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Evaluation of Sorbed Polycyclic Aromatic Hydrocarbons on Biochar

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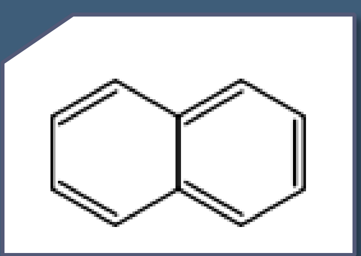
Introduction

- Polycyclic Aromatic Hydrocarbons (PAH)
  - 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




PAH Distribution

- **PAHs are among the most common organic pollutants**
  - Detected on every continent and virtually every location on the globe

- **Universal presence**
  - **Universal presence**
  - **Ease of transport**
  - **Stability**
- **USEPA lists 32 of these PAHs as priority pollutants**




PAH History

- **Some PAHs are known human carcinogens**

- **Sir Percival Pott (1755)**
  - **Postulated that the high incidence of cancer in chimney sweeps was caused by an agent in chimney soot (later shown to be PAHs on soot)**




PAH - Anthropogenic Sources

- **Largest stationary point sources**
  - **Paper mills**
  - **Factories of consumer wood products**
  - **Petroleum refining**


(ARB, 1997)




PAH Natural Sources

- **Present in Fossil Fuels**
  - Crude oil, coal, shale oils …
- **Present in gases (smoke) and ashes from**
  - Forest /Prairie fires
  - Volcanoes
- **Biological Routes**
  - Microbial degradation of black carbon
  - Microbial production during humidification (complex SOM)

(HSDB, 1995)




PAH Formation Processes

- **Incomplete combustion**
  - Burning fossil fuels
  - Biomass burning
  - Cooking for meal preparation

- **PAH production also occurs:**
  - Charcoal production
  - Present in bio-oil from biomass pyrolysis (e.g., Ré-Poppi and Santiago-Silva, 2002)

PAH Presence in Different Materials

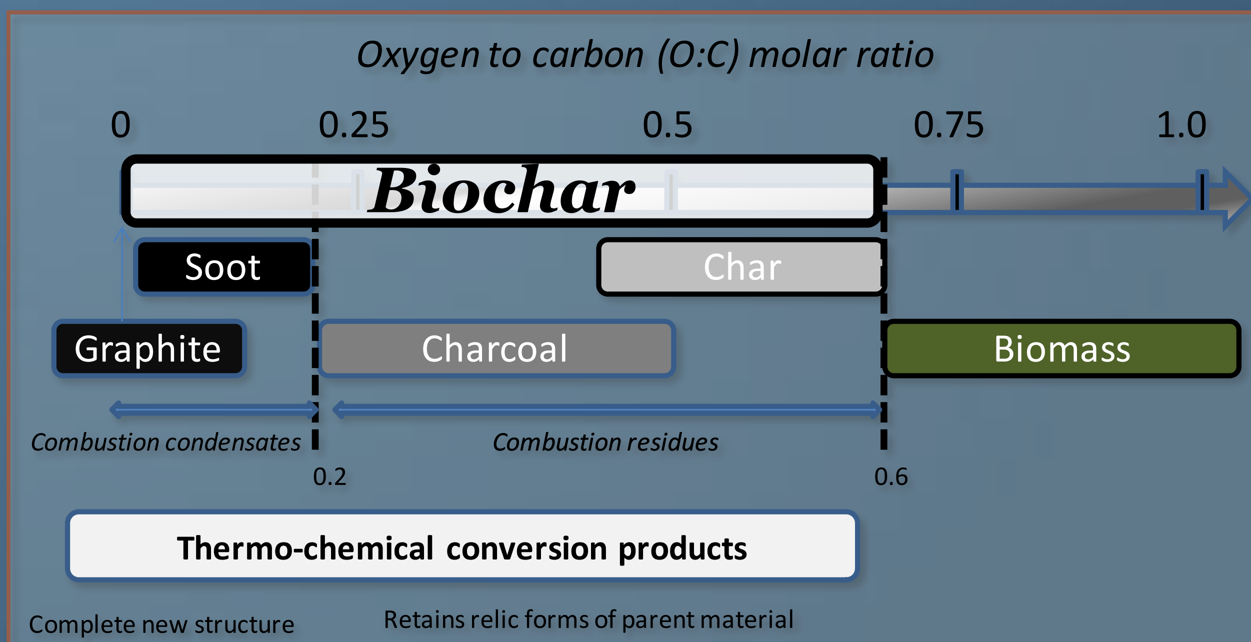
Material	Σ USEPA PAH [μg g^{-1}] ppm	Reference
Soils		
Urban soil (roadside)	0.04 to 13.5	(Ritschel, 2008)
Arable soil (farmland)	0.2 to 0.4	(Ritschel, 2008)
Terrestrial rocks	<0.1 to 45	(Mahajan et al., 2001)
Other Biomass Materials:		
Pine Needles	0.04 – 1.9	(Ratola et al., 2010; Navarro-Ortega et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




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 carbon



Adapted from Hedges et al., 2000; Elmquist et al., 2006; Spokas 2010

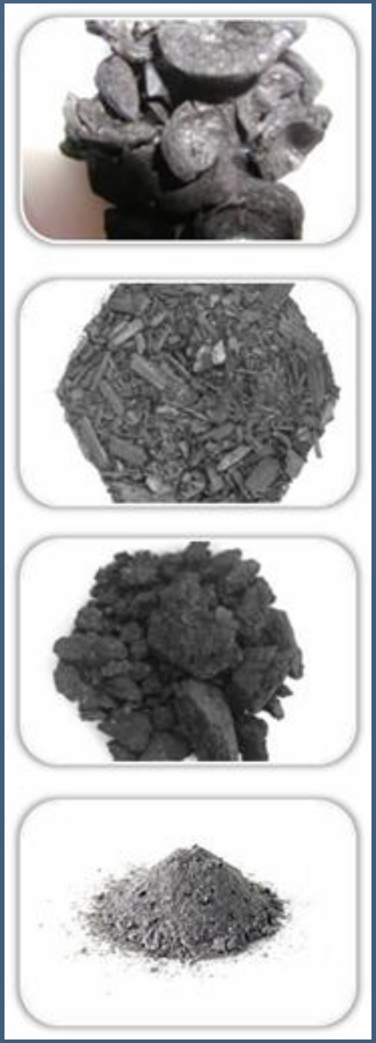
PAH Presence in Black Carbons

	Σ USEPA PAH [μg g^{-1}] ppm	Reference
Black Carbon Form		
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}

