PAHS AND CORN STOVER BIOCHAR

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POLYCYCLIC AROMATIC HYDROCARBONS

- Produced in combustion and pyrolysis
  - Including biochar production
- Some PAHs are carcinogenic
  - Regulations, clean-up objectives
  - IBI test category B, toxics
PAHS – USEPA PRIORITY POLLUTANTS

- Naphthalene
- Acenaphthylene
- Phenanthrene
- Anthracene
- Acenaphthene
- Chrysene
- Fluorene
- Pyrene
- Indeno (1,2,3,c,d) perylene
- Benzo (a) pyrene
- Benzo (a) anthracene
- Benzo (b) fluoroanthene
- Dibenz (a,h) anthracene
- Benzo gh perylene
- Fluoranthene
CHARACTERIZATION & EXPERIMENTS

- Total PAH profiles
- Bioaccessibility
- Sorption/solubility
BIOCHAR PREPARATION

- Corn stover
- Slow Pyrolysis
  - 450 °C
  - 550 °C
  - 750 °C
- N$_2$ atmosphere
ARTIFICIAL AGING

- 40% field capacity (moisture)
- Incubate 1 month
  - Freeze/Thaw Daily
  - 60°C
  - 110°C

Hale et al. (2011) Env. Sci. & Technol. 45:10445
CORN STOVER BIOCHAR PAH PROFILES

Concentration (mg/kg) vs. Temperature:

- 450°: Sum = 1.4
- 550°: Sum = 0.2
BIOCHAR AND ILLINOIS BACKGROUND SOILS

*Illinois Environmental Protection Agency
ECOLOGICAL SCREENING LEVELS

USEPA (2007)

Concentration (mg/kg)

29 - 100
BIOLOGICAL EFFECTS OF PAHS

- Uptake, toxicity unrelated to total concentrations
- Correlate with dissolved concentrations.
- Bioavailable → Freely dissolved
BIOACCESSIBLE PAHS

- Longer-term processes
- Correlate with uptake, degradation
- Bioaccessible → “Mild” extraction
- Bioaccessible ≥ Bioavailable
Pyrene probe compound

Added to biochar

Extract with 2-hydroxypropyl-β-cyclodextrin (HPCD)
HPCD EXTRACTION

HPCD-extractable Pyrene vs. Pyrene Spike (mg/kg)

- 550° char
- Un-aged
BIOACCESSIBLE PYRENE IN BIOCHAR

The diagram illustrates the relationship between pyrolysis temperature and bioaccessible pyrene in biochar. The x-axis represents the pyrolysis temperature (°C), while the y-axis shows the HPCD-extractable pyrene. The data points are differentiated by aging status: un-aged (blue diamonds) and aged (red circles). The graph shows a decrease in bioaccessible pyrene as the pyrolysis temperature increases.
SORPTION EXPERIMENTS

- Pyrene probe compound
- Control and measure dissolved pyrene by passive sampling
**ADSORPTION ISOTHERM**

![Graph showing sorbed pyrene (µg/kg) versus dissolved pyrene (µg/L) for 550° un-aged samples. The Freundlich Isotherm is depicted with a curve fitting the data points.](attachment:adsorption_isotherm.png)
ISOTHERM, LOG-LOG

Sorbed Pyrene (µg/kg)

Dissolved Pyrene (µg/L)
SORPTION ISOTHERMS, UN-AGED CHAR

![Graph showing sorbed and dissolved pyrene](image)

- **Y-axis**: Sorbed Pyrene (µg/kg)
- **X-axis**: Dissolved Pyrene (µg/L)

Legend:
- **450°**
- **550°**
- **750°**
SORPTION ISOTHERMS, AGED AND UN-AGED 750° CHAR

SORPTION ISOTHERMS, AGED AND UN-AGED 750° CHAR

 Sorbed Pyrene (µg/kg)

 Dissolved Pyrene (µg/L)

 Un-aged
 Frz-Thaw
 60 C
 110 C
CONCLUSIONS, PAH SORPTION

- PAHs sorb strongly to corn stover char
- Freundlich isotherm
- $6 < \log K_d < 8$ for 10 ng/L
- For native PAHs, solubility $<< 1$ ng/L
APPLICATION

- Use biochar for soils & sediment remediation
Small fraction of added pyrene is bioaccessible (HPCD-extractable)

- 10-15% 450° char
- 1-3% 550°, 750° chars
Biochar field trials
- Total PAHs
- Bioavailable PAHs
- Bioaccessible PAHs
- PAHs in crop
CONCLUSIONS, CHAR AGING

- Small effects on pyrene sorption
  - $\Delta \log K \leq 0.5$
- Bioaccessibility
  - $450^\circ$ & $750^\circ$ chars small decreases
  - $550^\circ$ char large decrease (?)
ACKNOWLEDGEMENTS

- Support: Illinois Sustainable Technology Center, Hazardous Waste Research Fund
- Jill O’Connell
“That’s all Folks!”

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EXTRA SLIDES
PAH CONCENTRATIONS IN CORN STOVER CHAR

ΣPAH

450°  1.4

550°  0.2
POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Naphthalene  Acenaphthylene  Acenaphthene  Fluorene

Phenanthrene  Anthracene  Fluoranthenone
MORE PAHS

Pyrene

Chrysene*

Benz[a]anthracene*

Benzo[k]fluoranthene*

Benzo[b]fluoranthene*
EVEN MORE PAHS

Benzo[a]pyrene**

Indeno[123-cd]pyrene*

Dibenzo[ah]anthracene*

Benzo[ghi]perylene
ECOLOGICAL SCREENING LEVELS

USEPA (2007)

Concentration (mg/kg)

0.0

0.5

1.0

1.5

2.0

29 - 100
PAHS IN BIOCHAR AND ILLINOIS BACKGROUND SOILS

Total PAH (mg/kg)

- Phenanthrene
- Pyrene
- Chrysene
- Benzo [a] pyrene

- CS450
- Chicago
- Metro
- Non-metro
- Non-metro
- TACO*

*Illinois Environmental Protection Agency
OED Online Word of the Day

The March 2012 quarterly update is now available. New words and meanings include dataveillance, LARP, ludology, schoolboy error, soz, and yakisoba. Find our word of the day:

Your word for today is: biochar, n.

biochar, n.

Pronunciation: Brit. /ˈbaɪərətʃər/, U.S. /ˈbɛərəˌtʃɑːr/

Etymology: < bio- (in biomass n.) + char- (in charcoal n.).

Charcoal produced from plant matter and typically buried under the atmosphere carbon dioxide (fixed during photosynthesis) that greenhouse effect.
OED Online Word of the Day

The March 2012 quarterly update is now available. New words: dataveillance, LARP, ludology, schoolboy error, soz, and yah.

Your word for today is: doh, int.

doh, int.

Pronunciation: Brit. /dəʊ/, U.S. /dou/


Etymology: Imitative. Compare OH int., DUH int.

Popularized by the American actor Dan Castellaneta who provided the voice for U.S. cartoon series The Simpsons. The quotation below is his: