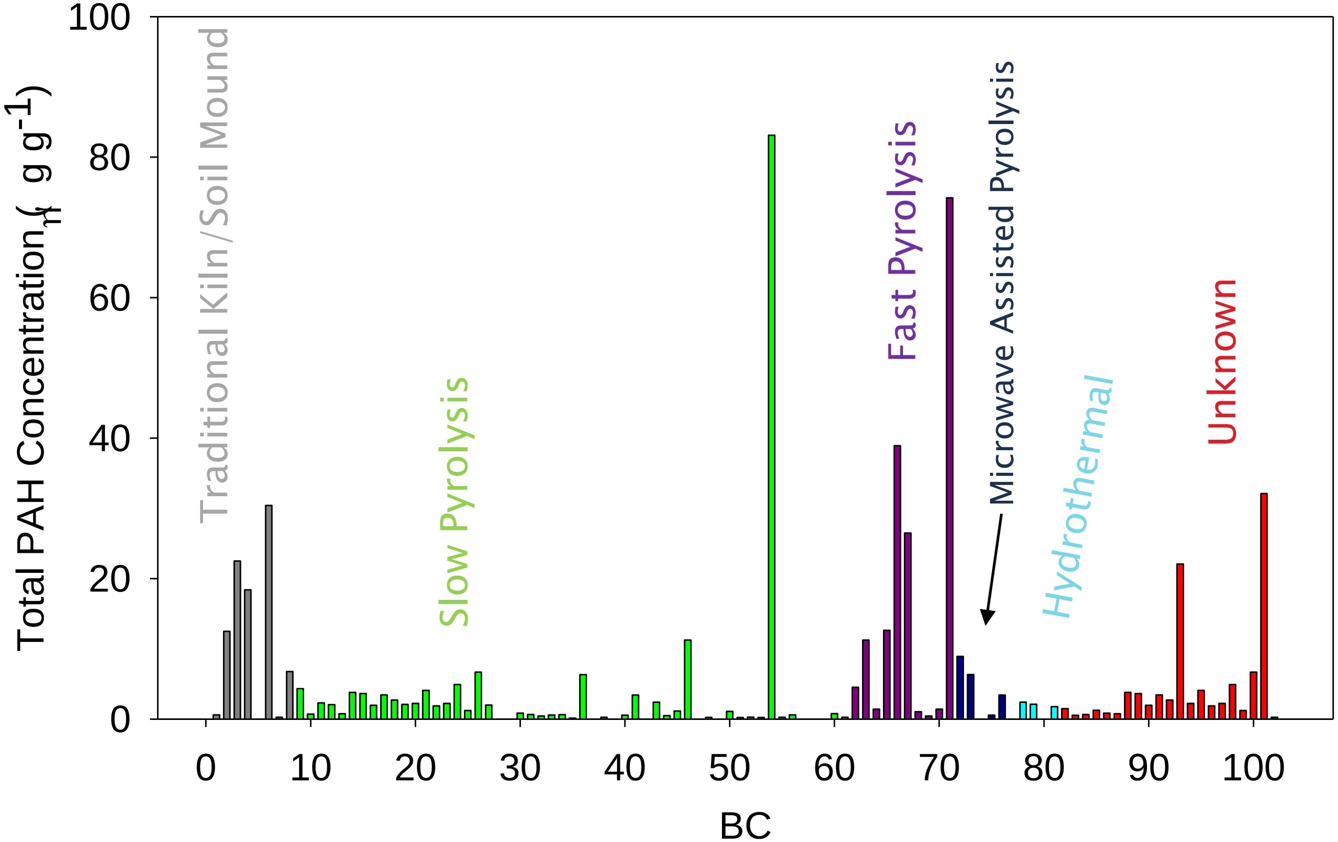
Biochars Examined

- ≈100 different biochars
- 50+ different pyrolysis units
  - Laboratory scale
  - Entrepreneur scale (homemade units)
  - Pilot scale
  - Small industrial scale units (tons/day)
  - Wood fired boilers (high C wood ash)
- Analyzed by multiple methods
  - Various solvent extraction/clean-up methods examined

