Soils in fire-prone ecosystems – Where does all the charcoal go?

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The Impact of Fire on the Landscape

Sierra de Aznalcollar
Southern Spain

September, 2004

July 2004
Duration: 2 weeks
Area: 26 000 ha (2.5 ha min⁻¹)

April, 2006
Long Term Impact?

….If Black Carbon has been produced since the last glacial maximum via biomass burning at the same rate as it is now produced, BC should account for 25 – 125% of the total soil organic carbon pool……

(Masiello and Druffel, 2003)

Where does all the charcoal go?
Erosion with Post-Fire Runoff

Post-fire runoff, Victorian Alps, Australia.

Image courtesy of Rob Ferguson and Stefan Doerr
Deposition and Accumulation in Sediments
Burrying under Sediments (Fossil Paddy Soils, China, Yangtze River)

Recent Paddy Field: river sediment

Ancient Paddy Field: flood deposits (3320 BP)

Prehistoric Rice Field: loess (6280 BP)

Parent Material: loess

(Cao et al., Naturwissenschaften, 93, 232-236, 2006)
Ditch around a Neolithic Settlement (Murr, Southern Germany)

Schmid et al., Soil Science 166, 569-584, 2001
Charcoal as New Litter Layer

Incorporation into newly formed humus?

Cambisol, Central Spain, 2 years after the last fire

Cambisol, Central Spain, 24 years after the last fire
Former Charcoal Production Site
Rio de Janeiro, Brazil
The Impact of Charcoal on Soil Organic Matter

Cambisol, Central Spain

- Difference in color → Difference in chemistry and soil properties
- Changes in C-concentration (depends on fire conditions)
- C-sequestration potential of soils
- Soil organic matter (SOM) quality
Solid-State Nuclear Magnetic Resonance Spectroscopy

- non-degradative technique

- Qualitative Information: Assignment of signals
- Quantification: Signal intensity
Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy

- Considerable difference between “natural” and “pyrogenic” SOM
- Identification of PyOM by aromatic C content (unburnt soils < 25%)

Unburnt Cambisol (Aznalcollar, Spain)

Burnt (3 weeks) Cambisol (Aznalcollar)
Common Model for Black Carbon (Soot)

Barbeque charcoal

H/C = 0.48

H/C < 0.2

- Electrical conductivity disables NMR spectroscopy
- Atomic H/C ratio is too low for biochars

(according to Sergides et al., 1987)
H/C of Charcoals

Maximal cluster size for PyOM: 4-6 rings

\[ \text{H/C}_{\text{PyOM}} > \text{H/C}_{\text{BC-Model}} \]

(Knicker et al., 2005, Org. Geochem. 36, 1359-1377)
High Variability of PyOM Composition

PyOM ≠ PyOM

Occurrence of “Black N”

(Knicker et al., Geoderma, 2007)
Charring of Lignin (5-20% of Plant C)

- Dehydroxylation
- Demethylation
- Cleavage of side chains
- Cleavage of ether bonds and dehydroxylation of ring
- Formation of biphenyls

(Knicker et al., 2008, Org. Geochem. 39, 935)
Charring of Proteins (1-20% of Plant C)

**Casein:**
- 450°C/4 min
  - Recovery:
    - C: 29%
    - N: 45%
  - Alkyl
  - O/N-alkyl
  - Aromatic
  - Carboxyl

**Atomic C/N**
- 4.0

**13C NMR**
- HNOC-CH-R
- I
- NH₂

**Pyridine,** **Nitrile,** **Pyrrole,** **Amide,** **15N NMR**
- 300, 200, 100, 0 ppm
- -260, -233, -347 ppm

**19N NMR**
- HNOC-R

**350°C/4 min**
- Recovery:
  - C: 66%
  - N: 51%

**450°C/4 min**
- Recovery:
  - C: 29%
  - N: 23%

*Organic Geochemistry*, 41, 947-950.
New Conceptual Model of PyOM

Lignin

Benz (a) anthracene

Cellulose

Benzofuran

Pyranone

Structure depends on:

- source material
- charring intensity

Alternative Concept for Char Structure

- Char presents an heterogenous mixture of heteroaromatic structures (Knicker, 2007, Biogeochemistry 85, 91)

- High potential for biotic oxidation

Degradation by lignin-degraders?
Biochemical Degradation of Aromatic Structures

- Anthracene
- Naphthalene
- Phenanthrene
- Benzoic acid
- Salicylic acid
- 4-Hydroxytoluene
- 4-Hydroxybenzoic acid
- Benzoic acid
- 3-Hydroxybenzoic acid
- Protocatechulic acids
- Pyrocatechol
- Anilic acid
- Tryptophane
- Biphenyl
- Benzene
- Phenol
- Naphthalene
- Phenol
- Benzoic acid
- Salicylic acid
- Anilic acid
- Tryptophane
- Biphenyl
- Benzene
- Phenol
- Naphthalene
- Phenol
- Benzoic acid
- Salicylic acid
- Anilic acid
- Tryptophane
- Biphenyl
Incubation of Grass PyOM

