Biochar: Contaminant source or sink?

Isabel Hilber, Franziska Blum, Hans-Peter Schmidt, Sarah Hale, Gerard Cornelissen, Diane Bürge, Thomas D. Bucheli

September 20 2012
Biochar & activated carbon (AC)

Similarities
- Pyrolysed organic material
- Same chemical structure

Differences
- Activation of AC by steam at around 1000 °C
- $\text{AC}_{\text{surface}} > \text{biochar}_{\text{surface}}$

Activated carbon  Biochar
Organic contaminants

- Organic contaminants
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Dioxins
  - Polychlorinated biphenyls (PCBs)
  - Pesticides
  - Etc.

Naphtalene, phenanthrene, fluoranthene

Dibenzo-p-dioxine

DDT

PCB
PAHs

- Formation due to incomplete combustion of organic material
- Soot particles are PAHs agglomeration
- Ubiquitous → water, soil, air, food

- Adverse health effects such as
  - Carcinogenic → lung cancer
  - Immunosuppressive

Biochar: Contaminant source or sink?
Isabel Hilber | © Agroscope Reckenholz-Tänikon Research Station ART
Common properties PAHs - biochar

- Formed during pyrolysis
- Condensed carbonaceous material
- Similar chemical structure consisting of aromatic rings
- Lipophilic → almost insoluble in water
Total concentrations of PAHs

Premium biochar
4 mg/kg

Basic grade biochar
12 mg/kg
PAHs fingerprints
Inorganic contaminants

- **Heavy metals originating from feedstock**
  - Non-essential or toxic elements such as cadmium (Cd), arsenic (As), lead (Pb), etc.

- **Heavy metals from abrasion during pyrolysis**
  - Chromium (Cr), nickel (Ni)

- **Essential elements at too high concentrations like cupper (Cu), zinc (Zn), etc.**
### Pb, Cu and Zn in biochars

<table>
<thead>
<tr>
<th>Material</th>
<th>ChemRRV 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood residues</td>
<td>120</td>
</tr>
<tr>
<td>Wood residues, biogas digestate</td>
<td>100</td>
</tr>
<tr>
<td>Coniferous &amp; deciduous residues, biogas digestate</td>
<td>400</td>
</tr>
</tbody>
</table>

ChemRRV: Chemikalien RisikoReduktionsVerordnung (CH)
Ni concentrations in 53 biochars

Threshold value of Ni set of Swiss ChemRRV at 30 mg/kg_{dw}
- 9 out of 28 wood samples surpassed threshold
- All lop samples surpassed threshold
Carbonaceous geosorbents (charcoal, biochar, coke, AC, graphite, soot etc.) exhibit highly nonlinear and strong sorption for organic contaminants (Endo et al., ES&T, 2009)

Freely dissolved PAHs reduced by 56-95% in activated carbon amended and 0-57% in biochar amended sewage sludge (Oleszczuk et al., Bioresource Technology, 2012)

Organic contaminants sink
Possible biochar amendments
Inorganic contaminants sink

- Biochar in contrast to metals non-ionic material → functionalization by steam activation and other methods
- Functionalized flax & cotton seed biochar bind Pb, Cu and Zn in soil (Uchimiya et al., JAFC, 2012)

Clay minerals naturally in soil or functionalized biochar
Summary source contaminants

PAHs
- Two thirds of the biochars contained >4 mg/kg for the Σ16 US EPA PAHs indicating a need to decrease the total concentration to produce premium biochar
- 40% of the samples contained >12 mg/kg PAHs and surpassed the threshold for basic grade biochar
- The majority of the concentrations consists of light PAHs

Heavy metals
- Non-essential elements (Cr, Pb) no problem
- 28% of 53 biochar samples exceeded Ni threshold value
Summary sink contaminants

Of PAHs and other organic contaminants

- High sorption affinity
- Surface area usually smaller than activated carbon
- Binding and problems such as fouling similar to activated carbon

Of non-essential elements

- Ionic interactions low because biochar surface not functionalized
- Functionalized biochar only effective in degraded soils with low clay mineral content
- pH normally $\geq 7 \rightarrow$ anionic heavy metals such as antimony (Sb) or arsenic (As) mobilized
Conclusions & outlook

Firstly,
- Biochar is still a source and a sink of contaminants
- Formation process of PAHs during pyrolysis known in order
- To reduce PAHs in biochars → ongoing investigations
- Extraction method to determine PAHs in pyrolised biochar must be established incl. sampling

Then,
- Biochar can be used without problem as soil improver and/or
- Sink for organic (inorganic) contaminants

Still,
- Ambivalence of binding or degradation especially of organic pollutants
Thank you!

ART – Research for Agriculture and Nature

isabel.hilber@art.admin.ch
Phone +41 44 344 76 06
Total PAH concentrations

Optimized extraction method for PAHs in soils  Hilber et al., JAFC, 2012

- Toluene (100%) as extraction solvent
- Soxhlet extraction for 36 h
- Quantification by GC-MS with isotope labeled internal standard for 16 EPA PAHs
Bioavailable PAHs – passive sampler

Not all of PAHs concentrations available for organisms → Bioavailable PAHs

- Determined in aqueous suspension with polyoxymethylene (POM)

Jonker & Koelmans, ES&T, 2001
Hale et al., ES&T, 2012
PAHs in different acts

- Swiss ordinance on reduction of risks (ChemRRV):
  - 4 mg/kg ($\Sigma 16$ EPA PAHs) guide value in compost and digestate

- Swiss ordinance values related to impacts on soils (VBBo):
  - Guide value: 1 mg/kg ($\Sigma 16$ EPA PAK)
  - Application of 20 t/ha mit 10 mg/kg $\rightarrow$ +40 $\mu$g/kg

- International Biochar Initiative:
  - Maximum allowed threshold value: 6 - 20 mg/kg
  - European Biochar Certificate: „premium“ biochar: < 4 mg/kg; „basic“ biochar: < 12 mg/kg
Activated carbon

inner surface

outer surface

inner surface

outer surface

Sub-micro pores \((r < 0.4\text{nm})\)

Micro pores \((0.4\text{nm} < r < 1\text{nm})\)

Meso pores \((1\text{nm} < r < 25\text{nm})\)

Macro pores \((r > 25\text{nm})\)

Biochar

Biochar: Contaminant source or sink?
Isabel Hilber | © Agroscope Reckenholz-Tänikon Research Station ART
Percentage PAHs bioavailable

Fraction of PAHs dissolved in water

- Miscanthus
- hard- and pinewood and mixed with compost
- composites only
- lop
- sieved coniferous wood residues
- beech wood
- sugar beet
- miscellaneous

Biochar: Contaminant source or sink?
Isabel Hilber | © Agroscope Reckenholz-Tänikon Research Station ART
Bioavailable PAHs in biochars

Bioavailable concentrations of biochars

Σ8 US EPA PAH [ng/L]

MISCANTHUS
hard- and pinewood and mixed with compost
composts only
LOP
sieved coniferous wood residues
beech wood
sugar beet
miscellaneous

Biochar: Contaminant source or sink?
Isabel Hilber | © Agroscope Reckenholz-Tänikon Research Station ART
Pb, Cu and Zn in biochars

- 2 g of biochar incinerated at 650 °C and extracted by 6M HCl, filtrated and
- Measured by ICP-OES

<table>
<thead>
<tr>
<th>Material</th>
<th>ChemRRV 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood residues</td>
<td>120</td>
</tr>
<tr>
<td>Wood residues, biogas digestate</td>
<td>100</td>
</tr>
<tr>
<td>Coniferous &amp; deciduous residues, biogas digestate</td>
<td>400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Out of 53 biochars [mg/kg dw]</th>
<th>Material</th>
<th>ChemRRV 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>156 Wood residues</td>
<td>120</td>
</tr>
<tr>
<td>Cu</td>
<td>183, 104 Wood residues, biogas digestate</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>4360, 4019 Coniferous &amp; deciduous residues, biogas digestate</td>
<td>400</td>
</tr>
</tbody>
</table>