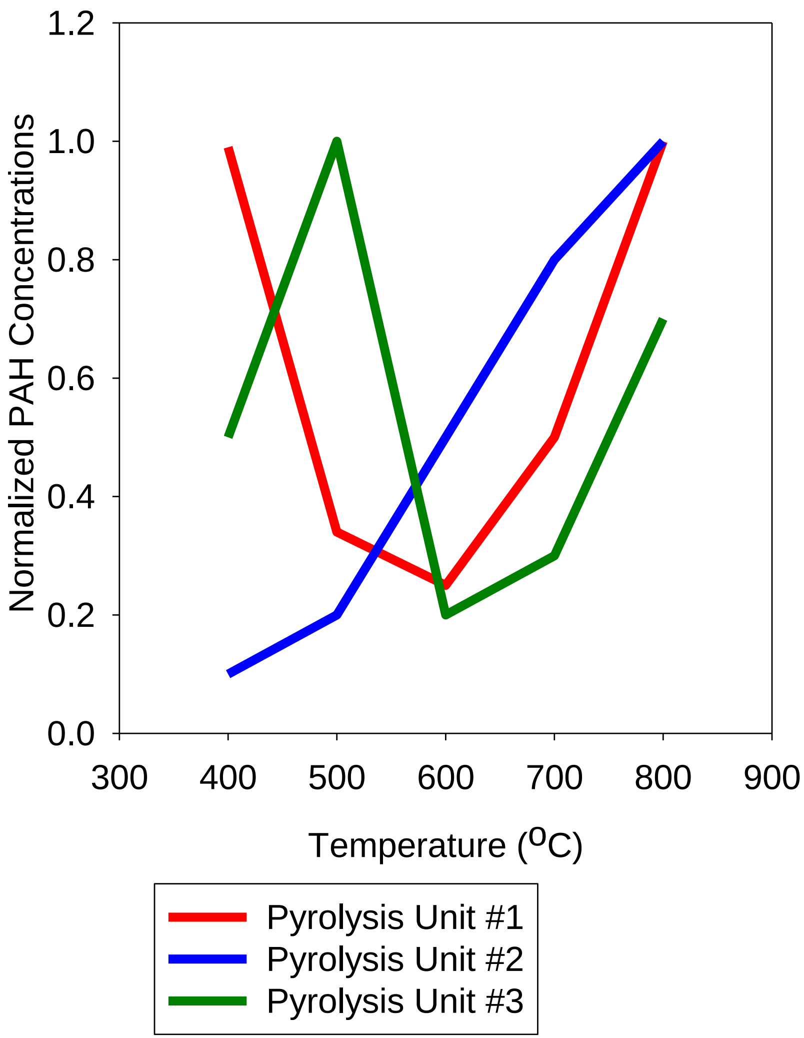


Sorbed PAH on Biochar

- Sum of total PAH range from 0.01 to 83 μg g^{-1}
- Naphthalene was present on all biochars
- Possible influence of production technique
  - Not statistically significant within this sample pool



PAH formation during pyrolysis

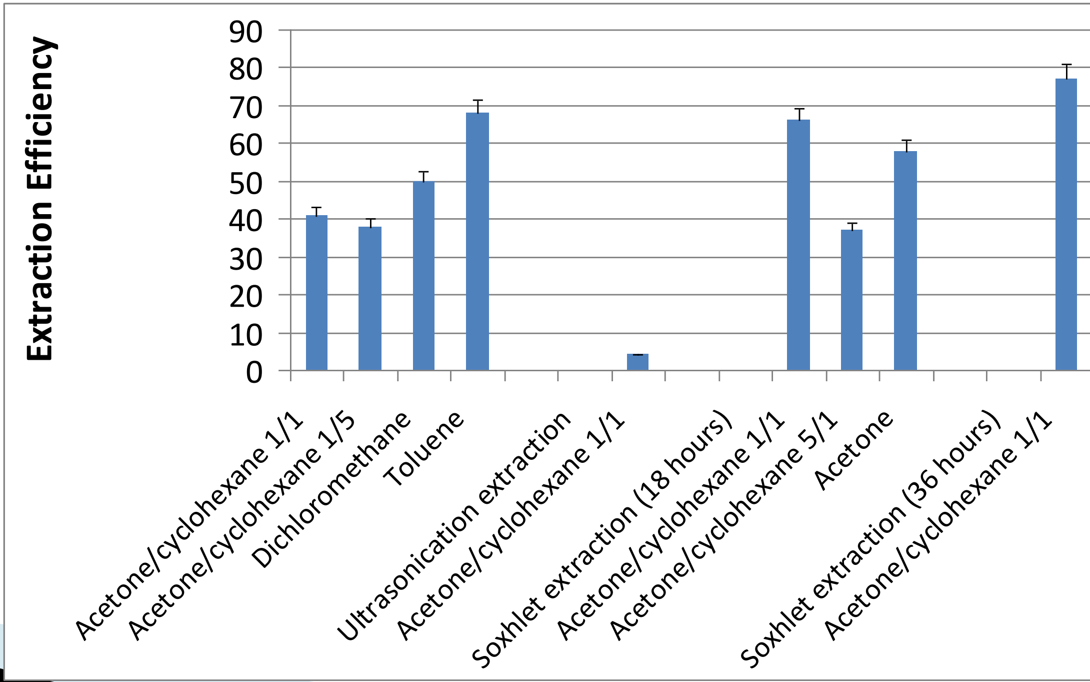


- PAH formation initially linked to higher production temperatures
- However, not all data follows this trend
- There are some hints on how to reduce PAH content

Analytical Difficulties

- Extraction of PAH from biochar
  - Since each biochar possesses unique properties
  - Also possesses different extraction efficiencies
  - Optimal solvent for one biochar might not be best for another

(Fabbri et al., 2012 – Submitted)