Incubation time: 7 weeks

Under oxic conditions char is relatively quickly oxidized
Impact of Regeneration Time on SOM Composition (Pine, Cambisol, Central Spain)

(1982)
- Control
  - Alkyl
  - O/N-Alkyl
  - Aromatic C
  - Carboxyl
  - C mg g\(^{-1}\)
  - 63

(2005)
- Burnt
  - 1 year
    - Alkyl
    - O/N-Alkyl
    - Aromatic C
    - Carboxyl
    - C mg g\(^{-1}\)
    - 14
  - 24 years
    - Alkyl
    - O/N-Alkyl
    - Aromatic C
    - Carboxyl
    - C mg g\(^{-1}\)
    - 59

- Erosion?
- Degradation?
Respiration Experiments

Multimeter

Incubation vessel

KOH

CO₂

soil

Respicond (25°C)
Respiration of a Soil without PyOM (7 month)

\[ C_r (\%) = C_f e^{(-k_f t)} + C_s e^{(-k_s t)} \]

Degradation rate constant

Fast pool

Slow pool

Mean Residence Time (MRT): $1/k$

\[ R^2 \approx 0.998 \]
Sierra de Aznalcóllar, S-Spain, After a Severe Fire, 2004

(Knicker et al. 2013, Soil Biology and Biochemistry, 197-198, 43-50.)
Mean Residence Time (1/k) (years)

- **MRT of PyOM is only slightly higher than MRT of SOM**
- **Charcoal as long-term C-sink?**

Knicker et al. 2013, Soil Biology and Biochemistry, 197-198, 43-50.
Changes of PyOM/SOM during Degradation

Knicker et al. 2013, Soil Biology and Biochemistry, 197-198, 43-50.
Changes of PyOM/SOM during Degradation

Pine

<table>
<thead>
<tr>
<th>Compound</th>
<th>0 days</th>
<th>7 months</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Carboxyl/Amide</td>
<td>10</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Aromatic</td>
<td>49</td>
<td>44</td>
<td>5</td>
</tr>
<tr>
<td>O-Alkyl</td>
<td>14</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>N-Alkyl/OCH₃</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Alkyl</td>
<td>19</td>
<td>17</td>
<td>2</td>
</tr>
</tbody>
</table>

Oak

<table>
<thead>
<tr>
<th>Compound</th>
<th>0 days</th>
<th>7 months</th>
<th>Difference</th>
</tr>
</thead>
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<tr>
<td>Carbonyl</td>
<td>4</td>
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<tr>
<td>Aromatic</td>
<td>39</td>
<td>34</td>
<td>5</td>
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<td>19</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>N-Alkyl/OCH₃</td>
<td>5</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Alkyl</td>
<td>24</td>
<td>21</td>
<td>3</td>
</tr>
</tbody>
</table>
Vertisol:

1-2% $C_{\text{org}}$

$^{14}C$-age: $\approx 5000$ years

(Prof. D. Faust, personal communication)

Former management:

After-harvest burning

(since Roman times)
Tierra Negra Andaluza

Utrera (Sevilla)

C_{arom}: 19%

C_{arom}: 28%
Chemical Oxidation (60°C; $K_2Cr_2O_2 + H_2SO_4$; 6 h):

If source material is known
COREC$_{arom}$ allows determination of PYOM by using a correction factor $f$

Chemical Oxidation of Tierra Negra

\[
\begin{array}{c}
\text{Carboxyl} \quad \text{O/N-Alkyl} \\
\text{Aromatic} \quad \text{Alkyl}
\end{array}
\]

\[C_{\text{arom}}: 19\%\]

\[
\begin{array}{c}
\text{Carboxyl} \quad \text{O/N-Alkyl} \\
\text{Aromatic} \quad \text{Alkyl}
\end{array}
\]

\[C_{\text{arom}}: 32\%\]
Selective enrichment of PyOM

Increase of aromaticity of SOM due to removal of fresh litter
Chronosequence: Ceasing Biannual Burning (Planalto, Brazil)

Time after last fire:

<table>
<thead>
<tr>
<th>Time</th>
<th>1 year</th>
<th>2 years</th>
<th>5 years</th>
<th>22 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>New</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post fire</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre fire</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Soil (1 year after last fire)

Humic Leptosol

(0-5 cm): 12.1%
(15-30 cm): 6.4%
(30-45 cm): 3.7%

- No clear indication for PyOM

Fast degradation of PyOM?