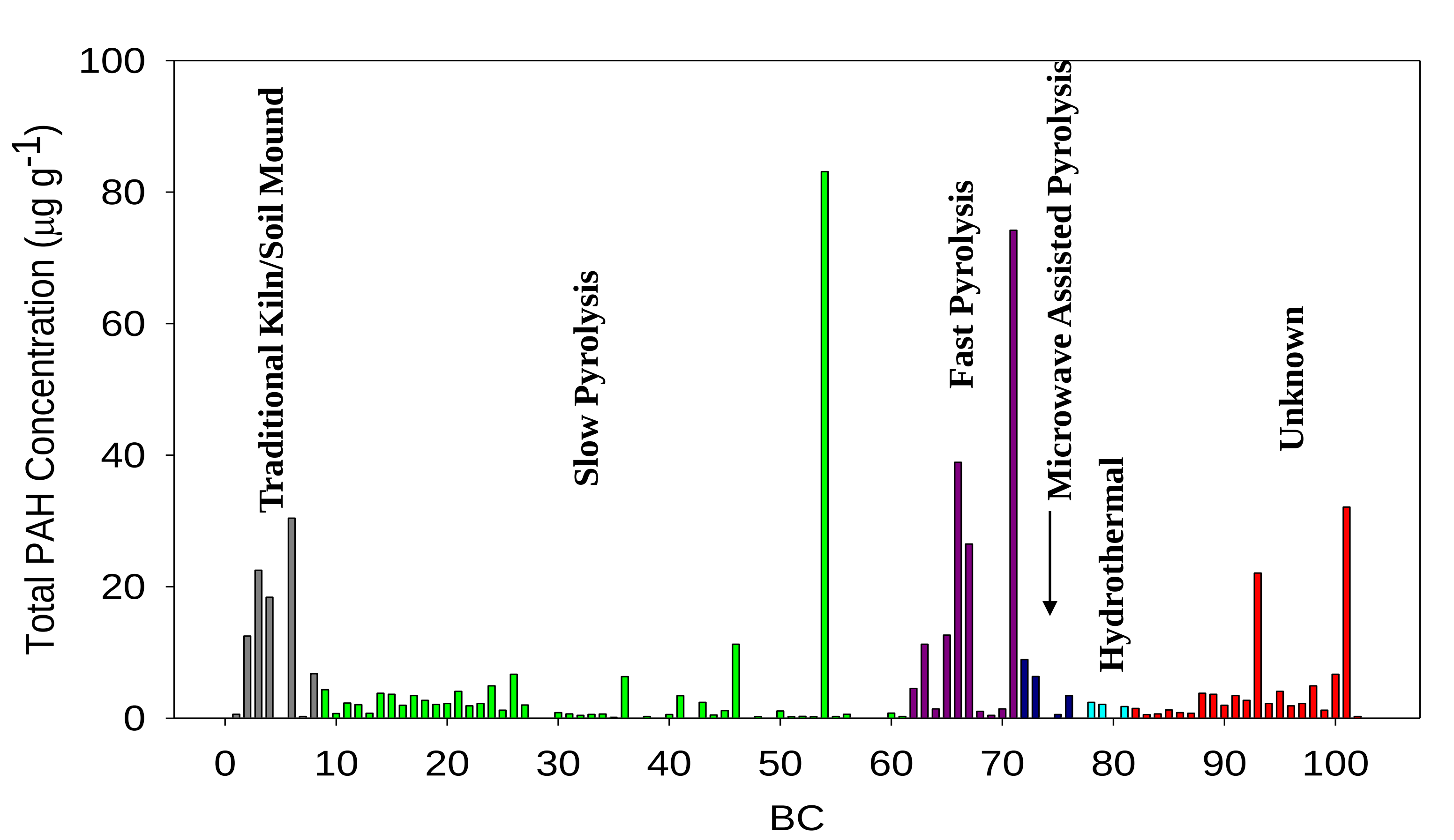
Biochars Examined

- ≈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