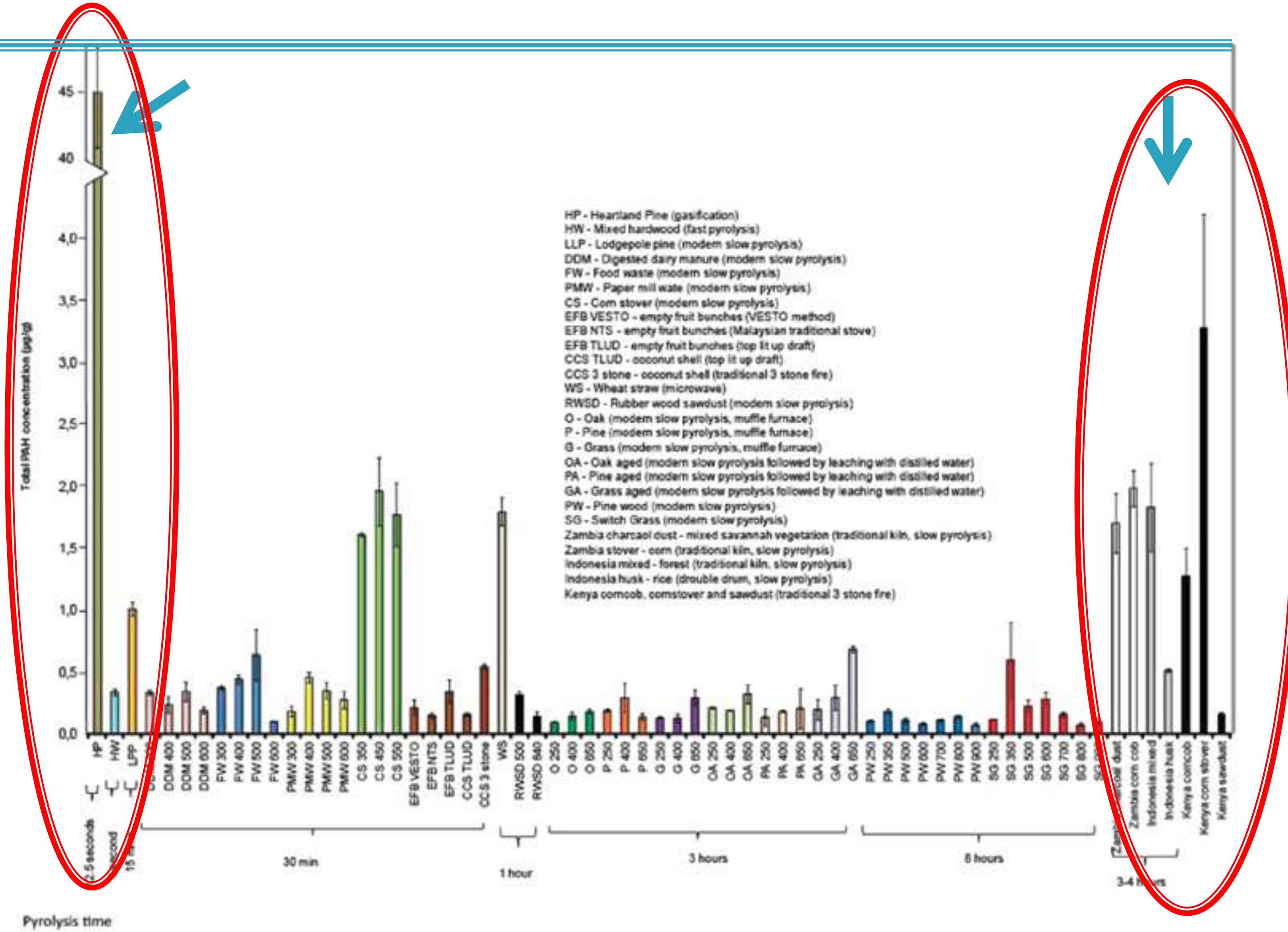


Highest PAH containing biochar

- Producer commented about flames in hardwood chips while producing biochar

- Agrees with data in the literature
  - Flame increase PAH content of the residuals (indication of oxygen presence)

Hale et al. (2012) Biochar Data



Factors impacting PAH formation?

- Presence of <u>oxygen</u> is necessary to create PAH compounds

(Rey-Salgueiro et al., 2004)

- <u>Moisture content</u> of the biomass prior to pyrolysis has been observed to be a vital factor
  - Dryer biomass producing lower levels of PAH

(Bignal et al., 2008)

PAH Impacted by O_2 and H_2O

- Post-production handling of biochar
- Cooling biochars in oxygen (air) environment
  - Increases sorbed PAH content
  - Lower PAH content in biochars cooled under anaerobic inert (N_2) environment
- Moisture differences in the feedstock lead to differences in the PAH content
  - In general, wetter feedstock leads to increased PAH levels
- PAH compounds can undergo abiotic oxidation while sorbed to biochar
  - Time since production important factor; reduces PAH levels

Importance of PAH presence

- Accumulation of PAH compounds by vegetation grown on biochar amended soils
  - Topic will be discussed Wednesday 10:00 am (Cooperage)

Conclusions

- Sorbed PAH levels on biochar can be minimized through feedstock, pyrolysis, and storage conditions

- Production conditions are critical
  - <u>Exclusion of oxygen</u> is the most important
    - Many sources – air, water, carbohydrates, etc…
    - Biochar cooling – avoid air (O_2) contact until cool

- Use of dry feedstocks to avoid PAH formation

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"The nation that destroys its soil destroys itself."
--Franklin D. Roosevelt