- Increase of aromatic C with depth

- Translocation?
- Selective enrichment?
- Humification?
PyOC Stocks in Comparison with non-PyOC (0-30 cm)

Burning leads to C increase

C increase is due to addition of carbohydrates (input of unburnt necromass of dead roots)

New litter input “masks” PyOM
PyOC in Soils under Cerrado (Viracopos)

PyOM in subsoil as efficient C sink

Velaso et al. submitted
PyOC in Soils under Cerrado

<table>
<thead>
<tr>
<th>%</th>
<th>clay</th>
<th>silt</th>
<th>sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_T</td>
<td>-0.86</td>
<td>0.30</td>
<td>0.59</td>
</tr>
<tr>
<td>carboxyl</td>
<td>0.52</td>
<td>0.16</td>
<td>-0.55</td>
</tr>
<tr>
<td>aryl</td>
<td>0.36</td>
<td>-0.52</td>
<td>-0.01</td>
</tr>
<tr>
<td>O - alkyl</td>
<td>-0.46</td>
<td><strong>0.58</strong></td>
<td>0.06</td>
</tr>
<tr>
<td>N - alkyl</td>
<td>-0.42</td>
<td>0.50</td>
<td>0.07</td>
</tr>
<tr>
<td>alkyl</td>
<td>-0.38</td>
<td>0.30</td>
<td>0.16</td>
</tr>
</tbody>
</table>

- In addition to PyOM-mineral interaction other mechanism must occur
- Accumulation due to low biochemical activity?

*Velasco-Molina et al. in preparation*
Planosol, Pantanal (Brazil)

last burning: 1999
 Sampling: 2002

Ah
Sand: 91%

E
Sand: 95%

BC (T)
Clay: 52%

C1 (T)
Clay: 47%

C2
Clay: 19 % Sand: 68 %

Residue after $H_2O$-Extraction

H$_2$O-Extract

C of C$_{\text{bulk}}$

0.8%

1.8%

2.2%
Conclusion: PyOM in Soils

- We have evidence for oxidation of the aromatic network

  On a larger time scale degradation processes may level out the differences between PyOM and SOM in the topsoil

- Once oxidized, the increasing solubility allows leaching of PyOM to the deeper soil

  High PyOM content in subsoil as a typical feature of soils with frequent char input?

  Fire (biochar input) as soil forming factor?
Fate of PyOM in Soils


Selective enrichment of PyOM (Andalusia)

"Masking" (Brazil, Planalto)

Absorption to mineral phase, stabilization

Accumulation (Pantanal)
The Ecological Role of Black Nitrogen?
Modell of Charred Proteins

$^{13}$C chemical shift
$^{15}$N chemical shift

Pyrrole (C/N: 4:1)

4-Hydroxytoluene

2,5-Diketopiperazine (C/N: 2:1)

Imidazole (C/N: 1.5:1)

Pyridine (C/N: 5:1)

Relative Contribution of BN to BC

Charring, 2 min, 350°C, oxic conditions

Charred grass

Charred peat

Atomic C/N: 5.1 (casein-BC)

BN ≈ 60% of $C_t$

BN ≈ 13% of $C_t$
Contribution of BN in Burnt Soils

Control (A horizon, Cambisol, Central Spain)

1 year:
(33% char)

C/N 22

27% of char C = heteraromatic C (9% of $C_{tot}$)

24 years:
33% of char C = heteraromatic C (7% of $C_{tot}$)
Pot Experiments with $^{15}$N-PyOM

125 g dry soil + 0.5 g seeds + 150 mg $^{15}$N-enriched PyOM.

Plant Availability of PyOM - $^{15}$N

$^{15}$N$_{add}$ present in grass (%)

Plants can use $^{15}$N of PyOM

Bioavailability of $^{15}$N-PyOM ($^{15}$N NMR)

Amides are newly formed from $^{15}$N-PyOM (20% of $^{15}$N$_{tot}$)

Planosol, Pantanal (Brazil)

Almost all aromatic C is N-heteroaromatics
Conclusions (BN)

- Peptides are precursors of Black Nitrogen
- “BN” is an important and integral part of “BC”
- BN is quantitatively relevant in fire-affected soils
- BN can be biochemically degraded, providing N for the build-up of new biomass
BN as a “Slow-release” Fertilizer for Providing N after Vegetation Fires

Need to use heterocyclic N after fires is in contrast to a high biochemical recalcitrance!
Conclusions (Summary)

- PyOM ≠ PyOM

- Behaviour of PyOM depends on source material and environmental conditions

- Degradability of PyOM is related with its ecological function

Low PyOM levels can be explained with:
- *Transport to the Ozean*
- *Lower biochemical recalcitrance of PyOM than thought*
- *Leaching and accumulation in deeper soils with low biological activity*
- *DOM in rivers?*

- The role of BN as a post-fire fertilizer should not be underrated
Thanks to:
- CITIUS (University of Sevilla)
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- IHSS for supporting the travel

Thanks for Your Attention !!!