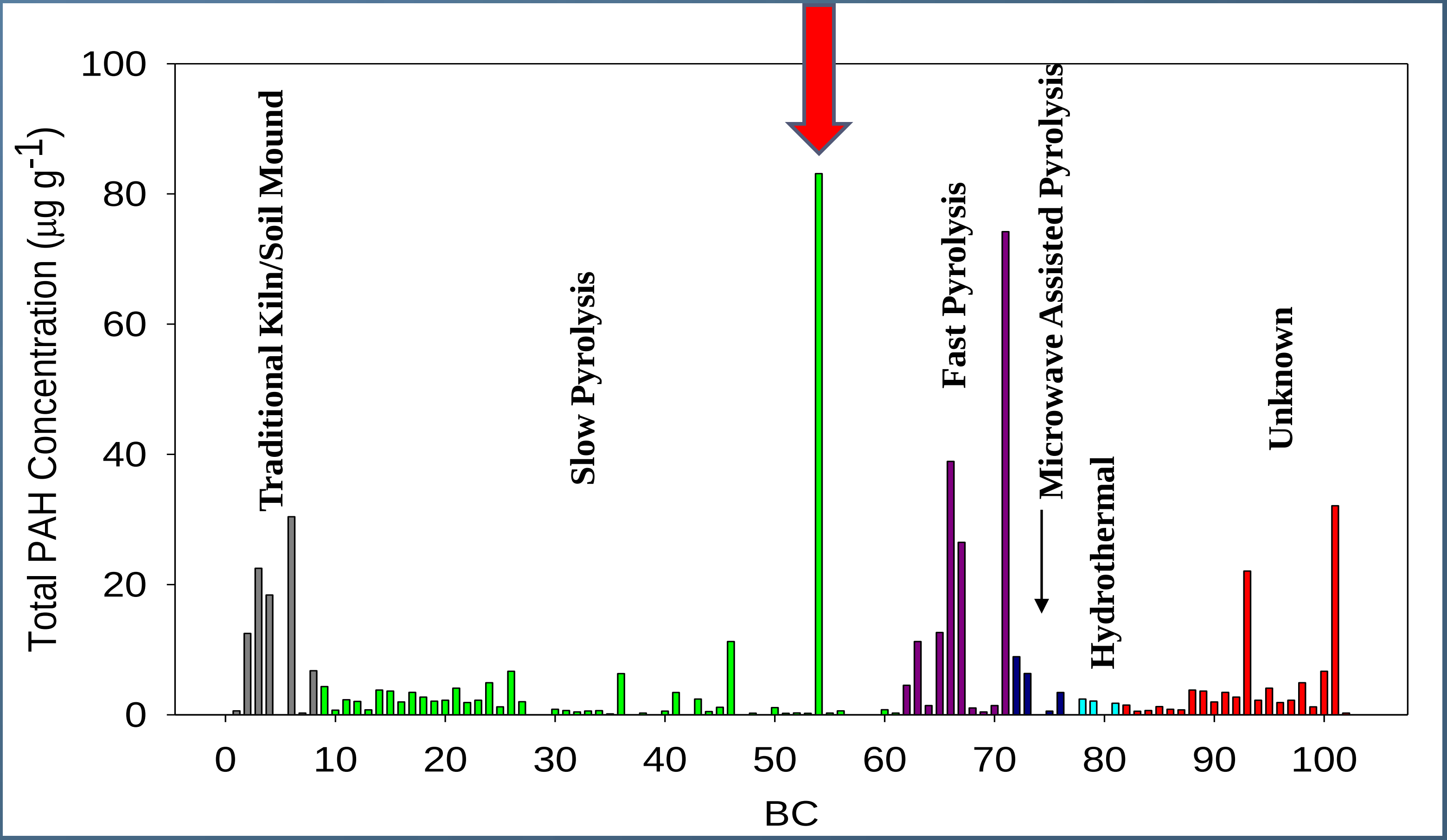


Total sorbed PAH on Biochar

- **Sum of total PAH range from 0.01 to 83 μg g^{-1}**

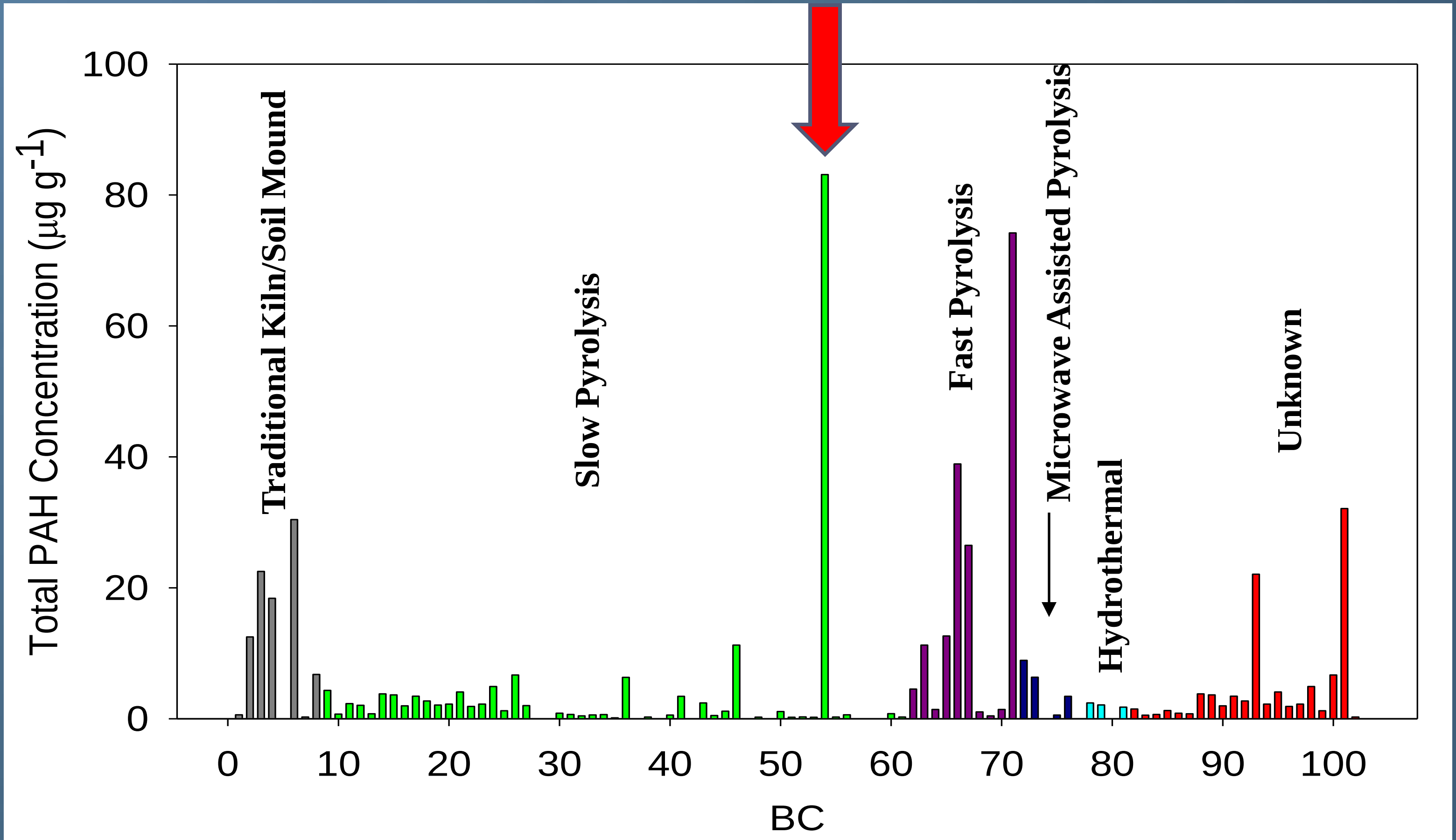


Total sorbed PAH on Biochar



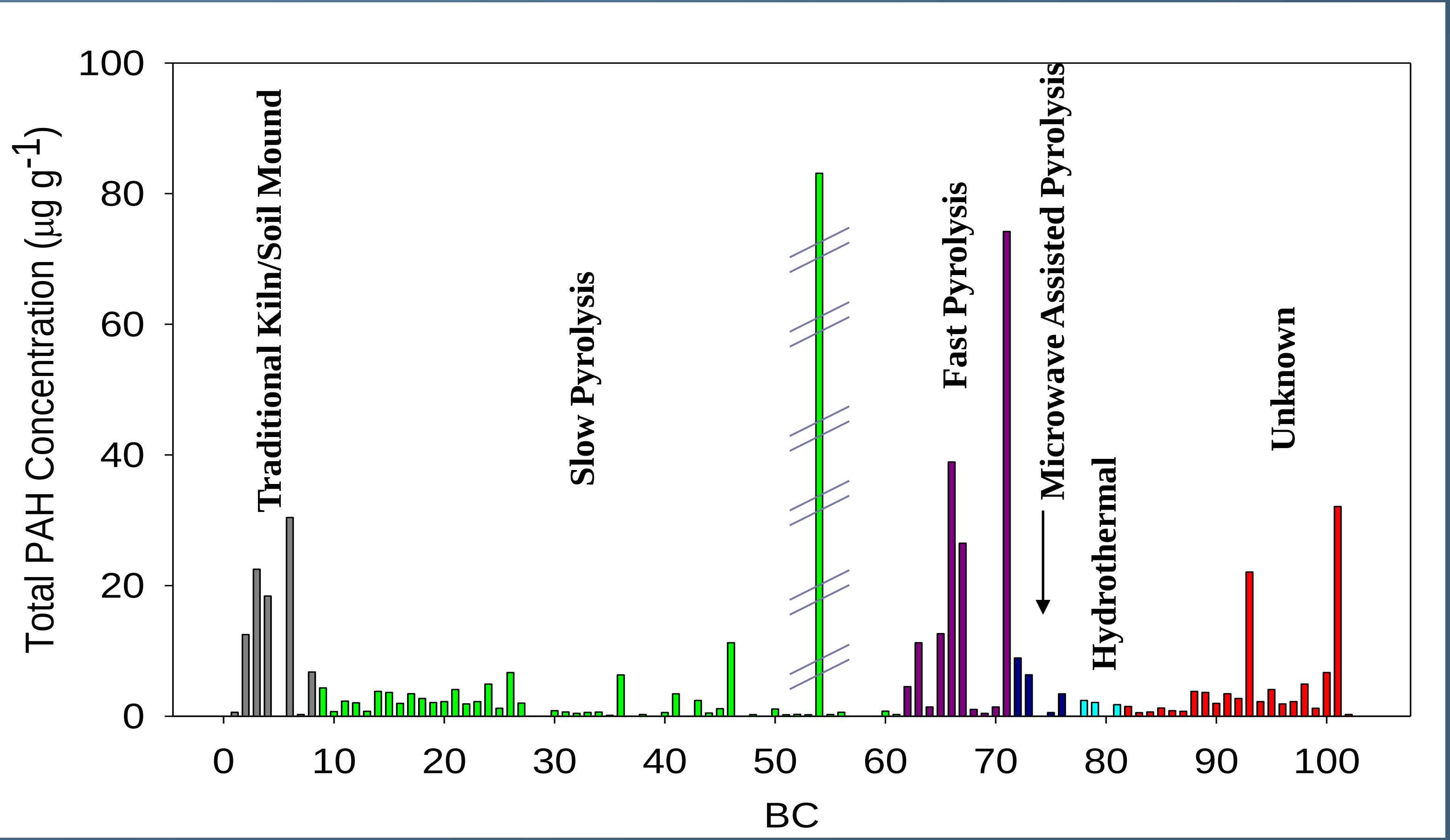
Total sorbed PAH on Biochar

- Highest sorbed PAH content: Slow Pyrolysis
  - Producer noted: Fire in the reactor that was extinguished with water during production/cooled

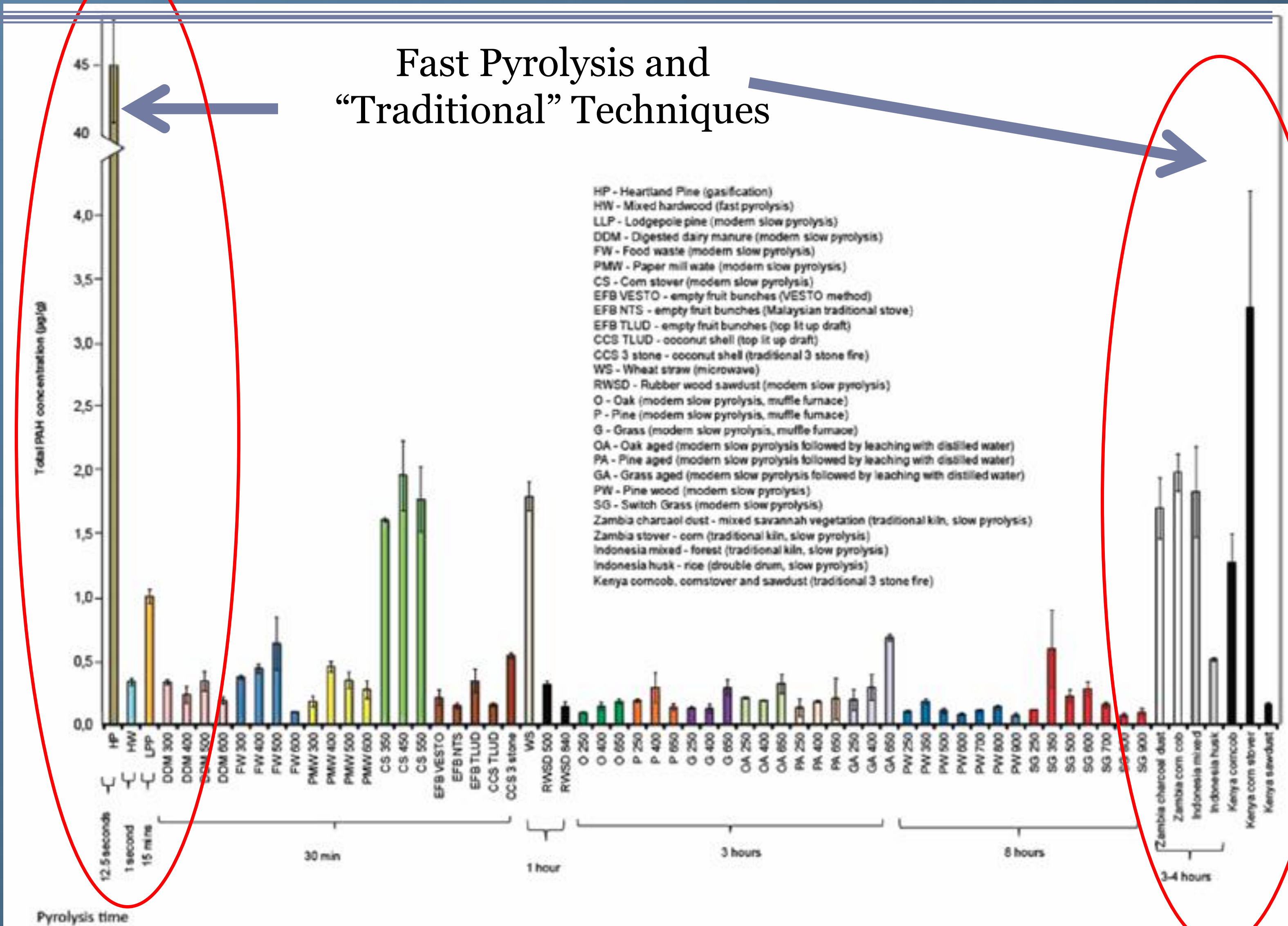


Total sorbed PAH on Biochar

- MAP and Hydrothermal produced lower amount of PAH
  - Conditions not favorable for the production of PAH (?)
  - Some of these used sewage sludge (2 to 126 ppm)

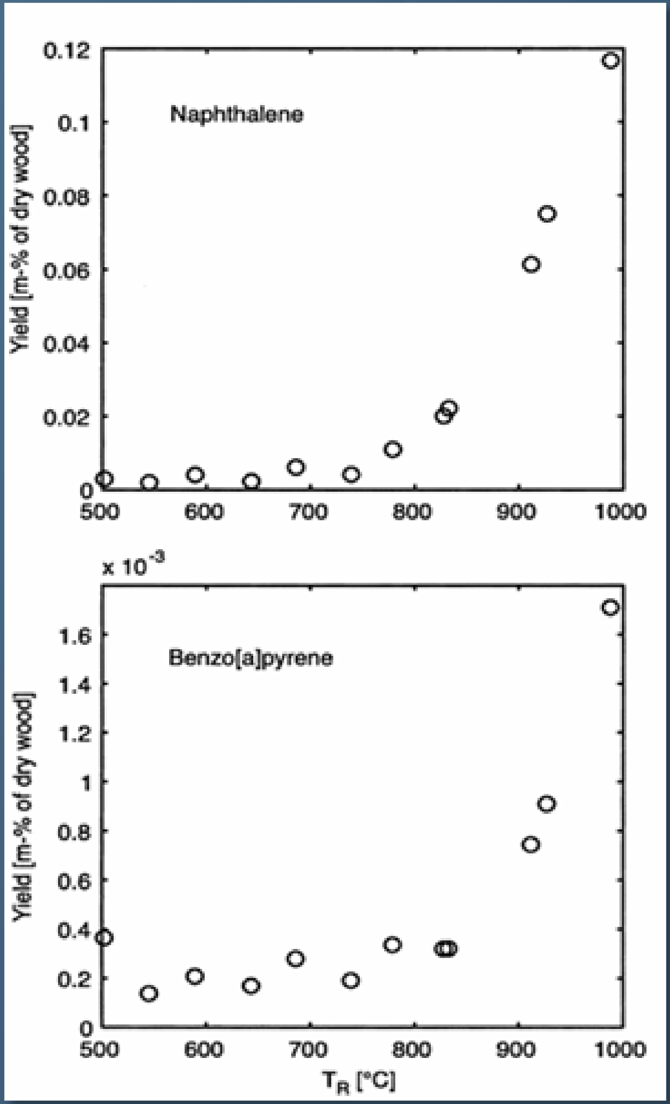


Other studies – Hale et al. (2012)



Temperature Dependence

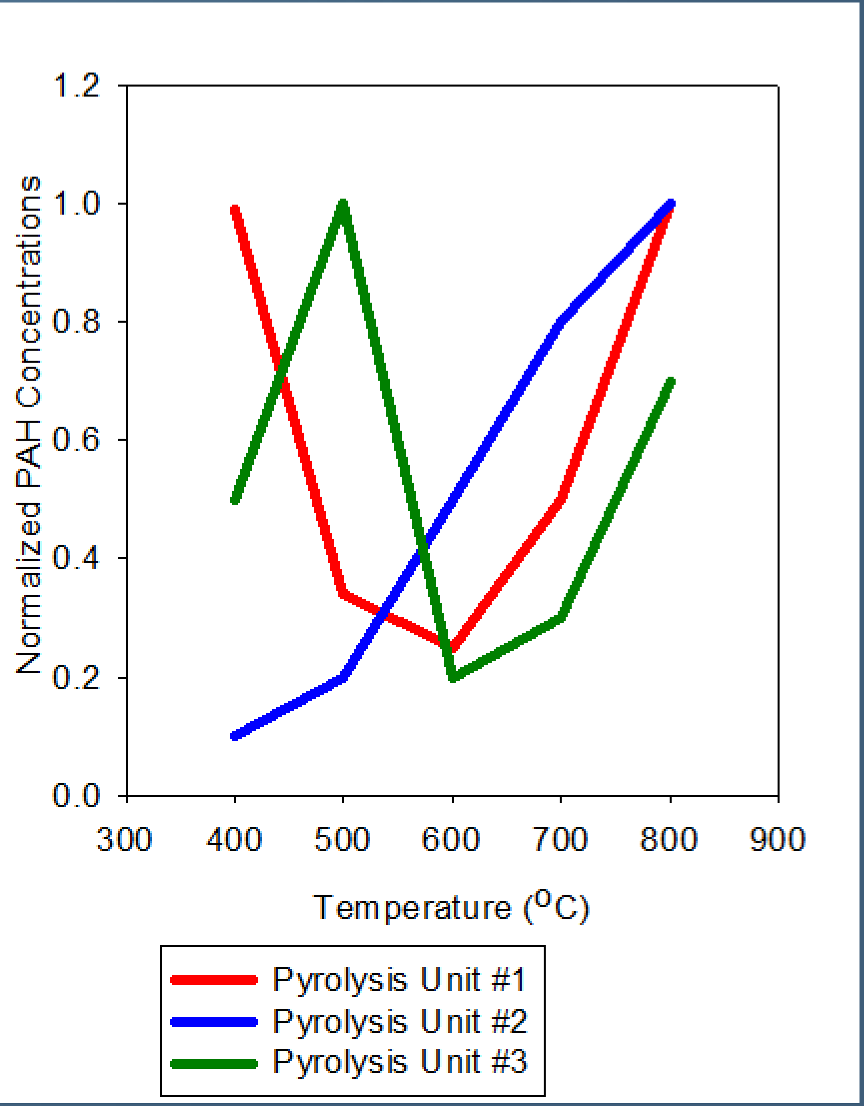
- PAH formation historically linked to higher production temperatures
  - Higher production temperatures lead to higher PAH levels



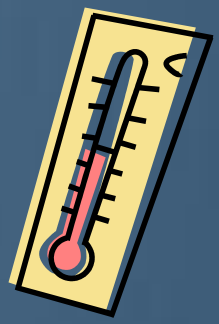
(Morf et al., 2002)

Temperature Dependence

- PAH formation historically linked to higher production temperatures
- However, there are exceptions
  - **Not all pyrolysis units follow this trend**



Factors in PAH formation



Not solely production temperature

- **Original feedstock – PAH levels ?**
- **Presence of <u>oxygen</u> is necessary to create PAH compounds**
  - **Presence of O_2 leads to increase PAH production**

(Rey-Salgueiro et al., 2004)

- **<u>Moisture content</u> of the feedstock**
  - **Dryer biomass producing lower PAH levels**

(Bignal et al., 2008)

PAH Presence in Ashes

Material	Σ USEPA PAH [μg g^{-1}] ppm	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)

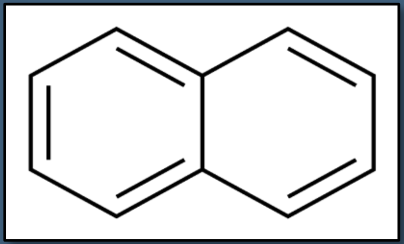
- Incineration and gasification residues contain higher amounts of PAH compounds (0.5 to 185 μg g^{-1})

PAH Formation for Biochar

- **Cooling biochars in oxygen (air) environment**
  - Increases sorbed PAH content

- **Moisture differences in the feedstock**
  - Wetter feedstock leads to increased PAH levels

- **Abiotic oxidation while sorbed to biochar**
  - Time since production = important factor



Conclusions

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

- Production conditions are critical
  - **Exclusion of oxygen** is the most important, both during production AND cooling
    - Many sources – air, water, carbohydrates, etc…
    - Biochar cooling – avoid air (O_2) contact until cool

  - Use **dry feedstocks** to minimize PAH formation

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